CHEMICAL PERFORMANCE OF CEMENT STABILISED CONTAMINATED CLAY

by

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ABSTRACT

Urban demand has increased the need to redevelop contaminated land. New legislation for land management has actively discouraged previously acceptable dig and dump practices. This has encouraged in-situ remediation approaches, for which stabilisation / solidification (S/S) is particularly suitable for treating metal contamination. However, concerns over long-term effectiveness and durability of S/S need to be addressed, because contamination is contained but not removed. This requires effective chemical assessments to inform design.

This study aims to design a suitable method for assessing S/S effectiveness, using a holistic risk based approach, for use during performance based S/S design. The processes that induce containment were evaluated, by assessing the solubility controlling mechanisms, and undertaking geochemical speciation modelling, to determine solubility controlling minerals. These findings can be used at the design stage to engineer S/S application to particular sites, and ensure long-term performance with minimal risk. The release controlling mechanisms include equilibrium (pH dependent) and disequilibrium (chemical kinetics – dissolution, diffusion, surface wash-off) leaching conditions. The pH dependent leaching test (CEN/TS 14429) was used to obtain equilibrium leaching data; the dynamic monolithic leaching test (CEN/TS 15863) was used to obtain time dependent disequilibrium leaching data; and the upflow percolation leaching test (CEN/TS 14405) was used to obtain porewater equilibrium leaching data. Extractions were then undertaken for available reactive surfaces (hydrous ferric oxides and organic carbon), and the results were combined with equilibrium leaching data to undertake geochemical speciation modelling using ORCHESTRA embedded in the leaching expert system LeachXS.

Evaluations for structural master species (Al, Si, and Ca) and contaminants (Zn^{2+}, Cr^{3+}) in cement stabilised contaminated kaolin were undertaken. The influences of common soil components (humic acid and sodium sulphate), and increasing hydration durations were also assessed, to inform containment effectiveness and chemical durability. Amphoteric leaching trends were not observed for zinc and chromium releases, under equilibrium pH dependent leaching. These were expected based on the theoretical solubility of their hydroxides, and suggested their partitioning under an alternative or combination of mineral phases.

The introduction of additives modified the availabilities of the contaminants at early hydration durations. Humic acid increased the availability for both contaminants, due to increased complexation with particulate organic matter. Increased sulphate content decreased zinc availability at the early hydration period, due to increased silicic acid releases from kaolin dissociation, for use in the formation of insoluble zinc silicates. However, increasing hydration cancelled the effects of additives on contaminant containment, and releases at advanced hydration durations were comparable to those observed for matrices without additives. Also, increasing hydration durations induced improved contaminant containment, resulting in reducing contaminant availability for leaching. Results for the structural master species showed increasing kaolin dissociation with hydration. However, the released silica was used up in the pozzolanic reaction with calcium, for formation of stable cementitious minerals, which improved the chemical durability of the stabilised kaolin clay matrices.

Speciation modelling was used to determine the solubility controlling phases for the contaminants, which can be used during field application of S/S, to minimise the potential for accidental releases, based on the mineral phase solubility properties. Findings showed that the assessment method was suitable for chemical characterisation of stabilised matrices, as a tool for informing design and application. However, limitations were observed in the leaching assessment and modelling tools, due to limited thermodynamic information for some expected mineral phases (variety of zinc silicates), and limitation for assessing chromium as chromate instead of Cr^{3+}.

DEDICATION

To my parents – Prof Elerius E John (RIP) and Prof Mildred E John for your incredible love, support and guidance, you truly are inspirations beyond comprehension.

None of this would be possible without your backing, rest in peace dear Father knowing your good work bore the very best fruit.

To God almighty, for grace mercies, health and provision

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To my dear friends – Lucie, Nsikak, Ukpono, Nkanta, Charles, Marianne, Eteka, Odudu, Azoi and Jyro to name a few

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Abbreviations

ANC / BNC	Acid / Base Neutralisation Capacities
AVS	Acid Volatile Sulphates
CAH	Calcium Aluminate Hydrate
CAS	Calcium Aluminosilicates
CEC	Cation Exchange Capacity
CEN/TS	European Committee for Standardisation / Technical Standards
cf	Concentration Factor
CSH	Calcium Silicate Hydrate
De	Diffusion Coefficient
DOC	Dissolved Organic Carbon
Eh	Redox Potential
EU	European Union
HFO	Hydrous Ferric Oxyhydroxides
ICP (OES)	Inductively Coupled Plasma (Optical Emissions Spectroscopy)
kPa	Kilopascal
L/A	Liquid / Surface area ratio
L/S	Liquid / Solid Ratio
LeachXS	**Leach**ing E**x**pert **S**ystem
mol	Molarity
ORCHESTRA	**O**bjects **R**epresenting **Che**mical **S**peciation and **Tra**nsport Models
pE	negative log of the electron activity
pH	Acidity / Alkalinity of system / $-\log_{10}$ of hydrogen ions activity
POM	Particulate Organic Matter
ppm	Parts per million (mg/kg)
rc	Slope
rpm	Revolutions per minute
S/S	Stabilisation / Solidification
SHA	Solid Humic Acid
SSA	Specific Surface Area
TOC	Total Organic Carbon
US EPA	United States Environment Protection Agency
XRF	X-ray Fluorescence

Chemical Abbreviations

Al, Al^{3+} -	Aluminium, Aluminium ion
$Al(OH)_3$	Aluminium hydroxide (Gibbsite)
Al_2O_3, AlO_4^{5-}	Alumina (Aluminium oxide), Aluminium oxide ion
$Al_4Si_4O_{10}(OH)_8$	Kaolinite
Ba	Barium
Ca	Calcium
CaO, $Ca(OH)_2$	Quick lime, Slaked lime
Cd	Cadmium
$Cr(OH)_3$	Chromium (III) hydroxide
Cr, Cr^{3+}, Cr^{6+}	Chromium, Chromium (III) ion, Chromium (IV) ion
CrO_4^{2-}	Chromate ion
Cu	Copper
Fe, Fe^{2+}, Fe^{3+}	Iron, Ferrous ion, Ferric ion
Fe_2O_3, $Fe(OH)_3$	Iron (III) oxide, Iron hydroxide
H^+, OH^-	Hydrogen ion, hydroxide ion
$H4SiO_4$	Silicic acid
HNO_3	Nitric acid
K	Potassium
Mg	Magnesium
Mn	Manganese
Na	Sodium
Na_4SiO_4, Na_2SiO_3	Sodium silicates
Na_2SO_4	Sodium silicate
NaOH	Sodium hydroxide
Ni	Nickel
Pb	Lead
S	Sulphur
Si, Si^{4+}	Silicon, Silicon ion
SiO_2	Silica (Silicon oxide)
SO_4^{2-}	Sulphate
$Zn(OH)_2$	Zinc hydroxide
Zn, Zn^{2+}	Zinc, Zinc ion

CHAPTER ONE

1.0 INTRODUCTION

The need for sustainable development often requires the redevelopment of Brownfield (previously developed) sites, to meet the demands of increasing urban expansion. The contaminant histories vary with the previous land use, and require unique site based evaluations, as part of the contamination assessment. Where contamination is deemed to pose a significant threat to human and environmental health, remediation is required to mitigate the risks. Recent EU and UK legislations discourage offsite disposal, and has actively encouraged the use of in-situ source control approaches for remediation (Harbottle *et al.,* 2007).

While organic contaminants can be destructively remediated on site, heavy metals are more problematic, and require modifications or containment to remove the risk. Stabilisation / solidification (S/S) remediation techniques provide viable and relatively economical options, and are particularly effective for heavy metal fixation and immobilisation (Bone *et al.,* 2004b, Harbottle *et al.,* 2008). However, since these contaminants are not removed from site, there is a need to validate the performance of the technique, and ensure long-term effectiveness during design.

1.1 BACKGROUND

Contamination legacies on sites vary with industrial processes that prevailed. S/S is more likely to be applied on sites with heavy metal contamination, or in combination with other remediation techniques for mixed contamination. The current study evaluated S/S effectiveness for application during remediation. This required tailoring the study to specific waste streams, from specific industrial processes. Undertaking laboratory based studies for translations to field applications are often challenging, and for the current study, clay contamination due to processes from electric arc furnace industrial processes was simulated.

Contaminants typical to electric arc furnace dusts were selected, in view of migration and subsequent groundwater pollution, and implications for human and environmental health. These include arsenic, cadmium, chromium, lead, mercury, selenium, silver, vanadium and zinc (US EPA, 1991), which cannot be destructively remediated. The next step was evaluating site investigation processes, to evaluate possible release mechanisms, migration pathways, and S/S containment processes, through use of diagrammatic conceptual models for risk management.

1.2 CONCEPTUAL MODELLING AND RISK MANAGEMENT

Conceptual studies show simplified descriptions of environmental conditions, to provide visualisations for site conditions. It is a vital aspect for simulation studies, and requires accurate definition of modelling requirements, and validation against actual conditions (Robinson, 2006). It has also gained increasing interest for use in knowledge acquisition and model abstractions (Kotiadis, 2008). It can depict information on contaminants, migration pathways and receptors, and is updated to show remediation influences during treatment. One key requirement is simplification, and for the current study, a visual depiction of conditions and pathways are shown in Figure 1.1. Stabilisation and changes with hydrations are depicted in Figure 1.2, while Figure 1.3 shows an expansion for the containment mechanisms and products.

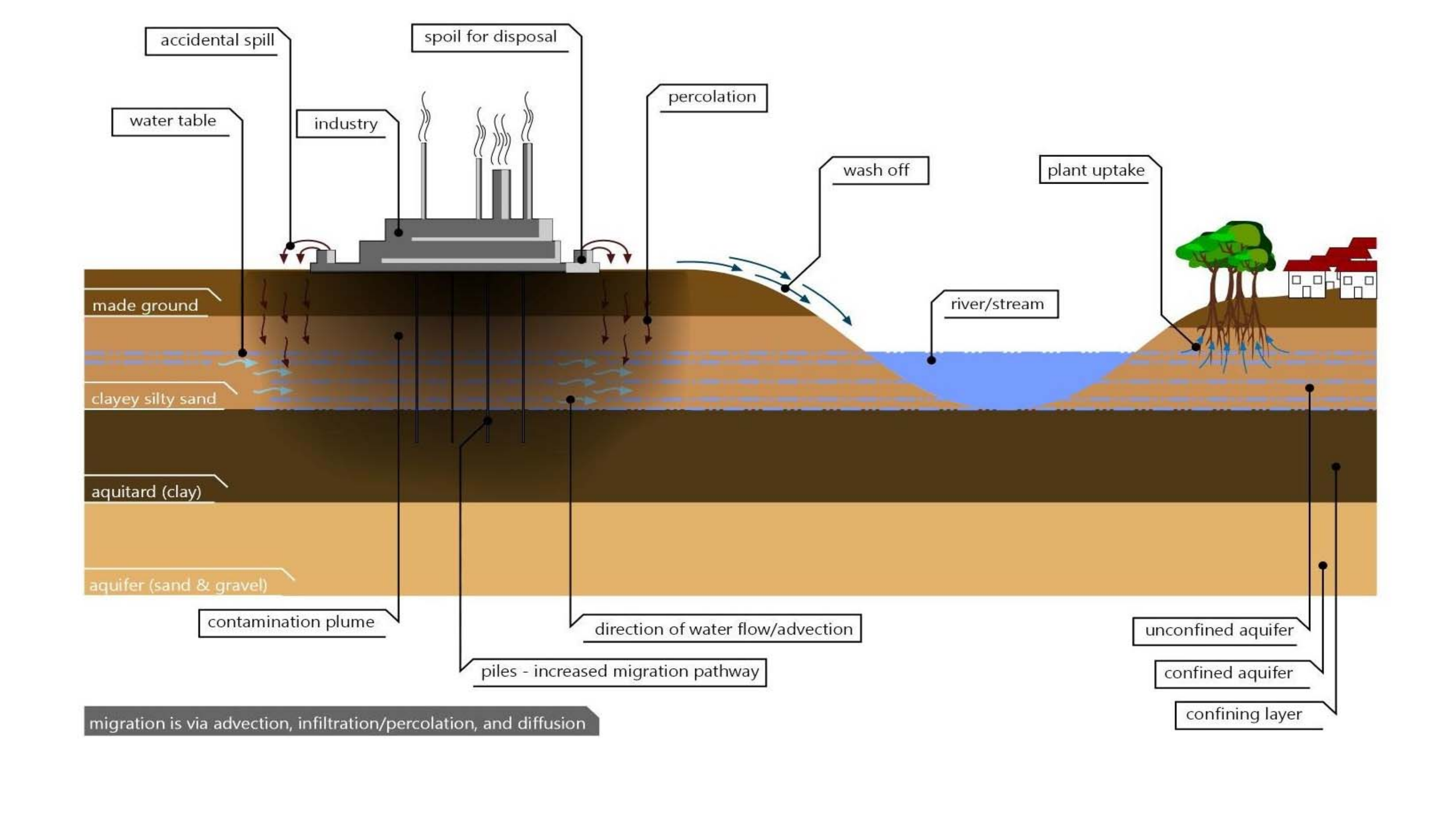

Figure 1:1: Conceptual model of site conditions, migration pathways and possible implications

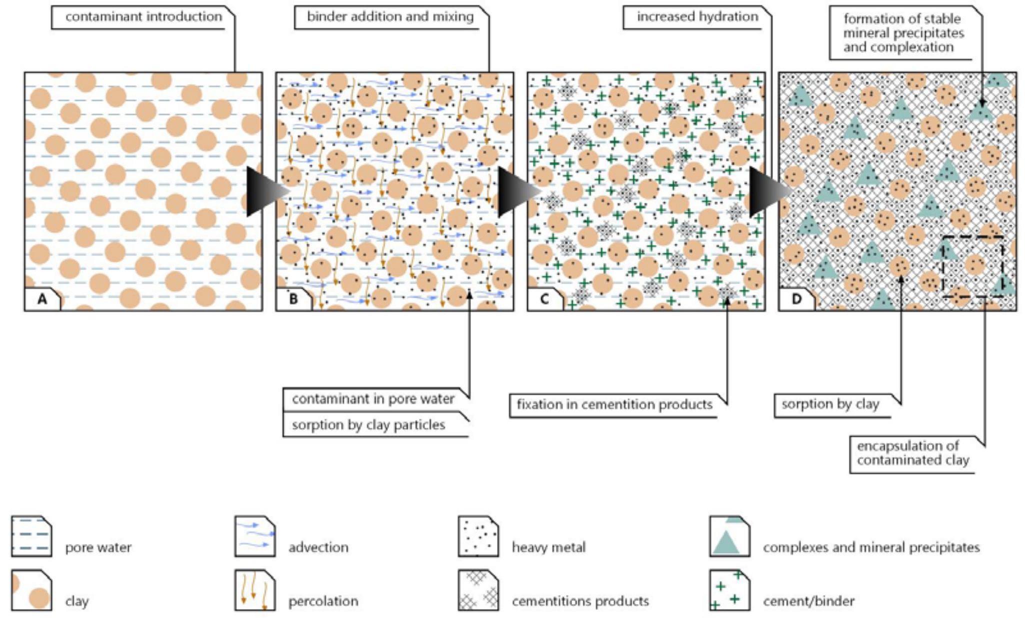

Figure 1:2: Stabilisation / solidification treatment, and changes with hydration

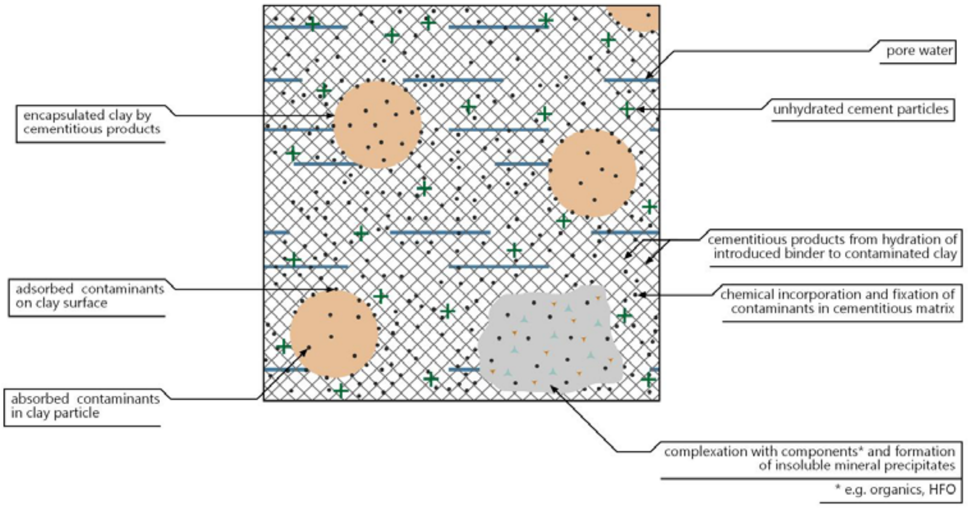

Figure 1:3: Contaminant containment mechanisms, within the stabilised material

1.3 RESEARCH PHILOSOPHY

S/S with cement is relatively common, due to the universal availability, desirable hydration properties, suitability for heavy metal immobilisation, and ready adaptability of hydraulic cements (Conner, 1990). S/S is particularly suitable for heavy metal remediation, and has been applied extensively over several decades, especially in the US. However, the interactions that induce immobilisation are not fully understood by the engineers who utilise the technique, which has limited the ability to evaluate and predict long-term effectiveness and durability. Considering that contamination are not removed, but rather immobilised, this evaluation and certification is necessary as part of design. This has limited acceptance in some countries, particularly from regulators, who fear that the method is not permanent, and will degrade over time and release contaminants (Nathaniel and Bardos, 2004).

Current assessment methods and tools do not fully characterise treated soils during S/S treatment to inform design, and emphasis has more traditionally been on the physical properties of the stabilised material. Various chemical processes occur during S/S, which induce contaminant containment, and these reactions and interactions are influenced by equilibrium within the pH domain. These chemical properties are more influential in determining contaminant containment and releases, and information from equilibrium properties and disequilibrium chemical kinetics will inform design, on actual containment properties and mechanics.

Leaching tests have been designed to address releases due to these constraints, and harmonisation of these tests has been undertaken, to tailor suites suitable for complete chemical characterisation of materials. These studies have mostly been applied for waste and treated waste characterisation, to evaluate environmental impact. However, given the similarities in chemical properties and prevailing kinetics, they can be adapted for use in evaluating contaminated soils, and S/S treated contaminated soils. Inherent heterogeneity of these materials makes the process complex, hence to understand the evaluation and assessment process, least complex materials are required, and then translated for application for contaminated land treatment.

1.4 HYPOTHESIS, AIMS AND OBJECTIVES

The aim of this study is to assess cement stabilisation / solidification treatment of heavy metal contaminated clay, to evaluate effectiveness, time dependent performance and chemical durability of the material. As part of the process, risk based assessments will be adopted, to allow risk based engineering approaches, during holistic S/S system designs.

To achieve this aim, the following objectives will be achieved:

- Design and adopt a suite of leaching tests and effective assessment method suitable for assessing releases from stabilised clay, based on the prevailing release controlling mechanisms.
- Assess the leachability of structural master species (aluminium and silicon) for stabilised kaolin clay, and introduced calcium from stabilising agent – CEM II Portland limestone cement.
- Assess the containment and leachability of two heavy metal ion contaminants (zinc as Zn^{2+} and chromium and Cr^{3+}) from the stabilised kaolin clay.
- Evaluate the implications of soil components (humic acid and sulphate) as additives, on the contaminant containment, and stability of the stabilised clay.

- Investigate the soluble chemistry during leaching of the stabilised clay, and chemically characterise the stabilised matrices, at different hydration periods, to evaluate changes in leachabilities with increasing hydration.
- Undertake geochemical speciation modelling using the leaching expert system LeachXS, embedded with the speciation modelling tool ORCHESTRA, to evaluate the solubility controlling mineral phases for component releases.
- Draw the findings together, for use in overall assessment during S/S design.

The hypothesis for the current study is that effectiveness, long-term performance and chemical durability of stabilisation / solidification treated clays can be evaluated using leaching assessments and speciation modelling, using information from a limited number of carefully selected leaching tests.

1.5 CONTRIBUTIONS TO KNOWLEDGE

This study generated a number of findings, which can be applied towards improving S/S assessments and informing performance-based site remediation designs. Some of these contributions include:

- Designed and adopted effective leaching assessment and evaluation methods and tools, as a means for stabilised material characterisation to inform design.
- Showed the suitability and effectiveness of geochemical speciation modelling as tool for predicting component releases from S/S treated materials, and predicting the solubility controlling mineral phases.
- Demonstrated the need to increase design emphasis on chemical characterisation, showing that these control component releases to greater degrees than variations in physical properties for the stabilised materials.

- Highlighted shortcomings in available assessment tools, proffering recommendations for increasing the resultant database to accommodate the variety of minerals encountered in soils. These included information on leaching trends for zinc, where amphoterism was not observed with pH leaching due to complexation.

1.6 THESIS OUTLINE

To effectively evaluate S/S treatment, and evaluate containment and releases of components, detailed investigations of current research trends and a robust experimental design were required. This thesis is divided into 9 chapters, where Chapter 1 introduces the scope for work undertaken. Chapter 2 presents a review of literature on land contamination, assessing contaminants and contaminant properties. Clays and clay properties are then evaluated, along with the interactions between clays and contaminants. Chapter 3 presents a review on stabilisation / solidification, reviewing interactions between clay – contaminants – binders, stabilisation of contaminants, S/S applications and evaluations, long-term performance and durability, and reviews a case study on evaluation of long-term performance for in-situ S/S application on a contaminated site.

Chapter 4 details the laboratory experimental methodology, covering material characterisation, sample preparation, and the extractions and leaching tests undertaken. Details of materials and analytical techniques used are also presented here. Chapter 5 presents the rationale and methodology for undertaking chemical leaching assessments and speciation modelling. The modelling and assessment tools are described here, including details on requirements and operations.

Results from laboratory experiments are presented in Chapter 6, which is followed by results for the leaching assessments and speciation modelling, which are presented in

Chapter 7. Experimental results, leaching assessments, and speciation results are discussed in Chapter 8, which are followed by conclusions in Chapter 9.

CHAPTER TWO

2.0 REVIEW OF BACKGROUND LITERATURE

2.1 LAND CONTAMINATION

Land contamination describes areas with elevated concentrations (above normal background levels) of substances, which may have arisen from previous land use. Key questions in assessing contaminated land include:

1. Does the contamination matter?
2. What needs to be done about it?

The answers depend on type and extent of contamination, and proposed land use. Contaminated land evaluations are based on assessments of risks posed by contamination, and action is determined based on the degree of risk (Environment Agency, 2004, Nathanail and Bardos, 2004). Criteria for land classification as contaminated are given in Part IIA of Environment protection Act (OPSI, 1990), based on significant risk to human and environmental health. For risk to be significant, there must be contamination linkage using Hazard – Pathway – Receptor model, and risk assessment allows for site specific evaluations to proffer appropriate solutions (Environment Agency, 2004).

The Contaminated Land Regulations (OPSI, 2006), and Environmental Damage (Prevention and Remediation) Regulations (OPSI, 2009) which transposed requirements of the EU Environmental Liabilities Directive (DEFRA, 2006a) to UK law, require remediation where risk is unacceptable to human health and the environment. These legislation, changes to the landfill directives (OPSI, 2005), and changes in landfill taxation (OPSI, 2009b), have resulted in a shift from previously convenient excavation and landfill disposal practices. These regulations and changes make it less economical to dispose large quantities of contaminated soils and wastes to landfill, requiring that alternative economical and sustainable options are sought. UK government targets of undertaking construction of 60% of about 2.4 million new homes by 2016 on Brownfield sites (Harbottle *et al.,* 2007) are therefore likely to require extensive in-situ process based remedial techniques.

The Contaminated Land Regulations give legal criteria for designation of special sites (Bone *et al.,* 2004a), and remediation notices can be issued on the Environmental Protection Act and Environmental Damage Regulations (DEFRA, 2006, OPSI, 2009a).

2.2 CONTAMINANTS

Contaminants are substances that are on, in or under the ground, and which have potential to cause harm, and or pollution to specific receptors (British Standards Institution, 2001). Contaminants can be broadly categorised into Organic and Inorganic contaminants, and include naturally enhanced concentrations of potentially harmful substances and those from anthropogenic activities. A review of potential contaminants for assessment of land in the UK was published by DEFRA and Environment Agency (2002), providing selection of key contaminants in view of potential human and environmental receptors. The source and nature of contaminants in the environment are variable, generated by a wide range of industries with a range of waste streams.

2.2.1 Organic Contaminants

Organic contaminants are carbon based, and could be natural or anthropogenic in existence. Their presence in wasteforms may be as a single contaminant associated with inorganic contaminants, or a suite of complex mixtures which may be toxic at very low concentrations. Organics of greatest environmental concern are usually refined petroleum products, chlorinated and non-chlorinated solvents, manufactured biocides, organic sludges and substances from manufacturing processes. Most contamination due to organics are associated with accidental spills and leaks, originating from equipment cleaning, maintenance, storage tanks, residue from used containers and outdated material (Bone *et al.,* 2004b, Yong and Mulligan, 2003). Transport and fate of organic contaminants are important, and models are used to assess migration plumes based on the target goals of the developer. Organic contamination migrations are due to advection (by fluid flow through soil) and diffusion, but other forms of transport e.g. infiltration may also contribute to migration (Environment Agency, 2002).

2.2.2 Inorganic Contaminants

Inorganic contaminants are non-carbon based, dominated by heavy metals and metalloids, which are often toxic and can bioaccumulate. Their cations tend to be strongly sorbed onto organic matter and clays, which can reduce their mobility, but the formation of metal-organic complexes[1] may increase mobility (Bone *et al.,* 2004b, Yong and Mulligan, 2003). Complexes are important in determining and controlling toxicity, bioavailability and solubility of cations, and some elements like iron and lead occur more often in solution as complexes rather than free ions (Langmuir, 1997). Typically, inorganic heavy metal contaminants in soils and waste are relatively immobile when present in native form, as large particles e.g. slag, in low solubility phases such as silicates, and where sorbed by clay minerals, immobile organic matter or hydrous ferric oxides (HFO) coating. Metals in relatively mobile phases are present as free aquo ions, complexed with inorganic ligands

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[1] A complex is a dissolved species that exists because of association of a cation and an anion or neutral molecule (Ligand). A ligand is an anion or neutral molecule that can combine with a cation to form a complex (Langmuir, 1997)

like chlorides, and complexed with soluble organics like humic and fulvic acids (Jared West *et al.,* 1999). Principal mechanisms involved in heavy metal adsorption and retention include ion exchange, precipitation and complexation reactions. Complexation is the processes by which substances are converted to other substances, with constituents that are more intimately associated than those in simple mixtures (US EPA, 1993).

MacDonald (1994) investigated the precipitation of heavy metals in aqueous solution, and indicated that the pH at which metals transmit from soluble form to precipitate forms varied for the different metals investigated. It was also discovered that the presence of other heavy metals in solution affected the precipitation behaviour of individual metals and their salts. For contaminated land, availability and mobility of inorganic contaminants are largely dependent on how they are bonded with the various soil fractions (Yong, 1999). Other influencing factors include; hydrogeological setting, system pH (acidity / alkalinity), ionic strength, Eh (oxidation / reduction potential) and formations of complexes (Yong and Mulligan, 2003). The chemical form (speciation) of these components, ultimately determines their behaviour in the environment. Knowledge of speciation for metals is required in order to assess the risk from existing contamination. Speciation will depend on the original chemical form, most thermodynamically stable form, and local environmental factors influencing equilibrium (Jared West *et al.,* 1999).

Properties of contaminants relevant to S/S are discussed in detail by Bone *et al.* (2004b) in terms of influencing contaminants partitioning between solid, liquid and gaseous components of soils. Some properties of contaminants, relevant for S/S include solubility, volatility and miscibility in water. Focus of the current study will be on inorganic contaminants, in view of the scope and aim of research undertaken.

2.3 SOILS

'Soil' means different things to different people, depending on the usage, i.e. for agricultural purposes, mineral processing or construction of the built environment. Wild (1993) defines soil as loose material composed of weathered rock and other minerals, as well as partly decayed organic matter. It is essentially a natural body of mineral and organic constituents, produced by solid material recycling during a myriad of complex weathering (physical / mechanical, chemical and biological) processes of crustal material closely related to the hydrological cycle (Mirsal, 2004). Soils cover most of the Earth's land surface, varying in depth from a few centimetres to several, varying in type based on composition, depending on sand, silt, clay, organic matter, water and air content. The main components of soil solids are shown in Figure 2.1 (Yong *et al.,* 1996).

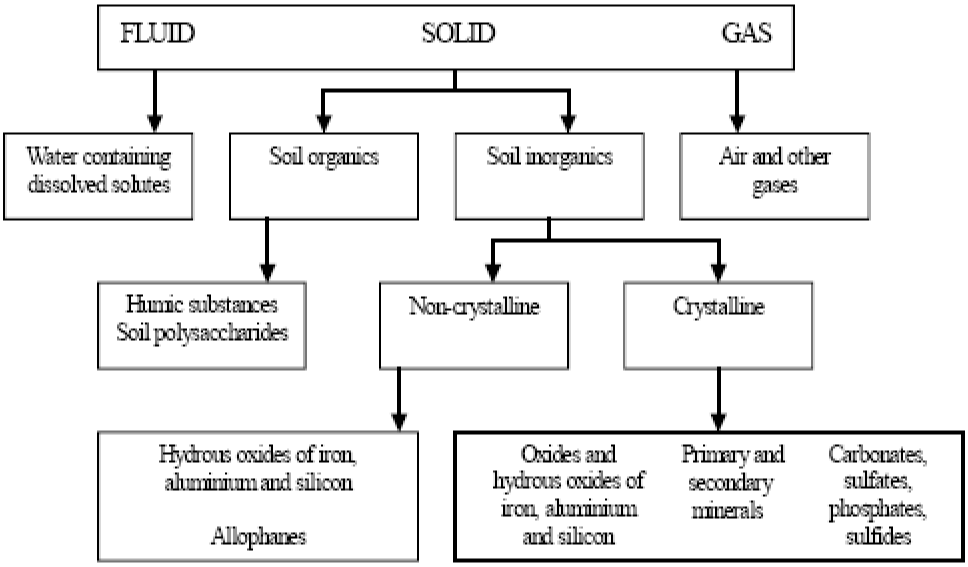

Figure 2:1: Soil constituent, showing the main composition of the soil solids (Yong *et al.,* 1996)

Interactions between soil particles and contaminants occur through three major processes: sorption, complexation, and precipitation. In this context, sorption describes the partitioning of solutes between the liquid phase and the solid particle interface, and could be through physical or chemical adsorption (ion adhesion to soil surface). Transition and alkaline earth metals can be complexed by inorganic ligands, and these complexes are much weaker compared to those formed with organic ligands. Precipitation is a key mechanism for metal retention in soils, and the solute concentration, together with soil and porewater pH are important controlling factors (Yong *et al.*, 1996, Bone *et al.*, 2004b).

Soils can retard leachate[2] flow, and chemically attenuate contaminant transport through various sorption processes. The most suitable soils are those with high cation exchange capacity (CEC), large specific surface area (SSA) and high chemical buffering capacity. Yong *et al.* (2001) used selective sequential extraction to assess the retention mechanism of heavy metals in soil solids, and found them to rank in the following order based on the surfaces: carbonates > amorphous > organic > ion exchangeable. Elzahabi and Yong (2001) also found that moisture content, wetting time, pH and heavy metal concentration were important factors that could control sorption characteristics in soils. They also found that the presence of carbonates and high soil pH increased metal retention, providing the soil had buffering capacity to acid attack.

Physical properties of soils are important in influencing their engineering behaviour and attenuation of contaminants. Physical properties relevant for remediation include: particle size; plasticity (property of fine soils, granular soils that contain sufficient fines to show plasticity are classified as fine soils) (BS 5930, 1999); moisture content; permeability (determined using constant and falling head methods or in a cell under known stress conditions) (BS 1377, 1990); strength – ability of the soil to withstand stress (normal and / or shear stresses) without collapse or deformation; compaction; and other properties which includes shrinkage and swelling, frost heave and frost shattering, and temperature (Bone *et al.*, 2004b).

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[2] Liquid produced due to action of leaching

2.3.1 Chemical and Mineralogical Composition

With the exception of highly organic soils, most solid soil material is inorganic, derived from solid geological deposits, and composed of minerals which are divided into two groups: Primary minerals and Secondary minerals. Primary minerals are derived unaltered during physical weathering. They include quartz and feldspars, with particles of relatively low specific surface area, and considered inert with minimal chemical interactions (Yong *et al.,* 1996). Secondary minerals, however, are derived as altered products of physical, chemical and/or biological weathering processes. They include clays (layer silicates), which have small particles and large specific surface areas. This property combined with a surface charge make them important for contaminant attenuation (Yong *et al.,* 1996, Yong and Mulligan, 2003, Bone *et al.,* 2004b). Typical soil minerals include: clay minerals, carbonates, oxides and hydroxides, and sulphates. The soil organic matter is very important, as well as pH in view of contaminant attenuation and soil chemistry.

2.4 CLAYS

The term 'clay' refers to naturally occurring deposit, composed primarily of fine grained minerals, which is generally plastic at appropriate water contents, and will harden when fired or dried (Reeves *et al.,* 2006). Although clays usually contain phyllosilicates (group of silicate minerals with layered structure composed of shared octahedral and tetrahedral sheets), they also contain other materials such as organic matter which could impart plasticity. Associated phases in clay may include materials which do not impart plasticity, and clays (including shales) constitute over 50% of sedimentary deposits, which occupy over three quarters of the world's land surface.

2.4.1 Clay Mineralogy

Clay minerals are a group of hydrous aluminosilicates, which are characteristically found in the clay fraction of sediments and soils. They have similar structure to mica i.e. sheeted layer structures with strong intra and inter sheet bonding but weak inter layer bonding (Reeves *et al.,* 2006). The majority of clays have sheet silicate structures (Figure 2.2) which consist of "composite layer" sheets of tetrahedrally coordinated Si and Al, and octahedrally coordinated cations (principally Fe^{3+}, Fe^{2+}, Al, Mg). These composite layers are stalked together and linked by cations and/or water molecules in the interlayer sites. The basic units are one tetrahedron to one octahedron in a 1:1 layer silicate structure, or one octahedron to two tetrahedral in a 2:1 layer silicate. Clay minerals are usually stacked / linked laterally to form the structural building blocks of clays, and characterise the nature and properties of the minerals (Reeves *et al.,* 2006).

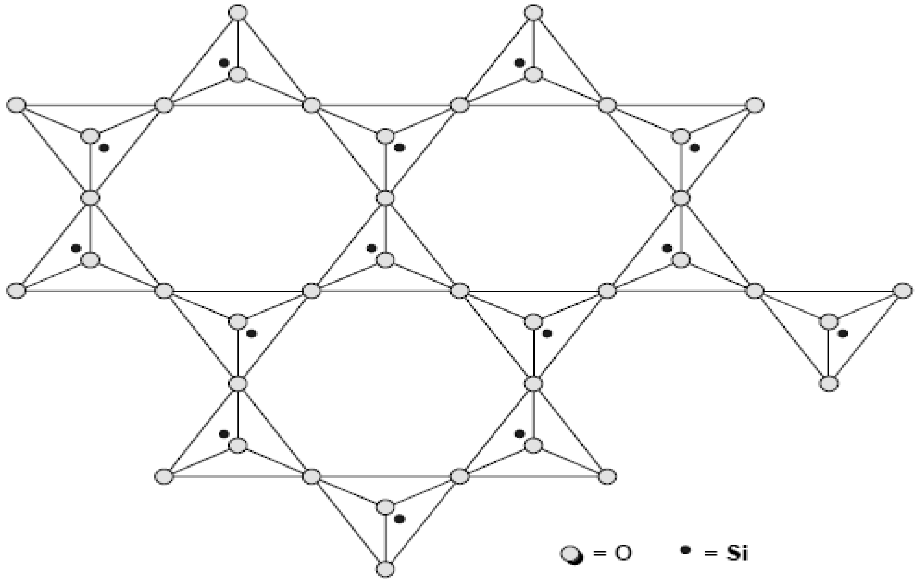

Figure 2:2: The Silica sheet (Ciullo, 1996)

Clay minerals are usually amorphous, and due to isomorphous substitution of Si and Al or dissociation of hydroxyl ions, carry a residual negative charge. This results in the attraction of cations from solution to the clay mineral surface, forming a double layer of tightly bound ions on the clay particle surface and a dispersed layer of cations (Reeves *et al.,* 2006). Clays have reactive surfaces, and carry surface charges at particle edges and broken bonds, with the nature of the charge being traceable to the structure of the layer lattice (Yong and Mulligan, 2003). Surface charges for clays are shown in Section 2.6.1. Clay mineral groups include:

- KAOLIN and SERPENTINE GROUP – The kaolin group are isometrical 1:1 layer silicates ($Al_4Si_4O_{10}\{OH\}_8$) but not isostructural. They have a dioctahedral structure with no net negative charge on the composite layer, and consequently no compensating interlayer cations or water layers (Reeves *et al.,* 2006). These clays are derived from the weathering of granites and alkali feldspars under acidic conditions, and lack structural cations except relatively insoluble Al and Si (Langmuir, 1997). Residual positive charge can occur on the edge of kaolinite in low pH environment, promoting edge-to-face attraction. These are non-swelling clays with an interlayer spacing of 7Å, though halloysite (kaolin mineral) contains one water layer in the interlayer sites producing 10Å interlayer spacing. Serpentine group of minerals are trioctahedral equivalents of Kaolin. The most important member of this group is Berthierine [$\{(Fe^{2+}, Mg)_{6-X} (Fe^{3+}, Al)_X Si_{4-X}) O_{16}(OH)_8$] (Reeves *et al.,* 2006, Mitchell and Soga, 2005).
- ILLITE – MICA GROUP – Illite is generally used to describe clay grade micas, and have a dioctahedral 2:1 composite layer structure. They are derived from weathering of silicates (including mica and alkali feldspars) under alkaline condition. They have a general formula of [$K_{1-1.5} Al_4(Si, Al)_8 O_{20}(OH)_4$] with a non-exchangeable cation of K with subordinate Na and Ca. Substitution of $[Si^{4+}]^{IV}$ by $[Al^{3+}]^{IV}$ and $[R^{3+}]^{IV}$ by $[R^{2+}]^{IV}$ produces a net negative charge of 0.7 – 10meq per $O_{10}(OH)_2$ formula unit. K is the principal interlayer cation, and layers of water may also be present. Illites are non-

swelling, but are often present as mixed-layers with montmorillonite and/or chlorite (described later). Typical minerals include; Sericite, Glauconite, illite and muscovite.

- SMECTITE (Montmorillonite) GROUP – These have a similar basic structure to illites i.e. 2:1 layer silicates, but with partial replacement of Al by Mg in the octahedron with water and exchangeable ions occupying the space between combined sheets. Smectites are most commonly dioctahedral, but trioctahedral varieties exist. They have an interlayer charge of 0.2 – 0.6meq per $O_{10}(OH)_2$ unit of structure, which is offset by hydrated interlayer cations, principally Na and Ca. The hydration of the interlayer cations causes the interlayer crystalline swelling that characterises smectites. Smectites have a general formula of $[M\ \frac{2}{3}(X,Y)_{4-6}\ (Si, Al)O_{20}\ (OH)_4.nH_2O]$, where M = Na or ½ Ca, X = Al or Fe^{3+}, Y= Mg or Fe^{2+}.
- VERMICULITE GROUP – These have a similar structure to smectites, but have Mg as the principal interlayer cation, and higher negative charge on the composite layer of 0.6 – 0.8meq per $O_{10}(OH)_2$. They are products of alteration in biotite mica by removal of K in the interlayer. They exhibit similar swelling to smectites, but to lesser degree due to higher layer charge. They are trioctahedral with general formula of $Mg^{(x-y)}/_2\ (Mg, Fe^{2+})_{3-5}\ (Al, Fe^{3+})Y\ (Si_{4-X}\ Al_X)\ O_{10}\ (OH)_X.nH_2O$.
- CHLORITE GROUP – These consist of a heterogeneous group of layer silicates with general formula $[(Mg, Fe)_{10}\ Al2(Si, Al)_8\ O_2\ (OH, F)_{16}]$. They have a 2:1 structure type, with a second octahedral layer in the interlayer sites having a net positive charge to offset the net negative charge on the 2:1 layer. Majority of chlorites are trioctahedral, but some dioctahedral and mixed dioctahedral 2:1 layer – trioctahedral (interlayer) forms are known. They are common products of alteration from ferromagnesian minerals, and may be present as mixed layer clays with Illite and Montmorillonite (Reeves *et al.*, 2006, Mitchell and Soga, 2005).

2.4.2 Clay Properties

Clay minerals can exhibit swelling properties due to sorption of water onto their surface or into their interlayer sites. However, not all clays exhibit this behaviour, resulting in a broad classification of clays into swelling and non-swelling varieties. Swelling clays include smectites and vermiculites, while non-swelling clays include kaolin, illites and chlorites. Illites may include water lenses in the interlayer site and halloysite contains a water layer, but are not classed as swelling clays. All clay minerals can show inter-particle swelling, governed by similar factors to intra-particle swelling. Inter particle associations of clay control their flocculation and dispersion properties (Reeves *et al.,* 2006).

Clays also exhibit ion exchange properties, especially 2:1 clay minerals, which have a net negative charge on the composite layer due to cation substitution (e.g. Al^{3+} for Si^{4+}; Fe^{2+} for Al^{3+}, Fe^{3+}). In smectites and illites the net negative charge is offset by interlayer cations, and in chlorites, by the inter-layer octahedral sheet. Kaolin ideally has neutral composite layer structure, but in reality, limited cation substitution may occur, producing a very small net negative charge on the composite layer offset by a small number of interlayer cations (Reeves *et al.,* 2006). Broken bond edge sites which may be positively or negatively charged are produced on the edge of the clay particles, due to disruption of the clay structure. The nature of the clay is determined by the presence of certain ions, notably H^+, OH^-, Al^{3+} and AlO_4^{5-}, with presence dependent on pH. This results in being negatively charged in alkaline solutions, and being positively charged in acidic solution. The pH dependent charge accounts for only a small percentage of the total charge in Illites and Smectites, but are more significant for Kaolins and Chlorites. It is also possible to have anion exchange but usually to a lesser extent than cation exchange (Reeves *et al.,* 2006). More detail on ion exchange is included in Section 2.6.1.

2.5 CLAY – WATER INTERACTIONS

Water and soil particles are not chemically inert, and react with each other due to a strong attraction of water molecules and sorption onto the surface of the soil particle, and these interactions influence the physical and physicochemical behaviour of the mixture (Mitchell and Soga, 2005). Clays are considered to be hydrophobic or lyophobic (fluid halting) colloids, even though water wets clays and is adsorbed on the particle surface (Mitchell and Soga, 2005). Colloids characteristically have large surface areas and a strong tendency to adsorb other material. They also exhibit Brownian movement (constant motion of particles suspended in water when viewed under a microscope) in a completely unpredictable fashion (Steedman *et al.,* 1980). Hydrophobic colloids are two-phase systems with behaviour dominated by surface forces, and can flocculate in the presence of small amounts of salts. Two particles in close proximity exhibit respective force fields which overlap and influence the behaviour of the system if the magnitude of the forces exceeds the weight of the particles (Figure 2.3). Clay particles are small and platy with a large surface area, and are especially influenced by these forces (Shaw, 1992). During mixing with water, clay can form spherical peds[3] separated from each other along zones of weakness which can result in increased pore spaces and permeability (Mirsal, 2004).

Due to the uneven charge distribution and dipolar characteristics of water molecules, they are attracted to ions in solution leading to ion hydration, where positive ions attract negative corners of water molecules and vice versa (Mitchell and Soga, 2005). Possible mechanisms for soil - water interactions include: hydrogen bonding, hydration of exchangeable cations, osmotic attraction, charged surface – dipole attraction, and attraction by Van Der Waals force. Mitchell and Soga (2005) indicate that water held in clays have different thermodynamic, hydrodynamic and spectroscopic properties. However, there is

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[3] individual units of soil aggregates, with clay or humus holding the particles together

no evidence of abnormal viscosity or failure of Darcy's law in clays of the type usually encountered in geotechnical practice. The viscosity and diffusion properties are for 'practical' purposes the same as those for pure water (Mitchell and Soga, 2005).

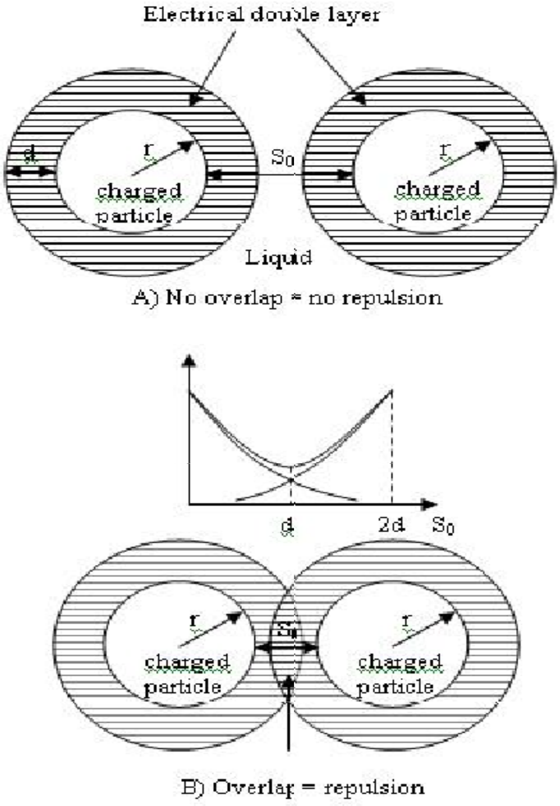


Figure 2:3: Overlapping Charged Particles (University of Washington, 2000)

Most surfaces acquire an electric charge when exposed to a polar medium, which could be due to ionisation, ion adsorption or ion dissociation. The surface charge influences the distribution of nearby ions in the medium, with counter-ions being attracted to the surface, and co-ions being repelled. This in collaboration with thermal motion leads to the formation of the Electric Double Layer (Shaw, 1992). Yong and Mulligan (2003) state that understanding the nature and mechanism of interactions between soil particles and electrolyte in water will give an indication of how reactive surfaces of the soils react with chemical properties of the water in the soil pores. Isomorphous substitution of the ions in the tetrahedral and octahedral layers of clays by lower valency ions result in the development of electric charges on the siloxane surfaces, and electric charges can also be developed on the edges of clay particles. The nature and magnitude of the charge is dependent on the basic structure of the clay, and the pH of the immediate surrounding (Yong and Mulligan, 2003). When the sum of negative charges is equal to the sum of positive charges, then the 'point of zero charge' (pzc) is attained. In clays like Kaolinite, 'charge reversal' (situation where net charge on a particle switches from positive to negative and vice versa) can occur as the clay progresses from a pH system below the pzc to one above the pzc. The 'Isoelectric Point' (IEP) is the pH at which the electric potential developed at the solid – liquid interface, as a result of movement of colloidal particles in one direction and counter-ions in the opposite direction becomes zero. At this point, a balance between positive and repulsive energies can be attained. Kaolinite particles in water have a positive charge below pH of 4.1, pzc between pH 4.1 and 4.2, and negative charge (which can vary with degree of order) above pH 4.2 (Yong and Mulligan, 2003).

2.5.1 Diffuse Double Layer

Though there is a minor difference in details concerning the type and distribution of the various ions adjacent to the reactive surface, there is a general agreement on the altered or structured water layer adjacent to the reactive surface, and swarm of counter-ions forming a diffuse layer of ions (Yong and Mulligan, 2003, Mitchell and Soga, 2005). Dry clays have adsorbed cations held tightly by negatively charged clay particles, with excess cations needed to neutralise the electro negativity of the clay particles and associated anions present as precipitated salts. When clay is placed in water the precipitated salts go into solution, adsorbed cations produce higher concentration near the particle surface, and try to diffuse away in order to equalise concentrations. However, the freedom to do this is restricted by the negative electrical field originating on particle surface, and this charged surface and adjacent phase of distributed ions make up the "Diffuse Double Layer" (Mitchell and Soga, 2005).

Due to the thermal motion of water molecules, the layer of counter-ions is diffuse, with the concentration of counter-ions decaying exponentially away from the surface. Since overall charge within the solution must be maintained, net charge on the surface is balanced by net charge in the diffuse layer. The electric double layer is then essentially the arrangement of the charge on the colloidal surface, and the counter-ions in the diffuse layer. To account for the finite volume of counter-ions, a Stern layer is introduced to the diffuse layer, which can be subdivided into the inner and outer Helmholtz planes (IHP and OHP), resulting in separation the diffuse layer from the surface of the colloid by the stationary layers of dehydrated and hydrated ions (Figure 2.4) (Snoswell, 2003).

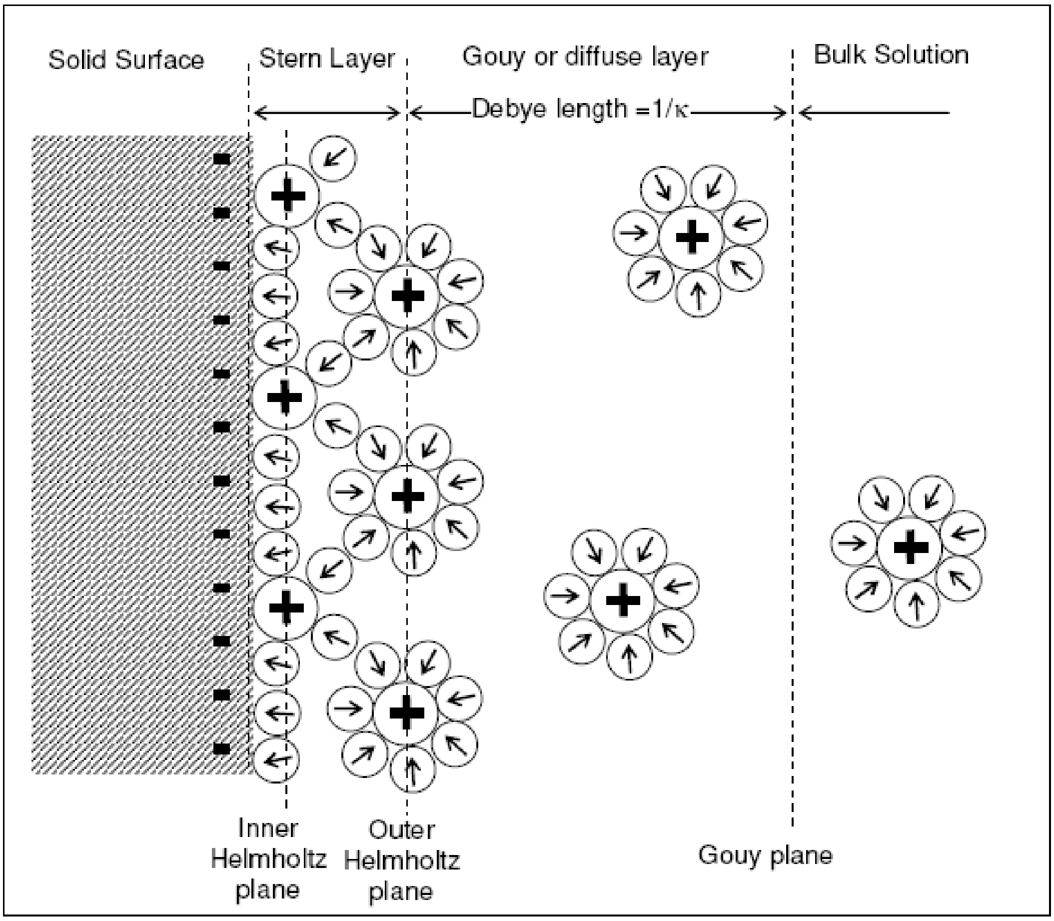


Figure 2:4: Diagrammatic representation of the Electric Double layer (Snoswell, 2003)

2.5.1.1 Inner Part of the Double Layer

Evaluation of the Gouy – Chapman diffuse double layer is based on assumption of point charges in the electrolyte medium. The finite size of the ions will limit the inner boundary of the diffuse part of the double layer, since the centre of an ion can only approach the surface of the clay particle to within its hydration radius without being specifically adsorbed. Stern proposed a model in which the double layer is divided into two parts, separated by a plane (the Stern plane) located at about one hydration ion radius from the surface and also considered the possibility of specific ion adsorption (Shaw, 1992). Specifically adsorbed ions are those attached to the surface by electrostatic and/or Van Der Waals forces, strong enough to overcome thermal agitation. These may be dehydrated and have their centres located in the Stern layer (between the surface and the Stern plane). Ions with centres beyond the Stern plane form the diffuse part of the double layer (Shaw, 1992).

The surface charge σ_o associated with the surface of the particle is balanced by the sum of the Stern layer charge σ_d at the OHP, and the diffuse layer charge σ_{ddl}. The surface potential ψ_o, which is associated with the surface of the particle, varies with the electrolyte concentration and the nature of the charge on the clay particle (Yong and Mulligan 2003). The potential drops from ψ_o at the surface to ψ_i at the IHP, and then changes to ψ_d at the OHP (Figure 2.5) (Yong and Mulligan, 2003, Schoch *et al.,* 2005). Beyond the OHP, the potential ψ is described by the Gouy – Chapman diffuse double layer model. ψ_d is considered to be equal (or almost equal) to the zeta potential ξ, from the view point of electrokinetics (Yong and Mulligan, 2003). The zeta potential (ξ) of a surface is the value of the position dependent electric potential within the space charge region at the plane of shear (location near the surface of the solid, where velocity deviates from zero, where there is flow of liquid in the vicinity of the solid surface). In other words, zeta potential is the electric potential at the plane of shear (Carnegie Mellon University, 2007). Quantitative treatment of the electric double layer is extremely difficult, and in some respects unsolved. The Gouy - Chapman model presents the simplest quantitative treatment of the diffuse double layer, though with severe limitations (Shaw, 1992).

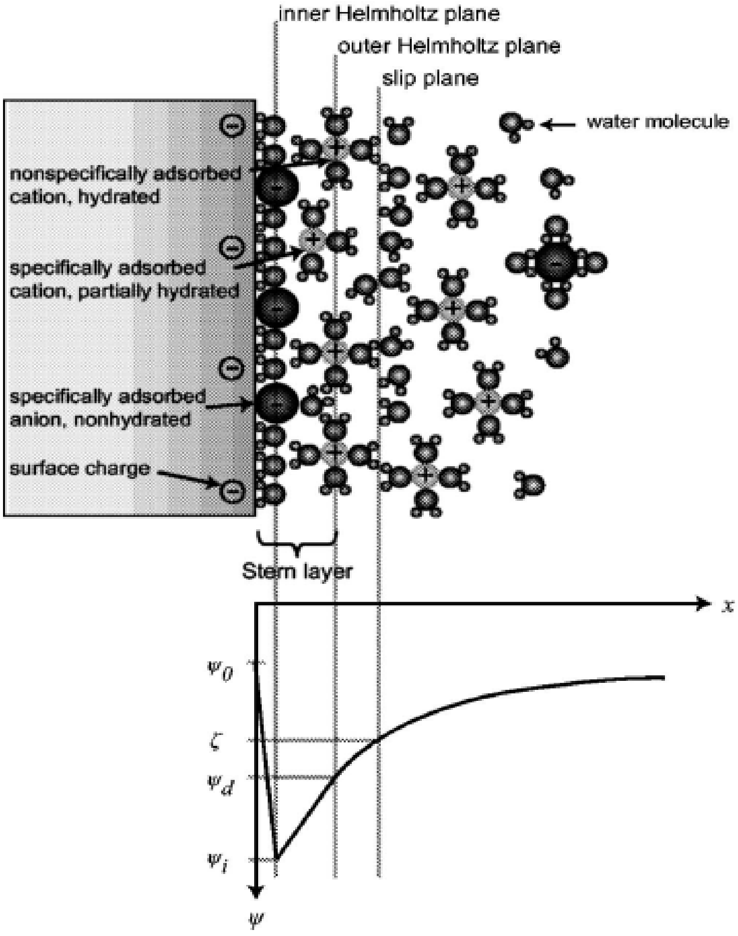


Figure 2:5: Electric potentials in the double layer (Schoch *et al.,* 2005)

ζ – Zeta potential

ψ – Electric potential

ψ_d – Potential at Outer Helmholtz Plane

ψ_0 – Surface potential

ψ_i – Potential at Inner Helmholtz Plane

2.5.1.2 Diffuse Part of the Double Layer

The Gouy - Chapman theory is the most widely accepted model and has received the most attention for the electric diffuse double layer, although the theory has been shown to accurately describe actual distribution of ions only for smectite particles at low concentrations (< 100mol/m^3) (Mitchell and Soga, 2005). It however provides useful basis for understanding flocculation and deflocculation, and relationships of these processes to the formation of structure and aspects of clay compression and swelling. Mathematical description of the diffuse double layer has been developed for both planar and spherical surfaces, and the procedures for calculations are detailed in Mitchell and Soga (2005).

2.5.1.3 Effects of System Variables on the Double Layer

- Effect of electrolyte concentration – Increase in electrolyte concentration results in reduced surface potential and rapid decay in potential with distance from surface.
- Effect of cation valency – Changes in cation valency affects surface potential and thickness of the double layer, for solutions of same molarity and constant charge.
- Effect of dielectric constant – The dielectric constant influences surface potential and thickness of the double layer, especially for clays in contact with contaminants, where porewater may be replaced by oils, solvents and organics.
- Effect of temperature – Increase in temperature will result in increase in the dielectric constant, but small variations in dielectric constant should not greatly influence the diffuse double layer. However, increase in temperature should increase thickness of the diffuse double layer and decrease surface potential for condition of constant surface charge, assuming all other factors remain constant.
- Additional factors: These include; size of ion, clay platelet associations and particle interference, and effect of pH (Mitchell and Soga, 2005).

2.6 CLAY – CONTAMINANT INTERACTIONS

Chemical reactions between contaminants and soils depend on the phase of the compound, speciation, mineralogy, pH and amount of organic matter present. These interactions and their variations with environmental conditions are important in determining contaminants fate and risk to human health and environment. The main reactions between contaminants, porewater and soils include: sorption, oxidation – reduction, precipitation, complexation, hydrolysis, and biological degradation (Bone *et al.,* 2004b). One major concern in contaminated land management is the partitioning of contaminants by chemical and physical mass transfer during contaminant transport in soils. Partitioning of contaminants by retention results from irreversible sorption by soil fractions, which prevents plume recharge and results in attenuation of the contaminant (Jared West *et al.,* 1999). Interactions between soils and organic or inorganic contaminants differ, and are discussed under cation exchange for inorganic contaminants, and clay – organic interactions for organics.

2.6.1 Inorganic Interactions and Cation Exchange

Ion exchange occurs between ions in the diffuse layer and surfaces of reactive soil particles due to charge imbalances. In clays, cation exchange occurs due to attraction of positive ions in porewater to negatively charged clay surfaces (Yong and Mulligan, 2003). Exchangeable cations are associated with charged sites of clay particles, and the quantity of exchangeable cations held by clay is called Cation Exchange Capacity (CEC) expressed in milliequivalents (meq) per 100g of soil. Table 2.1 adapted from Yong and Mulligan (2003) shows the CEC, Specific Surface Area, and the source of charge for different clays.

Table 2.1: Charge Characteristics, SSA and CEC of clays (Yong and Mulligan, 2003)

Soil Fraction	Cation Exchange Capacity (CEC), meq/100g	Total Surface Area (m^2/g)	Range of Charge (meq/100g)	Reciprocal of Charge Density (nm^2/charge)	Isomorphous Substitution	Source of Charge
Kaolinite	5 - 15	10 - 15	5 - 15	0.25	Dioctahedral: ⅔ of positions filled with Al	Surface silanol, edge silanol and aluminol groups. Ionisation of hydroxyls and broken
Clay Micas and Chlorite	10 - 40	70 - 90	20 - 40	0.5	Dioctahedral: Al for Si Trioctahedral or mixed Al for Mg	Silanol groups plus Isomorphous substitution and some broken bonds at edges
Illite	23 – 30	70 – 90	20 – 40	0.5	Usually octahedral substitution Al for Si	Isomorphous substitution, silanol groups and some edge contribution
Montmorillonite	80 - 100	800	80 – 100	1.0	Dioctahedral; Mg for Al	Primarily from Isomorphous substitution, with very little edge contribution
Vermiculite	100 – 150	700	100 – 150	1.0	Usually trioctahedral substitution Al for Si	Primarily from Isomorphous substitution, with very little edge contribution

The total number of charges on clay particles surfaces divided by total surface area of the particles involved provides a quantitative determination of the surface charge density, and the common procedure is to present this in terms of its reciprocal (Yong and Mulligan, 2003). Under set environmental conditions, clays will adsorb cations of specific type and amount, with the total adsorbed amount balancing the charge deficiency on the clay surface (Mitchell and Soga, 2005). Exchange reactions could be in response to changes in environmental conditions, and are also influenced by compositional factors, resulting in clays not having a fixed or single value for CEC. Clay CEC ranges from 1 – 150meq/100g, and represents the amount of readily exchangeable ions by leaching with a solution, containing other dissolved cations of higher replacing power (Mitchell and Soga, 2005). An exchangeable cation can be replaced by another of greater valency, and this mechanism plays a significant role in the heavy metal partitioning (Yong and Mulligan, 2003). The cation replaceability / lyotropic series (Mitchell and Soga, 2005) is given below in order of replacing power, and suggests that smaller cations tend to replace larger cations.

$Na^+ < Li^+ < K^+ < Rb^+ < Cs^+ < Mg^{2+} < Ca^{2+} < Ba^{2+} < Cu^{2+} < Al^{3+} < Fe^{3+} < Th^{4+}$

Ease of replaceability depends on valency, relative abundance of ion types, and ion size. However, it is possible to replace a cation of higher valency by another of lower valency e.g. Na^+ for Al^{3+} by mass action, as long as concentration of lower replacing power cation in solution is higher than that of the higher replacing cation (Mitchell and Soga, 2005). Exchange rates vary with clay type, depending on exchange sites, solution concentration, temperature, etc. In kaolin, exchange reaction may be almost instantaneous, illites may take few hours due to some exchange sites being located in between unit layers, and smectites take longer as most of the exchange sites are located in interlayer sites. Ion exchange reactions usually occur in an aqueous environment, but clays can adsorb ions from trace constituents that go into solution from rather insoluble substances (e.g. steel Shelby containers), even in the presence of very little moisture (Mitchell and Soga, 2005). Bischoff *et al.* (1970) discovered during investigation of interstitial water of marine sediments, that the selectivity of clay surfaces for different ions is temperature dependent. Fanning and Pilston (1971) also suggest that testing is carried under in-situ temperature, to ensure that representative values and properties are measured.

Most heavy metals become mobile at low pH, and sorption on clay particles becomes less effective. The presence of other components like oxides / hydroxides, carbonates and organic matter enhances retention. Changes in environmental conditions may alter clay retention capacities, but clay systems may exhibit dynamic mechanical and rheological behaviour, due to physicochemical changes of particle to changes in pore fluid characteristics (Ouhadi *et al.,* 2006).

2.6.2 Clay – Organic Interactions

Organics interact with clays by adsorption onto clay surfaces via hydrogen bonding, ion exchange, attraction of molecules to clay surface by Van der Waals force, and intercalation (Lagaly, 1984). Intercalation in this context is the entry of organic molecules between silicate layers, and is particularly important to kaolin minerals. Clay – organic interactions are important in geotechnical and geoenvironmental engineering, in view of contaminant migration, containment, clean-up, use of organics and polymers in S/S, and influence of organics on physical properties of soils (Mitchell and Soga, 2005). Adsorption of organics onto the clay particle surface depends on the availability of the surface, and ability of the organic molecule to displace water molecules. Cationic organics can exchange for inorganic adsorbed cations, but if the organic cation is larger than the cation site, all exchangeable cations cannot be displaced. Important properties of organics for interactions with clays include: Polarity, polarisability, solubility, size and shape (Mitchell and Soga, 2005).

Organically modified / organophilic clays can be used as adsorbents for organic compounds. Stockmeyer (1990) investigated the behaviour of organophilic bentonites in contact with aqueous solutions of organic compounds, and the findings give indications of factors affecting clay – organic interactions. Organophilic clays are formed by exchanging the original metallic counter-ions of natural clays with organic alkyl chain bearing cations, making the clay surface organophilic (Stockmeyer, 1990). This results in attraction of organic compounds to clay surfaces, and interlayering of these organic species in the organophilic interlamellar spaces. Ion – dipole interactions, dipole – dipole interactions and non – polar interactions are the main attracting forces between the adsorbate and adsorbent. Stockmeyer (1990) found that the adsorption of organics on organoclays depended on several factors. These factors include: type of interlayer cation and degree of organophilic exchange; equilibrium between adsorption on clay and desorption by water, which is controlled by the organophilic or hydrophilic character of adsorbent molecules; and the polarity of the adsorbate and ability for hydrogen bonding (Stockmeyer, 1990). Organophilic or organically modified clays are used for a variety of usages, which include the construction of barriers, liner systems, and in soil stabilisation.

After reviewing clay properties and contaminant interactions, the next requirement is assessing binder introduction and interactions which effect contaminant containment, and these will follow in Chapter 3.

CHAPTER THREE

3.1 SOIL STABILISATION / SOLIDIFICATION (S/S) PROCESSES

Land contamination presents great concern in the UK, and with growing environmental awareness and recent government legislation, there has been an increasing encouragement for utilisation of more sustainable and economical technologies in Brownfield redevelopment (Harbottle *et al.,* 2008). Destructive remediation approaches are useful in ameliorating unacceptable risk from organic contaminants, but cannot be applied for heavy metal remediation. Increased costs and changes in UK and EU environmental regulations have made disposal to landfill undesirable, promoting the use of process based in-situ approaches (Harbottle *et al.,* 2007). S/S provides a viable, relatively sustainable and economical option, which has been found to be particularly effective for amelioration of unacceptable risk from heavy metal contamination (Bone *et al.,* 2004b, Harbottle *et al.,* 2008). The technique has found extensive application in the US, being utilised over the last three decades (CL:AIRE, 2004), including use on 24% of source control remediation for the Superfund project (US EPA, 2004). However, previously low disposal costs for contaminated material to landfill, concerns over immobilisation rather removal, and uncertainties in assessing long-term effectiveness had limited its extensive utilisation in the UK (Al-Tabbaa *et al.,* 2005).

S/S was identified by DEFRA (2004) as the most suitable treatment process for wastes that were being landfilled. The technique modifies physical and chemical properties of contaminated material, with the broader objective being containment (Malviya and Chaudhary, 2006b). S/S relies on binders to chemically fixate or physically encapsulate contaminants within treated material, thereby converting toxic materials into more chemically and physically stable forms, to achieve desired properties (Connor, 1990).

Stabilisation (Fixation) involves reagent addition to produce more chemically stable constituents in contaminated soils, by chemical fixation into the matrix. Solidification (Encapsulation) involves reagent addition to impart physical stability to contaminated material, physically containing them in the matrix by cementation and reducing external influences (Bone *et al.,* 2004b).

However, the remedial approach is limited by inability to establish long-term effectiveness, performance and durability, especially for in-situ treated material. Limited data from treated sites of substantial age, and fears of litigation regarding remnant contamination further increased the problem. Short-term treatability studies (28 day hydration), without considerations of complex interactions and chemistries of treatment, do not inspire design confidence. It is important to understand containment, releases and fate of contaminants in S/S treated materials to inform predictions on long-term effectiveness, durability and performance. Having assessed soil and contaminant properties (Chapter 2), evaluation of interactions with binder addition to effect containment will be addressed in this Chapter, giving indications of modifications that induce containment. The most complete and holistic review on S/S to date was undertaken by Bone *et al.,* (2004b), hence most of the information presented here is derived from this publication.

3.2 BINDERS AND CLAY – BINDER INTERACTIONS

Binders are substances that cause components of a mixture to cohere, and for use in S/S are reagents added to impart physical, chemical or physicochemical stabilising effects on materials (Bone *et al.,* 2004b). Various binders are used in S/S applications, and these could be either primary or secondary stabilising agents. Appropriate selection of binders and operating parameters for S/S, depend on understanding the S/S processes and chemistry (Chen *et al.,* 2008).

3.2.1 Primary Stabilising Agents

These are reagents that can be used alone to induce required stabilisation action during S/S treatment. The uses of cement or pozzolans have been shown to provide the best treatment for reducing contaminant mobility in soils (Stegemann and Zhou, 2008). Some examples of primary stabilising agents include:

(1) Portland Cement: Typical composition of CaO (67%), SiO (22%), Al_2O_3 (5%), Fe_2O_3 (3%), and other components (<3%), and contains four major phases – Alite (C_3S), Belite (C_2S), Aluminate (C_3A) and Ferrite (C_4AF) (Bone *et al.,* 2004b). Detailed characterisation of the hydration process are discussed in Chen *et al.,* (2008), with relevance to implications for heavy metal immobilisation via S/S. 65% hydration is achieved after 28 days, with an excess of 90% after one year (Bone *et al.,* 2004b). The main mineral considered during hydration is colloidal calcium silicate hydrate (CSH), and mechanisms for formation from tricalcium and dicalcium silicates have strong implications on S/S (Mollah *et al.,* 1995, Hills *et al.,* 1996). Cement hydration can be divided into four stages of overlapping reactions (Cocke and Mollah, 1993):

Stage 1: $C_3A + 3(CS) + 32H \rightarrow C_6ASH_{32}$

Stage 2: $2(C_3S) + 4H \rightarrow C_3S_2H_3 + 3CH$

$2(C_2S) + 4H \rightarrow C_3S_2H_3 + CH$

Stage 3: $3(C_3A) + CH + 12H \rightarrow C_4AH_{13}$

$C_4AF + 4CH + 22H \rightarrow C_4AH_{14} + C_4FH_{13}$

Stage 4: $2(C_3A) + C_6ASH_{32} + 4H \rightarrow 3(C_6ASH_{12})$

Reaction products of C_3S and C_2S are CSH and Portlandite (CH), while C_3A and C_4AF hydrate to ettringite where excess sulphate is available, with C_4AF having higher iron content (Cocke, 1990, Bone *et al.,* 2004b). During hydration, CSH formation is accompanied by pH increase up to 12 – 13, and hydroxides react with silica derived from clays for production of a gel phase which cements the soil matrix. Kamruzzaman *et al.* (2006) investigated the microstructure of Singapore marine clay (composed of kaolinite and illite) treated with Portland cement, using x-ray diffraction (XRD), Scanning Electron microscopy (SEM), Mercury Intrusion Porosimeter, and laser diffractometer. Obtained results showed that kaolinite content decreases in treated soil with increasing hydration, suggesting that it is exhausted by pozzolanic reaction. The findings also suggest that Illites are less involved in the pozzolanic reaction, confirming previous suggestions by Porbaha *et al.* (2000). Kaolin which is stable under acidic conditions becomes destroyed by loss of silica under induced alkalinity, becoming unstable relative to gibbsite (Langmuir, 1997), with released silica being used up for formation of cementitious products. Bell (1996) also suggests formation of cementitious minerals with aluminium. Rapid increase in formation of cementitious products at lower cement contents was also observed (Figure 3.1).

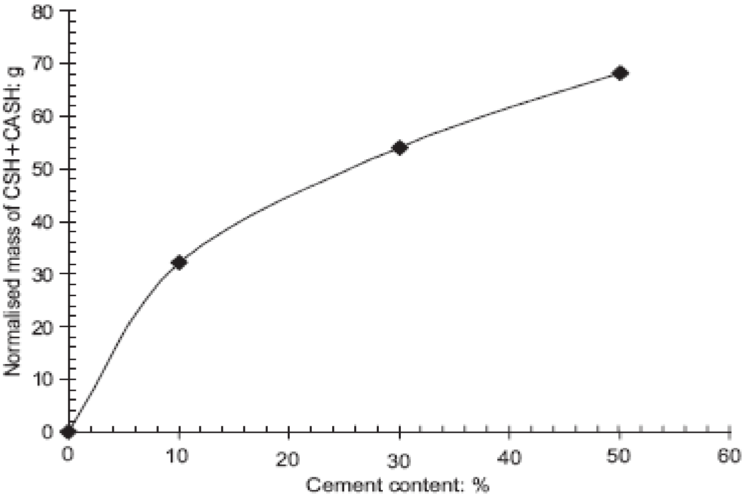


Figure 3:1: Mass of CSH + CASH versus cement content (Kamruzzaman *et al.*, 2006)

Interactions between soil and cement are not thought to be detrimental, though in some cases stiffening of the mix may occur (Bone *et al.*, 2004b). Presence of heavy metals are largely considered to be hydration inhibitors (Chen *et al.*, 2008), and these interactions are discussed in Section 3.4. Organics in soils may affect cementation processes, retarding hydration and formation of hydration products. They retard hydration by forming a protective layer around cement grains, inhibiting the formation of calcium hydroxide (Montgomery *et al.,* 1991, Natali Sora *et al.,* 2002). Clays can sorb organics, which may be problematic for hydration during S/S, and these organics also immobilise contaminants that can become released with pH modification during S/S (Bone *et al.,* 2004b).

(2) Lime: Widely used in the UK for S/S of contaminated soils (Sherwood, 1993, Reid and Brookes, 1999). Interactions with soils are similar to that of cement, but cement has lower free lime content. Interactions are two staged, and the first involves reaction of lime with water within a time scale of minutes to hours. The reaction is exothermic, and in some cases quicklime (CaO) is added to soils purely as a dewatering agent. The second stage of reaction involves solidification, and is as a result of pozzolanic reactions, occurring over days and weeks (Glendenning and Boardman, 1996, Bone *et al.,* 2004b, Rogers *et al.,* 2006). Pozzolans are material capable of reacting in the presence of water at ordinary temperatures to form cementitious compounds (Sherwood, 1993). Addition of lime to clay will result in a pH increase over 12.5, which promote silica and alumina dissolution, producing a water insoluble gel that cements the soil particles (McKinley *et al.,* 2001, Bone *et al.,* 2004b, Rogers *et al*., 2006).

3.2.2 Secondary Stabilising Agents

These stabilising agent are not effective as stand alone binders, but are useful when used in conjunction with lime or cement. They may require very little amount of cement or lime activators, and have numerous technical advantages such as reduced permeability and improved strength (Bone *et al.,* 2004b). Pollard *et al.* (1991) indicates that use of Portland cements and pozzolans results in improved durability, sulphate resistance, and obvious economic benefits. Research on use of wastes and by-products with pozzolanic properties in S/S include; spent oil-cracking catalysts (Wu *et al.,* 2003), rice husk (Yin *et al.,* 2006), phosphogypsum (Degiremenci *et al.,* 2007). Some Secondary stabilising agents include:

(1) Ground Granulated Blast furnace Slag (GGBS): By-products of iron manufacturing, trapped as a molten liquid (Bone *et al.,* 2004b). The slag is rapidly quenched in water, which optimises cementitious properties and produces granules similar to coarse sand. This granulated slag is dried and ground to fine powder. BS 6699 (1992) provide specifications for manufacture, and the physical and chemical properties of GGBS. GGBS reacts slowly with water, but this reaction increases drastically above pH 12, and both cement and lime are sufficiently alkaline to activate cementitious properties of GGBS (Bone *et al.,* 2004b). Wild *et al.* (1998) indicates that GGBS provides enhanced durability, including high resistance to chloride penetration, resistance to sulphate attack, and protection against alkali silica reactions (ASR). Tasong *et al* (1999) demonstrated through microstructural analysis that GGBS prevents sulphate attack on lime stabilised clays by preventing formation of ettringite, and its hydration activated by lime is more rapid than the pozzolanic reaction of lime and clay.

(2) Pulverised Fuel Ash (PFA): Separated from flue gases of pulverised coal burning power stations, distinct from bottom ash which is coarser. Mineralogy and phase compositions depend on those of the associated coal and furnace burning conditions (Bone *et al.,* 2004b). Relevant uses of PFA are covered in BS 3892, Parts 1 – 3 (1996, 1997). The potential for use of low grade PFA in S/S are discussed by Poon *et al.* (2003) and effects of PFA on water demand may also be important (Bone *et al.,* 2004b). PFA improves workability of mixes during S/S treatment, and whilst 28 day strength may be reduced, long term strength is increased (Taylor, 1997).

(3) Organoclays: Due to the large specific surface area of clays and ability to bind charged species on these surfaces, organically modified clays have been developed

for use in earth works (Bone *et al.,* 2004b). These are prepared by exchanging cationic ammonium compounds with mineral cations normally associated with negatively charged clays (Gullick and Weber Jr, 2001). The commonly used organic quaternary cationic ammonium cations are $[(CH_3)_3NR]^+$ and $[(CH_3)_2NR_2]^+$, where R is an aromatic or alkyl hydrocarbon group (Natali Sora *et al.,* 2005). Organics interfere with cement hydration, and do not bind firmly to the formed siliceous matrix. A viable way to overcome this problem is to pre-sorb organic contaminants on organoclays (Botta *et al.,* 2004) prior to S/S treatment (Bone *et al.,* 2004b). The use of modified bentonite was found to be successful, for containment of aromatic organics in soils prior to S/S with Portland cement (Gitipour *et al.,* 1997).

3.3 CLAY – CONTAMINANT – BINDER INTERACTIONS

Physical and chemical processes by which ions interact with cementitious binders allow S/S treatment of contaminated soils and wastes to be evaluated and predicted. Mollah *et al.* (1995), examined cation sorption by cementitious materials, identifying sorption behaviours, induced changes due to sorption, and leaching behaviours of sorbed cations. Influence of soil components must be considered during treatment, and reactions between clays and binders can provide long-term stabilising processes through adsorption and precipitation. Interactions between contaminants and clays or binders involve: sorption to binder / soil matrix; pH dependent and redox controlled precipitation; sorption to CSH; and incorporation into crystalline hydration products (Bone *et al.,* 2004b).

High early strength, reduced permeability, relatively high durability and universal availability makes hydraulic cement good binders for remediation purposes (Conner, 1990). Portland and other cement types are often used as binders for S/S of contaminated materials (Zhou *et al.,* 2006). CSH gels are formed during hydration of cementitious binders, and are mixtures of poorly crystallised particles with different morphologies, including fibrous, reticular network, grain morphology and inner product morphology (Taylor, 1997, and Chen *et al.,* 2008). During hydration, CSH gels contain the bulk of micro-porosity, and gel pores give rise to high surface areas, largely controlling sorption properties. Almost all Ca^{2+} in natural crystalline phases of CSH can be replaced (Viehland *et al.,* 1996, Viehland *et al* 1997). During precipitation of cementitious products, heavy metal ions may become sorbed to surfaces, or incorporated into crystalline lattices, forming crystallised gel which alters solubility (Kitamaru *et al.,* 2002).

Ettringite is one of the main components of expansive, shrink resistant, rapid hardening, high early strength, low energy cements. Average ettringite content in modern cements have increased as more sulphate is added to control set time of clinkers and improve early strength gain (Glasser, 1997, Chen *et al.,* 2008). Examination of ettringite minerals show evidence of compositional changes at ion sites, and Table 3.1 shows reported ion substitutions (Chen *et al.,* 2008).

Table 3.1: Reported ion substitution in ettringite (Chen *et al.,* 2008)

Ca^{2+} sites	**Al^{3+} sites**	**SO_4^{2-} sites**
Sr^{2+}	Cr^{3+}	CO_3^{2-}
Ba^{2+}	Si^{3+}	Cl^-
Pb^{2+}	Fe^{3+}	OH^-
Cd^{2+}	Mn^{3+}	CrO_4^{2-}
Co^{2+}	Ni^{3+}	AsO_4^{3-}
Ni^{2+}	Co^{3+}	NO_3^-
Zn^{2+}	Ti^{3+}	SO_3^{2-}

Adsorption of cationic species from aqueous media by cementitious substances is strongly dependent on: surface chemical characteristics; electric double layer at solid – liquid interface; adsorption site densities; media composition and pH (Mollah *et al.,* 1995). Table 3.2 shows adsorption selectivity for metals on different soils (Yong *et al.,* 1996), and Figure 3.2 shows theoretical solubilities for some metal hydroxides as a function of pH (US EPA, 1986).

Table 3.2: Adsorption selectivity for metals on soils (Yong *et al.*, 1996)

Material	Selectivity order
Kaolin Clay (pH 3.5 – 6.0)	Pb > Ca > Cu > Mg > Zn > Cd
Kaolin Clay (pH 5.5 – 7.5)	Cd > Zn > Ni
Illite Clay (pH 3.5 – 6.0)	Pb > Cu > Zn > Ca > Cd > Mg
Smectite Clay (pH 3.5 – 6.0)	Ca > Pb > Cu > Mg > Cd > Zn
Smectite Clay (pH 5.5 – 7.5)	Cd = Zn > Ni
Amorphous Al Oxide	Cu > Pb > Zn > Cd
Mn Oxide	Cu > Zn
Amorphous Fe Oxide	Pb > Cu > Zn > Cd
Goethite	Cu > Pb > Zn > Cd
Humic Acid	Cu > Pb > Cd > Zn
Mineral Soils (pH 5.0, with no organics)	Pb > Cu > Zn > Cd
Mineral Soil (20 – 40 g/Kg organics)	Pb > Cu > Cd > Zn

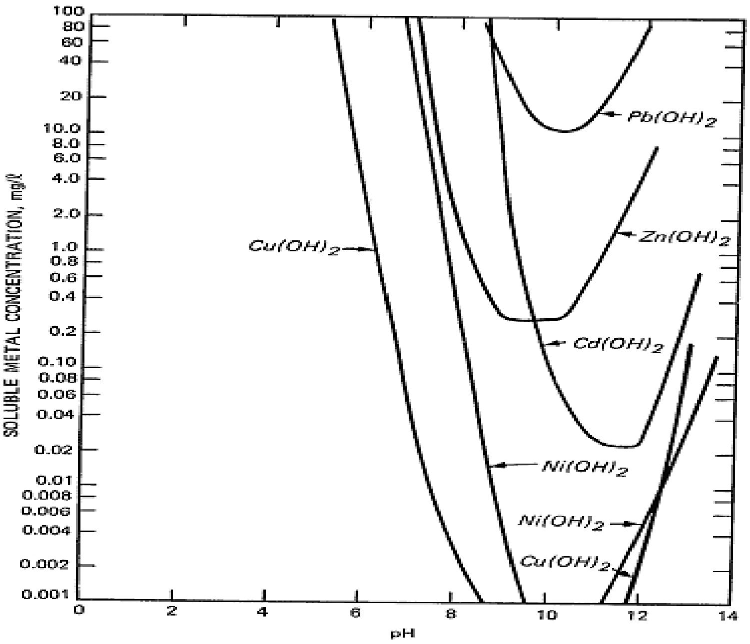


Figure 3:2: Theoretical solubility of metal hydroxides as a function of pH (US EPA, 1986)

Many toxic metals show amphoterism (increased solubility at high and low pH), and by adjusting the pH it is possible to induce minimum leachability to solution, with optimum pH varying from 9.5 – 11.0 dependent on metals present (US EPA, 1986). Presence of other heavy metals may affect precipitation behaviours of individual cations, and MacDonald (1994) showed this graphically using single metallic cations of zinc, lead and copper, and a mixture of the three cations. Solubility of zinc was most influenced with pH in the mixture, with lesser influence on lead and copper solubility (Yong and Mulligan, 2003). Precipitation behaviours are likely to be complex, varying with cation speciation, complexation with other components, and intrinsic / extrinsic factors (e.g. porosity, permeability, pH and Eh).

Several processes in soils combine with binders to facilitate S/S, dominated by clay fractions. Li *et al.* (2001) reported that metal retention in S/S forms is controlled by alkalinity and acid buffering capacity of the matrix, as these promote precipitation of insoluble species, particularly metal hydroxides. Interactions during S/S are discussed in Sections 3.4 and 3.5 for organic and inorganic contaminants.

3.4 STABILISATION/SOLIDIFCATION OF ORGANIC CONTAMINANTS

S/S treatment of organic contaminated soils / waste is less common, and has a shorter track record than for inorganics (Bone *et al.,* 2004b). However, many contaminated materials contain organics, and must be considered as part of the remedial strategy (Connor, 1990). However, S/S has been successfully used for the remediation of organics at the high profile superfund sites in the USA (US EPA, 2000). Conner (1990) suggests that besides adsorption and volatilisation, other reactions in S/S of organics include: Hydrolysis; Oxidation; Reduction; and Salt formation. Studies on use of S/S with organics have been carried out by several authors (Al-Tabbaa and Rose, 1996, Gitipour *et al.,* 1997, Bates *et al.,* 2002, Natali Sora *et al.,* 2002 and Botta *et al.,* 2004), but are less extensive than those for inorganic contaminants. Authors have reported difficulties using cementitious binders alone for S/S of organic contaminants, due to interference with hydration processes, resulting in setting retardation and strength reduction (Bone *et al.,* 2004b). Some organics that interfere with hydration include organic acids, alcohols, aldehydes, amides, amines, carbonyls, chlorinated hydrocarbons, ethers, hydrocarbons, lignin, oil, starches and sugars (Connor, 1990, Bone *et al.,* 2004b).

Hills *et al.* (1995) investigated setting retardation and strength characteristics of ordinary Portland cement with additions of seven toxic organic compounds. It was found that these organics modified properties of hydration products at early age, but the modifications in aged samples were less significant. Mechanisms for cement hydration retardation could include:

- Adsorption of retarding compound on surface of cement particles, forming a protective skin which slows down hydration reactions
- Adsorption of retarding compound on nuclei of calcium hydroxide, retarding growth, which is essential in hydration after the induction period.
- Formation of complexes with calcium ions, increasing their solubility and preventing formation of calcium hydroxide nuclei
- Precipitation of insoluble derivatives, forming a protective skin around cement particles due to reactions of retarding compound with alkaline solution; and
- Incorporation of retardant in the protective membrane, which rapidly forms around cement particles in water, modifying them and retarding continued growth of hydration products (Young, 1972, Bone *et al.,* 2004b).

Organic matter influences distribution of heavy metals in soils and stabilised soils, through complexation, precipitation and chemical incorporation (Peng *et al.,* 2009). Cement based S/S treatment of organic contaminants may be through direct immobilisation, immobilisation after sorption, or immobilisation using oxidising / reducing agents, and details of these can be found in Paria and Yuet (2006). Detailed discussions of interactions and important characteristics of aromatic, non-aromatic and volatile organics during S/S are given in Chapter 5 of Bone *et al.* (2004b). Besides setting retardation and strength development, retention problems are also encountered, since organics do not undergo chemical interactions to the extent of inorganics during S/S. This will result in encapsulation rather than fixation, allowing potential for leaching, as encapsulation depends on physical properties of the matrix.

3.5 STABILISATION/SOLIDIFICATION OF INORGANIC CONTAMINANTS

S/S of inorganic contaminants has found widespread acceptability as a cost effective remediation method. This process encapsulates / fixates cationic contaminants through sorption, hydrolysis and precipitation reactions (Bone *et al.,* 2004b). Successful extensive utilisation on the Superfund sites demonstrated its efficiency for a wide range of inorganic contaminants (US EPA, 2000). S/S is usually categorised based on additives employed for containment (Sharma and Lewis, 1994), and cement / pozzolan based techniques are preferred due to relatively low material and equipment costs, and good solidification characteristics (Paria and Yuet, 2006).

Lime / cement based S/S systems induce high pH environments, which favour precipitation of many cations as hydroxides, hydrous oxides or carbonates. Soluble salts may be incorporated into cementitious mineral phases, and the properties of the contaminants will influence how they are contained within S/S products (Bone *et al.,* 2004b). Table 3.3 shows the effects of high pH on solubility of some transition metals in their common oxidation states. The solubility of some soil mineral species are shown in Figure 3.3 (Bone *et al.,* 2004b), and this variability in solubility is important for the S/S process due to induced binder alkalinity (Mollah *et al.,* 1995). Various investigations for S/S of inorganic contaminants have been conducted, and a detailed review can be found in Bone *et al.* (2004b). Successful use of S/S requires containment of target contaminants, without compromising strength, durability or leachability of components. Retardations in setting may not necessarily affect leaching characteristics or buffering capacities of treated material.

Table 3.3: Behaviour of aqueous species at high pH for common oxidation states (Bone *et al.*, 2004b, after Glasser, 1997)

Group	**Element**	**Behaviour**
III	Sc, Y, La, Ac	Precipitates
IV	Ti, Zr, Hf	Precipitates
V	V Nb, Ta	Amphoteric (May be soluble as complex) Precipitates
VI	Co, Mo, W	Amphoteric (May be soluble as complex)
VII	Mn, Tc Re	Precipitates Amphoteric (May be soluble as complex)
VIII	Fe, Ru	Precipitates
IX	Co Rh	Precipitates Precipitates as hydrous oxide or metal
X	Ni Pd	Precipitates Precipitates as hydrous oxide or metal
XI	Cu Ag	Precipitates Precipitates as hydrous oxide or metal
XII	Zn Cd, Hg	May be soluble as complexes Precipitates as hydrous oxide or metal

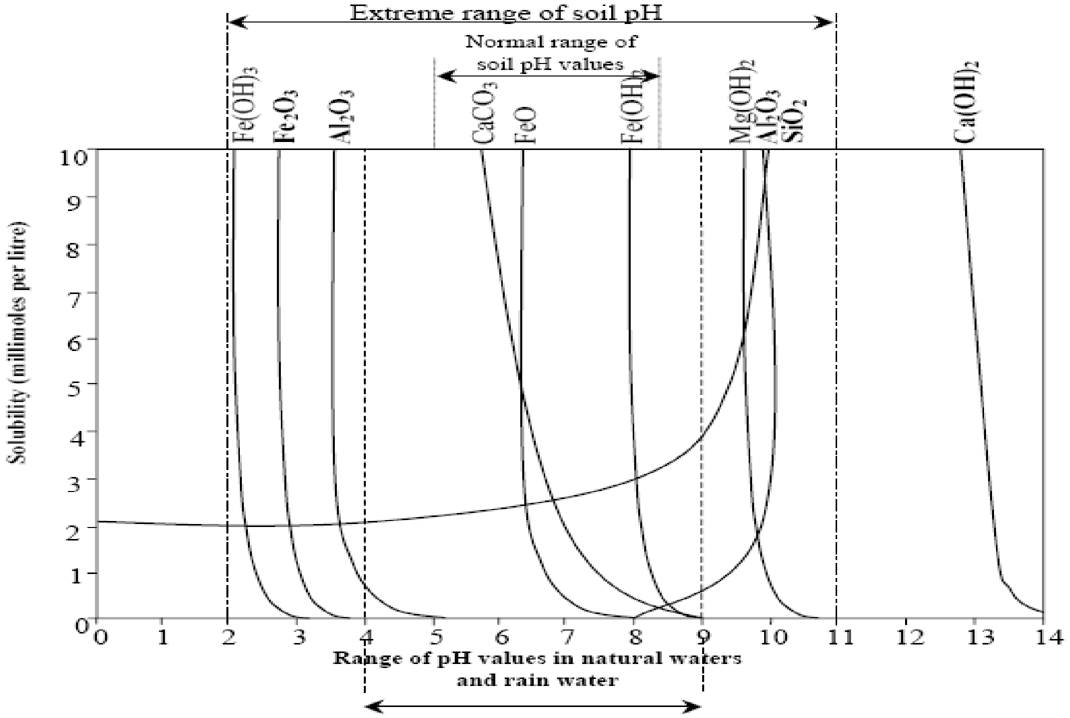
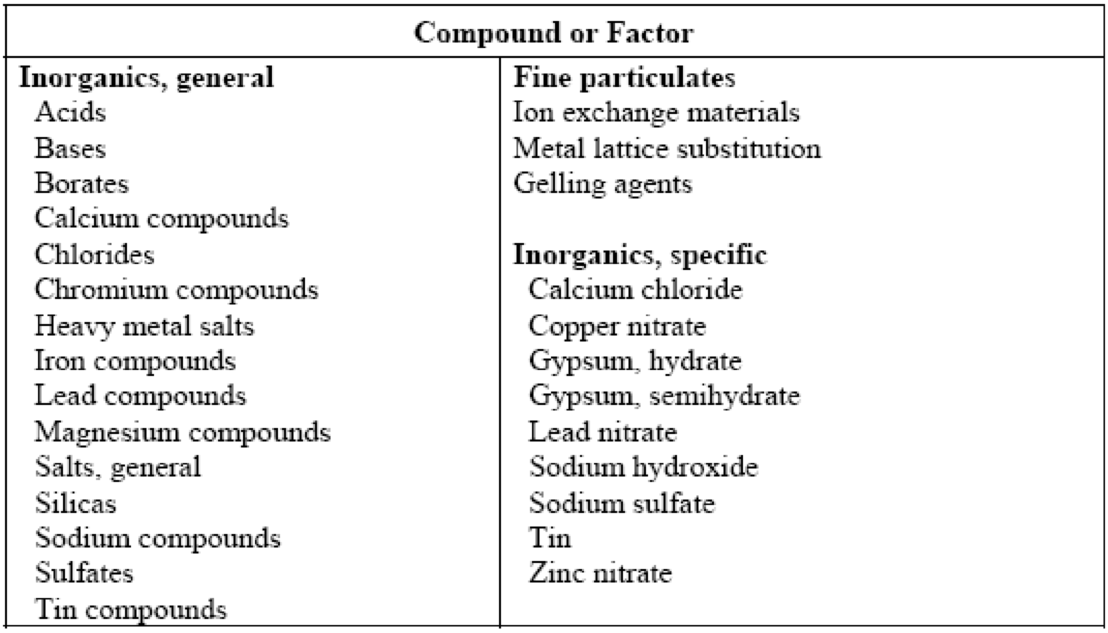


Figure 3:3: Solubility of soil mineral species in relation to pH (Loughnan, 1969)

Physical or chemical limitations can be imposed on characteristics of treated materials. Physical limitations include: physical characteristics of material being treated; prevailing environment; and economical or time constraints. Chemical limitation mechanisms involve sorption, complexation and precipitation reactions (Bone *et al.*, 2004b). A number of inorganic compounds can interfere with S/S processes, and examples that can affect solidification are shown in Table 3.4 (Conner, 1990).

Table 3.4: Inorganic contaminants which can affect solidification (Connor, 1990)



Compound or Factor	
Inorganics, general	**Fine particulates**
Acids	Ion exchange materials
Bases	Metal lattice substitution
Borates	Gelling agents
Calcium compounds	
Chlorides	**Inorganics, specific**
Chromium compounds	Calcium chloride
Heavy metal salts	Copper nitrate
Iron compounds	Gypsum, hydrate
Lead compounds	Gypsum, semihydrate
Magnesium compounds	Lead nitrate
Salts, general	Sodium hydroxide
Silicas	Sodium sulfate
Sodium compounds	Tin
Sulfates	Zinc nitrate
Tin compounds	

Heavy metals can cause environmental damage due to their mobility / solubility, and selecting appropriate remediation methods depend on site characteristics, contaminant concentrations and type, and end-use of the contaminated material (Mulligan *et al.,* 2001). Of particular importance in this research is the S/S of two heavy metals – Chromium (III) and Zinc (See Section 4.2.3 for selection reasons). Murat and Sorrento (1996) investigated effects of high concentrations of cadmium, lead, chromium and zinc on the composition and properties of calcium silicate and calcium aluminate cements. Calcium silicate cements were found to accept Cd, Cr and Zn into its crystalline matrix, with modification of hydration behaviours (Cd and Zn caused slower setting and reduced strength, while Cr caused faster setting and higher early strength). Given the implication of heavy metals on cements, understanding how they behave or influence binders during S/S are imperative for assessing long-term performance.

3.6 SITE SPECIFIC STABILISATION / SOLIDIFICATION APPLICATION

S/S relies on careful characterisation of contaminants to optimise the treatment process, and hence efficiency of employment will depend on:

- Good characterisation of material to be treated;
- Selection of most appropriate binder formulations;
- Effective contact between contaminants and treatment reagents;
- High degree of physical and chemical consistence of the feedstock;
- Use of appropriate mixing equipment and good working practice;
- Control over external factors such as temperature, humidity and degree of mixing, which affect setting, strength development and durability of products;
- Absence / control of substances that inhibit S/S processes and product properties (Bone *et al.,* 2004b).

One limiting factor for employment of S/S technologies in the UK had been lack of published information efficiency and durability. However, this is being addressed, with publications of two Environment Agency documents on scientific literature and guidance (Bone *et al.,* 2004a, 2004b), STARNET (http://www-starnet.eng.cam.ac.uk/), publications of state of the practice reports (CL:AIRE, 2004), and research and publications on leaching evaluations for stabilised materials. Whilst S/S has fared better in USA, viability of assessment criteria and leaching assessments undertaken are questionable, based on recent developments in leaching evaluations and material characterisation, for site specific impact assessments (see Van der Sloot *et al.,* 2007). Contaminants encountered on sites vary widely, and in some case prove difficult to treat by only one remediation process (Bone *et al.,* 2004b). Moreover, long term durability and performance of S/S is vital to ensure success, and this has been a cause for concern. Treatability and pilot studies are undertaken prior to S/S implementation, to evaluate binder suitability and optimise treatment conditions (Fleri and Whetstone, 2007), and these will now be briefly reviewed.

3.6.1 Treatability Study

Treatability studies have been used extensively in the chemical and remediation industries to determine efficacy of potential treatment processes. Potential benefits far exceed the relatively low costs for undertaking these studies, and obtained data for S/S are critical in determining compliance with design criteria, binder type, quantity, and delivery method (Fleri *et al.,* 2005a). Since S/S does not remove contaminants, binder selections must address compatibility with material to be treated, presence of components that may interfere with binder hydration and durability, and anticipated long-term ground and groundwater conditions (Bone *et al.,* 2004b). To design treatability studies, key factors must be addressed, which must include:

- Performance criteria – S/S designs physical and chemical performance criteria.
- Analytical methods – Performance criteria are specified using a variety of test methods e.g. British Standards Institution, ASTM, Environment Agency, etc.
- Binder selection – Knowing the performance criteria and analytical method allows preliminary selection of reagents for S/S. Additives may also be included to meet the specification, e.g. Pozzolans to increase strength and durability, and thinners to reduce clay plasticity and increase workability.
- Sampling protocol – determining the type of sampling to be employed is important, prior to any S/S application. Pre-solidification sampling is easier to employ, less expensive and uses hydraulic samplers to collect samples prior to solidification, which are remoulded for testing. This does not provide information on in-place columns, but rather provides data on the ability of the mix to achieve performance criteria. Post-

Treatability studies are generally undertaken at 28 days of binder hydration, and mixes are selected based on ability to meet physical and chemical performance criteria, and the availability and costs of reagents (Conner, 1990, Fleri and Whetstone, 2007). Studies usually include cost benefits analysis, and some ensure that physical performance criteria are met, before undertaking chemical analysis, in order to minimise costs.

3.6.2 Pilot Studies

Pilot studies are employed to confirm results of treatability studies, optimise mix designs, and give contractors experience with proposed full scale operation (Fleri *et al.,* 2005b). Following selection of design mixes from treatability studies, pilot studies are undertaken to scale up these mixes for application under field conditions. This determines operational parameters, and could include factors such as: Mixing tool diameter; Cycle time; Rotation speed; Penetration and withdrawal speed; Optimisation of grout density and viscosity; Exposure of test columns for visual inspection, to determine lateral stabilisation, mix homogeneity, and presence of voids and inclusions; Development of work platform; and Consideration of column sampling (Fleri *et al.,* 2005b, Fleri and Whetstone, 2007). Following completion of the pilot study, full implementation of S/S is undertaken, which could be on or off-site, depending on the binder application method.

3.6.3 Binder Application

Binder application to contaminated soils can be undertaken in two ways: ex-situ – where the soil is removed from its original location, treated and replaced or disposed of; and in-situ – where the soil is treated in place, with addition of the binder without excavation. Reagents can be added in dry or slurry form; dry reagents rely on water in the soils for hydration, while slurry forms are pumped in through in-situ delivery devices, whilst being mixed into the soil (Bone *et al.,* 2004b). Al-Tabbaa and Evans (1999) found that in-situ mixing of dry reagents required more vigorous mixing compared to slurry reagents, to attain similar level of consistency. Reagents are mixed in grout plant, and delivery usually involves use of weigh batching equipment to ensure that accurate proportions are delivered to achieve desired efficiency.

3.6.3.1 Ex-Situ S/S Techniques

There are three main methods of ex-situ S/S process:

1. Direct Mixing – this involves excavation and transportation of contaminated soil to disposal areas, either on-site or off-site. The material is layered along with the binder and mixed in place, and then compacted and left to cure in place.
2. In-Drum Processing – this involves addition of binder to contaminated material which is stored in a container. When mixing and setting is complete, the container and its contents are disposed of appropriately. The mixing paddles are usually left in the container, and disposed of with the treated material.
3. Plant Processing – this involves use of fixed or mobile treatment plants, where contaminated material are excavated, transferred to the plant, treated with appropriate

binders and additives using mechanical mixers, and then taken to final disposal sites (Al-Tabbaa and Perera, 2005a, CL:AIRE, 2004, Bone *et al.,* 2004b).

The employment of the different ex-situ treatment methods will depend on the type of contamination being remediated, and the disposal type to be employed.

3.6.3.2 In-Situ S/S Techniques

There are two methods for in-situ mixing of reagents to contaminated soils:

1. Mechanical Mixing. This approach utilises mechanical mixing augers, blenders and backhoes:
    1. Mechanical mixing using augers are employed to form S/S monolithic columns, by injecting binders into contaminated soils during mixing through hollow mixing augers. These are usually used for deep mixing S/S method, using single or multi-shafted augers of varying diameters. Figure 3.4 shows in-situ deep mixing solidification of contaminated soil.
    2. Mechanical mixing using blenders, backhoes and mixers are usually used for shallow mixing of contaminated soils. Backhoes and blenders were considered crude, and usually resulted in poor mixing, dust generation or reagent loss. Sophisticated design modifications have been made by operation companies to address these problems. Figure 3.5 shows an in-situ blender head in operation.
2. Pressure Mixing. This reagent application method is similar to conventional grouting, and involves direct injection of binder mixes under pressure to contaminated material. The method is however not developed on a commercial scale, due to difficulty in ensuring even permeation of binders in the soil. The method requires the soil to have sufficient overburden pressure to withstand injection pressure, with treatment requiring depths over 2m (Bone *et al.,* 2004b, CL:AIRE, 2004, Al-Tabbaa and Perera, 2005a)

Figure 3:4: In-situ deep mixing of solidification columns (Wilk, 2005)

Figure 3:5: In-situ blender head in operation (Portland Cement Association, 2007)

Table 3.5 shows a comparison by Evans *et al.* (2001) between in-situ and ex-situ S/S applications. Selection of appropriate S/S conditions depends on a wide range of factors, including material characterisation, handling and processing, objectives, regulatory requirements and economics (CLAIRE, 2004). Ex-situ applications have been applied more commonly than in-situ applications in the UK.

Table 3.5: In-situ versus Ex-situ S/S advantages and disadvantages (Evans *et al.*, 2001)

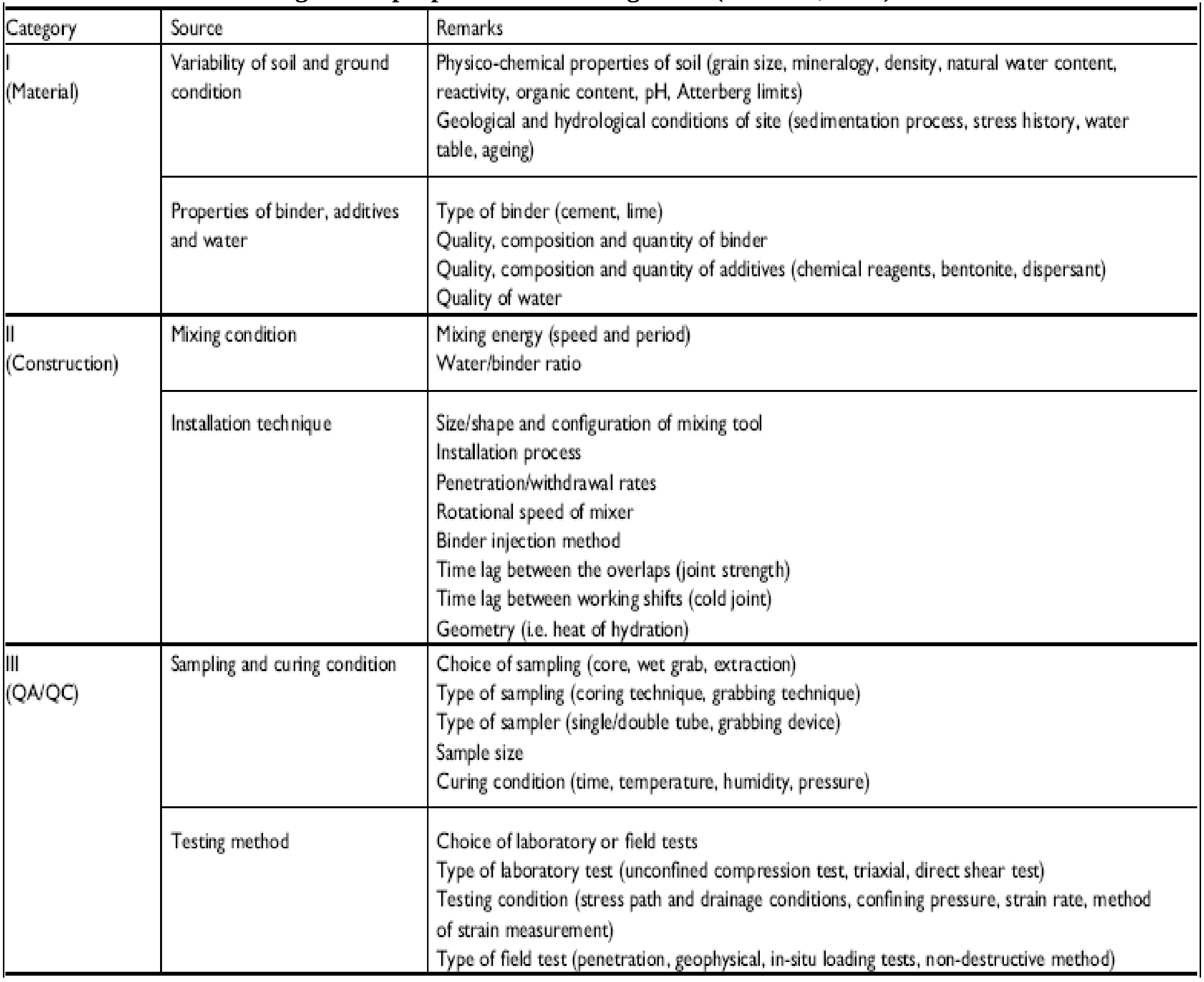
In-Situ S/S	**Ex – Situ S/S**
Advantages	Advantages
Lower costs for larger and deep remediation projects.	Single plants in central locations can treat material from many sources.
Recently developed in-situ equipment allows for controlled reagent injection and mixing, as well as emission control.	Provide better control of reagent addition.
Little or no secondary spoils generated.	Quality control sampling is easier.
Low noise and vibration levels.	Suitable for shallow depth remediation, where groundwater and support of adjacent land is not an issue.
Allows treatment close to structures where excavation would cause damage.	Tolerant to unstable soil surfaces with low bearing pressure.
No requirement for excavation or ground control.	May be included as an additional component of other treatment processes.
Disadvantages	**Disadvantages**
Cost for small projects may be influenced by equipment mobilisation.	Significantly larger costs than in-situ for large remediation works at substantial depth.
Small sites may not accommodate in-situ mixing equipment.	Materials may have to be excavated and transported to treatment plant
Bearing capacity of the ground must be sufficient to support mixing equipment.	Practical considerations regarding excavation may affect option, as regards the depth of contamination.
Physical obstructions, clays, oily sands and cohesive soils may reduce auger penetration rate and depth.	Disposal arrangements must be made for the treated wastes.
Made ground may have to be excavated in advance of mixing.	

3.6.4 In-situ Deep Mixing Stabilisation / Solidification Application

Al-Tabbaa (2003) discussed the research, development and application for S/S deep mixing technology in the UK, using case studies of projects that utilised the technology.

Given the dynamics of in-situ operations, it is imperative to evaluate consistency and development of material characteristics to ensure effectiveness of in-situ S/S applications. For example, Porbaha (2002) indicated that strength development for in-situ treated soils differs significantly from those treated under controlled laboratory conditions. This is due to differences in mixing energy and processes, mixing tools, material volume, construction procedure and curing environment, inherent soil heterogeneity and relatively lower degree of in-situ mixing. Table 3.6 shows the various factors that could affect in-situ properties of treated ground.

Table 3.6: Factors affecting in-situ properties of treated ground (Porbaha, 2002)



Category	Source	Remarks
I (Material)	Variability of soil and ground condition	Physico-chemical properties of soil (grain size, mineralogy, density, natural water content, reactivity, organic content, pH, Atterberg limits) Geological and hydrological conditions of site (sedimentation process, stress history, water table, ageing)
	Properties of binder, additives and water	Type of binder (cement, lime) Quality, composition and quantity of binder Quality, composition and quantity of additives (chemical reagents, bentonite, dispersant) Quality of water
II (Construction)	Mixing condition	Mixing energy (speed and period) Water/binder ratio
	Installation technique	Size/shape and configuration of mixing tool Installation process Penetration/withdrawal rates Rotational speed of mixer Binder injection method Time lag between the overlaps (joint strength) Time lag between working shifts (cold joint) Geometry (i.e. heat of hydration)
III (QA/QC)	Sampling and curing condition	Choice of sampling (core, wet grab, extraction) Type of sampling (coring technique, grabbing technique) Type of sampler (single/double tube, grabbing device) Sample size Curing condition (time, temperature, humidity, pressure)
	Testing method	Choice of laboratory or field tests Type of laboratory test (unconfined compression test, triaxial, direct shear test) Testing condition (stress path and drainage conditions, confining pressure, strain rate, method of strain measurement) Type of field test (penetration, geophysical, in-situ loading tests, non-destructive method)

Estimating in-situ properties is difficult, resulting in discrepancies with laboratory prepared sample results. Some factors affecting estimation of in-situ properties include:

- Effect of heat of hydration – temperature changes in treated soils differ between field and laboratory samples, and may affect hydration and strength development.
- Effect of joint strength – construction patterns influences material shear strength, with strength reduction at the joint-lap face, compared to the centre of the column.
- Effect of core sampling – core samples for analyses may be influenced by cracks / micro-fractures which occur during sampling. This may be due to sample rigidity, bend in the borehole, locking of sampler, and rotation of core with the sampler.
- Effect of sample size – The size of samples may affect results obtained, especially for strength tests (Porbaha, 2002).

Larson *et al.* (2005) suggest that in-situ S/S installation processes, especially for deep mixing columns, influence stabilisation effectiveness. These were for variations in auger designs including the number of mixing blades, rotating speeds and retrieval rates, and the original properties of the treated soil. Auger design is particularly important in ensuring effectiveness of mixing processes, as well as consideration of soil heterogeneity, stratification, and contaminant distributions (Al-Tabbaa *et al.,* 2000). Soils are usually stratified and heterogeneous, with varying contaminant distributions, making it imperative to ensure proper characterisation for effective treatment. A review of S/S deep mixing construction and installation processes is given in Porbaha *et al.,* (2001), and the factors found to influence column quality include: Binder injection method; Degree of mixing; Number of shafts; Configuration of mixing blades, Rotation speed of shafts; and the penetration / withdrawal speeds. Strength development is influenced by mixing and curing conditions, which differ with machinery and soil properties, thus making it difficult to predict (Kitazume and Hayoko 2007). This requires individual site evaluation for treated material properties, and where coring is employed for analyses, large diameter coring tools are likely to yield better results (O'Rourke and McGinn, 2006).

In-situ S/S processes usually result in treated material volume increases, with a documented average increase of about 20% (Fleri and Whetstone, 2007). Volatilisation of organics may also occur during mixing, and the utilisation of a shroud with an off gas collection facility should reduce this problem (OSTI, 1996). Quality assurance is very important for in-situ S/S deep soil mixing, and assessments of column integrity may be via in-situ or laboratory testing (Porbaha *et al.,* 2001). In-situ assessment methods can include non-destructive methods (e.g. sonic integrity test), loading methods, geophysical methods and penetrative test methods. Laboratory based assessments involve analyses of core samples, wet grab samples, and samples from column extraction. Column extractions are relatively expensive, and only undertaken for industrial research (Porbaha *et al.,* 2001). However, they offer advantages for: Evaluating column uniformity with depth; Sampling in different directions for testing; Checking diameter variations; and Examining binder distribution along length and cross-section (Holm, 2001).

It is important to note that these deep mixing evaluations are typically directed towards assessments of physical properties and column consistency, and little is said about assessing the material chemical characteristics. However, for contaminant containment, the material chemical characteristics and alterations with hydration and time will ultimately determine containment and leachability. This combined with the material physical properties (such as permeability, porosity and tortuosity) and prevailing environmental conditions will control the partitioning and release of components (Van der Sloot *et al.,* 2005). Deep mixing offers advantages of modifying physical and mechanical properties of treated soils, thereby reducing pathways for infiltration and component leaching, but chemical modification and alterations in these properties will control solubility and components releases.

Analysis of project life cycle for typical in-situ deep mixing S/S processes are given in Fleri and Whetstone (2007), using experiences from treatment at a number of Manufactured Gas Plants (MGP) in the USA. In-situ S/S using deep soil mixing has gained wide acceptance, especially in the MPG sector, to reduce need for material disposal off-site. This saves on backfill and disposal costs, reduces odour emissions during remediation, and has reduced implementation costs compared to other in-situ technologies like chemical oxidation and thermal desorption, especially for large or deep site remediation operations (Bone *et al.,* 2004b, Fleri and Whetstone, 2007). Project lifecycles for in-situ S/S in the USA are often overlooked, due to: Remediation being driven by regulation, with parties involved usually only doing what is minimally required by law; Site clean-up does not increase profitability; Remediation is usually considered the last step in compliance; and Post-remediation sampling focuses on groundwater release criteria for evaluating effectiveness, rather than the treated material integrity (Fleri and Whetstone, 2007).

3.8 LONG-TERM PERFORMANCE AND DURABILITY

S/S with cement based binders is being used for contaminated land remediation, typically based on treatability studies undertaken at 28 days of binder hydration (Fleri and Whetstone, 2007). This raises concerns over long-term effectiveness, due to uncertainties of test methods, observed deficiencies in application processes, observed lack of chemical binding in tested crushed samples, and uncertainty in performance arising from anticipated degradation with time (Al-Tabbaa *et al.,* 2005). Validating the long-term performance of any remediation method is essential for its success, but literature on long-term efficiency of in-situ S/S is limited, even in the USA where the technology has an application history over three decades (Al-Tabbaa and Boes, 2002). Various factors can affect S/S durability, and cement based S/S in deleterious environments with acidic / saline soils or zones of fluctuating groundwater conditions can compromise effectiveness (Klitch *et al.,* 1999). Adverse environments may promote / accelerate physical and chemical degradation of cementitious matrices, resulting in contaminant leaching. Dry environments are more favourable for contaminant containment, and contact of treated material with flowing water constitutes a realistic worst case scenario (Glasser, 1997).

Most tests carried out to assess long-term performance of S/S are based on results for relatively short binder hydration durations. However, increasing cementitious hydration results in physical, chemical and mineralogical modifications (Mollah *et al.,* 1995), which influence S/S processes. Pereira *et al.* (2007) indicates that most long-term S/S behaviour assessments are based on accelerated ageing, mathematical models or aggressive durability tests on fresh samples. Accelerated ageing prior to testing normally allows only brief curing periods, at which stage hydration is ongoing, which ultimately determines long-term behaviour. Lack of understanding of the complex interactions between binders, soils and contaminants, coupled with environmental behavioural variations, make it difficult to establish suitable tools for assessing long-term durability. Complex S/S system chemistries are made even more complicated, when considered within dynamic environment conditions (Al-Tabbaa *et al.,* 2005). Contaminant properties may also change during these interactions, and the altered contaminants may have different effects on the binder system (Conner, 1990).

Klitch *et al.* (1999) undertook microstructural analysis of a 6 year old environmentally exposed Portland cement S/S heavy metal contaminated industrial waste. Results indicated slight to moderate degradation, and found that degradation mechanisms were similar to those affecting concrete. Material vulnerability to degradation was found to be dependent on permeability, mineralogy, cement paste microstructure, and the cement – waste aggregation. Investigations utilised microstructural analyses of ultraviolet (UV) dye impregnated samples via SEM (scanning electron microscopy) and EDX (energy dispersive x-ray), with little information given on the original material, material chemistry and leaching behaviour. The basis for suggesting slight to moderate material degradation was on the material physical integrity, though numerous other factors are responsible for contaminant release from S/S treated materials.

Pereira *et al.* (2007) investigated short and long-term performance of fly ash, lime and cement S/S treated electric arc furnace ash, over 9 years after treatment. The ash contained Cr, Cd, Pb and Zn contaminants, with different mix designs employed for treatment. pH alterations with time were observed for the different mixes, as well as increased contaminant leachability. pH reduced in mixes from around 12 at 30 days to below 7 at 9 years, yielding decreased buffering capacities and increased contaminant leaching potential. Effects of curing conditions were also investigated in the short-term based on curing temperatures, with samples cured in plastic bags at ambient temperature, and others cured in ovens at 40 and 60 °C with or without air renewal, and tested at 28 days and 9 months. Curing temperatures and conditions were found to influence pH and contaminants containment, with ambient temperature humid curing conditions yielding higher pH and contaminant containment effectiveness.

Fitch and Cheeseman (2003) undertook analysis of 10 year old environmental exposed Portland cement and PFA S/S treated metal bearing waste filter cake. The surface regions were found to be severely degraded and carbonated, with reduced acid neutralising capacity compared to bulk samples. Large plate-like portlandite deposits with calcite rich top surfaces were found close to, but below the environmentally exposed surface. Calcite was the only mineral phase detected at both 28 days and 10 years, and surface metal concentrations were reduced compared to bulk samples, due to leaching. Integrity was severely compromised at exposed surfaces, and the changes in mineralogy and physical properties constituted likely detrimental implications. Little information was given on the original material properties, and the chemical properties investigated were based on leaching tests aimed at providing information on variations between different parts of the treated material.

