THE STRUCTURE AND PROPERTIES OF TINPLATE

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S Y N O P S I S

A study has been carried out relating to various methods of detinning scrap tinplate. Assessments of chemical and electrochemical techniques have been made with special relevance to recycling of the used can.

It has been found that the electrolytic dissolution of both tin and the iron-tin intermetallic compound is Coulombic in alkaline conditions. The addition of oxidising agents does not generally increase the rate of alloy dissolution under alkaline electrochemical conditions, although free tin dissolution is aided.

Parameters associated with an industrial electrolytic detinning plant have been studied, and it was found that optimum temperature and current density values exist for the dissolution of alloy in alkali.

The effect of thermally treating tinplate has been studied, and some reactions of the intermetallic layer have shown the possible presence of other stoichiometric alloys. Activation energies for one alloy ($FeSn_2$) have been calculated at above and below 232°C. Alkaline attack of the intermetallic layer has been shown to be very similar to that of iron.

The presence of lead and calcium has been found in tinplate; the relevance of the apparent lead content is discussed and assessed.

Conditions have been established for a viable industrial process for the reclamation of tin and clean scrap steel from urban refuse.

Necessary instrumentation for an industrial process is discussed.

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1. INTRODUCTION

Every year over 6,000 tons of tin are used in the United Kingdom to produce over 1 million tons of tinplate. Due to the high cost of tin, (currently about £7,000/ton), the amount applied to the steel substrate has decreased to such an extent that the value of the tin on the tinplate is about the same as the scrap steel, but it only corresponds to a thickness of about 10 μ.

The biggest single contribution towards the decrease in the amount of tin on tinplate has been the electrolytic tinning process, as this allows well controlled, but small, amounts of tin to be deposited onto steel sheet. The tinplate is then flash melted, when the surface obtains the characteristic shine and reduced porosity, but at the same time an intermetallic alloy is formed. As the quantity of tin has decreased, the relative amount of tin associated with the alloy layer has decreased, making reclamation more difficult.

With the cost of tin increasing, the amount of tin applied to steel for tinplate has decreased, making reclamation more difficult due to the increase in the relative amount of alloy. However, as the price of tin increases, recycling becomes more economical.

The amount of tin has been reduced to such a low quantity that further protection has to be provided; a layer of either polyvinyl or polyacrylic lacquer is usually applied to the can to prevent corrosion by the contents. If the tin overlay is dissolved, the blue/grey alloy layer is exposed. Further corrosion of the alloy, and ultimately the steel, would be possible if the lacquer were not present. As the thickness of tin has decreased, the stability of modern lacquers has increased, and present lacquers are capable of withstanding temperatures of over 300^{o}C. The role of the tin has become much more cosmetic, although its presence does assist can production, because it acts as a lubricant.

During the last ten years steel production in the United Kingdom has become more reliant upon the electric arc furnace, which requires relatively pure raw materials and large amounts of high quality scrap steel. The presence of tin affects the properties of the steel, so it is of paramount importance to ensure that the steel is as free of tin as possible. The maximum acceptable tin level for recyclable steel is about 0.03%, which represents about 5% of the total applied tin on tinplate. In order to attain this low value the detinning process must be extremely efficient, but nevertheless, the inherent tin content in recycled steel is gradually increasing, due to the increasing proportion of secondary steel being recycled.

1.1. Recycling as a Source of Tin

Due to the depletion of natural resources, such as rich alluvial deposits, the cost of tin is increasing, therefore the amount of tin which is utilised in the manufacture of cans will decrease until it becomes too expensive to use. The energy required to extract and refine tin from poorer ores is more than to remove it from used cans and refine it. Although more cans are becoming, at least partially, manufactured from aluminium or blackplate, the problems involved in their production are a lot more than those of tinplate cannisters. Unless there is a rapid redevelopment in the container industry, tin cans will retain a high degree of importance for a long time.

Nearly all manufactured tinplate is ultimately deposited in a dustbin. Analysis of urban waste has shown about 9% of the mass to be metallic, of which the majority is ferrous based metal. Local Government refuse collections are based on a daily total production of 7 lbs of waste per person, which has to be treated and disposed of. The easiest disposal method is to bury it in worked-out gravel pits or other convenient holes, or to dump it at sea. Local pits are becoming less available, and hence Local Governments have to transport their waste further distances, incurring high transport costs. The bulk density of untreated refuse is very low, making the cost per unit weight much higher than necessary. One way to reduce the cost is to increase the density by incineration and compression, using the heat generated for local consumption by residents. The bulkiest component of the waste is, however, tin cans, which can be magnetically separated and recycled.

Once the can has been removed from the bulk of the waste, it still has a high dirt content, this being in the form of paper, food, and other organic materials. To ensure a good recycling method, much of this has to be removed before any detinning can commence.

1.2. The Structure of Tinplate

The coating of tinplate consists of four components, excluding the steel base which represents the bulk volume of the tinplate. These four components are: (1) the alloy layer; (2) free tin; (3) an oxide layer, and (4) the surface layer, which is usually lacquer or oil.

In order to get an approximate idea of the relative thicknesses, the steel is about 2,540,000 Å, the alloy 1200 Å, free tin is about 12,000 Å, the oxide film is 25 Å and the oil about 50 Å. Obviously the free tin and alloy layer thicknesses will alter with variation in the amount of tin deposited, but over 99.5% of the tin present is in one of these two forms. Consequently, with respect to a recycling process, the major interest relating to tinplate structure is in the free tin and alloy layers.

The oxide layer is stannous oxide, although the passive film on the tinplate is undoubtedly affected by the presence of the oil film. The oil film is applied to the strip to aid de-piling of plates and to aid fabricability in can production. However, neither of these layers are of great consequence in tin reclamation from tinplate.

Most tin cans have at least one soldered seam; the solder used is usually 95:5 Sn:Pb, although baby food cans are totally tin soldered. Dissolution of solder is very important, because a lot of tin is present, but the structure of the seam renders this difficult. In order to attack the solder, the seam has to be exposed, and this is conveniently carried out by shredding the can. Fortunately, most of the lead in the solder is precipitated as "tank-bottoms" during detinning processes, so virtually none is deposited with the refined tin.

Recycling of tin cans has been practised, with varying degrees of success since 1854.[113] Consequently a lot of old literature is available relating to various processes, a substantial amount of which is in the form of patents. Numerous methods have been used to reclaim tin, but most early workers were only concerned with removal of the free tin, and not the alloy. With modern technology and increased availability of a wider range of chemicals, however, some older methods may be applicable, at least in part, to modern recycling. Since the amount of tin being applied to tinplate is decreasing, the problem is becoming more complex because of the greater proportion of alloy present.

Due to the applied nature of reclamation it is more logical to study the problem using commercial tinplate rather than synthesised, "ideal" material, as in earlier researches. However, the inhomogeneity of commercial material, revealed in the present work, made sophisticated kinetic studies unrealistic. It also necessitates the study of literature dating from 1854.

2. LITERATURE SURVEY

2.1. Introduction

The work carried out in this study relates to the industrial aspect of detinning scrap tinplate. Various processes have been previously employed, improved and rejected as tin reclamation has evolved. By necessity most are described only in the patent literature. Consequently, few objective accounts have been published on the effectiveness of the process, although novel aspects have been stressed with optimism. It is therefore difficult to assess the real degree of efficiency of the industrial processes without carrying out experimental comparisons on them all, but some comments relating to their effectiveness at detinning and attack of the plant can be offered.

This survey also contains an account of the literature on the alloying of tin with iron, a result of one stage of the manufacturing process, and the consequence of thermal manipulations. Again this relates to the technology of reclamation, due to the required heat treatments of used cans.

2.2. Chemical Detinning

Chemical detinning of scrap tinned iron was the first method employed to recycle the waste material, and started in the middle of the nineteenth century.[133]

The proposed methods can be categorised into four main classes: namely, acid, basic, neutral or non-specified pH and non-aqueous systems.

Within each class there are a variety of methods available, particularly where chemical oxidants are included. The majority of these variations have been patented, and a list of the relevant patents can be found in Appendix 1. However, a general survey of the known processes can be covered.

2.2.1. Acidic Liquors

Due to the enormous range of acidic processes employed, this group can be sub-divided into further sections; hydrochloric acid, sulphuric acid, nitric acid, hydrofluoric acid and organic acids. By far the most prevalent is hydrochloric acid because tin readily reacts to form tin chloride, which was a very important chemical in the chemical industry and especially in the silk dyeing industry.

2.2.1.1. Hydrochloric Acid

Hydrochloric acid reacts with tin in two ways, these being dependent upon the acid concentration:

$$Sn + 4HCl \rightarrow SnCl_4 + 2H_2 \qquad \text{eqn. 2.1}$$

$$Sn + 2HCl \rightarrow SnCl_2 + H_2 \qquad \text{eqn. 2.2}$$

Reaction 2.1 is with concentrated acid, and 2.2 with dilute acid.

Tin reclamation from tinned iron or tinplate using hydrochloric acid has been patented since the early stages of tinplate recycling.

The first patent was issued in 1872[1], which was followed rapidly by others.[2,3,4] Further patents were issued very soon afterwards describing methods whereby the tinplate was rotated to ensure a more even attack of the tin, and not of the iron.[5,6,13] Later[59], the use of dilute acid was described, whereby the tin, in the stannous form, was recovered by either electrolysis of the liquor or by addition of zinc. It was even suggested that addition of lump coke catalysed the stripping.[59]

Regeneration of the liquor became an important factor in detinning. One method was to add, either continuously or intermittently, an oxychloric acid, such as chloric or perchloric acid, or their salts (with or without hydrochloric acid).[7] The beneficial addition of oxidants such as potassium perchlorate ($KClO_4$) has been refuted, although it has been suggested that the addition of nitric acid is beneficial.[8,9]

It was recognised at an early stage that the presence of chloride ions increases the rate of detinning, and it has been suggested[10] using either concentrated acid or dilute acid with chlorine gas added to it. The excess acid in the tin-rich liquor was neutralised with either sodium hydroxide or calcium oxide, and the tin extracted by hydrolysis from the resulting stannic oxide.

Hydrogen chloride gas has also been used to detin iron, either at temperatures below $50^{\circ}C$[11], or at elevated temperatures.[12]

Recently hydrochloric acid has been suggested as an additive in rather involved processes, dissolving "stannic acid", which is prepared by saturating an alkaline stannate liquor with carbon dioxide, in hot hydrochloric acid to produce stannic chloride. This is diluted with water, and aluminium added to precipitate free tin.[14]

Lawson[15] has suggested using hydrochloric acid, instead of sulphuric acid, as a tin leaching agent. However, the methods suggests that the scrap is heated in a furnace to alloy it, and the metal chlorides extracted from the resulting mixture, using either ligand or chelating agents.

2.2.1.1.1. Hydrochloric Acid with Inhibitors

The major difficulty with a hydrochloric acid based process is that the acid will also dissolve the iron, hence wasting liquor. To overcome this the use of inhibitors has been advocated[13,16], one of the first being thiocarbanilide.[17] Others have been antimony salts[18], antimony oxide[19,20] and antimony oxide in a liquor of hydrochloric and sulphuric acids, as suggested by Mathers[21] who does concede it is very difficult to inhibit iron against attack in preference to tin, and that furthermore it is more difficult to obtain differential dissolution in hydrochloric acid than it is in sulphuric acid. Other inhibitors, such as formaldehyde[22,44], glycerine foots (the waste from the preparation of glycerine), and quinoline ethoxide. have also been suggested.[21]

The use of antimony trichloride has also been suggested.[23] As with all the antimony based inhibitors, the precipitated antimony metal can easily be washed off the iron, and the relevant salt obtained.

One interesting inhibiting system involved the unlikely mixture of hydrochloric acid, cupric sulphate and ammonia[24]; it is probable that the cupric sulphate acts as an oxidising agent for the tin, but little is actually known of the process.

2.2.1.1.2. <u>Hydrochloric Acid with Oxidising Agents</u>

The reason for addition of an oxidising agent is to reduce the liquor content time, and hence improve the throughput rate. The most readily available oxidant is oxygen, which can be pumped into the liquor[25]; the cheapest source of oxygen being air.

Other oxidants have been transition metal chlorides, such as ferric chloride[26,27,28], and chromic chloride.[29,30] In addition tin chloride, presumably stannic chloride, has been proposed.[31,32] It is probable that addition of such compoumds causes auto-reduction to occur, with the effect of oxidising tin metal to divalent tin, and if the reduction potentials are sufficient, to tetravalent tin.

Mixtures of tin and ferric chlorides in the presence of chloride gas have been suggested.[7,33] Other patents[10,34,35] have advocated using dilute hydrochloric acid with chlorine gas added, and one liquor[36] used nascent chlorine, claimed to be produced from the acid.

Further oxidising agents such as sodium nitrate[36] and sodium chloride[36] have been suggested. Bischitzky[37] patented a range of oxidants covering chloride, sulphate, phosphate, perborate, and other salts such as calcium chloride, sodium sulphate and magnesium chloride, all of which have high ionisation constants.

Alonzo[8] suggests a mixture of hydrochloric acid and nitric acid, whilst Lassaigne[38] advocated the use of hydrochloric, nitric and sulphuric acids, either as a mixture or by themselves.

Other oxidising agents have been suggested, such as sodium hypochlorite[40], to give either nascent or free chlorine; sodium permanganate[40], which can be reduced easily to manganese dioxide; metal dichromates[40,42], the chromium being reduced from Cr^{VII} to Cr^{III} in acid; manganese dioxide[42], which gives manganese dichloride in hydrochloric acid, with a corresponding reduction from Mn^{IV} to Mn^{II}; sodium chlorate[41], which readily decomposes to yield oxygen and sodium chloride.

2.2.1.2. Sulphuric Acid

Sulphuric acid does not dissolve tin as fast as hydrochloric acid[21], and has been the subject of only a few processes, although it does dissolve tin in preference to iron.[21] Both dilute[21,38,45] and concentrated acids[46,47,162] have been suggested. The first patent[45] was offered in 1887, for dilute acid, whilst the use of concentrated acid was not introduced until 1920.[46] The early patents for concentrated acid specifically refer to either oleum, or acid with sulphur trioxide added.

As with hydrochloric acid, inhibition of the liquor is important, so that the liquor is not wasted on dissolving iron. Mathers[21] used a series of inhibitors such as arsenious oxide formaldehyde, glycerine foots and quinoline ethiodide, the most effective being arsenious oxide. However, arsenic salts are toxic and quinoline ethiodide very expensive.

Only a few oxidising agents, except for oleum and sulphur trioxide, have been recommended, these being nitrate[48] and ferric sulphate[49], the latter being easily reduced to the ferrous state, and the former to lower nitrogen oxides, ammonia or even free nitrogen.

2.2.1.3. Nitric Acid

This has only been the subject of one patent[38], but nitric acid has been recommended as an oxidant in conjunction with hydrochloric acid.[8,9]

2.2.1.4. Hydrofluoric Acid

Hydrofluoric acid is very reactive, but with the increasing demand for stannous fluoride for toothpaste, a process was developed[50] whereby tin scrap is attacked by both a liquid mixture of hydrofluoric acid and stannous fluoride, and also by hydrogen fluoride gas.

2.2.1.5. Organic Acids

There are only a few processes using organic acids for tin reclamation, the earliest being one for tartaric acid with air as an oxidant.[51] Later a general patent[52] offered vapourised low aliphatic acids, such as acetic acid, in the presence of air or oxygen as a possibility. A mixture of sodium sulphide, ammonium nitrate and acetic acid has been used[21], the first two constituents acting as the active, oxidising species. There has also been the suggestion of acetic acid with nitrite as the oxidant.

2.2.1.6. Other Acidic Liquors

A few acidic liquors cannot be easily catagorised into the above groups. These involve the use of hydrochloric acid with additives such as sodium chloride and air[54], stannous chloride and air[55,56] and stannic chloride[57], the most active constituent being air, or stannic chloride.

2.2.1.7. Overall Assessment of Acidic Processes

The use of acids on an industrial scale for the detinning of tinplate would be very costly due to plant renewal because of acid attack of any exposed steel. Chemical protection of the plant would not be possible due to the ineffectiveness of passivating agents in acid and also because if they passivate plant attack, they would almost certainly reduce, or prevent, attack of the alloy.

The addition of oxidants to improve the rate of detinning may be beneficial, but plant dissolution has not been prevented! Neither sulphuric or nitric acids show any major advantage over hydrochloric acid, except possibly in cost if the latter acids can be prepared on, or near to, the plant. Hydrofluoric acid is both corrosive and an environmental problem, but if stannic fluoride is required in any quantity, no doubt a small detinning plant may be economically viable. Organic acids will only react relatively slowly with tinplate, and will not effectively attack the alloy layer, leaving an unacceptably high tin content in the base steel.

Acid plants do have the advantage of operating at lower temperatures, and hence a reduction in heating costs is possible. It is doubtful whether this would outweigh the other disadvantages, although alloy dissolution does occur readily in acid, even at normal temperatures. Acid dissolution of solid tin in solution with iron would require the wasted consumption of acid, and this should be prevented as far as possible.

2.2.2. Alkaline Liquors

Alkaline detinning of waste tinned iron is more popular than the acidic path because the iron is not so readily attacked by alkali, although under certain electrochemical conditions it is possible to generate the ferrate ion (Fe^{VI} or FeO_4^{2-}).[60,168]

The rate of chemical reaction on tin, and especially the alloy, demands that the stripping time is measured in hours, even at near boiling point temperatures; this time can be reduced with the addition of oxidants. Once the tin, and alloy, have reacted with alkali, which is usually sodium hydroxide, the solution is rich in sodium stannate; the tin is then recovered either electrolytically or by the addition of chalk or lime to produce a precipitate of calcium stannate.[78]

The reaction mechanism of tin in alkali is rather complicated and open to wide discussion[163-167,301], but it is generally agreed that the initial reaction involves the formation of the stannate ion;

this is then oxidised, either by air or auto-oxidation to stannate (Sn^{IV}).

2.2.2.1. Sodium Hydroxide Liquor

This process has been subjected to numerous patents[61-66] using the liquor at near its boiling point, and even in pressure vessels[67,68] to elevate the liquor temperature. One method suggested fusing sodium hydroxide onto the tinplate and washing off the resulting sodium stannate for recovery.[69]

The rate of detinning can be increased by use of oxidising agents such as air.[71-74] Another early oxidant was soluble lead, or plumbite,[75,76] which was popular because the lead in solution will precipitate out, and in doing so oxidise the tin. Hinchley[75,76] noted, however, that a minimum temperature of 56.7°C was needed for this reaction, although at 90°C most of the tin had dissolved in seconds. Other sources of soluble lead in alkali have been from lead oxide,[77-80] or lead acetate[81,82], both of which, once in hot alkali, form plumbite or plumbate ions. The use of other oxidants with lead oxide, such as sodium nitrate[83] have also been proposed.

The use of nitrate or nitrite as an oxidising agent has been long established, although some workers used it in conjunction with sodium chloride.[84,85] Using nitrate alone was first proposed in 1884[86] and since then has been the subject of numerous patents.[87,88,89] As with the acid process, the need to agitate the tinplate in the liquor has been established.[90,169]

Other variations on the use of nitrate have included a nitrate/nitrite mixture[91], or specifically potassium nitrate.[92] One method[91] was to react nitrous gases with the liquor to precipitate tin oxide. Stoyanov[93] has patented a method for treatment of incinerated tinplate which involves the use of a boiling alkali-nitrite liquor, which is subsequently treated with carbon dioxide to produce stannic acid. This is collected in hot concentrated hydrochloric acid and the tin recovered by addition of an electronegative element such as zinc or aluminium.

Sodium hydroxide solution absorbs carbon dioxide from the atmosphere to form sodium bicarbonate, which reacts with more liquor to form sodium carbonate. Initially, such a reaction may appear wasteful for the liquor, but addition of either carbon dioxide or sodium carbonate has been employed.[63,66]

Sodium carbonate enriched liquor has been used to wash tinplate before the detinning operation, hence employing what would otherwise be spent liquor, due to its unacceptably high carbonate concentration.[110] The earliest known use of this method is 1917[95], when the cleaned tinplate was then detinned in alkaline sodium hypochlorite. A later patent[96] included the use of other oxychlorides such as chlorite (ClO_2^-) and chlorate (ClO_3^-).

The action of sulphides and oxysulphur compounds on tin is very rapid, and consequently various detinning methods have been based on their use.[97,98] One patent[98] covers a whole range of oxy-sulphur compounds, including persulphate ($S_2O_8^{2-}$), pyrosulphate ($S_2O_7^{2-}$), thionate ($S_2O_6^{2-}$), pyrosulphate ($S_2O_5^{2-}$), thiosulphate ($S_2O_3^{2-}$) and sulphite (SO_3^{2-}) in the presence of sodium hydroxide and sodium chloride. Combinations of these oxysulphides is also known[99], and the addition of wetting agents such as sodium lauryl sulphate has been suggested.[100]

Nitrogen containing additives have also been used, such as ammonia[102,92] and nitrous gases[92], the latter being compared with the use of manganese dioxide. Nitro-aromatic compounds have been used as additives, examples being nitrobenzoates[104], nitrobenzoic acid[105,106,107,108], nitrophenates[104], nitrosulphonic acid[106], and nitrophthalic acid.[106] The attraction of the range of organic compounds is that the 'spent' reagent, which is believed to be meta-azobenzoic acid or a similarly corresponding group[109], can be reactivated by bubbling air or oxygen into the solution. Nitrobenzene, which probably undergoes a similar type of reaction as the nitro-organic acids has also been suggested.[110] A possible reason for the increase in detinning rate in the presence of nitrocompounds is that these establish redox systems assisting the oxidation of tin. A similar mechanism can be proposed for the use of 3-nitrophthalic acid.[111] A process based on nitro-organic compounds is operated in the U.S.S.R.[112]

Other alkaline chemical methods for detinning have been developed over the years, such as the use of the oxidative properties of stannic chloride[113], but the remaining alloy had to be removed electrolytically in hydrochloric acid. The use of an alkali liquor with the scrap in contact with a more electropositive element has been suggested, such as copper[114] in the presence of a depolarising material such as cupric oxide. This method has been extended[115,116] to include silver, gold, aluminium, iron, magnesium, nickel and chromium, or an oxide, alloy or salt of the same, but often with an oxidising agent present in the liquor. The common principle is that an electrical couple is established between the metals.

Modern technology has not been overlooked; ultrasound has been employed to increase the rate of detinning[117], whereby the concentration profile of the tin/liquor interface is disrupted.

2.2.2.2. Assessment of Alkali Chemical Processes

Alkali reactions with tin and the alloy layer are generally slow, and have to be carried out at elevated temperatures. Attack of a steel plant will not be so excessive as with an acid process.

Addition of oxidants is essential to maintain an economic throughput of tinplate. As the quantity of tin on tinplate decreases the cost of reclamation will increase due to the higher proportion of alloy present.

An alkali process is almost certainly cheaper than an acid process due to the lower initial costs incurred in the quantity of steel used for an acid process, and because the liquor will not be consumed on plant dissolution. Nevertheless, the cost of oxidants and heat have to be taken into account.

The use of recyclable organic compounds as oxidants should be carefully reviewed, due to their suspected carcinogenic properties.

2.2.3. Neutral or Non-specified pH Aqueous Methods

Although the pH of a liquor is not always specified, the literature does often state whether it is acidic or alkaline.

2.2.3.1. Copper-based Liquors

Copper sulphate solution was first used in 1894[118] to detin scrap tinplate. The tin dissolved as copper was deposited, but it is unlikely that any alloy attack would take place. A later development[119] incorporated copper sulphate with alkaline chloride or alkali earth metal chlorides, but it is unlikely that alloy attack would be increased.

Copper deposition onto steel would reduce the value of the steel, as copper is regarded as a steel pollutant. The process would be expensive, as copper is relatively costly.

2.2.3.2. Solutions of Chlorine and Chloride

Clerc[120] used a solution of stannic chloride, which was reduced to stannous chloride, to attack tinplate. The tin was recovered by precipitation after addition of waste iron or other suitable precipitating agents. The use of ferric chloride solution, either in conjunction with stannic chloride, or alone has also been suggested. Vigorous agitation is required, and the optional use of low pressure has been included.[120] Addition of magnesium oxide to the liquor causes stannous oxide to be precipitated, and the resulting magnesium chloride can be used to regenerate hydrochloric acid and chlorine.[121]

Various chlorine based liquors have been used in conjunction with additives such as iron and tin chlorides[23,123], ferric chloride with ammonium chloride[124] and ferric sulphate with ammonium sulphate. The reactivity of these liquors is not sufficient to attack the alloy, although tin dissolution would occur.

Liquors using "polysulphide" have been successfully used to attack both tin and the alloy layer, the first patent being in 1876[125], but others have followed.[20,97,101,126,127] "Polysulphide" is produced by dissolving flowers of sulphur in aqueous solutions of soluble sulphides such as sodium or ammonium sulphide; the resulting liquor is very reactive towards tinplate, but recovery of tin from the resulting sulphide is difficult.

2.2.4. Non-aqueous Systems

This group involves the attack of tinplate by gas, non-aqueous liquors and liquid metals.

2.2.4.1. Extraction by Chlorine Gas

Dry chlorine gas is a very good detinning agent, reacting rapidly with tin at low temperatures to produce volatile stannic chloride, which was an important chemical in the chemical and silk dyeing industries. The first patent was held in 1854[133] and a chlorine detinning plant operated in New York in 1873[134], but it was not until about 1906, when Goldschmidt introduced a chlorine process in preference to an electrolytic one, that the process became realistic.[128,129,130,131,132]

In the process the stannic chloride, being a liquid at normal temperatures, causes the pressure of chlorine in a sealed vessel to fall, until the reaction is complete.

One disadvantage with dry chlorine is that it reacts with iron, so Kugelgen[136] suggested keeping the reaction temperature as low as possible to prevent this attack; the reaction between tin and dry chlorine is exothermic. Various other patents[135,136,137,138] have been concerned with the design of the plant and methods of introducing the chlorine. Various methods to control the temperature by diluting the chlorine with air have been used, and at the same time the air stream can be used to carry out the stannic chloride as it is produced.[138,140] Zacharias[139] passed chlorine over finely divided tinplate in order to keep the temperature down, whilst Carrier[140] diluted the chlorine with air for the tin, but had to have a high concentration for the alloy, presumably because of its inertness.

One attempt to increase the attack rate was to elevate the reaction temperature to over 114°C[143], so that the stannic chloride remained volatile, and was swept out by the air stream, whilst the ferric chloride dissociated to return to ferric oxide and chlorine. Other references[39,142,144,145] and patent[141] are known, but few chlorine based extractions have been caried out since World War II.

2.2.4.2. Extraction by Hydrogen Chloride Gas

During the 1880's this process became relatively popular, with three patents being offered[146,147,148], and another was awarded in 1938[11], whilst in 1968 a reference was made abouts its feasibility.[38] In 1974 a report by Warren Springs Laboratories[12] also suggests hydrogen chloride to be a viable process.

The principle is that hydrogen chloride is pumped onto hot tinplate, and the resulting tin chloride washed off with water to yield stannic chloride. To ensure maximum conversion, a mixture of hydrogen chloride and chlorine has been used.[35]

2.2.4.3. Extraction by Stannic Chloride

Stannic chloride, under certain conditions, can be reduced to stannous chloride, and in doing so can oxidise tin to its divalent state. Such a process has been patented[129,149,150], using such methods as vacuum processes[121] or mixtures of chlorides, such as ferric and stannic chlorides.[150] Once the tin attack has occurred, zinc or iron is added to the liquor to precipitate the tin.

2.2.4.4. Extraction by Sulphur Dioxide Gas

This has been suggested as a detinning agent[39], but since it is only a mild oxidising agent itself it would be of little effect. However, in the presence of water, a mixture of sulphurous and sulphuric acids is produced, which is much more effective in detinning.

2.2.4.5. Extraction by Other Metals

When detinning first started there were attempts to react the tin with mercury to form an amalgam.[150,151,152] Besides being a rather slow method if it is not heated, it is also very poisonous, and besides, it does not readily affect the alloy layer.

One patent[154] has suggested using a molten lead bath to dissolve the free tin, but this would probably not dissolve the alloy and it is possible that further alloying may occur due to the elevated temperature (>320°C).

2.2.4.6. Extraction by Thionyl Chlorides

Only one patent has described thionyl chlorides being used[155], employing sulphur monochloride (S_2Cl_2) either alone or with sulphur dichloride (SCl_2). Presumably the sulphur dichloride undergoes dissociation to yield sulphur monochloride and chlorine, whilst the sulphur monochloride reacts with tin to form a mixture of sulphides and chlorides.

2.2.4.7. Extraction by Nitrogen Oxides

A suggestion has been made[39] for dinitrogen trioxide to detin tinplate; the dinitrogen trioxide (N_2O_3) readily dissociates into nitrogen dioxide (NO_2) and nitric oxide (NO), the latter readily reacting with oxygen to yield nitrogen dioxide, which in turn reacts with water to give a mixture of nitric and nitrous acids. It is probably the acids which are the active detinning agents.

2.2.4.8. Extraction by Organic Reagents

A liquor of carbon tetrachloride with 10% chlorine dissolved in it has been used to detin tinplate by Rondelli[156,157], although the process was first patented in 1909.[158,159] By using carbon tetrachloride as the solvent, dirty cans are cleaned in situ. Reaction of the dissolved chlorine on the tin yields stannic chloride.

A method of detinning using tars, mineral oils and coal products under pressure has been developed[160,161], but the essence of the process is that it is reliant upon organic acids such as phenolics and naphthenics being present. The temperature needed by these processes are in excess of 50°C.

2.3. Electrochemical Detinning

The majority of liquors used in electrolytic detinning can be categorised in the following groups: acidic, basic and neutral, each group having the optional use of oxidants.

2.3.1. Acidic Processes

Electrolytic acidic detinning processes are relatively rare, the only known ones being for hydrochloric acid[170,171] and a mixture of ortho-phosphoric acid being present to passivate the steel.

One other process has been suggested, where the scrap tinplate is cast into anodes and subsequently dissolved in phenosulphuric acid[173]; this method has obvious difficulties regarding the accessibility of the previously free tin.

The problems involved in acidic electrolytes are the same for acidic chemical processes, namely the dissolution of the plant and of base steel, but little can be done to successfuly prevent this occurring.

2.3.2. Alkaline Processes

Numerous references and patents have been produced regarding commercially viable processes using electrolytic alkaline processes, many of which are minor modifications of previously known processes.

2.3.2.1. Pure Alkali Processes

Due to the low cost, sodium hydroxide is preferred to potassium hydroxide as a detinning liquor, although potassium hydroxide has been used.[174,175]

The first electrolytic-based patents were awarded in 1883/4[176,177,178,179], but these were very straightforward alkali bath-type systems. It soon became apparent that scrap movement in the liquor bath was important to increase the rate and quality of detinning.[180,189]

As the quantity of tin overlay decreased, due to both the cost of tin increasing, and the onset of electrolytic tinplate as opposed to hot dipped plate, it became more difficult to recover the tin, so improved agitation methods, such as rotating drums were introduced.[113,182,183,184]

Often scrap tinplate is recovered by the detinners in the form of bales; this is done to increase bulk density and hence reduce transport costs, but it does create problems in trying to detin the bales, because they are do dense. One way to ensure efficient detinning is to break them open with a flyhammer, but a novel way is to stack the bales in closed tanks and evacuate the vessels. Alkali electrolyte then filled the vessels and the gaps in the bales at a pressure at least equal to atmospheric. The bales were made anodic and stripped.[185]

As the amount of tin decreased on tinplate alternative coverings had to be found to prevent corrosion through the inherent pin-pricks through the tin layer. Various lacquer coatings have been applied with a high degree of success, but unfortunately these lacquers tend to be inert to chemical attack and hence cause difficulties in detinning. One way of removing the lacquers, and in fact other surface coatings such as oxides, is to impart a cathodic, or reducing, current on the tinplate for about 5 minutes, after which time the tinplate is made anodic.[186]

Other ways of using pure alkali as a detinning electrolyte have involved elevating the temperature, and hence increasing the reaction rate, and at the same time recovering the tin in a molten state, by employing autoclaves operating at 30-35 atmospheres.[187,188]

2.3.2.2. Alkali Plus Oxidants

Various attempts have been made to increase the rate of chemical detinning by imparting a current across the reaction cell. If a chemical liquor detins quickly, the same liquor with a current applied may react more quickly, and hence reduce detinning times. It also has the advantage, as with all electrolytic detinning, that the stripping and the recovery of tin is done in one operation.

Typical oxidising agents that have been suggested include cobalt oxide (CoO)[190], sodium nitrate[191,192,193], potassium nitrate[92] and organo-nitro compounds such as m-nitrobenzoic acid[195] and m-nitrophthalic acid[175]. The relative merits of nitrate and nitrite oxidants have been compared and analysed.[206]

2.3.2.3. Alkali with Methanol

During the early 1960's it was suggested that addition of methanol[196,197,198,199,200] to detinning liquor would enhance the reaction rate. The reason for this is probably two-fold, one being that the methanol, which was between 5 and 20% by volume, would loosen, and even dissolve, the applied lacquers, and the other being that it lowered the viscosity of the liquor, allowing better penetration into tinplate bales.

2.3.2.4. Other Alkaline Solutions

Although sodium hydroxide has been shown to be the most economical liquor to use, others have been suggested, such as alkaline pyrophosphate[201,202], pure sodium carbonate[203] and sodium carbonate mixed with sodium chloride[204], sodium chloride by itself[186], alkaline sodium sulphate[203], alkaline sodium silicate[203], and alkaline sodium acetate.[330]

2.3.2.5. Assessment of Electrolytic Alkaline Detinning Processes

Alkaline electrolytic processes are faster than the corresponding chemical processes, and have the advantage that addition of oxidants does not generally increase the detinning rate. The liquor temperature can be reduced, and maintained by current losses in the plant.

The disadvantage of an alkali electrochemical process is that electricity is expensive; and plant insulation would be required. There are also difficulties in using an electrochemical continuous process, although these are not unsurmountable. A batch process is relatively easy to operate, but it is labour intensive.

An electrochemical process is more controllable than a chemical process, due to an extra independent variable, which is either potential, or more feasibly in an industrial process, applied current.

2.3.3. Neutral or Non-specified pH Electrolytes

Some patents use a range of chemicals, either by themselves or as mixtures, and hence cover a variety of conditions. A wide range of such liquors have been reported to be suitable for electrolytic detinning, including solutions of sodium chloride(203), sodium sulphate(203), sodium silicate(203), alkali metal salts of pyrophosphoric acid(172), ammonium, amino, alkali or alkaline earth salts of the following acids: acetic, citric, lactic, oxalic, tartaric, formic, nitric, phosphoric, hydrochloric, hydrochlorous or thiocyanic.(205) It is difficult to assess their activity, but they are not as efficient as either acid or alkali liquors due to their pH ranges.

2.3.4. Variations in the Electrolytic Process

Due to the need for patenting detinning processes, many of which are virtually identical in real terms, it has become necessary to alter one aspect of the method. The most readily variable aspect of an electrolytic detinning process is the cathodic, or deposition electrode, and a range have been suggested, such as carbon[194,207,208], iron[208,209] and even mercury.[210] A further variation can include electrode arrays, whether the electrode is stationary or rotating and other design features.

Similarly, the anodic aspect can be modified slightly to render a "new process" by altering the basket design[183,184,211] or methods of imparting a current into the reaction cell.[212,213]

2.4. General Comments about Detinning Literature

The available literature on detinning covers a very wide range of techniques, some of which are viable and some of which are not. Acidic plants, although they can operate at low temperature, are expensive, due to the acidic corrosion of the plant. There is no known method of ensuring passivation of steel from attack by hydrochloric acid. The use of sulphuric acid may reduce the attack due to its preferential attack of tin. Organic acids do not attack the alloy readily.

Alkaline processes are slower than acid ones, and require heat. Even the addition of oxidising agents does not substantially reduce the operating temperature. Early detinning processes were mainly concerned with the dissolution of free tin, but as this has decreased in quantity, dissolution of the alloy layer has become more important. Due to the necessity to patent processes various claims relating to additives have been made; the only effective ones have been shown to be oxidising agents such as organic acid salts, nitrite, persulphate, polysulphides and oxy-sulphur compounds and oxychlorides. A limited benefit may be possible from metal salts.

Electrolytic alkaline detinning solutions have been heavily patented, although relatively few include the addition of oxidising agents. This is because most oxidising agents are not beneficial when an applied current is imposed on the system. Electrolytic processes do, however, allow for a reduction in temperature. Good electrolytic processes have been patented, but then broken by the use of different cathodes; it is difficult to assess the effectiveness of the cathode unless long-term plant studies are carried out.

The use of gases, such as chlorine, to detin scrap tinplate is effective. Goldschmidt rejected alkaline electrolytic processes in favour of chlorine processes in the early Twentieth Century, but the inherent problems associated with gaseous processes restrict their use.

2.5. The Alloy Layer

When a mixture of iron and tin are thermally treated, they combine to form a range of alloys, or intermetallic compounds. During the flow melting process for electrolytic tinplate, the alloy formed is almost totally $FeSn_2$ [214,215,216], although Trilliat and Mihama [214] have claimed some evidence for the presence of an iron-rich alloy. Thwaites and Speight [217] have shown the existence of FeSn and Fe_3Sn_2 at higher temperatures, whilst Alesksanyan and Kuz'min[218] have detected, and identified, the existence of Fe_3Sn, Fe_5Sn_3, FeSn and Fe_3Sn_2, at high temperatures, by using X-ray diffraction, microscopy and differential thermal analysis techniques.

Studies of Ehret and Westgren[219] have shown the existence of five phases, some of which may have been a mixture of phases, whilst Jones and Hoare[220] repeated the work and only confirmed the presence of Fe_2Sn, FeSn and $FeSn_2$ at 850°C.

By studying the equilibrium diagram for iron-tin, one would expect two intermetallic compounds, FeSn and $FeSn_2$, to be present at room temperature. Due to the temperature of flow melting (about 330°C) only $FeSn_2$ is formed, by direct reaction between liquid tin and solid iron, but FeSn must form by diffusional processes in the solid state, that it is a much slower process indicates that most of the alloy layer should be $FeSn_2$. However, Clarke[222] found the iron content of the alloy to be higher than that required for stoichiometric $FeSn_2$. Covert and Uhlig[223] found a similar anomaly, but concluded that the alloy must, nevertheless, be in excess of 95% $FeSn_2$. Romig and Rowland[224] have shown the presence of other alloy phases by using etching techniques, but do not suggest any structures. Thwaites[225] has, unsatisfactorily, suggested a mechanism whereby $FeSn_2$ changes into FeSn at 496°C, and remains in existence due to a rapid quench. Electrochemical data from potential-time curves have indicated the existence of a constituent more noble than $FeSn_2$, which could be FeSn.[226,227]

Electron and X-ray diffraction analyses of the alloy have not been conclusive; it is known that $FeSn_2$ is tetragonal in structure, but under certain conditions it can exhibit hexagonal symmetry.[228] Also, FeSn exhibits a hexagonal structure, which further complicates analysis. Various workers[214,228,229,230,231,232] have shown the alloy structure to be that which would be expected of either tetragonal or hexagonal $FeSn_2$, whilst Kokorin and others[233,234,235] have shown the existence of non-equilibrium phases in tinplate. It is apparent that the constitution of the alloy remains confused, although it can be said to be over 95% $FeSn_2$ under normal circumstances.

Analysis of the alloy layer has been carried out by numerous methods, including chemical etching and optical microscopy[220,224,226,227], electron microscopy[221,239,240,241], radiotracer techniques[242], electrolytic stripping[234,244,245], X-ray diffraction[214,218,219,228,229,230,231,232,234,246,251], and electron re-emission Moessbauer Spectroscopy.[247,248,249] All the techniques show the same net result, but non, to-date, are a definitive solution to the problem of the alloy constitution. Asano[250] has reviewed the techniques available for studying the properties and structure of tinplate.

Gabe[221] compiled the data available for the structure of the alloy and analysed the results. He concluded that the structure is either tetragonal ($a = 6.533$ Å, $c = 5.321$ Å, $\frac{c}{a} = 0.815$) or pseudo-hexagonal ($a = 5.321$ Å, $c = 9.236$ Å, $\frac{c}{a} = 1.737$). Ehret and Westgren[219] have calculated the density for $FeSn_2$ to be $7.6\,g/cm^3$, and show a unit cell corresponding to pseudohexagonal, comprising of 12 atoms. Kanuyuki and Hiroshi[296] have shown the magnetic unit cell to be twice as large as the chemical cell, it being doubled along the c-axis.

The kinetics of alloy growth appear to follow an approximately parabolic relationship, as described in Fick's laws of diffusion:

$$x^n = Kt \qquad \text{eqn. 2.3}$$

where x is the diffusion distance, t is time, K is a constant (which includes the diffusion coefficient) and n is the power index.

Early work was carried out on both flow melted plate[243,253,254] and on unflow melted plate.[225,252,255,256] It was generally noted that the power index suggested a parabolic relationship. However, both Thwaites[225] and Frankenthal and Loginow[252] noticed that during thermal treatment of unflow melted tinplate this relationship was not obeyed, and hence indicated that the interface reaction between iron and tin did not obey simple first order kinetics.

Gabe[255] proposed a three stage mechanism for alloy formation, the first stage being a rate controlling mechanism involving tin itself, and involving nucleation of the alloy at discrete sites; the second stage being a wholly diffusion controlled process during which crystallites grow along three axes under approximately parabolic kinetics; the third being a predominantly unidirectional growth, when the growth rate power index increases substantially.

Biber[256,257,258] also studied the kinetics of the early stages of alloy formation and noted the parabolic growth only occurred if the rate of heating was slow.[258] He also showed that the growth rate of the alloy was different at different crystal faces of the iron, the growth rate on the (100) and (110) faces showarrests, compared to the rate of the (111) face due to the base metal being covered by the alloy. Luner and Murray[259] had also noticed this effect and suggested a degree of epitaxy in the formation of $FeSn_2$ when the tin melted onto the steel substrate, this degree being dependent on the mode of deposition of the tin, and the presence of impurities.

Teindl[260] and others[264,265,266] have shown that the morphology of the alloy is characteristic of how the samples are prepared prior to coating, and on the thermal effects in the bath. Schuez[261] showed that the production of electrolytic tinplate caused tetragonal $FeSn_2$ to be formed as a direct effect of the melting of the tin, and that the c-axis of the $FeSn_2$ runs parallel to the (100) and the iron surface if the surface orientation of the iron is (100). Further work on heating effects by Tissier[262] show that it is essential for good corrosion protection to allow Gabe's second stage[255] to be effective. Recently, Saito[263] has used micro-autoradiography to determine the diffusion coefficient of tin in the grain boundaries of iron between 200 and 600°C; he also calculated the apparent activation energy to be 10.1 kcal/mol.

One variation on the proposed kinetic formation of the alloy layer has been developed by Jolly and others.[267,268,269] It has been shown that an iron-tin mixture can form a range of carbides, and Jolly et al[268] have shown that the diffusion rate of tin is controlled by the formation and decomposition of iron-tin carbides; whilst only successfully identifying, by X-ray diffraction, Fe_3SnC_x. Other workers[269] have identified $Fe_3Sn_2C_y$, and shown evidence for $FeSnC_z$ (x, y and z are the carbon ratios in the carbides. They are probably integers, making the compounds stoichiometric, but this has not been verified.)

The presence of alloy in hot dipped tinplate would be expected, but Vitkin and Morgan[270] insist that the alloy is composed of two types of crystal, one being formed by diffusion of the tin into the iron;

$$2Sn + Fe \rightarrow FeSn_2 \qquad \text{eqn. 2.4}$$

as in electrolytic tinplate and one by the chemical effect of fluxing during hot tinning[236,237,238,273]:

$$Fe \xrightarrow{flux} FeCl_2 \qquad \text{eqn. 2.5}$$

$$FeCl_2 + 3Sn \rightarrow FeSn_2 + SnCl_2 \qquad \text{eqn. 2.6}$$

The flux in hot dipped plate is either hydrochloric acid or a molten active chloride. Men'shikova et al[271] have shown that the presence of tin chloride does not affect the rate of $FeSn_2$ formation.

Studies by Slivkov et al[272] have shown only one form of $FeSn_2$ in hot dipped tinplate, this form being due to the first, diffusion based, mechanism. They also point out the adverse effect of temperature on the alloy formation, because if the temperature exceeds 280°C, the diffusion coefficient of tin in iron, which increases exponentially, becomes unacceptably high.

The alloy is antiferromagnetic, and has a Neel temperature of 384°K. (The Neel temperature is the temperature at which there is an abrupt change in the magnetic susceptibility/temperature relationship above this temperature the substance acts as a simple paramagnetic one.)[274,275,276,277]

Both and Trumpy[278] have studied the magnetic structure and electron properties of Fe-Sn alloy, as have many others, such as Fabri[279], Shcherbina[280], Djega[281], and has determined internal magnetic fields, isomer shifts and quadrupole splotting of ^{57}Fe and ^{119}Sn along with the magnetic moment for each iron atom, for solid solutions of tin in iron and for stoichiometric compounds. They found that an increase in the tin content at 0-8% (atomic %) resulted in an anomolous increase in the iron magnetic moment, but this is due to the reduction of the 4s electron polarisation during the formation of Fe-Sn bonds. The hyperfine magnetic moments at the iron sites are proportional to the number of nearest neighbours, and inversely proportional to the square root of the number of next nearest neighbours.

Polarisation studies of the conductance electrons have been carried out by Werkheiser[282], and resistivity studies of the single crystals by Stenstrom.[283]

Corrosion of intermetallic compounds of the $FeSn_2$ type has not been exhaustively carried out, however Cherkashin[284] reported that silver-aluminium and magnesium-lead alloys react in such a way with water as to oxidise the more electronegative metal, and precipitate the pure metal of the lower constituent. This has been verified over a greater range of alloys by Löhberg.[285] Studies of the electrochemical reactivity of Fe-Cr alloys by Kolotyrkin[286] show that the dissolution of the least noble constituent, iron, from the alloy takes place in a kinetic manner, and is limited by the reaction where the hydroxide ions participate directly. There is also some indication that the reaction potential is related to the alloy composition.

Couvert and Uhlig[287] and Clarke and Britten[288] have studied the electrochemistry of alloy dissolution, both noting the high hydrogen overpotential. Couvert and Uhlig quote the steady potential as -0.271V, whilst Clarke and Britten quote +0.294, this was explained by postulating an oxide layer over the alloy. If an anodic current is applied, the sluggishness of cation movement from the lattice will favour diversion of the whole of the energy supplied to oxide formation, and hence it seems that the oxidation state of the film is raised until the field strength is sufficient to overcome this sluggishness. In the case of NiSn alloys, they suggest that nickel acts independently during oxidation, to form nickel hydroxides, and expect $FeSn_2$ to behave similarly, as the chemical corrosion of the alloy would suggest. Golubev[289] has suggested that the transition from metallic to atomic bonds may occur during deformation along grain boundaries of grains and the planes then acquire the other physico-chemical properties. Under certain corrosion conditions such an alloy can decompose into zones of non-metallic bonds, and hence have an increased tendency to selective corrosion. Clarke and Elbourne[290] note the low passivation potentials of some intermetallic tin compounds, and suggest the reason to be an overlay, in the case of NiSn, to be:

$$HO - Ni - O - Sn \begin{smallmatrix} \nearrow O \\ \searrow OH \end{smallmatrix}$$

which is followed by formation of nickel hydroxide ($Ni(OH)_2$) and then Ni - O - OH.[288]

A study has been made of the kinetics of chlorination of tin and $FeSn_2$ by Otooni.[291]

The formation of the alloy from a lead-tin mixture has been studied by Popel et al[292,293], who have shown that the liqu~~us~~idus-iron interaction is not adversely affected by the presence of lead, whilst Eremenko[294] has shown stability regions to be present, which would be expected from the Fe-Sn-Pb phase diagram. Thwaites[295] reports that the lead does not, in fact, take part in alloying, but the lower the tin content of the liquus, the lower the alloying. He concludes that tin is more soluble in iron than in lead.

3. EXPERIMENTAL PROCEDURES

3.1. Laboratory Procedures

3.1.1. Chemical Procedures

3.1.1.1. Acid Liquors

The rate of detinning tinplate in a laboratory glass beaker was compared between hydrochloric acid with and without various additives to improve the rate of detinning and also decrease the rate of steel dissolution.

Solutions of 2% antimony trichloride, bismuth trichloride and aluminium trichloride respectively were compared against 10N hydrochloric acid as both an oxidant and passivator. Other solutions tested were cobalt nitrate, cupric chloride, chromium trichloride, nickel sulphate, ammonium molybdate, lead sulphate, ferrous sulphate, magnesium sulphate, zinc sulphate and cadmium sulphate, all of which were 2% solutions in 5N HCl.

The effect of orthophosphoric acid as a passivator was also studied.

3.1.1.2. Basic Liquors

A range of experiments were conducted where the relative detinning rates of 2N sodium hydroxide were compared with rates obtained when additives such as potassium aluminium sulphate, sodium carbonate, sodium chlorite, sodium nitrate, sodium nitrite, sodium perborate, sodium perchlorate, sodium persulphate, sodium hexametaphosphate, sodium diorthophosphate, sodium monorthophosphate, sodium polysulphide, sodium sulphate and sodium sulphite. All the additives were 8% solutions ($^{w}/v$) and experimentation was carried out in laboratory glassware at either room temperature or 95^{o}C. Clean tinplate was immersed in the liquor, and the time taken for total detinning measured.

3.1.1.3. Preparation of Sodium Polysulphide

Flowers of sulphur were added to a boiling saturated aqueous solution of sodium sulphide until a saturated solution was obtained. The resultant liquor has a characteristic red colour. A similar solution of ammonium polysulphide can be prepared by an identical methods, although this liquor should be avoided due to a highly noxious smell.

3.1.2. Electrochemical Procedures

3.1.2.1. Acid Electrolytic Liquors

Comparisons were made in laboratory glassware between electrolytic detinning rates obtained using a galvanostatically controlled cell containing hydrochloric acid at different temperatures and anodic current densities. Additions of orthophosphoric acid and other organic compounds were made to prevent dissolution of the steel substrate of the tinplate. Details of the galvanostatic circuit are in Section 3.1.3.1. A silver/ silver chloride reference electrode was often used to monitor the reaction.

3.1.2.2. Alkaline Electrolytic Liquors

A series of previously used chemical oxidants were added to 2N solution of sodium hydroxide in a glass beaker. The oxidants were all

8% ($^{w}/v$) in strength and were; sodium nitrite, sodium hypochlorite, sodium chlorite, sodium chlorate, potassium perchlorate, sodium carbonate, ammonium molybdate, sodium orthophosphate, sodium polysulphide and sodium persulphate. Each liquor was compared with sodium hydroxide at different temperatures and anodic current densities.

