

The removal of anionic impurities from liquid metals using fused salt electrolysis

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THE REMOVAL OF ANIONIC IMPURITIES
FROM LIQUID METALS USING
FUSED SALT ELECTROLYSIS

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This is to certify that the work presented in this thesis was performed by the candidate in the School of Metallurgy at the University of New South Wales, and has not been submitted to any other University or Institute for a higher degree.

A.N. PARRY

ABSTRACT

The desulphurisation of a liquid copper cathode by electrolysis of a magnesium fluoride-calcium fluoride eutectic salt melt above the copper, using a graphite anode, was investigated at 1423K under an inert argon atmosphere.

Most electrolyses were carried out at a constant cell potential of 2.500 V. It was found that very low sulphur levels (< 1.5 ppm) could be obtained, and that electrolytic discharge of sulphide out of the fused salt was also occurring, meaning that the electrolyte was effectively 'self cleaning'.

Two different cathodic sulphur transfer mechanisms were identified. With high sulphur levels in copper, essentially direct cathodic transfer of sulphur atoms at the cathode interface occurs at a rate determined by the anode reactions, with a high current efficiency for sulphur transfer. With low sulphur levels in copper, 'indirect' desulphurisation occurs, by chemical combination of dissolved sulphur with cathodically discharged magnesium and calcium. This occurs at a low current efficiency for sulphur transfer, and at a rate determined by the diffusion of sulphur in copper to the cathode interface.

A build-up of dissolved sulphide in the fused salt phase resulted in an increase in the anodic current efficiency for sulphur discharge to the extent that efficient 'cleaning' of the electrolyte is indicated.

In the early stages of electrolysis it was found that discharge of fluoride ions from the electrolyte could occur at a cell potential 0.5 V below the experimentally determined decomposition potential of the melt (2.65 ± 0.04 V), due to the low cathode potential required for direct sulphur transfer.

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CHAPTER 1

INTRODUCTION

1.1 ELECTROMETALLURGY IN EXTRACTIVE METALLURGY

The use of electrometallurgical techniques in extractive metallurgy has found widespread application, with many metals currently electrowon or electrorefined on a commercial scale^{1,2,3}.

Table 1.1 shows the range of metals processed.

1.1.1 Electrowinning

Electrowinning from aqueous solutions is limited to those metals that can be cathodically deposited from aqueous solutions at a cathode potential lower than that for hydrogen evolution, and generally provides the final reduction step in hydrometallurgical extraction routes where a compound of the metal has been leached in an aqueous electrolyte. Zinc and copper are the main tonnage examples, although in the latter case most of the crude metal production comes from a purely pyrometallurgical route.

The use of fused salt electrolytes in electrowinning is necessary for metals which cannot be cathodically deposited from aqueous solution due to the predominance of the hydrogen discharge reaction. The major tonnage example is the production of aluminium from alumina by the Hall-Heroult process⁴ utilising a molten cryolite (Na_3AlF_6) electrolyte, which accounts for essentially all of the primary production of aluminium. Carbothermic reduction of alumina is not a viable alternative process, due to the very high temperatures (>2273K) required for this⁴.

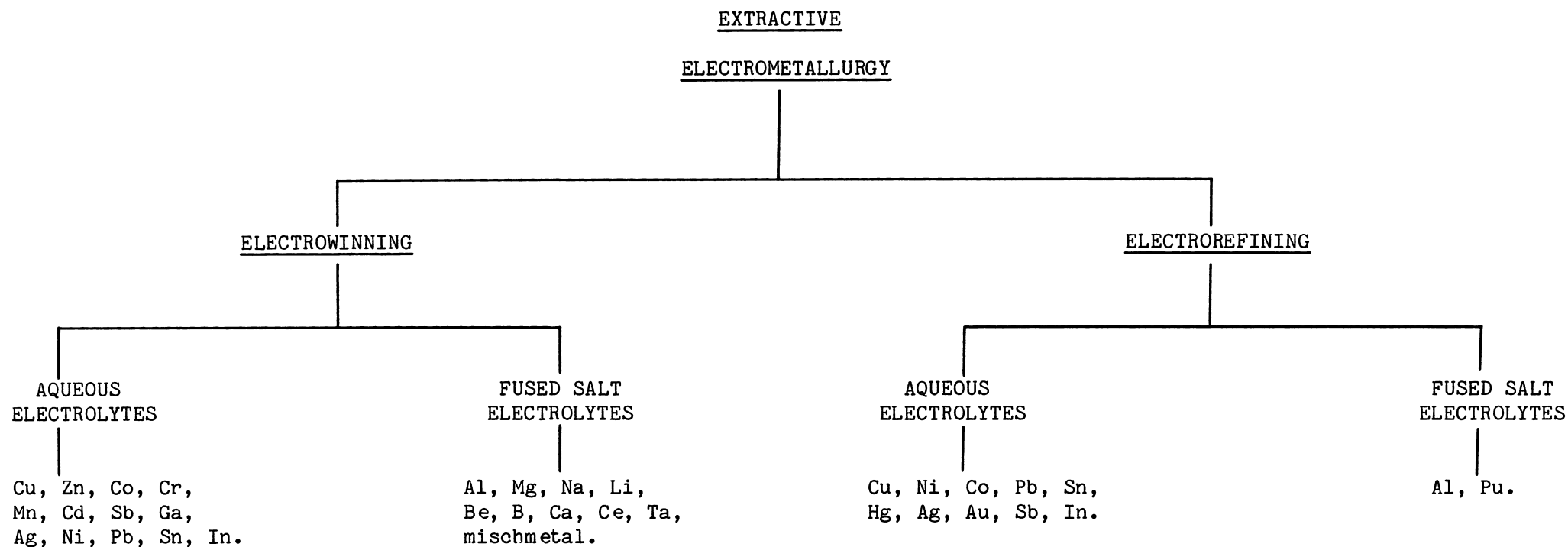


TABLE 1.1

CURRENT COMMERCIAL USE OF ELECTROMETALLURGY

IN EXTRACTION METALLURGY

The other metals in this category listed in Table 1.1 are electrowon from fused chloride electrolytes after first obtaining the metal as a chloride compound in a relatively pure form. Fused chloride electrolytes are well suited to this application due to their relatively low melting points and high electrical conductivity.

1.1.2 Electrorefining

As can be seen in Table 1.1 electrorefining in aqueous electrolytes is widely used on a commercial scale for the production of high purity metals. In all cases the feed is an impure metal anode with refining occurring through dissolution of the anode metal in the electrolyte and deposition of pure metal on the cathode.

Theoretically the cell potential for such a process is very close to zero as the activity of the metal in both electrodes is effectively unity. In practice the main role of the applied potential is to overcome the ohmic potential drop in the electrolyte, electrode polarization and ohmic potential losses in the cell hardware⁵. For example, in copper electrorefining cell potentials in the range 0.25 - 0.30 volts are applied⁶ with ohmic potential drop in the electrolyte the main component of this.

The Three-Layer Process for the electrorefining of aluminium^{7,8} is the only tonnage commercial process in which fused salt electrolytes are used. The electrolyte is either a mixture of aluminium fluoride with other fluorides (e.g. NaF, BaF₂, CaF₂) or with fluorides and chlorides (e.g. NaF, BaCl₂, NaCl). This electrolyte has a higher density than pure aluminium and therefore the cathode metal floats on top of it (see Figure 1.1). The impure aluminium anode metal is alloyed with copper such that it is more dense than the electrolyte and therefore forms a metal layer

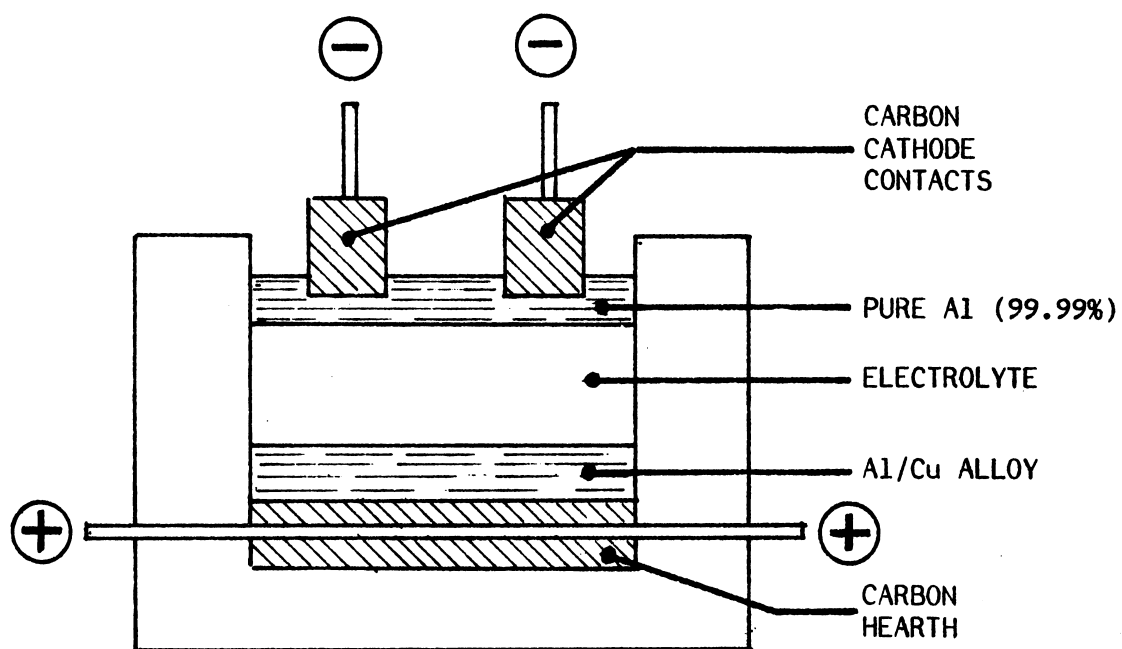


FIGURE 1.1

SCHEMATIC REPRESENTATION OF THE
THREE-LAYER CELL FOR
ELECTROREFINING ALUMINIUM

underneath it. This novel approach is obviously only applicable to a low density metal such as aluminium.

Cell temperatures may be in the range 973-1273K. Fairly high cell voltages are applied (of the order of 5 - 6 volts) to ensure generation of enough heat in the relatively small cells to maintain operating temperature. The current efficiency is 93 - 98% and the purity of the product is very high (99.99%+). This process is only used when 'super purity' aluminium is required. Sufficient purity is obtained in the Hall-Heroult process for most commercial applications of aluminium metal.

On a much smaller scale the Lamex process is used to electrorefine plutonium⁹. In this case the impure Pu metal or Pu alloy anode undergoes electrochemical dissolution in a molten NaCl-KCl electrolyte at 1013K followed by cathodic deposition to produce a metal product of greater than 99.99% purity.

1.2 THE USE OF FUSED ELECTROLYTES FOR ELECTROREFINING

Despite the fact that, to date, commercial application of electrorefining using fused salt or fused slag electrolytes has been very limited, considerable interest has been shown in the use of these high temperature electrolytes for the electrorefining of metals in the molten stage. The sizeable amount of published work reflecting this interest is reviewed later, but at this stage it is worthwhile to examine why this degree of interest has been shown, that is, what are the advantages to be gained in using fused electrolytes rather than aqueous electrolytes? These, as well as the comparative disadvantages of the use of fused electrolytes, are summarised in Table 1.2 and discussed below.

(1) High exchange current densities: Exchange current densities

for electrode reactions in fused electrolyte systems are generally higher than those encountered in aqueous systems^{10,11}

ADVANTAGES OF FUSED ELECTROLYTES	DISADVANTAGES OF FUSED ELECTROLYTES
1. High exchange current densities 2. High diffusivities 3. High electrical conductivity 4. Direct treatment of molten metal 5. Refining of the less noble metals 6. Non-conventional refining techniques are applicable	1. Cell heating requirements 2. Corrosive nature of fused electrolytes 3. Electrode configuration 4. Pollution

TABLE 1.2

COMPARISON OF FUSED ELECTROLYTES WITH
AQUEOUS ELECTROLYTES IN ELECTROREFINING

This is particularly true with metal/metal ion electrode reactions which are "fast" and therefore exhibit negligible activation polarization, but the exception is some gaseous discharge reactions (e.g. O^{2-} discharge) that have only slightly higher exchange current densities in fused systems. Higher exchange current densities indicate higher rates of charge transfer reactions and thus higher current densities can be maintained in fused electrolyte systems without suffering from increased activation polarization.

(2) High mass transport rates: Self-diffusion co-efficients and diffusivities of dissolved species are normally greater in fused electrolytes than in typical aqueous systems¹² thus comparatively higher current densities can be achieved in fused electrolytes without the penalty of increased concentration polarization.

(3) High electrical conductivity: The ionic conductivities of fused electrolytes are typically of the order of two orders of magnitude greater than those encountered in aqueous systems¹³, which is advantageous in terms of a reduced "IR" voltage drop through the electrolyte.

(4) Direct treatment of molten metals: The electrorefining of metals in the liquid rather than the solid state enables impure molten metal from a smelting process to be treated directly. This raises the possibility of a continuous electrorefining process utilising a "flow through" cell (which is not possible in the aqueous electrorefining of metals) and also eliminates the need for casting of anodes and remelting of cathodes.

(5) Electrorefining of the less noble metals: Due to the comparatively high cathodic potentials required for electrodeposition of the less noble metals (e.g. Al), these cannot be electrorefined using aqueous electrolytes due to the hydrogen discharge reaction. This is not a complication in the electrolysis of fused electrolytes.

(6) Use of 'non-conventional' electrorefining techniques: With high temperature molten systems a liquid metal electrode can be refined by electrolytic transport of the impurities out of the metal phase into the electrolyte. This is not possible in low temperature aqueous systems due to the prohibitively slow rates of solid state diffusion of the impurities in the solid metal electrode.

These potential advantages of using fused electrolytes as opposed to aqueous electrolytes in electrorefining obviously have to be considered in the light of inherent disadvantages associated with the use of fused electrolyte systems. These are:

(1) Cell heating requirements: Heat must be generated within the electrolysis cell by resistance heating of the electrolyte or by external supply to maintain operating temperatures (and also to melt the impure metallic feed if this is not already in the molten state). The specific energy demand associated with this is dependent upon the rate of electrorefining achievable and suggests that for large scale tonnage applications of fused electrolyte electrorefining, rapid refining rates are a requirement.

(2) Corrosive nature of fused electrolytes: Generally fused electrolytes are highly corrosive and comparatively difficult to handle compared with aqueous electrolytes.

(3) Inflexibility of electrode design: Liquid metal electrodes are physically limited to being metal pools and therefore horizontally oriented. In contrast to this, few design restrictions are imposed on solid metal electrodes used in aqueous electrorefining and the vertical electrode configuration normally employed represents a more compact cell design.

(4) Pollution aspects: The possibility of atmospheric contamination from:

- (i) release of volatiles from the high temperature electrolyte, or
- (ii) discharge of undesirable gaseous species at the electrodes

is greater with molten electrolyte systems.

1.3 GENERAL OVERVIEW OF FUSED SALT ELECTROREFINING

Hart, Hills and Tomlinson¹⁴ have reviewed much of the work aimed at developing fused salt electrorefining processes for metals. However, no mention is made in their review of any work carried out on the removal of anionic impurities from liquid metals. This work has been carried out in two specific areas, namely, the desulphurisation of molten pig iron and the removal of anionic impurities from molten copper. The reasons why this work was not reviewed by these authors is probably due to the fact that, in that case of desulphurisation of molten pig iron, most of the work was carried out using blast furnace slag type electrolytes and not fused salts as such, and in the case of removal of anionic impurities from copper, only one paper had been published at the time of writing their review.

Much of the published work reviewed by Hart, Hills and Tomlinson¹⁴ has been concerned with the electrorefining of the lower melting-point metals and in particular lead (m.pt. = 600K¹⁵) which

has been extensively studied in Russia by Delimarskii and his co-workers. This work has also been reviewed by Amstein, Davis and Hillyer¹⁶. Other lower melting-point metals which have been studied are zinc (m.pt. = 692K¹⁵) and plutonium (m.pt. = 913K¹⁵). In these low-melting systems the metal electrodes were liquid, and chloride electrolytes were generally used allowing operation at a cell temperature in the region of 773K for lead and zinc electrorefining and 973-1013K for plutonium electrorefining.

Electrorefining by transfer of metal from an impure anode to a pure cathode is the technique which has been employed almost exclusively in these works. In this thesis this method will be referred to as 'conventional' refining, while other electrorefining methods will be referred to as 'non-conventional'.

Amstein, Davis and Hillyer¹⁶, in their pilot plant work using an electrolytic cell with the two liquid metal electrodes separated by a horizontal diaphragm permeable to the electrolyte but not the liquid metal, found that current densities of 2-3 A/cm³ could be used as compared to 0.015 - 0.025 A/cm² in aqueous lead electrorefining. It was concluded that specific energy consumption for this type of cell would always be greater than that for aqueous cells due mainly to cell heating requirements (the cell voltage was 2.4 V as opposed to 0.35 - 0.70 V for aqueous electrorefining), but overall the fused salt system could have lower energy requirements due to the elimination of the casting and recasting of electrodes and anode slime treatments.

As previously discussed, the physical limitations and difficulties associated with the configuration of liquid metal electrodes are a potential problem area in molten salt electrorefining techniques. This is particularly so with conventional electrorefining

where separation of two liquid metal electrodes is required. Apart from the diaphragm type cells as used by Amstein, Davis and Hillyer other cell configurations investigated for the electrorefining of lead have comprised adjacent liquid metal pools separated by vertical insulating walls (e.g. the work of Panchenko and Delimarskii¹⁷) and the use of vertical graphite cathodes with "collectors" (Roms, Belen'kii and Delimarskii¹⁸). These three approaches to the problem of electrode configuration are diagrammatically shown in Figure 1.2. All three have inherent difficulties associated with them.

The diaphragm type cell requires a diaphragm material impermeable to the liquid metal but permeable to the fused salt and with sufficient mechanical strength and resistance to chemical degradation to give a satisfactory diaphragm life. Further, any gases evolved at the cathode (e.g. hydrogen¹⁶) are not released readily and the voltage drop across the diaphragm is a major component of cell voltage. The other two types of cell configuration suffer from the major difficulty of a long and tortuous current path with an uneven current density through the cell cross-section. A minimum electrode separation and minimum volume of electrolyte are desirable to reduce the "ohmic" drop and heat losses.

The physical limitations described above are particularly acute when liquid metal electrodes are used in conventional electrorefining. The elegant approach to these limitations applied in the "Three-Layer" process for aluminium electrorefining is obviously not applicable in these cases as there is no possibility of obtaining a fused electrolyte of higher density than lead. It is worth noting that the cell configuration limitations are much less severe if 'non-conventional'

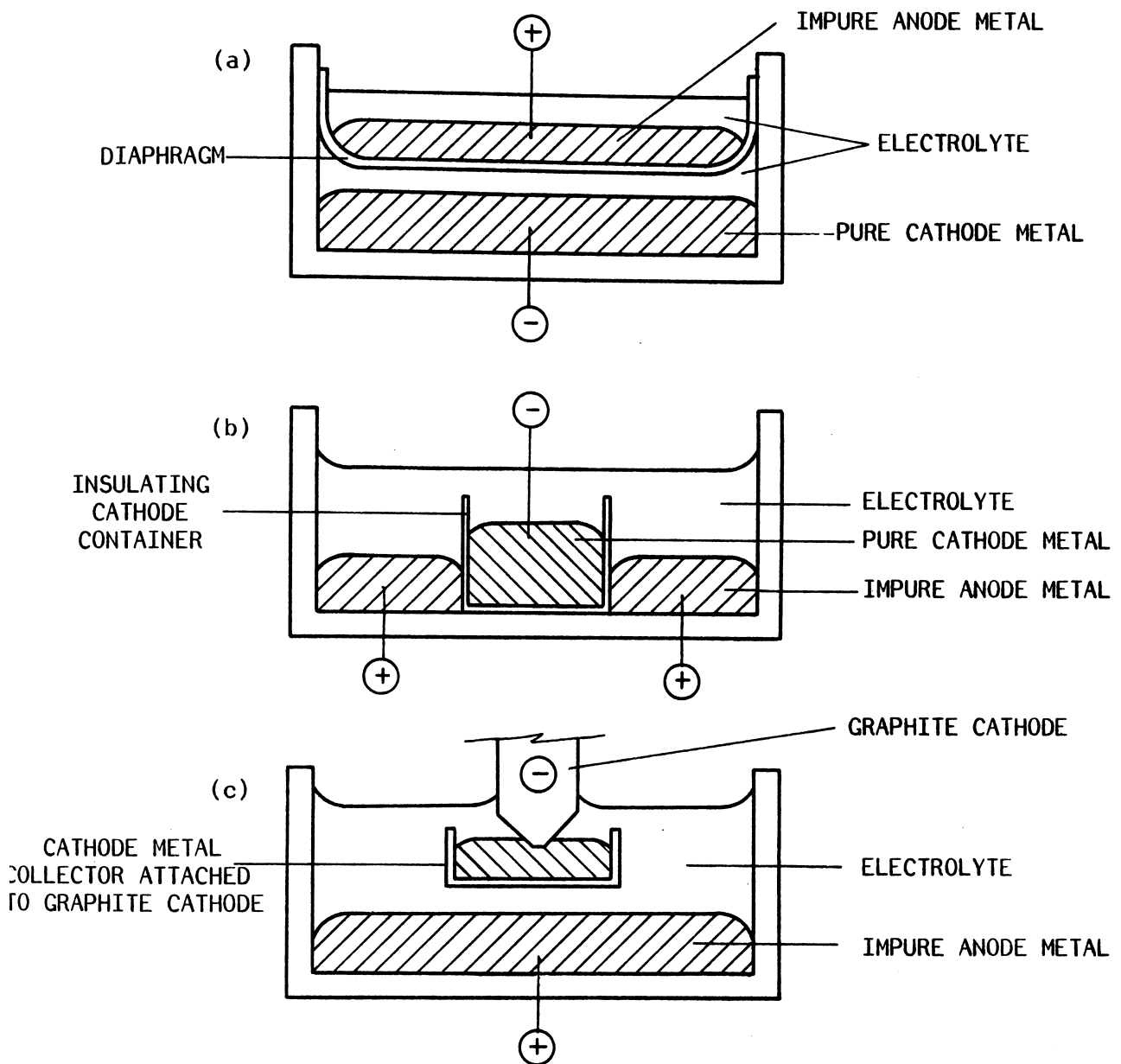


FIGURE 1.2

SCHEMATIC REPRESENTATION OF CELL CONFIGURATIONS USED FOR
FUSED SALT ELECTROREFINING OF LIQUID LEAD

- (a) Diaphragm Cell (after Amstein, Davis and Hillyer ¹⁶)
- (b) Adjacent Metal Pools (after Panchenko and Delimarskii ¹⁷)
- (c) Inert Cathode with Collector (after Roms, Belen'kii and Delimarskii ¹⁸)

electrorefining techniques are applied to liquid metal electrodes, with the liquid metal serving as a single electrode with no electrotransport of metal from one region of the cell to another.

Numerous papers have been published describing investigations into fused salt electrorefining of high melting-point metals¹⁶. These include beryllium, uranium, niobium, vanadium, tungsten, titanium and zirconium. Fused salt electrorefining of chromium has also been reported¹⁹. In all cases fused chloride electrolytes were used and the cell temperature was below the melting point of the metal being refined, (all cell temperatures reported being in the range 713-1128K). The electrorefining process in each case can be classified as 'conventional', with dissolution of a solid impure anode and electrotransport of the metal ions through the fused electrolyte followed by solid deposition (i.e. crystal growth) on the pure cathode.

Only three investigations utilising non-conventional electrorefining techniques have been described in the previously mentioned reviews of fused salt electrorefining^{14,16}. These are the removal of bismuth from molten lead²⁰, electrorefining of impure bismuth melts²¹ and gold recovery from molten electronic solder scrap²². The salient features of these processes are discussed below.

Removal of bismuth from molten lead²⁰ (Delimarskii, et. al.) was achieved in an electrolytic cell at a temperature of 613K with the stirred impure lead metal serving as the cathode and a small pool of molten lead serving as the anode. The cell voltage was 2.4 V at a typical current of 50A, which resulted in a cathodic current density of $\sim 1\text{A/cm}^2$.

Removal of the more electropositive bismuth from the cathode lead is a consequence of liberation of metallic sodium at the cathode/electrolyte interface during electrolysis. The sodium metal reportedly alloys with the liquid metal and forms a complex intermetallic compound of the type $\text{Na}_x \text{Pb}_y \text{Bi}_z$ which passes into the molten electrolyte, and is subsequently oxidised at the liquid anode to form a lead-bismuth alloy. Thus the bismuth concentration in the electrolyte initially increased to a maximum in the early stages of electrolysis and then decreased as the lead cathode became depleted in bismuth.

It was reported that the crude lead could be refined to 5 p.p.m. Bi by a sufficiently lengthy electrolytic treatment (which would appear to be at least 10 hours for an initial Bi content of 0.5% and a minimum of 5.5 hours for an initial content of 0.1%), and that the anode lead metal could be enriched to 10-15% Bi if it was re-used in multiple batch electrolyses.

The electrefining process for bismuth melts investigated by Delimarskii et. al.²¹ involved the anodic oxidation of dissolved Pb, Ag, and Cu impurities in the impure anode metal, resulting in their transfer into the fused chloride electrolyte. The experiments were carried out at 773-823K and current efficiencies of 80-92% were reported with a high purity Bi product melt obtained. The cathode consisted of a molten lead pool which acted as an impurity metal 'collector' due to the cathodic deposition of the Pb, Ag and Cu dissolved in the electrolyte. The cell configuration was of the type represented in Figure 1.2(b).

The authors reported that current densities of up to 1.0 A/cm^2 could be used. In one experiment using a current density of 0.83 A/cm^2 the lead was virtually completely eliminated from the anodic

bismuth melt (originally containing 15 wt% Pb) in under one hour. It was also reported that the current efficiency dropped sharply towards the end of the process due to an increase in the rate of anodic dissolution of bismuth as the concentration of lead in the anode approached low values.

The process reported by Kleespies et.al.²² for recovery of gold from scrap solder utilised a chloride electrolyte at 723-773K. The gold-containing molten solder served as the anode, while the cathode was a liquid pool of refined solder in a cell configuration similar to Figure 1.2(b) except that the central electrode was the anode. Electrolysis at an anode current density of $0.5 - 1.0 \text{ A/cm}^2$ (cell voltage = 6 - 12 V) resulted in anodic oxidation of the less noble Sn and Pb which passed into the electrolyte and subsequently were cathodically deposited. Thus the process achieved an enrichment in the gold content of the anode melt (an increase from 60 oz/ton to 15 000 oz/ton was reported) allowing the gold to be recovered subsequently by fire-refining, and at the same time refined solder was collected at the cathode. The reported current efficiency for combined Sn and Pb removal was 93%.

This process possesses some interesting features, namely that it can be considered both an anodic electrorefining and a conventional electrorefining process. The main material to be recovered is partially refined (i.e. concentrated) in the anode through anodic dissolution of the 'impurities' which comprise the bulk of the anode material. The two major impurities (Sn and Pb) are themselves electrorefined by conventional electrotransport from the anode and deposition at the cathode.

The two anodic electrorefining processes described above utilise electrotransport of cationic impurities out of the liquid metal electrode to be refined. Recovery of these impurity species is desirable and therefore the second electrode is also a liquid metal where deposition of the impurity cations dissolved in the electrolyte takes place.

In the chemical electrorefining process described above for removal of bismuth from molten lead²⁰, the semi-metallic bismuth is effectively behaving as an anionic species, since a chemically reactive metallic species is generated at the metal/electrolyte interface to achieve refining by reaction with the dissolved bismuth. Here again, a second liquid metal electrode is utilised as a collector for the impurity species which is transported through the electrolyte and anodically oxidised.

The use of two liquid metal electrodes in these processes introduces some of the difficulties and inflexibilities of liquid metal electrode configuration as discussed previously. In contrast to this, non-conventional electrorefining techniques for removal of true anionic impurities (as opposed to semi-metallic elements) from liquid metals will not encounter these difficulties as only one liquid metal electrode is required. Thus the liquid metal to be refined will serve as the cathode (in either cathodic or chemical electrorefining) with discharge of anionic species, typically in gaseous form, occurring at the anode.

1.4 THE REMOVAL OF ANIONIC IMPURITIES FROM LIQUID METALS

This work was commenced to investigate some fundamental aspects of the removal of anionic impurities from molten metals using non-conventional fused salt electrorefining techniques. Interest in

this type of electrorefining process stems mainly from two potential areas of application; viz:

- (1) Electrolytic desulphurisation of molten pig iron
- (2) Continuous electrorefining of impure molten copper

The published literature describing previous investigations into these two processes is reviewed in detail in the following chapter. However, in broad terms it can be said that the main impetus for their development is, in both cases, the desirability of a rapid, simple and efficient refining process capable of treating a continuous (or semi-continuous) molten metal stream in a "flow-through" type reactor.

1.4.1 Desulphurisation of Pig Iron

Sulphur removal from steel poses considerable problems to the steel-maker, because unlike most other impurity elements encountered in steel-making, sulphur is not removed by oxidation. Historically, desulphurisation has been approached from consideration of the slag/metal distribution of this element, with attempts to adjust conditions in the steel-making process to shift the equilibrium more strongly in favour of sulphur distribution to the slag phase. This has mainly been achieved through the use of higher basicity slags.

However, for over twenty years it has been recognised that the demands for low sulphur steels are increasing while the sulphur input from the raw materials used in iron and steel-making are also increasing²³, a continuing trend which has forced steel-makers to look beyond the use of high basicity slags as a sulphur sink. Because molten pig iron from the blast furnace is the major contributor to the sulphur input to steels most recent attempts at reducing sulphur levels in steels have been aimed at desulphurising pig iron by external treatment in batches between the blast furnace and the

steel-making process²⁴. The basis of the processes is the introduction into the pig iron of a species which has a high affinity for sulphur, resulting in the formation of a sulphide compound which reports to the slag phase. This can be done as a batch treatment through the direct injection of the reactive species.

Most interest has been in the use of magnesium, calcium carbide and lime as injectants. A major problem with the use of calcium carbide and lime is the high specific consumption of these desulphurising agents which becomes very much more pronounced as lower ultimate sulphur levels are approached, as does the required treatment time. Thus, typically, from data presented in the literature^{24,25} it would appear that at least five times the minimum theoretical requirement of these compounds is required for adequate desulphurisation. Magnesium injection²⁶ or the use of the "mag-coke" process gives a more efficient usage of reactant but has not gained widespread acceptance due primarily to the high cost of magnesium metal.

It is not suprising, therefore, that in a review of iron desulphurisation practice published in 1976, Kurzinski²⁴ wrote that: "To date, none of the existing desulphurizing methods offer a good solution to the production, metallurgical and economic factors raised by the iron sulphur problem".

Electrochemical removal of sulphur from molten pig iron through either cathodic or chemical electrorefining is one possible alternative sulphur removal process that can be considered and could be utilised in a continuous refining cell. Thus the molten pig iron would serve as the cathode with direct electrolytic transfer of sulphur

from the metal to the electrolyte occurring in cathodic refining or electrolytic generation of a reactive species at the metal/electrolyte interface to effect desulphurisation in a chemical electrorefining process. The anodic reaction would be the discharge of an anionic species from the electrolyte. Significant discharge of dissolved sulphide at the anode would result in a "self-cleaning" effect in the electrolyte.

As is discussed in the following chapter, the possibility of utilising such an electrolytic refining process has been recognised for many years and a significant amount of work has been done. However, there has been a general lack of agreement as to whether the refining process is occurring through a cathodic or chemical electrorefining mechanism and little work has been done on the involvement of sulphur in anode reactions. Further, it appears that utilisation of fused salts as electrolytes rather than molten blast furnace slag type electrolytes (which has characterised the bulk of the work) could yield more promising results.

1.4.2 Refining of Copper

The use of a high temperature molten salt electrorefining process for molten copper essentially entails consideration of the potential advantages and disadvantages associated with 'non-conventional' fused salt electrorefining as opposed to conventional aqueous electrorefining. These are summarised in Table 1.3.

Data published in 1977³⁴ showed that conventional copper electrorefining plants accrued capital-related operating costs that were significantly more dominant refining cost components than the electrical energy costs. The capital-related operating costs arise mainly from tankhouse depreciation and interest, and the interest from

POTENTIAL ADVANTAGES OF NON-CONVENTIONAL ELECTROREFINING TECHNIQUES	POTENTIAL DISADVANTAGES OF NON-CONVENTIONAL ELECTROREFINING TECHNIQUES
. Lower coulombic requirements . Less refining time . Simultaneous discharge of impurities from the electrolyte.	. Higher cell potential . Only one type of impurity (cationic or anionic) removed in a single stage.

TABLE 1.3

COMPARISON OF NON-CONVENTIONAL ELECTROREFINING
TECHNIQUES (CATHODIC, ANODIC OR CHEMICAL) WITH CONVENTIONAL
ELECTROREFINING

(See text for discussion)

the very large copper inventories in tankhouses. Even allowing for a threefold increase in electrical energy costs since the 1977 data was published, with no assumed increase in the capital-related costs, the capital-related operating costs would still predominate. This feature of conventional copper electrorefining plants, coupled with their associated very high labour costs²⁷, indicates that major cost savings could be gained if an inherently more rapid, higher intensity electrorefining process using a more compact plant with a smaller copper inventory and lower labour costs could be developed. A continuous molten salt electrorefining process has the potential to achieve this, as well as to reduce electrical power costs, if 'non-conventional' electrorefining techniques are utilised. The energy intensive cathode remelting operation would also be eliminated.

Direct treatment of blister copper from Pierce-Smith converters or a continuous smelting process⁶ would typically involve two molten salt electrorefining stages - the first using cathodic or chemical electrorefining to eliminate the anionic impurities (sulphur, oxygen, selenium, tellurium) and the second using anodic or chemical electrorefining to recover valuable cationic impurities (gold, silver) present in the copper. Obviously the second stage would not be required in cases where insufficient amounts of these valuable metals were present to make it economically attractive.

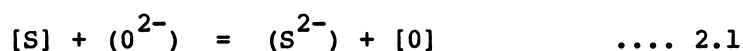
The small amount of work published in the literature describing investigations into such a process is reviewed in the following chapter.

CHAPTER 2

REVIEW OF PREVIOUS WORK

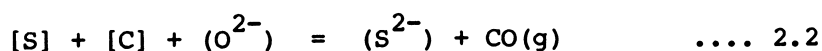
2.1 DESULPHURISATION OF PIG IRON

Prior to the development of the ionic theories of slag constitution the electrochemical nature of the slag/metal transfer reaction was not recognised because slag constituents were considered to be neutral molecular species. However, the acceptance of the ionic theories of slag constitution^{28,29} prompted a reappraisal of ideas on slag/metal transfer reactions and in 1950 Rosenquist³⁰ suggested that the sulphur transfer reaction from metal to slag could be represented as an ionic exchange reaction:



occurring through an electrochemical mechanism.

Following from this, in 1956, Wagner³¹ proposed an electrochemical or "local cell" mechanism for the kinetics of slag/metal reactions and pointed out the need for its experimental verification. He proposed that the overall desulphurisation reaction for pig iron in contact with slag:



was occurring as coupled cathode and anode reactions at different sites, as shown in Figure 2.1.

In the same year Ramachandran et al³² published the results of what is now regarded as a classical piece of work which gave experimental confirmation of the electrochemical nature of the slag/metal sulphur transfer reaction.