Designing effective S/S requires knowledge of the system physical and chemical properties, and the way contaminants are bound in the material. Information on different leaching mechanisms is useful, for projections of long-term contaminants immobilisation (Mollah *et al.,* 1993). The availability of components for leaching, rather than total concentration in materials, is the most important factor for accessing release and subsequent environmental pollution (Van der Sloot and Dijkstra, 2004). This availability and leaching of contaminants to the aqueous phase, and susceptibility for transport depends on their solution speciation, and affinity to bind to reactive surfaces of the matrix (Dijkstra *et al.,* 2004). Given this factor, assessing speciation and alterations in speciation of components are the most important considerations when assessing contaminant release. Complexation reactions between the components and organic complexants are also important pathways, and determine to large extents their speciation and bioavailability (Peng *et al.,* 2009). Some mechanisms responsible for S/S matrix degradation, which could compromise containment, are discussed below.

3.8.1 Degradation Mechanisms

Degradation of S/S treated materials range from two extremes: rapid degradation which is unacceptable with sudden release of contaminants; and gradual degradation over time with gradual release of components, at concentrations which do not pose significant risk (Bone *et al.,* 2004b). Degradation of S/S material can be due to physical, chemical and biological action, and could be intrinsic (due to material properties) or extrinsic (due to environmental factors). Degradation can modify material properties to yield conditions, which are not desirable for containment, usually by modification of cementitious products. Board *et al.* (2000) suggest that the key factor controlling physical characteristics of hardened cement is the water: cement ratio (w/c), and initial w/c ratio controls eventual porosity and strength. pH controls are normally considered for inorganic contaminant fixation, and ideally a pH system of 7.5 – 11.0 is desirable (Connor, 1990). Cement based binder systems usually have high pH, and even though this reduces with ageing due to diffusion and leaching, it usually decreases within acceptable levels due to buffering capacity (Al-Tabbaa *et al.,* 2005). Factors that influence contaminant immobilisation, interactions between contaminants and binders, and mode of immobilisation are important in contaminant retention during degradation. Degradation mechanisms that normally affect S/S wasteforms include: carbonation, oxidation, hydrolysis, soluble salts, alkali / aggregate reactions, organic acid attack, sulphate attack, chloride attack, freeze / thaw cycles, wet / dry cycles and biological attacks (Bone *et al.,* 2004b).

Since S/S degradation mechanisms are similar to those for concrete, their mechanisms can be divided into primary and secondary degradation mechanisms.

Primary degradation mechanisms:

1) Carbonation – process where CO_2 reacts with cement based material, and mainly involves CSH and $Ca(OH)_2$, which are converted to $CaCO_3$. Whilst carbonation may induce permeability reduction and strength increase via precipitation of $CaCO_3$ in pores, it reduces pH, which may mobilise contaminants. Carbonation is generally a slow process except at high temperature or where accelerated (Bone *et al.,* 2004b, Al-Tabbaa *et al.,* 2005, Al-Tabbaa and Perera, 2005b). The pH decrease may also prevents / reduces pozzolanic reactions, which occurs between dissolved soil minerals and $Ca(OH)_2$ (Barnard, 2008).

2) Sulphate Attack – process where natural occurring sulphates or those present in the binder, chemically react with compounds in cement based material. Soluble sulphates have deleterious effects on Portland cement, and the mechanism and severity of effect varies with the bases present. Sulphate reactions with Portland cement result in ettringite or thaumasite formation, which occupy about twice the volume of hydrated aluminates it replaces, resulting in expansion, cracking, spalling / softening, and disintegration. Usually, sodium and magnesium sulphates are most active in sulphate attack (Bone *et al.,* 2004b, Al-Tabbaa *et al.,* 2005).
3) Alkali – Aggregate Reaction – process where hydroxyls in pore solutions react with minerals in aggregates. The most important of these reactions are Alkali – Silicate Reactions (ASR), although reactions can also take place between alkalis in cement and carbonates in aggregates. Alkali – silicate reactions occur only in the presence of water and calcium ions, and results in alkali – silicate gel being formed in planes of weakness, aggregate pores or on aggregate surfaces (Taylor, 1997). Factors affecting alkali – silicate reaction rate include: presence of other ions, pH, permeability, availability of alkali and silicate, size of siliceous particles and temperature. The best prevention is removal of causative agents (Bone *et al.,* 2004b, Al-Tabbaa *et al.,* 2005).
4) Chloride Attack – Chloride penetration and attachment to cementitious materials are only significant at low pH, due to effects such as carbonation, and not really important for S/S processes, due to pH buffering (Bone *et al.,* 2004b, Al-Tabbaa *et al.,* 2005).

Secondary degradation mechanisms: these include freeze – thaw and wet – dry cycle damage, shrinkage settlement, biological attack, loading and fire damage (Bone *et al.,* 2004b, Al-Tabbaa *et al.,* 2005).

3.8.2 Leaching

Contaminant leaching is of primary concern when considering degradation of stabilised materials, and is influenced by material properties and degradation mechanisms. Carbonation is one of the most important and controversial mechanisms that influences S/S. Kumar and Bhattacharjee (2003) found that leaching and carbonation with ageing alters material characteristics (such as porosity and permeability), and occur intermittently and alternately during the treated material lifecycle. Pore structures also change with carbonation and leaching, modifying porosity and pH, where pH reduction or porosity increase increases leachability (Van Gerven *et al.,* 2007). Porosity and pore size distributions affect component transport and strength of monoliths, with pore systems of compacted cementitious materials consisting of gel and capillary pores (Kumar and Bhattacharjee, 2003).

Carbonation results in calcite formation, reduces pH, modifies solubility, and decreases porosity via calcite precipitation in pores (Van Gerven *et al.,* 2004). It is strongly influenced by wasteforms complexity, binder type and waste / binder ratios, and these determine CO_2 diffusivity within treated material. The amount of water present in crucial for carbonation, as water is necessary for the reaction, but excesses will limit reaction rates by reducing the diffusion rate (Lange *et al.,* 1996, Malviya and Chaudhary, 2006a). Carbonation rates and extent depend on prevailing environmental conditions (e.g. temperature and wetting) and is increased at warm temperatures with low relative humidity (Sanchez *et al.,* 2002, Gervias *et al.,* (2004).

Lange *et al.* (1997) suggest that curing cementitious material in carbon dioxide rich environment can increase strength and enhanced mechanical properties and toxic metal binding capacity. This has resulted in the employment of accelerated carbonation for S/S treatment processes, which is the controlled accelerated version of natural carbonation.

Fernandez Bertos *et al.* (2004) undertook a review of accelerated carbonation for S/S treatment of contaminated materials and found that accelerated carbonation positively influences heavy metal immobilisation in contaminated soils. It was also suggested that the method resulted in increased strength gains up to 70%, occurring rapidly, which allowed for immediate site use. However, Barnard (2008) found that effective accelerated carbonation of S/S treated fine grained soils resulted in properties (compaction, particle density, shear strength, shrink / swell, pH and conductivity) closer to those for unstabilised materials. Due to formation of peds when mixing clays, Barnard (2008) found that only outer shells of peds were carbonated, and the process limited formation of bonds between clay peds. Breakdown of the peds resulted in pH increase, due to increased Ca^{2+} concentration with water access to un-hydrated cores. Alba *et al.,* (2001) also found that carbonation processes could result in increased leachability of sulphates and heavy metals like Zn and Cr from S/S treated municipal solid wasteforms.

Evaluations of contaminant retention in S/S materials are based on leaching tests, mostly undertaken on freshly stabilised samples, assuming limited post S/S alteration (Bonen and Sarkar, 1995), and do not simulate long-term leaching behaviour. Use of accelerated aging or modification of leach tests have been employed to simulate long-term component releases, for example via the use of equivalent time to elucidate long-term fate of stabilised wasteforms (Badreddine *et al.,* 2004). This involved use of leachant at comparative volumes to annual rainfall to simulate leaching timeframes under anticipated exposure conditions. Whilst this can yield valuable insight to time dependent leaching, constant sample saturation during testing does not simulate cyclic conditions anticipated under field exposure, and slow transformation processes within the material with increasing hydration. This approach does not address the necessary release controlling mechanisms and processes (See Sections 4.5 and 5.2).

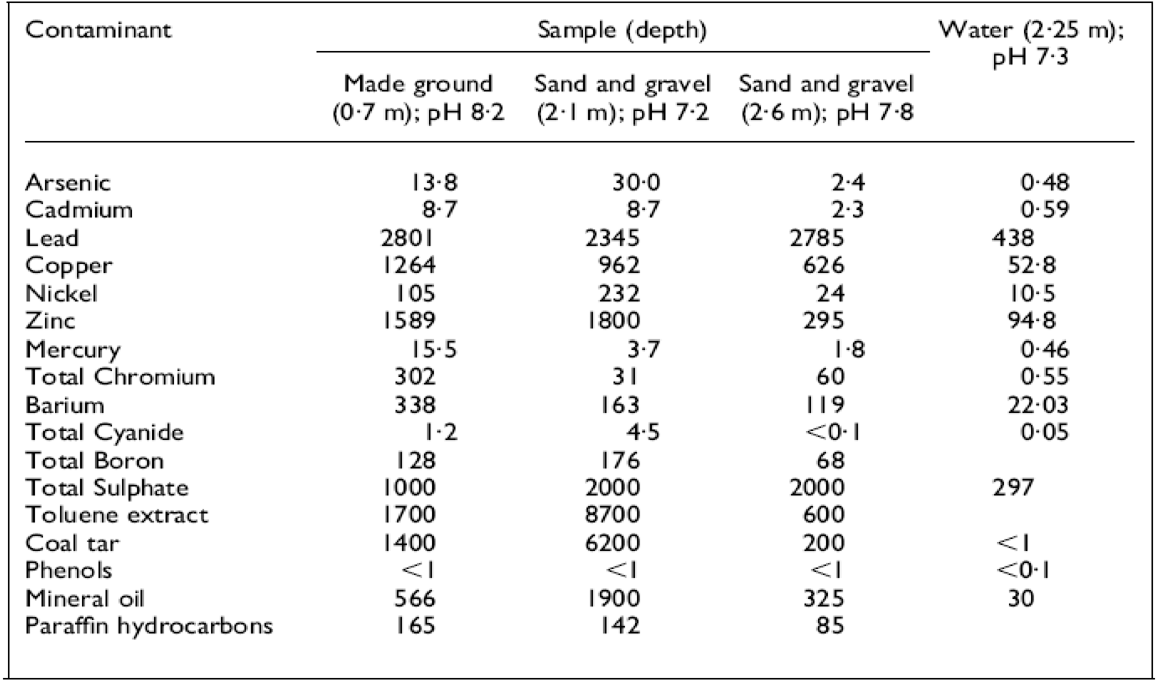
Often, hydration conditions affect contaminant partitioning and release, and Pereira *et al.* (2007) suggest that this has noticeable influences on leaching characteristics of wasteforms. Physicochemical changes in material properties with time, due to alteration via factors such as loss of alkalinity and carbonation, induce these modifications (Pereira *et al.,* 2007). Curing temperature and properties such as porosity influence degradation and leaching processes. Yokozeki *et al.* (2004) found that calcium leaching from CSH decreased at increased temperature, and degradation with leaching from cementitious products increased with time. However, degradation depth was porosity dependent, and diffusion rates increased with temperature even though solubility was decreased.

pH modification influences stability of most components, and thus solubility, and most cementitious products are only stable within narrow pH bands. Cementitious products, e.g. ettringite and monosulphate are capable of partitioning oxyanions (e.g. chromates) and undergo cation substitutions (e.g. Al^{3+} replaced by Cr^{3+}), but are only stable within tight high alkaline pH bands (11 – 13) (Chrysochoou and Dermatas, 2006). Decalcification of CSH, dissolution of Portlandite and calcium aluminosulphates like ettringite (dissolves below pH 10.5) and monosulphate occur as pH decreases from over pH 12 to around pH 9.5. This results in increased leachability of calcium and sulphur, yielding 70 – 80% of their total availability in the material (Engelsen *et al.,* 2009, Martens *et al.,* 2010). Temperature is also important in view of cementitious mineral formation, and ettringite is favoured over monophase minerals like monosulphate at curing temperatures below 50°C (Chrysochoou and Dermatas, 2006). With cementitious products degradation, partitioned components can be mobilised. These could be reprecipitated as hydroxides or other stable minerals e.g. elements like zinc (Ziegler and Johnson, 2001), or leached out, e.g. oxyanions like chromates (Chrysochoou and Dermatas, 2006). The different leaching mechanisms and assessment methods are addressed in Sections 4.5 and 5.2.

3.8.3 Case Study – 5 Year In-situ Stabilisation / Solidification Performance

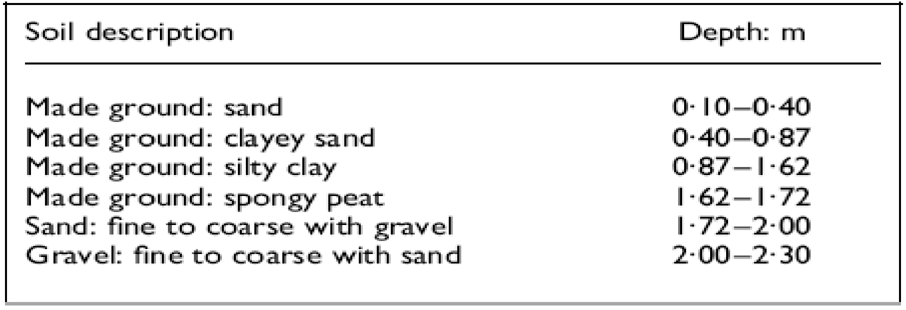
Al-Tabbaa and Boes (2002) undertook analysis to investigate long-term performance of S/S, on a site at West Drayton, Middlesex, UK, on information for physical and chemical properties of cored samples. This was the first investigation of its kind in the UK, aimed at assessing S/S effectiveness at meeting the design criteria, and assessing development of treated materials properties. Test specimens were cored from in-situ auger mixed S/S treated soils 4.5 years after installation, and tested at 5 years. Results were compared to those obtained from analyses of samples cored at 55 days at a depth of 1.2m, cured under laboratory conditions, and tested at 0.2, 1.2 and 2.4 years of hydration respectively. Contaminants present on site before treatment are shown in Table 3.7, and composition of the soil strata are shown in Table 3.8.

Table 3.7: Contaminants in soil and groundwater on test site (Al-Tabbaa and Boes, 2002)



Contaminant	Sample (depth)			Water (2·25 m); pH 7·3
	Made ground (0·7 m); pH 8·2	Sand and gravel (2·1 m); pH 7·2	Sand and gravel (2·6 m); pH 7·8	
Arsenic	13·8	30·0	2·4	0·48
Cadmium	8·7	8·7	2·3	0·59
Lead	2801	2345	2785	438
Copper	1264	962	626	52·8
Nickel	105	232	24	10·5
Zinc	1589	1800	295	94·8
Mercury	15·5	3·7	1·8	0·46
Total Chromium	302	31	60	0·55
Barium	338	163	119	22·03
Total Cyanide	1·2	4·5	<0·1	0·05
Total Boron	128	176	68	
Total Sulphate	1000	2000	2000	297
Toluene extract	1700	8700	600	
Coal tar	1400	6200	200	<1
Phenols	<1	<1	<1	<0·1
Mineral oil	566	1900	325	30
Paraffin hydrocarbons	165	142	85	

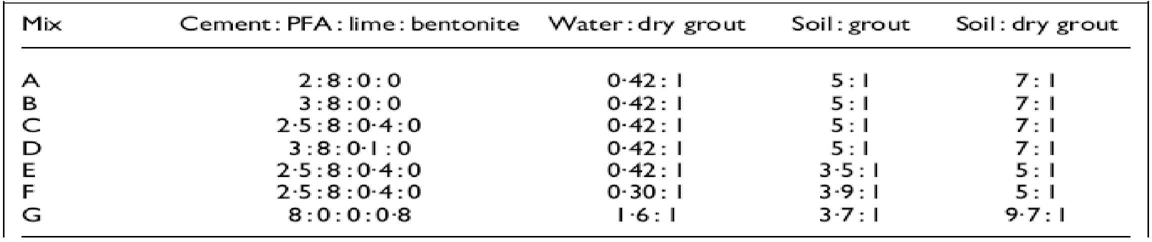
Table 3.8: Soil composition with depth on test site (Al-Tabbaa and Boes, 2002)



Soil description	Depth: m
Made ground: sand	0·10–0·40
Made ground: clayey sand	0·40–0·87
Made ground: silty clay	0·87–1·62
Made ground: spongy peat	1·62–1·72
Sand: fine to coarse with gravel	1·72–2·00
Gravel: fine to coarse with sand	2·00–2·30

Integrity of core samples and implications of curing under laboratory conditions are likely to have implications of samples tested at 1.2 and 2.4 years, but this evaluation focuses on testing undertaken at 5 years for treated made ground, and does not address storage conditions. Coring using water as the lubricant yielded highly fragmented cores, and thus a polymer was used, with samples washed prior to analysis. Microstructural analysis indicated that the polymer did not penetrate the core samples, and should not affect concentrations. However, washing to remove the polymer can result in wash-off of components, and could potentially influence measured concentrations. Grout mixes use for treatment are shown in Table 3.9, and 1m long 100mm diameter cores were attempted, which was trimmed with a diamond saw cutter to required dimensions prior to analyses. However, due to installation processes, loss of grout, and sample fracturing during coring, it was not possible to obtain intact 1m samples.

Table 3.9: Grout mixes used on test site (Al-Tabbaa and Boes, 2002)



Mix	Cement : PFA : lime : bentonite	Water : dry grout	Soil : grout	Soil : dry grout
A	2 : 8 : 0 : 0	0·42 : 1	5 : 1	7 : 1
B	3 : 8 : 0 : 0	0·42 : 1	5 : 1	7 : 1
C	2·5 : 8 : 0·4 : 0	0·42 : 1	5 : 1	7 : 1
D	3 : 8 : 0·1 : 0	0·42 : 1	5 : 1	7 : 1
E	2·5 : 8 : 0·4 : 0	0·42 : 1	3·5 : 1	5 : 1
F	2·5 : 8 : 0·4 : 0	0·30 : 1	3·9 : 1	5 : 1
G	8 : 0 : 0 : 0·8	1·6 : 1	3·7 : 1	9·7 : 1

Design criteria for the site are shown in Table 3.10, and employed ASTM tests for UCS and durability assessment, and TCLP (toxicity characteristic leaching procedure) and NRA (National River Authority) leach tests for leachability. All measured UCS measurements exceeded the design criteria (350kPa), undertaken on 100mm diameter and

100mm long samples. Mix designs result in variable UCS trends with time, yielding three distinct trends, with all mixes showing sharp increases between 0.2 and 2.4 years. Mixes B and D show constant increasing with time, mixes G and A show UCS decrease after 2.4 years, whilst the remaining mixes show relatively smaller increases (levelling off) between 2.4 and 5 years. UCS Trend variations are essentially due to mix designs, and Figure 3.6 shows the treated made ground results with time.

Table 3.10: West Drayton design criteria (after Al-Tabbaa and Boes, 2002)

Test	Criterion	Method	Comments
UCS (Soaked)	350kPa	ASTM	Used 100mm diameter and 100mm high samples
Permeability	$< 10^{-9}$ m/s	Flow Pump Method	Using flexible wall permeameters, at hydraulic gradient of 10 – 40
Durability - Wet –dry and Freeze - thaw	Pass ASTM tests of 12 cycles	ASTM	Used 100mm diameter and 60mm high samples, freeze – thaw temperature was – 10°C instead of – 20°C
Leachability	Leachate concentrations ≤ 50 greater than drinking water standard	TCLP and NRA	TCLP test using dilute acid at pH 4.9 ± 0.2, and NRA test using deionised water modified to pH 5.5 ± 0.2
Leachate pH	7 – 11		Measured at end of leaching tests

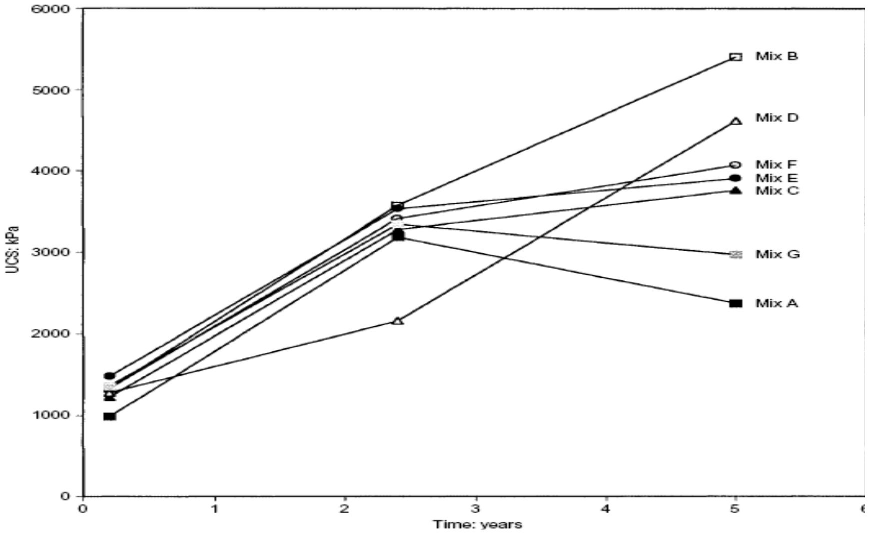


Figure 3:6: UCS results for made ground at 0.2, 2.5 and 5 years (Al-Tabbaa and Boes, 2002)

Implications of mix designs on properties can be draw from binder mix composition, cement content, water - grout ratios and soil - dry grout ratios. This case study does not address these implications, but rather highlights their importance and implications on sample properties and trend modifications. Results for permeability changes with time are shown in Figure 3.7. Three alteration trends are observed, where mixes F and mix B show increases with time, mixes A and G appear to stabilise at 2.4 years, and mixes D, C and E show decreases with time increase.

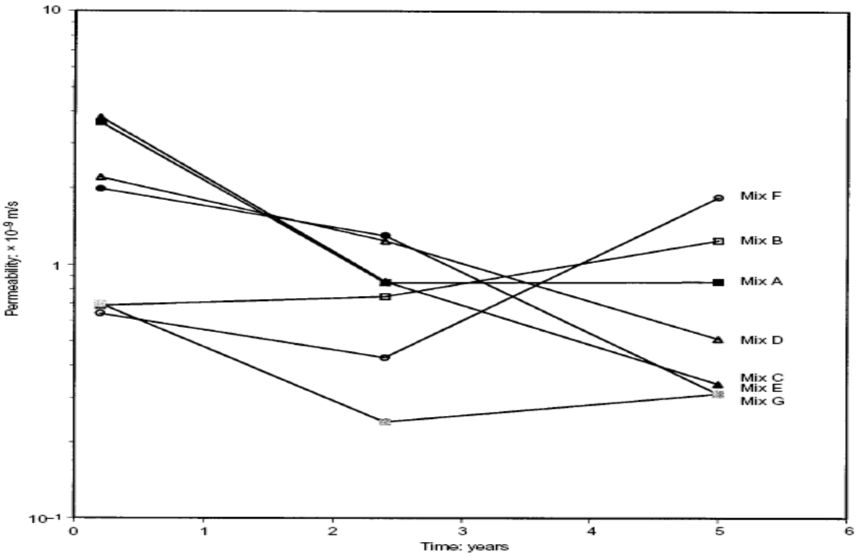
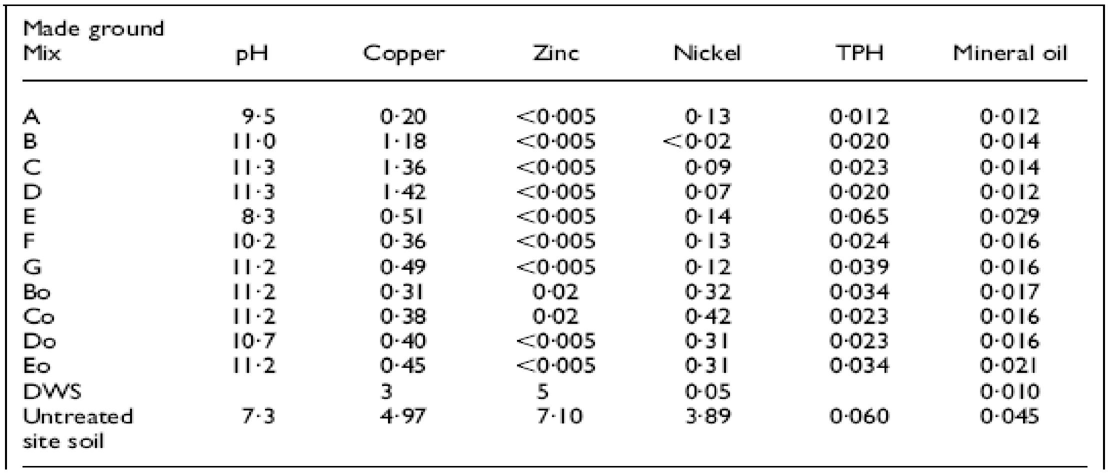


Figure 3:7: Made ground Permeability results at 0.2, 2.5 and 5 years (Al-Tabbaa and Boes, 2002)

To evaluate chemical modifications and contaminant containment effectiveness in treated samples, TCLP (toxicity characteristic leaching procedure) and NRA (National River Authority) leach tests were employed. These tests were suitable for use at the time of employment, since more detailed chemical characterisation tests have only been developed and come into force over the last decade. TCLP offered suitability for use as a land disposal compliance test in view of component releases, while NRA test yielded component leachabilities at pH close to expected under field conditions for leaching by acidic rainwater. NRA leach tests were only used at 5 years, thus correlations cannot be shown for modifications with time. Table 3.11 shows the leachate pH, heavy metal and total petroleum hydrocarbons (TPH) concentrations for mixes at 5 years, while Table 3.12 shows the leachate pH and heavy metal content at 0.2 and 5.0 years. pH modifications within a single made ground column are shown in Figure 3.8, at 0.2, 2.4 and 5.0 years after installation. These are similar to the findings by Pereira *et al.,* (2007), where big pH reductions are observed, but are still within desired pH ranges (7.5 – 11.0) Conner, 1990), except mix E. However, buffering capacities will be decreased at these pH values.

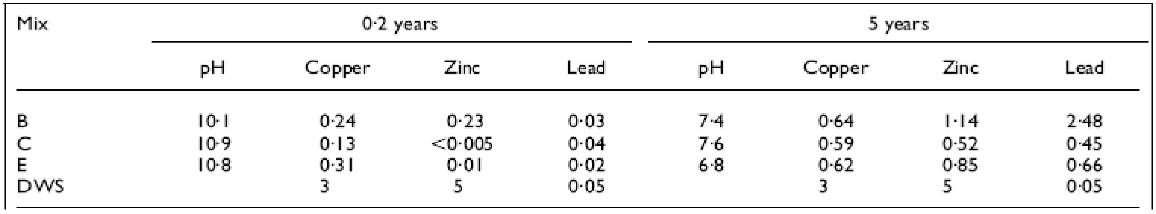
Table 3.11: Made ground NRA leachate pH, with heavy metals and hydrocarbons leachability at 5 years (mg/l) (Al-Tabbaa and Boes, 2002)



Made ground Mix	pH	Copper	Zinc	Nickel	TPH	Mineral oil
A	9·5	0·20	<0·005	0·13	0·012	0·012
B	11·0	1·18	<0·005	<0·02	0·020	0·014
C	11·3	1·36	<0·005	0·09	0·023	0·014
D	11·3	1·42	<0·005	0·07	0·020	0·012
E	8·3	0·51	<0·005	0·14	0·065	0·029
F	10·2	0·36	<0·005	0·13	0·024	0·016
G	11·2	0·49	<0·005	0·12	0·039	0·016
Bo	11·2	0·31	0·02	0·32	0·034	0·017
Co	11·2	0·38	0·02	0·42	0·023	0·016
Do	10·7	0·40	<0·005	0·31	0·023	0·016
Eo	11·2	0·45	<0·005	0·31	0·034	0·021
DWS		3	5	0·05		0·010
Untreated site soil	7·3	4·97	7·10	3·89	0·060	0·045

NB – DWS – Drinking Water Standards

Table 3.12: TCLP leachate pH and heavy metal leachability for made ground (mg/l) (Al-Tabbaa and Boes, 2002)



Mix	0·2 years				5 years			
	pH	Copper	Zinc	Lead	pH	Copper	Zinc	Lead
B	10·1	0·24	0·23	0·03	7·4	0·64	1·14	2·48
C	10·9	0·13	<0·005	0·04	7·6	0·59	0·52	0·45
E	10·8	0·31	0·01	0·02	6·8	0·62	0·85	0·66
DWS		3	5	0·05		3	5	0·05

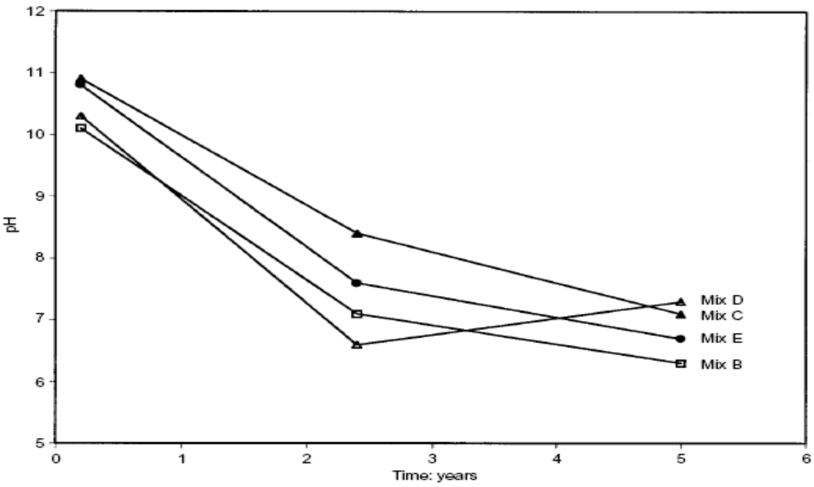


Figure 3:8: TCLP leachate pH with time for made ground columns (Al-Tabbaa and Boes, 2002)

TCLP results show increased metal leachability, and decreased pH between 0.2 to 5.0 years, with decreasing pH time trend (Figure 3.8) except for mix D, which shows slight increase between 2.4 and 5.0 years. No evidence of physical deterioration was observed with ageing, which suggests that chemical characterisation of matrices is of utmost importance in evaluating S/S effectiveness. Microstructural analyses (XRD and SEM) show increased calcite content at 5 years, due to carbonation of Portlandite, compared to earlier time scales, with a dominant CSH content and less evidence of Portlandite and calcium aluminates. Decreased strength and durability were also observed with increased permeability and component leachability, and column overlaps showed poor mixing efficiency of grout with contaminated soils.

3.9 SUMMARY

Using findings from the case study (Section 3.8.3) (not withstanding method and assessment limitations), and previous leaching and containment factors from review of literature in this chapter, effective chemical characterisation (including component speciation, complexation and alteration with time) and leaching evaluations are required to validate S/S durability and effectiveness. However, given complexities of S/S systems and inherent soil heterogeneity, there is need to evaluate S/S treatment of relatively well understood and simple matrices, before scaling up by introducing complexities.

CHAPTER FOUR

4.0 METHODOLOGY

This chapter provides details of materials and methods employed as part of the experimental procedures. Within this chapter, the laboratory aspects of the investigation, including material properties and characteristics, sample preparation, storage, sampling and testing, eluate preservation and analyses are presented.

4.1 EXPERIMETAL METHOD DEVELOPMENT

To assess efficiency and chemical durability of S/S treatment of contaminated land via leaching assessment and speciation modelling, it was essential to provide sufficient information to validate subsequent assessments and modelling methods (see Chapter 5 for details). Following detailed review of S/S (see Chapter 3), a careful selection of materials for sample preparation was undertaken, with consideration of suitability for the information required, whilst ensuring least chemical complexity. A suite of leaching tests was determined and adopted based on likely properties of the treated material (monolithic), to provide information for undertaking the assessments.

4.2 MATERIAL SPECIFICATION

The need to thoroughly characterise the system required use of least chemically complex material, likely to have the least effect on the bulk matrix. This allowed ease of characterisation and evaluation against the backdrop of dynamism and complexity of possible chemical interactions during stabilisation and material hydration.

4.2.1 Clay

Kaolin clay was selected for use due to its well defined physical and chemical properties, and minimal potential for alterations. PolWhite–E English China Clay refined clay) was used, supplied by IMERYS Minerals Ltd, Cornwall, UK, and is a high quality medium particle size kaolin product (IMERY, 2004). The mineralogy of the clay is given in Table 4.1 (IMERY, 2008).

Table 4.1: PolWhite-E Mineral Composition (IMERY, 2008)

Mineral	%Presence
Kaolin	74-80
Feldspar	5-12
Quartz	1-2
Mica	5-15
Montmorillonite	2-3

The typical properties of the kaolin product are given in Table 4.2, and a typical particle size distribution curve shown in Figure 4.1 (IMERY, 2004). All clay used in the study was mined from the same batch by the manufacturer, and supplied product was stored in sealed bags in a cool dry environment prior to testing.

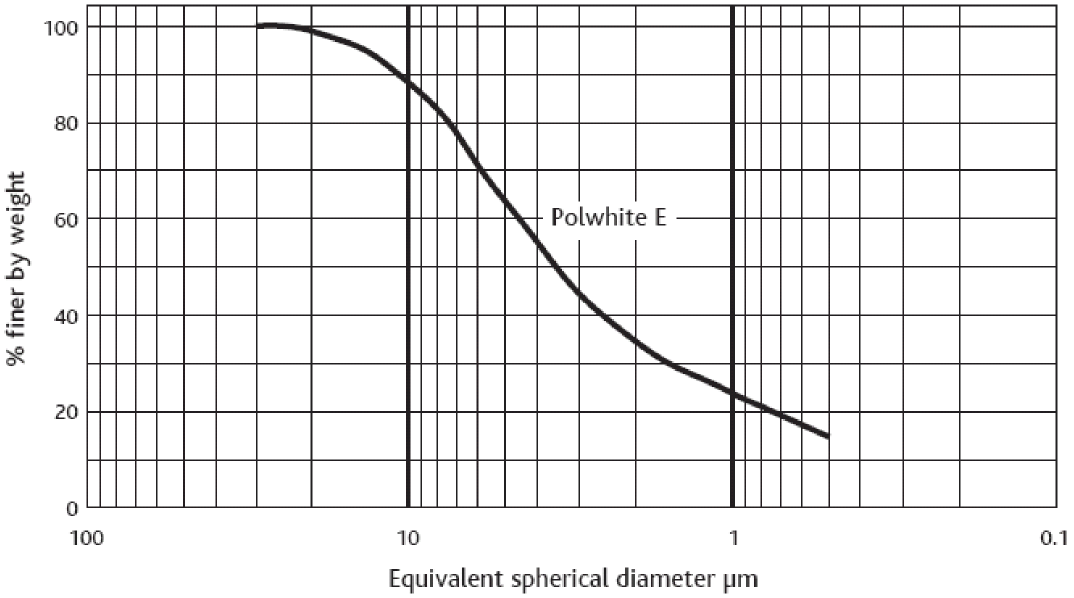


Figure 4:1: Typical PolWhite E Particle size distribution curve (IMERY, 2004)

Table 4.2: Typical Properties for PolWhite E (IMERY, 2004)

Parameter	**Values**
SiO_2 (%) via XRF (x ray fluorescence)	50
Al_2O_3 (%) via XRF	35
Water content (%)	1.5
pH	5.0
Yellowness	7
Specific Gravity	2.6
Surface Area (BET; m^2/g)	8
Oil Absorption (g/100g)	33
Water Soluble Salt Content (mass %)	0.15
Aerated Powder Density (kg/m^3)	360
Tapped Powder Density (kg/m^3)	810
Brightness (ISO R475)	78.5 ± 1.5
% Maximum > 10μm	35
% Minimum < 2μm	25

The significant properties likely to influence the S/S of the kaolin clay include: high silicate and aluminate content; high concentration of relatively non-reactive kaolin; low cation exchange capacity; low quartz but significant mica content; acidic pH; and low specific surface area compared to other clays.

4.2.2 Cement

The term ‘cement’ for work undertaken in thesis refers to CEM II – Ordinary Portland Limestone Cement (BS EN 197-1 – CEM 11/A-L 32, 5 R), a premium high quality lighter colour cement supplied by CEMEX UK Cement Ltd, Rugby, Warwickshire, UK. Some physical properties and Cr^{6+} content are given in Table 4.3, and the cement is a mixture of $3CaO - SiO_2$, $2CaO - SiO_2$, $3CaO - Al_2O_3$, and $4CaO - Al_2O_3 - Fe_2O_3$ (CEMEX, 2006). Mineral composition of the supplied cement was determined by the manufacturer via XRF analyses, undertaken over 3 months around production of the utilised batch (June to August 2008), and results for the average mineralogy are shown in Table 4.4. Chloride was observed in only 4 of 25 biweekly analyses, and the presented value is an average for the 4 measurements.

Table 4.3: Physical Properties of Portland Limestone Cement (CEMEX, 2006)

Parameter	Value
Mean Particle Size	5 – 30 Microns
pH	12 – 14
Density	2800 – 3200 kg/m^3
Dry Bulk Density	1100 – 1600 kg/m^3
Silica	< 1% crystalline silica
Soluble Chromium VI	< 2 mg/kg (2ppm)

Reducing agents (ferrous sulphate) are added to cement to keep the soluble Cr^{6+} below 2 mg/kg in compliance with UK regulation 2003/53/EC (CEMEX, 2006). These reducing agents have limited shelf life, requiring the cement be used within this period, to avoid detrimental implications such as skin irritations and dermatitis. Obtained cement was used within 2 weeks of purchase, with COSHH (control of substances hazardous to health) and risk assessments undertaken prior to use.

Table 4.4: Three Month Average concentration of Portland Limestone Cement (CEMEX, 2008)

Mineral	Concentration (%)
$Si0_2$ – Silicon Oxide	16.9
Al_20_3 – Aluminium Oxide	4.3
Fe_20_3 – Ferric Oxide	2.9
CaO – Calcium Oxide	61.9
MgO – Magnesium Oxide	1.0
SO_3 - Sulphate	2.7
Na_2O – Sodium Oxide	0.66
LOI – Loss on Ignition	9.2
Free CaO	2.1
Cl – Chloride *	0.06

NB: * Average of 4 measurements where Cl was observed

4.2.3 Contaminants

To evaluate performance and efficiency of the S/S process, two metallic contaminants were selected for addition to clay prior to treatment. This allowed assessment of partitioning / release potentials from treated matrices (See Section 4.4.1). The contaminants selected were Chromium (Cr^{3+}) and Zinc (Zn^{2+}) of analytical grade, in the form of hydrated nitrate salts, to ensure solubility in soil prior to stabilisation. Impurities and assay concentrations for Chromium nitrate nonahydrate ($Cr(NO_3)_3.9H_2O$) and zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) used are given in Tables 4.5 and 4.6 respectively (Fisher Scientific, 2008).

Table 4.5: Composition of Chromium III nitrate nonahydrate specified (Fisher Scientific, 2008)

Constituent	**Concentration**
Assay	≥95%
Chloride	≤0.003%
Iron	≤500ppm
Sulphate	≤0.01%

Table 4.6: Composition of Zinc nitrate hexahydrate specified (Fisher Scientific, 2008)

Constituent	**Concentration**
Assay	≥97%
Calcium	<50ppm
Chloride	<0.005%
Copper	<20ppm
Iron	<20ppm
Lead	<50ppm
Magnesium	<100ppm
Phosphorus (Total P)	<100ppm
Potassium	<50ppm
Silicon	<100ppm
Sodium	<100ppm
Sulphur (Total S)	<200ppm

The choices of contaminants for this study are due to differences in leaching characteristics, valency and oxidation properties, and presence in electric arc furnace ash contamination simulated in this study (Pereira *et al.,* 2001 and 2007).

4.2.3.1 Chromium

Usually occurs in two oxidation states - trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) varieties (Jing *et al.,* 2006). Cr^{6+} is acutely toxic as a respiratory carcinogen, while trivalent Cr^{3+} though less toxic may also be carcinogenic, causing allergic skin reactions with long-term exposure. Several studies have been conducted on S/S of chromium, and effects on different binder systems (Omotoso *et al.,* 1998, Wang and Vipulanandan, 2000, Halim *et* *al.,* 2004, Swarnalatha *et al.,* 2007, Luz *et al.,* 2007). Reinhart *et al.,* (1997) indicated that Chromium toxicity, solubility and mobility are dependent on oxidation state, and showed that Portland cement was ineffective in Cr^{6+} immobilisation, requiring reduction to ensure containment. However, Cr^{3+} was found to be successfully immobilised using Portland cement (Olmo *et al.,* 2003, Luz *et al.,* 2007), and accelerates C_3S hydration (Chen *et al.,* 2008). Leaching is strongly dependent on pH, and Jing *et al.,* (2006) found that Cr^{3+} leachability decreased with pH increase from 3.0 to 5.0, and then remained at similar levels between pH 5.0 and 10.5 before decreasing above pH 10.5. Modelling indications from the study indicated adsorption controlled releases below pH 10.5, and precipitation controlled releases above pH 10.5. Dermatas and Meng, (2003) suggest that immobilisation mechanisms for Cr^{6+} are through surface adsorption or reduction, while that for Cr^{3+} is through hydroxide precipitation. Use of Portland cement with other binders like GGBS (Laforest and Duchesne, 2006), and fly ash (Dermatas and Meng, 2003) may be suitable for immobilisation of Cr^{6+}, but these binders may not be suitable for use alone e.g. alkali activated fly ash (Palomo and Palacious, 2003).

4.2.3.2 Zinc

Often associated with cadmium, and occurs naturally in divalent form which is mobile under acidic conditions. Zinc hydrolyses at pH 7.0 – 7.5, forming zinc hydroxides above pH 8 (Mulligan *et al.,* 2001). Zinc is bio-available at high pH due to solubility of its organic and mineral colloids, and is toxic to plants at concentrations above 400ppm. Zinc can be sorbed by clays, and is sorbed by kaolin clay via lattice penetration and complex adsorption (Yong and Mulligan, 2003). Several investigations have been undertaken on zinc immobilisation in contaminated materials, with particular emphasis on leaching characteristic, which is observed to be amphoteric (Olmo *et al.,* 2003, Dutra *et al.,* 2006, Yin *et al.,* 2007, Olmo *et al.,* 2007, Battaglia *et al.,* 2007). Murat and Sorrento (1996) indicated acceptance of zinc into crystalline lattice of calcium silicate cement during hydration effectively removes zinc from the mobile phase depending on prevailing conditions. Diet *et al.* (1998) showed that zinc appeared to accelerate setting of calcium aluminate cements, and retard setting of calcium silicate cements. Retardation of C_3S is likely due to precipitation of calcium zincate, retarding hydration at early stages, but promoting hydration at later stages due to dissolution of calcium zincate with pH increase by C_3S hydration (Chen *et al.,* 2008). Carbonation can be good for zinc immobilisation by pH modification and chemical redistribution (Mollah *et al.,* 1993, Ecke, 2003), but can also increase leachability (Alba *et al.,* 2001) and compromise neutralisation capacity. Li *et al.* (2001) suggest that hydroxyl complexes $Zn(OH)_4^{2-}$ and $Zn(OH)_5^{2-}$ can be present in a strong alkaline solution, and their anionic properties preclude their adsorption to CSH, but they may form calcium zinc complexes during hydration (Mollah *et al.,* 1992, Mollah *et al.,* 1993, Paria and Yuet, 2006).

Health and safety concerns limited contaminants that could be used, with safer Cr^{3+} preferred over Cr^{6+}. Concentration used for each cationic contaminant was 500 mg/kg of clay, with risk and COSHH assessments undertaken prior to sample preparations.

4.2.4 Additives

To assess the implications of soil constituents on S/S processes, additives were introduced to kaolin clay prior to stabilisation. Two constituents known to influence cement hydration were selected – sulphate and humic acid (organics). These constituents influence hydration either by retardation or alterations in products formed (see Section 3.2). These constituents also form complexes with cations, and thus have significant implications on partitioning and release of contaminants. Due to time constrains, it was not possible to undertake testing with additive combinations, and further work is required for implications from multiple additives on S/S effectiveness.

4.2.4.1 Sulphates

Sodium sulphate decahydrate was used as a sulphate salt source. This was due to two main reasons; introduction of sulphate as a salt of a relatively non-reactive cation (sodium); and addition of salt in hydrated form to prevent drying by anhydrous varieties. The salt was in a crystalline form prior to mixing with the soil, and Table 4.7 shows the chemical properties of the salt and contained impurities.

Table 4.7: Specification for Sodium Sulphate decahydrate (VWR, 2009)

Characteristics	**Specification**
Assay - acidimetric	Min 99.0%
Appearance of Solution (10% water)	Conforms
pH at 5% water content	5.0 – 8.0
Chloride	Max 0.0003%
Phosphate	Max 0.001%
Nitrogen	Max 0.0005%
Heavy Metals (as Lead)	Max 0.0005%
Arsenic	Max 0.0001%
Calcium	Max 0.002%
Copper	Max 0.0002%
Iron	Max 0.0005%
Potassium	Max 0.002%
Magnesium	Max 0.001%
Lead	Max 0.0005%
Zinc	Max 0.002%

4.2.4.2 Humic Acid

Humic acids are complex mixtures of partially decomposed and transformed organic material, containing sulphur, nitrogen and phosphorus. They have high chelating properties for heavy metals, and a large fraction of its components belonging to carboxylic acid functional group. Compositions vary with location, and given its formation process, have no fixed chemical composition. Humic substances are extracted from soils with reagents, are insoluble in acid below pH 2.0 (Langmuir, 1997), with humic acid being the major extractable component. It is usually dark brown to black in colour, with high CEC (400 – 870 meq/100g) and ability to partition heavy metals. Technical grade humic acid (Sigma Aldrich, 2008) was used in this study, and being an irritant required use of personal protective equipment.

4.2.5 Extractions, Processing and Preservation

Primary leachant used for chemical testing was demineralised water, obtained via reverse osmosis (RO) using an ELGA PRIMER RO machine. Measured conductivity over one year testing period range between 4 and 8µS (micro Seimen). RO water was collected in 50 litre capacity HDPE (high density polyethylene) aspirators due to volume requirements, and used as needed. RO columns were changed when conductivity exceeded 8µS, to minimise ion introduction during extractions. Obtained eluates from chemical testing were filtered through 47mm diameter 0.45µm cellulose nitrate gridded filter paper, using 250ml polycarbonate filter funnels via vacuum filtration. 150ml of obtained eluates were preserved using 1ml of 50% Nitric acid (HNO_3), and stored at 21 ± 1°C to prevent re-precipitation of leached ions.

No re-precipitation was observed after acidification of samples obtained from time dependent and pH dependence extractions. However, gelatinous dark brown precipitates were observed from up-flow percolation extractions from humic acid samples. This did not influence analytical results, as analyses were undertaken after eluate collection, but may have implications if any subsequent analyses are required. 10% HNO_3 solution was used for cleaning glassware after tests, to minimise cross contamination. Due to high conductivities (>2000µS) of some eluates, dilutions were undertaken after filtration prior to analyses. It was found after a series of analytical trials for cationic analyses, that a 1 in 10 dilution was sufficient to give reliable and repeatable results. Ultra pure water was used for dilution, obtained using an ELGA UHQ ultra pure water machine. DOC analyses were undertaken without dilutions, due to equipment suitability for analyses within observed concentrations. 50ml of sample was separated for cation analyses, and an additional 0.5ml 50% HNO_3 was added to prevent any precipitation in analytical equipment tubing.

4.3 MATERIAL CHARACTERISATION

It was expected that contaminants or additives addition would influence clay properties. However, for the current study, characterisation tests were only undertaken to determine clay and stabilised clay properties as part of requirements for sample preparation. Influences of additive and contaminants were not considered. Compaction and particle density tests were undertaken to determine index properties of kaolin clay and stabilised kaolin clay, for use in sample preparation. Compaction tests were undertaken in accordance with BS 1377:4 for clay and BS 1924:2 for stabilised clay using a 2.5kg hammer to determine dry densities and optimum water contents. Particle densities were determined in accordance with BS1377:2 using the small pyknometer method for both treated and untreated clay samples. To determine porosity of stabilised matrices, particle density testing was also undertaken at the different duration of hydration required. De-aired water for pyknometer tests were obtained under a continuous vacuum in a desiccator. The pyknometer test was also undertaken under continuous vacuum to remove air from the sample and water, stirring slowly at intervals to remove air bubbles from the samples.

Prior to testing, elemental compositional analyses of matrices were undertaken using x-ray fluorescence (XRF), to determine concentrations for comparison with releases.

4.3.1 Composition Evaluation

XRF analyses was undertaken to provide information on quantitative elemental composition (%) of the different matrices (shown in Section 4.4.1) prior to analyses. The analyses were undertaken using a SPECTRO – XEPOS XRF instrument at the School of Applied Sciences laboratories, University of Wolverhampton. Sample preparation for analyses utilised the briquette method, which involved drying and crushing the solid sample, which were then briquetted using a 15 Ton hydraulic press prior to analyses using 8.5g sample and 1.5g Hoechst wax (HWC) wax binder.

4.4 LABORATORY EXPERIMENTATION

To achieve effective stabilisation, a method for sample preparation, packing and storage for hydration had to be developed (see Section 4.4.2). A suite of physical and chemical testing was required to obtain required information for material characterisation and leaching evaluation. Given requirements for effective chemical characterisation and leaching evaluation (see Section 3.9), bias for chemical testing over physical testing was necessary, in view of time constraints, as these determine component releases.

4.4.1 Sample Preparation

To ensure suitability for use in the suite of tests to be undertaken on stabilised matrices, treatability and consistency evaluations had to be undertaken to determine a suitable mix and sample preparation method. Kamruzzaman *et al.* (2006) indicated that 10% cement content was optimal for formation of cementitious products with kaolin minerals in mixed marine clay. This cement content was trialled with kaolin clay, during treatability studies, for 500mg/kg zinc and 500mg/kg chromium contaminations. Results at

28 days hydration showed that after agitation at 10rpm for 48 hours, contaminants were successfully partitioned within samples at natural pH, with release concentrations below detection. Consistency evaluations were then undertaken to optimise mixing and sample preparation, to reduce influence of heterogeneity.

4.4.1.1 Sample Mixing

Changes due to additive / contaminant inclusions were not assessed during consistency evaluations to ensure adoption of a single consistent sample preparation approach for all the matrices. Compaction testing results (Section 6.1.1) showed optimum water content of 28%, but mixing, storage for cation exchange and packing resulted in water losses of 1 – 2%. 30% water content was subsequently used for all sample preparation to mitigate this loss, which also improved workability during mixing. Mixing optimisation was undertaken using 50ml of 40% methyl blue solution in 5kg of clay-cement mixes in 35l capacity Hobert mixer (H300) with 30cm diameter paddle. Visual observations of even colour distribution were used, with considerations of reasonable mixing durations to prevent moisture loss. Optimum mixing was attained using 40rpm speed for 1 minute to allow water distribution, and 70rpm for 3 minutes, with a pause at 2 minutes to scrape peds off sides of the mixing bowl. Starting at the lower speed also reduced dust generation, with water introduced to dry clay in the bowl before mixing, and a damp plastic sheet wrapped around (Figure 4.2) to prevent dust escape. This process was used for preparation of all mixes (Table 4.8), without considering influence of inclusions on mixing consistency.

For matrices with contaminants / additives, clay was premixed at 20% water content with required inclusions, then stored in sealed plastic bags for 48 hours at laboratory temperature (20 ± 5°C) to allow cation exchange. Cement was then mixed in as slurry, with remaining water to make 30% water content to consistency. The mix designs are given in Table 4.8, and the Hobert mixing bowl had an optimum capacity to mix 11.05kg of sample, which sufficed for preparation of sample batches for testing over 3 hydration durations. Water content corrections were made for sulphate samples due to use of hydrated sodium sulphate. Batches were mixed in bulk for relative homogeneity prior to packing and storage, and the mixing bowl and paddle was washed with demineralised water and dried after each episode to prevent cross contamination. The mixing bowl and paddle were made of aluminium, while the top fitting section designed to contain spillage was made of steel.

Figure 4:2: Hobert H300 Mixer with sample in bowl

Table 4.8: Mix Design

Mix	Clay (g)	Additive (g)	Contaminant Metal (g)	Cement (g)	Water (ml)
Kaolin	8500				2550
ECC Zn	8500		4.25 - Zn		2550
ECC Cr	8500		4.25 - Cr		2550
EO	7650			850	2550
EOZ	7650		4.25 - Zn	850	2550
EOC	7650		4.25 - Cr	850	2550
EOS	7267.5	382.5 - Sulphate		850	2330
EOSZ	7267.5	382.5 - Sulphate	4.25 - Zn	850	2330
EOSC	7267.5	382.5 - Sulphate	4.25 - Cr	850	2330
EOH	7565	85 – Humic acid		850	2550
EOHZ	7565	85 – Humic acid	4.25 - Zn	850	2550
EOHC	7565	85 – Humic acid	4.25 - Cr	850	2550

NB: ECC – Kaolin clay, EO – Stabilised Kaolin, S – Sulphate, H – Humic acid, Z – Zinc, and C – Chromium. All mixes stabilised at 10% cement content, as ratio of total mass.

4.4.1.2 Sample Packing, Curing and Sampling

After mixing, samples were packed in 100mm diameter pvc-u (polyvinyl chloride) pipes using an ENERPAC PAMG1405N hydraulic ram. However, optimum compaction conditions could not be achieved in the pipes using this arrangement. Trials were undertaken using 2068kPa compressive pressure, with pipes wrapped in wire mesh to prevent rupture, and yielded optimum bulk density of 1.6Mg/m^3. Bulk densities were used during the preparation trials, since dry densities will vary due to variations in mix designs. 300mm extensions were fitted to the ram with 99mm circular base (Figure 4.3), and a 100mm top appendage was attached to tops of sample pipes for sample introduction. This allowed loose material to be packed into pipes, and vertical pressures applied to compress the material. Samples were prepared in two lengths, 100mm (monolithic tests) and 300cm (additional testing). Samples were introduced in even layers, 3 for 100mm samples, and 5 for 300mm samples. After introducing each layer, vertical pressure was applied until refusal, and pressure sustained for 30 seconds before release.

Figure 4:3: Hydraulic Ram equipment with fitted extension

Bulk densities employed were for averages across the whole sample, Figure 4.4 shows the completely packed and sealed samples, and extruded 100mm sample with clearly defined layering. After compressing the final layer, the top of the sample was trimmed of excesses and capped with low density polyethylene caps, and sealed with silicon sealant to prevent air ingression during hydration. Samples were labelled, dated and stored in a temperature controlled room at 21 ± 1°C, which corresponded to temperatures at which the European Committee for Standardisation (CEN) leaching tests used in the study are undertaken (Section 4.5.1, 4.5.2 and 4.5.3). At time of sampling for testing, the cap was slit with a cutting knife and removed, and the sample fitted to a hydraulic compaction sample extruder with a 100mm diameter uplift plate and extruded. This hydraulic extruder is used for removal of compaction samples from the proctor mould, and extruded samples were weighed and measured prior to testing.

Figure 4:4: Packed, capped and sealed samples in drain pipes, and extruded 100mm sample

4.4.2 Sample Testing

Three hydration durations were selected to test samples over one year period: 28 days, 150 days and 300 days. The selections of test employed were based on obtaining minimum information required for chemical characterisation matrices and assessments of component leaching. Physical tests selected were based on information required for incorporation in chemical leaching evaluations, with primary focus being chemical testing. All equipment was prepared for this research, to ensure control and repeatability, with focus on chemical testing. Desirable physical parameter tests like permeability, diffusion coefficient, and physical durability tests could not be undertaken due to time and resource constraints. However, these tests were not absolutely required, since assessments were primarily for release evaluations rather than release mechanisms influence estimation.

4.4.2.1 Physical Parameters

Physical parameters measured for stabilised matrices were based on requirements for evaluating matrix properties and component leaching. These included weights and dimensions, water content, particle density (BS 1377:2), Porosity and Tortuosity.

Porosity estimations were required for diffusion controlled release assessments for monolithic material, and were estimated from the bulk and particle density of the materials. The bulk densities of monolithic 100mm specimen were obtained using water content, weight and volume, and particle densities calculated (BS 1377:2). Obtained values provide average porosities for matrices, considering that samples were packed in layers, with observed discontinuities at the interface between layers.

Tortuosity is a measure of physical retardation, and gives indication of the path length which diffusing ions must cover in a porous matrix. It is a material property, and therefore is not ion specific. For calculations the least reactive ion in the material is selected (Environment Agency, 2005). In most cases, this is sodium (Na), which shows lowest diffusion coefficient and highest free mobility in water. It is often ideal to calculate diffusion coefficients for several ions to validate use of Na, and tortuosity of monolithic material can be calculated using the formula:

$$T = \frac{D_{Na}}{De,_{Na}} \qquad 4.1$$

Where: T – Tortuosity of the material,

D_{Na} – diffusion coefficient of Na in water – $10^{-8.88}$ m^2/s (Environment Agency, 2005)

$D_{e,Na}$ – calculated effective diffusion coefficient of Na in material (m^2/s)

4.4.2.2 Chemical Parameters

To obtain required chemical information for leaching assessments, it was necessary to collect information on the chemical properties that influence releases of components from stabilised matrices. These parameters are influenced by prevailing extrinsic and intrinsic parameters, so prevailing conditions were controlled to represent testing conditions e.g. temperature control. Chemical parameter measurements collected include pH, conductivity and Eh (redox potential).

pH is the measure of acidity or alkalinity of a solution, defined as the negative, base-10 logarithm of the hydrogen-ion activity, and controls or is involved in controlling most chemical reactions (Langmuir, 1997). Due to pH temperature sensitivity, all measurements were undertaken in the temperature controlled room, at a temperature of 21 ± 1°C, with calibrations referenced to 20°C. An ORION Bench-Top pH meter model 520A was used, with a VWR 662 1780 pH high accuracy fixed cable sealed flat double junction combined pH electrodes with a Bayonet Neill Concelman connector. The electrode was fluoride resistant, with 95% measurement stability at less than 5 seconds for measurements, and recalibration was undertaken on after every 10 measurements, using 3 standard calibration buffers (pH 4.0, 7.0 and 12.6).

Electrical conductivity (EC) of a solution is the measure of its ability to conduct electricity, and serves to estimate the total dissolved salts (TDS), or total amount of dissolved ions. EC was measured in Micro Siemens per centimetre (µS/cm), and measurements of test eluates were aimed at yielding indications of increasing / decreasing dissolved salts concentrations during the leaching. EC is temperature sensitive due to solubility levels being temperature dependent, so measurements were taken at constant temperature (21 ± 1°C). A HANNA HI 9033 multi range portable conductivity meter was employed for eluate measurements during testing.

Redox potential (Eh) in volts is the measure of oxidation – reduction potential. Most reactions involve electrons and protons, and oxidation releases protons which induces acidity while reduction consumes protons which induce alkalinity. Redox reactions involve oxidising and reducing agents, and most literature has abandoned the use of Eh in favour of pE which is the negative logarithm of electron concentration [$pE = -\log_{10}(e^-)$]. pE is related to Eh at 25°C by the expression (Langmuir, 1997):

$$pE = \frac{Eh(volts)}{0.05916} \qquad 4.2$$

Using the pE approach avoids the issue of whether or not Eh is measureable, and if measured, is thermodynamically meaningful. Stable Eh measurements are only possible in optimised systems, described by high redox capacities which tend to resist Eh changes (Langmuir, 1997). However, stable and repeatable Eh measurements were not achievable during measurements of eluates, with rapid changes observed over short durations from test completion. pE estimations for speciation modelling were undertaken by ORCHESTRA (see Section 5.4.3).

4.5 CHEMICAL TESTING

Chemical tests were employed to investigate stabilised matrices chemical characteristics. Tests selections were based on information requirements, i.e. component availabilities and pH dependent releases, time dependent leaching, and porewater chemistry under prevailing conditions. Complexation with HFO was also considered, requiring extractions to determine available reactive HFO content. Leaching test was selected from harmonised EU CEN (European Committee for Standardisation) leaching protocols, obtained from Energy Commission of the Netherlands (ECN), that hosts the leaching protocol technical committee. These standards were still in production at start of this research. Information on selection rationale, leaching assessments and geochemical modelling methods are given in Chapter 5.

The suite of tests selected compromised of the dynamic monolithic leaching test (DMLT) CEN/TS 15863 for time dependent aspects; the upflow percolation CEN/TS 14405 for porewater chemistry; and pH dependence leaching test CEN/TS 14429 with initial acid / base additions for pH dependent release, acid / base neutralising capacities (ANC / BNC) and availability. pH dependent information were also be used for speciation evaluations and leaching predictions. HFO determinations were undertaken using dithionite, ascorbate and oxalate extractions, along the guidelines of Dzombak and Morel (1990). Clay affinities for introduced contaminants were also assessed to determine sorption capacities, using ASTM contaminant sorption capacity test D4646 – 03 (2008).

4.5.1 Dynamic Monolithic Leaching Test

The dynamic monolithic leaching test (DMLT) CEN/TS 15863 (2008) was employed to determine time dependent aspects of leaching from stabilised matrices. This test is suitable for monolithic specimens of known dimensions, with low hydraulic conductivity (less than 10^{-8} m/s) and minimum side dimensions of 40mm. Where new sample surfaces are exposed through trimming / cutting to attain required dimensions, component releases may increase and should be considered. The test is not suitable for materials which generate excessive heat or gas emissions in reactions with utilised leachants. This test can also be used to determine leaching mechanisms, distinguishing between dissolution, diffusion and wash off controlled releases, to evaluate the materials intrinsic properties (CEN/TS 15863, 2008).

Testing was undertake in leaching vessels at fixed liquid (L) to specific surface area (A) ratios under temperature control, with leachant renewal at specific time intervals. Obtained eluates were filtered, analysed, and released constituents evaluated in view of release from geometric surface area. From components cumulative releases, leaching mechanisms controlling release can be identified e.g. diffusion through pores from test specimen surfaces, constituent dissolution / solubility controlled release, initial wash-off, and dissolution of material matrices (Environment Agency, 2005).

Leaching tanks were designed for testing, based on the expected monolithic specimen size. A non-reactive (glass or plastic) container, which can be closed to avoid prolonged contact with air, capable of holding test specimen with leachant at L/A of 8 ± 0.1 was used. A minimum space between the sample and walls of leaching tank of 20mm was used, based on the method requirements. This was a PVC cube measuring 220mm on all sides on the outside and 200mm on all sides on the inside (Figure 4.5A). A 10mm hole was drilled at top corner of vessel lids, to allow for removal and renewal of eluates and leachant without excessively disturbing test specimens. PVC supports were centrally fixed to bottom plate of vessels, to suspend 100mm diameter sample 20mm above the vessel bottom, in line minimum space requirements for CEN/TS 15863 (See Figure 4.5B).

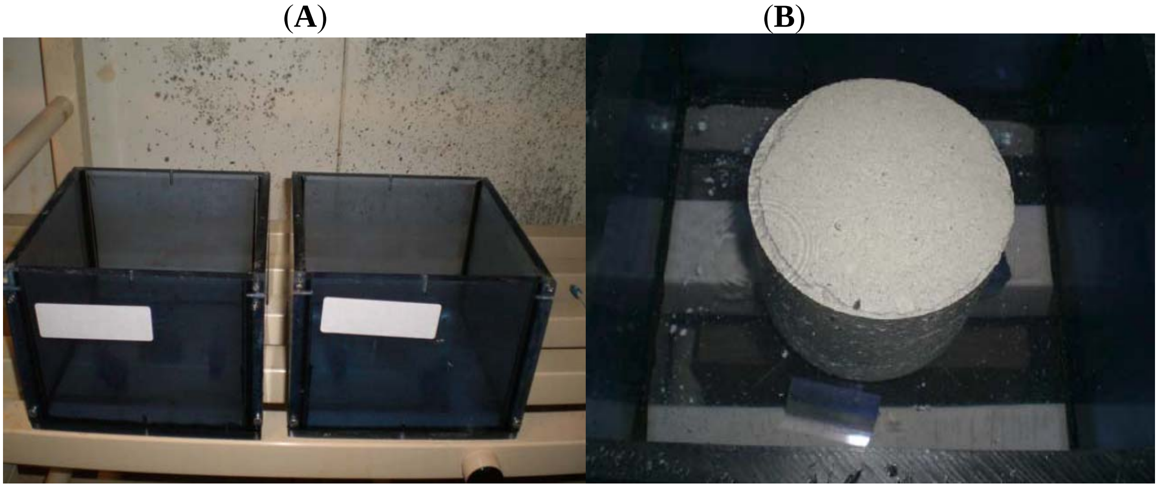


Figure 4:5: (A) Leaching vessels (B) Sample on support in leaching vessel

Leaching tanks were washed with demineralised water, rinsed with 1mol HNO_3 and filled with demineralised water for 24 hours prior to use. A peristaltic pump was required for eluate and leachant removal or renewal, and the piping was cleaned with 1mol HNO_3, soaked in demineralised water prior to use, and continually flushed with demineralised water for 10 minutes after each sampling episode.

100mm diameter and 100mm long samples (Figure 4.4) were used in testing, extruded using a 100mm diameter plate on a hydraulic extruder. Multiple samples were required for each matrix, with one being crushed for use in the determination of intrinsic material properties required for the test, such as particle density and water content. Measurements of sample dimensions, volume and weight were taken after extrusion, and brushed to remove lose particles prior to loading in the leaching vessel. Leachant volumes were determined based on specific surface area (A) for cylindrical samples [$2\pi r$ ($r + h$)], and an average from 5 random samples was used, which gave height of 104mm, and radius of 52mm. This yielded specific surface area of 50990mm^2, and leachant volumes of 4.08L at 8:1 L/A. To maintain at least 20mm of leachant over tops of samples, 4.4L demineralised water was used for all fractions, which conformed to L/A 8.1:1.

At commencement of testing, leachant was added to the sample in the tank, which was then labelled accordingly, noting sample matrix, date and time. Unstabilised clay samples did not retain integrity during testing, and as a result testing was discontinued after collection of first eluate fraction (6 hours) to assess releases from the unstabilised material. Table 4.9 shows the leachant renewal periods employed for testing over 64 days, and Figure 4.6 shows the disassociated clay peds from an unstabilised clay sample. Measurements of chemical properties (pH, Eh and conductivity) were undertaken on obtained eluates after each fraction, which was then filtered and acidified to prevent precipitation before undertaking chemical analyses.

Table 4.9: Leachant renewal times for the DMLT

Fraction	Duration of specific fraction ± 5% (days)	Cumulative Duration ± 5% (days)
1	0.25	0.25
2	0.75	1
3	1.25	2.25
4	1.75	4
5	5	9
6	7	16
7	1	17
8	19	36
9	28	64

Figure 4:6: Unstabilised clay sample after 6 hours of testing

A blank test was run for 24 hours at different sampling periods, to evaluate effects of leachant, leaching vessel and eluate collection processes. Factors that control release in monolithic specimens include shape, dimensions, porosity, tortuosity, pH, redox, availability, temperature, degree of water contact, nature of material, type of leachant, solubility of material, ability to undergo wash off and diffusion (CEN/TS 15863, 2008). After test completion, it is important to determine leaching mechanisms responsible for release, to assess if releases are diffusion controlled or other leaching mechanisms contribute. To determine release mechanism, cumulative releases of component for first 8 fractions (over 36 days) were used, grouped based on guidelines for DMLT, and are shown in Table 4.10 (Environment Agency, 2005).

Table 4.10: Fraction grouping for release mechanism evaluation

Order	Eluate fraction	Increment a – b (cumulative)
1	Fraction 2 to 7	Increment 2 – 7
2	Fraction 5 to 8	Increment 5 – 8
3	Fraction 4 to 7	Increment 4 – 7
4	Fraction 3 to 6	Increment 3 – 6
5	Fraction 2 to 5	Increment 2 – 5
6	Fraction 1 to 4	Increment 1 - 4

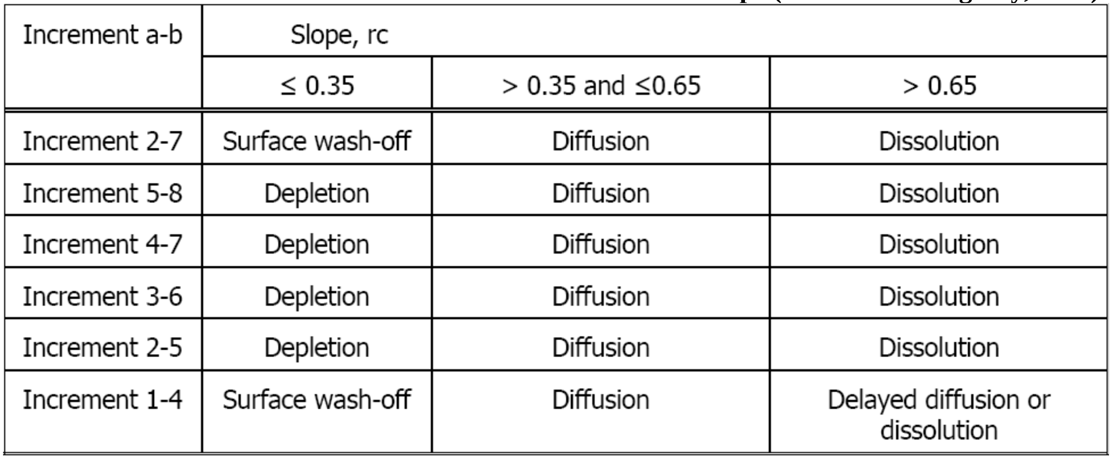
The concentration factor (cf) and slope (rc) of the linear regression line for plots of log concentration (□) versus log time (t) for each cumulative increment (a-b) of each component are then calculated, along with standard deviation of the slope (sd_{rc}).

Where $$cf_{a-b} = \frac{M}{LD} \qquad 4.3$$

M = mean concentration in the increment, and LD = lowest limit of determination.

Next, it is important to check for material dissolution by checking if $cf_{5-8} > 3.0$ and $rc_{5-8} > 0.8$, and if the material does dissolve the criteria will be met. Once no dissolution is observed, release mechanisms can be determined using Table 4.11 (Environment Agency, 2005) based on the calculated slopes.

Table 4.11: Determination of release mechanism based on the slope (Environment Agency, 2005)



Increment a-b	Slope, rc		
	≤ 0.35	> 0.35 and ≤0.65	> 0.65
Increment 2-7	Surface wash-off	Diffusion	Dissolution
Increment 5-8	Depletion	Diffusion	Dissolution
Increment 4-7	Depletion	Diffusion	Dissolution
Increment 3-6	Depletion	Diffusion	Dissolution
Increment 2-5	Depletion	Diffusion	Dissolution
Increment 1-4	Surface wash-off	Diffusion	Delayed diffusion or dissolution

For fully diffusion controlled release system the slope is exactly 0.5, and other criteria include: $cf_{a-b} \geq 1.5$, $sd_{rc} \leq 0.5$ and $0.35 < rc \leq 0.65$. However, given the nature of the test matrices, some dissolution is expected from the stabilised matrices (See Section 6.3.2). To assess effective diffusion coefficient of components, it must first be established that diffusion is the release controlling parameter. The availability of components is also required, determined via pH dependence leaching test (Section 4.5.3). For calculating tortuosity, the average effective diffusion coefficient $p\mathrm{D}_e$ are used:

$$\mathrm{D}_e = \left(\frac{\varepsilon 64}{2653 \times p \times Uavail} \right)^2 \times f \tag{4.4}$$

This is expressed in the form of negative logarithm where $p\mathrm{D}_e = -\log \mathrm{D}_e$

Where: D_e – Average effective diffusion coefficient for a given component

□64 – Derived cumulative leaching of the component over 64 days in mg/m^2

p – Density of the material in kg dry matter per m^3

U_{avail} – Leachable available quantity of the component

f – Is a factor equals to 1 s^{-1} (Environment Agency, 2005)

4.5.2 Up-Flow Percolation Leaching Test

Even though stabilised matrices were monolithic in form, it was important to assess equilibrium conditions, not just in terms of pH dependency, but also for releases to porewater. This can be realised using suitable percolation tests, using data for the first two eluate fractions up to a liquid (L) to solid (S) ratio of 0.3 or cumulative L/S ratio of 0.5. The upflow percolation leaching test CEN/TS 14405 (2008) was employed on crushed samples (<4mm particle size), along the prescribed method guidelines.

The test required the use of leaching columns of fixed diameter and height, and the current study employed 100mm diameter 320mm high columns (Figure 4.7). The leaching columns were made of non-reactive PVC-u pipes with top and base plates, with allowances for tubing and fitting of 100mm diameter 0.45µm pore glass-fibre filters to filter leachant pumped through samples. Flanges were prepared with rubber seals to make the arrangement watertight. Prior to testing, leaching columns were washed with 1mol HNO_3 and filled with demineralised water to stand for 24 hours, repeated at the end of each testing episode. 10mm polyethylene pipes were used to convey the leachant to and from leaching columns, soaked in HNO_3 and rinsed with demineralised water before and after each test episode.

Figure 4:7: Assembled leaching columns, and a complete arrangement of the test apparatus

Testing required linear flow velocity of 150mm a day through the empty column, which varies between 40 and 60ml/h with packed material in 350mm high columns. For the current test a flow capacity of 48ml/h through the packed column was used, obtained using a peristaltic pump (Figure 4.7B) calibrated using yield volumes with time for each sample batch. Testing required samples sizes with 95% passing through 4mm sieve, requiring size reduction (crushing) of the monolithic material. It was important to minimise excessive aeration of samples during crushing, which could alter the alkaline samples due to carbonation. Contamination and cross contamination of samples during crushing were also considered. To crush samples, vertical compressive force was employed, using the hydraulic ram at 6550kPa with a 450mm by 150mm and 15mm thick steel base plate, in a stainless steel box with dimensions of 480mm by 180mm by 150mm (length - width - height). Samples were crushed to large chunks, and then further reduced in size by crushing with a Kangol compaction hammer before sieving through 4mm sieve. The Kangol hammer was wrapped with LDPE sheet during crushing to prevent cross contamination, and the steel box was washed, dried and filled with anhydrous silica gel to prevent rusting after each episode. Water content measurements were taken before crushing, and the crushed sample air dried at 21 ± 1°C before packing into columns to prevent thermal alterations of samples. All equipment used for sample preparation was washed and dried after preparation processes, to prevent cross contamination.

After air drying, water contents of samples were determined, before samples were packed into leaching columns to start the test. The bases with rubber seals are fitted first to columns using 40mm screws, to suspend the columns above ground, allowing for leachant pumping through piping fitted at the bottom of the column (Figure 4.7). 100mm glass-fibre filters are then placed at the base to prevent back wash of material to the pipes, and 10mm of inert fine quartz sand (prewashed with demineralised water and dried at 105°C) is added to the base to aid in even permeation of water up the column. The arrangement was weighed, and then test specimens introduced as 5 equal layers to make up 300mm in the column. Each layer was subdivided into 3, each levelled off after introduction to column. After introducing each layer, a 500g weight was used to compact the material, via a vertical drop 3 times down a height of 200mm. Approximately 600g of material were selected for each layer with 200g sub-layer determined by trials, with the last layer was levelled off to yield a height of 320mm before compaction. The column was then weighed to determine the sample mass, and 10mm of sand added to the top to fill the column before fitting the filter paper and sealing the top section of the column. Figure 4.8 shows a cross-section of the material introduced to the column, before sealing to commence testing.

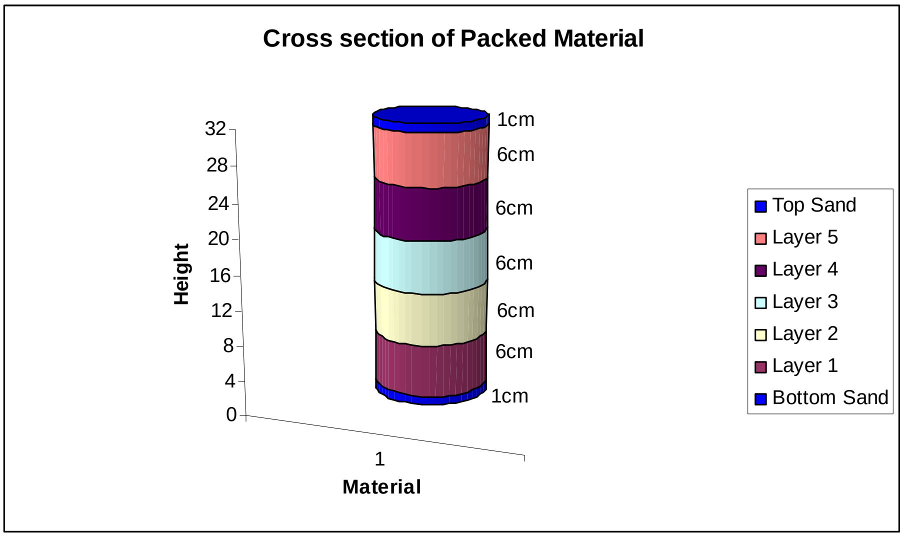


Figure 4:8: Cross section of packed material in columns

To start up the test, pre-saturation of columns was required to allow for sample equilibration over a period of 4 days. This was achieved by connecting a reservoir of demineralised water to the columns to saturate samples (Figure 4.9A), constantly topping up the reserve until eluate is observed in the top outflow pipe. At this point equilibration commences, allowing even water permeation under constant head. After 4 days of equilibration, columns were connected to the pump and the test started at 48ml/hr flow rates under temperature control.

Taps were put in place to prevent backflow from saturated columns, ensuring that columns could be isolated and connected to pumps without eluate loss. Eluates were collect in 1L Duran volumetric bottles (Figure 4.9B), and verification of equilibration was determined by measuring the pH of the first 0.1 L/S fraction, and comparing this to the next 0.1 L/S fraction. If the pH values do not vary by more than 0.5 units, the eluates are combined as the first 0.2 L/S fraction, with chemical parameters measured and the eluate acidified. The test is continued to obtain the next fraction of 0.3, yielding cumulative L/S ratio of 0.5 at which point the test is terminated after chemical parameter measurements. The Duran 1L glass bottles were filled with nitrogen to prevent eluate carbonation, prior to starting test commencement, and after each eluate fraction collection.

A B

Figure 4:9: A. Column with leachant reservoir to achieve saturation B. Testing in progress

Collected eluates were then filtered and prepared for analyses (dilutions and preservation), and the columns emptied and washed with water, rinsed with HNO_3, then filled with demineralised between test episodes.

4.5.3 pH Dependence Leaching Test

To evaluate pH dependent equilibrium leaching properties of the stabilised matrices, the CEN/TS 14429 (2008) pH dependence leaching test with initial addition of acid / base was employed. The test required a minimum of 6 leachate fractions with typical final pH values between 4.0 and 12.0, and a maximum pH variation of 1.5 units between fractions. However, during testing, it was not always possible to maintain a maximum pH variation of 1.5, considering that consumption of acid / base requirements were determined by preliminary titrations and test trials, and the samples exhibited significant buffering over the test duration (48 hours). However, no observed pH variation exceeded 2 units, with fraction numbers varying between 7 and 10, and observed values between 3.9 and 12.7 for equilibrium leaching over 48 hours.

Acids or bases were required for pH modification, and for acid 0.1 and 2mol HNO_3 were used, and for base 0.1 and 1mol Sodium hydroxide (NaOH) were used. Demineralised water was the primary leachant, and required amounts of acid or base to meet desired end pH values were added prior to test commencement. Testing procedures require agitation over 48 hours at 10rpm (rotations per minute) using an end over end shaker (Figure 4.10) under constant temperature. 270ml internal capacity polyethylene wide mouth bottles were used for samples, and were washed with water and rinsed with HNO_3 and demineralised water prior to tests.

Test procedures required samples of particle size with 95% $\leq$ 2mm. Samples crushed for use in percolation tests were further reduced using a mortar and porcelain bowl to prevent excessive alteration or contamination. This was then sieved through a 2mm sieve after water content determination, sealed in plastic bags and stored at 20 ± 1 °C. An average water content of 20% was observed for crushed samples of the different matrices, and tests were undertaken using 15g of sample, leached with 250ml of leachant to give an L/S ratio of 20 ± 1: 1 prescribed by CEN/TS 14429. Leachants were prepared in 250 volumetric flasks, by adding required amounts of base / acid to obtain end pH values of interest for the different fractions, and made up to 250ml using demineralised water for addition to the test specimens (Figure 4.10).

Figure 4:10: Batch extraction end over end shaker, and test fractions during leachant addition

After weighing 15g of samples (at 20% water content) into leaching containers, and preparing leachants to obtain end pH values of interest, tests were started at t_0 (time zero) by adding a third of the leachants to test specimens. These were then loaded into the end over end shaker and agitated at 10rpm for 30mins, and then another third of leachant added to samples at t_{30mins}, taking care when opening the container to dispose of any generated gases safely. The remaining leachant was added at t_{2hours}, with agitation continued after each leachant addition. pH values for different fractions were measured and documented at t_4, t_{44} and t_{48hrs} at completion, where t_{44} is a measure to validate equilibration. The difference in pH between t_{44} and t_{48hrs} should not exceed 0.3 pH units if equilibration has been attained. This criterion was achieved in all samples tested. Demineralised water blanks were run along with all matrices, to evaluate effects of test processes on releases. Eluates were allowed to settle for 5mins and chemical measurements taken, before being filtered, preserved and analysed.

4.5.4 Hydrous Ferric Oxides/hydroxide Extraction

To undertake speciation evaluations, complexation of components to HFO have to be evaluated, requiring extractions to determine their available amounts. HFO requirements for modelling are discussed in Section 5.4.2, and extractions were undertaken along the guidelines of Dzombak and Morel (1990) for ascorbate, oxalate and dithionite extraction procedures. Leachants used for extractions prepared for each new experiment, and test samples crushed below 2mm size and oven dried prior to testing. Cation analyses of obtained eluates for Fe, Al and Mn were undertaken, and results used in calculating total HFO for speciation modelling (Section 6.3.4).

Ascorbates are salts of ascorbic acid, which is a sugar acid (monosaccharide with a carboxyl group) with antioxidant properties. The ascorbate extraction test is used for the extraction of amorphous ferric oxide using analytical grade sodium hydrogen carbonate, tri-sodium citrate dihydrate and ascorbic acid. To prepare leachant, 10g of sodium hydrogen carbonate was mixed with 10g of tri-sodium citrate dihydrate in 500ml wide mouth polyethylene bottles. 200ml of nanopure water was then added to the mixture, and then deaerated for 4 hours by bubbling nitrogen through the sample. After deaeration, 4g of ascorbic acid was added to the solution, and then the solution deaerated again for 1 hour, yielding a final pH 8.0. Then 3g of test samples were weighed into 80ml wide mouth polypropylene bottles, and 60g of prepared solution added to the sample. This mixture was then agitated end over end at 25rpm for 24 hours and allowed to settle, before filtrating using a 50ml syringe and syringe filter with 0.45µm filter paper. Filtered eluates were preserved and diluted prior to analyses, and blanks of prepared leachant solutions were processed similarly and analysed.

Dithionite is an oxoanion of sulphur, and dithionite HFO extraction process determines amorphous and crystalline ferric oxides content. Reagents used for extraction included analytical grade sodium acetate anhydrous, tri-sodium citrate dihydrate, and sodium dithionite. To prepare the extractant, 5.72g of anhydrous sodium acetate was mixed with 12.08g tri-sodium citrate dihydrate in 250ml wide mouth polyethylene bottle. 200ml of nanopure water was added to the mixture, and 10.06g sodium dithionite added to the solution. However, the mixture pH was 7.0 instead of 4.8 described by Dzombak and Morel, and as such 8ml of glacial acetic acid was added to adjust pH (Van der Sloot, 2008). 60g of leachant solution was added to 3g of test specimens in 80ml wide mouth polypropylene bottles, and agitated in a water bath at 60°C for 3.5 hours, ensuring solids remained in suspension. This was allowed to settle, before filtering using 50ml syringes through 0.45µm filter paper for analyses. Blanks were prepared similarly, and analysed for process implications.

Oxalates are deprotonated charged forms of oxalic acids, which are strong carboxylic acids or ester of carboxylic acid. The oxalate HFO extraction process is used for extraction of acid volatile sulphides (AVS). This yields amorphous aluminium for speciation calculations, and reagents used are analytical grade di-ammonium oxalate monohydrate and oxalic acid dihydrate. To prepare extractant, 9.68g di-ammonium oxalate was mixed with 6.51g oxalic acid in 1L wide mouth polyethylene bottle, and 600ml of nanopure water added. 3g of samples were then added to 500ml wide mouth polyethylene bottles with 300g of extractant solution, and the mixture agitated in the dark, using an end over end shaker at 25rpm for 4 hours. This was allowed to settle, and then filtered using 50ml syringe with filter through 0.45µm filter-paper. Blanks were leachants processed in the same way, and obtained eluates were preserved and analysed.

4.5.5 Contaminant Sorption Capacity

To assess clay sorption capacity for contaminants of interest, a 24 hour batch measurement of contaminant sorption was undertaken along the guidelines of ASTM D4646–03 (2008). This test assesses sorption affinity of contaminants by unconsolidated geologic material (geomedia) in aqueous suspension. The test requires agitation (end over end) of geomedia in suspension with contaminant solution, in polyethylene containers to ensure non-reactive interactions with the container. The test determines the sorbable amount of contaminant by geomedia, in a rapid agitation test under environmental (temperature) control. The sorption affinity of trivalent chromium and zinc by oven dried kaolin clay was tested, at L/S of 20:1. 662.5mg of contaminant per kg of clay were used for testing, using 6.625mg (weighed from made up standard solutions) of zinc or chromium contaminants with 10g of clay in 200ml of demineralised water. This was then agitated end over end at 30rpm at 21±1°C for 24 hours. The test was used to determine distribution coefficient K_d, which is a ratio of contaminants sorbed by clay, compared to the original amount in solution.

$$K_d = \frac{(A-B)V}{(Ms)B} \qquad 4.5$$

Where: A – Initial concentration of the contaminant in the solution

B – Final concentration of the contaminant in the solution

V – Volume of solution used

Ms – Mass of soil expressed on an oven dried basis

K_d – Distribution coefficient (mL/g – millilitres per gramme)

K_d represents non-equilibrium 24 hour distribution coefficient, and requires that both initial and final contaminant concentrations are reported along with the extraction pH.

4.6 ANALYSES

To evaluate releases of components from the different leaching and extraction tests, chemical analyses of obtained eluates were required. Information for elemental components and organic carbon releases were required, to evaluate the leaching properties of the different matrices. Due to time and resource constrains, anion analyses were not undertaken during the current study. Some common anions found in soils include chloride, sulphate, phosphate and nitrate. However, since introduced contaminants were in nitrate form, and nitric acid was used in washing equipment and for pH adjustments, nitrates were not measured. Also, measures of sulphates and phosphates could be estimated from cation analytical results for sulphur and phosphorus.

Preliminary measurements were undertaken to assess chloride content in obtained eluates via ion chromatography (IC) analyses. This also included combination of eluates with standard chloride solutions, to evaluate sensitivity of the IC column for measuring chloride. pH provided a challenge, initially due to high alkalinity of samples, and subsequent acidic pH due to preservation to prevent precipitation. Results from analyses of 20 eluates showed huge nitrate and sulphate peaks, but no chlorides. Analysis of kaolin eluates also yielded no chloride, except for eluates doped with chloride solutions for validation. It was concluded that no significant chloride was present in matrices, unless introduced as impurity, and thus it was considered inefficient to undertake extensive IC analyses given prevailing constrains.

Information from the XRF analyses was used to evaluate components leachable fractions, in comparison to availabilities obtained from leaching tests. However, analyses were only undertaken on samples pretesting, and no additional measurements were taken on samples that had been chemically tested. Also, analyses of the kaolin for particulate organic carbon and total humic acid content may have been useful for speciation evaluations of component partitioning. However, due to minimal organic carbon in the processed kaolin, and complexities of resin extractions for organic carbon determinations, these were not undertaken.

4.6.1 Organic Carbon Analyses

Eluate organic carbon contents were required for use in speciation evaluations and leaching assessments, with analyses undertaken for total organic carbon (TOC), using PC (personal computer) controlled high sensitivity SHIMADZU TOC-V CPH total organic carbon analyser. The equipment has an ASI-V SHIMADZU auto sampler, capable of holding 93 samples. The NPOC (Non Purgeable Organic Carbon) method was used, where TOC was measured after sample acidification with hydrochloric acid (HCL) and oxygen sparging to remove inorganic carbon, which is converted to carbon dioxide. Total carbon was then measured, which represents TOC.

The equipment uses TOC control V SHIMATZU software, and acid used for sample acidification was TOC grade HCL, stripped of all organic carbon. To ensure accuracy and equipment sensitivity to samples, blanks were run along side samples. These were TOC grade water, obtained using MILLIPORE–MILLI Q Gradient A10 Q-Gard TOC water equipment, with 2ppb TOC and 18.2µS/cm conductivity. Calibration standards were prepared for each run, using SHIMATZU 1000ppm TOC calibration standard, diluted 1 in 10 to make 100ppm solutions. The equipment was then set to undertaken dilutions to yield TOC concentrations 1, 2.5, 5, 10, 50 and 100ppm for calibration. Prior to each measurement, the equipment rinses sampling piping with distilled water then flushed with the sample to prevent contamination and improve accuracy.

4.6.2 Cation Analyses

Releases of components (elemental) from the different matrices during leaching were required, to undertake leaching assessments and evaluations of containment / stabilisation effectiveness. Due to the large number of obtained eluates, it was necessary to adopt an analytical method that was both cost and time effective, without the need for excessive eluate preparation. The choice of ICP – OES (Inductively Coupled Plasma – Optical Emissions Spectroscopy) was adopted, given its suitability for use with type of eluate obtained, suitability for use in multi-quantitative evaluation of multiple elements of interest, and comparatively lower cost in relation to other methods available for this research. ICP analyses were undertaken at the University of Wolverhampton School of Applied Sciences laboratories, using the inductively coupled Plasma SPECTRO CIROS CCD (charged coupled detector) O.E.S (optical emission spectrometer) machine. Detection limits for components used in speciation evaluation are shown in Section 7.6.1 (Table 7.3).

CHAPTER FIVE

5.0 LEACHING ASSESSMENT AND MODELLING

5.1 INTRODUCTION

To evaluate partitioning and release of components from different stabilised matrices, extensive leaching evaluations are required, using a tailored suite of leaching tests depending on the material type tested, followed by geochemical speciation modelling to determine solubility controlling mineral phases. This approach allows reliable predictions of component releases under various environmental conditions, dependent on intrinsic material properties and external parameters. The role of modelling in evaluating S/S effectiveness is important for assessing dominant geochemical processes controlling porewater chemistry, long-term leaching performance, and the fate and transport of contaminants from stabilised materials (Bone *et al.*, 2004b). This section evaluates the methodology for the evaluation of laboratory experimentation data (Chapter 4) to fulfil chemical characterisation and leaching assessment requirements (See Section 3.9).

5.2 LEACHING EVALUATION

Kosson *et al.* (2002) devised a framework for an integrated assessment approach to leaching, taking into account: problem definition and test selection; data collection and management with management scenario description; intrinsic and extrinsic material properties; direct data evaluation, parameter derivation and comparative data sets (pH and L/S dependent release); release with time; and impact evaluation, using site specific information to provide release estimates. When undertaking leaching evaluations, understanding and inclusion of the interactions between components and reactive surfaces, e.g. clays, HFO and organic matter are required (Van der Sloot *et al.,* 2005). This provides a holistic characterisation of component release behaviours under prevailing environmental conditions.

A limited number of chemical and physical factors control releases from materials, which can be identified and quantified through a limited number of tests. Two types of matrices control release behaviours – monolithic and granular. Monolithic matrices often show diffusion dominated release, while granular materials show percolation dominated release (Van der Sloot and Dijkstra, 2004). Cementitious products have monolithic behaviour, and based on sample preparation methods employed, test specimens in this study were monolithic in behaviour. These mandated the suite selection for leaching tests employed in the study (See Section 4.5). Releases of constituents from monolithic materials to aqueous phase are controlled by chemical processes (minerals dissolution, sorption and availability) and physical transport processes (advection, surface wash-off and diffusion) (Van der Sloot and Dijkstra, 2004).

To assess component releases due to mass transfer from stabilised materials, tests should be designed based on material type i.e. monolithic or granular, at appropriate L/S ratio, and used in combination with tests for release under equilibrium conditions. In designing equilibrium release tests, considerations should be made for relationships between particle size, sample size and contact time, selection of appropriate L/S ratio, selection of appropriate leachants (acid and alkali) for pH adjustment, and practical mechanical limitations of test equipment (Kosson *et al.,* 2002, Van der Sloot *et al.,* 2006, Van der Sloot *et al.,* 2007). Specific materials exhibit systematic leaching behaviour, which are not obvious from a single step test results, but emerge from more detailed characterisation tests. Combinations of different tests are required to provide information on leaching characteristics of materials. Leaching tests are often carried out at relatively high L/S ratios, and do not give insight to leaching behaviour under often low L/S conditions encountered in the field (Van der Sloot *et al.,* 2006). This requires that information on the porewater chemistry is evaluated and incorporated into leaching evaluations, for releases under low L/S conditions.

When evaluating leaching to aqueous phases, due consideration must be made to processes that influence release. These include chemical and physical processes, and external influencing factors. Table 5.1 shows mechanisms and parameters for these processes (Van der Sloot and Dijkstra, 2004).

Table 5.1: Processes that control leaching behaviour (Van der Sloot and Dijkstra, 2004)

Processes	Mechanisms	Parameters
Chemical Processes	Mineral dissolution (solubility control), Sorption control and Component availability	pH, Speciation, Total concentration, Eh, Acid/Base buffering, Organic matter, and composition and ionic strength of aqueous phase
Physical Processes	Surface wash-off, Advection (high permeability) and Diffusion (low permeability / porosity)	Varies dependent on nature of material – Particle size, Tortuosity, Shape and size of specimen, Sensitivity to erosion and Salt intrusion
External Factors	Prevailing environmental conditions	Water volume, Contact Time, pH of environment, Temperature, Eh, Sorption and DOC

To incorporate environmental influences, it is important to assess leaching under different chemical constraints, i.e. pH for equilibrium conditions, and diffusion, dissolution and mass transfer for disequilibrium conditions. This will allow evaluation of leaching under appropriate field exposure conditions, after incorporating extrinsic factors such as oxidation, hydrology and mineralogical changes (Van der Sloot *et al.,* 2007). pH is one of the main controlling factors in metal partitioning between solid and aqueous phases, and different surface processes occur within the pH domain, such as ion exchange, complexation, precipitation, sorption and chemical incorporation (Dijkstra *et al.,* 2004, Ziegler and Johnson, 2001). pH and organic matter directly influence metal distributions in soils, whilst Eh indirectly alters distribution, mainly through modification of pH (Peng *et al.,* 2009), resulting in metal fixation through precipitation and co-precipitation (Hwang *et al.,* 2008). Eh modification can therefore be estimated with changes in pH, in view of containment implications (Also see Section 5.4.3). Evaluating leaching after incorporating these factors and considering extrinsic parameters will provide useful insight into material behaviour, under field exposure conditions, for use in predictive release modelling.

5.3 MODELLING

The information required to undertake release predictions for S/S treated materials are dependent on intrinsic and extrinsic influencing factors. Modelling the material behaviour can be via equilibrium thermodynamic predictive tools for equilibrium conditions, and/or chemical kinetics for interactions controlled by kinetic constrains and disequilibrium conditions. Thermodynamic equilibrium reactions include precipitation – dissolution and other chemical interactions between contaminated soils / wastes, contaminants, binders and groundwater. This is an active area of chemical model development, mainly through application of geochemical codes (Bone *et al.,* 2004b). Extensive works on speciation evaluations for stabilised waste and cementitious materials have been undertaken (See Dijkstra *et al.,* 2004 and 2008, Van der Sloot *et al.,* 2005, 2006, and 2007). Chemical kinetics are concerned with reaction rates, and are important in disequilibrium conditions over considerable periods due to slow reaction rates e.g. contaminant diffusion from monolithic material (Bone *et al.,* 2004b).

Understanding component leaching and release controlling mechanisms are important in undertaking modelling and predictions. Multi component interaction tools are required, which incorporate ion sorption to HFO and natural organic matter (humic and fulvic acids), in addition to component release assessments. These models will have better success when applied to evaluate speciation of metals in soils and wastes (Van der Sloot *et al.,* 2005). Geochemical reaction / transport modelling form a basis for prediction of long term release behaviour, as laboratory tests cannot mimic the various exposure conditions with reasonable chance of success (Van der Sloot *et al.,* 2006). Impact evaluations require identification of solubility controlling processes and component availabilities, and this information can be used for equilibrium modelling to determine solubility as function of pH at given L/S ratio. Information from this modelling can then be combined with disequilibrium release to predict environmental impact (Kosson *et al.,* 2002, Van der Sloot *et al.,* 2006). Complex interactions for variety of components present during S/S should be evaluated, and then modelling undertaken with consideration of environmental influences.

5.3.1 Disequilibrium Release Modelling

Where reactions are not sufficiently defined and chemical equilibrium cannot be attained, interpretations may be required via use of kinetic models / tools (Langmuir, 1997). Kinetic modelling approaches are based on the kinetics of component releases from materials such as monoliths, where leaching is not solely controlled by solubility, but rather by diffusion from the matrix, where thermodynamic equilibrium is not achieved. The inclusion of kinetic considerations allow robust prediction of leaching rates, and these combined with mass transfer predictions can provide a source term for contaminant transport calculations (Bone *et al.,* 2004b). Tests to determine releases controlled by mass transfer rates in monolithic material are required (See Section 4.5.1), and obtained results are used to determine or estimate intrinsic mass transfer parameters such as observed diffusivities of constituents, cumulative releases and flux (concentration flow through the material) as a function of prevailing pH and time (Kosson *et al.,* 2002).

Information required for mass transfer estimates from solid low permeability non-percolation controlled releases include; Material geometry; Material density; Initial leachable content (component availability); and Observed diffusivities of species (Kosson *et al.,* 2002). Release controlling mechanisms are complex and constituent specific, and diffusion rates through the material can be retarded by surface reactions or precipitation of insoluble compounds. Mass transfer can also be enhanced by species complexation or mineral phase dissolution (Kosson *et al.,* 2002). Using results from monolithic leaching assessments, bulk diffusion based modelling can be undertaken. These use Fickian diffusion model, based on Fick's second law of diffusion, which predicts how diffusion causes concentration fields to change with time (Kosson *et al.,* 2002, Bone *et al.,* 2004b). Assumptions for this approach include:

- Uniform distribution of species in a homogeneous porous matrix
- Mass transfer occurrence in response to concentration gradient of porewater
- Only high solubility species are a concern, or there are no significant extrinsic factors such as changes in Eh or pH (Kosson *et al.,* 2002).

This mass transfer approach to disequilibrium releases often overestimate actual releases (Kosson *et al.,* 2002). Other available approaches include advection – diffusion modelling (Yokozeki *et al.,* 2004), and use of activation energies (Chitambira *et al.,* 2007).

5.3.2 Thermodynamic Equilibrium Release Modelling

Thermodynamic equilibrium modelling relies largely on the numerical minimisation of Gibbs free energy of a system (Bone *et al.,* 2004b). Gibbs energy is the amount of energy released / consumed when a phase is created from another phase. Gibbs free energy (G) for a substances reaction is the maximum energy change for that reaction in terms of useful work (quantity of energy transferred by the system to another), at constant temperature and pressure (Langmuir, 1997). This is defined by the difference between changes in Enthalpy (ΔH) and Entropy (ΔS) of the reaction (r) at temperature T; where enthalpy is the heat transfer between the system and its surroundings at constant pressure but not constant temperature and volume, and entropy is the degree of randomness or disorder of a phase (e.g. thermal), and its change is equal to heat absorbed divided by absolute temperature (Langmuir, 1997).

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ \qquad 5.1$$

These reactions are affected by changes in temperature and pressure due to Le Chatelier's principle, where systems / reactions at equilibrium adjust themselves to changes in factors like temperature and pressure, to annul as far as possible the effects of these changes. The influence of chemical equilibrium and / or kinetics on the progress of chemical reactions often determines abundance, distribution and fate of substances in the environment. Understanding these basic concepts may therefore help to explain and predict environmental concentrations of species in aqueous systems (Langmuir, 1997). Chemical equilibrium is the time-invariant, most stable state of a closed system, which is the state of minimum Gibbs free energy. Whether a system can be considered as open or closed depends on the specific substances under study, the rate of flux of matter in and out of the system, and the time scale of interest. However, if reaction rates are much faster than flux rates of related components in and out of the system, the system can be assume to be closed (Langmuir, 1997).

Selections of relevant mineral phases are important in making predictions for geochemical equilibrium systems, for the assemblages of minerals present in the aqueous system. A phase is a restricted part of a system with distinct physical and chemical properties, made up of one or more components (Wood and Fraser, 1976). These components are simple chemical units that can be combined to describe the chemical composition of species or substances in the system. For example, kaolinite [$Al_2Si_2O_5(OH)_4$] can be formed from three oxides (Al_2O_3, SiO_2 and H_2O), or four ions (Al^{3+}, Si^{4+}, H^+ and O^{2-}) as components. Selecting the least components (Master Species) is one of the fundamental and essential input decisions in geochemical computer codes like MINTEQA2 (Langmuir, 1997).

The scope of work undertaken for this research did not cover calculations of parameters associated with equilibrium reactions, but provides indications of the important factors in thermodynamic equilibrium reactions. The research presented in this thesis, focuses on component releases evaluations, chemical durability and applicability for S/S systems. Specific interactions were not assessed, due to number and variety of interactions occurring, together with time and resource constrains in obtaining this information. Modelling equilibrium conditions for leaching were undertaken using the geochemical speciation tool ORCHESTRA, embedded in the leaching assessment tool LeachXS, using results from pH dependent leaching in closed systems under environmental control. This was chosen due to relative ease of use, flexibility, and capabilities for extension of the process models (See Section 5.4.1 below). Other geochemical tools available include VMINTEQ, MINTEQA2, PHREEQC, PHREEQC and SOLTEQ (Olmo *et al.,* 2007).

5.4 LEACHXS – ORCHESTRA

5.4.1 Introduction

For this study, ORCHESTRA (**O**bjects **R**epresenting **Che**mical **S**peciation and **Tra**nsport Models) (Meeussen, 2003) which uses an extended MINTEQA2 database with thermodynamic constants for inorganic reactions, embedded in the expert system /

database LeachXS (**Leach**ing E**x**pert **S**ystem) (Van der Sloot *et al.,* 2007) was employed for leach assessments and modelling. MINTEQA2 is the US EPA geochemical speciation code (McKinley *et al.,* 2001), a mass transfer code that can speciate aqueous solutions, and simulate solution chemistry changes caused by mass transfer processes. However, it does not consider solid solution mass transfer, and provides limited information on ion exchange / adsorption mass transfer. The system can predict overall geochemical behaviour of components, and whether reactions attain equilibrium, and is often used in reaction path modelling (Langmuir, 1997).

Leaching information was fed into LeachXS from which leaching assessments were undertaken, and geochemical modelling then undertaken using ORCHESTRA, which is a computer program for modelling geochemical speciation and mass transport processes. It consists of two components, a generic calculation kernel (Java executable) and a file with model definitions in object format (object database). This object database contains definitions of basic chemical model elements, such as "components", "species", "minerals", "surfaces", "sites", etc. which makes it possible to use ORCHESTRA in a similar way to other speciation modelling tools e.g. PHREEQC, MINTEQ, GWB or ECOSAT. The system offers the advantage of being flexible, and can be easily extended with new chemical, physical and biological process models. Model calculations are transparent, and all model equations are available in text format (Meeussen, 2009).

LeachXS database and expert system provides storage for material information, leaching data, and prevailing test chemical conditions. This system allows for matrix characterisation and environmental impact assessment, based on component releases during chemical leaching, and can be extended with relevant regulatory limits of components for comparison (LeachXS). The fundamental structure of LeachXS embedded with ORCHESTRA is shown in Figure 5.1.

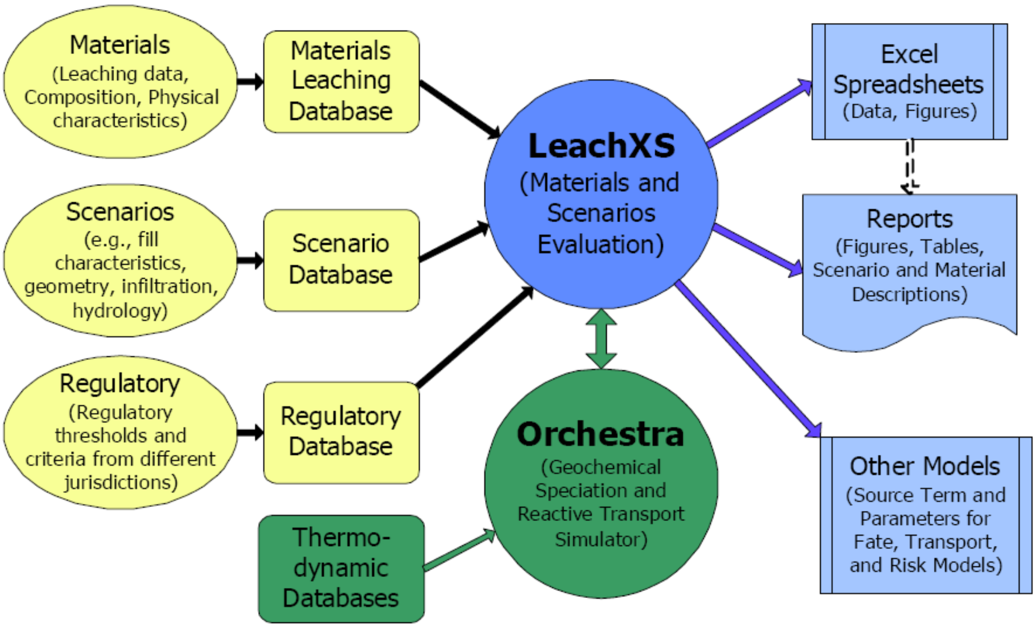


Figure 5:1: LeachXS - ORCHESTRA structure

LeachXS – ORCHESTRA combination provides quick data retrieval, automatic input generation for modelling, processing of calculated results and data presentations (Van der Sloot *et al.*, 2005). This allows for evaluation of solubility controlling mineral phases for different materials tested, evaluation of time dependent leaching characteristics, ANC / BNC, and comparisons of component leachability between and within materials. Input data from tailored leaching tests, and prevailing chemical conditions are used in modelling speciation and time dependent releases by ORCHESTRA, allowing users to undertake leaching evaluations via LeachXS after due consideration of relevant chemical interactions and solubility controlling mechanisms.

5.4.2 Modelling Requirements

During speciation evaluations, considerations for clay content, HFO and organic carbon are required, to assess complexation and sorption of components. Modelling of sorption to HFO surfaces and complexation with organic carbon are also undertaken by ORCHESTRA. Component binding to particulate and dissolved organics (POM and DOC) are modelled according to the NICA - Donnan model (Van der Sloot *et al.,* 2007). In the current study, all measured DOC was assumed to be composed of reactive humic substances, due to the low organic content of kaolin clay used, and the introduction of humic acid as an additive for evaluation of effects on S/S. Modelling of HFO used the generalised two layer model of Dzombak and Morel (1990).

Amorphous aluminium was used as a sorption site, due to its similarity in surface structure and reactivity to iron, and treated similar to HFO, where 1mol Fe – ASC ≈ 1mol Al – OX (Dijkstra *et al.,* 2004). The recommended specific surface area for Al is $600m^2/g$, whilst that for crystalline Fe is $100m^2/g$ (Meima and Comans, 1998). Measurements of these components were undertaken via HFO extractions (Section 4.5.4), where Ascorbate (ASC) extraction – Amorphous Fe, Dithionite extraction – Crystalline Fe and Oxalate OX – Amorphous Al. The equations for all modelling calculations are contained in the ORCHESTRA object database, and modelling was undertaken through LeachXS using leaching and reactive component extraction information. The input structure, object data, modelling layout and operation process for ORCHESTRA are shown in Meeussen and Van der Sloot (2008) for releases of inorganic substances from stabilised matrices.

5.4.3 Data Requirements

To facilitate leaching assessments, release predictions and speciation modelling, chemical data from leach tests and extractions were uploaded into LeachXS. Given use of computer programs, data had to be tailored in a way the relevant tools can understand, and homogenised to ensure consistency prior to uploading. Data required included: physical properties – particle density, bulk density, porosity, moisture content, particle size / physical dimensions, weight and tortuosity; chemical properties – pH, Eh and conductivity; leaching information; HFO and organic content; test conditions – flow rates, L/S ratios and temperature; extractant properties; and eluate analyses results. Due to difficulties in obtaining repeatable Eh results (see Section 4.4.2.2), estimations by ORCHESTRA were used. Eh modifies containment by altering pH, and as such its changes during interactions can be estimated from pH changes (See Section 5.2).

LeachXS provides a Material Exchanger System input template (Microsoft excel workbook) where all required information for assessments and modelling are entered. Entered information follows structured guidelines contained in the Material Exchanger System manual (LeachXS), using unique codes for each material and test, that can be understood by LeachXS software for assessments and modelling. The input workbook contains worksheets separated dependent on requirements i.e. individual worksheets for different tests, eluate analyses and material properties. The template used for this study included worksheets for material / matrix details, pH dependence leaching, Monolithic releases, Percolation / Porewater releases, Total compositional, and Eluate analyses.

5.4.4 Data Conversion

After uploading all required information for matrices and tests to the input template, the information has to be converted to a database (MS Access) from where the information can be utilised via LeachXS for evaluations and modelling. This was undertaken using LeachXS Material Exchanger System, designed to convert information about leaching data obtained from laboratory or field samples to a format compatible with LeachXS. The Material Exchanger software, user manual and LeachXS installation files are available for download at www.leachxs.org, and the guidelines for use are contained within. The system uses two modules, a reader module and a writer module. The heart of the system is an XML (Extensible Mark-up Language) – file that contains all input information, created using the Material Exchanger reader module from information in the input workbook. This XML file was then converted using the Material Exchanger writer module, transferring the information into a database file (Microsoft Access). Reader and writer plug-in were used during the conversions, and the system implements checks to ensure that all the input data are formatted in forms accessible by LeachXS.

5.4.5 Leaching Assessment

LeachXS expert system was used for leaching assessments, using a database for leaching information from test matrices. Guidelines on undertaking assessments, mineral phase selection, and comparisons are contained in the LeachXS user manual (ECN, 2008). LeachXS comparison facilities allow for: comparison and presentation of constituent releases and trends from individual samples; comparison and presentation of individual component releases and trends from different samples; estimation and comparisons of ANC / BNC; evaluation of releases during the different leach tests; evolution of pH during tests; and conversion of L/S ratio information to time release estimations. LeachXS also facilitates speciation modelling via ORCHESTRA, enabling selection of speciation controlling mineral phases, from where modelling is undertaken and results assessed for the different components within samples (See Chapter 7). For field samples, predictions for impact to groundwater can be evaluated, using releases and material properties.

5.4.6 Speciation Selection

To undertake evaluation of solubility controlling mineral phases for matrices, speciation determination for components in the matrices were required, using equilibrium results for releases during pH dependent leaching. Evaluations were only undertaken for elemental master species (aluminium, silicon, calcium and sulphur), and introduced contaminants (chromium and zinc) within matrices. To evaluate partitioning of components in matrices, the Speciation Finder on LeachXS was used to determine relevant stable minerals in the samples via ORCHESTRA, based on thermodynamic equilibrium under prevailing conditions. The process can be selected to run fully automated or interactive through all calculation phases, after which relevant minerals for the samples (based on expected mineralogy) are selected for modelling. This information was then used for undertaking pH dependent and time dependent partitioning and release predictions, requiring input of solid humic acid content, HFO content, clay content, L/S ratios, and other material physical and chemical properties for each matrix during the tests.

The selected solubility controlling mineral phases were then re-evaluated for the selected components, requiring knowledge of contained mineral phases in matrices, and stability of these minerals in the clay and cementitious matrices being assessed. ORCHESTRA (through LeachXS) was then used to model partitioning of the selected components within the selected mineral phases across the range of pH tested, and duration of the tests under prevailing pH and environmental conditions. This involves evaluating partitioning on clays, interactions with HFO and organic matter, sorption interactions, dissolution and precipitation (solubility) reactions, and other relevant chemical interactions. LeachXS was then used to assess and present partitioning results for components between the solid and liquid phase, fractionation in the solid phase, predictions and comparison of leaching trends, and evaluation of alterations / modification in mineral phases along the leaching interface during time dependent leaching.

5.4.7 Potential and Additional Benefits

LeachXS expert system and database also provides capabilities for evaluation of field monitoring data, leaching of components contained in landfills, road construction materials, ponds and impoundments. Leaching evaluation, speciation and prediction of releases from mixed waste materials can also be undertaken, for scenarios of co-disposal or mixtures of monolithic and granular material. Scenario calculations can also be undertaken for unsaturated flow through monolithic materials, road construction materials, and landfills. Groundwater impact assessments can also be undertaken using LeachXS, evaluating the impacts from both monolithic and granular material.

This tool provides a solution for quality control and compliance monitoring, and expansions are currently underway to allow selection and use of the leaching tools for this assessment. This involves inclusion of definitions for assessment goals and objectives; test methods, chemical analyses and quality control; data presentation and evaluation; and source term modelling and simulation. For the purposes of the research presented herein, LeachXS has been used to undertake all leaching assessments and comparisons for the different matrices and chemical tests employed, as well as the presentation of obtained information. Laboratory test results for the different matrices are presented in Chapter 6, and LeachXS - ORCHESTRA were then used to undertake assessments and speciation modelling, with results shown in Chapter 7 for the different matrices tested.

CHAPTER SIX

6.0 LABORATORY RESULTS

The findings and results from laboratory experimentation (see Chapter 4) are presented in 5 sections for ease of presentation:

1. Pre-stabilisation material characterisation and stabilisation evaluation results
2. Sample preparation and base compositional evaluation
3. Chemical leaching tests results
4. Physical parameter evaluations for leaching assessments, and
5. Eluate analyses results.

This chapter presents only select results from experimental processes, with the raw data and associated results given as appendices. Leaching evaluations for the information are shown in Chapter 7, and discussed in Chapter 8.

6.1 PRE-STABILISATION

Before undertaking clay stabilisation, it was necessary to assess the clay properties, to allow optimisation of sample preparation processes, ensure material efficiency, and assess implication of stabilisation. Physical tests were undertaken to assess compaction properties and particle density, along with chemical tests to assess pH development, and the sorption affinity of introduced contaminants to the clay.

6.1.1 Physical Tests

Compaction assessment was undertaken to determine optimum water content and maximum dry density of the clay, and the clay – stabiliser mix. In addition, particle density testing was undertaken, which was used for compaction evaluation, and for determinations of porosity in hydrated specimens. However, it was not possible to replicate optimum densities and water contents during actual sample preparation. Lower bulk density and higher water content were utilised due to equipment constrains. This however increased workability of the material during preparations.

6.1.1.1 Particle Density

The average value for particle density of kaolin clay was 2.6, with a range of 2.58 – 2.61. For stabilised samples, it was important to consider hydration with time, since the sample had to be dried at 105°C for 24 hours prior to testing. Using the average particle density of the mixture, where kaolin clay is 2.60 and cement is 3.12, a value of 2.64 is obtained based on 10% cement content (by weight). However, tests on samples dried immediately after stabilisation yielded particle density of 2.67, which varied from the calculated value due to particle hydration. This calculated value (2.64) was used during compaction evaluations, but particle density tests were undertaken on crushed stabilised samples after sampling at the different hydration duration. These yielded varying densities with matrix and hydration duration, with a range of 2.61 to 2.69.

6.1.1.2 Compaction

Compaction assessments were undertaken on 10% CEM II stabilised kaolin clay, to optimise preparation conditions. Tests on stabilised clay were undertaken immediately after mixing, with cement introduced as slurry with required water to attain required water contents. Care was taken to complete tests within 2 hours, to minimise cement hydration during the process. Results obtained are shown in Figure 6.1, for three unstabilised (ECC) and two stabilised clay samples with associated air void lines. Stabilised clay yielded slightly higher maximum dry densities (1.48Mg/m^3), at water contents similar to the optimum for unstabilised kaolin clay (28%). However, optimum conditions obtained could not be replicated using the hydraulic ram via compression during actual sample preparation for hydration (see Section 4.4.1.2). A dry density of 1.23 Mg/m^3 (1.6 Mg/m^3 bulk density) was achieved for stabilised kaolin without additives, at 30% water content.

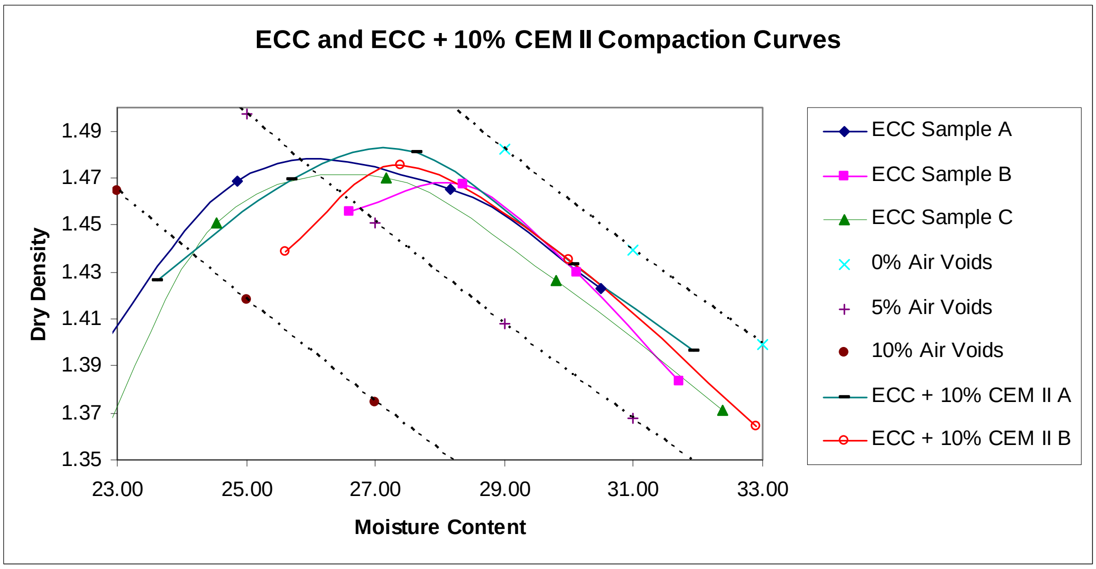


Figure 6:1: Compaction Chart for stabilised and unstabilised clay samples

6.1.2 Chemical Tests

Pre-stabilisation, chemical tests were undertaken to determine the sorption capacity of kaolin for introduced contaminants, using ASTM contaminant sorption capacity test (D4646–03, 2008). It was also important to evaluate kaolin pH development with additives introduction, in view of clay pH sensitivity for contaminants containment.