3.1.2.3. Alkaline Corrosion Couples

The corrosion couple between tin and steel was studied by immersing a divided cell containing sodium hydroxide in a water bath. A voltmeter and ammeter were connected between the electrodes. The two electrodes were also connected by wire. The effect of steel area was studied by varying the amount of steel in the liquor. Air was pumped into the cathodic side of the cell by a small air pump. A cadmium/cadmium hydroxide reference electrode was inserted into the split cell and connected to the i/p 'lo' terminal of a digital voltmeter, the tin and steel electrodes being connected to the i/p 'hi' terminal.

3.1.3. Electrochemical Apparatus

The basic equipment used in electrochemical experimentation was the 'Ministat' 257, a simple potentiostat supplied by H.B. Thompson and Associates of Newcastle-upon-Tyne, England. The digital voltmeter was Type SM211 supplied by Southern Electronics. The chart recorder was a high impedance model, Type PRO-12 supplied by Yew Electronics, Japan. The sweep generator was a Hi-Tek Type PPR 1.

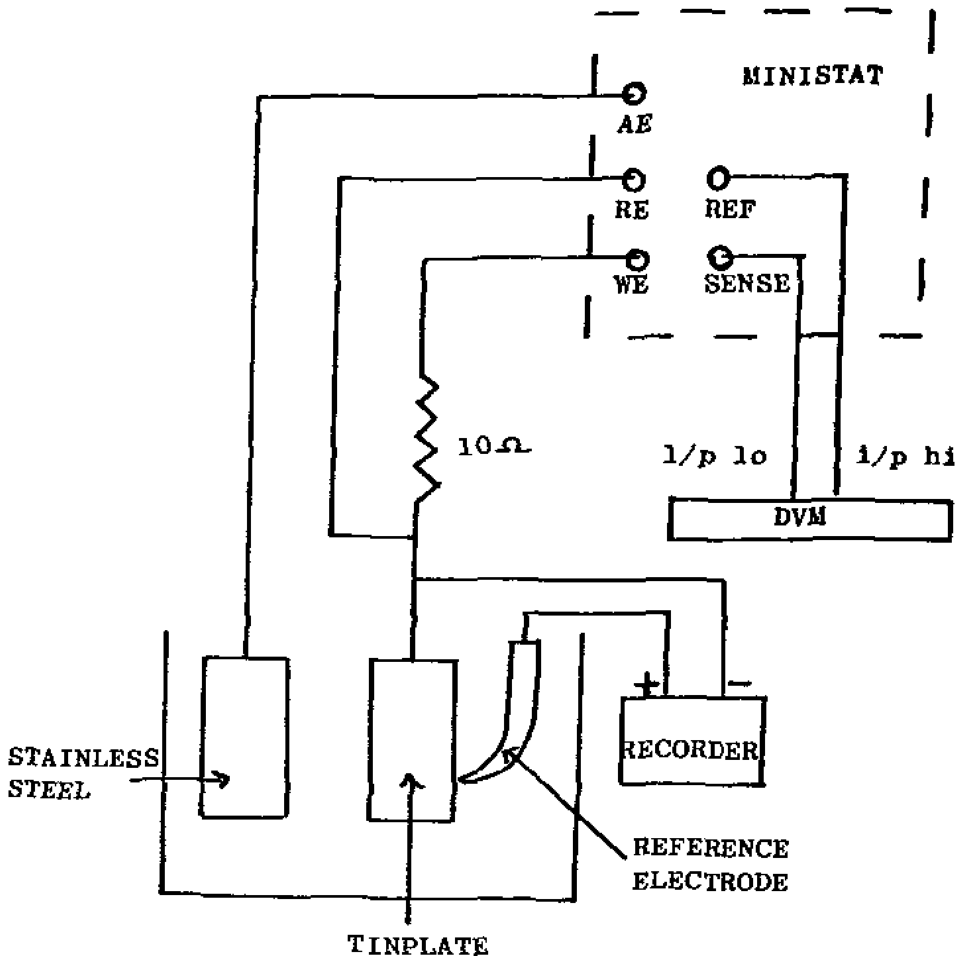


Fig. 3.1. A schematic diagram of the galvanostatic circuit.

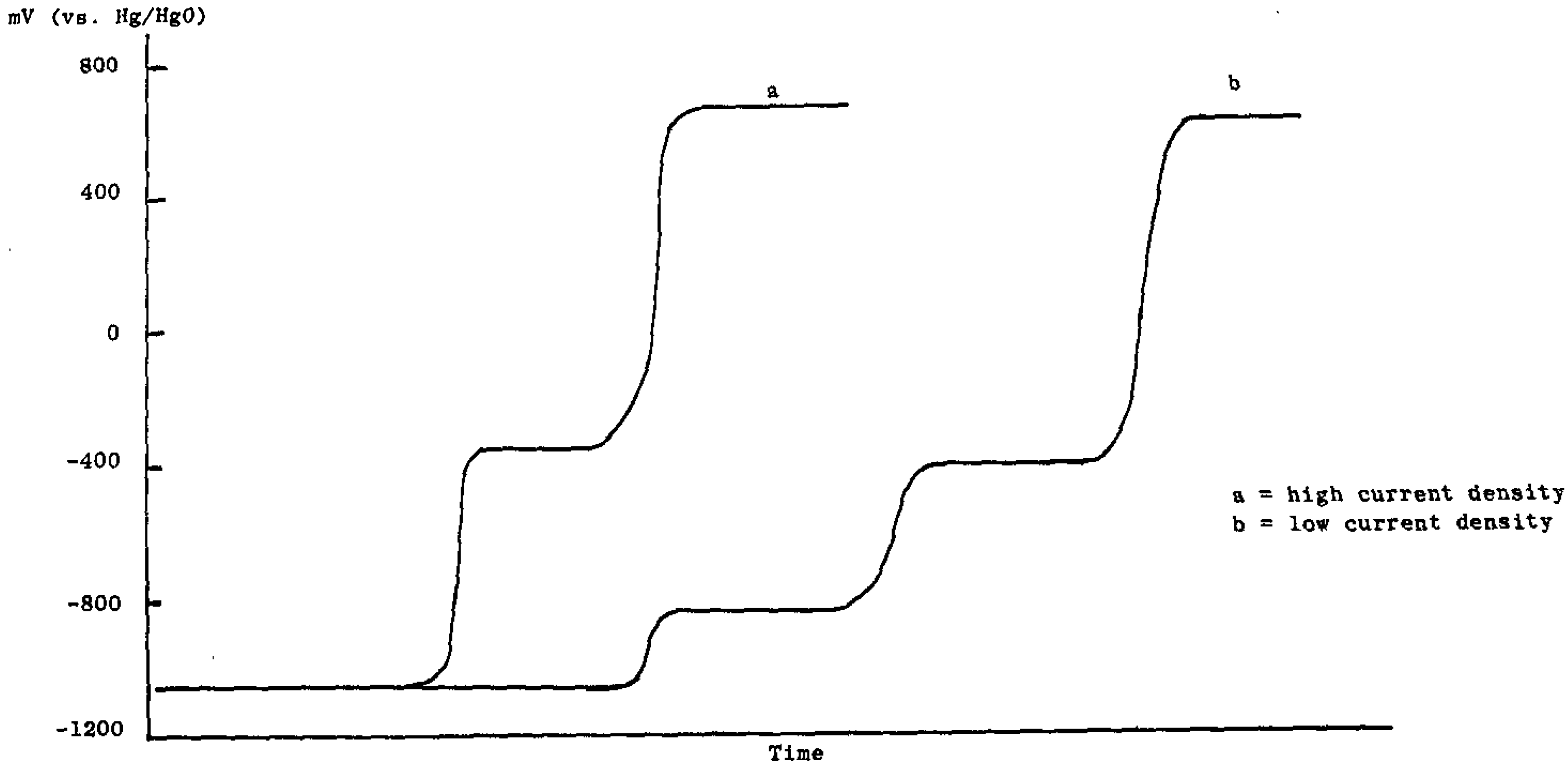
3.1.3.1. Galvanostatic Experiments

Most of the experimentation performed was galvanostatic. A galvanostat is essentially a two terminal device, capable of controlling the predetermined magnitude of a flow of current in an electronic circuit within very close limits. The principles of the galvanostatic mode are discussed by Von Frauenhofer.[55]

A schematic representation of the system is shown in Fig. 3.1. The auxiliary electrode, or counter, electrode was stainless steel, and the working electrode was tinplate. The current density applied to the working electrode was found by knowing the anodic surface area and the value of the counter resistor (R) which was generally 10Ω. By adjusting a dial and polarity switch, the current can be varied; it is measured on a digital voltmeter, connected between the "Ref" and "Sense" terminals. The applied current was then equal to the measured voltage divided by the counter resistor (R). The polarity of the working electrode, which is the common datum point of the instrument, can be altered by a switch. A positive reference polarity gave a cathodic reaction onthe working electrode. During tin dissolution the switch was negative.

A high impedance recorder (Yew X-Y recorder Type PRO-12) was connected across the cell. The positive terminal on the Y-axis was connected to the working electrode, and the negative terminal to the reference electrode, which was usually a mercury/mercuric oxide cell in 2N sodium hydroxide. The reference electrode was supplied by Russell pH Ltd., of Auchtermuchty, Fife. The x-axis was set to time, a convenient rate being 10 seconds/centimetre. The y-axis was usually

Fig. 3.2. Stylised electrochemical detinning profiles.



adjusted to cover 200 mV/centimetre. Such circuitry gave an inverted potential vs. time trace.

A second digital voltmeter was connected across the recorder terminals, to give a more precise potential reading.

Using the galvanostatic circuit, the detinning reaction could be followed. In order to prevent chemical dissolution of tin, the galvanostat was turned on as soon as possible after the tinplate had been put into the liquor; this would typically be two seconds after immersion.

After the tin overlay was removed, the potential increased to the dissolution potential of the alloy, which was characterised by its blue/grey colouration. At high current densities this increase would be about 600 mV, but at low current densities it would be 200 mV initially, but then rising to 600 mV. Once the alloy had been dissolved, the potential increased by about 1V, which corresponded to the steel/alkali potential. At this potential, oxygen was evolved from the steel base plate, whilst hydrogen evolved from the cathode.

A stylised detinning profile is shown in Fig. 3.2.

3.1.3.2. Potentiostatic Experiments

Using the Ministat as a potentiostat enables a closely controlled potential to be applied to an electrode, whilst the current varies. In the experiments carried out it was usual to apply a potential gradient across the reaction cell, from a Hi-Tek Wave Form Generator, Type PPR-1.

The output of the waveform generator was connected in parallel

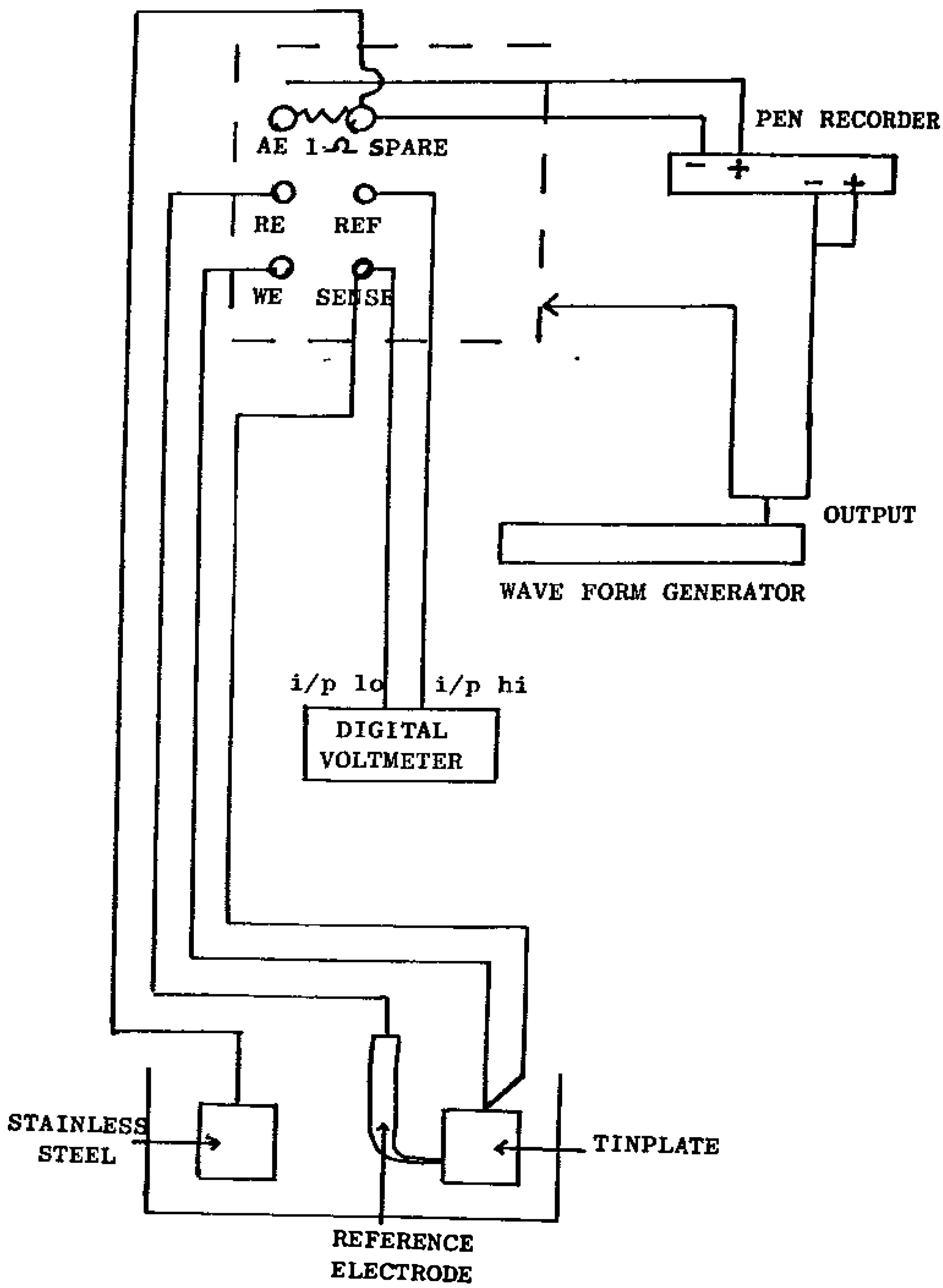


Fig. 3.3. A schematic diagram of the potentiostatic circuit.

to the x-axis terminals of the pen recorder and to the rear input of the Ministat. The screening of the co-axial cable from the generator inert to the negative terminal of the recorder, and the screening to the Ministat connection. The core led to the positive terminal of the recorder and the core of the Ministat lead.

A 1Ω resistor was connected between the auxiliary electrode and spare terminals on the Ministat. A connection from the 'spare' terminal was made to the negative terminal of the y-axis on the recorder and also to the stainless steel electrode. The positive terminal was connected to the auxiliary electrode terminal.

A reference electrode, usually Hg/HgO, was connected to the 'Reference electrode' terminal, whilst the working electrode was connected by two leads to the 'working electrode' terminal and the 'sense' terminal. This was to reduce the effect of any voltage drop along the working electrode supply lead. The common connection was made as near to the actual electrode as possible.

A digital voltmeter was connected between the 'Ref' and 'Sense' terminals, the former being on the positive side of the voltmeter. A schematic diagram is shown in Fig. 3.3.

The polarity switch was set to positive, and the Reference control potential set to zero. However, if a potential was required to be superimposed on the potential from the waveform generator, it could be set on the control potentiometer as long as it did not exceed $\pm$ 3 volts.

The function mode of the waveform generator was set to 'ramp', although other variations involving pulses can be obtained. The potential limits and gradients can be set by adjustment of their respective operative functions.

The equipment was usually used in an alkaline liquor cell, under the same conditions as the galvanostat. Whilst studying the electrochemistry of the alloy it was necessary to have a very small working electrode area. A Luggin capillary was employed to bring the reference electrode as near as possible to the electrode surface. When a small electrode was required, a larger working electrode was masked using Canning's "Fortolac", leaving only a small surface of unmasked electrode. This aided handling of the electrode and also obviated the edge effects on the current density distribution associated with an angular three dimensional electrode.

It was only possible to do a single potential sweep using the alloy, because the alloy would totally and irreversibly dissolve.

3.1.3.3. A Precision D.C. Voltage Amplifier

The Ministat, by making it act as a voltage amplifier, can be used to determine the specific conductance of liquors. A known voltage from an external source has to be introduced into the Ministat. In this case a standard nickel-iron cell of voltage 1.55 to 1.85 was used. Two resistors, R_1 and R_2, were connected between the working electrode and reference electrode, and the auxiliary electrode and reference electrode terminals respectively. The voltage between the auxiliary and working electrode terminals was measured. By knowing the value of R_1 and the two potentials, R_2 can be calculated:

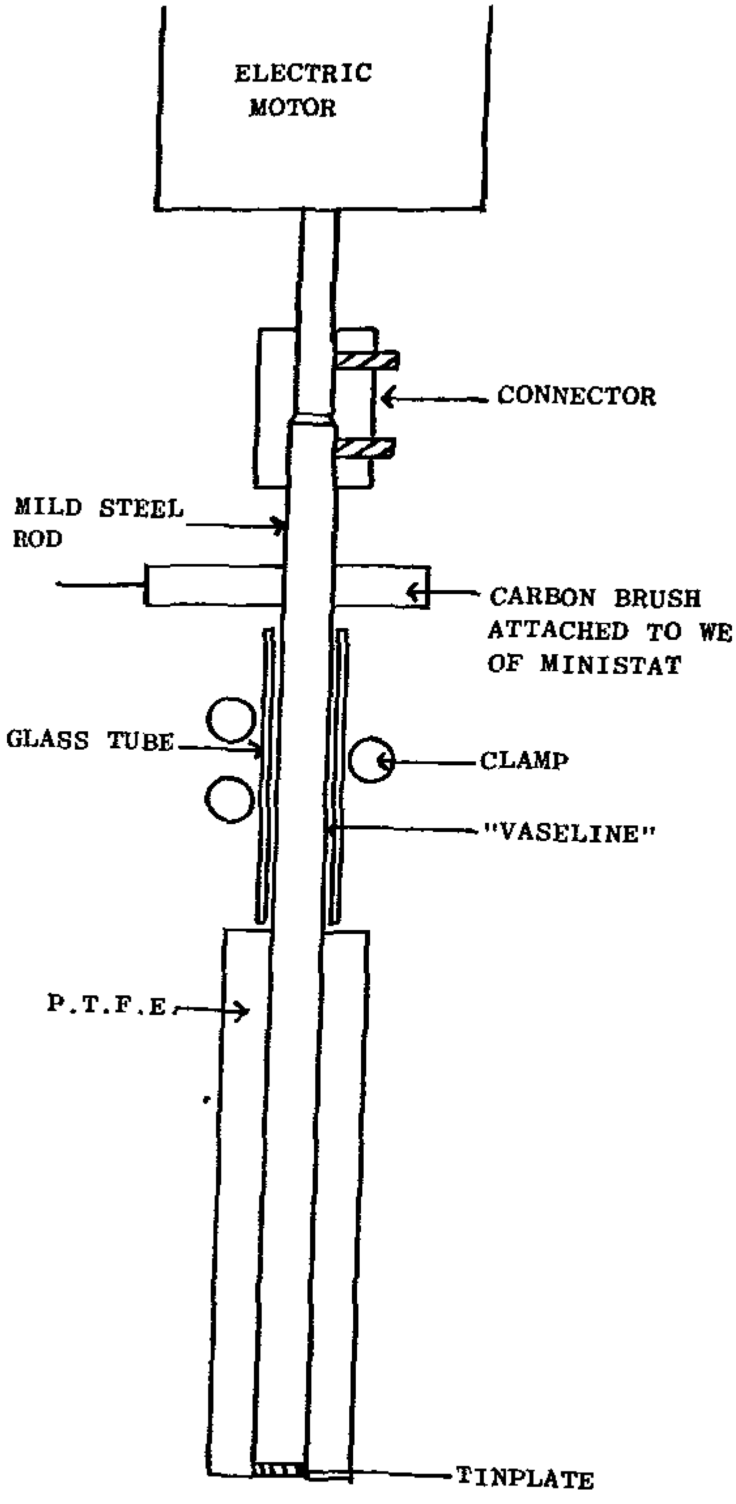


Fig. 3.4. The rotating disc electrode.

$$V_{out} = (1 + \frac{R_2}{R_1}) V_{in} \qquad \text{eqn. 3.1}$$

Resistance R_1 was the resistance between two 1 cm^2 platinum electrodes in hot alkali set at 1 cm apart. Hence the specific conductance could be evaluated.

Care has to be taken to ensure that the output voltage is not high enough to affect the platinum electrode surfaces, which have an oxidation potential of about 1-2 volts: a non-conducting oxide layer can form over the electrode, and give erroneous resistance results.

3.1.3.4. The Rotating Disc Electrode

A slow rotating disc electrode was made by sheathing a ¼" diameter mild steel rod with a 9/16" diameter P.T.F.E. sheath. A short piece of greased glass tubing was put onto the shaft, followed by a carbon brush with a ¼" diameter hole drilled into it. (See Fig. 3.4.) The carbon brush was connected to a potentiostat with a 100Ω counter resistor. To maintain good contact between the shaft and carbon brush, a drop of alkali was put into the hole. The shaft was driven by a variable speed electric motor, and its speed determined by a stroboscope.

A sample of the electrode surface to be examined was stamped out of a sheet using a ¼" diameter punch, and glued onto the shaft inside the P.T.F.E. sheath by silver filled epoxy resin, supplied by Radio Spares Ltd. A coating of "Fortalac" was applied to protect any exposed silver or mild steel from chemical attack. The electrode was cured at 80°C for 20 minutes.

The dissolution of both tin and alloy could be examined in different liquors, although the most usual ones were either just alkali or alkali with nitrite. The temperature was usually 85^{o}C.

By knowing the rotation speeds, the angular velocity (w) can be obtained. Analysis of the electrochemical reactions was obtained by plotting $w^{\frac{1}{2}}$ vs. current density on the rotating disc electrode.

3.1.3.5. Bulk Electrolytic Detinning

Electrochemical detinning in the laboratory gave an insight into the effects of various parameters on the detinning profile. A scaled-up test of the process was carried out in the laboratory before full test plant facilities were made available.

400 gms (2,400 cm^2) of unlacquered tinplate were packed into a container. The container was either a multi-holed plastic tube of volume 1810 cm^3, or a wire mesh basket made from 1/8" expanded steel mesh of volume 1960 cm^3.

A current was supplied to the tinplate by a mild steel rod being thrust into it; during one trial connections were made directly to the wire mesh basket.

The electrical circuit consisted of a 12V car battery with tappings on every cell. This made it possible to step the output voltage at 2 volt intervals. The anodic side of the battery was connected to a $10^{-3}\Omega$ series resistor (rating 100 A/100 mV). A pen recorder was connected across the resistor to measure the current.

Between the resistor and the anode basket was a 60 A/400 V switch box, which was connected to a $^7/8''$ mild steel bar thrust into the tinplate. The cathodic side of the battery was connected directly to a mild steel cathode, of effective total surface area of 100 cm^2. Appropriate heavy gauge wiring was used throughout.

The detinning liquor was 14 litres of 2N solution hydroxide (NaOH), with or without 8% sodium nitrite added ($NaNO_2$), and was kept in a soda glass water tank. The liquor was heated by means of a thermostatically controlled propellor-stirrer immersion heater which pumped the liquor at a rate of 11 litres/minute, and was limited to a maximum temperature control of 80°C ($\pm$1°C).

A series of experiments was carried out, to characterise the detinning profiles, the comparisons of which can be divided into the following groups:

3.1.3.5.1. <u>The Effect of Nitrite</u>

A comparison between 2N NaOH liquor with and without 8% $NaNO_2$ was made at 70°C and 80°C.

3.1.3.5.2. <u>Various Methods of Imparting the Current into the Cell</u>

This series was carried out at 80°C. Only three methods were studied:

(a) Imparting the current to the wire basket, where practicable.

(b) Inserting a $^7/8''$ mild steel bar into the tinplate mass.

(c) Inserting a $^7/8$" mild steel bar with a 5" diameter disc welded to the bar 1" from the bottom of it.

3.1.3.5.3. Effect of Liquor Agitation on the Rate and Degree of Detinning

This was carried out at 70°C, using an 8% alkaline nitrite liquor (2N NaOH + 8% $NaNO_2$).

3.1.3.5.4. The Effect of Applied Potential on the Detinning Rate

This was performed at 70°C, using 8% alkaline nitrite liquor (2N NaOH + 8% $NaNO_2$), and impressing voltages of 1.5 volts to 9.5 volts across the cell.

3.1.3.5.5. The Effect of Temperature on the Detinning Rate

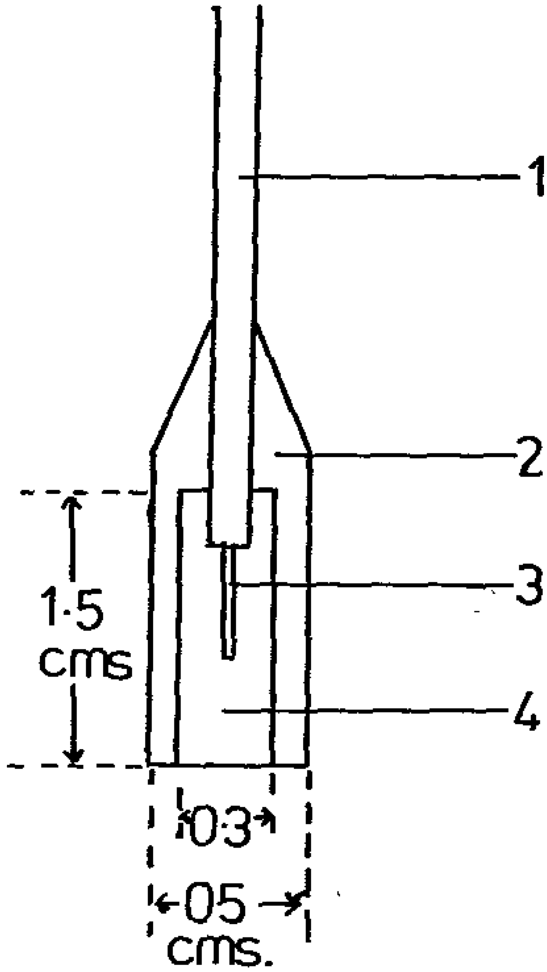
This series of experiments was carried out using an applied potential of 4.5 volts across the electrolytic cell of 8% $NaNO_2$ in sodium hydroxide liquor (2N NaOH) over a temperature range of 60°C to 80°C.

3.1.3.5.6. The Effect of Hydroxide/Nitrite Liquor Contact before Electrolysis

Samples of tinplate were soaked in the detinning liquor for a predetermined time before a current was applied. The liquor temperature was 70°C and the potential was 1.5V.

3.1.4. The Reference Electrode

In order to carry out electrochemical analyses on a pilot plant,



KEY

(1) insulated wire
(2) polythene
(3) bared wire
(4) cadmium head

Fig. 3.5. The Electrode.

a rugged, stable reference electrode was required. The reference electrode used in hot strongly alkaline liquors is usually mercury/mercuric oxide (Hg/HgO), but such a cell is not suitable for an industrial plant.

Elements from groups IB, IIB, IIIA, IVA and VA were preferred, due to the stability and low solubility of their oxides or hydroxides. Typical elements used were silver, zinc, cadmium, indium, lead, antimony and bismuth. Of these cadmium was considered to be the most reliable.

A few grams of cadmium metal were melted in a crucible and cast in a "Plasticene" mould which had some stripped, single core, 3 amp electric wire inserted in one end. Due to the toxicity of the metals, this operation should be carried out in a well ventilated room, or preferably in a fume cupboard. The size of the cast ingot was about 1.5 cm long and 0.3 cm in diameter (see Fig. 3.5.).

When the ingot had cooled, the "Plasticene" mould was removed, care being taken not to break the connection with the wire. After cleaning, the ingot and the first few inches of wire were immersed in molten polythene, and then removed. On cooling, the ingot was sheathed in a rugged inert casing, preventing alkali attack of both the wire and the electrode.

The end of the ingot was cut off, to expose cadmium metal encased in polythene. Any surplus polythene could be removed at this stage with a sharp knife. The ingot was then immersed in a 2N solution of sodium hydroxide and an anodic current density of about 10 mA/cm^2

impressed onto it galvanostatically. After 30 minutes the polarity of the ingot was reversed for 10 minutes. This was to prepare the exposed metal for oxidation. The ingot was then made anodic again for 45 minutes. In order to reduce hysterèsis of the electrode it was immersed in a boiling solution of sodium hydroxide for a few minutes, and then allowed to cool; this was repeated three times.

The electrode was tested against a standard Hg/HgO reference[94] electrode as supplied by Russell pH Ltd., Auchtermuchty, Fife, Scotland. The Hg/HgO electrode is reported not to suffer from hysteresis.[329] Typical hysteresis for the cadmium/cadmium hydroxide reference electrode was found to be about 15 mV when cycled between 80°C and 100°C. Different electrodes varied from each other by less than 25 mV at 95°C.

For further protection, the reference electrode was inserted into a piece of rugged nylon or P.V.C. tubing to reduce the possibility of damage by sharp tinplate. The electrode was found to be stable in hot alkali and did not deteriorate with time.

Due to the structure of the electrode, it is possible to reduce it, but care has to be taken to ensure that the electric wire is suitably wetted by the cadmium, and that the wire does not penetrate the head of the electrode.

Characterisation of the cadmium/cadmium hydroxide electrode had been carried out by de Bethune et al[103], who gave a value of -0.809V (vs. S.H.E.) at 25°C. They also calculated the potential shift due to temperature (25°C to 100°C) to be -0.143 mV per degree centigrade for a thermal shift, and -1.120 mV per degree centigrade for an isothermal shift. The temperature variance compares favourably with that given for the mercury/mercuric oxide values, which are -0.143 mV and -1.014 mV respectively. The isothermal shift at 95°C will be -78.4 mV for the cadmium reference electrode and -70.1 mV for the mercury electrode; this compares with -60.6 mV for the hydrogen electrode.[103]

It was found that the cadmium/cadmium hydroxide electrode is stable at elevated temperatures, and the potentials registered can be directly related to the standard hydrogen electrode.

There are both theoretical and practical advantages in using a reference electrode that avoids thermal junctions in a cell, because the electrodes would not be in thermodynamic equilibrium, and hence the Nernst potential cannot be determined in cells with a thermal junction.[122]

3.1,5. Analytical Procedures

3.1.5.1. Rutherford Back-scattering

Rutherford back-scattering (R.B.S.) is a technique giving semi-quantitative and qualitative information. A beam of alpha particles is fired at a target, which in this study was tinplate at different stages of being stripped. The energy spectrum of the particles scattered by Coulombic electrostatic repulsion from the atomic nuclei up to a depth of 3 μ from the surface, was analysed. The incident particle energy must be of sufficient magnitude not to interact with the electrons before reaching the atomic nuclei (i.e., >0.5 MeV) but must not be of sufficient energy to disrupt the nuclear structure (i.e., <3 MeV).

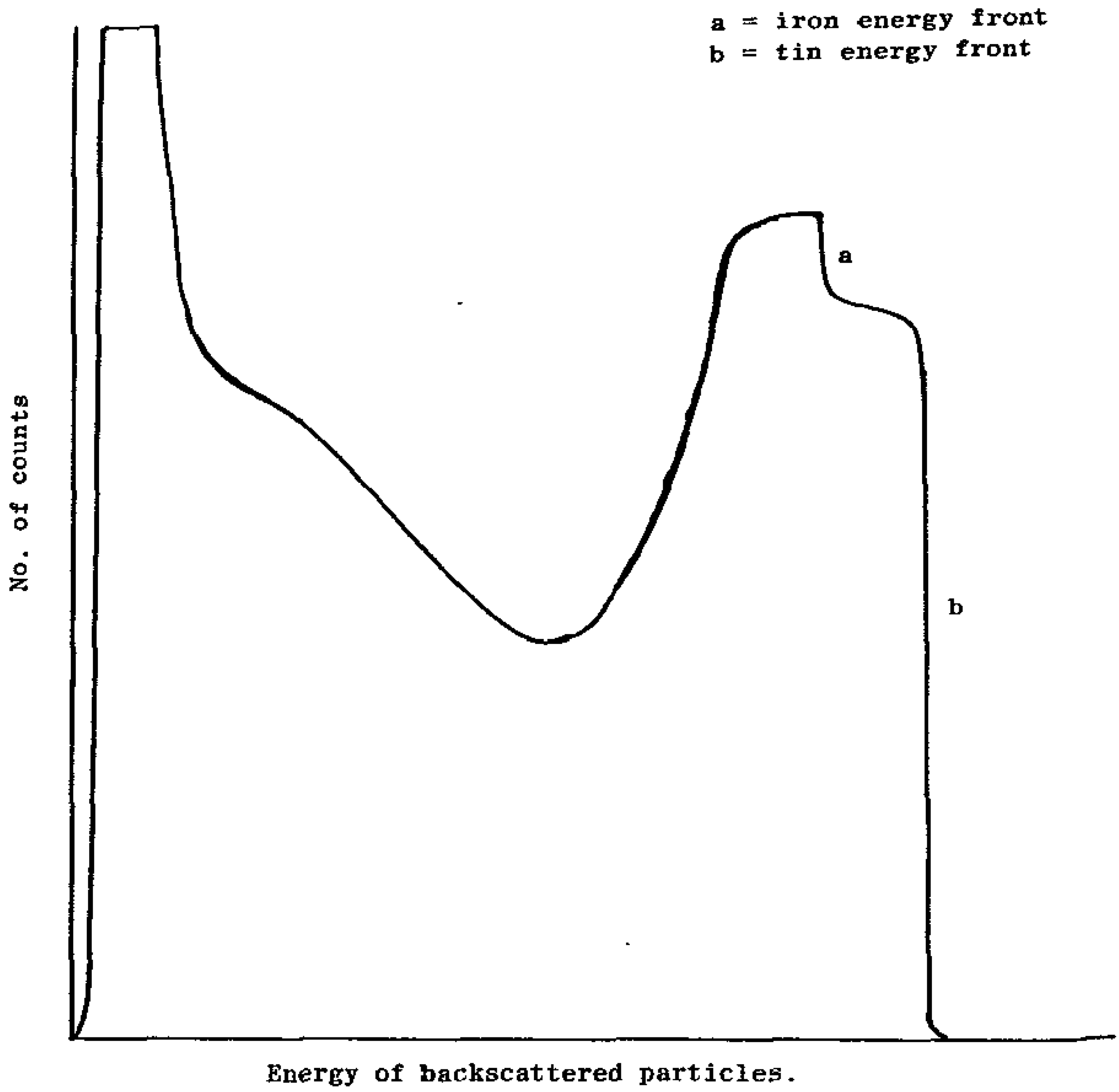


Fig. 3.6. A stylised Rutherford Backscattering Spectrum.

During scattering both momentum and energy of the system are conserved, with the result that the energy of the scattered particles is a function of:

(a) the incident radiation energy,

(b) the mass of the nucleus, and hence atomic number; the higher the mass, the greater the recoil energy,

(c) the scattering cross-section of the target nuclei, which is also a function of atomic number; the higher the cross-section, the higher the probability of a collision,

(d) the depth at which the nucleus is physically situated within the target; the deeper it is, the greater the energy loss in both penetration and escape,

(e) the angle of scattering.

In practice only (b), (c) and (d) are relevant to the results, as (a) and (e) are kept constant.

In practise a beam of alpha particles is accelerated and deflected so that it strikes a sample of tinplate, usually about 1 cm^2, suitably mounted in an evacuated reaction chamber. The resulting back-scattered particles are detected and a count at different energies is performed. The count is computer controlled, and can be either a total count value or a timed count. An idealised trace is shown in Fig. 3.6.

The maximum back-scattered energy is virtually specific for an element, and represents the atoms on the surface of the specimen. The more vertical this front is, the purer the surface coating is, as will be shown later. The build-up of energy behind this front is the result of scattering events within the target, the particles having lost energy due to depth of penetration and collision with electrons.

If the surface, or near surface, is composed of more than one element, this will manifest itself as a stepped front, the different energies relating to the elements present. The presence of light elements is difficult to detect and assess accurately, although their presence shows as a reduction in the sharpness of the heavier element energy front and possibly by a slight variation in the lower energy profile.

Quantitative analysis is complex due to the relatively large numbers of factors influencing the energy spectra. Some computer simulation is now available, whereby the target is theoretically divided into strata 1000 Å thick and the proportion of various elements within each layer calculated. To do this with any degree of certainty, one needs to know how the depth profile of the elements varies, and since this is not yet available, only semi-quantitative information about the concentration profile is available.

3.1.5.2. Auger Spectroscopy

Auger spectroscopy is a method of surface analysis whereby the energies of emitted electrons (Auger electrons) from the surface are measured. The Auger electron energies are specific for a particular element.

The emissions are stimulated by a fixed beam source of energetic radiation; primary emission occurs as electrons are ejected from the energy levels within the atom and thus creating 'holes' in the electronic structure, initiating a chain of electron transitions into lower energy levels with resulting loss of energy by the electrons. This loss of energy is accommodated by the atom by emission of a secondary, or Auger, electron.

The Auger spectrum is recorded differentially in order to magnify any variation in energy and show it as distinct peaks. Unlike Rutherford back-scattering, this technique is more sensitive towards lighter elements, due to their simplier electronic configuration, and hence their lack of ability to accommodate the energy released by any other means except Auger electrons.

The technique is suited to qualitative analysis of surfaces, although it is possible to extend it to semi-quantitative assessment by the use of standardised spectra; it cannot, however, give any indication relating to how the elements are interrelated.

Analyses using Auger were carried out using conventional techniques consisting of progressively sputtering away the surface of the sample by bombarding it with a 500 volt beam of argon ions (Ar^+). It was difficult to obtain full profiles of the specimens because the surface layer thicknesses were not suitable, so consideration was given to using "Scanning Auger Spectroscopy". This technique combines a method of grinding away the surface with a ball indentor to give a highly tapered penetration into the structure of the layers, and then scan the revealed surfaces. Dr. J.M. Walls (Loughborough Consultants Ltd.), was unsuccessful in this adaptation of the process due to excessive tin-smear of the plating.

3.1.5.3. Metallography

All specimens were mounted in cold thermosetting resin ('Araldite' HY 951 and MY 753) in order to reduce, as far as possible, the possibility of further thermal effects on the tinplate. Once set, the mounting was ground on 600 grit silicon carbide paper followed by diamond polishing on 6μ nylon and 1μ Selvyt. Final polishing was carried out with γ alumina on Selvyt.

If the specimen had free tin on the surface, it had to be protected from 'tin-smear' by electroplating it with a nickel overlay. This was carried out by degreasing the specimen ultrasonically in acetone with 10% Quadralene and then removing any surface oxides by cathodic treatment in a proprietary alkaline cleaner (Canning 10/55 metal cleaner) at 65°C for approximately 10 seconds with an applied current density of 40 mA/cm^2.

After surface preparation, deposition of nickel was anodically carried out in a proprietary nickel plating solution (Canning Sulfree 80) at 65°C for 2-3 hours with an applied current density of 40 mA/cm^2.

Specimens were either mounted vertically, or with a taper. If horizontal mounting was required, the specimen was attached to a scanning electron microscope stub by double-sided sellotape, and no surface treatment would be carried out. A vertical mounting (cross-section) was mounted by putting two or three specimens in a support cradle, mounting in resin and then grinding and polishing the specimen. For tapered sections, the recommended angle is 5^{o} 43'[215], which gives a magnification factor of X10. To obtain this the specimen was measured to find its length, and then the diameter of a piece of wire was calculated trigonometrically so that the wire would elevate one end of the specimen to give the required angle. The wire was fixed to the specimen by "Rapid Araldite" in order to ease mounting.

Both optical and electron microscopy were carried out on the specimen.

3.1.5.4. Scanning Electron Microscopy

Scanning electron microscopy has been used to study the morphology of tinplate, and in particular, the alloy. The instrument used was a Cambridge S4 MkII, and the usual magnification was between one and five thousand.

The specimen was mounted in cold setting thermoresin, which was in turn mounted on a suitable stub. Due to the insulative properties of the resin, the specimen was connected to the stub by applying a streak of conducting paint over the resin.

During microscopic examination line scans were occasionally carried out, using X-rays. These gave qualitative elemental analysis, although quantitative results could be obtained if required. During X-ray scanning the radiation from SnL_{α} and FeK_{α} emissions were used.

Electron probe microanalysis was also carried out on the stereo-scanning equipment, and by prior calibration using pure standards, it is possible to obtain an elemental ratio, and hence be able to speculate on the molecular structures present.

3.1.5.5. Transmission Electron Microscopy

Transmission electron microscopy (TEM) was the predecessor to scanning electron microscopy (SEM), and requires a much more intensive sample preparation. In order to prepare the samples, a replication technique was employed, whereby the specimen was "copied" onto a carbon/platinum backing. There are, in fact, two replication techniques currently carried out, a single stage and a double stage.

The single stage replication technique consisted of sputtering the sample with carbon/platinum at an angle of 45°, in order to obtain shadowing, until the sputtered coating was between 500 and 1000 Å thick. The surface was then scribed into 3 mm squares using a sharp scalpel and the specimen transferred to a solution of 3% bromine in methanol. This solution attacked the specimen and the carbon replicas floated off; once off they were collected and washed in methanol, methanol/water and finally distilled water, after which they were transferred to microscope grids.

The double stage replication technique involved applying a 3% solution of nitrocellulose in amyl acetate to the specimen and allowing it to dry for about half and hour. The resulting film was then sputtered with carbon/platinum until the overlay was between 500 and 1000 Å thick, and removed from the specimen by adhering it to "Sellotape". The "Sellotape", with the replica attacked, was then soaked in trichloroethylene to dissolve the "Sellotape" glue and free the replica, which was placed on a microscope grid, transferred to a filter paper and wetted with amyl acetate to dissolve the nitrocellulose.

The two techniques both have their advantages; the single stage one is better for visual microscopy on the electron microscope, as the replica is more exacting in its structure, but the two stage process has the advantage of removing samples of the specimen, on which electron diffraction patterns can be carried out, and hence, hopefully, the various structures can be determined.

3.1.5.6. Wet Analytical Techniques

3.1.5.6.1. Determination of Tin

Tin determination was carried out in two ways:

3.1.5.6.1.1. Titration

A 10.00 gm sample of tinplate was dissolved in 150 mls of hot hydrochloric acid (1:1). After cooling 2 gms of aluminium were carefully added and allowed to reduce for 15-20 minutes. The flask was then allowed to cool. The flask was then closed by a bung with a spray bulb attached, and reheated to dissolve the precipitated tin. Once dissolved the spray bulb was sealed and the flash cooled rapidly in a bath of cold water.

The bung was removed, and a marble cube, 1 ml of soluble starch solution (1g/litre) and 2 mls of potassium iodide solution (10g in 100 mls H_2O) added. The liquor was then titrated against standardised potassium iodate solution (6.010g/litre) to a blue end point. The tin content can then be calculated, as 1 ml of the iodate solution is equivalent to 0.01 gms of tin.

If detinned steel is being analysed, the potassium iodate solution is diluted by a factor of ten and restandardised.

If the tin content of alkaline detinning liquor is required, 10 mls of the liquor is pipetted into a 400 ml flask and 30 mls of hydrochloric acid (1:1) added to neutralise the alkali and destroy any sodium nitrite which may be present. After the evolution of brown nitrogen dioxide has stopped, 2 gms of aluminium are added and the method carried on as above.

3.1.5.6.1.2. Atomic Absorption Spectroscopy

A known weight of tinplate (2.5 gms) was dissolved in 100 mls of 10N hydrochloric acid, and the resulting solution diluted by a factor of ten.

The instrument was calibrated, using standard solutions of tin in 1N hydrochloric acid, ranging in concentration from 0.25M to 0.0079M. The tin radiation monitored was from a tin lamp of wavelength 2246.1 Å.

The unknown tin analysis was then determined by comparison with the standard results.

3.1.5.6.2. Analysis of Lead in Tin

Conventional atomic absorption spectroscopy was not sufficiently sensitive for lead, especially in strong alkali, so work was carried out[300] to determine the optimum process. The original liquor was 2N NaOH, which was treated with conc. nitric acid to reduce the pH to a range of 8-10. 10 mls of 10% ammonium citrate solution were added and the pH adjusted again to the required value, with 25% ammonium hydroxide.

1 ml of 10% hydroxylammonium chloride is added and 2 drops of thymol blue indicator and aqueous ammonia until the solution turns to a blue-violet colour.

The solution is then extracted with several portions of a 0.001% solution of dithizone in carbon tetrachloride. Final extraction was made by 10 mls of dil. nitric acid from the combined organic extracts, and this solution was analysed for lead using an A.A-6 Atomic Absorption spectrophotometer equipped with a Perkin Elmer G.P.A.-72 graphite furnace and a Baird Atomic hollow cathode lamp (2833 Å). The graphite furnace was used for drying at 90°C (30 secs.), ashing at 550°C (35 secs.) and atomisation at 2000°C (15 secs.).

3.1.6. Heat Treatment of Tinplate

A study was carried out to ascertain the effect of thermal treatment of flow melted tinplate under conditions similar to those anticipated in incineration of used cans. Samples of E5.6/5.6 tinplate (5.6 gms of tin per square metre on each side of the plate) were supplied by British Steel Corporation Tinplate Division in Swansea, and specimens 2 cm x 18 cm cut from the sheets. The strips were drilled in one corner, whereby they were suspended by wire into an air circulating furnace which had been preheated to the required temperature. The wires were attached to the outside of the furnace in order to facilitate easy and rapid loading and removal from the furnace.

A range of temperatures, from 100°C to 600°C were examined, with samples of tinplate being held at these temperatures for between one minute and four hours. Temperature control was estimated at ± 5°C. To minimise errors in treatment periods, the approximate time taken for a specimen to reach the specified temperature was determined by means of a thermocouple welded to the surface of a dummy specimen, and connected to a chart recorder. Once established, actual thermal treatment times started after this heating-up period, which varied from ½ to 1½ minutes.

Analysis of the thermally treated strips was mainly carried out using a galvanostatic detinning process (see Section 3.1.3.1.), although other analytical techniques described in Section 3.1. were carried out. Control samples for each sheet were also analysed.

3.2. Industrial Experiments

A test plant was made available, by Batchelor Robinson, at their Llanelli plant, to undertake a series of electrochemical batch detinning experiments. The plant was managed with a high level of expertise, and it was not expected that the experiments would reveal any significant scope for improvement, but could nevertheless complement the laboratory studies.

The plant consisted of a tank of hot (about 95°C) 2N sodium hydroxide with four baskets 3' x 2' x 3' in it; between the baskets were steel cathodes, with one other at each end. A current was introduced by means of bus-bars to the baskets and the cathodes.

A 3 x 3 x 3 electrode array was wired into a detinning basket before being charged with scrap, clean, tinplate. The electrode used was cadmium/cadmium hydroxide ($Cd/Cd(OH)_2$), the details of which may be found in Section 3.1.4. Each vertical set of three electrodes was held in a perforated polythene tube of adequate rigidity that prevented the actual contact of the electrode with the scrap, although it did allow the active electrode head to be very close to the tinplate. The positions of the electrodes were reproducible from one experiment to the other.

A good voltmeter was used (Southern Electronics Ltd., SM 211) with a simple rotary switch connecting to each electrode in turn. So far as possible the voltage measurements were timed.

A series of experiments was carried out, using a standard which was the normal electrolytic detinning process as employed on the plant. This consisted of four baskets, each loaded with about 220 lb of scrap, and five cathodes; the current to each basket was 250 amps. Potentials were measured at convenient intervals, whilst the applied current was manually held constant.

The second experiment involved using one basket and two cathodes, and applying a total current of 250 amps to each side of the basket; this was to determine if the charge distribution could be improved.

The third experiment was essentially the same as the second, but with double the current applied, whilst the fourth experiment halved the applied current density by using two, connected, baskets, but with only 250 amps applied.

Expt.	No. baskets	No. cathodes	Wt. tinplate per basket	Temp. (°C)	Current input per exptl. basket
1	4	5	220 lb	95.5	250 A
2	1	2	237 lb	87.7	250 A
3	1	2	213 lb	98.8	500 A
4	2	2	246 + 245 lb	96.1	250 A (total)
5	1	2	205 lb	96.1	250 A

TABLE 3.1.

The final experiment was essentially the same as the second again, but the basket was insulated and the current introduced to the bulk by a copper bar thrust into the centre of the basket.

In experiment 1 the cathodes (2'4" x 2'4") were placed between the baskets and at the ends of the baskets; in all other experiments the cathodes were placed at either end of the experimental basket. In experiment 4 the two baskets were placed as close together as possible without allowing them to "short out".

The average surface of tinplate in each basket was 667 square feet (620,000 cm^2); hence, with a 250 amp input, the current density was about 0.38 A/ft^2 (0.38 mA/cm^2).

The basket conditions are summarised in Table 3.1.

4. RESULTS AND DISCUSSION

4.1. Chemical Acidic Detinning

A series of experiments were conducted to evaluate the possibility of using an acid system for the removal of both tin and alloy from tinplate. Hydrochloric acid attacks tinplate readily, but it also attacks the base steel, as well as the plant if it is metal. Consequently, it is imperative that the detinned tinplate and plant are protected from unnecessary dissolution.

The samples of tinplate used in this study were type D8.4/2.8, having an average tin coating of 5.6 g/m^2. Total dissolution of tin and alloy at room temperature, using 10N hydrochloric acid, took over 4 hours.

4.1.1. The Use of Antimony and Bismuth Salts to Inhibit Attack of the Steel

Antimony has been used[222] to protect steel from acid attack during analysis of tinplate. A 10N hydrochloric acid solution was used as a detinning standard for assessment of rates.

A 2% solution of antimony trichloride was prepared in 10N hydrochloric acid. It was found that the antimony solution removed the overlays in less than 30 minutes at room temperature, whereas the 10N hydrochloric acid took over 4 hours under identical conditions.

If antimony trichloride is replaced by bismuth trichloride the rate of tin dissolution is more rapid, indicating a catalytic effect as well as the reported protective effect.[223]

Antimony trichloride is known to form a complex acid ($HSbCl_4$) in the presence of hydrochloric acid. In the presence of tin, the acid may undergo the following reactions:

$$HCl + SbCl_3 \rightarrow H^+ + SbCl_4^- \qquad \text{eqn. 4.1}$$

$$2SbCl_4^- + Sn \rightarrow Sn(SbCl_4)_2 + 2e^- \qquad \text{eqn. 4.2}$$

$$Sn(SbCl_4)_2 + 4H^+ \rightarrow SnCl_4 + 4HCl + 2Sb \qquad \text{eqn. 4.3}$$

The presence of the tin antimonyl chloride intermediate has not been verified, as it is unstable and readily reduces to metallic antimony, which precipitates onto the steel as a black sponge which can easily be removed. An identical mechanism can be postulated for bismuth trichloride.