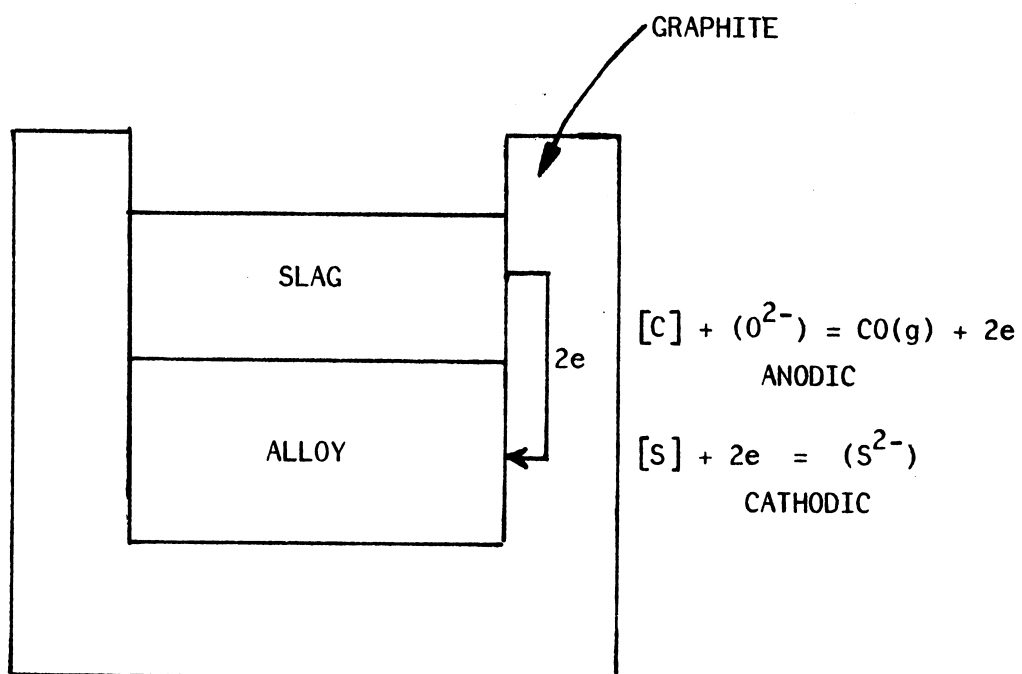
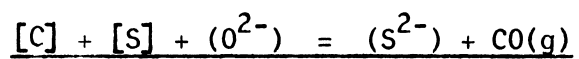


FIGURE 2.1

LOCAL CELL ACTION FOR THE REACTION



AS PROPOSED BY WAGNER³¹

They showed that the cathodic transfer of sulphur across the slag/metal interface was accompanied by simultaneous coupled anodic electrochemical reactions in order to maintain electroneutrality in the slag. Thus, the faradic equivalent of sulphur transferred to the slag was equal, within the limits of error, to the sum of the faradic equivalents of CO gas produced and Fe, Si or Al transferred from iron to slag. It was also proposed that different coupled reactions predominate depending on whether the slag/metal desulphurisation process is in the initial or final stages. These reactions are summarised in Table 2.1.

A qualitative interpretation of this behaviour has been given in terms of the relative shifts in the polarisation curves of the various electrochemical reactions as the desulphurisation process continues^{33,83}.

Further evidence of the electrochemical mechanism of sulphur transfer was given by Wynnyckyj and Roy³⁴. Their work confirmed Wagner's concept of "local cell action" involving cathodic sulphur transfer across the metal/slag interface with anodic oxide ion discharge to form CO gas occurring at the interface between the slag and the graphite crucible sidewalls. Conduction of electrons from the anodic to cathodic sites was thus occurring through the graphite crucible sidewalls and the molten metal.

The recognition of the electrochemical nature of the sulphur transfer from liquid iron to slag as the cathodic charge transfer reaction:



was the impetus for subsequent experimental work aimed at accelerating this charge transfer reaction by applying a potential difference

	CATHODIC	ANODIC
INITIAL STAGES	$[S] + 2e = (S^{2-})$	$[C] + (O^{2-}) = CO + 2e$ $[Fe] = (Fe^{2+}) + 2e$ $[Si] = (Si^{4+}) + 4e$ $[Al] = (Al^{3+}) + 3e$
LATER STAGES	$[S] + 2e = (S^{2-})$ $(Fe^{2+}) + 2e = [Fe]$ $(Si^{4+}) + 4e = [Si]$ $(Al^{3+}) + 3e = [Al]$	$[C] + (O^{2-}) = CO + 2e$

TABLE 2.1
REACTIONS OCCURRING WHEN SULPHUR IS
TRANSFERRED FROM IRON TO SLAG⁵

between the metal and the slag such that the liquid metal was cathodic with respect to the slag. Most of the work to-date has been carried out on desulphurisation of molten pig iron using a blast furnace type slag as an electrolyte. However, some workers have investigated the use of molten salts as electrolytes and produced significantly better results.

2.1.1 Desulphurisation of Pig Iron using Blast Furnace Slag

Electrolytes

In most of this work a 'standard' cell configuration as shown in Figure 2.2 was used, with the molten pig iron serving as the cathode and a conducting rod (usually graphite) immersed in the molten slag as an anode. Electrical contact to the liquid metal was through the base of the crucible which was typically fabricated from graphite.

In most cases the slags used were based on the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ ternary system, often with minor additions of oxides such as MgO , MnO and FeO . In all cases galvanostatic (i.e. constant current) electrolysis was applied and consequently the cell voltage was variable.

The major experimental details of the work reported using a 'standard' cell configuration are summarised in Table 2.2.

In all cases it was found that the application of an impressed current to the circuit resulted in:

1. A significant increase in the rate of sulphur transfer from metal to slag above that achieved through simple slag/metal contacting.
2. The attainment of much lower ultimate sulphur levels in the metal than could be achieved with slag/metal contacting.

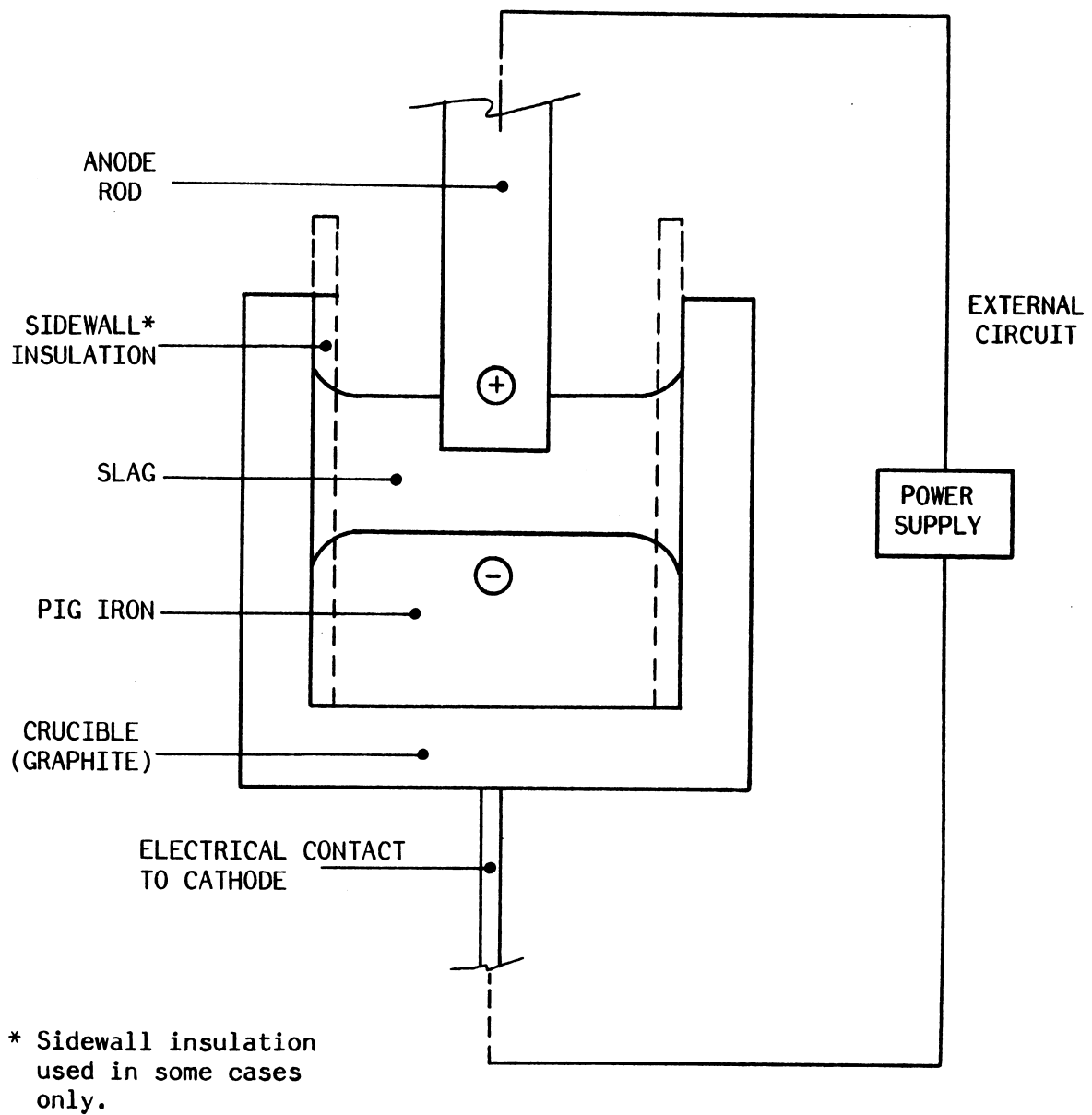


FIGURE 2.2

'STANDARD' ELECTROLYSIS CELL FOR
THE DESULPHURISATION OF PIG IRON

WORKERS	DATE	CELL TEMP (°C)	ANODE MATERIAL	CATHODE CURRENT DENSITY (A/cm ²)	CELL POTENTIAL (V)	TYPICAL SULPHUR LEVELS IN PIG IRON (wt% [S])		CATHODE CURRENT EFFICIENCY FOR S-TRANSFER (%)	REF.
						INITIAL	FINAL		
Esin et al	1958	N.D.	Graphite Rod	3.0	25-50	0.03-0.04	0.017	10-20 (max.)	35
Ohtani and Gokcen	1959	1500	Graphite Rod	N.D.	6.6-15	0.6 -0.8	0.01	50 (See note 4)	36
Homma et al	1960	1250-1350	Silicon Carbide or Graphite Rod	0.5	5	0.03-0.13	0.005-0.009	N.D.	37
Ginsburg and Gokcen	1962	1500	Graphite Rod	N.D.	N.D.	0.05-1.1	0.23	N.D.	38
Ward and Salmon	1963	1400	Graphite Rod	0.17-0.51	N.D.	0.1 -0.25	0.03 -0.04	10	39
Dobryden et al	1964	1470	Silit Rod	0.5	N.D.	0.12-0.14	0.01 -0.02	3.25	40,41
Nishiwaki et al	1970	1450-1570	Graphite Rod	0.56	N.D.	0.4	0.02 -0.03	N.D.	42
El Gammal et al	1973	1300-1400	Graphite Rod	0.05-0.8	10-45	0.32	0.01	N.D.	43
Gatellier & Olette	1977	1600	Platinum	N.D.	N.D.	0.45	N.D.	N.D.	44

TABLE 2.2

ELECTROLYTIC DESULPHURISATION OF PIG IRON USING A BLAST FURNACE
SLAG ELECTROLYTE AND A STANDARD ELECTROLYSIS CELL (Fig. 2.2)

NOTES

1. "N.D." = No data.
2. All experiments carried out at constant current.
3. The figures presented are typical values for the experimental work reported.
4. The maximum value of cathodic current efficiency reported by Ohtani & Gokcen of approximately 50% was only achieved at the start of electrolysis when the sulphur level in the pig iron was high.

This behaviour is typified in Figure 2.3 from the work of Ward and Salmon³⁹ in which the slag and metal were equilibrated with respect to sulphur during an initial holding period (approximately 180 minutes) and then current was applied (point A) producing a cathodic current density of 0.51 A/cm^2 for a period of approximately 130 minutes. The initial equilibration produced only a slight decrease in the sulphur content of the metal at a slow rate, while the application of current produced a dramatic decrease in the sulphur content at a much increased rate.

Other significant findings of the work summarised in Table 2.2 are discussed below.

(a) Kinetics of Sulphur Transfer

Ohtani and Gokcen³⁶ first established that the rate of sulphur transfer during electrolysis was proportional to the sulphur concentration in the liquid iron. Thus the kinetics could be characterised by a linear relationship between $\log [\%S]$ and electrolysis time, that is, "first-order" kinetics[†]. This is shown in Figure 2.4 from the work of these authors.

Subsequently other workers who have investigated the kinetics of electrolytic sulphur transfer^{38,40,41,42} have confirmed that first order kinetics are obeyed.

The rate of sulphur transfer from metal to slag is also dependent on the cathodic current density applied. Most workers^{35,36,39,40,41,42,43}

†

NOTE: Although strictly speaking the term "first order" kinetics applies only to chemical controlled (or activation controlled) reactions, it is more generally applied to all cases where linearity between $\log$ (concentration) and time is observed (e.g. for diffusion controlled reactions where the equilibrium concentration is much smaller than the bulk concentration of the diffusing species). It is in this more general sense that the term "first order" is used here.

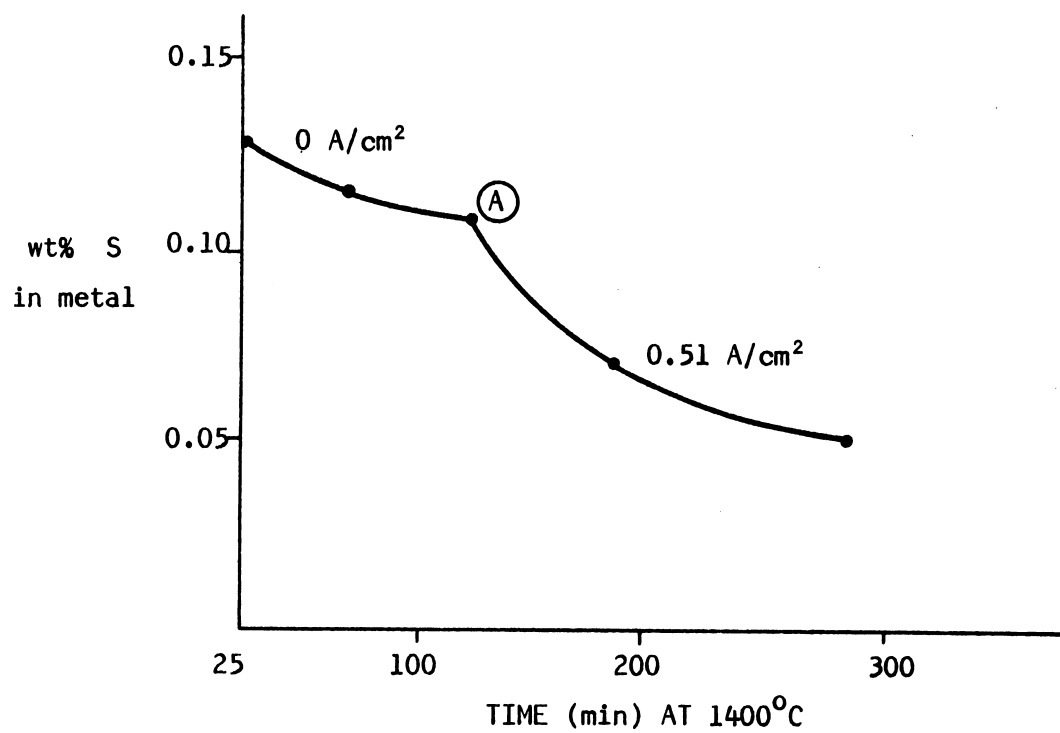


FIGURE 2.3

EFFECT OF APPLICATION OF CURRENT AFTER

EQUILIBRATION OF METAL AND SLAG

(after Ward and Salmon³⁹, run 'B2')

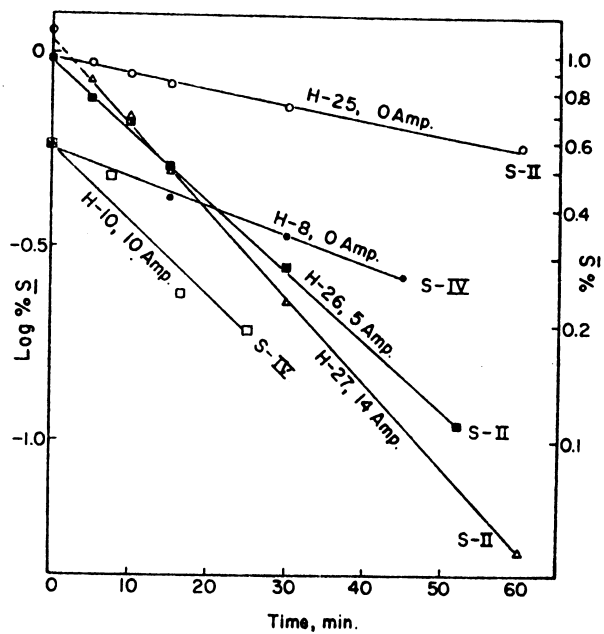


FIGURE 2.4

FIRST ORDER KINETICS OBSERVED FOR
ELECTROLYTIC DESULPHURISATION OF PIG IRON

(After Ohtani and Gokcen³⁶)

have reported that increased cathodic current densities result in an increase in sulphur transfer rate, with the relationship approximately linear. Nishiwaki et al⁴², in a treatment of data they obtained, showed that a plot of the rate constant for sulphur transfer (K_m) versus the current density could be closely approximated by a straight line, with an increase in the current density by a factor of two nearly doubling the value of the rate constant.

(b) Current Efficiency for Sulphur Transfer

A major difficulty encountered in the work with blast furnace slags has been the low current efficiencies achieved for sulphur transfer from the metal to the slag. Esin et al³⁵ reported maximum current efficiencies in the range 10-20% while Ward and Salmon³⁹ achieved no better than 10% in their experiments and Dobryden et al^{40,41} reported a maximum of 3.25%. No current efficiency figures were given by Gatellier and Olette⁴⁴ but they reported that current efficiencies of the order of "a few per cent" were achieved.

Better results were gained when sulphur concentrations in the molten iron were high. Thus Ohtani and Gokcen³⁶ found that current efficiencies of the order of 50% could be attained in the early stages of electrolysis of a high sulphur (0.6-0.7 wt% S) pig iron melt, but that the current efficiency subsequently decreased rapidly as sulphur was removed. Similarly Nishiwaki et al⁴² reported a current efficiency of 60% during the first 10 minutes of electrolysis which was effective in reducing the sulphur concentration of the pig iron from 0.4% S to $\sim$ 0.2% S. However, after 30 minutes electrolysis the sulphur concentration was still $\sim$ 0.08% and the overall current efficiency (i.e. the average current efficiency for the entire process) was then only 20%. These results indicate that for the

levels of sulphur commonly found in pig iron (typically ~ 0.15 wt% S) low current efficiencies for sulphur transfer would be expected using these electrolysis techniques.

This strong dependence of current efficiency on sulphur concentration in the pig iron which has been reported by most authors is to be expected. It can be readily shown that a linear relationship would be expected during galvanostatic electrolysis if the rate of sulphur transfer obeys first order kinetics. Thus, the current efficiency for sulphur transfer is given by:

$$\eta = i_s / i_t \quad \dots 2.4$$

where i_s is the sulphur transfer current and i_t is the total electrolysis current (constant). Further,

$$i_s = \dot{n}ZF \quad \dots 2.5$$

where $\dot{n}$ is the rate of sulphur transfer, Z the number of electrons required for electrochemical transfer and F Faraday's constant.

Combining these two equations with the defining equation for first order reaction kinetics; which in this case is:

$$\dot{n} = k_r [\%S] \quad \dots 2.6$$

(where k_r is the rate constant) gives the following equation for the current efficiency:

$$\eta = \frac{k_r ZF}{i_t} [\%S] \quad \dots 2.7$$

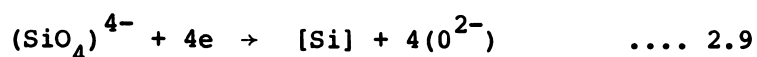
OR

$$\eta = \text{const.} [\%S] \quad \dots 2.8$$

Thus the current efficiency for sulphur transfer should be directly proportional to the sulphur concentration of the pig iron. A graphical plot given by Ohtani and Gokcen³⁶ of current efficiency during the first 10 minutes of electrolysis versus the initial sulphur

content of the metal did show an approximately linear relationship between these variables, although there was considerable scatter in the data points (see Figure 2.5).

The main reason for the low current efficiencies achieved in the work with blast furnace slags is the occurrence of competing non-sulphur-transferring cathode reactions, and in particular the reduction of silicate ions in the slag which can be represented by the following equation:[†]



This is the major current-consuming reaction and results in a steady build-up during electrolysis of reduced silicon metal dissolved in the pig iron^{36,39,42}.

Current efficiencies for silicon transfer in the range 70-80% have been reported^{40,41}, while data for one typical electrolysis experiment reported by Ward and Salmon³⁹ gives a calculated current efficiency for silicon transfer of 67% as opposed to only 2.5% for sulphur transfer. Gatellier and Olette⁴⁴ indicated that current efficiencies for silicon transfer were of the order of 50% in their work, while Nishiwaki et al⁴² reported values in the range 38-53%, more than double the current efficiencies for sulphur transfer which were in the range 13-18%.

Moderately increased current efficiencies for sulphur transfer were obtained by increasing the basicity of the electrolysis slags^{38,42}, due to the decrease in the activity of silicate ions in the melt and a resultant reduction in the rate of reaction (2.9).

[†]NOTE: This is only one of many possible representations of the silicate ion-silica reduction reaction. Similar equations could be written for many other types of silicate ion that possibly exist in these slags, e.g. $\text{Si}_3\text{O}_9^{6-}$, $\text{Si}_4\text{O}_{12}^{8-}$, etc.

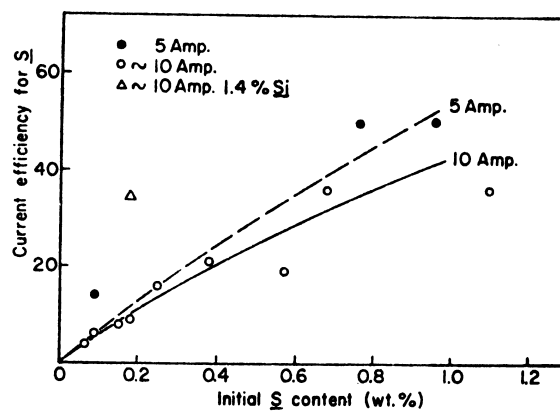


FIGURE 2.5

VARIATION OF CURRENT EFFICIENCY FOR
SULPHUR WITH INITIAL SULPHUR DURING
THE FIRST 10 MINUTES OF ELECTROLYSIS

(After Ohtani and Gokcen³⁶)

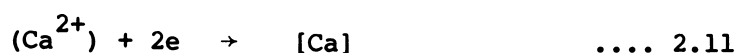
Similarly, pre-doping of the pig-iron with silicon³⁶ gave higher sulphur-transfer efficiencies due to a decrease in the rate of reaction (2.9), as did electrolysis with an Al_2O_3 - CaO slag containing no silica³⁶. In this latter case the current efficiency for sulphur transfer in the early stages of electrolysis was $\sim 35\%$ as opposed to $\sim 10\%$ using a silicate slag (in each case the initial sulphur content of the pig iron was similar, approximately 0.2 wt%).

Evidence for cathodic manganese transfer according to the equation



was given by Ward and Salmon³⁹ in electrolysis experiments with a silicate slag containing 11 wt% MnO . In this case both the silicon and manganese contents of the pig iron increased markedly during electrolysis and the sulphur current efficiency was very low - approximately 1.5%. It is interesting to note that the ultimate sulphur level achieved was much lower than that obtained for the Mn-free slags, presumably due to the chemical desulphurising effect of the dissolved manganese in the iron.

Very little data has been presented on other possible cathode reactions occurring (apart from sulphur and silicon transfer) but it appears that the combined efficiencies for silicon and sulphur transfer fall well short of 100%^{39,42}. However, some interesting results were published by El Gamall et al⁴³ who electrolysed a $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag using a pure molten silver cathode and a graphite anode at 1573K. A considerable build-up of reduced calcium metal dissolved in the molten silver was found, with an increase in the calcium concentration in the silver from 0.0% to 2.3% during 45 minutes electrolysis at 0.8 A/cm^2 cathodic current density, thus giving direct evidence of cathodic calcium discharge according to the equation:



It was postulated that only part of the cathodically discharged calcium dissolved in the silver bath, the rest reacting with the slag phase to produce a cathodic slag layer of high basicity. This cathodic slag (comprising one or two distinct layers) was readily separated and chemically analysed and had completely different physical and chemical properties from the bulk of the slag. The amount of calcium dissolution in the silver phase and amount of cathodic slag formed decreased with increasing temperature such that above the boiling point of calcium (reported as 1758K) these electrolysis phenomena did not occur - reportedly due to the rapid vaporisation of any metallic calcium formed. It was also suggested that this formation of calcium vapour at the slag/metal interface resulted in a "metallic cloud" forming in the molten slag, providing an electronic conduction path, suppressing ionic conduction and therefore ionic discharge reactions.

In experiments with pig iron as the cathode metal, the cathodic slag was found to be very rich in carbon, present in the form of CaC_2 , due to reaction at the slag/metal interface of discharged calcium with dissolved carbon in the pig iron. Electrolysis with pig iron doped to 0.32 wt% sulphur (1623K, cathodic current density = 0.8 A/cm^2) resulted in a rapid reduction of the sulphur concentration in the metal to approximately 0.01% in 12 minutes. Most of the sulphur transferred to the slag phase was found to be in the cathodic slag layer, retained as CaS . For example, one electrolysis experiment produced a cathodic slag containing $\sim 1.75 \text{ wt\% S}$ while the bulk of the slag contained $\sim 0.42 \text{ wt\% S}$.

The authors concluded that the rapid and efficient desulphurisation was achieved through the formation of a cathodic slag of high desulphurising power, highly basic and rich in CaC_2 , as well as through the release of elemental calcium which could react directly with the sulphur present in the pig iron.

(c) Desulphurisation using a 'Non-standard' Electrolysis Cell

Some desulphurisation work has been reported using a 'non-standard' electrolysis cell configuration as shown in Figure 2.6, with both electrodes immersed in the slag phase, producing electrolysis of the slag with no direct passage of current through the molten metal sub-layer.

It has been found that the kinetics of desulphurisation of the molten pig iron using this cell configuration are quite similar to the desulphurisation kinetics using the 'standard' cell configuration. This is a significant observation in terms of identifying the mechanism of sulphur transfer from the metal to the slag.

As an example, Esin and co-authors³⁵ using this type of electrolysis cell with two graphite anodes, reduced the sulphur concentration of the pig iron from 0.028 wt% to 0.018 wt% in 8.5 minutes with a cathodic current density of $1.8\text{--}1.9 \text{ A/cm}^2$ (run 15). Using a similar slag and cathodic current density in a 'standard' cell (run 9) a reduction in sulphur concentration from 0.030 wt% to 0.017 wt% in 7 minutes was achieved. Thus, although the rate of desulphurisation using the 'standard' cell was higher, there was not a great difference between the two.

Dobryden et al also achieved results with a 'non-standard' cell⁴⁵ comparable to those obtained with the 'standard'

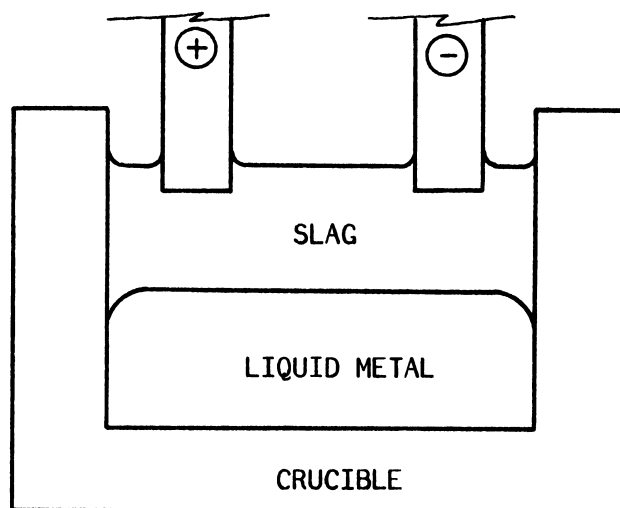


FIGURE 2.6

'NON-STANDARD' ELECTROLYSIS

CELL CONFIGURATION

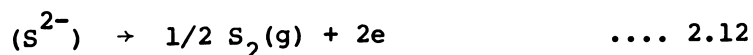
configuration⁴⁰. The kinetics of desulphurisation were found to be first order and the rate could be increased by using higher current densities.

One significant difference observed⁴⁵ was that no build-up of silicon in the metal phase was observed with a 'non-standard' cell, and in fact the silicon concentration in the metal was slightly lower at the completion of electrolysis. Further, electrolysis with alternating current produced more efficient desulphurisation than electrolysis with direct current, an opposite effect to that observed in electrolysis with 'standard' cells in which D.C. electrolysis was more efficient in desulphurisation of the pig iron⁴⁰.

Gattellier and Olette⁴⁴ indicated that equally good results for the desulphurisation of pig iron with a $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag were achieved with a 'standard' cell (Pt anode, pig iron cathode), and with a 'non-standard' cell consisting of two platinum electrodes immersed in the slag phase. No specific details of experimental results for this latter cell configuration were given, but it should be noted that results using the 'non-standard' cell were no worse than those achieved with the 'standard' cell.

(d) Anode Reactions

Little quantitative data has been presented in the work summarised in Table 2.2 on the anode reactions occurring during electrolysis, however, most workers have reported evidence of sulphur discharge at the anode according to the reaction



From a mass balance derived from sulphur analyses of metal and slag recovered from one electrolysis run, Ward and Salmon³⁹ concluded that an amount of sulphur equivalent to approximately half of the sulphur transferred from the metal to the slag phase was

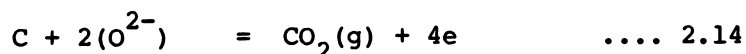
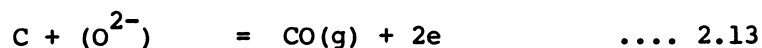
discharged from the slag at the anode during reduction of the sulphur in metal from ~ 0.25 wt% to ~ 0.012 wt%. However, using a slag of similar composition Nishiwaki et al⁴² found a lesser degree of anodic desulphurisation with 12% of the total sulphur in the system discharged at the anode during electrolysis in which the sulphur content of the pig iron was reduced from ~ 0.4 wt% S to ~ 0.05 wt% S. This is the only quantitative data available for the degree of slag desulphurisation, but most other workers^{35,37,38,43,44} reported that some of the sulphur did report to the gas phase, usually detected by observation of condensed sulphur in the cold regions of the furnace.

It is interesting to note that Esin et al³⁵ found that in some electrolysis experiments the sulphur concentration in the slag showed an initial decrease after the commencement of electrolysis, indicating that a higher rate of desulphurisation of the slag at the anode than desulphurisation of the iron at the cathode was occurring at this stage. However, in this work the slag was pre-doped with sulphide, and in fact the initial sulphur concentration of the slag (typically ~ 0.2 wt%) was significantly greater than the initial sulphur concentration of the molten metal (0.03 - 0.04 wt% S).

Ohtani and Gokcen³⁶ reported that discharge of sulphur at the anode did not occur in their work, sulphur analyses of slag showing that all the sulphur leaving the metal was found to be in the slag. There appear to be no unique experimental conditions in this work which would obviate the possibility of obtaining anodic sulphur discharge, in fact in some experiments the high initial sulphur levels of the molten iron (0.6 - 0.8 wt%) resulted in very high sulphide concentrations in the slag being achieved during electrolysis (above 2 wt% S for some runs), conditions favourable for the anodic discharge of sulphur. Thus these results appear to be anomalous.

Current efficiency data for sulphur discharge at the anode were reported by Ward and Salmon³⁹ and Dobryden et al^{40,45}. The former authors stated that the anodic current efficiency for sulphur discharge was very low, a value of 1.6% being obtained for one run, which was significantly less than the cathodic current efficiency. The latter authors reported higher anodic current efficiencies of up to 6% using a 'standard' cell⁴⁰ which is higher than the maximum reported cathode current efficiency for sulphur transfer of 3.25%. However, in that work slags pre-doped to sulphur concentrations (as dissolved sulphide) of approximately 0.9 wt% S were used, so these higher anodic current efficiencies can be attributed to the high initial sulphur content of the slag. Similar results were obtained using a 'non-standard' cell⁴⁵ with anodic current efficiencies for sulphur discharge of up to 10% reported for slags pre-doped to sulphur concentrations of 0.85 - 0.97 wt%.

The major current-consuming reaction at the anode is reported to be oxide ion discharge^{36,39,42}, according to equations (2.13) or (2.14) below, which are those that would occur with a graphite anode:



Thus most workers reported significant consumption of the graphite anode due to these discharge reactions occurring.

Only Dobryden and co-workers^{40,45} reported kinetic data for the anodic desulphurisation of the liquid slag phase. They found that at constant current the rate of sulphur extraction from the slag obeys first order kinetics with the rate proportional to the sulphur concentration of the slag. Their results also indicated that the rate

of slag desulphurisation was approximately proportional to the applied current. Both of these observations are identical to those found for the kinetics of cathodic sulphur transfer.

2.1.2 Desulphurisation of Pig Iron using Fused Salt Electrolytes

Due to the low current efficiencies for sulphur transfer attained with the use of blast furnace slag electrolytes, work was carried out using fused salt electrolytes with the aim of increasing the current efficiency for sulphur transfer by eliminating some of the non-sulphur-transferring cathodic reactions (in particular reduction of silica). The main details of this work are summarised in Table 2.3.

The current efficiencies reported, (Homma et al³⁷ reported no current efficiency data), are significantly higher than most of the values reported for electrolysis with blast furnace slag electrolytes (Table 2.2). To give a comparison, the 12% current efficiency for sulphur transfer from metal to slag reported by Ward and Salmon³⁹ using a fused barium chloride electrolyte (run "K" in their work) can be compared to the 1.5% current efficiency achieved using a blast furnace slag electrolyte with a similar initial sulphur concentration and similar current density (run "C2" in their work)³⁹.

The work summarised in Table 2.3 is discussed in detail below.

Homma et al³⁷ gave very little detail of the results they achieved using various different electrolyte compositions. However, significant desulphurisation was found when potentials of five volts or greater were applied, with final levels in the range 0.005-0.009 wt% [S]. It was also noted that the electrolyte itself was desulphurised during electrolysis. The proposed mechanism for pig iron desulphurisation was reduction and deposition of reactive

WORKERS	DATE	CELL TEMP (°C)	ELECTROLYTE	ANODE MATERIAL	CATHODE CURRENT DENSITY (A/cm ²)	CELL POTENTIAL (V)	TYPICAL SULPHUR LEVELS IN PIG IRON (wt% S)		CATHODE CURRENT EFFICIENCY FOR S-TRANSFER (%)	REF.
							INITIAL	FINAL		
Homma et al	1960	1250-1350	NaCl CaCl ₂ Na ₂ O/K ₂ O-SiO ₂ (See note 2)	SiC or Graphite rod	0.12-0.29	5	0.03-0.13	0.005-0.009	N.D.	37
Ward and Salmon	1963	1310	BaCl ₂	Graphite rod	0.13	N.D.	0.075	0.04 (see note 3)	12	39
Bills and Littlewood	1965	1250	CaCl ₂	Graphite rod	0.1-0.345	2.5	1.0	0.002 (see note 3)	53-100	46
Gatallier and Olette	1977	1400	CaCl ₂	Graphite rod	N.D.	N.D.	1.12	0.1 (see note 3)	8-28	44

TABLE 2.3

ELECTROLYTIC DESULPHURISATION OF PIG IRON USING FUSED SALT ELECTROLYTES

NOTES:

1. "N.D." - No data.
2. Homma et al used various electrolyte compositions.
3. This is the value when electrolysis was stopped. It is not necessarily the minimum value attainable.
4. Some runs were performed at cell potentials of 5-9 V.

metallic species (Na, Ca, Ba, Mg) at the metal/salt interface with subsequent chemical desulphurisation of the pig iron (i.e. chemical electrorefining).

Ward and Salmon³⁹ briefly investigated the use of a barium chloride electrolyte at 1583K. The carbon saturated iron had an initial sulphur content of approximately 0.075 wt%. Significant non-electrolytic desulphurisation was observed during an initial contact period between the two phases, with the sulphur level decreasing to approximately 0.04 wt% in the first 80 minutes of contact. This demonstrated that the barium chloride melt did have a significant sulphur capacity. Subsequently, current was passed between the graphite anode immersed in the fused salt and the liquid iron cathode. The graphite was sleeved with mullite to prevent short-circuiting between the anode and the crucible walls. A cathodic current density of 0.13 A/cm^2 maintained for a period of about 50 minutes resulted in a large increase in the rate of desulphurisation with a final sulphur level of approximately 0.01 wt% achieved at an overall current efficiency of 12%. Apart from this being a much higher current efficiency than achieved with a blast furnace slag electrolyte, the results also indicated that lower ultimate sulphur levels could be obtained with the use of the fused salt electrolyte. The minimum ultimate sulphur levels attainable with the blast furnace slag electrolyte were 0.03-0.04 wt%³⁹.