6.1.2.1 Contaminant Sorption Capacity

Sorption capacity evaluations were undertaken for the two contaminants used, with testing undertaken in triplicate for each contaminant. Results from ICP analyses in micrograms per litre (µg/L) are shown in Table 6.1, for sorption of contaminants by clay from the solution, along with calculated distribution coefficients (K_d) in millilitres per gramme (mL/g), and the standard deviation and variance of distribution coefficients. The average concentrations of contaminants (see Section 4.5.5) remaining in solution were used to calculate the percentage sorbed by clay, and thus maximum sorbable concentrations by the clay under prevailing conditions (Table 6.2).

Table 6.1: Results from sorption capacity test for kaolin clay with zinc and chromium solutions

Elements (µg/L)	**Zn**	**Cr**	**K_d mL/g**	**Std Dev**	**Variance**
Sample					
Clay + Cr III A		11806	32.771		
Clay + Cr III B		11940	32.179		
Clay + Cr III C		11771	32.928	0.40	0.156
Clay + Zn A	15612	23	21.048		
Clay + Zn B	16809	88	18.125		
Clay + Zn B	16883		17.958	1.74	3.020
Blank Zn Solution	32049				
Blank Cr III Solution		31151			
Blank Clay		122			

Table 6.2: Sorbable contaminant concentration by the Kaolin Clay

Contaminant	Fraction in Solution %	Fraction Retained by clay %	Sorbable concentration (mg) per kg of clay
Chromium	38.01	61.99	410.72
Zinc	51.28	48.72	322.77

6.1.2.2 pH Development

Due to pH sensitivity during chemical interactions, it was necessary to evaluate the implications of additive inclusions on kaolin natural pH. However, no standard tests were found for this determination, and thus guidelines from CEN/TS 14429 (2008) were adapted for use. This involved end over agitation of samples with demineralised water, at L/S ratio of 20 ± 1 for 48 hours, under temperature control at 20 ± 2°C, with pH measurements after 1, 24 and 48 hours. Results for this are shown in Table 6.3, for the kaolin clay, and kaolin clay with introduced additives. Samples were dried at 105°C for 24 hours prior to testing.

Table 6.3: pH development for the clay and admixtures

	pH			Conductivity μS
Sample	1 Hour	24 hours	48 Hours	
Kaolin Clay	5.37	5.57	5.41	55
Kaolin Clay + 5% Sulphate	4.66	4.71	4.72	2080
Kaolin Clay + 1% Humic Acid	5.14	5.06	5.04	72

6.1.3 Compositional Analyses

This section provides compositional information for the different matrices used for chemical leaching tests. It was imperative to demonstrate availability and leachable fractions of components during leaching, which determines stabilisation effectiveness and environmental contamination implications (See Section 3.8). Elemental compositional analyses via XRF were undertaken, to show component concentrations and variations. Analyses were undertaken after 28 days hydration, and compositional results major elemental contents in the different matrices shown in Tables 6.4 and 6.5. To ensure repeatability, stabilised zinc contaminated clay with 2.5% sulphate was analysed in 5 replicates. The calculated means, medians, standard deviations and variances for selected elements are shown in Table 6.6.

Table 6.4: XRF compositional analyses for Na, Mg, Al, Si, S and K (%)

Element	**Na**	**Mg**	**Al**	**Si**	**S**	**K**
ECC	1.7500	0.2180	18.4000	22.2600	0.0002	2.4410
ECC-Cr	1.6200	0.1790	16.3000	19.7200	0.0002	2.2180
ECC-Zn	1.6600	0.1980	17.2700	20.9300	0.0002	2.3170
ECC - OPC	1.5680	0.2528	18.7420	22.8980	0.0449	2.5580
ECC-OPC-Cr	1.5100	0.1980	16.3800	20.2400	0.0418	2.2540
ECC-OPC-Zn	1.6700	0.2330	16.9000	20.6800	0.0250	2.3620
ECC-OPC-HA	1.5800	0.1920	17.1400	21.1300	0.0498	2.4030
ECC-OPC-HA-Cr	1.5000	0.2110	17.4600	21.5500	0.0577	2.4010
ECC-OPC-HA-Zn	1.8300	0.2520	17.6600	21.6400	0.0619	2.4260
ECC-OPC-SO_4	2.2900	0.1500	14.7300	18.7000	0.2790	2.1150
ECC-OPC-SO_4-Cr	1.5100	0.2130	15.8700	19.4200	0.2730	2.1800
ECC OPC SO_4 Zn	1.9340	0.1894	16.3640	20.2500	0.2299	2.2820

Where: ECC – English China Clay; Cr – Chromium, Zn – Zinc; OPC – CEM II Portland Limestone Cement; HA – Humic Acid; and SO_4 – Sulphate.

Table 6.5: XRF Compositional analyses for Ca, Cr, Mn, Fe and Zn (%)

Element	Ca	Cr	Mn	Fe	Zn
ECC	0.0202	0.0031	0.0136	0.5262	0.0024
ECC-Cr	0.0182	0.0437	0.0106	0.5003	0.0024
ECC-Zn	0.0214	0.0031	0.0119	0.5241	0.0520
ECC - OPC	1.8044	0.0033	0.0161	0.6496	0.0042
ECC-OPC-Cr	2.4420	0.0466	0.0139	0.6432	0.0040
ECC-OPC-Zn	1.8820	0.0034	0.0149	0.6364	0.0469
ECC-OPC-HA	2.0340	0.0033	0.0158	0.6738	0.0044
ECC-OPC-HA-Cr	2.0300	0.0492	0.0150	0.6439	0.0041
ECC-OPC-HA-Zn	2.0980	0.0034	0.0148	0.6644	0.0475
ECC-OPC-SO_4	2.8220	0.0033	0.0150	0.6339	0.0041
ECC-OPC-SO_4-Cr	1.8850	0.0431	0.0149	0.5972	0.0040
ECC OPC SO_4 Zn	1.9712	0.0033	0.0150	0.6165	0.0441

Table 6.6: Variability evaluation for stabilised zinc contaminated kaolin with 2.5% sulphate

Element	Mean (%)	Median	Standard Deviation	Variance
Aluminium	16.364	16.310	0.526	0.276
Manganese	0.015	0.015	0.001	0.000
Magnesium	0.189	0.203	0.043	0.002
Silicon	20.250	20.140	0.697	0.486
Iron	0.617	0.625	0.025	0.001
Sodium	1.934	1.920	0.109	0.012
Calcium	1.971	2.085	0.240	0.057
Potassium	2.282	2.283	0.062	0.004
Sulphur	0.230	0.240	0.027	0.001

6.2 CHEMICAL LEACHING TESTS

This section shows the results from chemical leaching tests undertaken as part of the current study, separated based on the test undertaken and the matrices evaluated.

6.2.1 pH Dependent Leaching

The chemical parameters for pH dependent leaching of kaolin clay are shown in Table 6.7, showing measured pH and conductivities of eluate fractions. Acid and base neutralisation capacities (ANC/BNC) were also measured, for comparisons between matrices, based on matrix type and increasing hydration. However, due to comparable trends and values being observed, results are not shown here, but rather grouped and discussed in Chapter 8 (see Section 8.2.3.2 Table 8.6). For kaolin clay, 1mol HNO_3 and 0.1mol NaOH were used to induce pH modification, while 2mol HNO_3 and 1mol NaOH was used for all stabilised matrices. Table 6.8 shows measured parameters for the eluates from stabilised kaolin clay, at the different hydration durations (28, 150 and 300 days).

Table 6.7: Kaolin clay pH dependent chemical parameters

Fraction	pH	Conductivity µS
Kaolin Clay		
1	2.53	1262
2	3.06	550
3	5.43	237
4	6.02	83
5	6.97	99
6	8.08	104
7	9.42	114
8	10.11	136
9	11.31	451
10	11.99	1562

Table 6.8: Stabilised clay pH dependent chemical parameters

Fraction	pH	Conductivity µS	Fraction	pH	Conductivity µS
EO 28 Days			EO 300 Days		
1	3.84	10430	1	3.85	8650
2	4.10	9390	2	4.54	7490
3	5.45	8460	3	5.81	6460
4	7.56	6750	4	6.79	5940
5	7.60	6960	5	7.00	5730
6	9.30	5670	6	8.83	5210
7	10.99	4130	7	9.31	5080
8	12.07	1844	8	10.66	4150
9	12.28	3030	9	11.99	1395
			10	12.35	3250
EO 150 Days					
1	4.01	8460			
2	5.53	7180			
3	6.53	6490			
4	7.83	5960			
5	9.40	5240			
6	10.72	4110			
7	11.96	1425			
8	12.28	3280			

NB: EO – Stabilised Kaolin Clay

Table 6.9 shows measured chemical parameters for stabilised clay with 1% humic acid, whilst parameters for stabilised kaolin clay with 2.5% sulphate are shown in Table 6.10. For matrices contaminated with zinc, Figure 6.11 shows chemical release parameters for stabilised zinc contaminated kaolin clay at 28 days, 150 and 300 days of hydration. Results for stabilised zinc contaminated kaolin clay with 1% humic acid are shown in Table 6.12, whilst those for stabilised zinc contaminated kaolin clay with 2.5% sulphate are shown in Table 6.13, for the different hydration durations.

Table 6.9: Stabilised clay with 1% HA pH dependent chemical parameters

Fraction	**pH**	**Conductivity µS**	**Fraction**	**pH**	**Conductivity µS**
EOH 28 Days			EOH 300 Days		
1	3.74	11060	1	3.97	8820
2	4.23	9730	2	5.18	7810
3	5.65	9180	3	6.20	6870
4	7.08	8020	4	7.02	6790
5	8.07	7310	5	8.46	6180
6	9.16	6540	6	9.85	510
7	10.55	5365	7	10.52	5020
8	11.14	4250	8	12.20	2180
9	12.24	2850	9	12.47	4250
10	12.37	4180			
EOH 150 Days					
1	3.91	9160			
2	5.59	7550			
3	6.24	7190			
4	7.57	6530			
5	8.54	6170			
6	9.86	5490			
7	10.68	4910			
8	12.14	2370			
9	12.37	4270			

NB: EOH – Stabilised kaolin clay with 1% humic acid

Table 6.10: Stabilised clay with 2.5% Sulphate pH dependent chemical parameters

Fraction	**pH**	**Conductivity µS**	**Fraction**	**pH**	**Conductivity µS**
EOS 28 Days			EOS 300 Days		
1	3.85	11310	1	4.01	9090
2	5.75	9120	2	5.39	8250
3	6.76	8190	3	6.58	6860
4	7.45	7500	4	7.41	6230
5	8.53	6610	5	7.70	5860
6	9.85	5790	6	9.15	5320
7	10.99	3240	7	10.46	4390
8	12.07	2480	8	12.13	2510
9	12.30	3910	9	12.46	4770
EOS 150 Days					
1	4.10	8970			
2	5.40	8060			
3	6.67	7100			
4	8.07	6010			
5	9.33	5370			
6	10.51	4320			
7	12.03	2365			
8	12.35	4740			

NB: EOS – Stabilised kaolin clay with 2.5% sulphate

Table 6.11: Stabilised zinc contaminated clay pH dependent chemical parameters

Fraction	**pH**	**Conductivity µS**	**Fraction**	**pH**	**Conductivity µS**
EOZ 28 Days			EOZ 300 Days		
1	3.76	9785	1	3.82	8520
2	4.58	8430	2	4.29	7570
3	5.62	7982	3	5.12	6960
4	6.41	7220	4	6.39	6330
5	7.74	6680	5	7.87	5620
6	9.33	5955	6	9.24	5000
7	10.45	5330	7	10.65	4250
8	11.14	4140	8	12.01	1433
9	12.22	1930	9	12.36	3280
10	12.51	3765			
EOZ 150 Days					
1	4.10	8420			
2	5.48	8240			
3	6.02	7300			
4	7.34	6320			
5	9.30	5510			
6	10.76	4220			
7	11.97	1492			
8	12.29	3340			

NB: EOZ – stabilised zinc contaminated kaolin clay

Table 6.12: Stabilised zinc contaminated clay with 1% HA pH dependent chemical parameters

Fraction	pH	Conductivity µS	Fraction	pH	Conductivity µS
EOHZ 28 Days			EOHZ 300 Days		
1	4.03	9460	1	4.00	8980
2	4.89	8910	2	5.47	7990
3	6.35	7950	3	6.36	7160
4	7.69	7170	4	7.89	6680
5	9.20	6400	5	9.41	6100
6	10.21	5620	6	10.53	4870
7	11.20	4540	7	12.26	2380
8	12.45	3170	8	12.50	4280
9	12.64	5110			
EOHZ 150 Days					
1	4.26	8710			
2	5.88	8040			
3	7.45	6910			
4	9.04	6150			
5	10.01	5490			
6	10.56	4600			
7	12.18	2440			
8	12.43	4340			

NB: EOHZ – stabilised zinc contaminated kaolin clay with 1% humic acid

Table 6.13: Stabilised zinc contaminated clay with 2.5% sulphate pH dependent chemical parameters

Fraction	pH	Conductivity µS	Fraction	pH	Conductivity µS
EOSZ 28 Days			EOSZ 300 Days		
1	4.01	9070	1	3.86	9200
2	4.76	8110	2	4.12	8060
3	5.80	7530	3	5.47	7220
4	6.54	7080	4	6.88	6160
5	7.54	6400	5	8.26	5490
6	9.50	5610	6	9.36	4740
7	10.94	3940	7	10.56	4080
8	12.31	2860	8	12.15	2750
9	12.60	5010	9	12.47	4710
EOSZ 150 Days					
1	4.07	8830			
2	5.20	8350			
3	6.14	7170			
4	7.41	6070			
5	8.92	5500			
6	9.97	4710			
7	10.58	4020			
8	12.06	2520			
9	12.37	4720			

NB: EOSZ – stabilised zinc contaminated kaolin clay with 2.5% sulphate

For stabilised matrices with chromium contamination, Table 6.14 shows chemical parameters for pH dependent leaching of stabilised chromium contaminated kaolin clay at 28 days, 150 days and 300 days hydration. Table 6.15 shows results for stabilised chromium contaminated kaolin clay with 1% humic acid, whilst results for stabilised chromium contaminated kaolin clay with 2.5% sulphate are shown in Table 6.16 for the different hydration durations. For pH dependent leaching assessments, validation of equilibrium conditions were required. Based on CEN/TS 14429 (2008) requirements, a maximum pH variation of 0.5 pH units was required between 44 and 48 hours leaching for each eluate. All eluate samples fulfilled this requirement, and to avoid excessive repetition and due to space constrains, raw leaching results are contained in Appendix 1 for all the matrices at different hydration durations. The pH values presented in the results are equilibrium values, obtained after test completion.

Table 6.14: Stabilised chromium contaminated clay pH dependent chemical parameters

Fraction	**pH**	**Conductivity µS**	**Fraction**	**pH**	**Conductivity µS**
EOC 28 Days			EOC 300 Days		
1	3.97	9110	1	4.00	8380
2	5.21	8460	2	5.55	7470
3	6.78	7240	3	6.20	6490
4	7.92	6480	4	7.25	5740
5	9.33	5680	5	7.70	5200
6	10.76	4330	6	9.48	5050
7	12.07	1600	7	10.34	4400
8	12.43	3290	8	11.99	1395
EOC 150 Days			9	12.36	3210
1	4.12	8080			
2	5.70	7070			
3	6.95	6250			
4	8.47	5520			
5	9.87	4920			
6	10.46	4270			
7	11.91	1416			
8	12.26	3250			

NB: EOC – stabilised chromium contaminated kaolin clay

Table 6.15: Stabilised chromium contaminated clay with 1% humic acid pH dependent chemical parameters

Fraction	**pH**	**Conductivity**	**Fraction**	**pH**	**Conductivity**
EOHC 28 Days			EOHC 300 Days		
1	4.03	9270	1	3.97	8790
2	5.62	8230	2	5.09	7760
3	6.03	7920	3	6.17	7090
4	6.82	7310	4	7.00	6480
5	8.24	6640	5	8.74	5810
6	9.86	5920	6	10.04	5160
7	10.97	4610	7	10.55	4350
8	12.29	2165	8	12.10	1768
9	12.55	4180	9	12.43	3710
EOHC 150 Days					
1	4.32	8590			
2	5.88	7570			
3	6.59	7180			
4	7.84	6360			
5	9.34	5770			
6	10.32	5120			
7	12.01	1778			
8	12.30	3740			

NB: EOHC – stabilised chromium contaminated kaolin clay with 1% humic acid

Table 6.16: Stabilised chromium contaminated clay with 2.5% sulphate pH dependent chemical parameters

Fraction	**pH**	**Conductivity**	**Fraction**	**pH**	**Conductivity**
EOSC 28 Days			EOSC 300 Days		
1	3.55	11120	1	4.14	8210
2	4.22	9410	2	5.43	7340
3	5.85	8470	3	6.62	6170
4	6.36	8260	4	7.80	5580
5	7.05	7600	5	9.39	4830
6	8.19	6820	6	10.34	4010
7	9.83	5780	7	12.14	2440
8	10.84	4360	8	12.49	4680
9	12.28	2840			
10	12.57	5040			
EOSC 150 Days					
1	3.89	8680			
2	5.06	7600			
3	6.02	7020			
4	6.70	6260			
5	8.30	5480			
6	9.56	4830			
7	10.42	4180			
8	12.05	2510			
9	12.37	4770			

NB: EOSC – stabilised chromium contaminated kaolin clay with 2.5% sulphate

Information from pH dependent leaching was used for leaching assessments and speciation evaluations, based on the results for prevailing chemical parameters and obtained eluates analyses. These results are presented in Chapter 7.

6.2.2 Time Dependent Leaching

Time dependent leaching results for samples are presented in this section, showing calculated and measured physical and chemical parameters obtained using CEN/TS 15863. The primary aim of this assessment method was the determination of cumulative releases and release trends from stabilised matrices, in view of environmental impact under the prevailing testing conditions. However, it is also possible to determine release controlling mechanisms using the test method, and undertake calculations and predictions of releases under the chemical kinetics of the test process. The first priority here will be establishing primary release controlling mechanisms, and where releases are predominantly diffusion controlled, calculating the diffusion coefficients. Sodium (least reactive component) was used for this calculation, along the guidelines from CEN/TS 15863 (see Section 4.5.1). Calculated diffusion coefficients are also used to calculate tortuosity, which are used in the time dependent leaching assessments. Table 6.17 shows the calculated parameters for sodium from stabilised kaolin clay, at the different hydration durations. Table 6.18 shows the cumulative releases for sodium used in the calculations at the different hydration durations. Where matrix dissolution is observed (cf > 3.0 at fraction 5-8), calculating diffusion coefficients are not possible. This was observed for all hydration durations (Table 6.17), which was expected given the nature of cementitious matrices. However, during leaching assessments, LeachXS was used to estimate tortuosity, using an assumption of purely diffusion controlled leaching, as a tortuosity value was required.

Table 6.17: Parameters for release mechanism estimations in stabilised kaolin clay

Order	Eluate fractions	Mean	Concentration Factor cf	Increment a – b
28 Days				
1	Fraction 2 to 7	6.192	3.469	201.794
2	Fraction 5 to 8	7.065	3.958	198.100
3	Fraction 4 to 7	6.204	3.476	165.412
4	Fraction 3 to 6	7.282	1.296	136.705
5	Fraction 2 to 5	6.692	1.191	103.011
6	Fraction 1 to 4	6.099	1.085	72.045
150 Days				
1	Fraction 2 to 7	4.979	3.083	159.953
2	Fraction 5 to 8	6.514	4.033	161.871
3	Fraction 4 to 7	5.196	3.217	131.732
4	Fraction 3 to 6	5.862	1.371	107.689
5	Fraction 2 to 5	5.342	1.249	80.567
6	Fraction 1 to 4	4.659	1.089	55.851
300 Days				
1	Fraction 2 to 7	4.822	4.832	162.020
2	Fraction 5 to 8	5.734	5.745	159.460
3	Fraction 4 to 7	4.748	4.757	132.930
4	Fraction 3 to 6	5.670	1.210	110.963
5	Fraction 2 to 5	5.746	1.226	84.728
6	Fraction 1 to 4	5.035	1.074	58.139

Note: for details on calculations, see Section 4.5.1

Table 6.18: Sodium releases from stabilised kaolin clay during time dependent leaching

Fraction	Release (mg/m^2)	Cumulative	Fraction	Release (mg/m^2)	Cumulative
28 Days			**300 Days**		
1	6.436	6.436	1	4.973	4.973
2	6.242	12.678	2	5.257	10.230
3	6.096	18.774	3	4.687	14.918
4	5.620	24.394	4	5.222	20.139
5	8.812	33.206	5	7.820	27.959
6	8.600	41.806	6	4.951	32.910
7	1.785	43.591	7	0.998	33.908
8	9.062	52.653	8	9.166	43.074
9	6.999	59.652	9	17.584	60.658
150 Days					
1	5.248	5.248			
2	4.812	10.060			
3	4.277	14.337			
4	4.301	18.638			
5	7.978	26.615			
6	6.892	33.507			
7	1.615	35.122			
8	9.571	44.692			
9	8.303	52.995			

Whilst diffusion is likely to be the primary release controlling mechanism, it is not the only mechanism responsible for release. A slope of 0.5 is expected for a purely diffusion controlled system (See Chapter 4, Table 4.11, Section 4.5.1), and Figure 6.2 shows cumulative releases of sodium, with inclusion of 0.5 slope trend line.

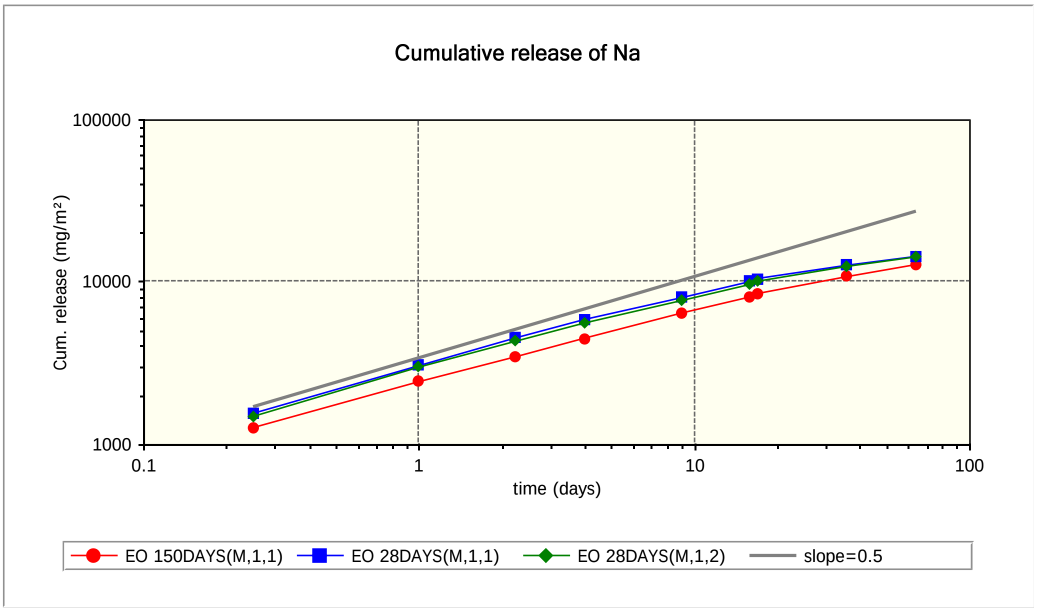


Figure 6:2: Cumulative release of sodium from cement stabilised clay at different test intervals

To assess repeatability during testing for eluate fractions, a triplicate run for stabilised chromium contaminated clay with 2.5% sulphate at 300 days hydration is shown in Table 6.19, for measured chemical parameters (pH and conductivity). Measured and calculated physical properties of the test samples are shown in Table 6.20.

Table 6.19: Measured Chemical Parameters for EOSC 300 days test replicates

Parameters	**pH**			**Conductivity µS**		
Sample	**A**	**B**	**C**	**A**	**B**	**C**
1	11.70	11.73	11.72	921	996	946
2	11.80	11.81	11.80	1127	1188	1128
3	11.72	11.73	11.70	959	1007	930
4	11.72	11.77	11.69	1035	1130	996
5	11.97	11.94	11.94	1607	1602	1530
6	11.91	11.91	11.71	1451	1494	1199
7	11.27	11.27	11.20	339	356	312
8	11.93	11.94	11.72	1658	1692	1430
9	11.67	11.78	11.01	1394	1481	1120

Table 6.20: Measured and calculated physical parameters for EOSC 300 days replicates

Parameters		**A**	**B**	**C**
Measured	Length (cm)	10.55	10.49	10.52
	Diameter (cm)	10.29	10.30	10.35
	Weight (g)	1628.30	1635.00	1638.10
Calculated	Bulk Density (Mg/m^3)	1.31	1.33	1.31
	Porosity	0.51	0.50	0.51
	Particle Density (Mg/m^3)	2.67	2.67	2.67
	Surface Area (cm^2)	507.68	506.06	510.50

Unstabilised samples did not retain integrity for use in time dependent leaching evaluations, losing monolithic form within 6 hours of testing. However, it was important to assess the contaminants leachable fractions to obtain background values. Table 6.21 shows results at measured chemical parameters of eluates after 6 hours of leaching from unstabilised matrices at 28 and 150 days, whilst the results for major constituents (mg/kg) from eluate analyses are shown in Table 6.22.

Table 6.21: Measured chemical parameters for unstabilised clay sample eluates at 6 hours

Sample	**Time**	**pH**	**Conductivity μS**
Clay	28 Days	6.45	90
	150 Days	5.67	67
Clay + Zinc	28 Days	4.67	290
	150 Days	4.69	149
Clay + Chromium	28 Days	3.86	281
	150 Days	3.83	289

Table 6.22: Measured concentrations of components from unstabilised clay samples (mg/kg)

Element	**Na**	**Ca**	**S**	**Si**	**Al**	**Zn**	**Cr**
Sample							
Clay 28 Days	33.82	0.00	35.83	5.35	0.21	0.00	0.00
Clay 150 Days	27.71	1.02	19.97	3.57	0.17	0.00	0.00
Clay + Zn 28 days	55.04	13.32	21.52	5.08	2.92	72.23	0.02
Clay + Zn 150 Days	29.32	5.92	9.18	2.14	0.84	31.65	0.00
Clay + Cr 28 Days	31.18	15.90	3.91	4.00	15.57	0.02	6.89
Clay + Cr 150 Days	35.73	19.05	3.11	3.39	15.04	0.17	3.66

Stabilised matrices retained integrity during testing, and the current evaluations (since no diffusion coefficients could be calculated) show pH development and cumulative release trends for clay minerals (Al and Si) and contaminants (Zn and Cr) during time dependent leaching for the different matrices. For matrices without additives, Figure 6.3 shows the pH development during time dependent leaching. Figure 6.4 shows development in matrices with 1% humic acid, whilst those with 2.5% sulphate content are shown in Figure 6.5. Cumulative aluminium releases from matrices without additives during time dependent leaching are shown in Figure 6.6, with the inclusion of a 0.5 slope trend line. Releases from matrices with 1% humic acid are shown in Figure 6.7, whilst those with 2.5% sulphate are shown in Figure 6.8.

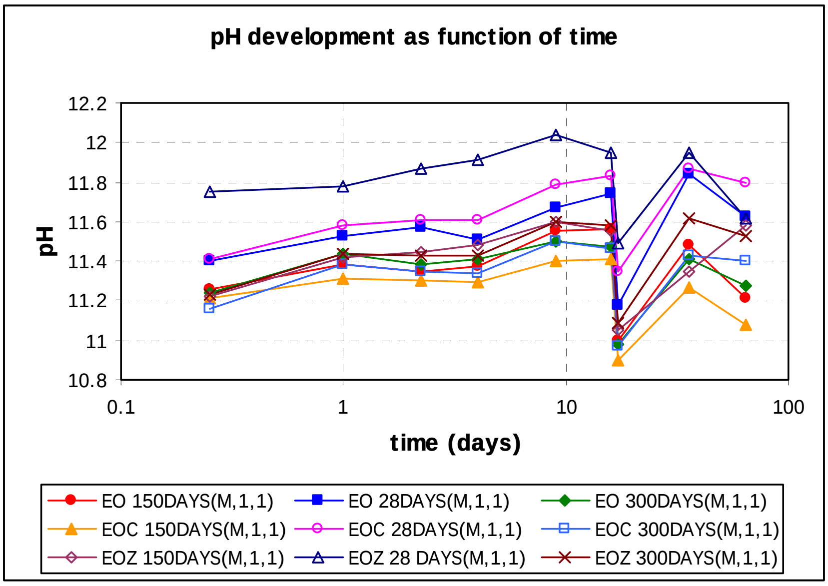


Figure 6:3: pH development for stabilised matrices without additives during leaching

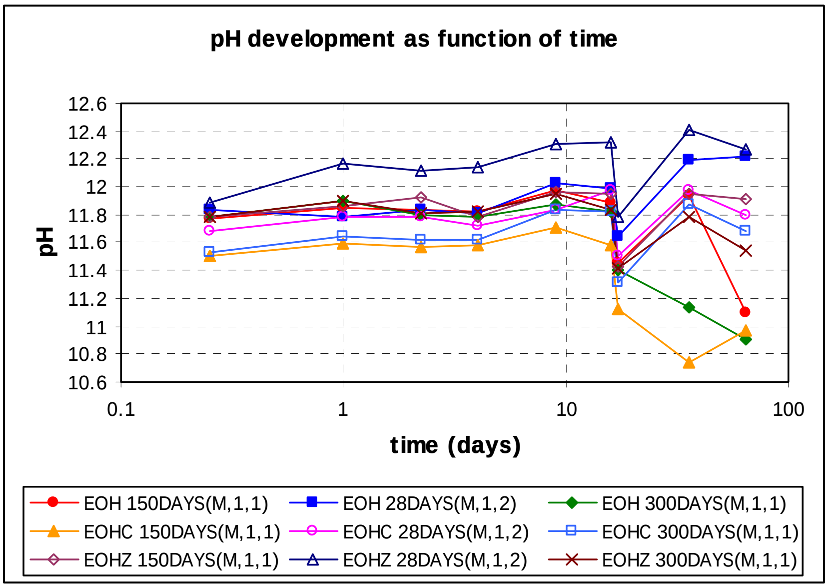


Figure 6:4: pH development for stabilised matrices with 1% humic acid during leaching

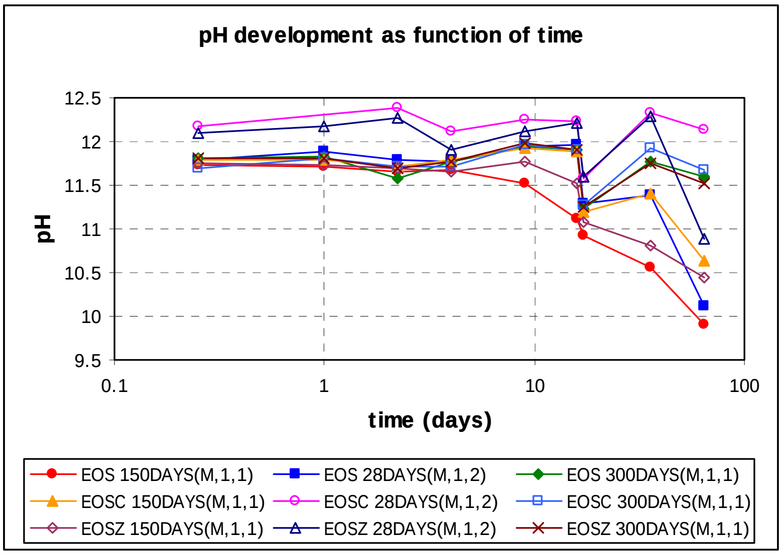


Figure 6:5: pH development for stabilised matrices with 2.5% sulphate during leaching

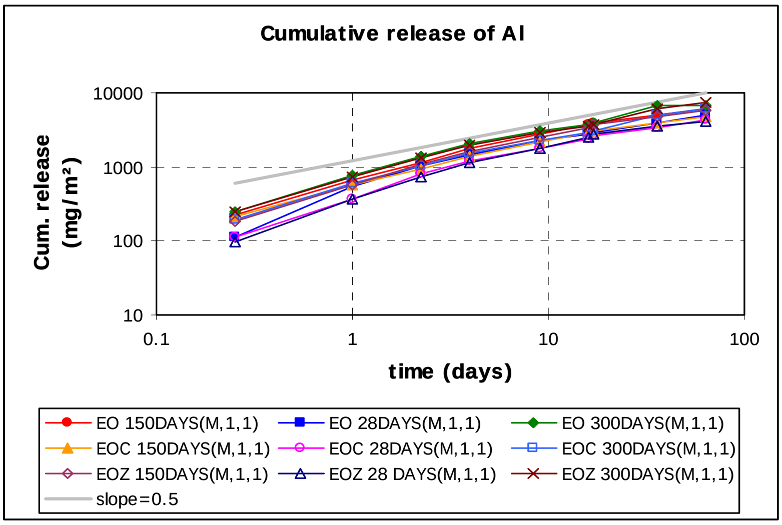


Figure 6:6: Cumulative aluminium release from stabilised matrices without additives

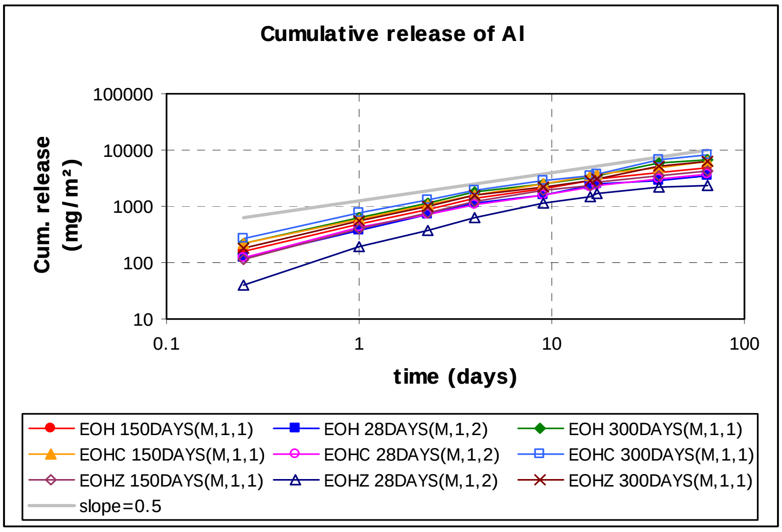


Figure 6:7: Cumulative aluminium releases from stabilised matrices with 1% humic acid

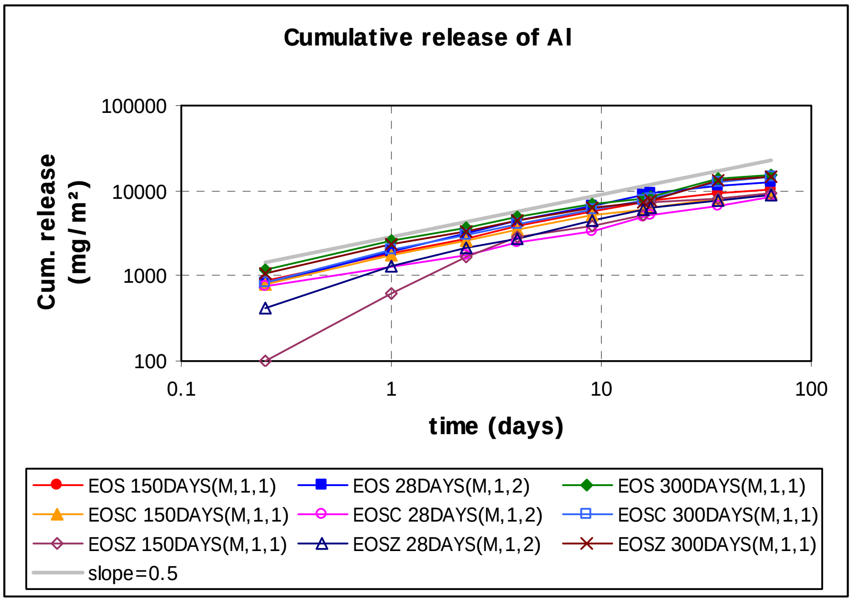


Figure 6:8: Cumulative aluminium release from stabilised matrices with 2.5% sulphate

For releases of silica, precipitations of calcium silicates were observed on walls of the leaching tanks at the end of tests (Figure 6.9), for stabilised matrices without additives, and stabilised matrices with 1% humic acid. This precipitation descended down the waterline, and was also observed on sample surfaces. This precipitation was however not observed in sulphate additive matrices leaching, and is discussed in Chapter 8, Section 8.2.3.1.

Figure 6:9: Calcium silicate precipitation on walls of monolithic test leaching vessel

This suggests that silica solubility depends on its speciation in the eluate solution, and the concentrations of other salts in the solution (See Section 8.2.3.1). Cumulative silica releases from stabilised matrices without additives are shown in Figure 6.10, whilst releases from stabilised matrices with 1% humic acid and 2.5% sulphate are shown in Figures 6.11 and 6.12 respectively.

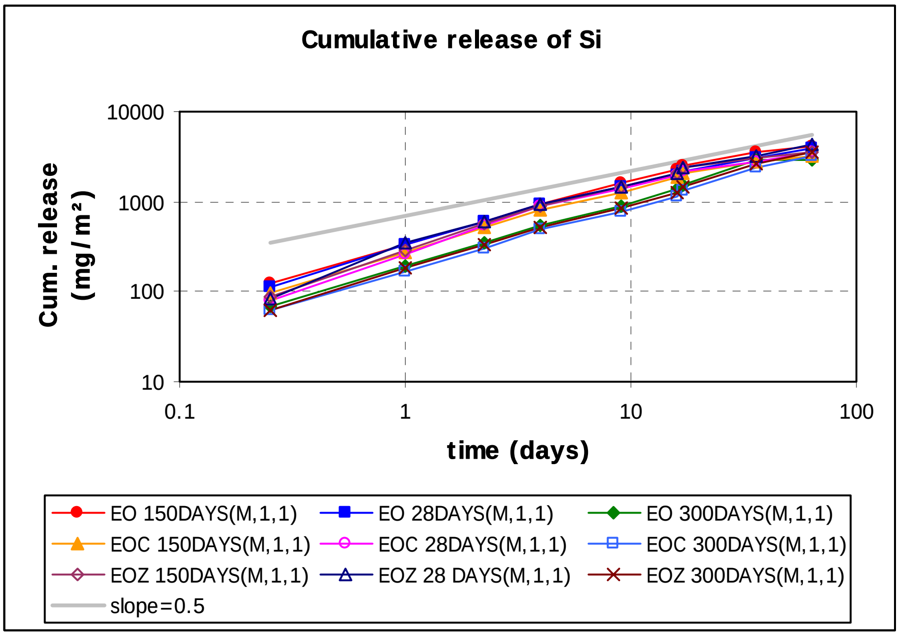


Figure 6:10: Cumulative silica releases from stabilised matrices without additives

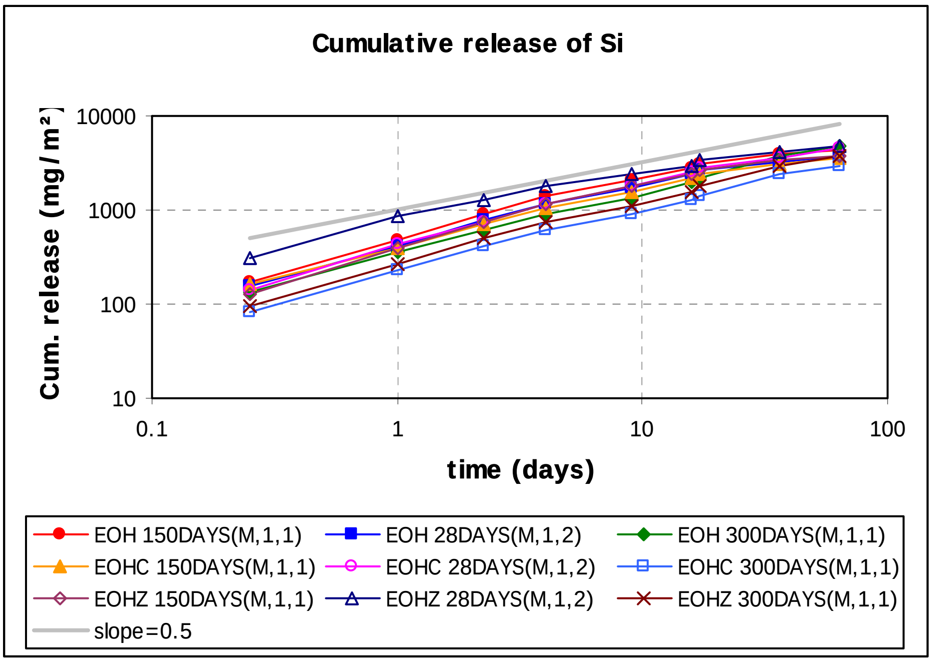


Figure 6:11: Cumulative silica releases from stabilised matrices with 1% humic acid

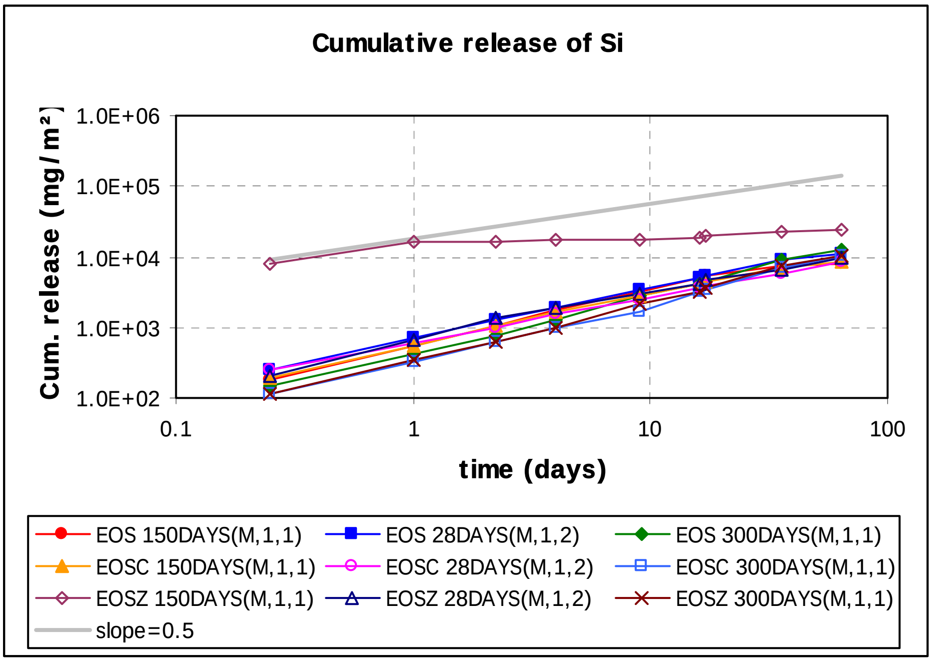


Figure 6:12: Cumulative silica releases from stabilised matrices with 2.5% sulphate

To evaluate releases of contaminants from the different matrices during time dependent leaching, cumulative releases of zinc and chromium are presented, for both contaminated and uncontaminated matrices. For zinc releases, Figure 6.13 shows cumulative releases from stabilised zinc contaminated and uncontaminated matrices without additives. Releases from matrices with 1% humic acid, and 2.5% sulphate are shown in Figures 6.14 and 6.15 respectively.

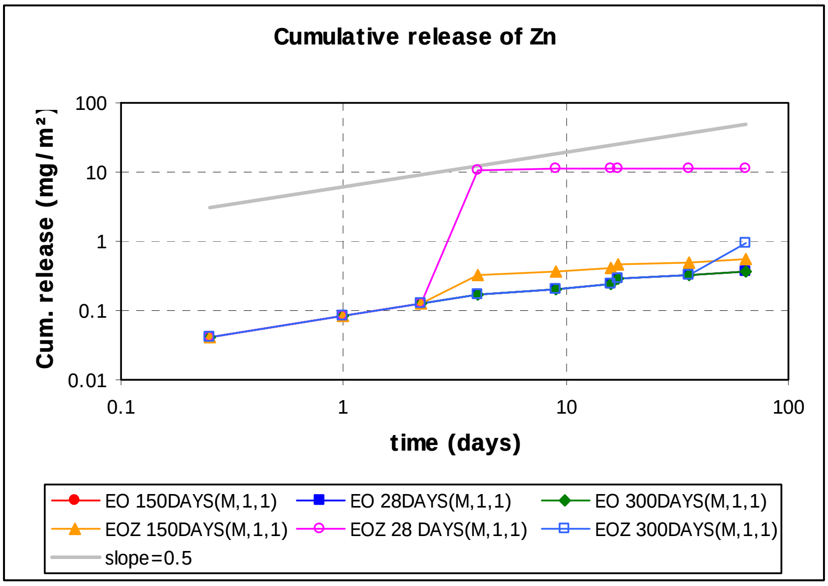


Figure 6:13: Cumulative zinc releases from stabilised matrices without additives

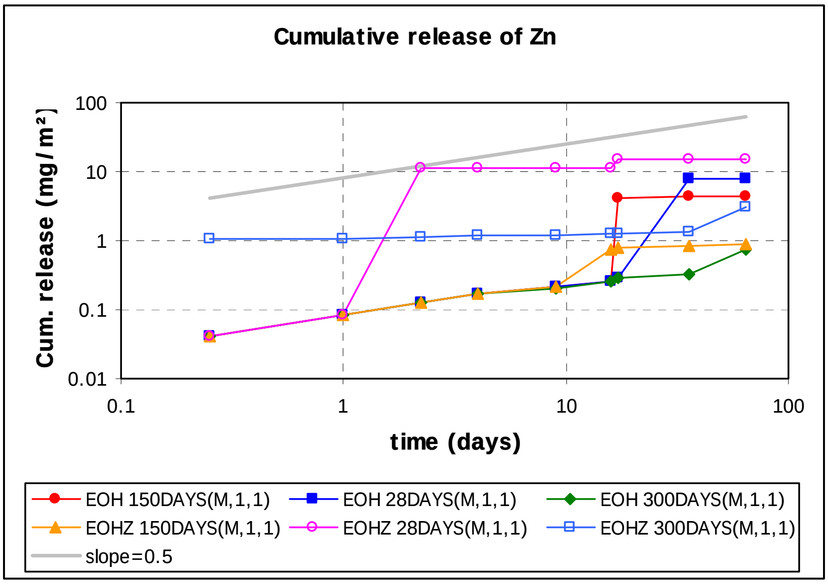


Figure 6:14: Cumulative zinc releases from stabilised matrices with 1% humic acid

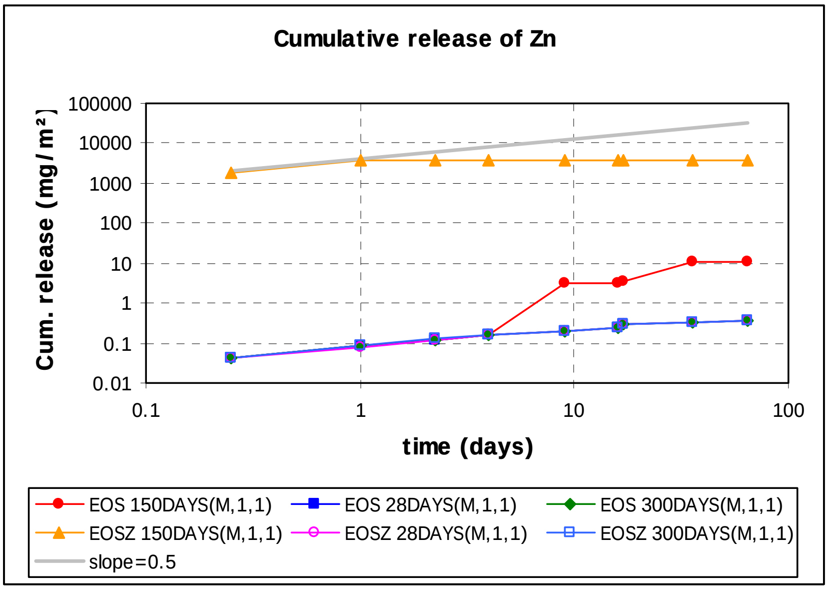


Figure 6:15: Cumulative zinc release from stabilised matrices with 2.5% sulphate

For evaluations of chromium releases, Figure 6.16 shows cumulative chromium releases from chromium contaminated and uncontaminated matrices. Releases from matrices with 1% humic acid, and 2.5% sulphate additives are shown in Figures 6.17 and 6.18 respectively. For leaching assessments and release / speciation modelling from the monolithic specimens, measured and calculated physical properties were required. These included parameters shown in Table 6.20, and were input for all samples, to calculate releases from specific surface areas for known sample volumes.

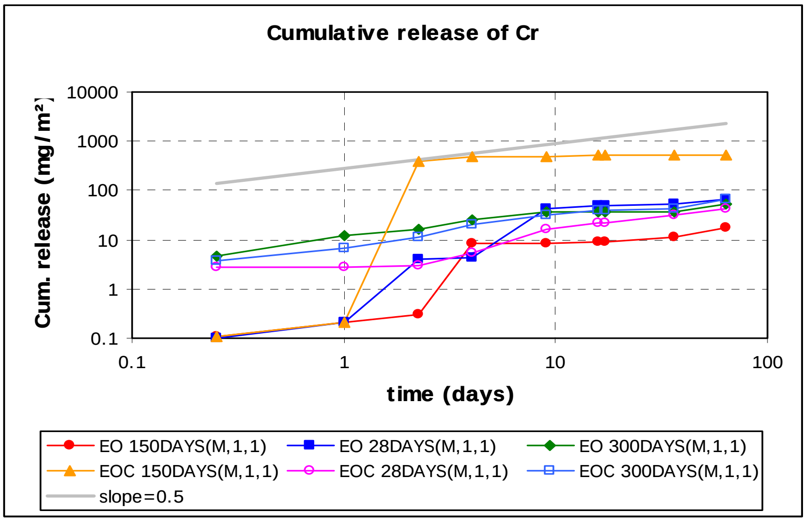


Figure 6:16: Cumulative chromium releases from stabilised matrices without additives

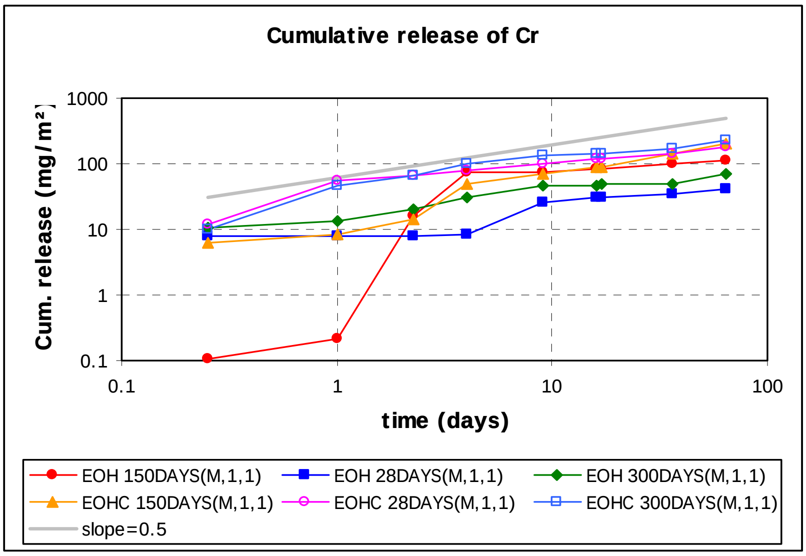


Figure 6:17: Cumulative chromium releases from stabilised matrices with 1% humic acid

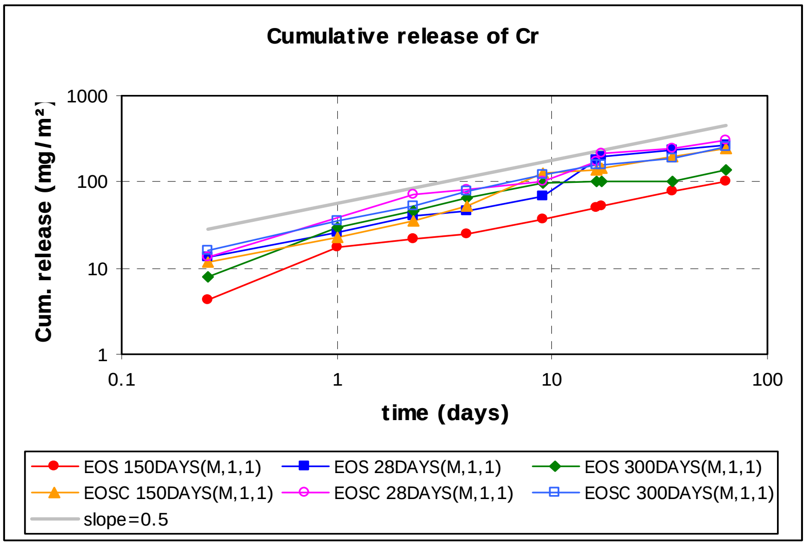


Figure 6:18: Cumulative chromium releases from stabilised matrices with 2.5% sulphate

Assessing releases of contaminants during time dependent leaching assessments is also beneficial, as this yields information on accidental releases via initial dissolution of mineral and wash off, which are not apparent from cumulative releases. Results for time dependent releases of zinc, from zinc contaminated matrices are shown in Figure 6.19, for the different hydration durations. Releases for chromium, from chromium contaminated matrices are shown in Figure 6.20, at the different hydration durations.

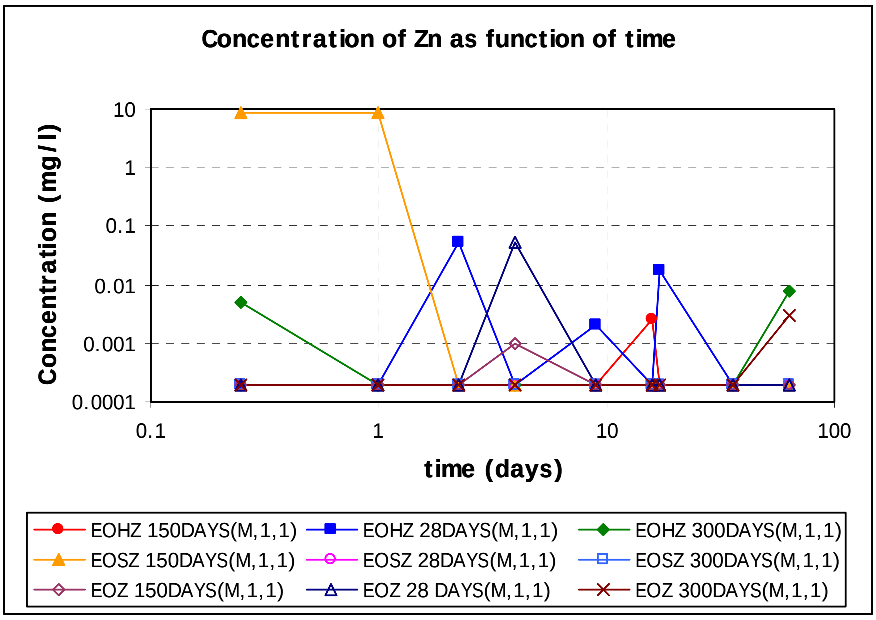


Figure 6:19: Zinc Release from cement Stabilised Clay and Zinc Contaminated Clay Samples

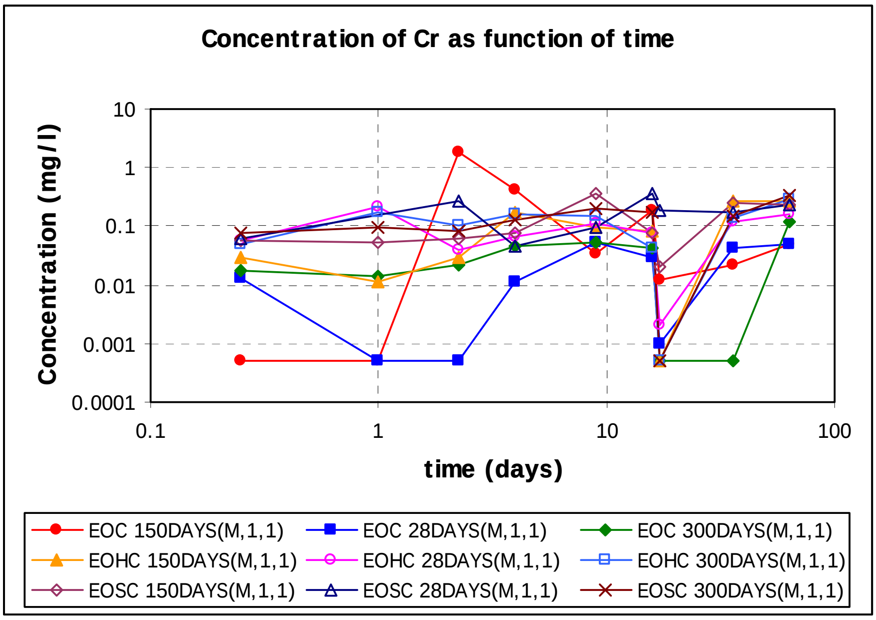


Figure 6:20: Chromium Release from Cement Stabilised Chromium Contaminated Clay Samples

These results were used for release assessments and release trend evaluations, during time dependent leaching (See Chapter 8, Section 8.2.3.1 and 8.3.3). Implications of contamination and additives were also drawn, but ultimately the information on cumulative releases was useful in view of environmental impact. Matrices degradation can also be evaluated, by assessing cumulative releases of structural components.

6.2.3 Porewater Leaching

To evaluate leaching to porewater, this section shows results from up-flow percolation tests CEN/TS 14405 (2008), at low L/S ratios. Results are presented based on matrix type (presence and type of additive), at the different hydration durations. Samples were crushed and air dried prior to testing, thus it was important to show results for physical parameters of the samples during testing. Table 6.23 shows results for physical parameters of stabilised matrices without additives.

Table 6.23: Measured physical parameters for stabilised matrices without additive

Sample	**EO 28 Days**	**EO 150 Days**	**EO 300 Days**
Physical parameters			
Weight (g)	2609.00	3037.00	3178.70
Porosity	0.61	0.60	0.58
Water content (%)	2.40	13.40	14.84
Bulk Density (Mg/m^3)	1.02	1.06	1.09
Sample	**EOC 28 Days**	**EOC 150 Days**	**EOC 300 Days**
Physical parameters			
Weight (g)	3024.90	2966.90	3023.30
Porosity	0.58	0.57	0.56
Water content (%)	8.69	4.02	5.51
Bulk Density (Mg/m^3)	1.11	1.15	1.15
Sample	**EOZ 28 Days**	**EOZ 150 Days**	**EOZ 300 Days**
Physical parameters			
Weight (g)	2770.30	2988.10	2967.40
Porosity	0.59	0.56	0.57
Water content (%)	4.05	5.14	5.18
Bulk Density (Mg/m^3)	1.07	1.14	1.13

These tests are designed to evaluate leaching to porewater from matrices under natural equilibrium conditions, and thus the prevailing chemical conditions were likely to influence component releases. Results for chemical parameters of obtained eluates, for stabilised matrices without additives are shown in Table 6.24, at different hydration durations. Fractions 1 and 2 are used to evaluate equilibration (See Chapter 4, Section 4.5.2), where each represents 0.1 L/S (0.2 cumulative L/S), while fraction 3 represents cumulative 0.5 L/S.

Table 6.24: Measured chemical parameters for stabilised matrices without additives

Chemical Parameters		**pH**	**Conductivity**
Sample	**Fraction**		
EO 28 Days	1	11.84	2120
	2	11.89	2120
	3	11.95	1795
EO 150 Days	1	11.69	1790
	2	11.87	1997
	3	11.94	2010
EO 300 Days	1	12.08	2730
	2	12.20	2980
	3	12.19	2770
EOC 28 Days	1	11.71	4310
	2	11.86	4010
	3	11.93	3220
EOC 150 Days	1	10.94	5540
	2	11.01	4660
	3	11.32	3190
EOC 300 Days	1	11.10	5100
	2	11.34	4070
	3	11.46	3100
EOZ 28 Days	1	12.19	4250
	2	12.27	3780
	3	12.29	3170
EOZ 150 Days	1	11.36	4020
	2	11.41	3100
	3	11.58	2290
EOZ 300 Days	1	11.90	4580
	2	12.07	5780
	3	12.16	5380

Cumulative releases of master species are discussed in Chapter 8 Section 8.5, with no zinc releases observed for all matrices, whilst chromium releases were comparable for both contaminated and uncontaminated matrices (See Chapter 8 where they are discussed, Table 8.2). These results were not presented in this section, with the priority given here to measured physical and chemical parameters for obtained eluates. Table 6.25 shows the measured chemical parameters for stabilised matrices with 1% humic acid, and the measured physical parameters are shown in Table 6.26.

Table 6.25: Measured chemical parameters for stabilised matrices with 1% Humic Acid

Chemical Parameters		**pH**	**Conductivity**
Sample	**Fraction**		
EOH 28 Days	1	11.88	3720
	2	12.07	4430
	3	12.10	4140
EOH 150 Days	1	12.00	4210
	2	12.09	4120
	3	12.06	3490
EOH 300 Days	1	12.24	6700
	2	12.40	6770
	3	12.38	5470
EOHC 28 Days	1	12.03	6010
	2	12.14	5250
	3	12.23	4110
EOHC 150 Days	1	11.57	5250
	2	11.60	4840
	3	11.74	3600
EOHC 300 Days	1	11.62	8600
	2	11.69	7650
	3	11.92	5110
EOHZ 28 Days	1	12.69	7610
	2	12.72	8910
	3	12.77	9140
EOHZ 150 Days	1	11.93	4210
	2	11.93	3850
	3	11.94	3630
EOHZ 300 Days	1	11.72	3710
	2	11.82	3340
	3	11.95	2710

Results for physical parameters of stabilised matrices with 2.5% sulphate additives are shown in Table 6.27, and the measured chemical parameters shown in Table 2.68. All presented results include both contaminated and uncontaminated samples for matrices, at the different hydration durations.

Table 6.26: Measured physical parameters for stabilised matrices with 1% Humic Acid

Sample	**EOH 28 Days**	**EOH 150 Days**	**EOH 300 Days**
Physical parameters			
Weight (g)	2807.60	2900.10	2830.20
Porosity	0.58	0.57	0.58
Water content (%)	1.90	2.73	3.35
Bulk Density (Mg/m^3)	1.11	1.14	1.10
Sample	**EOHC 28 Days**	**EOHC 150 Days**	**EOHC 300 Days**
Physical parameters			
Weight (g)	2986.00	2996.10	2831.40
Porosity	0.55	0.55	0.59
Water content (%)	3.25	2.50	4.41
Bulk Density (Mg/m^3)	1.16	1.18	1.09
Sample	**EOHZ 28 Days**	**EOHZ 150 Days**	**EOHZ 300 Days**
Physical parameters			
Weight (g)	2832.90	2751.70	2793.60
Porosity	0.63	0.59	0.59
Water content (%)	14.67	2.22	3.29
Bulk Density (Mg/m^3)	0.97	1.08	1.09

Table 6.27: Measured and physical parameters for stabilised matrices with 2.5% Sulphate

Sample	**EOS 28 Days**	**EOS 150 Days**	**EOS 300 Days**
Physical parameters			
Weight (g)	2791.10	2909.10	3036.50
Porosity	0.59	0.59	0.57
Water content (%)	2.60	5.64	5.37
Bulk Density (Mg/m^3)	1.09	1.11	1.16
Sample	**EOSC 28 Days**	**EOSC 150 Days**	**EOSC 300 Days**
Physical parameters			
Weight (g)	2818.40	2758.10	2972.80
Porosity	0.59	0.62	0.57
Water content (%)	2.67	2.79	3.66
Bulk Density (Mg/m^3)	1.10	1.02	1.15
Sample	**EOSZ 28 Days**	**EOSZ 150 Days**	**EOSZ 300 Days**
Physical parameters			
Weight (g)	2779.80	2958.40	2963.90
Porosity	0.60	0.59	0.61
Water content (%)	4.50	6.63	11.68
Bulk Density (Mg/m^3)	1.07	1.11	1.05

Table 6.28: Measured chemical parameters for stabilised matrices with 2.5% Sulphate

Chemical Parameters		**pH**	**Conductivity**
Sample	**Fraction**		
EOS 28 Days	1	11.40	20800
	2	11.59	17500
	3	11.70	13840
EOS 150 Days	1	11.77	21300
	2	11.99	19400
	3	12.09	14210
EOS 300 Days	1	12.46	22900
	2	12.51	19800
	3	12.49	14400
EOSC 28 Days	1	12.65	22000
	2	12.57	22800
	3	12.59	16840
EOSC 150 Days	1	11.94	24600
	2	12.05	21300
	3	12.17	15400
EOSC 300 Days	1	11.91	18740
	2	11.97	19450
	3	12.03	15860
EOSZ 28 Days	1	12.41	21200
	2	12.53	19320
	3	12.50	14300
EOSZ 150 Days	1	12.33	29300
	2	12.40	23800
	3	12.47	16990
EOSZ 300 Days	1	12.38	24400
	2	12.36	18760
	3	12.39	13710

Measured pH values for fraction 1 of eluates are equilibrium pH after 4 days of saturation, and the pH for fraction 2 used for validation. The pH variation should not exceed 0.5 pH units, and all measured eluates conformed to this requirement. Releases of aluminium, silicon and calcium are used to evaluate chemical durability and resistance to leaching with increasing hydration. These are discussed in Chapter 8 Section 8.5, for the different stabilised matrices. Releases to porewater can also be included for speciation evaluation of component releases, since testing were undertaken under equilibrium conditions. However, for the current study, no detrimental contaminant releases were observed, hence no speciation evaluations were required.

6.2.4 Hydrous Ferric Oxide / Hydroxide Extraction

Components can be sorbed onto surfaces of hydrous oxides of iron, aluminium and manganese (broadly termed hydrous ferric oxides – HFO), which alter their retention or release behaviour. To assess the amount of available HFO in matrices, extractions were undertaken using ascorbate (amorphous iron), dithionite (total iron) and oxalate (amorphous aluminium) extraction processes (Chapter 4 Section 4.5.4). Manganese measurements were also taken from extracted eluates, due are its surface sorption properties. However, due to the inability to establish specific surface properties for manganese, these results were not included when calculating HFO for use in speciation modelling as part of the current study. Results presented in this section are for uncontaminated samples, using representative matrices based on presence and type of included additives. This was done to prevent inclusions of soluble iron and aluminium contents, introduced with contaminants and minimise error. Representative values were used for each matrix during modelling, and evaluations for possible changes in HFO content with hydration were not undertaken.

Table 6.29 shows measured (ICP OES) concentration for Al, and Fe (mg/L), obtained through HFO extractions, and show sample weights and leachant volumes with extraction L/S ratios for unstabilised and stabilised kaolin matrices. From the measured component releases and sample volume, the available surface content in the test specimens can be estimated. These are shown in Table 6.30 (mg/kg), for the unstabilised and stabilised kaolin clay matrices.

To calculate HFO content for use in modelling, information on amorphous aluminium, amorphous iron and crystalline iron contents were required. The concentrations were obtained from analyses of eluates from HFO extraction. For this modelling approach, amorphous aluminium is treated similar to amorphous iron, due to similarities in surface structure and reactivity. Here, 1mol of amorphous iron from Ascorbate extraction is treated as almost equal to 1mol of amorphous aluminium from Oxalate extraction. The recommended surface area for sorption sites of the amorphous ions (Al and Fe) are 600m^2/g, whilst that of crystalline iron is 100m^2/g (Meima and Comans, 1998).

Table 6.29: HFO extraction parameters with measured eluate concentrations for Al, Fe and Mn

Sample	Extraction	Sample Mass (g)	Extractant Volume(g)	L/S ratio	Al (mg/L)	Fe (mg/L)
	Ascorbate	3.0	60.0	20.0	0.987	0.756
Clay	Dithionite	3.0	60.0	20.0	2.235	0.951
	Oxalate	3.0	300.0	100.0	0.311	0.322
	Ascorbate	3.0	60.0	20.0	13.219	9.385
EO	Dithionite	3.0	60.0	20.0	31.718	11.617
	Oxalate	3.0	300.0	100.0	5.496	1.413
	Ascorbate	3.0	60.0	20.0	8.383	7.073
EOH	Dithionite	3.0	60.0	20.0	25.511	13.598
	Oxalate	3.0	300.0	100.0	1.007	0.374
	Ascorbate	3.0	60.0	20.0	12.238	7.571
EOS	Dithionite	3.0	60.0	20.0	44.513	13.864
	Oxalate	3.0	300.0	100.0	6.589	1.309

Table 6.30: Concentrations of released components for the different HFO extractions

		Al(mg/kg)	Fe(mg/kg)
Sample	**Extraction**		
	Ascorbate	20	15
Clay	Dithionite	45	19
	Oxalate	31	32
	Ascorbate	264	188
EO	Dithionite	634	232
	Oxalate	550	141
	Ascorbate	168	141
EOH	Dithionite	510	272
	Oxalate	101	37
	Ascorbate	245	151
EOS	Dithionite	890	277
	Oxalate	659	131

To determine total HFO content, available Al and Fe concentrations are converted from mg/kg to mol/kg, achieved by dividing concentration (g/kg) by molecular weight, where Al is 26.98 (27 used in calculations) and Fe is 55.85. To determine crystalline iron content, amorphous iron content (ascorbate extraction) is subtracted from total iron content (dithionite extraction). Obtained ion releases (mol/kg) are then converted to HFO content in the material, as oxide/hydroxides of the ions in kg/kg of the dry solid material. This is done by multiplying concentrations in mol/kg by molecular weights of the oxyhydroxides, and dividing the obtained content by 1000. Since amorphous aluminium is treated as almost equal to amorphous iron, the molecular weight for Goethite [FeO(OH)] was used (88.86 but 89 used in calculations). However, crystalline Fe has specific surface area (SSA) of 100m^2/g while amorphous Fe and Al have 600m^2/g, and thus HFO for crystalline Fe was divided by 6 (Meima and Comans, 1998). Table 6.35 shows the calculated HFO for the different matrices, including individual concentration for HFO components in mol/kg.

Table 6.31: Calculated HFO for the Different Sample Matrices (kg/kg)

		Al(am) (mol/kg)	Fe(mol/kg)	Fe(cryst) (mol/kg)	HFO (kg/kg)
Sample	**Extraction**				
	Ascorbate		0.00027		2.41E-05
Clay	Dithionite		0.00034	6.98925E-05	1.04E-06
	Oxalate	0.00115			1.03E-04
				Total HFO	1.28E-04
	Ascorbate		0.00336		2.99E-04
EO	Dithionite		0.00416	0.00080	1.19E-05
	Oxalate	0.02036			1.81E-03
				Total HFO	2.12E-03
	Ascorbate		0.00254		2.26E-04
EOH	Dithionite		0.00487	0.00234	3.47E-05
	Oxalate	0.00373			3.32E-04
				Total HFO	5.92E-04
	Ascorbate		0.00271		2.42E-04
EOS	Dithionite		0.00497	0.00226	3.35E-05
	Oxalate	0.02440			2.17E-03
				Total HFO	2.45E-03

6.3 ELUATE ANALYSES, REPEATABILITY AND ACCURACY

This section presents results of eluate analyses for dissolved organic carbon (DOC) and cation analyses. These include release trends and repeatability of DOC analyses from different matrices at different hydration durations, evaluations of repeatability and precision for cation analyses, and analyses of blanks for impacts on measurements.

6.3.1 Dissolved Organic Carbon

DOC analyses were undertaken on eluates obtained from leaching tests, to assess the implications of organic carbon on component containment and releases. Obtained results were included for speciation modelling (NICA Donnan model), of component complexation with organics, where release DOC is assumed to be from reactive humic substances (See Chapter 5 Section 5.4.2). Raw results are not shown in this section, but rather release trends for different matrices (based on additives) are presented. Considering that kaolin contains very small organic content being process clay, small DOC releases from the stabilised matrices were expected, except from stabilised matrices with 1% humic acid additives. Table 6.32 shows the measured DOC released (mg/kg) from stabilised kaolin clay at the different hydration durations, while Figure 6.21 shows the release trends at the different hydration durations. Similarly, Table 6.33, 6.34 and 6.35 show DOC releases from the stabilised humic acid matrix, stabilised sulphate matrix, and from kaolin clay respectively. Figures 6.22, 6.23 and 6.24, show the corresponding release trends, for releases against changes in pH during leaching.

Table 6.32: Measured DOC releases from stabilised kaolin clay

Sample	pH	Release mg/kg	Sample	pH	Release mg/kg
EO 28 days	3.84	44.12	EO 300 Days	3.85	21.14
	4.10	27.42		4.54	19.98
	5.45	105.90		5.81	26.53
	7.56	60.52		6.79	36.36
	7.60	53.42		7.00	24.89
	9.30	51.50		8.83	31.10
	10.99	44.39		9.31	33.40
	12.07	83.45		10.66	30.11
	12.28	63.99		11.99	32.01
				12.35	17.82
EO 150 Days	4.01	26.17			
	5.53	26.97			
	6.53	29.67			
	7.83	45.62			
	9.40	41.45			
	10.72	30.68			
	11.96	29.44			
	12.28	25.13			

Table 6.33: Measured DOC releases from stabilised kaolin clay with 2.5% Sulphate

Sample	pH	Release mg/kg	Sample	pH	Release mg/kg
EOS 28 Days	4.01	85.75	EOS 300 Days	3.85	30.14
	5.39	43.32		5.75	38.97
	6.58	55.70		6.76	33.82
	7.41	45.82		7.45	16.91
	7.70	47.14		8.53	38.32
	9.15	52.72		9.85	28.12
	10.46	36.95		10.99	40.27
	12.13	37.98		12.07	39.33
	12.46	45.21		12.30	29.82
EOS 150 days	4.10	27.31			
	5.40	19.08			
	6.67	25.63			
	8.07	45.18			
	9.33	23.04			
	10.51	29.11			
	12.03	42.28			
	12.35	32.84			

Table 6.34: Measured DOC releases for stabilised kaolin clay with 1% humic acid

Sample	pH	Release mg/kg	Sample	pH	Release mg/kg
EOH 28 Days	3.74	122.91	EOH 300 Days	3.97	116.89
	4.23	140.91		5.18	148.37
	5.65	191.51		6.20	239.46
	7.08	316.79		7.02	276.74
	8.07	369.52		8.46	350.88
	9.16	357.18		9.85	320.66
	10.55	279.18		10.52	285.17
	11.14	202.34		12.20	155.82
	12.24	180.68		12.47	140.09
	12.37	205.34			
EOH 150 Days	3.91	150.25			
	5.59	162.64			
	6.24	233.26			
	7.57	318.18			
	8.54	343.95			
	9.86	295.57			
	10.68	241.86			
	12.14	149.68			
	12.37	135.29			

Table 6.35: Measured DOC releases for kaolin clay

Sample	pH	Release mg/kg
Kaolin Clay	2.53	55.49
	3.06	41.28
	5.43	47.44
	6.02	38.77
	6.97	22.42
	8.08	53.63
	9.42	52.62
	10.11	57.98
	11.31	51.92
	11.99	69.57

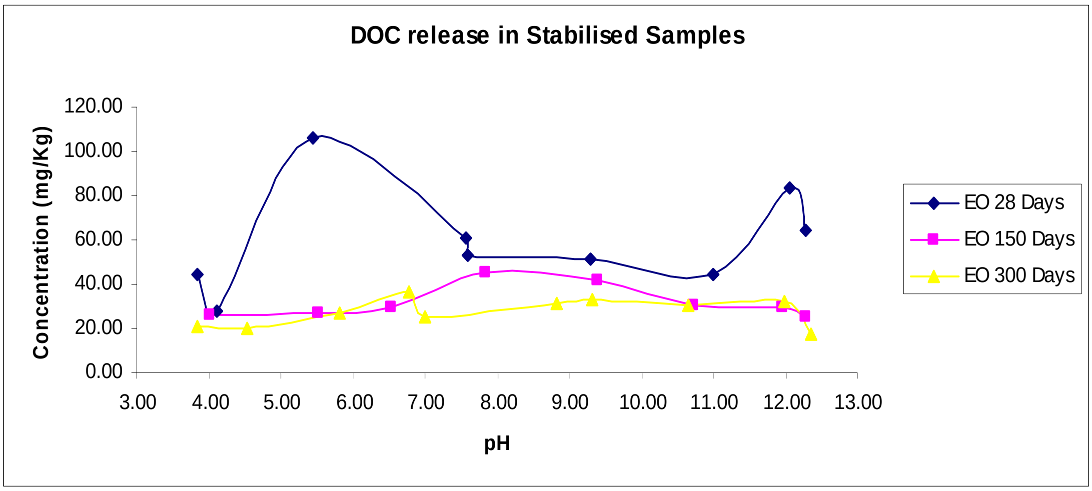


Figure 6:21: DOC release trends from stabilised clay at different hydration durations

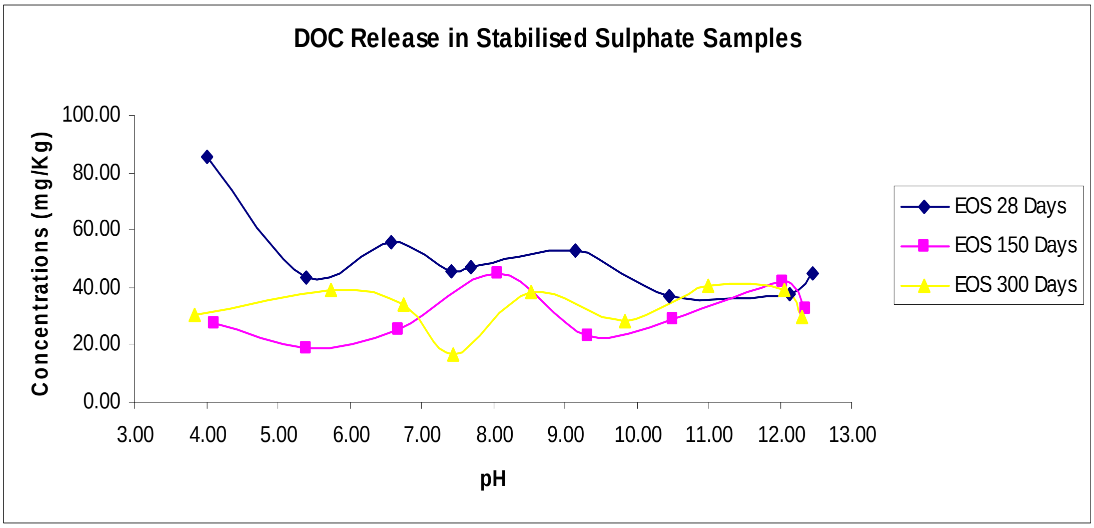


Figure 6:22: DOC release trends from stabilised kaolin with 2.5% Sulphate at different durations

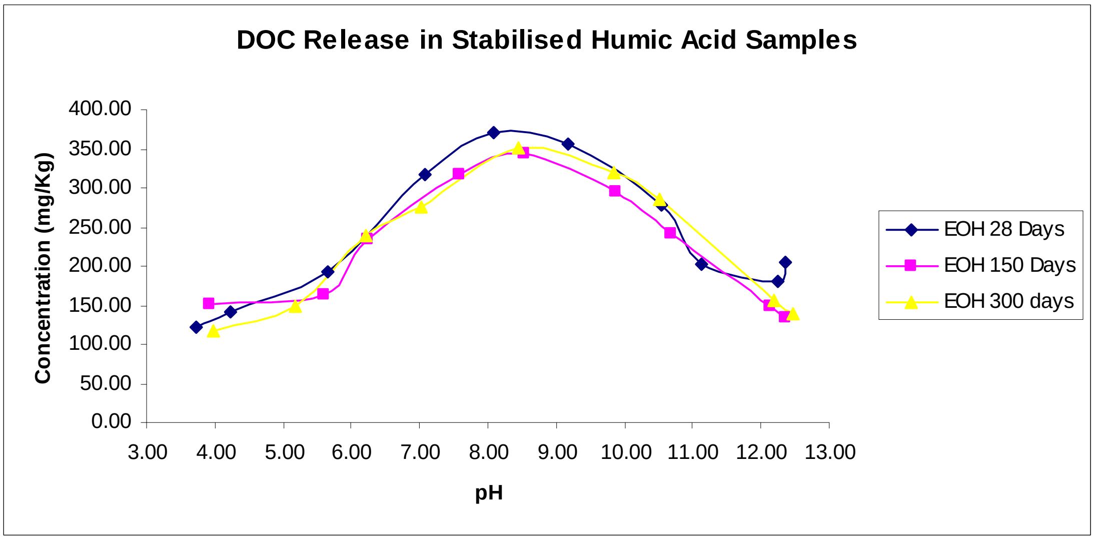


Figure 6:23: DOC release trend from stabilised kaolin with 1% humic acid at different durations

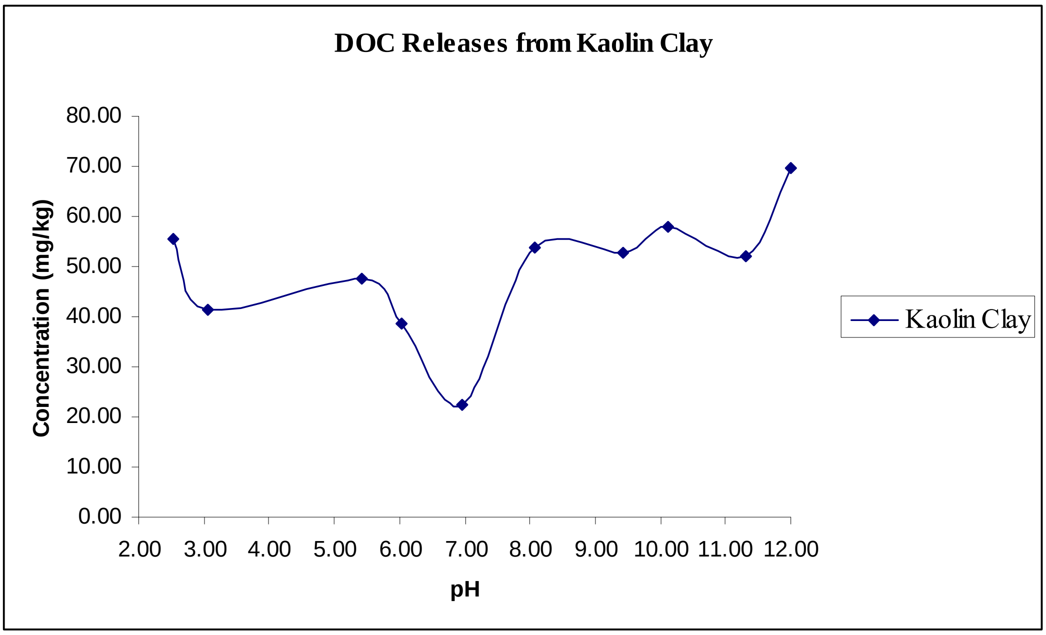


Figure 6:24: DOC release trend from kaolin clay

To evaluate impacts of leachants, preservatives and leaching containers on DOC measurements, analyses on control from time dependent leaching tanks, demineralised water (reverse osmosis RO water), and acidified demineralised water were undertaken. Table 6.36 shows measured DOC concentrations for monolithic leaching vessel controls, demineralised water, and acidified demineralised water (to assess preservation influence).

Table 6.36: Measured DOC concentrations in leachant, preserved leachant and leaching vessel

	Concentrations mg/l		
Sample	Tank Controls	RO Water	Acidified RO Water
	0.00	0.00	0.22
	0.15	0.02	0.25
	0.16	0.05	0.37
	0.20	0.21	0.41
	0.21	0.33	0.53
	0.21	0.33	0.58
	0.22	0.35	0.68
	0.24	0.38	1.27
	0.64	0.40	2.94

During DOC analyses, blanks (DOC removed water) were analysed with samples, to assess for cross contamination during analyses. Sorted results DOC analyses (mg/l) of these blanks, along with the variance, mean, standard deviation, median and count are shown in Table 6.37. The maximum observed measure was just over 2mg/l

Table 6.37: Measured concentrations for DOC Analyses blanks (mg/l)

Parameters		**Concentrations**			
Variance	0.2983	0.00	0.00	0.22	0.65
Mean	0.39	0.00	0.00	0.23	0.82
Std Dev	0.5461	0.00	0.00	0.26	0.88
Count	47	0.00	0.00	0.27	0.92
Median	0.22	0.00	0.00	0.34	0.94
		0.00	0.00	0.36	0.98
		0.00	0.00	0.38	0.98
		0.00	0.01	0.41	1.18
		0.00	0.13	0.45	1.64
		0.00	0.13	0.52	1.90
		0.00	0.16	0.53	2.40
		0.00	0.22	0.56	

To ensure repeatability of obtained DOC results, repeats for eluates were undertaken, and results evaluated for consistency. Also, during analyses, 5 measurements were taken for each eluate, and the average of 3 values with least deviation was used as the eluate concentration. Table 6.38 shows the concentrations, means, standard deviations and variances of some eluates analysed for DOC releases in replicates.

Table 6.38: Measured DOC repeats, mean, standard deviation and variance

Sample	1	2	3	4	5
Releases	193.37	4.04	8.43	1.39	175.91
	193.59	3.98	8.00	1.49	184.71
	192.73	4.09	8.50	1.41	176.80
					196.80
Mean	193.23	4.03	8.31	1.43	183.56
STD	0.45	0.06	0.27	0.05	9.67
Variance	0.20	0.00	0.07	0.00	93.60

6.3.2 CATION ANALYSES

Cation analyses via (ICP – OES) were undertaken on obtained eluates, to obtain information on component releases, for use in leaching assessments and speciation evaluations. To ensure that measured concentration were within reasonable accuracy, a standard iron solution, prepared at 10mg/l was analysed, and shown in Table 6.39.

Table 6.39: Measured Iron standard concentrations, mean, standard deviation and variance

Elements (mg/l)	**Na**	**Ca**	**S**	**Si**	**Al**	**Fe**	**Zn**	**Cr**
Iron standard 1	7.63	0.00	0.27	0.00	0.00	10.81	0.00	0.05
2	7.75	0.00	0.28	0.00	0.00	10.37	0.00	0.06
3	7.43	0.00	0.26	0.00	0.00	10.53	0.00	0.06
4	7.84	0.00	0.31	0.00	0.00	11.26	0.00	0.07
5	7.55	0.00	0.27	0.00	0.00	10.96	0.00	0.07
Mean	7.64	0.00	0.28	0.00	0.00	10.79	0.00	0.06
STD	0.16	0.00	0.02	0.00	0.00	0.35	0.00	0.01
Variance	0.03	0.00	0.00	0.00	0.00	0.12	0.00	0.00

Results show concentrations of selected components in the solution, with measurements ranging between 10.37 and 11.26, and iron concentration accuracy of about 10% (Table 6.39). To assess implications of leachants and preservative on results, Table 6.40 shows cation analyses results for leachants and control blanks. Some anomalous concentrations of elements were observed in eluates, which are expected during these types of analyses due to sample preparation and processing. However, measures were put in place during sample preparation, storage and processing to minimise contamination. To evaluate repeatability of obtained results, Table 6.41 shows results for cation analyses of 14 select samples analysed in replicates. Analyses of the obtained results for standard deviations, means and variances are shown in Table 6.42. Cation analyses for each eluate were run 5 times, and where variations exceeded 20% between measures for major components, results were discarded and the eluate reanalysed. Since analyses were undertaken at an external laboratory, it was important to ensure that results obtained were representative for eluates analysed, and putting these controls in place improved confidence in the obtained results. These data were loaded into LeachXS (Chapter 5 Section 5.4) for use in leaching and speciation evaluations presented in Chapter 7.

Table 6.40: Measured concentrations of selected components in control samples and blanks

Elements (mg/l)	**Na**	**Ca**	**S**	**Si**	**Al**	**Fe**	**Zn**	**Cr**
RO Water	0.52	0.00	0.28	0.12	0.00	0.13	0.07	0.00
RO Water	1.09	0.00	0.00	0.09	0.00	0.00	0.00	0.00
RO Water	0.18	0.00	0.00	0.11	0.00	0.13	0.00	0.04
RO Water	0.49	0.00	0.02	0.14	0.00	0.02	0.00	0.00
RO Water	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RO Water	**7.14**	**0.64**	**4.01**	**0.31**	**0.00**	**0.00**	**0.00**	**0.00**
RO Water	0.00	0.00	0.00	0.11	0.00	0.00	0.00	0.00
RO water	**1.36**	**0.41**	**0.07**	**0.32**	**0.17**	**0.20**	**0.04**	**0.15**
Acid RO Water	0.50	0.00	0.02	0.12	0.01	0.19	0.00	0.00
Acid RO Water	0.31	0.00	0.00	0.15	0.01	0.07	0.00	0.01
Acid RO Water	0.53	0.00	0.00	0.00	0.00	0.02	0.00	0.00
Acid RO Water	**18.57**	**0.77**	**3.74**	**0.21**	**0.00**	**0.02**	**0.00**	**0.04**
Acid RO Water	0.00	0.00	0.00	0.20	0.00	0.00	0.00	0.00
Acid RO water	**2.16**	**0.55**	**0.13**	**0.37**	**0.19**	**0.22**	**0.05**	**0.14**
Acid RO water	0.55	0.00	0.06	0.13	0.00	2.02	0.00	0.33
Acid RO water	0.70	1.90	2.05	0.11	0.00	0.90	0.00	0.19
Acid RO water	0.78	0.28	0.23	0.11	0.01	0.06	0.00	0.00
Filtration Blank	0.75	0.00	0.04	0.00	0.00	0.04	0.00	0.00
Filtration Blank	0.38	0.00	0.11	0.00	0.00	0.14	0.00	0.00
Filtration Blank	0.37	0.00	0.00	0.00	0.00	0.02	0.00	0.00
Filtration Blank	0.75	0.00	0.01	0.00	0.00	0.03	0.00	0.00
Filtration Blank	0.52	0.00	0.07	0.11	0.00	0.28	0.02	0.09
Tank Test Blank	**1.03**	**4.31**	**0.28**	**0.13**	**0.00**	**0.20**	**0.00**	**0.03**
Tank Test Blank	0.47	0.00	0.03	0.09	0.00	0.06	0.00	0.00
Tank Test Blank	0.69	0.00	0.09	0.11	0.05	0.05	0.00	0.00
Tank Test Blank	0.68	0.00	0.19	0.00	0.00	0.03	0.00	0.00
Tank Test Blank	0.50	0.00	0.09	0.00	0.11	0.17	0.00	0.00
Tank Test Blank	0.81	0.00	0.14	0.00	0.00	1.32	0.00	0.36
Tank Test Blank	0.72	0.00	0.08	0.00	0.00	0.01	0.00	0.00
Tank Test Blank	0.75	0.00	0.04	0.00	0.00	0.04	0.00	0.00

Table 6.41: Measured concentrations for selected cations in analysed replicates (mg/l)

Sample	Na	Ca	S	Si	Al	Fe	Zn	Cr
1	335.89	2.05	216.38	1.91	3.84	0.26	0.00	0.30
	333.71	2.10	216.91	1.93	3.88	0.13	0.00	0.33
	328.63	2.40	211.79	1.90	3.76	0.06	0.00	0.30
2	1.19	109.80	6.18	5.47	2.36	0.00	1.35	0.00
	1.20	109.92	6.12	5.43	2.31	0.44	1.30	0.18
	1.21	109.88	6.18	5.48	2.36	0.28	1.32	0.07
	1.26	109.87	6.21	6.19	2.40	0.33	1.34	0.03
	1.26	109.84	6.17	5.48	2.41	0.68	1.33	0.32
3	1.04	103.84	7.68	2.81	0.00	0.00	0.81	0.00
	1.08	103.73	7.89	2.93	0.02	0.02	0.84	0.01
	1.07	103.75	7.90	2.89	0.02	0.05	0.85	0.01
4	11.57	55.03	2.03	3.70	4.68	0.05	0.00	0.01
	11.56	57.07	1.96	3.72	4.91	5.48	0.00	1.84
	11.55	55.71	2.04	3.70	4.76	0.21	0.00	0.02
5	9.97	14.27	2.80	2.71	3.67	0.04	0.00	0.05
	9.83	14.22	2.87	2.72	3.63	0.05	0.00	0.02
	9.82	14.13	2.83	2.70	3.56	0.04	0.00	0.03
6	11.31	54.75	2.16	3.55	4.86	0.02	0.00	0.01
	11.33	54.98	2.19	3.54	4.89	0.01	0.00	0.00
	11.35	54.49	2.19	3.55	5.07	0.06	0.00	0.01
7	9.44	49.23	2.83	2.25	5.12	0.01	0.00	0.02
	9.30	48.17	2.84	2.29	5.40	0.00	0.00	0.03
	9.39	48.82	3.05	2.30	5.47	0.09	0.00	0.04
8	27.29	104.11	30.85	3.96	0.06	0.00	0.87	0.00
	27.27	104.06	30.90	3.94	0.05	0.00	0.87	0.00
	27.03	104.13	31.33	3.93	0.26	0.13	0.88	0.00
9	4.68	104.06	7.84	3.15	0.00	0.02	0.88	0.00
	1.21	104.10	7.69	2.78	0.03	0.00	0.82	0.00
	4.79	104.07	7.75	3.18	0.01	0.02	0.88	0.00
10	4.96	103.67	8.33	7.28	1.95	0.29	2.23	0.04
	5.02	103.75	8.19	7.27	1.92	0.27	2.19	0.03
	4.73	103.67	8.40	7.71	1.92	2.25	2.22	0.65
11	91.14	4.94	4.39	0.92	0.99	0.30	0.00	0.09
	90.89	4.68	4.44	0.89	0.99	0.19	0.00	0.08
	91.37	4.71	4.37	0.89	0.97	0.03	0.00	0.02
	90.00	4.80	4.31	0.91	1.00	0.07	0.00	0.02
12	86.27	4.81	5.26	0.99	0.84	0.05	0.00	0.03
	86.06	4.79	5.29	0.94	0.81	0.19	0.00	0.05
	86.79	4.91	5.33	0.99	0.85	0.44	0.00	0.12
13	5.23	102.72	5.24	1.00	0.00	0.32	0.00	0.16
	5.23	102.59	5.41	1.00	0.00	0.01	0.00	0.00
	6.14	107.95	3.97	0.96	0.00	0.05	0.00	0.00
14	194.20	13.54	29.37	5.49	7.46	0.18	0.00	0.15
	194.84	13.60	27.92	5.45	7.47	0.98	0.00	0.76
	193.90	13.55	28.81	5.46	7.77	0.10	0.00	0.14

Table 6.42: Standard deviations, variances and means for replicates of cation analyses

Sample		Na	Ca	S	Si	Al	Fe	Zn	Cr
1	SDV	3.73	0.19	2.81	0.02	0.06	0.10	0.00	0.01
	Variance	13.88	0.03	7.91	0.00	0.00	0.01	0.00	0.00
	Mean	332.74	2.18	215.02	1.91	3.82	0.15	0.00	0.31
2	SDV	0.03	0.05	0.03	0.32	0.04	0.25	0.02	0.13
	Variance	0.00	0.00	0.00	0.10	0.00	0.06	0.00	0.02
	Mean	1.22	109.86	6.17	5.61	2.37	0.35	1.33	0.12
3	SDV	0.02	0.06	0.12	0.06	0.01	0.02	0.02	0.00
	Variance	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
	Mean	1.06	103.77	7.82	2.88	0.01	0.02	0.83	0.00
4	SDV	0.01	1.04	0.04	0.01	0.12	3.09	0.00	1.05
	Variance	0.00	1.08	0.00	0.00	0.01	9.54	0.00	1.11
	Mean	11.56	55.93	2.01	3.71	4.78	1.91	0.00	0.62
5	SDV	0.08	0.07	0.03	0.01	0.05	0.00	0.00	0.01
	Variance	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mean	9.87	14.21	2.83	2.71	3.62	0.04	0.00	0.03
6	SDV	0.02	0.25	0.01	0.01	0.12	0.03	0.00	0.01
	Variance	0.00	0.06	0.00	0.00	0.01	0.00	0.00	0.00
	Mean	11.33	54.74	2.18	3.55	4.94	0.03	0.00	0.01
7	SDV	0.07	0.53	0.12	0.02	0.19	0.05	0.00	0.01
	Variance	0.01	0.29	0.02	0.00	0.04	0.00	0.00	0.00
	Mean	9.38	48.74	2.91	2.28	5.33	0.03	0.00	0.03
8	SDV	0.15	0.03	0.27	0.01	0.12	0.08	0.01	0.00
	Variance	0.02	0.00	0.07	0.00	0.01	0.01	0.00	0.00
	Mean	27.20	104.10	31.03	3.94	0.12	0.04	0.87	0.00
9	SDV	2.04	0.02	0.07	0.22	0.02	0.01	0.03	0.00
	Variance	4.15	0.00	0.01	0.05	0.00	0.00	0.00	0.00
	Mean	3.56	104.07	7.76	3.04	0.01	0.01	0.86	0.00
10	SDV	0.15	0.05	0.11	0.25	0.02	1.14	0.02	0.35
	Variance	0.02	0.00	0.01	0.06	0.00	1.29	0.00	0.12
	Mean	4.90	103.70	8.30	7.42	1.93	0.94	2.21	0.24
11	SDV	0.60	0.11	0.05	0.01	0.01	0.12	0.00	0.04
	Variance	0.36	0.01	0.00	0.00	0.00	0.01	0.00	0.00
	Mean	90.85	4.78	4.38	0.90	0.99	0.15	0.00	0.05
12	SDV	0.38	0.06	0.03	0.03	0.02	0.20	0.00	0.05
	Variance	0.14	0.00	0.00	0.00	0.00	0.04	0.00	0.00
	Mean	86.38	4.83	5.29	0.97	0.83	0.23	0.00	0.07
13	SDV	0.52	3.06	0.79	0.02	0.00	0.17	0.00	0.09
	Variance	0.28	9.35	0.62	0.00	0.00	0.03	0.00	0.01
	Mean	5.53	104.42	4.87	0.99	0.00	0.13	0.00	0.05
14	SDV	0.48	0.03	0.73	0.02	0.17	0.49	0.00	0.36
	Variance	0.23	0.00	0.53	0.00	0.03	0.24	0.00	0.13
	Mean	194.31	13.56	28.70	5.47	7.57	0.42	0.00	0.35

CHAPTER SEVEN

7.0 LEACHING ASSESSMENT AND MODELLING RESULTS

7.1 INTRODUCTION

Using results from pH dependent leaching of matrices, leaching assessments and geochemical speciation modelling for solubility controlling mineral phases were undertaken. Releases for the Master Species were evaluated (See Chapter 5 Section 5.4.6 for selection rational), showing comparisons between measured releases and predicted trends. However, this required the use of large numbers of figures to show comparisons required for validation of the specific elements solubility controlling phase predictions. These were required to draw out information on trends and speciation, used for the discussion presented in Chapter 8. However, to limit the number of figures presented, results for all master species were only shown for stabilised matrices without additives, due to observed similarities in trends and phases for calcium and sulphate. The presented leaching and speciation evaluations show:

- Baseline assessment for releases of master species from unstabilised kaolin
- Measured releases, predictions and speciation results for stabilised matrices, separated for presentation based on presence and type of additives, and subdivided based on contaminant inclusions.
- Trend comparisons for pH and time dependent releases from the different stabilised matrices, with increasing durations of hydration
- And, a consistency evaluation for time dependent releases, to validate obtained information on measured cumulative trends and measures.

Primarily, results presented in this chapter are from pH dependent leaching information, for releases under equilibrium leaching conditions, to determine speciation.

7.2 ASSESSMENTS FOR UNSTABILISED KAOLIN CLAY

Before introducing contaminants / additives, it was important to undertake assessments for releases and speciation of master species and contaminants of interest for the unstabilised kaolin clay. Figure 7.1 shows the measured releases and trends for these components, due to the influence of pH, from the unstabilised kaolin clay. Where no releases were observed in eluates, the detection limit of the analytical instrument for the element (presented in Section 7.6.1) was used as the lower limit instead of zero. Speciation modelling was then undertaken using ORCHESTRA embedded in LeachXS, using pH dependent releases and other modelling parameters (See Chapter 5 Section 5.4.2). Modelling parameters used for matrices are shown in Table 7.1, and discussed in Chapter 8 Section 8.6 during evaluations for components speciation in the matrices.

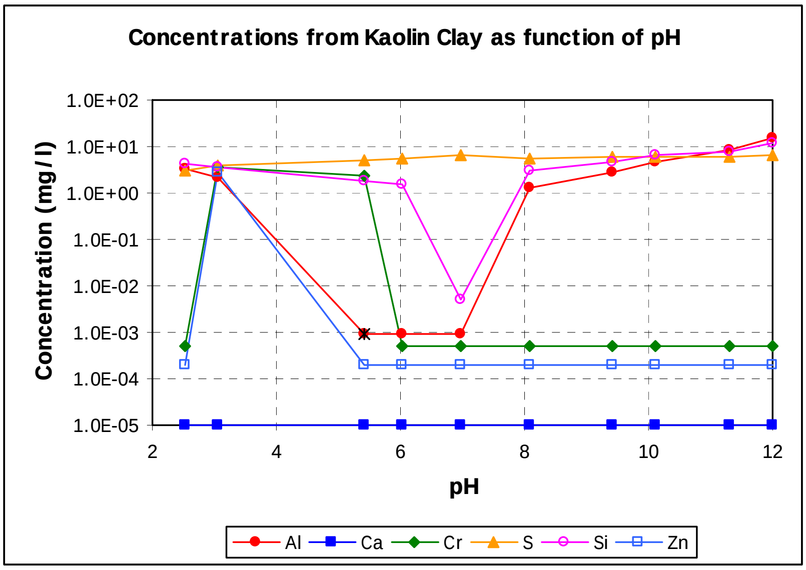


Figure 7:1: Releases for selected components from kaolin clay due to influence of pH

Table 7.1: Modelling parameters used for geochemical speciation modelling via ORCHESTRA

Model Parameters	Clay Content (kg/kg)			SHA (g/kg)	HFO (g/kg)
	28 days	150 days	300 days		
Kaolin clay	0.7			0.010	0.128
No Additive Matrices	0.60	0.40	0.30	0.010	2.120
Humic Acid Matrices	0.65	0.45	0.35	10.010	0.592
Sulphate Matrices	0.60	0.40	0.30	0.010	2.450

The variable clay contents in Table 7.1 for the different hydrations durations were based on assumptions of kaolin degradation in stabilised matrices with increasing hydration duration. Leaching results (Figure 7.1) show no available calcium releases from kaolin, and thus no speciation evaluation could be undertaken. Figure 7.2 shows speciation modelling prediction (broken line) and measured releases (joined dots) for aluminium from kaolin. Figure 7.3 shows the predicted solubility controlling mineral phases for aluminium, for partitioning between the solid and liquid phases.

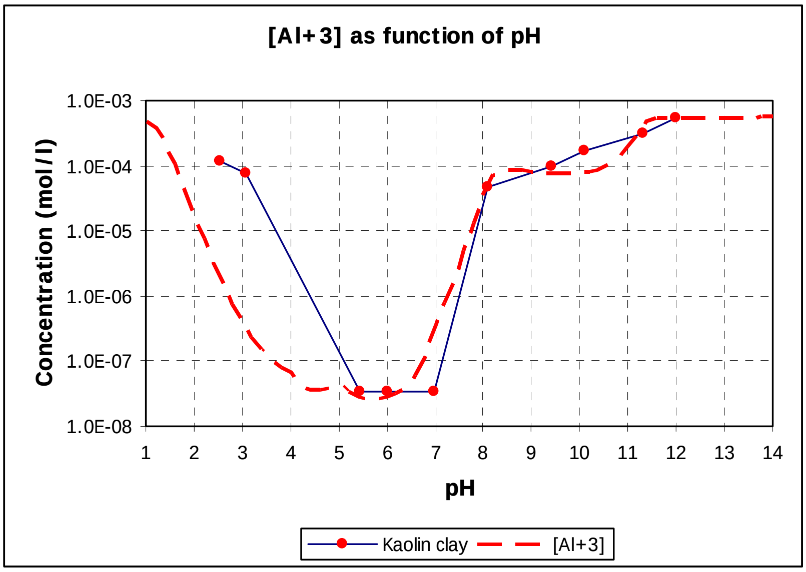


Figure 7:2: Aluminium predicted and measured release trend from kaolin clay

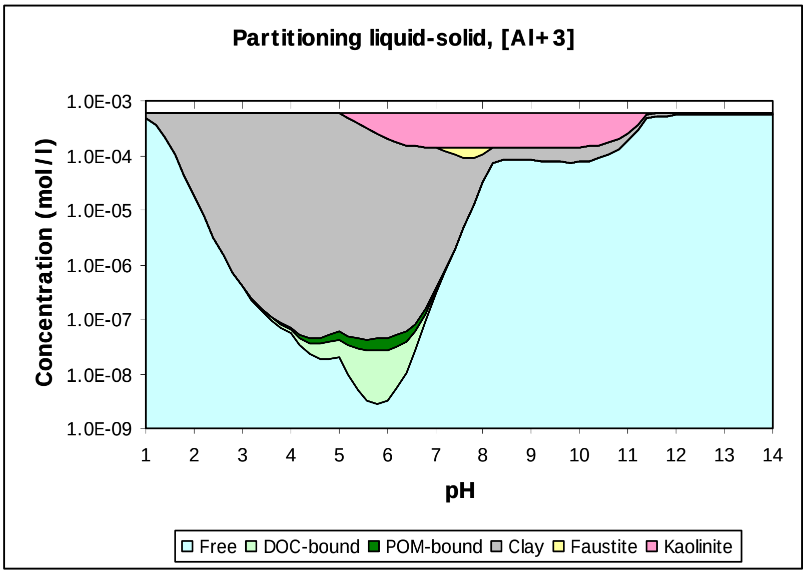


Figure 7:3: Solubility controlling mineral phases for aluminium leaching from kaolin clay

Results for silicon are shown in Figure 7.4, and the solubility controlling phases (as ortho-silicic acid - H_4SiO_4) from kaolin clay shown in Figure 7.5. Predictions for sulphate speciation indicated a total availability as free ion, with minimal release variation with pH (Figure 7.1), and thus were not presented. The mineral phase 'clay' represents generalised reactive clay minerals, not specified in the resultants database, which control solubility.

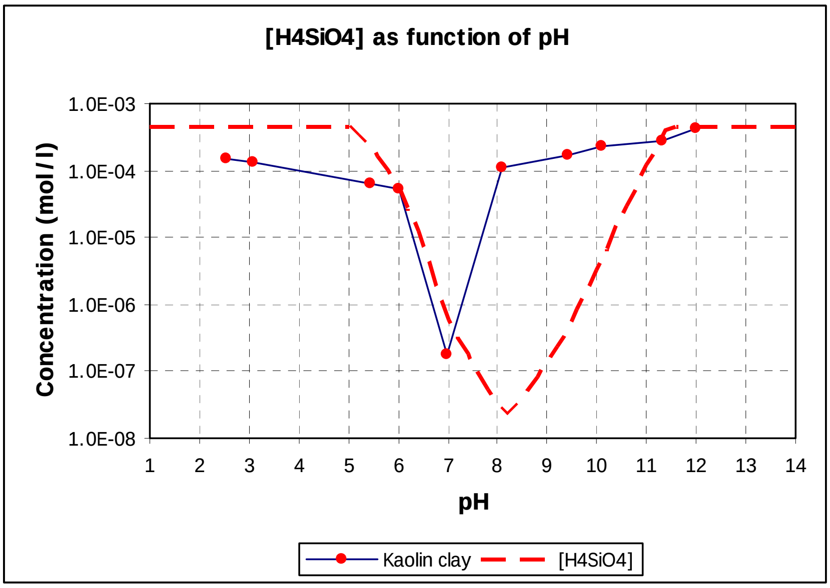


Figure 7:4: Silicon predicted and measured release trend from kaolin clay

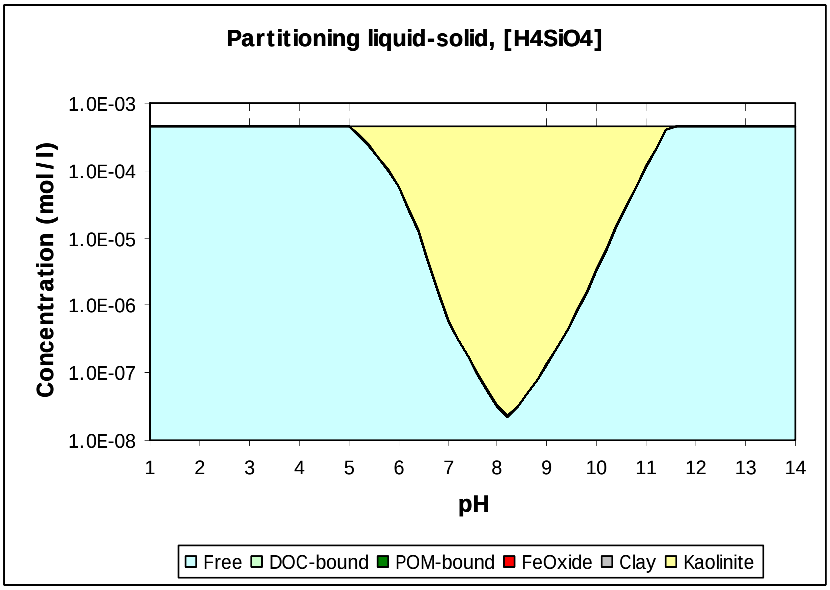


Figure 7:5: Solubility controlling mineral phases for silicic acid leaching from kaolin clay

Zinc measured and predicted releases are shown in Figure 7.6, with the solubility controlling phases shown in Figure 7.7. Corresponding results for chromium are shown in Figures 7.8 and 7.9 respectively. However, chromate ($CrO4^{2-}$) was used to evaluate chromium speciation due to imposed constraints by the modelling tool. Since qualitative comparisons were required, only relevant Cr^{3+} solubility controlling mineral phases were selected during speciation selections (See Chapter 5 Section 5.4.6).

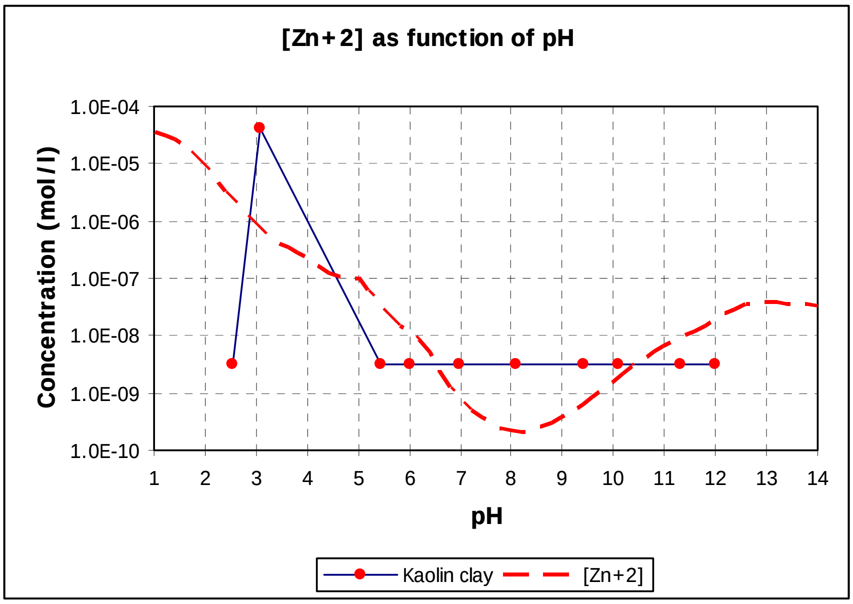


Figure 7:6: Zinc predicted and measured release trend from kaolin clay

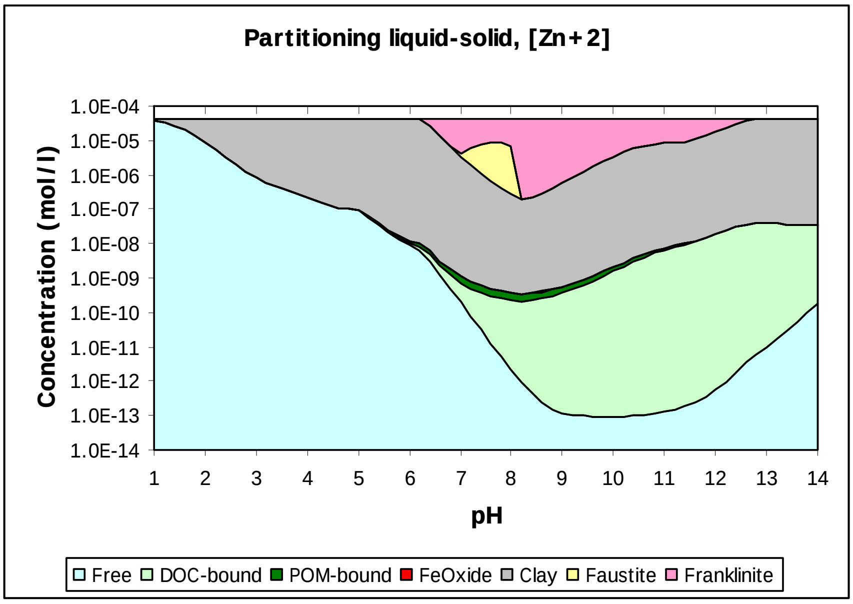


Figure 7:7: Solubility controlling mineral phases for zinc leaching from kaolin clay

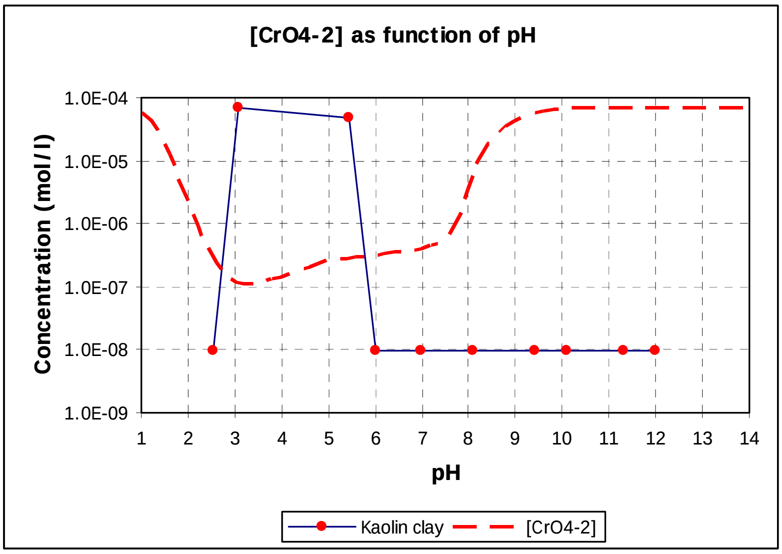


Figure 7:8: Chromate predicted and measured release trend from kaolin clay

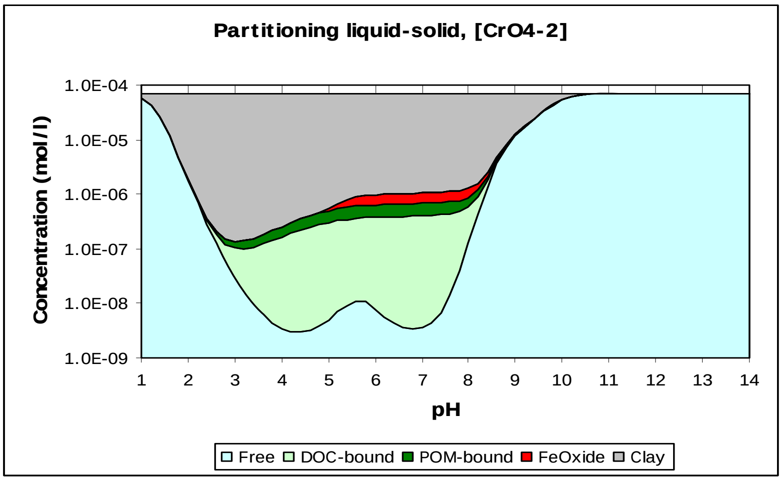


Figure 7:9: Solubility controlling mineral phases for chromate leaching from kaolin clay

7.3 ASSESSMENTS FOR STABILISED KAOLIN CLAY

This section presents results for stabilised matrices without additives, subdivided for presence and type of introduced contaminants, at the different hydration periods. The modelling parameters used for matrices with additives are shown in Table 7.1.

7.3.1 Uncontaminated Stabilised Kaolin Clay

Results for stabilised kaolin clay (EO) at different hydration periods are presented. Figures 7.10, 7.11 and 7.12 show measured releases for selected components at 28, 150 and 300 days hydration respectively. Release and speciation predictions were subsequently undertaken and presented for the different hydration periods. Even though presented results are for uncontaminated samples, trace concentrations of zinc and chromium were present in the matrix (See Chapter 6, Section 6.1.3). However, no chromium releases were observed at 28 days, and no zinc releases observed at 300 days hydration (Figures 7.10 and 7.12). Results for these contaminants at those hydration durations are not presented.