4.1.2. The Use of Transition Elements Salts

In order to protect the detinned steel from unwanted dissolution, it was decided to examine 2% solutions of cobalt nitrate, cupric chloride, chromium trichloride, nickel sulphate, ammonium molybdate, lead sulphate, ferrous sulphate, magnesium sulphate, zinc sulphate and cadmium sulphate dissolved in 5N HCl.

When lead and copper salts were present, visible elemental deposition occurred on the tinplate, but the metals then redissolved. Manganese, zinc and chromium salts had little effect on steel passivation, which would be expected due to their more negative reduction potentials relative to iron. However, the presence of cadmium, cobalt, molybdenum and nickel all appeared to reduce the steel dissolution, as predicted by the more anodic reduction potentials of these metals relative to iron. These results are based on purely qualitative observations of the amount of hydrogen evolved from the dissolving steel after being stripped of tin and alloy: the greater the degree of attack, the more hydrogen is evolved.

Due to contamination of the scrap steel, and the rigid compositional restrictions imposed on recycled steel, this method has been rejected as not industrially viable, but passivation should not be rejected. A stationary current-potential (overpotential-current) curve for iron in 1N H_2SO_4, under potentiostatic conditions, indicates that at potentials of up to 460 mV primary passivating films are formed[313], such that the current in the pores just compensates for the dissolution of the porous film in the electrolyte. Corrosion rate is independent of the potential, so the equivalent "corrosion-current density" remains constant until a secondary passivation layer begins to precipitate, at which point the primary passivation layer begins to redissolve (about 500 mV). The current density decreases owing to the low rate of corrosion of the secondary layer, and finally assumes a secondary, lower constant value corresponding to this new rate of corrosion, until oxygen begins to be evolved. By monitoring these reactions, passivation of iron is possible. If it is assumed that the Flade Potential is the same, numerically, as the passivation potential, then the potential required to passivate the iron can be determined at various pH's, and with the addition of phosphoric acid, the passivation may well be easier. There are numerous other passivating agents which may be applicable to the proposed acid system, such as nitrogen or sulphur containing organic molecules, ferricyanide, ferrocyanide, nitrates and nitrites. However, inhibitive anions are only effective at pH's more alkaline than a value which is dependent upon the anion. For chromate this is pH 1, for benzoate pH 6, phosphate pH 7.2 and hydroxide pH 12. Other factors affect the efficiency of the passivating agent, such as temperature and concentration; the effect of a potential will almost certainly affect the apparent range at which the reagent is active, but to what degree is not known.

4.1.3. The Use of Aluminium Trichloride

Since antimony and bismuth compounds catalysed the removal of tin by acting as a Lewis acid, the usage of aluminium trichloride was considered. Using 2% $AlCl_3$ in 10N HCl, it was noticed that the tin was effectively removed, but liquor preparation was rather violent for an industrial process if not carried out with extreme caution, so further studies were not pursued.

4.1.4. The Use of Phosphoric Acid

Immersed tinplate was detinned in 5% orthophosphoric acid in 5N HCl, but the alloy layer was not attacked. The alloy is clearly definable by its characteristic blue/grey colouration. This indicated that the alloy has some properties more closely related to iron than to tin.

4.2. Electrochemical Acid Detinning

Strips of tinplate were stripped in a glass laboratory beaker using varying strengths of hydrochloric acid at different current densities and temperatures.

The acid concentration was varied by simple dilution, whilst the temperature was maintained by a water bath.

4.2.1. Hydrochloric Acid

At room temperature (24°C) it was found that no matter what current density was imposed, if the acid concentration fell below 1.25N, the time required to totally detin was prohibitively long. Above 2.5N the rate did not significantly increase. If the current density was below 8 mA/cm^2 ($\sim$8 A/ft^2) detinning times were also excessively long, no matter what temperature or concentration of acid was used. At 50°C, using 1.25N HCl, the total detinning time required for 1 cm^2 of tinplate (D8.4/2.8) was 2.7 seconds at 12 mA/cm^2, but at 15 mA/cm^2 it was only 1.67 secs., whilst if the current density was reduced to 6 mA/cm^2, the time increased to 6.3 seconds. If the current density is increased from 12 mA/cm^2 by 25% the detinning rate is increased by a factor of 3, but if it is reduced by 50%, the rate decreases by almost 60%.

If an active liquor is used (i.e., stronger than 1.25N HCl) there is little difference in performance between 36°C and 48°C, but above and below these temperatures the rate increases or decreases accordingly. If the acid is less than 0.625N, total detinning may not occur, leaving the alloy layer as a residue on the steel.

Kunze and Willey[263] have suggested that the alloy layer may be more noble than the steel substrate, and hence protect the steel; this is in agreement with the above results, for even dilute hydrochloric acid reacts with iron, but it does not attack the alloy. Hence, if the alloy is to be removed, further dissolution of steel will be promoted, so it will have to be either passivated or removed from the liquor to prevent excessive dissolution. Due to the variability of tinplate on an industrial scale, removal is not a viable method, so chemical passivation would be required. It is known that phosphoric acid will passivate steel, so it was added to 5N HCl.

4.2.2. Hydrochloric Acid with Phosphoric Acid

The addition of 10N phosphoric acid (H_3PO_4) to 5N HCl at 24^{o}C, with an imposed current density on the tinplate of 9 mA/cm^2 did not appreciably affect the removal of tin, but alloy attack rate was reduced. At low concentrations of phosphoric acid (4%) the total detinning time per square centimetre was 3.65 seconds, compared with 2.85 seconds for 5N HCl, but if 10% phosphoric acid was present the time only increased to 4.16 seconds. At high phosphoric acid contents (20%) a steady detinning time of about 4 seconds is established.

4.2.3. Phosphoric Acid with Hydrochloric Acid

When 5N HCl was added to 10N phosphoric acid it was found that the very low amounts of hydrochloric acid (0 to 5%) had little effect on the tinplate. Phosphoric acid alone attacks tin with

Additive	Potential (mV)
none	-560
p-chloronitrobenzene	-55
m-nitroaniline	-60
o-nitrophenol	-75
m-nitrobenzoic acid	-90
p-aminophenol	-210
acetic acid	-210
thiourea	-215
o-dichlorobenzene	-260
urea	-270
oleic acid	-350

TABLE 4.1.

difficulty. Alloy layer attack was minimal at low hydrochloric acid concentrations; at 4% HCl content the detinning rate was 12 seconds/cm^2, but with 10% HCl, the rate was increased to 5 seconds/cm^2. If the hydrochloric acid concentration exceeds 6% by volume, the rate of tin removal increases, as does the alloy attack. The rate of tin dissolution is greater than that in hydrochloric acid alone. This trend continues until the hydrochloric acid volume percentage in the liquor exceeds 25%, at which point the relationship between the rate of tin removal and the overall rate of dissolution is constant, showing no passivation of the alloy by phosphoric acid.

4.2.4. Passivation of Iron in Acid by Organic Compounds

A range of organic molecules containing nitrogen, sulphur and/or halogens and carboxylic acids can passivate iron.[105,314,315] This can involve either physically adsorbing the molecule on to the surface of the electrode, or the formation of an inert layer which is chemically bound to the electrode. Various organic compounds, or ranges of compounds have been patented, and some typical ones have been studied, taking as a standard the reaction with 2.5N HCl at room temperature with an imposed current density of 8.5 mA/cm^2. No reference electrode was employed, but the potential across the reaction cell was measured, so the values quoted in Table 4.1. are suitable for comparison.

Under the strongly acidic conditions employed, the Flade Potential for iron is -0.58V[302], and this compares well with the potential across the cell of -0.56V.

The concentration of the passivating agent was 0.75% ($^{w}/v$) and was added to 2.5N HCl. The tinplate was then stripped galvanostatically with an applied current density of 8.5 mA/cm^2. The alloy dissolved at a potential about 180 mV more anodic than tin, the anode would then briefly become more anodic, but then revert to a more cathodic potential if it passivated; the lower the potential, the greater the degree of passivation.

p-chloronitrobenzene is the best inhibitor, although m-nitrobenzoic is the preferred reagent in industrial processes.[17] One factor worthy of note, however, is their toxicity. All aromatic compounds, including m-nitrobenzoic acid are at least moderately toxic, whilst m-nitroaniline and p-aminophenol are very toxic. O-dichlorobenzene has a 50 ppm permitted ceiling concentration in the atmosphere, implying that if breathed even for a short period it is dangerous, and p-chloronitrobenzene is highly toxic if adsorbed by the skin.

4.3. Overall Summary of Acidic Liquors

If all the factors are considered, it is difficult to suggest that an acidic process would be economically viable, because not only is there a base steel dissolution problem, but also possible dissolution of the plant. Passivation will not be very effective.

Chemically detinning plants are easier to passivate than are electrochemical processes, but the relative rates of reaction result in a variance of between factors of 5 and 20 in respect of the time required. The electrochemical rates are comparable between hydrochloric acid at room temperature and hot alkali liquours, the latter processes having the advantage that the liquor is not nearly as corrosive towards either the stripped steel or the metallic plant components. Hot acid can also produce highly corrosive vapours, which are industrially undesirable, so after assessing the problems involved in an acidic process, it was decided to examine the alkaline liquors as these would be more practical on an industrial scale.

4.4. Alkali Chemical Detinning

4.4.1. *Alkali Chemical Detinning Processes*

Although sodium hydroxide attacks tin at room temperature, it *has no effect on the* alloy layer. If the alloy layer is to be dissolved, the liquor has to be over 70°C to ensure a reasonable rate. The use of additives have shown some improvement on total detinning rate compared with alkali but at room temperature in laboratory glassware, detinning times were still very long (over 60 hours).

The most effective additive was sodium chlorite, followed by sodium persulphate and sodium polysulphide. The effect of polysulphide, however, was to form ferric sulphide on the base steel, reducing the value of it due to the high residual sulphur. All of the phosphate salts are effective detinning agents, and are capable of removing both tin and alloy without attack of the steel. Sodium nitrate and nitrite were also found to perform satisfactorily. Nitrite was better than nitrate because nitrate is reduced to nitrite before attack on tinplate occurs.[206] None of the other additives attacked the alloy at room temperature, even though tin dissolution occurred.

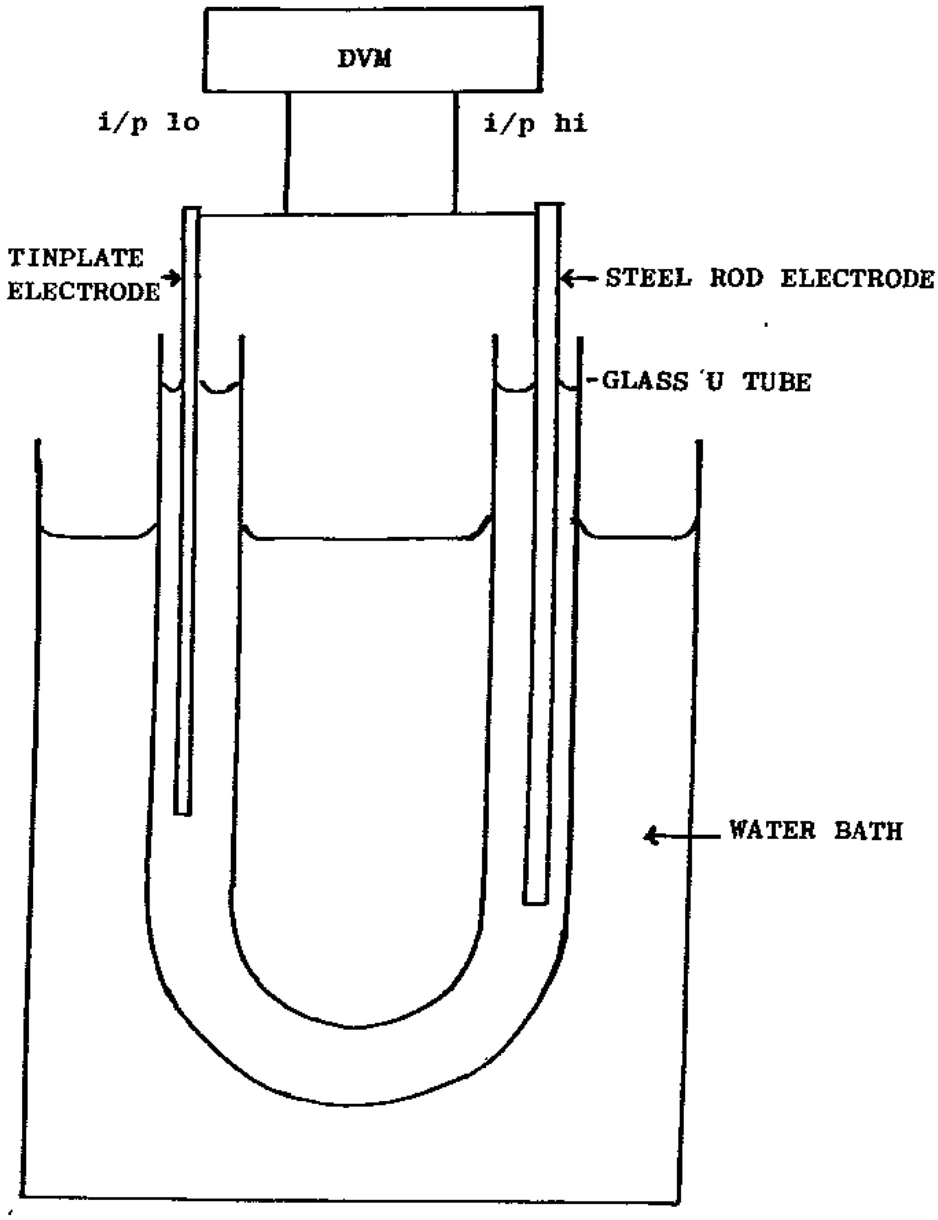


Fig. 4.1. The corrosion cell.

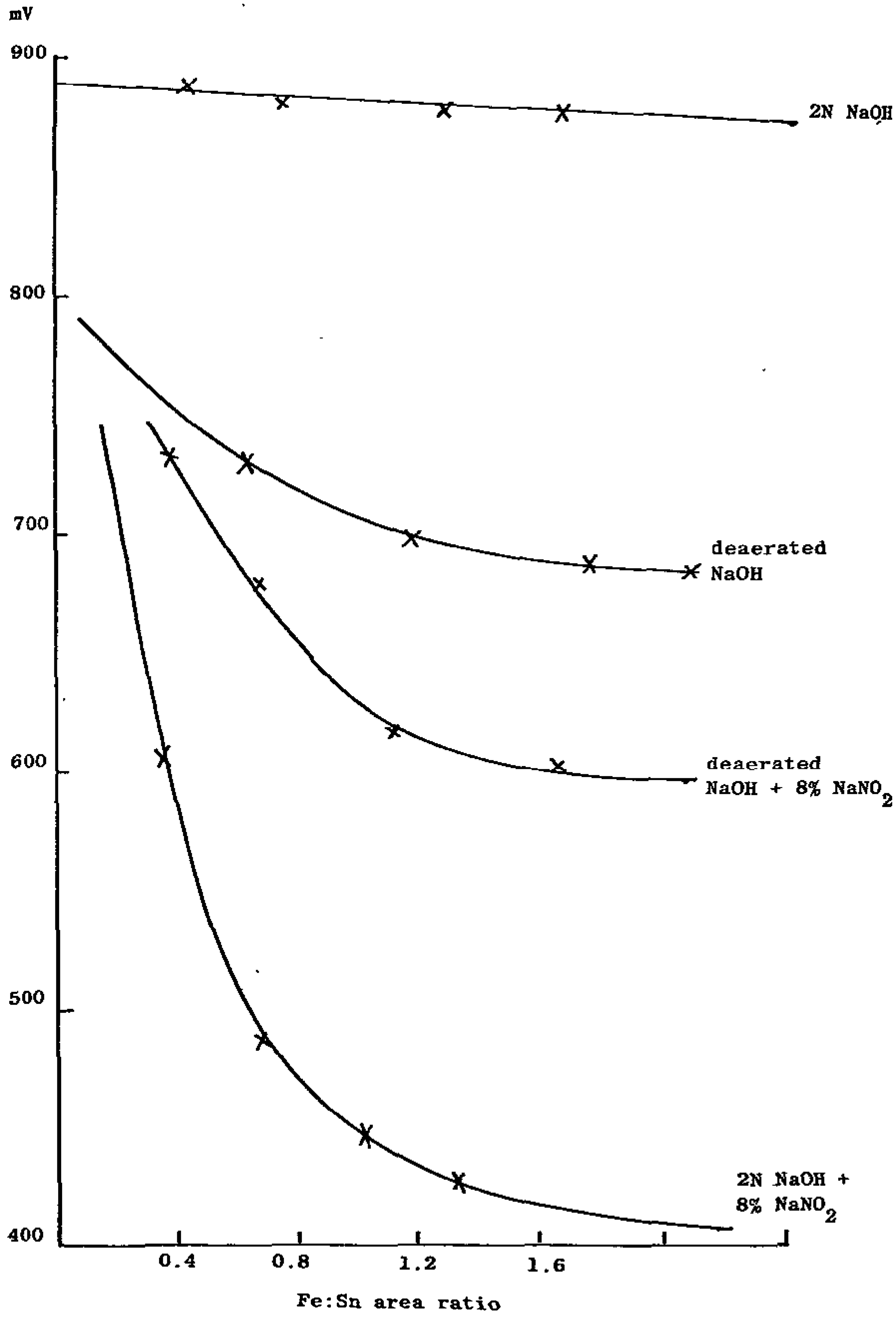


Fig. 4.2. Potential across cell at 85°C.

At elevated temperatures (95^{o}C) the rates of attack increased markedly, although the time generally required was still too long for an industrial process. It was noted that the region of tinplate just above the liquor surface invariably detinned much more rapidly than the immersed areas; this is due to the presence of oxygen.

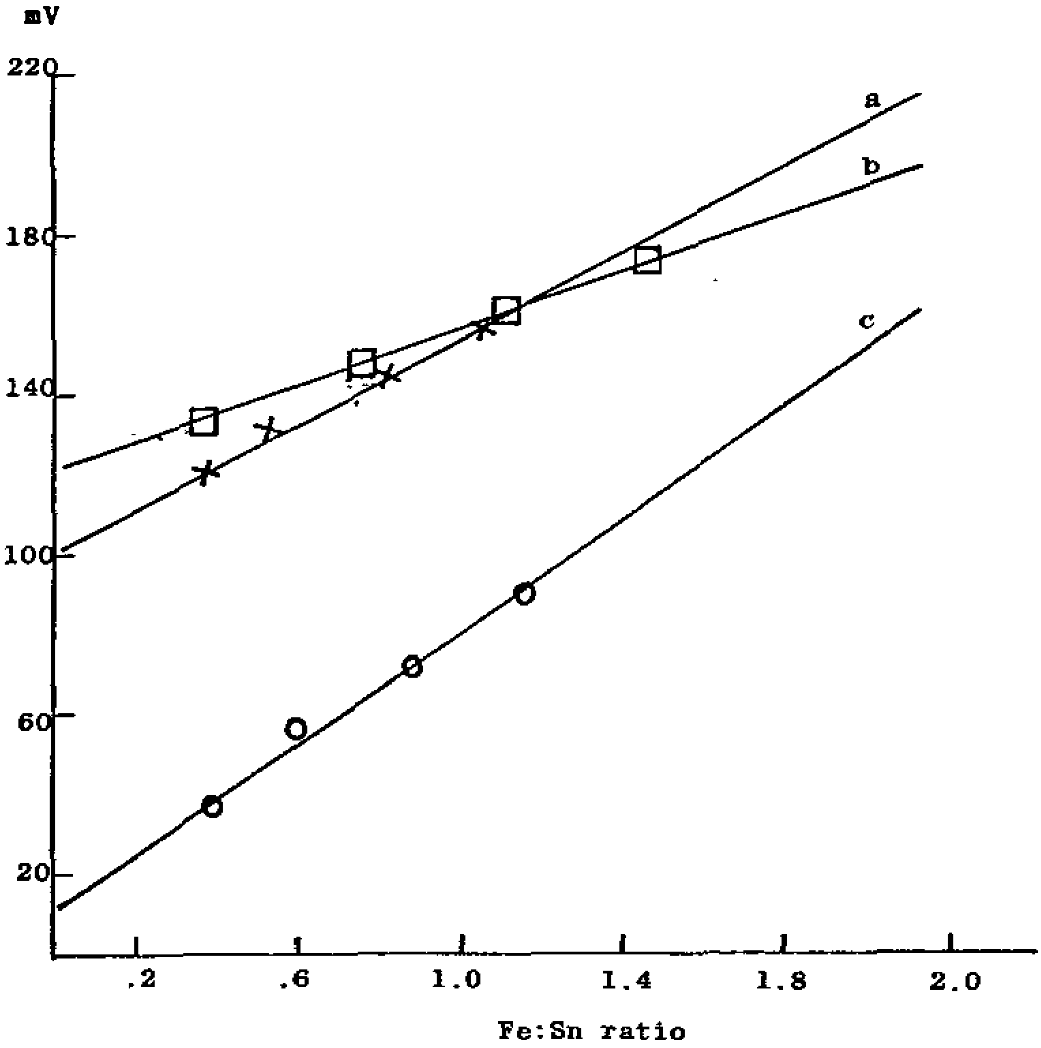
Alkali liquors have the advantage that they do not, generally, attack the base steel, and often have the property of protecting the steel from further atmospheric oxidation. In order to obtain comparable detinning rates to those of acidic liquors at room temperature, the alkaline liquor has to be as hot as possible.

Results obtained in laboratory glassware relating to chemical detinning rates were not consistent with those obtained on an industrial plant. This is due to the industrial plant being made of steel, so that a tin-steel corrosion couple is established.

4.4.2. The Tin-Steel Corrosion Couple

By using a split cell, comprising of a U tube filled with liquor, with an electrode inserted into each arm, and the whole system immersed in a water bath at 85^{o}C, it was possible to study the electrochemical couple.

A positive potential registered between the steel and tin electrodes if the tin was connected to both the steel electrode and the i/p lo terminal of a digital voltmeter (Figs. 4.1. and 4.2.). The potential increased as the amount of steel exposed to the liquor decreased. The current density on the tinplate increased as the amount of exposed steel increased.

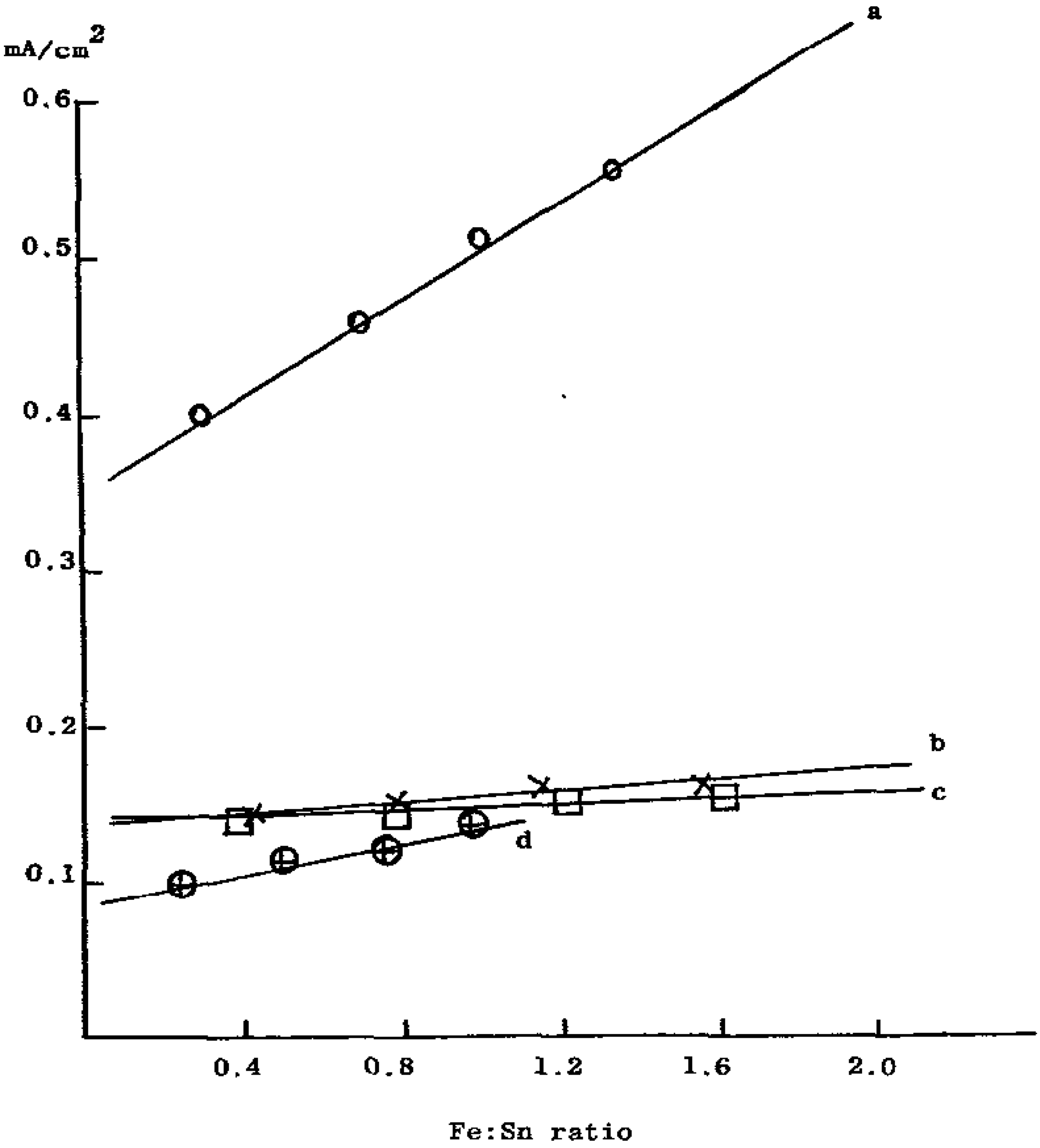


a = 2N NaOH + 3% $NaNO_2$ deaerated

b = 2N NaOH + 3% $NaNO_2$

c = 2N NaOH + 3% $NaNO_2$ + air on steel

Fig. 4.3. Affect of Fe:Sn on potential on the tin anode, measured against $Cd/Cd(OH)_2$ reference electrode (85^oC).



a = 2N NaOH + 8% $NaNO_2$

b = deaerated 2N NaOH

c = 2N NaOH

d = deaerated 2N NaOH + 8% $NaNO_2$

Fig. 4.4. Effect of Fe:Sn ration on current density on tinplate (85^{o}C).

If a cadmium/cadmium hydroxide reference electrode was inserted into the cell and connected to the i/p 'lo' terminal of the D.V.M. the potentials on both electrodes increased linearly with the amount of exposed steel in the presence of nitrite (Fig. 4.3.). The results indicate that the more steel available in the couple, the higher the current density will be on the tinplate, and hence the greater corrosion. This accounts for the high detinning rates claimed by Batchelor-Robinson on their chemical plants.

Since the current density increased on the tinplate as the amount of steel available for the couple increased, it can be inferred that the reaction creating the current was limited by the cathodic element of the couple. It can be shown (Fig. 4.4.) that the presence of oxygen in 2N NaOH causes an increase in current density on the tinplate, and aids the anodic dissolution reaction. The presence of nitrite in the liquor probably acts as a depolariser, accounting for the reduction in current density when it is present.

4.4.3. The Effect of the Couple on Detinning

The effect of the couple was compared for different liquors. Additional effects of air and the quantity of steel were also examined. A two litre beaker was filled with 360 gms of tinplate, and a perforated steel tube was forced into the centre of the mass. A $Cd/Cd(OH)_2$ reference electrode was placed in the mass, protected by a PVC sheath. The hot liquor (85^{o}C) was added, and the detinning process monitored both visually and by the potential established between the reference electrode and the tinplate.

Additive to 2N NaOH	Steel wool	Air	Detinning pot (mV)	Total time (mins)	Comments
None	no	no	-	243	still free tin
None	yes	yes	-	207	still free tin
3% $NaNO_2$	no	no	507	186	
3% $NaNO_2$	yes	no	652	140	
3% $NaNO_2$	yes	yes	670	90	detinned from the top of vessel
3% $NaClO_2$	no	no	821	68	residual liquor
3% $NaClO_2$	no	yes	813	37½*	contained iron oxide
3% NaCl (0.5M)	yes	yes	-	293	still free tin
0.5M NaOCl	yes	yes	-	366	not fully detinned but iron corrosion visible
0.5M Na_2SO_3	yes	yes	-	225	tin virtually untouched

*analysis of sample for residual tin showed <<0.06%.

TABLE 4.2.

If the amount of available steel for the couple was to be increased, steel wool was inserted inside the tube. Aeration was by pumping air to the base of the tube and allowing it to rise up the interior.

The results are shown in Table 4.2. and show that alkali by itself is not a very good detinning agent, even in the presence of air. Neither are alkaline sodium hypochlorite, sodium chloride or sodium sulphate liquors, but the presence of sodium nitrite or chlorite increases the detinning rate. If compressed air and excess steel are available the reaction is even faster for both.

During nitrite liquor detinning with excess steel wool and air, the top half of the bulk detinned within half an hour, this can be explained by either good liquor agitation due to the air, or a greater availability of air for the cathodic reaction of the couple.

With such a marked increase in the detinning rates due to the presence of an electrochemical couple, the addition of an imposed current should be even more effective.

4.5. Alkali Electrochemical Detinning

A range of experiments were conducted to assess the relative reactivity of different liquors suitable for an industrial detinning process. Most of the additives have been used to increase chemical detinning rates, but not electrochemical rates. The most important aspect was the reactivity on the alloy, as this is the slowest stage of the process.

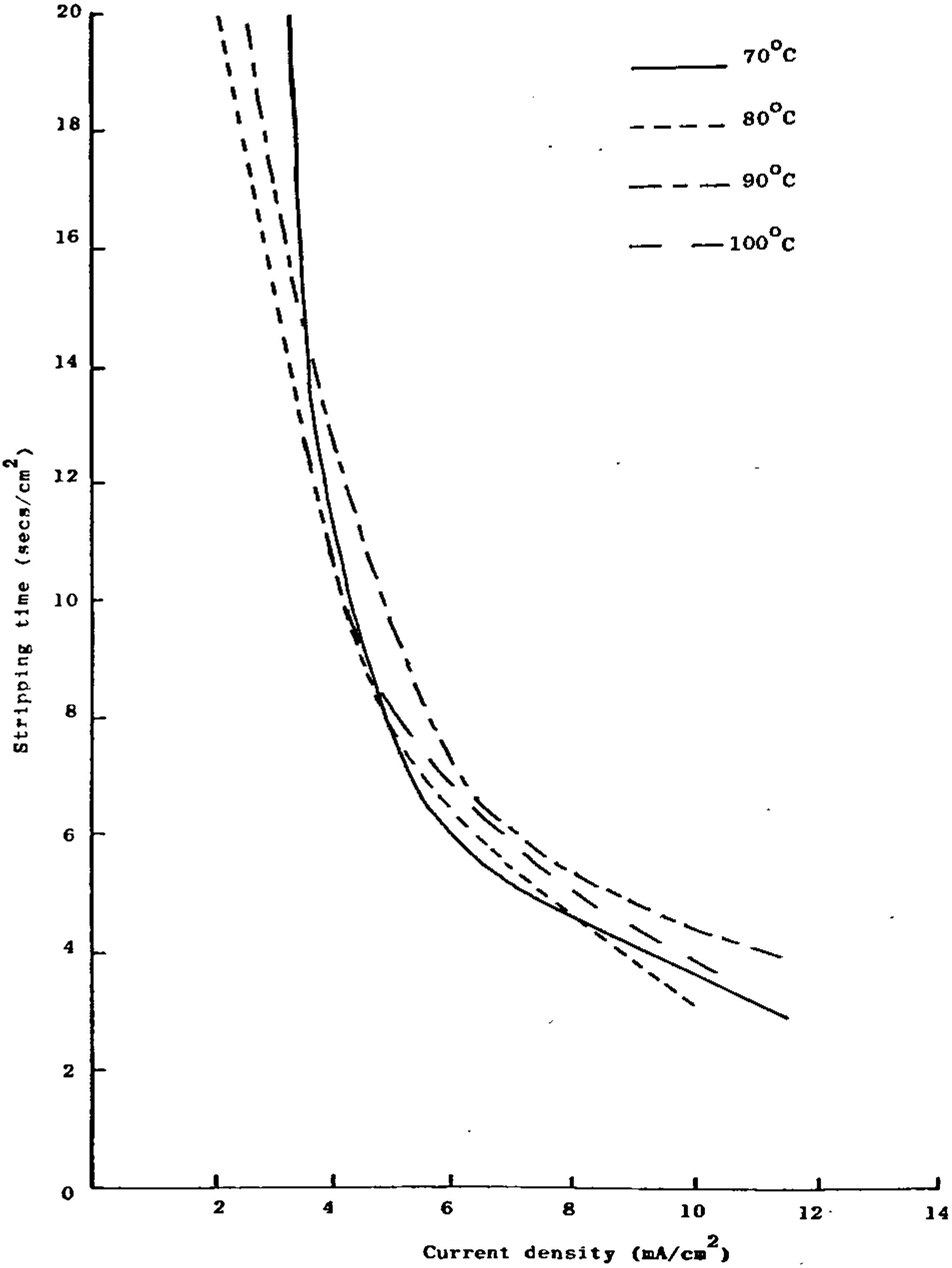


Fig. 4.5. Overall detinning rate vs. anodic current density for 2N NaOH at different temperatures.

The experiments were preformed galvanostatically in laboratory glassware, and hence are not directly comparable with plant results due to the effect of the iron-tin couple. Nevertheless, comparisons between individual liquors and relative dissolution rates can be made. A stylised detinning trace is shown in Fig. 3.2. The type of tinplate used was D8.4/2.8, which is equivalent to an overall tin covering of 0.56 mg/cm^2 or 5.6 g/m^2 (corresponding to a tin content of 0.5%), whilst a typical tin content of fully detinned steel was between 0.004 and 0.010% .

In order to assess the real detinning ability of electrochemical liquors, the overall reaction time has to be taken into account. It is possible that an electrochemically employed liquor has a chemical aspect of detinning, which would not be apparent on the electrochemical analyses. To account for this effect, the total experimental time to detin 1 cm^2 of tinplate was used, taking no account of the chemical or electrochemical components individually. In order to clarify the results, experimental points have been omitted, although the graphs have been plotted through the practical results.

4.5.1. Sodium Hydroxide

Although tin readily dissolves in alkali the alloy does not unless the liquor is hotter than 70^{o}C. Hence any electrolytic alkaline process ideally should be carried out at above 75^{o}C in order to avoid passivation of the electrode. Fig. 4.5. shows the effect of current density on stripping rate in 2N sodium hydroxide. The effect of temperature on the overall rate is slight, even at low current

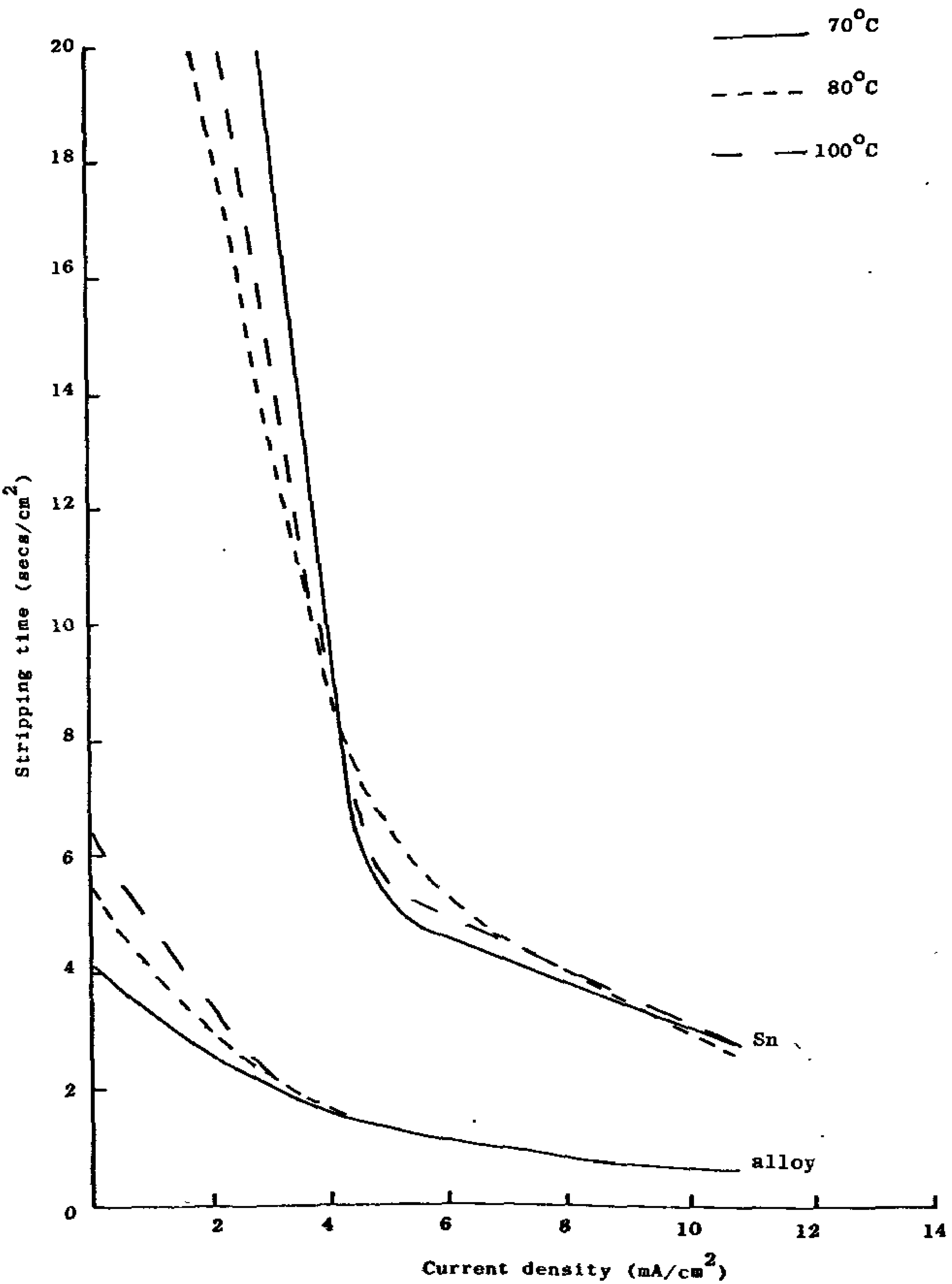


Fig. 4.6. Rate of attack of free tin and alloy vs. current density for 2N NaOH at different temperatures.

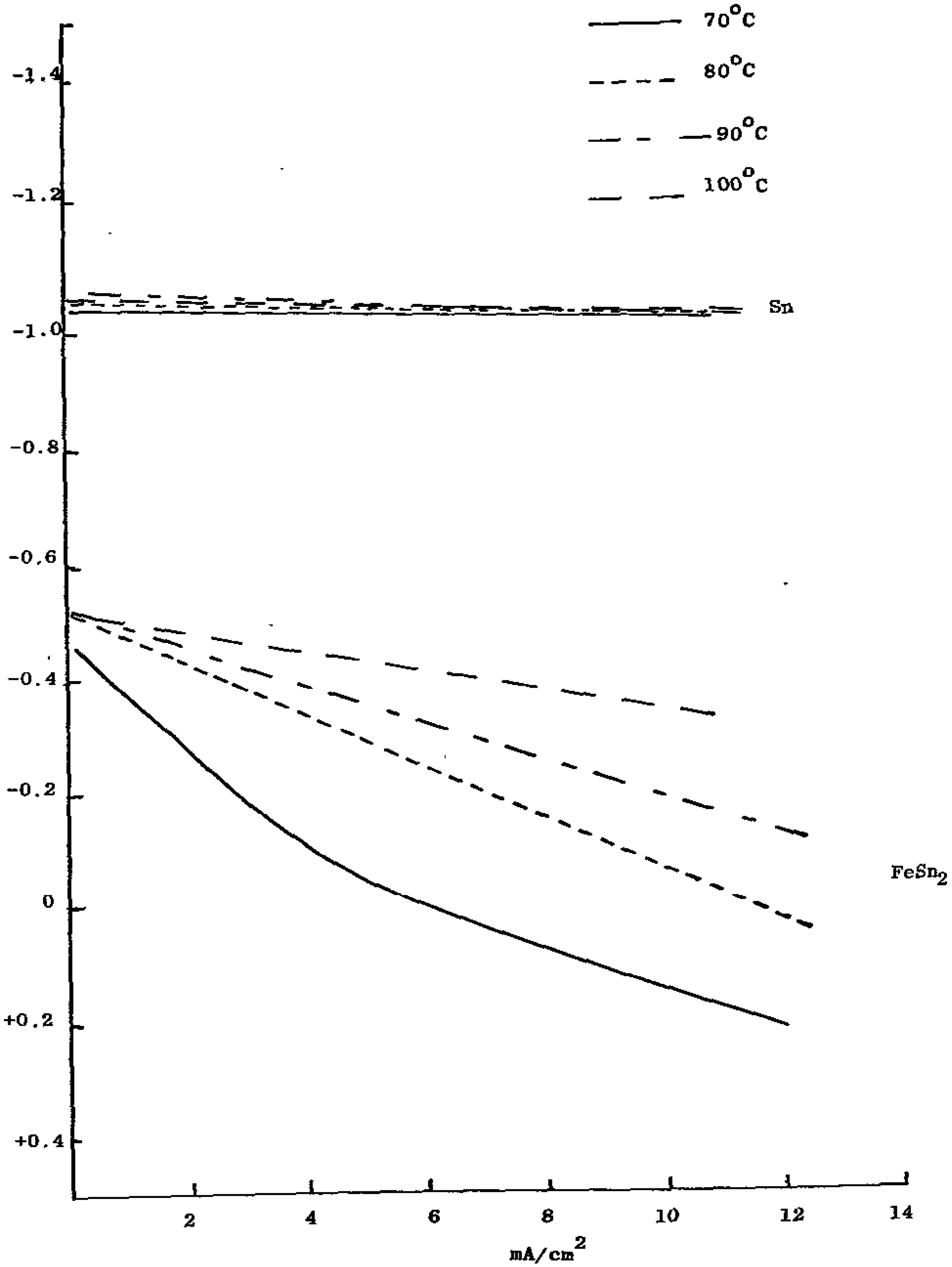
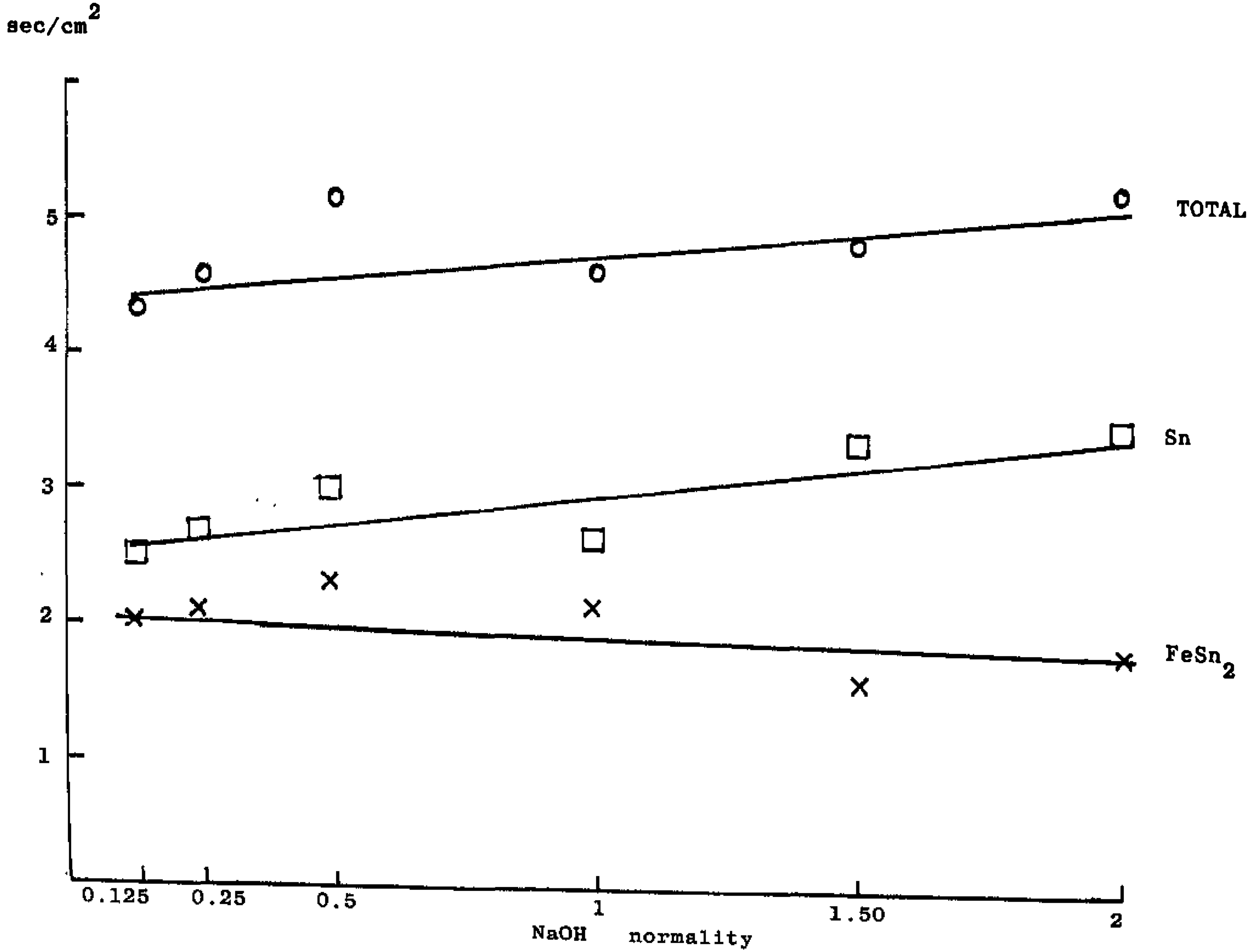


Fig. 4.7. Reaction potential (vs Hg/HgO) for tin (Sn) and alloy ($FeSn_2$) in 2N NaOH at different temperatures.

Fig. 4.8. Effect of concentration of sodium hydroxide on attack rates, at 90°C and an anodic current density of 9 mA/cm^2.



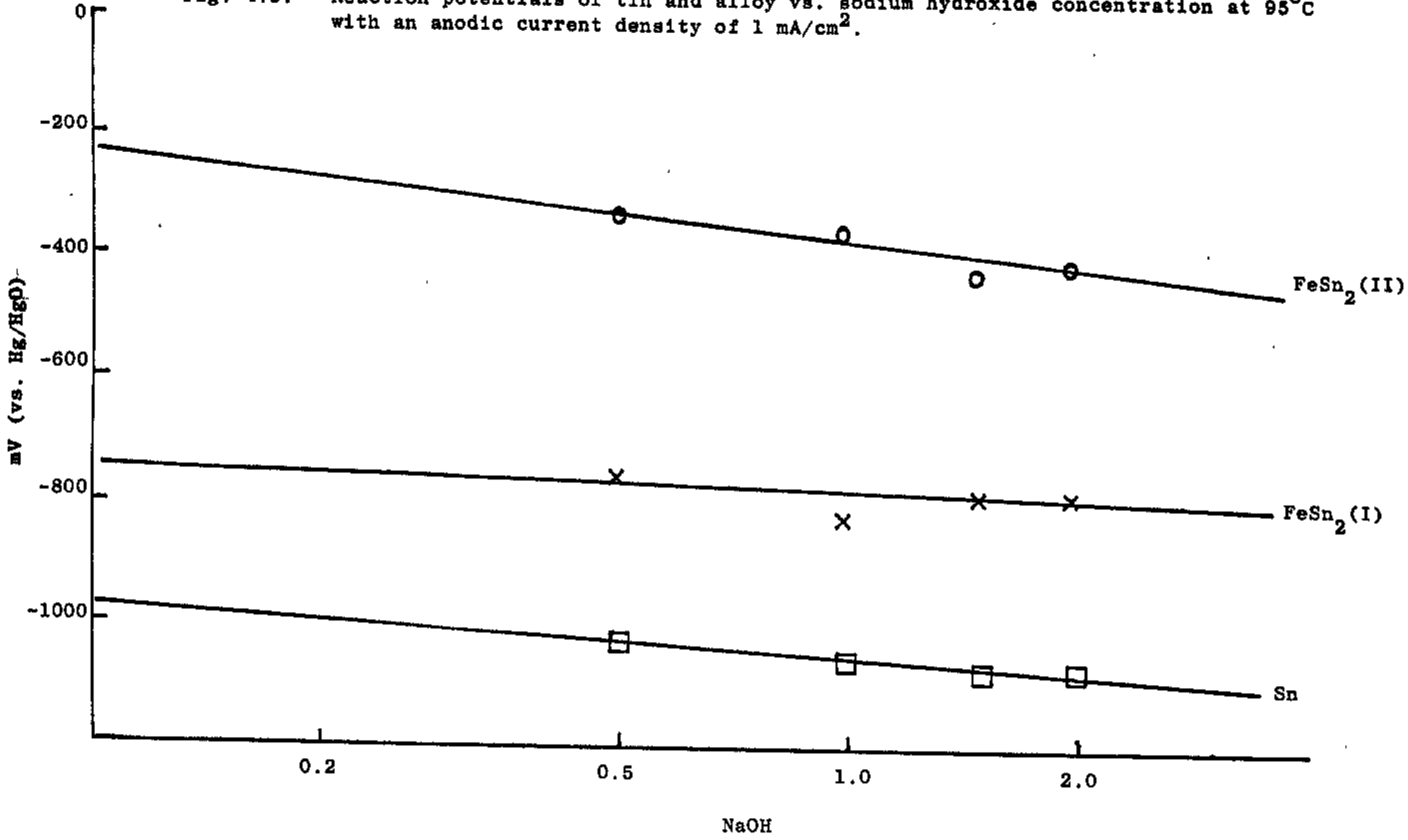
densities. The overall rate is composed of two fractions, the tin overlay and the alloy overlay, both of which dissolve Coulombically in alkali, although in other liquors tin may also dissolve chemically. Fig. 4.6. shows the relative rates of these two components. In clean tinplate the alloy represents between 10 and 20% of the total tin content, so the effective dissolution rate of alloy is approximately $^1/2$ or $^1/3$ that of pure tin, which would be expected.

The rate of alloy dissolution is not significantly dependent upon temperatures above 70°C at current densities is excess of 6 mA/cm^2. A constant stripping rate is also observed above 6 mA/cm^2.

The alloy reaction potentials (vs Hg/HgO) for tin and the alloy were studied at different temperatures. It was found that the tin potential did not vary significantly, remaining between -995 mV and -1120 mV over a wide range of current densities, as shown in Fig. 4.7. The alloy layer potential is more varied, showing both temperature and current density variations; at 6 mA/cm^2 a slight change in the potential vs. current density gradient occurs at all temperatures. The alloy layer reaction potential also becomes less anodic as the temperature increases.