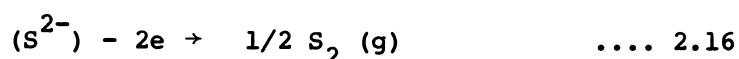
The authors assumed that sulphur transfer was occurring through direct electrochemical transfer (equation 2.3). The reduction of barium ions to barium metal at the cathode according to equation 2.15.



was assumed to be the cathodic reaction resulting in wastage of

current. It was considered that the metallic barium so formed dissolved in the fused BaCl_2 electrolyte (metallic barium has an extensive solubility in fused barium chloride³⁹) and subsequently recombined with the anodically evolved chlorine gas.

Anodic evolution of sulphur from the fused salt was also indicated. A mass balance showed that approximately half of the sulphur that was eliminated from the metal was removed from the system according to equation 2.16 below:



However, the calculated current efficiency for this anodic desulphurisation was only 1.6%.

Bills and Littlewood⁴⁶ have briefly described an investigation into the electrolytic desulphurisation of molten iron (3.3 wt% carbon) at 1523K using a fused calcium chloride electrolyte and a graphite anode. A significant feature of this work was the use of potentiostatic (constant voltage) electrolysis rather than galvanostatic electrolysis which was used by all other workers. A cell potential of 2.5 volts was applied in most of the experiments, this being below the decomposition potential of CaCl_2 which was reported to be about 3.0 volts at 1523K.

It was found that, with a pure CaCl_2 electrolyte, severe voltage and current fluctuations were unavoidable during electrolysis, a phenomenon attributed to the "anode effect" well known in the electrolysis of halide melts^{47,48}. In order to achieve stable electrolysis conditions, 5 wt% of lime was added to the chloride electrolyte thus promoting oxide ion discharge at the anode (equations 2.13 and 2.14) in preference to chloride ion discharge.

In experiments with no potential applied, substantial transfer of sulphur from the metal to the salt phase was observed which is indicative of a significant sulphide capacity of the oxide-doped salt.

Potentiostatic (voltage-controlled) electrolysis of the melt at a cell potential of 2.5 volts gave greatly accelerated rates of sulphur transfer with quite high current efficiencies. Table 2.4 summarises some results obtained. The sulphur concentration figures and electrolysis times given in this table were estimated from a graph given by the authors (Figure "A" in their work⁴⁶) and thus are only approximate.

It can be seen that in comparison to the other work described, much higher current efficiencies were obtained in this work. This was not gained at the expense of decreased cathode current density (c.f. Table 2.3). Thus by implication the rates of sulphur transfer were also much higher. It is also apparent that the average current efficiency for cathodic sulphur transfer decreases as lower sulphur levels are approached, which would be expected as the effects of depletion of sulphur in the metal phase become dominant. However, another possible contributing factor to the decreased average current efficiency in these cases is the use of a higher cathodic current density in these latter experiments. No discussion was presented by the authors as to the relative significance of these effects, nor were any reaction mechanisms proposed.

No quantitative data on sulphur discharge at the anode was given, although the authors did report that "sulphur losses from the system appeared to be small", which would indicate that anodic sulphur discharge was not a dominant anode reaction.

AVERAGE CATHODIC CURRENT DENSITY A/cm ²	TIME (min)	SULPHUR LEVELS IN IRON (wt%)		AVERAGE CURRENT EFFICIENCY (%)
		INITIAL	FINAL	
0	60 (simple contact)	1.0	0.7	-
0.1	60	1.0	0.2	100
0.4	30	1.0	0.015	73
0.45	25	0.4	0.001-0.002	53

TABLE 2.4

DATA FROM ELECTROLYTIC DESULPHERISATION EXPERIMENTS

OF BILLS AND LITTLEWOOD⁴⁶ USING A CaCl₂/5% CaO

FUSED ELECTROLYTE

Gatellier and Olette⁴⁴ briefly investigated the desulphurisation of pig iron containing approximately 1.1 wt% S using a fused CaCl_2 electrolyte at 1673K in a graphite crucible with an alumina sidewall insulating sleeve. The graphite crucible base served as the cathodic contact while a graphite anode rod was immersed in the fused salt. Metal samples were taken during electrolysis for progressive sulphur analysis but some doubt as to the accuracy of analyses was expressed due to the presence of slag inclusions in the samples.

Some initial desulphurisation was observed before a voltage was applied - approximately 10% of the sulphur was removed from the iron in the first hour of contact with no applied voltage. The subsequent passage of current (between 1.6 and 4.0 Amps - no figures for current density were given) produced a marked acceleration in the sulphur transfer rate, with an indication that higher rates could be achieved with higher applied currents. The current efficiency for sulphur transfer decreased with decreasing sulphur content of the metal. For example, during a 50 minute period when a constant current of 3 amps was applied, the calculated average current efficiency was 28% in the first 15 minutes, 12% in the next 15 minutes and 8% in the final 20 minutes. During this period the sulphur level of the metal was still quite high, decreasing from approximately 0.45 wt% to 0.20 wt%, unrealistically high for industrial pig irons and significantly higher than the initial level of 0.075% used by Ward and Salmon³⁹, who, as previously noted, achieved a current efficiency of 12% for electrolysis under molten BaCl_2 at 1583K.

The presence of sulphur deposits on the cold furnace parts indicated sulphur discharge at the anode had occurred, however no indication as to the amount of sulphur discharged was given.

2.2 REMOVAL OF ANIONIC IMPURITIES FROM LIQUID COPPER USING FUSED SALT ELECTROLYSIS

The first and most significant work in this area was reported by Ward and Hoar⁴⁹ in 1961. The study was initiated after some interesting results had been obtained in earlier work⁵⁰ aimed at the production of copper and sulphur by the electro-decomposition of molten cuprous sulphide dissolved in a fused barium chloride electrolyte at temperatures around 1423-1433K. In this earlier work molten copper was produced at the cathode and elemental sulphur evolved at the anode. However it was found that the sulphur content of the cathodically produced copper was often less than that found when copper was equilibrated with cuprous sulphide without any electrolysis, and further, if electrolysis was continued after the depletion of cuprous ions in the melt, sulphur was removed rapidly from the liquid copper resulting in extremely low sulphur levels in copper. This suggested that sulphur and the chemically related chalcogenide elements (oxygen, selenium and tellurium) could be removed from molten copper using fused salt electrolysis.

The electrolysis experiments were carried out at 1353-1423K under an inert nitrogen atmosphere in 'standard' electrolysis cells with a liquid copper cathode doped with one of the impurities, a pure barium chloride electrolyte and a graphite anode. All electrolysis experiments were carried out under galvanostatic conditions except for the two tellurium removal runs at constant voltage, with cathodic current densities in the range 0.16-0.31 A/cm².

The major results achieved in desulphurisation experiments were:

1. No spontaneous desulphurisation occurred when the liquid copper and fused BaCl₂ were held in contact without applied current.

2. With current applied, rapid desulphurisation of the copper occurred with very low final levels achieved - from initially 0.80-1.1 wt% S to less than 0.001 wt% S. The overall sulphur removal rates to achieve these levels were of the order of $2.5 \text{ mg/cm}^2 \cdot \text{min}$ (the area term refers to the cathode/electrolyte interfacial area).

3. The calculated overall current efficiency for sulphur removal was high - in the range 79-84%.

4. Desulphurisation of the chloride electrolyte due to anodic discharge of sulphide did not occur.

The proposed mechanism for sulphur transfer was diffusion of sulphur to the metal/salt interface followed by direct electrochemical transfer of sulphur from the liquid metal to the fused electrolyte according to equation 2.3 . In some experiments (Se and Te removal) in which electrolysis was continued for some time after effectively complete removal of the anionic impurity occurred, a significant build-up of barium was detected in the copper. Thus it was proposed that after depletion of the anionic impurity from the liquid copper the cathode reaction was barium reduction, but before depletion the cathode process was solely direct anionic transfer with no barium metal production (which, if occurring would give a 'chemical refining' effect due to the combination of this reactive metal with the anionic species).

The cell voltage was monitored during electrolysis and normally rose steadily from an initial value of $\sim 2.9 \text{ V}$ to 3.6 V . A sudden rise of $\sim 0.4 \text{ V}$ then occurred and the voltage subsequently remained constant. The sudden rise was attributed to the depletion of the

sulphur in the copper, i.e. the failure of sulphur diffusion and convection within the copper to keep pace with the rate of the sulphur discharge reaction (equation 2.3) required for electron transfer.

Thus it was proposed that barium discharge according to the equation:



became the new cathode reaction with a cathode potential 0.4 V higher.

At all stages of electrolysis it was proposed that chlorine discharge was the sole anode reaction, therefore after depletion of the anionic impurity from the copper the overall cell reaction was assumed to be decomposition of the BaCl_2 melt.

Similar results were obtained for removal of O, Se and Te from liquid copper, with rapid reduction to very low levels (<0.001 wt%) at high current efficiencies, although corrections had to be made to the calculated rates and current efficiencies for these three elements due to the fact that significant spontaneous transfer (i.e. non-electrolytic transfer) occurred when the melts were contacted, especially in the case of deoxidation.

It is interesting to note that in the detelluridation experiments crystals of tellurium were recovered from the cool 'condenser' region of the furnace indicating that elemental tellurium discharge at the anode was occurring in these experiments. No explanation was put forward for this supposedly unique behaviour in the Cu/Te system, but it is perhaps significant that tellurium is the least electro-negative of the four chalcogens and therefore its anodic discharge as an elemental species would be more thermodynamically favourable than for the other three elements assuming equal ionic activity in the melt.

Lapat has patented a method for the use of a fused salt electrolysis process to continuously refine liquid blister copper⁵¹.

The first stage of the proposed process is the removal of anionic impurities from a liquid copper cathode via cathodic electrorefining or chemical electrorefining using a fused chloride or fluoride electrolyte.

Brief results were given for one experiment in a 'standard' electrolysis cell. The cell temperature was 1423K, the electrolyte was fused barium chloride and the electrolysis was carried out at a cell potential of 3.3 volts giving a cathodic current density of 1.0 A/cm^2 . No details of electrolysis time or current efficiency were given. The elimination of sulphur, selenium and tellurium was very effective ($\text{S} < 0.0002 \text{ wt\%}$, $\text{Se} < 0.003 \text{ wt\%}$, $\text{Te} < 0.001 \text{ wt\%}$) from initial levels of 0.0341 wt%, 0.028 wt% and 0.029 wt% respectively. It is also interesting to note that the semi-metallic impurity elements in the copper were substantially eliminated by the electrolysis treatment, especially bismuth which was reduced from 0.056 wt% to 0.002 wt%. Arsenic decreased from 0.039 wt% to 0.013 wt% and antimony from 0.049 wt% to 0.011 wt%. This would suggest that these impurities are behaving as anionic species.

It was proposed that direct electrochemical sulphur transfer across the cathode interface was occurring. In addition the anode reaction was claimed to be chlorine discharge rather than discharge of S, Se or Te, resulting in a continuous build-up of these impurity species in the chloride melt and their eventual precipitation as barium compounds (e.g. BaS) due to the low solubility of these in chloride melts. This would result in fouling of the electrolyte and would require an electrolyte cleaning circuit, or discard of the used electrolyte. The use of a fluoride based electrolyte was proposed as a possible solution to this problem. It was argued that the higher

solubility of chalcogenide compounds in fluoride electrolytes and the higher decomposition potential of fused fluorides as compared to chlorides would mean that the anode reaction could be confined to discharge of the chalcogenide ions if the cell potential was maintained below the decomposition potential of the fluoride melt.

A chemical electrorefining variant of this process was proposed which would use to advantage the high degree of miscibility of the reactive metals (e.g. Ba or Ca) in their molten halide salts. Thus generation of dissolved metal in the fused salt would be carried out initially by decomposition of the molten salt in an electrochemical reactor. Subsequently the impure liquid copper would be intimately contacted with this fused salt to eliminate the chalcogenide impurities by a chemical refining effect.

In their work on electrochemical desulphurisation and deoxidation of molten iron, Gatellier and Olette⁴⁴ described one set of experiments in a 'standard' cell using a sulphur-doped liquid copper cathode under a $\text{CaO-CaF}_2\text{-Al}_2\text{O}_3$ slag at 1673K. The anode was graphite and the melt was contained in a molybdenum crucible.

Significant non-electrolytic desulphurisation occurred during an initial contact period of the slag with the molten copper, particularly when a highly basic slag composition was used which had a high sulphur capacity. Subsequent commencement of galvanostatic electrolysis produced a marked increase in the rate of desulphurisation with final sulphur levels of less than 0.001 wt% achieved.

The proposed mechanism for sulphur transfer was one of 'chemical' electrorefining rather than cathodic electrorefining, that is, it was proposed that desulphurisation was occurring due to cathodic discharge

of metallic calcium at the copper/slag interface, with subsequent formation of CaS which passed into solution in the molten slag. Quoted current efficiency for sulphur transfer was less than 30% for reduction of the sulphur level of the metal from 0.015 wt% S to 0.005 wt% S. This fairly low current efficiency was attributed to the use of non-insulated crucible sidewalls, allowing discharge of calcium metal to occur at the molybdenum/slag interface as well as the copper/slag interface.

Some desulphurisation of the slag also occurred due to anodic discharge of sulphur, since condensed elemental sulphur was detected in the cooler region of the furnace. No quantitative data was given, but it was stated that sulphur discharge was only a minor anode reaction, the major reaction being discharge of oxide ions to form CO gas.

2.3 CONCLUSIONS

At the cathode the contribution of direct electrochemical transfer or chemical reaction has not been clearly established. In addition the influence of electrolyte composition on the activity of the sulphide ion and the transport of the sulphide ion from the metal/electrolyte interface to the bulk of the electrolyte requires further investigation.

At the anode the dependence of the discharge mechanism on the electrolyte composition also requires further investigation.

CHAPTER 3

SYSTEM SELECTION

3.1 METAL-IMPURITY SYSTEM

This work was confined to an investigation of the removal of dissolved sulphur from liquid copper. The liquid copper-sulphur system was preferred to the liquid iron-sulphur system (or the liquid pig iron-sulphur system) due to the lower cell temperatures allowed for the former. Thus 1423K cell temperatures were used as opposed to approximately 1673K that would be required for the ferrous system.

Sulphur was the only anionic impurity species considered in this work.

3.2 CHOICE OF ELECTROLYTE

In all previous work reported on the electrolytic desulphurisation of liquid metals using fused salts (Sections 2.1.2 and 2.2), electrolytes based on single component alkaline earth chloride melts were used with the exception of the work by Homma³⁷ in which a sodium chloride electrolyte and some binary oxide-silicate electrolytes were briefly investigated.

In this work the fused salt electrolyte used was a CaF_2 - MgF_2 binary mixture of the eutectic composition. The phase diagram for the CaF_2 - MgF_2 system is shown in Figure 3.1. The reported eutectic composition is 55.6 wt% CaF_2 -44.4 wt% MgF_2 which has a melting point of 1253K.

A fluoride electrolyte was chosen mainly for the low vapour pressure, high stability (i.e. high decomposition potential) and the high solubility for impurities that fluoride based electrolytes exhibit in comparison to chlorides and other halide electrolytes.

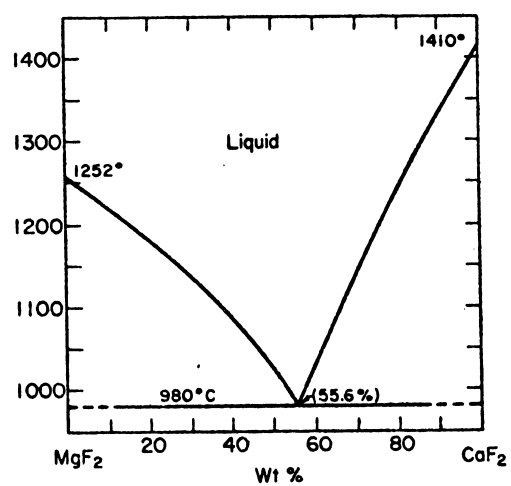


FIGURE 3.1

CaF₂-MgF₂ PHASE DIAGRAM⁽⁵²⁾

In considering the properties of the $\text{CaF}_2\text{-MgF}_2$ eutectic, no quantitative data pertaining to the "ideality" of the $\text{CaF}_2\text{-MgF}_2$ system (e.g. conductance isotherms, molar volume isotherms, integral enthalpy of mixing data) were available. However, major departures from ideal solution behaviour would not be expected in this system because:

1. The phase diagram is that of a simple binary eutectic system with no incongruently melting compounds or evidence of a tendency to complex formation.
2. The divalent calcium and magnesium cations are quite similar in terms of ionic radius ($\text{Ca}^{2+} = 99 \text{ pm}$, $\text{Mg}^{2+} = 72 \text{ pm}$)¹⁵.

It is also worth noting when considering $\text{Ca}^{2+}/\text{Mg}^{2+}$ ionic interactions in molten salts with a common anion, that integral enthalpy of mixing isotherms in the $\text{CaCl}_2\text{-MgCl}_2$ system do not exhibit marked departures from ideality⁵³.

3.2.1 Vapour Pressure

The values given in Table 3.1 show that at corresponding temperatures the vapour pressures over alkaline earth chlorides are at least one order of magnitude greater than for the alkaline earth fluorides. From this data the calculated vapour pressure (assuming ideal behaviour) over a $\text{CaF}_2\text{-MgF}_2$ eutectic melt at 1423K is 0.67 Pa, which is negligible, while at the higher temperature of 1623K more appropriate for desulphurisation of pig iron, it is still very low at 20.0 Pa. In contrast to this, of the alkaline earth chlorides, only CaCl_2 has a very low vapour pressure at 1423K while all have significant vapour pressures at 1623K.

COMPOUND	MELTING POINT (K) (From Ref. (15))	LIQUID PHASE VAPOUR PRESSURE (Pa)		VAPOUR PRESSURE REF.
		1423K	1623K	
CaF ₂	1696	0.04*	2.67*	56
MgF ₂	1534	1.33*	36.0	57
CaCl ₂	1055	50.6	959.7	56
BaCl ₂	1236	426	10660	58
MgCl ₂	987	15330	79980	58

TABLE 3.1

MELTING POINT AND VAPOUR PRESSURE DATAFOR ALKALINE EARTH HALIDESNOTE:

- (1) Asterisk (*) indicates these values are extrapolated from liquid phase data and therefore represent predicted vapour pressures for the supercooled liquid phase.
- (2) The values for BaCl₂ and MgCl₂ are only approximate ($\pm 10\%$)
 - determined from graphical interpolation of data given by Brewer⁵⁸.

3.2.2 Decomposition Potential

Table 3.2 gives calculated values of the decomposition potentials of pure liquid alkaline earth fluorides and chlorides at 1423K. The compilations of " β -functions" by Barin and Knacke^{54,55} were used to calculate the standard free energy and decomposition potential values in this table. Appendix I gives details of the methods of calculation of thermodynamic data using these β -functions and the values of all the β -functions used for thermodynamic calculations at 1423K in this work. The free energy and decomposition potential data for CaF_2 , MgF_2 and BaF_2 at 1423K were calculated from extrapolated liquid phase data and thus refer to the supercooled pure molten fluoride at 1423K as the standard state.

It is evident from Table 3.2 that the alkaline earth fluorides are significantly more stable than the corresponding alkaline earth chlorides, exhibiting a decomposition potential of the order of two volts greater in magnitude. Ignoring polarisation or depolarization effects, this allows correspondingly higher potentials to be applied in fused salt electrolysis processes using fluoride melts without resulting in decomposition of the salt melt.

A theoretical decomposition potential for the CaF_2 - MgF_2 eutectic at 1423K can be calculated from the data in Table 3.2 assuming ideal behaviour and Temkin activities⁵⁹ for the ionic species in the melt. The eutectic composition of 55.6 wt% CaF_2 /44.4 wt% MgF_2 corresponds to 50.0 mole% CaF_2 /50.0 mole% MgF_2 , giving Temkin activities for both cationic species of 0.50. From the Nernst equation, this reduced cationic activity will result in an increase in the magnitude of the decomposition potential of $RT/nF \ln 1/0.5$ volts, which is equivalent

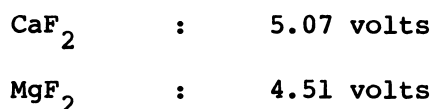
DECOMPOSITION REACTION	ΔG°_{1423K} (kJ)	$-E^{\circ}_{1423K}$ (Volts)
$\text{CaF}_2^*(l) \rightarrow \text{Ca}(l) + \text{F}_2(g)$	970.11	5.03
$\text{MgF}_2^*(l) \rightarrow \text{Mg}(g) + \text{F}_2(g)$	862.74	4.47
$\text{BaF}_2^*(l) \rightarrow \text{Ba}(l) + \text{F}_2(g)$	974.46	5.06
$\text{CaCl}_2(l) \rightarrow \text{Ca}(l) + \text{Cl}_2(g)$	608.43	3.15
$\text{MgCl}_2(l) \rightarrow \text{Mg}(l) + \text{Cl}_2(g)$	432.18	2.24
$\text{BaCl}_2(l) \rightarrow \text{Ba}(l) + \text{Cl}_2(g)$	638.24	3.31

TABLE 3.2
CALCULATED THERMODYNAMIC DATA FOR
DECOMPOSITION REACTIONS^{54,55}

NOTE:

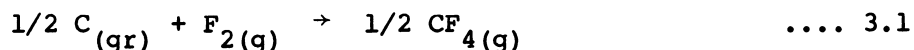
Asterisk (*) indicates the reference state for these compounds is the supercooled liquid at 1423K, unit activity.

to 0.04 volts for $T = 1423\text{K}$, $n = 2$, $R = 8.3143 \text{ J.K}^{-1}\text{mole}^{-1}$ and $F = 96487.0 \text{ C. mole}^{-1}$. Thus, in the eutectic mixture at 1423K , assuming ideality, the decomposition potentials of the two melt components are:



With the application of a rising potential to the eutectic melt, decomposition of the least stable compound (MgF_2) will occur first. Thus the theoretical reversible decomposition potential of the eutectic melt, assuming ideal solution behaviour, is 4.51 volts.

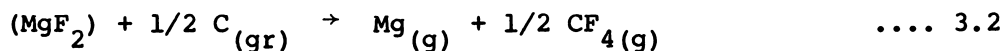
With the use of a graphite anode significant depolarization will result from the rapid chemical reaction of evolved fluorine gas with the anode carbon to form gaseous carbon tetrafluoride, represented in equation 3.1 below:



At 1423K

$$\begin{aligned} \Delta G_{3.1}^{\circ} &= -353.15 \text{ kJ}^{54} \\ \therefore E_{3.1}^{\circ} &= 1.83 \text{ V} \end{aligned}$$

Thus the overall decomposition reaction at 1423K is:



(where (MgF_2) represents 50 mole% MgF_2 in the CaF_2 - MgF_2 eutectic).

The theoretical decomposition potential is therefore $(4.51 - 1.83) \text{ V} = 2.68 \text{ V}$, assuming cathodic liberation of Mg gas at unit activity.

3.2.3 Solubility of Impurities

Among the halide salts the fused fluorides are the best solvents for other inorganic compounds⁶⁰. A high solubility of the chalcogenide compounds (oxides, sulphides, selenides and tellurides)

is desirable in the electrorefining process being considered as the possibility of fouling of the molten salt electrolyte due to precipitation of these compounds from solution is reduced.

No specific data for the solubility of sulphide compounds in fluoride melts or chalcogenide compounds generally in binary alkaline earth fluoride melts could be found in the literature. However, the high affinity for chalcogenides shown by fluoride melts is demonstrated by the fluoride-oxide phase diagrams shown in Figure 3.2.

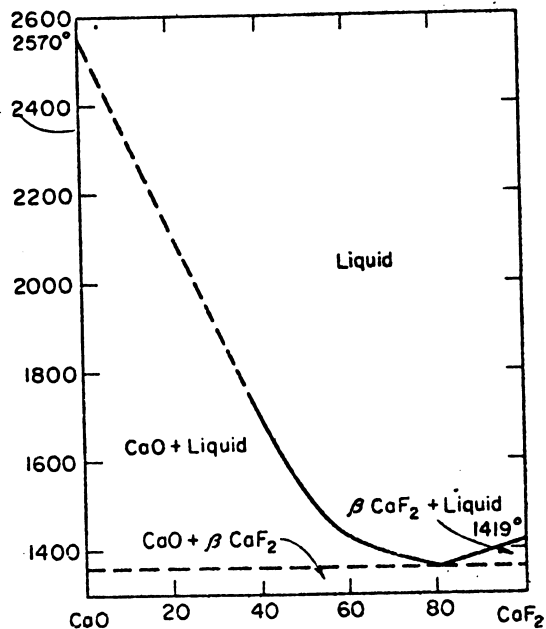
Significant solubility of reduced metal species (Mg, Ca) in the fluoride eutectic melt is also expected in this system. Again, no specific data on binary fluoride salt melts were available, but examination of the CaF_2 -Ca system⁶¹ (Figure 3.3) shows that CaF_2 and Ca exhibit complete miscibility in all proportions above the melting point of CaF_2 .

Rogers et al⁶² list two conditions for substantial metal-salt miscibility, viz:

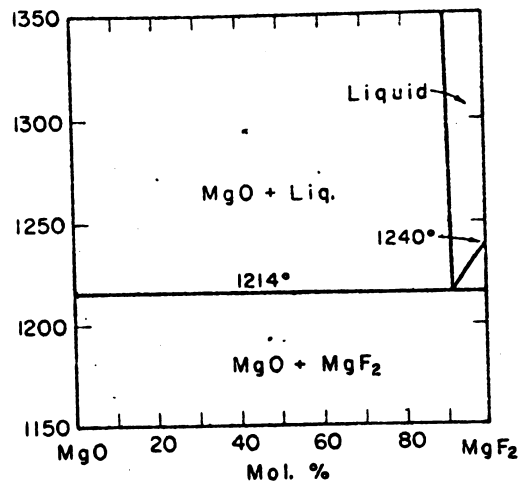
1. The internuclear separation of cations and anions should be sufficiently high to prevent anion-anion contact; miscibility will be limited when $r_+/r_- < 0.42$ but substantial when $r_+/r_- > 0.42$.
2. Strong interaction should exist between the two metals indicated by the formation of stable intermetallic compounds.

Considering the $\text{CaF}_2/\text{MgF}_2$ - Ca/Mg system, the ionic ratios r_+/r_- are 0.74 and 0.55 for CaF_2 and MgF_2 respectively, while the calcium-magnesium phase diagram⁶³ shows a stable intermetallic compound CaMg_2 is formed in alloys of the two metals. Thus it is likely that substantial metal-salt miscibility in the $\text{CaF}_2/\text{MgF}_2$ - Ca/Mg system will be observed.

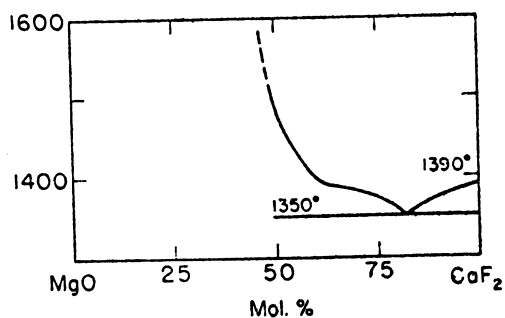
CaO-CaF₂



MgF₂-MgO



CaF₂-MgO



CaF₂-CaO-MgO

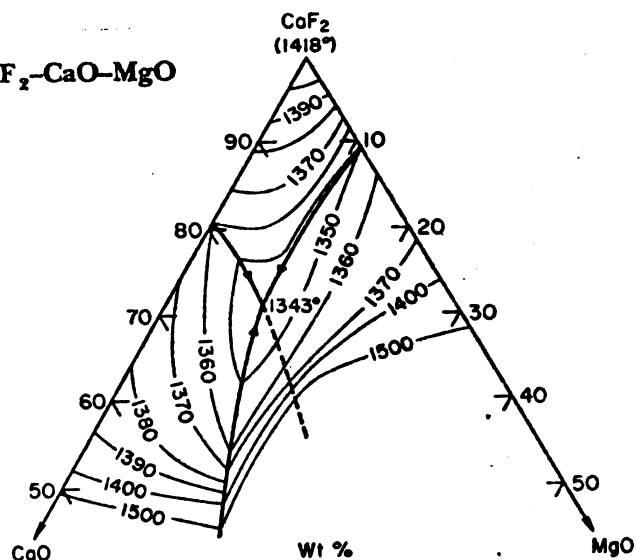


FIGURE 3.2

**PHASE DIAGRAMS SHOWING SOLUBILITY OF
OXIDES IN FLUORIDE MELTS (From Ref.(52))**

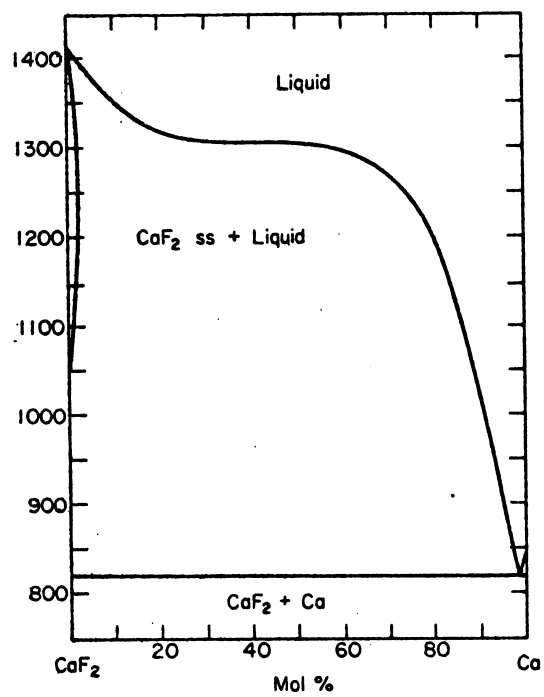


FIGURE 3.3

CaF₂-Ca PHASE DIAGRAM (52)

CHAPTER 4

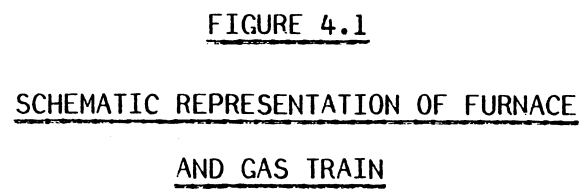
EXPERIMENTAL METHODS

4.1 FURNACE AND GAS TRAIN

A schematic representation of the furnace and gas train is shown in Figure 4.1.

All experiments were conducted with a continuous flow of inert argon gas. The gas (C.I.G. Special Grade Argon) from supply bottle (A) passed through two sets of twin 300 mm x 30 mm diameter drying columns (B) and (C), the first containing silica-gel beads and the second magnesium perchlorate ("Anhydrite") drying agent. It then passed through a 350 mm x 40 mm diameter deoxidation column (D) packed with 5 x 5 mm cylinders of B.T.S. catalyst at 513K. After a final drying stage of a second set of magnesium perchlorate drying columns (E) the gas flow was metered using a dibutyl-phthalate manometer flow meter (G) which was preceded by a bleed-off tube (F) used for fine adjustment of the flow to the furnace and to ensure a constant gas flow rate. All elements in the gas train were fabricated from pyrex glass and isolated when not in use with high vacuum stopcocks.

The recrystallised alumina furnace tube (K) was 800 mm long with an internal diameter of 38 mm. Machined brass flanges at either end (H) utilised 'o-ring' seals which were protected from excessive temperatures by water cooled sleeves (I). The design of these flanges is described in the following section. The gas flowed downwards through the furnace tube and out through an exit tube in the lower flange connected to a bubbler (M) in normal operation. A three-way tap also enabled connection to a vacuum pump (for evacuating the apparatus) or gas analysis equipment.



(See legend following page)

FIGURE 4.1

SCHEMATIC REPRESENTATION OF FURNACE
AND GAS TRAIN

LEGEND:

A	-	Gas supply
B	-	Silica gel drying columns
C	-	Anhydrite drying columns
D	-	B.T.S. catalyst deoxidation column
E	-	Anhydrite drying columns
F	-	Bleed-off tube
G	-	Manometer
H	-	Furnace tube flanges
I	-	Water cooled sleeves
J	-	Furnace
K	-	Furnace tube
L	-	Control thermocouple
M	-	Exit gas bubbler

The resistance heated furnace (J) was kanthal wound and the length of the constant temperature zone (within a range of $\pm 1\text{K}$) was 4.5 centimetres at 1423K, sufficient to ensure positioning of the electrolysis cell entirely within this region for all experiments. The temperature was controlled using an "Ether Mini" Type 17-98B controller using a Pt-Pt/13% Rh control thermocouple (L), which gave temperature control to $\pm 0.5\text{K}$.

4.2 ELECTROLYSIS CELL

Figure 4.2 is a schematic diagram of the complete electrolysis cell assembly for two-electrode work.

The top flange (B) was machined from brass with an 'o-ring' seal (C) to the outside of the furnace tube and a gas inlet (D). The 8.5 mm o.d. x 6.0 mm i.d. recrystallised alumina tube (E) through which the anode rod (F) was inserted was held in position by a rubber "squash gasket" seal (A). The anode was a 6.4 mm diameter Morganite EY9 grade graphite rod (bulk density = 1.70 g cm^{-3}) which had been partially shaved down to a reduced diameter of approximately 5.5 mm to allow insertion into the alumina tube. The length of anode rod projecting below the extremity of the alumina tube (approximately 100 mm) was not reduced in diameter.

The crucible base (K) was machined from A.T.J. grade graphite (bulk density = 1.73 g cm^{-3}) while the sidewalls (H) were boron nitride and machined to be a press-fit inside the graphite base. A $1\text{-}1/2^\circ$ taper (diverging from bottom to top) was machined on the inside surface of the boron nitride to facilitate removal of the solidified contents. The dimensions of the crucible were:

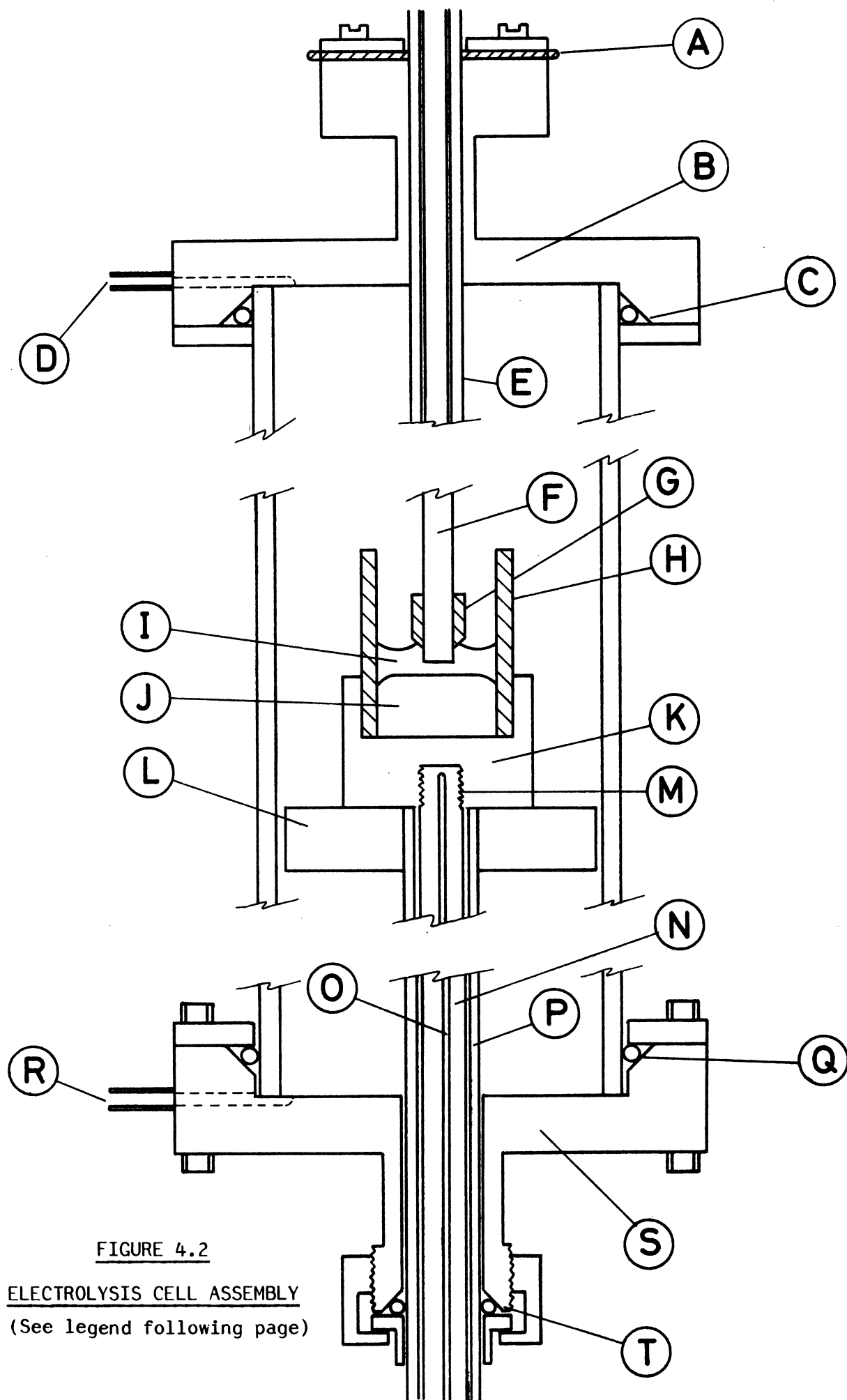


FIGURE 4.2
ELECTROLYSIS CELL ASSEMBLY
 (See legend following page)

FIGURE 4.2

ELECTROLYSIS CELL ASSEMBLY

LEGEND:

- A - "Squash gasket" seal
- B - Top brass flange
- C - Upper 'o-ring'
- D - Gas inlet
- E - Recrystallised alumina tube
- F - Graphite anode rod
- G - Boron nitride anode sheath
- H - Boron nitride crucible sidewalls
- I - Fused salt
- J - Liquid copper
- K - Graphite crucible base
- L - Sintered alumina crucible support
- M - 1/4 inch Whitworth thread
- N - Graphite cathode rod
- O - Pt-Pt/13% Rh thermocouple
- P - Recrystallised alumina tube
- Q - Lower 'o-ring' seal
- R - Gas exit tube
- S - Lower brass flange
- T - 'O-ring' seal

depth	-	36 mm
base	-	21 mm internal diameter
top	-	22 mm internal diameter

In most experiments approximately 40 g of copper and 10 g of salt were used, giving melt depths of 1.5 and 1.1 cm for the copper and salt respectively, and a nominal copper/salt interfacial area of 3.62 cm².