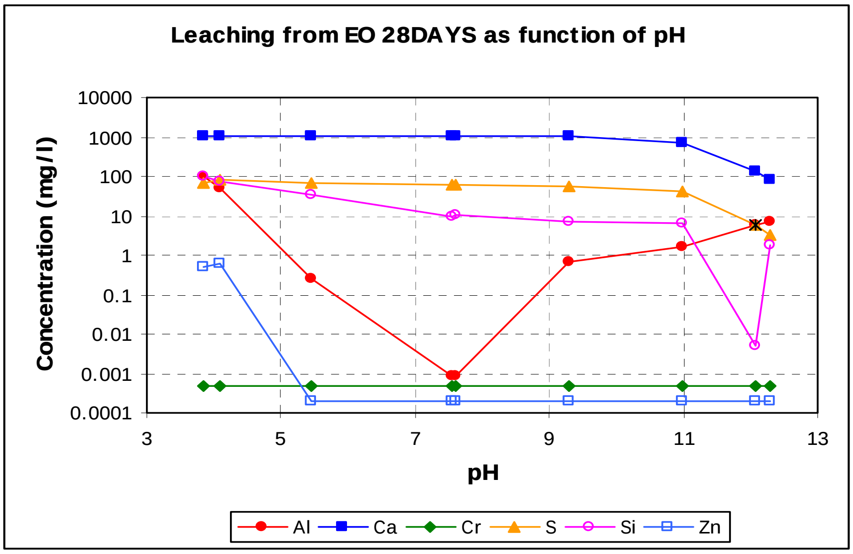


Figure 7:10: Releases of selected components from stabilised clay due to pH influence at 28 days

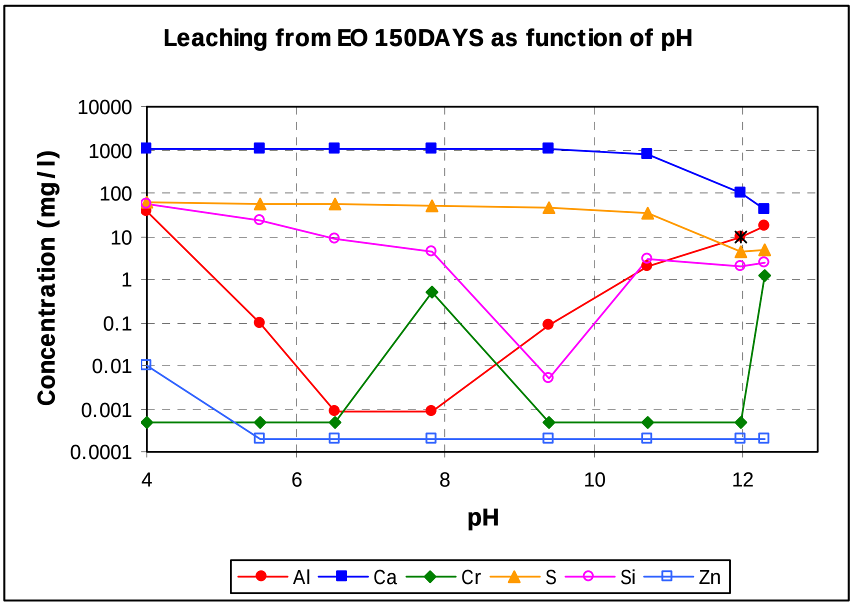


Figure 7:11: Release of selected components from stabilised clay due to pH influence at 150 days

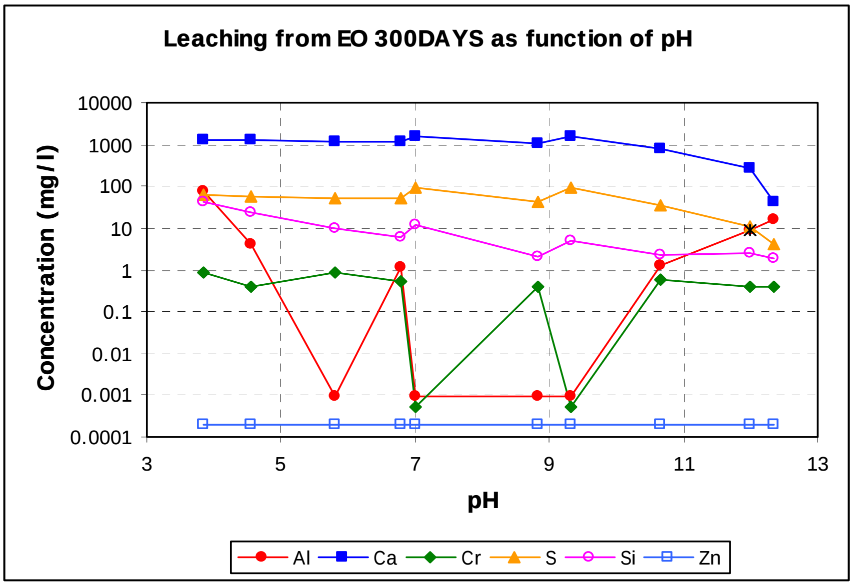


Figure 7:12: Release of selected components from stabilised clay due to pH influence at 300 days

While the clay contents of matrices were not measured with increasing hydration, induced alkalinity will increase kaolin dissociation with increasing hydration. These were considered for modelling parameters, with clay contents decreasing with hydration (Table 7.1). Figures 7.13 and 7.14 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively, at 28 days of sample hydration. Respective results for silicon releases are shown in Figures 7.15 and 7.16, and those for calcium releases shown in Figures 7.17 and 7.18.

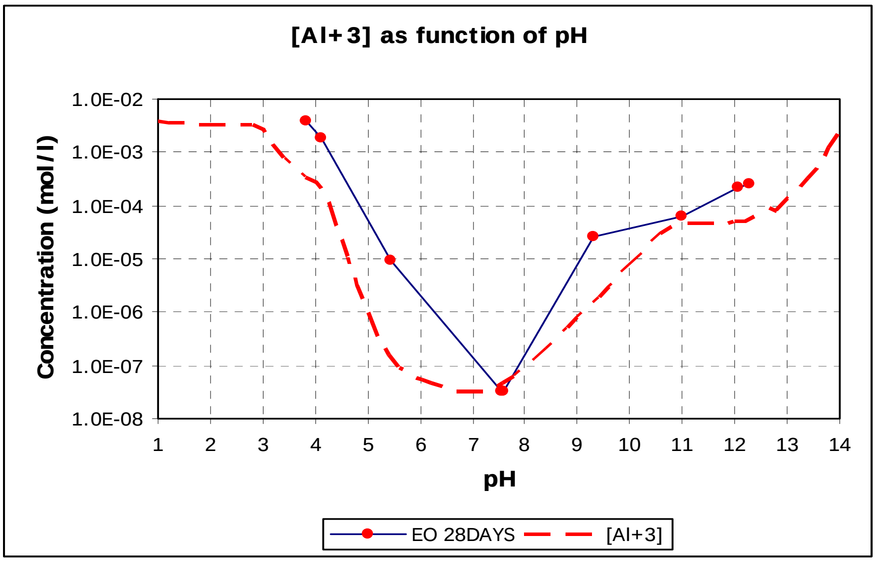


Figure 7:13: Aluminium predicted and measured release trend from stabilised clay at 28 days

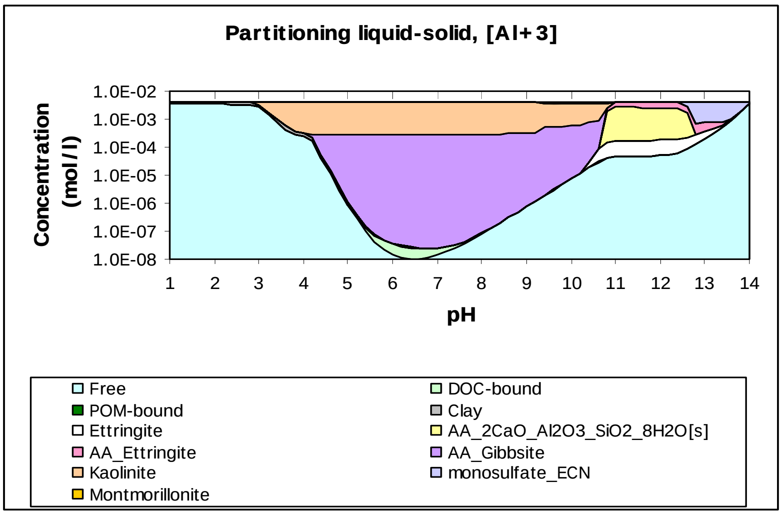


Figure 7:14: Solubility controlling mineral phases for aluminium leaching from stabilised clay at 28 days

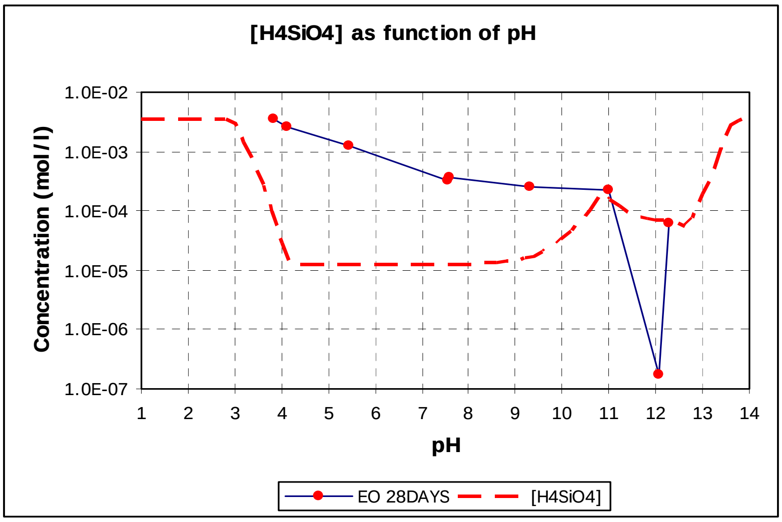


Figure 7:15: Silicic acid predicted and measured release trend from stabilised clay at 28 days

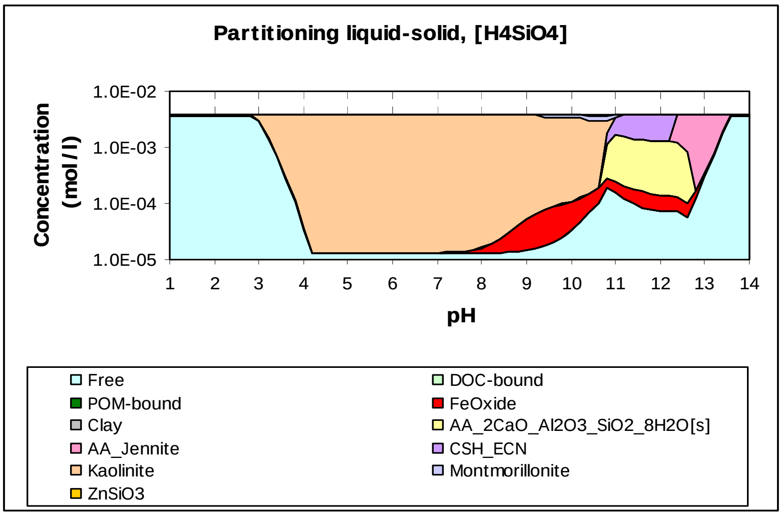


Figure 7:16: Solubility controlling mineral phases for silicic acid leaching from stabilised clay at 28 days

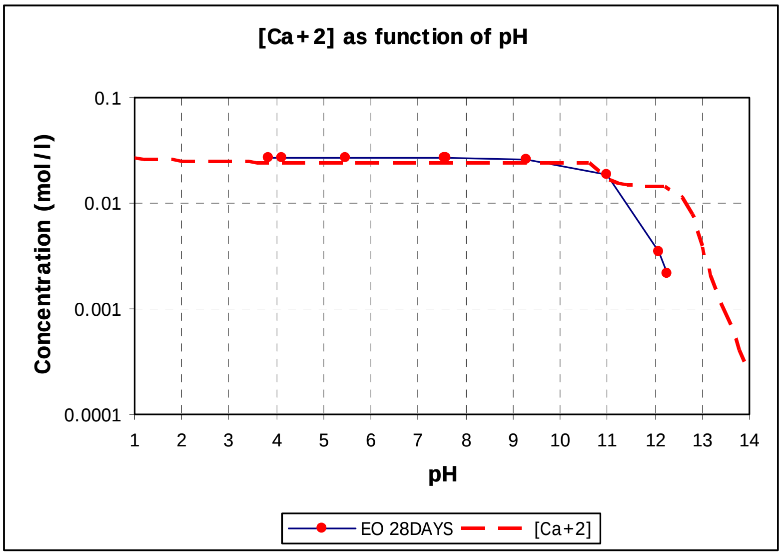


Figure 7:17: Calcium predicted and measured release trend from stabilised clay at 28 days

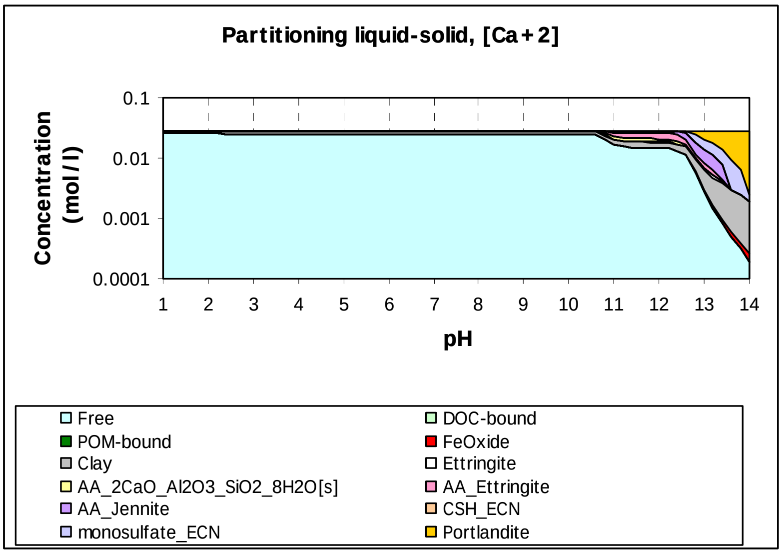


Figure 7:18: Solubility controlling mineral phases for calcium leaching from stabilised clay at 28 days

Figures 7.19 and 7.20 show measured and predicted sulphate releases, and the solubility controlling mineral phases respectively, at 28 days hydration. Respective results for zinc are shown in Figures 7.21 and 7.22. No chromium results are presented, since no releases were observed at 28 days hydration (Figure 7.10).

For leaching at 150 days hydration, Figures 7.23 and 7.24 show the measured and predicted aluminium releases, and the solubility controlling mineral phases respectively, at 150 days hydration. Respective results for silicon (as silicic acid) are shown in Figures 7.25 and 7.26 from the uncontaminated stabilised kaolin clay without additives.

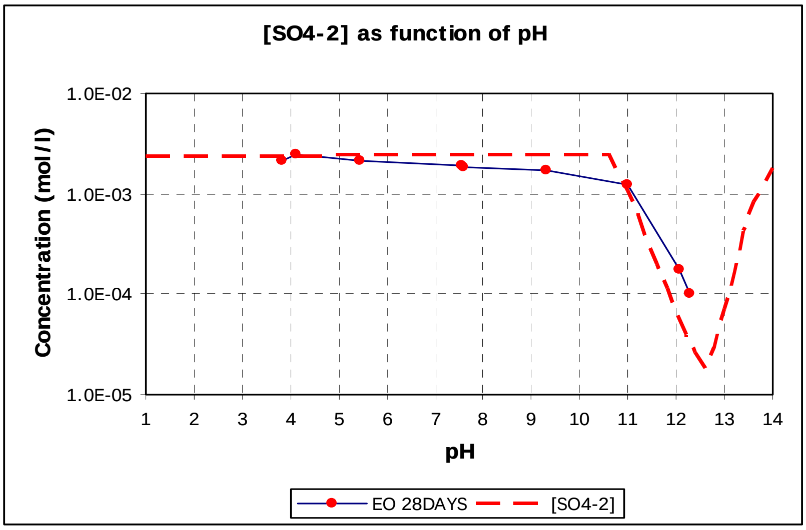


Figure 7:19: Sulphate predicted and measured release trend from stabilised clay at 28 days

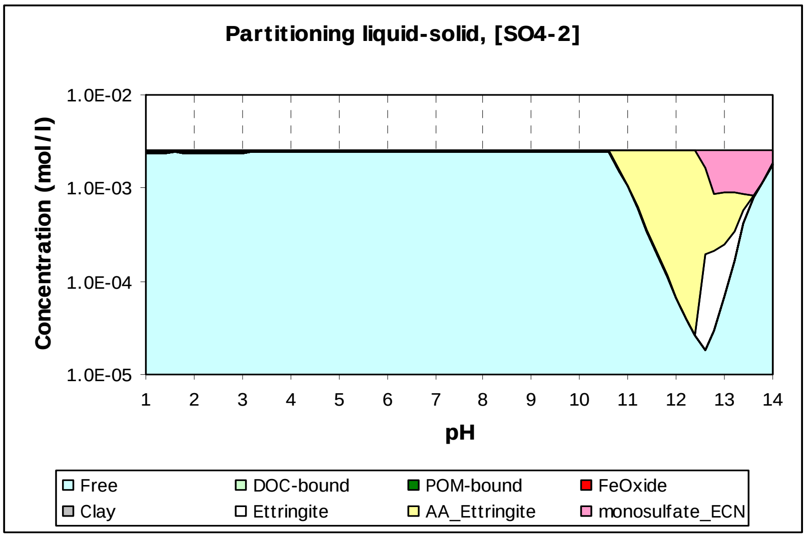


Figure 7:20: Solubility controlling mineral phases for sulphate leaching from stabilised clay at 28 days

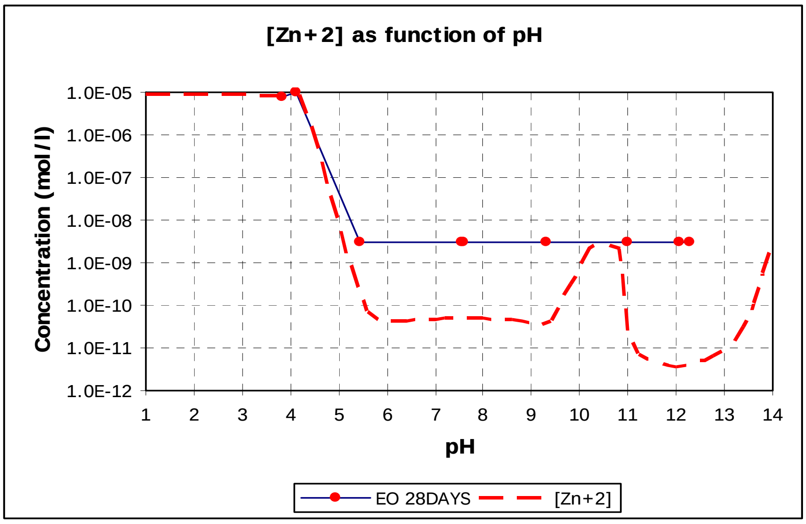


Figure 7:21: Zinc predicted and measured release trend from stabilised clay at 28 days

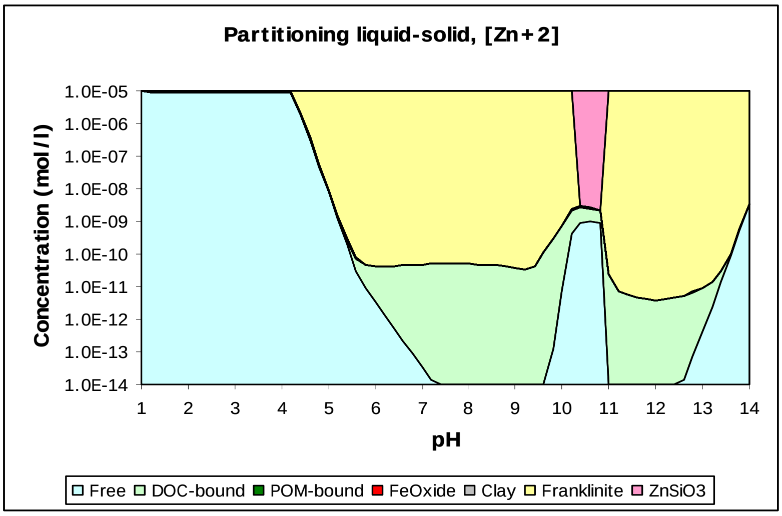


Figure 7:22: Solubility controlling mineral phases for zinc leaching from stabilised clay at 28 days

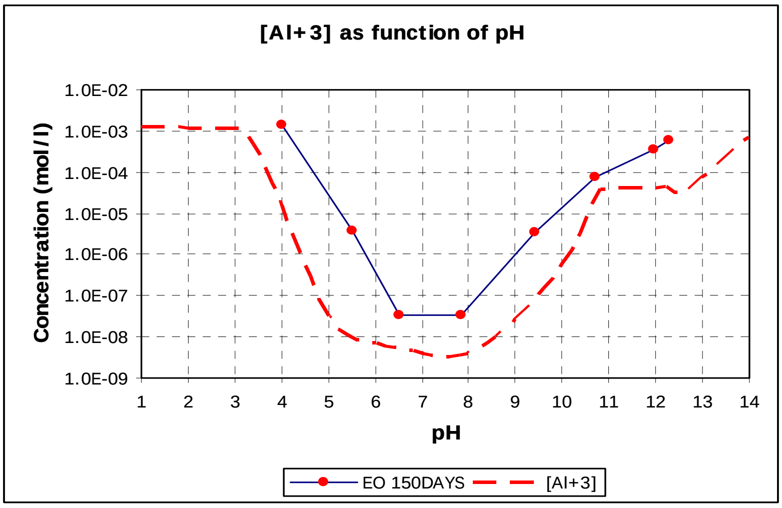


Figure 7:23: Aluminium predicted and measured release trend from stabilised clay at 150 days

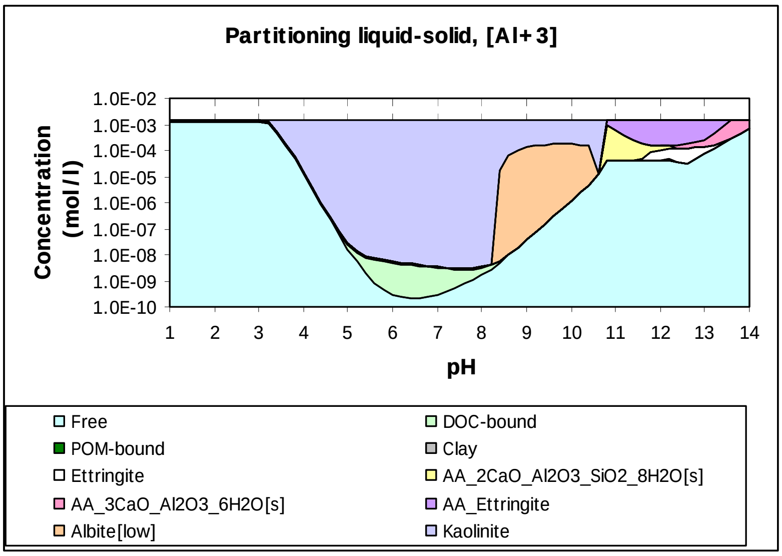


Figure 7:24: Solubility controlling mineral phases for aluminium leaching from stabilised clay at 150 days

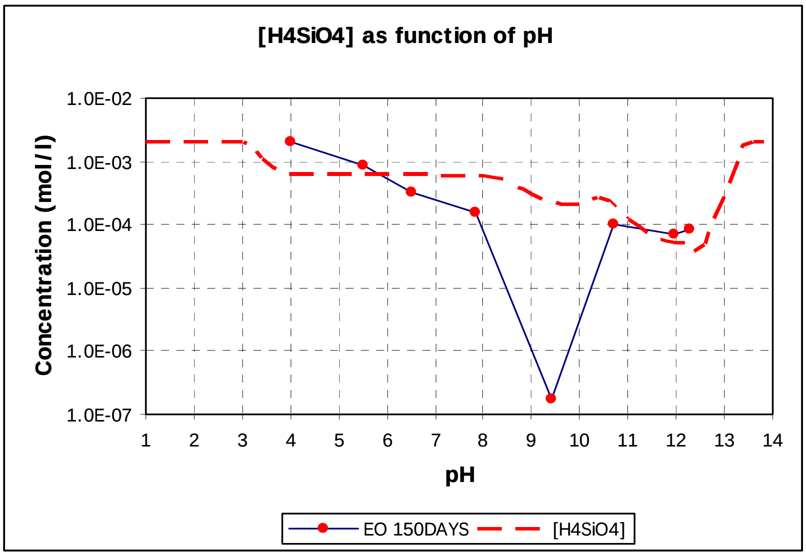


Figure 7:25: Silicic acid predicted and measured release trend from stabilised clay at 150 days

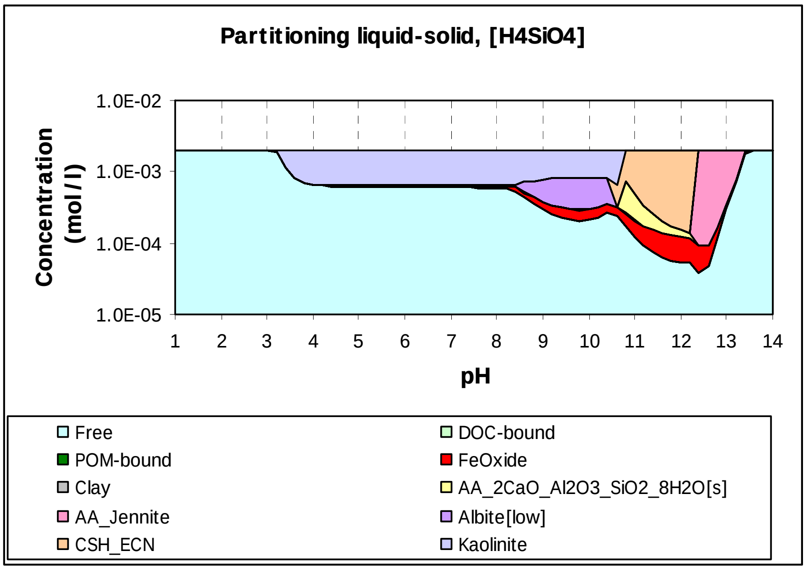


Figure 7:26: Solubility controlling mineral phases for silicic acid leaching from stabilised clay at 150 days

Figures 7.27 and 7.28 show the measured and predicted releases for calcium, and the solubility controlling mineral phases respectively, at 150 days hydration. Respectively results for chromium releases are shown in Figures 7.29 and 7.30, those for zinc releases shown in Figures 7.31 and 7.32, and those for sulphate releases shown in Figures 7.33 and 7.34. These results are for releases from the stabilised uncontaminated kaolin matrix with additives, leached after 150 days of hydration.

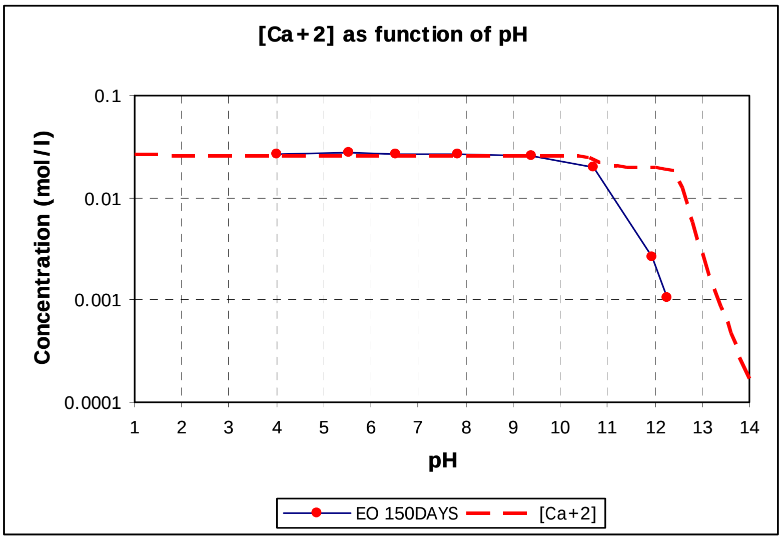


Figure 7:27: Calcium predicted and measured release trend from stabilised clay at 150 days

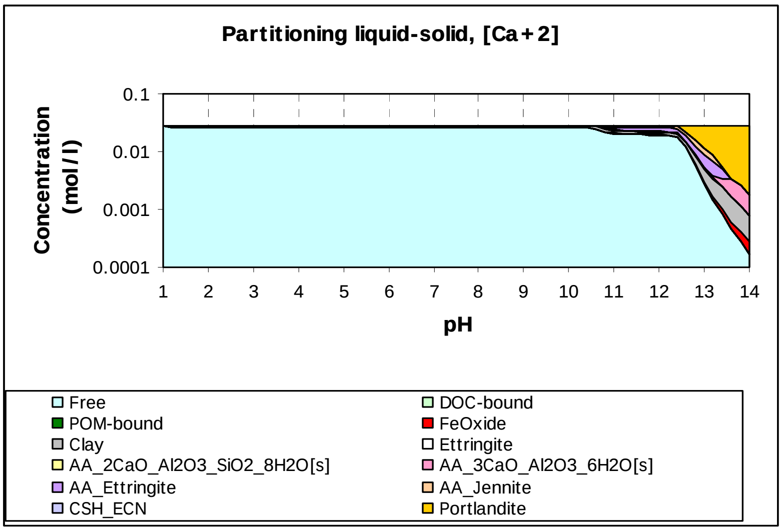


Figure 7:28: Solubility controlling mineral phases for calcium leaching from stabilised clay at 150 days

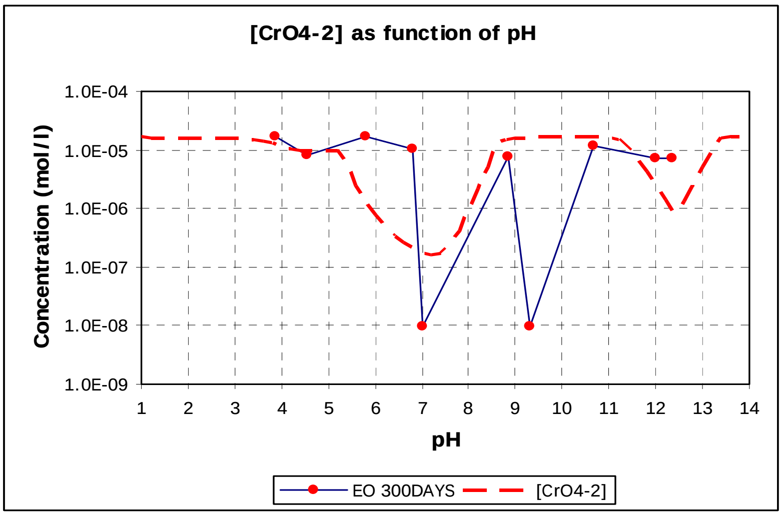


Figure 7:29: Chromate predicted and measured release trend from stabilised clay at 150 days

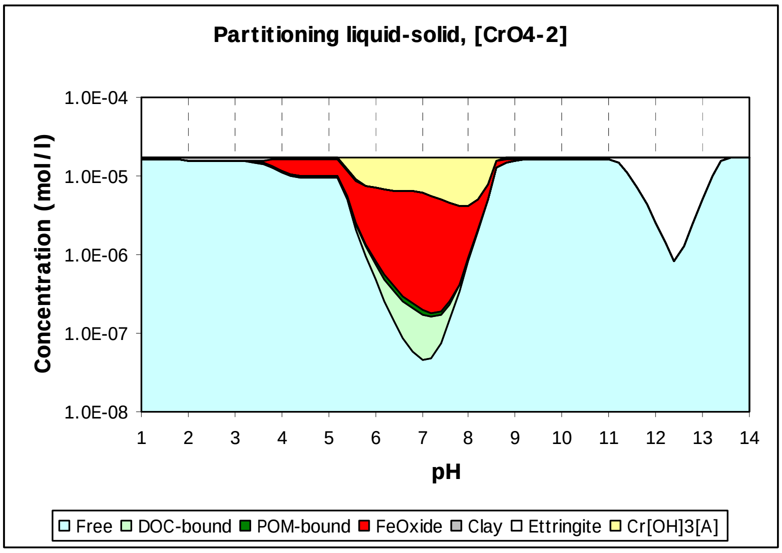


Figure 7:30: Solubility controlling mineral phases for chromate leaching from stabilised clay at 150 days

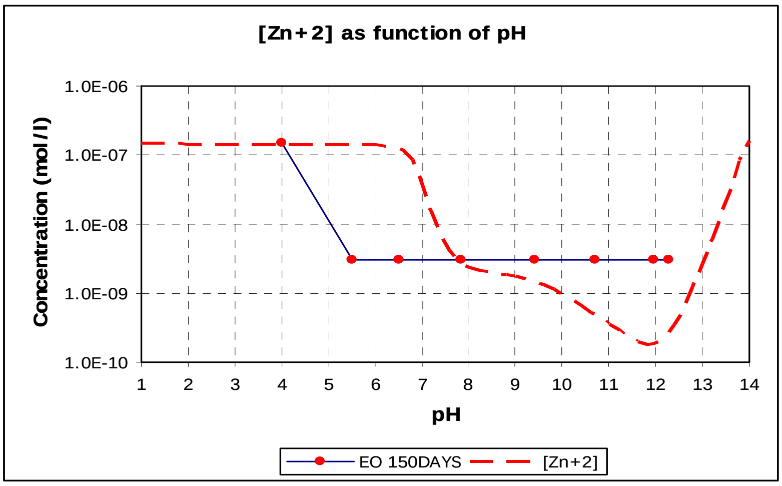


Figure 7:31: Zinc predicted and measured release trend from stabilised clay at 150 days

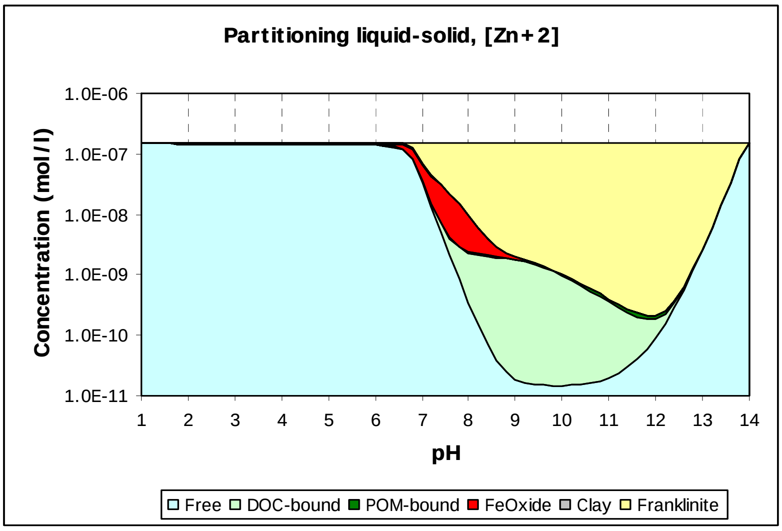


Figure 7:32: Solubility controlling mineral phases for zinc leaching from stabilised clay at 150 days

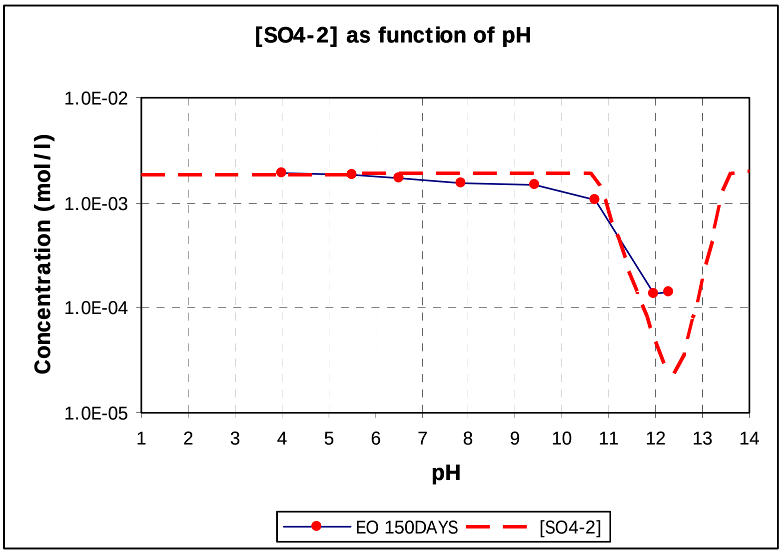


Figure 7:33: Sulphate predicted and measured release trend from stabilised clay at 150 days

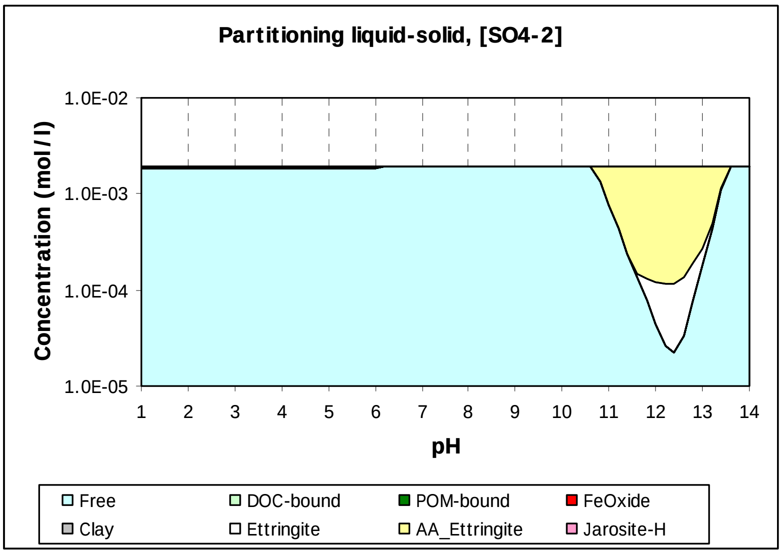


Figure 7:34: Solubility controlling mineral phases for sulphate leaching from stabilised clay at 150 days

For leaching at 300 days of hydration, Figures 7.35 and 7.36 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.37 and 7.38, calcium releases shown in Figures 7.39 and 7.40, and sulphate releases shown in Figures 7.41 and 7.42. No zinc releases were observed at 300 days hydration, and thus results are not presented for this period. The measured and predicted releases for chromium are shown in Figure 7.43, and the solubility controlling mineral phases shown in Figure 7.44, at 300 days of hydration.

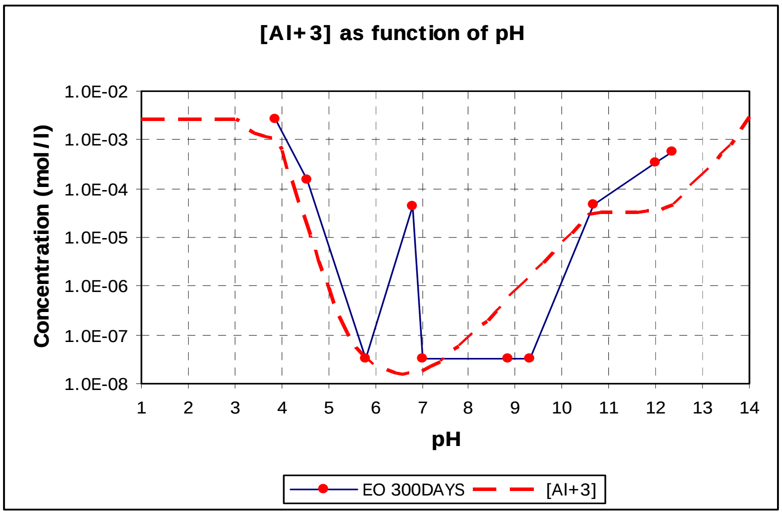


Figure 7:35: Aluminium predicted and measured release trend from stabilised clay at 300 days

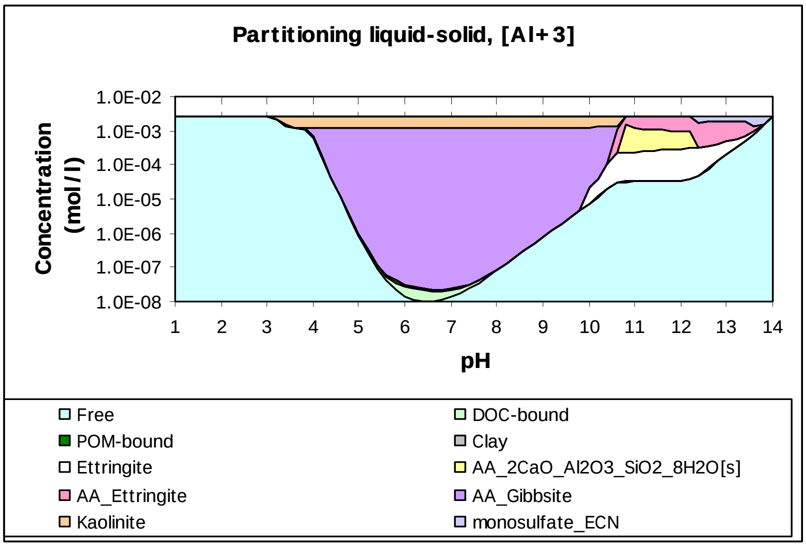


Figure 7:36: Solubility controlling mineral phases for aluminium leaching from stabilised clay at 300 days

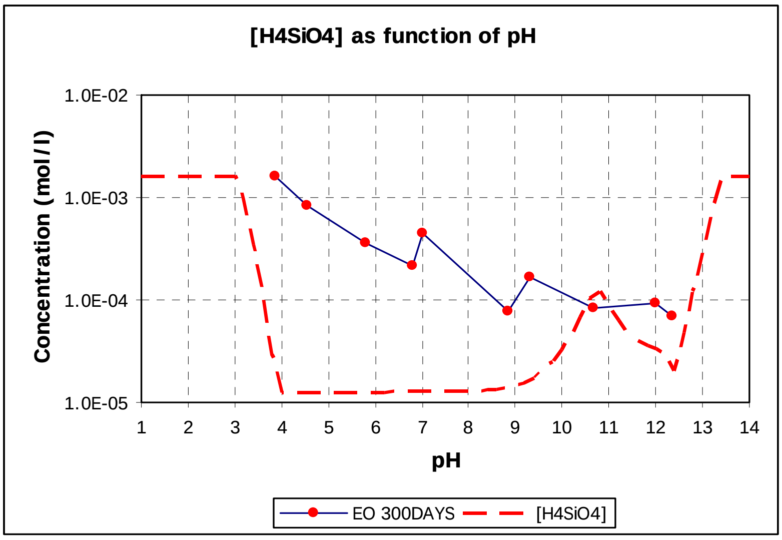


Figure 7:37: Silicic acid predicted and measured release trend from stabilised clay at 300 days

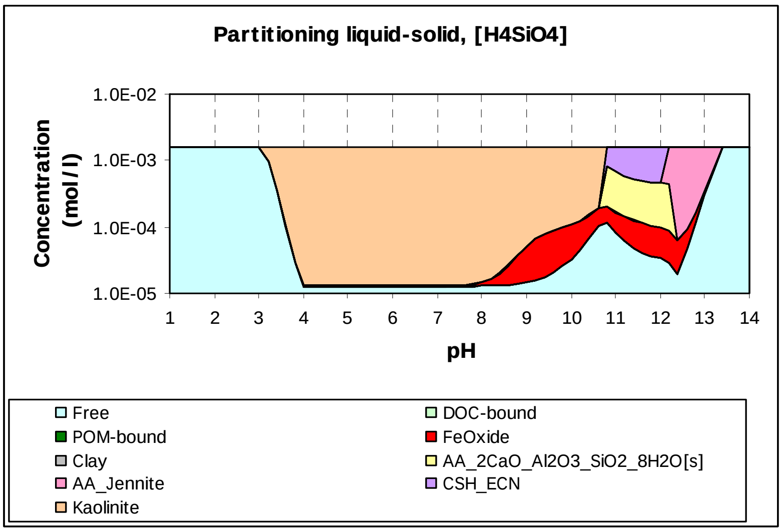


Figure 7:38: Solubility controlling mineral phases for silicic acid leaching from stabilised clay at 300 days

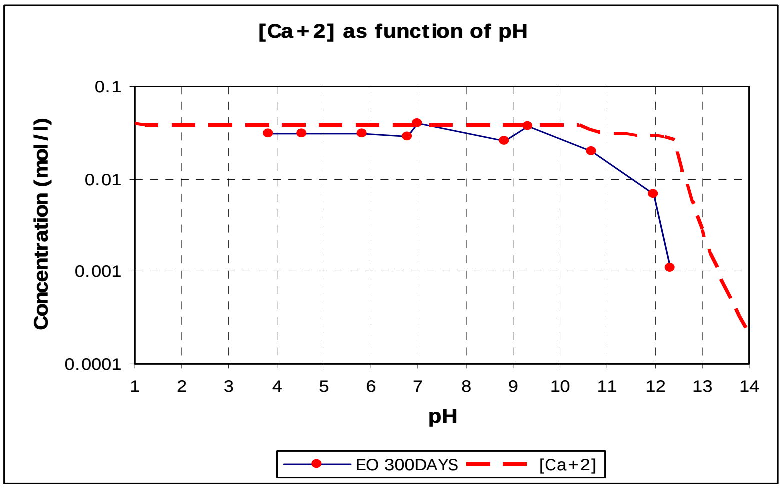


Figure 7:39: Calcium predicted and measured release trend from stabilised clay at 300 days

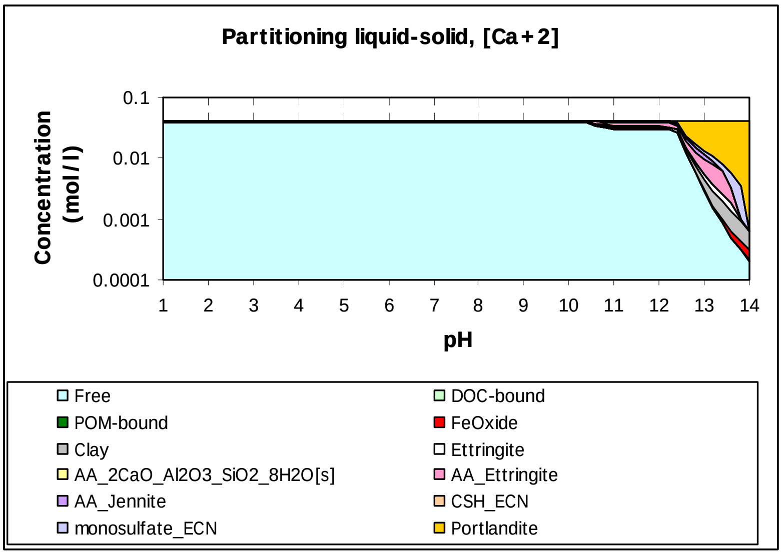


Figure 7:40: Solubility controlling mineral phases for calcium leaching from stabilised clay at 300 days

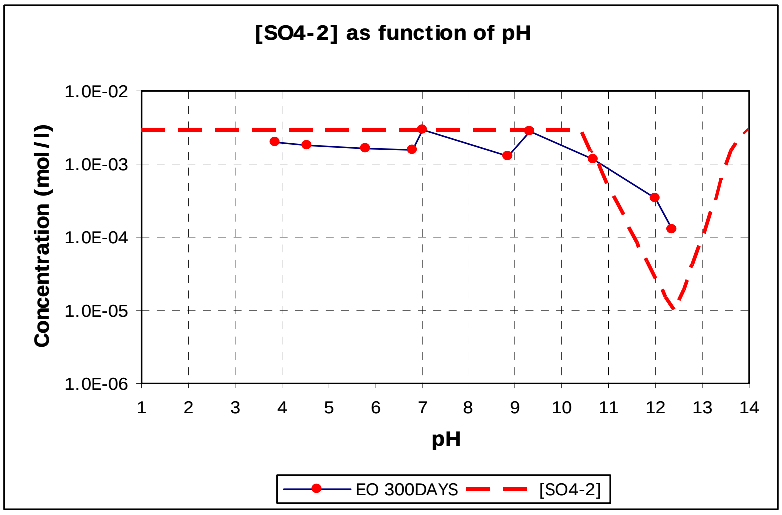


Figure 7:41: Sulphate predicted and measured release trend from stabilised clay at 300 days

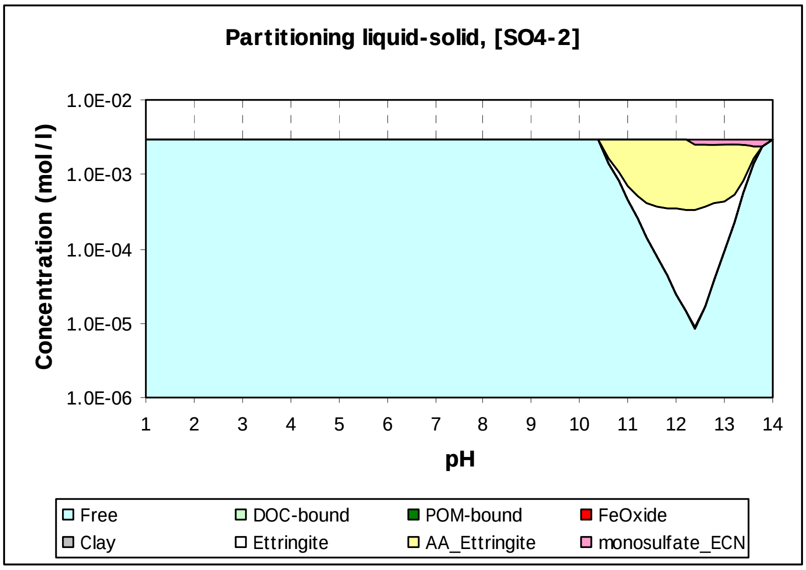


Figure 7:42: Solubility controlling mineral phases for sulphate leaching from stabilised clay at 300 days

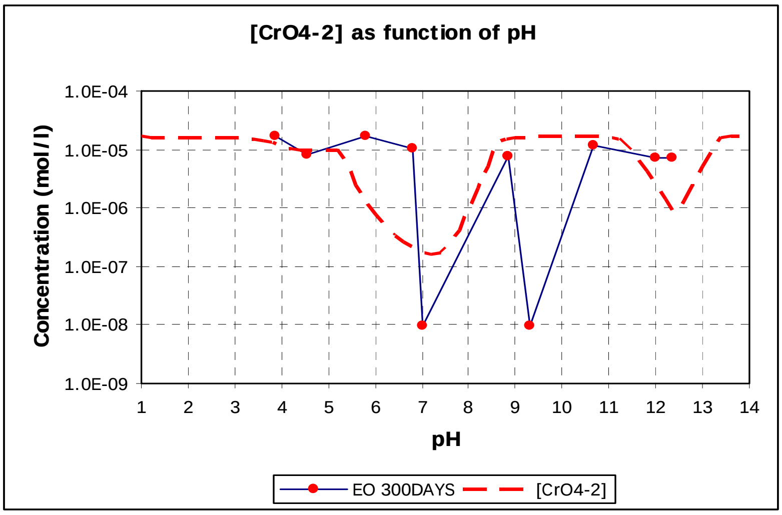


Figure 7:43: Chromate predicted and measured release trend from stabilised clay at 300 days

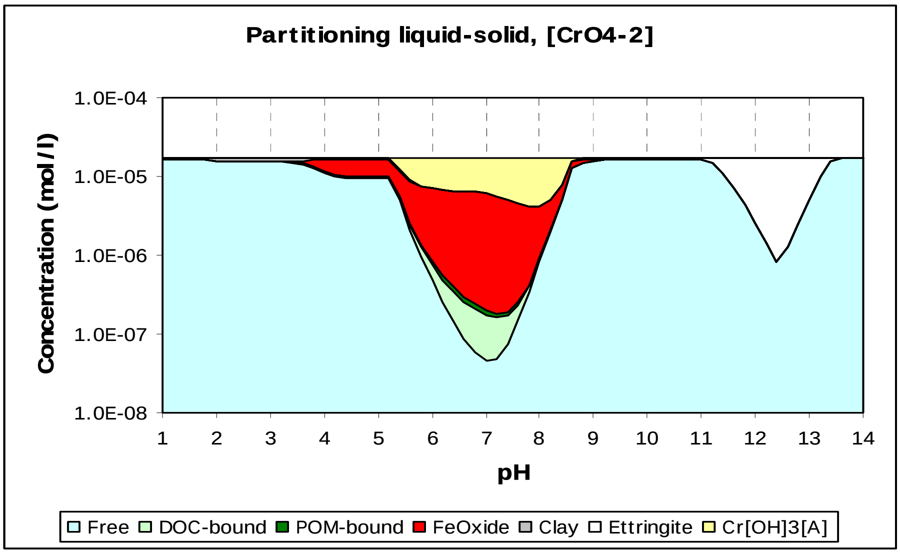


Figure 7:44: Solubility controlling mineral phases for chromate leaching from stabilised clay at 300 days

7.3.2 Stabilised Zinc Contaminated Kaolin Clay

To assess zinc partitioning and containment, leaching assessments and speciation evaluations were undertaken on zinc contaminated cement stabilised kaolin clay. Figures 7.45, 7.46 and 7.47 show the selected components leachability under pH influence, at 28, 150 and 300 days hydration respectively. Speciation evaluations were then undertaken to predict these components releases, and their solubility controlling mineral phases.

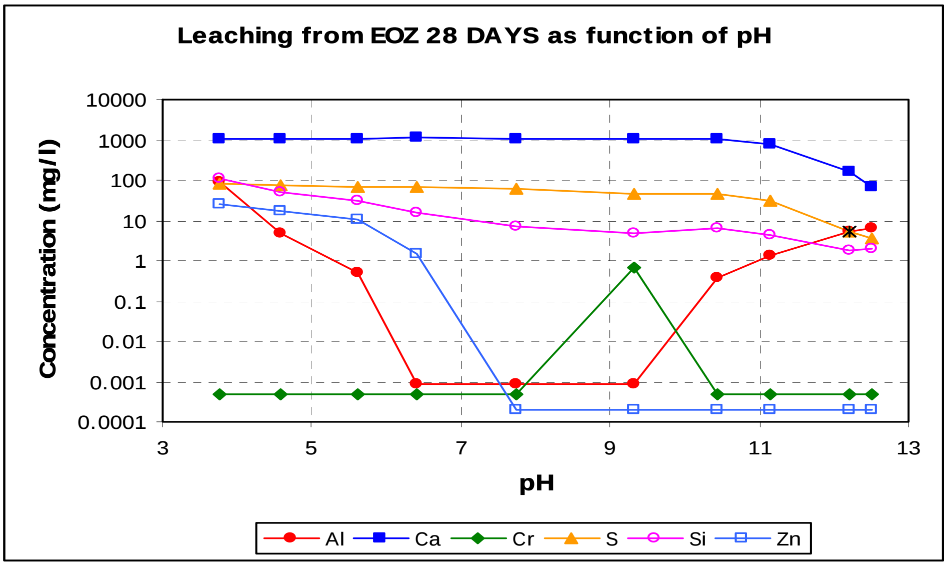


Figure 7:45: Releases of selected components from stabilised zinc contaminated clay due to pH influence at 28 days

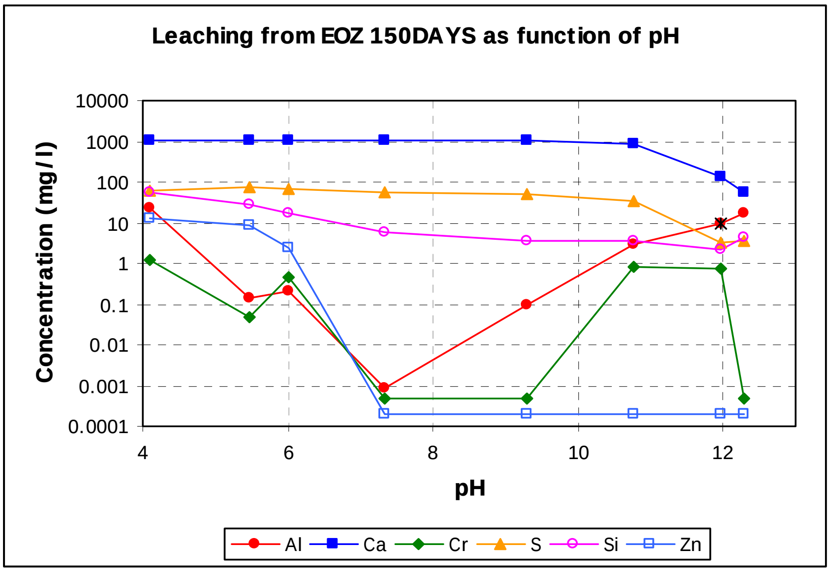


Figure 7:46: Releases of selected components from stabilised zinc contaminated clay due to pH influence at 150 days

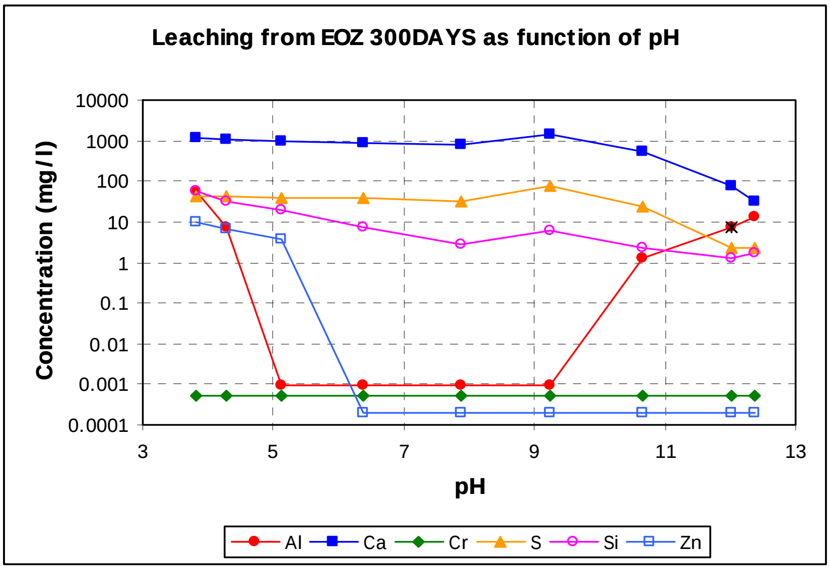


Figure 7:47: Releases of selected components from stabilised zinc contaminated clay due to pH influence at 300 days

Figures 7.48 and 7.49 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively, at 28 days hydration. Respective results for silicon releases are shown in Figures 7.50 and 7.51, those for calcium releases shown in Figures 7.52 and 7.53, and those for sulphate releases shown in Figures 7.54 and 7.55. Chromium release at 28 days hydration (Figure 7.45) appeared anomalous, and thus no results were presented. The measured and predicted releases for zinc are shown in Figure 7.56, and the solubility controlling mineral phases shown in Figure 7.57.

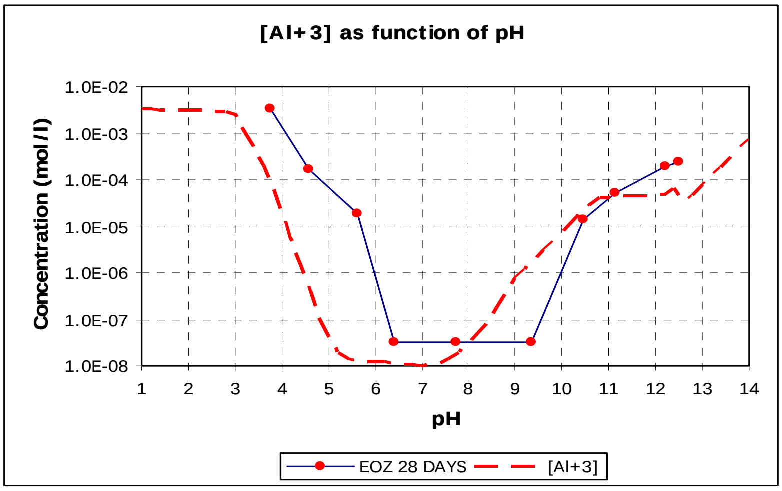


Figure 7:48: Aluminium predicted and measured release trend from stabilised zinc contaminated clay at 28 days

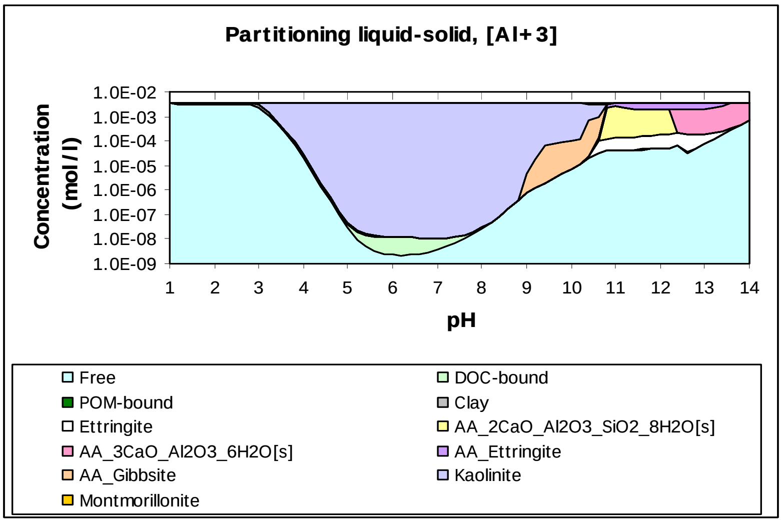


Figure 7:49: Solubility controlling mineral phases for aluminium leaching from stabilised zinc contaminated clay at 28 days

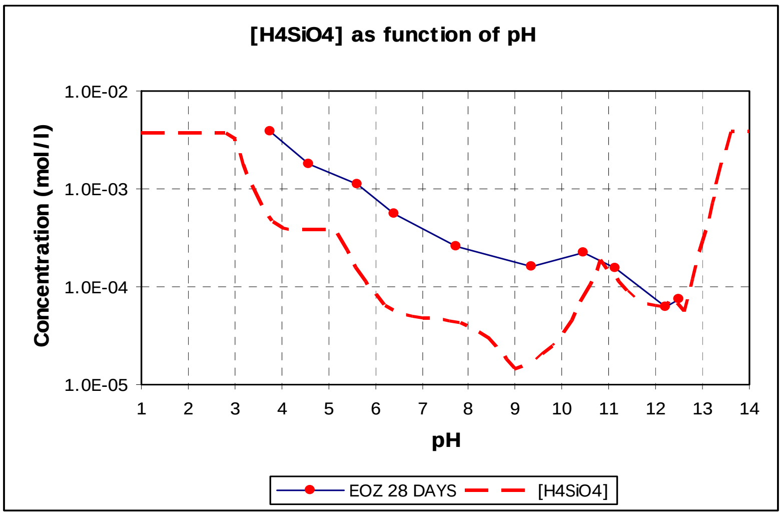


Figure 7:50: Silicic acid predicted and measured release trend from stabilised zinc contaminated clay at 28 days

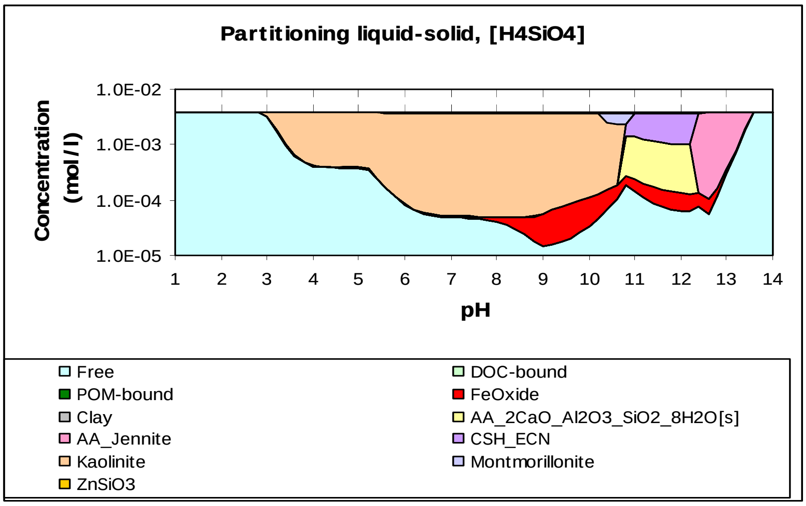


Figure 7:51: Solubility controlling mineral phases for silicic acid leaching from stabilised zinc contaminated clay at 28 days

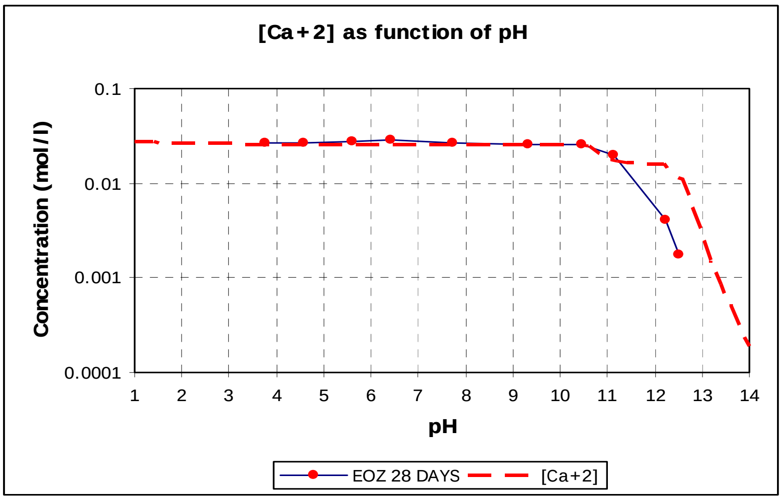


Figure 7:52: Calcium predicted and measured release trend from stabilised zinc contaminated clay at 28 days

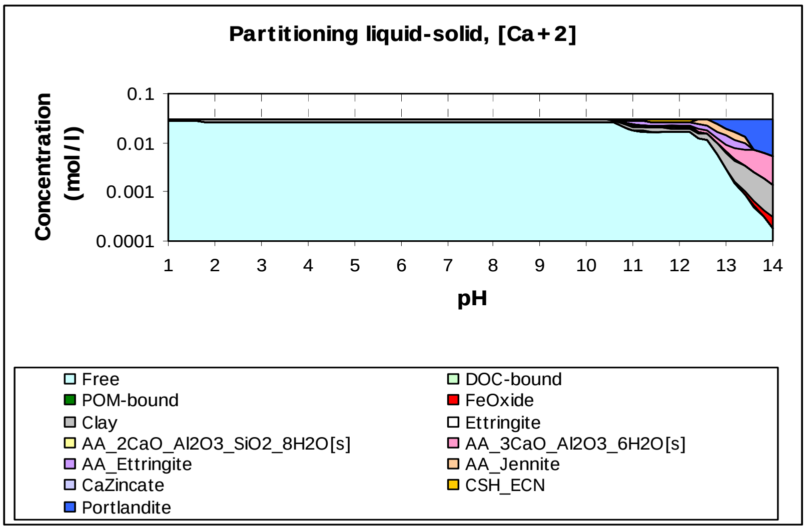


Figure 7:53: Solubility controlling mineral phases for calcium leaching from stabilised zinc contaminated clay at 28 days

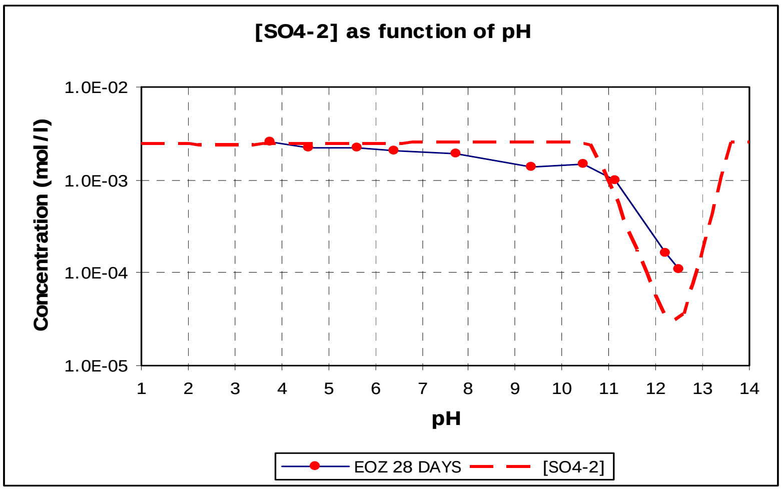


Figure 7:54: Sulphate predicted and measured release trend from stabilised zinc contaminated clay at 28 days

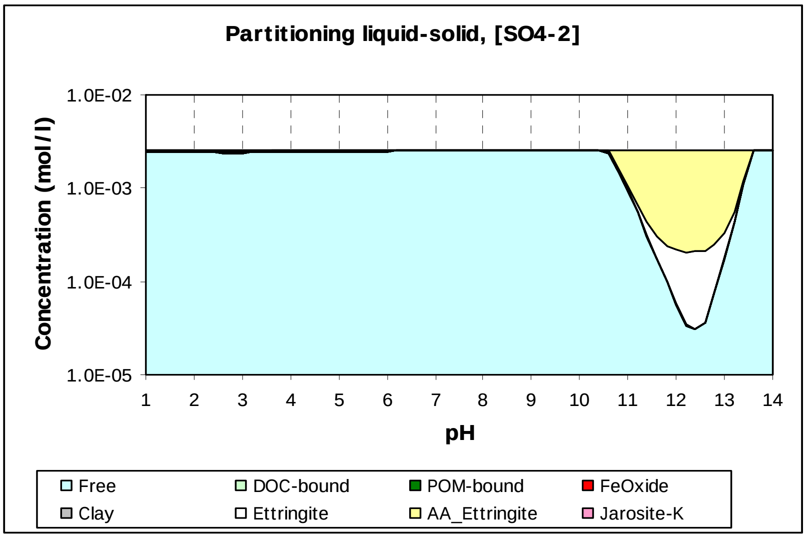


Figure 7:55: Solubility controlling mineral phases for sulphate leaching from stabilised zinc contaminated clay at 28 days

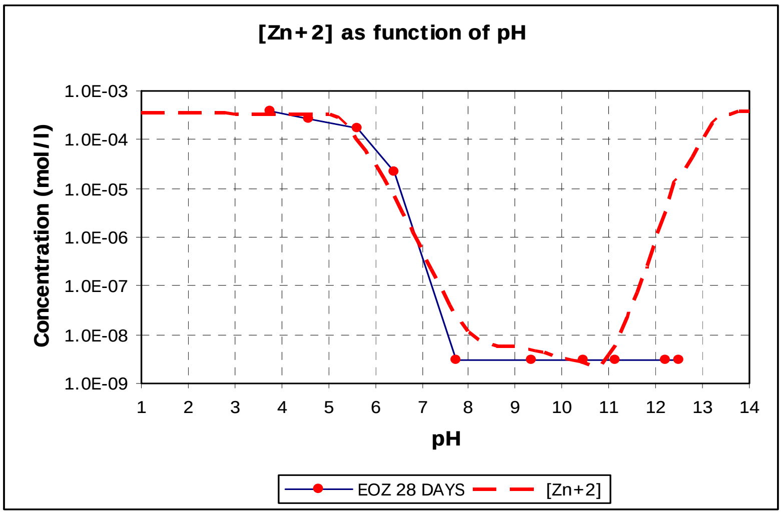


Figure 7:56: Zinc predicted and measured release trend from stabilised zinc contaminated clay at 28 days

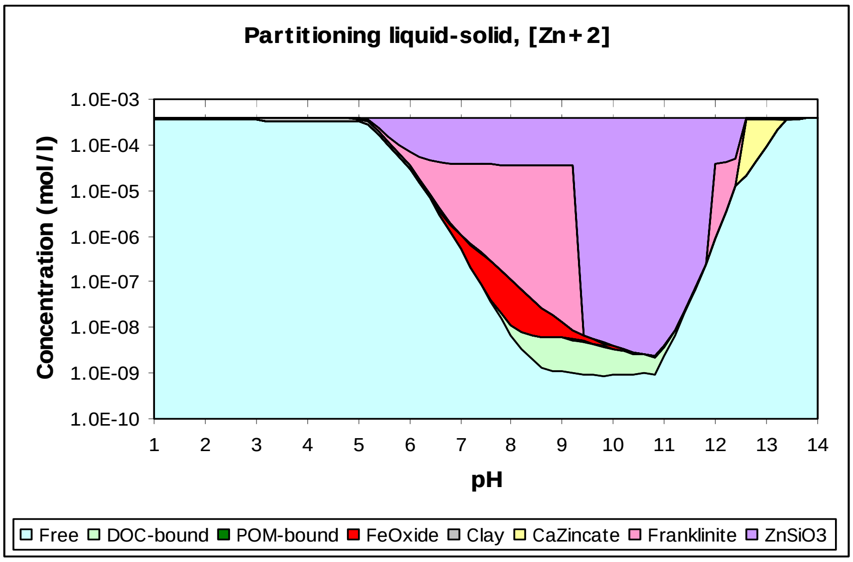


Figure 7:57: Solubility controlling mineral phases for zinc leaching from stabilised zinc contaminated clay at 28 days

For leaching at 150 days of hydration, Figures 7.58 and 7.59 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively, from the stabilised zinc contaminated kaolin. Respective results for silicon are shown in Figures 7.60 and 7.61, those for calcium releases shown in Figures 7.62 and 7.63, those for sulphate releases shown in Figures 7.64 and 7.65, and those for chromium releases shown in Figures 7.66 and 7.67. The measured and predicted releases for zinc are shown in Figure 7.68, and the solubility controlling mineral phases shown in Figure 7.69.

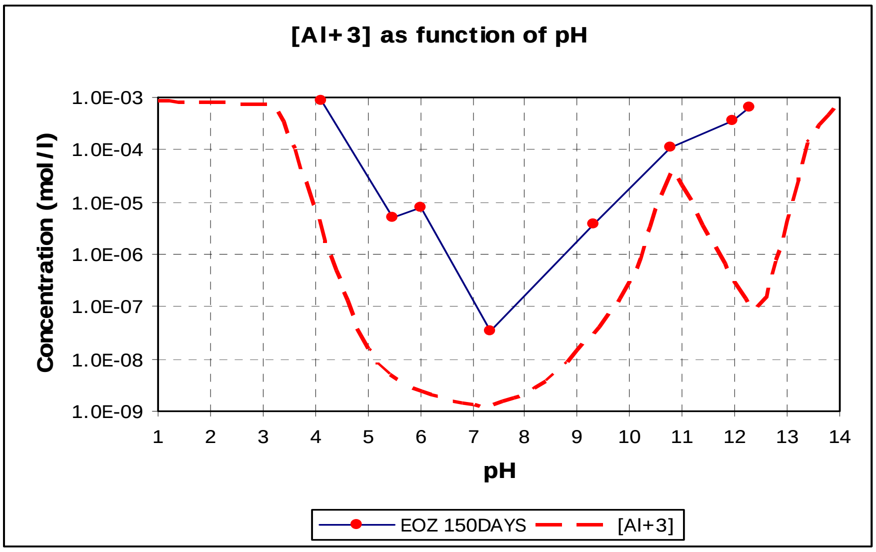


Figure 7:58: Aluminium predicted and measured release trend from stabilised zinc contaminated clay at 150 days

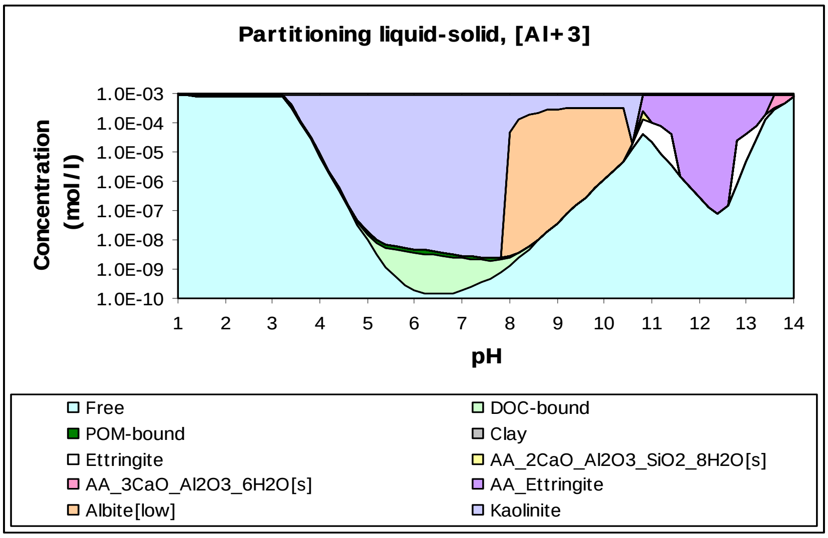


Figure 7:59: Solubility controlling mineral phases for aluminium leaching from stabilised zinc contaminated clay at 150 days

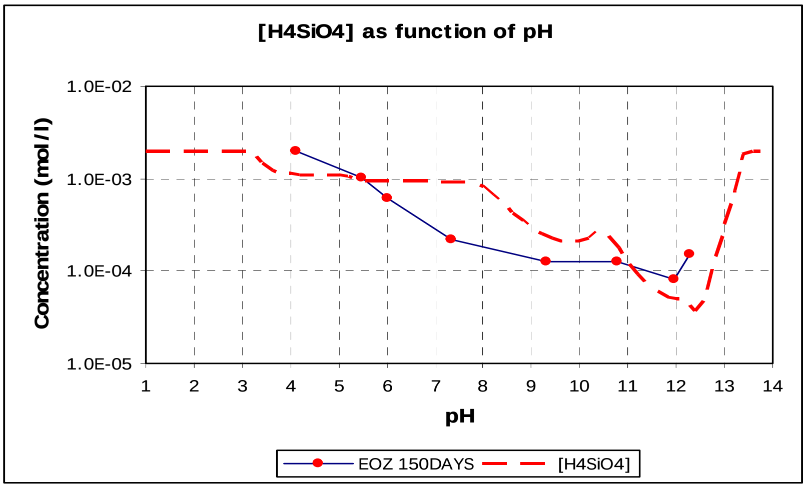


Figure 7:60: Silicic acid predicted and measured release trend from stabilised zinc contaminated clay at 150 days

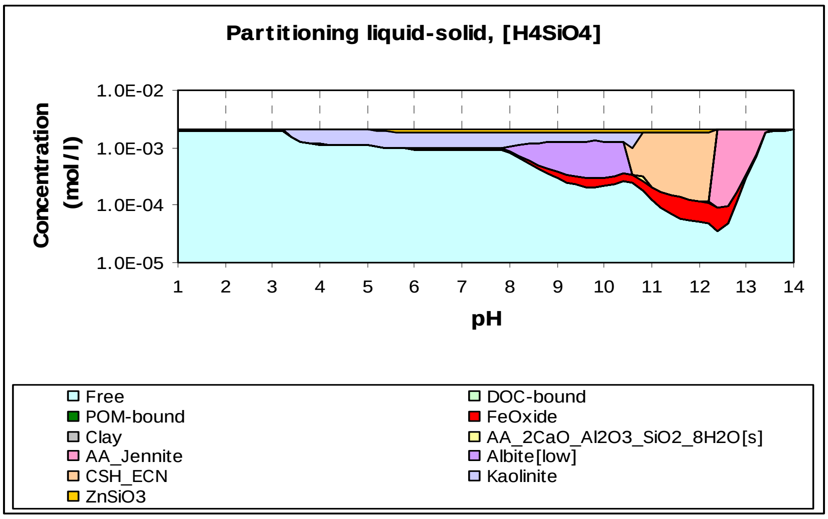


Figure 7:61: Solubility controlling mineral phases for silicic acid leaching from stabilised zinc contaminated clay at 150 days

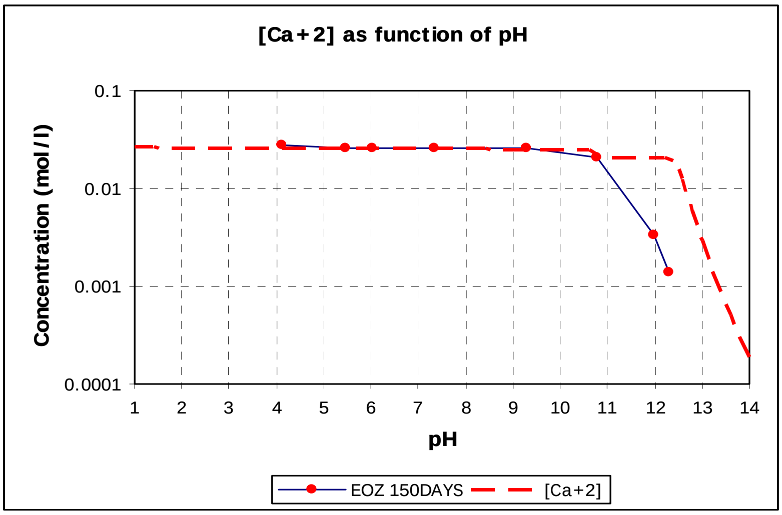


Figure 7:62: Calcium predicted and measured release trend from stabilised zinc contaminated clay at 150 days

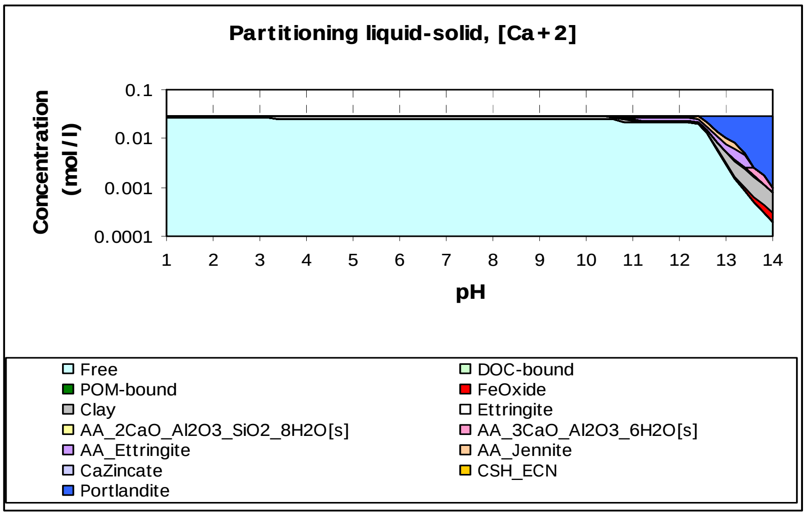


Figure 7:63: Solubility controlling mineral phases for calcium leaching from stabilised zinc contaminated clay at 150 days

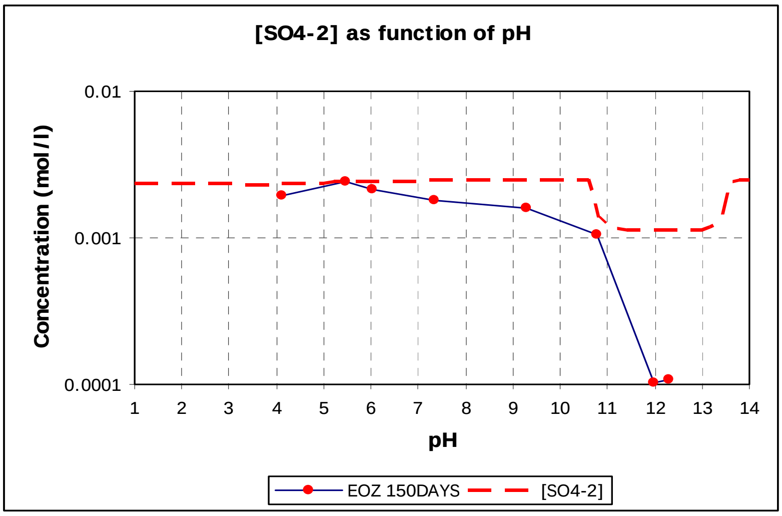


Figure 7:64: Sulphate predicted and measured release trend from stabilised zinc contaminated clay at 150 days

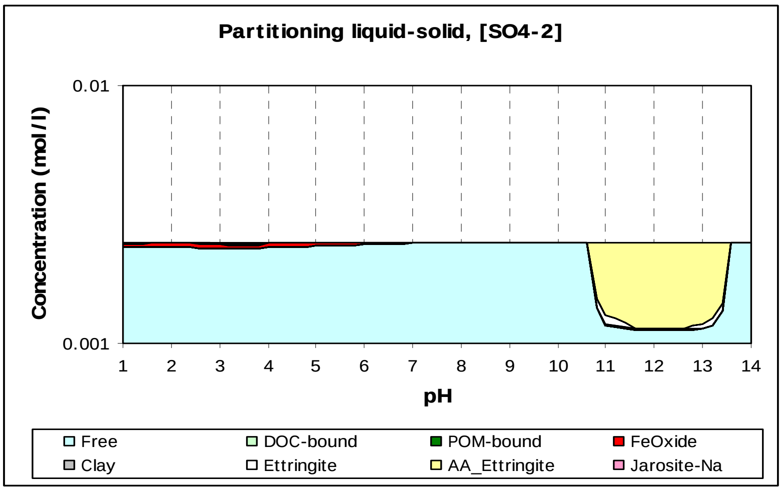


Figure 7:65: Solubility controlling mineral phases for sulphate leaching from stabilised zinc contaminated clay at 150 days

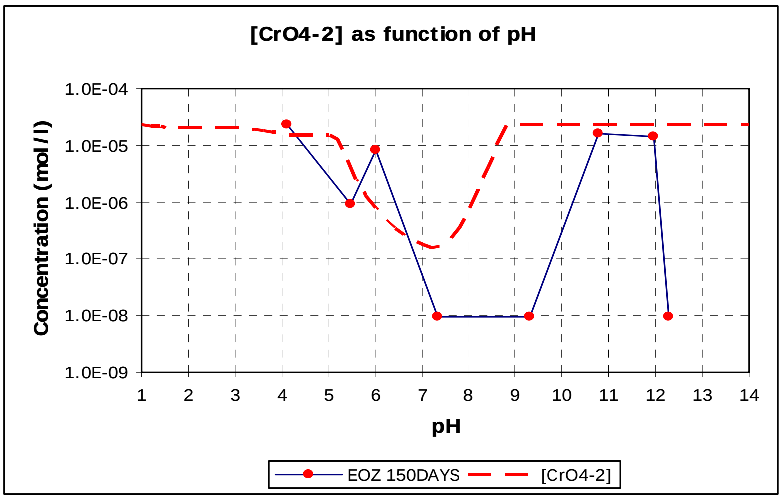


Figure 7:66: Chromate predicted and measured release trend from stabilised zinc contaminated clay at 150 days

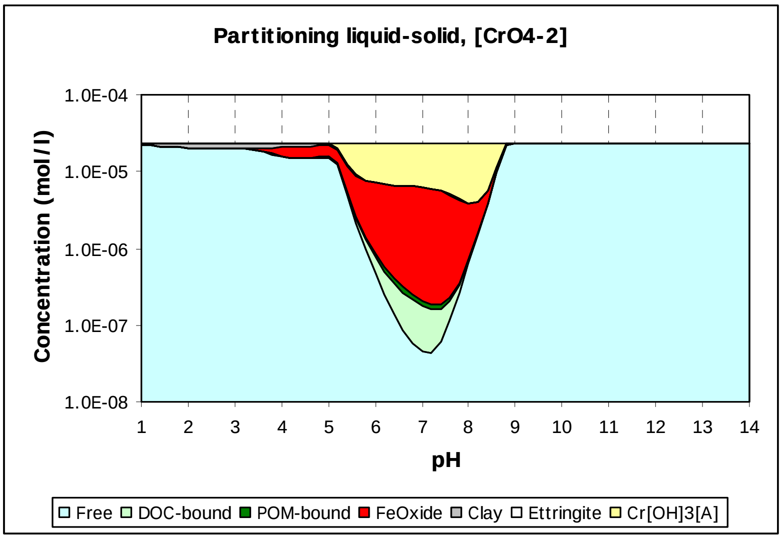


Figure 7:67: Solubility controlling mineral phases for chromate leaching from stabilised zinc contaminated clay at 150 days

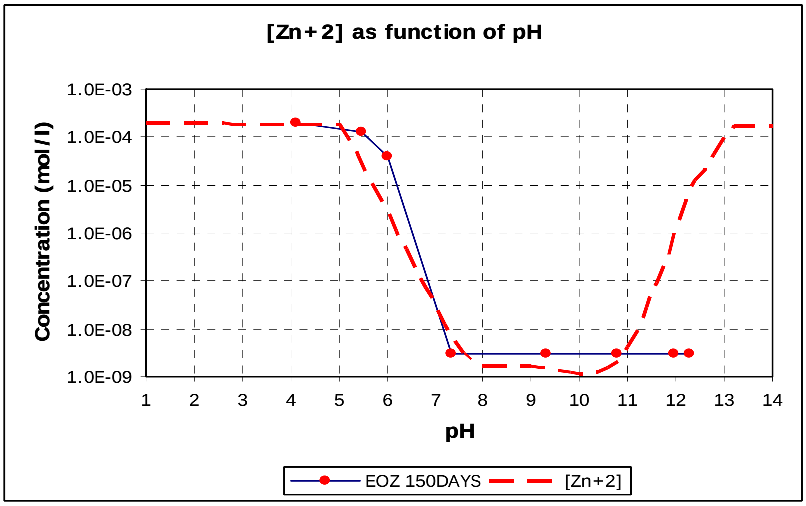


Figure 7:68: Zinc predicted and measured release trend from stabilised zinc contaminated clay at 150 days

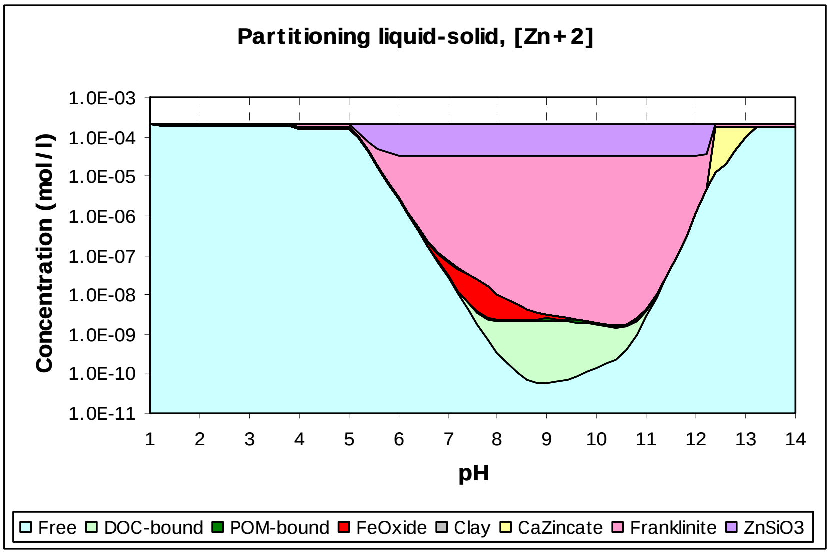


Figure 7:69: Solubility controlling mineral phases for zinc leaching from stabilised zinc contaminated clay at 150 days

For leaching at 300 days of hydration, Figures 7.70 and 7.71 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.72 and 7.73, those for calcium releases shown in Figures 7.74 and 7.75, and those for sulphate releases shown in Figures 7.76 and 7.77. No chromium releases were observed at 300 days of hydration, from the stabilised zinc contaminated kaolin clay, and thus no results are presented. The measured and predicted releases for zinc are shown in Figure 7.78, and the solubility controlling mineral phases shown in Figure 7.79.

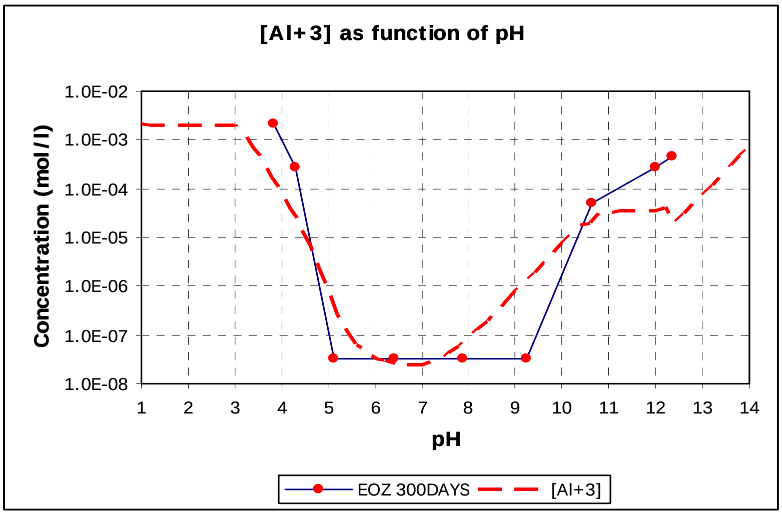


Figure 7:70: Aluminium predicted and measured release trend from stabilised zinc contaminated clay at 300 days

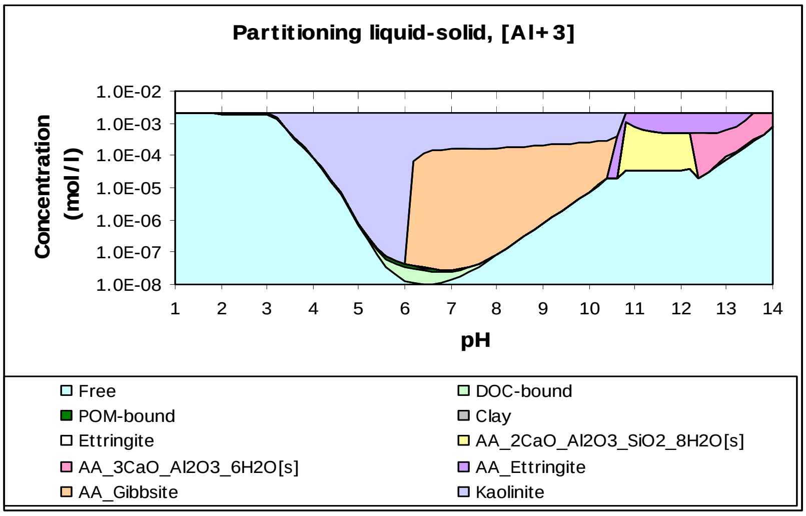


Figure 7:71: Solubility controlling mineral phases for aluminium leaching from stabilised zinc contaminated clay at 300 days

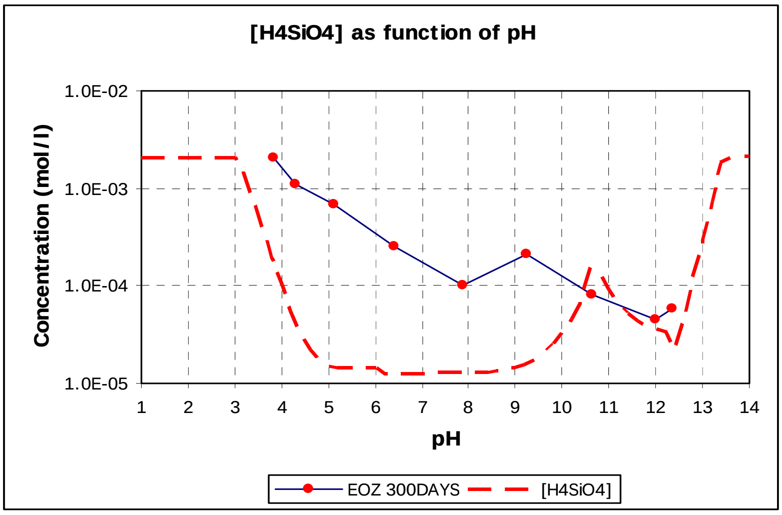


Figure 7:72: Silicic acid predicted and measured release trend from stabilised zinc contaminated clay at 300 days

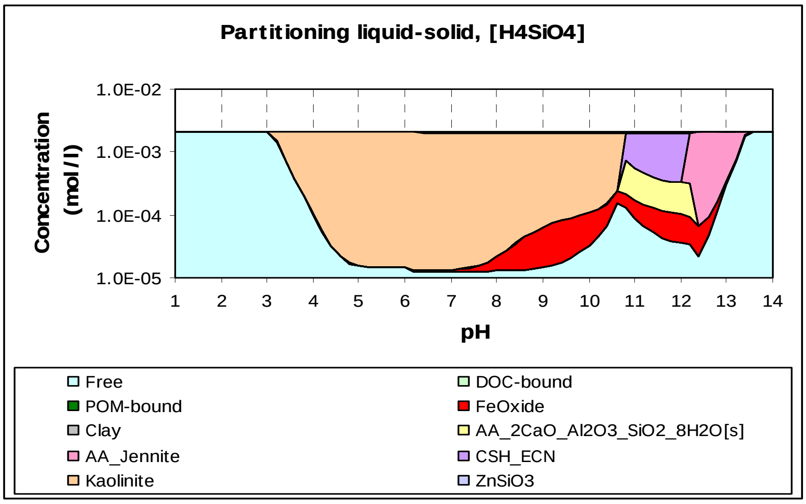


Figure 7:73: Solubility controlling mineral phases for silicic acid leaching from stabilised zinc contaminated clay at 300 days

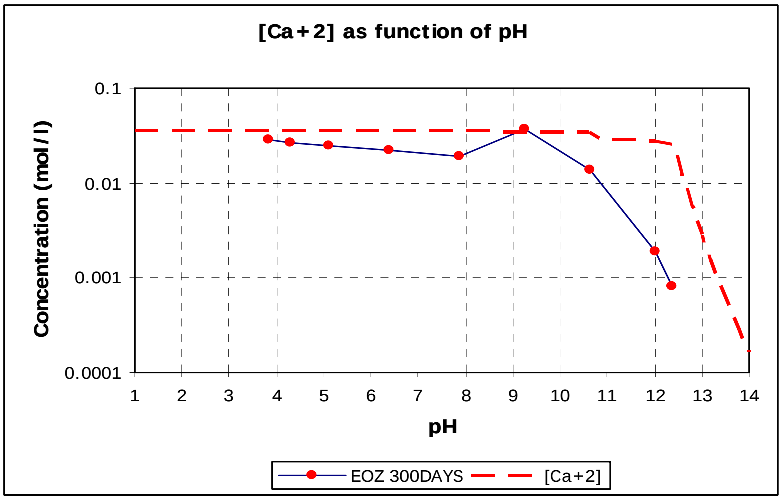


Figure 7:74: Calcium predicted and measured release trend from stabilised zinc contaminated clay at 300 days

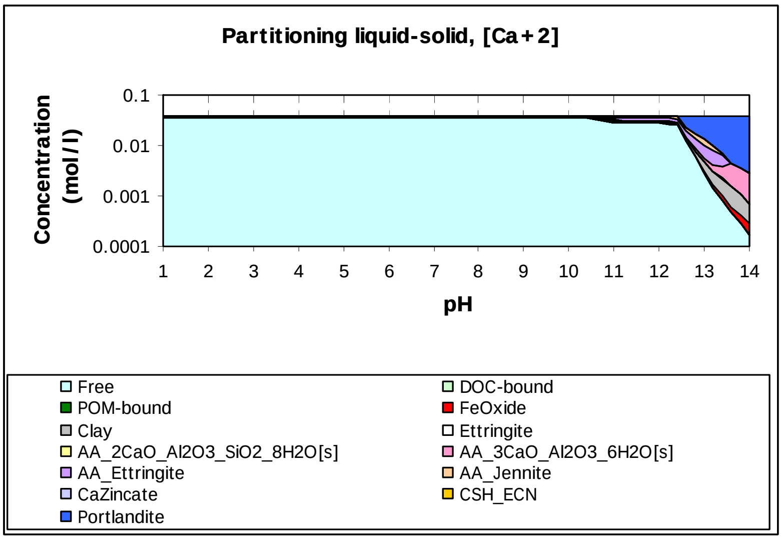


Figure 7:75: Solubility controlling mineral phases for calcium leaching from stabilised zinc contaminated clay at 300 days

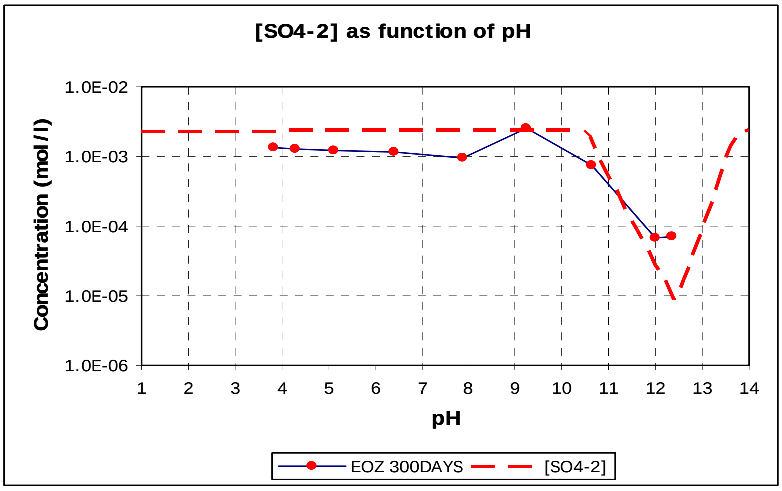


Figure 7:76: Sulphate predicted and measured release trend from stabilised zinc contaminated clay at 300 days

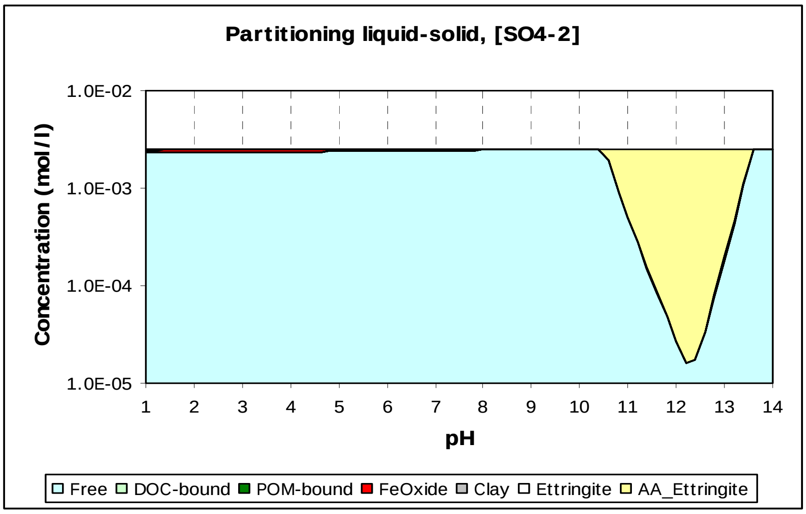


Figure 7:77: Solubility controlling mineral phases for sulphate leaching from stabilised zinc contaminated clay at 300 days

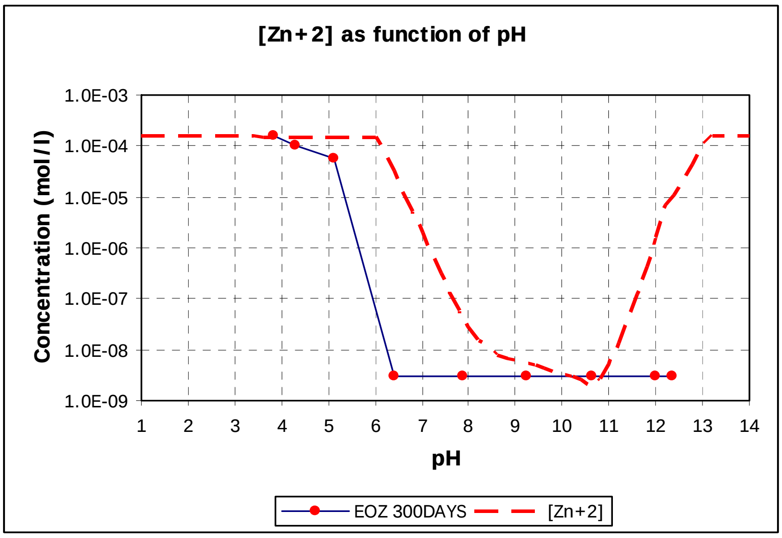


Figure 7:78: Zinc predicted and measured release trend from stabilised zinc contaminated clay at 300 days

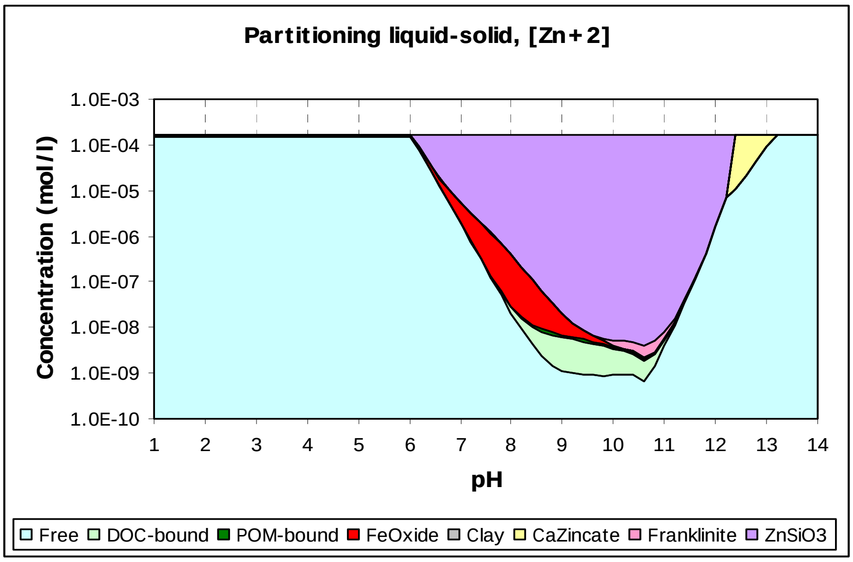


Figure 7:79: Solubility controlling mineral phases for zinc leaching from stabilised zinc contaminated clay at 300 days

7.3.3 Stabilised Chromium Contaminated Kaolin Clay

To assess chromium partitioning and containment, leaching and speciation evaluations were undertaken on stabilised chromium contaminated kaolin clay. Figures 7.80, 7.81 and 7.82 show the releases of selected components at 28, 150 and 300 days of hydration respectively. No trace releases for zinc were observed at 150 and 300 days (Figures 7.81 and 7.82), and thus no results are presented at these periods.

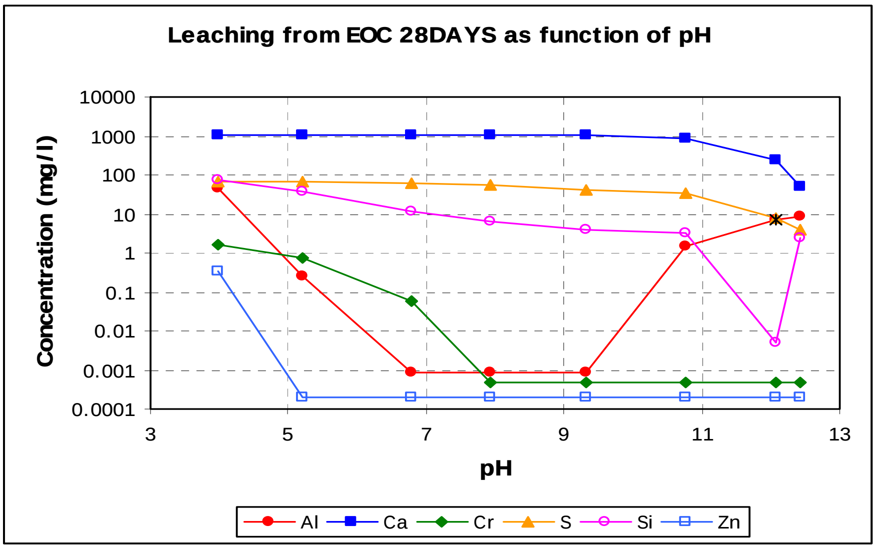


Figure 7:80: Releases of selected components from stabilised Chromium contaminated clay due to pH influence at 28 days

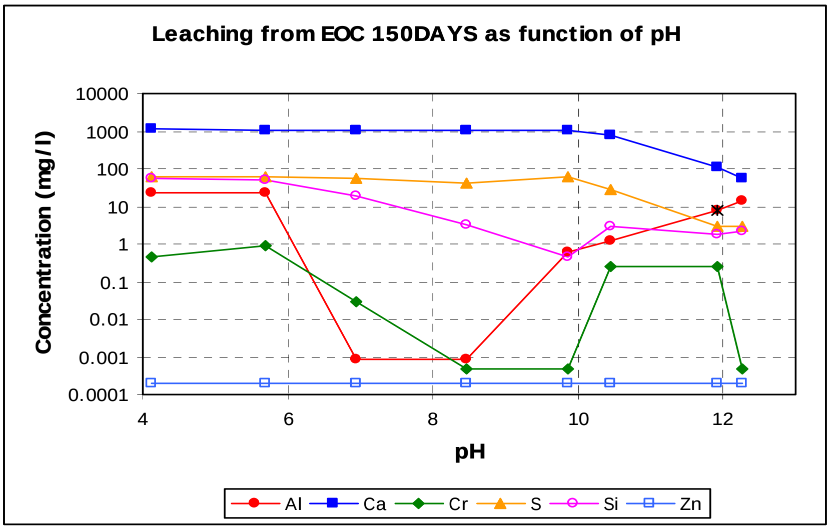


Figure 7:81: Releases of selected components from stabilised Chromium contaminated clay due to pH influence at 150 days

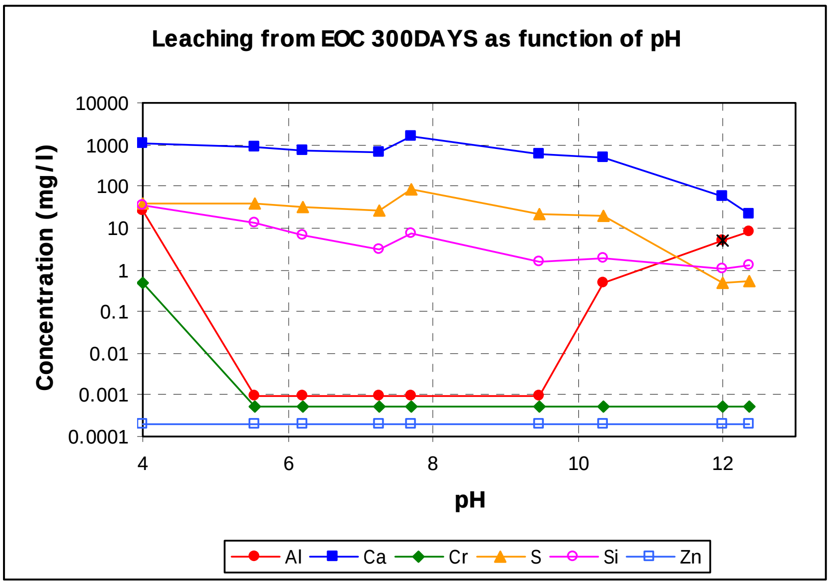


Figure 7:82: Releases of selected components from stabilised Chromium contaminated clay due to pH influence at 300 days

For leaching at 28 days of hydration, Figures 7.83 and 7.84 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.85 and 7.86, those for calcium shown in Figures 7.87 and 7.88, those for sulphate shown in Figures 7.89 and 7.90, and those for zinc shown in Figures 7.91 and 7.92. The measured and predicted releases for chromium (as chromate) are shown in Figure 7.93, and the solubility controlling mineral phases are shown in Figure 7.94.

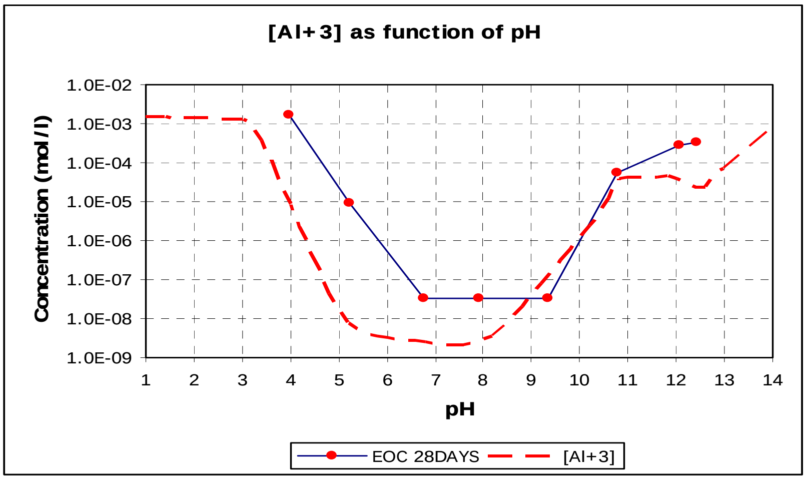


Figure 7:83: Aluminium predicted and measured release trend from stabilised chromium contaminated clay at 28 days

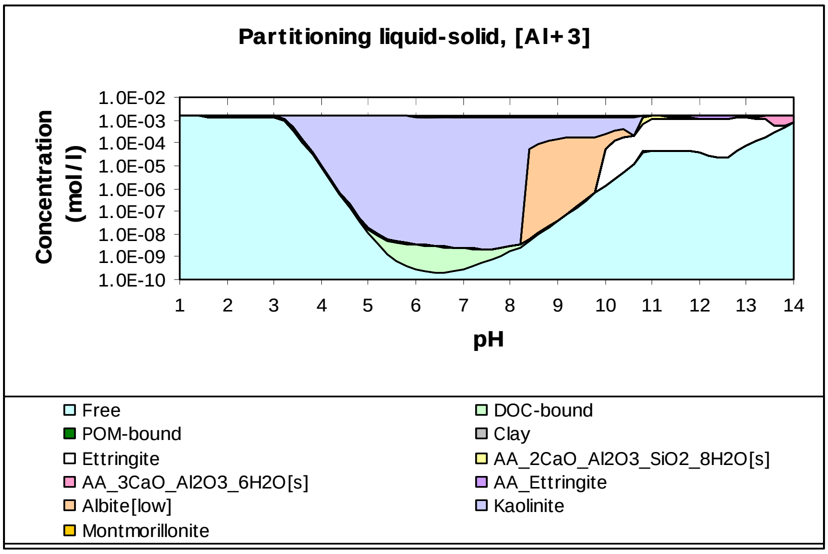


Figure 7:84: Solubility controlling mineral phases for aluminium leaching from stabilised chromium contaminated clay at 28 days

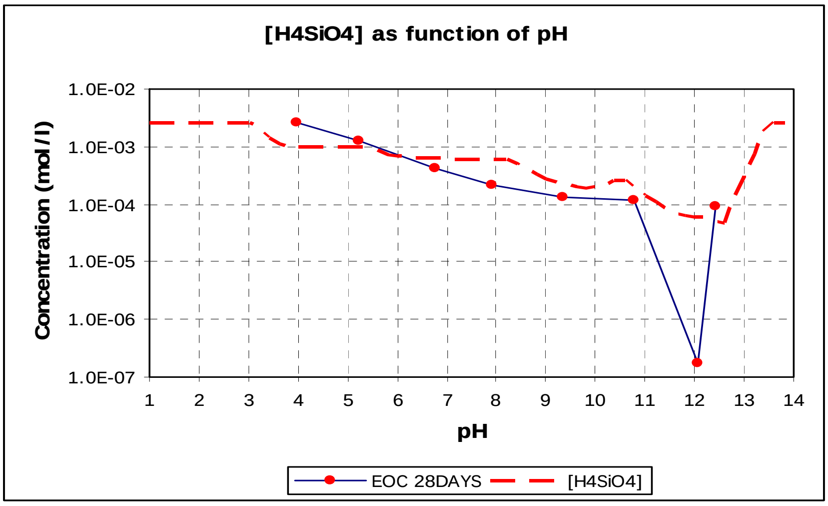


Figure 7:85: Silicic acid predicted and measured release trend from stabilised chromium contaminated clay at 28 days

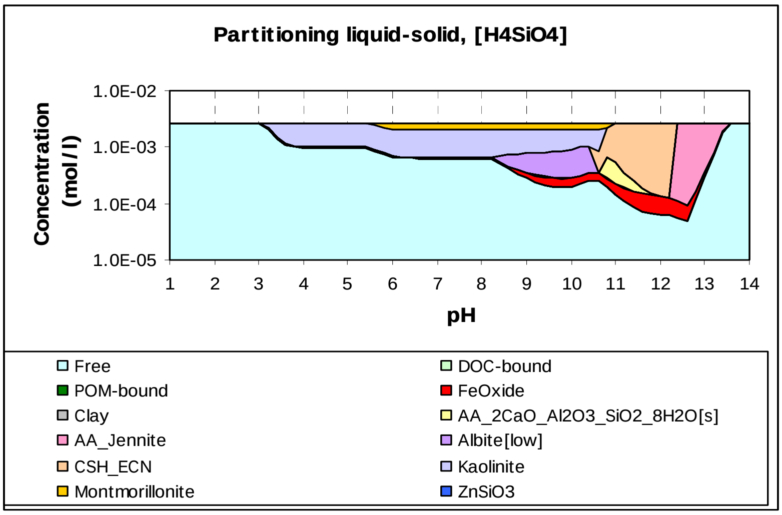


Figure 7:86: Solubility controlling mineral phases for silicic acid leaching from stabilised chromium contaminated clay at 28 days

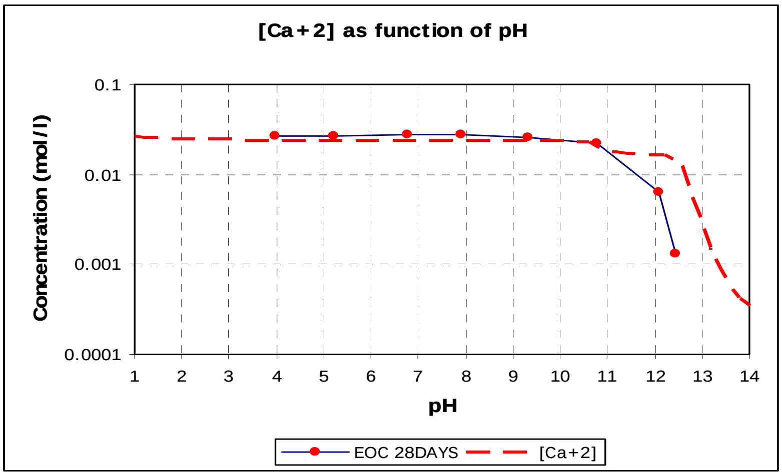


Figure 7:87: Calcium predicted and measured release trend from stabilised chromium contaminated clay at 28 days

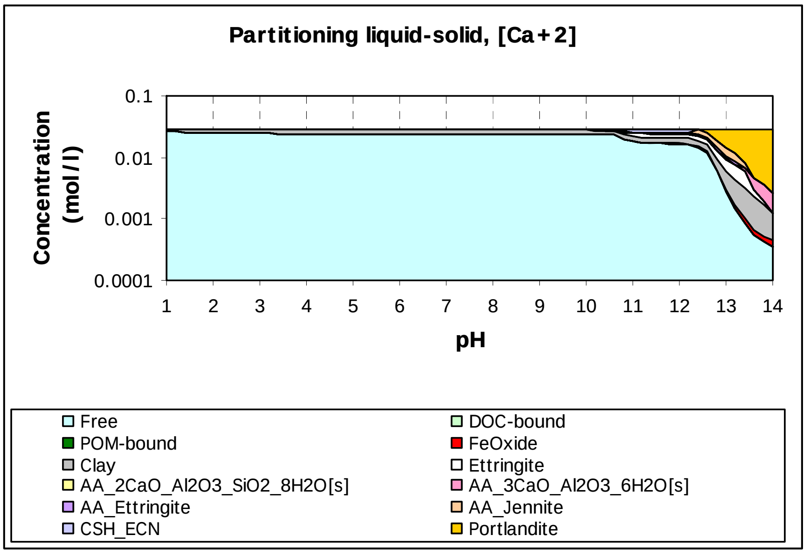


Figure 7:88: Solubility controlling mineral phases for calcium leaching from stabilised chromium contaminated clay at 28 days

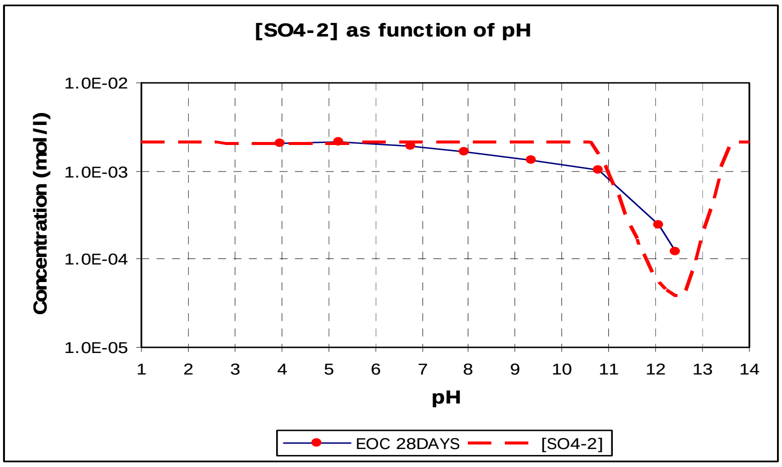


Figure 7:89: Sulphate predicted and measured release trend from stabilised chromium contaminated clay at 28 days

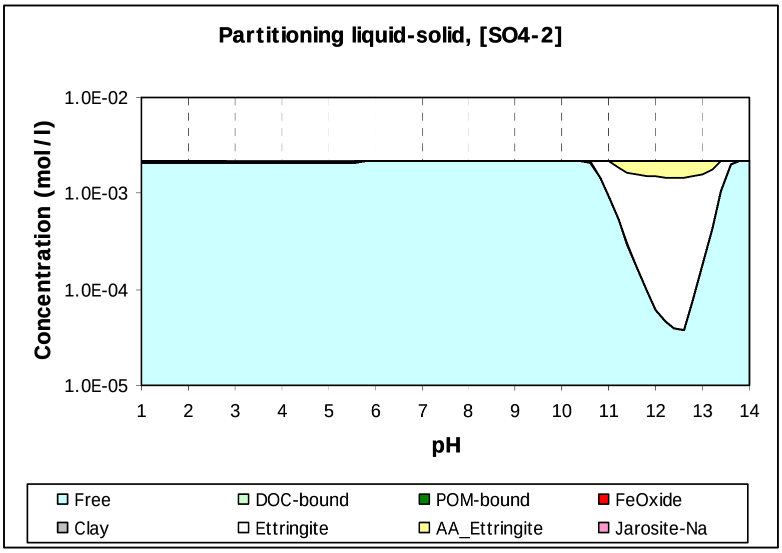


Figure 7:90: Solubility controlling mineral phases for sulphate leaching from stabilised chromium contaminated clay at 28 days

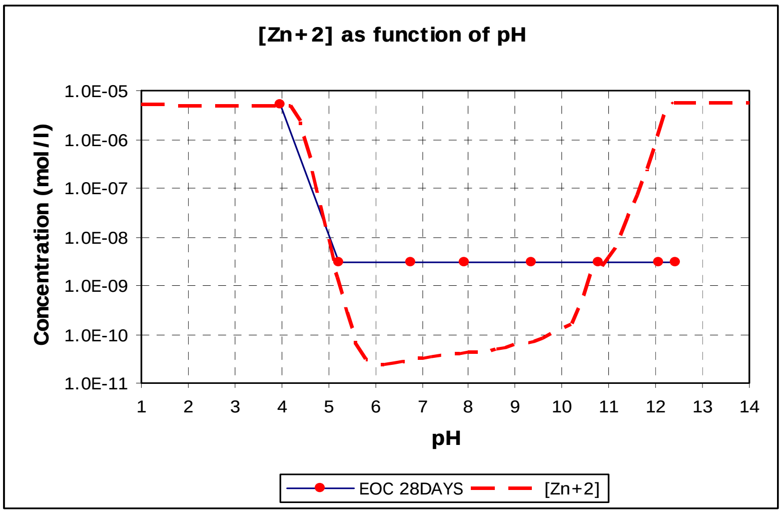


Figure 7:91: Zinc predicted and measured release trend from stabilised chromium contaminated clay at 28 days

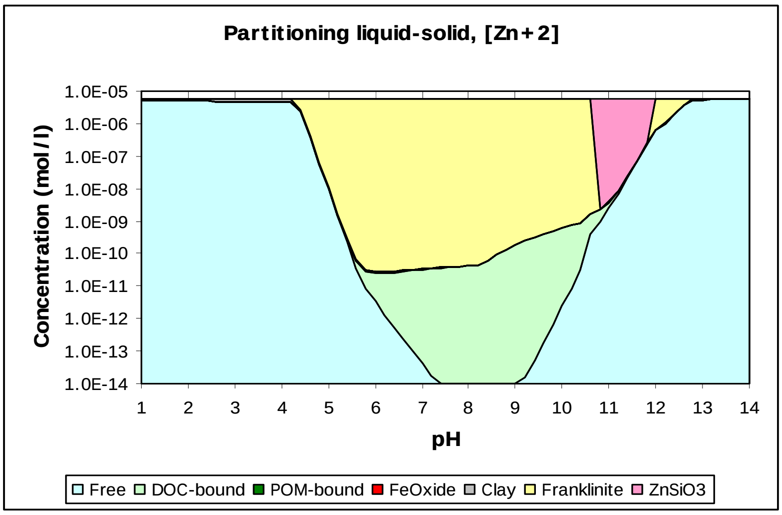


Figure 7:92: Solubility controlling mineral phases for zinc leaching from stabilised chromium contaminated clay at 28 days

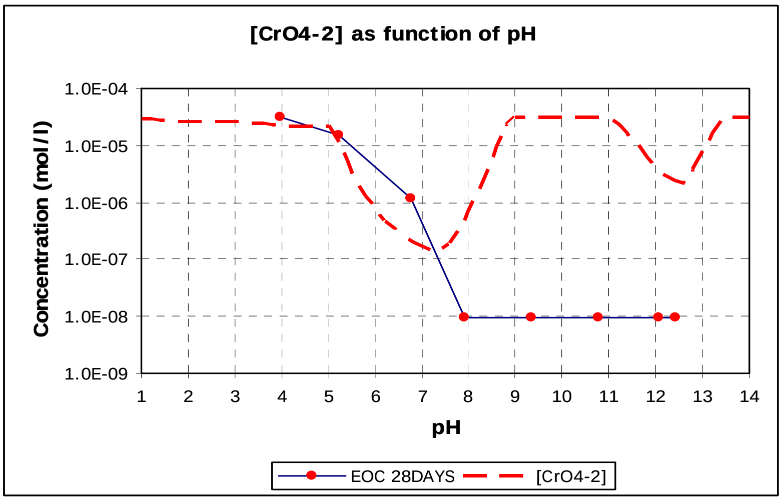


Figure 7:93: Chromate predicted and measured release trend from stabilised chromium contaminated clay at 28 days

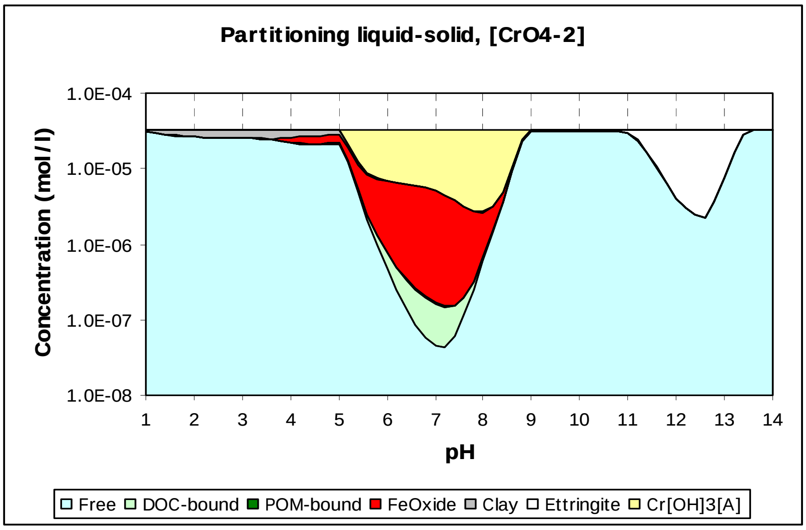


Figure 7:94: Solubility controlling mineral phases for chromate leaching from stabilised chromium contaminated clay at 28 days

For leaching at 150 days of hydration, Figures 7.95 and 7.96 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively, from the stabilised chromium contaminated kaolin clay. Respective results for silicon releases are shown in Figures 7.97 and 7.98, those for calcium shown in Figures 7.99 and 7.100, and those for sulphate releases shown in Figures 7.101 and 7.102. The measured and predicted releases for chromium are shown in Figure 7.103, and the solubility controlling mineral phases are shown in Figure 7.104.