Fig. 4.8. shows the effect of alkali concentration on overall detinning rate; the rate apparently decreased with increase in hydroxide concentration. This is due to the rate of attack on the tin, and not on the alloy, which is virtually independent of hydroxide concentration. This suggests that the alloy mechanism follows an adsorbtion path, whilst the tin dissolution rate is determined by the solubility of a product.

Fig. 4.9. Reaction potentials of tin and alloy vs. sodium hydroxide concentration at 95°C with an anodic current density of 1 mA/cm^2.



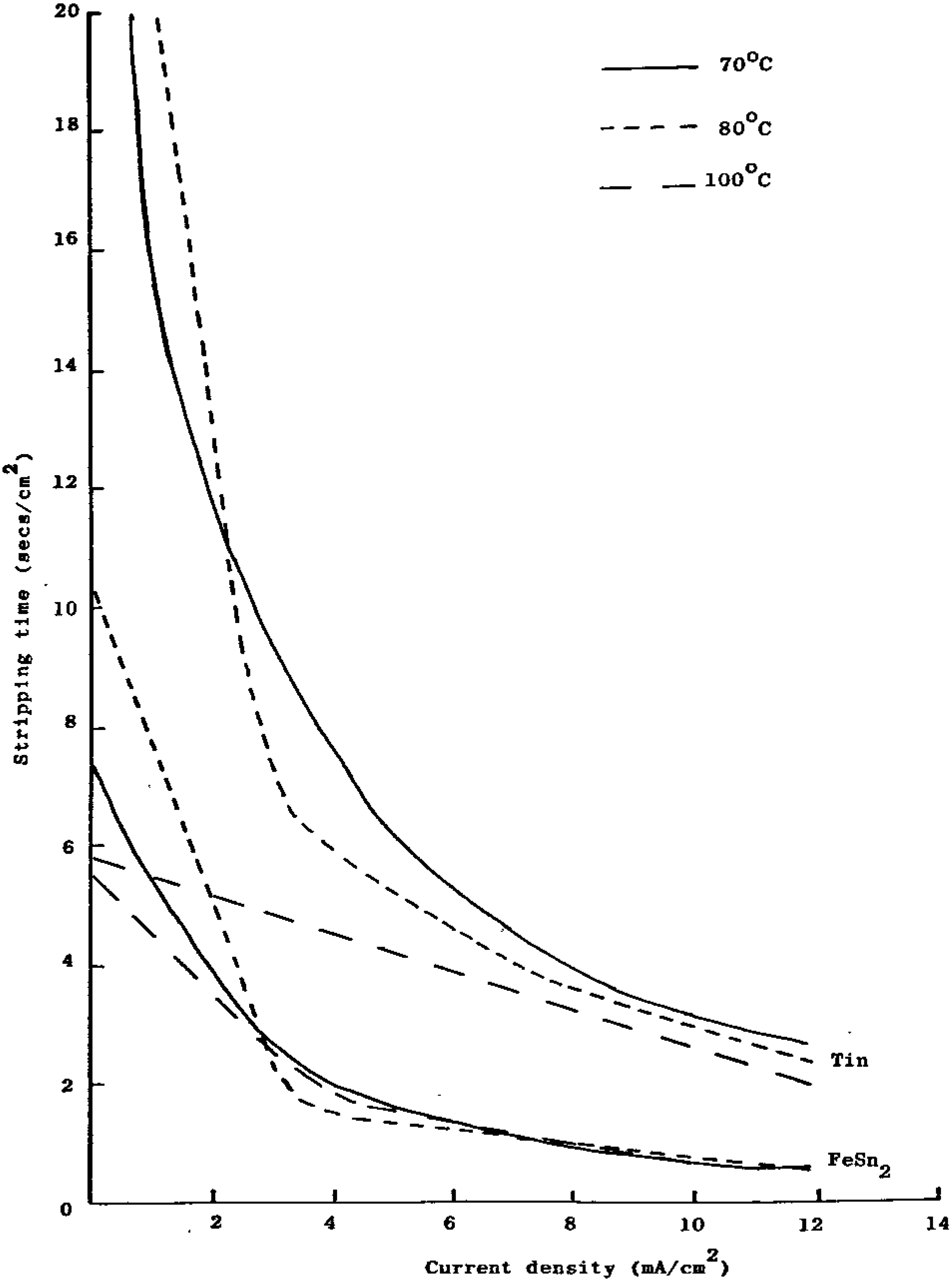


Fig. 4.10. Dissolution rates of tin and alloy vs. current density in 2N NaOH + 8% $NaNO_2$ at different temperatures.

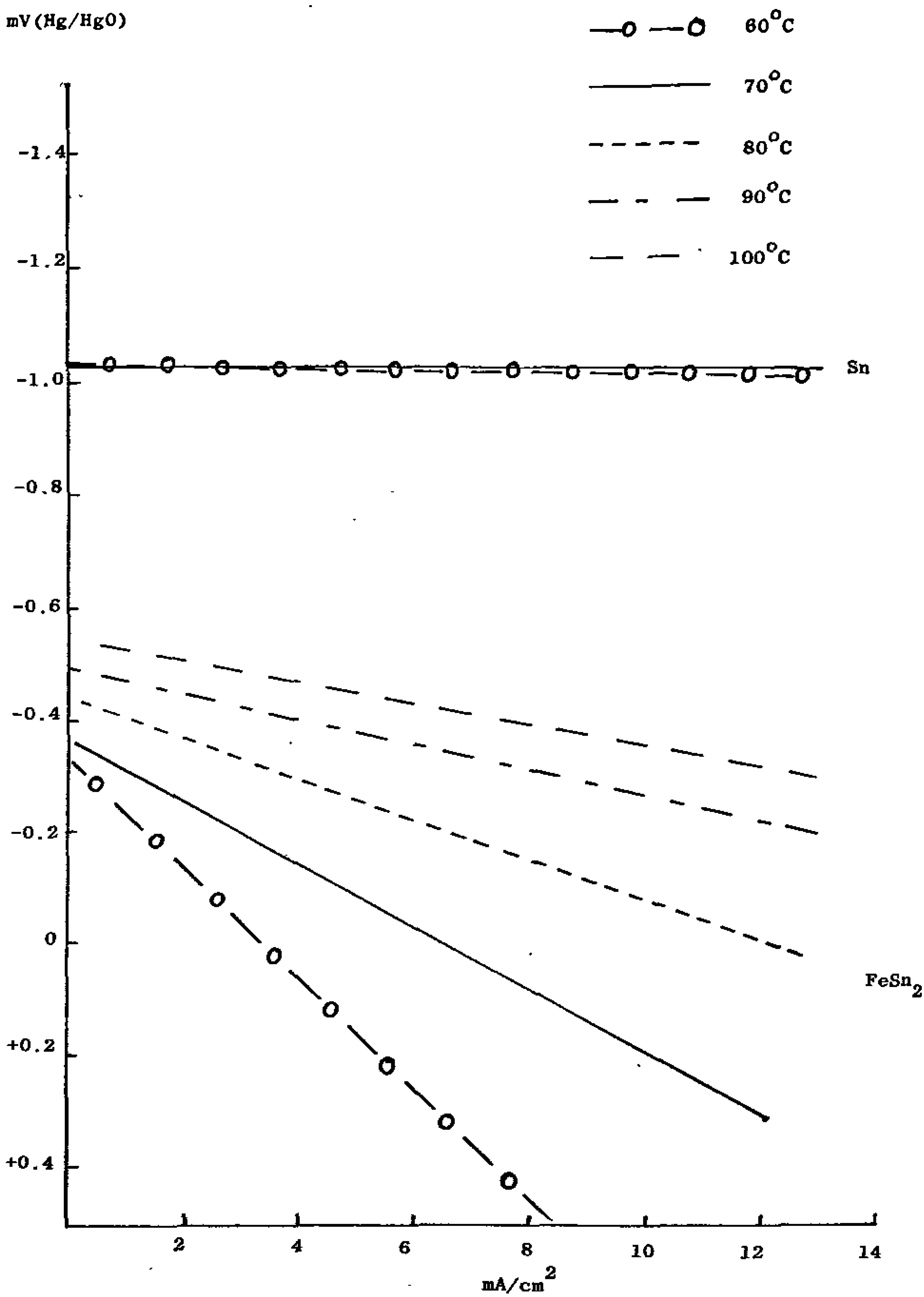


Fig. 4.11. Reaction potentials (vs Hg/HgO) for tin and alloy vs. current density in 2N NaOH + 8% $NaNO_2$ at different temperatures.

The effect of hydroxide concentration on the reaction potential at 1 mA/cm^2 current density at $95^{o}C$ is shown in Fig. 4.9. The tin potential varies by about 75 mV/decade, whilst the alloy varies about 150 mV/decade.

Between the stripping potentials of tin and the alloy is a plateau, which is only apparent at low current densities.

4.5.2. Sodium Hydroxide and Sodium Nitrite

Alkaline nitrite is usually associated with chemical detinning. The presence of nitrite improves the overall rate of detinning compared with ~~just~~ hydroxide, but the degree of improvement is dependent upon current density. At low current densities the improvement can be as much as 30%, whilst at high current densities it is only 10%. Fig. 4.10. shows the effect of nitrite on detinning times, but it should be noticed that any improvement in rate is only due to greater rates of dissolution of tin, and not alloy.

The reaction potentials for tin and the alloy are shown in Fig. 4.11. The tin potential remains relatively constant over a range of current densities and temperatures, but the alloy reaction potentials reveal a heavy dependence on both current density and temperature, as shown with alkali, strongly indicating that nitrite does not attack the alloy in an electrochemical process.

4.5.3. Sodium Hydroxide and Sodium Chloride

Alkaline sodium chloride is corrosive to tinplate, but in an

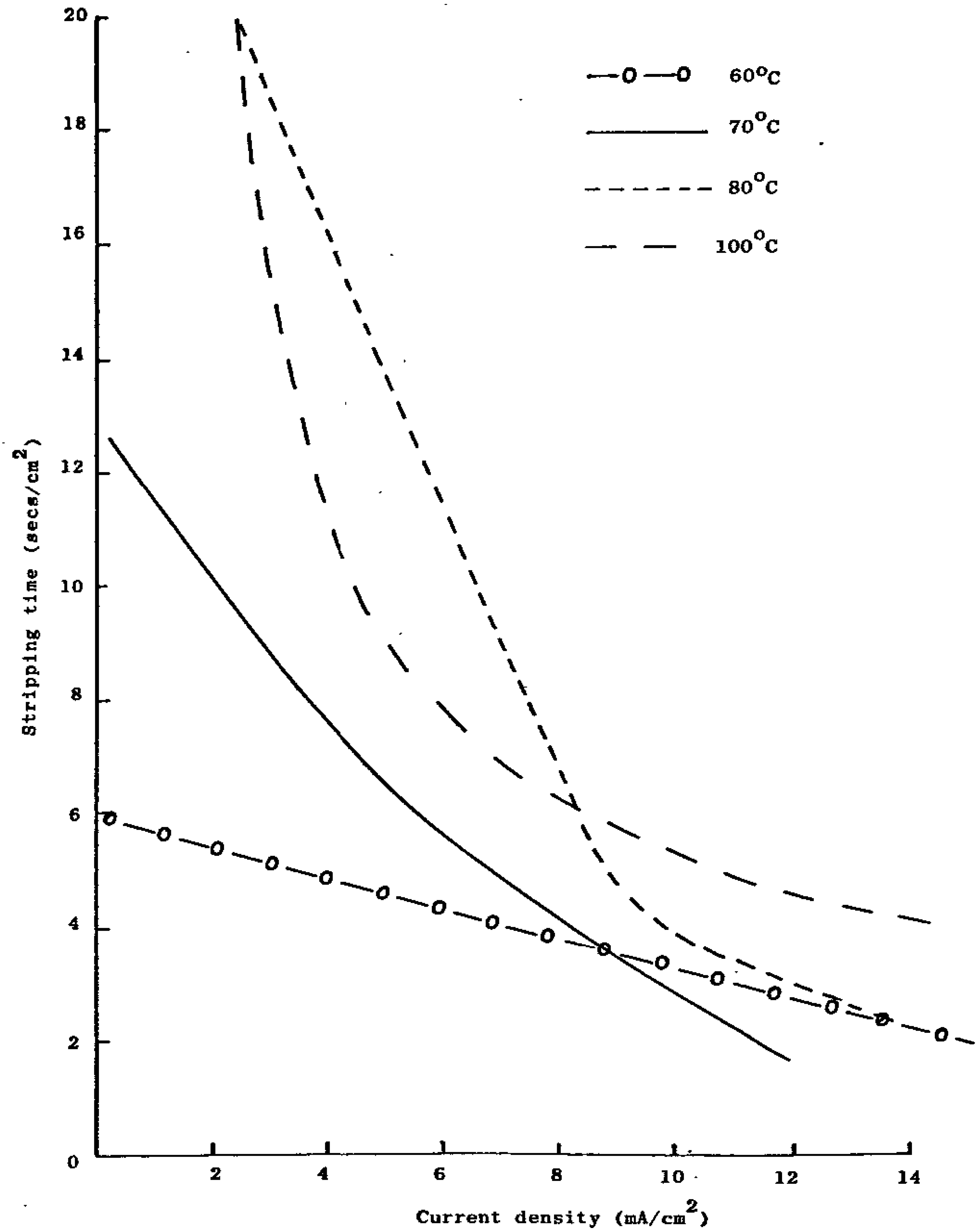


Fig. 4.12. Overall detinning rate vs. anodic current density in 2N NaOH + 8% NaOCl at different temperatures.

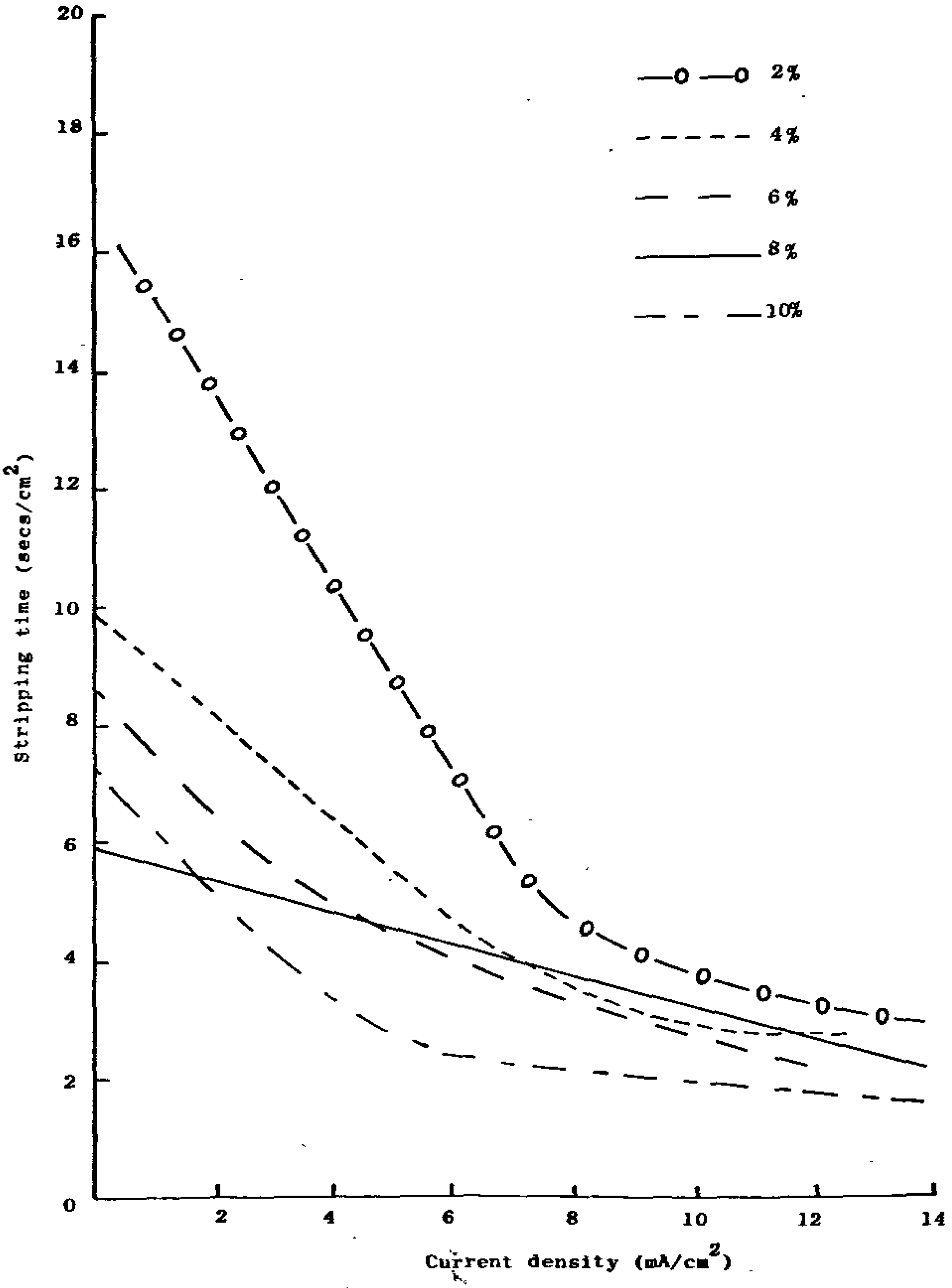


Fig. 4.13. Overall detinning rate vs. anodic current density for various concentrations of NaOCl in 2N NaOH at 60°C.

electrolytic process there is only a marginal improvement in rate. Corrosion of the steel through pinholes in the tin and alloy is marked, and causes the tinplate to appear blotchy with black or brown spots covering it.

Addition of 8% $NaNO_2$ to an alkaline solution of 20% sodium chloride had no effect on the detinning rate. This indicates that chloride ions do not affect electrolytic detinning processes.

4.5.4. Sodium Hydroxide and Sodium Hypochlorite

Alkaline sodium hypochlorite has been used as a chemical detinning agent[95], but not in electrochemical processes. As shown in Fig. 4.12., the reactivity of sodium hypochlorite is highly temperature dependent, below 50°C it does not fully detin the specimen regardless of current density, but at 60°C a linear relationship is assumed between overall detinning rate and current density. The most active range is between 60°C and 80°C; above this temperature range the hypochlorite is deactivated, and below it there is little attack on the alloy.

The effect of hypochlorite concentration at 60°C is shown in Fig. 4.13.; the rate of detinning is related to the concentration and current density, but at low current densities it is much faster than either alkali or alkaline nitrite. It is also active at lower temperatures.

At low concentrations (2 and 4%) a pink discharge was noticed

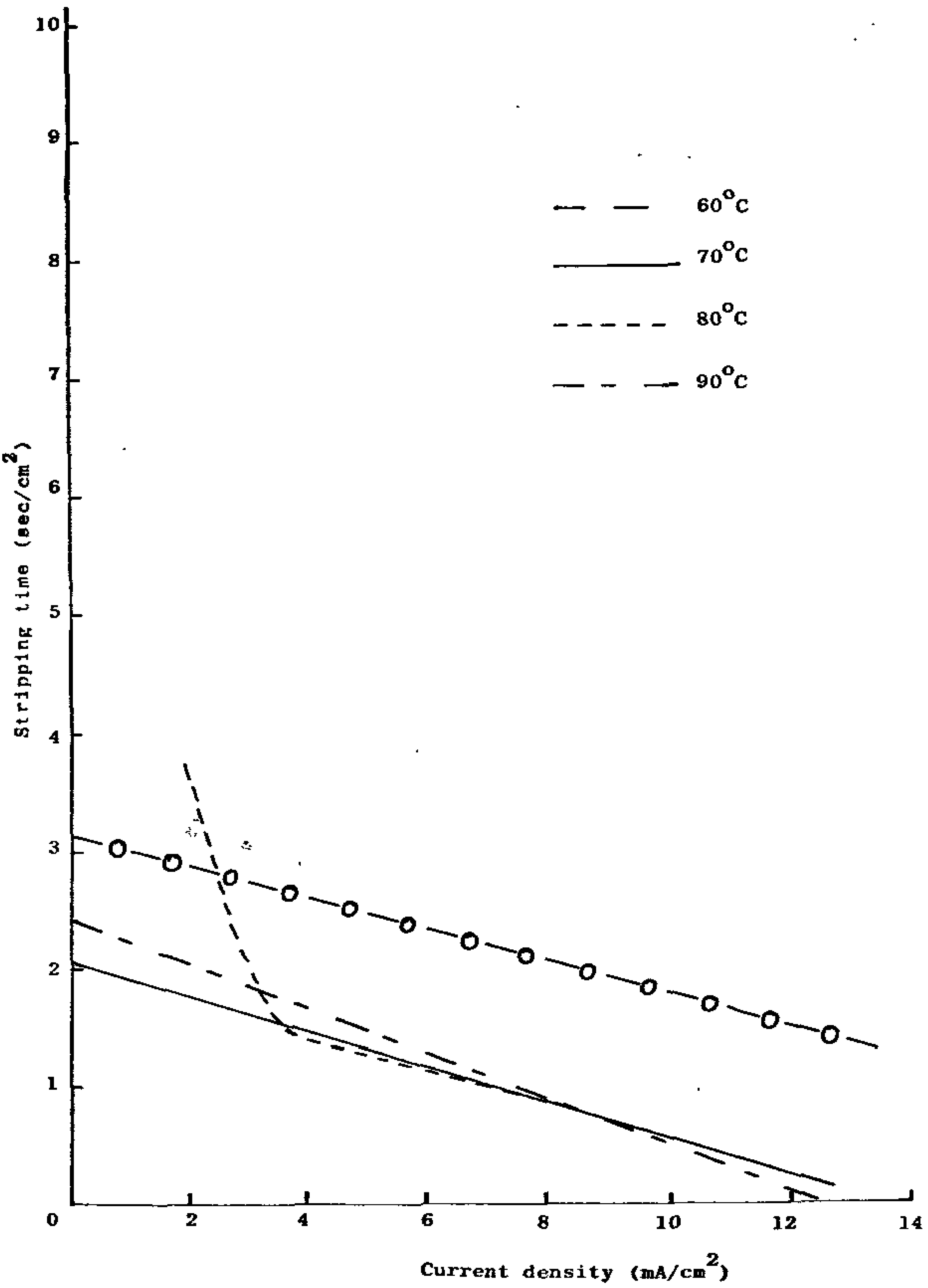


Fig. 4.15. Overall detinning rate vs. anodic current density for 2N NaOH + 8% $NaClO_2$ at different temperatures.

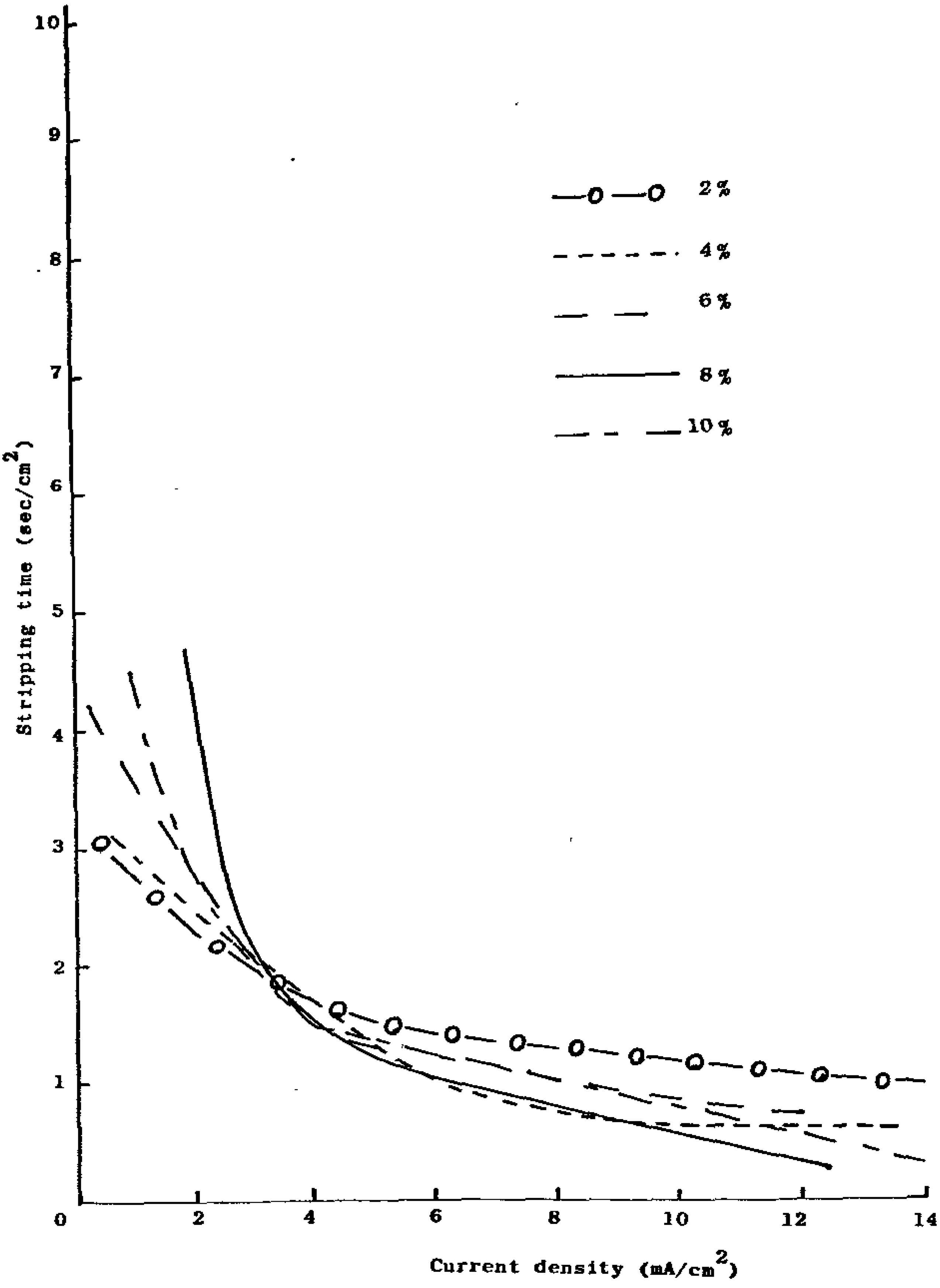


Fig. 4.14. Overall detinning rate vs. anodic current density for various concentrations of $NaClO_2$ in 2N NaOH at 80^oC.

at the anode; this was ascribed to the presence of the ferrate ion (Fe(VI) or FeO_4^{2-}).

Alkaline hypochlorite reacts at much lower temperatures than hydroxide alone, although at over 80°C the activity decreases. Hypochlorite attack is primarily on the tin overlay, and it has little effect on the dissolution of alloy.

4.5.5. Sodium Hydroxide and Sodium Chlorite

The use of alkaline chlorite has been patented[96] as a chemical detinning agent, but no reference is known relating to an electro-chemical process.

Fig. 4.14. shows that the overall rate for detinning in the presence of chlorite is much faster than for virtually all other oxidants. The rate is so rapid that the limiting factor is probably transport associated rather than kinetically linked. This is supported by the reaction potential being independent of the current density for both tin and alloy. These are -0.48V and +0.64V respectively (vs Hg/HgO) at 80°C, over a current density range of 3 to 10 mA/cm^2.

The final tin content of alkaline chlorite detinned steel was <0.005% for tinplate and 0.004% for totally alloyed tinplate at 250°C.

During the electrochemical detinning process the liquor appeared to turn a pale yellow colour, which was attributed to the evolution of chlorine dioxide.

Fig. 4.15. shows the rate of tin removal to increase with

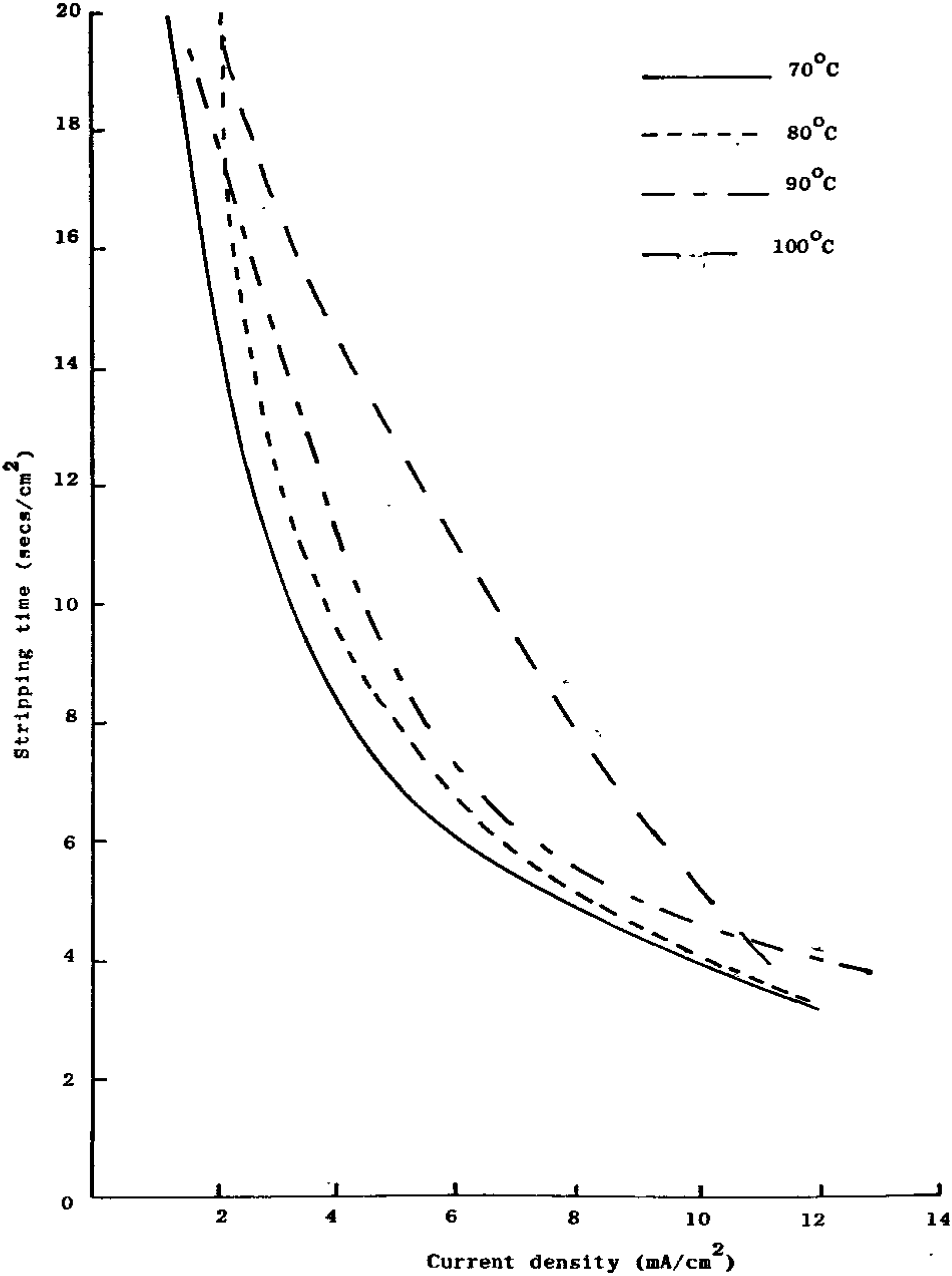


Fig. 4.16. Overall detinning rate vs. anodic current density for 2N NaOH + 8% $KClO_3$ at different temperatures.

temperature, whilst alloy attack rates do not increase greatly over $80^{o}C$; hence it is not worthwhile to exceed $80^{o}C$ on a plant. At above $90^{o}C$ it was noticed that the anode discharged a red colouration. This is attributed to the formation of the ferrate ion, as has been mentioned in Section 4.4.4. with respect to hypochlorite.

The effect of chlorite concentration at $80^{o}C$ was minimal, except for low concentration, as shown in Fig. 4.14., where the rate was less than for more concentrated liquors. The degree of error in detinning times is about 0.25 sec/cm^2, which is of little consequence when using conventional liquors, but when chlorite is used, this error represents nearly 50% of the quoted rates.

The advantage of chlorite is the rate of tin removal, which is increased by a factor of ten compared with alkali rates, but alloy attack is also increased by a factor of two. This would be advantageous in the treatment of used cans. The rate of alloy attack is related to both current density and temperature.

4.5.6. Sodium Hydroxide and Potassium Chlorate

The addition of chlorate to alkali had only a slight effect on the overall rate of detinning; the most obvious effect being at low temperatures ($70^{o}C$) as shown in Fig. 4.16. At higher temperatures it had little beneficial effect, and could be compared with hypochlorite in reactivity.

The lack of reactivity can be ascribed to chlorate, and perchlorate, being difficult to reduce, although it is possible to

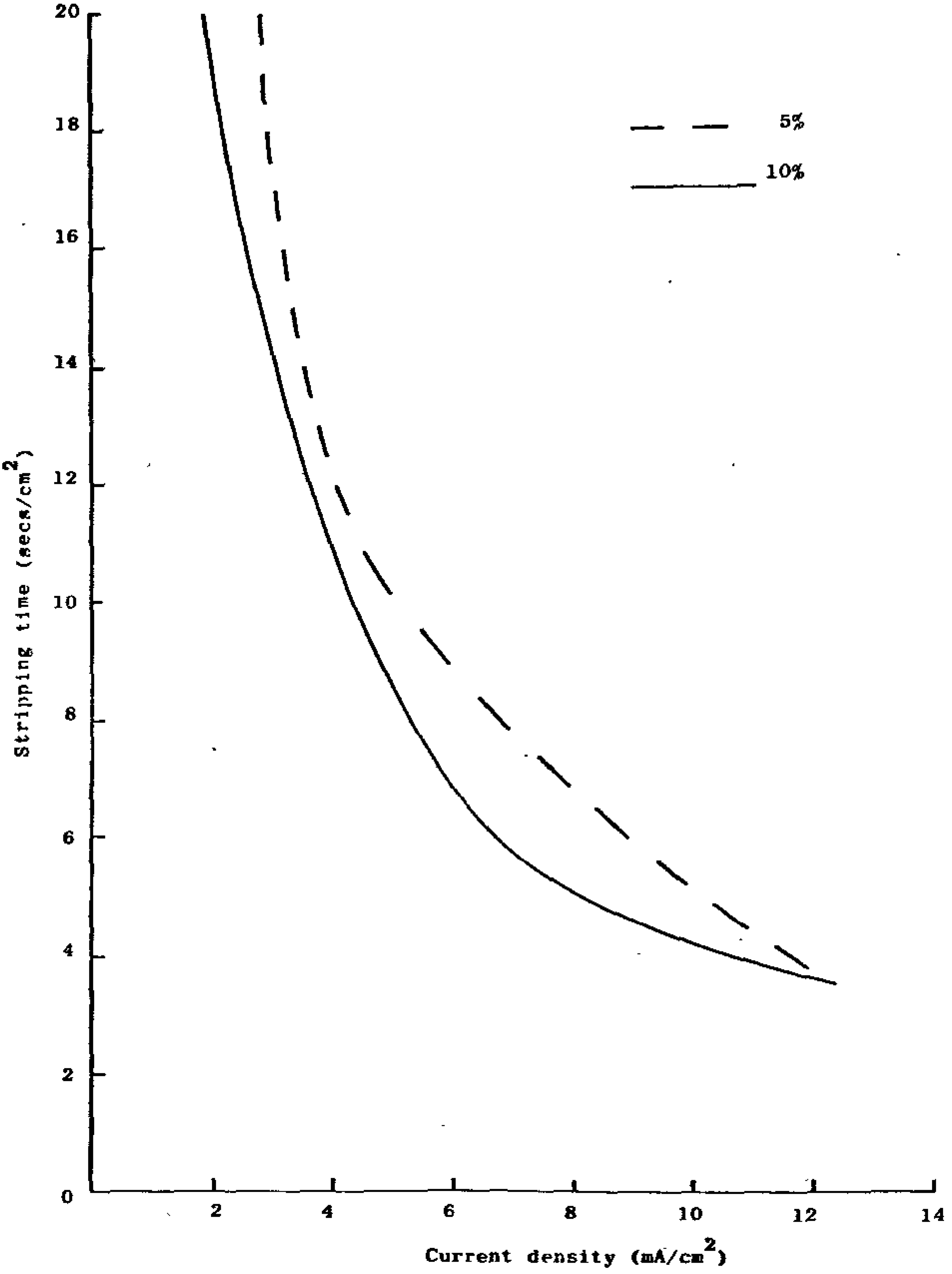


Fig. 4.17. Overall detinning rate vs. anodic current density for various concentrations of ammonium molybdate in 2N NaOH at 80^{o}C.

reduce chlorate to chlorine dioxide in the presence of trivalent vanadium.

The presence of chlorate does not increase the rate of attack of either tin or alloy compared with alkali.

4.5.7. Sodium Hydroxide and Potassium Perchlorate

The addition of perchlorate to alkali had no effect on the rate of detinning compared with alkali alone under the same conditions. This is because perchlorate is one of the most stable per-ions known.

4.5.8. Sodium Hydroxide and Ammonium Molybdate

Two concentrations of ammonium molybdate were studied, 5 and 10%. The results were superimposable upon each other and showed little difference compared with alkali alone, and alkali/nitrite liquors, as can be seen in Fig. 4.17.

Detinning was carried out at 80°C, and during the operation a smell of ammonia emanated from the liquor; this originated from the ammonium molybdate. A red discharge was produced on the anode; this could be either molybdenum oscillating between Mo(V) and Mo(VI) or, more likely, the discharge of ferrate ions. The liquor also foamed profusely. Addition of molybdate did not improve the corrosion rate of either tin or alloy.

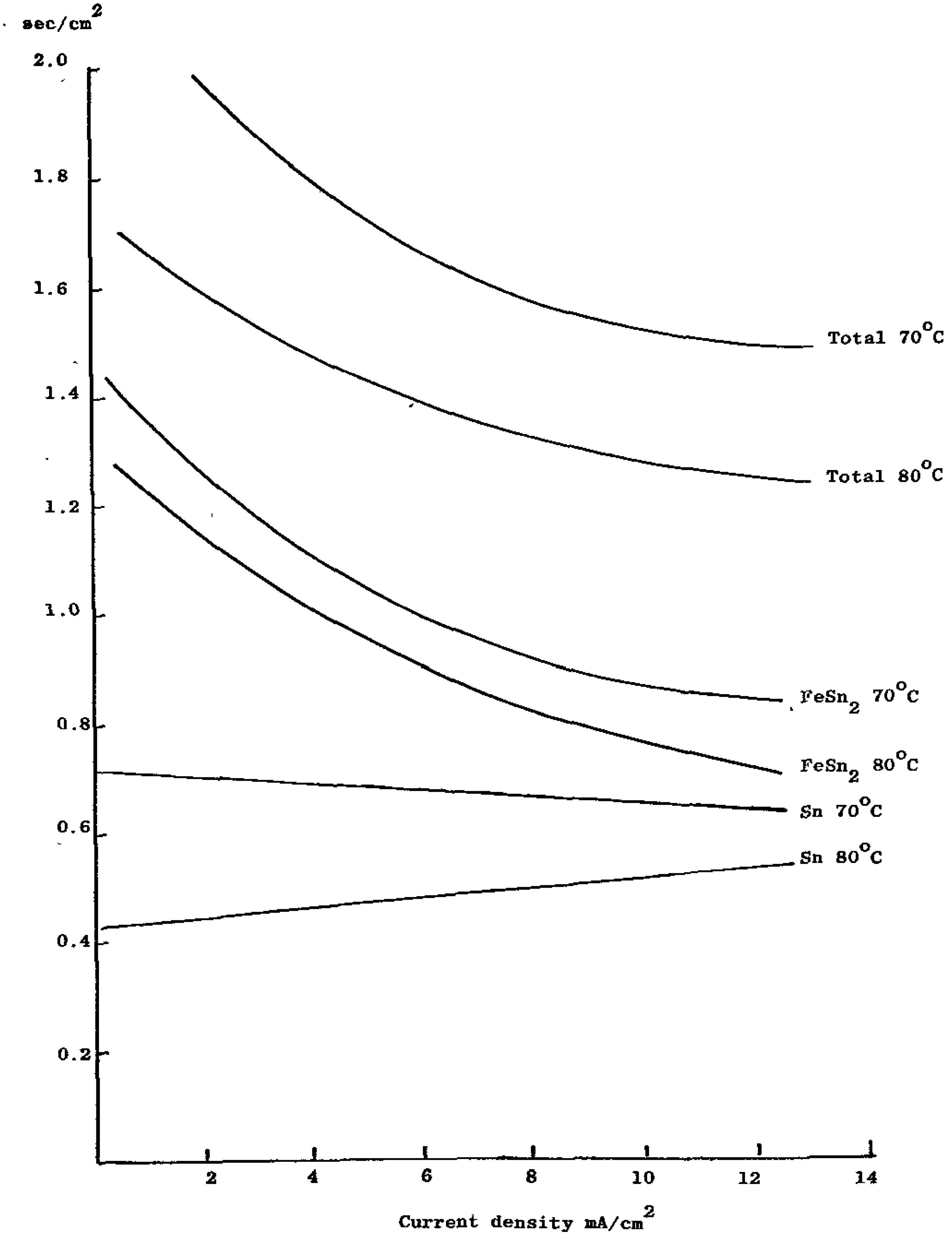


Fig. 4.18. Rate of attack of tin and alloy vs. current density for 2N NaOH + sodium polysulphide at different temperatures.

4.5.9. Sodium Hydroxide and 8% Sodium Carbonate

An 8% solution of alkaline sodium carbonate at 80°C had no effect on the electrochemical stripping of either tin or alloy compared with alkali alone.

4.5.10. Sodium Hydroxide and 8% Sodium Phosphate

Alkaline sodium phosphate at 80°C did not affect the electrochemical dissolution of either tin or the alloy compared with just alkali.

4.5.11. Sodium Hydroxide and 8% Sodium Polysulphide Solution

Akaline sodium polysulphide is known to be an efficient chemical detinning agent, which can be regenerated during electrodeposition of the tin. 25% ($^{v}/v$) of 30% ($^{w}/v$) sodium polysulphide was added to alkali and detinning performed at 70°C and 80°C. Attack was very rapid, and the rate was virtually independent of current density as shown in Fig. 4.18. It was found that the chemical and electrochemical detinning rates were identical, indicating the process is kinetically controlled, and not influenced electrochemically.

Once the tin overlay had been removed and the alloy layer exposed, copious amounts of a dark precipitate were formed at the anode; this being a mixture of Fe_2S_3, FeS, SnS_2 and SnS. When the liquor was filtered and the residue washed, the precipitate appeared golden brown, indicating the presence of SnS_2. When the steel anode was examined after detinning, a black overlay of iron sulphide was

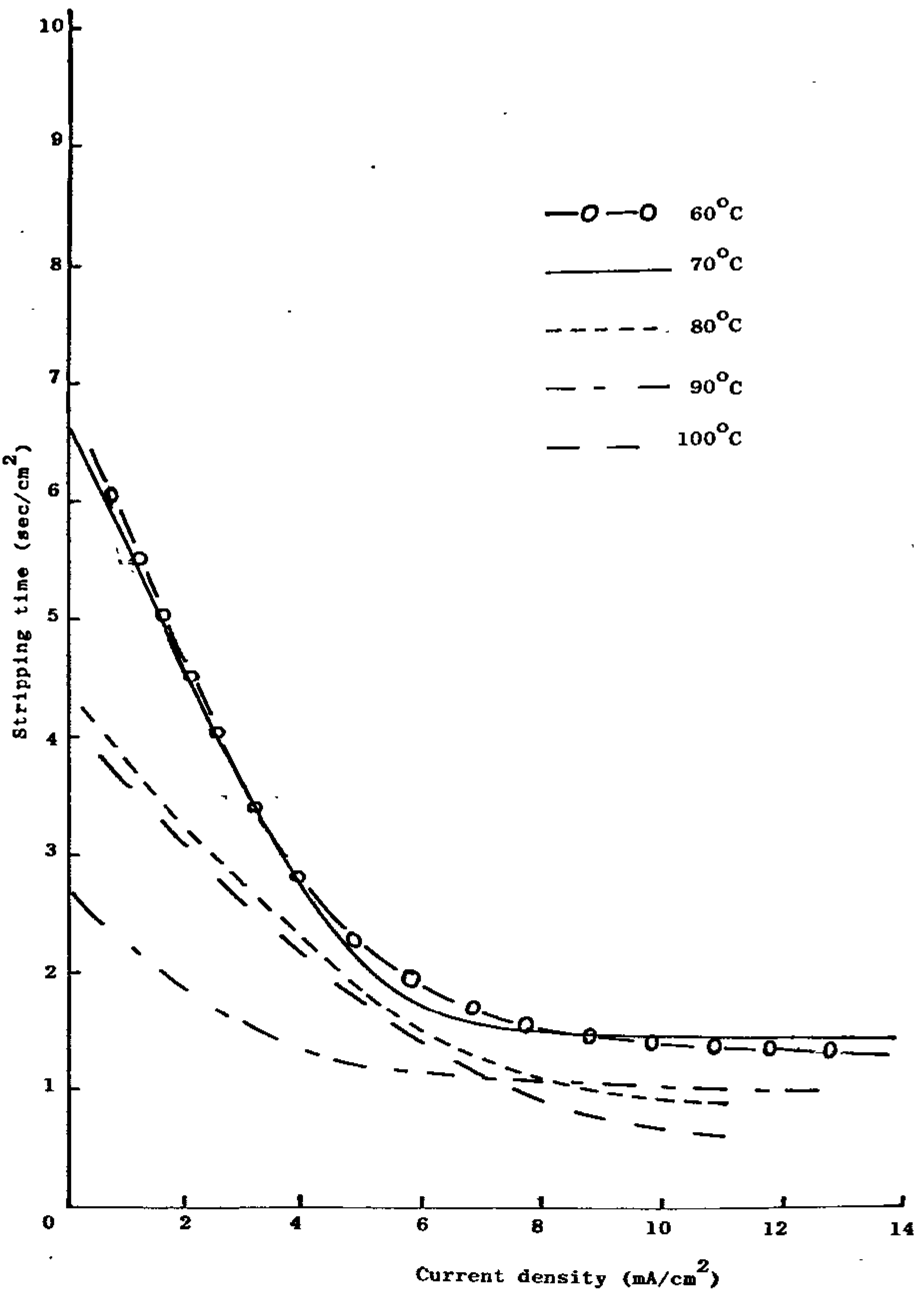


Fig. 4.19. Overall rate of detinning vs. anodic current density for $2N\ NaOH + 8\%\ Na_2S_2O_8$ at different temperatures.

noticed; there was also a layer of elemental sulphur present. During the electrolytic detinning the liquor darkened, and sulphurous fumes were detected.

Due to the presence of high residual sulphur on the scrap steel, further work was not carried out, although alloy attack rates were marginally faster than for just sodium hydroxide, whilst tin dissolution was faster, by a factor of ten. Electrochemical detinning has no benefit over chemical detinning when polysulphide liquors are used.

4.5.12. Sodium Hydroxide and Sodium Persulphate

The addition of sodium persulphate to sodium hydroxide enhanced detinning almost as much as chlorite. A minimum temperature of about 60°C was required to ensure detinning, whilst if the liquor exceeded 80°C the persulphate decomposed and oxygen was produced at the anode. At temperatures between 60°C and 80°C, the liquor in the vicinity of the anode turned purple, indicating the presence of the ferrate ion. No benefit was apparent if the liquor exceeded a temperature of 80°C, as shown in Fig. 4.19.

The overall rate of detinning is dependent upon current densities at low values (below 5 mA/cm^2), but independent at higher current densities. An increase in persulphate concentration increased the rate of overall detinning.

The rate of alloy dissolution is dependent on current density, but not greatly dependent on temperature, although an increase from 70°C

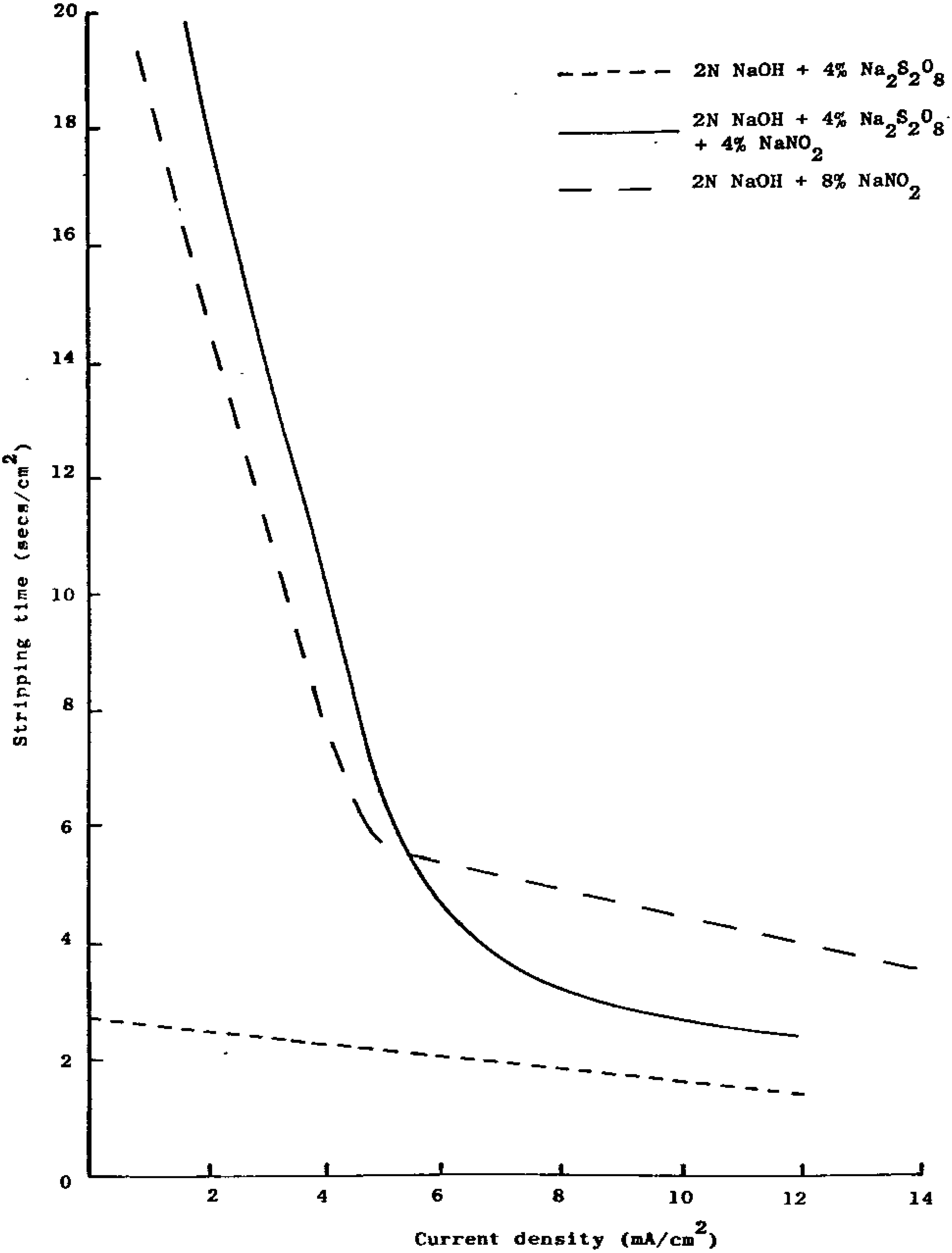


Fig. 4.20. The effect of nitrite on overall detinning rates of alkaline persulphate at 80°C.

to $100^{o}C$ increased the rate by 0.3 sec/cm^2 or up to 20%. The rate of alloy dissolution is approximately twice that of hydroxide under the same electrochemical conditions, but persulphate can operate at a lower temperature.