The anode was immersed in the molten salt (I), the projecting surface area geometrically defined by a boron nitride insulating sheath (G). Details of anode dimensions and of the different types of anodes used are given later (Section 4.3).

In most cases the boron nitride components were machined from Union Carbide HBN grade hot-pressed boron nitride rod. However, in some later experiments HBC grade hot-pressed boron nitride rod was used, which has a lower content of B₂O₃ binding agent.

Electrical contact to the liquid cathode copper (J) was made using a 6.4 mm diameter EY9 grade graphite rod (N) screwed into the base of the crucible with a 1/4 inch Whitworth thread (M). The crucible was supported on a circular disc (L) made from cast and sintered alumina cement. This had been cast onto the end of a 12 mm o.d. x 8 mm i.d. recrystallised alumina tube (P) which contained the cathode contact rod and served to support the complete crucible assembly. The total clearance between the sintered disc and the inner walls of the furnace tube was approximately 2 mm, thus ensuring central positioning of the crucible within the furnace tube.

Variable anode immersion was obtained by vertical repositioning of the crucible assembly which was clamped in position by an 'o-ring' seal (T) between the alumina tube and lower brass flange (S). This

lower flange was held and sealed to the furnace tube by an external 'o-ring' seal (Q) and contained the gas exit connection (R).

Temperature measurement was made using a Pt-Pt/13% Rh thermocouple contained in a 2.5 mm diameter twin-bore alumina sheath (O). A notch to accommodate the thermocouple sheath was cut along one side of the graphite cathode rod along its complete length allowing the thermocouple to be inserted into the graphite crucible base to the top of the thread hole (approximately 10 mm deep). The thermocouple junction was recessed 4 mm below the top of its alumina sheath and encased in alumina cement to prevent deterioration due to exposure to a reducing atmosphere in the presence of carbon.

Figure 4.3 depicts the method employed to obtain a gas-tight seal between the end of the alumina tubes and the projecting graphite rods contained within them. A tight fitting 'o-ring' (C) was placed over the graphite rod (A) and positioned against the end of the alumina tube (D). A layer of Dow Corning "Silastic R.T.V." silicon rubber sealing compound (B) was then placed over the 'o-ring' ensuring good contact was obtained with the top of the alumina tube and the graphite rod. This type of seal was air-dried for a minimum of 24 hours before use to ensure adequate 'setting' of the silicon rubber compound.

For three-electrode work the top assembly used is shown in Figure 4.4. The machined brass flange (C) was fitted to the furnace tube with an 'o-ring' seal (D). Two vertical holes were drilled in the fitting to accept two recrystallised alumina tubes (E) 8.5 mm o.d. x 6.0 mm i.d. These were fixed in position with high-temperature "Araldite" cement (A) which also gave a gas-tight seal. The brass flange was water-cooled (B) to prevent any possible over-heating of the araldite cement or silicon rubber seals.

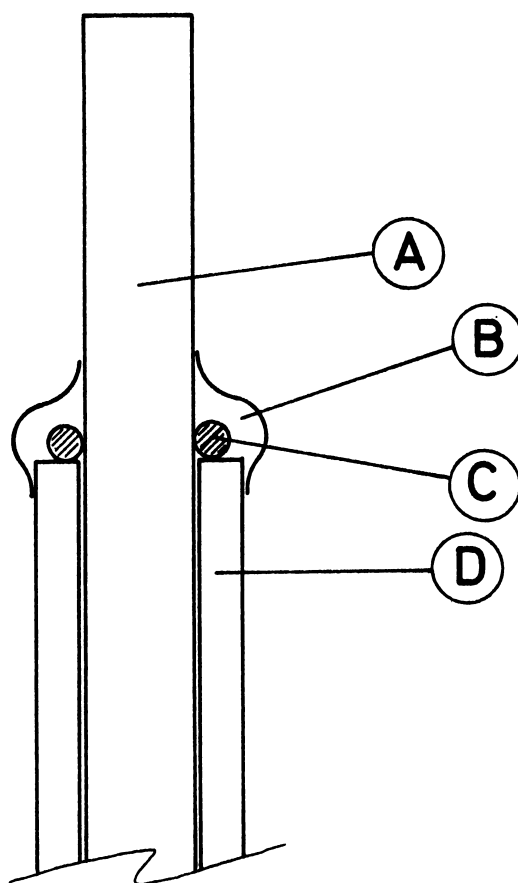


FIGURE 4.3

GAS-TIGHT SEAL FOR GRAPHITE ELECTRODE RODS

- Legend:
- A - Graphite rod
 - B - "Silastic" sealing compound
 - C - "O - ring"
 - D - Alumina tube

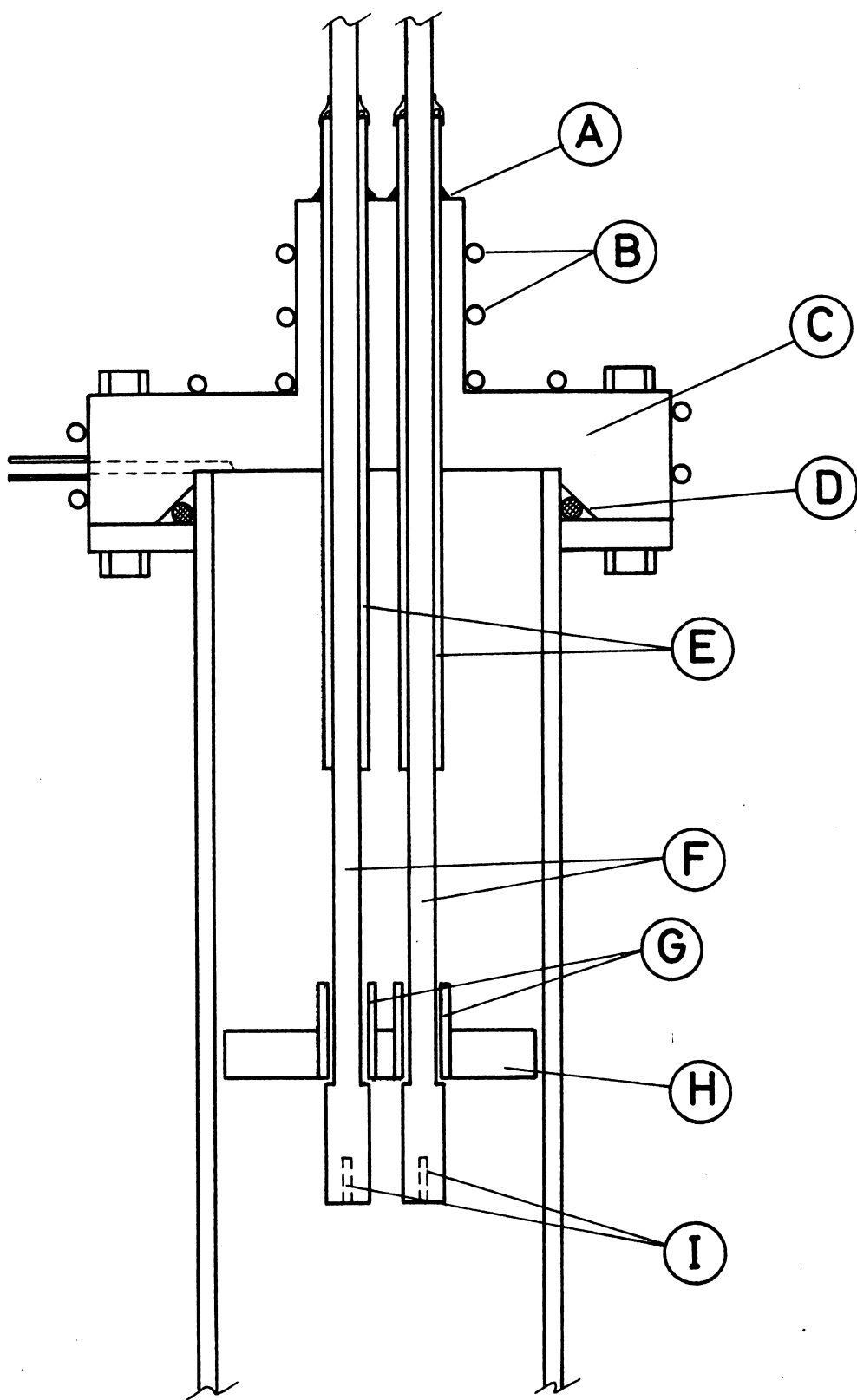


FIGURE 4.4

TOP-ASSEMBLY FOR THREE ELECTRODE WORK

(See following page
for legend)

FIGURE 4.4

TOP-ASSEMBLY FOR THREE ELECTRODE WORK

LEGEND:

- A - High temperature "Araldite"
- B - Water cooling
- C - Brass flange
- D - 'O-ring' seal
- E - Recrystallised alumina tubes
- F - Graphite electrode rods
- G - Alumina tubes
- H - Sintered alumina disc
- I - 4 b.a. female thread

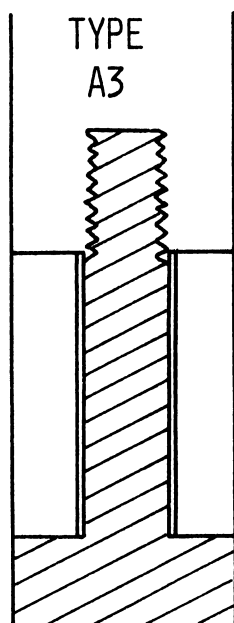
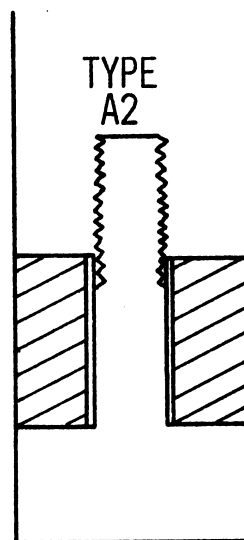
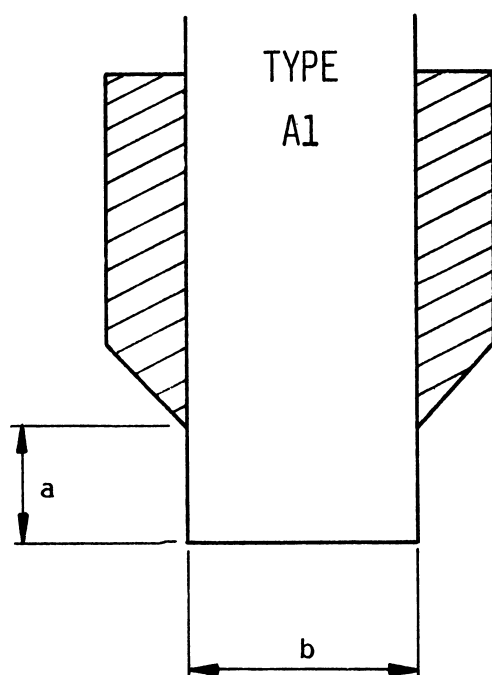
The 6.4 mm diameter graphite anode rods (F) were reduced in section (to approximately 5.5 mm to fit inside the alumina tubes) for the complete length apart from the lower 60 mm. To ensure central location and adequate separation of the two electrode rods at the lower end, a locating assembly consisting of two appropriately spaced alumina tubes (G) (20 mm long x 8.5 mm o.d. x 6 mm i.d.) cemented into a circular sintered alumina disc (H) was mounted on the electrode rods. The total clearance between this disc and the inner walls of the furnace tube was 2 mm maximum, thus fixed alignment of the electrodes was assured. The type of electrode rods as shown in Figure 4.4 had 4 b.a. threads tapped in the base (I), so that various types of anode tips could be screwed into the rods, as is described in the following section.

4.3 ANODE TYPES

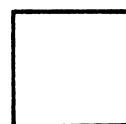
The different types of anode used in this work are shown in Figure 4.5 (schematic) and Figure 4.6.

The anode type which was generally used for 2-electrode electrolysis was type A1, consisting of a press-fit boron nitride sheath over the graphite electrode rod, with a 45° taper machined in the lower boron nitride surface to facilitate the escape of anode gases. These anodes were fabricated in three size ranges with the nominal dimensions shown in Table 4.1. (The dimensions 'a' and 'b' correspond to those indicated in Figure 4.5).

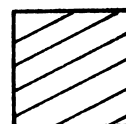
Anode types A2 and A3 utilised detachable tips that could be weighed for the purpose of determining electrode weight losses (i.e. carbon consumption) during electrolysis. With type A2 the graphite tip was threaded to screw into a hole tapped in the electrode rod



KEY



- GRAPHITE



- BORON
NITRIDE

FIGURE 4.5

ANODE TYPES

(a)

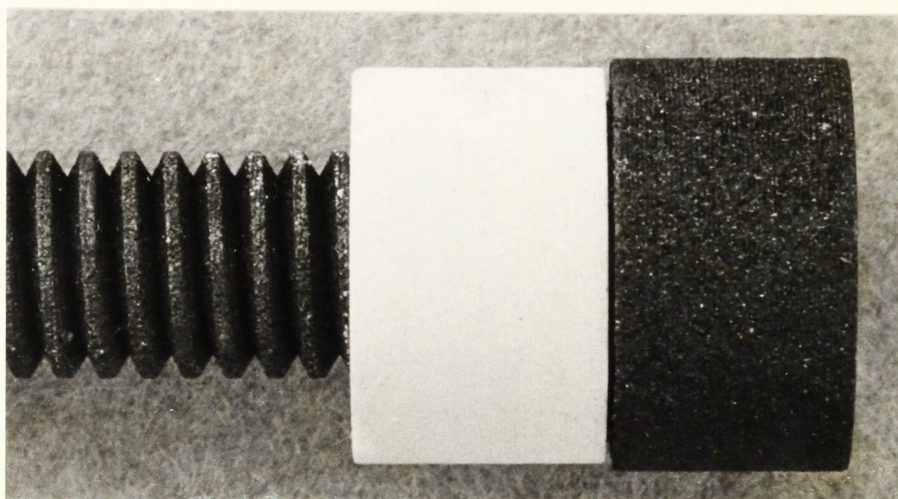
TYPE A1

(after electrolysis
run B4)



(b)

TYPE A2



(c)

TYPE 3

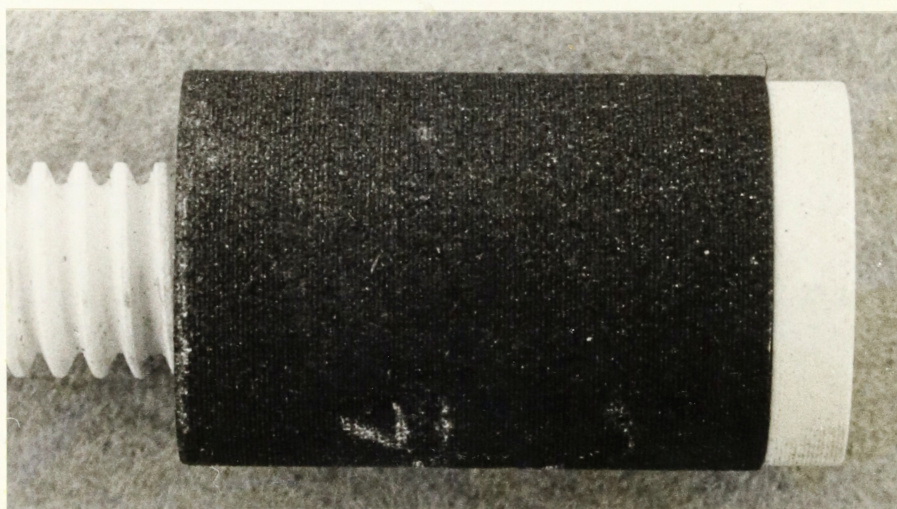


FIGURE 4.6

PHOTOGRAPHS OF ANODE TIPS

(approx. X12)

ANODE SIZE	NOMINAL DIMENSIONS (cm)		NOMINAL GEOMETRIC AREA (cm ²)		
	a	b	BASE	SIDES	TOTAL
Small	0.24	0.48	0.181	0.362	0.543
Medium	0.28	0.64	0.322	0.563	0.885
Large	0.45	0.64	0.322	0.905	1.227

TABLE 4.1NOMINAL ANODE DIMENSIONS

(4 b.a. thread). A hollow boron nitride cylinder of the same outside diameter as the electrode tip was clamped between the two graphite components to produce a geometrically defined nominal anode surface area. This type of configuration proved reasonably satisfactory for weight loss determinations, however extreme care was required to prevent an artificial weight loss through mechanical degradation of the fine graphite thread. Further, considerable difficulty was experienced in machining a good quality thread with no chipping or crumbling of the thread edges.

Although tests involving 'blank runs' (i.e. subjecting the electrode to a typical electrolysis temperature cycle with no melt immersion or electrolysis) showed that, with extreme care in electrode handling, no artificial weight losses were produced, to alleviate these restrictions in later work, electrodes of type A3 were used. These consisted of a hollow, cylindrical graphite electrode tip held in position with a boron nitride end-cap screwed into the electrode rod (4 b.a. thread). Machining of these fine threads in hot pressed

boron nitride was found to be much easier than with graphite, with less tendency to produce weak crumbly threads.

The simple design of the graphite tip with the type A3 electrode enabled very accurate anode weight-loss determinations with negligible artificial (mechanically induced) weight-losses. However, with no boron nitride sheath to produce a geometrically defined anode surface, the depth of immersion in the molten salt was the sole determinant of electrode area. This was not a significant disadvantage, as it was found that the benefits of having a geometrically defined anode surface area were normally reduced because of gas shielding effects. Furthermore, the true anode area could be readily determined from observation of the anode surface after electrolysis. These aspects are further discussed in Section 4.5.7.

The type A2 anode tips were made within three nominal size ranges, as with type A1, while when using type A3 anodes an attempt was made to immerse the electrode to a specific depth to give an anode area corresponding as closely as possible to one of these size ranges.

4.4 ELECTRONIC APPARATUS

Figure 4.7 is a schematic diagram of the electronic apparatus used in this work.

The power supply for electrolysis was a C.T.I.C. Type BK-51 Potentiostat/Galvanostat. This was used in conjunction with an Utah Electronics model 0151 Linear Sweep Generator which could produce half-cycle, full-cycle or cyclic (continuous) linear voltage changes with sweep rates from 0.001 volts/sec to 1000 volts/sec within the range -5.0 V to +5.0 V. This gave the capability of applying three different techniques in electrochemical investigations:

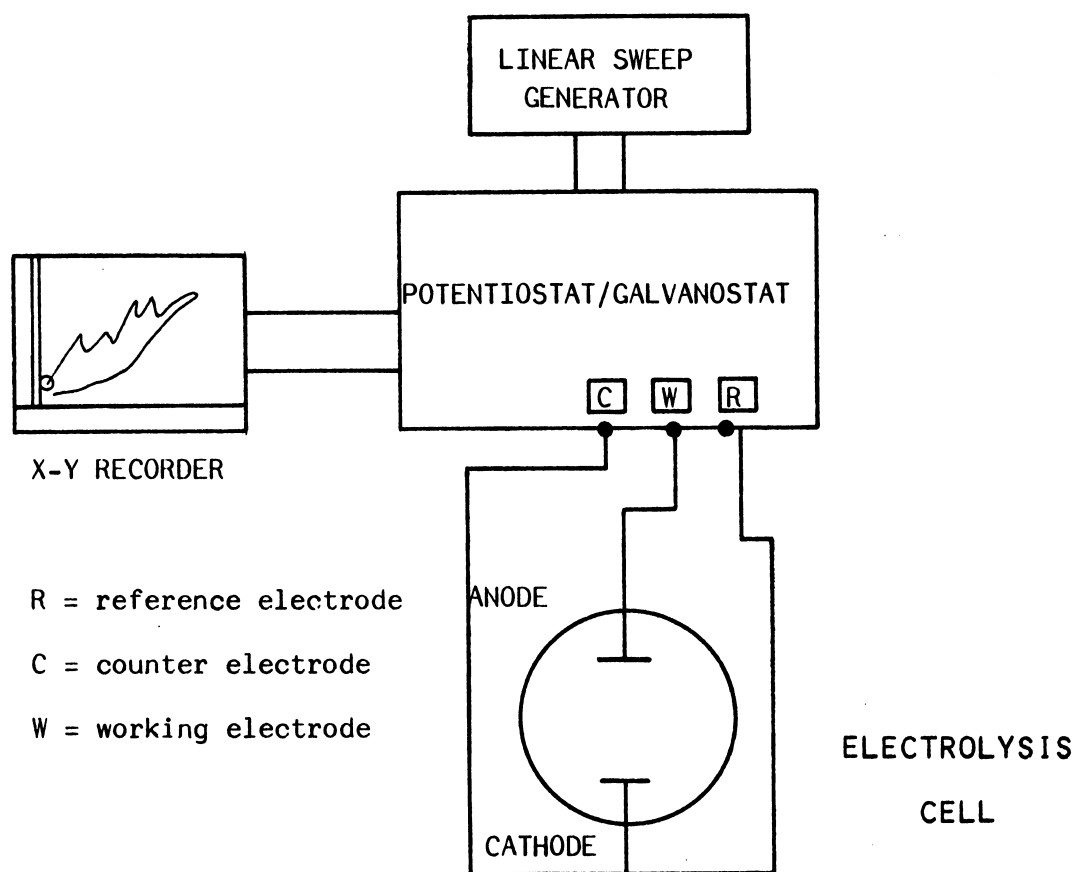


FIGURE 4.7

ELECTRONIC APPARATUS

1. Potentiostatic (voltage-controlled) electrolysis with a constant applied potential.
2. Potentiostatic electrolysis with linear voltage sweeps (linear sweep voltammetry).
3. Galvanostatic (current-controlled) electrolysis with a constant applied current.

For 2-electrode work the reference electrode output was shorted to the counter electrode output, as shown in Figure 4.7.

Current and voltage outputs were monitored on a Hewlett Packard Model 7045A X-Y recorder. A Solartron model LM1604 Digital Voltmeter was used for accurate current and voltage measurement. In the case of current measurement this involved determination of the potential drop across a standard resistor in the circuit, while voltage measurements were made directly at the output terminals of the potentiostat/galvanostat or at the exposed ends of the graphite electrode rods.

4.5 EXPERIMENTAL TECHNIQUES

The following describes only the normal techniques and procedures that were applied in the bulk of the experimental work. In some cases there was some deliberate variation from standard methods to enable further investigation of particular phenomena. Where this has been done it is noted in the presentation of results.

4.5.1 Copper Doping

The pure copper feed was cathode copper with a typical analysis listed in Table 4.2, the main impurity being oxygen. For each experiment in which sulphur-doped copper was used the following procedure was adopted.

<u>ELEMENT</u>	<u>CONCENTRATION (p.p.m.)</u>
O	< 150
S	4
Se	< 0.5
Te	< 0.5
Bi	< 0.5
As	2
Pb	5
Sb	< 0.5
Cd	< 0.5
Ag	6
Zn	< 0.5
Ni	3
Co	3
Fe	4

TABLE 4.2TYPICAL ANALYSIS OF PURE COPPER FEED

Approximately 60 g of copper feed in block form (weighed to ± 0.01 g) was placed in a graphite crucible with a weighed amount of pure cuprous sulphide (± 0.01 g) to produce a nominal sulphur level of 0.10 wt% in copper assuming complete dissolution of the Cu_2S in the copper. The graphite crucible was machined from A.T.J. graphite with an internal diameter of 21 mm, equivalent to the minimum internal diameter of the electrolysis crucibles. The Cu_2S was produced by reacting stoichiometric quantities of high purity copper wire and A.R. grade elemental sulphur in an evacuated glass ampoule. X-ray diffraction powder analysis confirmed it to be stoichiometric Cu_2S with no diffraction lines observed for any other Cu-S compounds.

The crucible and contents were sealed in the furnace and heated to 1423K under an inert argon atmosphere. This temperature was maintained for 10-12 hours to ensure complete dissolution and homogenisation of the Cu_2S in the liquid copper and virtually complete deoxidation of the copper by the graphite crucible (< 15 ppm [O]). The crucible was then lowered approximately 15 cm out of the furnace hot zone to produce solidification of the melt. The cooling rate achieved was approximately 80K/min during the initial decrease from 1423K to below the freezing point of copper.

The solidified copper billet was sectioned and drill samples were taken for sulphur analysis as shown in Figure 4.8, leaving approximately 40 g (± 3 g) of sulphur-doped copper for use in electrolysis. To ensure representative sampling three different drill samples were removed - one from the centre and two from the sides near the edge of the billet. However, in each case there was no significant difference between the sulphur assays of the three, indicating that macro-segregation of sulphur during solidification was not occurring to any

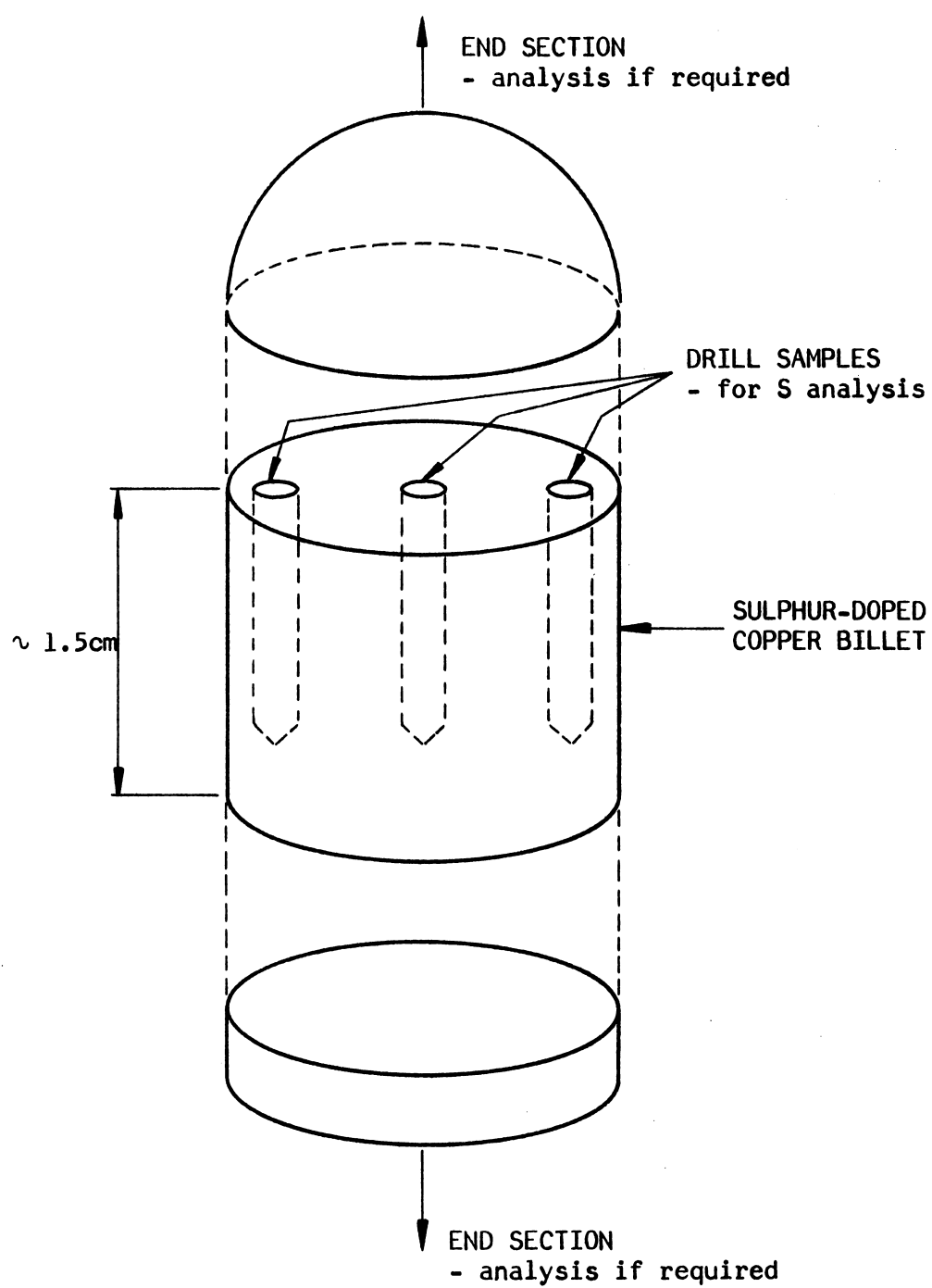


FIGURE 4.8

SECTIONING AND SAMPLING OF
THE DOPED COPPER BILLET

appreciable extent. This had previously been established by extensive sampling of solidified copper samples with microstructural examination of different regions.

4.5.2 Crucible and Electrode Preparation

After machining and assembly of the crucible and graphite electrode (two graphite electrodes in the case of three-electrode work), they were subjected to a high temperature 'boil' to remove volatile impurities. The empty crucible and electrode were sealed in the furnace in the normal experimental configuration (Figure 4.2) and heated to 1473K under an inert argon atmosphere (maintaining a continuous flow of 100 ml/minute). This temperature was held for 12-14 hours, after which the furnace power was switched off and the components removed after cooling and stored in a desiccator.

After this treatment it was found necessary to re-machine the inner surfaces of the crucible and the lower graphite and boron nitride surfaces of the electrode before using them in electrolysis, in order to remove a very thin surface layer of transparent material that had formed on the surface of the boron nitride. In some cases discrete solidified droplets of this material approximately 0.1-0.2 mm diameter were observed on the surface when it was viewed under a stereoscopic microscope. Surface scrapings analysed using X-ray diffraction powder techniques did not produce a positive identification - no diffraction lines other than for boron nitride were observed.

The removal of this layer from the inner crucible walls by lathe machining involved a light surface 'skim' to a depth of 0.1-0.2 mm.

For the boron nitride electrode surfaces it was found more convenient to lightly rub the surface with fine (600 grade) emery paper to remove the surface layer.

After this treatment the crucible and electrode were ultrasonically cleaned in S.V.R. 114 alcohol to remove finely divided graphite and boron nitride dust particles. This is a technique reported by Mamantov⁶⁴ and was found to be very effective. Examination of the machined surfaces under a stereoscopic microscope before and after ultrasonic cleaning confirmed that complete removal of the very fine surface particles was achieved, whereas these could not be removed by techniques such as air-blowing. The ultrasonic cleaning was done in two stages, each of approximately five minutes immersion in the alcohol with a fresh alcohol bath used for each stage.

After ultrasonic cleaning the components were oven-dried at 393K for a minimum of two hours before being used.

4.5.3 Melt Preparation

The high purity CaF_2 and MgF_2 salts were obtained in powdered form from Electronic Space Products Incorporated, with quoted purities of 99.95% and 99.98% respectively. At all times except when weighing batches for electrolysis runs they were stored in a desiccator to minimise atmospheric moisture pick-up.

For a typical electrolysis run, 10.00 g of binary salt mixture of eutectic composition (5.56 g of CaF_2 + 4.44 g of MgF_2) was weighed and after thorough mixing placed in a drying oven at 393K for a minimum of 24 hours prior to charging it into the electrolysis crucible. The salt mixture was placed in the crucible on top of the sulphur-doped copper billet with light compaction. The copper billet itself was given a final surface clean before placing it in the

crucible, by lightly filing all external surfaces with a clean file to remove any surface oxidation or contamination. The crucible loading procedure was carried out rapidly to minimise atmospheric moisture pick-up - the total time required was approximately one minute.

Immediately after loading the crucible it was sealed in the furnace which had been pre-purged for approximately 20 minutes with an argon gas flow of 500 ml/minute. The crucible was positioned 1-2 mm below the point of contact of the anode tip with the powdered salt surface. In order to enhance the purging of air from within the crucible (i.e. from the void spaces in the compacted salt powder) the furnace was evacuated twice to approximately 100 Pa and back-flushed with argon.

Before raising the cell temperature to 1423K the furnace was slowly heated (over a five hour period) to 823K and held at that temperature for 12-15 hours to achieve final drying of the fluoride salts. During this period an argon gas flow of 100 ml/minute was maintained.

Pre-electrolysis salt drying was carried out at a temperature no higher than 823K because it has been reported⁶⁵ that hydrolysis of MgF_2 to form oxide according to the equation



occurs at temperatures down to 900K (although temperatures of at least 1273K are required to produce a similar reaction with CaF_2 ⁶⁵).

However, a temperature of 823K was considered sufficient as the data reported by Duval⁶⁶ indicate that the thermogravimetric weight-loss curves for MgF_2 and CaF_2 become horizontal at 693-698K and 673K respectively.

After the 12-15 hour drying period the cell temperature was raised over a three hour period to 1423K, which was the temperature at which all electrolysis experiments were conducted. A potential of 0.200 volts was then applied across the electrodes and the crucible slowly raised until initial contact of the lower anode surface with the salt melt was indicated by the sudden commencement of a small "residual" current flow (typically 0.05-0.10 mA). The applied voltage was then removed and the crucible further raised to give the desired depth of immersion of the anode in the salt melt. This was typically 5 mm for type A1 and A2 anodes but variable for type A3 (depending on the required anode surface area) and was indicated by a graduated scale on the lower portion of the alumina tube supporting the crucible assembly.

Electrolysis was then commenced with the argon flow of 100 ml/minute maintained throughout.

4.5.4 Electrolysis Procedures

Most of the electrolyses were performed under potentiostatic (voltage-controlled) conditions with the application of a fixed cell potential. After setting the desired voltage output from the potentiostat the cell connector leads were plugged in to complete the circuit and commence electrolysis. This was done as soon as practicable after anode immersion.

Current versus time electrolysis curves were recorded on the X-Y recorder during electrolysis. When a new chart recorder sheet was required the electrolysis was interrupted for a short time (typically 30 seconds) by disconnecting one of the contact leads to the cell to allow this. With a typical time base of 25 seconds = 1 cm, this had to be done every 14 minutes.

For electrolysis over an extended time a continuous chart recorder was also used to record the complete current versus time electrolysis curve. In this case the X-Y recorder was only used to obtain a higher-resolution trace of the current versus time curve when necessary.

Electrolysis was terminated by unplugging the connector leads. After completion of electrolysis the melt was cooled immediately by lowering the crucible into the cool regions of the furnace tube. Initially a water-cooled quenching chamber was installed as part of the lower flange assembly, but it was found that rapid lowering of the crucible into this region frequently produced thermal shock induced cracking of the alumina support tube. To alleviate these problems, lowering of the assembly only into a cooler region of the furnace (973-1073K) was adopted. This gave sufficiently rapid solidification (the copper solidified in ~ 1 minute) to prevent sulphur reversion from the salt phase into the copper phase.