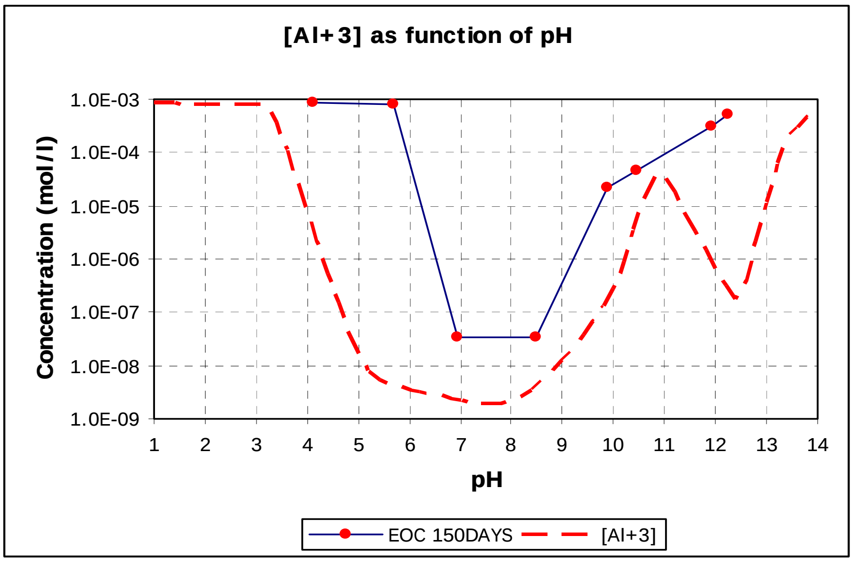


Figure 7:95: Aluminium predicted and measured release trend from stabilised chromium contaminated clay at 150 days

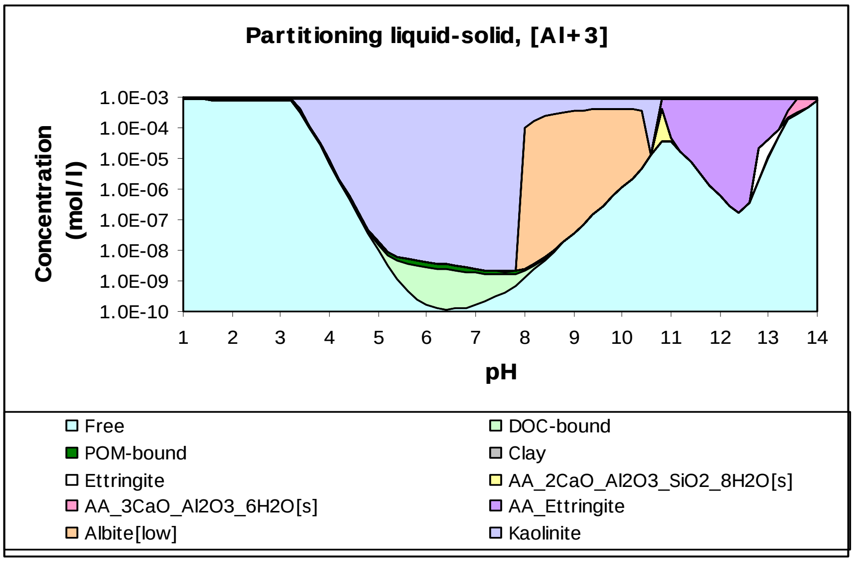


Figure 7:96: Solubility controlling mineral phases for aluminium leaching from stabilised chromium contaminated clay at 150 days

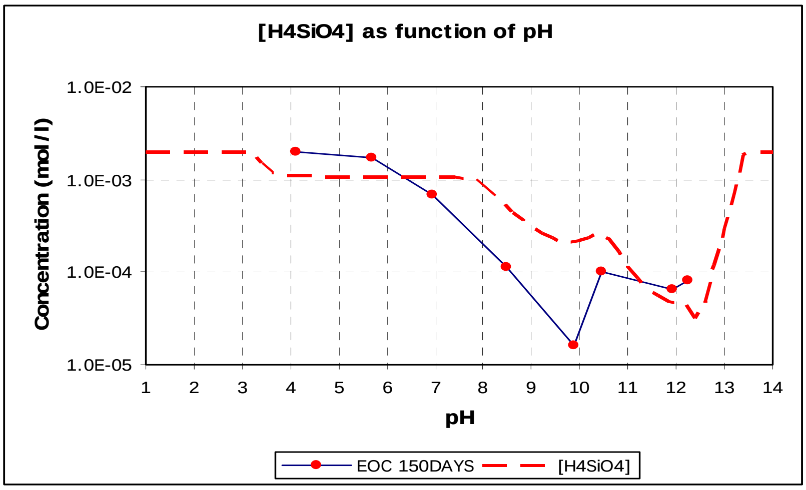


Figure 7:97: Silicic acid predicted and measured release trend from stabilised chromium contaminated clay at 150 days

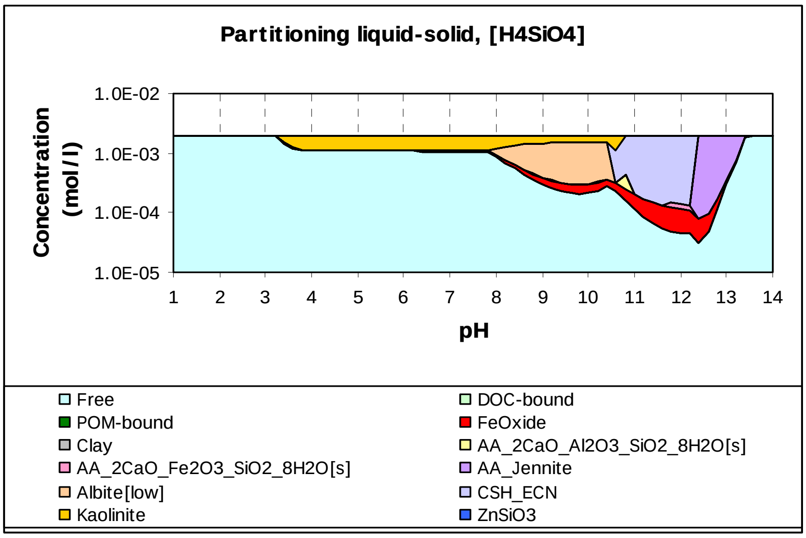


Figure 7:98: Solubility controlling mineral phases for silicic acid leaching from stabilised chromium contaminated clay at 150 days

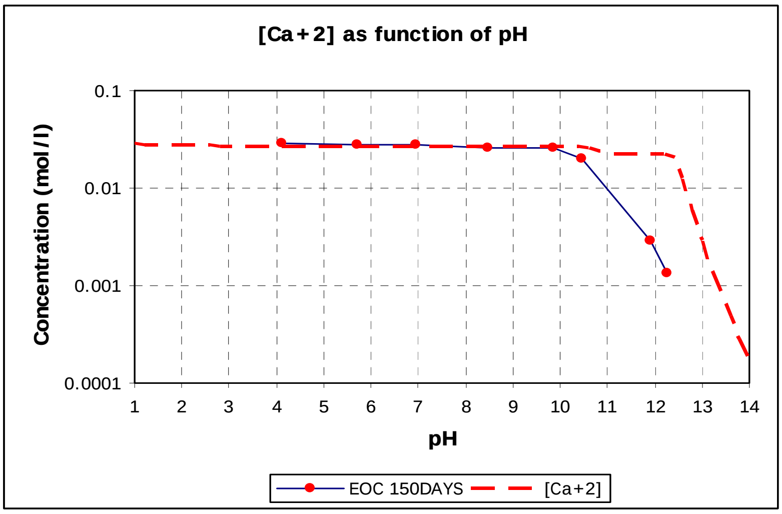


Figure 7:99: Calcium predicted and measured release trend from stabilised chromium contaminated clay at 150 days

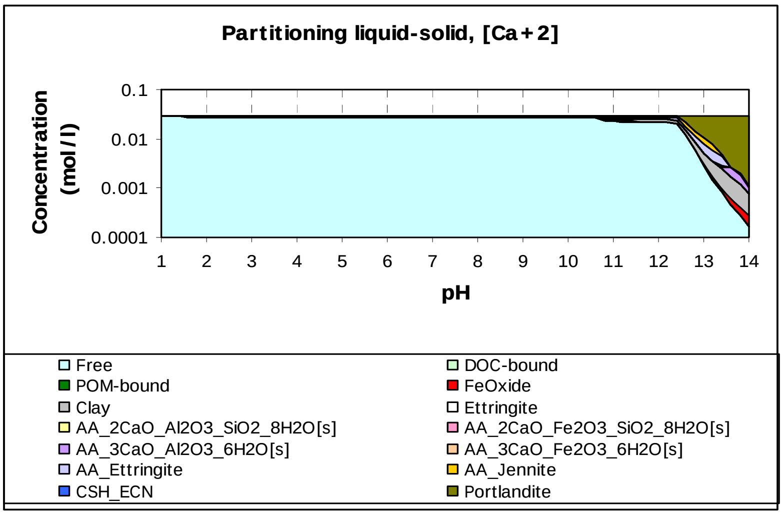


Figure 7:100: Solubility controlling mineral phases for calcium leaching from stabilised chromium contaminated clay at 150 days

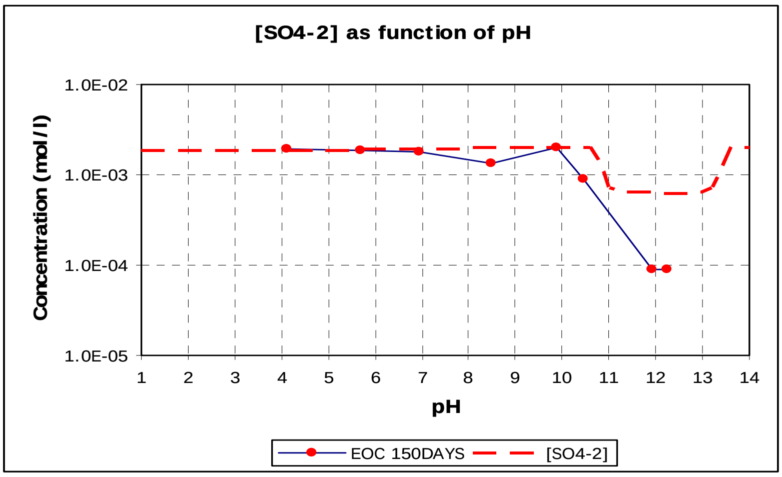


Figure 7:101: Sulphate predicted and measured release trend from stabilised chromium contaminated clay at 150 days

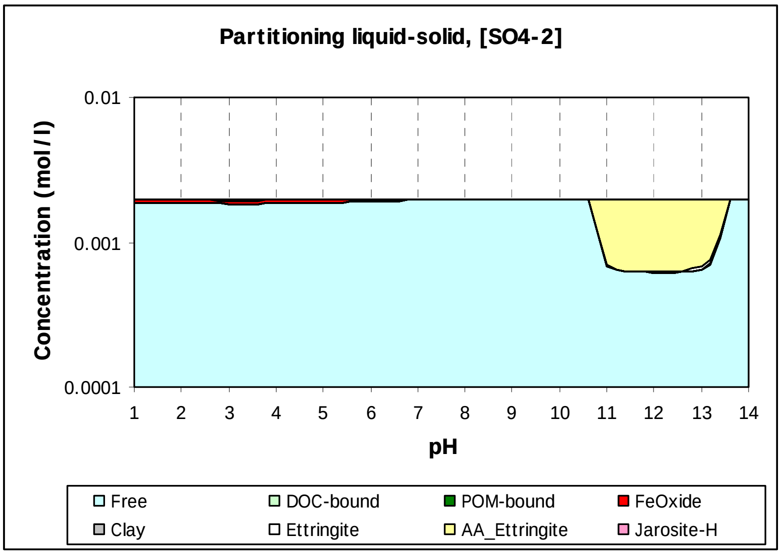


Figure 7:102: Solubility controlling mineral phases for sulphate leaching from stabilised chromium contaminated clay at 150 days

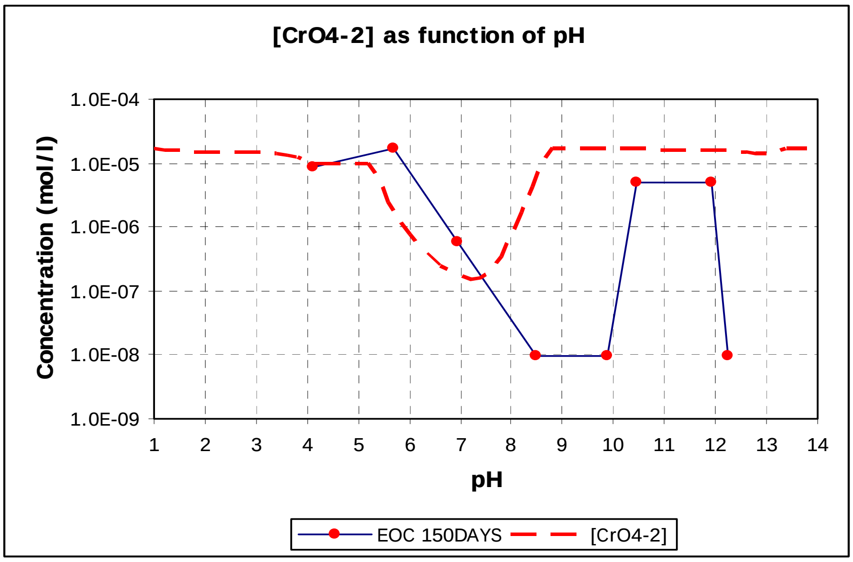


Figure 7:103: Chromate predicted and measured release trend from stabilised chromium contaminated clay at 150 days

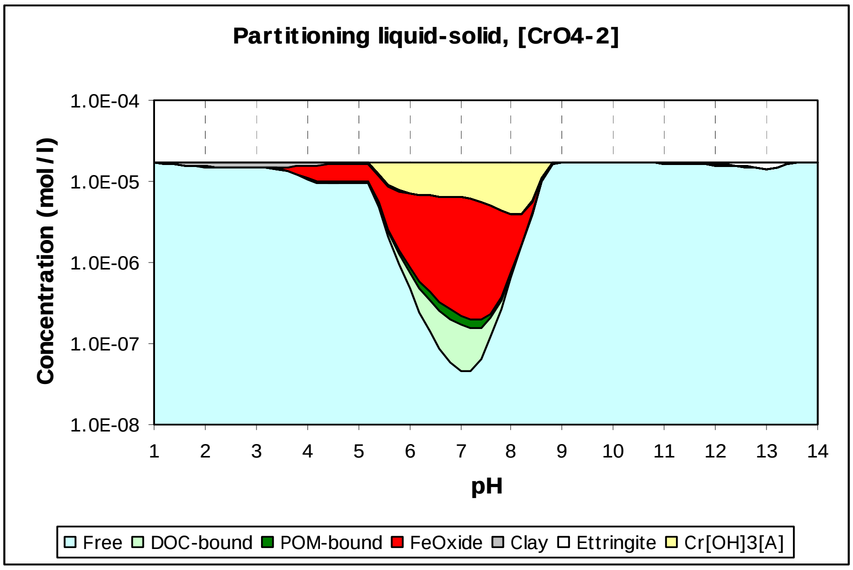


Figure 7:104: Solubility controlling mineral phases for Chromate leaching from stabilised chromium contaminated clay at 150 days

For leaching at 300 days of hydration, Figures 7.105 and 7.106 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.107 and 7.108, those for calcium shown in Figures 7.109 and 7.110, and those for sulphate shown in Figures 7.111 and 7.112. No zinc releases were observed at 150 and 300 days of hydration, and thus no results were presented. The measured and predicted releases for chromium are shown in Figure 7.113, and solubility controlling mineral phases shown in Figure 7.114.

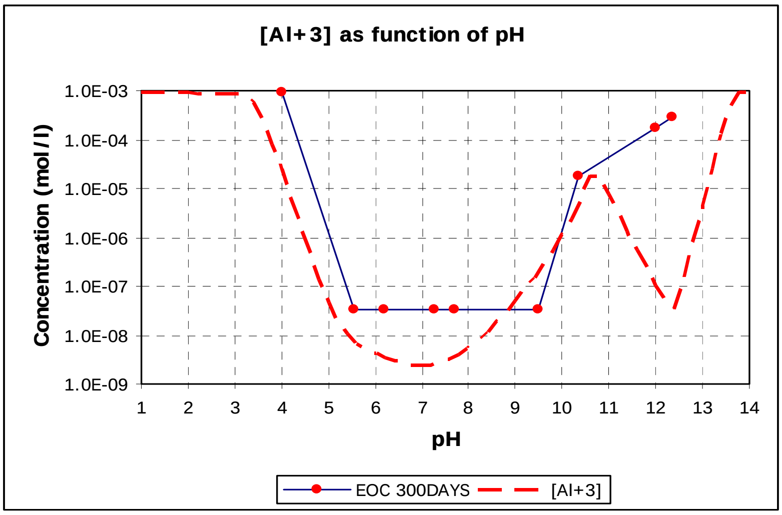


Figure 7:105: Aluminium predicted and measured release trend from stabilised chromium contaminated clay at 300 days

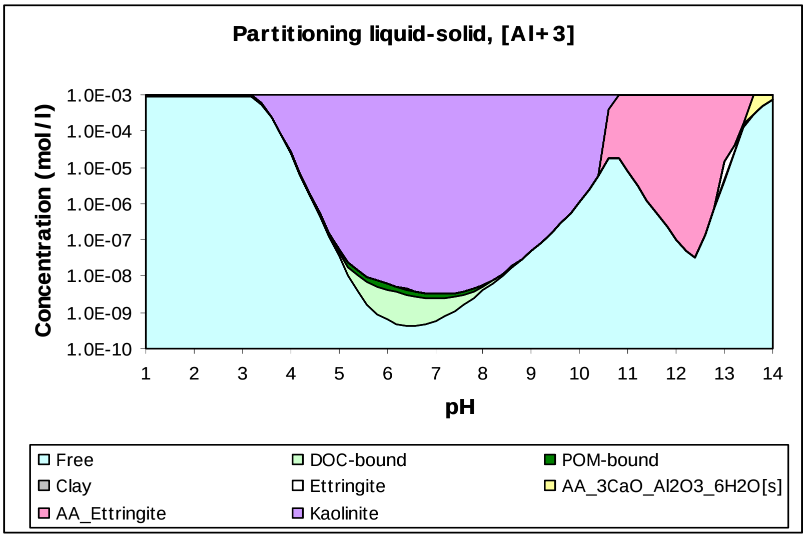


Figure 7:106: Solubility controlling mineral phases for aluminium leaching from stabilised chromium contaminated clay at 300 days

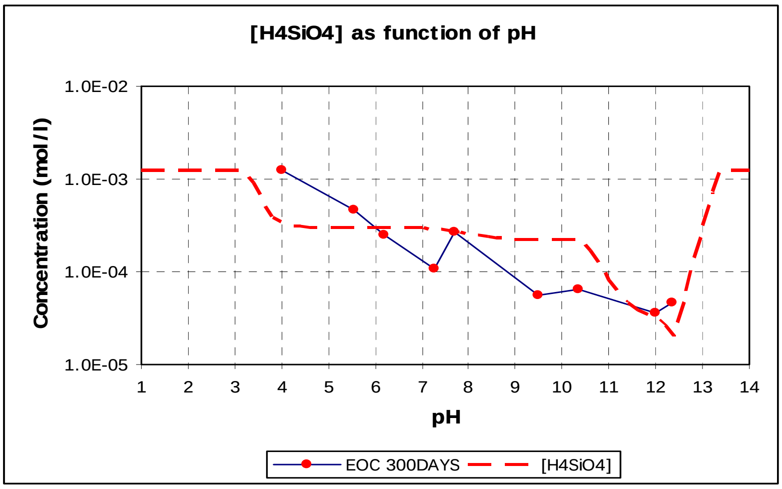


Figure 7:107: Silicic acid predicted and measured release trend from stabilised chromium contaminated clay at 300 days

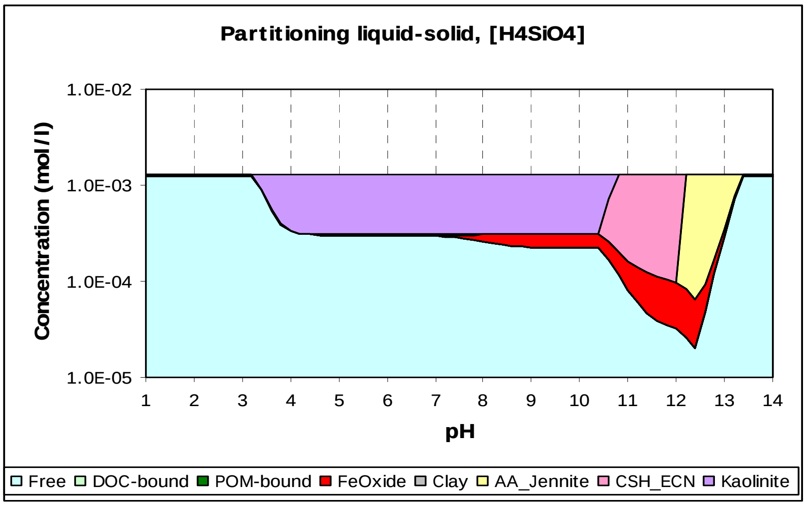


Figure 7:108: Solubility controlling mineral phases for silicic acid leaching from stabilised chromium contaminated clay at 300 days

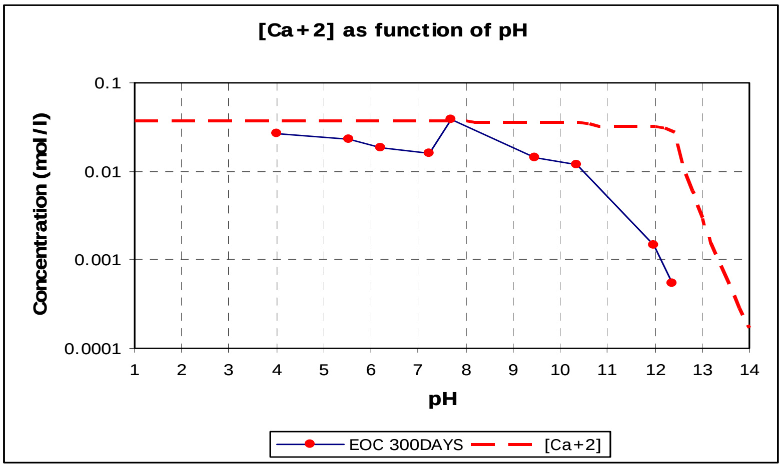


Figure 7:109: Calcium predicted and measured release trend from stabilised chromium contaminated clay at 300 days

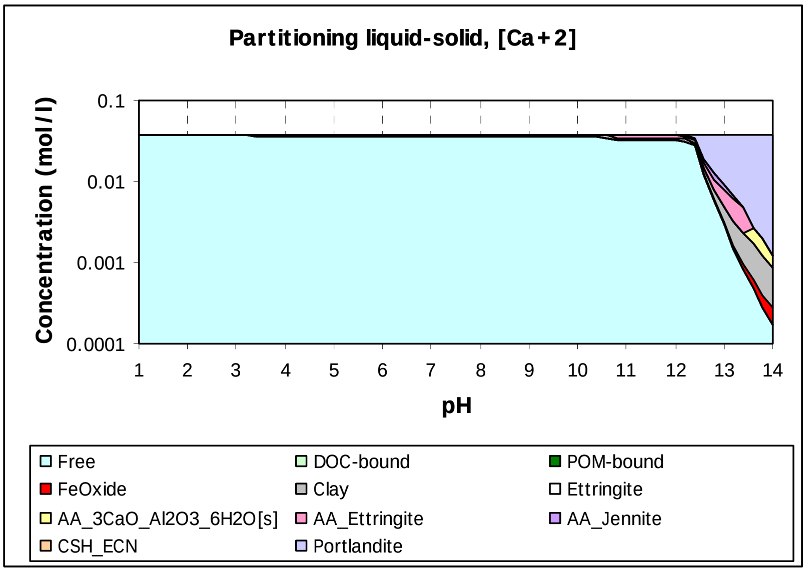


Figure 7:110: Solubility controlling mineral phases for calcium leaching from stabilised chromium contaminated clay at 300 days

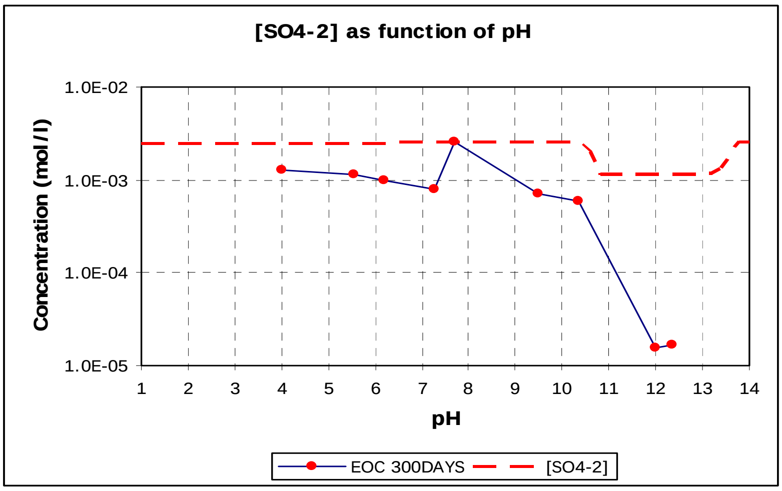


Figure 7:111: Sulphate predicted and measured release trend from stabilised chromium contaminated clay at 300 days

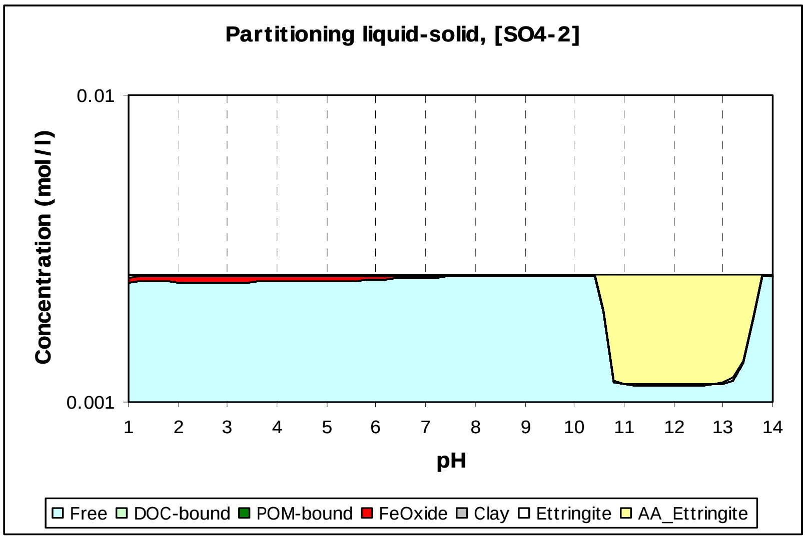


Figure 7:112: Solubility controlling mineral phases for Sulphate leaching from stabilised chromium contaminated clay at 300 days

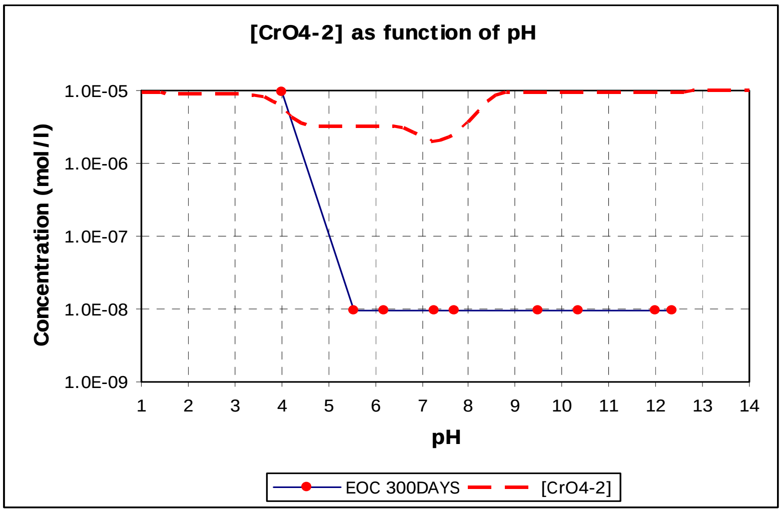


Figure 7:113: Chromate predicted and measured release trend from stabilised chromium contaminated clay at 300 days

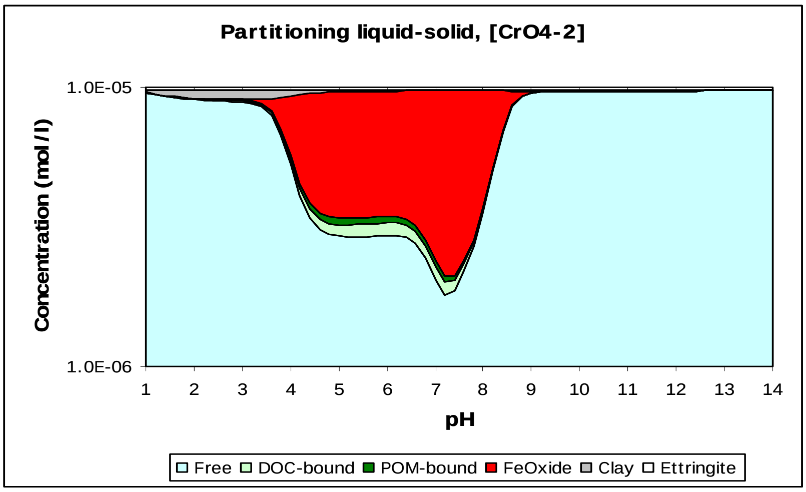


Figure 7:114: Solubility controlling mineral phases for Chromate leaching from stabilised chromium contaminated clay at 300 days

7.4 CEMENT STABILISED KAOLIN CLAY WITH 1% HUMIC ACID

To assess the influence of organic carbon on introduced contaminant partitioning and releases, leaching and speciation evaluations were undertaken on stabilised kaolin clay with 1% humic acid. However, for humic acid additive matrices, only results for aluminium, silicon and introduced contaminants (in contaminated matrices) are presented. This was due to observed similarities in trends and mineralogy, for calcium and sulphate releases, compared to matrices without additives. Modelling parameters employed for this matrix were shown in Table 7.1, and the increased clay contents (compared to other matrices) was due to the potential hydration retardation induced by introduced humic acid.

7.4.1 Uncontaminated Stabilised Kaolin Clay with 1% Humic Acid

Results for releases from uncontaminated kaolin clay with 1% humic acid are presented in this section. For the uncontaminated humic acid additive matrix, only results for aluminium and silicon trends and speciation are presented. Figures 7.115, 7.116 and 7.117 show the measured release trends for pre-selected components, at 28, 150 and 300 days respectively.

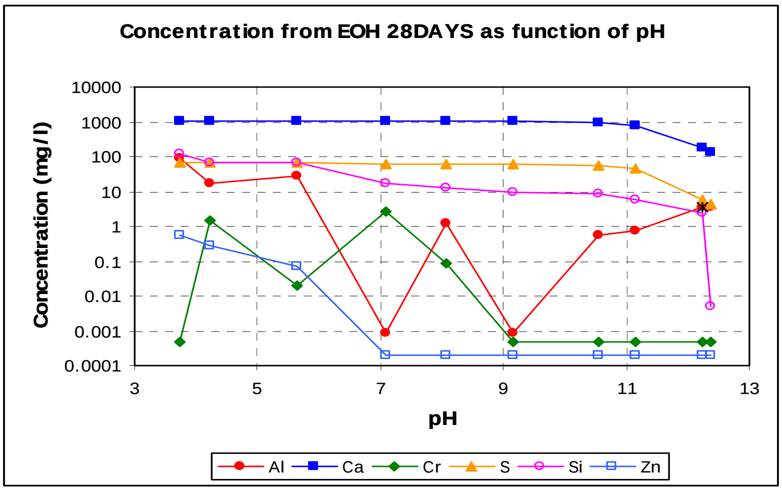


Figure 7:115: Releases of selected components from stabilised contaminated clay with 1% humic acid due to pH influence at 28 days

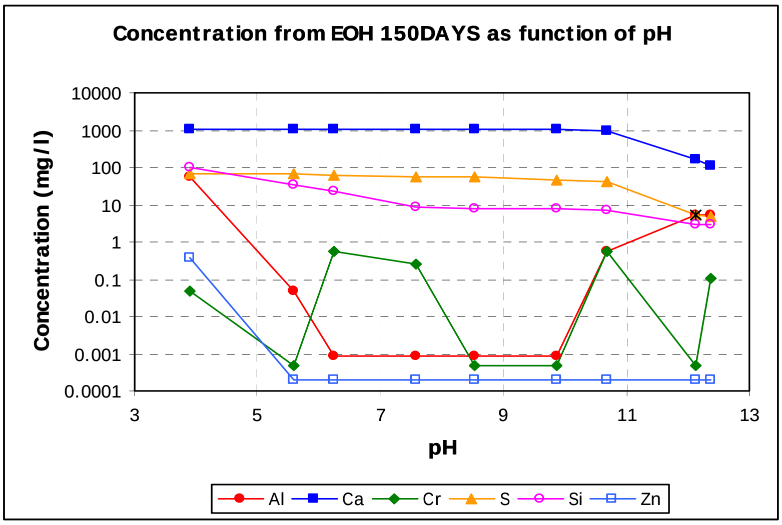


Figure 7:116: Releases of selected components from stabilised contaminated clay with 1% humic acid due to pH influence at 150 days

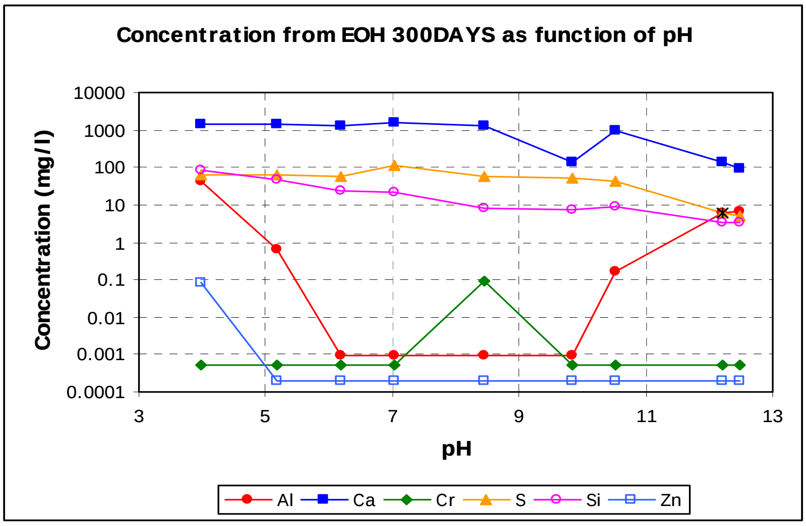


Figure 7:117: Releases of selected components from stabilised contaminated clay with 1% humic acid due to pH influence at 300 days

For leaching at 28 days of hydration, Figures 7.118 and 7.119 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon are shown in Figures 7.120 and 7.121. For leaching at 150 days of hydration, Figures 7.122 and 7.123 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon are shown in Figures 7.124 and 7.125. For leaching at 300 days of hydration, Figures 7.126 and 7.127 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon are shown in Figures 7.128 and 7.129.

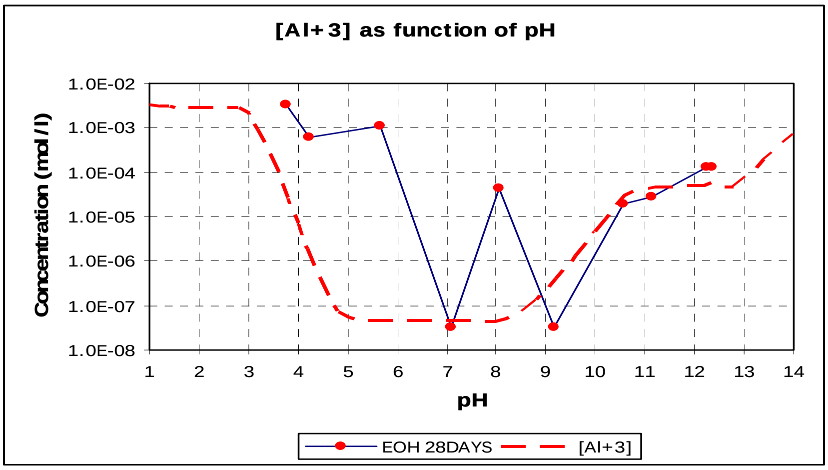


Figure 7:118: Aluminium predicted and measured release trend from stabilised clay with 1% humic acid at 28 days

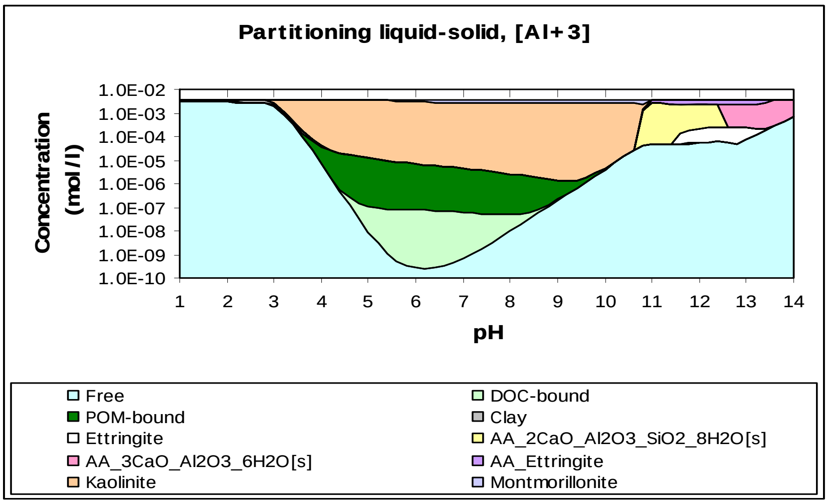


Figure 7:119: Solubility controlling mineral phases for aluminium leaching from stabilised clay with 1% humic acid at 28 days

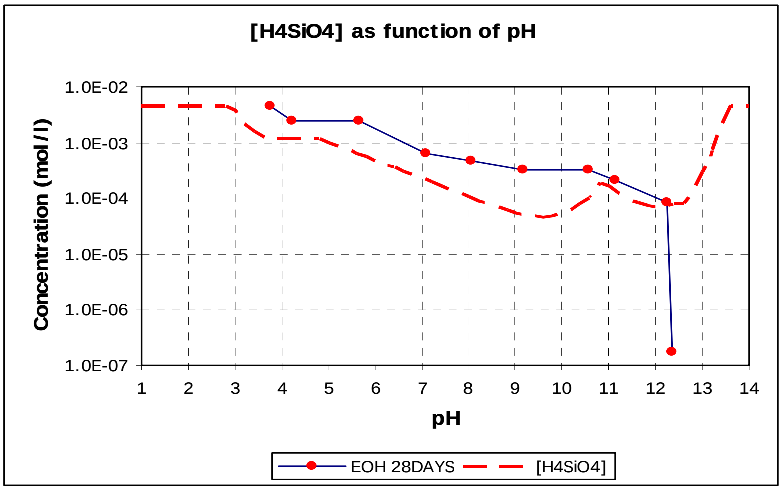


Figure 7:120: Silicic acid predicted and measured release trend from stabilised clay with 1% humic acid at 28 days

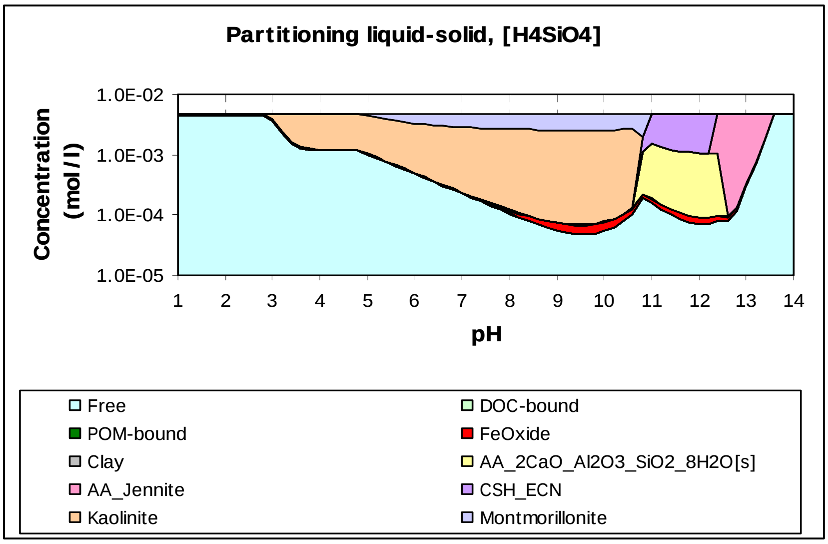


Figure 7:121: Solubility controlling mineral phases for silicic acid leaching from stabilised clay with 1% humic acid at 28 days

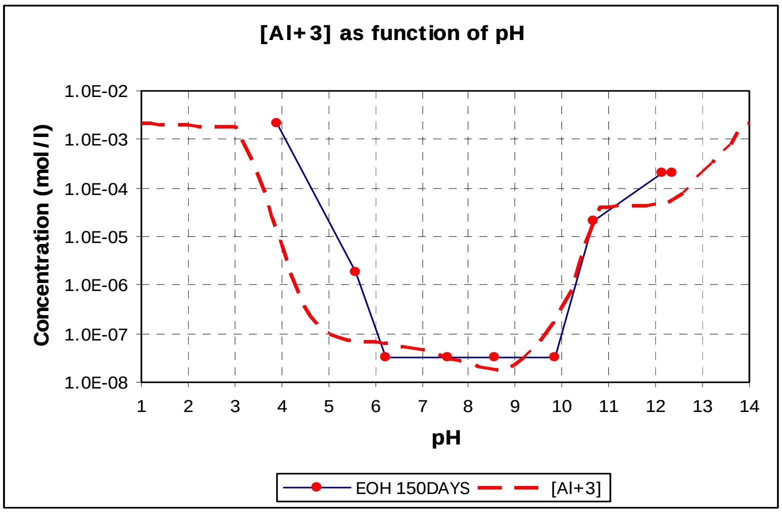


Figure 7:122: Aluminium predicted and measured release trend from stabilised clay with 1% humic acid at 150 days

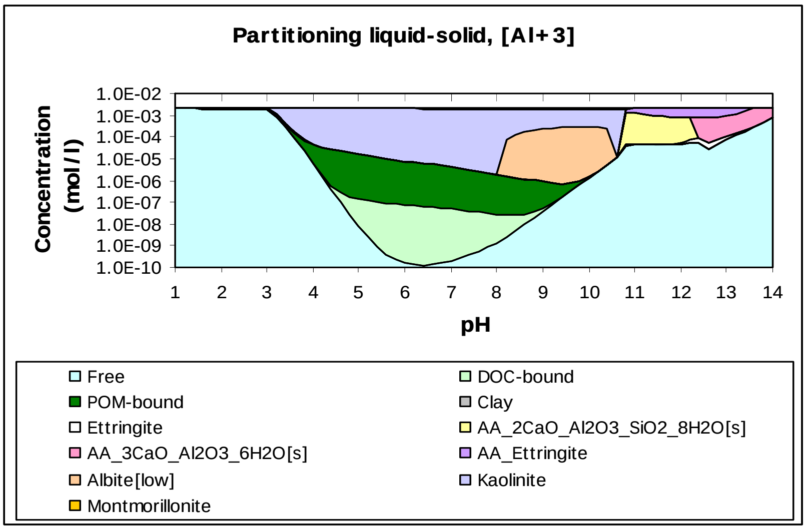


Figure 7:123: Solubility controlling mineral phases for aluminium leaching from stabilised clay with 1% humic acid at 150 days

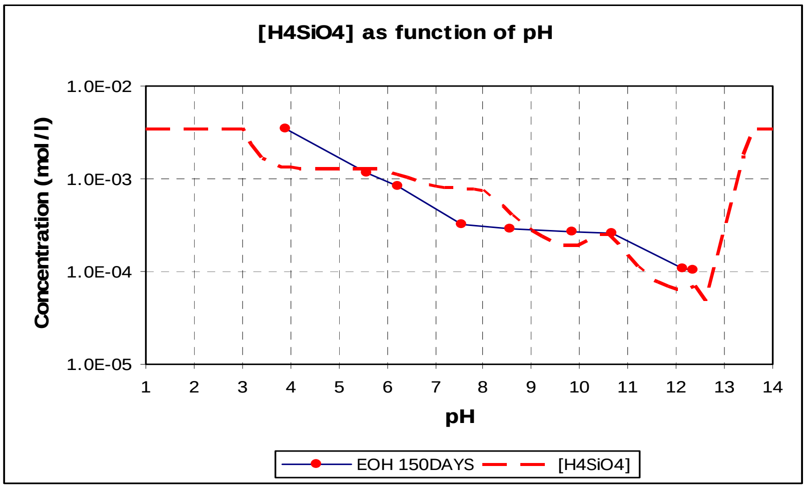


Figure 7:124: Silicic acid predicted and measured release trend from stabilised clay with 1% humic acid at 150 days

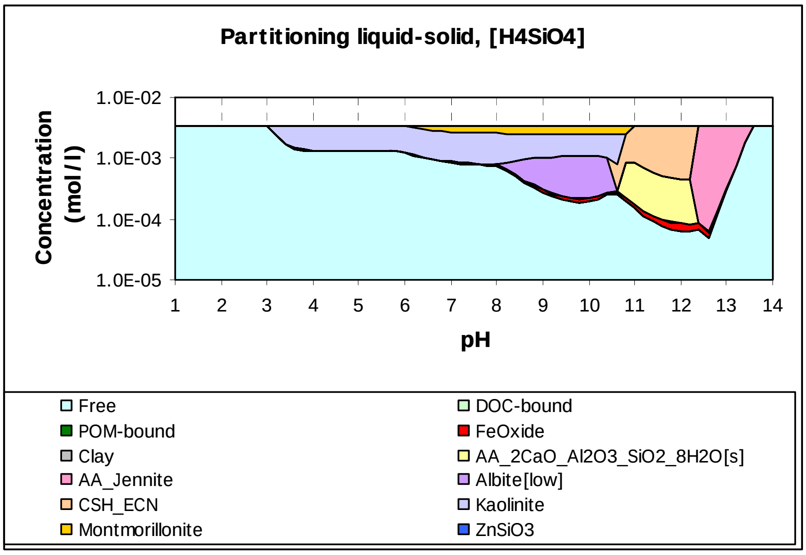


Figure 7:125: Solubility controlling mineral phases for silicic acid leaching from stabilised clay with 1% humic acid at 150 days

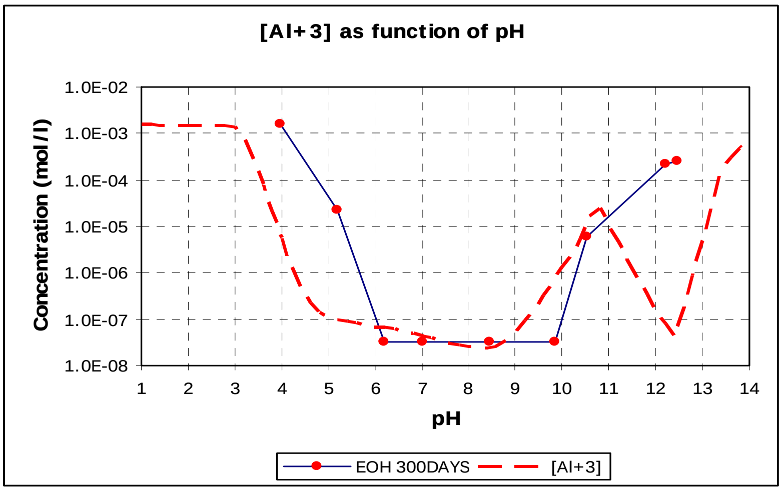


Figure 7:126: Aluminium predicted and measured release trend from stabilised clay with 1% humic acid at 300 days

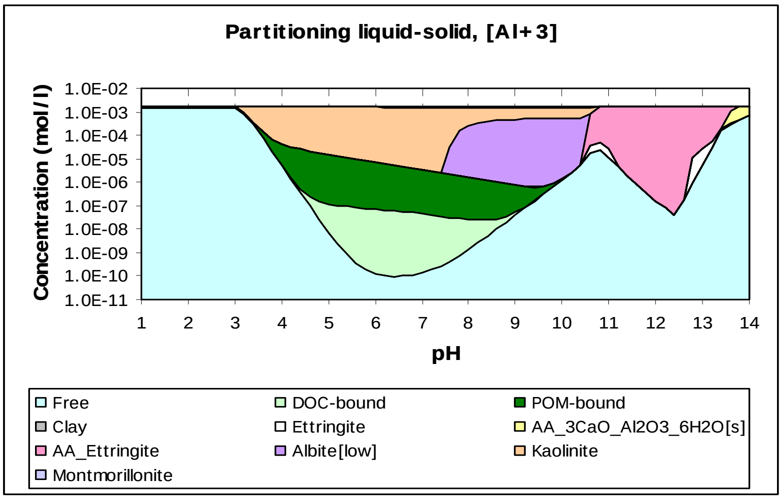


Figure 7:127: Solubility controlling mineral phases for aluminium leaching from stabilised clay with 1% humic acid at 300 days

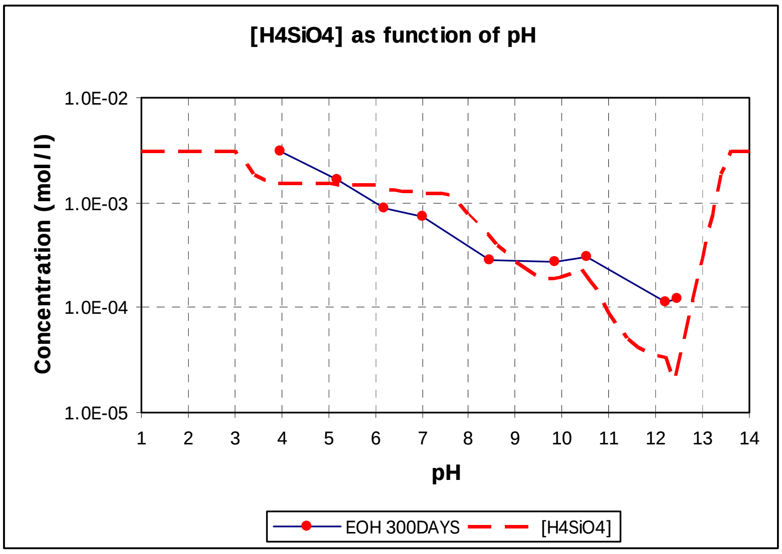


Figure 7:128: Silicic acid predicted and measured release trend from stabilised clay with 1% humic acid at 300 days

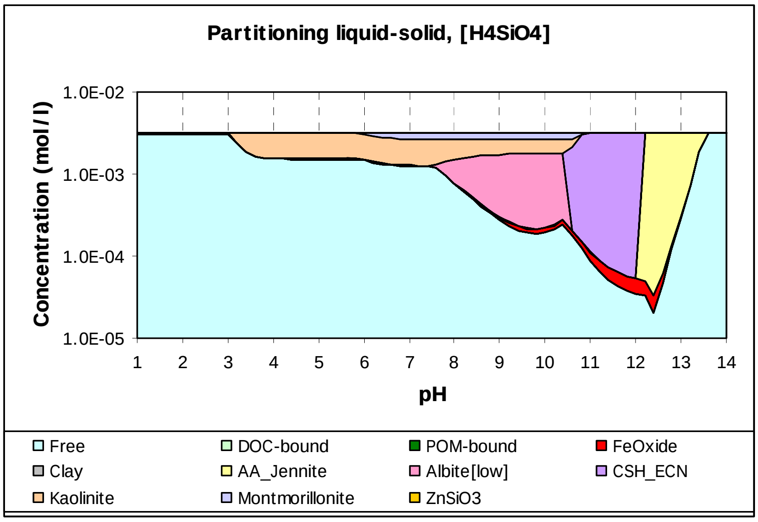


Figure 7:129: Solubility controlling mineral phases for silicic acid leaching from stabilised clay with 1% humic acid at 300 days

7.4.2 Stabilised Zinc Contaminated Kaolin Clay with 1% Humic Acid

To evaluate the implications of increased organic carbon on zinc containment, leaching and speciation evaluations were undertaken on stabilised zinc contaminated kaolin clay with 1% humic acid. Results for aluminium, silicon and zinc were then presented for different hydration durations. Measured releases and trends for all pre-selected components, due to pH influence are shown in Figures 7.130, 7.131 and 7.132, for leaching at 28, 150 and 300 days of hydration respectively.

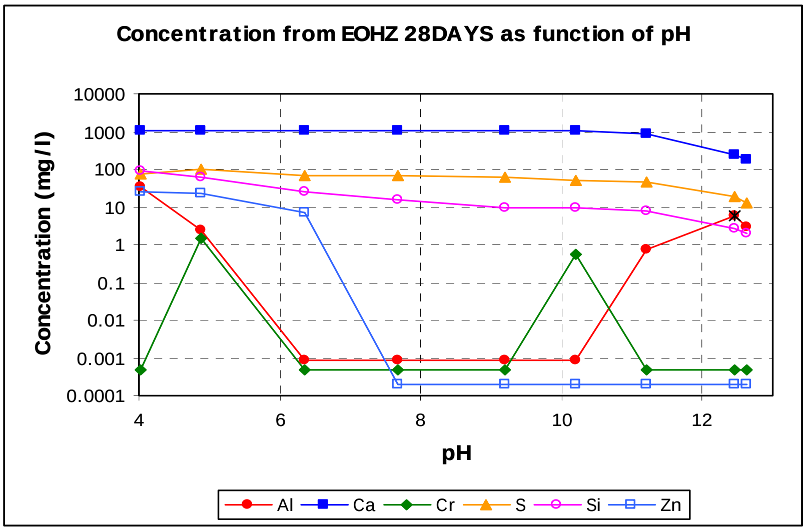


Figure 7:130: Releases of selected components from stabilised zinc contaminated clay with 1% humic acid due to pH influence at 28 days

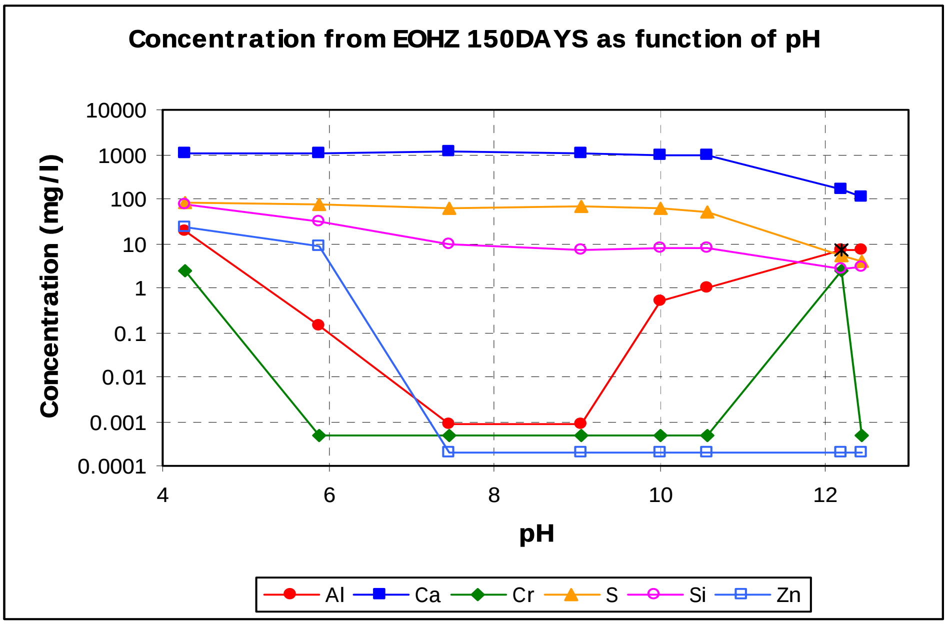


Figure 7:131: Releases of selected components from stabilised zinc contaminated clay with 1% humic acid due to pH influence at 150 days

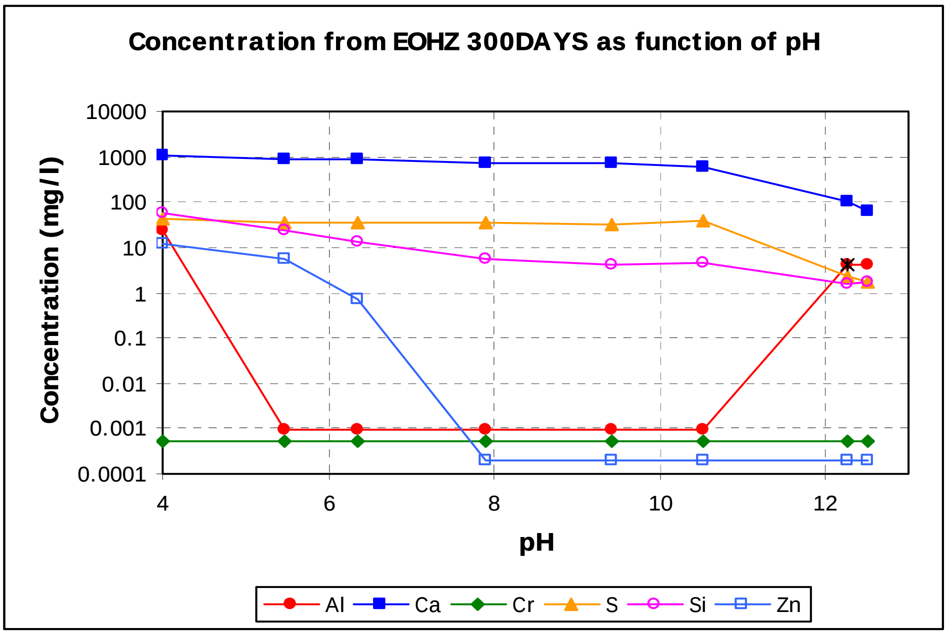


Figure 7:132: Releases of selected components from stabilised zinc contaminated clay with 1% humic acid due to pH influence at 300 days

For leaching at 28 days of hydration, Figures 7.133 and 7.134 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.134 and 7.135, and those for zinc releases shown in Figures 7.136 and 7.137.

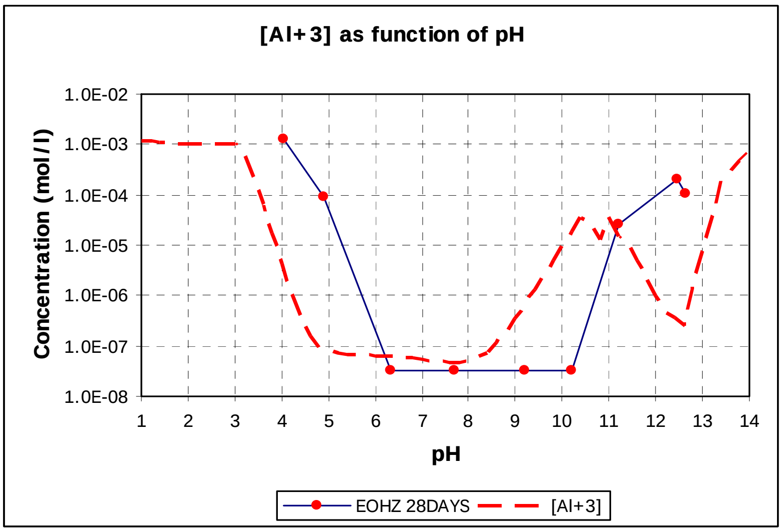


Figure 7:133: Aluminium predicted and measured release trend from stabilised zinc contaminated clay with 1% humic acid at 28 days

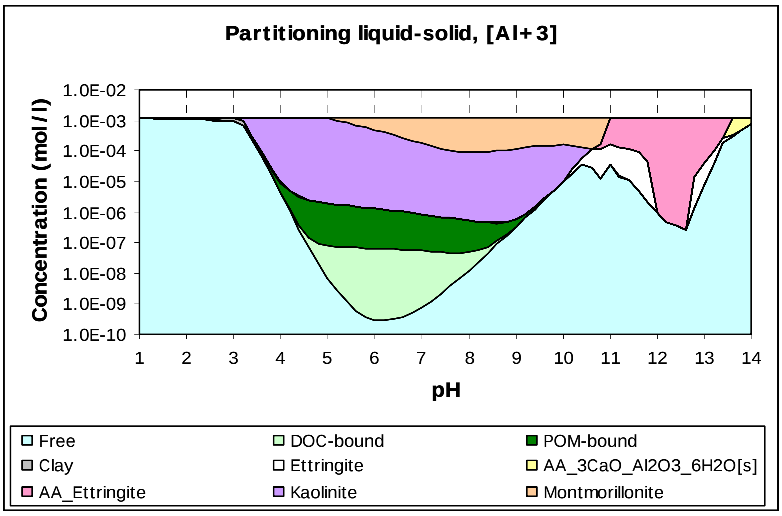


Figure 7:134: Solubility controlling mineral phases for aluminium leaching from stabilised zinc contaminated clay with 1% humic acid at 28 days

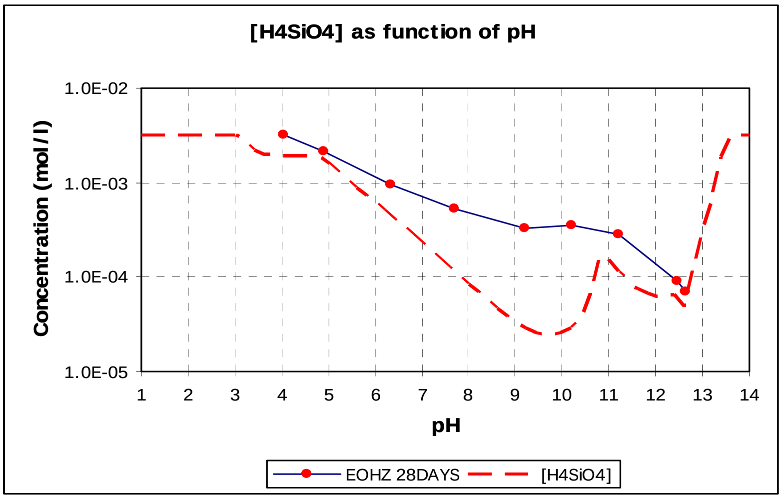


Figure 7:135: Silicic acid predicted and measured release trend from stabilised zinc contaminated clay with 1% humic acid at 28 days

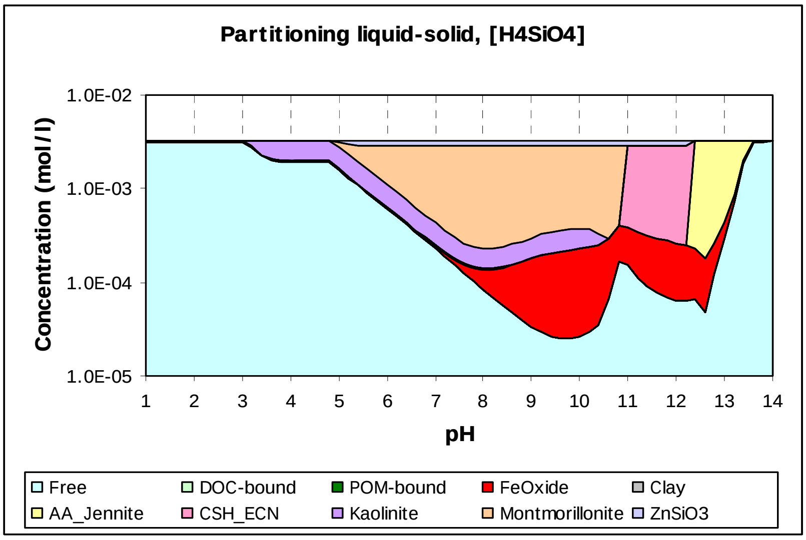


Figure 7:136: Solubility controlling mineral phases for silicic acid leaching from stabilised zinc contaminated clay with 1% humic acid at 28 days

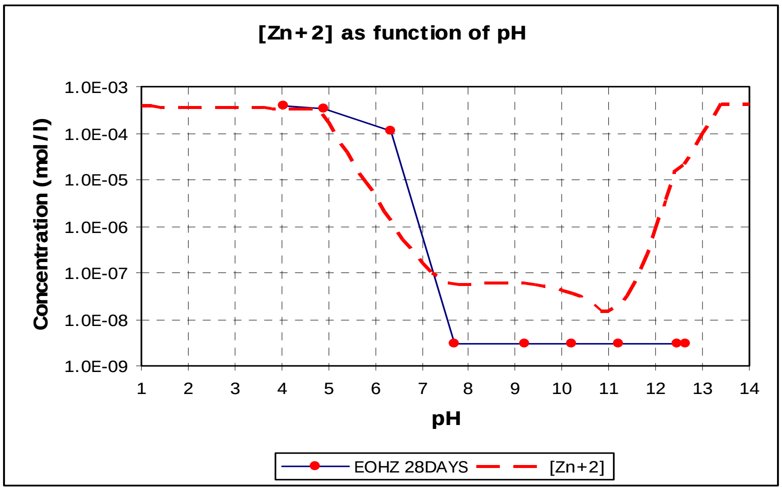


Figure 7:137: Zinc predicted and measured release trend from stabilised zinc contaminated clay with 1% humic acid at 28 days

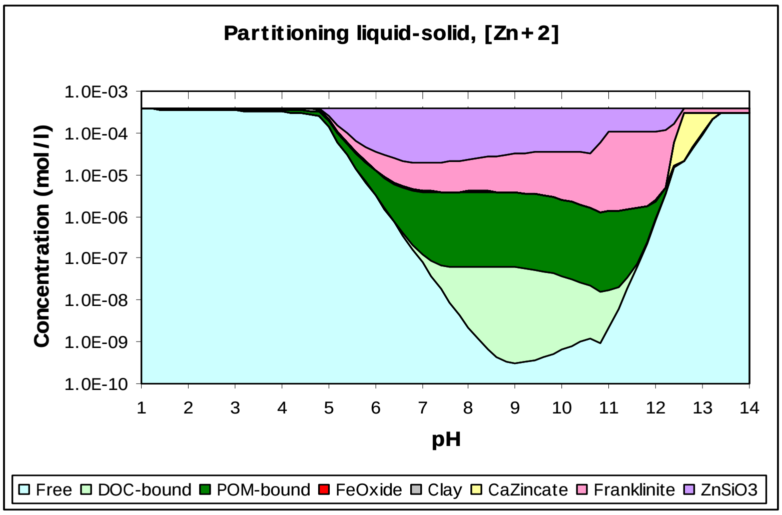


Figure 7:138: Solubility controlling mineral phases for zinc leaching from stabilised zinc contaminated clay with 1% humic acid at 28 days

For leaching at 150 days of hydration, Figures 7.138 and 7.139 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.140 and 7.141, and those for zinc shown in Figures 7.142 and 7.143.

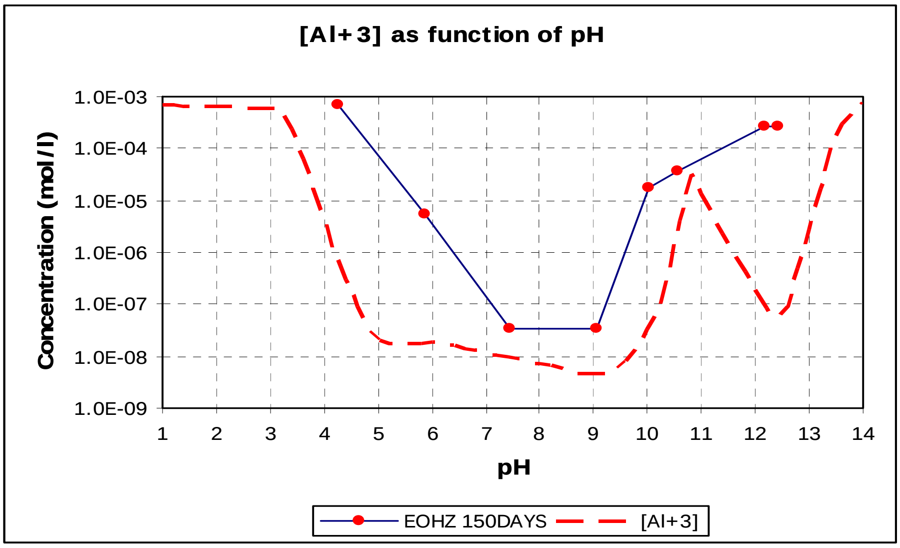


Figure 7:139: Aluminium predicted and measured release trend from stabilised zinc contaminated clay with 1% humic acid at 150 days

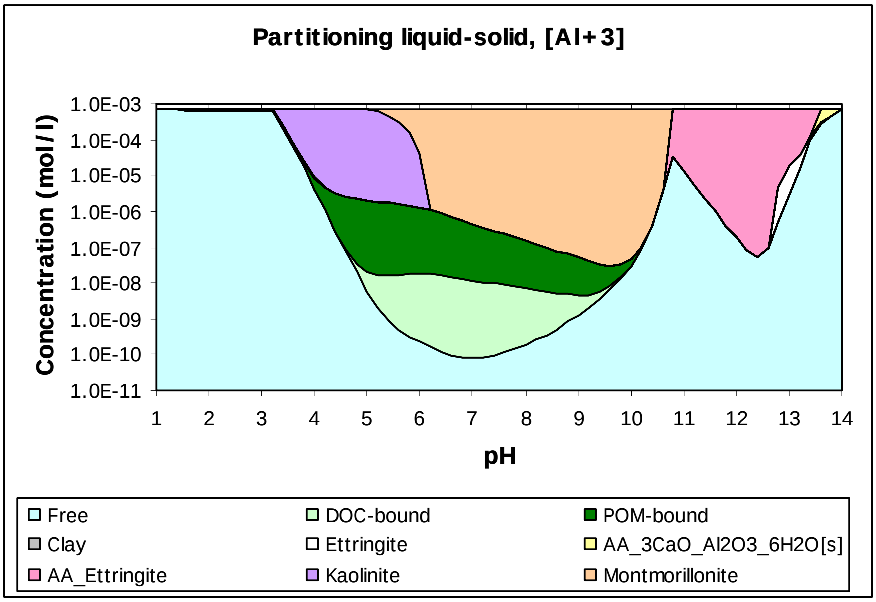


Figure 7:140: Solubility controlling mineral phases for aluminium leaching from stabilised zinc contaminated clay with 1% humic acid at 150 days

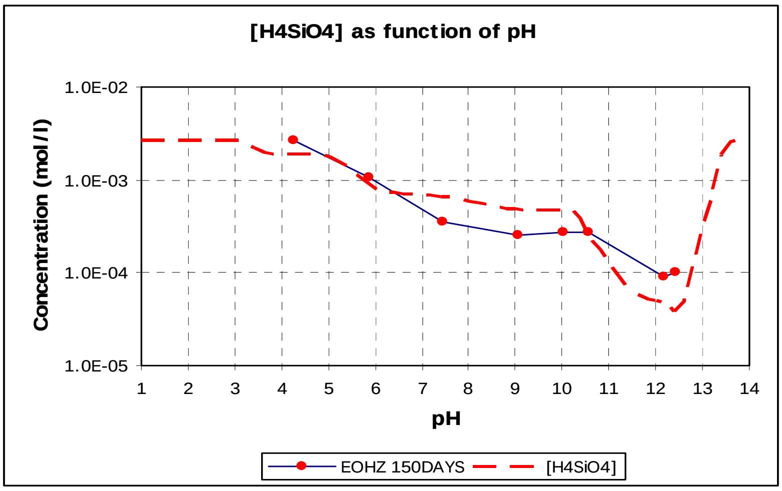


Figure 7:141: Silicic acid predicted and measured release trend from stabilised zinc contaminated clay with 1% humic acid at 150 days

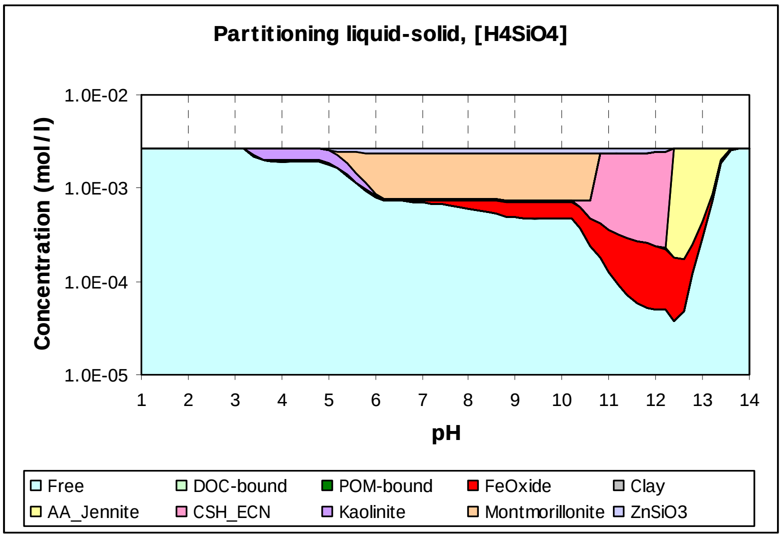


Figure 7:142: Solubility controlling mineral phases for silicic acid leaching from stabilised zinc contaminated clay with 1% humic acid at 150 days

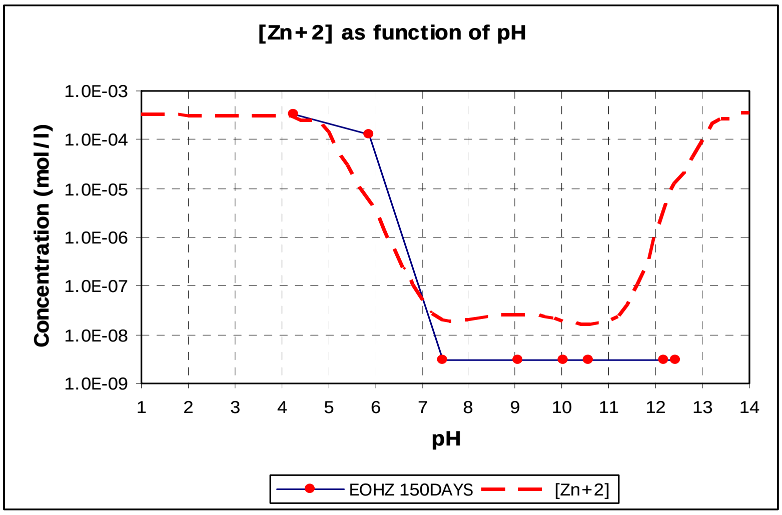


Figure 7:143: Zinc predicted and measured release trend from stabilised zinc contaminated clay with 1% humic acid at 150 days

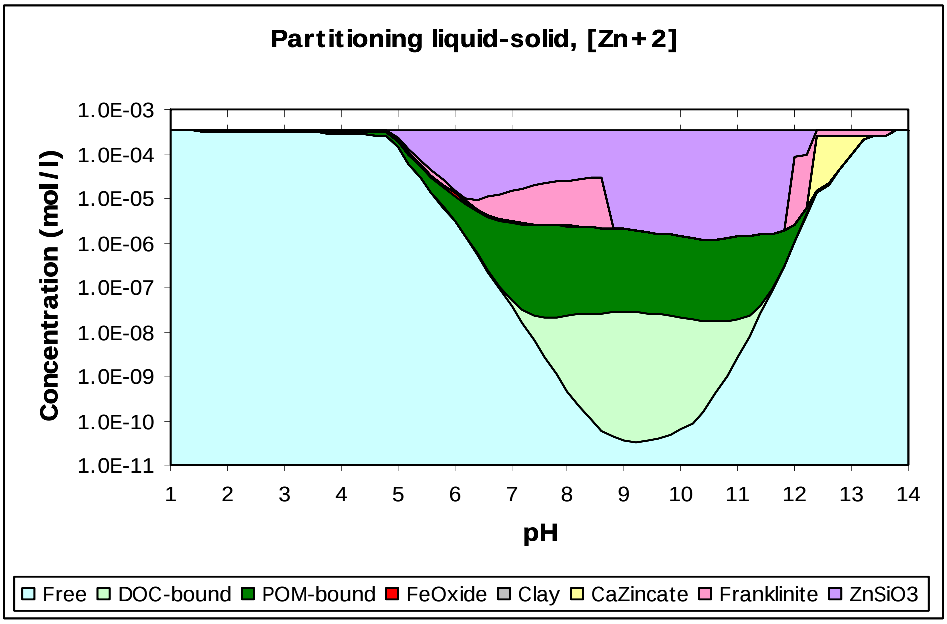


Figure 7:144: Solubility controlling mineral phases for zinc leaching from stabilised zinc contaminated clay with 1% humic acid at 150 days

For leaching at 300 days of hydration, Figures 7.144 and 7.145 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.146 and 7.147, and those for zinc shown in Figures 7.148 and 7.149, for leaching from the stabilised zinc contaminated kaolin clay with 1% humic acid.

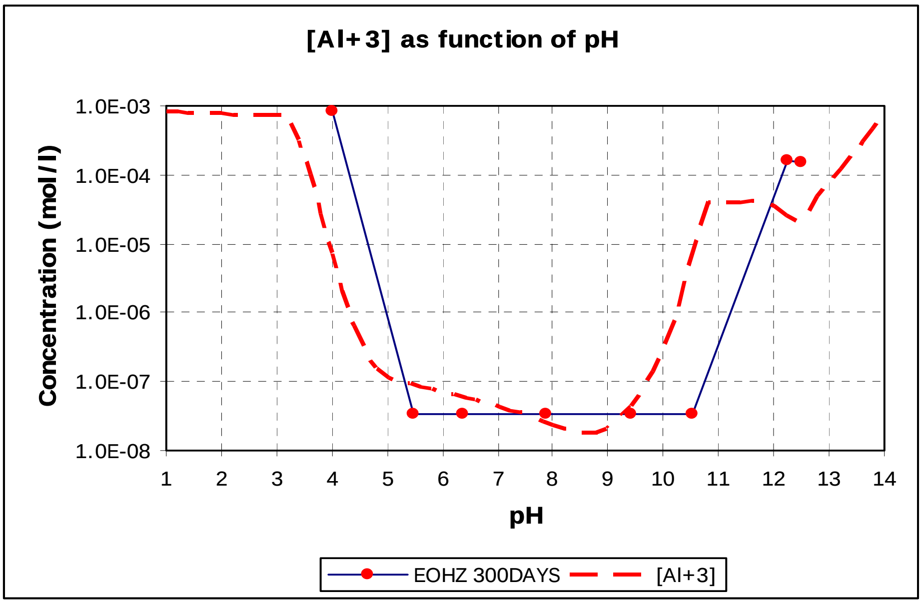


Figure 7:145: Aluminium predicted and measured release trend from stabilised zinc contaminated clay with 1% humic acid at 300 days

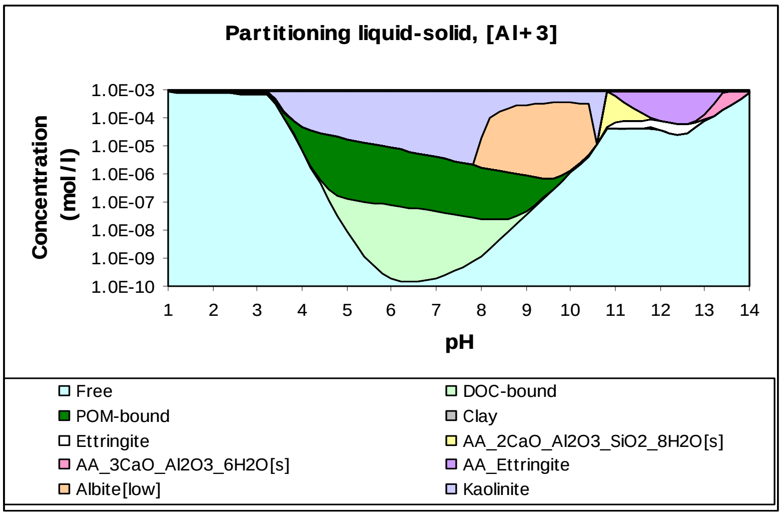


Figure 7:146: Solubility controlling mineral phases for aluminium leaching from stabilised zinc contaminated clay with 1% humic acid at 300 days

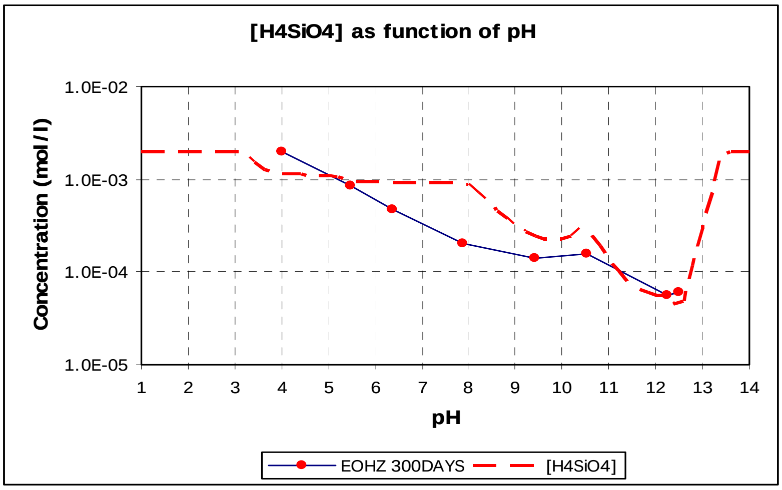


Figure 7:147: Silicic acid predicted and measured release trend from stabilised zinc contaminated clay with 1% humic acid at 300 days

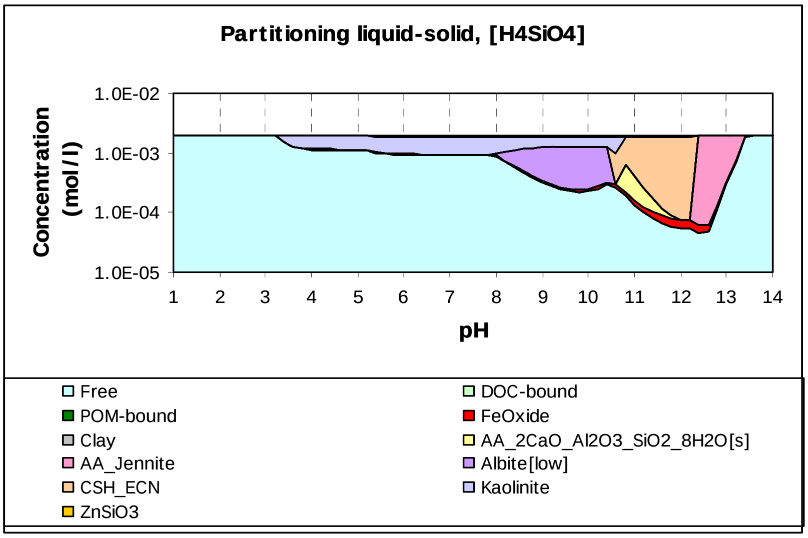


Figure 7:148: Solubility controlling mineral phases for silicic acid leaching from stabilised zinc contaminated clay with 1% humic acid at 300 days

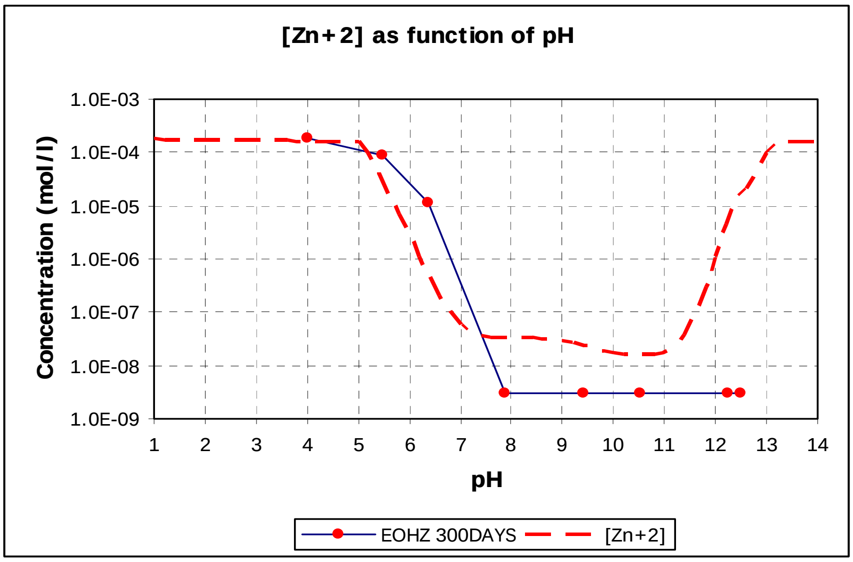


Figure 7:149: Zinc predicted and measured release trend from stabilised zinc contaminated clay with 1% humic acid at 300 days

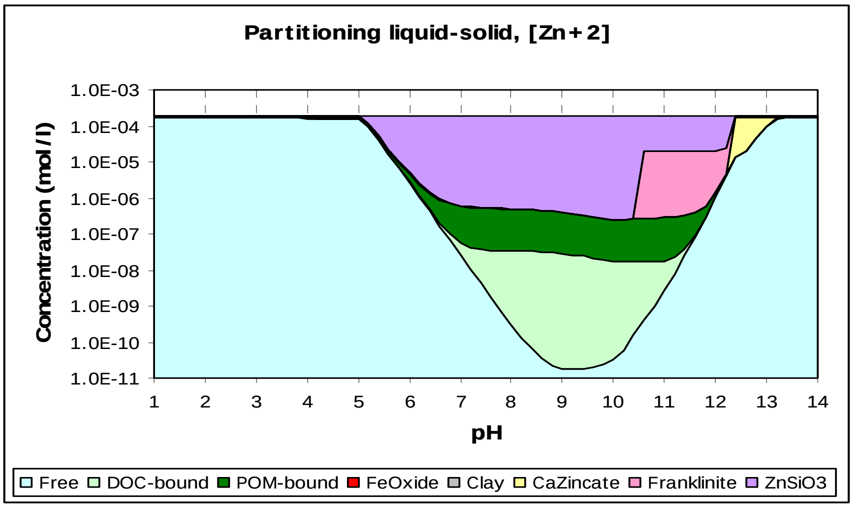


Figure 7:150: Solubility controlling mineral phases for zinc leaching from stabilised zinc contaminated clay with 1% humic acid at 300 days

7.4.3 Stabilised Chromium Contaminated Kaolin Clay with 1% Humic Acid

To evaluate the implication of increased organic carbon on chromium containment, leaching and speciation evaluations were undertaken on stabilised chromium contaminated kaolin clay with 1% humic acid. Results for aluminium, silicon and chromium were evaluated and presented for the different hydration durations. Results for releases and trends of pre-selected components, due to leaching under pH influence at 28, 150 and 300 days of hydration, are shown in Figures 7.151, 7.152 and 7.153 respectively.

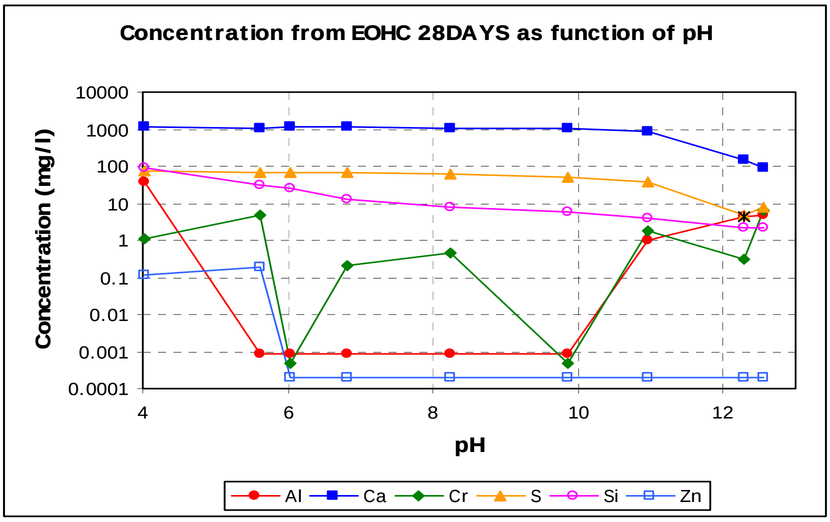


Figure 7:151: Releases of selected components from stabilised chromium contaminated clay with 1% humic acid due to pH influence at 28 days

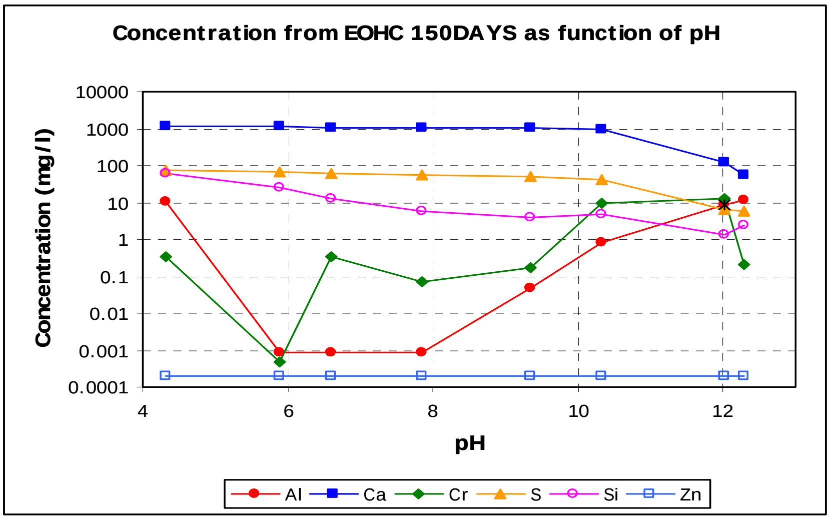


Figure 7:152: Releases of selected components from stabilised chromium contaminated clay with 1% humic acid due to pH influence at 150 days

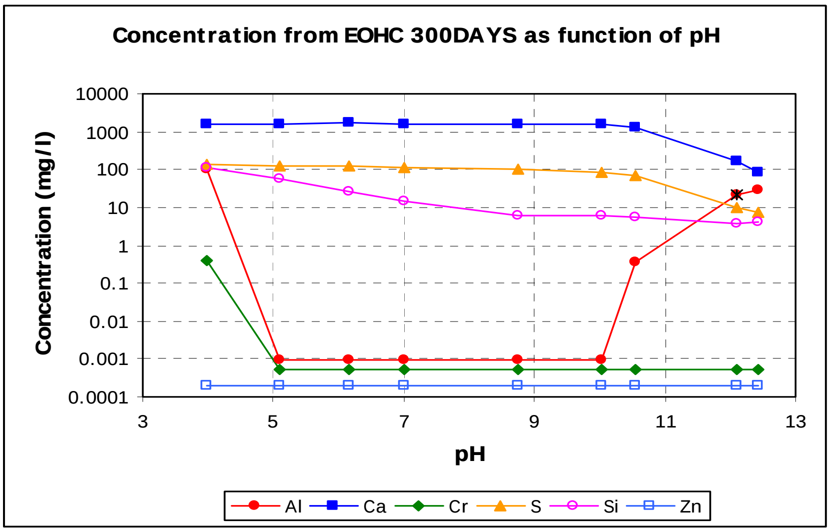


Figure 7:153: Releases of selected components from stabilised chromium contaminated clay with 1% humic acid due to pH influence at 300 days

For leaching at 28 days of hydration, Figures 7.154 and 7.155 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.156 and 7.157, and those for chromium shown in Figures 7.158 and 7.159.

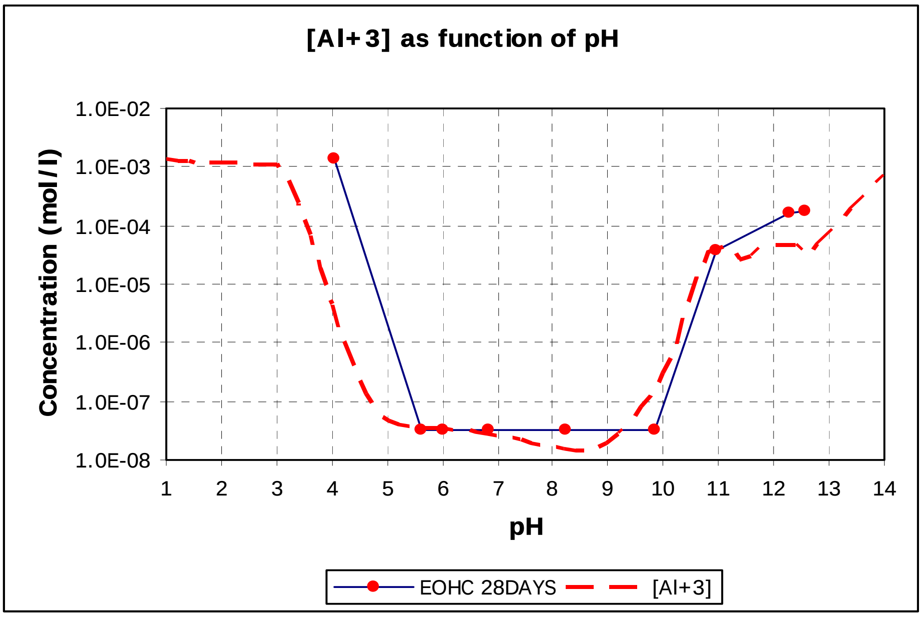


Figure 7:154: Aluminium predicted and measured release trend from stabilised chromium contaminated clay with 1% humic acid at 28 days

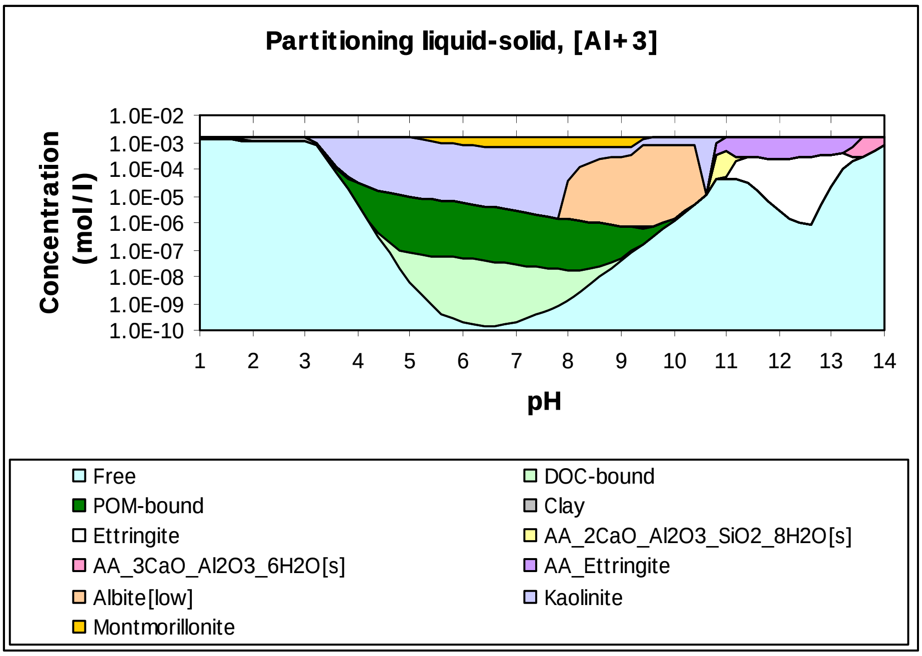


Figure 7:155: Solubility controlling mineral phases for aluminium leaching from stabilised chromium contaminated clay with 1% humic acid at 28 days

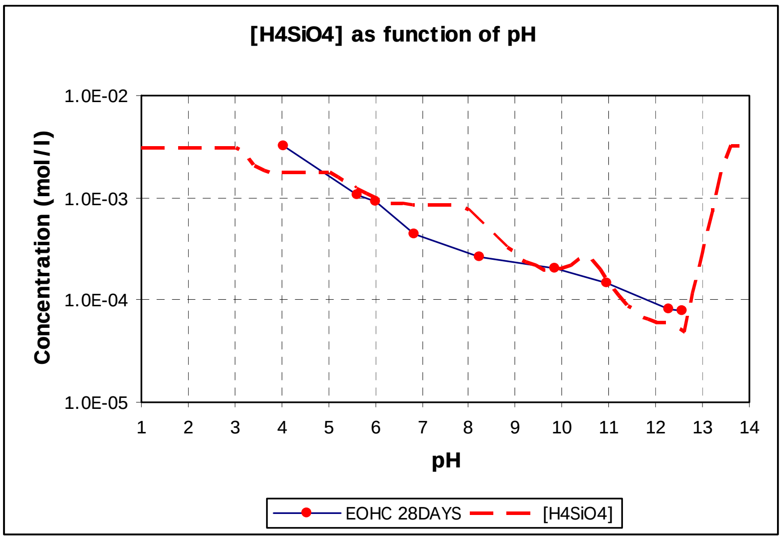


Figure 7:156: Silicic acid predicted and measured release trend from stabilised chromium contaminated clay with 1% humic acid at 28 days

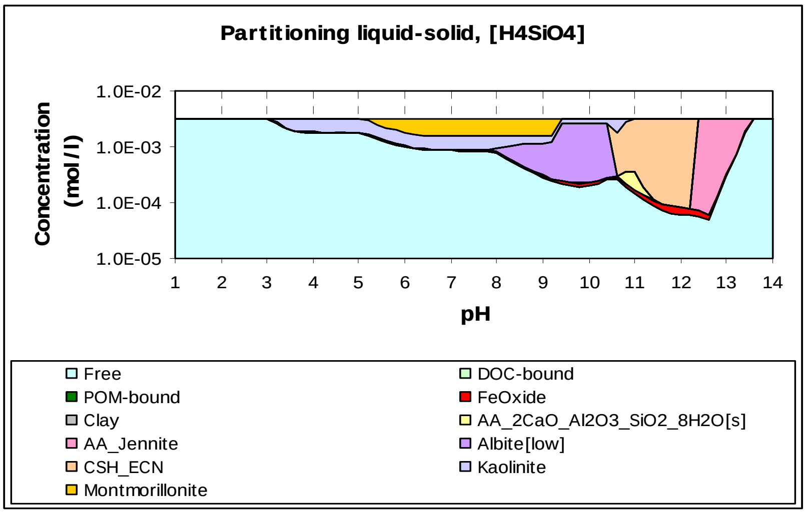


Figure 7:157: Solubility controlling mineral phases for silicic acid leaching from stabilised chromium contaminated clay with 1% humic acid at 28 days

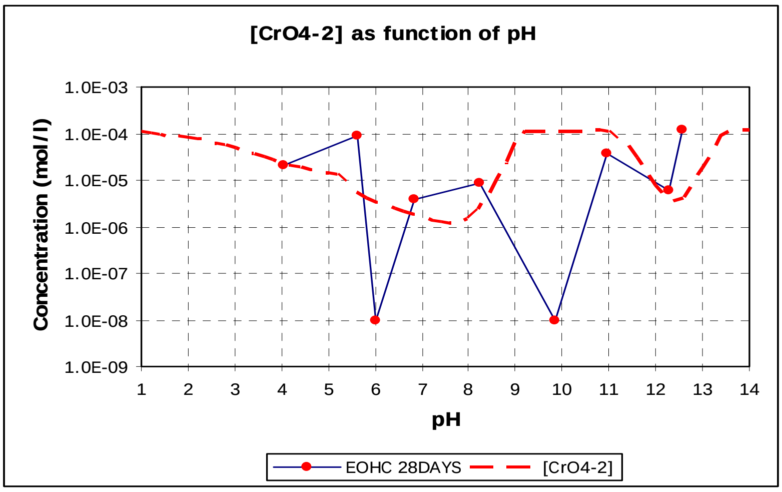


Figure 7:158: Chromate predicted and measured release trend from stabilised chromium contaminated clay with 1% humic acid at 28 days

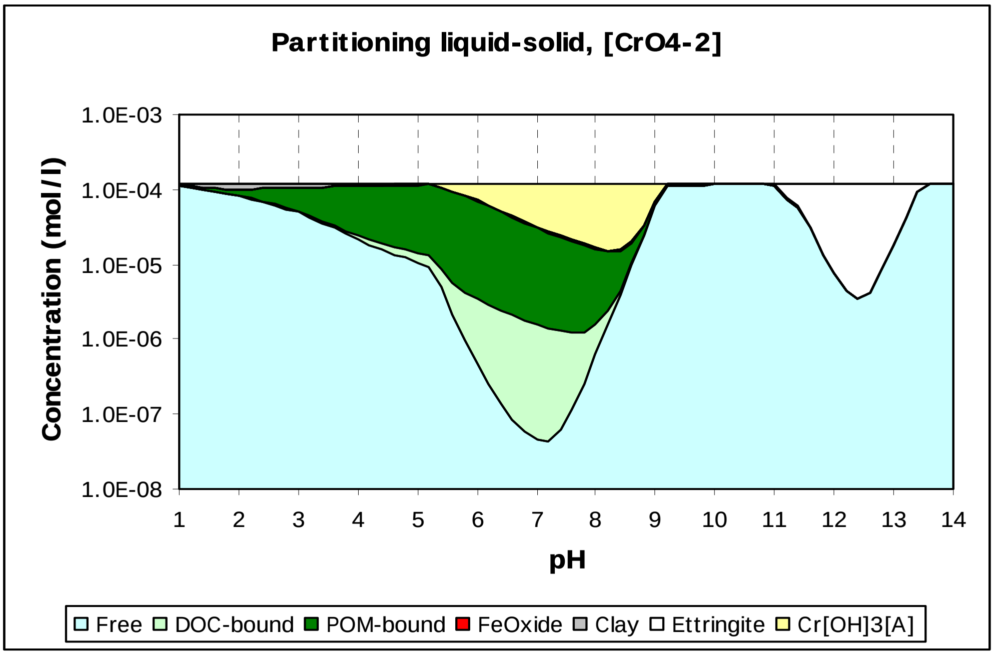


Figure 7:159: Solubility controlling mineral phases for chromate leaching from stabilised chromium contaminated clay with 1% humic acid at 28 days

For leaching at 150 days of hydration, Figures 7.160 and 7.161 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.162 and 7.163, and those for chromium releases shown in Figures 7.164 and 7.165.

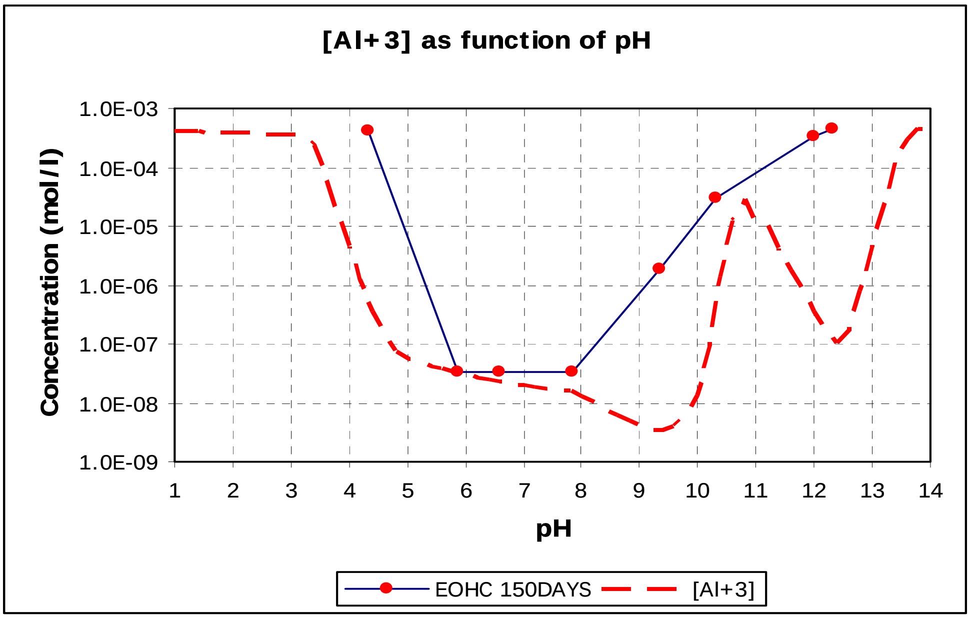


Figure 7:160: Aluminium predicted and measured release trend from stabilised chromium contaminated clay with 1% humic acid at 150 days

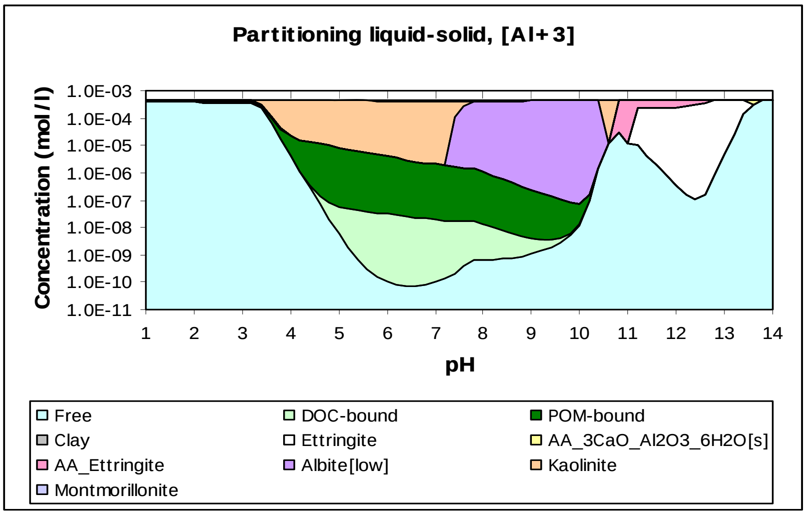


Figure 7:161: Solubility controlling mineral phases for aluminium leaching from stabilised chromium contaminated clay with 1% humic acid at 150 days

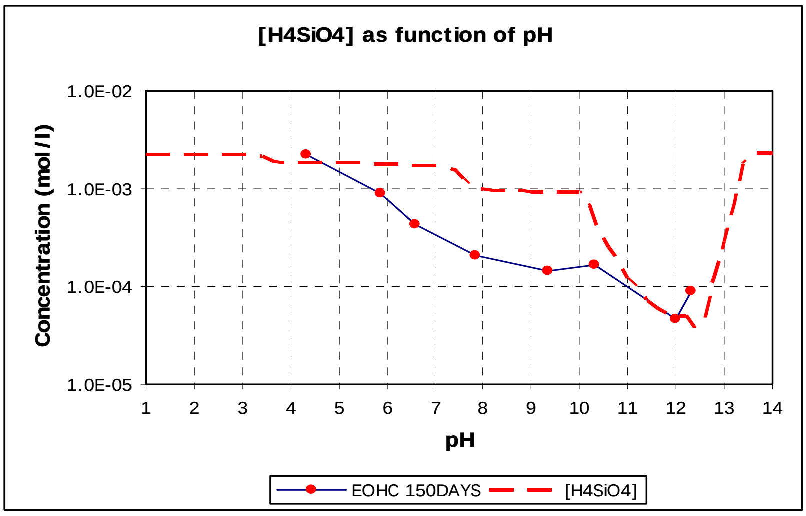


Figure 7:162: Silicic acid predicted and measured release trend from stabilised chromium contaminated clay with 1% humic acid at 150 days

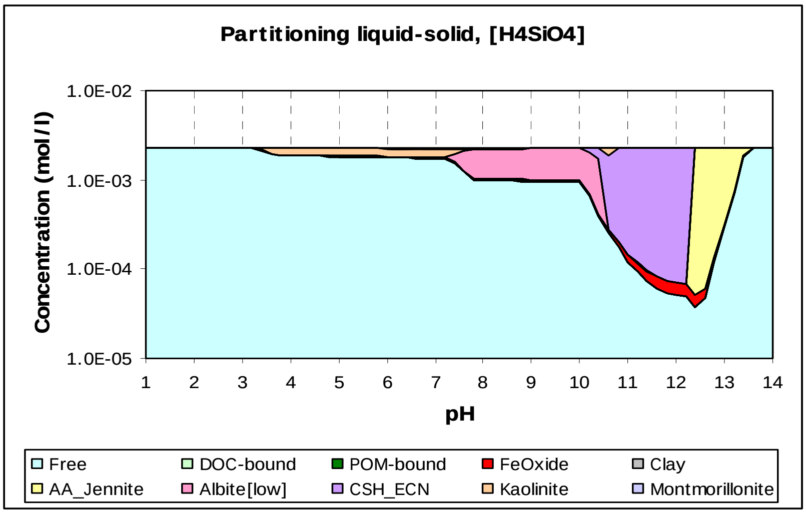


Figure 7:163: Solubility controlling mineral phases for silicic acid leaching from stabilised chromium contaminated clay with 1% humic acid at 150 days

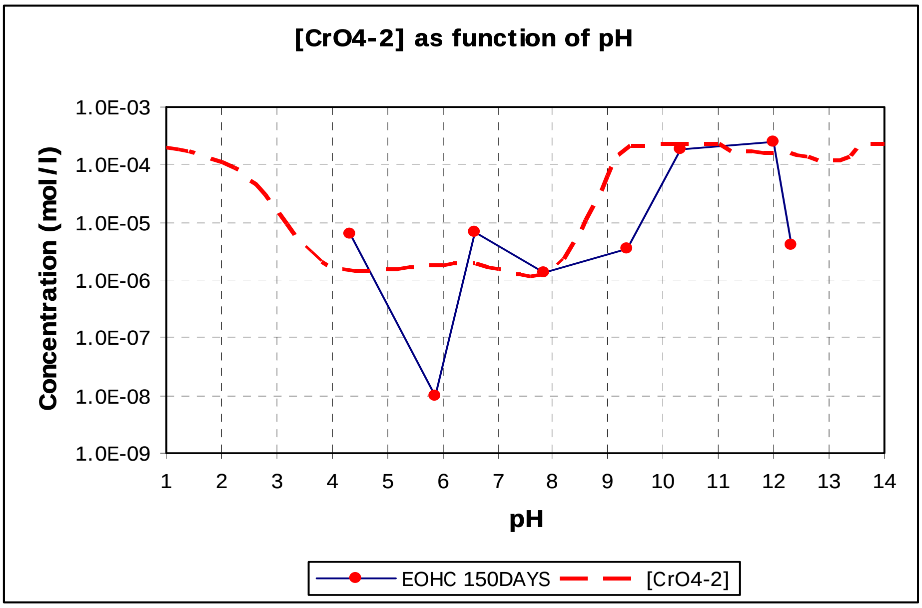


Figure 7:164: Chromate predicted and measured release trend from stabilised chromium contaminated clay with 1% humic acid at 150 days

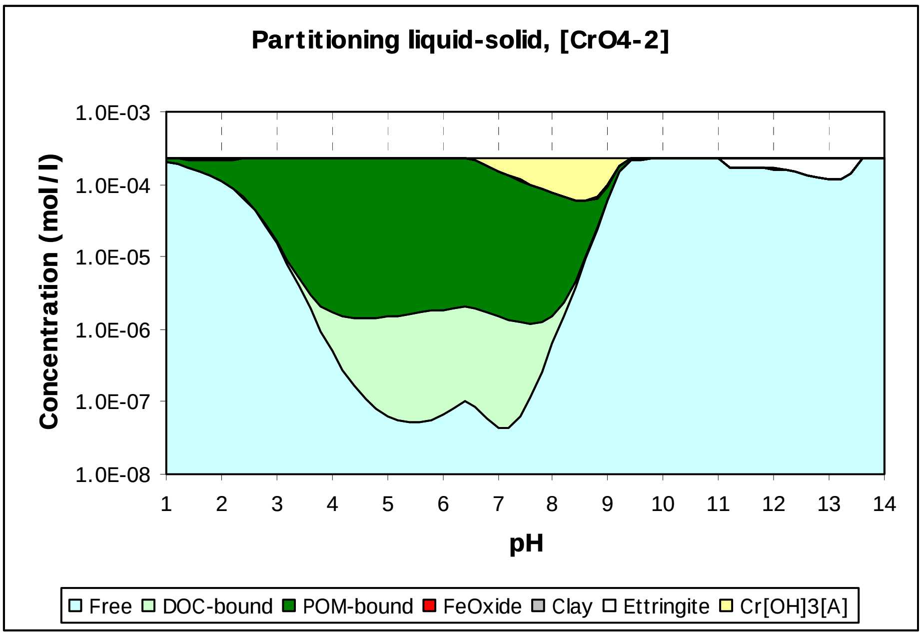


Figure 7:165: Solubility controlling mineral phases for chromate leaching from stabilised chromium contaminated clay with 1% humic acid at 150 days

For leaching at 300 days of hydration, Figures 7.166 and 7.167 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.168 and 7.169, and those for chromium shown in Figures 7.170 and 7.171, for leaching from the stabilised chromium contaminated kaolin clay with 1% humic acid.