If nitrate is added to the persulphate liquor, the rate of detinning decreased, as shown in Fig. 4.20., but not to the extent that it was equivalent to alkaline nitrite.

4.6. The Industrial Significance of Alkaline Process Results

Alkaline chemical process rates can be improved by addition of better oxidants, such as chlorite, persulphate and polysulphide. Laboratory experimentation relating to chemical detinning can be misleading, because in the industrial processes, the plant has a large quantity of steel available. This establishes a tin- iron corrosion couple leading to faster detinning rates.

Agitation of the tinplate can be beneficial as it not only causes less produce enriched liquor to be in contact with the plate, but it also causes air to dissolve, enhancing the cathodic reaction in the tin-iron couple.

The alloy layer is chemically a lot more inert than the tin, and its dissolution is more difficult in a truly chemical process. In an electrochemical process the dissolution has been found to be Coulombic unless a highly active oxidant such as chlorite or persulphate is present. Polysulphide liquors show no difference in detinning rate between chemical and electrochemical processes. The use of polysulphides, however, cause a build-up in residual sulphur associated with the steel, rendering it virtually worthless for re-cycling.

If highly alloyed tinplate is to be reclaimed, as the used can would be, in order to obtain sufficiently low tin levels, the present alkali nitrite process for chemical extraction will not be satisfactory. Replacement of nitrite by chlorite or persulphate will increase the rate of detinning. On the other hand, if the high alloy tinplate is to be treated electrochemically, the addition of most oxidants, with the exception of chlorite and persulphate, will not be beneficial. Electrochemical dissolution of alloyed tinplate will take about three times as long as electrochemical dissolution of clean tinplate, not taking into account the initial iron-tin corrosion couple effect.

4.7. The Chemistry and Applied Electrochemistry of Some Reactions

4.7.1. The Electrochemical Dissolution of Tin

The oxidation state of tin in the electrochemical rate determining step in alkali is two, indicating the formation of stannous oxide or hydroxide. The overall rate of dissolution is dependent upon the rate of dissolution of this product. Stirrup and Hampson[309] believe the final product to be stannite ($HSnO_2^-$), whilst Dickenson and Lofti[301] claim it to be $Sn(OH)_3^-$; the latter being in agreement with the solubility of stannous oxide as discussed by Garrett and Heilis[331] The authors[301,309] are in agreement, however, that stannous oxide is formed during anodic dissolution of tin in alkali.

The Pourbaix Diagram has been calculated for tin at elevated temperatures by Brook[149], and shows the tin/stannate reaction potential at 100°C and pH 14.15 (2N NaOH) to be about -1.160V (vs S.H.E.). This compares favourably with the experimental result of -1.060V (vs Hg/HgO), and indicates that the reaction is thermodynamically in equilibrium, hence a low electrical overpotential exists. As the temperature increases, the reaction potential becomes more Nernst-like. Auger spectroscopy has shown oxygenated species present on the surface of the tin electrode; this is consistent with the mechanisms proposed in the literature[301,309], and with the thermodynamic results.

In order to assess the suitability of oxidants as detinning agents, not only has the effect on the tinplate to be taken into account, but the final degradation products have to be assessed. If the products cannot be regenerated into usable oxidants, they have to be disposed of, and the question of environmental pollution has to be taken into account. Only the most effective oxidants are considered.

4.7.2. Nitrite

The reduction of nitrite can yield a wide range of products:

$NO_2^- + H_2O + e^- \rightarrow NO + 2OH^-$	-0.46V	(ref. 316)	eqn. 4.4
$2NO_2^- + 2H_2O + 4e^- \rightarrow N_2O_2^{2-} + 4OH^-$	-0.18V	(ref. 316)	eqn. 4.5
$2NO_2^- + 3H_2O + 4e^- \rightarrow N_2O + 6OH^-$	-0.15V	(ref. 316)	eqn. 4.6
$NO_2^- + 7H_2O + 6e^- \rightarrow NH_3 + 7OH^-$	+0.806V	(ref. 316)	eqn. 4.7
$NO_2^- + 2H_2O + 3e^- \rightarrow N_2 + 4OH^-$	+1.09V	(ref. 316)	eqn. 4.8

It has been noticed on a chemical detinning plant that the immediate surrounding atmosphere has an ammoniacal aroma. The presence of ammonia undoubtably arises from the reduction of nitrite, as shown above. It is probable that the potential established between the steel and tin in the corrosion couple is partially due to the reduction of nitrite to ammonia, or possibly nitrogen.

These products, whilst being unpleasant in large quantities are not dangerous, but care has to be taken in the disposal of spent liquor, as nitrites are believed to induce cancer.

4.7.3. Polysulphide

Gabe and Wolynec[307,308] have studied the attack of tin by polysulphide and conclude that the dissolution of tin is diffusion controlled, and related to the polysulphide concentration, as well as the hydroxide concentration. A mechanism is proposed for highly alkaline liquors, where a combination of hydroxide and polysulphide reacts:[307,308]

$$Sn + 4OH^- \rightarrow Sn(OH)_4^{2-} + 2e^- \qquad \text{eqn. 4.9}$$

$$S_x^{2-} \rightarrow S^{2-} + S_{x-1} \qquad \text{eqn. 4.10}$$

$$Sn(OH)_4^{2-} + S^{2-} \rightarrow SnS + 4OH^- \qquad \text{eqn. 4.11.}$$

$$SnS + 6OH^- \rightarrow Sn(OH)_6^{2-} + S^{2-} + 2e^- \qquad \text{eqn. 4.12}$$

Whether tin does dissolve in alkali as $Sn(OH)_4^{2-}$ is open to discussion, but the reaction has been well covered by Stirrup and

Hampson[309] and by Dickenson and Lofti.[301] The reversibility of the tin sulphide/hydroxide reaction explains the influence of the hydroxide concentration.

Alkaline polysulphide hence reacts to produce sulphide ions, which can be oxidised to sulphur, or react to form insoluble sulphides:

$$S^{2-} \rightarrow S + 2e^- \qquad \text{eqn. 4.13}$$

$$S^{2-} + Fe \rightarrow FeS + 2e^- \qquad \text{eqn. 4.14}$$

$$3S^{2-} + 2Fe \rightarrow Fe_2S_3 + 6e^- \qquad \text{eqn. 4.15}$$

$$S^{2-} + Sn \rightarrow SnS + 2e^- \qquad \text{eqn. 4.16}$$

$$2\,S^{2-} + Sn \rightarrow SnS_2 + 4e^- \qquad \text{eqn. 4.17}$$

The presence of free sulphur or sulphide on the detinned steel is highly damaging to its market value.

4.7.4. Hypochlorite

Hypochlorite can dissociate:

$$3NaOCl \rightarrow NaClO_3 + 2NaCl \qquad \text{eqn. 4.18}$$

and also reduce:

$$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \quad 0.90V \quad \text{(ref. 316)} \qquad \text{eqn. 4.19}$$

The presence of chloride from either reaction could be damaging to the plant. However, under anodic conditions, hypochlorite is believed to undergo the following reaction:

$$6ClO^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 6e^- + {}^3/2\ O_2 \quad \text{(ref. 332)} \quad \text{eqn. 4.20}$$

This may, however, be the result of two overlapping reactions:

$$6ClO^- \rightarrow 2ClO_3^- + 4Cl^- \quad \text{(ref. 332)} \quad \text{eqn. 4.21}$$

$$3H_2O \rightarrow {}^3/2\ O_2 + 6H^+ + 6e^- \quad \text{(ref. 332)} \quad \text{eqn. 4.22}$$

Anodic evolution of oxygen appears to be related to the concentration of hypochlorite, and involves the production of chloride ions.(303)

The following anodic reaction is also possible:

$$ClO^- \rightarrow Cl^-_{ads} + O_{ads} \quad \text{(ref. 332)} \quad \text{eqn. 4.23}$$

$$Cl^-_{ads} \rightarrow Cl_{ads} + e^- \quad \text{(ref. 332)} \quad \text{eqn. 4.24}$$

$$ClO^- + O_{ads} \rightarrow ClO_2^- \quad \text{(ref. 332)} \quad \text{eqn. 4.25}$$

$$ClO_2^- \rightarrow ClO_2 + e^- \quad \text{(ref. 332)} \quad \text{eqn. 4.26}$$

It is unlikely that much chloride dioxide would be produced from hypochlorite liquor, and since oxidation of hypochlorite has such high reaction orders that there are probably several steps involved.

The presence of chlorate on a plant would not be damaging, but care has to be spent in disposal of spent liquor.

4.7.5. Chlorite

The reduction of chlorite follows two mechanisms:

$$ClO_2^- + H_2O + 2e^- \rightarrow ClO^- + 2OH^- \quad 0.59V \quad \text{(ref. 316)} \quad \text{eqn. 4.27}$$

$$ClO_2^- + 2H_2O + 4e^- \rightarrow Cl^- + 4OH^- \quad 0.76V \quad \text{(ref. 316)} \quad \text{eqn. 4.28}$$

The ion can also be oxidised to:

$$ClO_2^- \rightarrow ClO_2 + e^- \quad -0.954V \quad \text{(ref. 316)} \quad \text{eqn. 4.29}$$

The high reduction potentials and low stability could account for the high reactivity of the species.

However in the presence of alkali, and pH's greater than 10.5[304], chlorine dioxide disproportionates by purely chemical mechanisms:

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \quad \text{eqn. 4.30}$$

to give chlorite and chlorate ions. Below pH 8.42, chlorine dioxide remains as a truly dissolved gas in aqueous solution.[305] Bigorgne[325] has discussed the chemistry of chlorite in alkali.

The products associated with chlorite reactions are not particularly harmful, with the possible exception of chlorate, and any hypochlorite-rich liquors could be used as a chemical detinning liquor, for tinplate. The initial cost of chlorite, however, may be prohibitive, but production of chlorine dioxide is relatively easy, and from there, chlorite is an easy product to obtain.

4.7.6. Persulphate

The reduction of persulphate follows a two stage mechanism:

$$S_2O_8^{2-} \rightarrow 2SO_4^{-} \text{ (fast)} \qquad \text{(ref. 333)} \qquad \text{eqn. 4.31}$$

$$2SO_4^{-} + 2e^{-} \rightarrow 2SO_4^{2-} \qquad \text{(ref. 333)} \qquad \text{eqn. 4.32}$$

the overall reaction being:

$$S_2O_8^{2-} + 2e^{-} \rightarrow 2SO_4^{2-} \quad 2.0V \text{ (ref. 316)} \qquad \text{eqn. 4.33}$$

The reaction is first order and is inhibited in potassium hydroxide.[306] The mechanism is probably one of dissociative chemisorption of the persulphate ion on, in this case, tinplate.

The reaction products of the highly oxidative reaction are safe, and of little pollution significance.

4.8. The Chemistry of Ferrate Ions

The ferrate ion is produced in highly alkaline conditions, by the reaction of hydroxide on iron. The presence of oxidising agents, such as chlorite, persulphate and hypochlorite catalyse its production. Kaufmann[310] has claimed that the intensity of the ferrate's red/purple colour is comparable with the permanganate ion. He[310] has also used three of the U.V. spectral peaks to analyse for ferrate, these being 390, 300 and 675 mμ. When this was attempted with presumed ferrate solutions, little more than peak inferences were observed. Carrington[311] has developed some relationship between the electronic specta and the structure of oxyanions, and gives data on the ferrate ion.

Uhlig and King[302] have proposed that iron is passivated under similar alkali conditions imposed during detinning, by chemisorbed oxygen, and their value for the Flade potential corresponds to the equilibrium:

$$3H_2O + Fe_{(surface)} \rightleftharpoons 0.0_{2(adsorbed\ on\ Fe)} + 6H^+ + 6e^- \qquad \text{eqn. 4.34}$$

The standard potential for this is -0.58V. The 0.0_2 signifies a complete, chemisorbed monolayer of oxygen atoms, onto which a further layer of oxygen molecules can be chemisorbed. This structure is consistent with the observed approximate $0.01C/cm^2$ apparent surface capacitance of passive film substance. If this passive layer fails, ferric hydroxide is produced, leaving a residual film of ferric oxide 60 Å thick.

Liquor	Temp. °C	Basket type	Time to remove Sn (mins)	Total detinning time (mins)	Time to remove $FeSn_2$ (mins)	Tin content of detinned steel
2N NaOH	70	wire	6.7	23.0	16.3	0.006%
2N NaOH	70	plastic	8.5	23.0	14.5	0.006%
2N NaOH	80	wire	5.3	20.0	14.7	0.005%
2N NaOH + 8% $NaNO_2$	70	wire	1.8	14.0	12.2	0.010%
2N NaOH + 8% $NaNO_2$	70	plastic	1.9	13.5	11.7	0.012%
2N NaOH + 8% $NaNO_2$	80	wire	1.0	10.0	9.0	0.012%
2N NaOH + 8% $NaNO_2$	80	plastic	1.0	9.0	8.0	0.010%

TABLE 4.3.

Under anodically polarised conditions in concentrated alkali, Uhlig[302] observed sodium ferrate on an iron electrode:

$$0.O_2 + 2Fe + 2NaOH \rightarrow Na_2FeO_4 + H_2O + Fe_{(surface)} \qquad \text{eqn. 4.35}$$

but in dilute alkali the ferrate passivates:

$$2Na_2FeO_4 + 5H_2O + Fe_{(surface)} \rightarrow 0.O_{2(ads\ on\ Fe)} + 2Fe(OH)_3 + 4NaOH \qquad \text{eqn. 4.36}$$

In the presence of strong oxidising agents, however, reaction 4.35 would be expected to predominate, due to the ease of forcing reaction 4.36 to produce the ferrate ion, unless a different reaction mechanism occurs involving the iron and the oxidising agent.

4.9. Laboratory Bulk Detinning

The samples of tinplate detinned in this study were inhomogeneous because they were off-cuts from a can producing plant destined to be chemically detinned by Batchelor-Robinson. In practical terms, the results are more aligned to the industrial process than to standardised laboratory processes. Chemical analysis indicated a total tin content of the scrap of 0.45%.

4.9.1. Comparison between Hydroxide and Alkaline Nitrite/Liquors

Table 4.3. shows that the presence of nitrite only appears to increase the rate of dissolution of the tin at a given temperature. This agrees with the laboratory results of single strip detinning. The

type of basket does not affect the rate of detinning, but this is possibly due to a heavy oxide layer on the mesh insulating the steel. The presence of nitrite appears to inhibit total dissolution of tin from the steel.

4.9.2. The Shape of the Anode

An alkaline nitrite liquor was used at 80°C with a 3 volt potential across the cell. The total detinning times using a mild steel rod and a rod with a disc welded to it were both very similar. The tin removal was complete in 2 minutes and total detinning in 5.2 minutes. By using the wire basket as the input source, the tin was removed in 2.3 minutes, but total detinning took 8 minutes. This could be due to the insulation properties of iron oxides on the wire basket reducing the amount of charge in the mass, or that a better charge distribution is obtained if the current is injected into the midst of the tinplate.

4.9.3. The Effect of Liquor Agitation

If an alkaline nitrite liquor is pumped, the total detinning time was 2.5 minutes, but if the liquor was stationary the time increased to over 3.5 minutes. The potential across the cell was 4.5 volts and the temperature was 70°C. The current was introduced by a steel rod thrust into the midst of the bulk.

In order to obtain better liquor movement in the bulk, it was pumped directly into the centre of the basket, down the anodic input

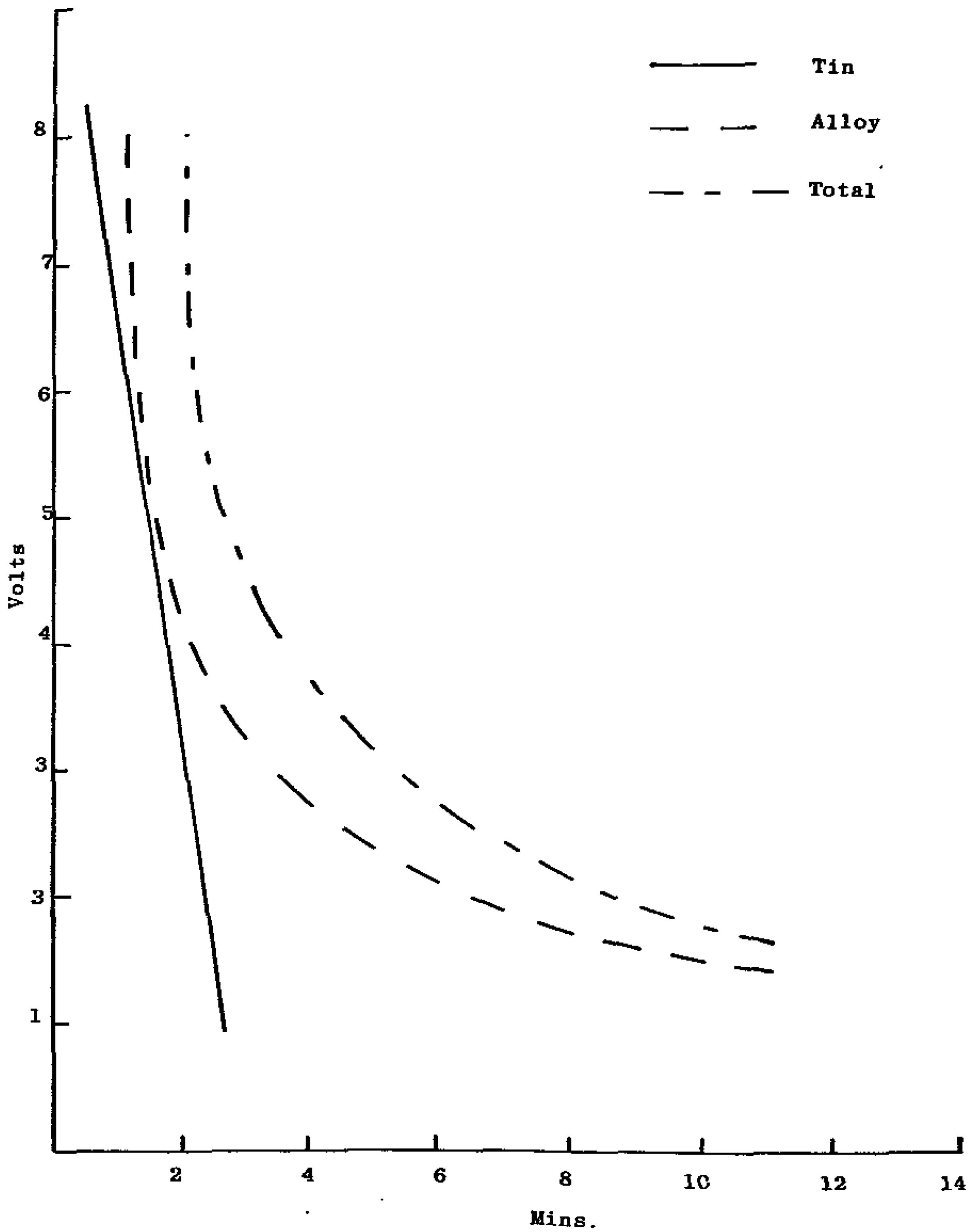


Fig. 4.21. Cell potential vs. detinning time for 2N NaOH + 8% $NaNO_2$ at 70°C.

Temp. °C	Sn removal mins : secs	Alloy removal mins : secs	Total detinning mins : secs
60	1.30	2.00	3.00
65	1.36	1.48	4.00
70	1.00	1.30	2.30
	1.06	1.29	2.35
	1.10	1.35	2.40
75	1.00	1.20	2.20
80	0.45	1.30	2.15

<u>TABLE 4.4</u>.

rod. Although the total detinning time did not vary greatly, the amount of residual tin on the stripped steel fell from about 0.010% to 0.004% when the liquor was pumped. These results suggest that liquor agitation within the bulk enhances the degree of detinning substantially and marginally reduces the time required.

4.9.4. The Effect of Potential on Detinning

Fig. 4.21. shows that the removal time of tin in an alkaline nitrite liquor is directly related to the potential applied, and hence the current density. This suggests that the tin reaction is weakly polarised.

The alloy layer relationship is not linear however; a minimum potential is required for practical attack, but if the potential exceeds 6 volts across the cell there is no further benefit in the rate. A potential of 6 volts corresponds to a current density of about 16 mA/cm^2, but even at 1.5 volts (4 mA/cm^2) the effect on alloy attack is very marked.

4.9.5. The Effect of Temperature

The temperature of an alkaline nitrite liquor with an applied potential of 4.5V across the cell had a marked effect on both tin and alloy attack as shown in Table 4.4.

The rate of tin dissolution is directly related to temperature, but the rate of alloy dissolution is limiting at 70°C. At temperatures over 80°C the liquor loss due to evaporation becomes marked, so liquor

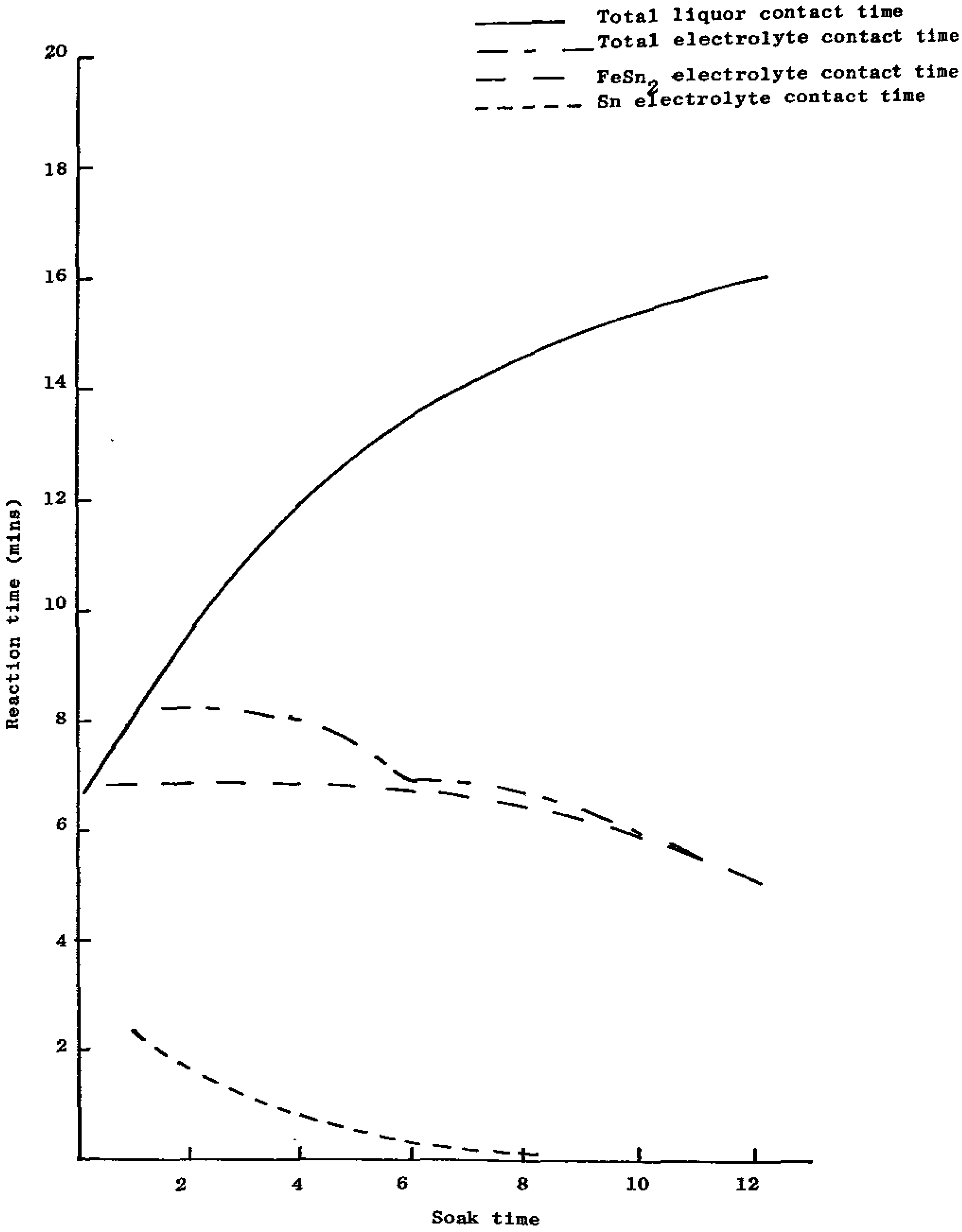


Fig. 4.22. Reaction time vs. pre-electrolysis soaking time for tinplate in 2N NaOH + 8% $NaNO_2$ at 70°C with 1.5 volts across the cell.

concentration would have to be continuously monitored.

4.9.6. The Effect of Pre-electrolysis Soaking

Bundles of tinplate were left to soak in an alkaline nitrate liquor for a prescribed time at 70°C before a potential of 1.5 volts was applied. The results are shown in Fig. 4.22. The removal of tin is initially slow due to the presence of a less reactive oxide film, but once the film has been removed, after about 4 minutes, the tin dissolution rate becomes a linear function. This suggests that tin dissolution is an active chemical reaction which is enhanced by application of a potential.

Once the alloy layer is exposed, further attack continues slowly. In the electrochemical process, dissolution of the alloy is delayed until the tin reaction is complete, unless the conditions are so forcing that the electrochemical differences between alloy and tin layers are overwhelmed.

4.9.7. Overall Comments

These results show that the laboratory trends exhibited by single strip detinning are followed by bulk detinning of tinplate. The corrosion-couple effect was not noticeable in these experiments due to the small quantity of exposed free steel in the equipment.

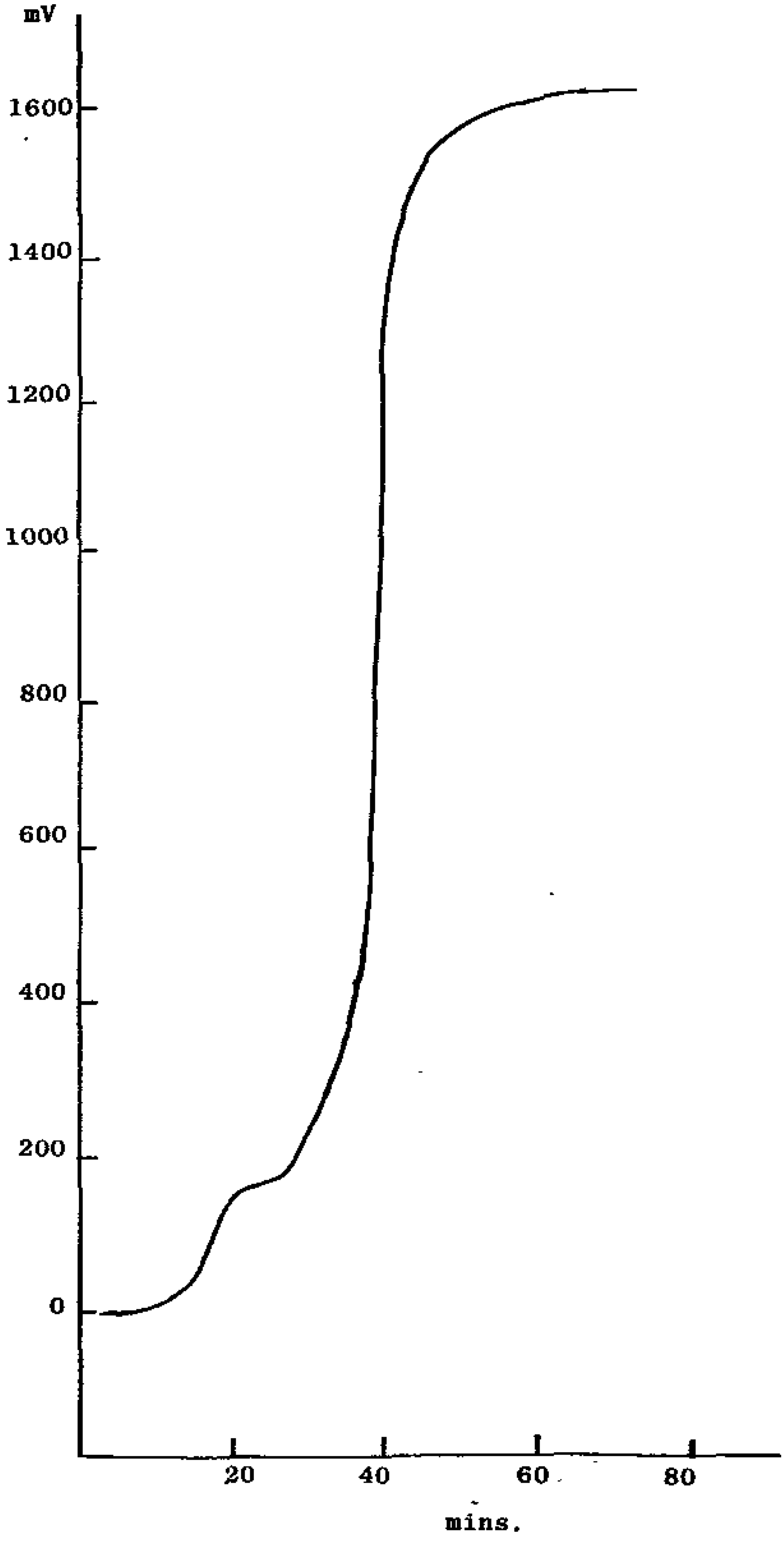


Fig. 4.23. Overall detinning of a single basket.

4.10. Industrial Electrolytic Detinning

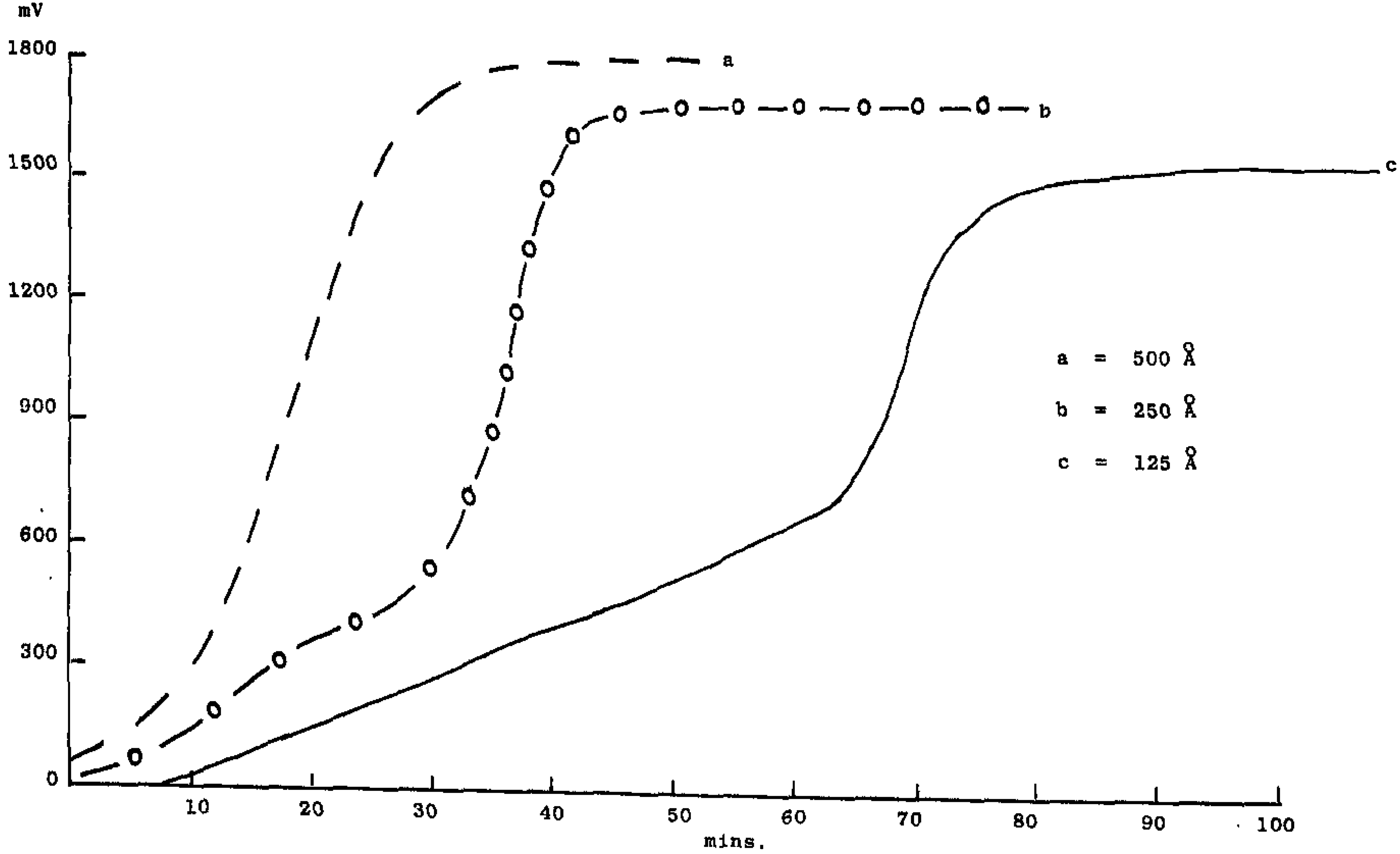
The industrial electrolytic plant used was a pilot plant owned and operated by Batchelor Robinson Metals and Chemicals Co., at Llanelli, South Wales, as described in Section 3.1.7.

It was found that averaging the final potential changes between the tinplate and all the reference electrodes, which were $Cd/Cd(OH)_2$, and examining the resulting total detinning profile, the method of current imput had little effect on the overall detinning rate. All three experiments carried out to examine this factor (experiments 1, 2 and 5) showed a sharp increase in potential after 40 minutes from the time at which the current was first applied, which indicated that both the tin and the alloy had been removed, as shown in Fig. 4.23.

A more detailed analysis of the measurements showed that the electrodes placed nearer the steel cathodes exhibited a much less well defined detinning curve, albeit marginally quicker than the ones farthest from the cathode. This indicated that the reaction went faster nearer the cathode, and also that the process did not go in such discrete steps as was originally shown with laboratory tinstrip.

The potentials obtained on the test plant were numerically different from the corresponding laboratory ones due to the fact that the potential is related to the current density on the tinplate, and the test plant current density was theoretically much lower than the laboratory one, these being 0.38 mA/cm^2 and between 1.5 and 10 mA/cm^2 respectively.

Fig. 4.24. Effect of applied anodic current on detinning time.



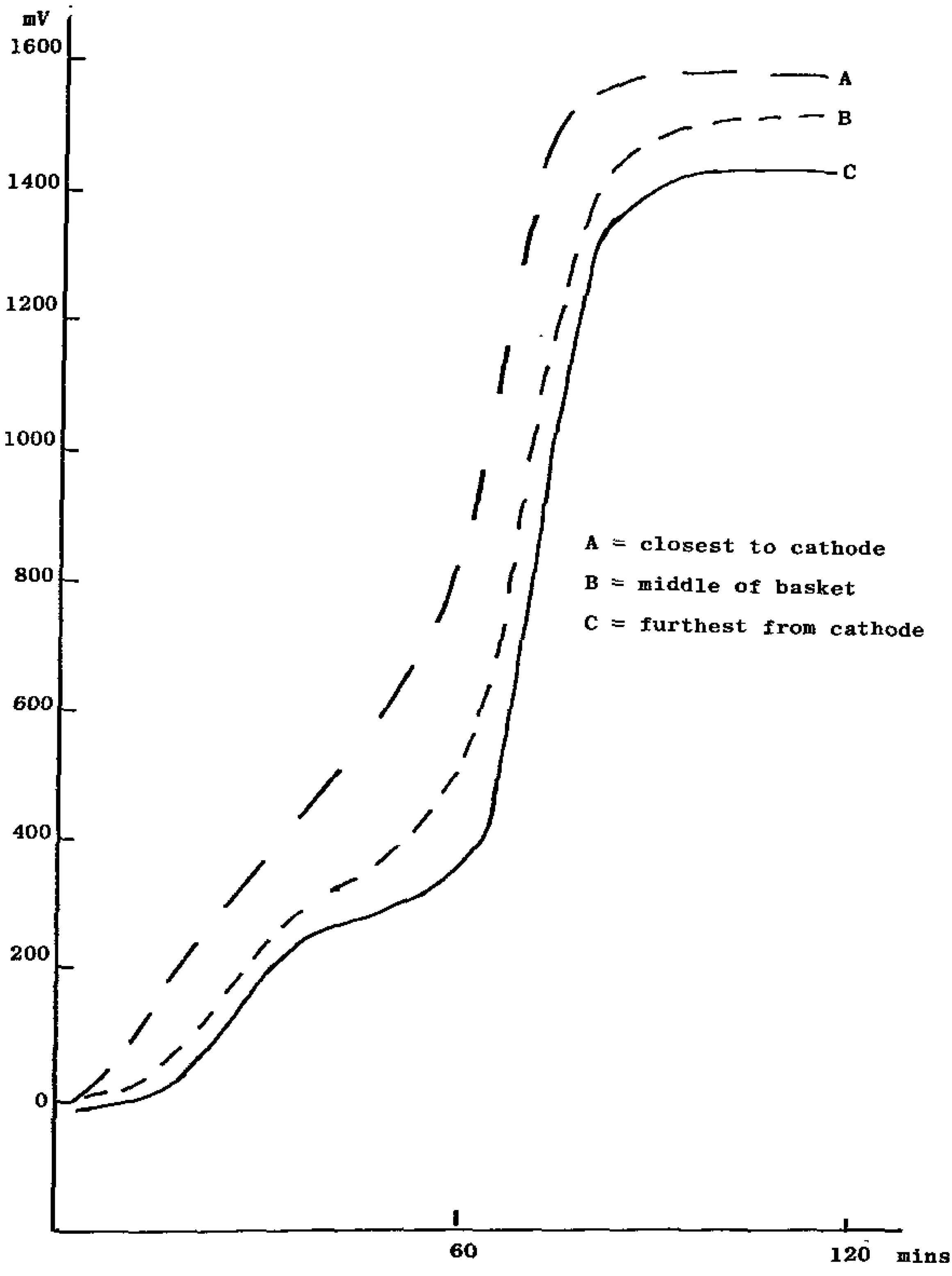


Fig. 4.25. Effect of distance on detinning time.

The amount of current consumed on the test plant per unit area of tinplate was calculated to be 3.3×10^{-4} Ahr/cm^2, ($1.2C/cm^2$) compared with a figure of 3.2×10^{-4} Ahr/cm^2 ($1.1C/cm^2$) for the laboratory detinning; this indicated that plant power consumption, and hence efficiency, was comparable with the laboratory.

The effect of varying the applied current is shown in Fig. 4.24. The total detinning time, which corresponded almost entirely to the removal of alloy, due to the rapid, couple induced, chemical removal of tin, is Coulombic.

Experiment 4, using the "double basket" produced results shown in Fig. 4.25. Accepting that a potential of 1600 mV (vs. $Cd/Cd(OH)_4$) corresponds to complete removal of the alloy layer, the difference in stripping time between the faces closest and furthest from the cathode is only 10 minutes. This suggested that larger loads could be detinned efficiently in the present bath. Even if the potential were not monitored, an "overkill" in time of 15% should be adequate to ensure good detinning.

Analysis of the scrap tinplate showed an average tin content of 0.49% before detinning, and the amounts shown in Table 4.5. on the steel after detinning.

The results in Table 4.5. indicate that the present methods of imparting a current into the tinplate bulk cannot be readily improved on. One interesting result was that of experiment 4; the outermost tinplate had more residual tin than the innermost. This result cannot be logically explained, except that it may be caused by the mixture of

Experiment	Experimental mode	Final tin content%
1	normal process	0.007
2	current to both sides of basket	0.004
3	double original current density	0.004
4	half original current density	0.0065 inside 0.024 outside
5	electrode in centre of mass	0.017

TABLE 4.5.

tinplate used. The amount of tin residual on the steel is well below that required by the electric arc furnace to recycle steel.

Traces A, B and C in Fig. 4.25. show that due to the more rapid detinning profile of A, the area nearest the cathode carried a higher current density. A degree of screening of material well inside the basket undoubtedly occurred, this is probably inevitable in a batch process, but not in a continuous one. The final potential of gas evolution is so high that the screening is not unacceptable, but during the early stages of detinning, as in Region A, as soon as the potential (vs. $Cd/Cd(OH)_2$) rose to over 300 mV, the current moved into the charge, causing a detinning "wave". This is analogous to the constriction of current in a porous electrode, the theory of which can be applied to the pilot plant results.

4.11. Application of the Porous Electrode Theory to Experimental Bulk Detinning

The distribution of current in porous or tortuous electrodes has received little theoretical attention, although such electrodes are enormously important industrially. An idealised, formal approach was due to de Levie, some of the indication of this, when applied to battery technology have been revealed experimentally.[181]

An electric current in a porous electrode can be transmitted by two paths, through the solid phase and through the electrolyte. The distribution of the current is related to the relative conductance of the two paths, and hence their impedance. Passage through the electrode is assumed to have a low resistance, but the electrolytic double layer

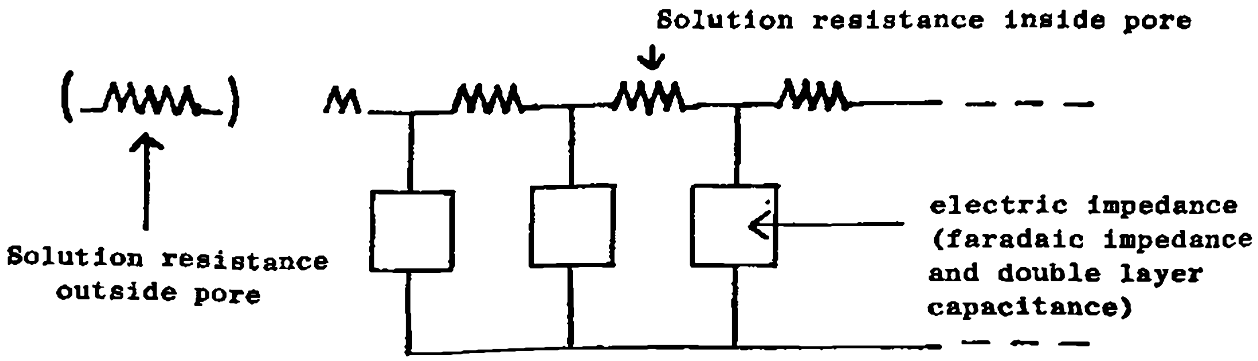


Fig. 4.26a. The equivalent circuit of a pore.

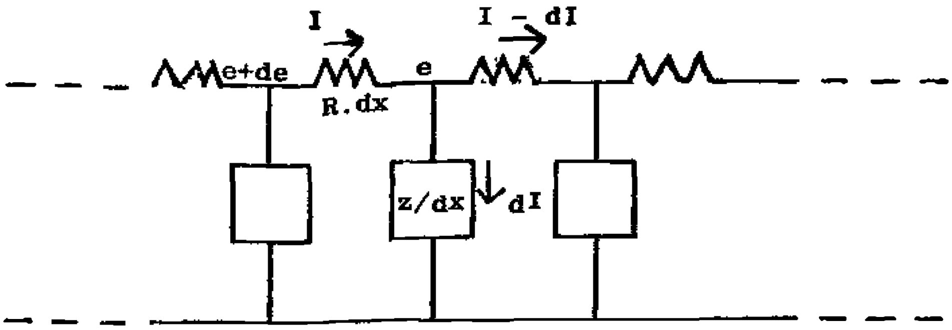


Fig. 4.26b. A section dx of the equivalent circuit of a pore. (e) Potential, (I) current, (x) distance along pore axis, (R) resistance per unit pore length, (z) electrode impedance per unit pore length.

From Fig. 4.26b. the following is derived:

$$de = -IR\,dx \quad \text{so that} \quad \frac{de}{dx} + IR = 0$$

$$dI = -\frac{e}{z}dx \quad \text{so that} \quad \frac{dI}{dx} + \frac{e}{z} = 0$$

If R and z are independent of x, then:

$$\frac{d^2e}{dx^2} - \frac{R}{z}e = 0$$

$$\frac{d^2I}{dx^2} - \frac{R}{z}I = 0$$

Fig. 4.26. The porous electrode (after de Levie[181]).

at the solid surface must be crossed, and this presents an impedance, as recognised by Frumkin[194] and de Levie.[181] De Levie considered an electrical analogue, as shown in Fig. 4.26.

It can be shown that the impedance of the interface (z) and hence the resistance (R') is related to the exchange current density (I^o)[181]:

$$\frac{1}{R'} = 2\pi a\ f\ I^o \qquad \text{eqn. 4.37}$$

where a is the radius of the pore and f is $^F/_{RT}$.

The conductance of the electrolyte in the pore is given by:

$$\frac{1}{R} = \pi a^2 K \qquad \text{eqn. 4.38}$$

where K is the specific conductance of the electrolyte. Hence the pore acts like a resistor.

Frumkin[194] has shown that the ratio of the electrolyte conductance to that of the electrode is related to the "penetration depth" of the pore.

$$^1/p = \left\{ \left(\frac{R}{R'}\right) \right\}^{\frac{1}{2}} = \text{penetration depth} \qquad \text{eqn. 4.39.}$$

The penetration depth is a measure of the effect of the pore on the electrode electrolyte reaction. Hence the penetration depth ($^1/p$)

$$1/_p = \left(\frac{aK}{2\pi f I^o}\right)^{\frac{1}{2}} \qquad \text{eqn. 4.40.}$$

decreases with decreasing specific ~~conductance~~ impedance and pore radius, and with increasing exchange current density. In practical applications, electrodes with a pore depth of the order of the penetration depth are more economical, because the large fraction of current flowing into the region $0 < x < {}^{1}/_{p}$, where x is the distance from the electrode surface.

If the electrolytic stripping of a typical mass of shredded tinplate is considered, using experimentally determined values for the specific conductance of the sodium hydroxide liquor to be $0.7\,\Omega^{-1}\,cm^{-2}$ at $95^{o}C$ and $0.5\,\Omega^{-1}\,cm^{-2}$ at $80^{o}C$, parameters relating to the porous electrode theory can be determined.

An exchange current density for free tin and for alloy was found by plotting the overpotential against current density, where

$$\frac{dI}{d\eta} = \frac{I^{o}\,z\,F}{RT} \qquad \text{eqn. 4.41}$$

R being the gas constant and T the temperature in degrees Kelvin. F is the Faraday, and z is the number of electrons involved in the reaction.

If the overpotential is plotted against log current density, the gradient is a constant (-b), as defined by the Tafel equation:

$$\eta = a - b \log I \qquad \text{eqn. 4.42.}$$

where

$$b = \frac{2.303\,RT}{\alpha z F} \qquad \text{eqn. 4.43}$$

and α is the transfer coefficient.

Temp:	80°C		95°C	
	Sn	$FeSn_2$	Sn	$FeSn_2$
I^o (Amps/cm^2)	3.45×10^{-5}	6×10^{-6}	7×10^{-5}	6.6×10^{-5}
z	2	6	2	6
α	0.55	0.028	0.64	0.025
$d\eta/dI$	440	850	225	800
$d\eta/d \log I$	0.060	0.42	0.058	0.49
$1/p$ (cm)	11.95	14.4	8.88	16.7

<u>TABLE 4.6.</u>

From the results obtained, and assuming the pore radius to be 1 cm in the electrolytic process, the results shown in Table 4.6. can be calculated.

The results for the penetration depth ($^1/p$) partially explain the results obtained on the pilot plant, and suggest the presence of a detinning wave moving through the tinplate. The penetration depth is numerically the same as the "wavelength" of the wave. However, a much more effective current constriction operates.

When free tin is present, the current density passes from the tinplate into the liquor. However, where there is no more remaining free tin, the alloy will not dissolve until the potential has increased by about 600 mV. Anode current is therefore deflected towards any free tin still present. The practical effect of this shift in dissolution potential (the effect of which is probably enhanced by the slight change in exchange current density of the alloy) is to establish penetration of an anodic wave from the externally stripped layer to the unstripped interior, until the mass is uniformly in the alloy surface condition, with no residual free tin.

An essential feature of the final rise of the overpotential under galvanostatic conditions is the evolution of oxygen. The same argument applies for the increase in potential, ensuring that the depths of the anodic charge are detinned and dealloyed before excessive wastage of current occurs in evolution of oxygen.

The adaptation of the porous electrode theory to the macroscopic scale can explain the rapid electrochemical dissolution rates on the pilot plant. The applied current would only be sufficient for an overall current density of 0.38 mA/cm^2, whilst if the basket is hypothetically divided into finite elements, each the width of the penetration depth, the current density would increase to 1.8 mA/cm^2. This current density corresponds to a required time of 20 minutes to remove the amount of alloy that would be associated with the overall tin overlay of 5.6 gms/m^2, which is the majority of tinplate produced in this country.[326] This calculated result is in agreement with the rate of detinning found in experiments conducted on the pilot plant, and accounts for the much higher than expected dissolution rates experienced on plant.

A variation in the pore radius of $\pm$50% effects the pore penetration depth, and hence the current density on the charge, by about 30%.

4.12. The Effect of Thermally Treating Tinplate

Preparation of used cans for detinning will possibly involve incineration in order to remove the remaining debris after initial separation from the bulk waste. Thermal treatment will also start lacquer degradation.