After cooling the crucible and contents inside the sealed furnace they were removed and weighed (± 0.01 g). The solidified copper and salt together were easily removed from the crucible as neither the boron nitride nor the graphite were wetted by the melt components. However, for mass balance purposes it was not possible to quantitatively separate the salt phase from the copper due to the presence of small amounts of molten salt in some surface holes and gaps that were invariably present in the copper. Due to the difference in freezing points, the copper solidified approximately 2-3 minutes before the fused salt, and this allowed some of the fused salt phase to flow down the shrinkage voids between the copper and the boron nitride crucible sidewalls. Further, the top surface of the

copper usually had a coarse dendritic structure which allowed some of the molten salt phase to flow into the interdendritic voids. The hard brittle salt phase could not be easily chipped off the surface of the copper and attempts at this usually resulted in compaction of the fine salt powder formed into the soft surface of the copper.

The copper and salt samples were then analysed as described in Section 4.6.

The same procedure was followed for galvanostatic (current-controlled) electrolysis except that in this case a constant cell current was set and maintained by the galvanostat after the circuit had been connected. Cell potential versus time curves were plotted on the X-Y recorder, while the continuous chart recorder was again used for lengthy electrolysis runs.

In some potentiostatic electrolysis runs the progress of electrolysis was monitored using linear sweep voltammetry (L.S.V.). This normally involved firstly obtaining linear sweep voltammograms prior to the commencement of electrolysis, with the I/V curves recorded on the X-Y recorder. Subsequently, at various stages of electrolysis, the cell potential was removed and further linear sweep voltammograms obtained, followed by recommencement of electrolysis as soon as was practicable. Typically this required the cessation of electrolysis for a period of 2-3 minutes.

4.5.5 Determination of Decomposition Potentials

The slow sweep (or "steady state") current-voltage curve technique⁶⁷ was used to determine decomposition potentials. In this method the decomposition potential is determined by extrapolating the

rapidly increasing (and approximately linear) region of the slow-sweep current-voltage curve to zero current, as shown in Figure 4.9(a). In this work a sweep rate of 0.02 volts/sec. was applied.

In the case where other reactions are occurring prior to the onset of a particular decomposition reaction, the decomposition potential is defined at the point of intersection of the extrapolated I/V curves before and after decomposition - as shown in Figure 4.9(b) - although in this case correction must be made for the component of the cell voltage due to the 'IR' drop through the electrolyte.

The slow sweep technique is simple and rapid, and is particularly suited to this work as any polarization or depolarization effects that result from the cell geometry and/or electrode materials used are included in the decomposition potential value obtained. Thus the decomposition potential determined is relevant to the particular experimental apparatus used.

One disadvantage of this technique is that its accuracy is limited as it involves linear extrapolation of current-voltage curves that are not strictly linear, and which may also exhibit rapid current fluctuations during the voltage sweep due to gas evolution effects occurring at one or both of the electrodes (as shown in Figure 4.9(b)). In this case a linear average-current line has to be estimated. It was found that the reproducibility of this technique was at best ± 0.04 volts (± 0.1 volts with significant gas evolution).

In 'rapid' linear sweep voltammetry where the onset of a particular electrode reaction during the forward voltage sweep is indicated by a sudden increase in current, the same linear extrapolation techniques were used to define the cell potential at which the reaction was considered to commence.

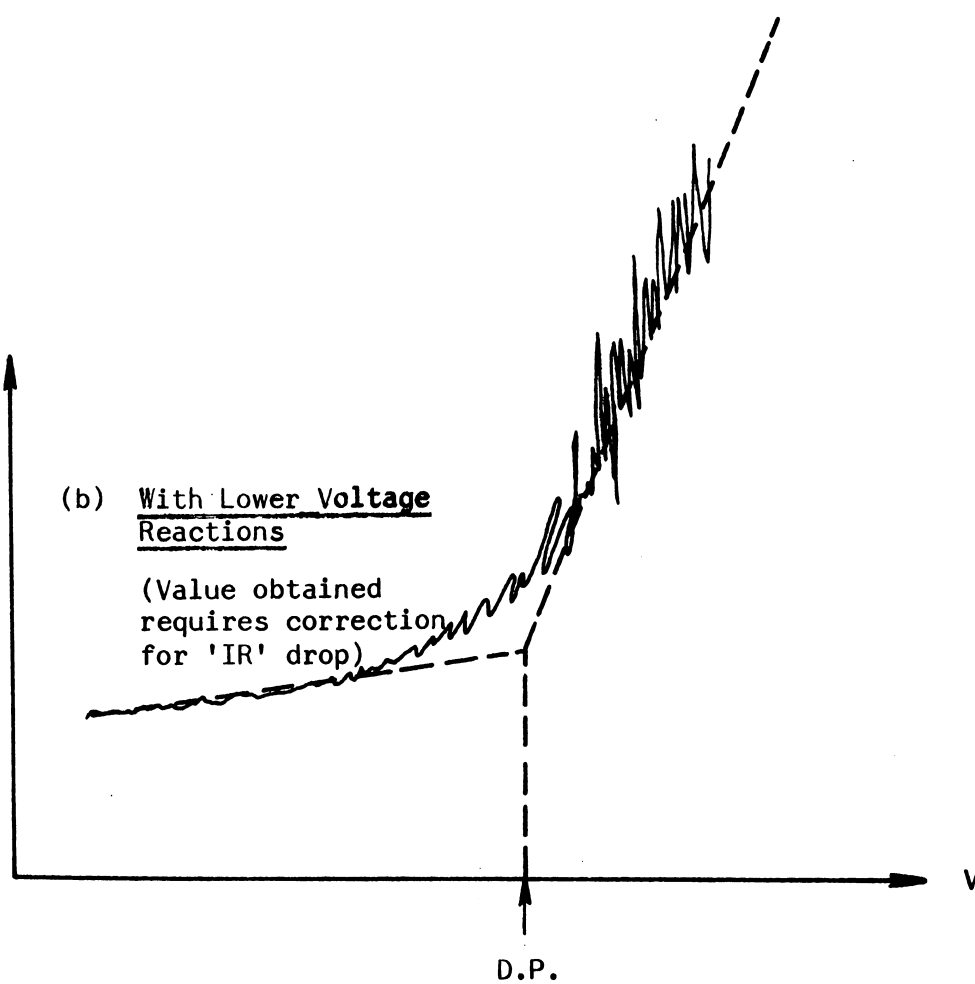
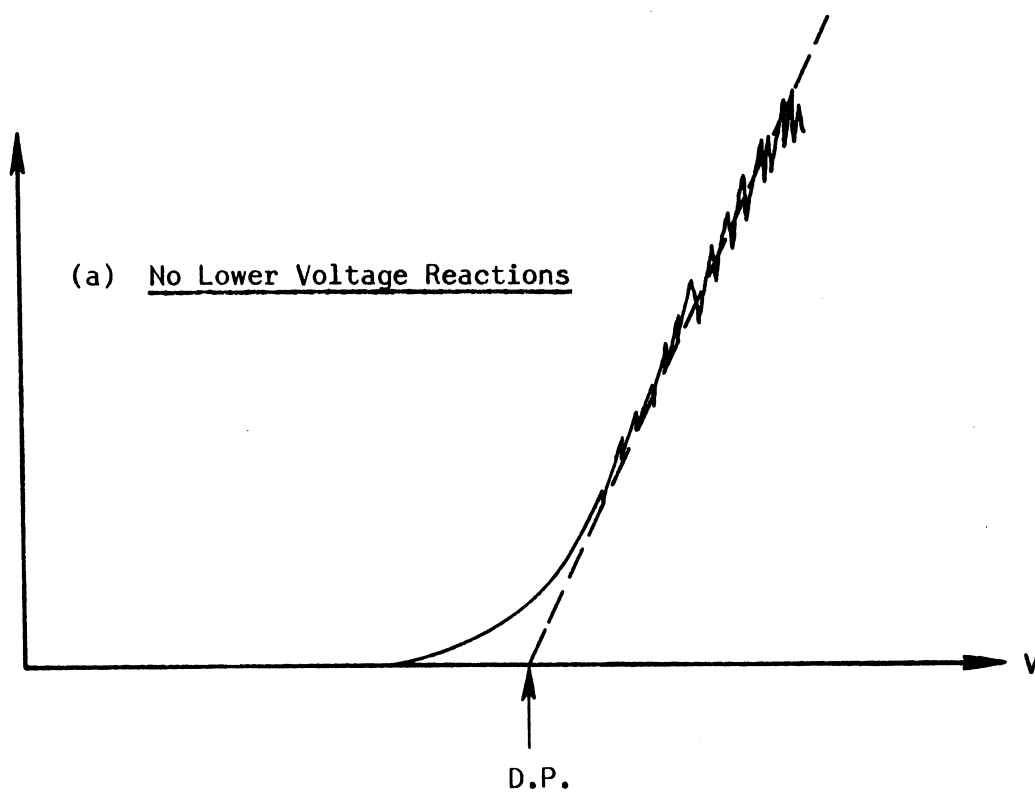


FIGURE 4.9

DETERMINATION OF DECOMPOSITION POTENTIALS
BY LINEAR EXTRAPOLATION OF I/V CURVES

4.5.6 Measurement of the Amount of Current Passed During Electrolysis

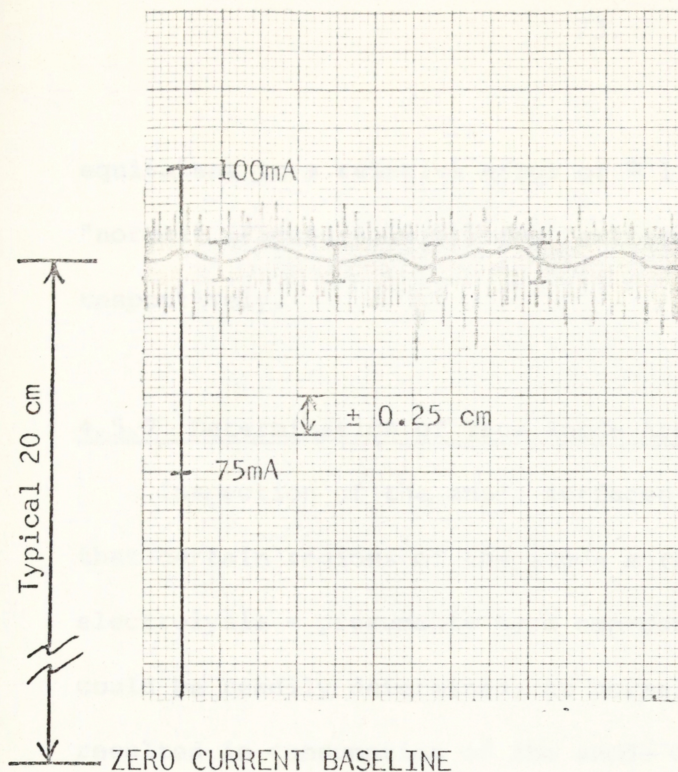
For galvanostatic electrolysis the total current passed during electrolysis (expressed in milliampere-hours (mAh) in this work) was determined from the product of the set electrolysis current and the electrolysis time at that current, determined with a stop-watch.

The current passed during potentiostatic electrolysis was determined by measurement with a planimeter of the total area under the current versus time electrolysis curves.

During plotting of these curves the time base and current scale of the recorder were chosen (and altered when necessary) so as to maximise the area under the curve and thus minimise the relative errors resulting from area measurement. Thus, typically the area measured for each full page trace from the recorder was at least 150 cm^2 . The accuracy of the planimeter for measurement of areas of that size was $\pm 0.2 \text{ cm}^2$ (determined from measurement of accurately known areas) giving a total planimeter error of less than $\pm 0.15\%$ for each determination.

The main source of uncertainty in planimeter area measurement resulted from the presence of rapid short-term current fluctuations during electrolysis which resulted in electrolysis curves of the type shown in Figure 4.10. These are actual size reproductions of sections of electrolysis curves, Figure 4.10(a) being typical of the fluctuations commonly observed and Figure 4.10(b) an extreme case where violent fluctuations were recorded. In these cases an average electrolysis curve was drawn in (as shown in these Figures) and the amount of current passed determined from the area under this.

The uncertainty associated with the positioning of this average electrolysis curve is indicated on Figures 4.10(a) and 4.10(b) and is



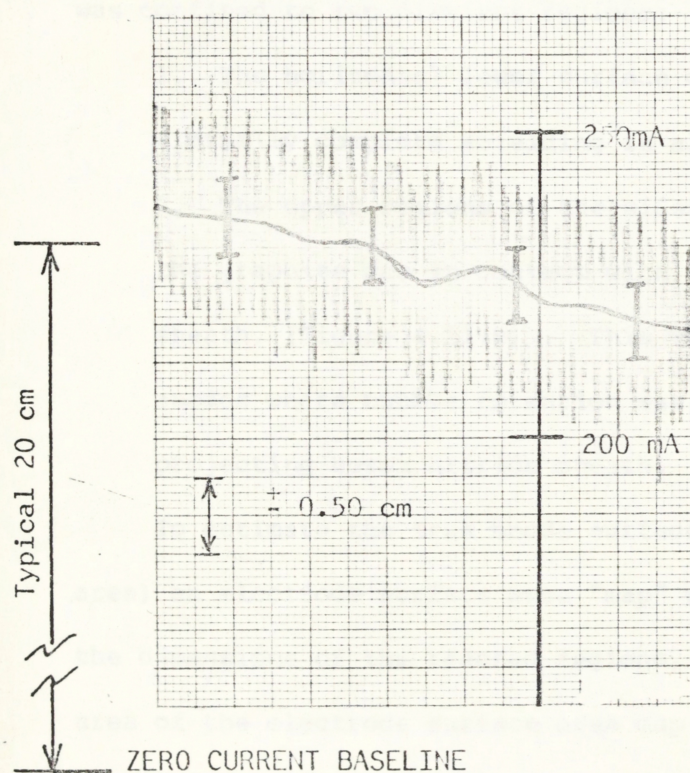
(a) 'normal' case

Maximum Uncertainty = ± 0.25 cm

Maximum Relative Error in Current Magnitude

$$= \frac{\pm 0.25}{20} \times 100\%$$

$$= \pm 1.25\%$$



(b) 'extreme' case

Maximum Uncertainty = ± 0.5 cm

Maximum Relative Error in Current Magnitude

$$= \frac{\pm 0.5}{20} \times 100\%$$

$$= \pm 2.50\%$$

FIGURE 4.10

ELECTROLYSIS CURVES WITH SHORT-TERM CURRENT FLUCTUATIONS
SHOWING PLACEMENT OF AVERAGE CURRENT CURVES

equivalent to a relative error of $\pm 1.25\%$ and $\pm 2.50\%$ for the "normal" (Figure 4.10(a)) and "extreme" case (Figure 4.10(b)) respectively.

4.5.7 Determination of True Anode Areas

Inspection of the anode surfaces after electrolysis indicated that certain regions of the anode surface were being shielded during electrolysis - presumably by a non-conducting gaseous film. This could be readily determined, as normally the anode reaction occurring resulted in consumption of the anode carbon and a marked change in the surface appearance of the graphite - to a smoother more shiny surface. Thus, non-wetted (i.e. non-reacting) areas of the anode surface could be easily identified, and in most cases the shielding was confined to two distinct regions:

1. The horizontal lower surface of the anode which experienced virtually complete shielding in all cases (see Figure 4.11(a)).
2. The upper regions of the sides of the graphite anode where the graphite was in contact with the boron nitride insulating sheath, (Figure 4.11(b)). This was most evident with type A1 anodes where bubble formation was presumably stabilised by the projecting boron nitride sheath.

To estimate the true anode surface area (i.e. the reacted surface area) an electrode surface area "map" was drawn from measurements of the dimensions of the reacted regions, as shown in Figure 4.12. The area of the electrode surface area map (which was drawn to scale) was then determined using a planimeter, thus giving an estimate of the true electrode surface area.

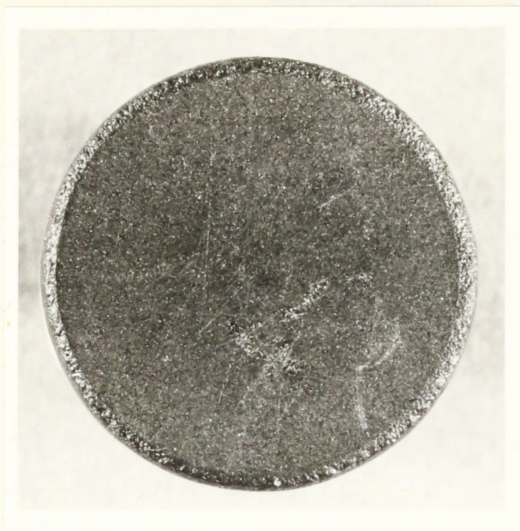


FIGURE 4.11 (a)

Photomicrograph of an anode base (x22). Most of the surface has been shielded (dull appearance) with only the outer edges reacted (shiny appearance).

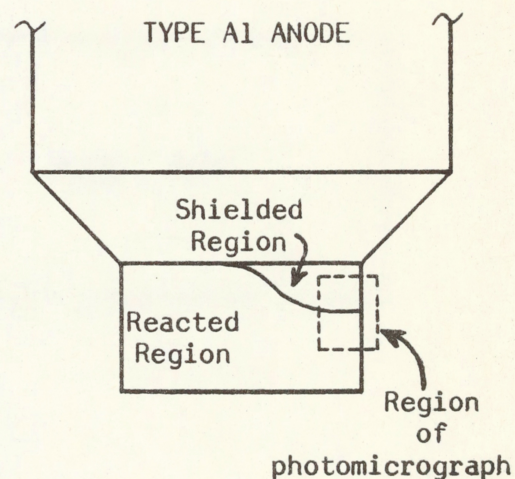
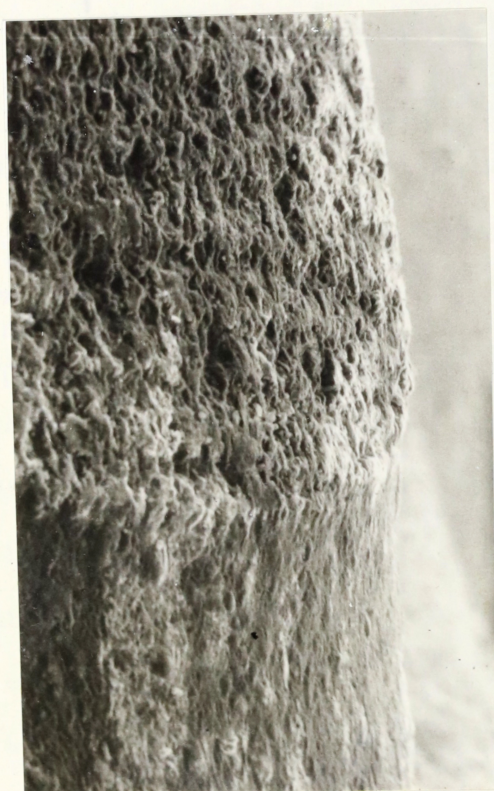
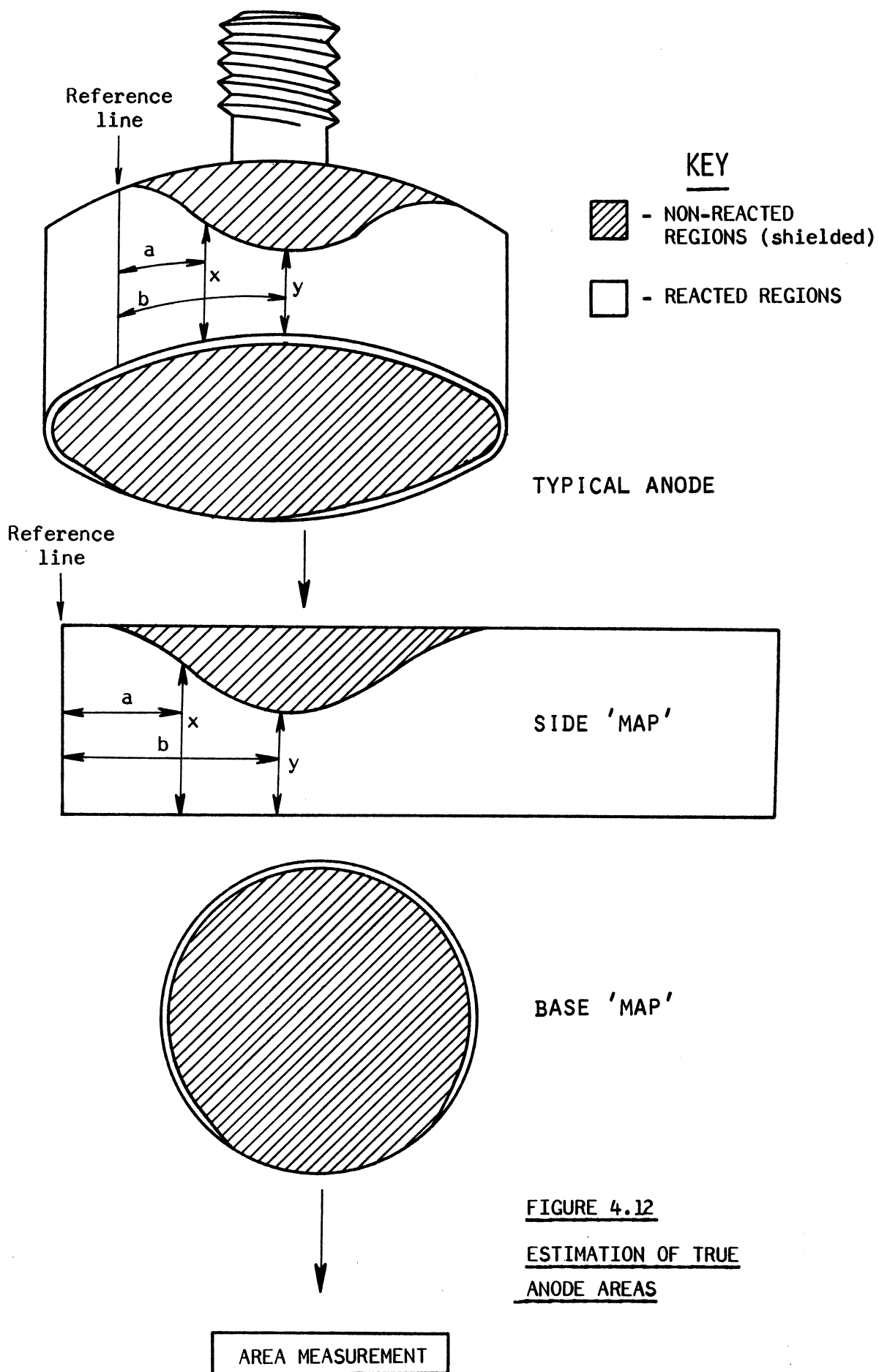


FIGURE 4.11 (b)

S.E.M. Photomicrograph of the horizontal edge of an anode (x150) corresponding to the region indicated in the sketch above. A clear distinction between the lower reacted region and upper shielded region is evident.

FIGURE 4.11

ANODIC SHIELDING PHENOMENA



4.6 CHEMICAL ANALYSIS

4.6.1 Determination of Sulphur in Copper

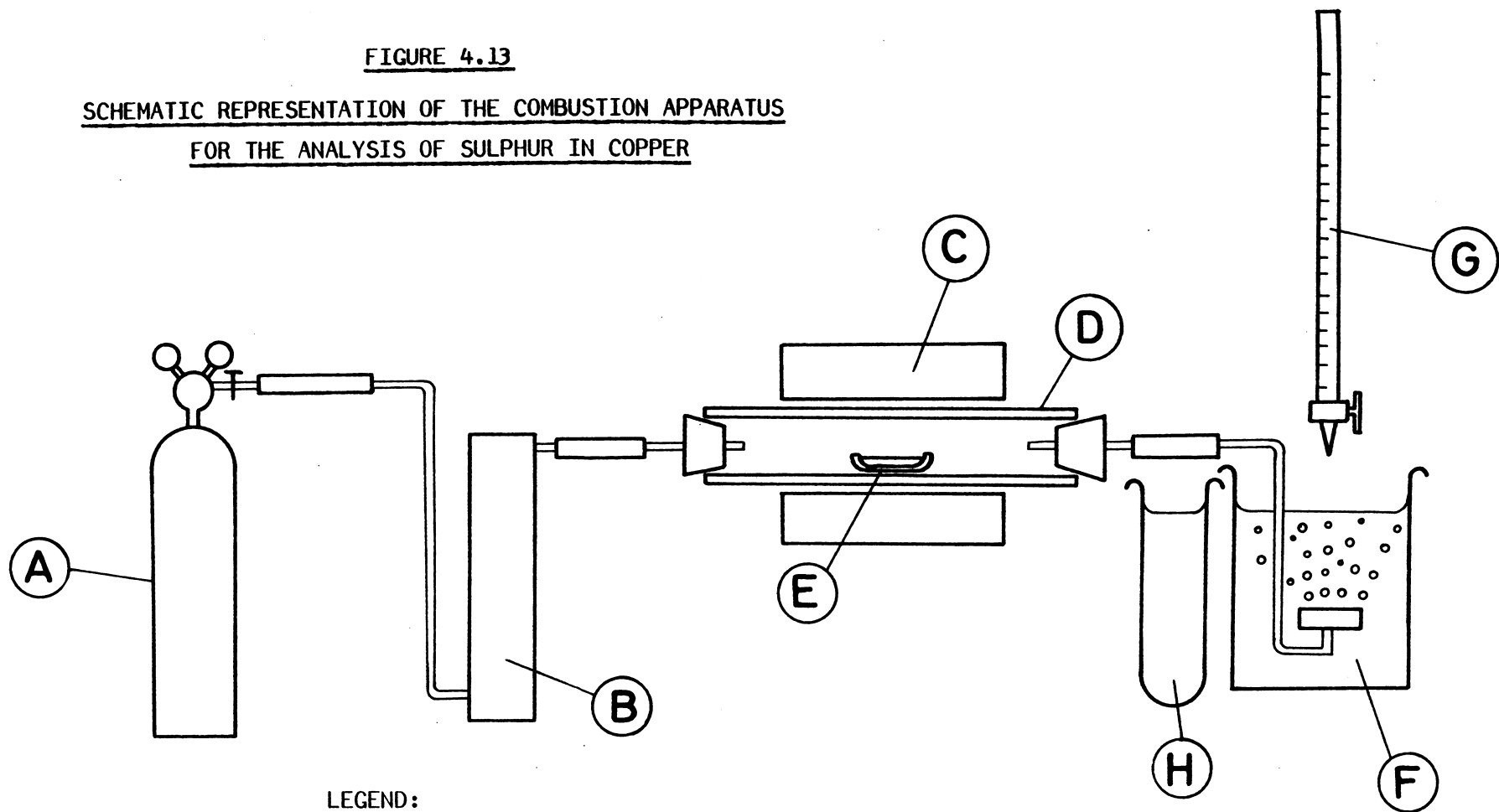
The copper samples were analysed for sulphur using a combustion technique^{68,69}. The apparatus used is schematically represented in Figure 4.13.

Combustion of the sulphur in copper was carried out at 1473K in an atmosphere of pure oxygen from supply bottle (A) at a flow rate of 600 ml/minute. The copper sample to be analysed (weighed to ± 0.001 g) was placed in a pre-fired porcelain boat (E) which was rapidly inserted into the furnace hot zone in the mullite furnace tube (D). Insertion was from the gas inlet end and the furnace was resealed immediately to resume the oxygen flow. The sulphur dioxide gas evolved was absorbed into 100 ml of 3% HCl solution (F) which contained starch solution as an indicator. Prior to commencing absorption a small amount of potassium iodate solution was titrated into the absorption solution to produce a blue colouration characteristic of the starch-iodate complex in the presence of excess iodate solution. The intensity of this initial blue colour was that of the end-point of the titration and was matched to that of an end point comparison solution (H). As SO₂ was absorbed into the solution it was continuously titrated with standard potassium iodate solution to maintain the blue end-point colour. The end-point (i.e. end of SO₂ absorption) was readily determined by the persistence of the blue colour, and was normally achieved in 3-4 minutes (although the bulk of the SO₂ was released within 30 seconds).

The standard potassium iodate solution was 0.00104N giving a titration equivalent of 1.00 ml per 100 μ g of sulphur. The mass of the copper sample used was dependent on the sulphur concentration

FIGURE 4.13

SCHEMATIC REPRESENTATION OF THE COMBUSTION APPARATUS
FOR THE ANALYSIS OF SULPHUR IN COPPER



LEGEND:

A - oxygen supply
B - calcium chloride drying column
C - carbolite furnace
D - mullite reaction tube

E - pre-fired poreclain boat containing the Cu
F - absorption solution
G - titration burette
H - end-point colour comparison solution

- ranging from 0.5 g for the sulphur-doped copper (typically about 0.085 wt% S) to approximately 4 g for very low sulphur levels (which was the maximum amount of copper one boat could hold). The analysis samples were drill turnings from the copper billets. Care was taken in sampling electrolysed copper billets to ensure there was no contamination from solidified fluoride salt particles on the surface of the copper. This salt also contained dissolved sulphur.

In each case corrections were made for blank determinations which were regularly checked. The blank determination generally required two drops (0.06 ml) of the iodate solution.

Because this technique required the assessment of the intensity of the final blue colouration (and not just the detection of the presence of a blue colouration) to determine the end point, the uncertainty in determining end points was reasonably high at ± 0.06 ml, even with a standard "end-point solution" of the same required blue colouration as the end-point used as a comparison standard situated next to the solution being titrated. Together with the possible errors in reading the initial and final burette readings (± 0.01 ml for each), this represents a total titration uncertainty of ± 0.08 ml. For a typical titre of 5-6 ml this gives a relative error of $\pm (1.3-1.5)\%$, which was considered satisfactory. The errors associated with weighing of the copper samples (weighed to ± 0.001 g) and preparation of the standard solution are not significant compared to this.

It should be noted that using a lower strength standard potassium iodate titration solution to give a larger titre did not significantly reduce the relative error associated with the titration as there was a

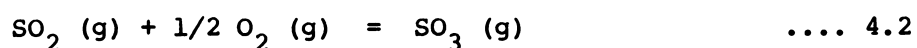
corresponding decrease in the sensitivity in detecting the end point, since the addition of a greater quantity of the weaker iodate solution was required to produce a detectable change in the blue intensity.

For very low sulphur concentrations in copper a lower detection limit of 1.5 p.p.m. could be achieved using the procedure described below.

Two drops (0.06 ml) of the potassium iodate solution were added to the absorption solution prior to combustion, producing a blue colouration that was just detectable. The accurately weighed copper sample (~ 4 g) was then placed in the hot zone and if the slight blue colouration persisted after five minutes and after an addition of iodate solution equivalent to a blank determination, then the sulphur concentration in the copper was recorded as "not detected", which in this case is less than:

$$\frac{0.06 \text{ ml} \times 0.0001 \text{ g/ml}}{4 \text{ g}} \times 100 \text{ wt\% S} = 1.5 \text{ p.p.m.}$$

Sulphur analysis by combustion in pure oxygen is not quantitative as the high oxygen partial pressure results in some degree of conversion of SO_2 to SO_3 according to the reaction:



Increased conversion of SO_2 to SO_3 is thermodynamically favoured as the temperature of the gas decreases on leaving the furnace hot zone. Figure 4.14 shows the variation of the equilibrium $P_{\text{SO}_2}/P_{\text{SO}_3}$ ratio with temperature at four different oxygen partial pressures from 1.0 atm. (line I) to 10^{-3} atm. (Line IV). As can be seen the equilibrium shifts rapidly to favour SO_3 formation as the temperature decreases and even at an oxygen partial pressure of 10^{-3}

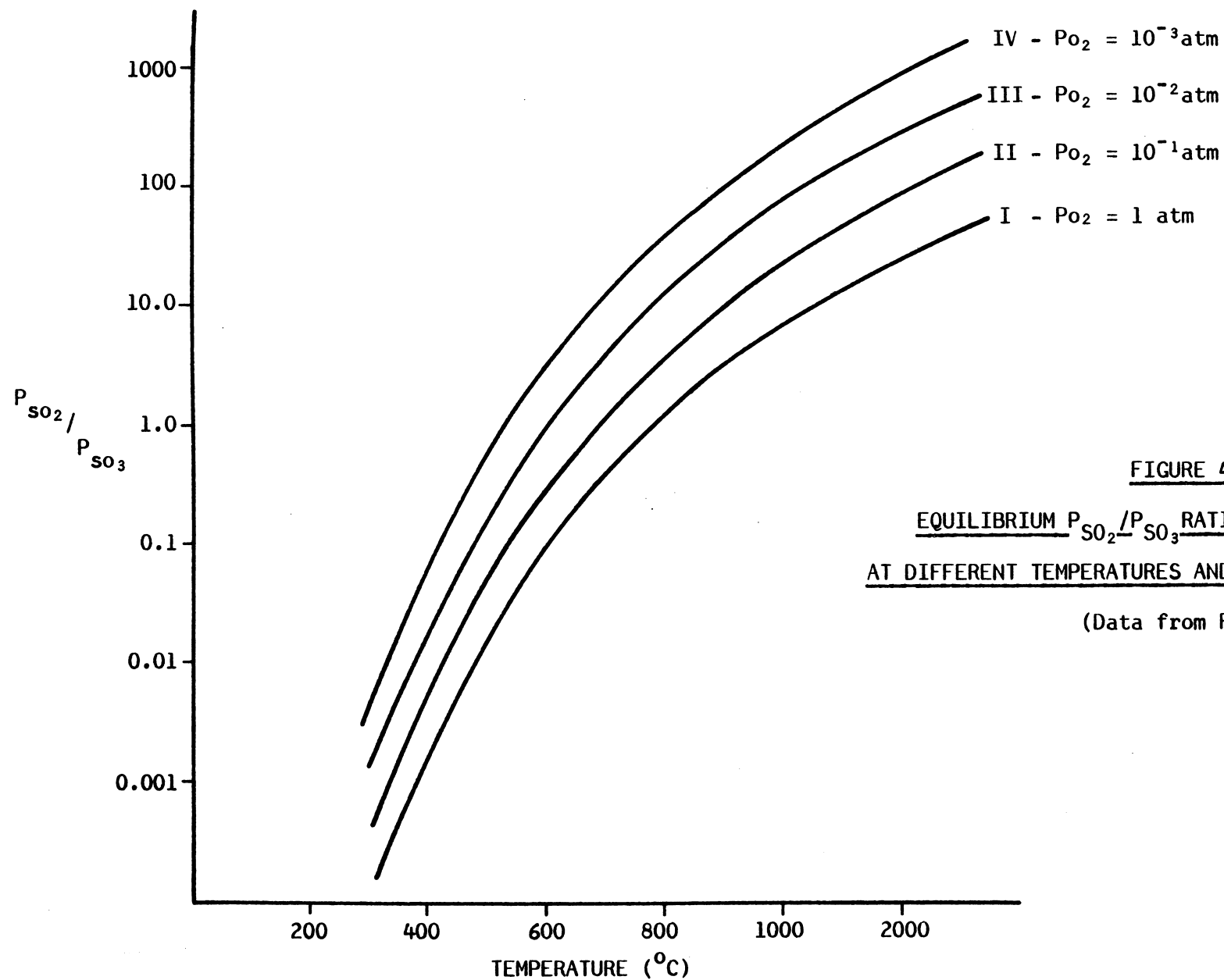


FIGURE 4.14
EQUILIBRIUM P_{SO_2}/P_{SO_3} RATIO FOR EQUATION (4.2)
AT DIFFERENT TEMPERATURES AND OXYGEN PARTIAL PRESSURES
(Data from Refs. 54, 55)

atmospheres a 10% conversion of SO_2 to SO_3 is possible at over 923K. However, the rate of conversion of SO_2 to SO_3 decreases rapidly as the temperature falls and as a result large losses of sulphur to SO_3 do not occur in practice.

The amount of conversion of SO_2 to SO_3 must be determined empirically by analysing material of accurately known sulphide concentration and is obviously dependent on the geometry of the apparatus and the gas flow rate, as these will determine the gas cooling rate. For this reason these two parameters were kept constant throughout this work. The separation between the furnace hot zone and the absorption solution was kept at a minimum (60 cm) to further reduce the degree of SO_2 conversion to SO_3 .

Calibration was performed with accurately weighed (± 0.02 mg) samples of pure Cu_2S - the stoichiometry of which had been confirmed by X-ray diffraction analysis. The amount of Cu_2S used was varied to give a range of titrations similar to those produced in the copper analyses. The time period over which the bulk of the SO_2 was evolved (~ 30 seconds) was similar to that for the copper analyses indicating that similar gaseous SO_2 concentrations were achieved with each.

The results of the calibration tests are summarised in Table 4.3.