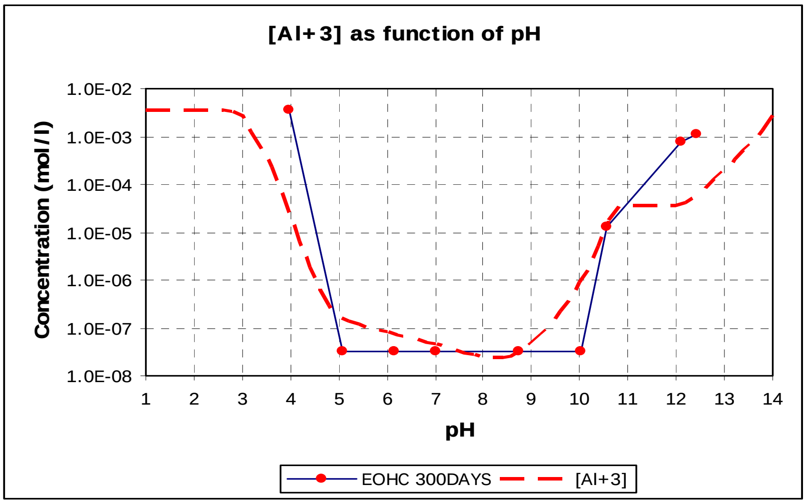


Figure 7:166: Aluminium predicted and measured release trend from stabilised chromium contaminated clay with 1% humic acid at 300 days

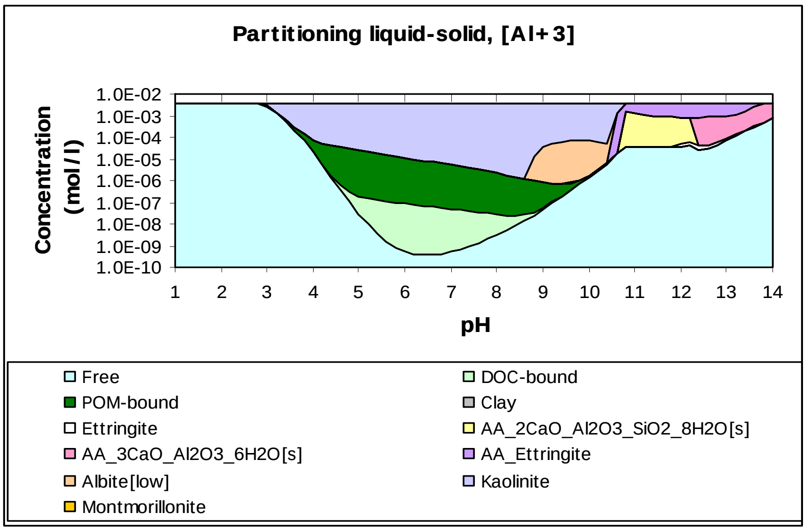


Figure 7:167: Solubility controlling mineral phases for aluminium leaching from stabilised chromium contaminated clay with 1% humic acid at 300 days

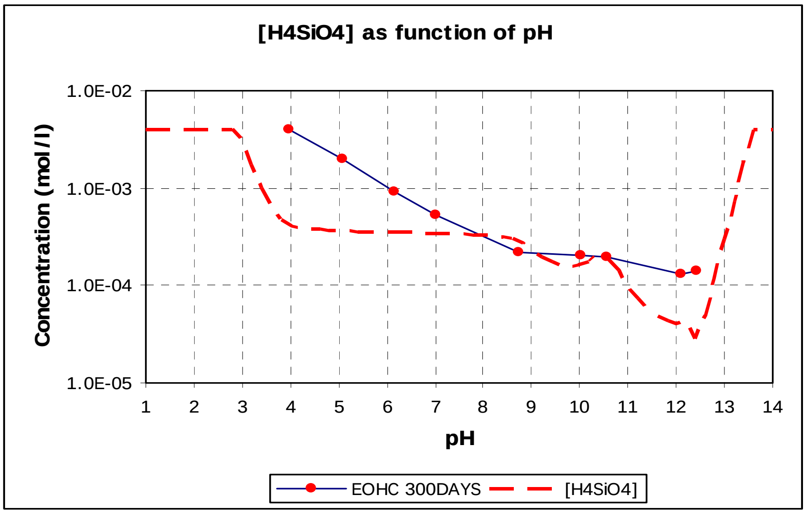


Figure 7:168: Silicic acid predicted and measured release trend from stabilised chromium contaminated clay with 1% humic acid at 300 days

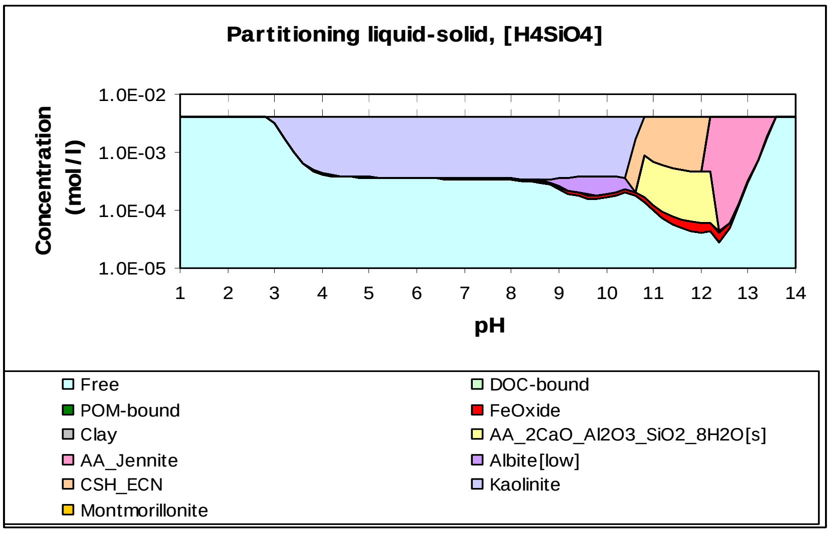


Figure 7:169: Solubility controlling mineral phases for silicic acid leaching from stabilised chromium contaminated clay with 1% humic acid at 300 days

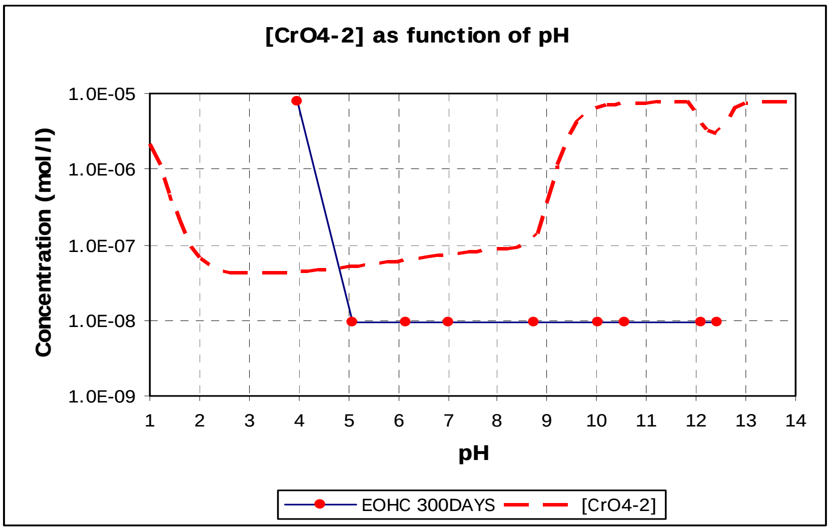


Figure 7:170: Chromate predicted and measured release trend from stabilised chromium contaminated clay with 1% humic acid at 300 days

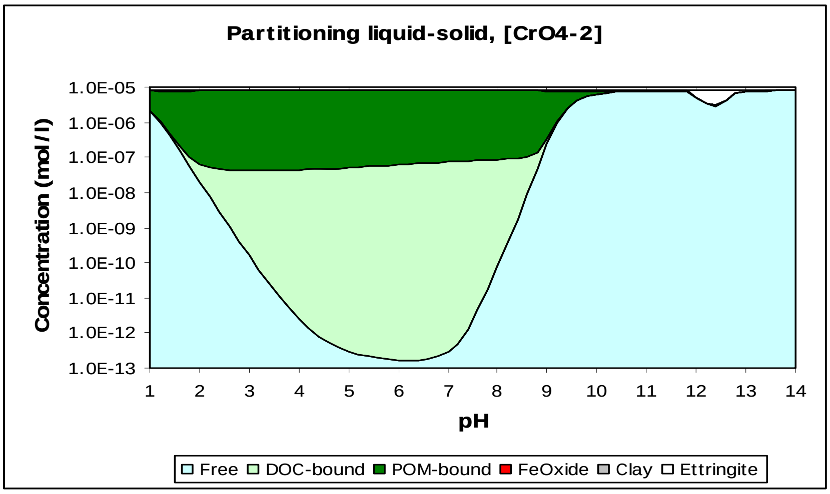


Figure 7:171: Solubility controlling mineral phases for chromate leaching from stabilised chromium contaminated clay with 1% humic acid at 300 days

7.5 CEMENT STABILISED CLAY WITH 2.5% SULPHATE

To evaluate the implications of increased sulphate content on components releases, leaching and speciation evaluations were undertaken on stabilised kaolin clay matrices with 2.5% sulphate. Results for aluminium, silicon and introduced contaminants (for contaminated matrices) were then evaluated and presented. However, while the matrices included an increased sulphate content, no changes in sulphur releases trends or speciation was observed. Expected increases in release concentrations were observed, but sulphate releases are not presented in this section. Modelling parameters used for speciation evaluations are shown in Table 7.1, and are similar to those for matrices without additives.

7.5.1 Uncontaminated Stabilised Kaolin Clay with 2.5% Sulphate

For uncontaminated sulphate matrices, evaluations for aluminium and silicon releases were undertaken, and results presented for different hydration durations. The releases and leaching trends of pre-selected components, due to pH influence, are shown in Figures 7.172, 7.173 and 7.174, for tests at 28, 150 and 300 days of hydration respectively.

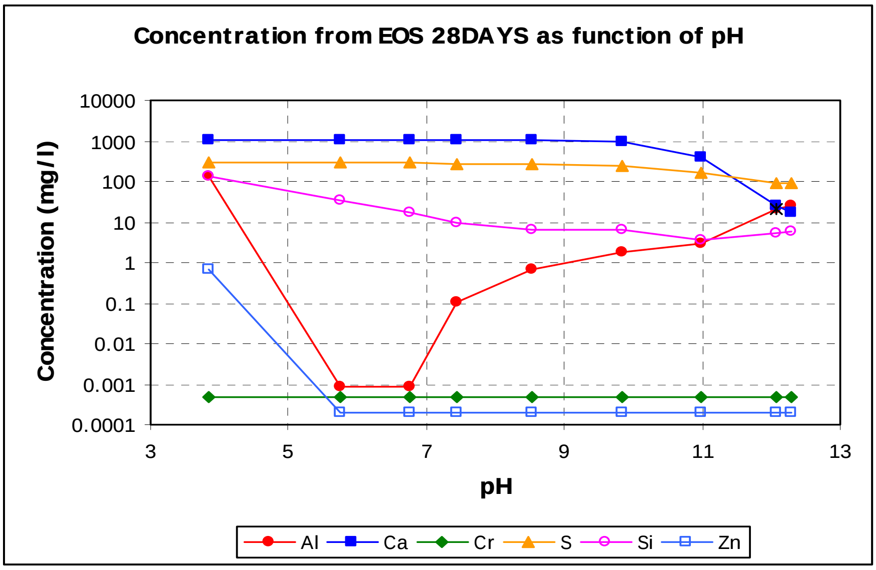


Figure 7:172: Releases of selected components from stabilised clay with 2.5% sulphate due to pH influence at 28 days

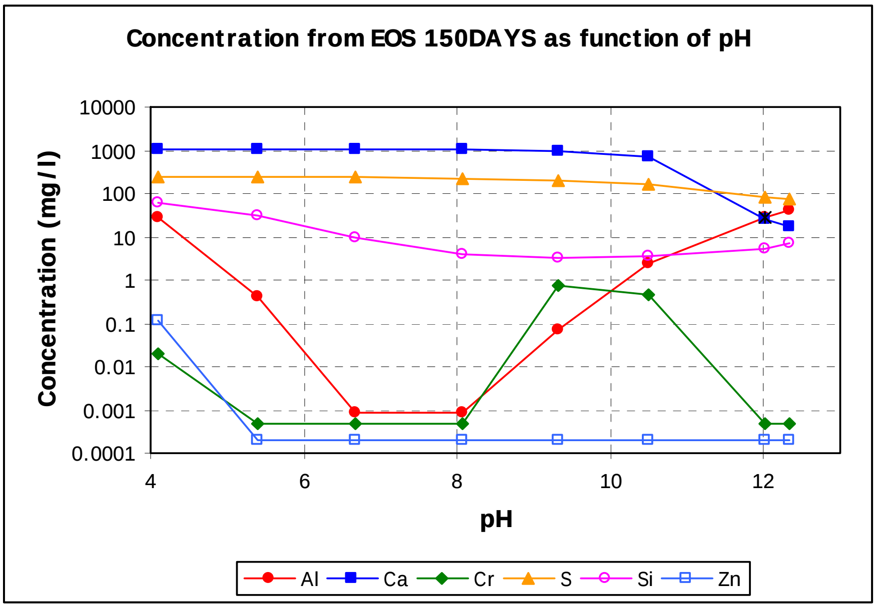


Figure 7:173: Releases of selected components from stabilised clay with 2.5% sulphate due to pH influence at 150 days

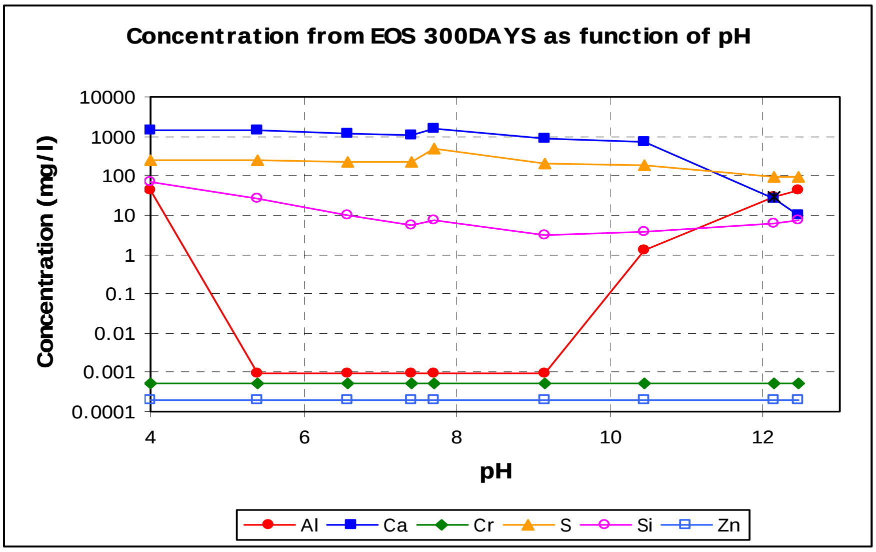


Figure 7:174: Releases of selected components from stabilised clay with 2.5% sulphate due to pH influence at 300 days

For leaching at 28 days of hydration, Figures 7.175 and 7.176 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.177 and 7.178. For leaching at 150 days of hydration, Figures 7.179 and 7.180 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.181 and 7.182.

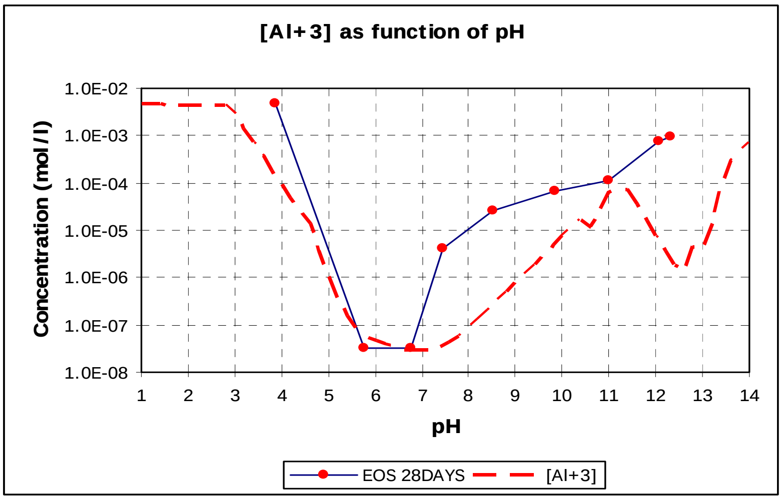


Figure 7:175: Aluminium predicted and measured release trend from stabilised clay with 2.5% sulphate at 28 days

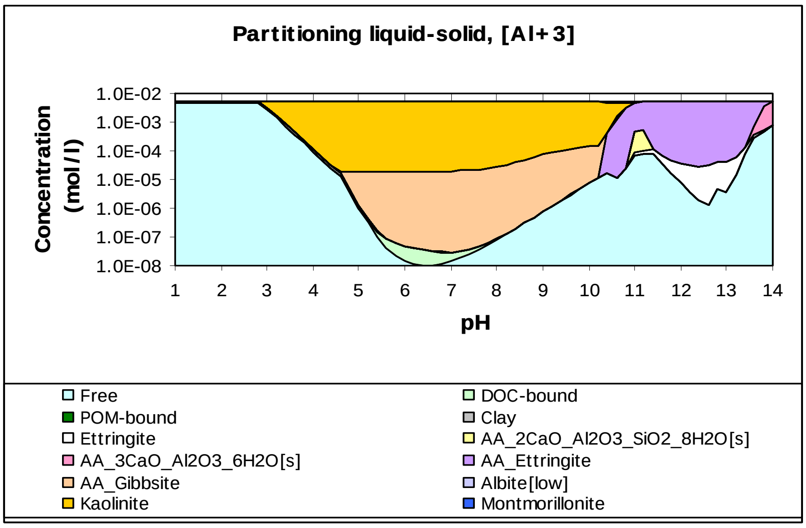


Figure 7:176: Solubility controlling mineral phases for aluminium leaching from stabilised clay with 2.5% sulphate at 28 days

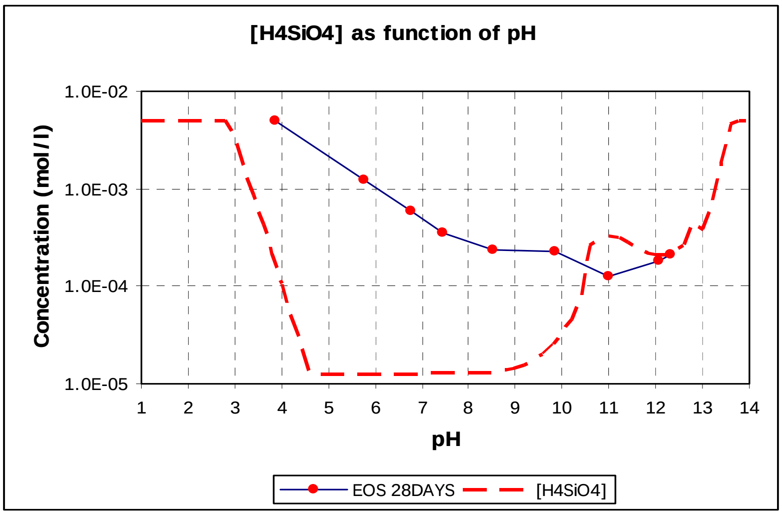


Figure 7:177: Silicic acid predicted and measured release trend from stabilised clay with 2.5% sulphate at 28 days

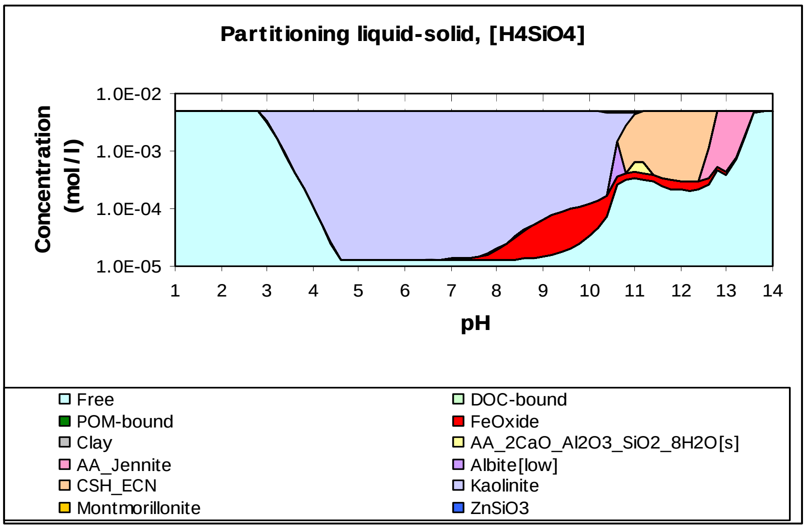


Figure 7:178: Solubility controlling mineral phases for silicic acid leaching from stabilised clay with 2.5% sulphate at 28 days

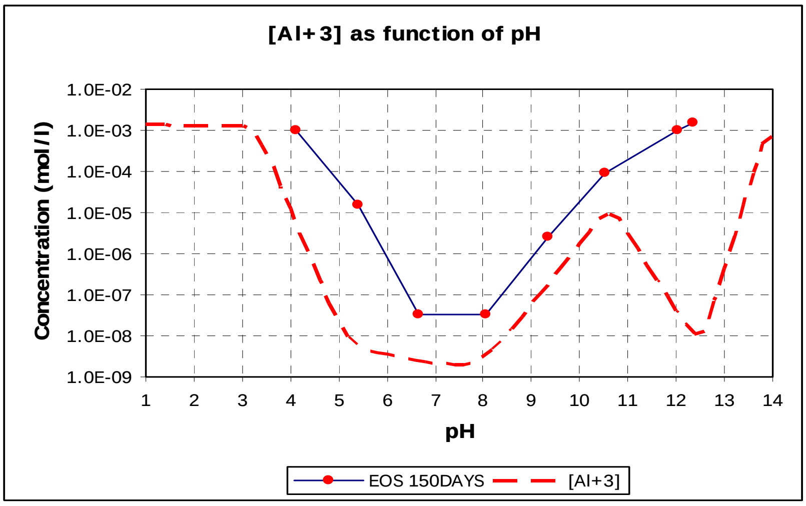


Figure 7:179: Aluminium predicted and measured release trend from stabilised clay with 2.5% sulphate at 150 days

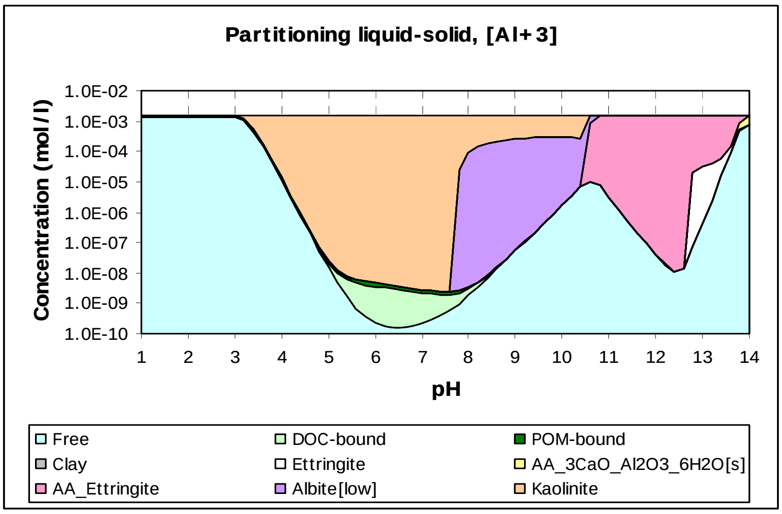


Figure 7:180: Solubility controlling mineral phases for aluminium leaching from stabilised clay with 2.5% sulphate at 150 days

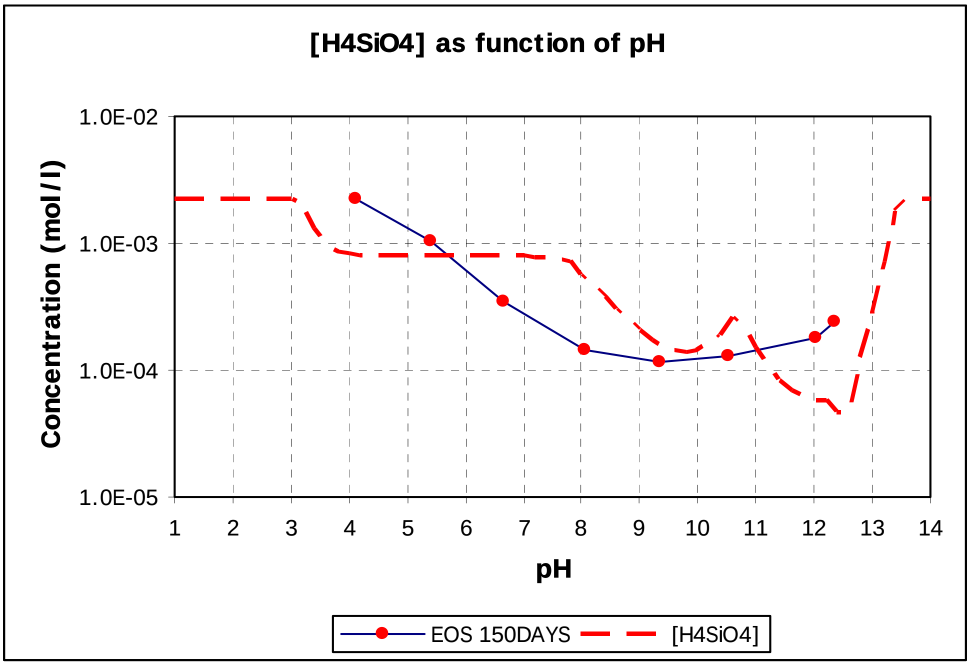


Figure 7:181: Silicic acid predicted and measured release trend from stabilised clay with 2.5% sulphate at 150 days

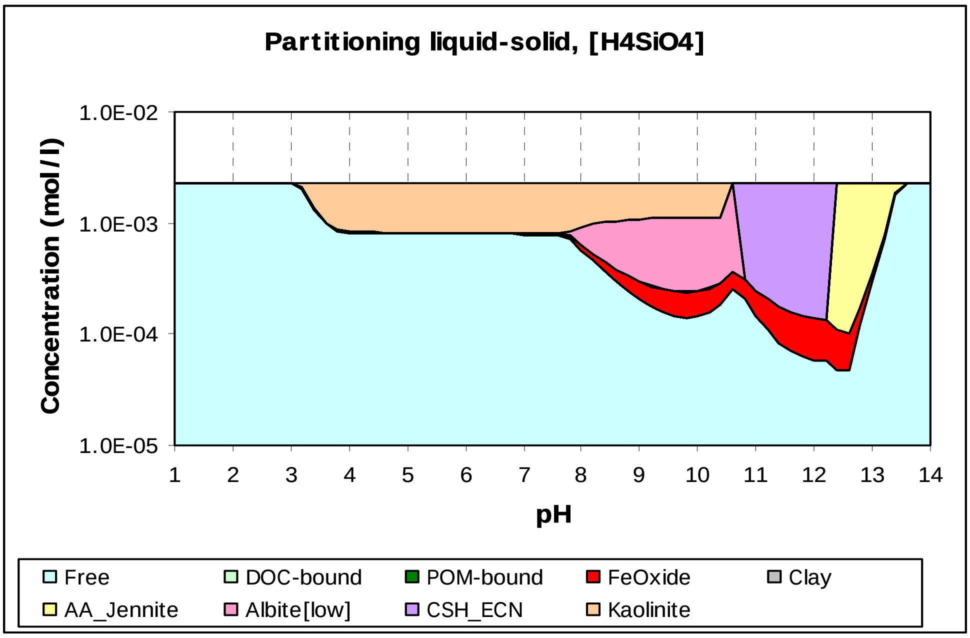


Figure 7:182: Solubility controlling mineral phases for silicic acid leaching from stabilised clay with 2.5% sulphate at 150 days

For leaching at 300 days of hydration, Figures 7.183 and 7.184 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figure 7.185 and 7.186, for leaching from stabilised kaolin clay with 2.5% sulphate.

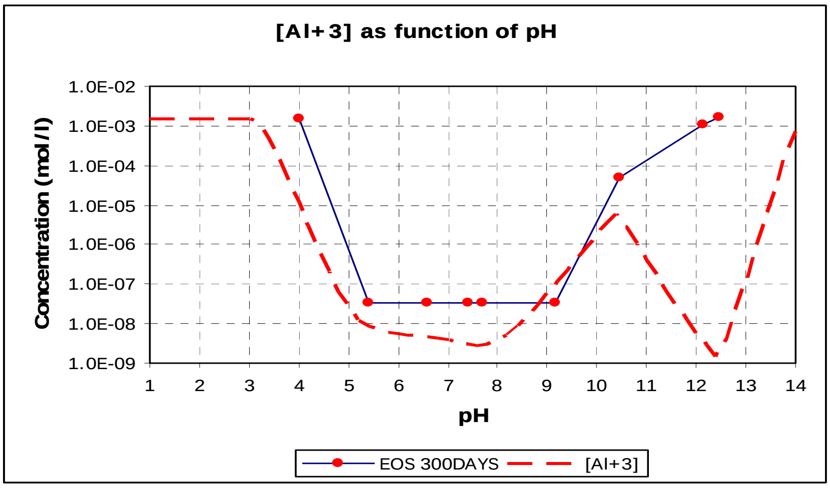


Figure 7:183: Aluminium predicted and measured release trend from stabilised clay with 2.5% sulphate at 300 days

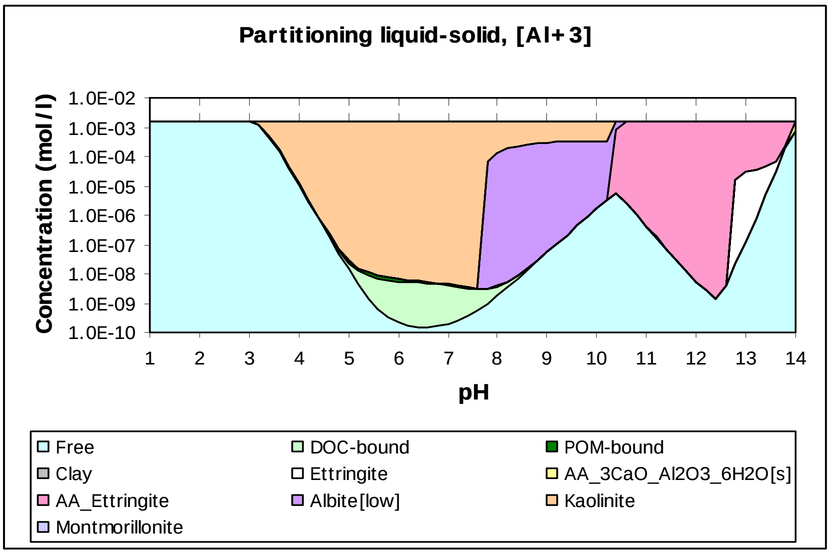


Figure 7:184: Solubility controlling mineral phases for aluminium leaching from stabilised clay with 2.5% sulphate at 300 days

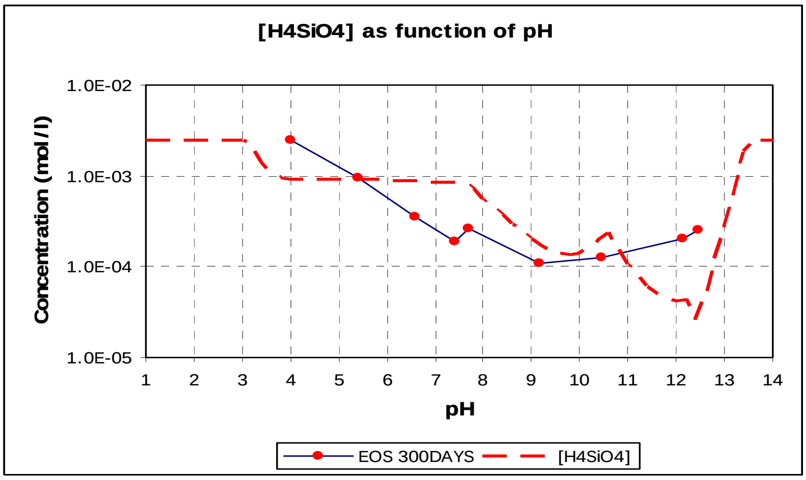


Figure 7:185: Silicic acid predicted and measured release trend from stabilised clay with 2.5% sulphate at 300 days

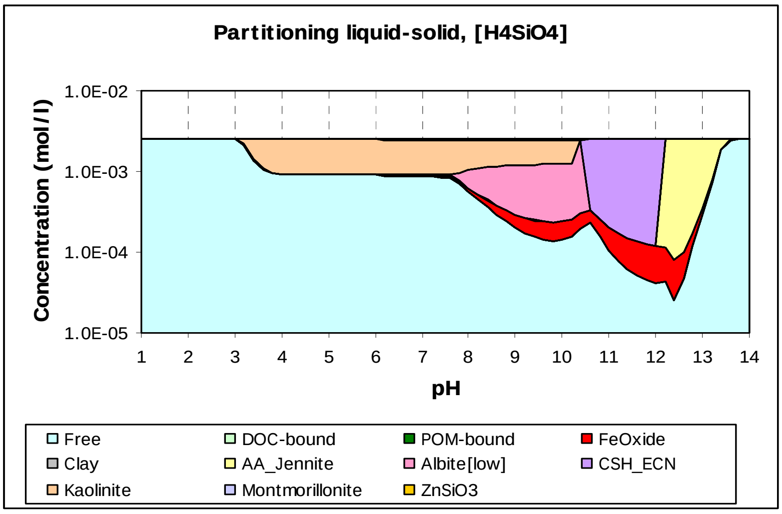


Figure 7:186: Solubility controlling mineral phases for silicic acid leaching from stabilised clay with 2.5% sulphate at 300 days

7.5.2 Stabilised Zinc Contaminated Kaolin Clay with 2.5% Sulphate

To evaluate the implications of the increased sulphate content on zinc containment, leaching and speciation evaluations were undertaken on stabilised zinc contaminated kaolin clay with 2.5% sulphate. Results for aluminium, silicon and zinc evaluations are presented in this section. The releases and release trends of all pre-selected components, due to the influence of pH dependent leaching, are shown in Figures 7.187, 7.178 and 7.189, for leaching at 28, 150 and 300 days of hydration respectively.

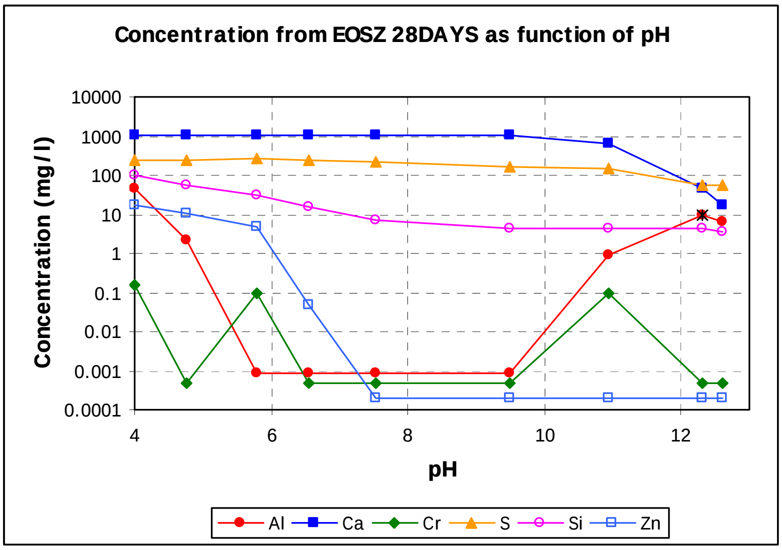


Figure 7:187: Releases of selected components from stabilised zinc contaminated clay with 2.5% sulphate due to pH influence at 28 days

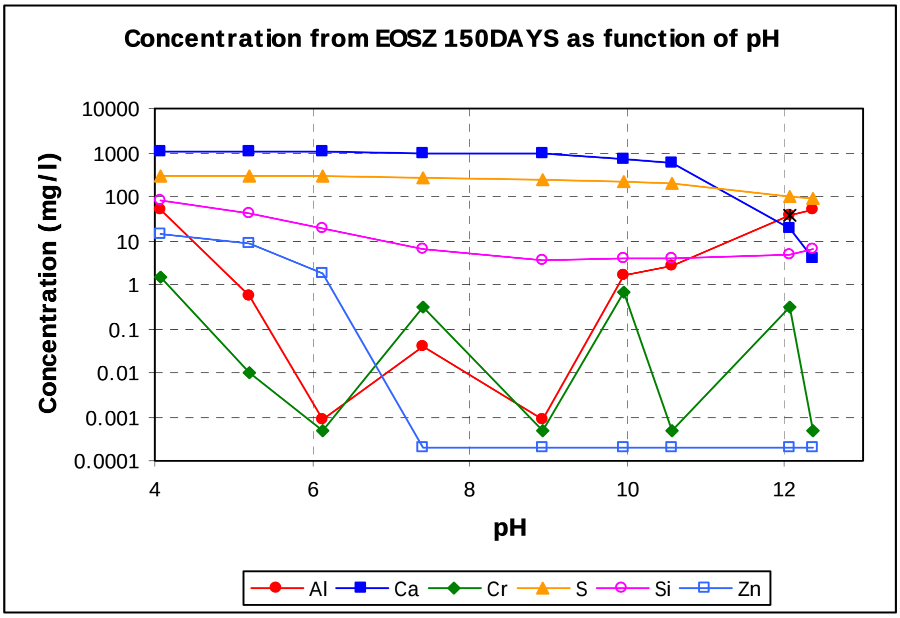


Figure 7:188: Releases of selected components from stabilised zinc contaminated clay with 2.5% sulphate due to pH influence at 150 days

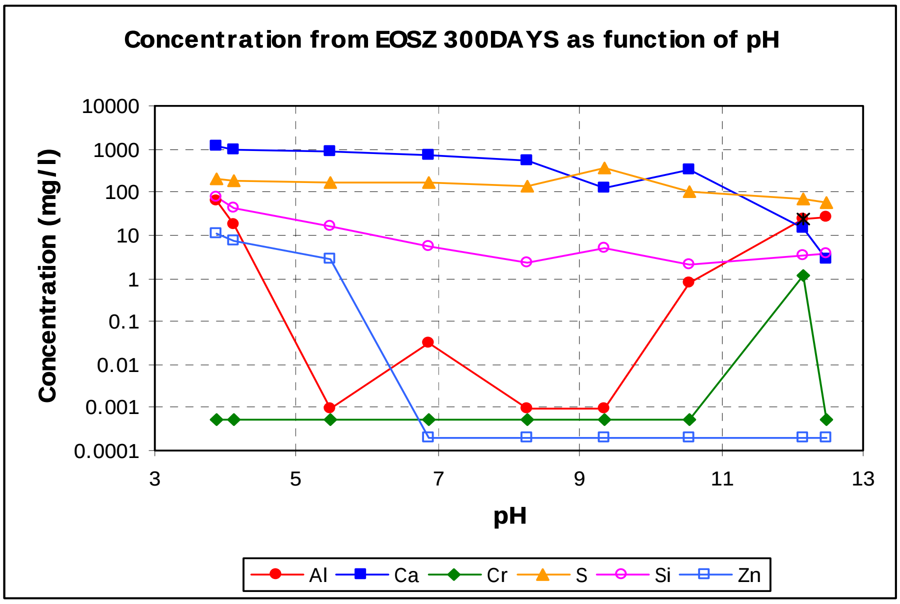


Figure 7:189: Releases of selected components from stabilised zinc contaminated clay with 2.5% sulphate at 300 days of hydration due to influence of pH

For leaching at 28 days of hydrations, Figures 7.190 and 7.191 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.192 and 7.193, and those for zinc releases shown in Figures 7.194 and 7.195.

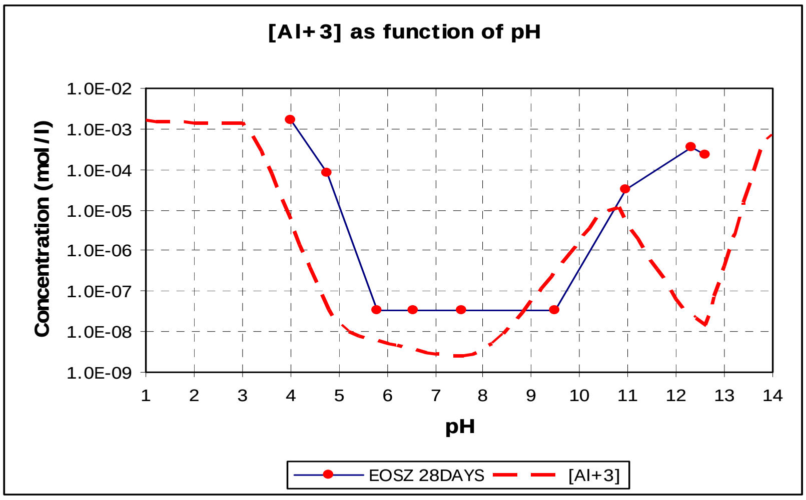


Figure 7:190: Aluminium predicted and measured release trend from stabilised zinc contaminated clay with 2.5% sulphate at 28 days

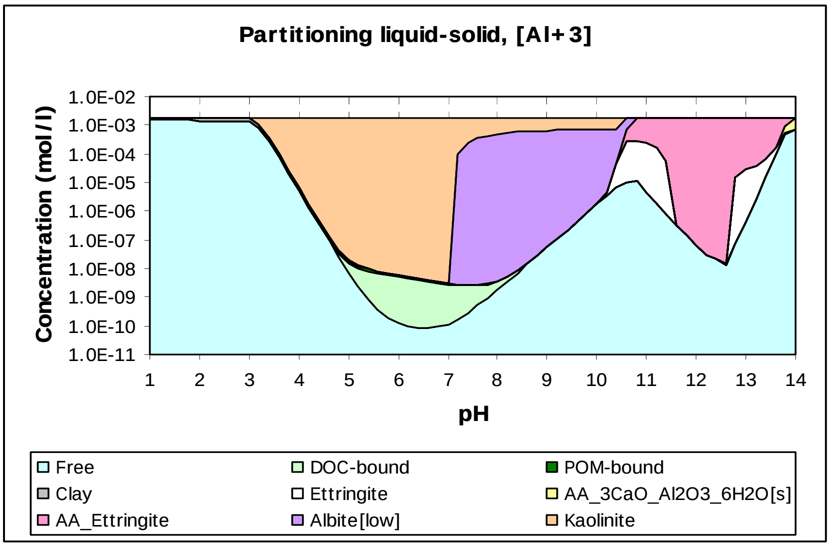


Figure 7:191: Solubility controlling mineral phases for aluminium leaching from stabilised zinc contaminated clay with 2.5% sulphate at 28 days

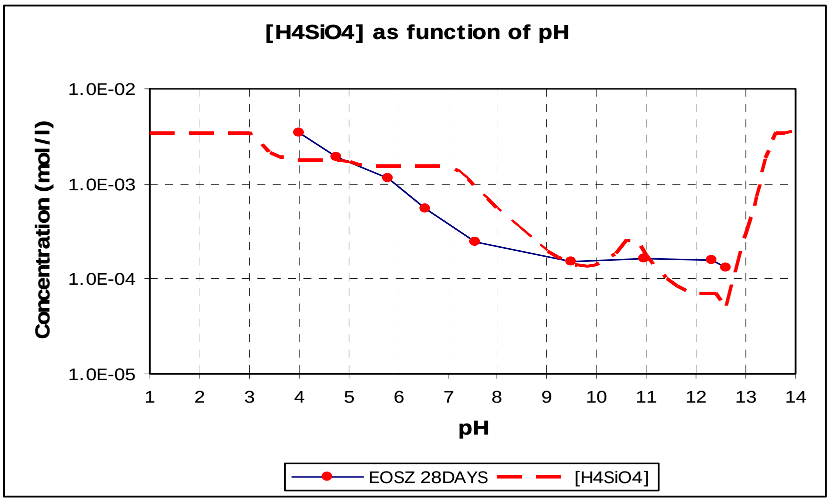


Figure 7:192: Aluminium predicted and measured release trend from stabilised zinc contaminated clay with 2.5% sulphate at 28 days

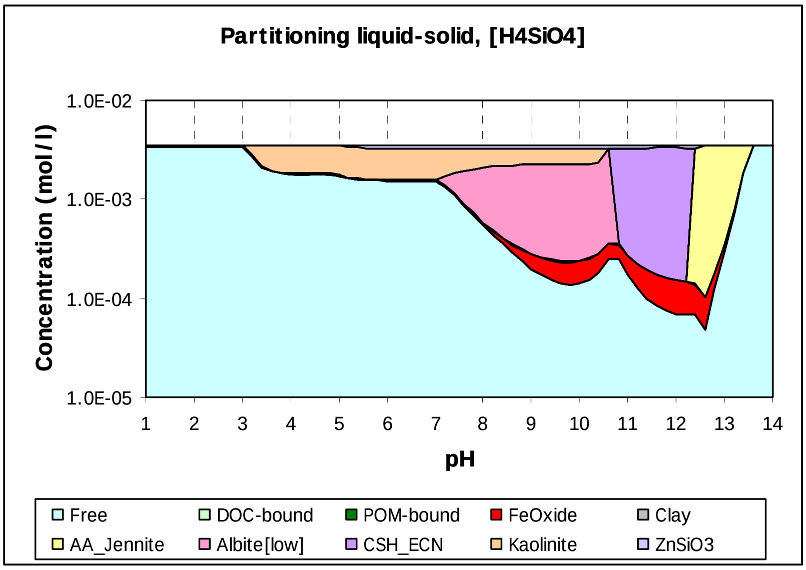


Figure 7:193: Solubility controlling mineral phases for silicic acid leaching from stabilised zinc contaminated clay with 2.5% sulphate at 28 days

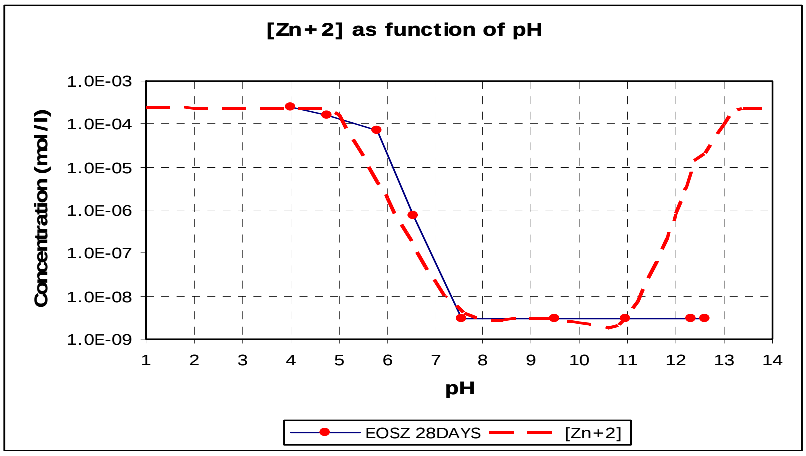


Figure 7:194: Zinc predicted and measured release trend from stabilised zinc contaminated clay with 2.5% sulphate at 28 days

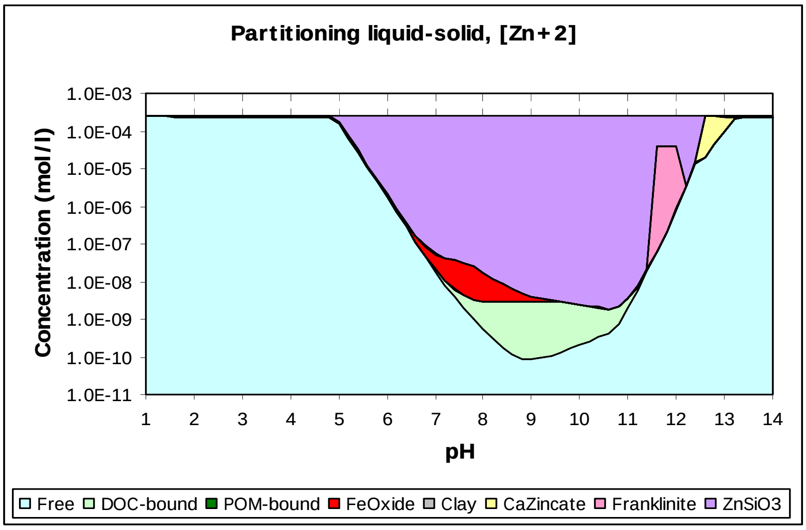


Figure 7:195: Solubility controlling mineral phases for zinc leaching from stabilised zinc contaminated clay with 2.5% sulphate at 28 days

At 150 days of hydration, Figures 7.196 and 7.197 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.198 and 7.199, and those for zinc releases shown in Figures 7.200 and 7.201.

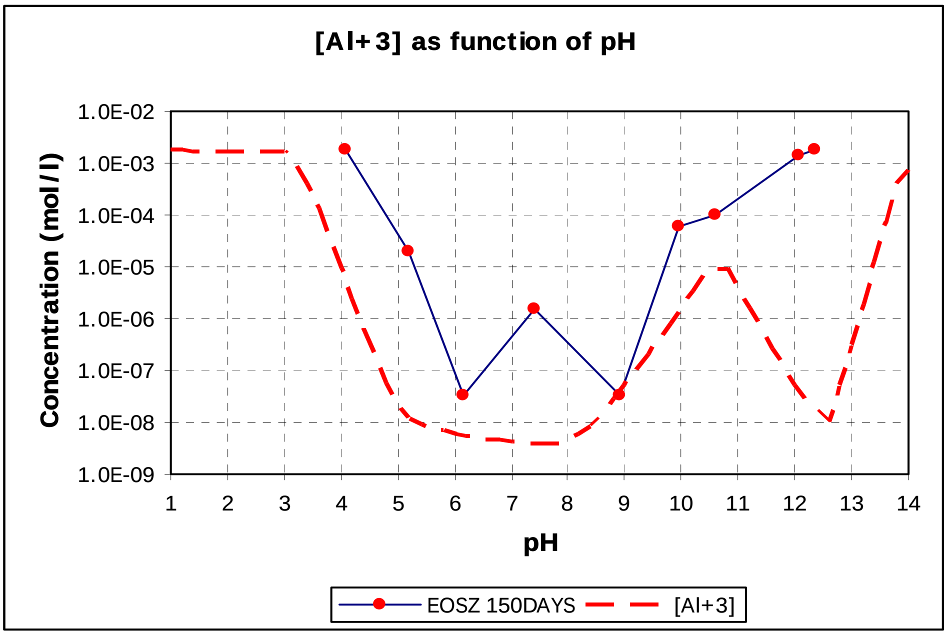


Figure 7:196: Aluminium predicted and measured release trend from stabilised zinc contaminated clay with 2.5% sulphate at 150 days

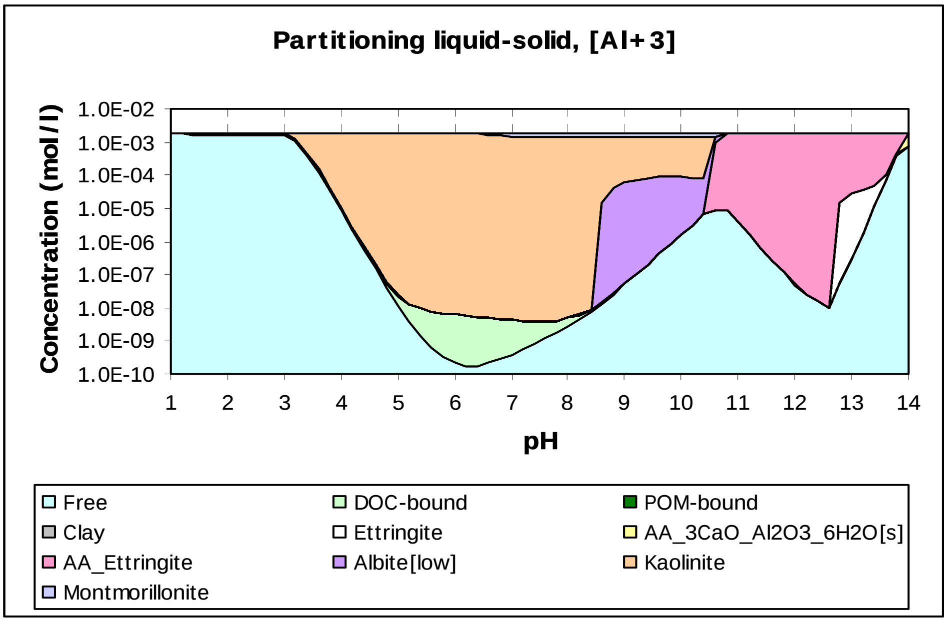


Figure 7:197: Solubility controlling mineral phases for aluminium leaching from stabilised zinc contaminated clay with 2.5% sulphate at 150 days

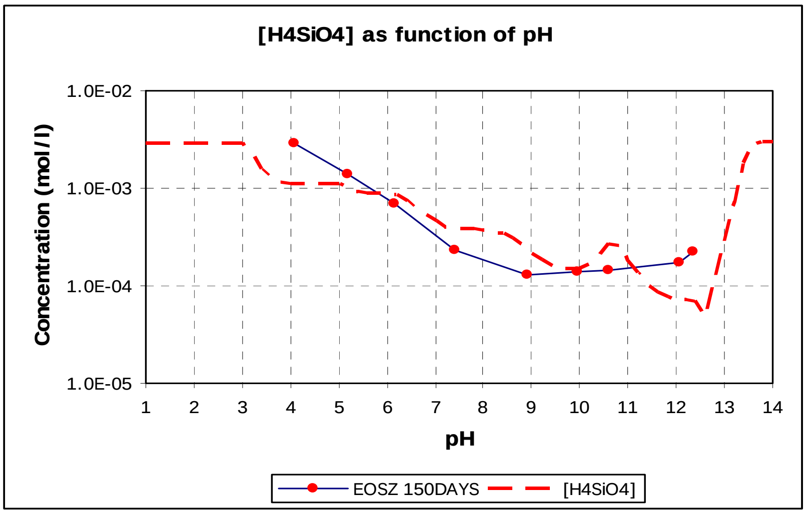


Figure 7:198: Silicic acid predicted and measured release trend from stabilised zinc contaminated clay with 2.5% sulphate at 150 days

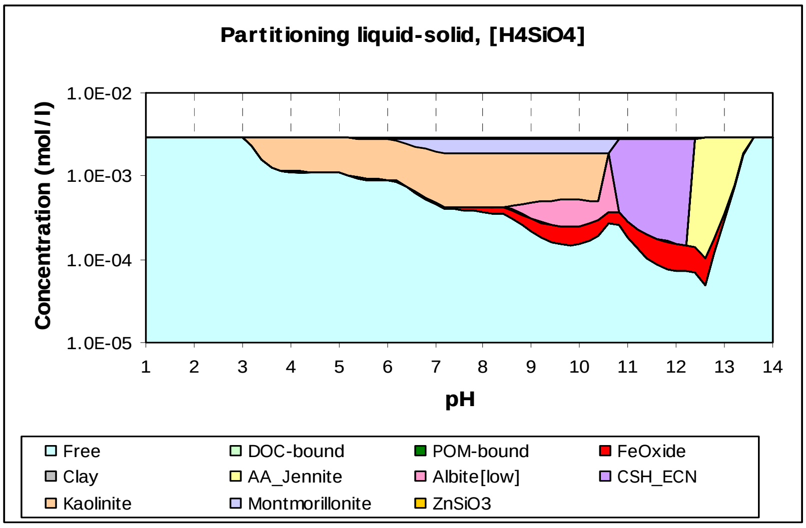


Figure 7:199: Solubility controlling mineral phases for silicic acid leaching from stabilised zinc contaminated clay with 2.5% sulphate at 150 days

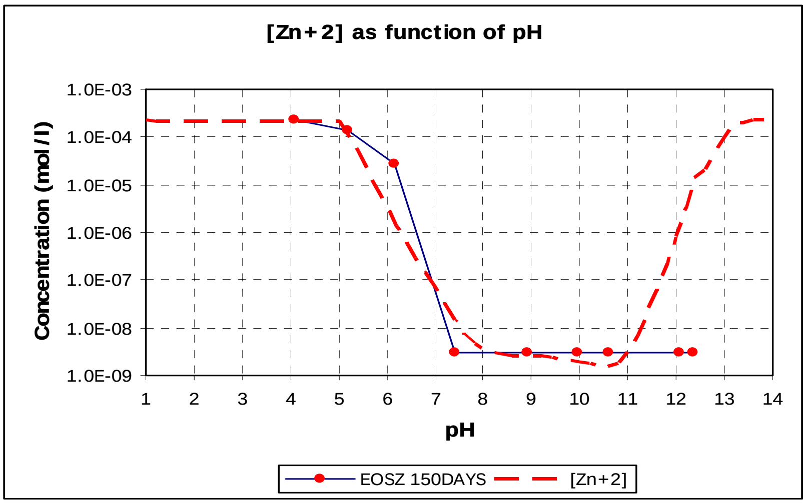


Figure 7:200: Zinc predicted and measured release trend from stabilised zinc contaminated clay with 2.5% sulphate at 150 days

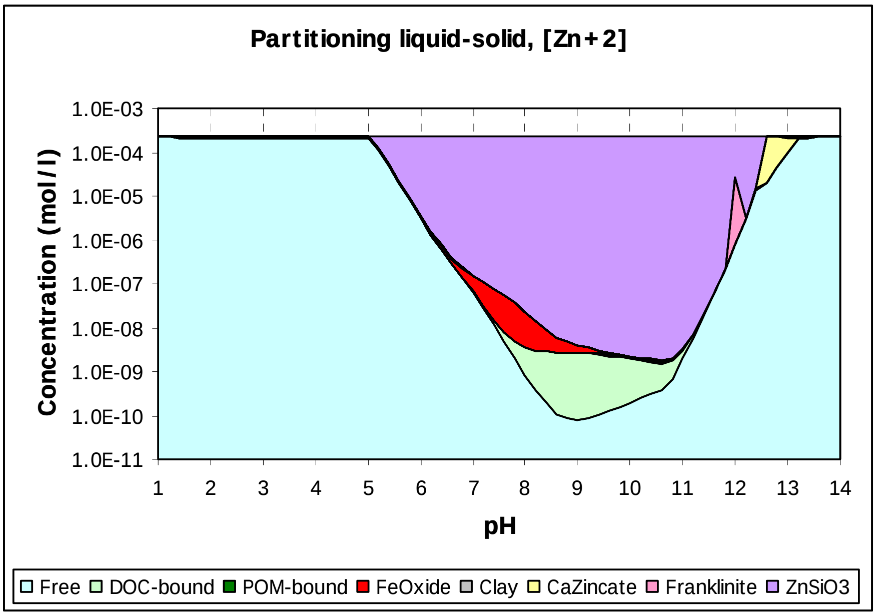


Figure 7:201: Solubility controlling mineral phases for zinc leaching from stabilised zinc contaminated clay with 2.5% sulphate at 150 days

For leaching at 300 days of hydration, Figures 7.202 and 7.203 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.204 and 7.205, and those for zinc releases shown in Figures 7.206 and 7.207, for leaching from the stabilised zinc contaminated kaolin clay with 2.5%.

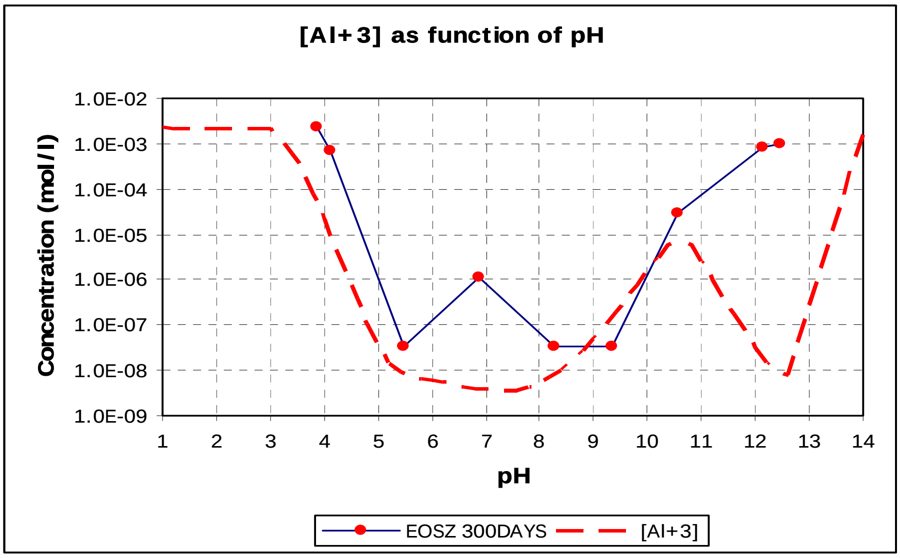


Figure 7:202: Aluminium predicted and measured release trend from stabilised zinc contaminated clay with 2.5% sulphate at 300 days

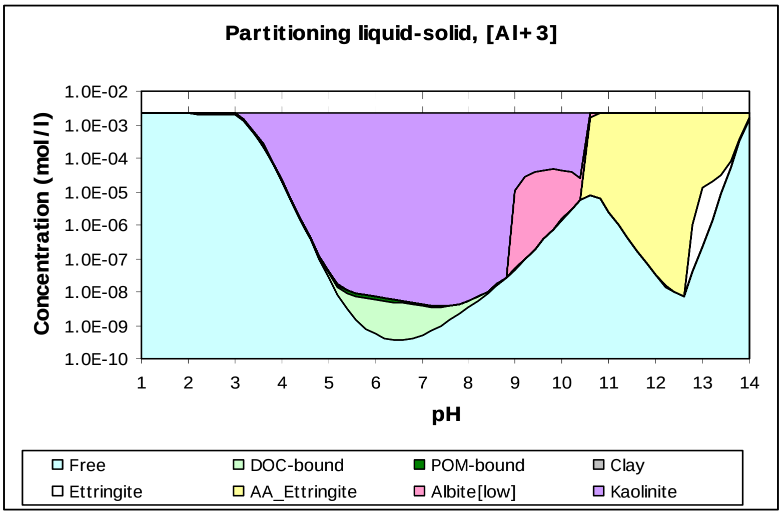


Figure 7:203: Solubility controlling mineral phases for aluminium leaching from stabilised zinc contaminated clay with 2.5% sulphate at 300 days

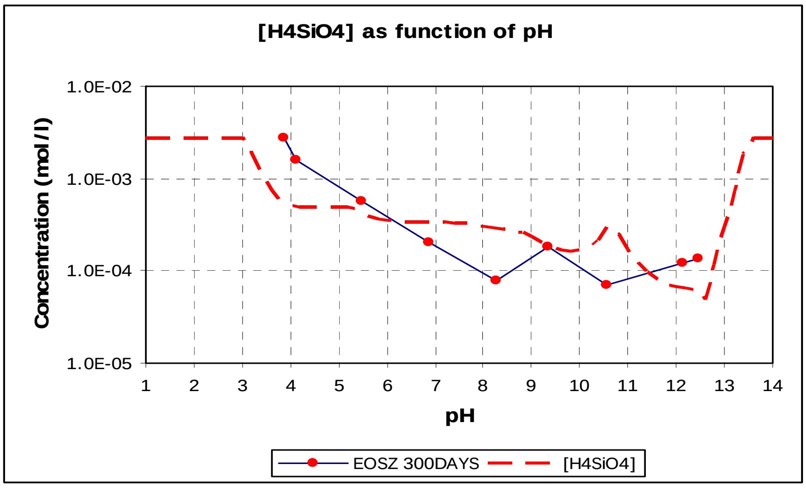


Figure 7:204: Silicic acid predicted and measured release trend from stabilised zinc contaminated clay with 2.5% sulphate at 300 days

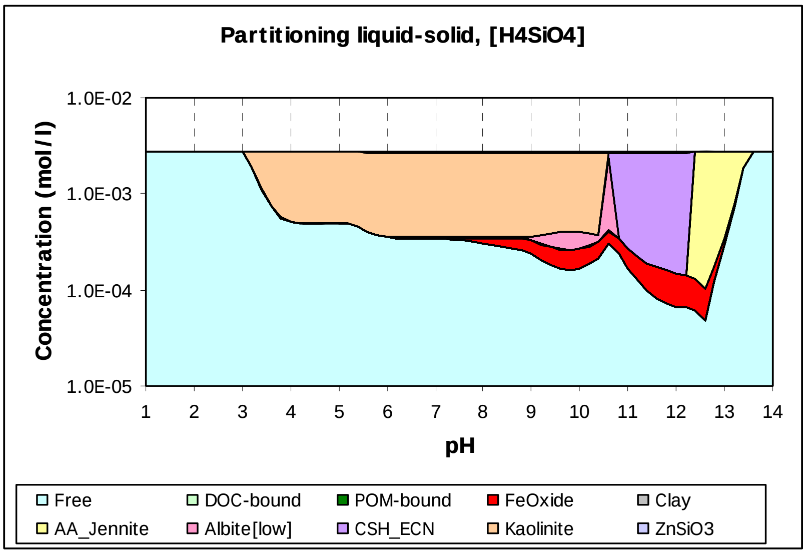


Figure 7:205: Solubility controlling mineral phases for silicic acid leaching from stabilised zinc contaminated clay with 2.5% sulphate at 300 days

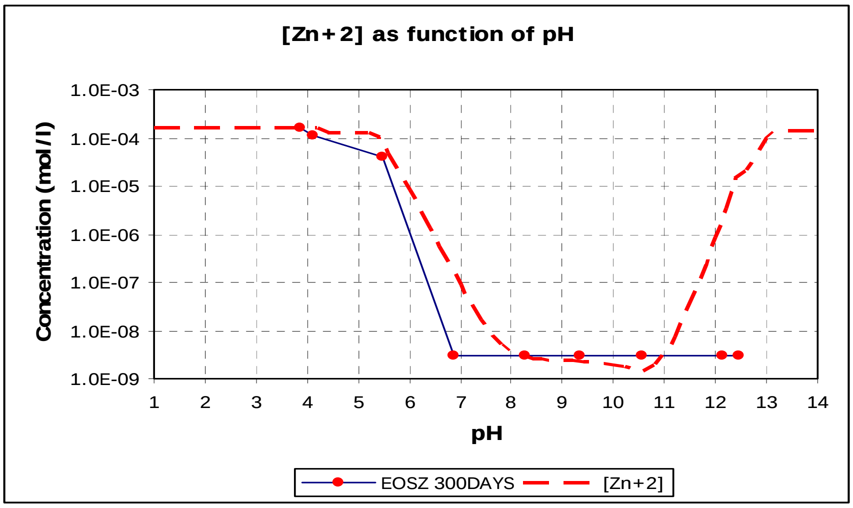


Figure 7:206: Zinc predicted and measured release trend from stabilised zinc contaminated clay with 2.5% sulphate at 300 days

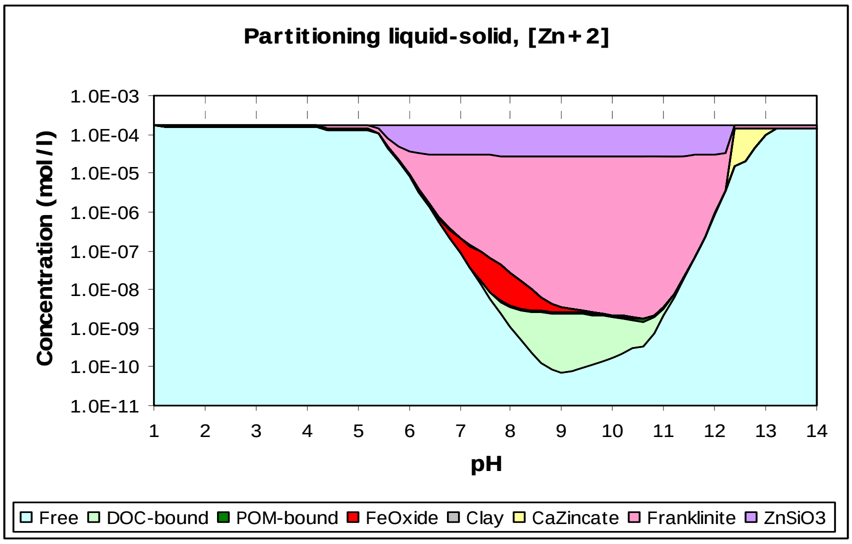


Figure 7:207: Solubility controlling mineral phases for zinc leaching from stabilised zinc contaminated clay with 2.5% sulphate at 300 days

7.5.3 Stabilised Chromium Contaminated kaolin Clay with 2.5% Sulphate

To evaluate the implications of increased sulphate content on chromium containment, leaching and speciation evaluations were undertaken on stabilised chromium contaminated kaolin clay with 2.5% sulphate. Results for aluminium, silicon and chromium evaluations are presented in this section. Releases and trends for preselected components due to influence of pH are shown in Figures 7.208, 7.209 and 7.210, for leaching at 28, 150 and 300 days of hydration respectively.

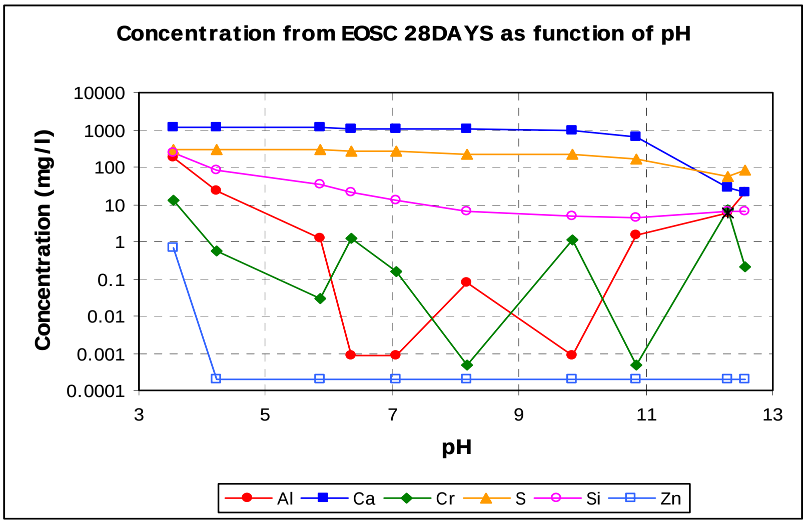


Figure 7:208: Releases of selected components from stabilised chromium contaminated clay with 2.5% sulphate due to pH influence at 28 days

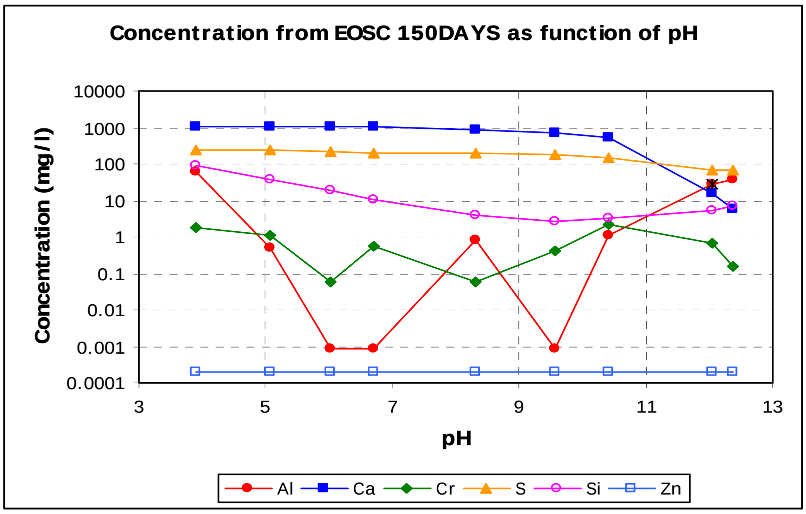


Figure 7:209: Releases of selected components from stabilised chromium contaminated clay with 2.5% sulphate due to pH influence at 150 days

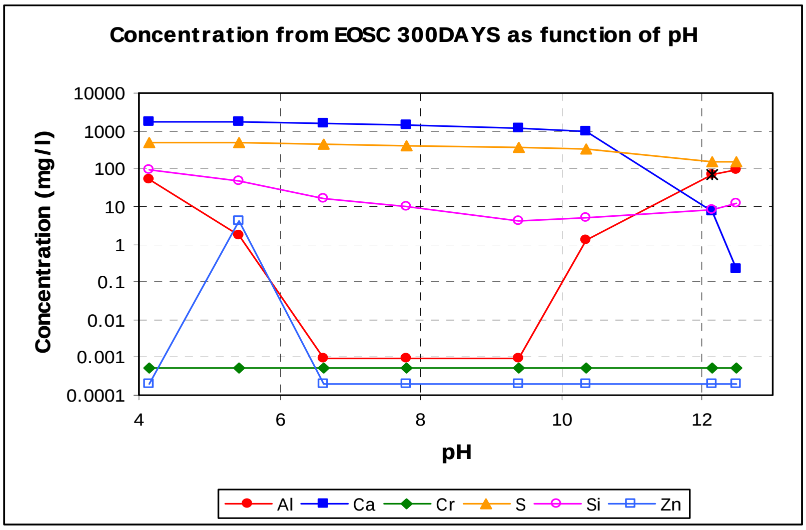


Figure 7:210: Releases of selected components from stabilised chromium contaminated clay with 2.5% sulphate at 300 days of hydration due to influence of pH

For leaching at 28 days of hydration, Figures 7.211 and 7.212 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.213 and 7.214, and those for chromium releases shown in Figures 7.215 and 7.216.

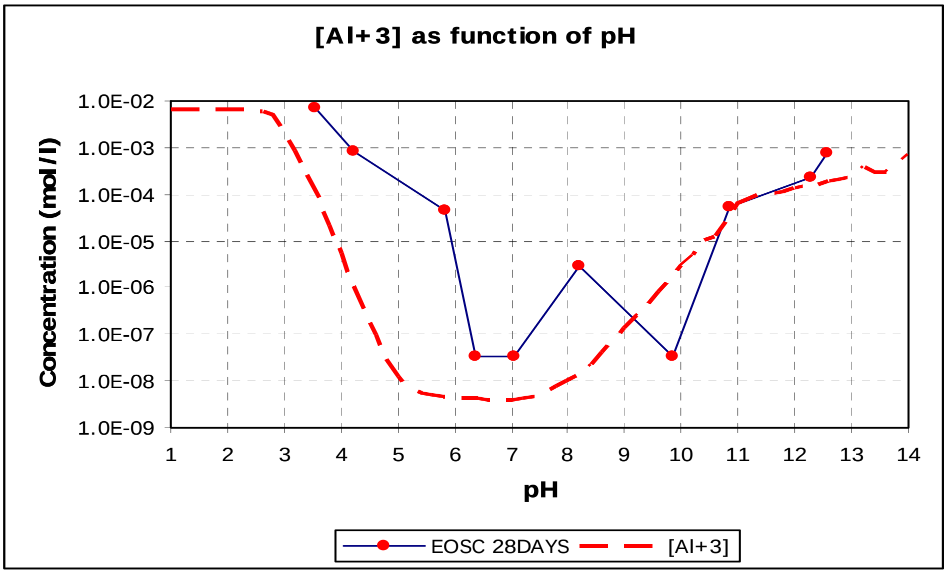


Figure 7:211: Aluminium predicted and measured release trend from stabilised chromium contaminated clay with 2.5% sulphate at 28 days

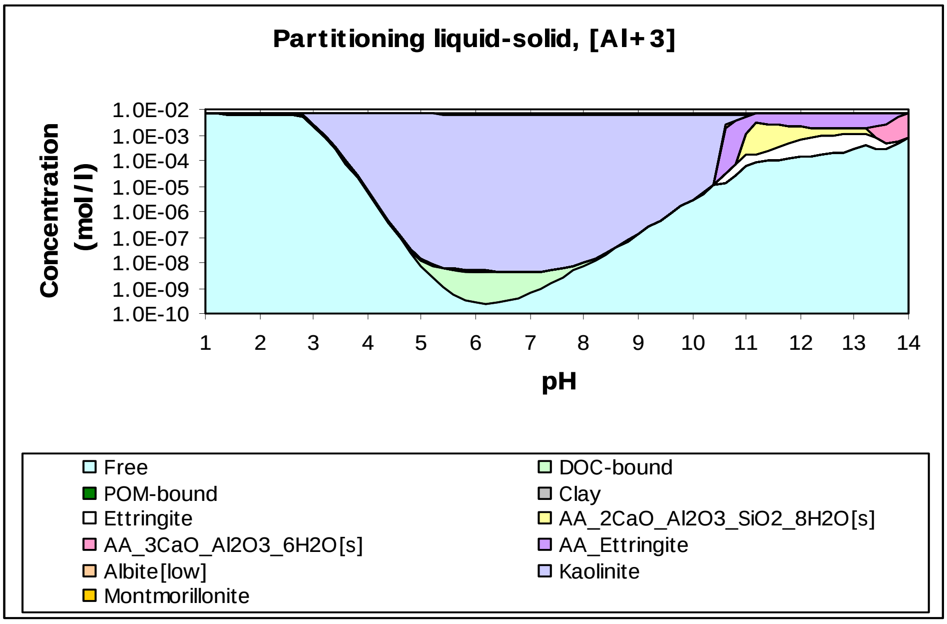


Figure 7:212: Solubility controlling mineral phases for aluminium leaching from stabilised chromium contaminated clay with 2.5% sulphate at 28 days

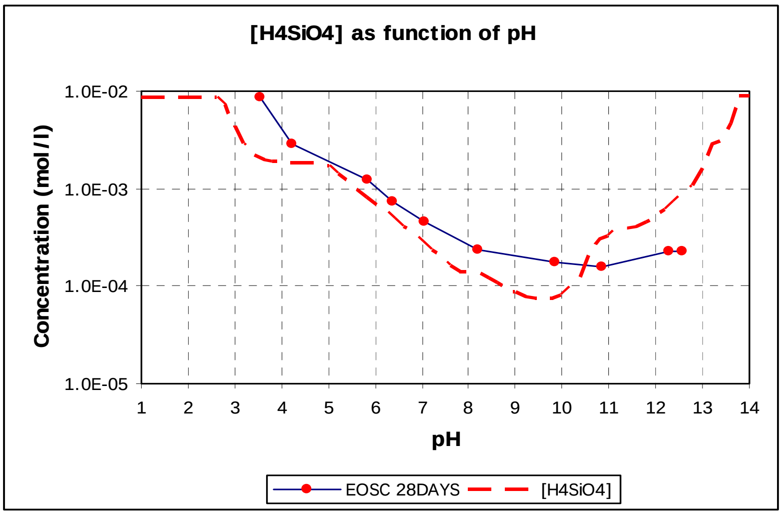


Figure 7:213: Silicic acid predicted and measured release trend from stabilised chromium contaminated clay with 2.5% sulphate at 28 days

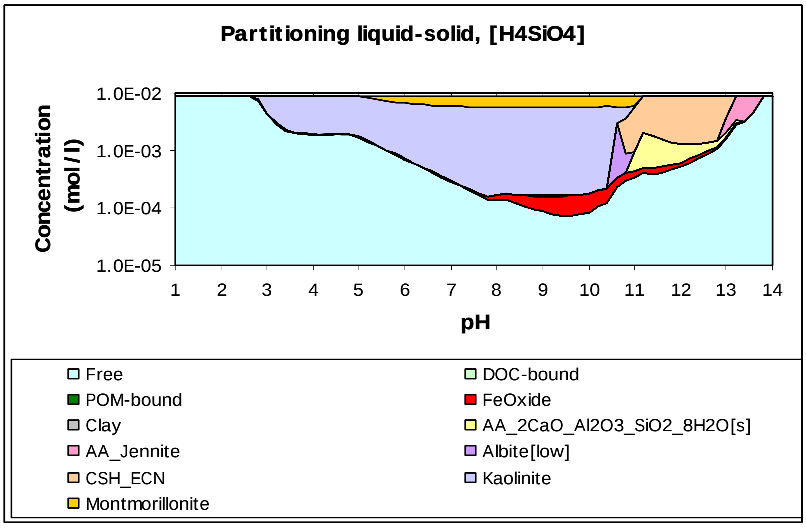


Figure 7:214: Solubility controlling mineral phases for silicic acid leaching from stabilised chromium contaminated clay with 2.5% sulphate at 28 days

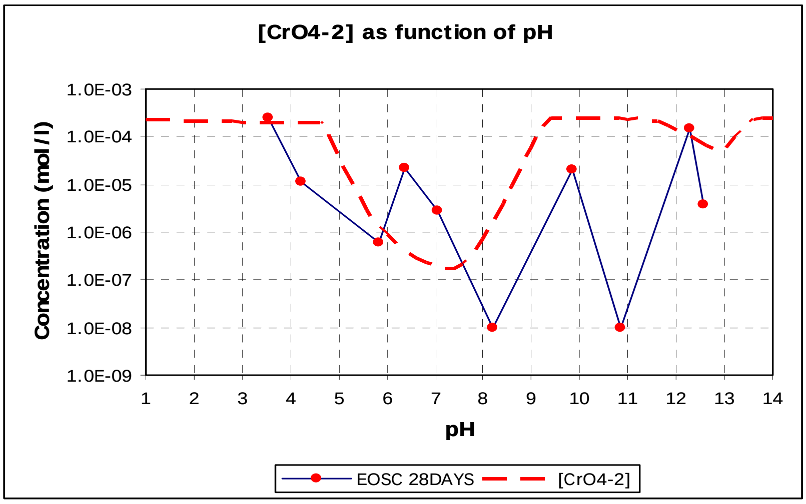


Figure 7:215: Chromate predicted and measured release trend from stabilised chromium contaminated clay with 2.5% sulphate at 28 days

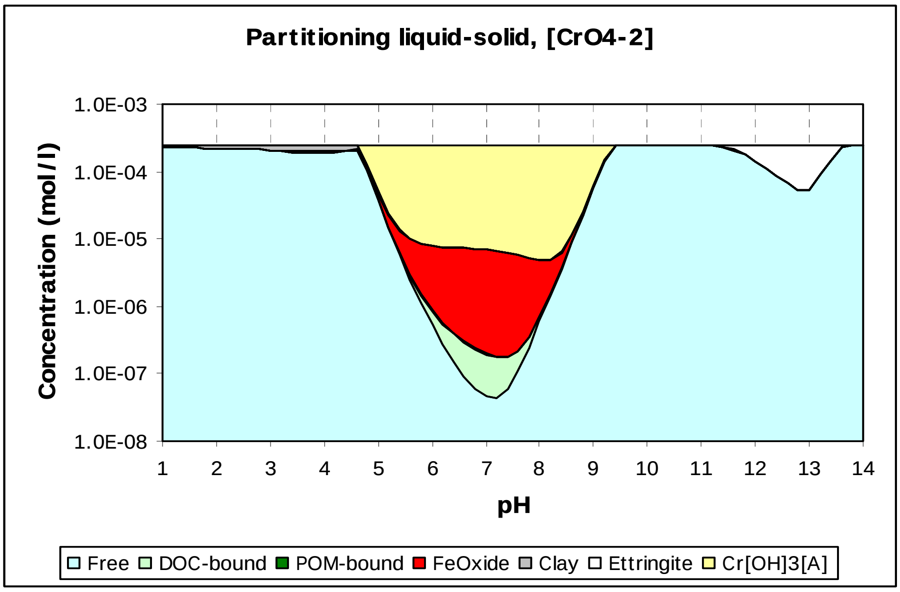


Figure 7:216: Solubility controlling mineral phases for chromate leaching from stabilised chromium contaminated clay with 2.5% sulphate at 28 days

For leaching at 150 days of hydration, Figures 7.217 and 7.218 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.219 and 7.220, and those for chromium releases shown in Figures 7.221 and 7.222.

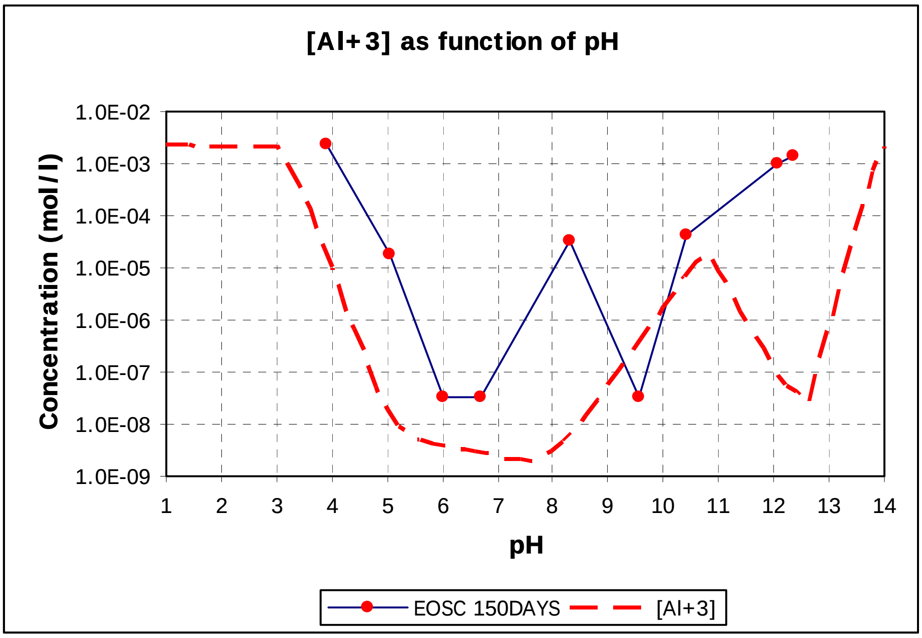


Figure 7:217: Aluminium predicted and measured release trend from stabilised chromium contaminated clay with 2.5% sulphate at 150 days

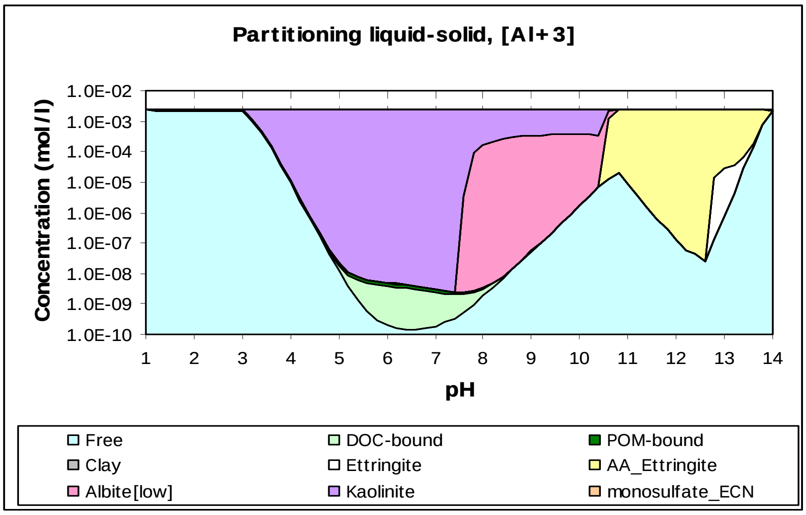


Figure 7:218: Solubility controlling mineral phases for aluminium leaching from stabilised chromium contaminated clay with 2.5% sulphate at 150 days

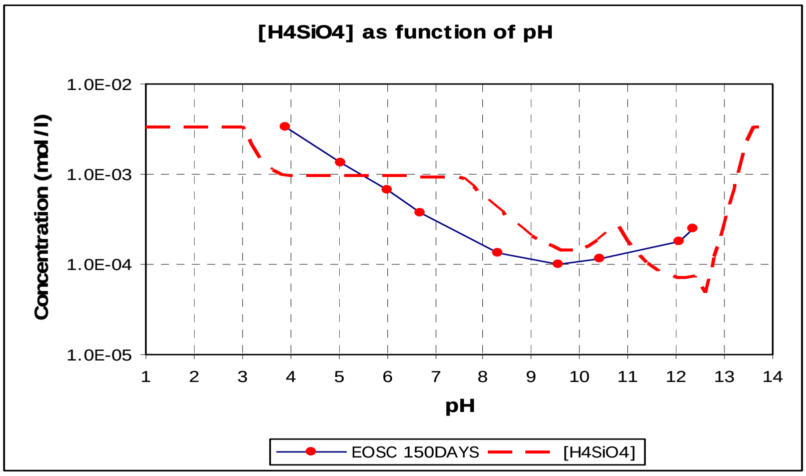


Figure 7:219: Silicic acid predicted and measured release trend from stabilised chromium contaminated clay with 2.5% sulphate at 150 days

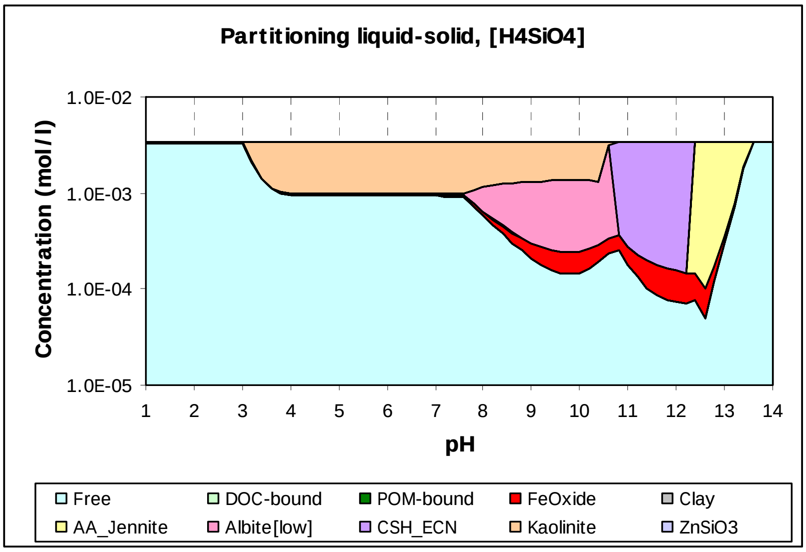


Figure 7:220: Solubility controlling mineral phases for silicic acid leaching from stabilised chromium contaminated clay with 2.5% sulphate at 150 days

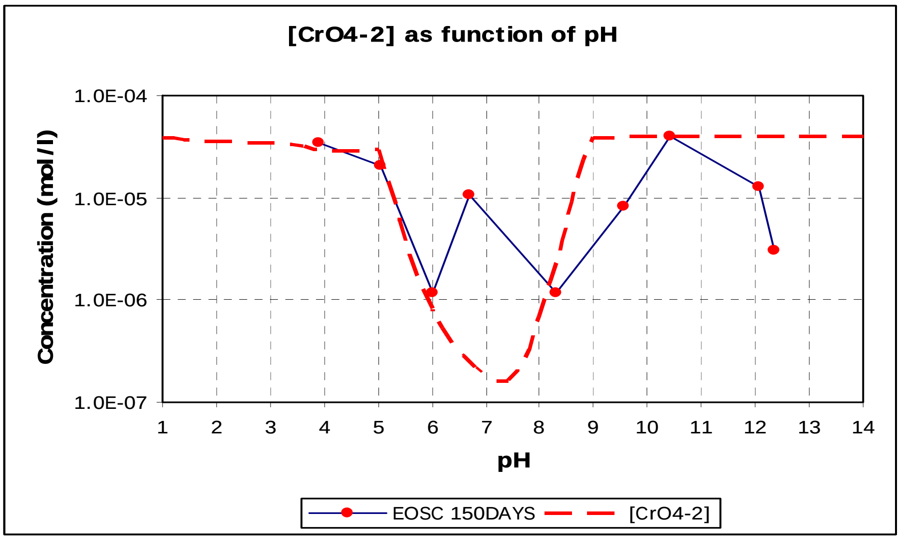


Figure 7:221: Chromate predicted and measured release trend from stabilised chromium contaminated clay with 2.5% sulphate at 150 days

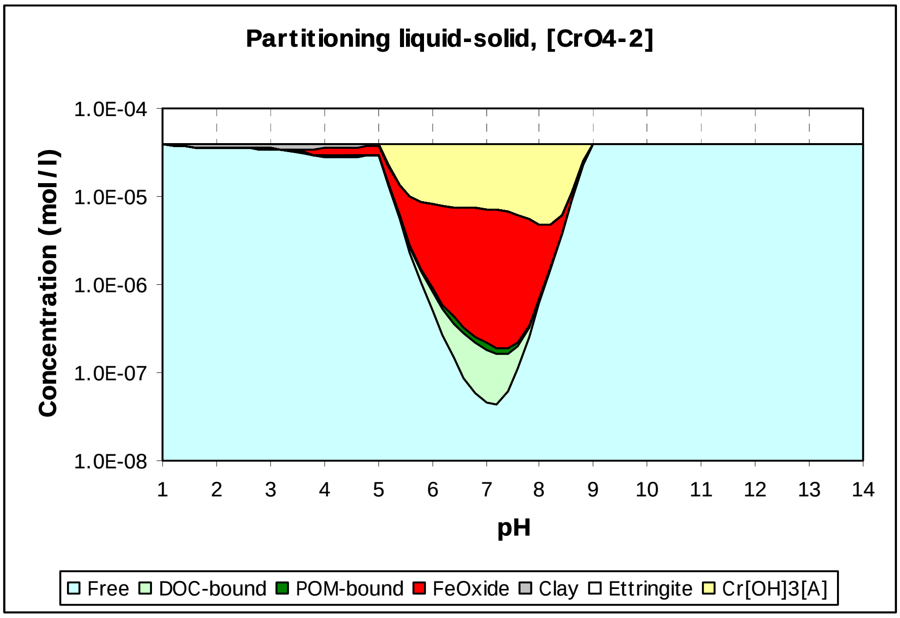


Figure 7:222: Solubility controlling mineral phases for chromate leaching from stabilised chromium contaminated clay with 2.5% sulphate at 150 days

For leaching at 300 days of hydration, no releases were observed for chromium (Figure 7.210), and thus no results are presented for this duration. Figures 7.223 and 7.224 show the measured and predicted releases for aluminium, and the solubility controlling mineral phases respectively. Respective results for silicon releases are shown in Figures 7.225 and 7.226, for leaching from the stabilised chromium contaminated kaolin clay with 2.5% sulphate.

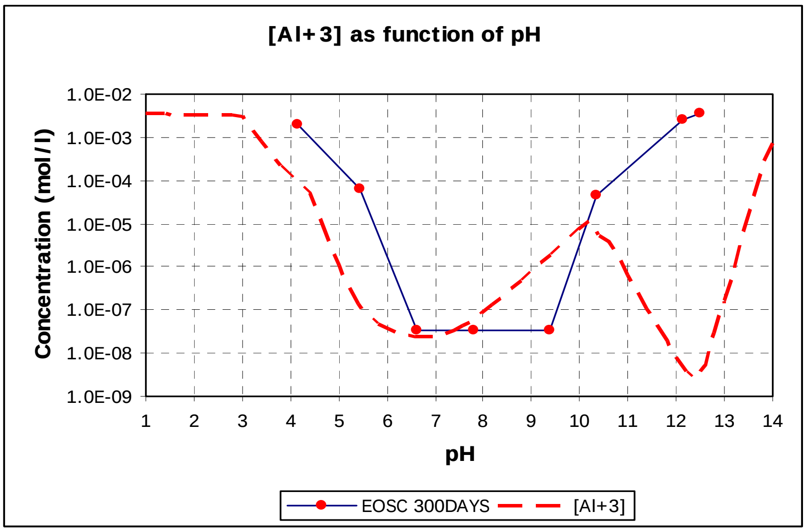


Figure 7:223: Aluminium predicted and measured release trend from stabilised chromium contaminated clay with 2.5% sulphate at 300 days

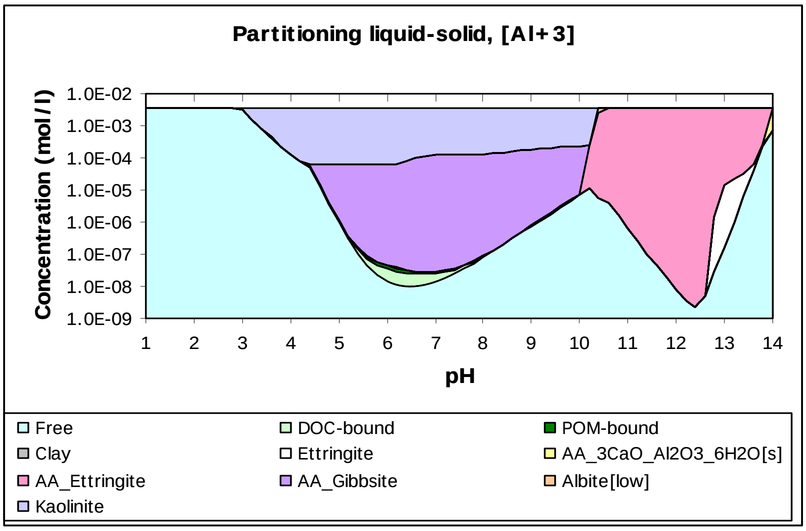


Figure 7:224: Solubility controlling mineral phases for aluminium leaching from stabilised chromium contaminated clay with 2.5% sulphate at 300 days

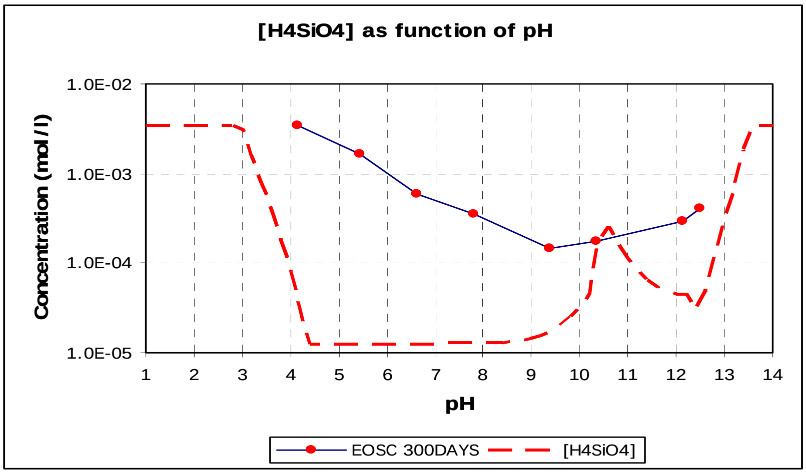


Figure 7:225: Silicic acid predicted and measured release trend from stabilised chromium contaminated clay with 2.5% sulphate at 300 days

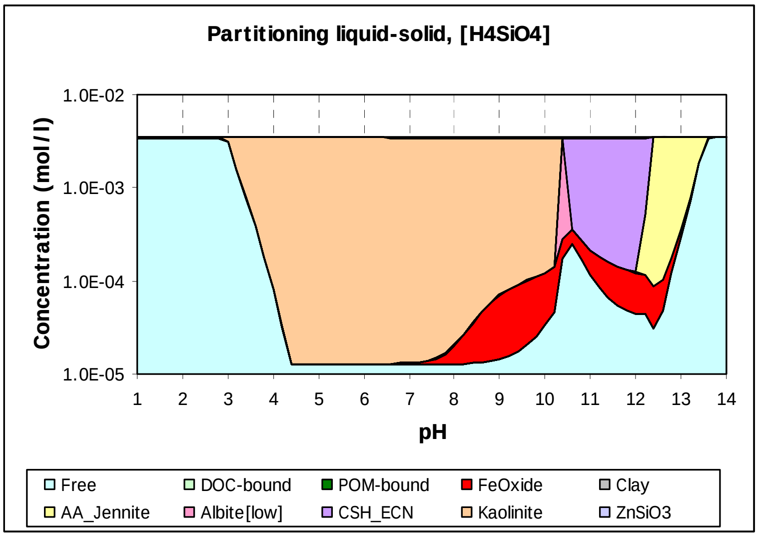


Figure 7:226: Solubility controlling mineral phases for silicic acid leaching from stabilised chromium contaminated clay with 2.5% sulphate at 300 days

7.6 COMPARISONS

Assessments for degradation of matrices can be inferred from releases and trend alterations for the structural components (Al, Si and Ca). Increases or decreases in releases with increased hydration duration were used to assess the formation of stable products, or the degradation of existing ones. Kaolin dissociates at high alkaline pH prevailing in stabilised matrices, yielding hydroxides of aluminium and silicon which can then be used in pozzolanic reactions. Implications of inclusions and inclusion type on chemical durability and contaminant releases were evaluated, via assessments of component availabilities and alterations in availabilities with hydration duration (Chapter 8 Section 8.2). These comparisons show releases and trend modifications for uncontaminated matrix controls and evaluations for the matrix influences on contaminant releases and trends.

7.6.1 Matrix Degradation and Trend Modifications

Components of interest for evaluating matrix durability (for CEM II stabilised kaolin clay) were aluminium, silicon and calcium. Aluminium and silicon are the structural components of kaolin clay, and calcium dominates during the formation of cementitious products during stabilisation. Alterations in release trends for these components due to influence of pH leaching were assessed and presented here, as well as changes in availability with increasing hydration (discussed in Chapter 8 Section 8.2.2 and 8.2.3.2). Releases from unstabilised kaolin clay (ECC) were also included for comparison, in view of availability and trend modifications with stabilisation. Cumulative releases of these components during time dependent leaching are also be presented in this section, to derive trends and modifications with increasing hydration (discussed in Chapter 8 Section 8.2.3.1 and 8.3). The pH evolutions during leaching of matrices are also presented here, due to the influence of prevailing pH on component solubility. Table 7.2 shows the availabilities of the components (g/kg) from kaolin clay and the stabilised matrices at different hydration periods, and the pH where the majority of component availabilities occur.

Table 7.2: Availabilities of Al, Si and Ca from the kaolin clay and stabilised clay matrices (g/kg)

Control Samples Availabilities (g/kg)				
Sample	pH	Al	Si	Ca
Kaolin Clay (ECC)	11.99	0.28	0.22	DL
EO 28 days	3.84	2.07	2.01	21.45
EO 150 days	4.01	0.72	1.09	21.17
EO 300 days	3.85	1.43	0.87	30.67
EOH 28 days	3.74	1.76	2.48	21.44
EOH 150 days	3.91	1.13	1.89	21.44
EOH 300 days	3.97	0.83	1.68	31.38
EOS 28 days	3.85	2.63	2.73	21.43
EOS 150 days	4.10	0.76	1.23	21.41
EOS 300 days	4.01	0.82	1.35	28.95

Note: Calcium availability at 300 days observed around neutral pH (Also See Chapter 8 Section 8.2.2)

DL in Table 7.2 indicates concentrations below equipment detection limits of the analytical equipment (Table 7.3). Detection limit values rather than zero were used as the lower leaching limit during assessments and modelling. Cumulative releases for aluminium, silicon and calcium (g/m^2), from surfaces of stabilised matrices controls during monolithic leaching at the material natural pH are shown in Table 7.4.

Table 7.3: ICP OES (SPECTRO CIROS CCD) detection limits (µg/l)

Element	Detection Limit (µg/l)	Element	Detection Limit (µg/l)
Sodium	0.250	Manganese	0.020
Magnesium	0.009	Iron	0.200
Potassium	0.800	Zinc	0.070
Calcium	0.010	Aluminium	0.040
Sulphur	1.900	Silicon	0.900
Chromium	0.180	Phosphorus	1.000

Table 7.4: Cumulative releases of the Al, Si and Ca from stabilised clay matrices (g/m^2)

Cumulative Releases (g/m^2)			
Sample	Al	Si	Ca
EO 28 days	4.94	3.98	91.93
EO 150 days	6.21	4.10	55.86
EO 300 days	6.88	2.98	41.41
EOS 28 days	12.82	11.39	11.70
EOS 150 days	10.47	8.05	7.37
EOS 300 days	15.58	12.18	9.82
EOH 28 days	3.53	3.81	157.44
EOH150 days	4.77	4.45	105.16
EOH 300 days	6.90	4.75	736.81

Results for component releases with hydration are presented based on the presence and type of additive included. pH dependent releases of the components from the different matrices will also show the releases from unstabilised kaolin clay for comparisons. For stabilised kaolin clay without additives, Figures 7.227 and 7.228 show the measured release trends due to pH influence, and cumulative releases for aluminium during time dependent leaching, at the different hydration durations respectively. Similarly, Figures 7.229 and 7.230 show the results for silicon releases. No calcium release was observed during pH dependent leaching of kaolin clay, and as such was not included for trend comparisons. Figures 7.231 and 7.232 show the release trends during pH dependent leaching, and cumulative releases for calcium during time dependent leaching respectively, at the different hydration periods. The evolution of pH during time dependent leaching for the stabilised kaolin clay is shown in Figure 7.233, for the different hydration durations.

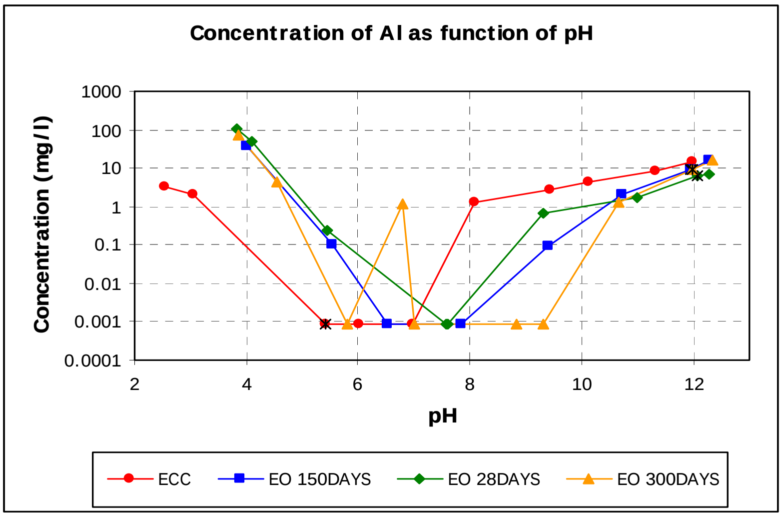


Figure 7:227: Release of aluminium due to pH influence from kaolin clay and stabilised kaolin clay at different hydration durations

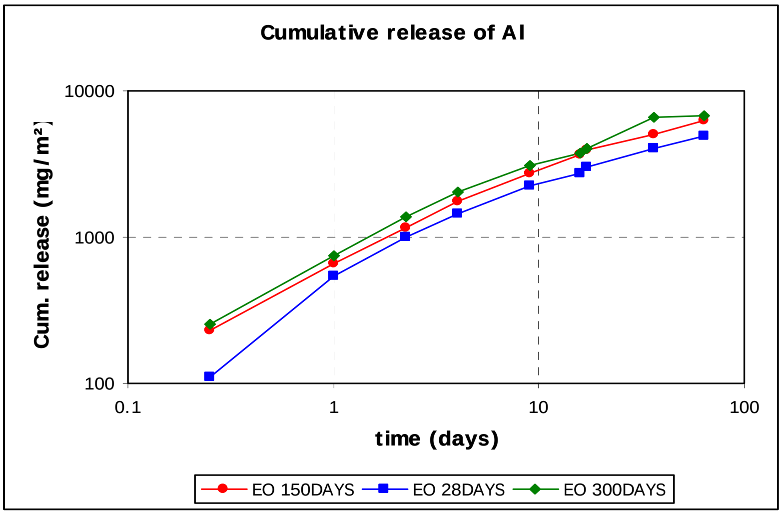


Figure 7:228: Cumulative releases of aluminium during time dependent leaching from stabilised kaolin clay at different hydration durations

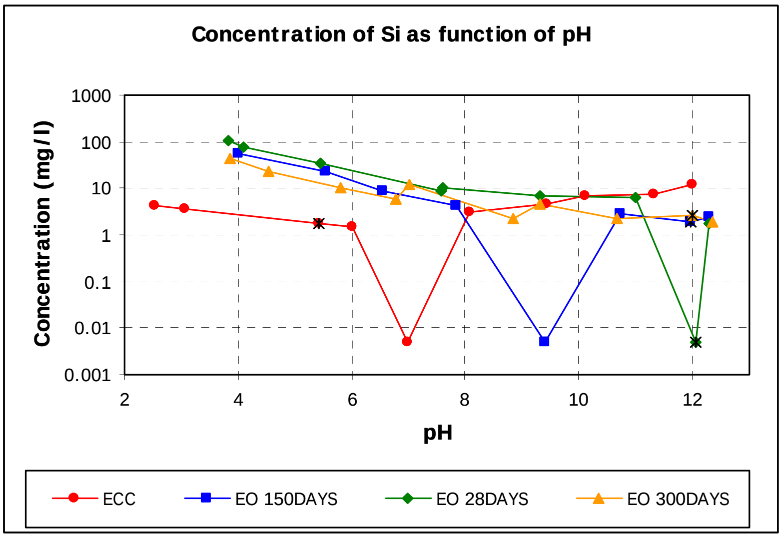


Figure 7:229: Release of silicon due to pH influence from kaolin clay and stabilised kaolin clay at different hydration durations

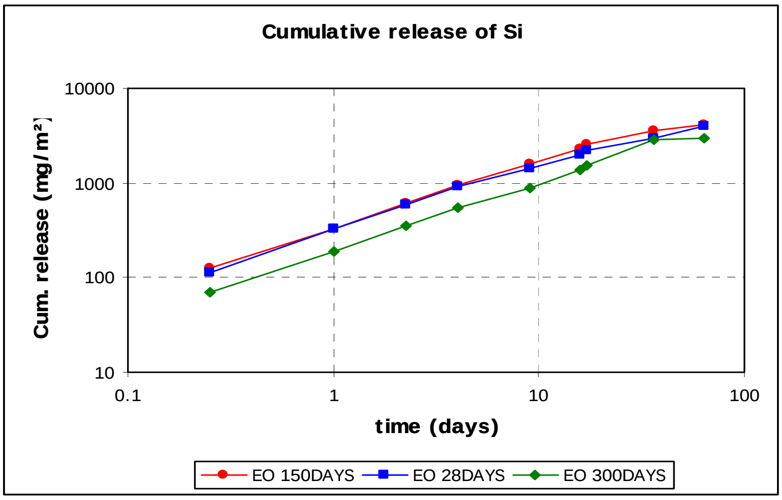


Figure 7:230: Cumulative releases of silicon during time dependent leaching from stabilised kaolin clay at different hydration durations

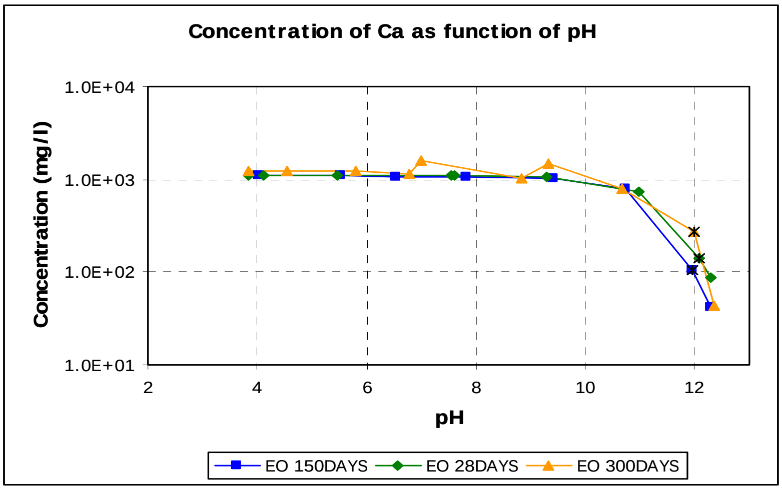


Figure 7:231: Release of calcium due to pH influence from stabilised kaolin clay at different hydration durations

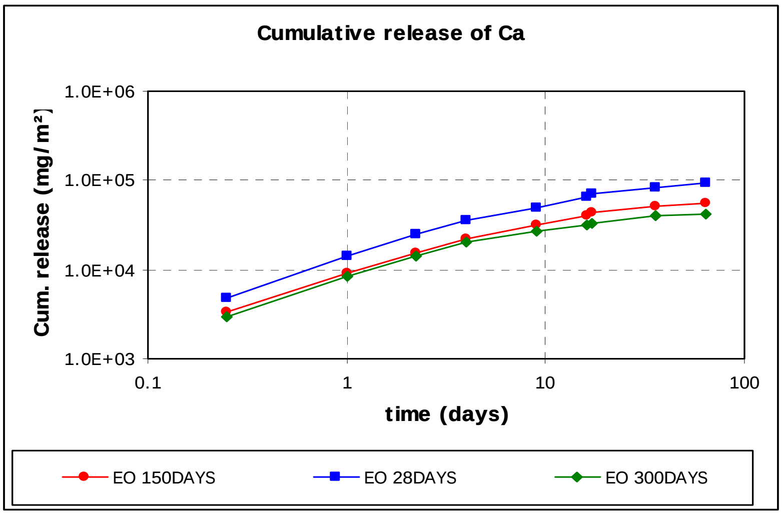


Figure 7:232: Cumulative releases of calcium during time dependent leaching from stabilised kaolin clay at different hydration durations

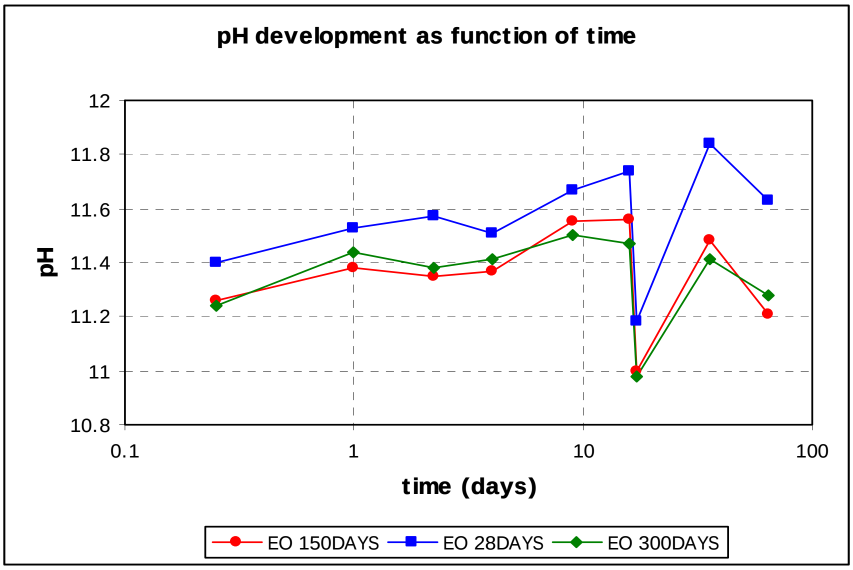


Figure 7:233: Evolution of pH during time dependent leaching of stabilised kaolin clay at different hydration durations

For 1% humic acid matrices, Figures 7.234 and 7.235 show the release trends during pH dependent leaching, and the cumulative releases for aluminium during time dependent leaching at different hydration durations. Similarly, respective results for silicon releases are shown in Figures 7.236 and 7.237, and those for calcium shown in Figures 7.238 and 7.239. Figure 7.240 shows the pH evolution during time dependent leaching, for the different hydration durations.