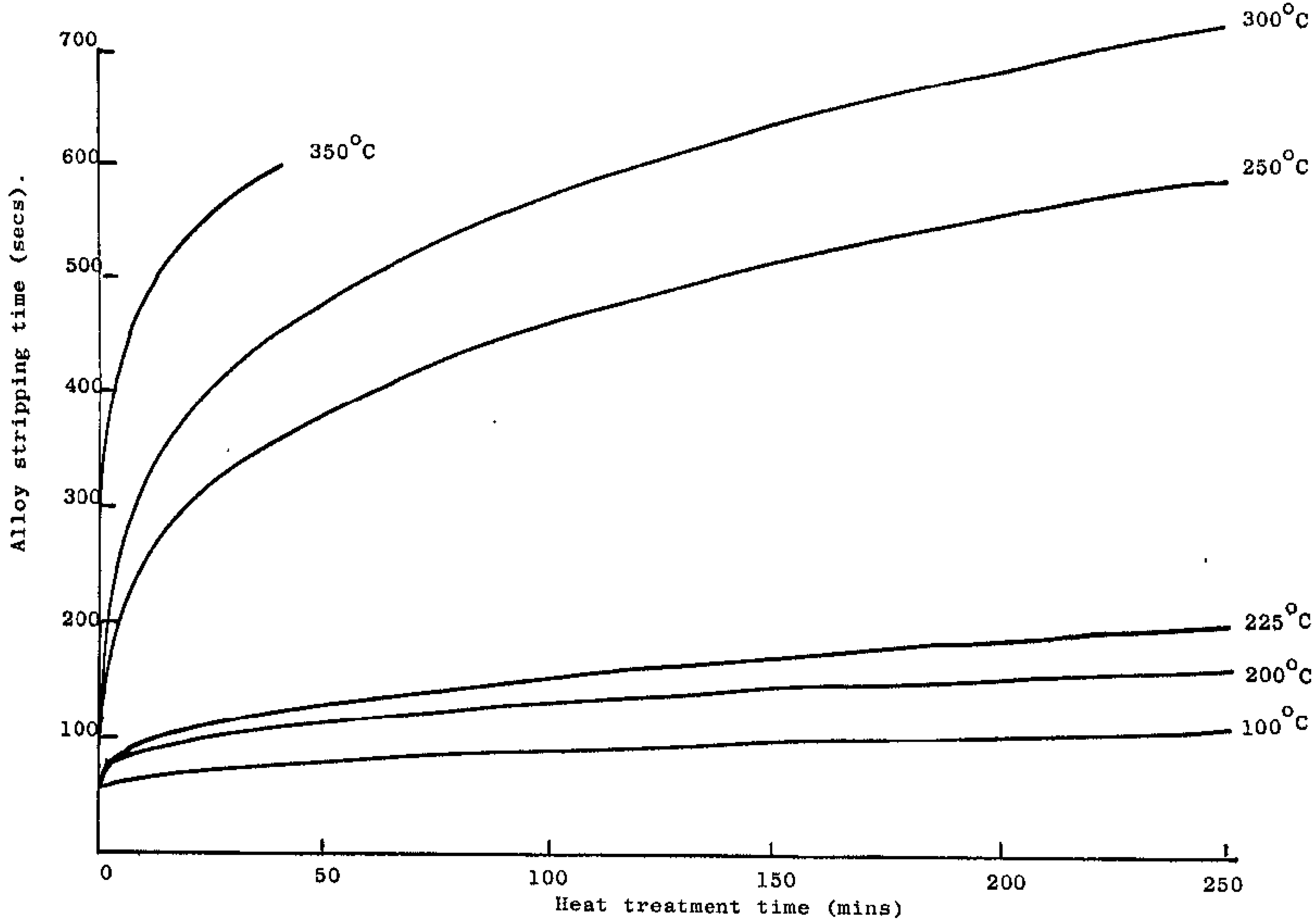
Type E5.6/5.6 tinplate was thermally treated and then galvanostatically stripped at 95°C in 2N NaOH, using a current density of 4 mA/cm^2.

The growth of the alloy can be determined by the time required for the potential to increase from -800 mV to +650 mV (vs. Hg/HgO) as shown in Fig. 3.2. These potentials are associated with the dissolution of alloy, whilst tin dissolved at about -1060 mV under the

Temperature	Growth rate exponent (n)	Rate constant (k)
100	1.9	1.06
200	2.5	331
225	2.3	266
250	3.2	2.0×10^6
300	3.5	2.73×10^6
350	5.6	6.32×10^6

TABLE 4.7.

Fig. 4.27. Heat treatment times vs. alloy stripping time.



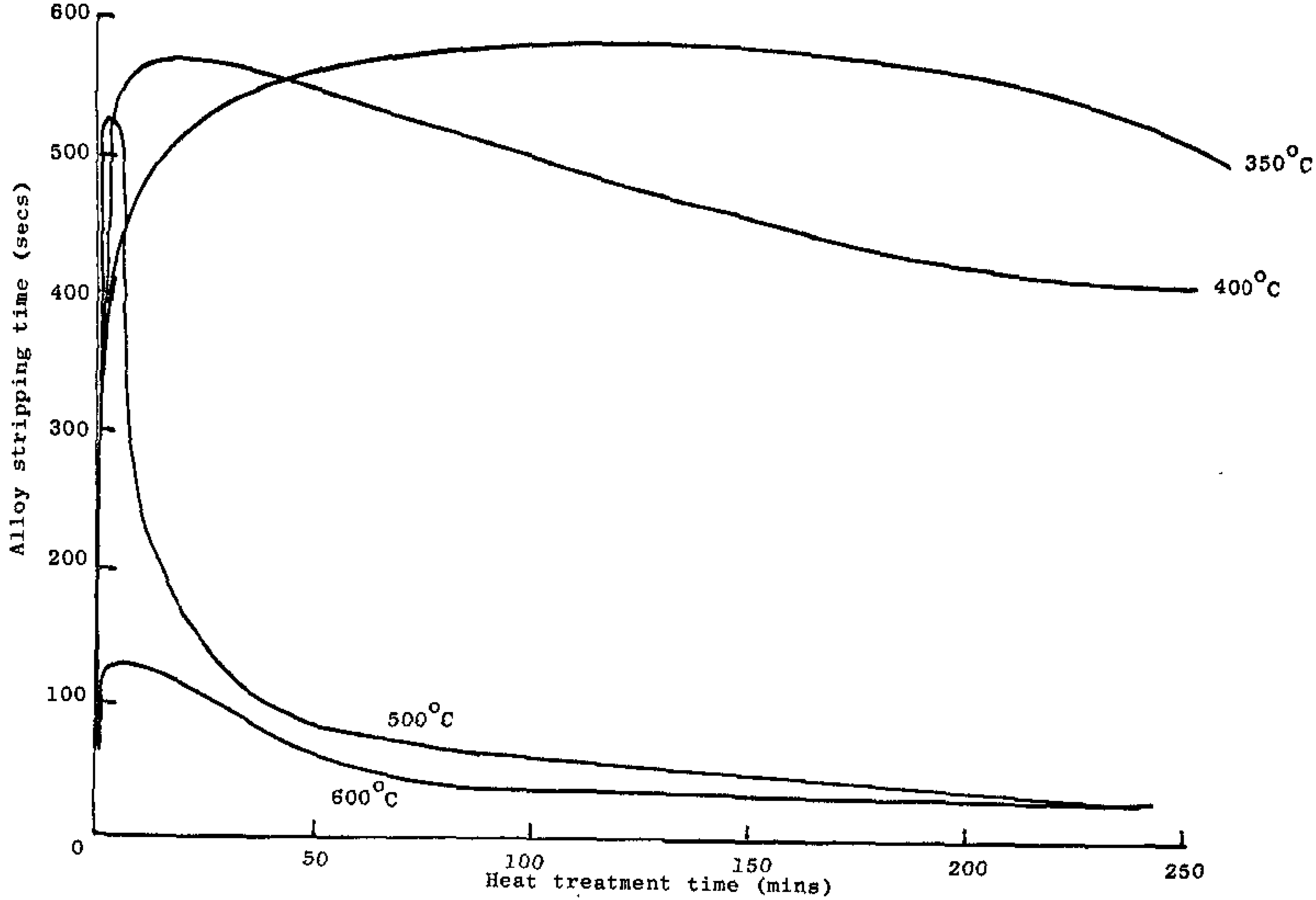


Fig. 4.28. Heat treatment times vs. alloy stripping times.

conditions. The alloy layer showed two characteristic stripping potentials, one at -800 mV and one at -400 mV. These correspond to the active dissolution of Fe to $Fe(OH)_2$ and $Fe(OH)_2$ being oxidised to $Fe(OH)_3$ respectively.

Calculations relating to alloy dissolution were performed, assuming the alloy was totally $FeSn_2$. Lubyova[245] reported that 0.68 µm of $FeSn_2$ on an area of 1 cm^2 would be dissolved by 1 Coulomb. Using this value, and knowing the total applied charge, the amount of alloy is calculable.

Figs. 4.27. and 4.28. show the rate of alloy formation is heavily dependent on temperature, and that it follows a parabolic relationship, as predicted by Fick's Law of Diffusion, indicating that the growth region being studied was diffusion controlled.

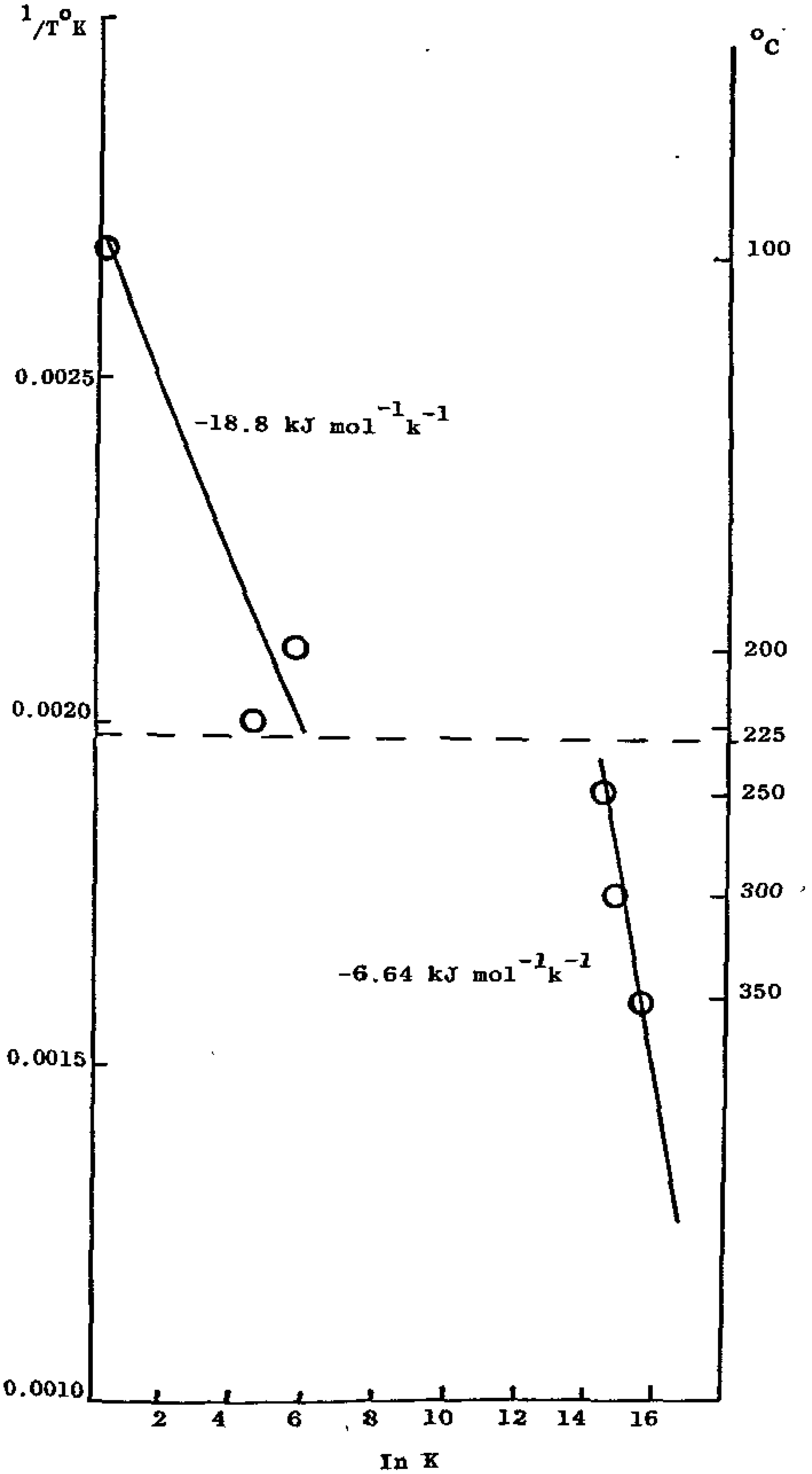
Statistical analysis of the data by log-log plots enabled determination of the growth law exponent, n, where:

$$x^n = Kt \quad - \text{ Fick's Law of Diffusion} \qquad \text{eqn. 4.44}$$

at each temperature, and the rate constant (K), as outlined in Appendix 2. The results are shown in Table 4.7. Fick's Law is a parabolic relationship, for which n = 2; this is adhered to below the melting point of tin (232^{o}C) but not above it.

Using the Arrenhius equation, the activation energies for the reaction were found to be 18.8 kJ $mol^{-1}k^{-1}$ (4.33 kc $mol^{-1}k^{-1}$) at temperatures below 232^{o}C, and 6.6 kJ $mol^{-1}k^{-1}$ (1.59 kc $mol^{-1}k^{-1}$)

Fig. 4.29. Arrenhius plot for the alloy ($FeSn_2$)



above 232°C, as shown in Fig. 4.29.

Few data are available for comparison, but the reaction corresponds to the third stage as defined by Gabe.[255] Activation energies have been calculated[255] based on studies by other workers. Kunze and Willey[243] studies yielded a value of 30.66 kJ $mol^{-1}k^{-1}$ whilst Adams[322] corresponded to 17.6 kJ $mol^{-1}k^{-1}$, both were carried out below 232°C. Saito and Ishida[263] report a value of 42.4 kJ $mol^{-1}k^{-1}$ between 200°C and 600°C.

Good correlation between the present work and previous work exists, although Thwaites[225] obtained a value of 89 kJ $mol^{-1}k^{-1}$ for a reaction carried out on flow melted tinplate above 232°C.

Since the mechanism of alloying is not fully understood, no firm conclusions can be drawn. The amount of carbon present in the steel is 0.04% to 0.15%[323], and this may catalyse alloy formation.[267,268,269]

Alloy formation during thermal treatment has been divided into three regions. The first region is below 232°C, where Fick's Law of Diffusion applies, the second is between 232°C and 300°C, and the third is above 300°C, where diffusion laws do not appear to be adhered to.

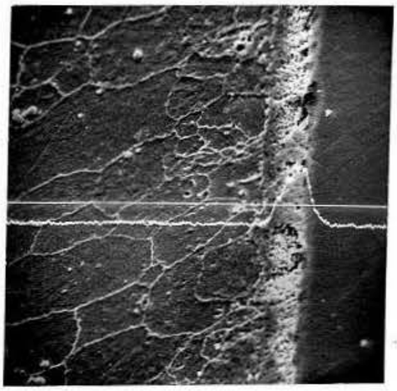
Alloy growth below 232°C follows a roughly parabolic law, where the growth rate exponent is equal to 2. For thickening of the layer to occur, free tin has to transfer through the alloy to the $Fe/FeSn_2$ boundary. The rate of thickening will be dependent on the availability of tin at the interface, and is hence related to the rate of tin diffusion.

At temperatures between 232°C and 300°C the growth rate is still parabolic but the growth rate exponent increases to between 3 and 6. The tin is molten and more mobile, allowing greater growth rates of alloy.

The growth rate of the alloy is dependent on either the rate of diffusion by the tin through the alloy, or the rate at which the tin and iron react to form further alloy. If the latter is the case, no reduction in growth rate would be expected with time, as shown by the parabolic type curves, so diffusion is still the rate determining factor. The growth rates are temperature dependent, but a sharp increase in growth rate at temperatures in excess of the melting point of tin cannot be totally accounted for by greater mobility of the tin, and another diffusion mechanism occurs.

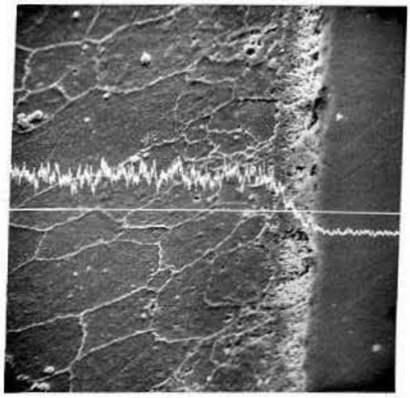
The parabolic growth rate applies at temperatures above 300°C for short treatment times, but as the temperature increases, the alloy layer apparently diminishes. Chemical analysis showed that the tin migrated into the steel substrate, forming the α solid solution.

The solid solution formation becomes significant when there is no free tin available, which will be dependent on the incineration temperature and the amount originally present, Once the free tin is exhausted, alloy growth is halted, and diffusion of the alloy into the steel substrate starts to predominate. Tin is exhausted after 10 minutes at 400°C, whereupon the alloy growth ceases. At 500°C the initial growth is rapid, but after 30 minutes virtually all the alloy is in solid solution with the steel. At 600°C the disappearance of alloy is so rapid that none exists after 2 minutes of thermal treatment.



(a) Untreated SnK_{α}

= 10μ

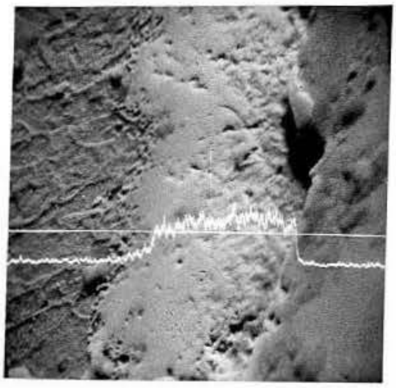


(b) Untreated FeK_{α}

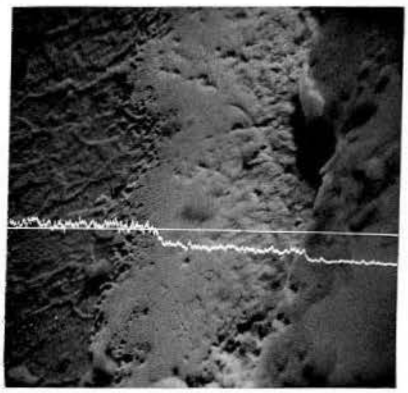
= 10μ

= 10μ

= 10μ

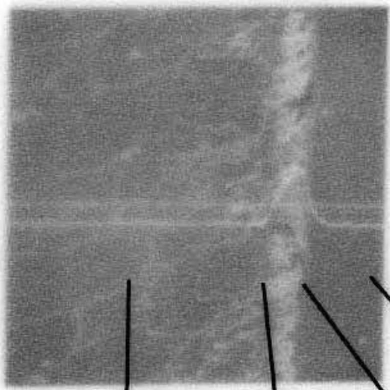


(c) Heat treated SnK_{α}



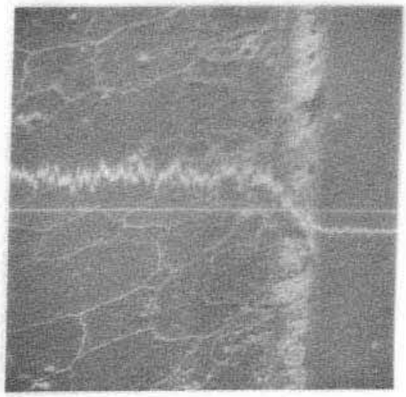
(c) Heat treated FeK_{α}

Fig. 4.30. Scanning electron micrographs of normal and heat treated (400°C, 3 hrs 45 mins) tinplate, showing SnK_{α} and FeK_{α} to emission lines, 1800X.



(a) Untreated SnK_{α}

= 10μ

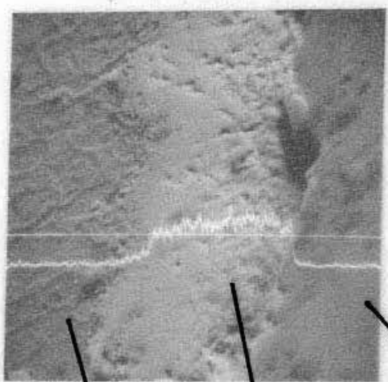


(b) Untreated FeK_{α}

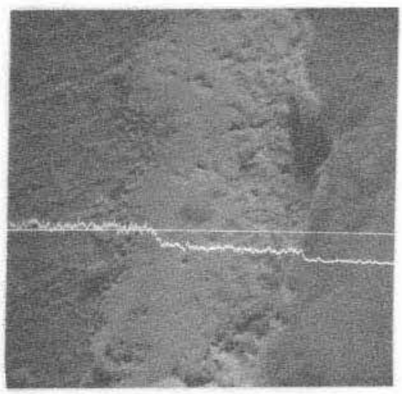
= 10μ

= 10μ

= 10μ



(c) Heat treated SnK_{α}



(c) Heat treated FeK_{α}

Fig. 4.30. Scanning electron micrographs of normal and heat treated (400°C, 3 hrs 45 mins) tinplate, showing SnK_{α} and FeK_{α} to emission lines, 1800X.

The length of time free tin remains as tinplate is shown in Table 4.8. After this time the alloy layer degrades to form less tin-rich, stoichiometric compounds, rendering it virtually unusable for reclamation.

The alloy forming processes were followed by Rutherford Back-scattering Analysis, which will be discussed in Section 4.16. The thickness of the alloy was determined by Scanning Electron Microscopy, (Fig. 4.30.), and the composition by electron probe micro-analysis; the results obtained compared favourably with those of electrolyte stripping. A range of iron-tin alloys could be detected using these methods of analysis.

Little work has been carried out on the effects of thermal treatments of tinplate, the ~~hottest~~ highest temperature study being carried out by Lambert[321] at 440°F (267°C) and below, the trends of which are also apparent in the present study.

Gabe[257] has postulated a three-stage alloy formation process; this work suggests that a fourth, diffusion controlled stage exists when the free tin is totally depleted and the $FeSn_2$ diffuses into the base steel to form new, stoichiometric compounds. Verbraak and Dapper[324] report that alloy formation is followed by oxidation, and that dissolution of the alloy did not occur until 750°C. Their results are in conflict with the present findings, but their work was performed in an oxidising atmosphere, where alloy degradation may occur preferentially by oxidation rather than dissolution.

Temperature ^oC	Maximum time for free tin (mins)
250	240
300	120
350	30
400	10
500	2
600	0

TABLE 4.8.

Specimen	Area	Measured values				Calculated values						Computed values			
		Peak height		Background		+Corrected peak height, I		++Standardised peak height, S		+++Normalised peak value, K		Weight %		Atomic %	
		SnLα	FeKα	Sn	Fe	Sn	Fe	Sn	Fe	Sn	Fe	Sn	Fe	Sn	Fe
Pure Sn standard	1	10392		344-888		9776									
Pure Fe standard	1		9391		253-312		9109								
	2		9216		226-285		8961								
250°C 120 mins	1	9240	2067	408-937	263-312	8668	1770	8011	1770	81.9	18.1	82.4	17.6	68.8	31.2
	2	8131	1988	309-709	217-276	7622	1742	7044	1742	80.2	19.8	80.8	19.2	66.4	33.6
300°C 4 hrs	1	8929	2586	397-813	277-310	8324	2293	7693	2293	77.0	23.0	77.7	22.3	62.1	37.9
	2	9870	2493	343-903	274-340	9248	2186	8547	2186	79.6	20.4	80.2	19.8	65.6	34.4
400°C 63 mins	1	7760	2001	350-706	198-229	7232	1788	6684	1788	78.9	21.1	79.5	20.5	64.6	35.4
	2	7375	2360	298-643	230-251	6905	2120	6382	2120	75.1	24.9	75.8	24.2	59.6	40.4
*400°C 125 mins	1	5827	5736	330-659	255-263	5333	5477	4929	5477	47.4	52.6	48.8	51.2	31.0	69.0
	2	7296	3569	336-722	216-277	6767	3323	6254	3323	65.3	34.7	66.3	33.7	48.1	51.9
	3	8453	2217	324-746	243-286	7918	1953	7318	1953	78.9	21.1	79.5	20.5	64.6	35.4

+ I = (Measured peak height - average background)

++ $S = \dfrac{I \text{ element}}{\alpha \text{ element}}$ where $\alpha_{Fe} = 1$ (by definition)

$\alpha_{Sn} = \dfrac{I \text{ Sn std}}{I \text{ Fe std}}$

+++ $K = \dfrac{S}{I_{Sn}/\alpha_{Sn} + I_{Fe}/\alpha_{Fe}}$

*Results suspect due to detachment of nickel plating from specimen edge during metallographic preparation.

TABLE 4.9.

Compound	Atomic percent	
	Fe	Sn
$FeSn_2$	3.33	66.7
FeSn	50.0	50.0
Fe_3Sn_2	60.0	40.0
Fe_2Sn	66.7	33.3
Fe_3Sn	75.0	25.0

TABLE 4.10.

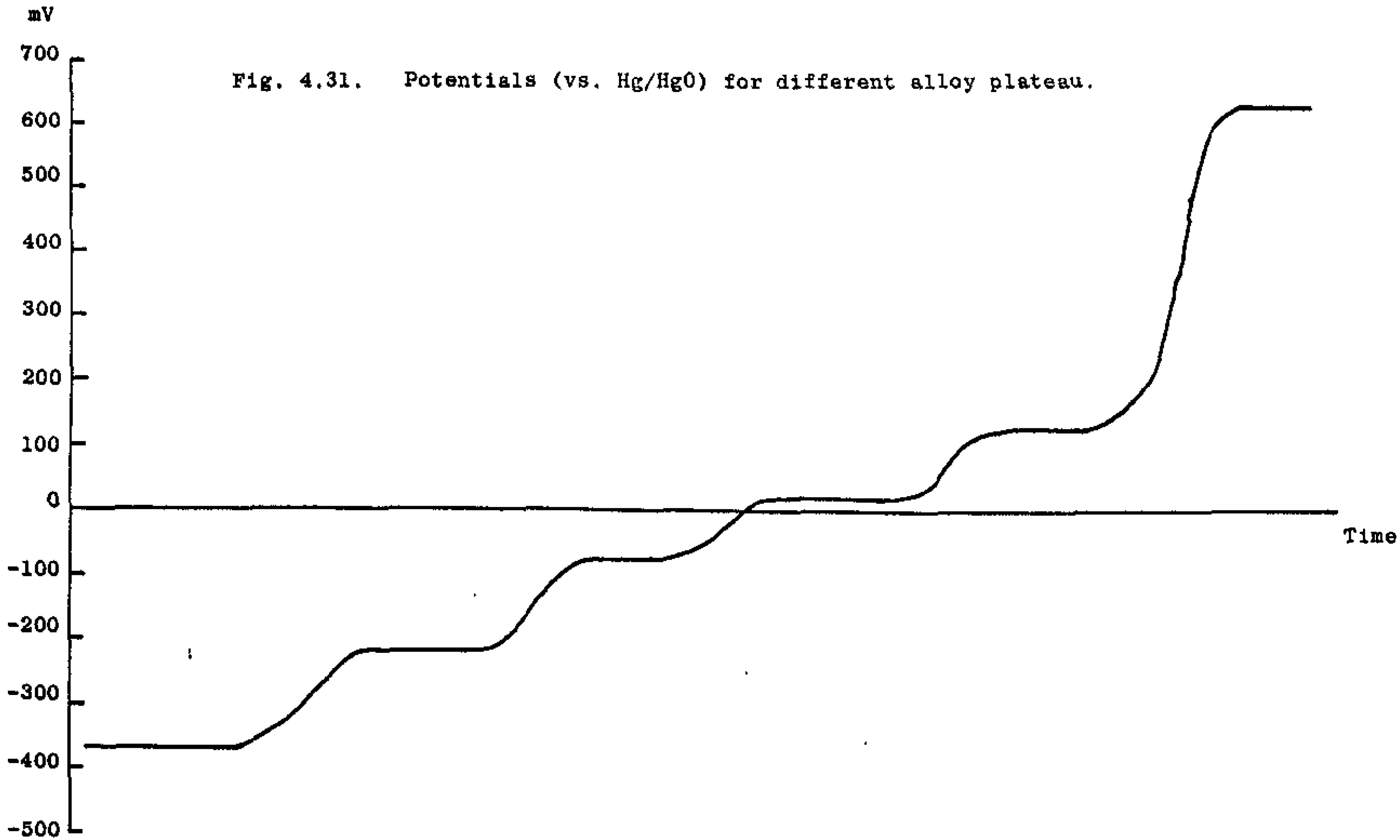


Fig. 4.31. Potentials (vs. Hg/HgO) for different alloy plateau.

If incineration is to be carried out, these results suggest that the temperature should not exceed 350°C, and that heat source dwell time should be carefully controlled.

4.13. Evidence for Intermetallics other than $FeSn_2$

The existence of intermetallics other than $FeSn_2$ in tinplate has been the subject of wide speculation.[222,223,224] During the detinning of certain thermally treated specimens of tinplate, the profile of the alloy changed from the typical anodic plateau at about -350 mV to -400 mV (vs. Hg/HgO) to a series of heavily stepped plateaux (Fig. 4.31.). The onset of these plateaux corresponded to depletion of the free tin layer during thermal treatment, and hence they may be due to the reduction of the tin content of the intermetallic compound, as further diffusion occurred.

During early formation of these plateaux, the plateau corresponding to free $FeSn_2$ at -840 mV (vs. Hg/HgO) was still present, but as the new plateaux became more predominant, the -840 mV plateau disappeared.

Analysis of the surfaces corresponding to the plateaux was made using electron probe microanalysis, the results of which are shown in Tables 4.9. and 4.10. The results confirmed that the predominant composition of alloy formed below 300°C was $FeSn_2$, but if the specimen was heat treated at 400°C for 63 minutes, the possible presence of small amounts of FeSn in addition to $FeSn_2$ was indicated. The specimen treated at 400°C for 125 minutes gave variable results from the three

Alloy	Atomic percent		Wt. percent	
	Fe	Sn	Fe	Sn
$FeSn_2$	33.3	66.7	19.18	80.82
FeSn	50	60	32.2	67.8
Fe_3Sn_2	60	40	41.49	58.41
Fe_2Sn	66.7	33.3	48.7	51.3
Fe_3Sn	75	25	52.74	41.26

TABLE 4.11.

Alloy	Potential (mV)	Electrochemical equiv. mg/C
$FeSn_2$	-350	0.507
FeSn	-120	0.452
Fe_3Sn_2	-80	0.419
Fe_2Sn	+5	0.397
Fe_3Sn	+130	0.371
Fe	+630	0.289

TABLE 4.12.

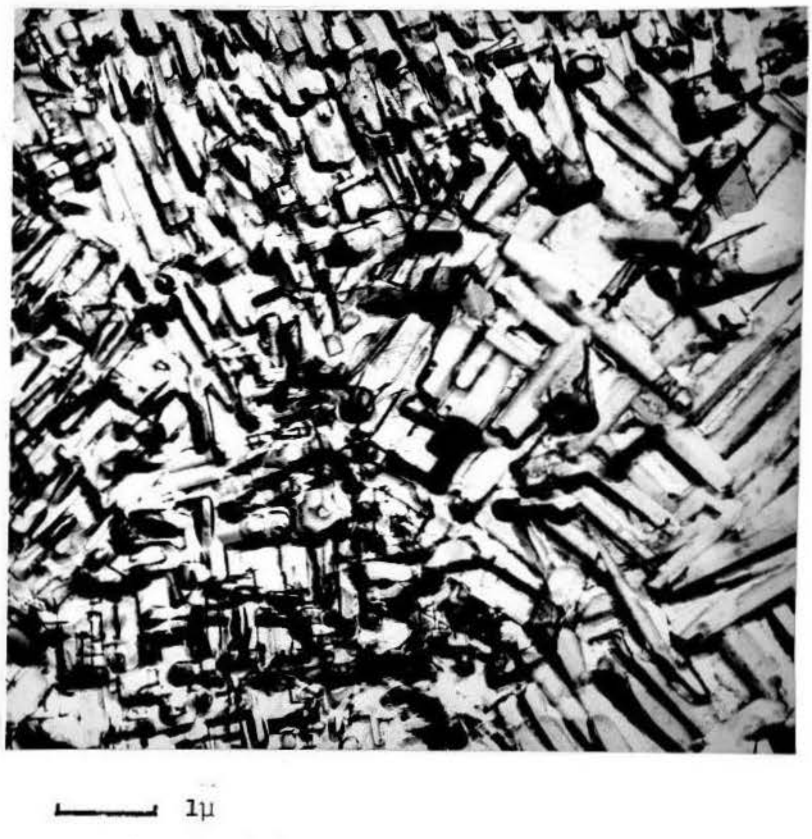


Fig. 4.32. Transmission electron micrograph of $FeSn_2$. (Single replication technique). 13,000X

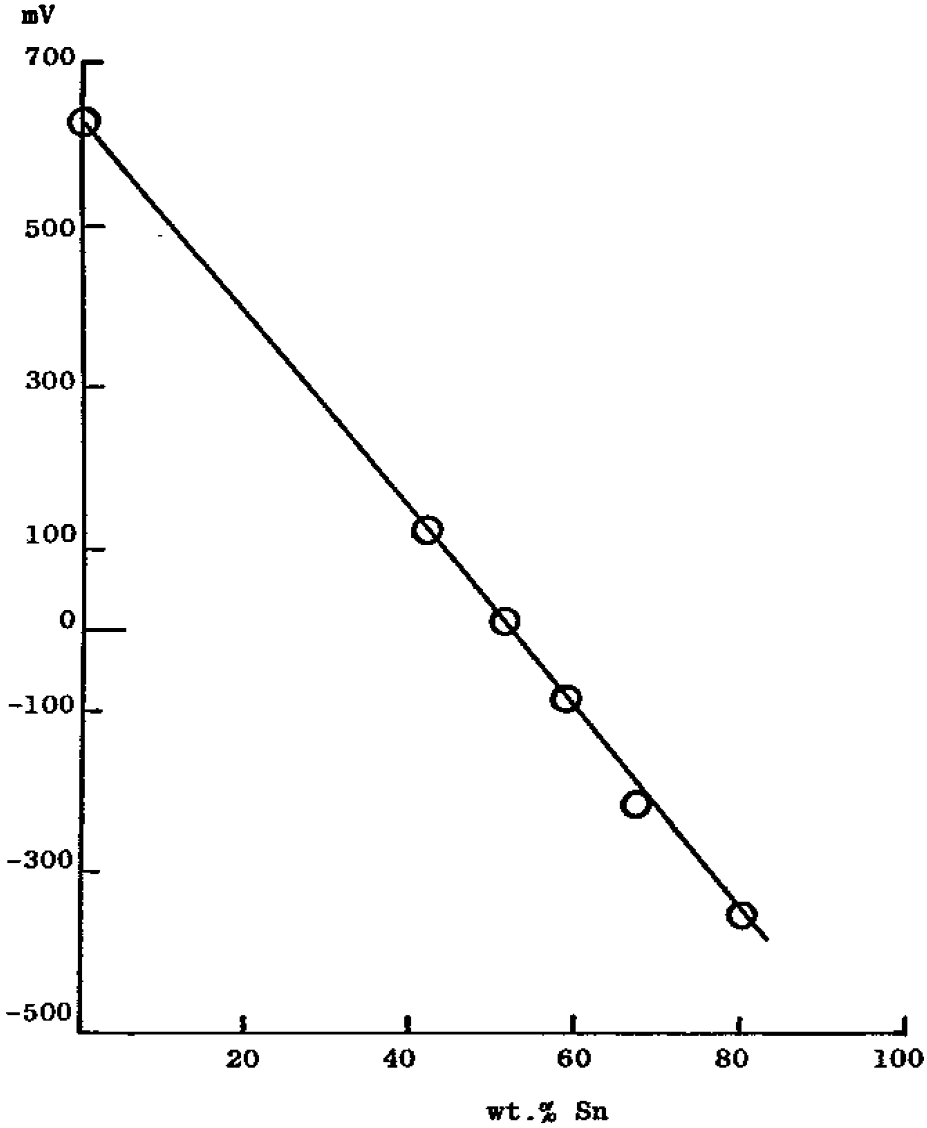
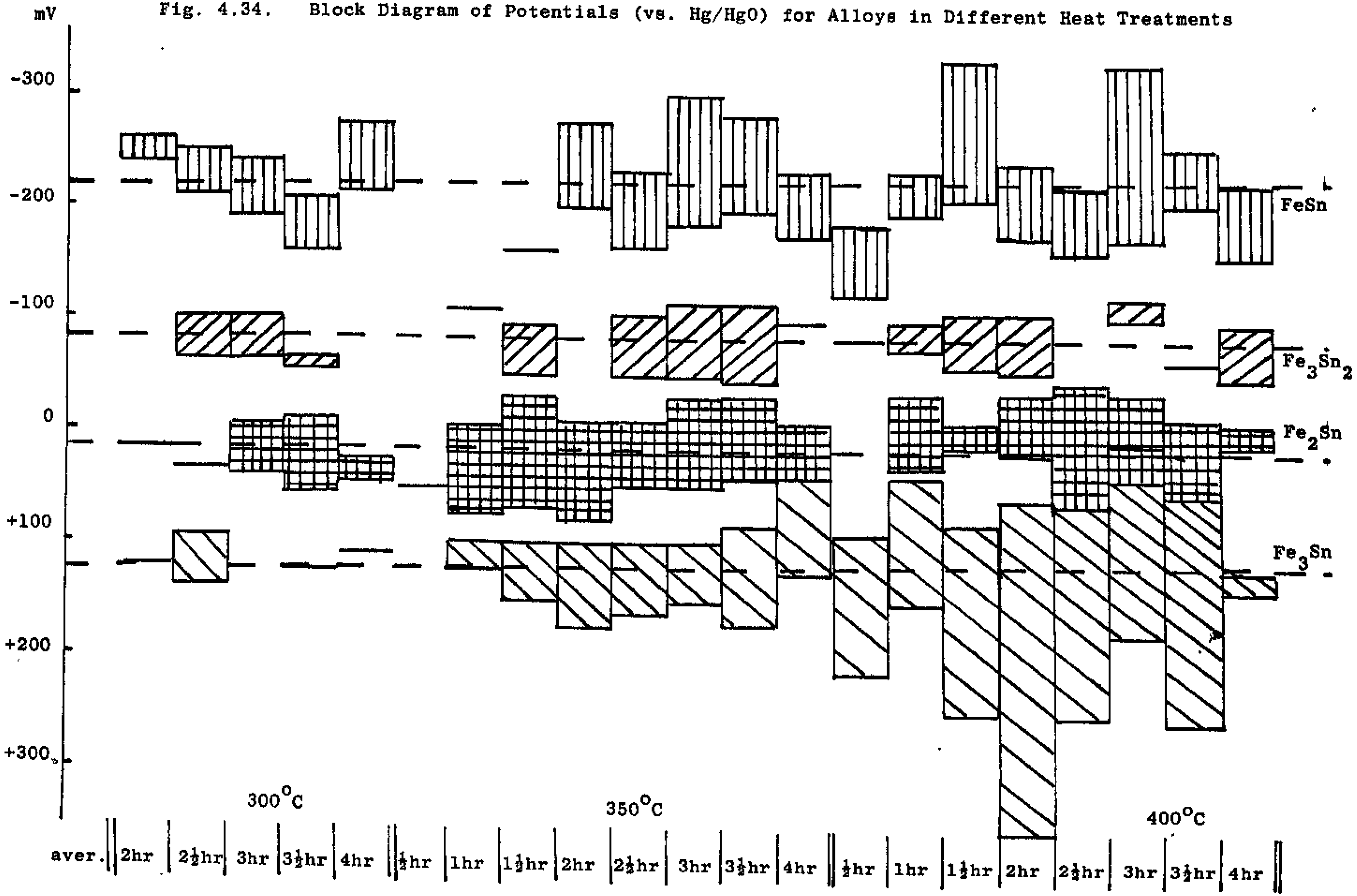


Fig. 4.33. Wt. % tin vs. Average Reaction Potentials for Alloys.

Fig. 4.34. Block Diagram of Potentials (vs. Hg/HgO) for Alloys in Different Heat Treatments



areas analysed, but suggested an iron:tin ratio of up to 2:1 (Fe_2Sn).

One major difficulty in obtaining conclusive evidence for the existence of other intermetallics is that the electron probe beam is relatively large compared to the area and depth of the regions of interest. Consequently, the beam is focussed on an inhomogeneous sample. A typical photograph obtained by transmission electron microscopy is shown in Fig. 4.32; the structure is very similar to that of $FeSn_2$ as obtained by Gabe.[221]

Results obtained by both scanning electron microscopy and transmission electron microscopy, including diffraction patterns, were less conclusive.

The compositions of known iron-tin alloys are shown in Table 4.11.

If it is assumed that the more iron present in the alloy, the more noble it will be in hot alkali, the potentials associated with the electrolytic plateaux can be assigned to known structures. A linear relationship is obtained between iron content and potential, as shown in Fig. 4.33. These potentials (vs. Hg/HgO) were estimated by observing the potential range over which the associated plateaux are present under the imposed stripping conditions, as shown in Table 4.12., and are based on the mean potentials obtained from the block diagram shown in Fig. 4.34. Little work has been published on potential/constitution relationships of alloys, although Stromberg and Zakharov[317] claim that the composition of amalgams can be predicted by the shape of the current-time stripping curves.

Kunze and Willey[243] have calculated the electrochemical equivalent of $FeSn_2$ to be 0.507 mg/C, which corresponds to the oxidation state of both components as being 2. Assuming the oxidation state does not vary, the electrochemical equivalents of the remaining alloys can be calculated, as shown in Table 4.12. It is, however, difficult to assess the quantity of alloy present, because as the more noble intermetallics become exposed, the potential becomes more anodic, forcing the dissolution of the less noble alloys. Non-destructive analyses, such as electron probe micro-analysis and diffraction patterns suggest that the quantities of alloy which are not $FeSn_2$, remain low, whilst galvanostatic stripping indicates that the amount of FeSn may be substantial, little current being consumed at the $FeSn_2$ potential. This apparent discrepancy can be explained by the presence of FeSn at the surface of the anode. It was also noticed that if the thermally treated tinplate was left for a period of time (about one month) the detinning characteristics altered, and the tinplate showed signs of rusting. This can be explained by the intermetallics formed during the heat treatment being unstable at room temperature and probably forming more stable compounds, as shown below:

$$Fe_3Sn \rightarrow Fe_2Sn + Fe \qquad \text{eqn. 4.45}$$

$$2Fe_2Sn \rightarrow Fe_3Sn_2 + Fe \qquad \text{eqn. 4.46}$$

$$Fe_3Sn_2 \rightarrow FeSn_2 + 2Fe \qquad \text{eqn. 4.47}$$

$$2FeSn \rightarrow FeSn_2 + Fe \qquad \text{eqn. 4.48}$$

Evidence for this is based on the fact that slow, but definite oscillations of the reaction potential occur between the different characteristic reaction potentials, both after storage and during initial detinning, indicating that higher alloy formation follows a similar, but reversed mechanism to that above.

4.14. Some Reactions of the Alloy Layer

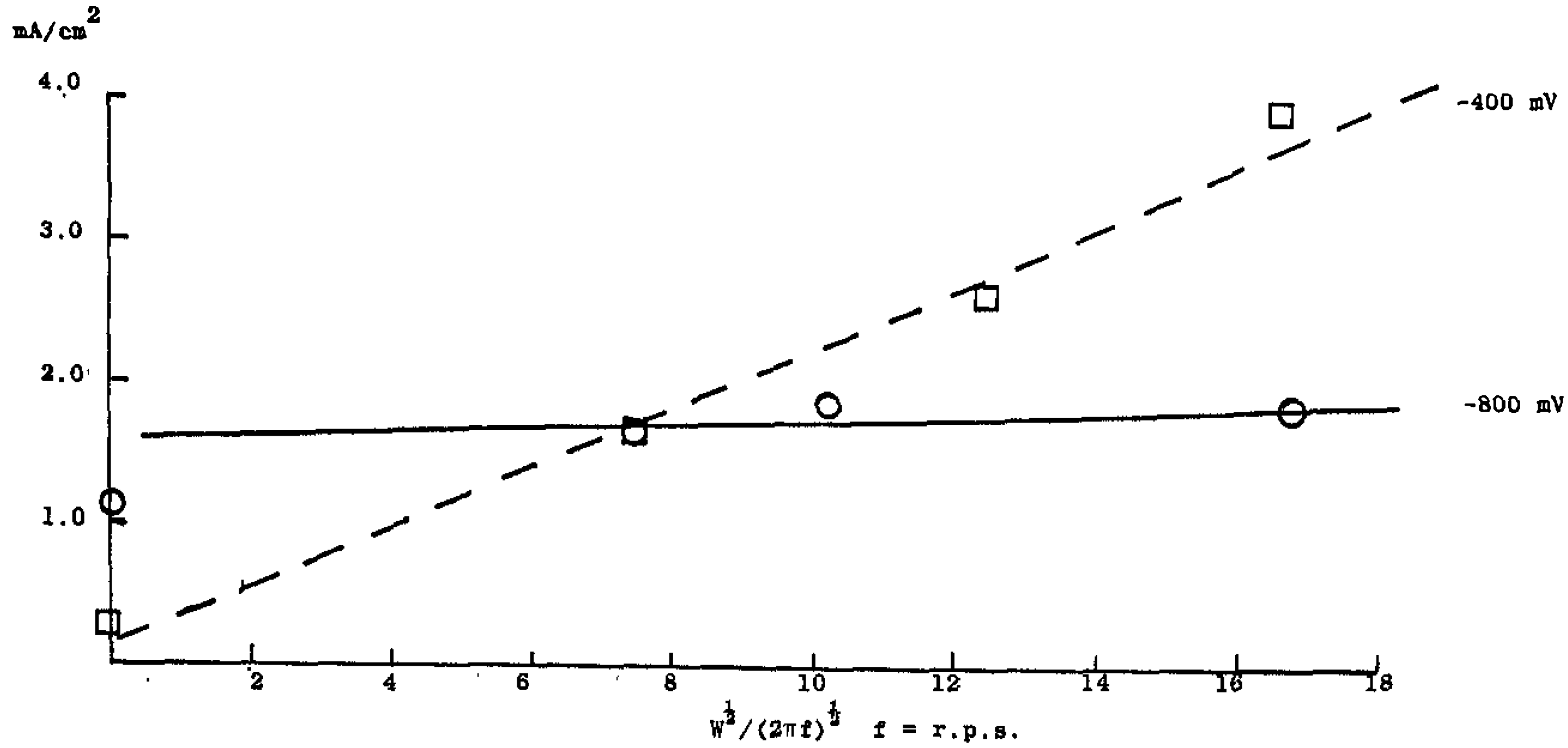
The dissolution of $FeSn_2$ in an alkaline electrochemical medium produces ions of the lowest oxidation state during the rate determining step[243], hence the oxidation number of the alloy is six. However, stannite ($HSnO_2^-$) is not stable in alkali and forms stannate ($HSnO_3^-$).[297]

Analysis of the rate of alloy electrochemical attack in most alkaline liquors, as discussed in Section 4.5.1., indicates that the rate is not highly dependent upon current density, but it is dependent upon temperature. In the majority of liquors the alloy will not dissolve at any appreciable rate below about 70°C.

The alloy dissolution rate is linearly related to the hydroxide concentration (Fig. 4.8.), and the gradient is found to be $^1/_6$. This indicates an adsorption mechanism, because the dissolution rate is virtually independent of hydroxide concentration.

During electrolytic attack at low current densities a plateau corresponding to -800 mV (vs. Hg/HgO) was observed. The size of the plateau was highly dependent upon the current density; at 5 mA/cm^2 the plateau was virtually undetectable, but at values below 0.5 mA/cm^2 it became the predominant feature of the alloy dissolution. The length of

Fig. 4.35. Effect of $W^{\frac{1}{2}}$ on anodic current density for reactions of the alloy at different potentials.



the plateau is independent of alkali concentration, suggesting that it is associated with adsorption of an overlay; it is also independent of temperature between 70° and 90°C. Above 90°C the dissolution time increases substantially, suggesting either a thicker adsorbed layer, or an insolubility effect. Below 70°C the dissolution of the alloy is very slow, and often the electrode passivated.

Studies at 80°C using a potentiostatically controlled rotating disc electrode showed that at low speeds of rotation (0 to 2,700 rpm), the current density did not vary with $w^{\frac{1}{2}}$ ($\sqrt{\text{angular}}$ velocity) for the plateau at -800 mV (Fig. 4.35.). This indicated that ~~the reaction was kinetically controlled, due to the electron transfer reaction being much slower than the rate of mass transfer~~, or that the reaction components had to pass through an inert passive layer. However, the reaction corresponding to -400 mV (vs. Hg/HgO) showed a linear proportionality between current density and $w^{\frac{1}{2}}$, indicating that the electron transfer reaction is the faster step, and that the reaction rate is determined by the rate of mass transfer, (Fig. 4.35.).

Cherkashin(284) has shown that the dissolution of some alloys in water follow a mechanism whereby the most electropositive component reacts to give the corresponding hydroxide and the free metal of the less electropositive element. Löberg(285) has suggested that the reaction of water vapour on intermetallics is stopped by the passivation of one, or both, components of the alloy. Lingstrom(318) claims that due to trivalent iron being more dense than divalent iron, the oxidation of $Fe(OH)_2$ to $Fe(OH)_3$, and further to FeO.OH, disrupts the structure; he also points out that $Fe(OH)_2$ is insoluble in alkali.

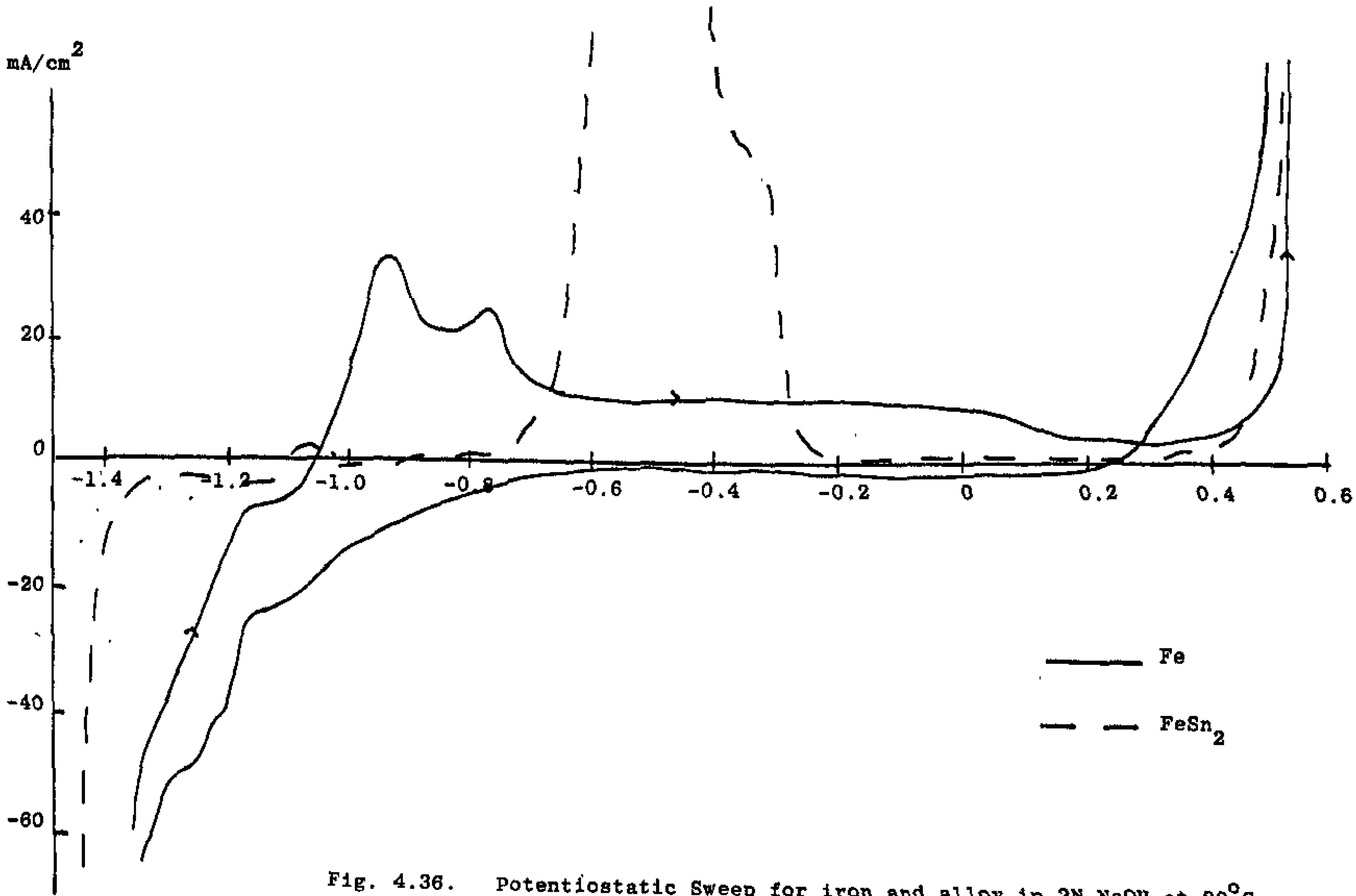


Fig. 4.36. Potentiostatic Sweep for iron and alloy in 2N NaOH at 80°C.