The data from tests S1-S6 were used to determine an empirical multiplication factor to enable correction of analysis results for SO_3 formation. (The values for S7 and S8 were not included in the mean value obtained due to large uncertainties associated with the mass and volume measurements.) The mean value of the ratio of (calculated %S) : (theoretical %S) so determined was 0.953 with a standard deviation = 0.004. Thus the multiplication factor used for

TEST NO.	MASS Cu ₂ S (g)	TITRE (ml)	CALC. %S	RATIO: CALC. %S THEORETICAL %S	UNCERTAINTY	
					IN Cu ₂ S WEIGHING (%)	IN TITRATION (%)
S1	0.00452	8.67	19.18	0.952	± 0.4	± 0.9
S2	0.00236	4.50	19.07	0.947	± 0.8	± 1.8
S3	0.00214	4.13	19.30	0.958	± 0.9	± 1.9
S4	0.00204	3.91	19.17	0.952	± 1.0	± 2.0
S5	0.00190	3.64	19.16	0.951	± 1.0	± 2.2
S6	0.00132	2.55	19.32	0.959	± 1.5	± 3.1
S7	0.0058	1.10	18.97	0.942	± 3.4	± 7.3
S8	0.00026	0.52	20.00	0.993	± 7.7	±15.4

TABLE 4.3

SUMMARY OF DATA FOR THE DETERMINATION OF AN
EMPIRICAL SO₃ CONVERSION CORRECTION FACTOR

NOTES

$$1. \text{ Theoretical wt\% S in Cu}_2\text{S} = \frac{32.064}{(32.064 + 2(63.54))} \times 100\%$$

$$= 20.146\%$$

2. For Tests S1-S6:

$$\text{Average ratio} : \frac{\text{Calculated wt\% S}}{\text{Theoretical wt\% S}} = 0.953$$

$$\text{Std. Deviation} = 0.004$$

correction of titration volumes in subsequent copper analyses was 1/0.953 or 1.049. This is similar to the multiplication factor determined by Alcock⁷⁰ of 1.047-1.053 for analysis of sulphur in copper in pure oxygen (500 ml/minute) at 1473K, but significantly lower than the value of 1.11-1.15 obtained by Fincham and Richardson⁷¹ for analysis of steel samples in oxygen (250 ml/minute) at 1673-1723K. The difference is probably attributable to the lower gas flow rate used by Fincham and Richardson and possibly differences in gas transport distances, although the latter could not be determined.

The conversion of SO_2 to SO_3 can be virtually eliminated in combustion analysis by using industrial grade CO_2 rather than oxygen as the combustion gas⁷⁰. However, analysis using CO_2 was found to be unsatisfactory in this work as the SO_2 release from the copper samples was very slow and apparently incomplete - especially when the larger copper samples were used (~ 2 g).

Whereas with oxygen combustion the rate of SO_2 release was very rapid due to the virtually complete wetting of the porcelain boat by the copper oxide "slag" formed, with CO_2 combustion negligible wetting of the porcelain occurred and the liquid copper remained as a large bead in the centre of the boat with an oxidised surface. The very slow SO_2 release rates resulted in considerable uncertainty in determining end-points which were approached very slowly and frequently not reached within 30 minutes. Further, analysis of copper samples from the same billet using both O_2 and CO_2 analyses in some cases resulted in the sulphur concentration determined from O_2 analysis being significantly higher than that determined from the CO_2 analysis - even when the sample had been left in the furnace for

~ 30 minutes during CO₂ analysis and no further change in the intensity of blue colour in the absorption solution was detected. These difficulties are similar to those experienced by Alcock⁷⁰, who found it preferable to use O₂ combustion with an empirical correction factor for analysis of sulphur in 'pure' copper.

Thus the oxygen combustion analysis technique was preferred for use in this work.

4.6.2 Analysis of Other Elements in Copper

4.6.2.1 Calcium and Magnesium

The analysis of copper samples for calcium and magnesium was done using atomic absorption spectrophotometry. The accurately weighed samples (~ 1 g) were dissolved in 5 ml of concentrated nitric acid which was diluted in a volumetric flask to 100 ml with distilled water after filtering to remove small quantities of undissolved solids. These solutions were then analysed on the A.A.S. unit using an air-acetylene flame.

Calibration standards were made from standard stock solutions containing 100 µg/ml of Ca or Mg. The required quantity of stock solution was added to 5 ml of a base solution of 1 g "spec. pure" Cu dissolved in 5 ml conc. HNO₃ and diluted to 100 ml to give the same concentration of Cu and HNO₃ as was present in the analysis solutions. Satisfactory linear calibration curves were obtained that showed good sensitivity, allowing concentrations to be determined to a lower limit of 4 p.p.m. Ca and 10 p.p.m. Mg.

4.6.2.2 Oxygen

Oxygen analyses in copper samples were determined using an industrial "Leco" infra-red oxygen analyser with a lower detection limit of

approximately 2 p.p.m. Care was taken in sample preparation to reduce contamination from surface oxidation of the samples by using block samples (rather than turnings). The samples were cleaned in nitric acid immediately before loading into the vacuum chamber.

4.6.3 Determination of Sulphide in the Fluoride Salt

Fluoride salt samples were analysed for dissolved sulphide after electrolysis using a hydrogen sulphide evolution technique^{72,73}. The apparatus used is depicted schematically in Figure 4.15.

The salt was ground to a fine powder (100% < 170# mesh) in a mortar and pestle. An analysis sample in the range 0.2-1.0 g (depending on sulphide concentration) was weighed to ± 1 mg and placed in the flask (B) and then heated to boiling in 100 ml of 1 : 1 HCl solution that was admitted through the thistle funnel (A). The gas released passed through a condensation bulb (C) to trap HCl vapours and was then bubbled through an ammoniacal zinc sulphate absorption solution (E) through the delivery tube (D) to absorb the SO₂. This was continued until pure HCl vapour was being transported through the tubes and condensing in the absorption solution (i.e. no gas bubbling was observed in the absorption solution), which was typically after 3-4 minutes of boiling. After disconnecting the delivery tube (keeping it in the solution) the absorption solution was acidified with 40 ml of 1 : 1 HCl and immediately titrated with a 0.0100N standard KIO₃ solution to a blue end point using starch solution as an indicator. All titration volumes were corrected for blank determinations which were typically 0.15 ml.

In most cases a small amount of white residue (up to 10% of the original sample weight) remained in the flask after the acid boil. X-ray diffraction powder analysis indicated this was MgF₂ with no

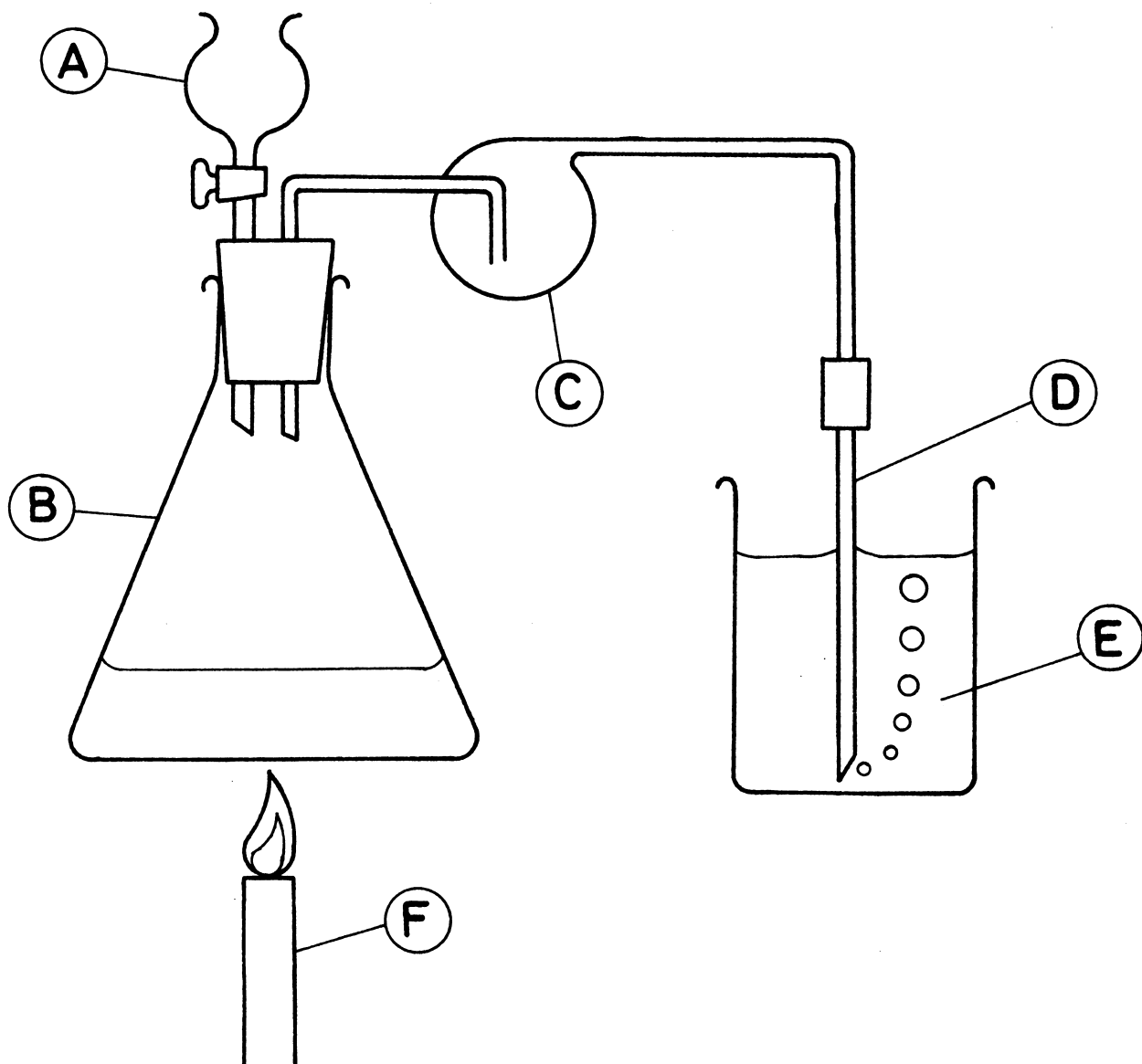


FIGURE 4.15

SCHEMATIC DIAGRAM OF EVOLUTION APPARATUS
FOR SULPHIDE ANALYSIS IN SALTS

Legend:

- | | | | |
|-----|-------------------|-----|---------------------|
| A - | thistle funnel | D - | delivery tube |
| B - | evolution flask | E - | absorption solution |
| C - | condensation bulb | F - | bunsen burner |

diffraction lines for CaF_2 detected. In some cases low concentrations of MgO were detected in the X-ray analysis. It was established that no further sulphide remained in this residue by regrinding and reboiling it in fresh acid solution and passing the gases into a fresh absorption solution. This was effective in completely dissolving the residue, but on no occasion was the required KIO_3 titration greater than that required for a blank determination.

Thus it appears that sulphide in the finely powdered salt sample (probably in the form of CaS and MgS precipitate) is effectively leached from the sample during the 3-4 minutes acid boil, with no indication of retained sulphide in the MgF_2 residue. S.E.M. examination of solidified CaF_2 - MgF_2 melt surfaces revealed a typical lath-like eutectic structure which appeared quite porous (see Figure 4.16) and therefore likely to experience rapid leaching of sulphide inclusions during an acid boil.

The H_2S evolution analysis technique gives a determination only of sulphide-sulphur and does not indicate total sulphur if sulphate ions are also present. To investigate the possibility of sulphate being present in the fluoride salt, some powdered salt samples were analysed for total sulphur using a quantitative fusion technique⁷³. Excellent agreement was achieved with the two techniques indicating that there is negligible sulphate-sulphur present in the fluoride salts. Appendix II gives the details of the fusion technique used and comparative results for fusion and evolution analyses.

These results are to be expected, as with a very low oxygen potential over the melt negligible sulphate formation would be expected. In investigating sulphur distributions in

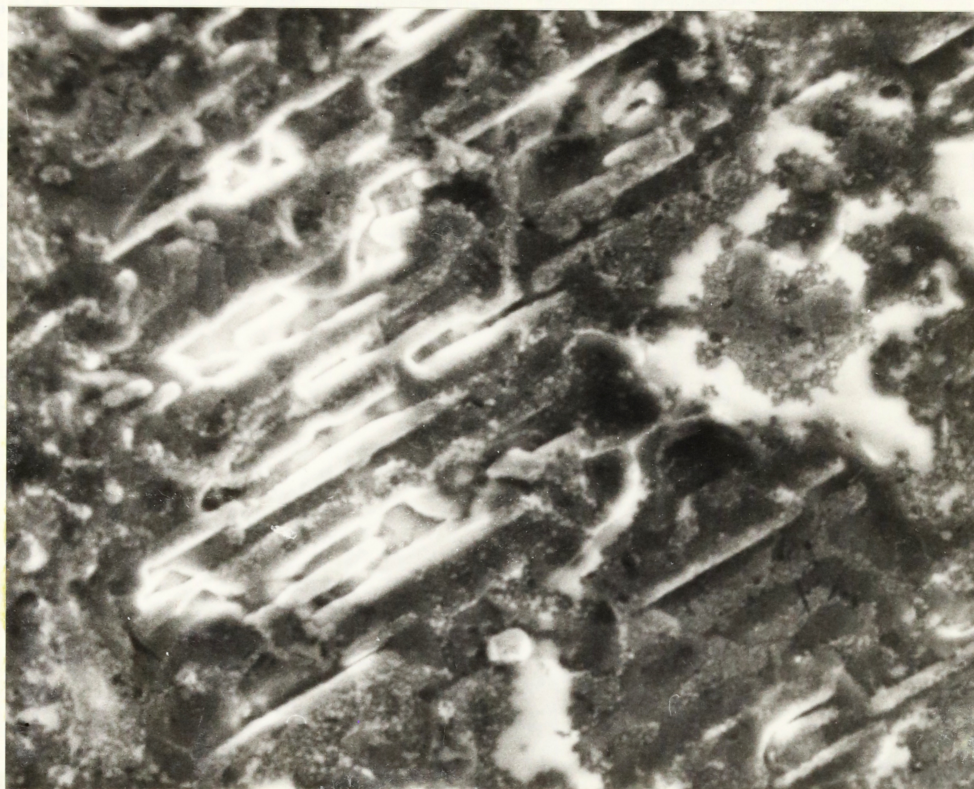


FIGURE 4.16

SCANNING ELECTRON PHOTOMICROGRAPH

OF THE SURFACE OF

THE SOLIDIFIED FLUORIDE SALT

(X2000)

CaO-Al₂O₃-SiO₂ slags at 1773K, Fincham & Richardson⁷⁴ showed that the sulphur/oxygen equilibrium strongly favours sulphide formation for $P_{O_2} < 10^{-6}$ atmospheres while sulphate formation is predominant for $P_{O_2} > 10^{-3}$ atmospheres. In this work where the deoxidised argon gas subsequently passed over graphite electrode fittings in the furnace at a temperature of 1273-1423K, oxygen partial pressures less than 10^{-10} atmospheres could be expected.

4.6.4 Determination of Carbon Tetrafluoride in Gases

During some electrolysis experiments the exit gases from the furnace were analysed for gaseous CF₄ using a simple absorption technique, utilising the slight solubility of CF₄(g) in water⁷⁵. The apparatus used is represented in Figure 4.17.

The exit gases were drawn through the absorption vessel (E) containing 150 ml of distilled water from the suction provided by a downstream vacuum pump. The suction was adjusted using a flow valve (C) to maintain approximately atmospheric pressure at the pressure gauge (A). Teflon (PTFE) tubing (D) was used where possible, while the gas delivery tube (B) was thoroughly dried before use to prevent CF₄ absorption occurring before contact with the absorption solution. All exposed metal surfaces such as the inside surface of the lower brass flange (F) and the inner surfaces of the gas exit tube (G) were sprayed with a PTFE coating to reduce the possibility of any metal/gas reactions.

The initial and final concentrations of fluoride ion in the absorption solutions were determined using a fluoride selective-ion

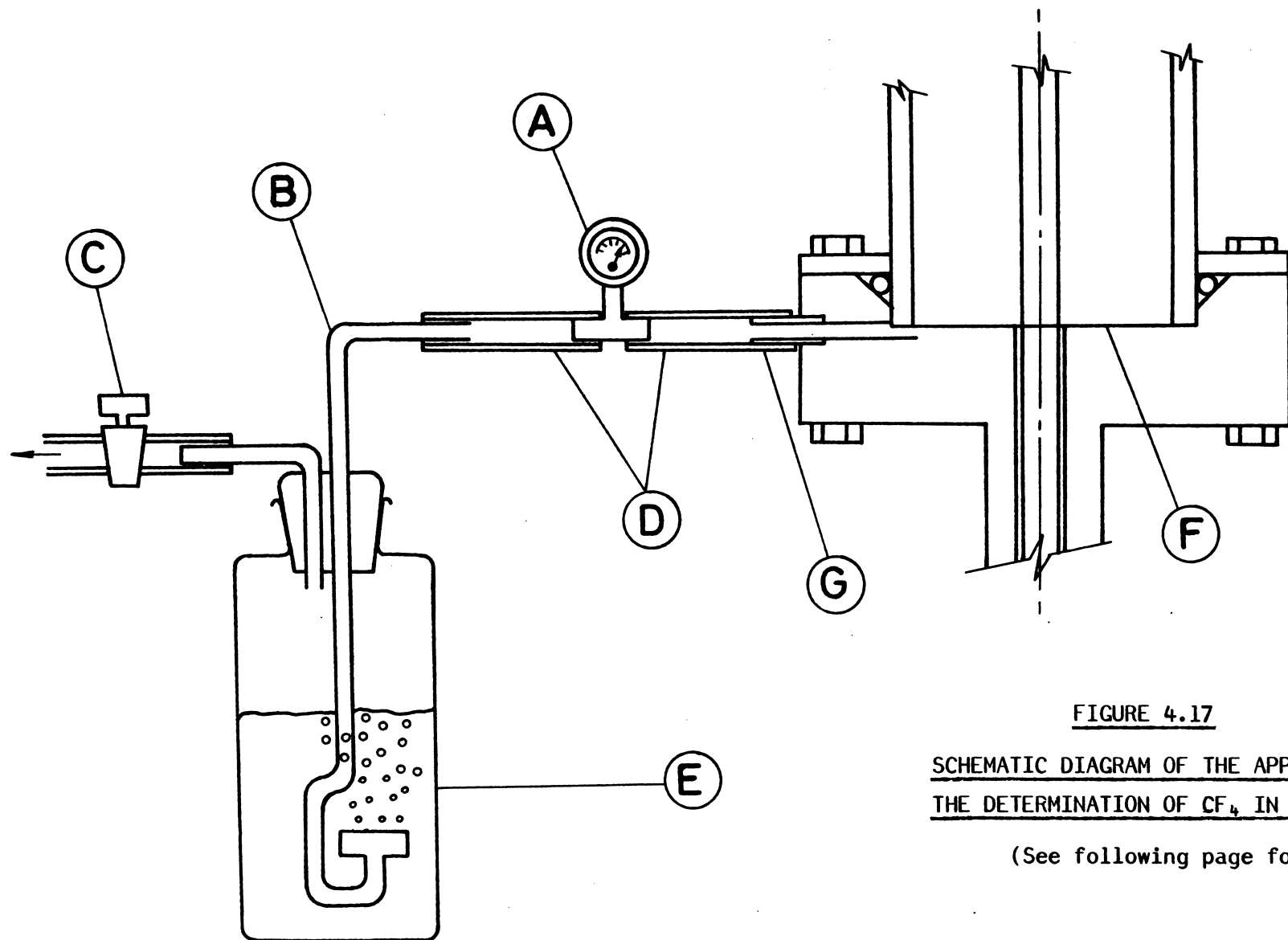


FIGURE 4.17

SCHEMATIC DIAGRAM OF THE APPARATUS FOR
THE DETERMINATION OF CF_4 IN EXIT GASES

(See following page for legend)

FIGURE 4.17

SCHEMATIC DIAGRAM OF THE APPARATUS FOR
THE DETERMINATION OF CF₄ IN EXIT GASES

LEGEND:

- A - Pressure gauge
- B - Pyrex gas delivery tube
- C - Flow control valve
- D - Teflon (PTFE) tubing
- E - Absorption vessel
- F - Lower brass furnace flange
- G - Furnace gas exit tube

electrode[†] in conjunction with a double junction silver/silver-chloride reference electrode. The solution was pretreated with a "total ionic strength adjustment buffer" (T.I.S.A.B.) which served to fix the ionic strength of the sample, to release fluoride from complexes and to buffer to a pH of about six. Details of the preparation of the T.I.S.A.B. solution are given at the end of this section.

The selective ion electrode shows a sensitive response to fluoride ion activity over the range saturated to 10^{-6} M. The relative accuracy achieved for low concentrations is the same as that for high concentration ranges due to the logarithmic relationship between activity and millivolts. For calibration of the electrode, solutions of known fluoride concentration made from a 1 g/l F^- standard stock solution (1.1053 g NaF dissolved in 500 ml distilled water) were used.

The completeness of absorption was checked with a second identical absorption bottle placed in series with the first. In cases when the first absorption solution showed a significant increase of fluoride ion concentration due to CF_4 absorption, no increase in fluoride ion concentration was detected in the second vessel, indicating that the gaseous CF_4 was effectively 100% captured in the first vessel.

[†] "Townson" fluoride selective ion electrode (type S-101); Manufactured by Townson and Mercer, N.S.W., Australia.

4.6.4.1 Preparation and Use of T.I.S.A.B. Solution

The T.I.S.A.B. solution was prepared as follows: 57 ml of glacial acetic acid, 58 g of NaCl and 0.30 g of sodium nitrate were dissolved in about 500 ml of distilled water. The pH was adjusted to 5-5.5 with 5 M NaOH, then the solution was allowed to cool to room temperature and made up to 1 litre in a volumetric flask.

For analysis work all standards and samples were diluted 1 : 1 with T.I.S.A.B. solution.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 DATA TREATMENT AND PRESENTATION

5.1.1 Sulphur Mass Balances after Electrolysis

In the following sections the sulphur mass balance after the completion of electrolysis is expressed as a final sulphur distribution, i.e. the percentage of the total initial sulphur in the copper reporting to the copper, salt and gas phase respectively after electrolysis. In calculating the sulphur distribution the following procedures were followed:

1. The respective masses of the copper and fluoride salt phases after electrolysis were assumed to be equal to the original masses of these two phases charged to the crucible before electrolysis.
2. The amount of sulphur reporting to the gas phase during electrolysis was calculated by difference from the total amount of sulphur initially in the system and the combined amounts of sulphur determined in the copper and salt phases after electrolysis.

The first procedure was necessary because complete separation and individual quantitative weighing of the solidified copper and salt phases after electrolysis was not possible (as described in section 4.5.4). It was not expected to introduce significant errors into the mass balances. Typically, the total weight loss of the copper and salt resulting from the salt pre-drying and subsequent

sulphur discharge during electrolysis totalled no more than 0.08 g. Thus it was considered reasonable for the purposes of mass balances to assume unchanged masses of copper and salt.

The second procedure described above was necessary because the sulphur discharged from the fused salt to the gas phase was not collected quantitatively due to the difficulties arising from condensation in the reaction tube and the small quantities (< 40 mg) of sulphur. Thus, calculation of this value by difference was considered adequate with accurate analyses of sulphur in the copper and salt phases.

5.1.2. Current Efficiencies

Unless otherwise stated in the following sections, it is assumed that the term "current efficiency" refers specifically to the current efficiency with respect to sulphur transfer at the electrode being considered.

The overall current efficiency is defined as the average current efficiency for the entire electrolysis, and thus is equal to the ratio (expressed as a percentage) of the faradic equivalent of sulphur transferred, to the total amount of current-passed. The overall current efficiency value for electrolysis gives no specific information as to the value of the instantaneous current efficiency at any particular stage of electrolysis, but if the rate of change of the overall current efficiency at any particular stage of electrolysis is known then the instantaneous current efficiency can be calculated.

5.1.3. Electrolysis Curves

In most cases the electrolysis curves presented in this section are average electrolysis current versus time curves and do not show the short term current fluctuations that normally are observed during

electrolysis. The average electrolysis curves were estimated as described in Section 4.5.6. The use of average electrolysis current curves makes the direct comparison of various types of electrolysis curves less complicated.

Where various experiments have produced a family of electrolysis curves of the one type, use has been made of a "typical" electrolysis curve to represent that type of curve in subsequent analysis of the basic features of the curves, and in comparisons with other types of electrolysis curves.

In each case the "typical" electrolysis curve has been constructed from a determination of the mean value of the electrolysis current for the individual electrolysis curves at various positions along the time axis.

5.1.4 Faradic Equivalents

Faradic (or coulombic) equivalents of electrochemically transported species are expressed in milliamperes-hours (mAh) in this work. They have been calculated using Faraday's law which can be expressed in the form:

$$I.t = \frac{gnF}{A} \quad \dots 5.1$$

where

$I.t$ = faradic equivalent (mA.h)

g = mass of transported substance (g)

n = number of electrons involved in electrochemical reaction

F = Faraday's constant (26802 mAh/mole)

A = atomic weight of the substance

The calculated multiplication factors (nF/A) used for conversion of masses to faradic equivalents are summarised below:

sulphur	:	$\text{mAh} = g_{\text{S}} \times 1672$	(n = 2)
calcium	:	$\text{mAh} = g_{\text{Ca}} \times 1337$	(n = 2)
magnesium	:	$\text{mAh} = g_{\text{Mg}} \times 2204$	(n = 2)
oxygen	:	$\text{mAh} = g_{\text{O}} \times 3350$	(n = 2)
fluorine	:	$\text{mAh} = g_{\text{F}} \times 1411$	(n = 1)
carbon	:	$\text{mAh} = g_{\text{C}} \times 4467$	(n = 2)
		$= g_{\text{C}} \times 8933$	(n = 4)

5.2 PRELIMINARY INVESTIGATIONS

5.2.1 Decomposition Potential of the Fluoride Melt

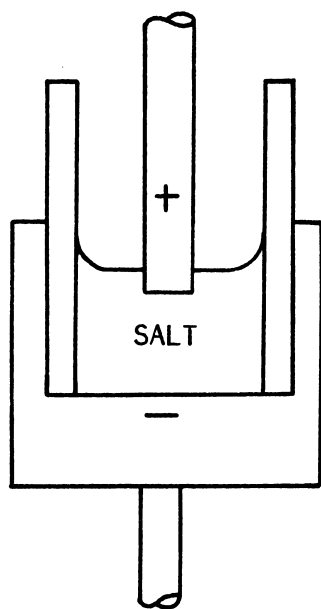
Two different cell configurations were used to determine the decomposition potential of the calcium fluoride-magnesium fluoride eutectic melt, as depicted in Figure 5.1. A graphite cathode was used in the type I, cell while a liquid copper cathode was used in the type II cell, both having a graphite anode. A nominal 7.5 g of salt mixture was used in each case and subjected to the normal pre-electrolysis drying treatment. The copper used in the type II cell (39.5 g) was cathode copper feed which had been deoxidised for 12 hours at 1423K in a graphite crucible.

The slow sweep current-voltage curves obtained are shown in Figure 5.2. In the initial sweeps obtained immediately after the cell temperature was reached, the onset of significant current flow was observed at fairly low voltages, viz:

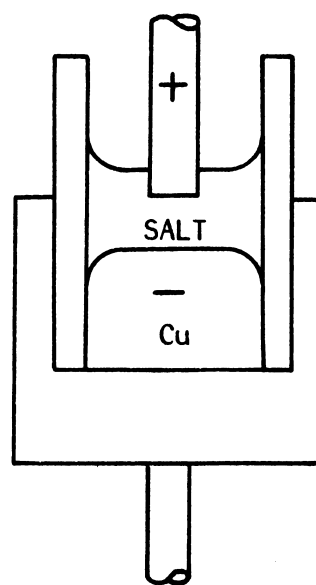
Type I cell - 1.15 V (Point B)

Type II cell - 0.95 V (Point A)

These low voltage decomposition reactions were attributed to the presence of low level impurities in the melt. In order to eliminate these impurities the melt was electrolysed at a constant potential of



TYPE I - GRAPHITE ANODE
GRAPHITE CATHODE



TYPE II - GRAPHITE ANODE
COPPER CATHODE

FIGURE 5.1

SCHEMATIC REPRESENTATION OF THE TWO CELL
CONFIGURATIONS USED FOR DETERMINATION OF
THE DECOMPOSITION POTENTIAL

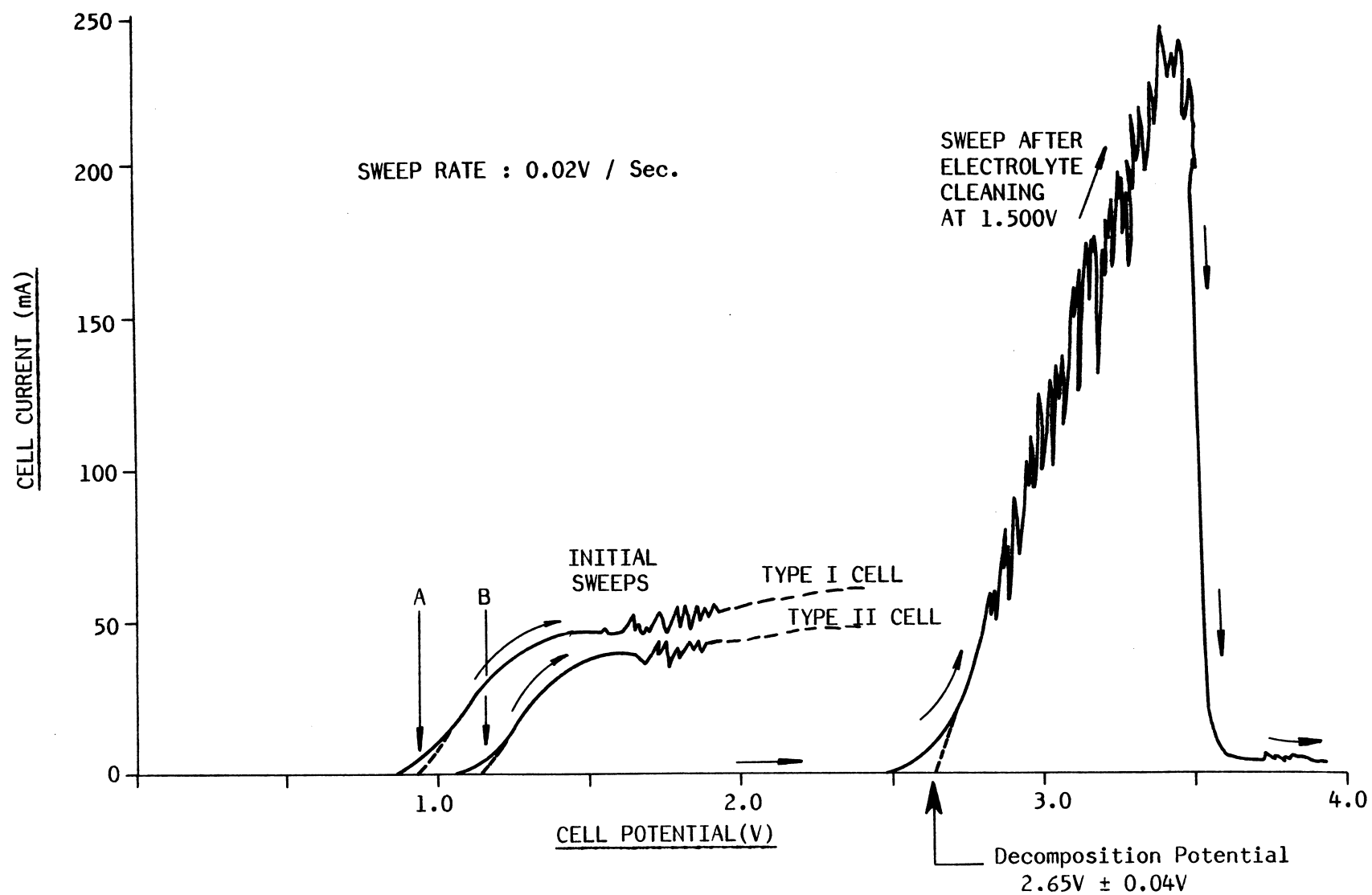


FIGURE 5.2
SLOW-SWEEP CURRENT/VOLTAGE CURVES

1.500 V for 3-4 hours. In this period the electrolysis current decayed from an initial level of 30-40 mA to less than 1 mA, indicating effective depletion of the impurity species.

Subsequent slow sweep current-voltage curves obtained with the cleaned electrolyte gave an indicated decomposition potential of the fluoride melt of 2.65 V with a reproducibility of ± 0.04 V. A typical curve obtained is shown in Figure 5.2. The same decomposition potential was obtained for both type I and type II cells. This value shows excellent agreement with the theoretical calculated value of 2.68 V (Section 3.2).

A sudden drop in current to low levels (approximately 10 mA) was observed when a cell potential of 3.3-3.4 V was reached (see Figure 5.2), and no further significant current flow was obtained until the cell potential dropped to below 3.2-3.3 V on the return sweep. This behaviour is typical of the "anode effect" commonly observed with electrolytic decomposition of fluoride melts^{47,76}, and is probably due to the formation of a non-conducting film of gaseous carbon-flourine compounds over the anode surface when high current densities are achieved, thereby preventing wetting of the anode surface by the electrolyte⁶⁷.

Chemical analysis of the cathode copper from the type II cell indicated a significant build-up of magnesium and, to a lesser extent, calcium. The analysis data and calculated faradic equivalents for electrochemical transfer of the Ca and Mg into the copper by a two-electron transfer reaction are summarised in Table 5.1.

These results show that the liquid copper phase is acting as a fairly effective sink for reduced magnesium and calcium metal liberated at the copper/salt interface. The faradic equivalent of

	Mg	Ca
INITIAL Cu ASSAY (wt%)	N.D.	N.D.
FINAL Cu ASSAY (wt%)	0.072	0.014
MASS TRANSFERRED IN 39.50 g Cu	28.4 mg	5.5 mg
FARADIC EQUIVALENT	62.6 mAh	7.4 mAh

TOTAL [Mg + Ca]_{Cu} FARADIC EQUIVALENT = 70.0 mAh

TOTAL CURRENT PASSED = 116.8 mAh

TABLE 5.1

CHEMICAL ANALYSIS AND CALCULATED FARADIC
EQUIVALENTS OF Ca AND Mg IN CATHODE COPPER
FROM TYPE II CELL DECOMPOSITION POTENTIAL DETERMINATIONS

these two metals transferred is 60% of the total current-passed, therefore it can be concluded that at least 60% of the combined magnesium and calcium liberated at the cathode dissolves in the liquid copper phase.

The results also show that magnesium reduction is the dominant cathode reaction, which is a consequence of the greater thermodynamic stability of calcium fluoride as compared to magnesium fluoride.

It is interesting to note that the same decomposition potential was obtained with both a graphite cathode and a liquid copper cathode. From this it can be concluded either that there is no significant cathodic depolarization occurring in either case or that the cathodic depolarization is identical in each case.

The former is more probable considering the good agreement between the experimentally determined value and the calculated theoretical value of the decomposition potential which was derived assuming no cathodic depolarization. Further, it is unlikely that the magnitude of cathodic depolarization (if occurring) would be identical for the two cell types.

As discussed in Section 3.1, the cathodic reaction occurring at the onset of decomposition is the liberation of magnesium vapour at the cathode interface. In the type II cell any depolarization must arise from dissolution of this magnesium in the liquid copper, and sufficiently rapid diffusion of the dissolved magnesium away from the cathode interface to maintain an activity of magnesium in the copper adjacent to the interface significantly less than unity. However, in the type I cell the only possible depolarization mechanism is rapid dissolution of the magnesium vapour in the molten salt and subsequent

rapid diffusion of the dissolved magnesium away from the cathode interface[†].

The likelihood of these two totally different depolarization mechanisms giving an identical cathodic depolarization potential would seem remote.

It is reasonable to assume that any cathodically liberated magnesium and calcium which did not report to the liquid copper phase would undergo dissolution in the molten salt phase, since the molten fluoride salt is expected to have a high affinity for these metallic species (Section 3.2). In this case the amount of current passed which was not accounted for by magnesium and calcium dissolved in the copper is $116.8 - 76.0 = 48.8$ mAh. If it is assumed that this current resulted in the reduction of magnesium and calcium at the cathode in the same relative proportions as indicated by the copper analysis, and that this reduced metal dissolved entirely in the fluoride salt (total mass = 7.49 g), then this would result in maximum concentrations of 0.26 wt% and 0.05 wt% for $(\text{Mg})_{\text{salt}}$ and $(\text{Ca})_{\text{salt}}$ respectively. These values are expected to be significantly lower than the saturation concentrations of Mg and Ca in the fused salt.