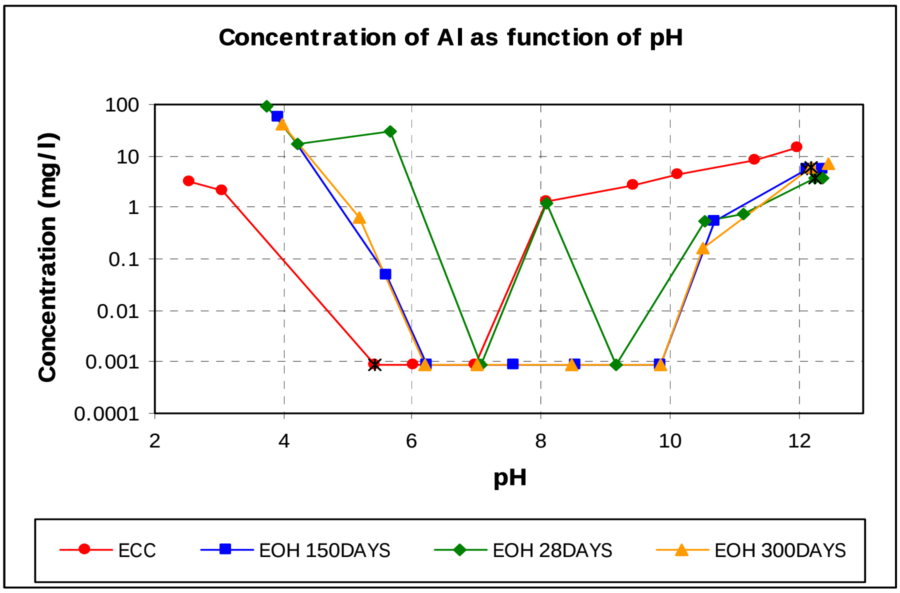


Figure 7:234: Release of aluminium due to pH influence from kaolin clay and stabilised kaolin clay with 1% humic acid at different hydration durations

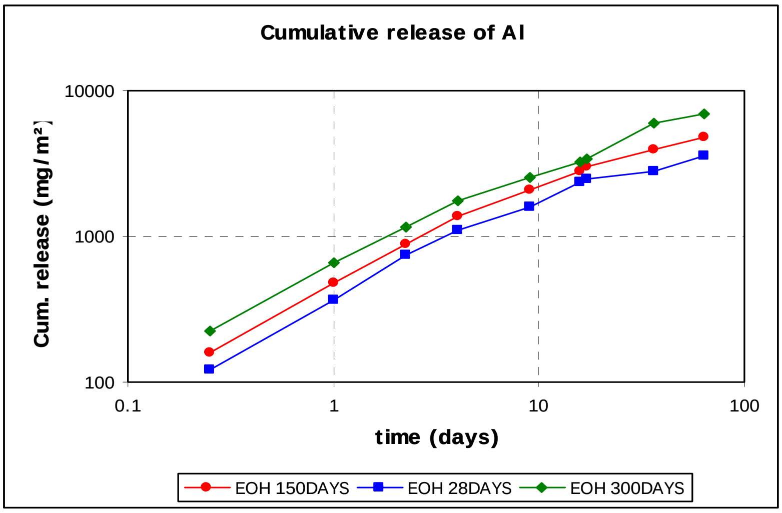


Figure 7:235: Cumulative releases of aluminium during time dependent leaching from stabilised kaolin clay with 1% humic at different hydration durations

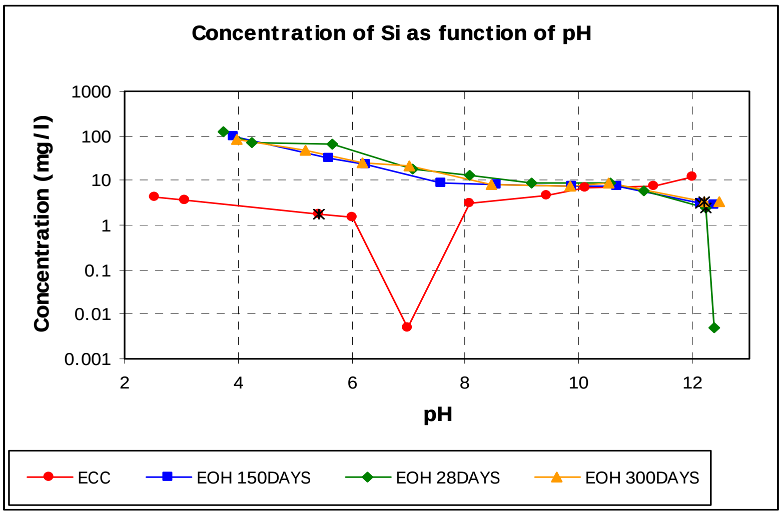


Figure 7:236: Release of silicon due to pH influence from kaolin clay and stabilised kaolin clay with 1% humic acid at different hydration durations

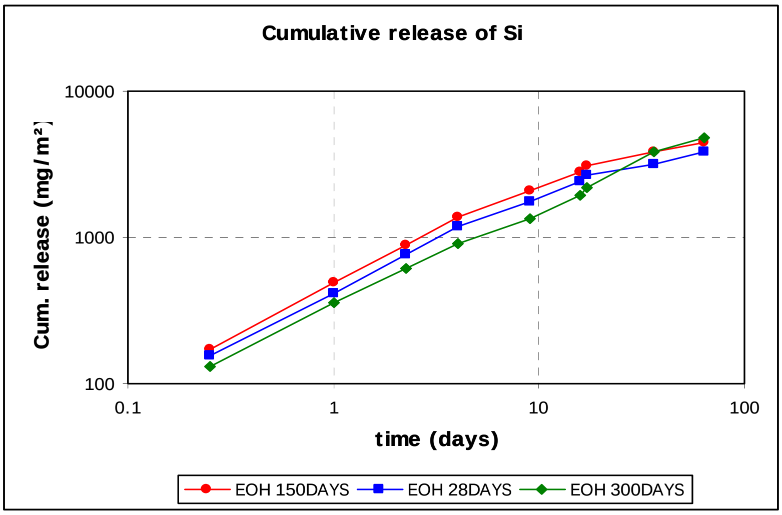


Figure 7:237: Cumulative releases of silicon during time dependent leaching from stabilised kaolin clay with 1% humic acid at different hydration durations

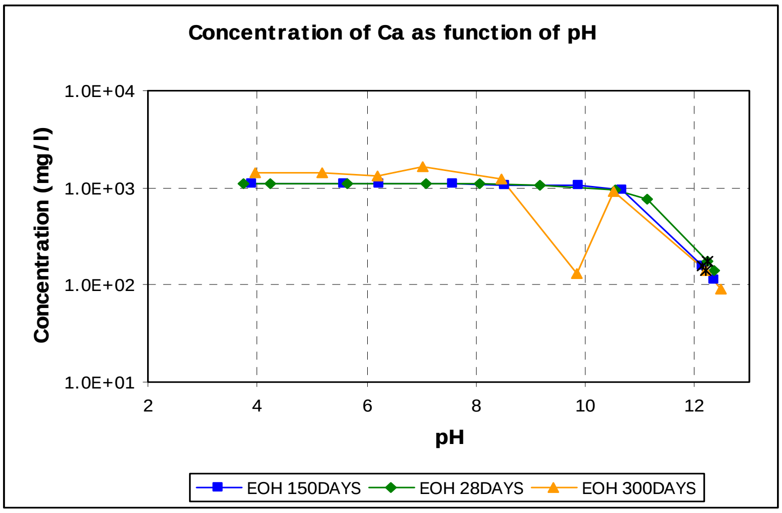


Figure 7:238: Release of calcium due to pH influence from stabilised kaolin clay with 1% humic acid at different hydration durations

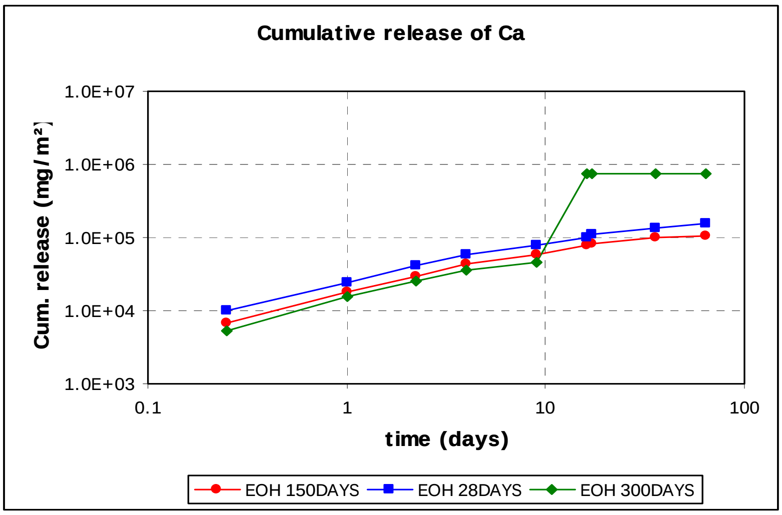


Figure 7:239: Cumulative releases of calcium during time dependent leaching from stabilised kaolin clay with 1% humic acid at different hydration durations

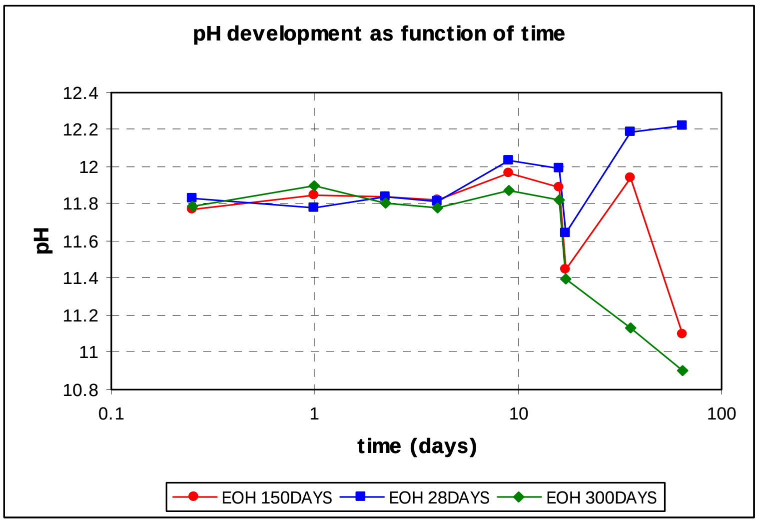


Figure 7:240: Evolution of pH during time dependent leaching of stabilised kaolin clay with 1% humic acid at different hydration durations

For 2.5% sulphate matrices, Figures 7.241 and 7.242 show the measured releases during pH dependent leaching, and cumulative releases during time dependent leaching, for aluminium at the different hydration durations. Similarly, results for silicon are shown in Figures 7.243 and 7.244, and those for calcium are shown in Figures 7.245 and 7.246. The evolutions of pH during time dependent leaching for the sulphate matrix are shown in Figure 7.247, for the different hydration periods.

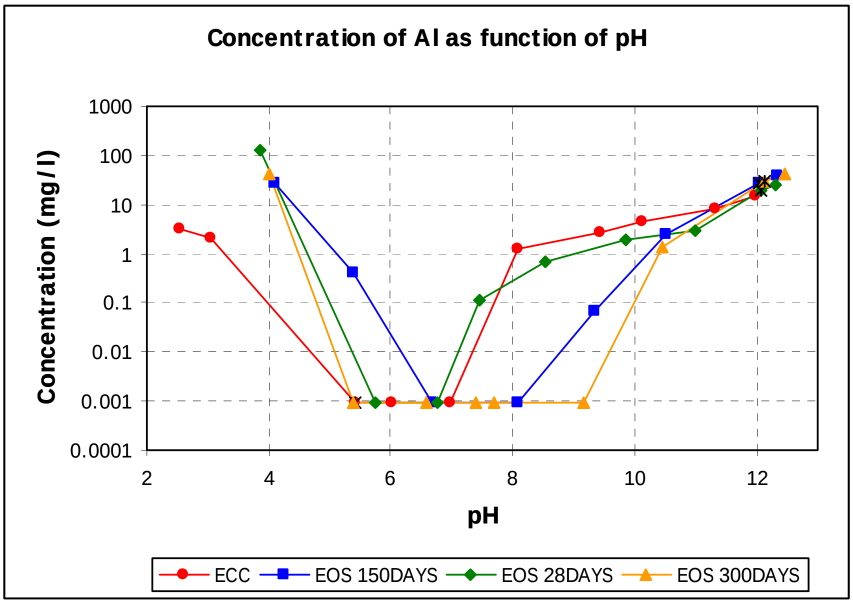


Figure 7:241: Release of aluminium due to pH influence from kaolin clay and stabilised kaolin clay with 2.5% sulphate at different hydration durations

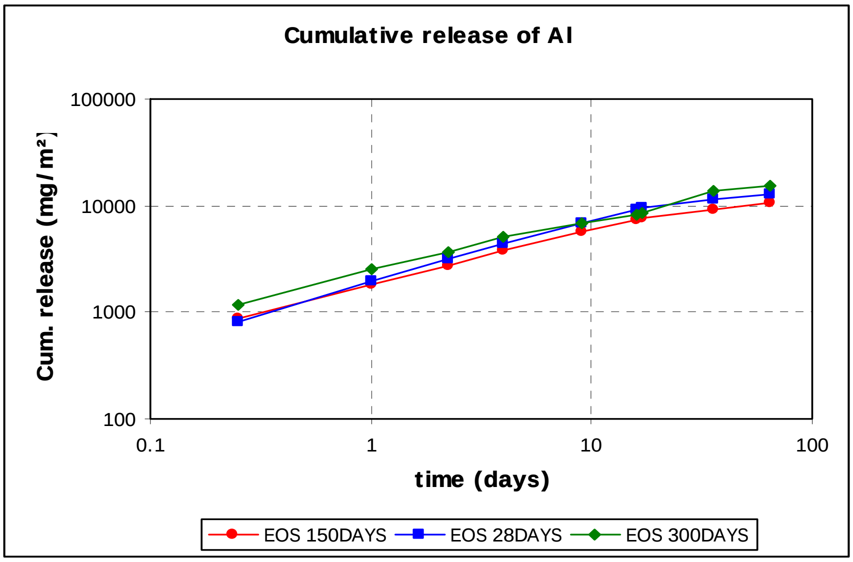


Figure 7:242: Cumulative releases of aluminium during time dependent leaching from stabilised kaolin clay with 2.5% sulphate at different hydration durations

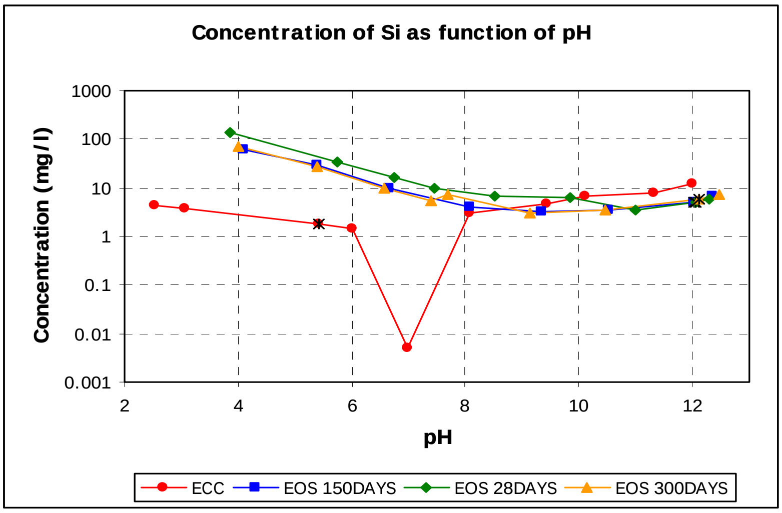


Figure 7:243: Release of silicon due to pH influence from kaolin clay and stabilised kaolin clay with 2.5% sulphate at different hydration durations

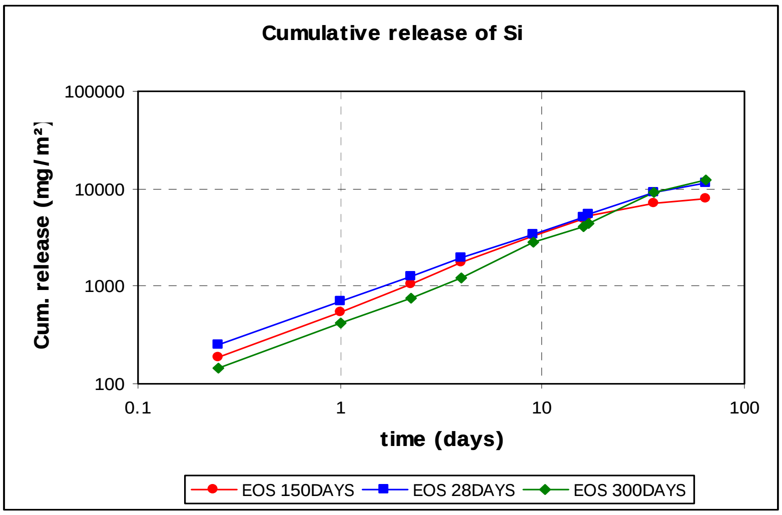


Figure 7:244: Cumulative releases of silicon during time dependent leaching from stabilised kaolin clay with 2.5% sulphate at different hydration durations

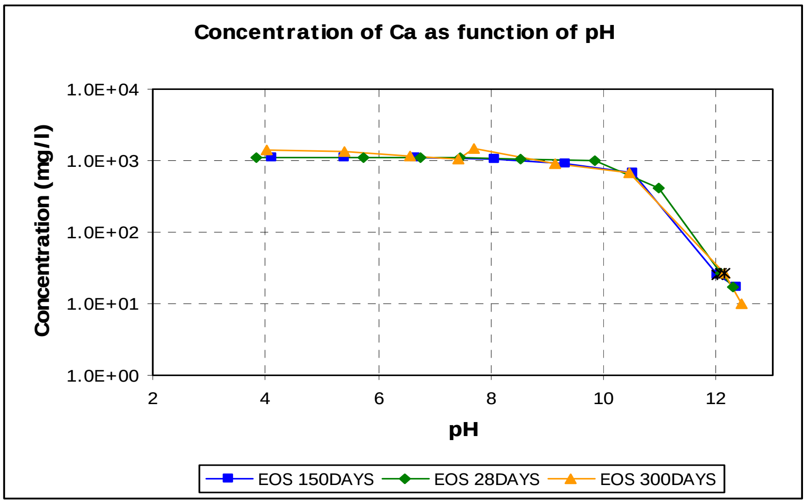


Figure 7:245: Release of calcium due to pH influence from stabilised kaolin clay with 2.5% sulphate at different hydration durations

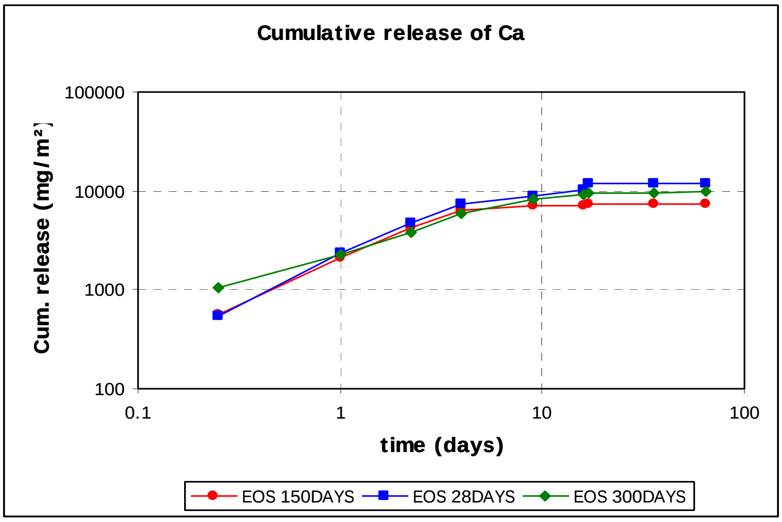


Figure 7:246: Cumulative releases of calcium during time dependent leaching from stabilised kaolin clay with 2.5% sulphate at different hydration durations

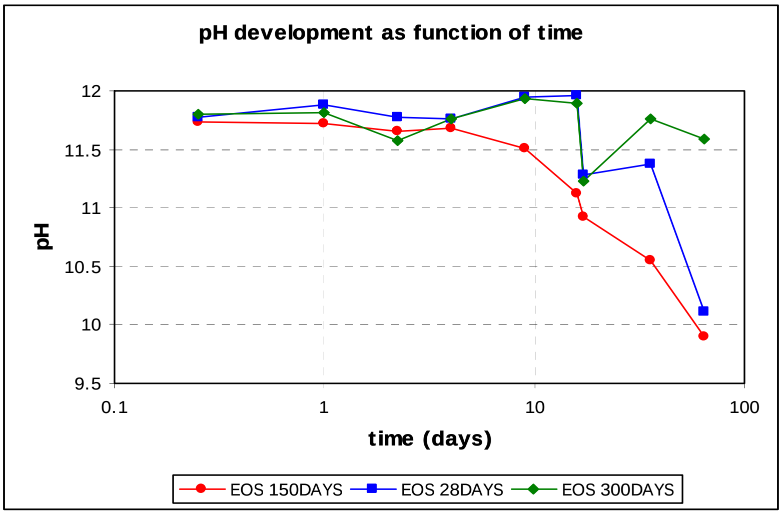


Figure 7:247: Evolution of pH during time dependent leaching of stabilised kaolin clay with 2.5% sulphate at different hydration durations

7.6.2 Zinc Contaminant Release

This section shows comparisons for zinc containment and releases, due to influences from variations in the matrices and increasing hydration. Availabilities (g/kg) of aluminium, silicon, calcium and zinc from pH dependent leaching of stabilised zinc contaminated stabilised matrices are shown in Table 7.5 for the different hydration durations. Cumulative releases (g/m^2) during time dependent leaching of zinc contaminated matrices are shown in Table 7.6, at the different hydration periods.

Table 7.5: Availabilities of Al, Si, Ca and Zn from stabilised zinc contaminated matrices

Zinc Samples Availabilities (g/kg)					
Sample	**pH**	**Al**	**Si**	**Ca**	**Zn**
EOZ 28 days	3.76	1.82	2.11	21.25	0.48
EOZ 150 days	4.10	0.46	1.09	21.40	0.26
EOZ 300 days	3.82	1.09	1.14	28.41	0.20
EOHZ 28 days	4.03	0.66	1.77	21.25	0.50
EOHZ 150 days	4.26	0.38	1.45	22.16	0.43
EOHZ 300 days	4.00	0.45	1.07	19.96	0.23
EOSZ 28 days	4.01	0.87	1.91	21.24	0.33
EOSZ 150 days	4.07	0.95	1.60	20.15	0.29
EOSZ 300 days	3.86	1.18	1.49	21.92	0.21

Table 7.6: Cumulative releases of Al, Si, Ca and Zn from stabilised zinc contaminated matrices

Zinc Samples Cumulative Releases (g/m^2)				
Sample	**Al**	**Si**	**Ca**	**Zn**
EOZ 28 days	3.72	3.91	142.70	0.0004
EOZ 150 days	5.33	3.63	61.13	0.0004
EOZ 300 days	7.36	3.53	64.63	0.0010
EOSZ 28 days	7.18	8.22	21.62	0.0004
EOSZ 150 days	9.44	23.80	439.38	3.6310
EOSZ 300 days	14.73	10.05	10.63	0.0004
EOHZ 28 days	2.29	4.78	185.14	0.0060
EOHZ 150 days	4.24	3.78	134.65	0.0009
EOHZ 300 days	6.21	3.72	94.05	0.0030

Note: Anomalous releases for EOSZ at 150 days, trend shown in Chapter 7 Figure 7.15. Discussed in Chapter 8 Section 8.2.3.1

To evaluate the influence of increasing hydration on zinc containment, Figures 7.248, 7.249 and 7.250 show the pH dependent releases of zinc from the different matrices, at the different hydration durations. These are for releases from stabilised zinc contaminated kaolin clay, stabilised zinc contaminated kaolin clay with 1% humic acid, and stabilised zinc contaminated kaolin clay with 2.5% sulphate respectively. The release of zinc during pH dependent leaching of the uncontaminated and unstabilised kaolin clay is also included for comparison.

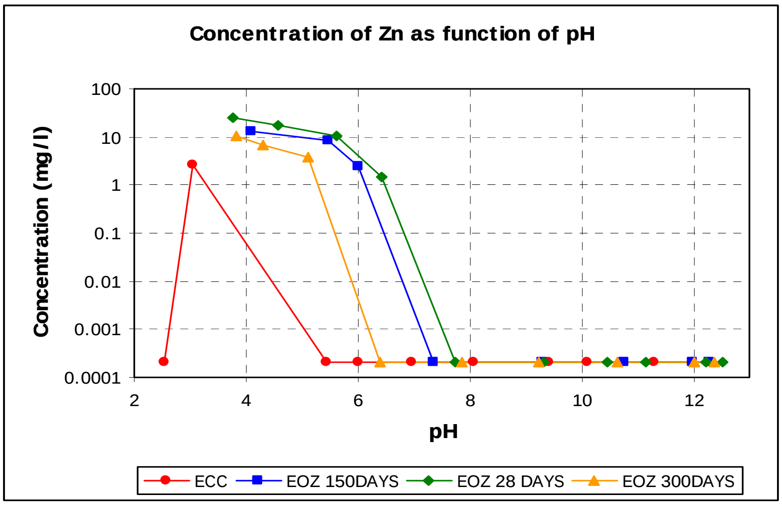


Figure 7:248: Releases of zinc from kaolin clay and stabilised zinc contaminated kaolin clay at different hydration durations

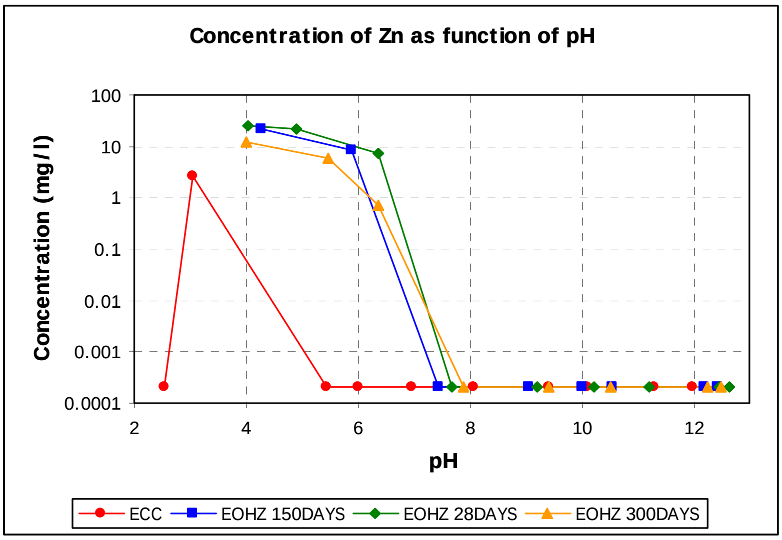


Figure 7:249: Releases of zinc from kaolin clay and stabilised zinc contaminated kaolin clay with 1% humic acid at different hydration durations

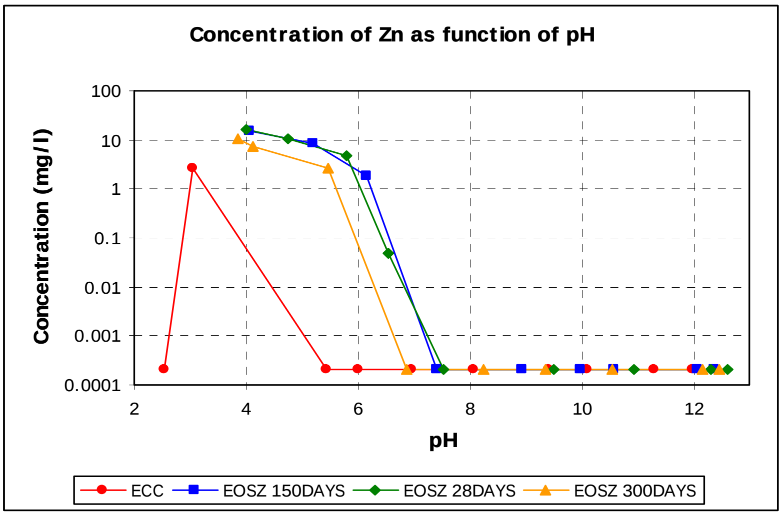


Figure 7:250: Releases of zinc from kaolin clay and stabilised zinc contaminated kaolin clay with 2.5% sulphate at different hydration durations

To evaluate the influences of introduced additives on zinc releases, comparisons were undertaken for zinc releases from the different matrices, at specific hydration periods. Figure 7.251 shows the pH dependent zinc releases from zinc contaminated and uncontaminated matrices at 28 days of hydration. Similarly, respective results for leaching at 150 and 300 days of hydration are shown in Figures 7.252 and 7.253. These results include zinc release trends from uncontaminated and zinc contaminated matrices without additives, matrices with 1% humic acid, and matrices with 2.5% sulphate.

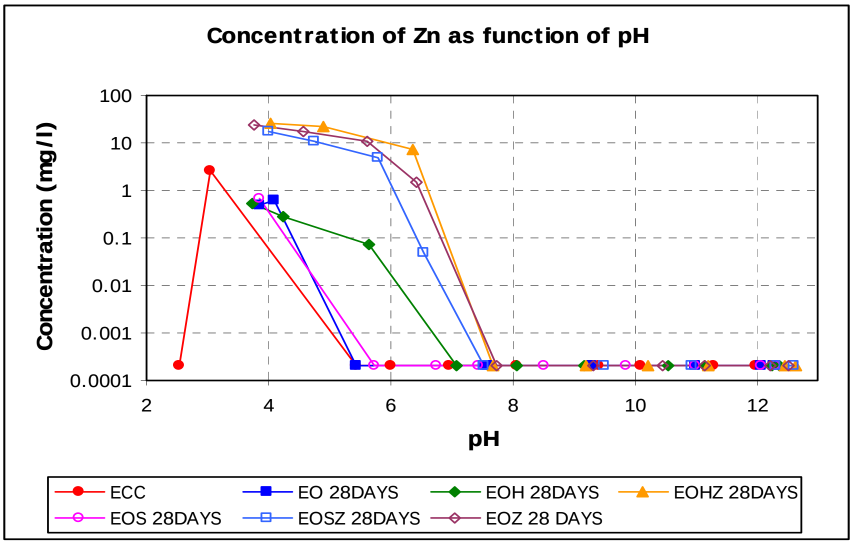


Figure 7:251: Releases of zinc from kaolin clay, stabilised zinc contaminated, and uncontaminated matrices, with and without additives at 28 days hydration

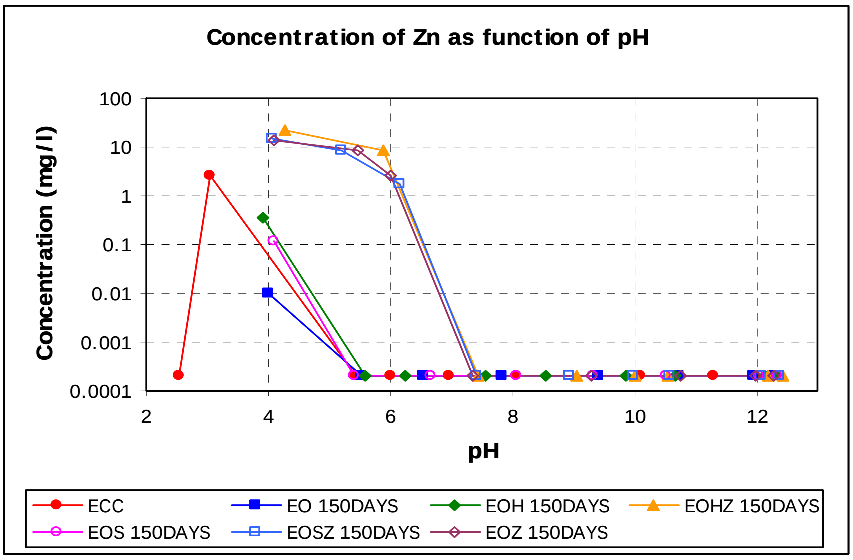


Figure 7:252: Releases of zinc from kaolin clay, stabilised zinc contaminated, and uncontaminated matrices, with and without additives at 150 days hydration

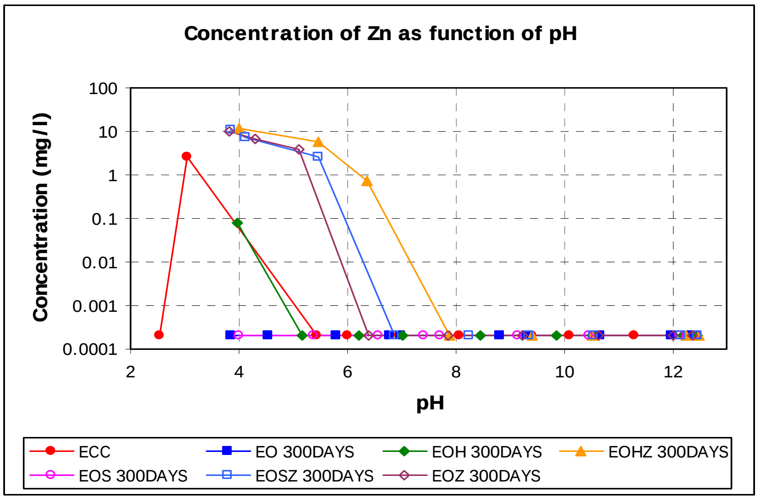


Figure 7:253: Releases of zinc from kaolin clay, stabilised zinc contaminated, and uncontaminated matrices, with and without additives at 300 days hydration

7.6.3 Chromium Contaminant Release

This section shows comparisons for chromium containment and releases, due to influences from matrix variations, and increased hydration. Availabilities (g/kg) of aluminium, silicon, calcium and chromium during pH dependent leaching of chromium contaminated matrices are shown in Table 7.7, at the different hydration durations. The cumulative releases (g/m^2) of these components, during time dependent monolithic leaching are shown in Table 7.8, for the different hydration durations.

Table 7.7: Availabilities of Al, Si, Ca and Cr from stabilised chromium contaminated matrices

Chromium Samples Availabilities (g/kg)					
Sample	**pH**	**Al**	**Si**	**Ca**	**Cr**
EOC 28 days	3.97	0.86	1.43	21.17	0.03
EOC 150 days	4.12	0.47	1.08	22.57	0.02
EOC 300 days	4.00	0.50	0.68	29.38	0.01
EOHC 28 days	4.03	0.73	1.74	22.57	0.12
EOHC 150 days	4.32	0.23	1.24	22.58	0.23
EOHC 300 days	3.97	1.91	2.17	31.99	0.01
EOSC 28 days	3.55	3.62	4.81	22.71	0.25
EOSC 150 days	3.89	1.25	1.82	21.42	0.04
EOSC 300 days	4.12	1.82	1.87	31.98	DL

Note: Chromium availabilities were variable, and did not always occur at the acidic pH extremes shown (Discussed in Chapter 8 Section 8.2.2)

Table 7.8: Cumulative releases of Al, Si, Ca and Cr from stabilised chromium contaminated matrices

Chromium Samples Cumulative Releases (g/m^2)				
Sample	**Al**	**Si**	**Ca**	**Cr**
EOC 28 days	4.24	3.60	113.09	0.041
EOC 150 days	4.73	3.20	61.68	0.534
EOC 300 days	5.97	3.17	61.81	0.065
EOSC 28 days	8.52	8.33	19.46	0.192
EOSC 150 days	9.43	8.49	12.00	0.244
EOSC 300 days	14.85	10.47	10.47	0.260
EOHC 28 days	3.80	4.56	123.77	0.105
EOHC 150 days	6.33	3.53	57.42	0.203
EOHC 300 days	8.35	2.93	78.83	0.231

To assess the influences of increasing hydration on chromium containment, Figures 7.254, 7.255 and 7.256 show the pH dependent chromium releases at the different hydration durations. These are for releases from stabilised chromium contaminated kaolin clay, stabilised chromium contaminated kaolin clay with 1% humic acid, and stabilised chromium contaminated kaolin clay with 2.5% sulphate respectively.

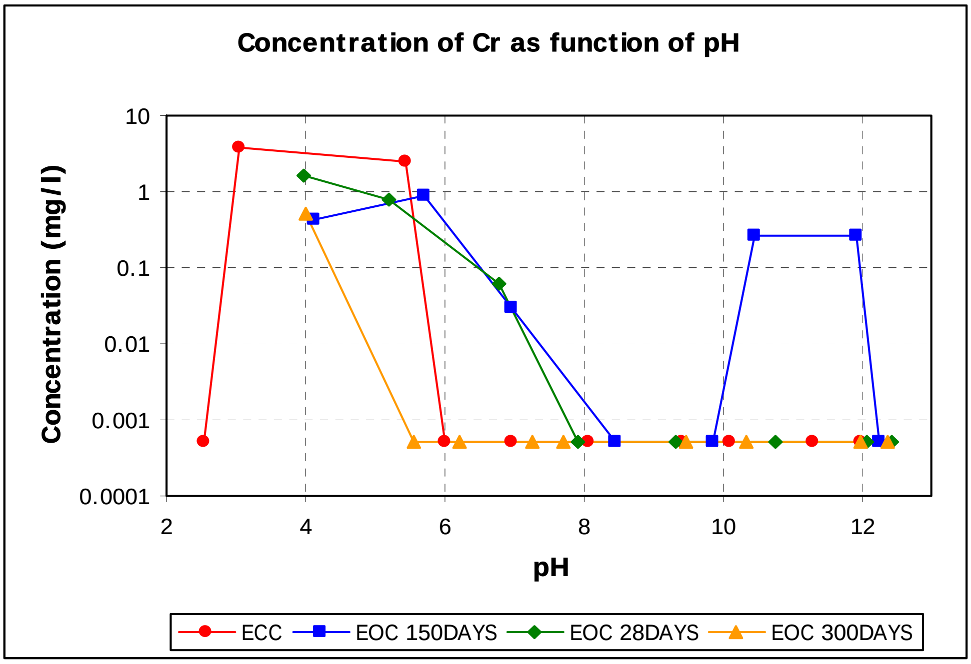


Figure 7:254: Releases of chromium from kaolin clay and stabilised chromium contaminated kaolin clay at different hydration durations

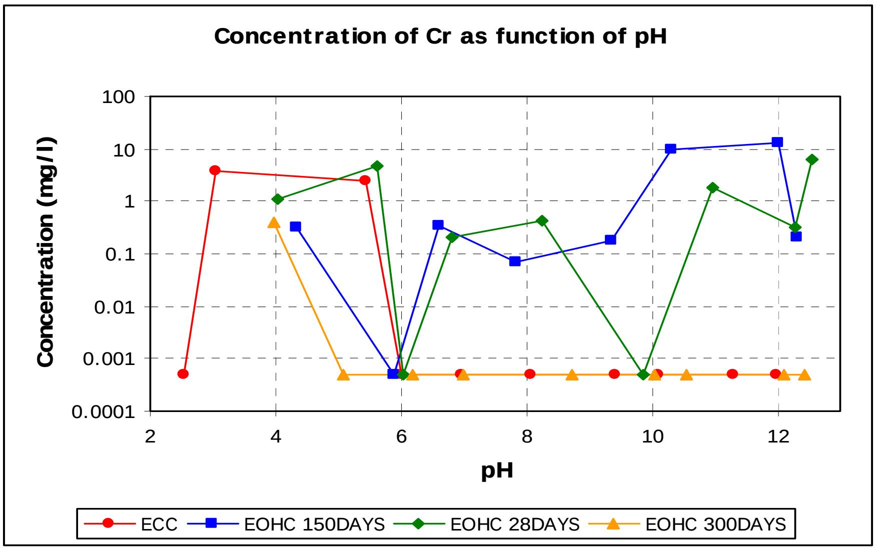


Figure 7:255: Releases of chromium from kaolin clay and stabilised chromium contaminated kaolin clay with 1% humic acid at different hydration durations

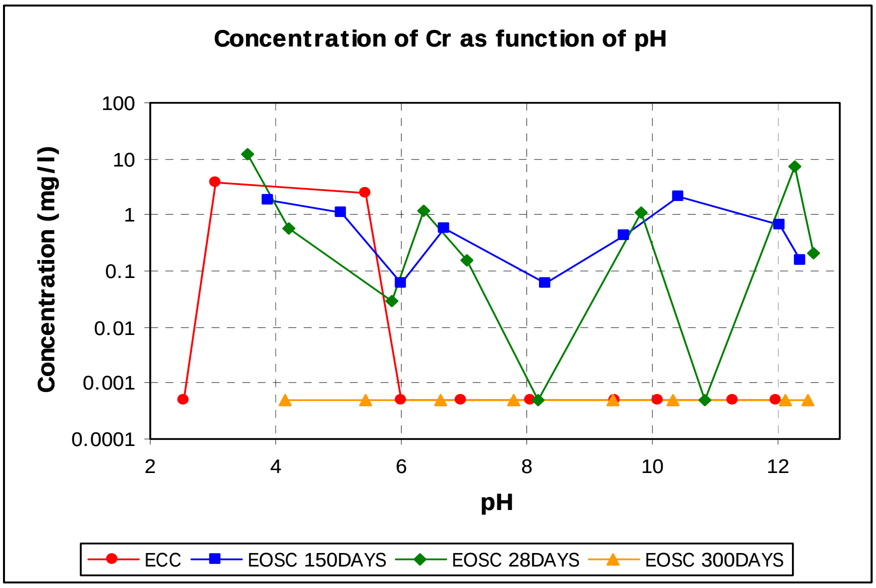


Figure 7:256: Releases of chromium from kaolin clay and stabilised chromium contaminated kaolin clay with 2.5% sulphate at different hydration durations

To evaluate the influences of introduced additives on chromium containment, releases from pH dependent leaching of different matrices are assessed, at specific hydration durations. Figure 7.257 shows chromium releases at 28 days of hydration from the different matrices. Chromium releases at 150 and 300 days of hydration, are shown in Figures 7.258 and 7.259 respectively. These include leaching results from uncontaminated and chromium contaminated samples, for the different stabilised matrices.

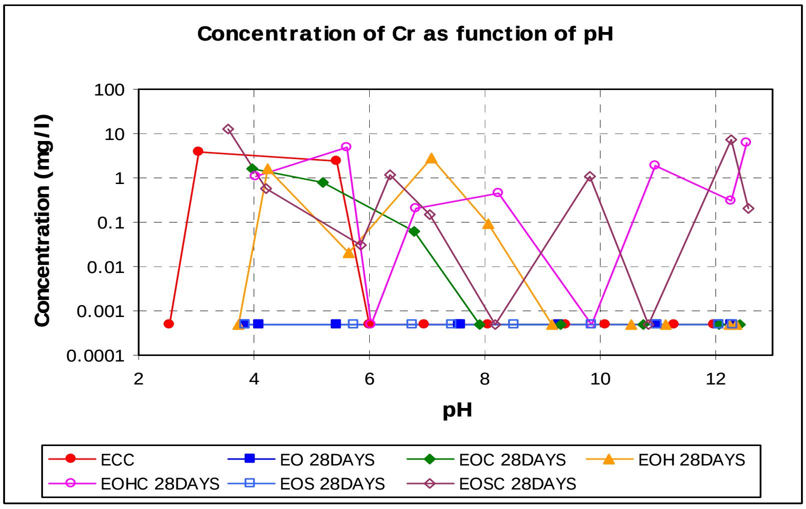


Figure 7:257: Releases of chromium from kaolin clay, stabilised chromium contaminated and uncontaminated matrices, with and without additives at 28 days hydration

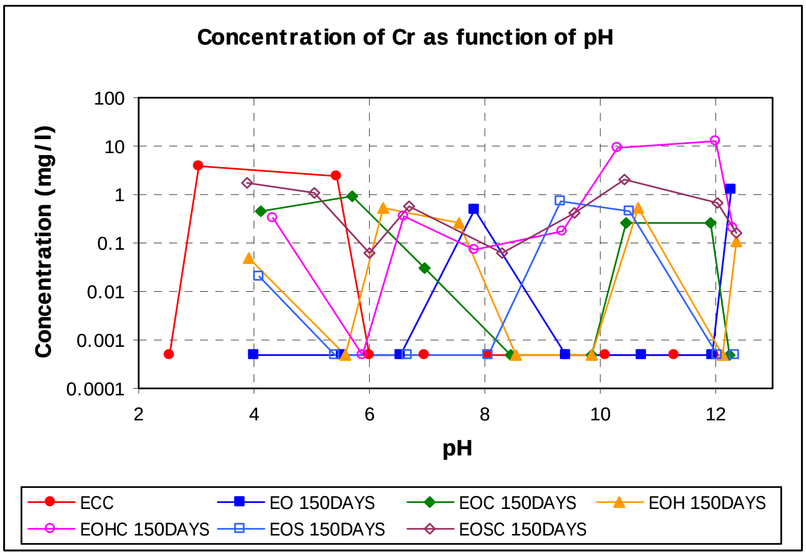


Figure 7:258: Releases of chromium from kaolin clay, stabilised chromium contaminated and uncontaminated matrices, with and without additives at 150 days hydration

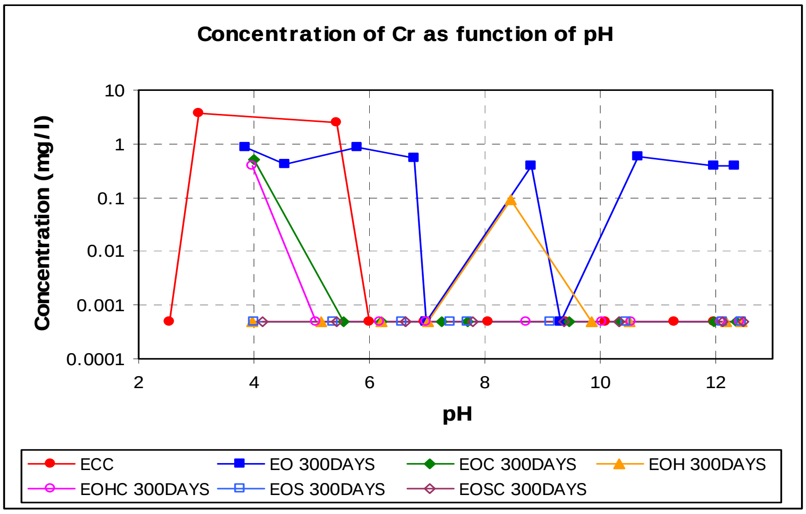


Figure 7:259: Releases of chromium from kaolin clay, stabilised chromium contaminated and uncontaminated matrices, with and without additives at 300 days hydration

7.7 TIME DEPENDENT LEACHING CONSISTENCY EVALUATION

To ensure reliability, repeatability and consistency for measured time dependent leaching results for stabilised matrices, triplicate repeats were undertaken on selected samples for comparisons. These were undertaken at different hydration durations, and for different matrices. The results for two matrices were evaluated and presented for illustrative purposes, and these included: stabilised zinc contaminated kaolin at 150 days of hydration; and stabilised chromium contaminated kaolin with 2.5% sulphate at 300 days of hydration. Comparisons for pH evolution and the time dependent and cumulative releases for aluminium and silicon are presented for comparison. Time dependent and cumulative releases for aluminium from stabilised zinc contaminated kaolin replicates at 150 days of hydration are shown in Figures 7.260 and 7.261 respectively. Respective results for silicon are shown in Figures 7.262 and 7.263, while the replicates pH evolutions are shown in Figure 7.264. Time dependent and cumulative releases for aluminium from stabilised chromium contaminated kaolin with 2.5% sulphate replicates at 300 days of hydration, are shown in Figures 7.265 and 7.266 respectively. Respective results for silicon are shown in Figures 7.267 and 7.268, while the replicates pH evolutions are shown in Figure 7.269.

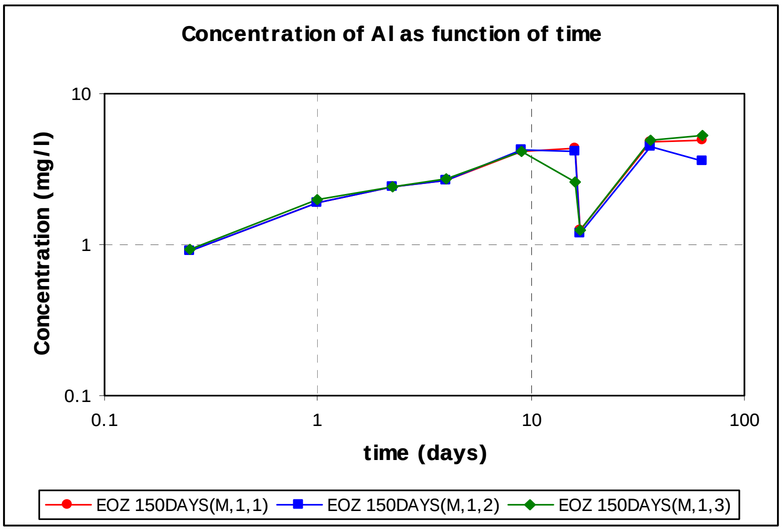


Figure 7:260: Releases of aluminium during time dependent leaching of stabilised zinc contaminated kaolin clay replicates at 150 days hydration

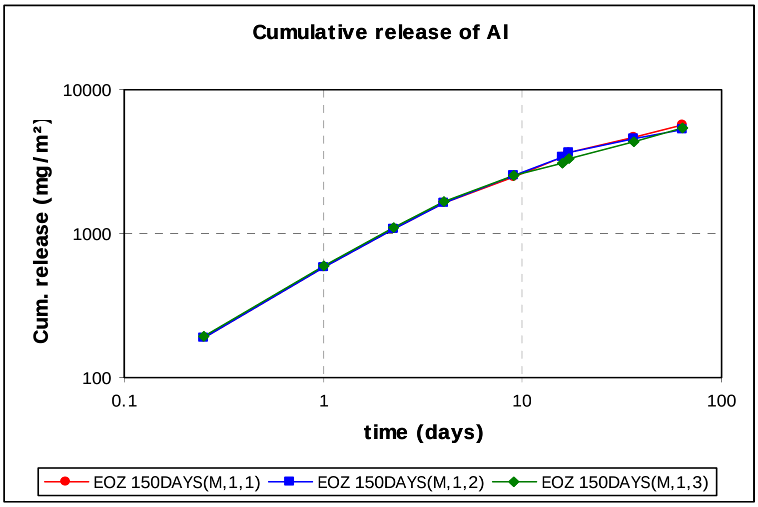


Figure 7:261: Cumulative releases of aluminium from time dependent leaching of stabilised zinc contaminated kaolin clay replicates at 150 days hydration

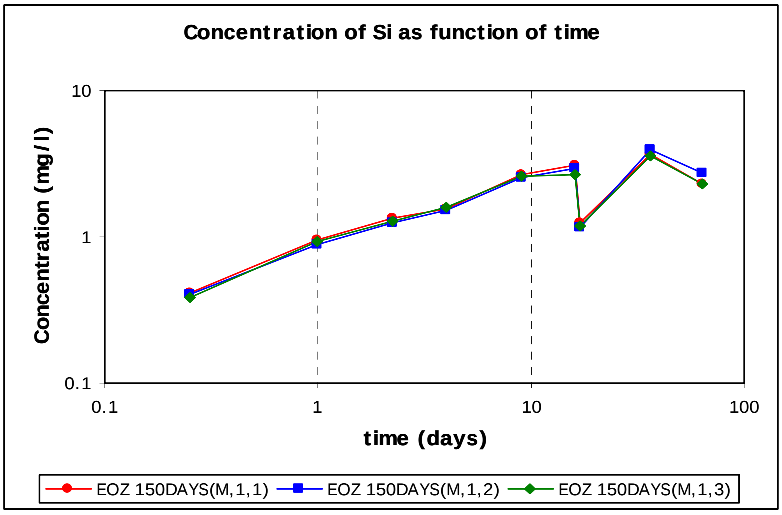


Figure 7:262: Releases of silicon during time dependent leaching of stabilised zinc contaminated kaolin clay replicates at 150 days hydration

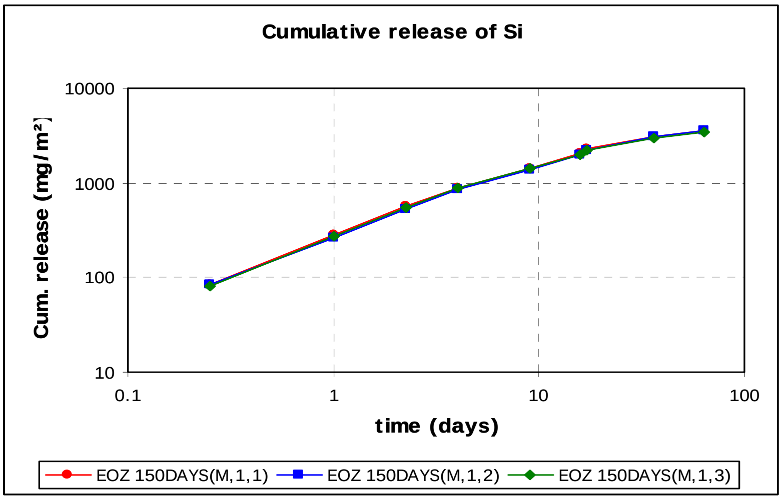


Figure 7:263: Cumulative releases of silicon from time dependent leaching of stabilised zinc contaminated kaolin clay replicates at 150 days hydration

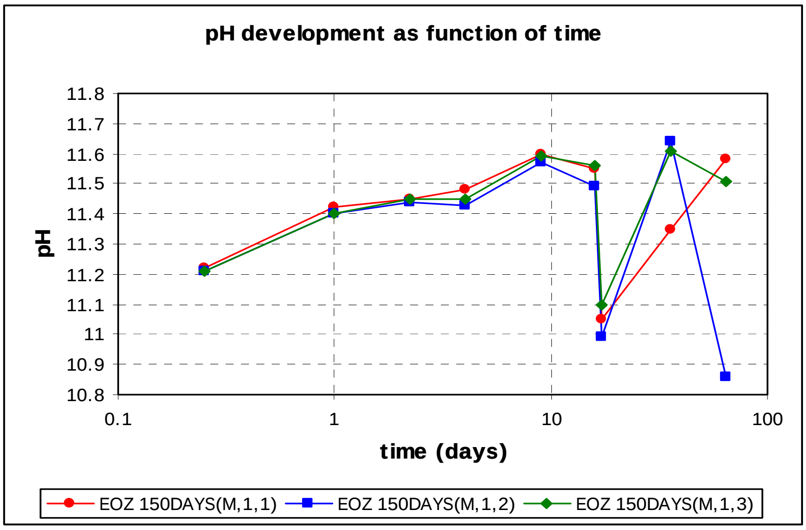


Figure 7:264: pH evolution for time dependent leaching of stabilised zinc contaminated kaolin clay replicates at 150 days hydration

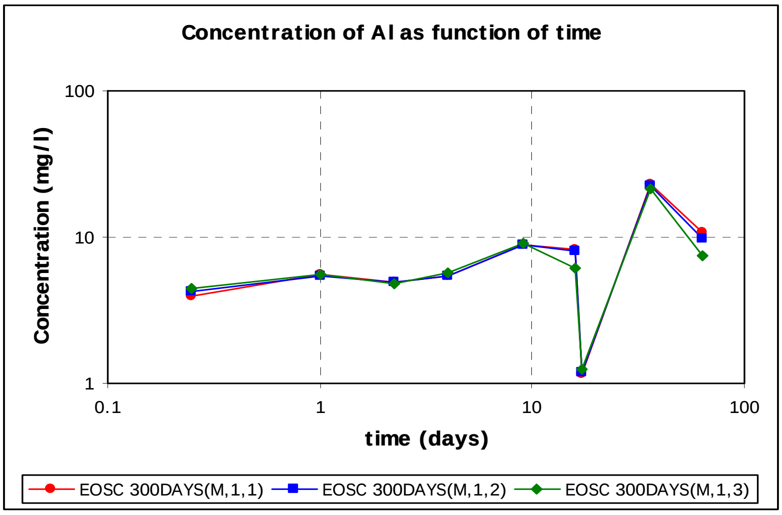


Figure 7:265: Releases of aluminium during time dependent leaching of stabilised chromium contaminated kaolin clay with 2.5% sulphate replicates at 300 days hydration

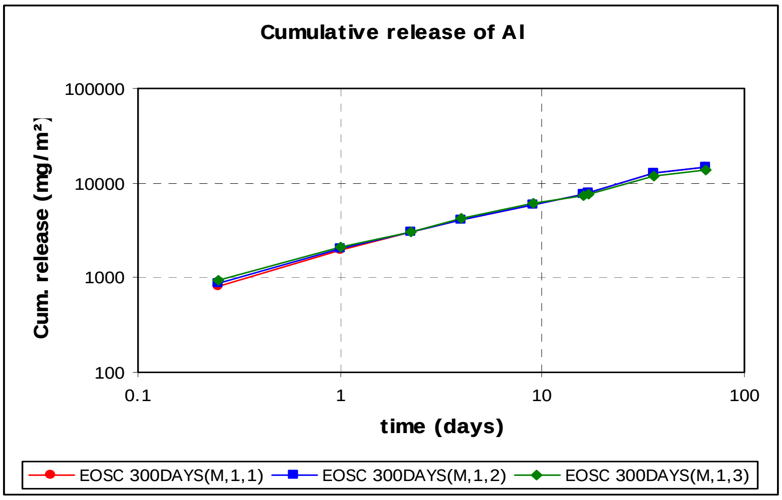


Figure 7:266: Cumulative releases of aluminium from time dependent leaching of stabilised chromium contaminated kaolin clay with 2.5% sulphate replicates at 300 days hydration

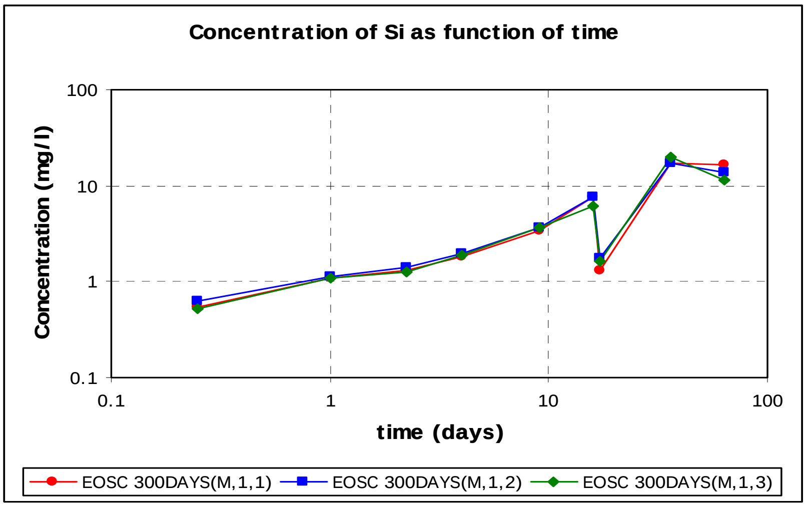


Figure 7:267: Releases of silicon during time dependent leaching of stabilised chromium contaminated kaolin clay with 2.55 sulphate replicates at 300 days hydration

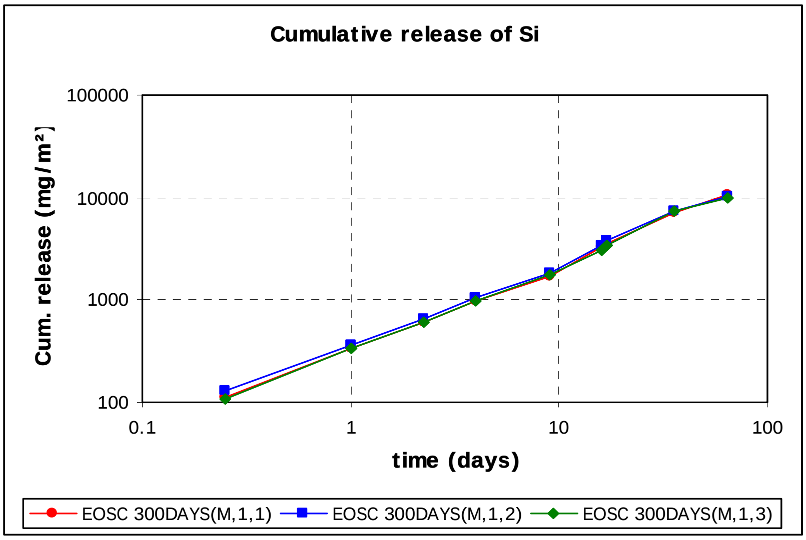


Figure 7:268: Cumulative releases of silicon from time dependent leaching of stabilised chromium contaminated kaolin clay with 2.5% sulphate replicates at 300 days hydration

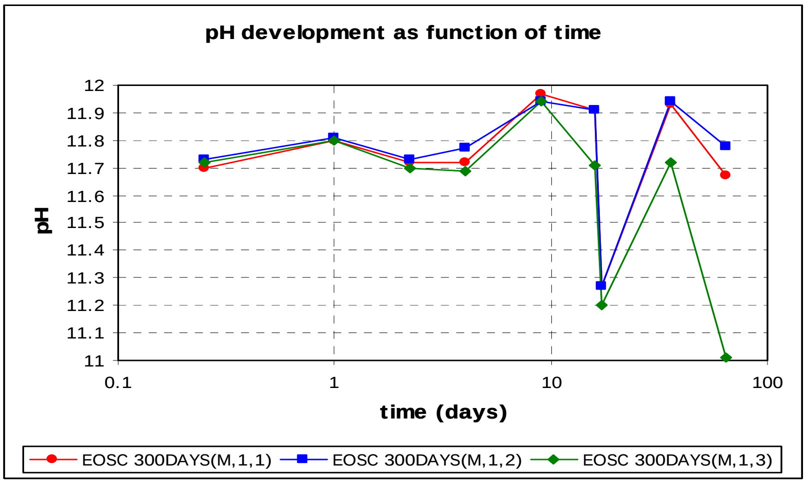


Figure 7:269: pH evolution for time dependent leaching of stabilised chromium contaminated kaolin clay with 2.5% sulphate replicates at 300 days hydration

The results presented in this chapter will now be considered in detail in Chapter 8, from where specific and key trends, together with their implications, will be discussed. These will include influences of additives and hydration on containment and leaching behaviours for the matrices, relevant mineral phases for solubility control, and evaluations of method effectiveness. Complete chemical characterisation could not be accomplished due to time, cost, testing and analytical constraints, but the use of master species for evaluation improved confidence in this approach, when applied to assess S/S chemical durability and effectiveness evaluation.

CHAPTER EIGHT

8.0 DISCUSSIONS

This chapter discusses the results from laboratory experimentations (presented in Chapter 6), leaching and geochemical speciation evaluations (presented in Chapter 7), and the implications of these findings for application to S/S. Primary focuses were on Zn^{2+} and CrO_4^{2-} releases from matrices, degradation of matrices with hydration (via releases of H_4SiO_4 and Al^{3+}), chemical durability, and implications of additives (humic acid and sulphate) and hydration increases on containment (to meet study objectives, Chapter 1 Section 1.4). However, whilst chromium was introduced as Cr^{3+} nitrate, LeachXS limitations only allowed assessments as chromate species. Care was taken to ensure that selected solubility controlling phases were specifically Cr^{3+} salts (see Chapter 7.3). Due to lack of published information for similar assessments on comparable matrices, comparisons of results with findings from other studies were not possible.

Master species were used during release assessments from the different matrices (see Chapter 5 Section 5.3), and calculations for individual interactions were not manually undertaken during this study. ORCHESTRA embedded in LeachXS was used for the geochemical calculations (dissolution – precipitation, sorption - desorption, ion exchange and complexation) to determine speciation (see Section 5.4). However, an understanding of the interactions that induce containment was required (reviewed in Chapter 3 Sections 3.3 and 3.4), prior to selections of solubility controlling mineral phases. Characterising and understanding the behaviour of stabilised matrices can be used to improve confidence in long-term S/S performance. These were addressed by assessing the different release mechanisms, evaluating the partitioning of components, and assessing the changes with increasing hydration time.

The discussions chapter is structured into 7 sections:

1. Preliminary Material Characterisation: It was necessary to discuss the potential for variability and error during experimentation and analyses, and these are discussed in this section. The section then discusses the implications of material properties, and the sample preparation process, on the measured releases of components and stabilisation effectiveness. The section also discusses the implications of the mixes on component releases, and the implications of eluates analyses.
2. Matrix Evaluation: Compositional evaluations for stabilised matrices are presented in this section, discussing the leaching availabilities for the master species. This section also discusses the variations in release availabilities with matrix variations, and increases in hydration. The chemical durability / leaching resistance of the different matrices are then discussed, with changes in hydration during pH and time dependent leaching, based on the leachability of structural components.
3. Time Dependent Leaching Evaluations: The results and trends from time dependent leaching of monolithic specimens, for the different matrices, are discussed in this section. The discussions are separated based on the matrix types, for components cumulative releases, and changes in releases with increasing hydration.
4. pH Dependent Leaching Evaluations: The results and trends from pH dependent leaching for the different matrices are discussed in this section. Similar to discussions for monolithic leaching, the discussions are separated based on the matrix types, and consider the leaching trends and changes in trends with increasing hydration.
5. Porewater Leaching Evaluations: The results from up-flow percolation leaching, to evaluate equilibrium leaching to porewater, are discussed in this section. Changes

in releases for structural components (no observed contaminant release, see Section 8.5) for the different matrices, with increasing hydration, are discussed here.

6. Speciation Evaluations: This section discusses the geochemical speciation of master species and introduced contaminants, comparing the measured and predicted leaching trends for the components, and the solubility controlling mineral phases. The calculations and estimations of HFO and organic carbon are also discussed here, in view of their implications on containment and requirements for use in modelling. The changes in speciation for the different matrix variations, and changes in hydration are also discussed, as well as the validation of predicted phases. These discussions are separated based on the matrix type (additives), with the discussions then tailored to the introduced contaminant. The speciation evaluations for kaolin clay are also discussed to assess the changes induced by stabilisation. A brief discussion on interfacial speciation changes for monolithic specimens is included in this section. This discusses kaolin degradation under prevailing alkalinity during monolithic leaching at the different hydration periods.
7. Key Findings and Implications for S/S Design: Findings from discussions in the different sections are drawn together. The implications for S/S design are considered, showing adaptations for application to the conceptual situations presented in Chapter 1 Section 1.2.

8.1 PRELIMINARY MATERIAL CHARACTERISATION

The potential for variability and error during testing and analyses are discussed in this section. The implications of the sample preparation processes, evaluations for matrix compositions, possible implications of additives and mix designs, and analyses of eluate are also discussed in this section, in relation to the stabilisation process.

8.1.1 Potential for Variability and Experimental Error

As in all scientific studies, it is necessary to evaluate the potential for error arising from laboratory experimentation, eluate analyses and the assessment methods. Repeatability and accuracy are particularly important for this study, due to the potential for variability imposed by the nature of tests undertaken (chemical assessments) and the analytical methods employed. Processed kaolin clay was used during sample preparation, ensuring that all material used was from a single batch (see Chapter 4 Section 4.2.1). The cement used was also from a single batch (see Chapter 4 Section 4.2.2), to minimise variability in prepared samples. Inherent heterogeneity was unavoidable, especially considering the sample preparation process, where formations of peds and the packing processes induced variability across samples. This resulted in variable moisture contents within the peds, limited water getting into unhydrated cement grains surrounded by clay, and prevented a consistent composition across the matrices (also see Chapter 4 Section 4.4.1). However, consistency evaluations were incorporated during sample preparation, using colour permeation (methyl-blue) to optimise mixing and packing processes. Compositional evaluations via XRF were also undertaken on stabilised matrices (Chapter 6 Section 6.1.3), and variability evaluations for test replicates are presented in Table 6.6. Concentrations of the evaluated components (Al, Si, Ca, Mn, Mg, P, S, Fe and Na) were repeatable and consistent for the replicates tested, but varied between the different matrices. Evaluations for matrix compositions are discussed in Section 8.2.1.

For the chemical leaching tests, it was important to ensure the consistency of samples used during the tests. During equilibrium leaching tests (pH dependent leaching and up-flow percolation leaching tests), crushed samples were required (see Chapter 4 Sections 4.5.2 and 4.5.3) for testing. These required sample extrusion and processing, and a representative sample used (after crushing and mixing) for the tests. To prevent thermal alterations, pH dependent test specimens were tested at the crushed and sieved water content, while the up-flow percolation specimens were air dried and mixed before packing. For these tests, replicates of tests were not undertaken, but rather eluates replicates for chemical analyses were used to assess repeatability. Also, due to the costs for undertaking chemical analyses, it was economical to test replicates rather than conduct replicate tests. Typically, pH dependent leaching tests generate 8 – 10 eluate fractions, so it was cheaper to replicate one fraction than replicate the test. For the percolation tests, variations in material densities and water conditions influenced releases. This was mitigated by ensuring column saturation and equilibration prior to test commencement (Chapter 4 Section 5.4.2), and calculating the releases based on prevailing physical parameters (see Chapter 6 Section 6.2.3). For disequilibrium leaching tests, monolithic specimens were tested, and thus it was necessary to replicate tests to evaluate consistency and repeatability of the measure chemical parameters and the eluates analysed (see Chapter 4 Section 4.5.1). Replicates were then evaluated for consistency, and the illustrative results for comparisons were presented in Chapter 7 Section 7.7. pH development and leachability trends were repeatable and comparable for the replicate fractions, when matching aluminium, silicon and calcium releases. Variations in physical properties are likely to have influenced the measured releases and measured chemical parameters. Table 6.19 and 6.20 (Chapter 6 Section 6.2.2) shows the measured chemical parameters for eluate fractions and the material physical properties. The chemical parameters show comparable values and trends during the tests, however, depletion sets in halfway through the tests (at 30 days – fraction 8), inducing variations in the parameters.

To ensure the accuracy of eluates analytical results, daily calibrations were carried out for both ICP cation analyses and DOC analyses. Daily calibration standards were run to prevent concentration drifts, and blanks were used to assess process anomalies and contamination. During DOC analyses, controls for the leachants used in the different tests were analysed to determine contaminations (Chapter 6 Section 6.3.1 Table 6.36). Most of the measures were below 1mg/l, indicating minimal potential for contamination from the testing processes. Measures from the unstabilised kaolin clay varied between 22 and 70mg/kg, and thus 1mg/kg was considered insignificant, in view of the expected limited organic content in processed kaolin clay. To ensure accuracy and evaluate cross contamination, blanks (DOC free water) were analysed along side test eluates. The obtained results (Section 6.37) show that almost half of the analysed blanks (47) were below detection by the highly sensitive Shimatzu DOC analyser, with 92% of the measurements below 1mg/l. For cation analyses, since testing was done in an external laboratory (University of Wolverhampton), it was necessary to determine the accuracy and precision of the eluate results. Given the cost implications, it was not economical to analyse each eluate in multiple replicates, but rather random selections of eluates were used to generate confidence in the obtained data. Eluates were analysed in batches, and replicates and controls were included in each batch, to ensure reliability of obtained results. To evaluate the influence of test processes on results, controls and blanks were analysed and presented in Chapter 6 Section 6.3.2 (Table 6.40). Measures were put in place during testing to minimise contamination, but for these chemical processes it was not always possible to completely negate external influences. Anomalous concentrations (bold highlight in Table 6.40) of salts were present in some of the analysed controls, which could have been introduced during acidification of eluates, or from leaching or storage containers. However, these were unlikely to have significantly affected measured concentrations, as eluate measurements were converted from mg/l to mg/kg of the solid sample. Repeatability evaluations were then undertaken on eluate replicates (Tables 6.41 and 6.42), and the results for the selected components (Na, Ca, S, Si, Al, Fe, Zn and Cr) showed significant repeatability and consistency. To ensure accuracy of obtained results, replicates of a standard iron solution (10mg/l) were analysed and the results presented in Table 6.39. Results were repeatable and consistent, showing 93% accuracy for the measured iron concentrations. This engendered confidence in the obtained measurements, which were subsequently used for assessments.

8.1.2 Material Properties, Mix Properties and Sample Preparation

The properties of the original material, variations in the mixes for the different matrices, and the processes and problems encountered during sample preparation, were likely to influence the containment and leachability of contained components. The kaolin clay used in testing had a composition of predominantly kaolin (74 – 80%), with inclusions of montmorillonite, feldspar, mica and quartz (See Table 4.1). Compositional evaluations show structural dominance of silica and alumina (85%) with a natural pH of 5.0 (Table 4.2). The affinity of the introduced contaminants for sorption by the kaolin clay (Zn^{2+} and Cr^{3+} at 662.5mg/kg) show that 411mg/kg Cr and 323mg/kg Zn were sorbable at the clay's natural pH (Table 6.2). Inclusion of additives influenced the natural development of pH for the clay (Table 6.3), reducing from 5.4 for kaolin, to 4.7 for sulphate samples, and 5.0 for humic acid samples. Evaluations for the implications of additives on contaminants containment post-stabilisation were undertaken, but the assessments for their implications on sorption capacities were not required. Whilst minor alterations in properties for clays may be expected with time, Boardman (1999) did not find these changes to be significant for kaolin clay properties.

The cement used for stabilisation of the kaolin clay contained 62.0% CaO, 16.9% SiO_2, 4.3% Al_2O_3 and 2.7% SO_3 on average (Table 4.4) at pH 12.0 – 14.0. This significantly increased the concentrations of Ca and S in stabilised matrices (Tables 6.4

and 6.5). It also increased the zinc content from 24mg/kg to over 40mg/kg, and chromium content from 31mg/kg to 33mg/kg, compared to unstabilised samples. The introduction of hydrated sulphates as an additive had a negligible impact on contaminant concentrations, but decreased the aluminium and silicon contents (Tables 6.4 and 6.5). This was due to the sodium sulphate contents used, which was 2.5% of the total matrix mass. These were considered during chemical durability evaluation for sulphate matrices (Section 8.2.3).

Peds of stabilised clays formed during mixing, prior to packing for curing, which was likely to result in varying properties on the exterior and interior of the peds. Variations in peds sizes were observed between matrices, varying with the presence of additives and introductions of contaminants. However, these were not measured for the matrices and are mentioned to highlight the implications of varying surface processes (agglomeration, flocculation, changes in the diffuse layer) occurring for the mixes. Barnard (2008) measured 5mm averages for peds during mixing of cement stabilised kaolin, and these peds can increase the porosity and permeability (Mirsal, 2004) when packing. Using 30% water contents (Chapter 4 Section 4.4.1.1) improved the workability during mixing, and also allowed sufficient water to permeate though the peds during stabilisation.

Implications of additive or contaminant inclusions on physical properties of matrices were not assessed. Similar preparation methods were employed for all mixes to ensure consistency (Section 4.4.1). These inclusions will impact on host soil properties, where additives like organics can significantly modify index properties and other physical and chemical properties (Mitchell and Soga, 2005, Peng *et al.*, 2009), and can enhance components leaching (Van der Sloot and Dijkstra, 2004). They can also influence hydration by retarding setting of cement and reducing the strength of products (Bone *et al.*, 2004b). This was particularly evident for humic additive mixes, which retained plastic deformation after 300 days of hydration, due to hydration retardation, as suggested by

Natali Sora *et al.* (2002). However, the focus of the study was on chemical implications of additives on components containment post-stabilisation. Also, feasibility assessments for humic matrices found that samples retained their monolithic form and integrity during leaching. The introduction of sulphate as sodium sulphate will result in the increased formation of expansive minerals (ettringite) during hydration. This can induce cracking, compromising porosity and permeability (Bone *et al.*, 2004b, Al-Tabbaa *et al.,* 2005), especially during leaching from monoliths.

During the characterisation of matrices (leaching assessments discussed in Sections 8.3, 8.4 and 8.5), emphases of sub-sections were on the implications of introduced additives on the leachability of contaminants.

8.1.3 Eluate Analyses

The eluates obtained from the different leaching and extraction tests were analysed using ICP-OES for cation analyses, and a Shimatzu DOC analyser for DOC analyses. However, the ICP analyses only provided information on cation releases, without information on anion releases. Anion analyses for sulphates, phosphates, sulphides, chlorides and nitrates were undertaken using ion chromatography (see Chapter 4 Section 4.6 for explanations). Since the contaminants were introduced in nitrate form, extractions undertaken using nitric acid, filtration glassware cleaned with nitric acid, and samples preserved using nitric acid, nitrate measurements were discounted. Estimates for sulphates and phosphates were obtainable, using measures for sulphur and phosphorous from ICP analyses, so the priority was the determination of chloride measures. From a selection of 20 eluate fractions from the uncontaminated kaolin and the different matrices and test types, anion analyses were undertaken specifically to determine the presence and concentration of chloride. Validations were undertaken using standard chloride solutions, including spiking samples with known concentrations to determine possibilities for ion suppression. No chloride measures were recorded for any of the 20 eluates, and thus anion analyses were discontinued.

All obtained eluates were analysed within two weeks of collection and processing, and the eluates were acidified during processing to prevent re-precipitation of dissolved salts during storage. Obtained eluates from the percolation tests for sulphate and humic acid matrices had high dissolved salt contents, due to the nature of the test specimens and the low L/S ratios of the tests. After test completion, the eluates were filtered and preserved with acid, and samples for cation analyses were diluted 1 in 10 (also see Section 4.2.5). DOC samples did not require dilution, due to the suitability of the equipment for the concentrations measured. However, it was observed that after a few months of storage (all analyses having already been completed) salt precipitations occurred at the bottom of sulphate matrix eluates, and gelatinous precipitates of humic substances were found in humic acid matrix eluates. While these were not significant for this study due to all analyses having already been undertaken, they indicated the changing dynamics for salts in the eluates, due to changes from equilibrium conditions sustained during leaching.

8.2 MATRIX EVALUATION

To delineate baseline properties and characteristics of stabilised matrices, it was important to assess composition and concentrations of components in kaolin clay (see Section 8.1.2) and the stabilised matrices (Section 8.2.1). The implications on the release and availability of structural components (Al, Si and Ca for the stabilised kaolin) and contained contaminants were then evaluated. This was then used to infer the chemical durability based on resistance to leaching of the components, with changes in the hydration duration. This evaluation required information from matrices compositional evaluations

(Section 8.2.1), information on availabilities (Section 8.2.2), and information on cumulative releases (Section 8.2.3.1).

8.2.1 Matrix Compositional Evaluation

In undertaking compositional evaluations, it was important to select relevant elements for comparing releases to total composition. These included the introduced contaminants (Zn and Cr) and additives (S), kaolin structural components (Al and Si), and the stabilising agent (Ca). Alterations in the leached calcium content, with changes in hydration, can be used to infer the formation and stability of cementitious products. Kaolin becomes increasingly dissociated at high alkalinity due to silica loss, becoming unstable relative to gibbsite (Langmuir, 1997). Considering the alkalinity of stabilised kaolin, dissolution and releases of alumina and silica with hydration (McKinley *et al.*, 2001) can also be used to infer stability. Introductions of additives modified the matrices, and required the evaluation of leached concentrations, for comparison to compositional contents, to assess their implications.

For samples containing sulphate additives, 5% sodium sulphate decahydrate was added to kaolin pre-stabilisation, which yielded approximately 2.5% sodium sulphate. For consistency, mixes were labelled as matrices with 2.5% sulphate, for which introduced sodium constituted 0.8% of the entire matrix (800 mg/kg introduced). However, impact of sodium on stabilisation was not considered due to it being the least reactive cation in the lyotropic series (Mitchell and Soga, 2005). However, mass transfer can induce replacements, as well as cation exclusion (retarding calcium release) during monolithic leaching. This was observed during assessments, and addressed in Section 8.2.3.1.

Repeatability of the compositional evaluations was addressed in Section 8.1.1, and the results were found to be repeatable. These results were then used for comparisons with availabilities (Section 8.2.2) to determine the fraction of components leachable from the stabilised matrices. However, different analytical methods were used for obtaining this information, i.e. ICP for cation analyses and XRF for compositional analyses. It must be stressed that these comparisons are for qualitative purposes and should not be treated as absolutes. Within the scope of this study, it was not possible to evaluate the error induced by comparing the results from the different methods. Rather, the repeatability and accuracy of the results from the individual methods were evaluated (Section 8.1.1) to inform reliability for the comparisons. These considerations should also be incorporated during S/S design, using material characterisation and release availabilities to evaluate environmental impact, rather than relying on numbers from compositional concentrations.

For the compositional analyses (XRF), obtained results were for elemental contents rather than their oxides, and did not account for hydration of salts. The obtained results were for the elements concentrations, as a percentage of the total content. This yielded approximately 40% aluminium and silicon content for kaolin (Table 6.4), compared to approximately 85% for their hydroxides (Table 4.2). Results were not corrected to hydroxides, since the comparisons required were for elemental releases. Information drawn from compositional evaluations, for the implications of stabilisation, included:

- Reductions in aluminium and silicon content for stabilised matrices, with the lowest content observed in sulphate matrices. This was due to the replacement of kaolin (predominantly composed of alumina and silica) with 10% (total weight) cement (lower alumina and silica content – see Chapter 4 Table 4.4) used for stabilisation. For sulphate matrices, 2.5% of the total content was further replaced by sodium sulphate.
- Increased total sulphate contents with stabilisation (approximately 0.05% in stabilised matrices, and 0.30% in sulphate matrices), which was expected with cement and additive introductions, compared to concentrations (2mg/kg) in unstabilised kaolin.

- Increased calcium content with stabilisation, constituting about 2% of total content, in comparison to about 0.02% in unstabilised kaolin, due to 10% cement addition.
- Consistent chromium concentrations were observed in uncontaminated matrices (31–34mg/kg), but contaminated samples results showed variability, with smaller contents measured (437 – 492mg/kg) than those expected (500mg/kg). Zinc contents also show consistency for uncontaminated matrices, increasing from 24mg/kg in unstabilised kaolin, to 40–44mg/kg with stabilisation. However, contaminated samples varied between 441 and 520mg/kg, compared to 500mg/kg introduced.

8.2.2 Component Leaching Availabilities

The equilibrium availability of components for leaching can be compared to their total concentrations, to give an indication of the components' leachable fraction. This maximum leachable content (availability) gives a clearer indication of environmental implications (especially for contaminants) than measured total contents (Van der Sloot *et al.*, 2007). Availabilities are speciation dependent, and determine susceptibility for release, transport and contamination (Dijkstra *et al.*, 2004). Table 8.1 provides a summary of measured availabilities from all matrices at different hydration durations. Knowing components availability pH is important when evaluating the environmental impact, to evaluate releases under local conditions. These can be incorporated during S/S design, for components of interest, to design out situations that can compromise containment. Most measured availability for components in this study occurred at the acidic leaching extreme. However, some were observed at neutral or alkaline pH and are discussed subsequently.

Due to small variations in the lowest pH values measured during pH dependent leaching (range of 4 – 12 required see Section 4.5.3), measured availabilities may vary slightly. A pH range of 4 – 12 was required to characterise equilibrium conditions for a material, and for cations with acidic availabilities, pH measures below 4 may increase the measured availability. However, whilst it was difficult to replicate a constant pH 4 for all matrices tested, the measured minimum pH values were sufficiently close, varying between 3.55 and 4.32 for the different matrices (Table 7.2, 7.5 and 7.7).

The availability of calcium was observed under neutral conditions at 300 days of hydration for most matrices, and was due to the increasing formation of cementitious minerals, which modified the mineralogy (also see Sections 8.4 and 8.5). The other assessed elements had their availabilities observed under acidic pH conditions, except chromium. Chromium availability was observed under acidic conditions for matrices without additives (comparable to uncontaminated samples, see Table 8.1), but the leaching trends were variable (discussed in Section 8.4). The availabilities in humic and sulphate matrices were observed under alkaline pH conditions, or had releases at alkaline pH comparable to those at acidic pH.

For the unstabilised kaolin clay, no calcium was available for release (below detection) (see Table 8.1), and less than 1% of the total aluminium and silicon content was leachable (Table 6.4 and 6.5). However, zinc and chromium availabilities were approximately double their compositional measures (trends discussed in Section 8.4). For matrices without additives, silica availability decreases with increasing hydration (Table 8.1). Aluminium availability decreases from 28 to 150 days, but increases at 300 days, and calcium availability increases with increasing hydration. These are due to increasing kaolin degradation with hydration, which increases aluminium availability. However, the released silica was used up in complexation (see Section 8.6.2), and pozzolanic reactions to form cementitious products, thereby decreasing with hydration (also discussed in 8.2.3)

Table 8.1: Summary of availabilities for all matrices at different hydration durations (g/kg)

Sample	Al	Ca	Cr	Si	Zn
Kaolin Clay	0.28	DL	0.06	0.22	0.05
EO 28	2.07	21.45	DL	2.01	0.01
EO 150	0.72	21.17	0.02	1.09	0.00
EO 300	1.43	30.67	0.02	0.87	DL
EOH 28	1.76	21.44	0.05	2.48	0.01
EOH 150	1.13	21.44	0.01	1.89	0.01
EOH 300	0.83	31.38	0.00	1.68	0.00
EOS 28	2.63	21.43	DL	2.73	0.01
EOS 150	0.76	21.41	0.01	1.23	0.00
EOS 300	0.82	28.95	DL	1.35	DL
EOC 28	0.86	21.17	0.03	1.43	0.01
EOC 150	0.47	22.57	0.02	1.08	DL
EOC 300	0.50	29.38	0.01	0.68	DL
EOHC 28	0.73	22.57	0.12	1.74	0.00
EOHC 150	0.23	22.58	0.23	1.24	DL
EOHC 300	1.91	31.99	0.01	2.17	DL
EOSC 28	3.62	22.71	0.25	4.81	0.01
EOSC 150	1.25	21.42	0.04	1.82	DL
EOSC 300	1.82	31.98	DL	1.87	0.08
EOZ 28	1.82	21.25	0.01	2.11	0.48
EOZ 150	0.46	21.40	0.02	1.09	0.26
EOZ 300	1.09	28.41	DL	1.14	0.20
EOHZ 28	0.66	21.25	0.03	1.77	0.50
EOHZ 150	0.38	22.16	0.05	1.45	0.43
EOHZ 300	0.45	19.96	DL	1.07	0.23
EOSZ 28	0.87	21.24	0.00	1.91	0.33
EOSZ 150	0.95	20.15	0.03	1.60	0.29
EOSZ 300	1.18	21.92	0.02	1.49	0.21

Note DL – below detection limits. Matrix definitions in Chapter 4 Table 4.8

For contaminated matrices, zinc availabilities decrease with increasing hydration, from 480mg/kg at 28 days, to 260 and 200mg/kg at 150 and 300 days respectively. This indicates that zinc containment improves with increasing hydration, due to increasing formation of insoluble mineral phases (discussed in Section 8.6). For chromium availability, the measured values were comparable to those observed in uncontaminated samples (Table 8.1), which indicates that the stabilisation method is effective in containing the introduced contaminant. Also, the availability decreases with increasing hydration, which indicates increasing partitioning effectiveness with hydration. The kaolin clay was also observed to have a high sorption affinity for the introduced chromium contaminant (see Section 8.1.2), due to lattice substitution of chromium for aluminium to immobilise the contaminant (also see discussions in section 8.6).

For matrices with humic acid, silica availability decreases with hydration, while alumina availabilities decrease from 28 to 150 days (similar to matrices without additives) and then increase at 300 days (uncontaminated sample decreases with hydration) (see Table 8.1). Calcium availability also increases with hydration, except in zinc contaminated matrices, where a decrease was observed at 300 days. These show that the presence of the additive does not significantly modify the availability trends, compared to those observed in the matrices without additives. Zinc availability also decreases with increasing hydration, reducing from 500mg/kg at 28 days, to 430 and 230mg/kg at 150 and 300 days respectively. Chromium availabilities were observed to increase from 120mg/kg at 28 days to 230mg/kg at 150 days, before decreasing to levels comparable to uncontaminated matrices at 300 days hydration. However, observed contaminant availabilities were higher than those observed in matrices without additives, indicating that the increased organic content increased availability. However, at 300 days availabilities were comparable to the other matrices, which showed increasing containment effectiveness with hydration.

For matrices with sulphate, alumina and silica availabilities change in trends similar to those observed in the uncontaminated and humic acid matrices, except for the zinc contaminated sample (Table 8.1). For this sample, aluminium availability increases with hydration, but this could also be due to the low availability pH at 300 days (see Chapter 5 Table 7.5). However, calcium availability decreases from 28 to 150 days, and then increases at 300 days of hydration. This trend was not observed in matrices without additives, or humic acid matrices, and was likely to be a function of mineralogical changes due to increased sulphate contents. For contaminant availabilities, zinc also shows decreasing availability with hydration, similar to the other matrices, decreasing from

330mg/kg at 28 days, to 290 and 210mg/kg at 150 and 300 days hydration respectively. Chromium availability also decreases with hydration, but the availability at 28 days (250mg/kg) was higher then the observed value for the matrix without additives. The availability however decreases to a level comparable to uncontaminated samples at 150 days, and was below detection at 300 days. These results show that increasing hydration improves the contaminant containment, and for zinc, the increased sulphate content improves early partitioning (28 days) compared to other matrices. However, the availabilities at 300 days were comparable to those for the other stabilised matrices, which indicated that increasing hydration negated the additives influences on containment.

To summarise findings from availability evaluations, the different matrices showed increased aluminium availability with hydration increase due to dissociation of kaolin at the induced alkalinity. However, silica availability decreased with hydration, due to its use in pozzolanic reactions and formation of complexes (for example with zinc, see Section 8.6.2). The increasing pozzolanic reactions with hydration also increased the availability of calcium, due to increased formations of cementitious minerals, which degrade with acidification (discussed in 8.2.3.2). Contaminant availabilities decreased with increasing hydration, indicating increasing partitioning effectiveness with hydration. Humic acid additives increased contaminant availabilities, but increasing hydration cancelled this effect, with availabilities at 300 days of hydration being comparable for all the matrices. Sulphate additives increased zinc containment effectiveness, but increased chromium availability at the early hydration period (also see Sections 8.2.3.1 and 8.3 for discussions).

8.2.3 Chemical Durability Assessments

To evaluate chemical durability and resistance to leaching, results from pH dependent leaching and cumulative monolithic releases were considered with increasing hydration. These evaluations were for contaminants of interest, and the structural components and master species (Al, Si and Ca). Increasing hydration was expected to induce kaolin dissociation, which releases aluminium and silicon, and these were then used for formation of stable hydration minerals. Chemical durability was inferred from the leachabilities of these components with hydration. Evaluations in this section are divided between releases observed during time dependent leaching and pH dependent leaching.

8.2.3.1 Time Dependent Leaching Durability Assessment

Cumulative releases of aluminium, silicon and calcium were used to evaluate chemical durability, for leaching at the stabilised material unaltered natural pH. No detrimental contaminant releases were observed during these tests (see Section 8.3), which supported the effectiveness of the treatment method (key factor for S/S design). The lack of contaminant releases indicated that the solubility controlling phases (see discussions in Section 8.6) were chemically durable under the prevailing chemical conditions, during leaching from monolithic specimens. pH alterations during time dependent leaching tests varied between pH 10.8 and 12.0 for matrices without additives, pH 10.7 and 12.4 for humic acid matrices, and pH 9.9 and 12.5 for sulphate matrices (Figure 8.1) at the end of testing.

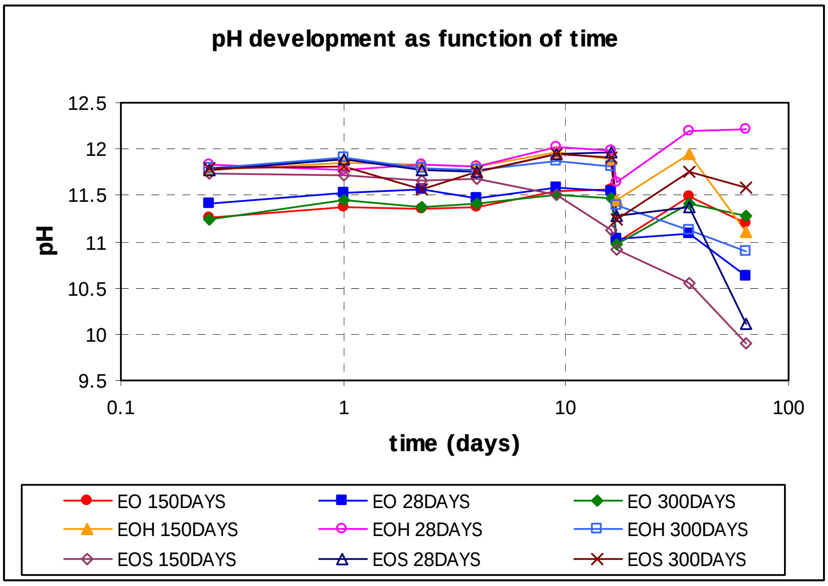


Figure 8:1: pH development during time dependent leaching tests for the different matrices

These changes in pH are due to changes in the prevailing conditions, at the leaching interface, and pH decreases are likely to be induced by depletions in free hydroxyl ions. Due to pH modifications and the associated stability of cementitious minerals, mineralogical changes were expected during leaching (also see Section 8.6.6). These included CSH decalcification, portlandite and monosulphate dissolution (Engelsen *et al*, 2009, Martens *et al*, 2010), and loss of silica due to kaolin degradation (Langmuir, 1997). With pH reductions below 10.5 for sulphate matrices at 28 and 150 days (Figure 8.1), significant breakdown of cementitious minerals were expected.

At the end of time dependent leaching tests (64 days), significant precipitation of calcium silicates (confirmed during evaluations of sulphate matrices on the next page) was observed on walls of leaching vessels and on surfaces of test specimens for matrices without additives and humic acid matrices. However, this precipitation phenomenon was absent for sulphate additive matrices, whose eluates also had significantly higher conductivities (indicating higher dissolved salt contents). Matrices without additives and humic acid matrices showed reduced aluminium and silicon cumulative releases at the different hydration periods compared those for sulphate matrices (Tables 7.4, 7.6 and 7.8).

Calcium releases were also significantly higher than those for sulphate additive matrices, and decrease with hydration (Figures 7.232, 7.239), except in the humic acid additive matrix at 300 days, where an anomalous release at 16 days of monolithic leaching (probably due to wash-off during leachant addition) increased the cumulative release. Precipitated silica was released due to kaolin degradation at the leaching interface (see Section 8.6.6), with the released silicic acid complexing with released calcium and precipitating as calcium silicates, which have low solubility under the prevailing alkalinity. Low cumulative releases of aluminium and silicon in porewater (see Section 8.5), and associated non-release of contaminants, indicated that matrices are chemically durable and resistant to leaching, at the stabilised pH (see alteration range Figure 8.1). Also, the decreasing calcium leachability with hydration suggests increasing formation of alkaline stable hydration (cementitious) minerals

For sulphate additives matrices, significant increases in aluminium and silicon releases were observed, with no associated silica precipitation and significant reductions in calcium leachability (Tables 7.4, 7.6 and 7.8). These did not affect contaminant leachability, except for an initial wash-off at leaching inception, from the zinc contaminated sample at 150 days (Figure 6.15), which also increased silicon, and decreased aluminium initial leachabilities (Figures 6.8 and 6.12) (this supports containment of zinc as a silicate, see Section 8.6). This increased leachability (Al and Si) was associated with increased kaolin dissociation with increased sulphate contents, resulting in aluminium and silicon release. However, the non-precipitation of salts, and significantly decreased calcium releases, suggested dominance of salts with higher solubility. The increased sodium contents in these matrices (see Section 8.1.2) induced calcium leaching retardation, due to mass action. This resulted in dominance of sodium in the leachant, inducing silicic acid complexation as sodium silicates (Na_4SiO_4, Na_2SiO_3). The decreased calcium content, and increased sodium and silica contents in eluates confirmed the precipitation as calcium silicates for the other matrices. Figures 8.2, 8.3, 8.4 and 8.5 show the respective cumulative releases for Na, Al, Si and Ca from stabilised matrices.

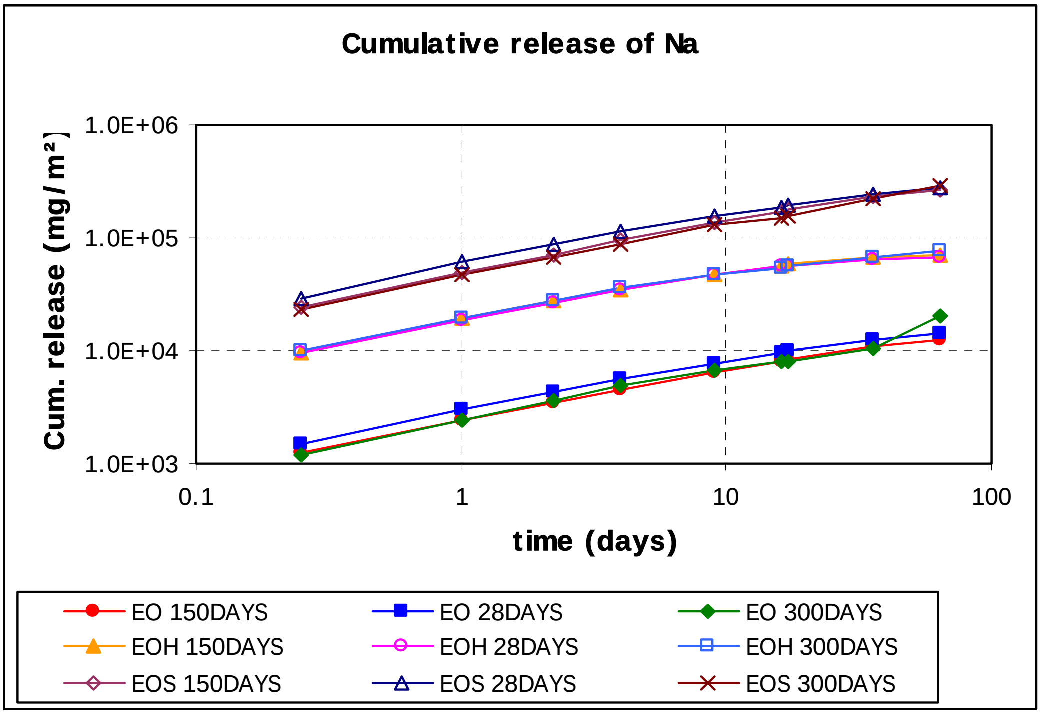


Figure 8:2: Cumulative Sodium releases for the different stabilised matrices

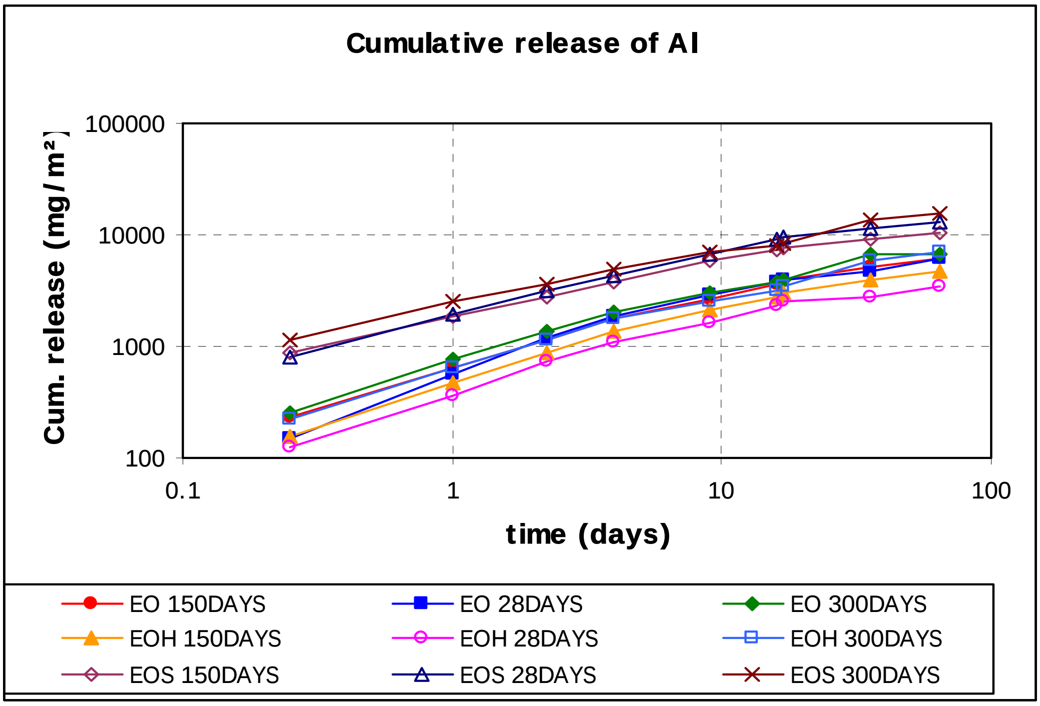


Figure 8:3: Cumulative Aluminium releases for the different stabilised matrices

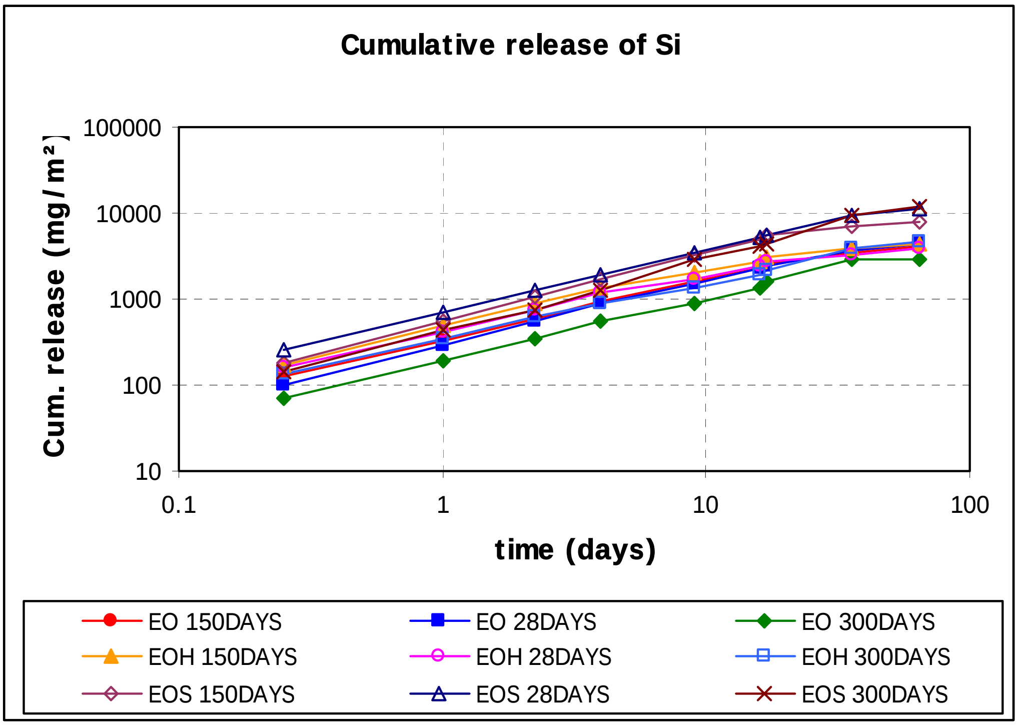


Figure 8:4: Cumulative Silicon releases for the different stabilised matrices

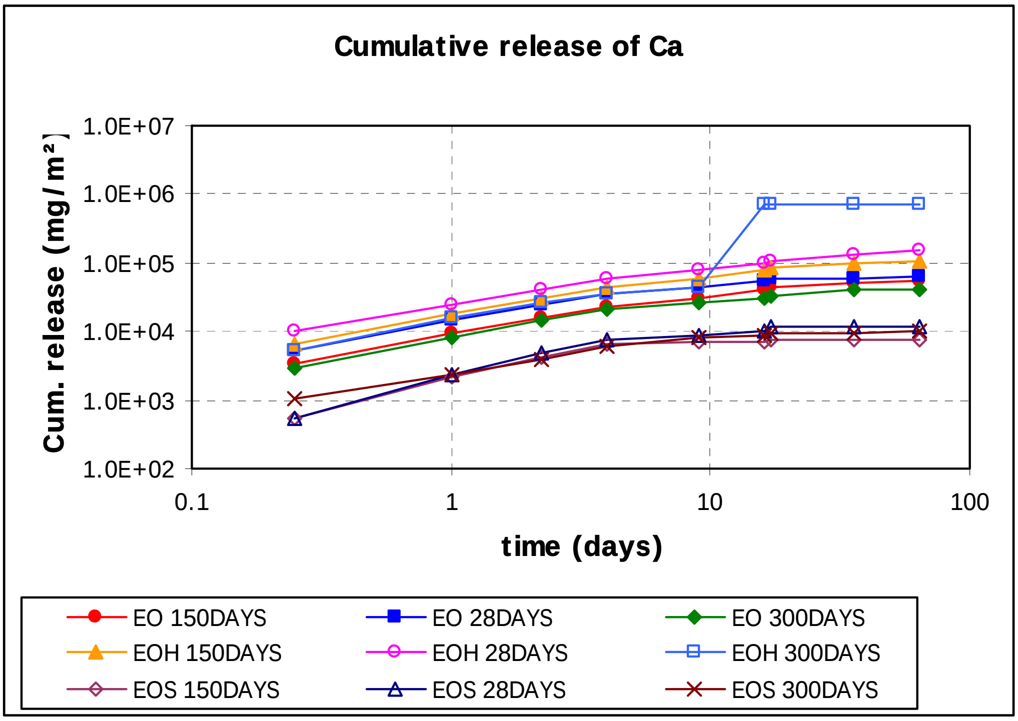


Figure 8:5: Cumulative Calcium releases for the different stabilised matrices

Figures 8.2 to 8.5 show clear trends of increased sodium, aluminium, and silicon cumulative releases for matrices with increased sulphate, and significantly reduced cumulative calcium releases. This supported deductions that the increased sulphate content induced increased degradation of the stabilised kaolin, and the increased sodium content increased solubility and retarded calcium leaching. Considering that sulphate matrices had lower aluminium and silicon contents (see Section 8.1.2), these findings showed that the introduction of sodium sulphate promoted kaolin degradation, but did not influence the releases of contaminants.

Humic acid additives in stabilised matrices were expected to retard hydration, and the sampled matrices remaining deformable under thumb pressure, even after 300 days of hydrations. In view of cumulative releases, humic acid did increase contaminant release (Tables 7.4, 7.6 and 7.6). However, the degradation of kaolin was retarded, with decreased aluminium cumulative releases (Figure 8.3). Also, due to hydration retardation, there were associated increases in calcium cumulative releases, decreasing with hydration due to formation of stable hydration minerals (Figure 8.5). The anomalous release at 300 days was likely due to wash-off during leachant additions, with releases from unhydrated cement particles with breakdown of peds. Increasing hydration also increases kaolin dissociation, with cumulative releases for increasing aluminium, confirming that the humic additive retarded the hydration processes.

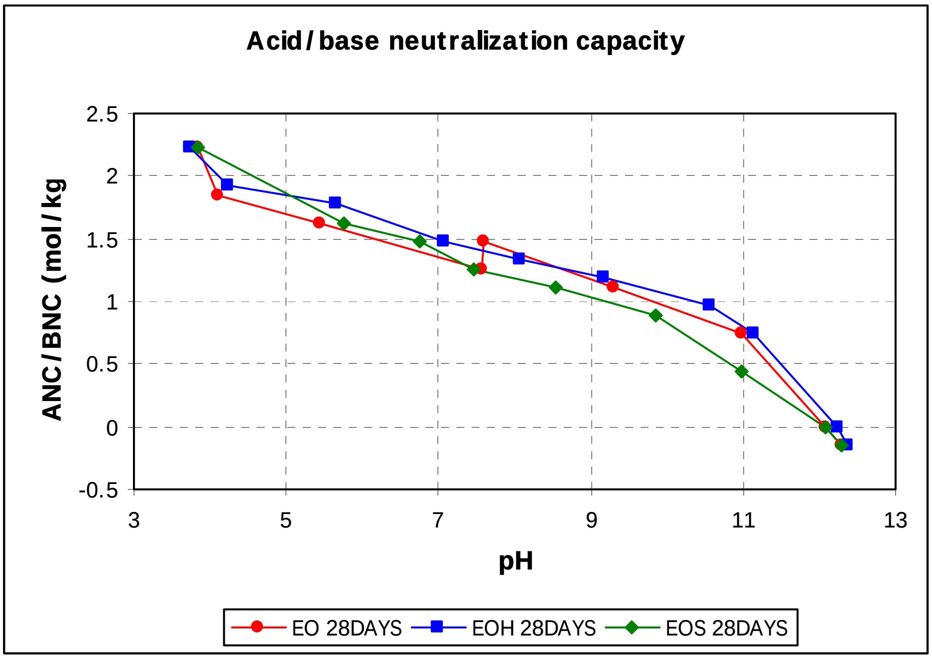
8.2.3.2 pH Dependent Leaching Durability Assessment

Changes in component availabilities, pH dependent leaching trends and neutralisation capacity with increasing hydration, was used to infer chemical durability. Leaching availabilities have already been evaluated for contaminant releases with hydration from matrices (See Section 8.2.2). Changes in leachability, trends and availability with hydration indicate mineralogical changes, due to formation of hydration minerals, and degradation or alteration of existing minerals (discussed in Section 8.6).

For matrices without additives, there were consistent release trends for aluminium and silicon, with decreased release availabilities at 300 days, relative to 28 days (Figures 7.227 and 7.229). Calcium release increased at 300 days, but showed consistent release trends at all durations (Figure 7.231). These trends were also observed for releases from humic acid matrices (Figures 7.234, 7.236 and 7.238), which suggests increased formation of durable cementitious products with hydration. This decrease in leachable aluminium and silicon, and increase in available calcium, was associated with the formation of cementitious products. 70 – 80% calcium is typically available for leaching with pH decrease from above 12 to 10.5, as observed by Engelsen *et al.* (2009) and Martens *et al.* (2010) due to degradation of cementitious products via dissolution and decalcification. Decreased aluminium leachability at this pH was due to insolubility of controlling phases (see Section 8.6), while silicon showed minimal leachability variation at this pH.

Similar to time dependent evaluations (Section 8.2.3.1), increased sulphate contents increased aluminium and silicon availabilities (Chapter 7 Tables 7.2, 7.5 and 7.7). Additionally, release trends were found to be similar to those observed for other matrices, consistent with decreased aluminium and silicon availabilities with increased hydration, and increased calcium availability (Figures 7.241, 7.243 and 7.245). Comparing leachable fractions to total concentrations (Chapter 6 Tables 6.4 and 6.5), the matrices were durable and resistant to leaching, increasing in durability with increased hydration. While kaolin degradation released aluminium and silicon hydroxides, these are used up for formation of cementitious mineral, yielding decreased availabilities at 300 days.

Comparisons for acid or base neutralisation capacities for matrices are shown in Figure 8.6, at 28 and 300 days. These neutralisation values indicate the ability of matrices to buffer acidity or alkalinity of prevailing environments, using information on leachant additions to adjust pH during leaching (Chapter 4 Section 4.5.3). Obtained results show that the measured neutralisation capacities for the different matrices were comparable at similar hydration durations, showing similar overall trends (Figure 8.6). However, comparisons of neutralisation using 1mol/kg of nitric acid showed that sulphate matrices had lower neutralisation capacities and humic acid matrices had higher neutralisation capacities, due to increased hydroxyl content in the humic matrices (retarded hydration).



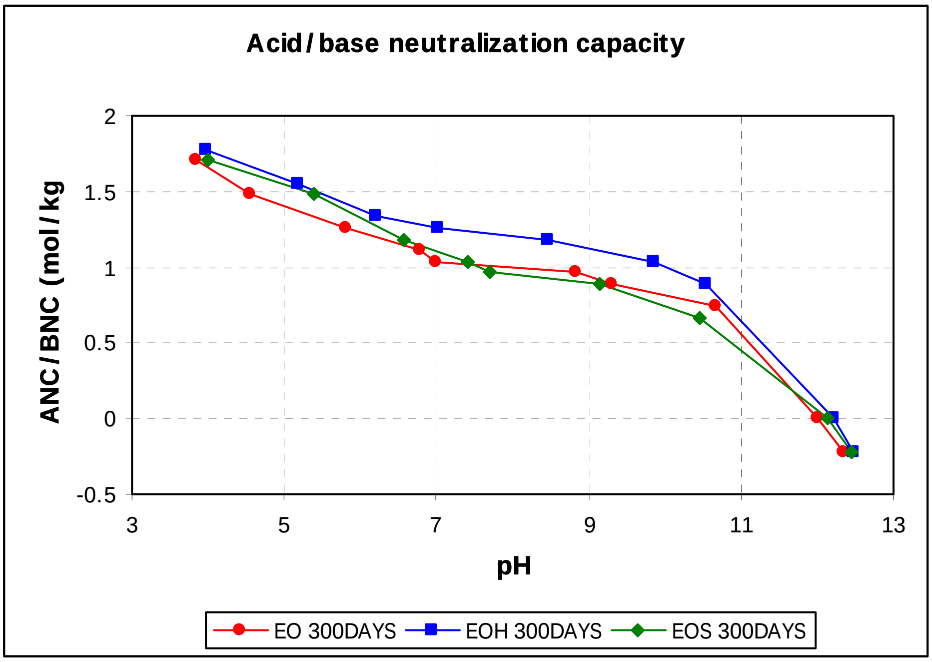


Figure 8:6: Acid and Base neutralisation capacities for the different matrices at 28 and 300 days. NB: ANC – acid neutralisation capacity, BNC – base neutralisation capacity

However, the neutralisation capacities are reduced at 300 days, requiring less than 2mol/kg of acid to reach pH around 4, compared to values around 2.25mol/kg at 28 days (Figure 8.6). Also, the pH values attained using 1mol/kg of nitric acid was decreased at 300 days, but the trends remained the same with humic matrices having the highest values. These results are shown for comparison purposes, and the ANC/BNC can be incorporated during S/S design, to mitigate possible environmental conditions, such as acid rain, contact with percolating water and groundwater. With increasing formation of cementitious products, the available free hydroxyl (OH^-) ions decrease, which will decrease the neutralisation capacities. However, the formed minerals will retain buffering properties, but are likely to be less than those values at early hydration periods.

8.3 TIME DEPENDENT MONOLITHIC LEACHING EVALUATION

Concentration factors for sodium, from the monolithic leaching of stabilised kaolin (Table 6.17) indicated that dissolution was taking place during leaching, which prevented calculations for diffusion coefficients (See Chapter 4 Section 4.5.1). This was expected, given expected mineralogy, with soluble salts (carbonates, oxides and hydroxides), and the degradation of kaolin under the prevailing conditions. This indicated that diffusion was not the sole controlling release mechanism. It was also expected that substantial dissolution and surface wash-off were taking place, with leachant replacements. Repeatability and consistency during time dependent leaching were addressed in Section 8.1.1, which informed reliability in the obtained chemical data.

Tests could not be undertaken on unstabilised kaolin, as the clay failed to retain integrity up to 6 hours during tests (see Chapter 4 Section 4.5.1 and Chapter 6 Section 6.2.2). Contaminant inclusions modified the prevailing chemical parameters (Tables 6.21), decreasing pH and increasing conductivity. This was expected, given the use of acidic contaminant nitrates for contamination, with more volume required to introduce 500mg/kg of chromium as chromium nitrate nonahydrate, than zinc as zinc nitrate hexahydrate. Measured elemental releases from kaolin and contaminated kaolin at 28 and 150 days of storage (Table 6.22), showed that kaolin retained more chromium than zinc (also see Section 8.1.2). Given the limited inclusions in the kaolin clay, and the stoichiometric properties of kaolin, chromium partitioning was likely due to lattice substitution with aluminium in kaolin. Contaminant releases also decreased with increasing time, releasing roughly half the measured releases from 28 days at 150 days. Considering the stability of kaolin under acidic conditions (Langmuir, 1997), increases in aluminium leachability for chromium contaminated kaolin (Table 6.22) can be attributed to the decreased pH, and substitution of Al^{3+} by Cr^{3+}. There was also an observed increase in calcium and a reduction in sulphur release, compared to uncontaminated kaolin. Zinc contaminated kaolin also shows an increase in calcium release, and reduction in sulphur. However, it was expected that contaminants would be incorporated into the crystalline lattice of kaolin and available HFO (see Section 8.6.2), despite the relatively non-reactive properties of kaolin (Langmuir, 1997). Evaluations for stabilised matrices are presented according to presence and type of included additives, at the different periods of hydration.

8.3.1 No Additive Monolithic Leaching Evaluation

For stabilised matrices without additives, changes in pH during leaching (Figure 6.3) show variations between pH 11 - 12, with higher pH measures at 28 days, compared to 150 and 300 days. These were due to decreasing hydroxyl ion content with formations of cementitious products (also see Section 8.2.3.2). Leaching trends for cumulative releases for aluminium and silicon were comparable for samples (Figures 6.6 and 6.10), with increased aluminium cumulative releases at 300 days (discussed in Section 8.2.3.1). No impact on trends was observed for aluminium or silicon, with inclusions of contaminants.

Cumulative releases for chromium (Figures 6.16) showed that chromium was effectively partitioned within stabilised matrices, with comparable releases between contaminated and uncontaminated samples. For EOC at 150days, there was a release of 1.9mg/l to eluates at 2 days of leaching due to surface wash-off with leachant replacement, increasing the measured cumulative concentration. However, this does not compromise the chemical durability of the matrix, which effectively retains chromium at other hydration periods. Cumulative releases for zinc showed that it was effectively partitioned within the stabilised matrix (Figures 6.13). There was a release of 0.1mg/l zinc from contaminated kaolin at 28 days, due to surface wash-off, which increased the cumulative release at this duration. However, this was insignificant in view of cumulative releases with hydration, and most measured zinc concentrations in eluates were below detection.

It was surmised that contaminant containment was successful during monolithic leaching at the matrices stabilised pH. The measured pH of the matrices decreased with hydration, due to decreasing availability of OH^- ions.

8.3.2 Humic Acid Additive Monolithic Leaching Evaluation

For humic acid additive matrices, cumulative release of aluminium and silicon showed consistent leaching trends (Figures 6.7 and 6.11), at the different hydration periods. Cumulative aluminium leachability increased with hydration time, while cumulative silicon releases decreased at 150 and 300 days, when compared to that at 28 days (discussed in Section 8.2.3.1). pH evolution during leaching (Figure 6.4), showed comparable trends at different hydration periods, varying between 11.0 and 12.4. Notable exceptions were observed for EOHC at 150 days and EOH at 300 days, and were likely due to OH^- depletion at the leaching interface. These samples pH values decreased below 11 at the end of testing. Start pH values were comparable for samples, varying between 11.5 and 12, with chromium contaminated samples having the lowest measures.

Similar to matrices without additives (Section 8.3.1), contaminants were effectively partitioned with humic acid matrices (Figures 6.14 and 6.17). Chromium and zinc releases were comparable to uncontaminated matrices. These results indicate that humic acid additives did not compromise containment of contaminants, nor significantly modify observed trends for the releases of the structural cations compared to those for matrices without additives (also see Section 8.2.3.1).

8.3.3 Sulphate Additive Monolithic Leaching Evaluation

For sulphate additive matrices, pH evolution during leaching (Figure 6.5), show comparable trends, with their start values varying between 11.5 and 12, with notable exceptions at 28 days for contaminated samples, where values over 12 were observed. End values at 150 days were decreased compared to other durations, as well as for the uncontaminated matrix (EOS) at 28 days. This was due to the prevailing mineral phases at this duration, which yielded reduced OH^- content at the leaching interface, at the completion of leaching tests. Cumulative releases for aluminium and silicon show consistent trends, at the different hydration periods. However, the initial leachability of aluminium was decreased at 28 and 150 days, for zinc contaminated samples (Figure 6.8). Initial high release of silicon at 150 days, from the zinc contaminated sample, increased the cumulative release for this matrix (Figure 6.12 discussed in 8.2.3.1). The reduced aluminium releases at 28 and 150 days, was likely due to zinc influences for the matrix, which suggests complexation of insoluble zinc aluminosilicates under alkaline conditions (discussed in 8.6.3). However, at 300 days, cumulative aluminium release was comparable, and all samples showed increasing aluminium cumulative leachability with hydration, and decreased silicon cumulative release at 300 days.