Schrebler-Guzman[168] has reported various potentials involved in the dissolution of iron in alkali, using cyclic voltammetry at 25°C. A mechanism is proposed:

$$Fe + OH^- \rightarrow Fe(OH)_{ads} + e^- \qquad \text{eqn. 4.49}$$

$$Fe(OH)_{ads} \rightarrow Fe(OH)_{ads}^{+} + e^- \qquad \text{eqn. 4.50}$$

$$Fe(OH)_{ads}^{+} + OH^- \rightarrow Fe(OH)_2 \qquad \text{eqn. 4.51}$$

$$Fe(OH)_2 + OH^- \rightarrow Fe(OH)_3 + e^- \qquad \text{eqn. 4.52}$$

$$Fe(OH)_3 \rightarrow FeO.OH + H_2O \qquad \text{eqn. 4.53}$$

The potentials reported, -0.78V, -0.62V and -0.4V (vs. S.H.E.), correspond to eqns. 4.49, 4.50 and 4.51 in the most cathodic cases and to eqns. 4.52 and 4.53 at the most anodic potential. This work was repeated in an open beaker at 20°C and 80°C, using a Luggin capillary. A shoulder plateau was noticeable at -0.94V, followed by a double peak at -0.72 and 0.56V (vs. Hg/HgO), as shown in Fig. 4.36., the latter of which had a tail extending to +0.3V on the anodic sweep. The intensity of the peaks increased greatly at 80°C compared to 20°C. These results are in agreement with previous workers.[319,320]

When the experiment was repeated with alloy ($FeSn_2$) at 80°C, a weak peak corresponding to -0.9V (vs. Hg/HgO) was visible, but a strong one at -0.42V (vs. Hg/HgO); these correspond to:

$$Fe(O) \rightarrow Fe(II) + 2e^- \qquad \text{eqn. 4.54}$$

and $Fe(OH)_2 + OH^- \rightarrow FeO.OH + H_2O$ eqns. 4.52 and 4.53 respectively; only one sweep was possible due to the irreversible dissolution of the alloy.

Clarke and Britten[288] have reported the dissolution of nickel-tin alloys at both 25°C and 71°C, where the following reactions occur:

$$SnNi + 4OH \rightarrow Sn(OH)_2 + Ni(OH)_2 + 4e^- \qquad \text{eqn. 4.55}$$

$$Ni(OH)_2 + OH^- \rightarrow NiO.OH + H_2O + e^- \qquad \text{eqn. 4.56}$$

The existence of $Fe(OH)_2$ during dissolution of $FeSn_2$ was confirmed during an experiment relating to the iron-tin couple (Section 4.4.2), for during attack on the alloy layer, a green overlay was visible; this corresponded to an increase in potential of about 180 mV above the dissolution potential for tin, which would thus correspond to the plateau at -800 mV.

Addition of oxidants to the electrolyte did not generally increase the dissolution rate of the alloy.

If the rate of dissolution is plotted against current density, and extrapolated to zero current density, and the corresponding rate then used for an Arrenhius plot, the activation energy can be calculated:

$$R = R_o \exp\left(-\frac{\Delta H}{RT}\right) \quad - \text{ Arrenhius eqn.} \qquad \text{eqn. 4.57}$$

$$\therefore \quad \ln R = \ln R_o - \frac{\Delta H}{RT} \qquad \text{eqn. 4.58}$$

The gradient is $-\frac{\Delta H}{R}$, and calculation of the activation energy (ΔH) yielded a value of +20 ($\pm$2) kJ k^{-1} mol^{-1}(+4.76 ($\pm$0.48) kc $mol^{-1}k^{-1}$) for sodium hydroxide with and without nitrite and other non-active electrochemical oxidants. The presence of an active electrochemical oxidant such as chlorite, reduced the activation energy to +12 kJ $k^{-1}mol^{-1}$(+2.86 kc $k^{-1}mol^{-1}$), showing the existence of another reaction mechanism. This explains the much more rapid dissolution rates in the presence of chlorite.

Kokorin and Vitkin[244] have postulated the existence of two forms of $FeSn_2$, tetragonal and hexagonal; if they exist there should be a detectable transition temperature between the two forms. A determination of this temperature was carried out by Differential Thermal Analysis, but no transition temperature was observed between 50°C and 250°C, even with the equipment operated at its most sensitive range. This indicates that either the transition temperature is below 50°C or above 250°C, or that there is no such transition, and that the evidence for the two forms is erroneous.

From the results of alloy dissolution, the reaction appears to follow a mechanism controlled by the reactivity of the most noble component of the alloy. During the electrochemical attack the iron matrix is disrupted, allowing free dissolution of the tin. The alloy shows more character associated with iron than with tin during alkaline electrochemical attack.

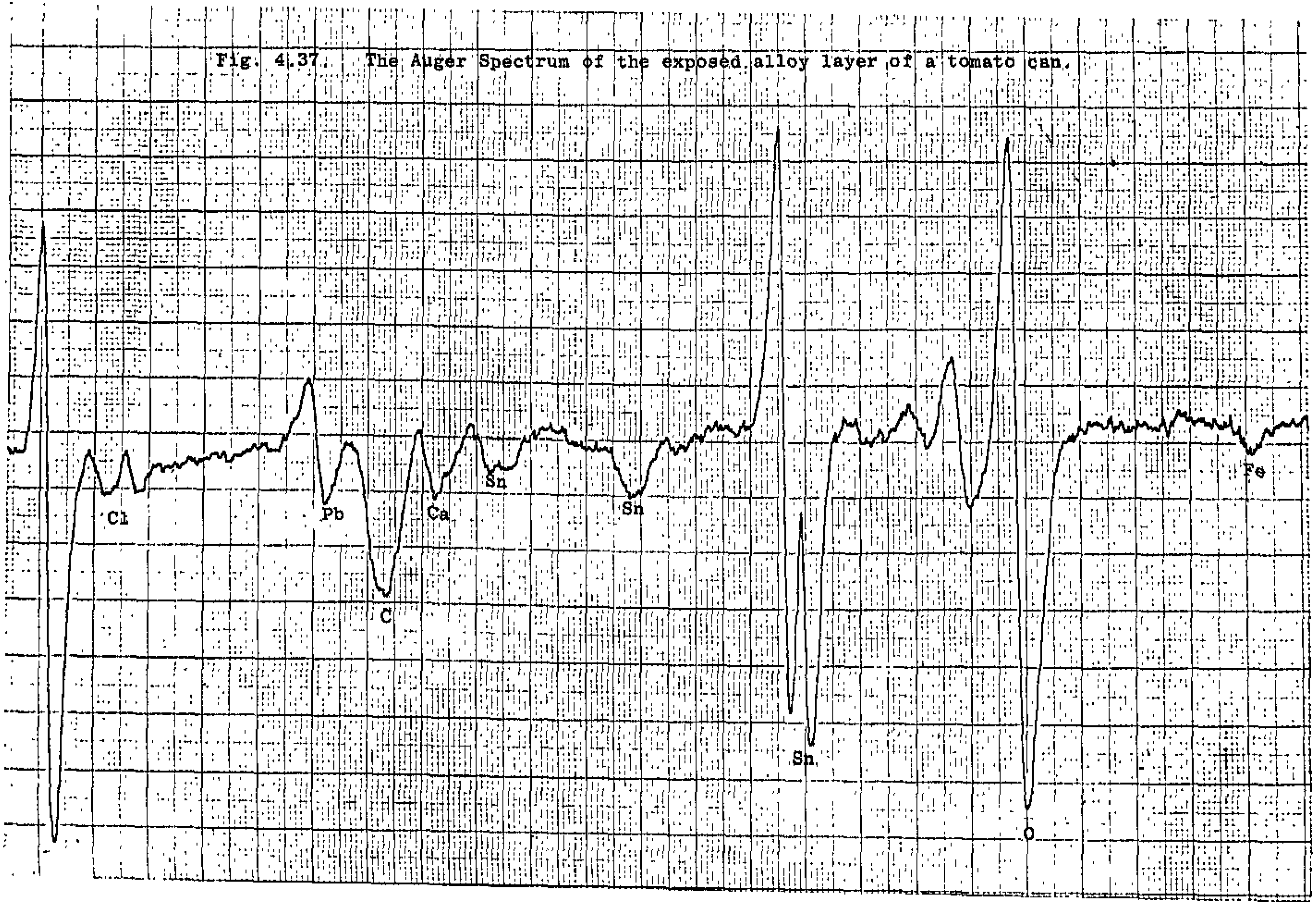


Fig. 4.37. The Auger Spectrum of the exposed alloy layer of a tomato can.

4.15. The Presence of Other Elements in Tinplate

During studies of tinplate surfaces by Auger Spectroscopy and Rutherford Back-scattering, iron, tin, oxygen, calcium, lead, sulphur, carbon and chlorine were detected. Fig. 4.37. shows the Auger spectrum of a sample of unlacquered tinplate where the contents (Italian tomatoes) had dissolved some of the free tin. A similar spectrum for clean tinplate galvanostatically stripped to -840 mV (vs. Hg/HgO) revealed only iron, tin, oxygen, calcium and lead, suggesting that the other elements originated from the food.

Iron and tin peaks are expected from the constitution of the can. Oxygen was probably in the form of oxide or hydroxide produced during waterline corrosion after opening. The presence of calcium, however, was not expected, although Habraken and Le Roy[327] have also reported its presence on blackplate after pickling in hydrochloric acid, and subsequent washing. A possible explanation is that after the pickling process, the steel plate is washed in water which may contain soluble calcium salts. These salts are then deposited on the plate, which then enters the plating section, where tin is deposited. Other explanations for its existence are that it originates from lubricating oils used during cold rolling of the steel plate before pickling, or the presence of organic calcium salts in the oil overlay of fresh tinplate.

The presence of lead was shown by both Auger spectroscopy and Rutherford Back-scattering. The amount of lead permitted in tinplate is 0.08%[328] of the total tin. Quantitative analysis by Auger spectroscopy revealed a surface lead content of 3% (atomic percent) on the used can. Definition of "the surface" is difficult, but it probably corresponds to a thickness of a few atomic layers. When the clean tinplate was examined, however, it was found that to eliminate the lead signal, 300Å had to be removed by sputtering from the alloy surface. This corresponds to a continuous layer equivalent to about 3% of the original tin thickness, and forty times the maximum expected from the British Standards Specification.

Two possible explanations exist for the high lead content. One is that there is a physical build-up of lead at the tin/alloy interface as the result of increased mobility of free lead in the tin during the flash melting process. The second is that as the lead is electrolytically stripped, it redecorates the surface of the specimen by a displacement reaction (see page 15, refs. 75, 76). The latter is not supported by Auger spectroscopy, although electrochemical data suggests it to be possible. Eremenko[294] has shown there to be regions of stability in the Fe-Sn-Pb phase diagram, suggesting that lead may be associated with the alloy, but Thwaites[295] claims the presence of lead reduces the quantity of $FeSn_2$ formed. Lead is not soluble in iron.

Brook[149] has adapted the Pourbaix Diagram for lead to account for increases in temperature, and has shown that the reaction potential of

$$HPbO_2^- + H_2O + 2e^- \rightarrow Pb + 3OH^- \quad (-0.54V \text{ at } 25^{\circ}C) \text{ ref. } 316$$

eqn. 4.59

decreases to about -0.7V (vs S.H.E.) at 102°C. This compares well with -0.8V (vs. Hg/HgO) as recorded in the detinning experiments at 95°C.

At such a potential, the electrochemical removal of lead will take place during the first oxidation stage of alloy dissolution; this would account for the misleading electrochemical results of the lead content, and also account for the apparent "decoration" of the alloy with lead.

Soluble lead salts have been used to aid tin dissolution on tinplate[75,76,83], the effect being due to the reduction potential of lead being more anodic than that of tin under the same conditions, hence lead will be deposited whilst tin dissolved. The alloy layer, however, would not be affected by the presence of lead, because the active dissolution potential of the alloy is about 350 mV more anodic than that of lead. By comparing the actual reaction potential of the $Pb/HPbO_2^-$ reaction with the theoretical potential at a given temperature and pH, it is possible to determine the extent of polarisation of the reaction.

Analysis by electron probe microscopy showed the presence of lead, but the background count was so high relative to the total count that no accurate quantitative measurements were possible.

Rutherford Back-scattering was able to detect lead on the surface of some specimens, but the penetration depth of the beam was relatively high, so quantitative analysis was difficult. The technique can also easily detect variations in tin concentration with depth in the steel. It was possible to detect some lead on the sample of a tomato tin where the free tin had been dissolved by the tomato juices; an approximate calculation indicated that the exposed alloy contained about 0.3% by weight of lead.

Analysis of a sample of unflashed E5.6/5.6 tinplate indicated the presence of lead, and electrochemical analysis yielded a figure of between 0.13% and 5% lead by weight; this is significant in as much as no alloy was present to interfere with the electrochemical determination, but nevertheless the result appears rather high. This may, however, be due to initial attack of the steel by alkali to produce ferrous hydroxide, followed by its passivation.

Chemical analysis, carried out by M. Saremi, indicated the presence of 0.215% lead by weight in a sample of D5.6/8.4 tinplate. Although these results may appear alarming, the evidence for widespread contamination of tinplate with lead is slight, and in practice the lead from the soldered seam is a lot more important than the electro-deposited lead on the can.

Elemental analysis of the surfaces by Auger spectroscopy has shown the presence of oxygen at depths of greater than 3000 Å in the alloy layer. Tables 4.13. and 4.14. show the atomic percentage of elements detected in lead free tinplate. The surface is systematically removed by sputtering, the sputtering time being in minutes, as shown in Column Sp. One minute of sputtering is equivalent to about 4 Å.

Both Tables show the presence of carbon, although the vast majority appears to be in the form of surface contamination, as the majority of it is removed in the first few atomic layers.

Sp (mins)	Fe	Sn	C	O	S	Cl	Depth (Å)
0	4	12	37	35	2	6	0
5	4	18	16	45	8	1	20
20	5	17	13	46	9	1	80
50	5	18	10	51	5	1	200
100	7	11	8	56	6	1	400
255	5	12	6	54	9	1	1020
435	19	12	9	41	5	1	1740
710	22	11	8	35	12	0	2840
1027	38	21	6	28	4	0	4108
1717	45	22	0	15	18	0	6868

Elemental atomic percent Auger analysis at various depths for the plateau corresponding to -800 mV.

TABLE 4.13.

Sp (mins)	Fe	Sn	C	O	S	Cl	Depth (Å)
0	4	14	28	42	5	1	0
7	6	18	13	49	9	0	28
20	9	18	7	53	7	0	80
50	9	18	4	55	7	1	200
100	12	12	2	53	10	2	400
280	16	6	0	52	15	2	1120
485	22	8	4	47	10	1	1940
1133	34	7	4	44	8	1	4532
1528	42	12	4	32	9	1	6112

Elemental atomic percent Auger analysis at various depths for the plateau corresponding to -360 mV.

TABLE 4.14.

Table 4.13. shows that the oxygen content is constant to a depth of over 3000 Å during stripping at -780 mV. The amount of tin also remains constant, whilst as sputtering occurs, the presence of iron progressively increases. This suggests an inhomogeneous surface of iron and alloy, as all the tin has been previously removed.

Once the reaction potential has increased to -360 mV (vs. Hg/HgO), further sputtering reveals a sharp decrease in the time content at depths in excess of 400 Å, with a corresponding increase in the amount of iron, (see Table 4.14.). The oxygen content, however, remains at a high level. Ratios of oxygen to iron and tin suggest that stannous hydroxide is found in conjunction with ferric hydroxide, or FeO.OH. These results complement the indications of mechanistic processes proposed in previous sections, but further studies and a deeper understanding of the effect of valence electrons on Auger spectroscopy have to be obtained.

4.16. Determination of the Degree of Dissolution of Tin in Steel by Rutherford Back-scattering

The Rutherford Back-scattering spectrum for untreated tinplate is shown in Fig. 4.38., but as the free tin migrates from the surface, and iron becomes closer to the surface, the spectrum alters to the shape shown in Fig. 4.39. Once the free tin has been removed from the surface, the front associated with free tin disappears to give a sharp iron front and a peak for tin, as shown in Fig. 4.40. The associated change in shape at lower energies is due to the increased depth the tin has penetrated, and consequential lower energy of back-scattered particles.

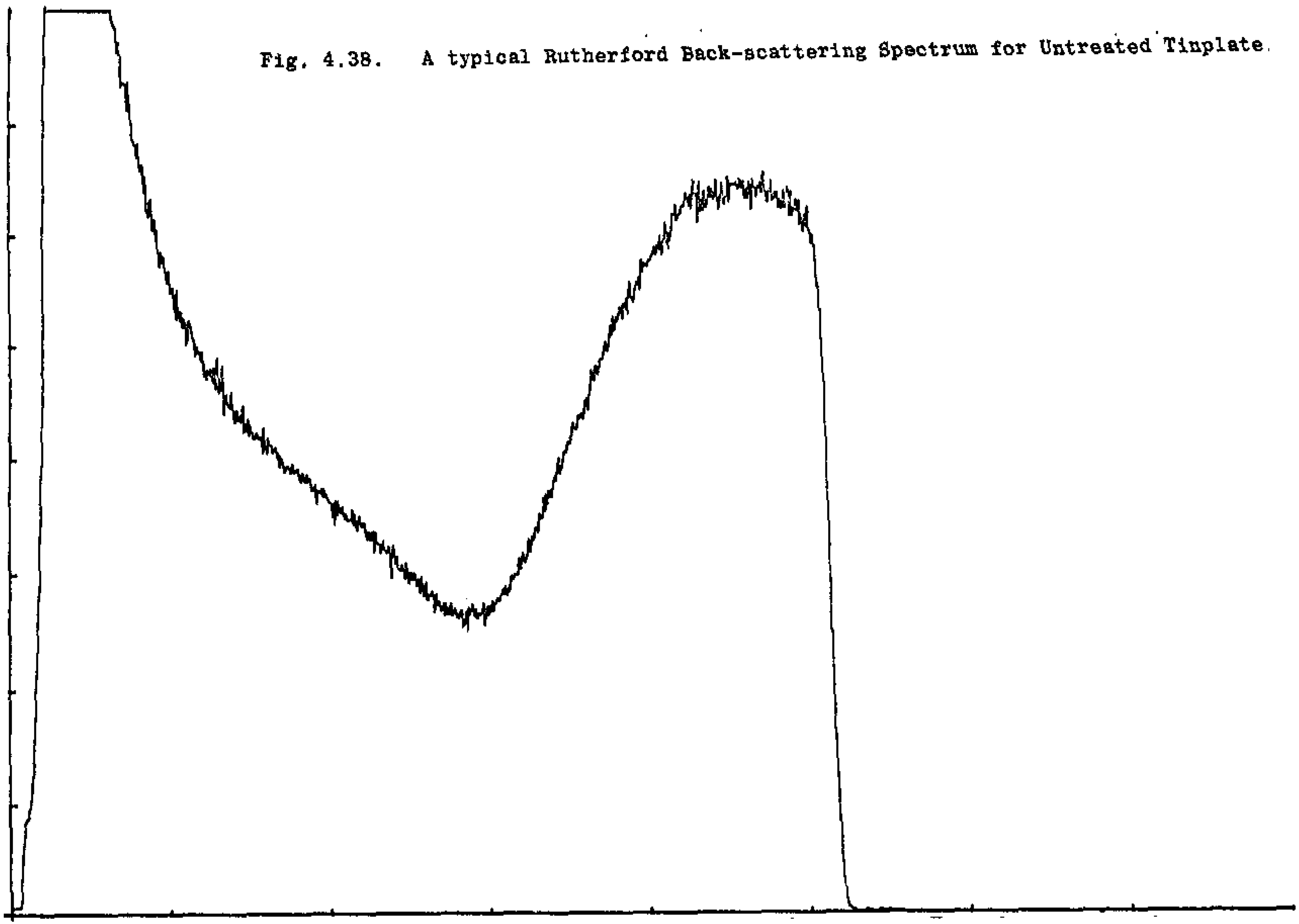
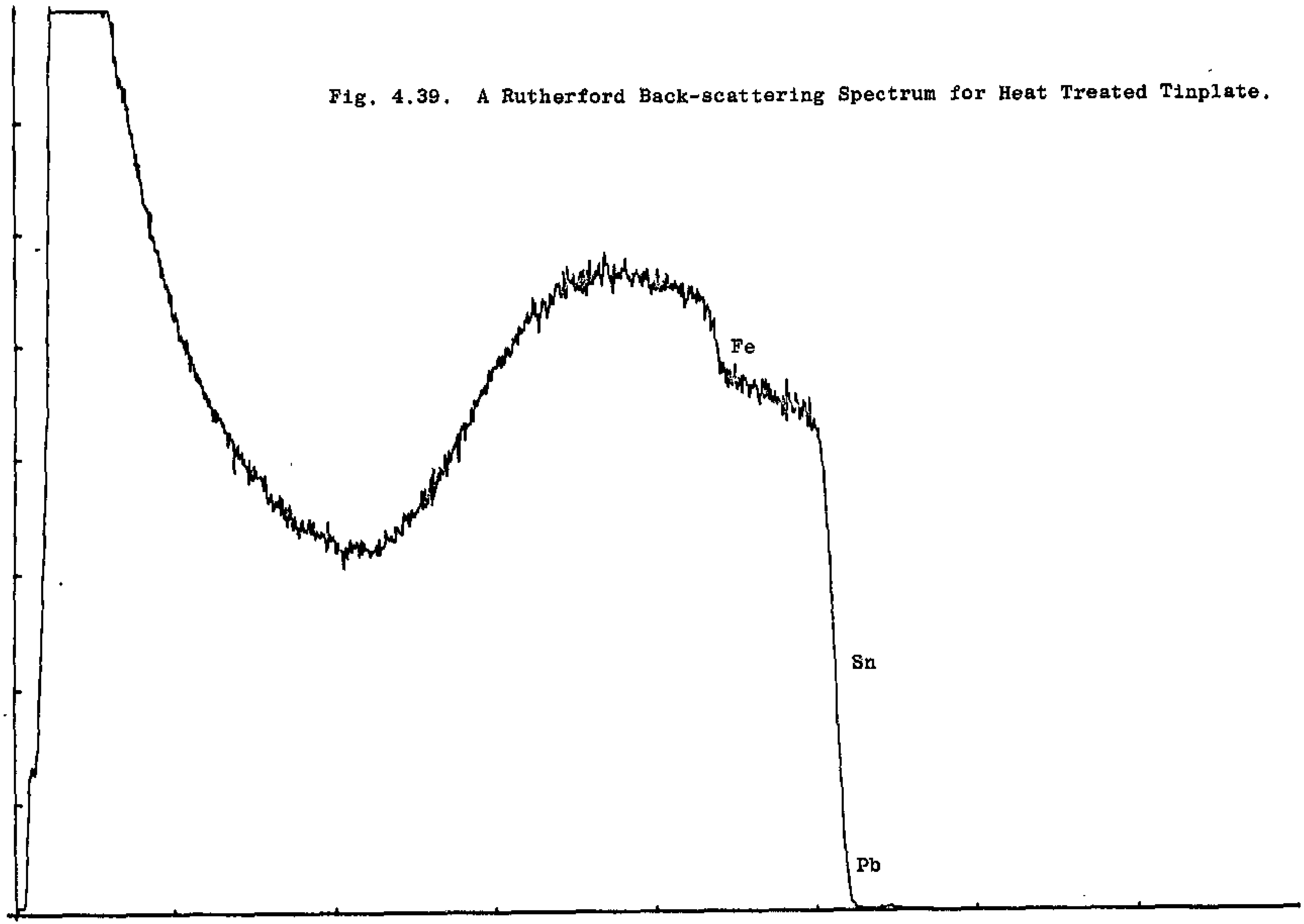


Fig. 4.38. A typical Rutherford Back-scattering Spectrum for Untreated Tinplate.

Fig. 4.39. A Rutherford Back-scattering Spectrum for Heat Treated Tinplate.



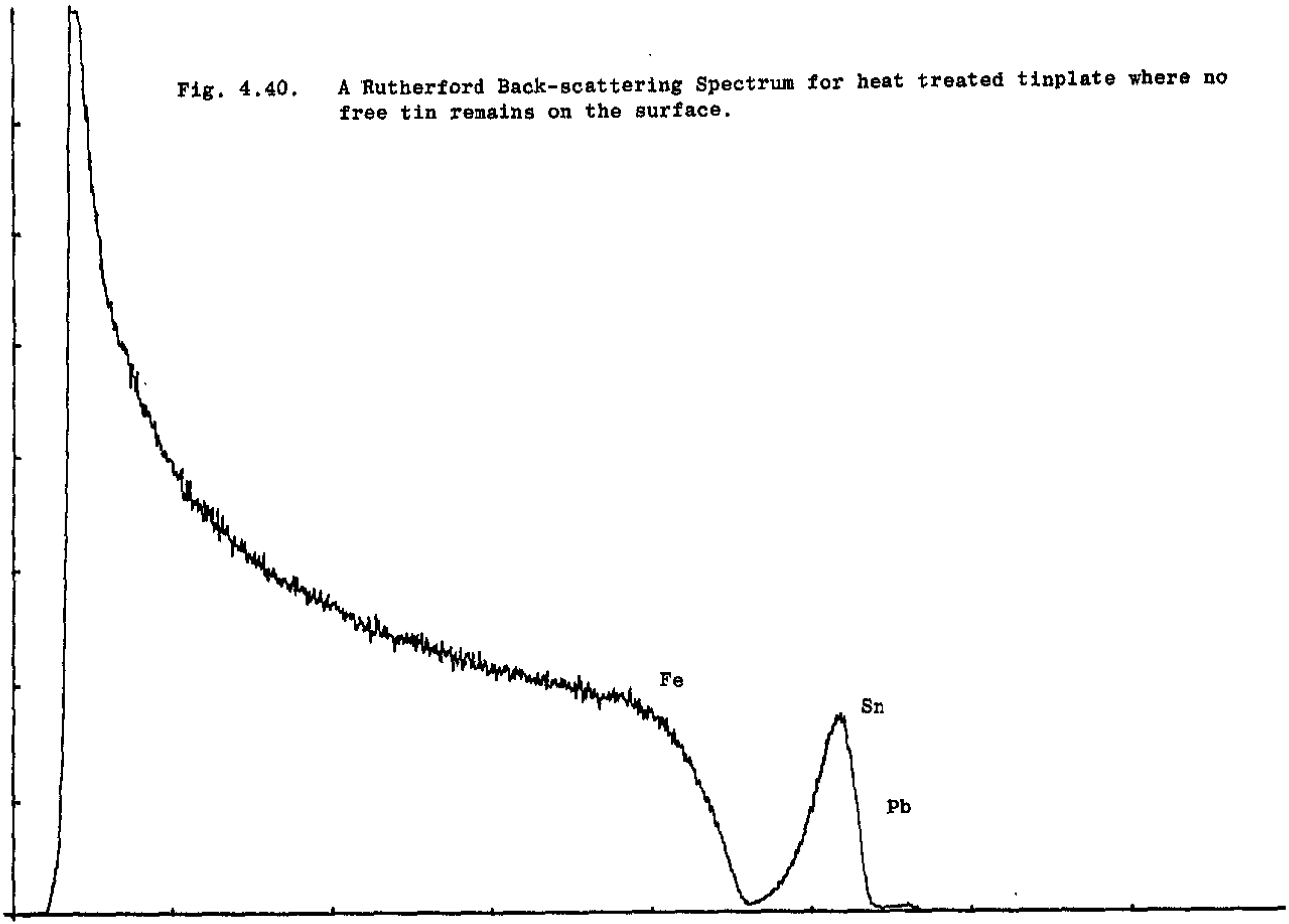


Fig. 4.40. A Rutherford Back-scattering Spectrum for heat treated tinplate where no free tin remains on the surface.

Fig. 4.41. Rutherford Back-scattering Spectra for tinplate heated to 200°C for 4 hrs.

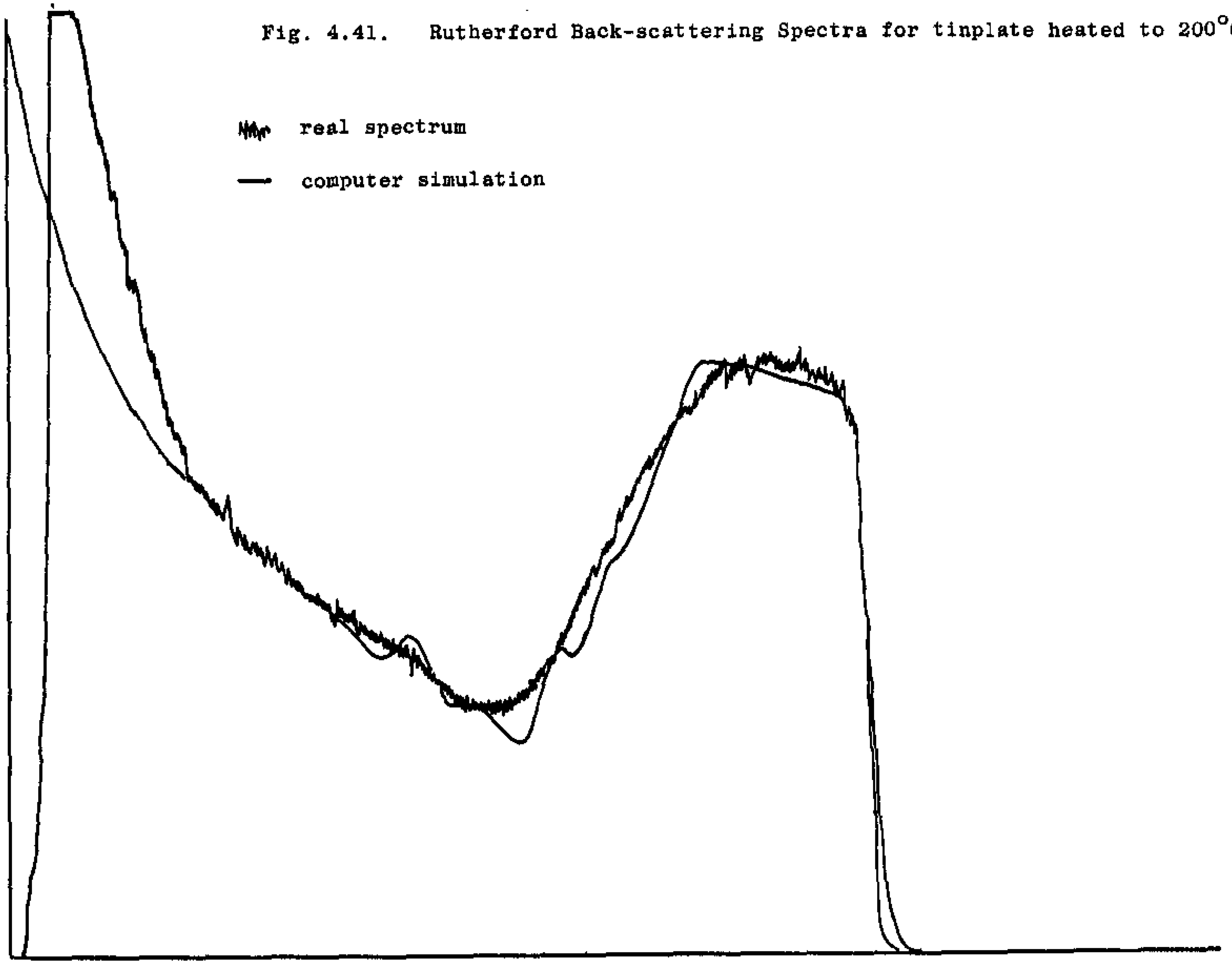
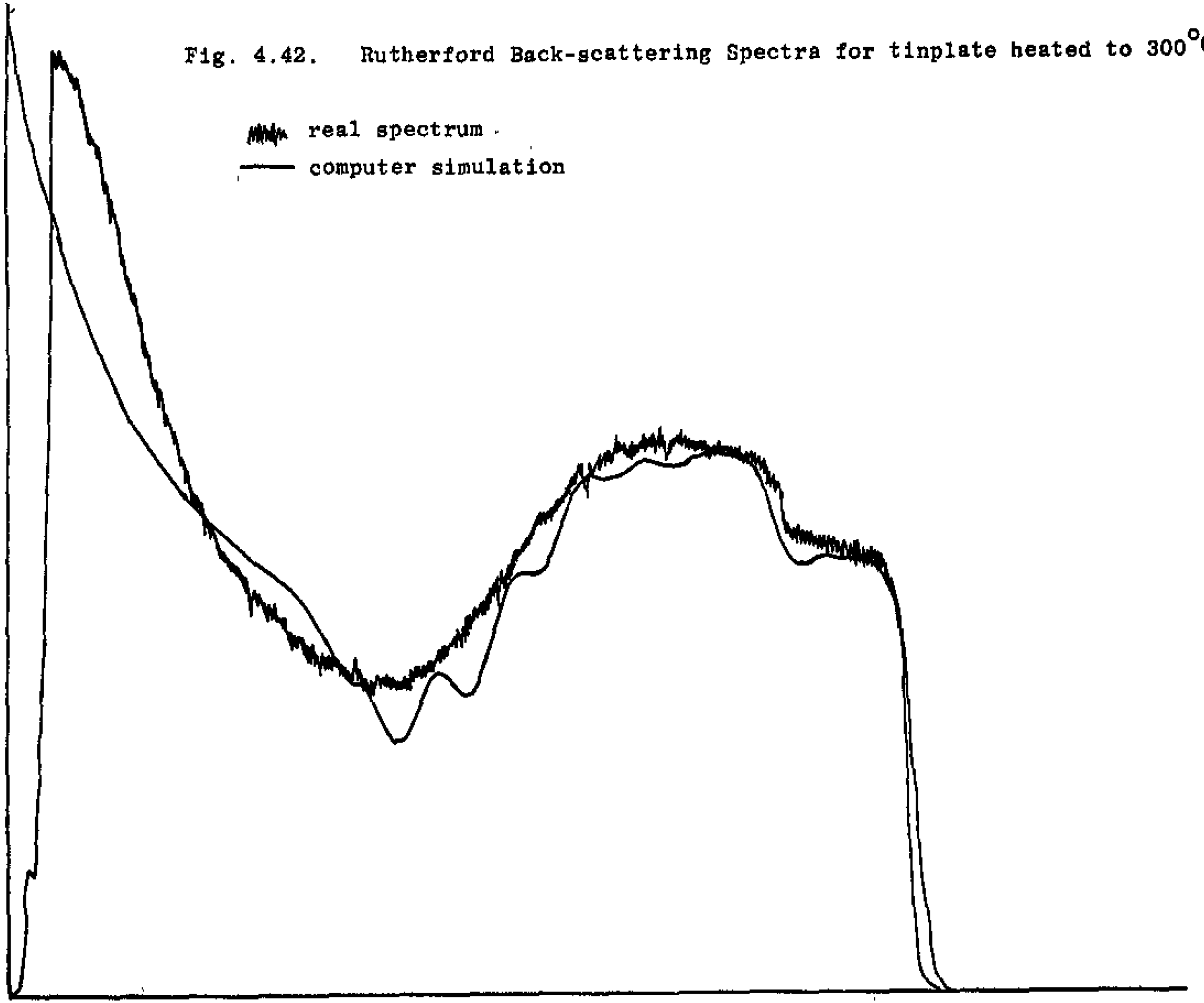


Fig. 4.42. Rutherford Back-scattering Spectra for tinplate heated to 300°C for 4 hrs.



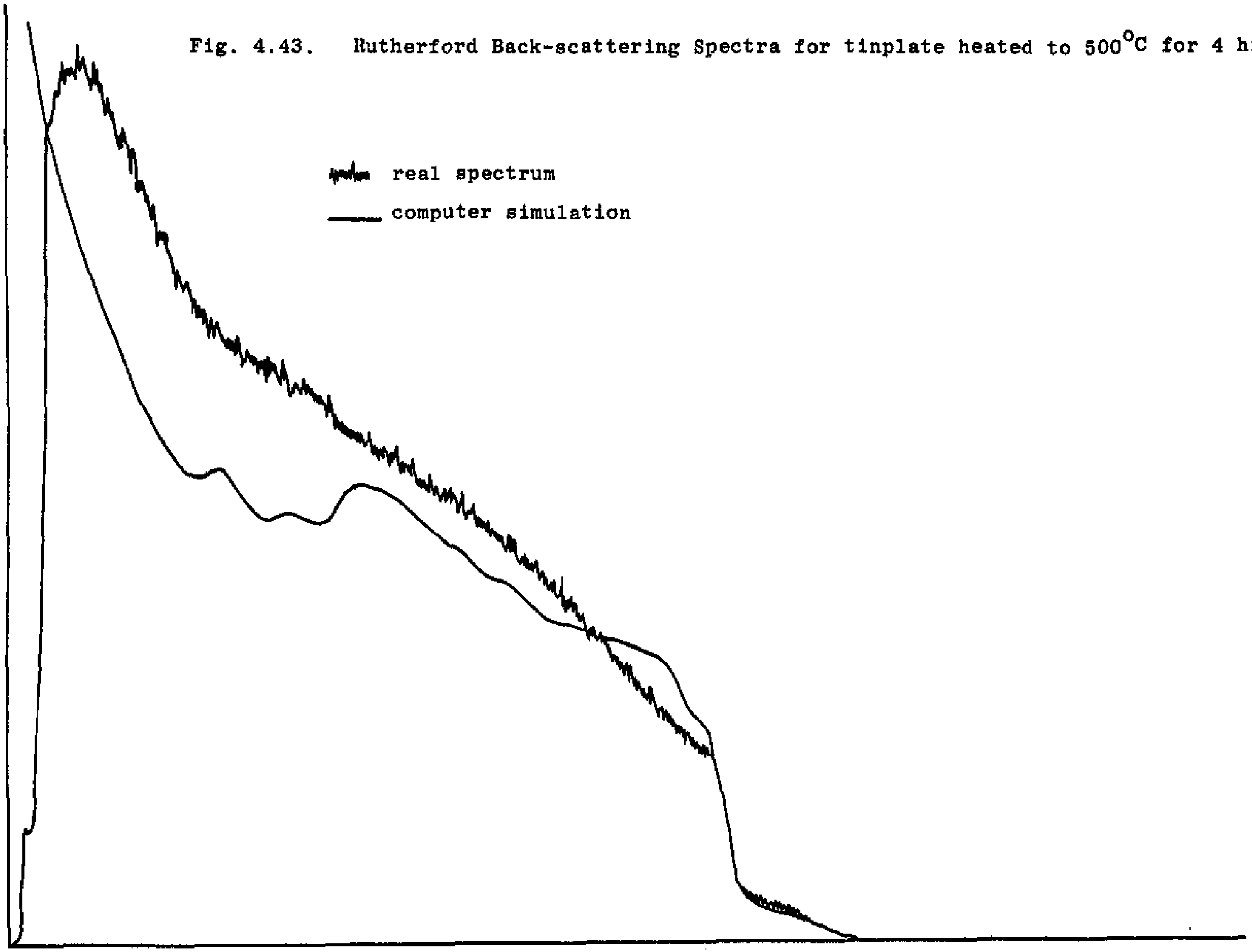
By altering the parameters of a computer programme to simulate the tin profile, it is possible to obtain a theoretical spectrum for tinplate. The amount of free tin and tin concentration gradient into the steel is varied. Each simulation is compared with the experimental one until a "best fit" is obtained. Due to the amount of computer time required to perform this, only a few have been done, but with a reasonable degree of success, as shown in Figs. 4.41., 4.42. and 4.43.

Fig. 4.41. shows the real and simulated spectra for tinplate that has been heat treated at 200°C for 4 hours. The simulation gave a free tin depth of 4000 Å, which correlates well with both the electrolytic and metallographic values of 5,500 Å. The simulation also indicated a fairly smooth decrease in the tin profile, for a further depth of 11,000 Å, at which point the tin concentration is zero. This does not agree with the electrochemical value of 5000 Å alloy layer.

Fig. 4.42. shows the real and predicted spectra for tinplate heated to 300°C for 4 hours. The simulation, metallographic and electrochemical results all suggest that the free tin has been totally removed to form alloy, which is present on the surface. It does also suggest a constant iron-tin ratio to a depth of 5000 Å, after which a tin gradient of a further 8000 Å exists. These results do not agree with either metallographic or electrochemical estimates of a total alloy thickness of 20,000 Å.

Fig. 4.43. shows the simulated and real spectra for tinplate

Fig. 4.43. Rutherford Back-scattering Spectra for tinplate heated to 500°C for 4 hrs.



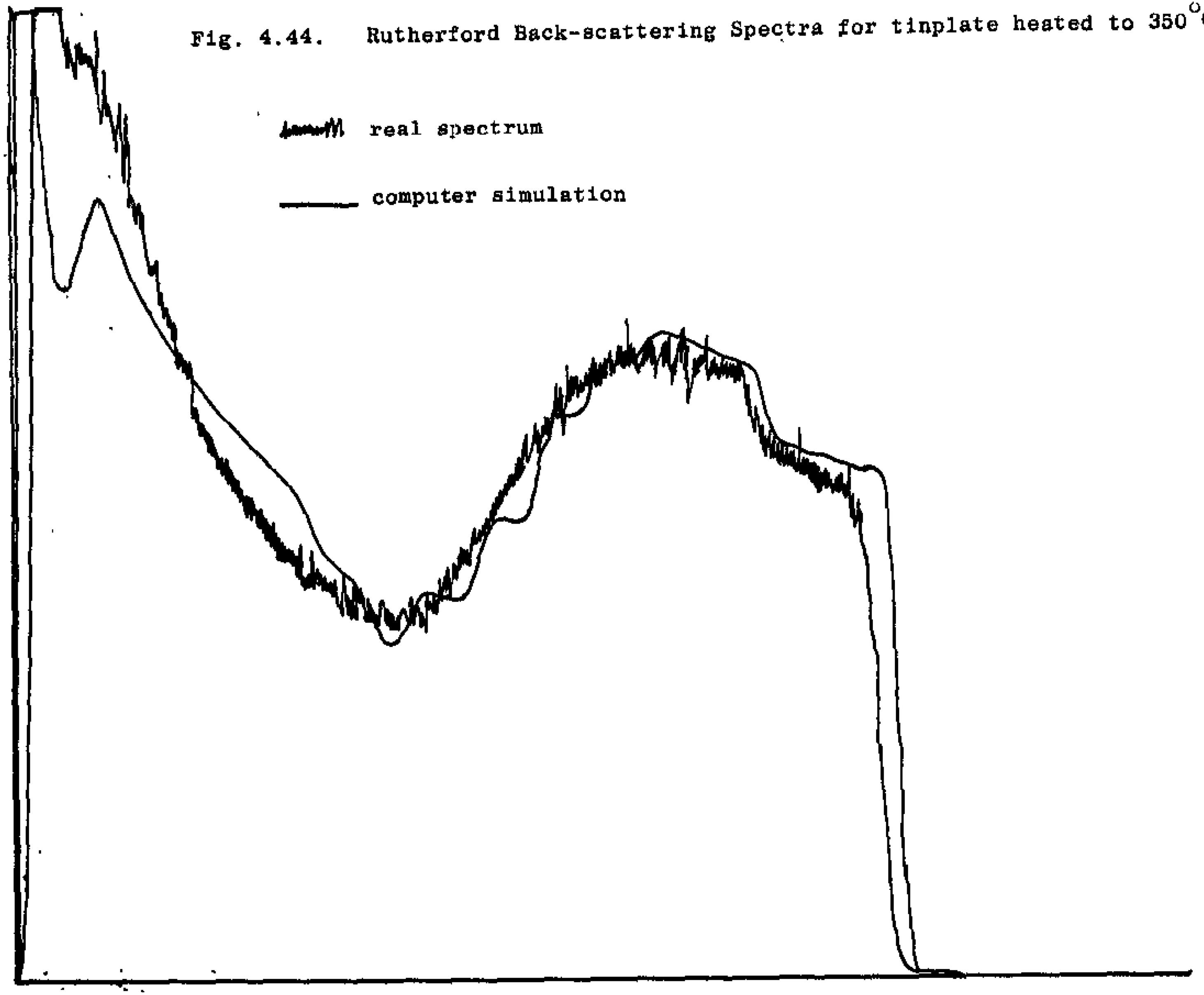


Fig. 4.44. Rutherford Back-scattering Spectra for tinplate heated to 350°C for 2½ hrs.

heated to 500°C for 4 hours. The simulation indicates an initial increase in the tin:iron ratio, but corresponding to a surface oxide layer of approximately 8000 Å. This is followed by an approximately constant tin profile for a further 3000 Å, and an exponential tail off in the tin profile for a total penetration depth of 25,000 Å. This compares with an electrochemical prediction of an alloy depth of 7000 Å. The comparison is unreasonable because the electrochemical results do not allow for the tin to be in solution with the iron, and for passivation of the electrodes by oxides.

Analysis of tinplate thermally treated at 300°C for 2½ hours (Fig. 4.44.) indicated, by electrochemical methods, a totally alloyed depth of 9000 Å, with a further 6,500 Å alloy of different forms, which were mainly Fe_3Sn and Fe_2Sn. Rutherford Back-scattering simulation, however, showed the existence of $FeSn_2$ to a depth of 5000 Å, with a diminishing tin gradient of a depth of 14,000 Å. Although the present simulation programme does not totally agree with other analyses, it does indicate that the programme can be developed to give more information regarding intermetallic formation than is at present available. Moreover, it shows that Rutherford Back-scattering will be a valuable asset in non-destructive analyses.

4.17. General Discussion of the Results with Respect to an Industrial Process

At present the majority of recycled tinplate originates from the off-cuts of clean tinplate. If reclamation is to be increased, alternative sources of tinplate have to be used.[312] The annual production of tinplate in the United Kingdom exceeds one million tons, the vast majority of which (over 90%) is finally deposited as urban waste. The amount of tin involved in this is in excess of 5,000 tons, and the value of the tin, (currently (Autumn 1980) about £7,000/ton), is about equal to that of the scrap steel.

For recycling in an electric arc furnace the detinned scrap steel should not contain more than 0.03% residual tin. The high degree of intolerance towards impurities is due to air not being pumped into the furnace to oxidise any impurities, as it is with the open hearth and Bessemer processes.

The used tin can has a dirt content of about 20%, the bulk of which is paper and organic materials. Most cans also have a coating of chemically and thermally stable lacquer applied to prevent corrosion of the container by its contents. To ensure a high degree of detinning, as much as possible of these contaminants have to be removed before metal separation can take place. The easiest way to clean such a can is to bake it, but it has been shown in the present study that both burn time and temperature must be carefully monitored. If the temperature exceeds 500^{o}C it is virtually impossible to recover the tin, whilst a dwell time of 30 minutes would be acceptable at 350^{o}C.

It has also been shown that the majority of the alloy formed during baking is $FeSn_2$. However, if no further free tin is available for alloying, other alloys, less rich in tin, are formed by diffusion into the steel. When this occurs, the tin becomes more dilute throughout the plate. The less rich alloys are more difficult to detin, and are unstable at normal temperatures.[223] If totally alloyed tinplate is left standing for any great time (less than one month), the alloy becomes more iron-like in character and passivates. Electrolytic alkaline treatment of such plate renders it passive, preventing or at least making more difficult, the recovery of free tin. Such plate would, however, be susceptible to acid dissolution.

The composition of the can is very important, because many cans have aluminium tops to them; if an alkaline liquor is to be used for tin recovery, it is essential that the aluminium is removed. If it is not, it will react violently, and wastefully, with the liquor. Aluminium can be removed by magnetic separation after the cans have been shredded.

Shredding of the cans is very important, for it not only increases the bulk density, but it also opens the seams of the cans allowing attack of the tin-lead solder.

The method employed for detinning will be dependent upon the volume, type and source of tinplate available. A purely chemical alkaline process would be suitable for clean tinplate, but if recycled cans are to be used, either an alkaline electrochemical, or acidic, process would be required. Acidic processes have the advantage of not requiring heat to maintain a good dissolution rate, but the processes do have the disadvantage of being difficult to control excessive dissolution of either the plant, if metallic, or the detinned plate. Passivation of acidic dissolution of steel has been shown to be very difficult. However, acid liquors can attack iron-tin solid solutions which would otherwise passivate in alkaline liquors.

Alkaline processes are required to be operated under hot conditions, but neither the plant, or detinned plate, is attacked by the liquor. In order to increase the chemical rate of attack, oxidising agents are often added. Electrolytic alkaline processes can, however, be operated at lower temperatures without the use of oxidising agents, as they do not generally appear to assist the reaction. It has been shown that the rate of electrochemical detinning does not benefit substantially if the anodic current density is over 6 mA/cm^2 or if the liquor is over 70^{o}C. This is in agreement with Singh and Chakravarti.[330]

Singh and Chakravarti[330] found that the most efficient cathodic current density was 13.5 A/ft^2 (13.5 mA/cm^2); this corresponded to an anodic current density of about 7 mA/cm^2. The optimum temperature in their study was 60^{o}C, using a liquor of 70 gms/litre of sodium hydroxide (1.75N) with 8 gms/litre sodium acetate (0.1N). These conditions resulted in a cathodic current efficiency of 71%, tin deposition of 96.4% of the total available tin, and a residual tin on the steel of 0.0125%. The remainder of the tin remained in solution as sodium stannate.