5.2.2 Desulphurisation with No Electrolysis

In order to determine the significance of non-electrolytic sulphur transfer from metal to salt in this system, the desulphurising

[†]NOTE: The formation of magnesium-carbon compounds at the cathode interface is not expected as these compounds are not thermodynamically stable at 1423K:

$(\Delta G_f^{\circ} \text{Mg}_2\text{C}_3(\text{s}) = + 54.53 \text{ kJ/mole}; \Delta G_f^{\circ} \text{MgC}_2(\text{s}) = + 71.40 \text{ kJ/mole at } 1423\text{K}^{54,55}.)$

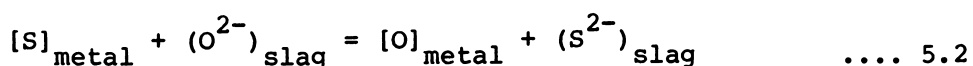
capacity of the fluoride melt in three liquid copper/molten salt contact runs with no electrolysis was investigated. The details of these runs are summarised in Table 5.2.

The results indicate:

1. The fluoride melt has a very low desulphurising capacity, with the sulphur distribution strongly favouring the metal phase after 5 hours contact (runs A1, A2).
2. The rate of sulphur transfer is slow with no detectable transfer after 20 minutes contact (run A3).
3. Similar sulphide concentrations in the molten salt were achieved with the high-sulphur run (A1) and the low sulphur run (A2) after five hours.

These results are consistent with those of other workers, who have investigated the desulphurising capacity of pure calcium fluoride melts in contact with liquid metals. Kor and Richardson⁷⁷ and Davies⁷⁸ concluded that pure CaF_2 melts do not take up sulphur and have a negligible sulphur capacity, while Zhmoydin and co-workers⁷⁹, in reviewing work by other Russian workers in this field, concluded that "it is unanimously noted that both high-silica slags and purely fluoride slags are poor desulphurisers".

It is recognised that any transfer of sulphur that does take place between liquid metal and a fluoride slag (or molten salt) is predominantly by sulphur-oxygen exchange^{77,78,80} via the reaction:



and that the activity of oxide ions in the slag phase is the dominant factor in determining desulphurising capacity. Hence it has been found that the presence of oxide impurities in CaF_2 melts leads to

RUN	MASS Cu (g)	MASS SALT (g)	MELT CONTACT TIME (MINS)	wt% S IN Cu		FINAL wt% S IN SALT	FINAL SULPHUR DISTRIBUTION	
				INITIAL	FINAL		COPPER (%)	SALT (%)
A1	45.02	8.46	300	0.651	0.651	0.030	99	1
A2	40.94	7.91	300	0.088	0.082	0.023	95	5
A3	41.21	7.93	20	0.084	0.084	N.D.	100	0

TABLE 5.2

NON-ELECTROLYSIS RUNS

- A1 - High sulphur, long contact
- A2 - Low sulphur, long contact
- A3 - Low sulphur, short contact

an increase in the desulphurising capacity of these melts^{77,78,79}, and fluoride slags with high lime levels have proved to be very powerful desulphurisers.

It is probable, therefore, that the dominant factor in determining the non-electrolytic desulphurising capacity of the $\text{CaF}_2\text{-MgF}_2$ melts in this work is the presence of low level oxide impurities in the melt. As previously discussed (Section 5.2.1) the presence of low level oxide impurities in the salt melt was indicated by a low-voltage current rise. Thus, a higher impurity concentration in run A2 as opposed to run A1 (which had a significantly higher sulphur concentration in the copper) could result in the indicated higher desulphurising capacity of the former.

5.2.3 Extended Potentiostatic Electrolysis

As a preliminary investigation in order to determine the minimum sulphur levels in copper attainable for electrolyses at different cell potentials below the decomposition potential of the fluoride salt, four extended-time potentiostatic electrolysis runs were carried out at cell potentials of 0.600 V, 1.500 V, 2.000 V and 2.500 V. In each case electrolysis was continued for a sufficient time to allow the cell current to drop to what was effectively a residual current ($\sim 2\text{mA}$), after which no further significant decrease in current occurred. This also gave a preliminary investigation of the "self-cleaning" capacity of the fluoride electrolyte, that is, the ultimate degree of elimination of sulphide from the fused salt resulting from anodic discharge.

In each case a small type A1 anode was used. The masses of copper and fluoride salt were approximately 40 g and 8 g

respectively. The copper was doped to nominally 0.1 wt% sulphur except in the case of the 0.600 V run in which a high sulphur (0.642 wt%) doped copper sample was used.

The electrolysis curves obtained are shown in Figure 5.3. Table 5.3 summarises details of these runs including the final sulphur mass balances calculated from the assay data.

Each of the electrolysis curves is characterised by an initial current rise to a maximum, followed by a steady current decay to a residual value. The effects of increased cell potential are:

1. Higher initial current
2. More rapid initial current rise
3. Higher peak current
4. More rapid current decay to residual levels

Very low ultimate sulphur levels in copper were achieved with less than 1.5 p.p.m. in runs B2, B3, B5 and 15 p.p.m. in run B1 which was the high-sulphur copper sample electrolysed at a cell potential of only 0.600 V. Further, for the range of cell potentials from 0.600-2.500 V, virtually complete anodic discharge of dissolved sulphide in the salt phase is achieved, ranging from 89.1% of total sulphur eliminated in run B3 (1.500 V) to 97.6% of total sulphur in run B2 (2.500 V). This clearly demonstrates that the electrolyte does have a "self-cleaning" capacity - even at applied potentials as low as 0.600 V.

No build-up of calcium and magnesium in the copper was detected in the 0.600 V electrolysis. However, in the other electrolyses at 1.500 V or greater, a significant build-up of these metals occurred, with magnesium dissolution predominating. These analyses confirm that

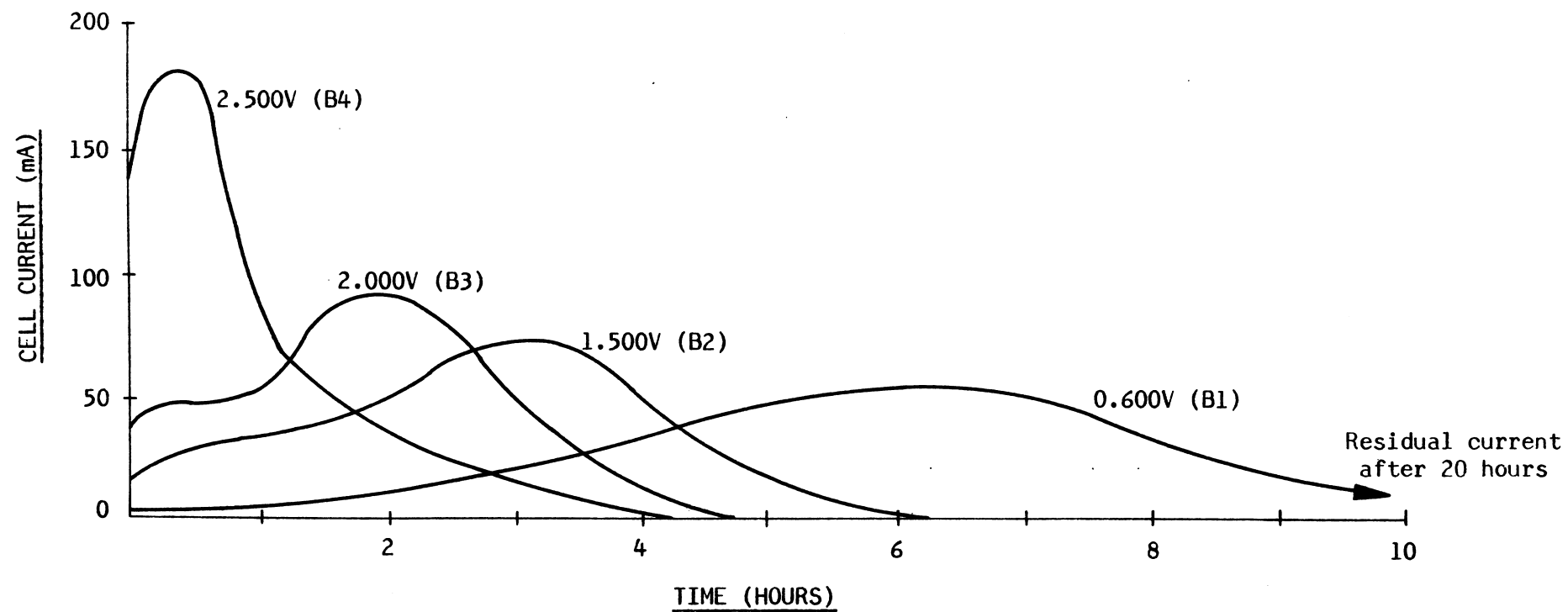


FIGURE 5.3

ELECTROLYSIS CURVES FOR EXTENDED POTENTIOSTATIC
ELECTROLYSIS BELOW THE DECOMPOSITION POTENTIAL

RUN	CELL VOLTAGE	ELECTROLYSIS TIME (hrs)	MASS Cu (g)	MASS SALT (g)	TOTAL CURRENT PASSED (mAh)
B1	0.600	20	40.10	8.02	490
B2	1.500	12	39.87	7.94	133
B3	2.000	5	39.92	7.88	108
B4	2.500	10	40.00	7.82	176

RUN	wt% [S] IN Cu		FINAL wt% (S) IN SALT	FINAL SULPHUR DIST. (% TOTAL SULPHUR)			FINAL Cu ASSAY (wt%)	
	INITIAL	FINAL		COPPER	SALT	GAS	Mg	Ca
B1	0.642	0.0015	0.303	0.2	9.8	90.0	N.D.	N.D.
B2	0.082	N.D.	0.010	-	2.4	97.6	0.020	0.0062
B3	0.089	N.D.	0.049	-	10.9	89.1	0.006	0.0032
B4	0.085	N.D.	0.011	-	2.5	97.5	0.036	0.0070

TABLE 5.3

DETAILS OF EXTENDED POTENTIOSTATIC ELECTROLYSIS RUNS

calcium and magnesium discharge reactions can occur at the cathode with an applied cell voltage as low as 1.500 V, but there is no evidence of these reactions occurring at a cell potential of 0.600 V.

The overall current efficiency data for these runs is summarised below:

<u>RUN</u>	<u>CATHODE C.E. (%)</u>	<u>ANODE C.E. (%)</u>
B1	88	87
B2	47	46
B3	55	49
B4	37	37

The low voltage electrolysis (B1) resulted in a high current efficiency at both electrodes, but sulphur transfer rates were very low. Higher cell potentials resulted in more rapid transfer rates but lower current efficiencies at both electrodes, with current efficiency values for run B4 (2.500 V) significantly lower than for runs B2 and B3 (1.500 V and 2.000 V respectively). This behaviour is indicative of a greater proportion of the current flow being utilised in non-sulphur transferring electrode reactions as the cell potential is increased.

In each case the values for the overall cathodic and anodic current efficiencies are quite similar - a necessary consequence of extended electrolysis runs in which the electrolysis is continued until virtually all the sulphur is electrolysed out of both the liquid copper and molten salt phases.

The fact that no sulphur was detected in the copper in runs B2, B3 and B4 obviates the possibility of significant sulphur reversion from the salt phase occurring during cooling of the melt after

completion of electrolysis in these runs, particularly in run B3 in which the sulphide concentration in the salt was the higher of the three (0.05 wt%).

In run B1 the sulphur level in the salt phase was significantly higher (0.303 wt%) and 15 p.p.m. sulphur was detected in the electrolysed copper. However, it is probable that this is due to incomplete removal of sulphur from the copper rather than reversion from the salt phase. Subsequent electrolysis experiments (see Section 5.3) in which similar final sulphur in salt levels were achieved produced no detection of sulphur in the copper phase after the standard cooling procedures.

The solidified copper recovered from each run was very clean with no evidence of surface oxidation or contamination (e.g. from precipitation of impurities during cooling). The solidified salt was dense and pure white with no discoloration. No trace of any precipitated sulphide phases was detected at the salt/copper interface or on the upper surface of the salt (confirmed through visual inspection and X-ray powder diffraction analysis of samples scraped from the surface) - which would be expected if precipitation of solid sulphides (CaS or MgS) from the salt melt was occurring.

Inspection of the lower regions of the alumina furnace tube revealed a soft yellow solid deposit on the inner surface in the region of the lower water cooled jacket after each electrolysis run. Samples of this deposit scraped off and analysed using X-ray powder diffraction techniques gave a positive identification as orthorhombic sulphur. The diffraction lines observed and relative intensities are listed in Appendix III, and it can be seen that all the lines detected correspond to orthorhombic sulphur diffraction lines with no other

lines observed. Condensation of any sulphur gas present (boiling point = 718K^{15}) was expected in this region with the constant flow of argon maintained during electrolysis from the top of the furnace tube to the exit near the base.

5.3 POTENTIOSTATIC ELECTROLYSIS AT 2.500 VOLTS

After determining that, for extended potentiostatic electrolysis, very low sulphur levels in copper and virtually complete discharge of the sulphide from the salt phase could be achieved over the range of cell potentials from 0.600 V to 2.500 V, the change in sulphur distribution during the progress of electrolysis at 2.500 V was investigated with a series of electrolysis runs.

Three different anode size ranges were used, and accordingly the results are divided into three series:

C Series - anode area approximately 0.25 cm^2 (small anode)

D Series - anode area approximately 0.50 cm^2 (medium anode)

E Series - anode area approximately 0.80 cm^2 (large anode)

The details of these electrolysis runs with initial and final analysis data, and the final sulphur distributions are given in Table 5.4, while the electrolysis curves obtained are shown in Figure 5.4. It should be noted that in Figure 5.4 different time and current scales are used on each of the three sets of axes.

It should also be noted in Table 5.4 that:

1. Due to the anode shielding phenomena (detailed in Section 4.5.7) it was not possible to achieve a constant true anode area for successive runs in one anode size range. Thus a significant variation in true anode area within each of the three anode size ranges is observed.

RUN NO.	ANODE AREA (cm ²)	ELECTROLYSIS TIME (min)	TOTAL CURRENT PASSED (mAh)	MASS COPPER (g)	MASS SALT (g)	wt% S IN Cu		FINAL wt% S IN SALT	FINAL SULPHUR DIST. (% OF TOTAL S)			FINAL Mg/Ca ANALYSES IN Cu	
						INITIAL	FINAL		IN Cu	IN SALT	IN GAS	wt% Mg	wt% Ca
C1	0.20	14.0	43.4	41.79	9.83	0.093	0.041	0.150	44.1	38.8	18.1	N.D.	0.0038
C2	0.24	29.0	54.0	39.58	7.82	0.085	0.014	0.196	16.5	45.6	37.9	N.D.	N.D.
C3	0.25	56.0	90.4	42.31	7.91	0.079	0.0009	0.130	1.1	30.8	68.1	0.007	N.D.
D1	0.48	4.0	24.8	38.69	9.82	0.089	0.051	0.089	57.3	25.3	17.4	N.D.	0.0062
D2	0.50	6.0	36.2	35.12	9.89	0.088	0.034	0.140	38.6	44.8	16.6	N.D.	0.0036
D3	0.51	10.0	79.8	40.73	7.98	0.088	0.010	0.220	11.4	49.2	39.4	N.D.	0.0071
D4	0.52	11.0	68.3	41.15	9.88	0.092	0.010	0.185	10.9	47.5	41.6	N.D.	N.D.
D5	0.49	22.0	85.0	40.12	9.69	0.084	0.004	0.109	4.8	32.0	63.2	0.012	0.0046
D6	0.53	35.0	101.6	43.43	7.84	0.084	N.D.	0.068	0.0	18.1	81.9	0.018	0.0062
D7	0.41	40.0	116.4	38.53	9.72	0.082	0.003	0.073	3.7	18.1	78.2	0.028	N.D.
D8	0.50	60.0	196.1	40.04	9.72	0.092	N.D.	0.020	0.0	5.3	94.7	0.026	0.0100
E1	0.82	2.5	38.0	41.36	9.78	0.087	0.038	0.141	43.7	38.3	18.0	N.D.	N.D.
E2	0.78	5.0	63.3	40.17	9.87	0.086	0.012	0.187	14.0	53.4	32.6	N.D.	0.0030
E3	0.83	7.5	85.0	39.92	9.72	0.083	N.D.	0.136	0.0	39.9	60.1	0.013	0.0028

TABLE 5.4

DATA FOR 2.500 V POTENTIOSTATIC ELECTROLYSIS RUNS

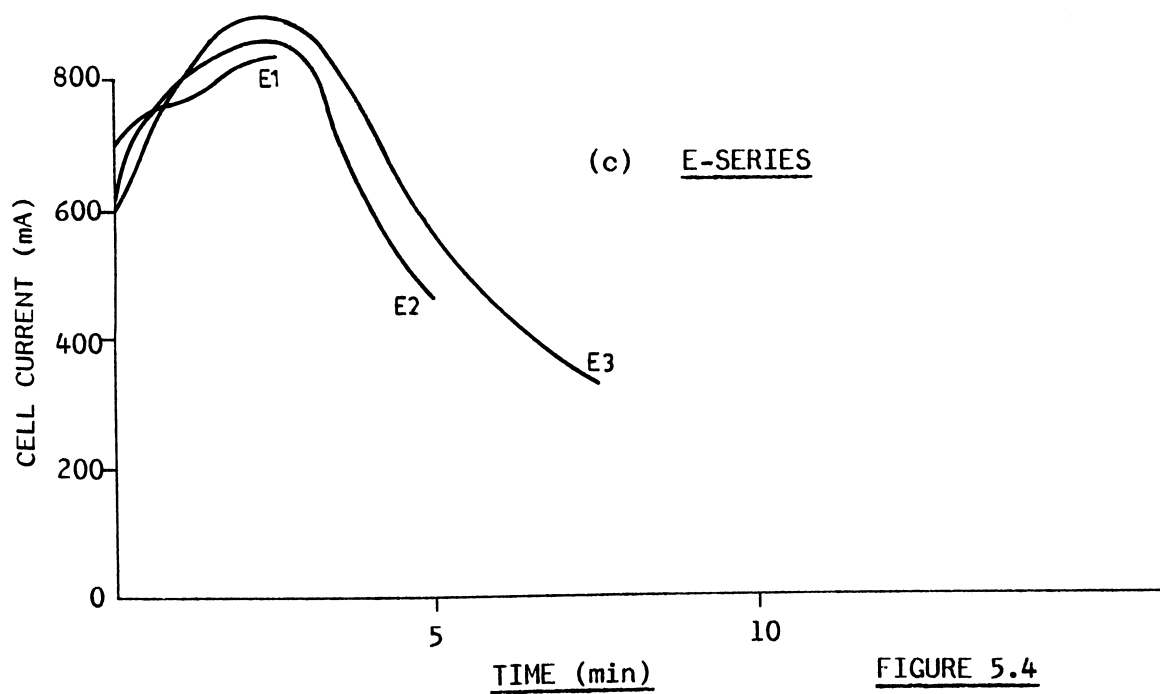
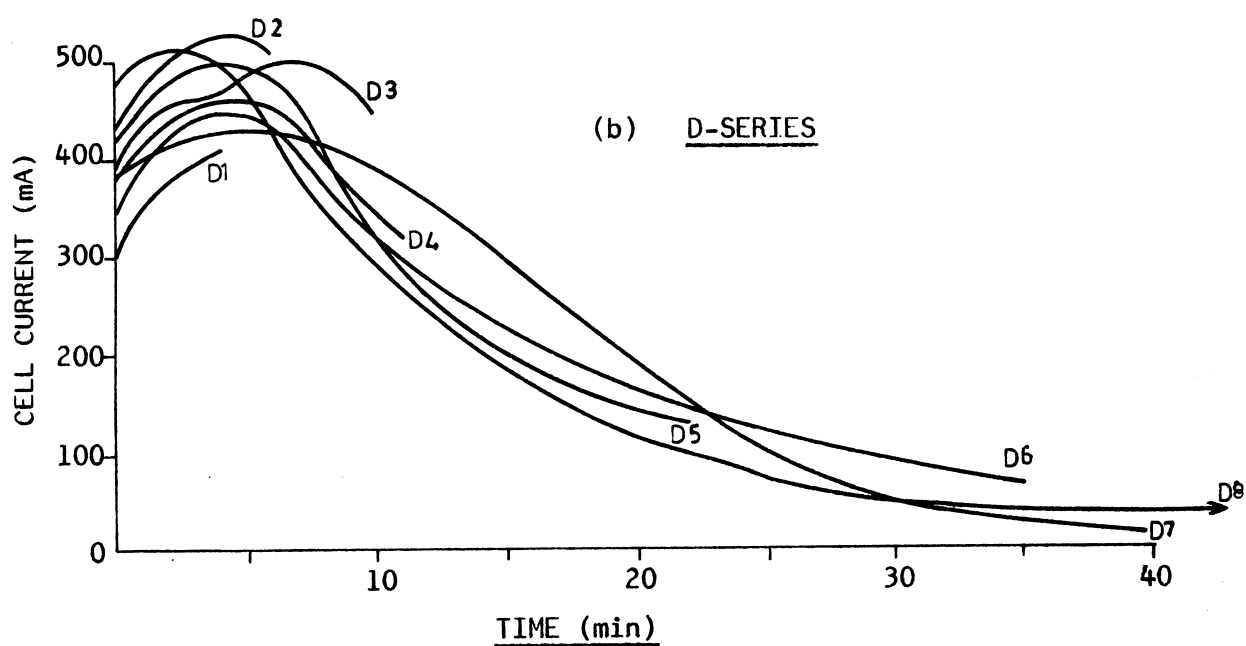
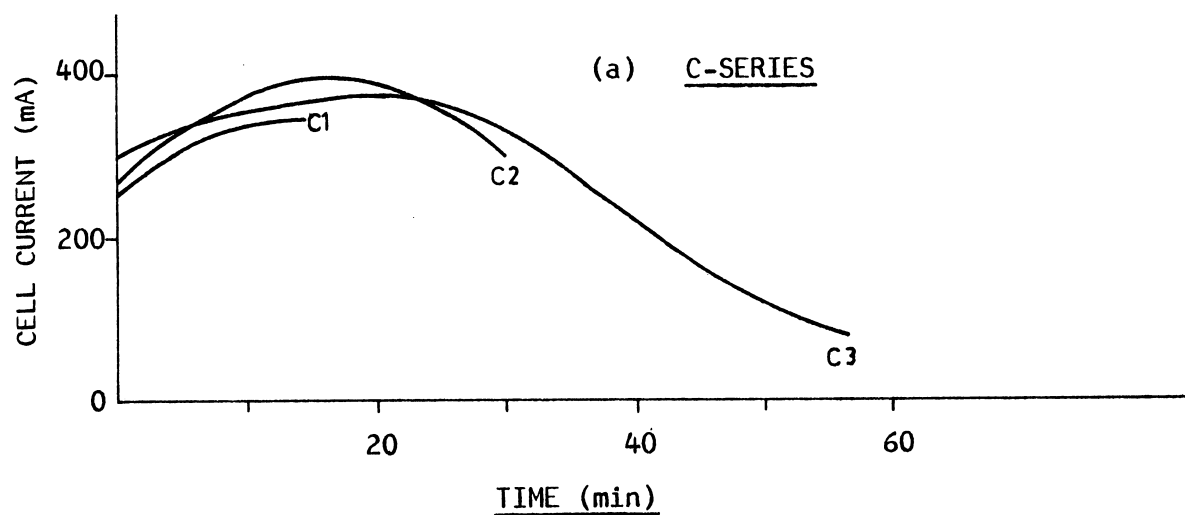


FIGURE 5.4
2.500V POTENTIOSTATIC ELECTROLYSIS
CURVES

2. Four of the runs (C2, C3, D3, D6) were made using approximately 8 g of fluoride salt. These were four of the initial electrolysis runs in which a smaller quantity of salt was used. In all subsequent runs approximately 10 g was used because increased fused salt depth was required for the large anode size and for three-electrode work in which two electrodes were immersed in the salt phase.

3. In run D7 jamming of the crucible support rod occurred which prevented the immediate lowering of the crucible out of the furnace hot zone after the completion of electrolysis. Thus a very slow melt cooling rate was achieved in this run.

Approximately 15 minutes elapsed between the completion of electrolysis and solidification of the copper, compared to less than one minute for the other electrolysis runs.

5.3.1 Discussion of the Electrolysis Curves

All the curves shown in Figure 5.4 have the same basic form as observed in run B4, with an initial current rise to a peak with a steady current decay for the remainder of electrolysis.

Although there is considerable scatter in the electrolysis curves within each of the three anode size ranges, it can be seen that each anode size range has produced a family of curves which is quite distinct from those of the other two anode sizes. The differences between the three sets of curves is more clearly illustrated in Figure 5.5, in which a single representative electrolysis curve (i.e. "typical" electrolysis curve) for each of the three anode sizes has been plotted on one set of axes. The three representative electrolysis curves were obtained as described in Section 5.1.3. Details of these three curves are summarised in Table 5.5.

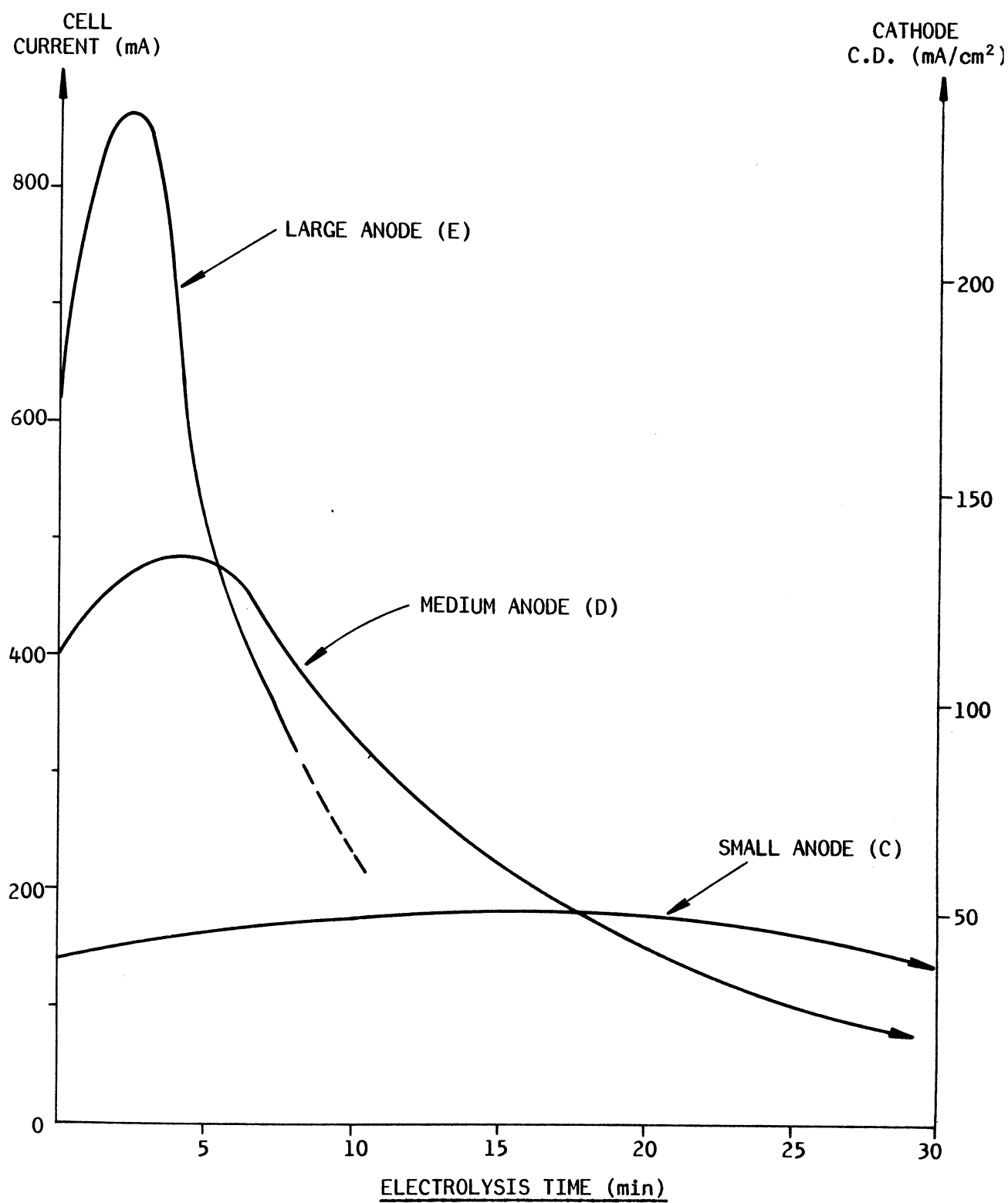


FIGURE 5.5
COMPARISON OF ELECTROLYSIS CURVES

RUN SERIES	AVERAGE ANODE AREA (cm ²)	INITIAL CURRENT DATA			PEAK CURRENT DATA			
		CURRENT (mA)	CATHODE C.D. (mA/cm ²)	ANODE C.D. (mA/cm ²)	CURRENT (mA)	CATHODE C.D. (mA/cm ²)	ANODE C.D. (mA/cm ²)	TIME TO PEAK (min)
C	0.23	140	38	608	185	50	804	16.0
D	0.49	398	108	812	481	130	981	4.5
E	0.81	620	168	765	861	233	1062	2.4

TABLE 5.5

DATA SUMMARY FOR ELECTROLYSIS

CURVES IN FIGURE 5.5

Because a constant liquid copper-fused salt interface area was used in these runs (nominally 3.62 cm^2), these three curves can also be represented as cathode current density curves, as indicated by the cathode current density scale placed on Figure 5.5. Clearly an increase in anode area produces a marked increase in cathode current density in these electrolyses, an indication that mass transfer and charge transfer reactions at the cathode are not current-limiting.

In Figure 5.6 the three representative electrolysis curves have been replotted to show anode current density versus the amount of current passed during electrolysis (expressed in milliampere hours). Also shown on this figure are the positions at which the peak electrolysis currents are reached (C_p , D_p and E_p for the C, D and E-series runs respectively).

It can be seen from this figure that:

1. The anode current density electrolysis curves are quite similar for each of the three anode size ranges, although the magnitude of the anode current density for the C-series electrolyses (small anode) is of the order of 20% lower than for the other two anode size ranges.
2. The current peak occurs after the passage of an amount of current that is significantly less than the total faradic equivalent of sulphur contained in copper ($C_{[S]}$, $D_{[S]}$ and $E_{[S]}$).
3. The current peak occurs after the passage of less current with a larger anode size.

The observation in (2) and (3) above can be confirmed by a comparison of the (mAh to peak) / (mAh [S] in Cu) ratios for each anode size range; viz:

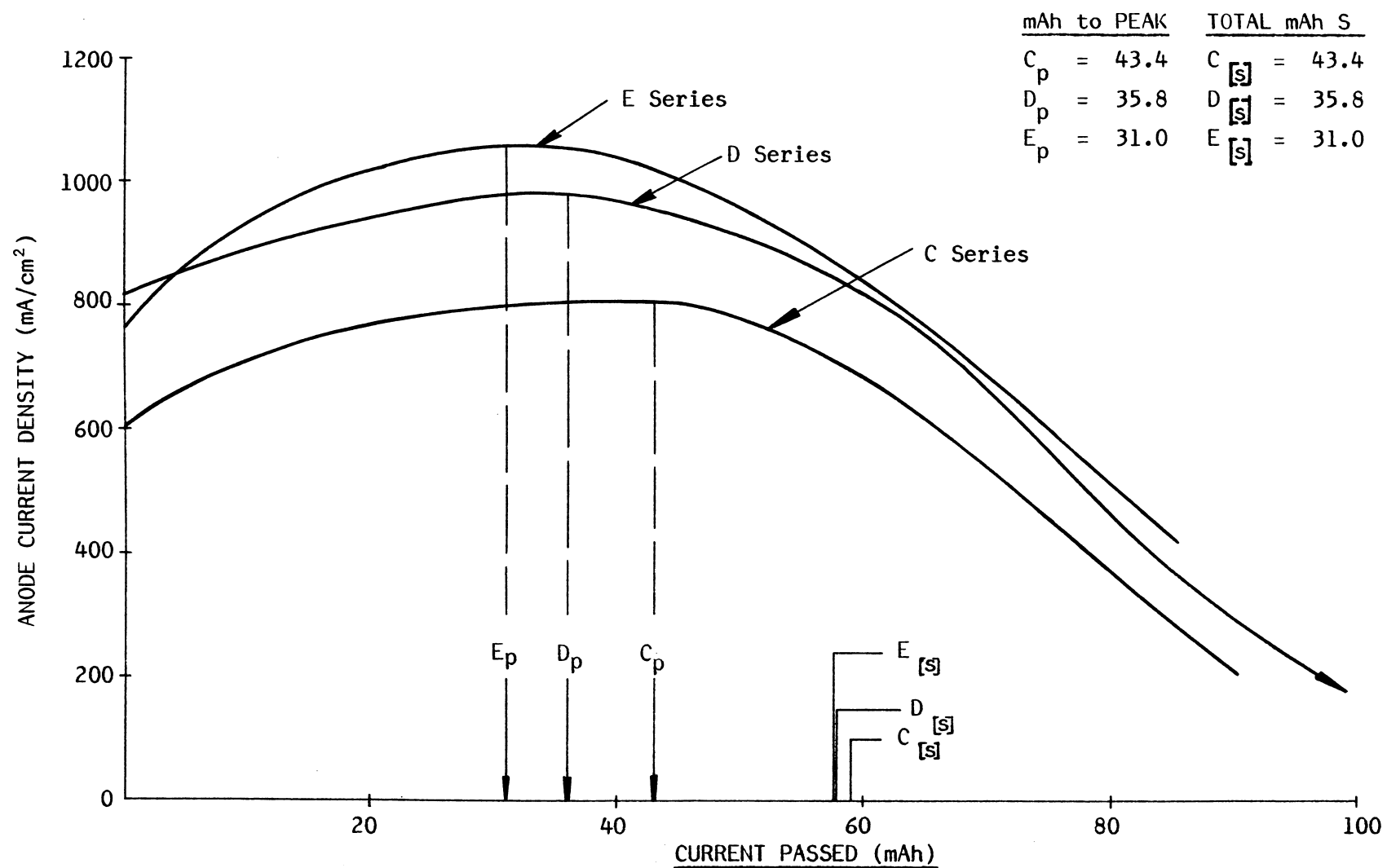


FIGURE 5.6
COMPARISON OF ELECTROLYSIS CURVES -
ANODE CURRENT DENSITY VERSUS CURRENT PASSED

$$\begin{array}{rclcl}
 \text{small anode} & - & \frac{C_p}{C_{[s]}} & = & 0.73 \\
 \text{medium anode} & - & \frac{D_p}{D_{[s]}} & = & 0.62 \\
 \text{large anode} & - & \frac{E_p}{E_{[s]}} & = & 0.53
 \end{array}$$

The overall similarity of the three anode current density versus current-passed electrolysis curves in Figure 5.6, in contrast to the marked dissimilarity in magnitude of the current density for the cathode current density electrolysis curves in Figure 5.5 is indicative of anodic control of the electrolysis process, that is, the anodic electrode reactions being current-limiting throughout electrolysis. Further, the presence of the current peak suggests a significant change in the nature of the anode reactions is occurring at this time, with this change occurring earlier (in terms of current passed) with a larger anode area.

Because the magnitude of the electrolysis current is dependant on the anode area it was thought that the reason for the considerable scatter observed in the cell current versus time electrolysis curves for each anode size range (Figure 5.4) might be the variation in true anode area within each anode size range. To further investigate this, the electrolysis curves in Figure 5.4 were replotted as anode current density versus time curves. However no significant reduction in the degree of scatter was observed, particularly with the D-series work in which most of the work was done and most of the scatter is observed. Thus, the variability in the cell current magnitude for the electrolysis curves within each anode size range in Figure 5.4 cannot be attributed solely to variability in true anode areas.

5.3.2 Sulphur Distribution Curves

From the final sulphur distribution data in Table 5.4, time-based sulphur distribution curves have been plotted for each anode size range, shown in Figure 5.7(a), (b) and (c). For comparison purposes the corresponding typical electrolysis curve for each series is plotted on each, with the same time scale but an arbitrary current scale. This allows the main feature of the electrolysis curves to be directly related to the changes in sulphur distribution in the three phases.