Similar to the other matrices, contaminants were effectively partitioned within stabilised sulphate matrices (Figures 6.15 and 6.18). Cumulative releases for zinc and chromium were comparable with those for uncontaminated samples. This indicated that increased sulphate contents did not compromise contaminant containment. However, the releases of structural components were modified, which were discussed in Section 8.2.3.1.

8.4 pH DEPENDENT LEACHING EVALUATION

Evaluations for leaching under the influence of pH were important to assess components speciation, availabilities, matrix buffering capacities, and leaching behaviours under different field exposure conditions. These provide information for equilibrium component releases, and data for speciation evaluations (Van der Sloot *et al.*, 2007). These are based on the different surface processes that occur within pH domain, e.g. ion exchange, complexation, precipitation, sorption and incorporation (Dijkstra *et al.*, 2004). Prior to evaluating release from stabilised matrices, information for leaching from uncontaminated and unstabilised kaolin was required. Given the expected low neutralisation and buffering properties of kaolin, contaminants were expected to be mobilised with increased acidification, given the measured natural kaolin pH, and reductions in pH with contamination (Table 6.21). Uncontaminated kaolin clay was tested, to use the obtained information as a baseline for comparisons with stabilised matrices.

The leaching behaviours for selected components from kaolin are shown in Figure 7.1. There was no available calcium release, with values below detection limits across the pH range. Sulphur release was also consistent across the pH range. Aluminium showed an amphoteric leaching trend, with the availability observed at pH 12, and insolubility between 5 and 7 (Figure 7.2). Silicon (as ortho silicic acid) also had maximum availability at the alkaline pH extreme, with a decreasing leachability away from alkaline. Measures at the neutral pH were below the detection limit (Figure 7.4). The occurrence of aluminium and silicon availabilities under alkaline conditions, were due to the dissociation of kaolin under these conditions. The kaolin clay contained small quantities of contaminants of interest. Zinc releases (Figure 7.6) were below the detection from above pH 5.43, and the maximum availability was observed at pH 3.06. This indicated that the contained zinc did not occur as a hydroxide, which should show amphoteric leaching, as theorised by US EPA (1986) (see Figure 3.2), and documented in Bone *et al.* (2004b) and Paria and Yuet (2006). Chromium showed leachability under natural and acidic pH, with the availability observed at pH 3.06 (Figure 7.8). This also did not follow the theoretical hydroxide solubility trends (Bone *et al.,* 2004b, Paria and Yuet, 2006, charts adapted from US EPA 1986). A pH below 4 (see Section 4.5.3) was not required when characterising the clay, but was difficult to attain (using 0.1mol nitric acid) due to the low buffering capacity of the clay.

8.4.1 No Additives pH Leaching Evaluation

Evaluations for component leaching from stabilised matrices without additives are presented in this section, at the different hydration periods. For the uncontaminated matrix, the natural pH changes from 12.07 at 28 days, to 11.96 and 11.99 at 150 and 300 days respectively (Table 6.8), decreased with increasing hydration duration. Results were sorted with decreasing acidity, where the penultimate pH is the natural, and the last shows alkalinity increase for all pH dependent leaching chemical parameter tables. Aluminium showed amphoteric leachability at the different hydration periods, with broadening of the insolubility region with increasing hydration. These change from pH 7.56 – 7.60 at 28 days, to 6.53 – 7.83 at 150 days, and 5.81 – 9.31 at 300 days (Figure 7.227). Leaching at alkaline pH was comparable to values obtained for kaolin. However, aluminium availabilities occur at the acidic extreme for stabilised matrices, and decreased with increased hydration (also see Section 8.2.2). Silicon release was comparable at different hydration durations, with decreasing availability with increasing hydration (Figure 7.229). Releases increased with acidification, and the availability was observed at the acidic extreme. Calcium release increased with pH decrease from alkaline conditions, reaching about 80% of the maximum availability at around pH 10.5 (Figure 7.231). These were in line with findings by Engelsen *et al.* (2009) and Martens *et al.* (2010) for cementitious materials, due to dissolution and decalcification. Calcium availability increased with hydration, due to increased formation of cementitious mineral, which are leachable with changes from alkaline conditions. Sulphate release showed comparable trends at different hydration periods (Figures 7.10, 7.11 and 7.12), increasing to 80% of maximum availability, as alkalinity decreases to around pH 10.5. This was due to the dissolution of ettringite and monosulphate (Engelsen *et al.,* 2009), and the maximum availabilities occurred under acidic extremes. These trends are important, for incorporation during S/S design, to design out possibilities for accidental releases, due to changes in prevailing field conditions. For components of interest, the observed leachability trends and changes in these trends with increasing hydration will show how the material behaves under equilibrium leaching with field exposure. The solubility of structural components may compromise the integrity of the matrices, and the obtained results showed that the decrease of pH below 10.5 compromised the insolubility of the cementitious minerals.

For zinc contaminated samples, the natural pH was increased compared to those observed in uncontaminated samples, ranging from 12.22 at 28 days, to 11.97 and 12.01 at 150 and 300 days respectively (Table 6.11). The contained contaminant did not influence the leachability trends of the structural cations (Al, Si and Ca), compared to those observed for uncontaminated samples (Figures 7.45, 7.46 and 7.47). Zinc releases showed consistent leaching behaviours at all hydration periods (Figure 7.248), but did not display the expected amphoterism. Theoretical solubility of hydroxides (US EPA, 1986) shows amphoteric leaching, as did findings by other authors, for release during pH dependent leaching for stabilised wastes and cement mortars (Meima and Comans, 1997, Olmo *et al.,* 2007, Dijkstra *et al.,* 2008, Buj *et al.*, 2010). Zinc substitution for calcium in CSH, and formations of calcium zincate was expected, and the dissolution of these minerals with decreasing pH should induce release. However, the released zinc can be reprecipitated as insoluble minerals. Zinc availabilities decreased with increasing hydration, and the insolubility pH decreased from 6.41 at 28 days, to 5.12 at 300 days (Figure 7.248). Similar to findings in Section 8.2.2, zinc availability decreases with hydration, which indicates increasing containment effectiveness with increasing hydration. Amphoteric leaching trends were not observed during pH dependent leaching, which indicated that solubility was not controlled by hydroxides, but rather as phases which are insoluble under alkalinity (see Section 8.6.3).

For chromium contaminated samples, measured natural pH was similar to those measured in uncontaminated samples, with 12.07, 11.91 and 11.99 measured at 28, 150 and 300 days respectively (Table 6.14). Chromium contamination did not affect the trends for the structural components, similar to those observed for uncontaminated samples (Figures 7.80, 7.81 and 7.82). Chromium releases showed releases and availability under acidic conditions, but the releases at 150 days also showed leachability under alkaline conditions. However, stabilisation effectively partitioned the introduced chromium, with maximum availabilities less than those observed from the uncontaminated kaolin clay (Figure 7.254). Amphoteric leachability was also expected for chromium (Bone *et al.,* 2004b, Paria and Yuet, 2006), with releases at alkaline pH due to the dissolution of ettringite and monosulphate, which can partition chromium (Chrysochoou and Dermatas, 2006). Consistent leaching trends at all hydration periods were also not observed (Figures 7.80, 7.81 and 7.82). These results indicated that chromium containment was effective at all hydration durations (also see Section 8.2.2), and the introduced chromium did not modify the behavioural trends for the structural components. However, the release trends were not those expected (amphoteric trends).

8.4.2 Humic Acid Additives pH Leaching Evaluation

It was expected that contaminants can be partitioned onto or complexed with organic carbon, thereby modifying their release and release behaviour (Peng *et al.*, 2007). For uncontaminated humic acid matrices, the natural pH was increased, compared to those measured for matrices without additives. These ranged from 12.24 at 28days, to 12.14 and 12.20 at 150 and 300 days respectively (Table 6.9). Leaching results (Figures 7.115, 7.116 and 7.117) show that the introduction of humic acid did not modify the leaching trends of the structural components, compared to matrices without additives (see Section 8.4.1). Decreasing aluminium and silicon availability and increasing calcium availability were also observed with increasing hydration durations (Figures 7.234, 7.236 and 7.238), similar to the observed trends for matrices without additives (also see Section 8.2.2). DOC releases during leaching from humic acid matrices, showed a decreasing release with increasing alkalinity and acidity, peaking under neutral conditions between pH 7 and 9 (Figure 6.23). However, the release from kaolin showed a reverse trend (Figure 6.24), which suggested that this trend was a function of humic acid, rather than a general trend for organic carbon. These findings indicated that increased humic acid contents did not modify the leaching trends of the structural components. Whilst humic acids showed high solubility under neutral conditions, the releases of the components were not affected.

For zinc contaminant samples, the natural pH was increased above values measured for uncontaminated samples, similar to observations for other zinc contaminated matrices (Sections 8.4.1 and 8.4.3). The pH ranged from 12.45 at 28 days, to 12.18 and 12.26, at 150 and 300 days respectively (Table 6.12). The introduction of zinc did not modify the leaching trends for the structural components (Figures 7.130, 7.131 and 7.132), similar to findings for the matrix without additives (Section 8.4.1). However, calcium availability at 300 days was lower than values at other periods (Table 8.1 also see Section 8.2.2). Due to zinc complexation with organic carbon, higher availabilities and leachabilities were expected, under neutral pH, where high DOC releases were observed (Chapter 6 Figure 6.23). However, the observed leaching trends were similar to those observed for matrices without additives (Figure 7.249). From these findings, it was found that the introduction of humic acid did not modify leaching trends, even though zinc availabilities were increased (see Section 8.2.2).

For chromium contaminated samples, the measured natural pH was comparably lower than those for uncontaminated and zinc contaminated samples. These ranged from 12.29 at 28 days, to 12.01 and 12.10 at 150 and 300 days respectively (Table 6.15). However, the leachability trends for the structural components were not modified by chromium addition (Figures 7.151, 7.152 and 7.153), similar to observations for matrices without additives (see Section 8.4.1). Chromium availabilities were significantly increased at 28 and 150 days, compared to measures from matrices without additives (Table 8.1 Section 8.2.2). However, the leaching trends did not show predictable trends, with variable releases across the pH range (Figure 7.255).

These results, for leaching from humic acid matrices, show that the introduction of humic acid did not modify the leaching trends for the components. The trends for the structural components were comparable to those observed for the matrices without additives (Section 8.4.1). While the availabilities of the contaminants were increased at the early hydration durations (see Section 8.2.2), the leaching trends were not modified. Similar to matrices without additives, the contaminants did not display the leaching trends expected for theoretical solubility of hydroxides, indicating that partitioning was due to different mineral phase.

8.4.3 Sulphate Additive pH Leaching Evaluation

Evaluations of stabilised sulphate additive matrices are presented in this section, to assess the implications on component partitioning and release. Sulphate inclusions were expected to increase formation of hydrated calcium aluminosulphates like ettringite, which can modify partitioning contaminants, and compromise their containment during leaching. Ettringite minerals are subject to compositional changes, and can substitute Zn^{2+}, Cr^{3+} and CrO_4^{2-} (Chrysochoou and Dermatas, 2006, Chen *et al.*, 2008).

Evaluations for uncontaminated samples showed natural pH values higher than those for matrices without additives, but lower than those for humic acid matrices. Measured values ranged from 12.07 at 28 days, to 12.03 and 12.13, at 150 and 300 days respectively (Table 6.10). The introduction of increased sulphate content did not modify the leaching trends of the components (Figures 7.172, 7.173 and 7.174), and were similar to those observed for the other matrices (Sections 8.4.1 and 8.4.2). However, the leachability of sulphur increased to about 70% at pH 10.5, compared to over 80% for the other matrices. This suggested the formation of sulphates minerals with cations, which had lower solubility at the alkaline pH, and were not degraded with cementitious minerals.

For zinc contaminated samples, the measured natural pH was higher than those observed for the uncontaminated sample, similar to observations for other zinc contaminated matrices (Sections 8.4.1 and 8.4.2). Measured values ranged from 12.31 at

28 days, to 12.06 and 12.15 at 150 and 300 days respectively (Table 6.13). Similar to the other matrices, the introduction of zinc did not modify the leaching trends for the structural components (Figures 7.187, 7.188 and 7.189). Also, calcium releases are similar to those observed for zinc contaminated humic acid matrices (Section 8.4.2), and did not show increased leachability at 300 days nor increased leachability at neutral pH. This supports mineralogical alterations with hydration, with increasing complexation of calcium and zinc as a mineral phase. Zinc releases show comparable trends to those observed for the other matrices (Figure 7.250). This indicated that while the presence of increased sulphate content reduced the availability of zinc (see Section 8.2.2), the leaching trends were not modified. Moreover, the zinc contaminated sulphate matrix had decreased zinc leachability at comparable pH values at the early hydration periods, compared to the other matrices (Figure 7.251).

For chromium contaminated samples, the measured natural pH was higher than those observed for uncontaminated samples, but lower than those for zinc contaminated samples. These ranged from 12.28 at 28 days, to 12.05 and 12.14, at 150 and 300 days respectively (Table 6.16). Similar to the other matrices (Sections 8.4.1 and 8.4.2) the introduction of chromium did not modify the leaching trends of the structural components (Figures 7.208, 7.209 and 7.210). However, initial availabilities of aluminium and silicon were elevated compared to other matrices, but decreased to comparable levels at 300 days (Table 8.1). While chromium availability decreased with hydration (Table 8.1), no clear trends could be drawn (Figure 7.256). No releases were observed at 300 days, which supports increased containment with increased hydration. Also, releases at 150 days, were comparable to those observed for uncontaminated samples and less than those uncontaminated and untreated kaolin (Figure 7.256). This indicated that whilst releases were observed, containment was effective, with levels below concern.

These results show that the introduction increased sulphate contents, did not significantly modify the leaching trends for the structural components. Zinc matrices also showed the highest natural pH values, consistent for all the different matrices (Sections 8.4.1 and 8.4.2). The introduction of increased sulphate improved containment of zinc (also see Section 8.2.2), but the leaching trend was not modified. However, the solubility of zinc was decreased at comparable pH, compared to measures for the other matrices. The leachability of chromium was modified at the early hydration period, compared to those for the matrix without additives. However, increasing hydration yielded measures comparable to those for uncontaminated samples. These trends can be incorporated when evaluation the speciation (Section 8.6), and used to inform S/S design, to prevent accidental releases under field exposure.

8.5 POREWATER LEACHING EVALUATION

Evaluations for release to porewater from stabilised matrices were undertaken, under the stabilised materials natural chemical conditions. Tables 6.23, 6.26 and 6.27 show the measured physical parameters, under which percolation tests were undertaken, for the different matrices. Difficulties in harmonising preparation processes, resulted in slight variations for porosity, packed bulk density, and water contents. However, packed columns were equilibrated for a minimum of 4 days, to equilibrate porewater chemical properties. Therefore, these effects due to variability were deemed insignificant over the full testing program. Tables 6.24, 6.25 and 6.28 show the measured chemical parameters, and the variations between pH for the first two eluate fractions, did not exceed 0.5 prescribed by CEN / TS 14405 (required to validate equilibration, see Chapter 4 Section 4.5.2).

Porewater releases were not included for use in speciation modelling, and this was done to simplify speciation findings, using only the pH dependent leaching information.

Instead, the focus was to assess contaminant releases under weathered and low L/S ratios, and the releases of master species (Al, Si and Ca, see Section 8.2.3), to infer durability with increasing hydration. Table 8.2 shows cumulative releases to porewater (mg/kg) at 0.5 L/S, from the different stabilised matrices, at the different hydration periods.

Aluminium leachability increased with hydration for all matrices due to increased kaolin degradation, but was insignificant compared to the total content (Table 6.4). Calcium leachability decreased with hydration for uncontaminated matrices, due to increased formations of stable cementitious minerals. However, release from contaminated matrices increased with hydration, except for the zinc contaminated sulphate matrix. This was likely due to increased calcium zinc complexation (also see Section 8.4.3). Silicon release was increased in sulphate and humic acid matrices, due to hydration retardation in humic matrices, and influence of sulphates during formation of cementitious minerals. Release increase with hydration in contaminated matrices, and decreased with hydration in uncontaminated matrices. This was also likely due to cation substitutions in cementitious minerals, at the prevailing pH conditions. However, degradation and releases were considered minimal and insignificant, compared to the measured total content (Table 6.4).

Contaminants were not leachable under the prevailing conditions, with comparable chromium releases between contaminated and uncontaminated samples, and zinc releases below the detection limit. This confirmed the findings from time dependent and pH dependent leaching (Section 8.3 and 8.4), which showed contaminant insolubility under the stabilised materials prevailing chemical conditions. Negligible degradation of stabilised matrices were observed (for releases of aluminium, silicon and calcium), compared to their total contents in the stabilised matrices, and no detrimental contaminant releases were observed. These results can then be incorporated during S/S design, to assess the release components to porewater, or under weathered conditions at prevailing low L/S ratios.

Table 8.2: Cumulative component releases to porewater from different matrices (mg/kg)

	Al	Ca	Cr	Si	Zn
EO 28	5.90	37.02	1.46	4.42	DL
EO 150	10.61	9.56	0.70	4.97	DL
EO 300	10.86	11.58	0.41	3.33	DL
EOH 28	2.44	40.37	0.58	9.93	DL
EOH 150	6.52	18.76	0.39	10.11	DL
EOH 300	8.98	11.03	0.46	7.57	DL
EOS 28	2.65	125.85	2.02	9.03	DL
EOS 150	18.14	21.42	2.17	9.91	DL
EOS 300	27.76	1.38	1.27	7.14	DL
EOC 28	3.71	125.15	1.14	2.42	DL
EOC 150	2.65	174.47	0.30	2.01	DL
EOC 300	5.91	253.20	DL	4.08	DL
EOHC 28	4.24	25.64	2.21	4.00	DL
EOHC 150	5.70	38.14	3.31	3.13	DL
EOHC 300	16.01	94.20	16.49	5.54	DL
EOSC 28	18.44	10.77	3.32	12.40	DL
EOSC 150	10.41	12.41	4.29	11.81	DL
EOSC 300	15.25	26.05	7.30	16.44	DL
EOZ 28	5.12	68.32	0.21	2.34	DL
EOZ 150	6.71	68.15	0.62	3.12	DL
EOZ 300	14.91	77.04	DL	3.65	1.07
EOHZ 28	5.56	29.87	0.37	5.86	DL
EOHZ 150	6.27	33.86	0.65	7.53	DL
EOHZ 300	17.36	47.44	0.17	11.07	DL
EOSZ 28	5.42	14.69	1.72	4.61	DL
EOSZ 150	43.68	3.80	2.83	14.05	DL
EOSZ 300	63.75	0.70	2.79	17.00	DL

8.6 SPECIATION EVALUATION

Effective leaching assessments (chemically characterised materials) can be used to inform decisions on environmental impact, ensure effective material characterisation, and provide information on releases under the different exposure conditions. These can then be combined with information on containment interactions, obtained from pH dependent equilibrium leaching, and extractions for interactive surfaces (HFO and organic carbon) to inform speciation (see Chapter 5, Section 5.2). These will improve confidence in view of environmental impact, especially for the containment of components which pose concerns. Complete chemical characterisation (addressing all release controlling mechanisms), effectively informs the equilibrium and disequilibrium release conditions, and combined with partitioning information for DOC and HFO, improves confidence and informs design. Releases under the various exposure conditions can then be assessed and addressed. Components leaching depend on speciation, which determine distribution, solubility, and transport (Dijkstra *et al.*, 2004, Van der Sloot *et al.*, 2007, Peng *et al.*, 2009).

The stabilised matrices were expected to contain variable solubility controlling mineral phases, and phase alterations were expected with changes in hydration durations. Geochemical speciation modelling was used to obtain information on these solubility controlling mineral phases, and phases changes with hydration. The research scope did not allow individual validations for geochemical interactions and calculations. The calculations were contained in algorithms for ORCHESTRA (Meeussen, 2009) embedded in LeachXS (see Chapter 5 Section 5.4). The prevailing mineral phases were selected for each matrix, based on the expected mineralogy and mineral alterations with stabilisation (see Section 5.4.6). These selected minerals (after speciation determinations), were then used to run the modelling process, to predict the solubility controlling mineral phases for the matrices.

Speciation discussions are divided based on the presence and type of introduced additives, to evaluate their implications on component partitioning. Aluminium, silicon and introduced contaminants speciation are then discussed. HFO and organic estimations are also discussed, along with an introduction to the monolithic leaching interfacial speciation.

8.6.1 Hydrous Ferric Oxides and Organic Carbon Estimations

To incorporate HFO for speciation modelling, extractions were undertaken to determine available amounts of crystalline and amorphous iron, and amorphous aluminium surfaces. Manganese surfaces which can also act as sorption sites were not included for this study (see Chapter 6 Section 6.2.4), and modelling was undertaken using the generalised two layer model of Dzombak and Morel (1990). Table 6.31 shows the values used during speciation modelling, for the different matrices and untreated kaolin. Whilst contaminant introduction and increasing hydration may affect available HFO, time and resource constrains did not allow additional assessments.

Most HFO in kaolin was present as amorphous aluminium (0.00115mol/kg). Also, for the stabilised matrices HFO was dominantly composed of amorphous aluminium, except for the humic acid matrix. This matrix also had the lowest HFO content, reduced by an order of magnitude, compared to the other stabilised matrices. This was due to the significant reduction in available amorphous aluminium released with kaolin degradation, due to hydration retardation. The highest HFO measures were observed in sulphate matrices, which also showed the highest available amorphous aluminium content due to increased kaolin dissociation (also see discussions in Sections 8.2.3.1 and 8.3.3). Also, matrices with introduced additives had lower amorphous iron contents compared to the matrix without additives, but also had higher crystalline iron contents (see Table 6.3.1). HFO was measured at 150 days for all matrices, using the midpoint for hydration periods (28, 150 and 300 days of hydration), as the representative measure for the samples.

Evaluations for component complexation with dissolved and particulate organics were undertaken via ORCHESTRA, using the NICA – Donnan Model, using information obtained from eluates DOC analyses (see Chapter 6 Section 6.3.1). Information on solid humic acid (SHA) content for materials were required for input during modelling, to evaluate complexation with particulate organic matter (POM). However, analyses for these, using resin extractions (complex extraction processes for total humic content), could not be done within the study scope. For matrices containing 1% humic acid, the introduced content was employed as SHA using a value of 0.01 kg/kg. Assuming low organic contents in kaolin clay, stabilising cement, contaminants and sulphate additives, and possibilities for other organic carbon sources e.g. fulvic acids, conservative estimates of 10 mg/kg SHA were used for matrices without humic acid. This was based on modelling assumptions of 20% solid humic content for natural organic matter, and an average DOC release of about 50 mg/kg from kaolin clay (see Chapter 6 Table 6.35).

8.6.2 Kaolin Clay

Speciation evaluations for releases of master species (Al and Si) and contaminants of interest from kaolin clay were undertaken, to assess solubility controlling phases under equilibrium conditions. Predicted leaching for aluminium closely resembles the measured trend (Figure 7.2), and the main solubility controlling phases are kaolinite and the other included clay minerals (Figure 7.3). Considering that natural kaolin pH was around pH 5.53, there was no significant degradation, which occurs under alkaline conditions (Langmuir, 1997). This resulted in the kaolinite phase being dominant at the alkaline end, where alkalinity induces degradation. Silica leachability also shows similar prediction and measured trends (Figures 7.4 and 7.5), with a broader predicted insolubility than measured (pH 6.0 – 8.0). The kaolin clay contained traces of assessed contaminants, and evaluations for their speciation were undertaken.

For zinc, amphoterism was predicted, with a lower leachability under alkaline conditions. However, the measured release only showed leachability under acidic conditions (Figure 7.6). Sorption to clay (and lattice substitution), franklinite (zinc iron manganese hydroxide) and faustite (zinc alumino phosphate hydroxide) were predicted as solubility controlling phases, with POM complexation (Figure 7.7). Faustite occurs in mines in Cornwall (mindat.org) where the kaolin clay was mined. Zinc can be sorbed by clay minerals via cation exchange, or incorporated in the crystalline lattice. This lattice substitution produces minerals like the zinc silicate mineral of the kaolinite – serpentine family Fraipontite - ($(Zn, Al)_3(Al, Si)_2O_5(OH)_4$) (McPhail *et al*, 2003). Franklinite occurs as a common zinc mineral, a component from granite and pegmatite degradation, during acidic weathering which forms kaolin clay. Predicted chromate release suggested low solubility under acidic and releases under alkaline conditions, and contradicted the measured release. This showed release under acidic conditions (Figure 7.8). Employed assessment tools limited evaluation of alternative chromium forms (See Section 8.0 and Chapter 7.3). These findings suggest that chromium does not occur as chromate in kaolin, and predicted partitioning phases include clay minerals, POM and HFO (Figure 7.9).

8.6.3 No Additive Speciation Evaluation

For speciation evaluations in stabilised matrices without additives, aluminium and silicon evaluations were undertaken for uncontaminated samples, and included the contaminants of interest for contaminated samples. For uncontaminated samples, aluminium predictions and measured release showed similar amphoteric trends, comparable for all hydration periods (Figures 7.13, 7.23 and 7.35). Assuming decreasing clay content with increasing hydration, assumptions for 60%, 40% and 30% clay contents were made at 28, 150 and 300 days respectively. This was based on an 80% original clay content (see Section 8.1.2 and Chapter 4 Table 4.1), and was likely to have over-estimated content decreases, since no measurements were taken post-stabilisation.

At 28 days, dominant solubility controlling mineral phases was kaolinite, gibbsite, calcium aluminosilicates hydrates (CAS), ettringite and monosulphate, with traces montmorillonite and clay minerals (Figure 7.14). These phases were predicted after geochemical speciation modelling, using the measured releases of components under the prevailing chemical conditions, using the selected mineralogy for components in the matrix, after speciation determination for stable minerals (see Chapter 5, Section 5.4.6).

Monosulphate and gibbsite were not dominant at 150 days (Figure 7.24), but were observed at 300 days with gibbsite being the dominant phase (Figure 7.36). Increased kaolin degradation increases gibbsite contents, which can result in the increased dominance of the phase. Albite (sodium plagioclase – $NaAlSi_3O_8$) dominance at 150 days was due to the degradation of feldspar, where the kaolin clay contained 5 - 15% feldspar (Table 4.1). Sodic feldspars occur in granites and pegmatite, and the acidic weathering of these rocks produce kaolin clay (Mitchell and Soga, 2005, Reeves *et al.,* 2006). At 28 days, silicon leaching was controlled by kaolinite, CAS, CSH, HFO, montmorillonite, clay minerals, and Jennite ($Ca_9Si_6O_{18}(OH)_6.8H_2O$) (Figure 7.16). Albite becomes dominant at 150 days (Figure 7.26), similar to aluminium, but was absent at 300 days (Figure 7.38). These suggest that dominant solubility controlling minerals for silicon are kaolinite, jennite, CSH, CAS and HFO, with comparable predictions at the different hydration periods. For aluminium, major solubility controlling mineral phases were kaolinite, gibbsite, ettringite, and CAS at different hydration periods. No major alterations in calcium and sulphate phases were observed, even with additive and contaminant inclusions, and hence these results were not included for evaluation. The dominant controlling mineral phases for calcium were jennite, monosulphate, ettringite, clay, CAS, CSH and portlandite (Figures 7.18, 7.27 and 7.40). Ettringite, jarosite (hydrous iron and potassium sulphate) and monosulphate were the dominant phases for sulphates (Figures 7.20, 7.34 and 7.42).

These results showed that the releases of the structural components are controlled by kaolinite, other present clay minerals (montmorillonite and clay alterations), available HFO, present feldspar minerals (albite), and the formed cementitious minerals (CSH, CAS, portlandite, ettringite and jennite). The dominance of these phases was modified with hydration, but the release trends were not modified (see Section 8.4). These phases can be incorporated when designing S/S for field application, taking into account the expected field exposure conditions, to evaluate the potential for degradation and component release.

The primary focus of speciation evaluations was the assessment of contaminant partitioning and alterations in partitioning, to evaluate the implications for leaching. For zinc contaminated stabilised clay matrices, calcium zincate becomes a dominant phase for the partitioning and release of calcium, but did not modify the released trend (Figure 7.53, 7.63 and 7.75). Predictions for aluminium release showed similar trend to that observed for uncontaminated stabilised samples, with the inclusion of albite at 150 days of hydration (Figure 7.59) and corresponding absence at 28 and 300 days of hydration (Figures 7.49 and 7.71). There is also the inclusion of calcium aluminate hydrate (CAH) as a controlling phase for aluminium releases, but the predicted and measured trends were consistent and comparable at the different durations of hydration (Figures 7.49, 7.59 and 7.70). The partitioning of silicon in zinc contaminated stabilised matrices were also similar to those observed in uncontaminated samples, with similar solubility controlling mineral phases at the different durations of hydration. However, there was the inclusion of zinc silicates ($ZnSiO_3$) as a solubility controlling phase, but it was not a dominant phase in view of partitioned silica concentrations (Figures 7.51, 7.61 and 7.73).

For partitioning of zinc in stabilised contaminated matrices, the dominant solubility controlling mineral phases were zinc silicates, franklinite, calcium zincate, HFO and clay (Figures 7.57, 7.69 and 7.79). Predictions suggest amphoteric leaching, with comparable solubility at acidic and alkaline pH (Figures 7.56, 7.68 and 7.78). The presence of calcium zincate was expected, due to complexation of zinc and calcium, coating CSH at alkaline pH (Mollah *et al.,* 1995, Zeigler and Johnson, 2001). Prevalence of franklinite and partitioning on HFO were due to formation of complexes with iron. The lack of measured solubility at alkaline pH was due to zinc partitioning in an insoluble phase (as a zinc silicate, see Section 8.2.3.1 and 8.3.3), which was not predicted. Not all zinc silicate ($ZnSiO_3$) phases are stable under low pressure and temperature conditions. High temperature and pressure monoclinic clino-pyroxene forms and orthorhombic metastable varieties exist, having the similar formula but different crystal forms (Morimoto *et al.,* 1975). Orthorhombic forms are metastable at all conditions, and may occur as complexes with magnesium - $(Zn,Mg)Si_2O_6$, as Willemite - Zn_2SiO_4, or as Hermimorphite – $Zn_4Si_2O_7(OH)_2.H_2O$. Karazhanov *et al.* (2009) confirmed metastable orthorhombic varieties, with stability determined by crystal structure of the mineral form, and the presence of willemite polymorphs. At high alkalinity, zinc hydroxides were expected, as well as zinc carbonates in the prevailing carbonate rich environment (McPhail *et al.,* 2003). Tiller and Pickering (1973), suggested that the presence of aluminium in the crystalline lattice, and availability of silicic acid in the equilibrium solution, will favour prevalence and stability of zinc silicates over carbonates. This was confirmed by McPhail *et al.* (2003), and where silica concentrations approach quartz saturation zinc silicates are likely to limit zinc solubility. Hermimorphite also has lower solubility at acidic pH than willemite. However, there is insufficient information on thermodynamic properties of hermimorphite and zinc clay minerals like Fraipontite (McPhail *et al*, 2003). It was concluded that under the prevailing conditions, zinc silicates (hermimorphite, fraipontite and willemite) will be present in the stabilised matrices.

The use of $ZnSiO_3$ as a solubility controlling phase for zinc has been shown by Comans *et al.* (1993) and Meima and Comans (1999), for leaching from MSWI residues. Given similarities in properties for metastable zinc silicates, $ZnSiO_3$ was used to represent all zinc silicates phases during speciation evaluations. Prediction trends were consistent at the different hydration periods, but phase dominances varied with hydration. Zinc silicates and franklinite dominate at 28 days, franklinite dominance increases at 150 days, while zinc silicates dominate at 300 days. These results showed that zinc was effectively partitioned in stabilised contaminated matrices, primarily as zinc silicates and franklinite, with minimal complexation as calcium zincate. While the prediction trends suggested amphoterism, the prevailing phases were accurately predicted, with due considerations of imposed limitations for the subtle variations in zinc silicate phases. Also, the presence of zinc contaminant did not significantly modify the mineralogy for structural component, although relevant zinc minerals contributed to solubility control, which was expected.

For chromium contaminated samples, aluminium solubility controlling phases were similar to those observed in uncontaminated samples. However, albite controls solubility at 28 and 150 days (Figures 7.84 and 7.96), but was absent at 300 day (Figure 7.106), compared to dominance at only 150 days for uncontaminated and zinc contaminated samples. Silicon solubility controlling phases are also similar, with associated dominance of albite at 28 and 150 days (Figures 7.86 and 7.98), but not at 300 days (Figure 7.108). Prediction trends were consistent for all hydration periods, similar to those observed for uncontaminated samples, with kaolinite, jennite, CSH and HFO controlling solubility. Given the low chromium availability in stabilised chromium contaminated samples (See Section 8.2.2), predicted leachability trends show partitioning between pH 5.0 – 9.0, and 11.0 – 13.0 at 28 days, and 5.0 – 9.0 at 150 days for the available chromium. Solubility phases include sorption and substitution by clay and HFO and precipitation as chromium hydroxide between pH 5.0 – 9.0, and substitution with ettringite between pH 11.0 – 13.0 (Figures 7.94, and 7.104). At 300 days, sorption to clay and HFO control solubility (Figure 7.114), but it was worth noting that the release was comparable to uncontaminated samples. Partitioning with ettringite, sorption on HFO and substitution in clays was expected for chromium (Bone *et al.*, 2004b), as well as precipitations of hydroxides (Dermatas and Meng, 2003). However, using chromate to evaluate Cr^{3+} speciation was unlikely to accurately predict partitioning, based on the determinations for stable mineral phases used for predictions.

While the phases predicted were those expected for containment of chromium within the stabilised matrices, predicted leaching trends were not comparable with hydration, similar to those measured which also showed no definable trends (also see Section 8.4). The introductions of the contaminants did not significantly influence the speciation of the structural components. The contaminant speciation and expected solubility controlling phase degradations can be incorporated during S/S design, putting in place measures to limit the conditions that can induce their accidental releases.

8.6.4 Humic Acid Additive Speciation Evaluation

For humic acid matrices, similar speciation evaluations were undertaken, and evaluations for aluminium and silicon speciation, and introduced contaminants presented. Higher clay contents of 65%, 45% and 35%, at 28, 150 and 300 days respectively, were assumed for humic acid matrices. This was due to hydration retardation considerations, and decreased rates for kaolin degradation (see Section 8.2.3.1), compared to other matrices. However, clay contents were not measured, and decrease over estimations were expected.

For uncontaminated samples, aluminium solubility at 28 days was controlled by kaolinite, ettringite, CAS, CAH, traces of clay and montmorillonite, and dominant POM influence (Figure 7.119). At 150 days and 300 days, albite also becomes dominant in controlling solubility (Figures 7.123 and 7.127). Increased organic content had significant implications on aluminium solubility, and partitioning trends were consistent at all hydration periods, though predictions at 300 days suggested greater ettringite influence (Figure 7.126). Predicted and measured trends for silica were also comparable at all periods (Figures 7.120, 7.124 and 7.128). The dominant solubility controlling phases were kaolinite, montmorillonite, CSH, CAS, HFO and jennite at 28 days (Figure 7.121). Albite also becomes dominant at 150 and 300 days (Figure 7.125 and 7.129), since it controls releases of both aluminium and silica, but CAS no longer controls solubility at 300 days. DOC was not observed to influence solubility for silica, even though the increased organic content influences mineralogy, which control silica solubility.

For zinc contaminated samples, aluminium releases follow similar speciation trends to those observed in uncontaminated samples. Minor variations in the dominance of prevailing mineral phases were observed, but these were not significant in view of trend modifications or solubility alterations (Figures 7.134, 7.140 and 7.146). For silica releases, predictions and trends were consistent at all periods (Figures 7.135, 7.141 and 7.147), with phases comparable to those observed for uncontaminated samples (Figures 7.136, 7.142 and 7.148). Zinc silicates were dominant for silica releases at all periods, and HFO controls solubility to greater extents, even though available HFO was lower in humic matrices. This increased HFO dominance was also observed for other zinc contaminated matrices, compared to similar uncontaminated matrices, and was likely due to sorption of zinc silicates onto HFO surfaces, which modified the silica solubility phases. Zinc prediction trends and partitioning were similar to those observed for matrices without additives, except that significant complexation with POM were observed. These were expected given the increased organic content, but HFO influence on zinc controlling solubility was decreased. Solubility controlling minerals (zinc silicate, franklinite and calcium zincate) varied in dominance with hydration, with zinc silicates increasing and POM decreasing in dominance with increasing hydration (Figures 7.138, 7.144 and 7.150).

These results showed that the increased organic content modified the solubility phases for zinc, and explains the increases in availability for this matrix (Section 8.2.2).

However, increasing hydration induced increasing formations of zinc silicates, which resulted in comparable speciation and solubility to matrices without additives.

For chromium contaminated samples, aluminium and silica solubility phases were comparable to those for the uncontaminated samples (Figures 7.155, 7.157, 7.161 7.163 7.167 and 7.169). The predicted and measured release for silica was also comparable at all hydration periods (Figures 7.156, 7.162 and 7.168). HFO influence on silica solubility was not as pronounced as observed for zinc contaminated samples, similar to those for the uncontaminated samples. High chromium leachability at 28 and 150 days (Table 8.1) produced an associated increased partitioning at these periods, with reasonably comparable releases and predictions (Figures 7.158 and 7.164). Speciation predictions suggested that solubility was controlled by POM and chromium (III) hydroxide under acidic and neutral conditions, and ettringite under alkaline conditions (Figures 7.159 and 7.165). However, at 300 days, predictions and releases were variable and non comparable (Figure 7.170), and speciation predictions suggest partitioned to POM and ettringite controlling phases for release. Also, the measured availability was comparable to those for uncontaminated samples (Table 8.1), which confirmed that while chromium was effectively contained, chromate assessment was not suitable for Cr^{3+} solubility controlling phase predictions.

The Speciation predictions showed that increased organic content significantly influence aluminium releases, becoming a dominant solubility controlling phase at all hydration periods. While silicon phases were not influenced by increased organics, zinc contaminated samples showed increased HFO dominance due to zinc silicates sorption. Increased organic content increased zinc complexation with POM, which decrease with hydration, with zinc silicates dominating solubility. This showed why releases and phases at 300 days were comparable, where the increased hydration produced phases comparable to those observed for matrices without additives. Speciation predictions for chromium showed that increased organic contents increased the complexation of chromium with POM. The releases and predictions were comparable at 28 and 150 days of hydration, and showed the dominance of POM in controlling solubility. However, increasing hydration improved containment (see Section 8.2.2), and releases at 300 days were comparable to those for uncontaminated matrices. However, predictions are this matrix showed similar problems to those for matrix without additives.

8.6.5 Sulphate Additive Speciation Evaluation

For sulphate matrices, evaluations for aluminium and silicon, and introduced contaminants speciation are presented to evaluate influences from increased sulphate. Clay contents similar to those for matrices without additives were used during modelling, with 60%, 40% and 30%, used at 28, 150 and 300 days respectively. Assumptions were made prior to modelling that sulphate influences would not affect kaolin degradation rates. However, leaching evaluations suggested alumina and silica release increases, suggesting increased kaolin dissociation (see Section 8.2.3.1, and 8.3.3). However, their availabilities and trends were not significantly modified (see Section 8.2.2 and 8.4.3).

For uncontaminated samples, aluminium predictions show that kaolinite, gibbsite, albite, CAS, CAH, ettringite and montmorillonite were dominant at 28 days (Figure 7.176), but CAS and gibbsite were not observed as controlling phases at 150 and 300 days (Figures 7.180 and 7.184). Leaching trend predictions suggested increased ettringite dominance at alkaline pH, which should reduce leachability for this range, but this was not observed for measured values (Figures 7.175, 7.179 and 7.183). Solubility controlling phases for silica included kaolinite, albite, CSH, jennite, CAS, montmorillonite and HFO at 28 days (Figure 7.178), but CAS were not observed at 150 and 300 days (Figures 7.182 and 7.186). Silica release predictions were also consistent and comparable at 150 and 300 days (Figures 7.177, 7.181 and 7.185), but predictions at 28 days of hydration suggests increased insolubility due to kaolinite (Figure 7.178). The increased sulphate was not observed to significantly modify speciation, compared to phases for the other matrices. The increased dominance of CAS for all hydration periods may be due to the utilisation of gibbsite for formation of hydrated calcium aluminates.

For zinc contaminated samples, aluminium and silica releases and predictions were comparable to those observed for uncontaminated matrices. However, CAH and montmorillonite were only present at 28 and 150 days (Figures 7.191, 7.197 and 7.203), for aluminium speciation. Zinc silicate was also observed as a silica solubility controlling phase, at all hydration periods (Figures 7.193, 7.199 and 7.205). For zinc partitioning and releases, predictions show that zinc solubility was controlled by zinc silicate, franklinite, calcium zincate and HFO at the different durations of hydration (Figures 7.195, 7.201 and 7.207). However, while zinc silicates dominate at 28 and 150 days, the influence at 300 days was dominated by franklinite and zinc silicate. The increased degradation of kaolin, compared to the other clays, was expected to increase the availability of silica in the ore solution, which was used up for the formation of zinc silicates and hydration products. This was likely to be the mechanism that influenced the improved early partitioning of zinc, compared to the other matrices.

For chromium contaminated samples, aluminium speciation predictions showed that kaolinite, ettringite, montmorillonite, CAS and CAH were the dominant phases at 28 days (Figure 7.212). However, at 150 days, CAS and CAH were replaced by monosulphate (Figure 7.218), and gibbsite becomes dominant at 300 days (Figure 7.224). Further predictions suggest the increased dominance of ettringite under alkaline pH at 150 and 300 days (Figures 7.217 and 7.223), but these were not observed for the measured releases. Silica predictions showed kaolinite, CSH, montmorillonite, jennite, albite and HFO as the solubility controlling phases at 28 days, with comparable leaching and prediction trends (Figures 7.213 and 7.214). However, montmorillonite was not observed at 150 and 300 days, while jennite was absent as a dominant phase at 150 days (Figures 7.220 and 7.226). Increased chromium availability at 28 days (Table 8.1) was observed for predictions, but useful correlation was not observed with measured releases (Figure 7.215). However, the predicted solubility controlling mineral phases were those expected (HFO, chromium (III) oxide and ettringite) (Figures 7.216 and 7.222), given the increased HFO content of sulphate matrices (Section 8.6.1), and increased ettringite contents. The results show that the increased leachability at early hydration may be due to the increased HFO content which sorbs the contaminant, and are mobilised under acidic conditions. However, this again showed the shortfalls of assessing Cr^{3+} using chromate species.

The obtained results showed that increased sulphate contents did not significantly modify the trends and speciation for the structural components, with only minor alterations observed for the solubility controlling phases, compared to the other matrices. The speciation for zinc contaminated samples, showed increased dominance of zinc silicate minerals at the early hydration period, due to increased availability of silica in the pore solution with increased kaolin degradation. The increased HFO content increases the availability and leachability of chromium at the early hydration periods, however, the partitioning of all contaminants improved with increasing hydration.

8.6.6 Monolithic Material Leaching Interface Development

As a way for demonstrating potential for the current employed assessment, i.e. using leaching evaluations for the different releases controlling mechanisms, the mineralogical development at the leaching interface, during monolithic leaching was evaluated. This was aimed at providing a brief introduction to the changes that occur in prevailing mineral phases, with leaching from the monolithic specimen at the liquid – solid interface. The structural components of kaolin (Al and Si) were evaluated, to assess the degradation of kaolin with increasing leaching. Figures 8.7, 8.9 and 8.11 show the changes in mineral phases for aluminium, at 28, 150 and 300 days respectively. The respective results for silica are shown in Figures 8.8, 8.10 and 8.12. With progressive leaching from test inception to 64 days, kaolin was increasingly dissociated at the leaching interface. This resulted in gibbsite becoming more stable, and silica being released as silicic acid. As a result, kaolin is replaced by gibbsite as the dominant release controlling mineral for aluminium, and silica becomes increasingly available as free ortho-silicic acid. The dominance of the phases changed with increased leaching, and also varied at the different hydration durations. Similar replacements were observed for the other matrices, and these results can be used to infer changes in degradation with increasing leaching or hydration.

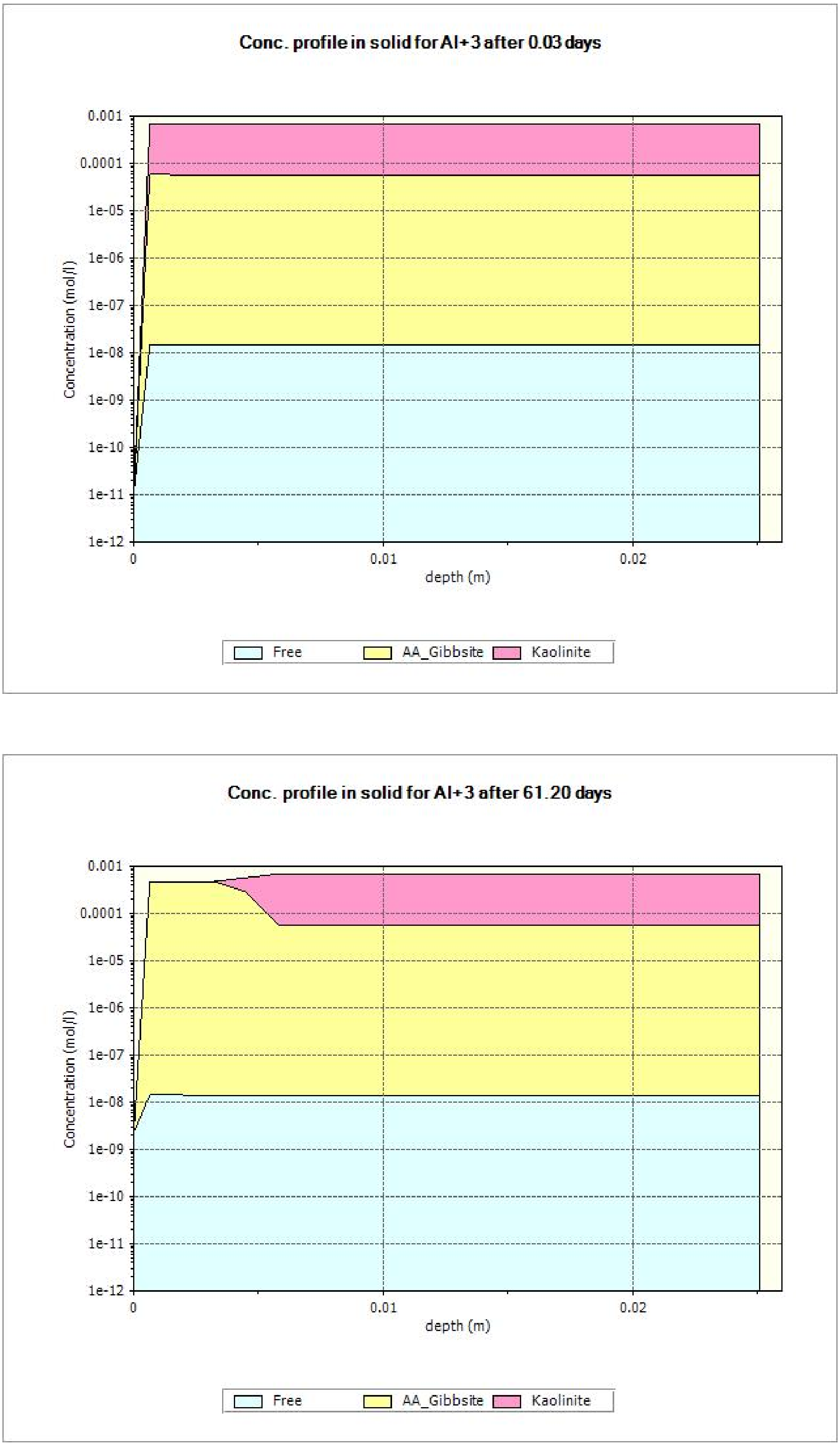


Figure 8:7: Aluminium mineral alterations at the monolithic leaching interface from EO at 28 days

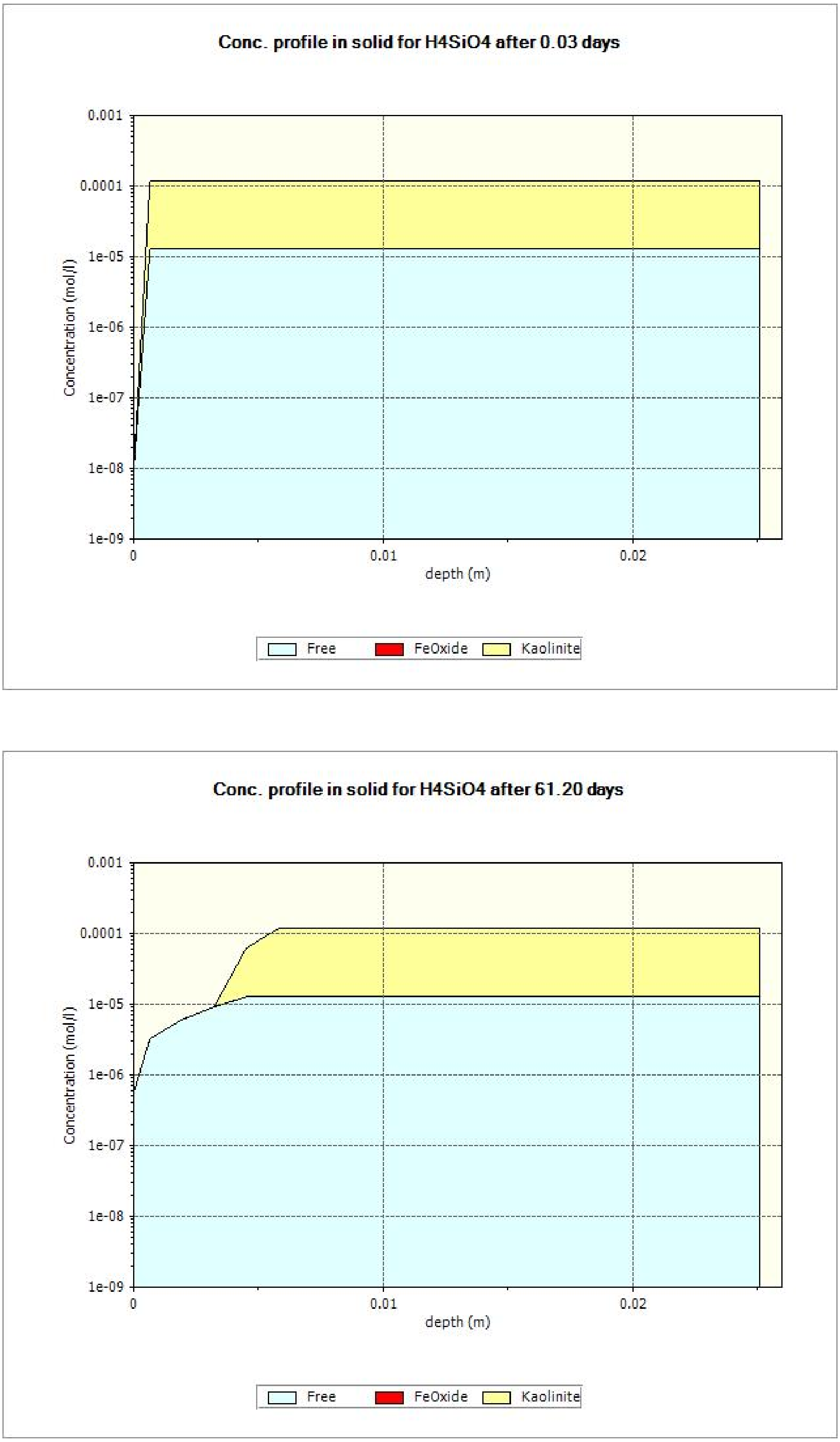


Figure 8:8: Silicon mineral alterations at the monolithic leaching interface from EO at 28 days

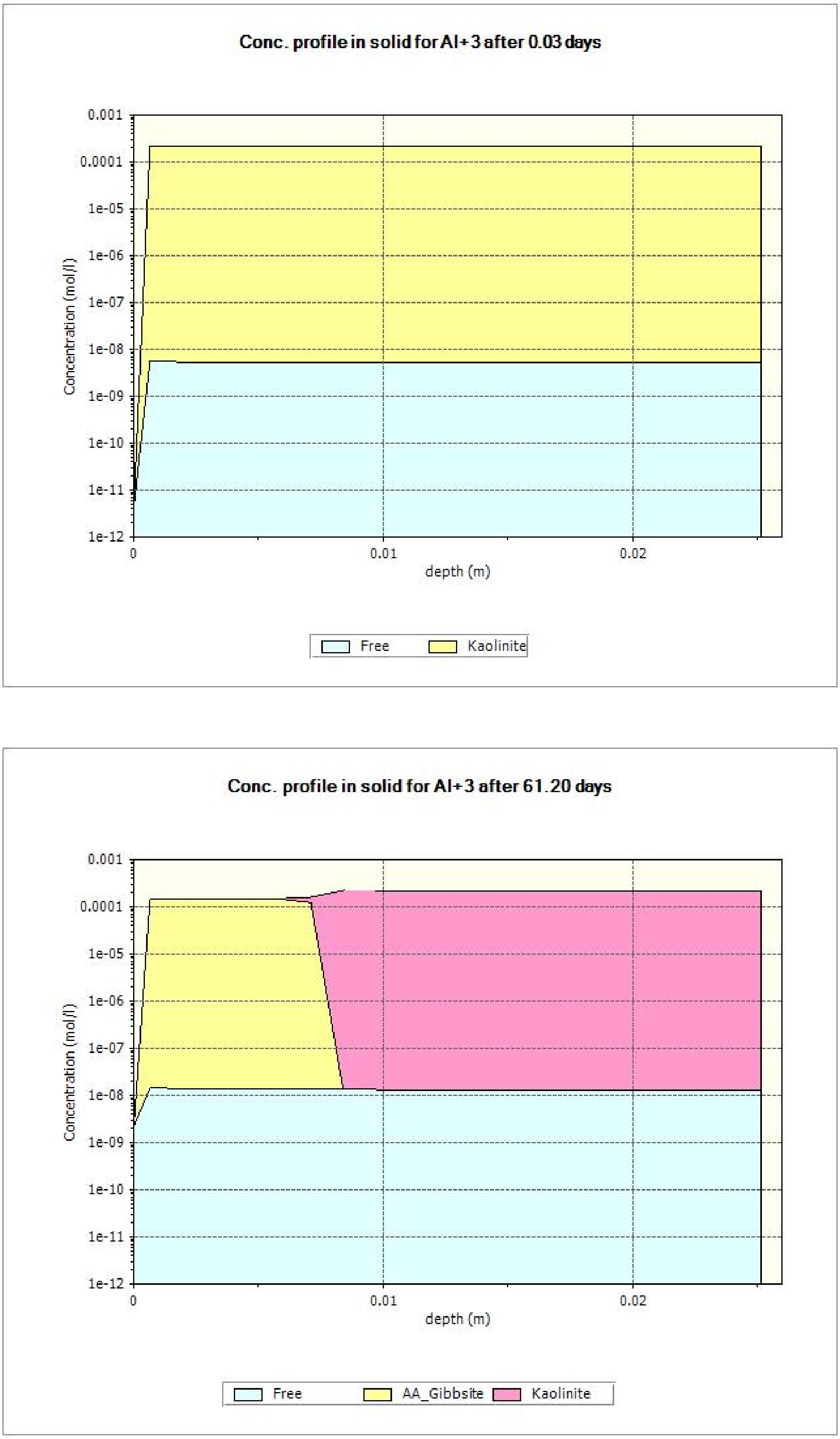


Figure 8:9: Aluminium mineral alterations at the monolithic leaching interface from EO at 150 days

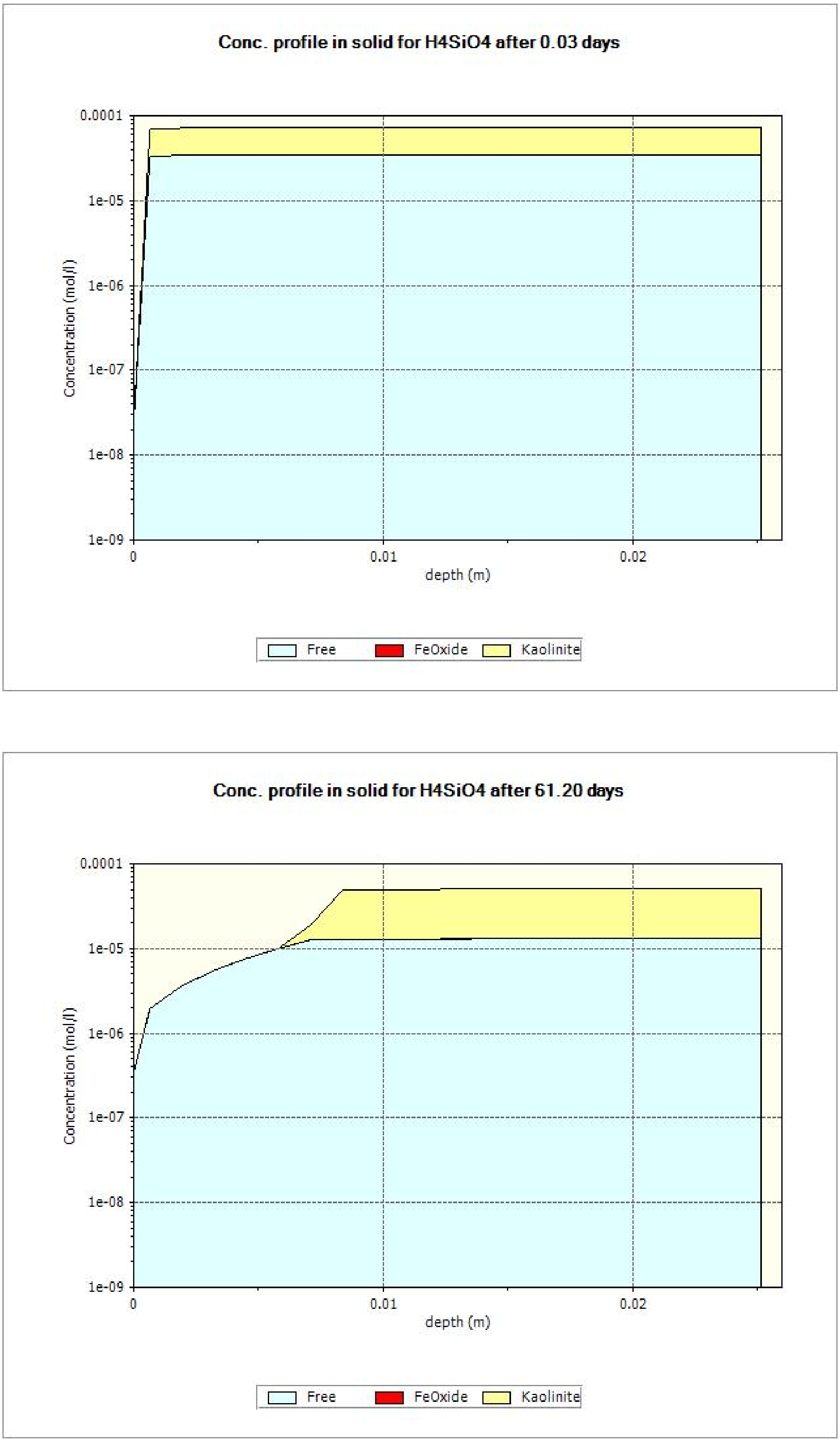


Figure 8:10: Silicon mineral alterations at the monolithic leaching interface from EO at 150 days

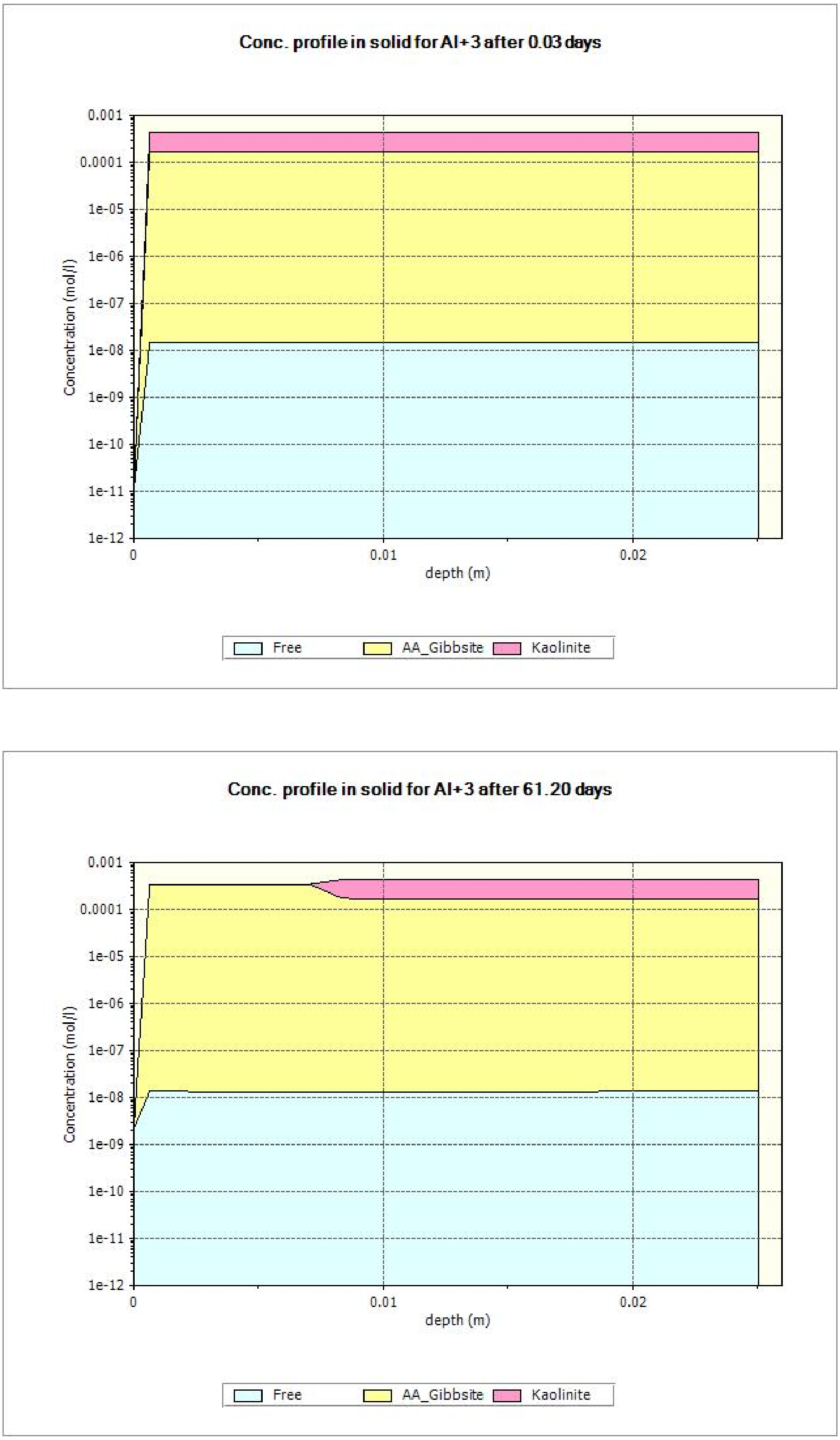


Figure 8:11: Aluminium mineral alterations at the monolithic leaching interface from EO at 300 days

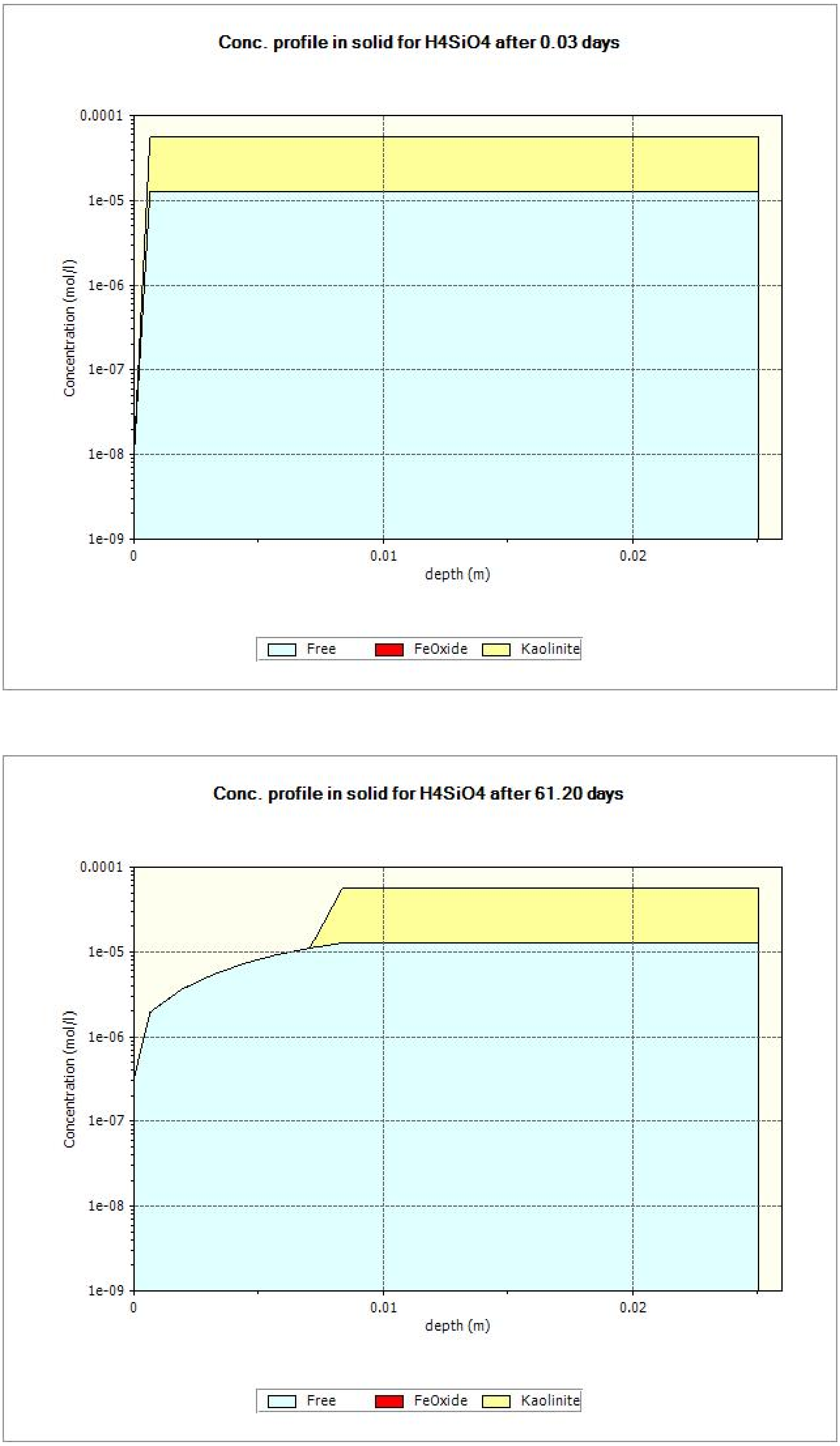


Figure 8:12: Silicon mineral alterations at the monolithic leaching interface from EO at 300 days

8.6 KEY FINDINGS AND IMPLICATIONS FOR STABILISATION / SOLIDIFICATION DESIGN

One of the objectives of the study was the design and adoption of a suitable suite of leaching tests, for the assessment of releases from stabilised kaolin clay matrices. These tests took into account the different mechanisms that influence releases for the stabilised matrices, which displayed monolithic properties after preparation and curing. The important mechanisms to consider related to the disequilibrium and equilibrium leaching conditions for components. For disequilibrium conditions, components released during monolithic leaching due to diffusion, dissolution and wash-off from the material surface were evaluated and discussed (Section 8.3). For equilibrium leaching conditions, leaching due to the influence of pH was evaluated and discussed in Section 8.4, and the leaching to porewater discussed in Section 8.5. No new leaching tests were devised for this study, but rather the harmonised leaching tests by the European Committee for Standardisation (CEN) were adapted and employed appropriately.

The leachabilities of structural master species were then undertaken, to determine releases, leaching trends and availability. These master species dominate composition, and for the stabilised kaolin clay matrices, were aluminium, silicon and calcium. Changes in the leachability and trends with hydration gave indications of the material degradation, or formation of stable / durable minerals. The increased cumulative releases of aluminium with increasing hydration (Section 8.2.3.1) indicated increasing kaolin degradation, due to dissociation under prevailing alkaline pH conditions. However, the released silica was used up in pozzolanic reactions for formation of cementitious products. This was observed during monolithic leaching tests, where precipitations of calcium silicate were observed during leaching, due to complexation of released silicic acid with calcium. Cumulative releases of calcium also decreased with hydration, due to the increased formation of stable cementitious products. These results were used to infer the chemical durability of the matrices, which increased with hydration, regardless of increasing kaolin dissociation.

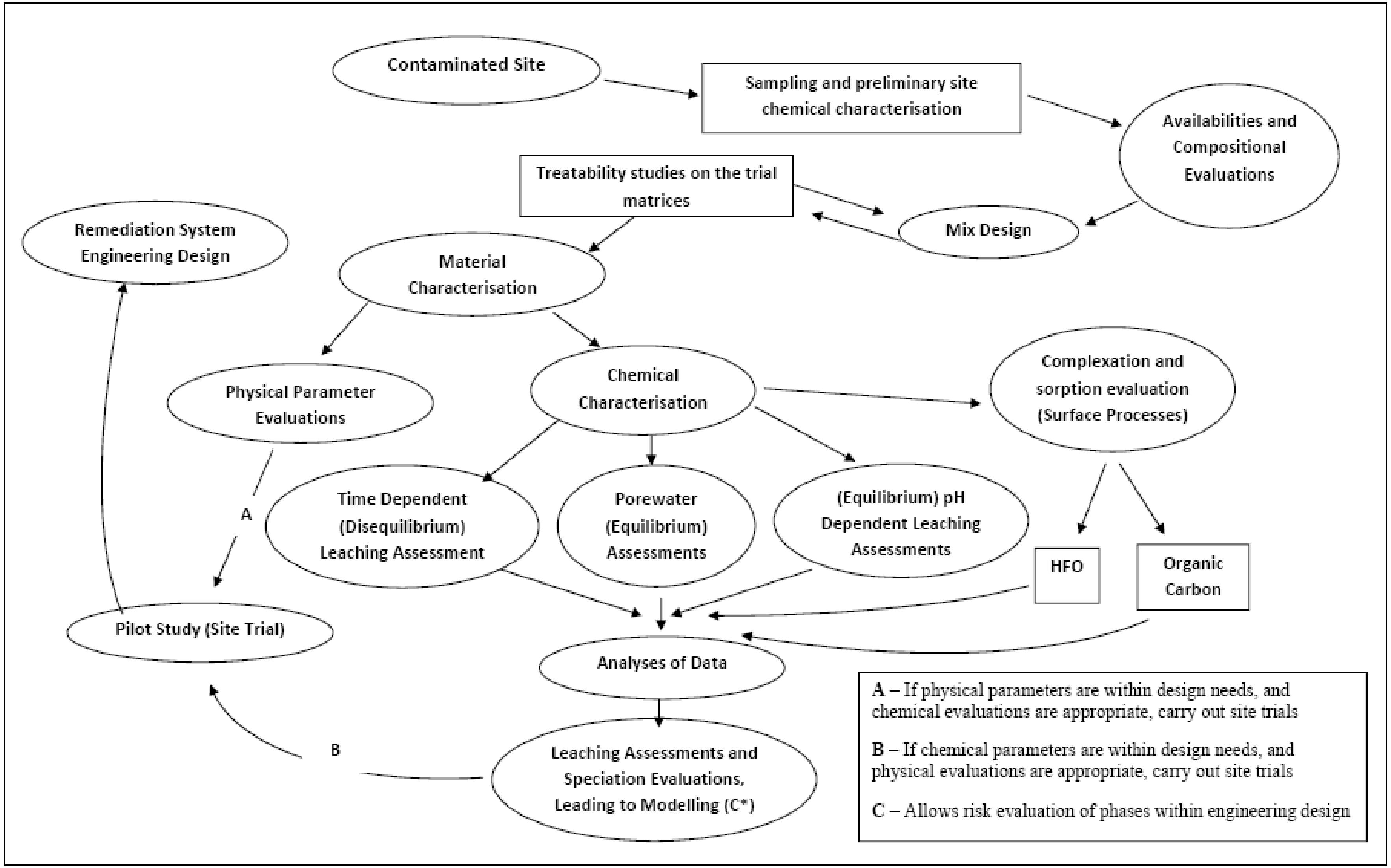
The containment and leachability of introduced contaminants were then evaluated, to determine the effectiveness of the treatment method. These were for introduced zinc nitrate and chromium (III) nitrate. The leaching assessment methods were successful in evaluating the leaching trends and availabilities for these components under pH and monolithic leaching conditions. The contaminants were effectively contained during monolithic leaching under the prevailing stabilised matrices natural alkaline pH conditions (Section 8.3), and had comparable releases to those for uncontaminated samples. However, during pH dependent leaching, the expected leaching trends were not observed. Zinc did not show amphoteric leaching behaviour, but rather was only soluble under high acidity (Section 8.4). This was validated and explained during speciation evaluations (Section 8.6), based on lattice conditions and prevailing components in pore solution (see Section 8.6.3). Chromium leaching did not show consistent trends during leaching at the different periods. However, the availabilities indicated effective containment (Section 8.2.2).

Additives were introduced to the mixes to determine implications on contaminants containment. These additives were organic carbon (as 1% humic acid) and sulphate (as 2.5% sodium sulphate). The presence of increased organic carbon increased the availability of both contaminants (Section 8.2.2), but did not compromise containment during leaching from monolithic specimens (Section 8.3). The humic acid matrices remained deformable under thumb pressure after 300 days of hydration, but retained integrity during monolithic leaching at all hydration durations. The presence of increased sulphate contents improved zinc partitioning (Section 8.4), but also increased the dissociation of kaolin, and subsequently increased the aluminium releases. During monolithic leaching, the increased sodium content (from sodium sulphate) induced cation (calcium) exclusion due to mass action, resulting in increased silica solubility (Section 8.2.3.1 and 8.3). This was due to the higher solubility of sodium silicates, and no calcium silicate precipitations were observed for sulphate matrices.

Increasing durations of hydration improved containment for both contaminants in the different matrices. The releases of zinc were comparable at 300 days of hydration, and the availabilities decreased with increasing hydration (Section 8.2.2). The leaching trends were also comparable at all hydration durations for the different contaminated matrices. The availability of chromium also decreased with hydration, with measured availability at 300 days being comparable to those observed for uncontaminated samples. Kaolin dissociation increased with hydration, yielding increased aluminium releases, but the released products were incorporated for formation of cementitious products. This resulted in decreasing calcium cumulative releases, but also increasing availability with increasing hydration, due to the formation of cementitious products, which were leachable with decreasing pH. The introduction of humic acid decreased aluminium cumulative releases, and increased calcium cumulative releases, due to hydration retardation (Section 8.2.3.1). However, increasing hydration durations increased aluminium releases, and decreases calcium releases, due to increasing hydration processes. These results showed that increasing hydration improved the chemical properties of the stabilised matrices. The acid neutralisation capacities were however decreased with hydration durations, due to reductions in free hydroxyl ions, to buffer induced acidity.

Results from geochemical speciation modelling were then used to evaluate the solubility controlling mineral phases for the different matrices. These phases show the sensitivity of partitioning minerals to changes in pH under equilibrium leaching conditions, and can be used to evaluate changes under field conditions. S/S designs can then be used to design out risks and susceptibilities, for specific phases of interest. For example, reducing agents can be introduced to ensure reduction of Cr^{6+} contaminants, and their complexation as Cr^{3+} salts. Predicted releases were compared to actual measurements, and the trends were comparable, for the master species evaluated. However, for the contaminants, variations were observed between measured and predicted releases. Amphoteric leaching was predicted for zinc, due to dissolution of calcium zincate and solubility of precipitated hydroxides. However, for the tested matrices, a variety of zinc silicates induced insolubility (Section 8.6.3), some of which lack sufficient thermodynamic information (Hermimorphite and Fraipontite). Trends for chromium were not comparable, due to the use of chromate for Cr^{3+} evaluation, but the predicted phases were those expected for the matrices tested. The high chromium sorption affinity by kaolin (8.1.1) suggests lattice substitution of Cr^{3+} for Al^{3+}, which makes the clay a dominant solubility controlling phase. Substitution of Cr^{3+} with Al^{3+} also occurs in ettringite, along with the precipitation of chromium (III) hydroxides. The phases predicted for the structural components were also validated, and conformed to expectations for speciation of the stabilised kaolin matrices. With changes in prevailing field pH conditions, the dominants phases (under these conditions) can be evaluated, and releases predicted in view of environmental impact.

Taking on board the findings from this research, these can then be integrated for application during S/S treatment of contaminated land. Figure 8.13 shows a hypothetical process application for characterisation and validation for S/S suitability and effectiveness, during treatability evaluations. These address the contamination and transport mechanisms shown in the conceptual study (Chapter 1 Figure 1.1), including the characterisation of stabilised products, and the various containment mechanics (Figures 1.2 and 1.3). These will improve confidence in the S/S application and inform design, in view of establishing and validating the effectiveness, long-term performance and chemical durability of stabilised material.



A – If physical parameters are within design needs, and chemical evaluations are appropriate, carry out site trials

B – If chemical parameters are within design needs, and physical evaluations are appropriate, carry out site trials

C – Allows risk evaluation of phases within engineering design

Figure 8:13: Flow diagram for effectiveness evaluation and material characterisation during S/S design

CHAPTER NINE

9.0 CONCLUSIONS

9.1 INTRODUCTION

Stabilisation / solidification techniques have been previously demonstrated as effective tools for the amelioration of unacceptable risk posed by heavy metals in contaminated soils. However, these methods induce containment, and do not remove contaminants. There is therefore a need to ensure effectiveness of the treatment in attaining and maintaining the design criteria for the long term. This study set out to devise a suitable chemical assessment method for S/S effectiveness, using a holistic risk based approach, for incorporation during whole system performance based S/S design. This required systematic evaluations of chemical containment processes, by assessing the various release controlling mechanisms and undertaking geochemical speciation modelling to allow risk evaluations for solubility controlling phases. To achieve this, kaolin clay (simple stoichiometric clay with well defined properties) was stabilised using CEM II Portland limestone cement, and assessments undertaken to characterise the stabilised material. The effectiveness of stabilisation was evaluated, and information on time dependent performance and chemical durability determined, using data on the containment of introduced contaminants (Zn^{2+} and Cr^{3+}) and the releases for structural master species (Al, Si and Ca).

Section 9.2 outlines the potential impact of the key findings and conclusions that are detailed in Sections 9.3 and 9.4, and as a design evaluation methodology, is a significant contribution to knowledge in its own right. Section 9.3 provides conclusions for the structural master species, while those for contaminants are presented in Section 9.4.

9.2 IMPLICATIONS OF COMBINING LEACHING ASSESSMENTS AND GEOCHEMICAL MODELLING ON S/S DESIGN

9.2.1 Introduction

Key to determining S/S effectiveness was the design and adoption of a suite of leaching tests to inform assessments of the different mechanisms that induce leaching from materials. For this evaluation, it was important to select the least amount of components that define the stabilised matrix (master species) and assess their releases under different release conditions. Also, the introduced contaminants were assessed to determine the containment effectiveness for different matrices. The influences of additives on containment were also undertaken, using common soil components (humic acid and sulphate). For the stabilised matrices, releases were controlled by equilibrium and disequilibrium conditions, and an understanding of these conditions was required to undertake assessments. The data for the releases controlling mechanisms can be used to determine susceptibility for environmental damage, and are dependent on the solubility controlling mineral phases. These phases were determined using geochemical speciation modelling from results for equilibrium leaching releases, for incorporation during S/S design to validation performance under field conditions.

9.2.2 Leaching Assessments

Equilibrium leaching is controlled by prevailing chemical conditions and the various surface processes that occur within the pH domain. To obtain this information, a pH dependent leaching test (CEN/TS 14429) was adopted, with initial additions of acid or alkali to induce pH modification. This test also informed the availability (maximum leachable content for leaching at pH range 4.0 – 12.0) for components, which are dependent on the speciation of the component in the material, and ultimately determines the environmental impact. The stabilised materials exhibited monolithic behaviours after sample preparation and storage for hydration. This therefore required information on disequilibrium releases for time dependent leaching from monolithic specimens, due to diffusion, dissolution and surface wash-off processes, which are not controlled by equilibrium. The dynamic monolithic leaching test (DMLT) with eluate renewal (CEN/TS 15863) was adopted to provide the information on time dependent releases of components, due to the prevailing chemical kinetic. Also, it was important to assess equilibrium leaching at low liquid to solid (L/S) ratios, to evaluate releases to porewater, and releases under weathered conditions. For this assessment, the upflow percolation leaching test (CEN/TS 14405) was adopted, using information for releases up to 0.5 L/S.

The obtained information for the different release controlling mechanisms was sufficient to characterise the stabilised matrices, providing information on the leachability of components under the prevailing conditions. Leaching assessments were then undertaken, to determine the stabilisation effectiveness. These assessments were effective for the stabilised clay matrices, and provided information on components availability, and changes in availability with increasing hydration (see Sections 9.3 and 9.4). Cumulative releases for structural master species were also obtained, along with information on changes in releases and release trends with increasing hydration. The implications of introduced additive on containment and leachability were also obtained. The stabilisation effectiveness was then validated, showing effective contaminants containment within the stabilised matrices under the stabilised materials chemical conditions. However, observed equilibrium leaching trends for contaminants were not those expected, based on theoretical solubility of their hydroxides. This required validation to determine the solubility controlling mineral phases which dictate releases within the pH domain (see Section 9.4).

9.2.3 Geochemical Speciation Modelling and Evaluation

To allow risk evaluations for components solubility controlling phases during S/S design, geochemical speciation modelling was undertaken for the stabilised matrices. Since components speciation determine their behaviour during leaching, it was important to evaluate these phases, to design out the risks that can induce their leaching under field conditions, during performance and risk based S/S designs. To undertake speciation evaluations, evaluations for interactions that induce containment were required. These included complexation with organics, sorption to reactive hydrous ferric oxides (HFO) surfaces, precipitation, sorption, chemical incorporation and substitution with clay minerals and formed cementitious minerals.

Extractions were done to determine available HFO and organic carbon, and speciation modelling undertaken, using pH equilibrium leaching information. This approach was effective for determining the releases controlling mineral phases, which determined how the components behaved under exposure conditions. This can be incorporated during S/S design to design out risks for accidental releases based on the stability of the predicted phases. Predictions for releases of the selected solubility controlling phases were then compared to the measured releases to validate components partitioning predictions and establish the modelling limitations. Speciation and trends for structural master species were accurately predicted based on the expected mineralogy for the matrices evaluated (see Section 9.3). For contaminants', limitations for evaluations were observed from the tools (LeachXS – ORCHESTRA). Assessment could only be undertaken for chromium releases as chromate (CrO_4^{2-}) species, while the contaminant was introduced as Cr^{3+} (see Section 9.4.2). Also, limitations were observed for zinc release, due to limited thermodynamic information for some of the expected solubility controlling phases (see Section 9.4.1).

9.2.4 Implications for Stabilisation / Solidification Design

Adopting an integrated holistic assessment approach to evaluate S/S effectiveness for contaminant containment proved ideal for characterisation of the stabilised matrices to inform S/S designs. Information on release controlling mechanisms was successfully obtained, and evaluations for releases due to their influences were addressed. The use of speciation modelling proved successful for evaluating components solubility controlling phases, and evaluations at the different hydration periods showed how these phases altered, for the different matrices. The obtained information can be adopted for use during field trials to inform effective performance and risk based S/S designs, to meet and sustain the required design criteria. The findings from this study highlighted the need for increased emphasis on chemical characterisation during S/S treatability studies, for evaluations of effectiveness, since the obtained information determines the environmental impact.

9.3 EVALUATIONS FOR THE STRUCTURAL MASTER SPECIES

9.3.1 Introduction

The assessment of master species during chemical characterisation ensures effective leaching assessment, for releases of the components that dictate material behaviour. For the stabilised kaolin clay matrices, these were aluminium, silicon and calcium. The influences of introduced contaminants and additives were then assessed, for leachability of these structural components with increasing durations of hydration. The availabilities and cumulative releases of these components were also used to infer the chemical durability for the matrices, with increasing durations of hydration.

9.3.2 Master Species without Additives or Contaminants

Under the induced alkalinity from stabilisation, increasing dissociation of kaolin was expected, which releases hydroxides of aluminium and silicon. The availability of aluminium increased with increasing hydration, which indicated the increasing dissociation / degradation of kaolin with increasing hydration. However, the availability of silica decreased with increasing hydration, which indicated its increasing use for the formation of cementitious products in the pore solution. The availability of calcium increased with hydration, which also indicated the increasing formation of cementitious minerals. This increases calcium availability for leaching due to the decalcification and dissolution of cementitious minerals (CSH and portlandite) with decreasing pH. The availabilities indicated increasing stability of the stabilised matrices, regardless of kaolin degradation. Also, the availabilities of kaolin components (aluminium and silicon) were less than 1% of the total content in the matrices.

Cumulative releases for the structural components during monolithic leaching also indicated increasing stability of matrices with increasing hydration. Cumulative releases for calcium and silica decreased with increasing hydration due to the increasing formation of cementitious minerals, which were insoluble under the prevailing alkaline conditions. Precipitations of calcium silicate were observed during monolithic leaching of stabilised matrices. These showed the pozzolanic interactions taking place within matrices, which decreased the solubility of calcium and silicon. Equilibrium leaching to porewater also showed increasing kaolin dissociation, with increasing formation of stable cementitious minerals. However, releases for master species were insignificant, compared to their total content in the matrices, which showed their chemical stability under prevailing conditions.

Accurate predictions for the leaching trends and solubility controlling phases for the structural components were observed, which can be used to infer behaviour the under field exposure conditions. The master species solubility controlling phases for aluminium were kaolinite, gibbsite, albite, and formed cementitious (aluminate) minerals. Those for silica were kaolinite, albite, HFO and the formed cementitious (silicate) minerals, while calcium was controlled by cementitious minerals, HFO and clay minerals. Phase dominance varied with hydration time, but the leaching trends remained consistent. These indicated that early hydration results may be useful in predicting longer term behaviour, if the phase dominance behaviour with time can be modelled confidently.

9.3.3 Influence of Contaminants and Additives

No significant modifications in the speciation and solubility controlling phases for structural master species were observed due to contaminant introductions. These findings were consistent for all the hydration periods. However, for zinc contaminated samples, zinc silicates (which control zinc solubility) also became minor solubility controlling phases for silica, and calcium zincate for calcium. Also, HFO became more dominant for silica in zinc contaminated sulphate additive matrices, due to the sorption of zinc and zinc silicates to the increased HFO surfaces in the sulphate matrices.

For additives, the introduction of humic acid decreased the early availability of aluminium and silicon, due to hydration retardation and decreased kaolin degradation. The acid neutralisation capacity for humic acid matrices was also higher than those for the other matrices, due to the increased hydroxyl availability, induced by unhydrated cement. However, sulphate matrices promoted kaolin dissociation, increasing the availability and cumulative releases for aluminium and silica. The increased sodium content from introduced sodium sulphates induced calcium cation exclusion, and here sodium dominated releases during monolithic leaching. This increased the cumulative release for silica, and no precipitations of calcium silicates were observed, due to the higher solubility of complexed sodium silicates in eluates. However, the effects from the additives were cancelled with increasing hydration, which resulted in the different matrices having comparable phases and properties at increased hydration periods (300 days).

9.4 CONTAINMENT AND LEACHABILITY OF CONTAMINANTS

9.4.1 Introduction

The employed assessment approach was effective for evaluating the trends and availabilities of introduced contaminants, and for the evaluation of modifications, due to introductions of additives, and increases in hydration. The contaminants were effectively contained within the stabilised matrices, and no detrimental releases were observed for leaching under the natural chemical conditions for the matrices (Porewater equilibrium leaching and monolithic disequilibrium leaching). Also, the degradation of kaolin with increasing hydration did not compromise contaminants containment. However, some limitations were observed during modelling. These limitations were due to evaluations of chromium as chromate (imposed by assessment tools), and the limited thermodynamic information for some expected zinc minerals.

9.4.2 Partitioning and Releases for Zinc from the Stabilised Matrices

Zinc availability decreased with increasing hydration, indicating increasing effective partitioning, within the stabilised matrices. However, amphoteric leaching trends were not observed during equilibrium leaching assessments, with no leaching observed under alkaline conditions. This was due to the insolubility of several forms of zinc silicates, formed due to the prevalence of silicic acid in the pore solution, and presence of aluminium in the crystalline lattice. However, some of the expected zinc silicate mineral phases (hermimorphite and fraipontite), expected to control solubility, had limited thermodynamic information, and could not be used in modelling because the phases could not be selected. The observed solubility controlling phases were zinc silicates, franklinite and calcium zincate, varying in dominance with hydration. The introduction of additives modified the availability of zinc, and dominance of the mineral phases, but did not alter the leaching trends. Humic acid increased zinc availability at early hydration periods, due to complexation of zinc with particulate organic matter. Increased sulphate content decreased zinc availability at early hydration periods, due to increasing kaolin dissociation, which increased the available silica in the pore solution, and the formation of zinc silicates. However, increasing hydration cancelled out the effects of additives, with comparable mineral phases and availabilities observed for the different matrices.

9.4.3 Partitioning and Releases for Chromium from the Stabilised Matrices

The containment for chromium was effective in the stabilised contaminated matrices, with observed availabilities that were comparable to those for uncontaminated matrices. The kaolin clay had a high sorption affinity for chromium prior to stabilisation, due to lattice substitution of Cr^{3+} for Al^{3+}. However, the measured leaching trends did not show expected amphoterism for theoretical solubility of chromium hydroxide, which suggested chromium partitioning as alternative phases. Speciation evaluations suggested that chromium solubility was controlled by clay containment (lattice substitution), precipitations as a hydroxide, incorporation and substitution with ettringite, and sorption to HFO. However, prediction trends were not comparable to those measured, due to limitations in assessment as a chromate, rather than as species for Cr^{3+}. This was mitigated by only selecting stable Cr^{3+} phases during speciation evaluations, based on the expected mineralogy for the matrices. The presence of additives modified the leaching of chromium at the early hydration phases, with humic acid increasing chromium availability due to complexation with particulate organic matter. The increased sulphate content also increased chromium availability at the early hydration period, due to the increased sorption to HFO, where releases were induced by HFO leaching. However, increasing hydration cancelled out the effects of the additives, resulting in releases at increased hydration periods, which were comparable to those observed for uncontaminated samples. These results can be incorporated during S/S design for field application, to mitigate risks that can mobilise the contaminants, but inducing solubility of their controlling phases.

9.4 FURTHER WORK

Whilst the work undertaken proved useful and significant, in view of testing the hypothesis on S/S characterisations and effectiveness evaluation, these were undertaken on a relatively simple mineral matrix, which does not represent expected field materials. Even with introduced complexities using additives, the degree of controls imposed to allow accurate evaluations, and singularity of additives and contaminants, still yielded comparatively simple materials in view of natural soils. However, given the inherent heterogeneity of natural materials, and the complex suite of contaminants encountered in natural contaminated soils, it was necessary to attempt characterisation for simple materials, to inform expansions to assess natural material. The complex chemistries involved during S/S, and variability in characteristics for individual components, provided challenges even for these relatively simple matrices.

Further work should attempt to characterise natural soils, containing a suite of components, with varying implications on S/S effectiveness. Various interactions are expected to occur during stabilisation of natural soils, which could influence S/S effectivenesss and dictate component alterations during hydration. These interactions could include: interactions between soil components e.g. organics and sulphate, with contaminant suites; interactions between the different organic and inorganic contaminants during treatment; implications from varying mixes of soil fractions (clays, silts, and sand); and degradation of soil components e.g. pyrites with oxidation and weathering, to yield gypsum and HFO. The use of 10% cement proved suitable for the current study, but this content would be too expensive for application under field conditions. Lower cement contents and mixes for binders, e.g. use of pozzolans and slag cements, would be more ideal, but these introduce additional complexity during assessments.

The need to introduce resilience and sustainability, during environmental design, has become increasingly important over recent years. This is due to the need to effectively manage resources, restore sites to original conditions, and protect the natural environment. The major challenge for S/S, in view of its adoption by operators, is to incorporate these factors and assessments during design. In its present form, evaluations are relatively expensive, difficult to undertake, and relatively confusing to most engineers who actually undertake process execution. There is therefore a need to adopt simple risk based evaluation approaches (similar to work undertaken), and thereby enable S/S treatments to be designed and engineered appropriately.

There is also a need to expand the current materials database on phases used in speciation evaluations, which are currently ongoing at research centres such as the Energy Commission of the Netherlands (ECN), including improvements to LeachXS capabilities for undertaking environmental impact evaluations. The current database has been developed over the last 30 years, using information from speciation evaluations undertaken using MINTEQA and MINTEQA2 by the US EPA. However, given inherent heterogeneity of soils, variability in component speciation, and complexities of various sorption, cation exchange and partitioning properties, it is understandable that there are still gaps in data in the current tool. Information from the current study will be included as part of these improvements, as well as any subsequent work, to improve predictions on components speciation, containment and releases. Also, specific species evaluations e.g. Cr^{3+} instead of Cr^{6+} or chromate, will be more accurate in predicting releases and speciation. This problem was encountered during for assessments and predictions of chromium leaching.

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APPENDIX 1

Monolithic Parameters and Equilibrium pH Data

APPENDIX 2

XRF Compositional Data

Appendix 1

Monolithic Parameters and Equilibrium pH Data

1. Stabilised Clay
2. Stabilised Clay with 1% Humic Acid
3. Stabilised Clay with 2.5% Sulphate
4. Stabilised Zinc Contaminated Clay
5. Stabilised Zinc Contaminated Clay with 1% Humic Acid
6. Stabilised Zinc Contaminated Clay with 2.5% Sulphate
7. Stabilised Chromium Contaminated Clay
8. Stabilised Chromium Contaminated Clay with 1% Humic Acid
9. Stabilised Chromium Contaminated Clay with 2.5% Sulphate

Sample 1	Stabilised Clay			pH Leaching Data		pH		Conductivity	Leachant
	Monolith Parameters			Fraction	Hours	44	48	µS	
28 Days	Length (cm)	10.48		1		12.06	12.07	1844	Natural
	Diameter (cm)	10.34		2		12.27	12.28	3030	2ml NaOH
	Radius (cm)	5.17		3		10.96	10.99	4130	5ml HNO3
	Surface Area (cm^2)	508.97		4		7.52	7.60	6960	10ml
	Weight (g)	1624.50		5		3.84	3.84	10430	15ml
	Bulk Density (Mg/m^3)	1.32		6		4.10	4.10	9390	12.50ml
	Particle Density Mg/m^3)	2.61		7		9.29	9.30	5670	7.5ml
	Porosity	0.49		8		7.58	7.56	6750	8.5ml
				9		5.35	5.45	8460	11ml
150 Days	Length (cm)	10.46		1		11.95	11.96	1425	Natural
	Diameter (cm)	10.33		2		12.30	12.28	3280	3ml NaOH
	Radius (cm)	5.17		3		10.70	10.72	4110	5ml HNO3
	Surface Area (cm^2)	507.34		4		7.54	7.83	5960	7.5ml
	Weight (g)	1626.00		5		6.56	6.53	6490	8.5ml
	Bulk Density (Mg/m^3)	1.34		6		3.99	4.01	8460	11.5ml
	Particle Density Mg/m^3)	2.63		7		9.59	9.40	5240	6.5ml
	Porosity	0.49		8		5.58	5.53	7180	9.5ml
300 Days	Length (cm)	10.54		1		12.00	11.99	1395	Natural
	Diameter (cm)	10.27		2		12.36	12.35	3250	3ml NaOH
	Radius (cm)	5.14		3		10.64	10.66	4150	5ml HNO3
	Surface Area (cm^2)	506.30		4		8.81	8.83	5210	6.5ml
	Weight (g)	1632.20		5		6.81	6.79	5940	7.5ml
	Bulk Density (Mg/m^3)	1.35		6		5.74	5.81	6460	8.5ml
	Particle Density Mg/m^3)	2.62		7		4.43	4.54	7490	10ml
	Porosity	0.48		8		3.84	3.85	8650	11.5ml
				9		9.23	9.31	5080	6ml
				10		6.93	7.00	5730	7ml

NB – 1M Sodium hydroxide and 2M Nitric acid used for leaching

Sample 2	Stabilised clay with 1% humic acid			pH Leaching Data		pH		Conductivity	Leachant
	Monolith Parameters			Fraction	Hours	44	48	µS	
28 Days	Length (cm)	10.34		1		12.34	12.24	2850	Natural
	Diameter (cm)	10.25		2		12.46	12.37	4180	2ml NaOH
	Radius (cm)	5.12		3		11.16	11.14	4250	5ml HNO3
	Surface Area (cm^2)	497.77		4		10.41	10.55	5365	6.5ml
	Weight (g)	1636.40		5		9.09	9.16	6540	8ml
	Bulk Density (Mg/m^3)	1.42		6		6.88	7.08	8020	10ml
	Particle Density Mg/m^3)	2.64		7		5.53	5.65	9180	12ml
	Porosity	0.46		8		3.71	3.74	11060	15ml
				9		8.08	8.07	7310	9ml
				10		4.22	4.23	9730	13ml
150 Days	Length (cm)	10.39		1		12.10	12.14	2370	Natural
	Diameter (cm)	10.31		2		12.36	12.37	4270	3ml NaOH
	Radius (cm)	5.16		3		10.66	10.68	4910	6ml HNO3
	Surface Area (cm^2)	503.67		4		9.90	9.86	5490	7ml
	Weight (g)	1642.90		5		8.59	8.54	6170	8ml
	Bulk Density (Mg/m^3)	1.40		6		6.25	6.24	7190	9.5ml
	Particle Density Mg/m^3)	2.61		7		3.94	3.91	9160	12.5ml
	Porosity	0.46		8		7.53	7.57	6530	8.5ml
				9		5.54	5.59	7550	10.5ml
300 Days	Length (cm)	10.36		1		12.18	12.20	2180	Natural
	Diameter (cm)	10.36		2		12.46	12.47	4250	3ml NaOH
	Radius (cm)	5.18		3		10.50	10.52	5020	6ml HNO3
	Surface Area (cm^2)	505.66		4		9.84	9.85	510	7ml
	Weight (g)	1638.20		5		8.44	8.46	6180	8ml
	Bulk Density (Mg/m^3)	1.38		6		6.15	6.20	6870	9ml
	Particle Density Mg/m^3)	2.64		7		5.04	5.18	7810	10.5ml
	Porosity	0.48		8		3.94	3.97	8820	12ml
				9		7.01	7.02	6790	8.5ml

Sample 3	Stabilised clay with 2.5% Sulphate			pH Leaching Data		pH		Conductivity	Leachant
	Monolith Parameters			Fraction	Hours	44	48	µS	
28 Days	Length (cm)	10.55		1		12.07	12.07	2480	Natural
	Diameter (cm)	10.35		2		12.31	12.30	3910	2ml NaOH
	Radius (cm)	5.17		3		11.00	10.99	3240	3ml HNO3
	Surface Area (cm^2)	511.44		4		8.51	8.53	6610	7.5ml
	Weight (g)	1632.50		5		6.69	6.76	8190	10ml
	Bulk Density (Mg/m^3)	1.30		6		3.84	3.85	11310	15ml
	Particle Density Mg/m^3)	2.67		7		9.78	9.85	5790	6ml
	Porosity	0.51		8		7.43	7.45	7500	8.5ml
				9		5.69	5.75	9120	11ml
150 Days	Length (cm)	10.60		1		12.06	12.03	2365	Natural
	Diameter (cm)	10.32		2		12.38	12.35	4740	3ml NaOH
	Radius (cm)	5.16		3		10.50	10.51	4320	4.5ml HNO3
	Surface Area (cm^2)	510.93		4		8.05	8.07	6010	7ml
	Weight (g)	1631.40		5		6.67	6.67	7100	8.5ml
	Bulk Density (Mg/m^3)	1.31		6		5.23	5.40	8060	10ml
	Particle Density Mg/m^3)	2.69		7		4.11	4.10	8970	11.5ml
	Porosity	0.51		8		9.26	9.33	5370	6ml
300 Days	Length (cm)	10.55		1		12.13	12.13	2510	Natural
	Diameter (cm)	10.35		2		12.43	12.46	4770	3ml NaOH
	Radius (cm)	5.17		3		10.47	10.46	4390	4.5ml HNO3
	Surface Area (cm^2)	511.31		4		9.15	9.15	5320	6ml
	Weight (g)	1634.20		5		7.40	7.41	6230	7ml
	Bulk Density (Mg/m^3)	1.30		6		6.54	6.58	6860	8ml
	Particle Density Mg/m^3)	2.67		7		5.25	5.39	8250	10ml
	Porosity	0.51		8		3.99	4.01	9090	11.5ml
				9		7.67	7.70	5860	6.5ml

Sample 4	Stabilised zinc contaminated clay			pH Leaching Data		pH		Conductivity	Leachant
	Monolith Parameters			Fraction	Hours	44	48	µS	
28 Days	Length (cm)	10.46		1		12.25	12.22	1930	Natural
	Diameter (cm)	10.34		2		12.54	12.51	3765	3ml NaOH
	Radius (cm)	5.17		3		11.13	11.14	4140	5ml HNO3
	Surface Area (cm^{2})	508.19		4		10.40	10.45	5330	7ml
	Weight (g)	1614.60		5		9.41	9.33	5955	8ml
	Bulk Density (Mg/m^{3})	1.32		6		7.70	7.74	6680	9ml
	Particle Density Mg/m^{3})	2.63		7		6.30	6.41	7220	10ml
	Porosity	0.50		8		5.46	5.62	7982	11ml
				9		4.43	4.58	8430	12ml
				10		3.78	3.76	9785	13ml
150 Days	Length (cm)	10.48		1		11.99	11.97	1492	Natural
	Diameter (cm)	10.31		2		12.32	12.29	3340	3ml NaOH
	Radius (cm)	5.15		3		10.78	10.76	4220	5ml HNO3
	Surface Area (cm^{2})	506.49		4		9.28	9.30	5510	7ml
	Weight (g)	1629.10		5		7.34	7.34	6320	8ml
	Bulk Density (Mg/m^{3})	1.34		6		6.02	6.02	7300	9.5ml
	Particle Density Mg/m^{3})	2.62		7		4.09	4.10	8420	11.5ml
	Porosity	0.49		8		5.41	5.48	8240	10.5ml
300 Days	Length (cm)	10.53		1		12.00	12.01	1433	Natural
	Diameter (cm)	10.32		2		12.36	12.36	3280	3ml NaOH
	Radius (cm)	5.16		3		10.62	10.65	4250	5ml HNO3
	Surface Area (cm^{2})	508.50		4		7.74	7.87	5620	7ml
	Weight (g)	1624.80		5		6.39	6.39	6330	8ml
	Bulk Density (Mg/m^{3})	1.33		6		5.00	5.12	6960	9ml
	Particle Density Mg/m^{3})	2.62		7		4.26	4.29	7570	10ml
	Porosity	0.49		8		3.82	3.82	8520	11.5ml
				9		9.10	9.24	5000	6ml

Sample 5	Stabilised zinc contaminated clay with 1% humic acid			pH Leaching Data		pH		Conductivity	Leachant
	Monolith Parameters			Fraction	Hours	44	48	µS	
28 Days	Length (cm)	10.45		1		12.51	12.45	3170	Natural
	Diameter (cm)	10.30		2		12.71	12.64	5110	3ml NaOH
	Radius (cm)	5.15		3		11.21	11.20	4540	5ml HNO3
	Surface Area (cm^2)	505.16		4		10.19	10.21	5620	7ml
	Weight (g)	1627.50		5		9.18	9.20	6400	8ml
	Bulk Density (Mg/m^3)	1.34		6		7.54	7.69	7170	9ml
	Particle Density Mg/m^3)	2.64		7		6.26	6.35	7950	10ml
	Porosity	0.49		8		4.77	4.89	8910	11.5ml
150 Days	Length (cm)	10.46		1		12.18	12.18	2440	Natural
	Diameter (cm)	10.25		2		12.42	12.43	4340	3ml NaOH
	Radius (cm)	5.12		3		10.55	10.56	4600	6ml HNO3
	Surface Area (cm^2)	502.03		4		9.99	10.01	5490	7ml
	Weight (g)	1622.20		5		8.99	9.04	6150	8ml
	Bulk Density (Mg/m^3)	1.35		6		7.37	7.45	6910	9ml
	Particle Density Mg/m^3)	2.61		7		5.82	5.88	8040	10.5ml
	Porosity	0.48		8		4.24	4.26	8710	12ml
300 Days	Length (cm)	10.53		1		12.24	12.26	2380	Natural
	Diameter (cm)	10.26		2		12.48	12.50	4280	3ml NaOH
	Radius (cm)	5.13		3		10.52	10.53	4870	6ml HNO3
	Surface Area (cm^2)	505.13		4		9.39	9.41	6100	7.5ml
	Weight (g)	1628.10		5		7.83	7.89	6680	8.5ml
	Bulk Density (Mg/m^3)	1.35		6		6.30	6.36	7160	9.5ml
	Particle Density Mg/m^3)	2.63		7		5.47	5.47	7990	10.5ml
	Porosity	0.49		8		3.99	4.00	8980	12ml

Sample 6	Stabilised zinc contaminated clay with 2.5% sulphate			pH Leaching Data		pH		Conductivity	Leachant
	Monolith Parameters			Fraction	Hours	44	48	µS	
28 Days	Length (cm)	10.57		1		12.32	12.31	2860	Natural
	Diameter (cm)	10.38		2		12.60	12.60	5010	3ml NaOH
	Radius (cm)	5.19		3		10.93	10.94	3940	4ml HNO3
	Surface Area (cm^2)	514.33		4		9.40	9.50	5610	6.5ml
	Weight (g)	1632.00		5		7.50	7.54	6400	7.5ml
	Bulk Density (Mg/m^3)	1.29		6		6.46	6.54	7080	8.5ml
	Particle Density Mg/m^3)	2.66		7		5.64	5.80	7530	9.5ml
	Porosity	0.51		8		4.56	4.76	8110	10.5ml
				9		3.98	4.01	9070	12ml
150 Days	Length (cm)	10.42		1		12.08	12.06	2520	Natural
	Diameter (cm)	10.37		2		12.38	12.37	4720	3ml NaOH
	Radius (cm)	5.18		3		10.56	10.58	4020	4ml HNO3
	Surface Area (cm^2)	508.17		4		9.94	9.97	4710	5ml
	Weight (g)	1620.40		5		8.88	8.92	5500	6ml
	Bulk Density (Mg/m^3)	1.31		6		7.35	7.41	6070	7ml
	Particle Density Mg/m^3)	2.69		7		6.09	6.14	7170	8.5ml
	Porosity	0.51		8		4.07	4.07	8830	11m
				9		5.07	5.20	8350	10ml
300 Days	Length (cm)	10.50		1		12.16	12.15	2750	Natural
	Diameter (cm)	10.37		2		12.48	12.47	4710	3ml NaOH
	Radius (cm)	5.19		3		10.55	10.56	4080	4ml HNO3
	Surface Area (cm^2)	511.26		4		8.09	8.26	5490	6ml
	Weight (g)	1631.00		5		6.84	6.88	6160	7ml
	Bulk Density (Mg/m^3)	1.31		6		5.31	5.47	7220	8.5ml
	Particle Density Mg/m^3)	2.68		7		4.11	4.12	8060	10ml
	Porosity	0.51		8		3.87	3.86	9200	11.5ml
				9		9.24	9.36	4740	5ml

Sample 7	Stabilised chromium contaminated clay			pH Leaching Data		pH		Conductivity	Leachant
	Monolith Parameters			Fraction	Hours	44	48	µS	
28 Days	Length (cm)	10.35		1		12.08	12.07	1600	Natural
	Diameter (cm)	10.41		2		12.43	12.43	3290	3ml NaOH
	Radius (cm)	5.20		3		10.78	10.76	4330	5ml HNO3
	Surface Area (cm^2)	508.49		4		9.37	9.33	5680	7ml
	Weight (g)	1599.00		5		7.78	7.92	6480	8ml
	Bulk Density (Mg/m^3)	1.30		6		6.74	6.78	7240	9ml
	Particle Density Mg/m^3)	2.64		7		5.04	5.21	8460	10.5ml
	Porosity	0.51		8		3.98	3.97	9110	12ml
150 Days	Length (cm)	10.51		1		11.91	11.91	1416	Natural
	Diameter (cm)	10.31		2		12.29	12.26	3250	3ml NaOH
	Radius (cm)	5.15		3		10.48	10.46	4270	5ml HNO3
	Surface Area (cm^2)	507.20		4		9.77	9.87	4920	6ml
	Weight (g)	1612.90		5		8.46	8.47	5520	7ml
	Bulk Density (Mg/m^3)	1.31		6		6.95	6.95	6250	8ml
	Particle Density Mg/m^3)	2.64		7		5.69	5.70	7070	9.5ml
	Porosity	0.50		8		4.11	4.12	8080	11ml
300 Days	Length (cm)	10.49		1		11.99	11.99	1395	Natural
	Diameter (cm)	10.29		2		12.36	12.36	3210	3ml NaOH
	Radius (cm)	5.15		3		10.31	10.34	4400	5ml HNO3
	Surface Area (cm^2)	505.77		4		9.46	9.48	5050	6ml
	Weight (g)	1609.40		5		7.20	7.25	5740	7ml
	Bulk Density (Mg/m^3)	1.31		6		6.16	6.20	6490	8ml
	Particle Density Mg/m^3)	2.63		7		5.50	5.55	7470	9.5ml
	Porosity	0.50		8		3.99	4.00	8380	11ml
				9		7.60	7.70	5200	6.5ml

Sample 8	Stabilised chromium contaminated clay with 1% humic acid			pH Leaching Data		pH		Conductivity	Leachant
	Monolith Parameters			Fraction	Hours	44	48	µS	
28 Days	Length (cm)	10.52		1		12.28	12.29	2165	Natural
	Diameter (cm)	10.31		2		12.56	12.55	4180	3ml NaOH
	Radius (cm)	5.16		3		10.94	10.97	4610	5ml HNO3
	Surface Area (cm^2)	507.88		4		9.75	9.86	5920	7ml
	Weight (g)	1612.80		5		8.12	8.24	6640	8ml
	Bulk Density (Mg/m^3)	1.37		6		6.77	6.82	7310	9ml
	Particle Density Mg/m^3)	2.60		7		5.95	6.03	7920	10ml
	Porosity	0.47		8		4.04	4.03	9270	12ml
				9		5.57	5.62	8230	11ml
150 Days	Length (cm)	10.45		1		11.99	12.01	1778	Natural
	Diameter (cm)	10.27		2		12.29	12.30	3740	3ml NaOH
	Radius (cm)	5.14		3		10.26	10.32	5120	6ml HNO3
	Surface Area (cm^2)	503.23		4		9.38	9.34	5770	7ml
	Weight (g)	1623.40		5		7.78	7.84	6360	8ml
	Bulk Density (Mg/m^3)	1.31		6		6.57	6.59	7180	9ml
	Particle Density Mg/m^3)	2.62		7		5.84	5.88	7570	10ml
	Porosity	0.50		8		4.28	4.32	8590	11.5ml
300 Days	Length (cm)	10.49		1		12.10	12.10	1768	Natural
	Diameter (cm)	10.34		2		12.43	12.43	3710	3ml NaOH
	Radius (cm)	5.17		3		10.01	10.04	5160	6ml HNO3
	Surface Area (cm^2)	508.84		4		8.71	8.74	5810	7ml
	Weight (g)	1605.80		5		6.98	7.00	6480	8ml
	Bulk Density (Mg/m^3)	1.30		6		6.15	6.17	7090	9ml
	Particle Density Mg/m^3)	2.64		7		5.04	5.09	7760	10ml
	Porosity	0.51		8		3.96	3.97	8790	11.5ml
				9		10.53	10.55	4350	5ml

Sample 9	Stabilised chromium contaminated clay with 2.5% sulphate			pH Leaching Data		pH		Conductivity	Leachant
	Monolith Parameters			Fraction	Hours	44	48	µS	
28 Days	Length (cm)	10.40		1		12.31	12.28	2840	Natural
	Diameter (cm)	10.27		2		12.59	12.57	5040	3ml NaOH
	Radius (cm)	5.14		3		10.84	10.84	4360	4ml HNO3
	Surface Area (cm^2)	501.30		4		9.83	9.83	5780	6ml
	Weight (g)	1611.30		5		8.07	8.19	6820	7.5ml
	Bulk Density (Mg/m^3)	1.33		6		6.97	7.05	7600	8.5ml
	Particle Density Mg/m^3)	2.67		7		6.28	6.36	8260	9.5ml
	Porosity	0.50		8		3.58	3.55	11120	14ml
				9		5.66	5.85	8470	10.5ml
				10		4.19	4.22	9410	11ml
150 Days	Length (cm)	10.46		1		12.07	12.05	2510	Natural
	Diameter (cm)	10.33		2		12.40	12.37	4770	3ml NaOH
	Radius (cm)	5.16		3		8.19	8.30	5480	6ml HNO3
	Surface Area (cm^2)	506.95		4		6.63	6.70	6260	7ml
	Weight (g)	1522.80		5		5.98	6.02	7020	8ml
	Bulk Density (Mg/m^3)	1.24		6		3.91	3.89	8680	11ml
	Particle Density Mg/m^3)	2.68		7		10.37	10.42	4180	4ml
	Porosity	0.54		8		9.50	9.56	4830	5ml
				9		4.90	5.06	7600	9ml
300 Days	Length (cm)	10.55		1		12.15	12.14	2440	Natural
	Diameter (cm)	10.29		2		12.49	12.49	4680	3ml NaOH
	Radius (cm)	5.15		3		10.33	10.34	4010	4ml HNO3
	Surface Area (cm^2)	507.68		4		9.36	9.39	4830	5ml
	Weight (g)	1628.30		5		7.74	7.80	5580	6ml
	Bulk Density (Mg/m^3)	1.31		6		6.56	6.62	6170	7ml
	Particle Density Mg/m^3)	2.67		7		5.38	5.43	7340	8.5ml
	Porosity	0.51		8		4.12	4.14	8210	10ml

APPENDIX 2

XRF COMPOSITIONAL (%) DATA

Element	Na	Mg	Al	Si	P	S	K	Ca	Cr	Mn	Fe	Zn	Sn	Pb
ECC	1.75	0.218	18.4	22.26	0.02438	< 0.00020	2.441	0.0202	< 0.0031	0.0136	0.5262	0.00237	0.00188	0.00189
ECC Cr	1.62	0.179	16.3	19.72	0.02108	< 0.00020	2.218	0.0182	0.0437	0.0106	0.5003	0.00241	0.00187	0.00165
ECC Zn	1.66	0.198	17.27	20.93	0.02181	< 0.00020	2.317	0.0214	< 0.0031	0.0119	0.5241	0.05199	0.00146	0.00173
EO 1	1.57	0.244	18.76	22.92	0.02744	0.05038	2.561	1.968	< 0.0034	0.0175	0.6545	0.00417	0.00181	0.00205
EO 2	1.65	0.253	18.79	22.94	0.02591	0.04674	2.529	1.839	< 0.0034	0.0175	0.6534	0.00419	0.00271	0.00179
EO 3	1.46	0.254	18.75	22.89	0.02642	0.04725	2.569	1.873	< 0.0035	0.016	0.6549	0.00429	0.00268	0.00206
EO 4	1.6	0.273	18.55	22.66	0.02536	0.03821	2.538	1.645	0.00329	0.0149	0.6388	0.00388	< 0.0016	0.00186
EO 5	1.56	0.24	18.86	23.08	0.02649	0.04169	2.593	1.697	< 0.0033	0.0146	0.6462	0.00425	0.00321	0.00189
EOC	1.51	0.198	16.38	20.24	0.02282	0.04184	2.254	2.442	0.0466	0.0139	0.6432	0.00402	< 0.0016	0.00194
EOH	1.58	0.192	17.14	21.13	0.02514	0.04979	2.403	2.034	< 0.0033	0.0158	0.6738	0.00438	0.00203	0.00206
EOHC	1.5	0.211	17.46	21.55	0.02636	0.05765	2.401	2.03	0.0492	0.015	0.6439	0.00405	0.00197	0.00155
EOHZ	1.83	0.252	17.66	21.64	0.02719	0.06189	2.426	2.098	< 0.0034	0.0148	0.6644	0.04749	0.00366	0.00174
EOS	2.29	0.15	14.73	18.7	0.0271	0.279	2.115	2.822	< 0.0033	0.015	0.6339	0.00414	0.00257	0.00159
EOSC	1.51	0.213	15.87	19.42	0.0252	0.273	2.18	1.885	0.0431	0.0149	0.5972	0.00401	0.0015	0.00187
EOSZ 1	2.03	0.234	15.85	19.41	0.02351	0.1825	2.222	1.547	< 0.0032	0.0152	0.574	0.04047	0.0029	0.00157
EOSZ 2	1.84	0.125	16.31	20.14	0.0271	0.2463	2.283	2.09	< 0.0033	0.0146	0.6176	0.04407	0.00265	0.00215
EOSZ 3	1.82	0.169	15.86	19.8	0.0281	0.2402	2.218	2.085	< 0.0033	0.0162	0.6249	0.04463	0.00151	0.00172
EOSZ 4	1.92	0.216	16.97	21.1	0.0262	0.2314	2.35	2.019	< 0.0032	0.014	0.6322	0.04692	0.00204	0.00186
EOSZ 5	2.06	0.203	16.83	20.8	0.0292	0.2491	2.337	2.115	< 0.0034	0.015	0.6338	0.04457	< 0.0016	0.00203
EOZ	1.67	0.233	16.9	20.68	0.02205	0.02499	2.362	1.882	< 0.0034	0.0149	0.6364	0.04687	0.00286	0.00177

ECC - Kaolin Clay, EO - Stabilised Kaolin clay, EOH - Stabilised Kaolin Clay with 1% Humic Acid, and EOS - Stabilised Kaolin Clay with 2.5% Sodium Sulphate

Z / Zn denote 500mg/kg zinc contamination, and C / Cr denote 500mg/kg chromium (III) contamination.