These results agree with those obtained in this study, although a higher optimum temperature (70^{o}C) and lower current density (6 mA/cm^2) has been found. It is worthy of note that the Batchelor Robinson experimental electrolytic detinning plant operated at a cathodic current density of about 18.4 A/ft^2 (18.4 mA/cm^2), although the corresponding anodic current density was about 0.4 mA/cm^2. The liquor was 2N sodium hydroxode heated to about 95^{o}C.

Since electrolytic attack of the alloy layer does not vary substantially at temperatures over 75^{o}C, a saving can be made on heating costs of the liquor. It was found that the ohmic losses incurred on the pilot plant were sufficient to maintain the liquor temperature at 95^{o}C; the plant operated at a potential of 3V and current of 1000 A. A time of 40 minutes was required to detin 840 lbs of tinplate, corresponding to 4 lbs of free tin, under these conditions. If a potential loss on both the anode and cathode is taken into account, the amount of energy used to maintain the temperature of the bath is about 1 kw; this is equivalent to the heat loss from the plant. If the liquor temperature is reduced to 75^{o}C, the heat loss is reduced by 25% assuming an ambient temperature of 15^{o}C, so the amount of energy consumed by the ohmic losses could be reduced by the same amount. Improvements in plant design relating to inter electrode distances would account for this.

The time required to fully detin the scrap using an industrial electrochemical process is about 40 minutes, whilst the industrial chemical process is about 90 minutes. Allowing for a degree of "over-kill" on the electrochemical plant, a saving in throughput time of about 50% seems possible. Since the presence of nitrite does not aid electrochemical dissolution of the alloy, savings can be made on the cost of the use of oxidants.

It can be seen that by careful control of an electrochemical plant, an overall energy saving of about 50% is possible. In order to achieve a careful control, the reaction potentials on the plant have to be carefully monitored. This can be achieved by using a rugged, stable reference electrode such as cadmium/cadmium hydroxide.

The adaption of the present screw thread drive system on the chemical detinning plants operated by Batchelor Robinson to an electrochemical process would save labour costs. The pilot plant test results also indicate that the degree of detinning is maintained at such a high level that the remaining tin on steel figure is of no consequence in relation to the value of the steel.

Alkali dissolution of tin on a chemical plant proceeds faster than would be expected. This is due to the establishment of an electrochemical corrosion couple between the tin, acting as the anode, and the steel of the plant. The cathodic reaction is either the reduction of dissolved oxygen in the liquor, or the reduction of any added oxidants. Agitation of the liquor aids dissolution of tin not only because it removed reaction products from the tin surface, but also because it dissolves more oxygen in the liquor. Analyses of electrochemical laboratory scale detinning with alkaline nitrite has shown that the removal of tin is not as good as without nitrite. This can be explained by the nitrite passivating the steel and any other noble compound which may be present. It is also probable that the nitrite reacts on the anode, hence lowering the anodic current efficiency for tin dissolution. The resulting tin on steel content is still, however, a lot less than the maximum required for recyclable steel.

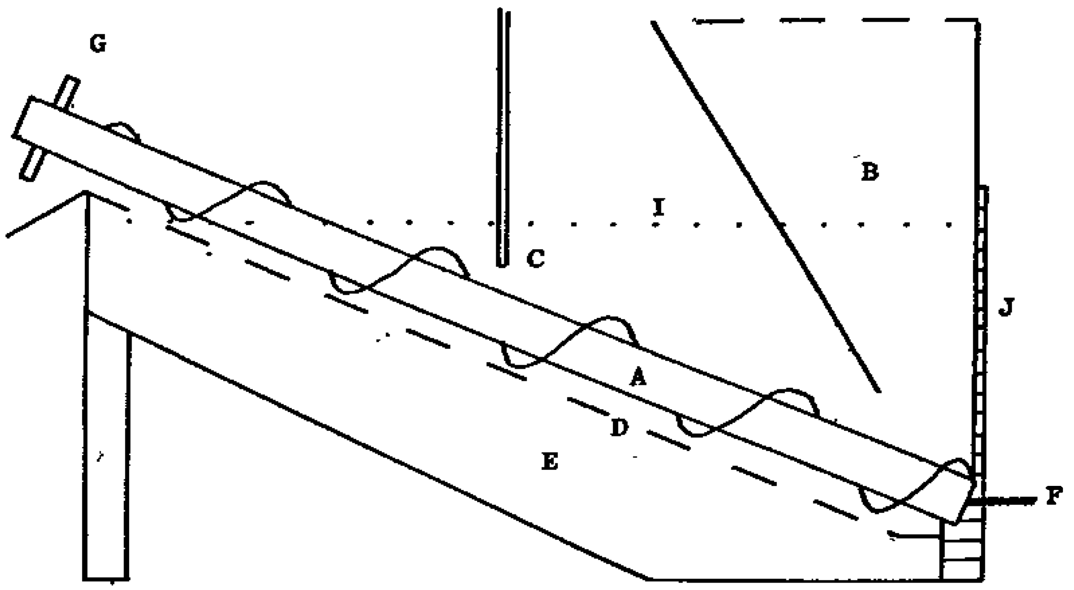
Due to the rapid dissolution of free tin in alkali, and the relatively slow reaction with alloy, consideration can be given to allowing tin to dissolve chemically in a holding tank before electrolytic attack of the alloy. This will also allow some cleansing of the tinplate to take place, as carbonaceous material will still adhere to the can.

Laboratory electrolytic results have shown that most oxidants used in chemical detinning processes are not beneficial to an electrolytic plant. Moreover, both tin and alloy dissolve Coulombically in most liquors, but the presence of strong oxidants, such as persulphate and chlorite, have been shown to be slightly beneficial.

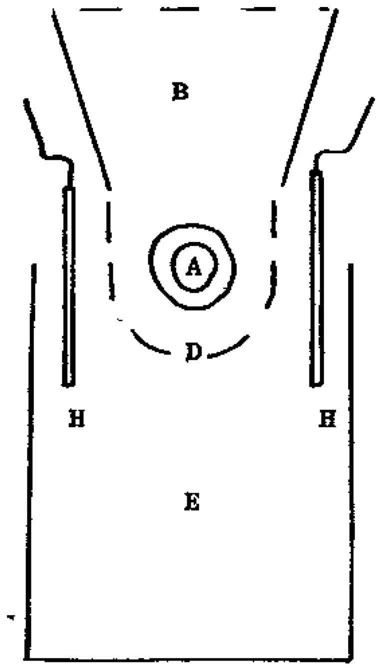
In order than an electrolytic process may be viable, certain important factors have to be taken into account. The present chemical process is adequate for clean tinplate, as long as the plant capacity is capable of processing the amount readily available. However, the chemical plant will need renewal, and consideration should be given to an electrolytic plant, whereby used cans will be able to be treated. In order to process used cans an evaluation of the energy requirements will have to be carried out; if the thermal capacity value of the used can is in excess of the recycled value of the metals, high temperature incineration is favourable. If, however, the value of the metal is greater, care has to be taken in the thermal treatment.

Further work is required in thermal treatment of used cans, but initial studies suggest that the temperature should not exceed 400^{o}C for any time longer than ten minutes. Lower temperatures have an increased dwell time. The process should be continuous, as this will reduce labour costs, and by careful monitoring of the potentials, optimum detinning times will be achieved.

Initial results have indicated that the concentration of tin, in the form of Sn (IV), can be determined by the variation in potential between a sulphide electrode and a suitable commercial reference electrode such as mercury/mercuric oxide. The potential was measured



SIDE VIEW



END VIEW

A - insulated anodic feed screw
B - storage hopper for tinplate
C - reference electrode
D - cradle for stripping tinplate
E - alkaline liquor bath
F - current input to screw
G - insulated drive system for screw
H - suspended cathodes
I - liquor level
J - electrical insulation

Fig. 4.46. Schematic diagram of envisaged plant.

on a digital voltmeter, and plotted against the concentration of tin (IV), which was in the form of sodium stannate (Na_2SnO_3) dissolved in 2N sodium hydroxide. The solution was heated to 80^{o}C.

The potential established should be dependent upon the log (SnIV) if the sulphide electrode is reactive to the presence of tin. Initial results show that it may be due to the affinity of sulphide by tin (IV). The results shown in Fig. 4.45. appear to confirm this belief.

A sketch of a possible plant is shown in Fig. 4.46.

The tinplate is transported by an anodically charged screw thread. To prevent the tinplate shorting to the cathodes, suspended vertically along the path of the screw, it is enclosed in a meshed metal carrier. A reference electrode is placed at a suitable distance from the end of the plant to ensure that the tinplate is wholly detinned. The monitored potential regulates the screw speed, by means of a programmed micro-processor, taking into account the liquor temperature and concentration. Once detinned, the scrap steel is baled.

Recovery of the tin is carried out by deposition on the cathodes, which are removable, and the tin is then melted off the electrode in a furnace. To ensure a good deposit, tin has to be cathodically deposited as Sn(IV).

Present evidence suggests that although tin is removed from the anode as Sn(II), it is oxidised to Sn(IV) whilst in the liquor.[297] Removal of the deposited tin requires removal of the cathode altering the charge distribution on a continuous plant. If the current is switched off, rapid dissolution of the reclaimed tin will occur. It is also possible that during electrolytic detinning operations, a steady state tin concentration will develop; the concentration increasing due to chemical attack of free tin whilst the plant is non-operative. If this occurs liquor depletion would have to be performed by electrolysis as with the present chemical plants, or by precipitating the soluble tin as an insoluble salt, such as calcium stannate.

A processing line as described might reduce the throughput dwell time for clean tinplate by nearly 50%, compared with conventional chemical detinning lines, or alternatively it could reduce the size of the plant by 50%.

5. CONCLUSIONS

(1) An acidic detinning process does not appear to be viable due to the highly corrosive nature of the liquor, and the difficulty in preventing wasteful loss of the acid in dissolution of steel base plate and possibly the plant.

(2) Alkaline chemical detinning rates can be improved by addition of chlorite or persulphate to sodium hydroxide. The operating temperature of the plant can also be reduced, saving energy.

(3) If the use of alkaline nitrite liquor is to be continued, greater detinning rates are possible by vigorous agitation of the liquor. On the present continuous detinning plants an electrochemical couple is established between the anodic tinplate and the cathode steel of the plant. Addition of oxidants such as nitrite or air aid the cathodic reaction of the couple, hence increasing the anodic, or tin dissolution, reaction.

(4) If reclamation of highly alloyed used cans is to be successfully continued on a large scale, electrochemical processes are required, due to the inert nature of the alloy. Preparation of the baked can should involve a "pre-electrolysis soak" in alkali, where any remaining free tin can be readily dissolved by the action of the corrosion couple, and any

remaining carbonised contaminant can be removed by the detergent attack of the alkali. Electrolytic recovery of the tin from the alloy can then be carried out by a continuous process, although the more labour intensive batch process is easier to design.

(5) Electrochemical alkaline dissolution of alloy does not require the addition of oxidants, and the optimum temperature is about 75°C. Once heated, the plant temperature will remain constant due to the ohmic losses incurred during the detinning.

(6) The optimum anodic current density is 6 mA/cm^2 ($\sim$6 A/ft^2), which can be achieved by careful design of the anodic aspect of the process, taking advantage of the control of current distribution due to the tortosity of the charge and polarisation. No benefit is obtained by exceeding this current density or temperature for alloy dissolution.

(7) Careful and rigid control of the plant is required. A sturdy reliable reference electrode, such as $Cd/Cd(OH)_2$, can be used to monitor the degree of tin dissolution from the tinplate, the results of which can be used to vary the throughput rate of the plant. By careful control, a residual tin-on-steel value of between 0.004% and 0.017% is obtainable; this is well below the maximum tin content for recyclable steel. A preliminary experiment suggests that the tin content of the liquor can be determined by a tin specific electrode.

(8) Preparation of the used can for detinning must be carefully controlled, and the temperature during thermal treatment should not exceed, ideally, 350^{o}C, although a short dwell time (not more than 10 minutes) at 400^{o}C would be permissible.

(9) During thermal treatment the formation of alloys other than $FeSn_2$ has been detected. Once the free tin layer is depleted during thermal treatment, the alloy diffuses into the steel base plate to form a series of stoichiometric alloys. Evidence has been obtained suggesting the presence of FeSn, Fe_3Sn_2, Fe_2Sn and Fe_3Sn, although none are thermodynamically stable at room temperature.

(10) Activation energies have been calculated for the formation of $FeSn_2$ above and below the melting point of tin. The lower temperature activation energy is 18.8 kJ mol^{-1}k^{-1}, which corresponds well with other published results, whilst the high temperature result is 6.59 kJ mol^{-1}k^{-1}.

(11) The reaction of $FeSn_2$ with alkali has been shown to follow a reaction path very similar to that of iron dissolution, whereby initial attack corresponds to formation of ferrous hydroxide. The reaction proceeds to form ferric hydroxide. The activation energy has been found to be +20 kJ mol^{-1}k^{-1} for alloy dissolution.

6. FURTHER WORK

(1) Elevated temperature studies relating to the kinetics and electrochemistry of tin dissolution in alkali.

(2) Further chemical and electrochemical studies of the alloy at both elevated and room temperatures.

(3) Analysis of thermally treated, or specially prepared, tinplate by Moessbauer Spectrocopy to establish the existence and stability of other intermetallic compounds.

(4) The development of a tin specific electrode for on-plant determination of free tin in the liquor.

(5) Refinement of a computer programme for Rutherford Back-scattering analysis.

(6) Industrial experiments relating to the thermal treatment of dirty cans. This should include thermal treatments and ease of removal of the carbonaceous material.

(7) Studies relating to the cathodic deposition of tin in liquors with different oxidants present, should be carried out.

(8) More analyses of tinplate for lead should be carried out, and attention should be drawn to the reactivity of the lead under detinning conditions observed in the corrosion of tinplate by food liquors.

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APPENDIX 1.

Patents

ref.		
(1)	F.G. Morton	Brit. Pats. 1739 and 3676 (1872) Tinplate is treated in hydrochloric acid and heated in a furnace. Then treated with further hydrochloric acid, to remove tin and alloy.
(2)	G. Haseltine	Brit. Pat. 4070 (1873) Dissolve tin in hydrochloric acid until the liquor is spent, and then add HNO_3 or $KClO_3$ until remainder dissolved.
(3)	A. Gutensohn	Brit. Pat. 4879 (1879) Add hydrochloric acid to tinplate, and then convert to a galvanic cell by insertion of a zinc rod to act as one electrode and tinplate the other.
(4)	B. Biggs	Brit. Pat. 321 (1880) Tinplate dissolved in hydrochloric, nitric or sulphuric acids, or mixtures of suitable acids. Tin is precipitated by addition of zinc, or the liquor is evaporated down to yield $SnCl_2$ crystals.
(5)	W. Barlow	Brit. Pat. 1576 (1882) Excess of hydrochloric acid with tin chloride is added to tinplate in a rotating drum. Process heated by a steam vessel.
(6)	R.H. Biggs	Brit. Pat. 4584 (1887) Detinning vats are coated with asphalte or similar internally to prevent acid attack. Tin dissolved in acid and precipitated by addition of nitric acid, or zinc.
(7)	L.U. La Corsa	Brit. Pat. 312 924 (1928) The use of hydrochloric acid or chloride solutions with stannic chloride. The liquor is regenerated continuously or intermittently by addition of oxyacids of chlorine, or their salts. Further hydrochloric acid may be added if desired.
(10)	A. Thomas	Brit. Pat. 460 072 (1937) Tinplate cleaned in NaOH. Tin dissolved in acid solvent such as HCl, dil HCl + Cl_2. Stannous chloride oxidised to stannic by excess chlorine. Acid neutralised by excess alkali, and tin

removed by hydrolysis. If Pb or Ca present, boil in HnO_3 or NH_4NO_3 to convert to nitrate, which remains soluble.

(11)	D. De Lape	U.S. Pat. 2 096 090 (1938) Wet tinplate exposed to hydrogen chloride gas at temperatures below 50°C.
(14)	Stoyanov et al	Ger. Pat. 2 647 005 (1977) Heat tinplate scrap for 60 mins in aqueous solution of 4 to 7N NaOH with 0.2 to 0.75N $NaNO_3$ at 100-105°C. Saturate with CO_2 and dissolve acid ("stannic acid") in hot conc. HCl. Resulting stannic chloride treated with scrap metal, after dilution to ppt tin. See also 2,647,006 and 2,647,007.
(24)	A. Gutensohn	Brit. Pat. 1901 (1877) An earthenware vessel is filled with tinplate and hydrochloric acid. Once spent, the liquor is evaporated to yield tin chloride which is treated with liquid ammonia and copper salts to regenerate the liquor.
(25)	J. Stuart	Brit. Pat. 1276 (1874) Separation of tin from steel by sulphuric, nitric or hydrochloric acids, with air pumped into the mass. Can either be done in a crate process, or by a tumbling vessel.
(26)	E. Edwards	Brit. Pat. 6803 (1886) The use of iron perchloride in the presence of hydrochloric acid. The process also separates tin from other metals or alloys.
(27)	M. Ramos-Garcia	Brit. Pat. 18 726 (1890) The cans are cleaned by incineration, and then treated with hydrochloric acid with ferric chloride added. Also uses chlorine and hydrogen chloride gas to attack tinplate.
(28)	M. Adam	Brit. Pat. 154 242 (1919) Tin dissolved by strong solution of tin and iron chlorides, preferably in hydrochloric acid. Tin electrodeposited on rotating cathode. See also Brit. Pat. 209 124 (1922)
(29)	E. Blundstone	Brit. Pat. 11 624 (1885) Addition of hot solutions of chromium (preferably perchloride) salts to tinplate, waste tin, terneplate. Contact with air is avoided during the process.

(30) P. Marino — Brit. Pat. 14 231 (1915)
Tin removed by liquor of alkali metal dichromate in hydrochloric acid at 50-80°F.

(31) R.T. Robinson — U.S. Pat. 2 308 138 (1941)
Dissolve tin in a solution of free hydrogen chloride, stannic chloride and ferrous chloride.

(32) J. Stevenson — Can. Pat. 223 600 (1922)
Dissolve tin in strong solutions of tin and iron chlorides with hydrochloric acid present.

(33) M. Adam — Can. Pat. 245 637 (1924)
Treat tin with aqueous solutions of iron and tin chlorides in which chlorine is added by adsorption.

(34) J. Jacobson — Dutch Patent 22 288 (1930)
Chlorine gas added to hydrochloric acid at 40-70°C as required. Tin recovered by electrolysis after partial neutralisation and addition of sulphuric acid.

(35) J. Jacobson — Brit. Pat. 255 092 (1925)
See (34) Dutch Pat. 22 288.

(36) T.A. Eklund — Brit. Pat. 138 622 (1920)
Tin, in the form of sulphide, oxide or chloride, dissolved in hydrochloric acid in presence of oxidising agent. Solution is heated and reduced to $SnCl_2$, which is electrolysed using carbon, scrap tinplate or iron-tin alloy anode and sheet iron or tin cathode.

(37) F. Bischitzky — Brit. Pat. 288 049 (1927)
Tin dissolved by treatment with hydrochloric acid with Cl^-, SO_4^-, PO_4^{3-}, BO_4^{3-} catalysts. Also used additives with high ionisation constants, such as $CaCl_2$. Stannous oxide precipitated by lime or chalk.

(38) L. Lassaigne — Fr. Pat. 870 350 (1942)
Tin dissolved in a mixture of H_2SO_4, HNO_3 and HCl. Stannic oxide washed and reduced to tin.

(40) G. Maranca — It. Patent 423 066 (1947)
Three detinning baths, first is 6-8% sodium chlorate with MnO_4^-, $Cr_2O_7^{2-}$, OCl^- as oxidants, second is hydrochloric acid and third is water. Tin recovered as stannous chloride.

(41) C.L. Bertou — Brit. Pat. 15 174 (1890)
Hydrochloric acid with nitrates, chlorates or other suitable oxidants added is used to attack tinplate. Initial temperature not over 30°C,

		but specifies the liquor should not boil.
(42)	P. Marino	Can. Pat. 250 691 (1925) Tinplate immersed in alkali dichromate with manganese dioxide and hydrochloric acid, at 70-90°C. Tin recovered electrolytically.
(43)	G. Guastella	It. Pat. 609 851 (1960) The use of Cu_2OCl_2HCl complex copper salt to act as a replenishible oxygen carrier.
(44)	N. Venkatakrishnan	India Pat. 101 628 (1968) The use of formaldehyde to inhibit acid attack of steel.
(45)	C.B. Schultze	Brit. Pat. 3 669 (1887) Tinplate treated with cold dil. sulphuric acid, and tin recovered by neutralisation and precipitation by iron. Lacquers destroyed by hot sulphuric acid.
(46)	P.A. Mackay	Brit. Pat. 161 654 (1920) Dissolve tin in oleum.
(47)	P.A. Mackay	U.S. Pat. 1 387 443 (1921) Dip tinplate for short times into sulphuric acid with free sulphur trioxide dissolved in it. Wash iron plate in water. Tin recovered from dil. liquor.
(48)	H.A. Martin	Brit. Pat. 7 544 (1894) Tin scrap treated in dilute sulphuric acid with nitrate or chlorate present. Hydrochloric acid can be added.
(49)	H.W. Hemmingway	Brit. Pat. 8 759 (1902) Tin dissolved in acidified ferric sulphate solution, and recovered by electrodeposition. Liquor recovered by addition of nitrate and more sulphuric acid at 170°F.
(50)	J.E. Gilliand	U.S. Pat. 3 097 063 (1963) Detin using hydrogen fluoride or hydrofluoric acid. Stannous fluoride produced.
(52)	P. Dekker	Ger. Pat. 604 463 (1934) Tinplate treated with vapourised low aliphatic acids such as acetic acid in presence of oxygen or air. Temperature above 80°C.
(53)	N. Korobkov	U.S.S.R. Pat. 123 004 (1959) A chemical process using alkali metal nitrites which is added to 6% acetic acid.

(56) C.T. Batchelor — Brit. Pat. 2 366 (1899)
Tinplate put in acid-resistant cage and rotated in bath of hydrochloric acid. Contact with air is important.

(57) C.T. Batchelor — Brit. Pat. 21 497 (1909)
Scrap placed in stannic chloride until 90% tin removed. Resulting $SnCl_2$ removed and crystallised. Remaining tin removed electrolytically in alkali.

(58) P. Marino — Brit. Pat. 225 499 (1923)
Treat tinplate with hydrochloric acid containing nascent chlorine produced in alkali dichromate and manganese dioxide being present. Tin recovered by displacement by zinc or electrolysis. (See ref. 42)

(59) T. Twynam — Brit. Pat. 297 528 (1927)
Diluted hydrochloric acid at 80-89^{o}F dissolved tin, which was precipitated as $SnCl_2$ by addition of zinc to liquor. Tin recovered by electrolysis. Addition of lump coke accelerates acid attack.

(61) L. Poensgen — Brit. Pat. 4684 (1884)
Tin scrap is heated in closed vessel and exposed to action of alkali liquors. The vessel is rotated, and the resulting ammonia collected.

(62) Les Petits — Brit. Pat. 304 639 (1928)
Hot alkaline solution of sodium carbonate used for detinning.

(63) E. Scarez — Belg. Pat. 361 710 (1929)
Clean cans detinned by alkali, followed by removal of solder by heating. Second detinning with alkali in presence of excess tin. Dissolved tin and lead recovered by pptn. with sodium bicarbonate.

(64) K. Goldschmidt — U.S. Pat. 2 055 732 (1936)
Hot alkaline liquor pumped into a pressure vessel containing bales of scrap tinplate. The reaction pressure is in exess of one atmosphere.

(65) F.D. Murphy — Brit. Pat. 756 863 (1953)
To increase the detinning rate, the alkaline liquor is heated, under pressure to over 100^{o}C, whilst in contact with scrap tinplate.

(66) Zaklady
Pol. Pat. 51 266 (1966)
6.5-9% vol. NaOH with 1.5-2% Na_2CO_3.
Rotating drum used with liquor at 90°C.

(67) L. Riveere
Brit. Pat. 10 309 (1906)
Tinplate pulverised and enriched, then treated in a digester in the presence of alkali, which was regenerated.

(68) G. Spitz
Brit. Pat. 5 273 (1907)
Metal coatings treated at over 100°C at pressures between 7-15 atmospheres with dil. acid or alkali.

(69) Benson
U.S. Pat. 2 355 777 (1944)
Thin coatings of caustic alkali applied to, and fused upon, the surface of tin scrap to convert tin to alkali metal stannate.

(70) I. Bang
Brit. Pat. 70 (1890)
The scrap is heated in oxygenated alkali liquors. Tin precipitated by action of lime.

(71) I. Bang
Brit. Pat. 12 553 (1890)
Similar to Brit. Pat. 70, but allows liquor to trickle over tinplate and escape from bottom of vessel to be detinned.

(72) F.E. de Fursac
Brit. Pat. 2 583 (1893)
Tinplate put into suitable receivers and alternately exposed to liquor and air.

(74) W.G. Norlander
U.S. Pat. 2 350 918 (1944)
Immerse tinplate in sodium hydroxide liquor, containing a foaming agent, and pass air through it. Remove lead and tin by addition of calcium hydroxide.

(76) J.W. Hinchley
Brit. Pat. 346 674 (1930)
Spongy lead dissolved in excess alkali solution with aid of air or oxygen.

(77) A.M. Gillies
Australia Pat. 118 756 (1944)
Cleaned tinplate immersed in hot alkaline solution with catalyst. Tin precipitated by addition of calcium hydroxide.

(78) H.A. Schulte
Brit. Pat. 777 (1882)
An alkali liquor of 15-20% sodium hydroxide with an excess of lead oxide is heated to boiling point before detinning starts. The drum rotates to aid air contact.

(79) C.D. Abel	Brit. Pat. 4 400 (1882) A mixture of sodium hydroxide and lead oxide, in a rotating drum is used to detin tinplate.
(80) A. McDougall	Brit. Pat. 10 783 (1890) Tinned scrap immersed in alkali with lead oxide. The resulting liquor is treated with galvanised strip to precipitate tin.
(81) W.B. Ballantine	Brit. Pat. 327 997 (1929) Tin recovered by alkaline solution of lead acetate. Alkali added until the white cloud formed just disappears.
(82) Africa Tin Recovery Co.	Fr. Pat. 683 900 (1929) Tin dissolution was carried out in sodium hydroxide with lead acetate added.
(83) J.M. Creusot	Fr. Pat. 1 179 673 (1959) A solution of 1N NaOH with either 1 g/litre PbO or 80 g/litre $NaNO_3$ used for detinning. Tin recovered by electrolysis.
(84) C.V. Zenger	Brit. Pat. 3 384 (1873) Tinned scrap treated with mixture of sodium chloride and sodium hydroxide with some sodium nitrate or manganese dioxide present. The bath is above the melting point of tin.
(85) S.L. Baliicki	Pol. Pat. 57 212 (1969) Use 4 NaOH: 1 Cl^- : 1 NO_3^- (or NO_2^-), as oxidising liquor; precipitate tin by addition of calcium hydroxide.
(87) W.J. Butterfield	U.S. Pat. 1 511 590 (1925) 1-5% $NaNO_3$ dissolved in hot 5-10% NaOH.
(88) M. Klinger	Fr. Pat. 811 023 (1937) Detinning carried out with such strong sodium hydroxide the alkali stannate is pptd. $NaNO_3$ may be added as oxidant.
(89) H. Wakae	Jap. Pat. 654 (1961) Recommends the use of alkaline sodium nitrate for rapid detinning.
(90) W.S. Leinhardt	U.S. Pat. 3152 888 (1964) Using a rotatable pear shaped vessel with an aqueous solution of 1.25-3N NaOH with 0.125-0.625N $NaNO_3$ at 200°F. Lacquer removed by tumbling, and CO_2 removed to increase efficiency.

(91) W.T. Little — U.S. Pat. 1 811 142 (1931)
Tinplate reacted with NaOH, NO_3^-, NO_2^- mixture and resulting stannate reacted with nitrous gases to ppt. SnO, which is removed and liquor recycled.

(92) E. Kardos — U.S. Pat. 1 798 607 (1931)
Tinplate reacted in alkali with "vitreous gases" dissolved in it, such as N_xO_y from ammonia oxidation.

(93) I. Stoyanov et al — Ger. Pat. 2 647 006 (1977)
See Ref. 14.

(95) M. Pierson — Brit. Pat. 113 951 (1917)
Degrease tinplate with sodium carbonate, then treat plate with liquors of NaOH and NaOCl at 85°F. Partly spent liquors regenerated by treatment with chlorine. Stannous oxide ppted by liquor treatment with excess chlorine. Tin can also be ppted by addition of calcium hydroxide.

(96) E. Ruf — *Brit. Pat. 1 250 863 (1971)*
Sodium hydroxide liquor with sodium chlorite added, heated to between 50 and 100°C. Air passed through the liquor.

(97) A. Kissock — U.S. Pat. 1 501 413 (1924)
Scrap tinplate treated with sodium polysulphide in alkali. Tin recovered and polysulphide regenerated by electrolysis.

(98) W.C. Gregory — U.S. Pat. 2 229 073 (1941)
Electrolytic detinning by alkaline solution of halogen salts. Tin deposited directly onto cathode.

(99) L.M. Edwards — U.S. Pat. 3 121 005 (1963)
Thiosulphate in alkali solution as a chemical detinning liquor.

(100) L.M. Edwards — *Brit. Pat. 938 203 (1963)*
Hot alkaline liquor with 50-200 g/litre thiosulphate. Other salts suggested are $S_2O_7^{2-}$. A wetting agent is added.

(101) W.C. Gregory — *Brit. Pat.* 128 833 (1918)
Tinplate treated with hot ammonium polysulphide. Sodium hydroxide can be added if desired. Tin recovered as sulphide by neutralisation.

(102) E.G. Hickey — U.S. Pat. 1 592 935 (1926)
Ammonia dissolved in sodium hydroxide used to detin scrap.

(104) A. Vollmer — U.S. Pat. 2 200 782 (1940)
Substituted organic compounds of the benzene series, dissolved in sodium hydroxide using electrolytic process with tinplate as anode.

(107) S. Swierezynski — Pol. Pat. 54 229 (1967)
Chemical dissolution of tin and alloy from tinned iron by alkaline liquor with meta-nitrobenzoic acid as an oxidant.

(110) Vlascu — Rom. Pat. 61 458 (1972)
Scrap washed in hot water and in hot sodium carbonate solution with sodium stearate and m-dinitrobenzene to remove grease. Detinning done in 1.5% NaOH with 0.1% m-dinitrobenzene; tin recovered electrolytically, and lead as solid residue.

(113) A.S. John — Brit. Pat. 204 387 (1922)
Detinning in 6-9% NaOH with 1% $SnCl_4$. Continued in 1-2% HCl. Electrolysis at 150^{o}F. Tin deposited on cathode.

(114) R.A. Holland — U.S. Pat. 1 511 967 (1925)
Scrap immersed in alkaline solution in direct contact with copper or other electro-positive metals to iron and tin. Cupric oxide aids *removal of tin.*

(115) P. Marth — Ger. Pat. 572 749 (1928)
Alkali wash in presence of metal such as copper, silver, gold, which have as small solution tension as tin. Oxidising agents can be added.

(116) P. Marth — Fr. Pat. 8 33 024 (1938)
Dissolve tin in hot alkali containing a metal, alloy, oxide or salt that forms a compound with iron as a catalyst. Addition of oxidants suggested.

(117) M. Lipser — Czech. Pat. 1 73, 256 (1974)
Use ultrasound to reduce reaction time. Yield increased by 20-50%.

(118) T.G. Hunter — Brit. Pat. 132 (1894)
A solution of copper sulphate is sprayed onto tinplate. The copper is precipitated by the tin, which is in turn precipitated by the iron.

(119) Reymersholms Gamla Ind. — Swed. Pat. 59 586 (1925)
Scrap tinned iron treated with copper sulphate solution with chloride of alkali metal present.

(120) C. Clerc — U.S. Pat. 1 413 555 (1922)
Tin scrap treated in vacuo with stannic chloride. Tin ppted by action of Zn, Fe, or other precipitating agents.

(121)	C. Clerc and Nihoul	Brit. Pat. 181 722 (1922) Dissolve tin in solution of $FeCl_3$ and $SnCl_4$. Liquor is agitated. Stannous oxide precipitated by addition of MgO, the resultant $MgCl_2$ used to regenerate MgO and obtain HCl and Cl.
(123)	M. Adams and H. Davies	U.S. Pat. 1 565 425 (1926) The scrap is immersed in a solution of saturated iron and tin chlorides in a stripping vessel, and chloride is injected in.
(124)	L.U. La Corsa	Brit. Pat. 284 691 (1927) Tinplate leached with ferric chloride solution, and electrolysed for tin recovery. Other additives include ammonium chloride, ferrous sulphate and ammonium sulphate.
(125)	E.A. Parnell	Brit. Pat. 3 183 (1876) Cages of tinplate are passed through tanks with alkaline polysulphide liquor being pumped around the plant. The cases go in the opposite direction of flow. Tin is recovered by evaporation.
(126)	W.P. Thompson	Brit. Pat. 1913 (1890) Tinplate treated in hot alkaline polysulphide with ammonium chloride added. Tin precipitated, after liquor decanted off, by addition of hydrochloric acid.
(128)	K. Goldschmidt	Brit. Pat. 1 2868 (1905) Tinplate exposed to chlorine gas, which permeates through baled scrap.
(129)	K. Goldschmidt	Brit. Pat. 1 2869 (1905) Scrap tinplate reacted with carbon tetrachloride or other suitable solvent.
(130)	K. Goldschmidt	Brit. Pat. 1 2870 (1905) Dry chlorine, diluted with air, reacts with tinplate to form stannic chloride. The detinned bales are dipped in alkali to protect them from further attack.
(131)	K. Goldschmidt	Brit. Pat. 2 3449 (1906) The tinplate was vigorously agitated in the presence of chlorine in a closed receptacle.
(132)	K. Goldschmidt	Ger. Pat. 466 904 (1924) Dry chlorine, diluted with air, is allowed to react with baled tinplate in a closed vessel.

(133) J. Higgins — Brit. Pat. 766 (1854)
Tin scrap treated with hydrochloric acid and sodium nitrate. Chlorine gas can be used as an alternative, if it is dried over calcium chloride beforehand.

(134) Seeley — U.S. Pat. 127 375 (1873)
Dry chlorine reacts with tinplate to form stannic chloride which is collected and refined. This was the basis for a plant operated in New York in 1896.

(135) E. Sperry — Brit. Pat. 25 496 (1907)
Process consisted of employing chlorine to obtain stannous chloride from tinplate. The product needs purification to obtain other chlorides.

(136) F.W. Kugelgen — Can. Pat. 17 771 (1917)
Dry chlorine gas passed through a succession of tanks of tin scrap. The temperature is below that of attack on the iron.

(137) Buckau — Ger. Pat. 309 277 (1918)
Dry chlorine is used to detin tin plated iron; the tin is recovered as stannic chloride.

(138) Von der Linde — Swiss Pat. 78 890 (1917)
Action on tin by chlorine which has been mixed with air before being brought into contact with tinplate.

(139) W.C. Zacherias — U.S. Pat. 1 283 016 (1919)
Temperature regulated by addition of finely divided tin in sufficient quantities to prevent chlorine attack of iron.

(140) C.E. Carrier — U.S. Pat. 1 358 136 (1921)
Treat tin scrap with dilute anhydrous chlorine, and then attack alloy with concentrated chlorine.

(141) L.U. La Corsa — Fr. Pat. 640 205 (1927)
Oxidise tin to stannous chlorine by addition of stannic chloride, using chloride as a catalyst.

(143) T. Mitchell — U.S. Pat. 1 961 065 (1935)
Treat residual tin plating with chlorine and oxygen in excess of the quantity to react with steel present. Temperature above 114^{o}C to dissociate ferric chloride product.

(146) H.H. Lake — Brit. Pat. 10 018 (1885)
Scrap heated to 400^{o}C and reacted with dry hydrogen chloride gas.

(147) S.T. Montagne — Brit. Pat. 6370 (1887)
Scrap treated with hot hydrochloric acid gas, and the tin recovered by treatment with zinc or lime of the liquor.

(148) L.A. Groth — Brit. Pat. 13 234 (1888)
Tin recovered from scrap by the action of dry hydrochloric acid, resulting liquor treated with zinc.

(150) H. Davies and M. Adam — Brit. Pat. 209 124 (1922)
Tinplate treated with iron and tin chloride solution and chlorine injected into the liquor. Hydrochloric acid is also added and maintained in the solution.

(151) W. Robinson — Brit. Pat. 1 708 (1873)
Tin recovered from tinplate by reacting it with mercury in a sealed vessel, and distilling the amalgam.

(152) H.W. Hambery — Brit. Pat. 2 775 (1873)
Tinplate treated in a sealed furnace with a mercury vapour; once condensed, tin can be recovered.

(153) C. Madge — Brit. Pat. 3 160 (1876)
A mixture of scrap tinplate, gravel, or grit and mercury are rotated in a drum. The amalgam is heated to recover the tin and mercury.

(154) J.F. Duke — Brit. Pat. 7 151 (1892)
Tinplate is immersed in a bath of molten lead, the lead alloying with the tin, to form solder.

(155) Du Pont — Brit. Pat. 880 470 (1960)
A chemical process, using SCl_2 or S_2Cl_2, often containing $TiCl_4$ or Et_2O as a diluent. Scrap washed in carbon tetrachloride operating temperature is 138^{o}F.

(157) T. Rondelli — Brit. Pat. 232 281 (1923)
Dissolve 10% chlorine in carbon tetrachloride. Tin removed quickly, but iron not attacked. Solvent also cleans the plate.

(158) W. Murray and H. Fernberger — U.S. Pat. 913 275 (1909)
Stannic chloride is removed from surface of tinned iron after treatment with chlorine by washing with carbon tetrachloride with chlorine dissolved in it.

(159)	Dubois and Kaufmann	Ger. Pat. 228 952 (1911) Used carbon tetrachloride or tetrachloroethane as diluent for chlorine. Tin can be recovered from a saturated solution by electrolysis, whereby chlorine is recycled, or by addition of water and pptn. of $Sn(OH)_2$.
(160)	Farben Ind.	Brit. Pat. 466 284 (1937) Detinning of scrap by tars, mineral oils, coal products by virtue of their acidic content at above 50^oC.
(161)	Farben Ind.	Fr. Pat. 813 460 (1837) See (160)
(162)	J. Jackson	Brit. Pat. 1 532 876 (1979) Immerse tinplate in H_2SO_4. Scrap conveyed through three tanks by high pressure water jets.
(169)	Schmeduk	Brit. Pat. 2 012 815 (1980) Delacquering and detinning carried out by passing shredded scrap along a rotating drum. Liquor is a solution of alkali and quinone, which is electrolysed to recover tin.
(170)	E.L. Cleaver	Brit. Pat. 5033 (1883) Tinplate cleaned with hydrochloric acid, and then treated with sodium or potassium hydroxide. Tin recovered by electrolysis.
(171)	T. Fenwick	Brit. Pat. 8988 (1886) Tin partly removed by electrolytic action, the remainder by strong hydrochloric acid.
(172)	H.G. Orlik	U.S. Pat. 2 578 898 (1951) Electrolytic detinning using a liquor of orthophosphoric acid, acetic acid and water, with glycerine to inhibit acid attack of the iron.
(173)	L.S. Deitz	U.S. Pat. 2 403 586 (1946) The tinplate is melted and 1% aluminium added; the recast ingot is then electrolytically detinned in phenolsulphonic acid. Aluminium reduces loss of tin in slime.
(175)	H. Rogers et al	Brit. Pat. 122 618 (1918) Recovery of tin by using 7-10% NaOH or KOH with 1% $SnCl_2$ dissolved in it at 180^oF. Heated by steam pipe.
(176)	Lainder	Brit. Pat. 3552 (1883) An electrolytic bath technique, using warm sodium hydroxide liquor, and the tinplate as the anode. The patent was withdrawn.

(177) Price — Brit. Pat. 5847 (1883)
Anodic tinplate is attacked in warm alkali. The patent was withdrawn after initial submission.

(178) Price — Brit. Pat. 5849 (1883)
Warm sodium hydroxide is used to detin tinned iron plate. The patent was withdrawn.

(179) Price — Brit. Pat. 2119 (1884)
A static bath of hot alkali, dissolving anodically polarised tinplate. The patent was withdrawn.

(180) W. Beatson — Brit. Pat. 11 067 (1885)
To ensure good electrolytic detinning in alkali, the liquor should be warm, and the scrap agitated.

(182) F.A. Lowenheim — U.S. Pat. 2 665 473 (1953)
Good detinning accomplished in a rotating drum, anodically charged, and immersed in hot alkali.

(183) G. McClaugan and D. Read — Brit. Pat. 1 533 727 (1976)
A continuous electrolytic plant using a rotating drum.

(184) G. McClaugan and D. Read — Brit. Pat. 1533 728 (1976)
A rotating drum for continuous electrolytic detinning.

(185) G. Knippers — Ger. Pat. 1 148 756 (1963)
Baled tinplate stacked in closed tanks and put under vacuum. Alkaline electrolyte pumped into vacuum vessel under pressure. Electrolytic detinning, using bales as anodes.

(186) T. Yoshita — Jap. Pat. 18 848 (1971)
Initially treat tinplate cathodically to remove films (lacquers, etc.) then treat anodically in 10% NaOH, KOH or NaCl.

(187) P. Kaesermann — Swiss Pat. 243 879 (1949)
Scrap is detinned electrolytically under pressure in a closed system providing for collection of the spongy tin.

(188) J.C. Groeber — Brit. Pat. 1013 521 (1964)
Sodium hydroxide electrolyte is used to detin anodically charged tinplate in an autoclave operating at 30-35 atmospheres.

(189) Speler Ind. — Ger. Pat. 570 619 (1933)
An electrolytic application for dissolving tinned material at the anode in alkali.

(190) M. Mandl — U.S. Pat. 2 243 165 (1941)
Treat material anodically in aqueous electrolyte of caustic alkali with traces of cobalt oxide as a catalyst.

(193) Hosada and Mukai — Jap. Pat. 654 (1961)
Leach tinned scrap with sodium hydroxide and sodium nitrate liquor at 105-125^{o}F to remove tin. Allow to cool and redissolve pptd. salt in hot water. Extract tin by electrolysis.

(195) Berzelius mbH — Ger. Pat. 709 569 (1949)
Scrap cleaned and dissolved in alkali bath of nitro substituted organic compould. When the solution is nearly saturated with tin it is electrolysed. The solvent is regenerated.

(196) Cremades y Cia — Spanish Pat. 280 064 (1962)
Alkaline electrolytic process with methanol (5-20%).

(197) G. Knippers — Ger. Pat. 1 135 181 (1962)
Solution of 5-6% NaOH with 15-20% methanol used to penetrate mass. Reaction performed under vacuum to remove gases.

(198) G. Knippers — Ger. Pat. 1 146 261 (1963)
An electrolytic process, using 30-35 g/litre of Na_2CO_3 with 5-20% methanol in water. It is carried out at 80-100^{o}C.

(199) G. Knippers — Ger. Pat. 1 146 262 (1963)
A current of 2,500 A applied to a tinplate anode using the liquor of ref. 198.

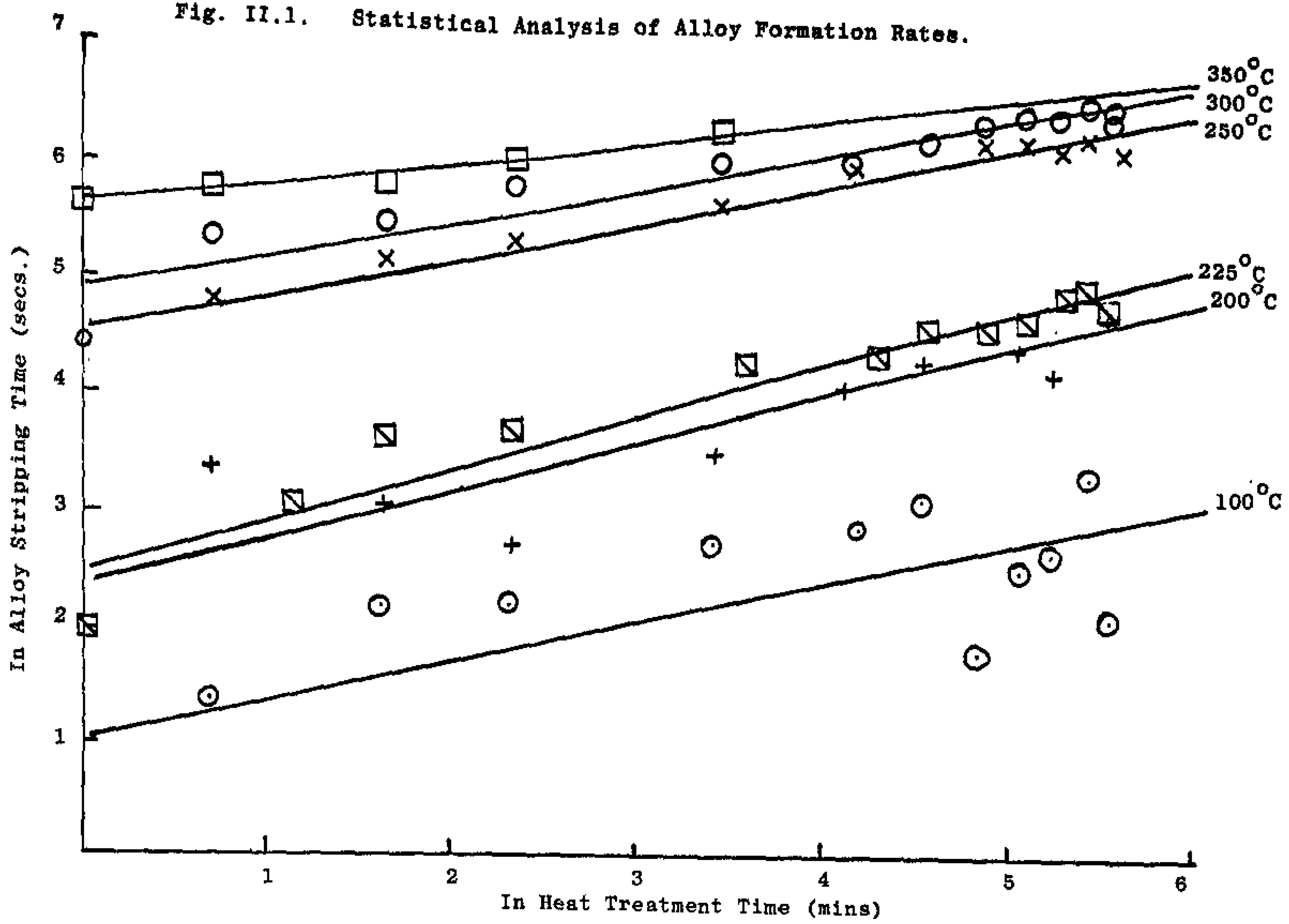
(201) J.E. Starek — Can. Pat. 432 632 (1946)
Scrap detinned anodically in an aqueous solution of alkali metal pyrophosphate.

(202) M.C. Blume — U.S. Pat. 3 394 063 (1968)
1.5 to 5% of potassium pyrophosphate at pH 10-11. Liquor between 54 and 89^{o}C. Current density on anode 2A/ft^2.

(203) C.F. Bohnhardt — U.S. Pat. 1 457 688 (1923)
Detinning metal plates by electrolytic use of a bath consisting of sodium sulphate, carbonate and silicate.

(204)	A.E. Veloso	U.S. Pat. 3 707 448 (1972) Using an aqueous solution of sodium chloride and carbonate, with a current density of 40-80 A/ft^2. Temperature of the liquor is 30-90°C.
(205)	H. Dillenburg	Ger. Pat. 2 254 398 (1974) Acidic liquors containing alkaline, or alkali metal salts of nitric, orthophosphoric, hydrochloric, hypochloric, or thiocyanic acids. The pH range for the chemical plant is 4.0 to 7.0.
(207)	C.P. Tatro	U.S. Pat. 1 316 926 (1919) Subject to the scrap, while in contact with carbon, to action of either sodium or potassium hydroxide solution at 50-65°C. Tin is deposited on the cathode.
(211)	J.P. Worthley	Brit. Pat. 2 000 809 (1979) Use a titanium basket coating in plastic for electro-recovery of secondary metals.
(212)	Victoria Rolling Co.	*Brit. Pat. 170 861 (1921)* Dissolve tin in contact with electro-negative element, such as copper, in sodium hydroxide. Carbon impregnated with copper oxide can replace copper.
(213)	R.A. Holland	U.S. Pat. 1 511 967 (1923) A general electrolytic patent.
(315)	Ketjen	Dutch Pat. 45 549 (1939) The use of thiocarbanilide to prevent iron attack in acid liquors.

Fig. II.1. Statistical Analysis of Alloy Formation Rates.



APPENDIX II.

Statistical Analysis of Kinetic Data

The growth rates of the alloy can be described by Fick's Law of Diffusion for temperatures below 350°C.

$$x^n = kt \qquad \text{eqn. 2.3}$$

Taking logs:

$$n \ln x = \ln k + \ln t \qquad \text{eqn. II.1}$$

Hence, if ln x vs. ln t is plotted, the gradient will be n, and the intercept ln k. Table 4.7. shows the values for n and k, obtained from Fig. II.1. The best-fit straight lines are drawn using linear regression, whereby deviations in the dependent variable (ln x) are minimised.

Some inaccuracies will be caused in transforming these data back in order to draw the growth curves (Figs. 4.27. and 4.28.), as this method of regression does not correctly accommodate an error term to allow for deviation of the points from the regression line. However, even noting the short-comings of the method, it is the generally accepted method.

To account for the fact that the growth curves do not pass through the origin, due to alloy formation during flow melting, an average stripping time corresponding to un-heat treated alloy content samples has been subtracted from the experimental stripping times.

Logarithms were then taken of the corrected times.

From the values of k obtained, activation energies can be calculated from the Arrenhius equation, as shown in Fig. 4.29.

APPENDIX III.

Production and classification of tinplate in Great Britain is categorised in Table III.1

Type	% by area	Total tin per m^2 (gms)
E2.8/2.8	37.2	5.6
E5.6/5.6	5.3	11.2
E8.4/8.4	0.4	16.8
E11.2/11.2	0.4	22.4
E1.4/1.4	0.8	2.8
E4.2/4.2	3.7	8.4
E5.0/5.0	1.4	10.0
D2.8/5.6	27.1	8.4
D2.8/8.4	2.1	11.2
D2.8/11.2	4.2	14.0
D5.6/8.4	3.2	14.0
D5.6/11.2	6.7	16.8

TABLE III.1

The balance of production, as a percentage is made up by Tin Free Steel and blackplate.(334)

Ref: (334) Mr. L.M. Warner, British Steel Corporation, Private communication.