Scales showing the approximate sulphur concentration in copper and salt corresponding to the percentage of total sulphur in these phases have been placed on the right hand side of these graphs. These scales are based on the average masses of copper and salt and total sulphur for each series and therefore are not exact in terms of defining the sulphur concentration in copper or salt for each plotted point. However, the 'internal' variation in copper, salt and sulphur masses for each series was such that these scales can be considered accurate to within $\pm 5\%$ for the sulphur in copper and $\pm 10\%$ for the sulphide in salt.

The 'best fit' curves drawn on these Figures 5.7(a), (b) and (c) show the general trends in sulphur distribution changes during electrolysis. A rigorous quantitative analysis of the features of these 'best fit' curves is not appropriate. In the case of Figures 5.7(a) and (c) only four and three data points respectively have been used, while in Figure 5.7(b) the scatter in the plotted points is substantial - due to the use of end-point data from

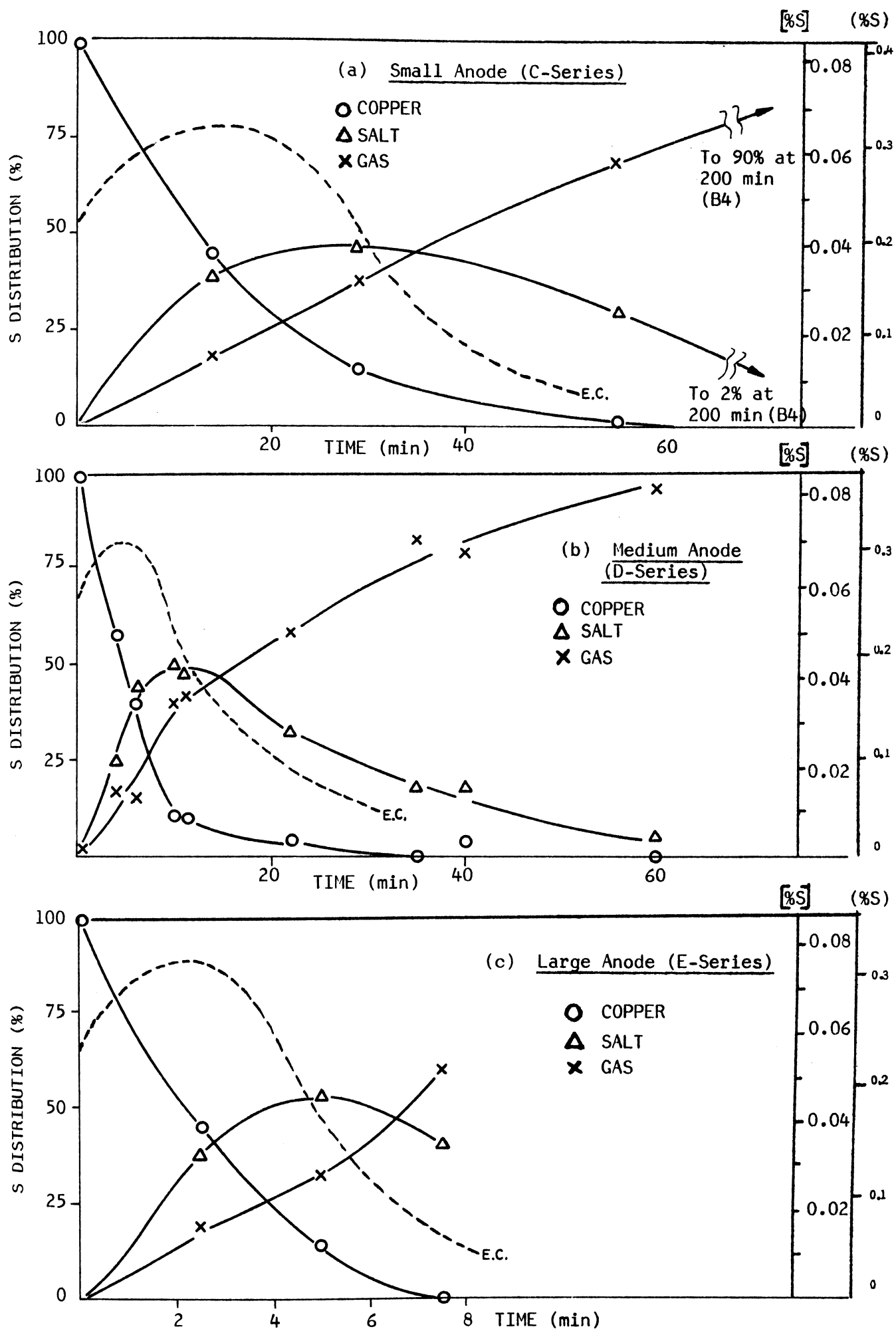


FIGURE 5.7
TIME-BASED SULPHUR DISTRIBUTION CURVES
 (E.C. = ELECTROLYSIS CURVE)

individual runs to characterise continuous progress of a hypothetical single run. However, the curves clearly show the nature of the changes in sulphur distribution during electrolysis.

The sulphur in copper curves indicate that the initial rate of removal of sulphur from copper is rapid and that the rate of sulphur transfer does appear to decrease when lower sulphur levels in copper (~ 0.02 wt%) are reached. Discharge of sulphide from the fused salt electrolyte is initially slower than the rate of sulphur transfer from the copper into the fused salt, resulting in a significant build-up of sulphide in the fused salt. In each case the salt concentration reaches a peak of 0.18-0.20 wt% S when the sulphur in copper has decreased to approximately 0.01 wt%. Subsequently the sulphide is electrolysed out of the fused salt at a relatively slow rate. This discharge continues after the copper is effectively depleted in sulphur (at which point the fused salt contains approximately 0.10 - 0.15 wt% S).

In considering the shape of the electrolysis curves in relation to the changes in overall sulphur distribution, again fairly consistent behaviour is observed for each of the three series.

The initial increase in electrolysis current coincides with a period of rapid increase in the sulphide concentration of the fused salt. However, in each case the electrolysis current peak is reached while sulphide is still accumulating in the fused salt and well before the maximum sulphide concentration in the fused salt is reached. The point of maximum sulphide concentration in the salt phase occurs when the cell current has decreased to less than 70% of the peak value. In addition it is evident that the maximum sulphide in salt concentration is reached in a period when the rate of decrease of the cell current is at a maximum.

The electrolysis current peak occurs when there is a significant amount of sulphur remaining in the copper; of the order of 50% of total sulphur (i.e. ~ 0.045 wt% S) for the medium and large anode electrolyses (D and E series) and approximately 40% of total sulphur in copper (i.e. ~ 0.035 wt% S) for the small anode electrolyses (C series).

In Figure 5.8 the sulphur distribution curves have been plotted on a current-passed basis, showing the change in sulphur distribution to the copper, salt and gas phases in Figures 5.8(a), (b) and (c) respectively. The data for each of the three sizes have been plotted on these curves. Although a reasonable amount of scatter is observed in the points plotted from individual runs, the 'best fit' lines drawn on these figures clearly show the trends in sulphur distribution changes

The data from run B4 (Section 5.2.3 - 2.500 V extended electrolysis, small anode) have also been included on these curves. In this run the total current passed was 176 mAh and the final sulphur distribution was 0.0, 2.5, 97.5% for the copper, salt and gas phases respectively.

As was the case with the anode current density curves plotted on a current-passed basis (Figure 5.6), the plotting of the sulphur distribution curves in this manner shows that a similar and consistent behaviour is observed with each of the three different anode sizes. Thus the actual utilisation of the electrolysis current in producing changes in the sulphur distribution during electrolysis does not differ markedly for the three anode sizes, despite the significant differences in the rates of sulphur transfer.

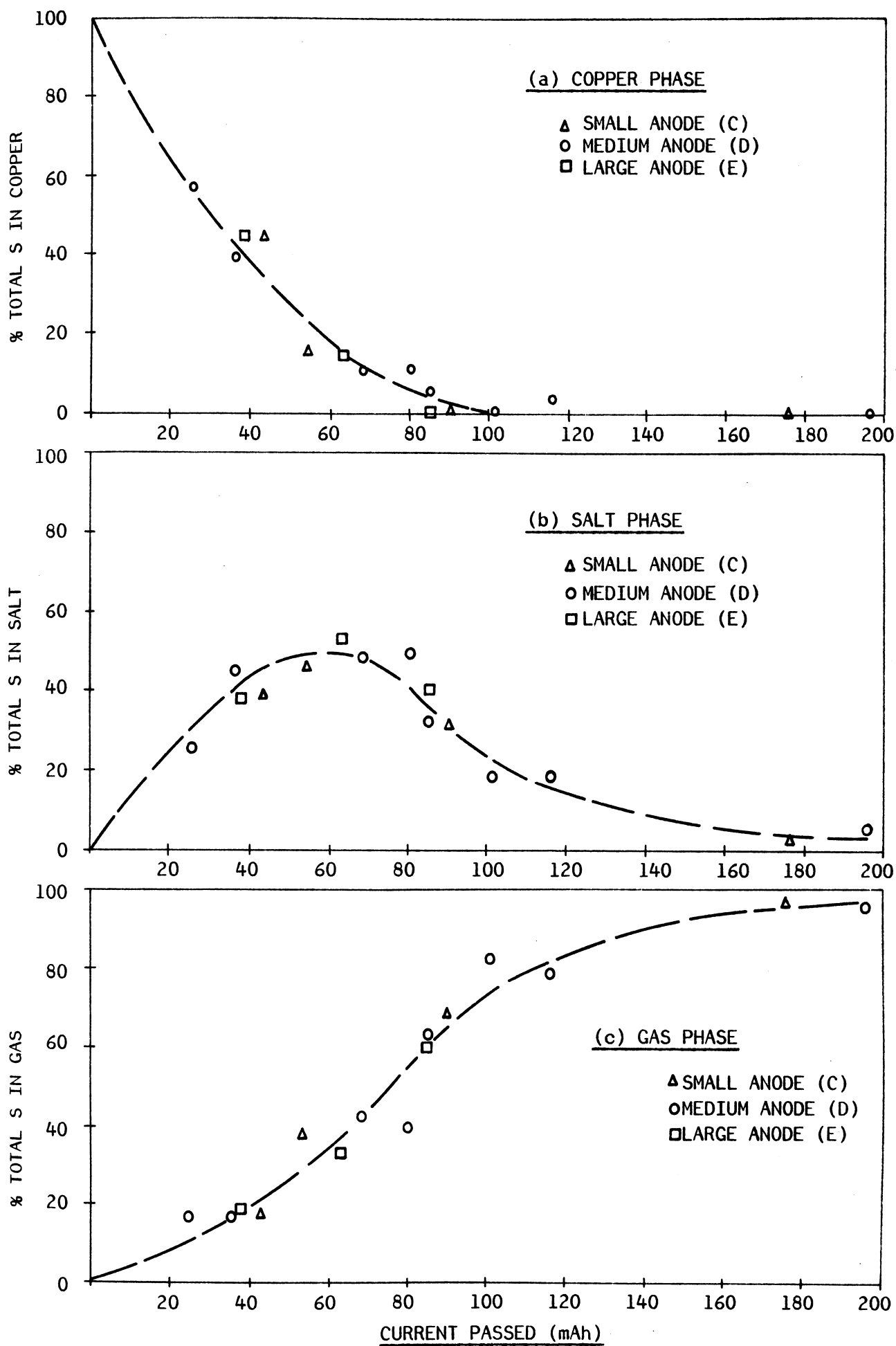


FIGURE 5.8

CURRENT-BASED SULPHUR DISTRIBUTION CURVES

The degree of scatter of points in the current-based sulphur distribution curve for the copper phase can be significantly reduced if the amount of current passed in each electrolysis run is re-calculated relative to the ratio of the actual faradic equivalent of sulphur in each run to the average faradic equivalent of sulphur in all the runs. This eliminates some of the variation due to differing amounts of sulphur present in each run.

Thus the "corrected current passed" is defined as follows:

$$\int I_c = \int I \cdot \frac{\overline{\text{mAh}}_{[s]}}{\text{mAh}_{[s]}} \quad \dots 5.3$$

where $\int I_c$ = corrected current passed (mAh)
 $\int I$ = actual current passed during electrolysis (mAh)

$\overline{\text{mAh}}_{[s]}$ = average total faradic equivalent of sulphur
 for all runs

$\text{mAh}_{[s]}$ = total faradic equivalent of sulphur for that
 run

Figure 5.9 shows the sulphur distribution curves plotted on the basis of "corrected current passed". The average total faradic equivalent of sulphur in copper is 58.2 mAh for all runs in Table 5.4. In comparison with Figure 5.8(a) there is significantly less scatter in the copper-phase sulphur distribution curve (Figure 5.9(a)). However, there does not appear to be any reduction in scatter of points for the distribution curves of the salt and gas phases (Figures 5.9(a) and (b)).

Current efficiency data can be derived from the current-based sulphur distribution curves, since the slope of these curves at any point is proportional to the current efficiency at that point. Thus,

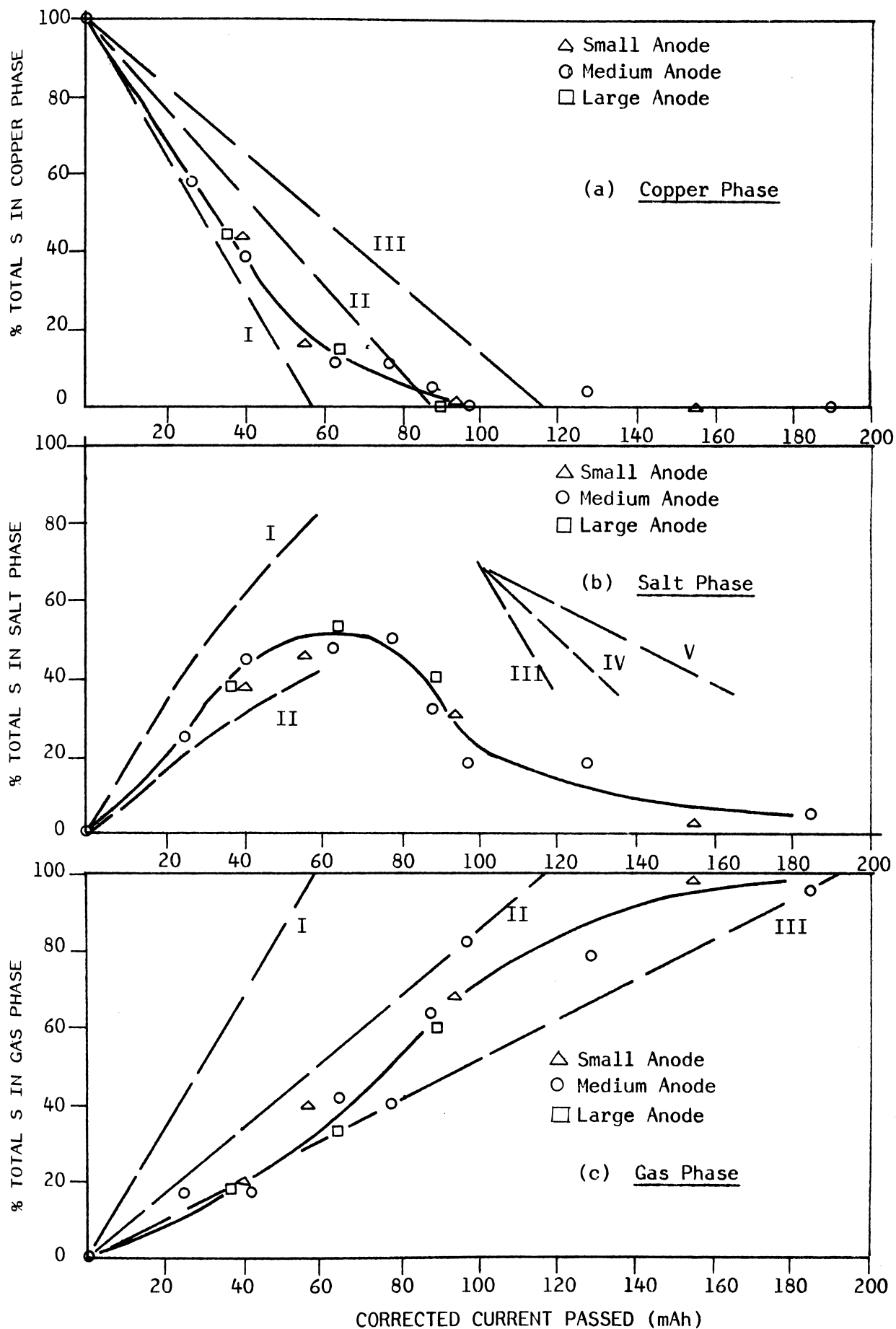


FIGURE 5.9

CURRENT-BASED SULPHUR DISTRIBUTION CURVES
USING "CORRECTED" CURRENT PASSED

(See text for explanation of dashed lines)

calculated (i.e. theoretical) sulphur distribution curves at specific current efficiencies assuming a total faradic equivalent of sulphur of 58.2 mAh have been superimposed on Figure 5.9 (dashed-lines). The details of the calculated curves are as follows:

Figure 5.9(a)

Curves I, II, III - theoretical sulphur distribution curves for transfer of 58.2 mAh equivalent of sulphur from copper at cathodic current efficiencies of 100%, 75% and 50% respectively.

Figure 5.9(b)

Curves I, II - theoretical sulphur distribution curves for discharge of sulphide out of the fused salt phase at anodic current efficiencies of 0% and 50% respectively, assuming sulphur transfer into the fused salt according to the 'best fit' curve for sulphur in the copper phase (Figure 5.9(a)).

Curves III, IV, V - show the theoretical slope of sulphur distribution curves for discharge of sulphide out of the fused salt phase at anodic current efficiencies of 100%, 50% and 25% respectively, assuming no transfer of sulphur from the copper to the salt is occurring (i.e. copper is depleted in sulphur).

Figure 5.9(c)

Curves I, II, III - theoretical sulphur distribution curves for the discharge of sulphide from the fused salt phase at anodic current efficiencies of 100%, 50% and 30% respectively.

The 'best fit' sulphur distribution curves representing actual electrolysis behaviour can be compared with the theoretical curves to give a qualitative analysis of the variations in cathodic and anodic current efficiencies during electrolysis:

. Cathode Current Efficiency

From Figure 5.9(a) it can be seen that the bulk of the cathodic transfer of sulphur out of the copper occurs with a high current efficiency of approximately 90%. After $\sim 80\%$ of the sulphur in copper has been transferred ($[s]_{Cu} = 0.015 - 0.02 \text{ wt\%}$) the cathode current efficiency decreases rapidly, with most of the remaining sulphur transferred with a cathode current efficiency of significantly less than 50% (c.f. slope of line III).

Virtually complete removal of sulphur from the copper ($< 1.5 \text{ p.p.m.}$) is expected after the passage of $\sim 100 \text{ mAh}$, which represents an overall cathode current efficiency of 60%.

. Anode Current Efficiency

From Figures 5.9(b) and 5.9 (c) it appears that the anode current efficiency during the early stages of electrolysis (20 - 50 mAh) is low - clearly less than 50% and of the order of 30%. After the maximum sulphide concentration in the salt phase has been reached, the sulphide level of the salt decreases relatively rapidly (70 - 100 mAh/period). If the slopes of the 'best fit' lines in this period (Figures 5.9(b) and (c)) are compared to the slopes of the theoretical lines, it appears that the anode current efficiency during this period is significantly greater than in the initial stages of electrolysis. The curves indicate that an anode current efficiency greater than 50% is achieved.

In subsequent stages of electrolysis (> 100 mAh) when the sulphide in the salt is discharged relatively slowly and with an apparently decreasing rate, a comparison of the curves indicates that the anode current efficiency also decreases to less than 30%.

If the two 'best fit' curves drawn on Figures 5.9(a) and 5.9(b) are considered to represent the progress of a single hypothetical 2.500 V electrolysis run (with an initial faradic sulphur-equivalent of 58.2 mAh contained in the copper), then predicted cathode current efficiency and anode current efficiency data for the hypothetical electrolysis can be calculated from the relative changes in sulphur distribution to the two phases during successive discrete periods of electrolysis. This has been done for successive 20 mAh periods and the data obtained are summarised in Table 5.6. The calculated cathodic and anodic current efficiencies are represented graphically in Figure 5.10.

The general trends of variation in current efficiencies as shown in this figure are consistent with the discussion above and are obviously significant in characterising the cell reactions occurring during 2.500 V potentiostatic electrolysis. This is further discussed in Section 5.6 in which the probable cell reactions are reviewed.

5.3.3 Magnesium and Calcium Build-up in Copper

The magnesium and calcium analysis data summarised in Table 5.4 indicate that a significant build-up of magnesium in the liquid copper occurs in the lengthier electrolysis runs for each series. Calcium, at a lower concentration, is also detected in these runs, although very low levels of calcium in copper are also evident in some of the shorter electrolysis runs.

ELECTROLYSIS PERIOD	$-\Delta[S]_{\text{Cu}}$ (mAh)	$\Delta(S^{2-})_{\text{salt}}$ (mAh)	$\Delta\{S_2\}_{\text{gas}}$ (mAh)	CATHODE C.E. (%)	ANODE C.E. (%)
0 - 20 mAh	18.0	+ 14.0	+ 4.0	90	20
20 - 40 mAh	18.0	+ 11.6	+ 6.4	90	32
40 - 60 mAh	14.5	+ 4.7	+ 9.8	63	49
60 - 80 mAh	5.8	- 4.1	+ 9.9	34	50
80 - 100 mAh	2.5	- 11.6	+ 14.1	12	70
100 - 120 mAh	0.0	- 5.0	+ 5.0	0	25
120 - 140 mAh	0.0	- 2.9	+ 2.9	0	15

TABLE 5.6

AMOUNTS OF SULPHUR TRANSFERRED AND CALCULATED CATHODE

AND ANODE CURRENT EFFICIENCIES FOR HYPOTHETICAL

ELECTROLYSIS BASED ON THE 'BEST FIT' CURVES IN FIGURES 4.9(a) AND (b)

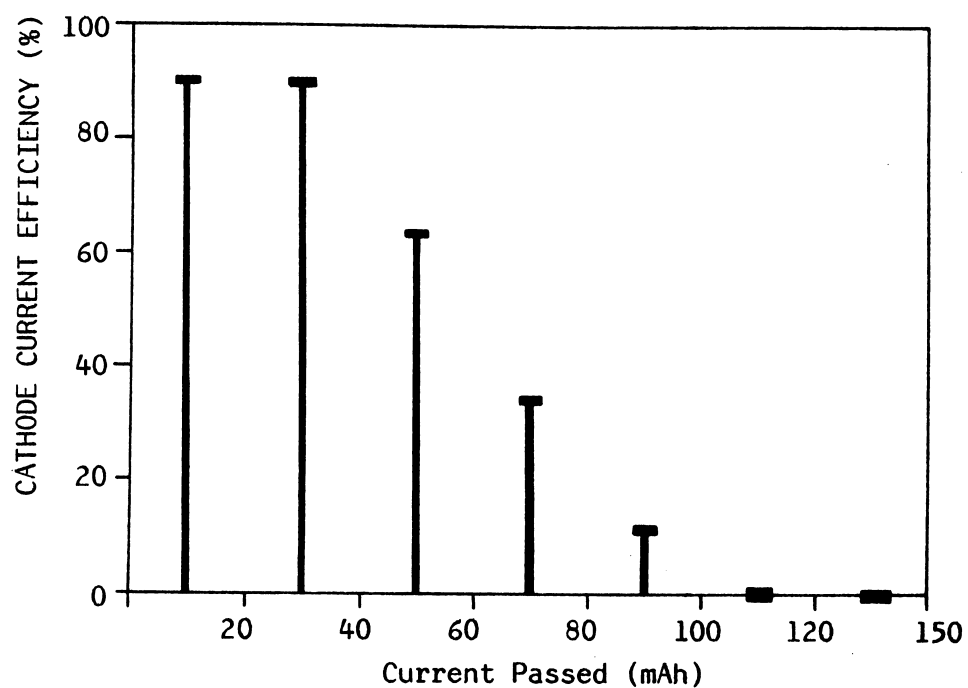
$-\Delta[S]_{\text{Cu}}$ = faradic equivalent of the amount of sulphur transferred out of the copper during the 20 mAh electrolysis period (from Figure 5.9(a))

$\Delta(S^{2-})_{\text{salt}}$ = faradic equivalent of the overall change in the amount of sulphur in the fused salt during the 20 mAh electrolysis period (from Figure 5.9(b))

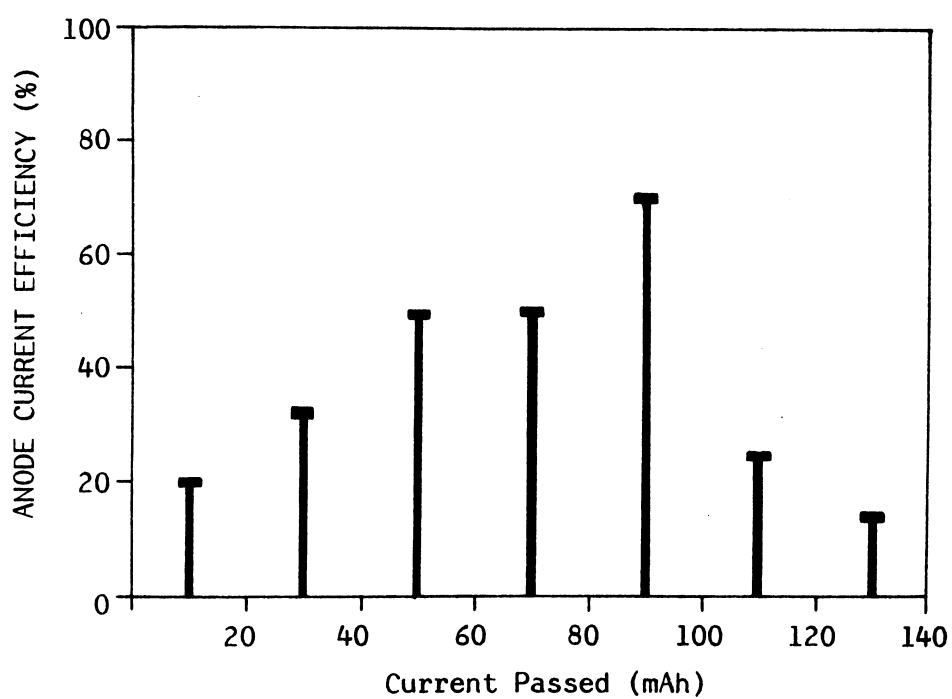
$\Delta\{S_2\}_{\text{gas}}$ = $-\Delta[S]_{\text{Cu}} - \Delta(S^{2-})_{\text{salt}}$
= faradic equivalent of the amount of sulphur discharged to the gas phase during the 20 mAh electrolysis period

Cathode C.E. = $(-\Delta[S]_{\text{Cu}} / 20.0) \times 100\%$

Anode C.E. = $(\Delta\{S_2\}_{\text{gas}} / 20.0) \times 100\%$



(a) CATHODE CURRENT EFFICIENCY



(b) ANODE CURRENT EFFICIENCY

FIGURE 5.10

GRAPHICAL REPRESENTATION OF CURRENT EFFICIENCY

DATA IN TABLE 5.6 FOR HYPOTHETICAL

2.500V ELECTROLYSIS

In Figure 5.11 the total amounts of magnesium and calcium in the final copper for each run have been converted to a combined (Ca + Mg) faradic equivalent and plotted against the corrected current passed. Also included in Figure 5.11 is the data for the extended electrolysis runs (B2 (1.500 V), B3 (2.000 V) and B4 (2.500 V)) in which a significant build-up of magnesium and calcium in copper was also observed (Table 5.3).

If all the current passed above that of the average faradic equivalent of 58.2 mAh sulphur in copper is considered as "excess current" then the rate of build-up of Ca/Mg in the copper can be compared to the two theoretical lines drawn in Figure 5.11:

- I - theoretical line for (Ca + Mg) equiv. = 100% utilisation of excess current
- II - theoretical line for (Ca + Mg) equiv. = 30% utilisation of excess current

From this it can be seen that the magnesium and calcium build-up in the copper (which obviously occurs predominantly only once the bulk of the sulphur is removed from the copper) represents significantly less than 100% utilisation of the excess cathode current. The maximum is 50% (D6), and the average for the points in Figure 5.11 where excess current was passed is approximately 30%, although a large degree of variation is observed. In electrolysis runs where excess current was passed, the ratio of faradic equivalents

$[Mg]_{Cu} : [Ca]_{Cu}$ is 5.4 : 1.

5.3.4 Electrode Weight-loss Data

Anode weight-loss data were obtained for seven of the 2.500 V potentiostatic electrolysis runs in Table 5.4, and are summarised in Table 5.7 below:

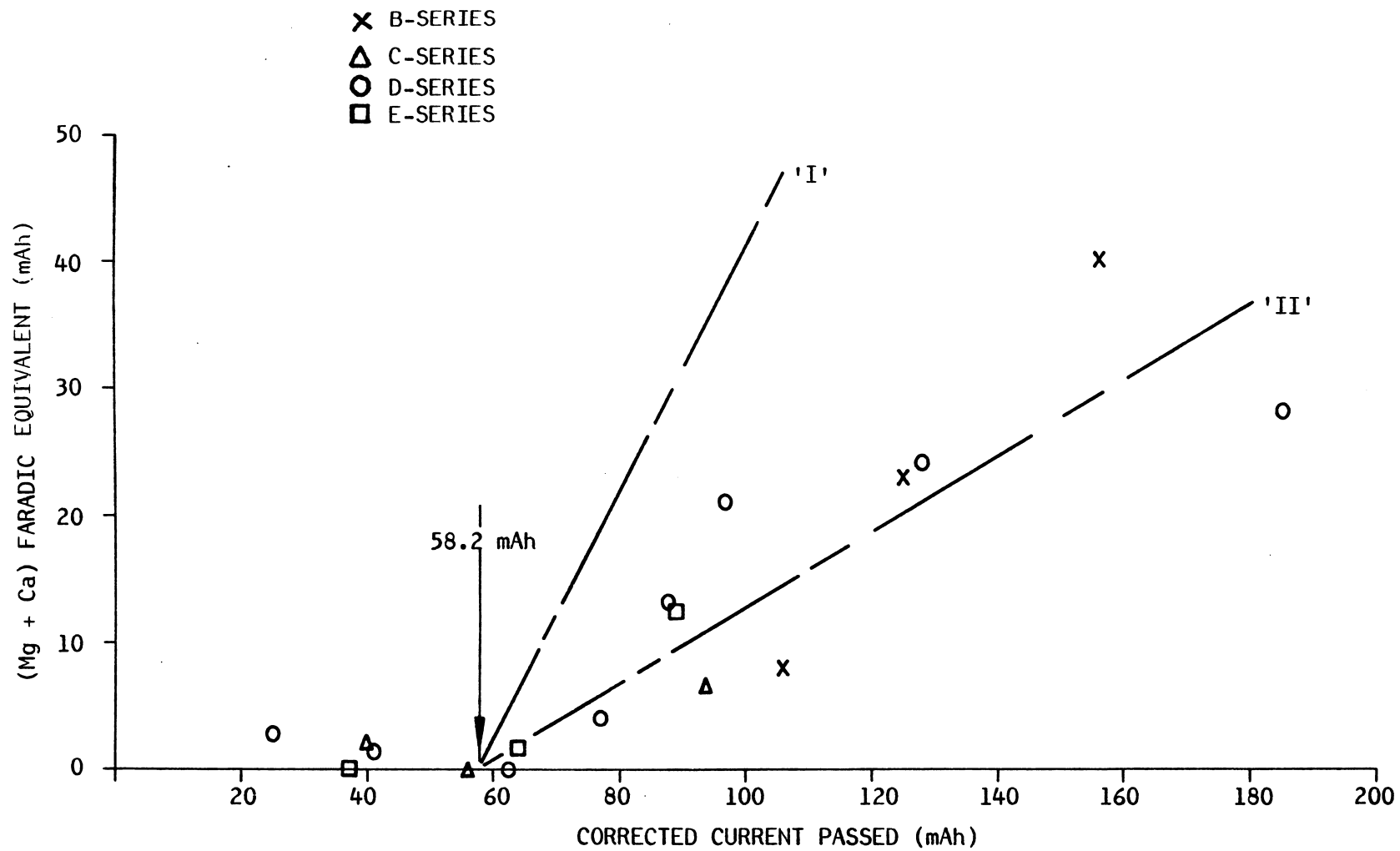


FIGURE 5.11

LINE I - (Ca + Mg) = 100% of excess current

LINE II - (Ca + Mg) = 30% of excess current

RUN	ANODE TYPE	ELECTRODE WEIGHT LOSS (g)
C1	A2	0.00460
D1	A3	0.00300
D2	A3	0.00395
D4	A2	0.01150
D8	A3	0.01720
E2	A3	0.00870
E3	A3	0.00865

TABLE 5.7ANODE WEIGHT LOSS DATA

(NOTE: Initial and final anode weights determined to ± 0.05 mg.)

Significant anode carbon consumption is evident in these runs with the D-series results showing increased consumption with increased electrolysis time.

It had previously been confirmed that the anode weight loss was solely due to electrochemical reactions at the anode with no 'artificial' component resulting from purely chemical interaction of the anode carbon with its environment. This was done in potentiostatic electrolysis experiments using the three-electrode cell assembly (Figure 4.4). Identical anode tips were mounted on both anode rods. During electrolysis, a potential was applied to only one anode rod, the other serving as a 'dummy' anode immersed in the salt melt, which was re-weighed after cooling in the furnace. In each case when this was done no significant change in the dummy electrode weight

(i.e. >1 mg) was detected even for fairly lengthy electrolysis runs - as was the case for run D8 (60 minutes) in which a second dummy anode was used.

From the anode weight-loss data and the amount of current passed during electrolysis, a theoretical electron transfer number (n-value) for the electrochemical consumption of the graphite carbon can be calculated from Faraday's Law (equation 5.3). This will represent an overall or average n-value for whatever carbon-consuming reactions are occurring during the progress of electrolysis. This has been done and the results summarised in Table 5.8.

In this case two separate average n-values have been calculated for each run. The first, designated n_1 , was calculated assuming the total anode current-passed results in carbon consumption. The second, designated n_2 , was calculated assuming only the non-sulphur anode current (i.e. fluoride or oxide ion discharge) produces carbon consumption, that is, assuming that the sulphide does not discharge as $\text{Cs}_2(\text{g})$.

It can be seen from Table 5.8 that four of the n_1 values are greater than 4, whereas not one of the n_2 values is greater than 4 and all but one (D4) are within the range 2-4.

From consideration of the possible gaseous reaction products formed from a combination of carbon with the three-component system S, O, F (see, for example, gaseous species listed in Barin and Knacke^{54,55}), it is evident that an average n-value for electrochemical carbon consumption greater than 4 is not possible, and that an n-value in the range 2-4 would be expected, assuming negligible formation of $\text{CF}(\text{g})$ which is relatively unstable compared to $\text{CF}_4(\text{g})$, and the other C/F compounds possible^{54,55}.

RUN	TOTAL ANODE CURRENT (mAh)	NON-SULPHUR ANODE CURRENT (mAh)	THEORETICAL n-VALUE n_1	THEORETICAL n-VALUE n_2
C1	43.4	24.7	4.23	2.40
D1	24.8	16.3	3.70	2.43
D2	36.2	27.0	4.10	3.06
D4	68.3	42.3	2.66	1.64
D8	196.1	137.8	5.11	3.59
E2	63.3	45.6	3.26	2.35
E3	85.0	60.0	4.40	3.10

TABLE 5.8THEORETICAL n-VALUES FOR ANODE CONSUMPTION

- n_1 - Calculated using total anode current-passed
- n_2 - Calculated using only non-sulphur anode current-passed

Thus the data in Table 5.8 do suggest that sulphide ion discharge at the anode does not result in the formation of $\text{CS}_2(\text{g})$ as the predominant gaseous sulphur species. This is supported by the observation of elemental sulphur condensed in the carbon regions of the reaction tube.

It should be noted that in run D4 ($n_2 = 1.64$) a type A2 anode tip was used. As discussed in Section 4.3, these anode tips are more likely to result in an artificial weight-loss than the type A3. An artificial weight-loss will result in the calculated n-value being lower than the actual n-value.

5.3.5 Analysis of Fluoride in Furnace Off-Gases

The furnace gases were analysed for gaseous CF_4 in three of the 2.500 V potentiostatic electrolysis runs using the procedure described in Section 4.6.4. The results (summarised in Table 5.9) show that discharge of gaseous fluoride is occurring during 2.500 V potentiostatic electrolysis, with significant amounts of fluoride reporting to the absorption solution.

It had been previously confirmed that this evolved fluoride was discharged only during electrolysis by analysing furnace off-gases with a fluoride melt in the crucible at 1423K with no electrolysis. In each case there was no significant increase of fluoride concentrations detected in the absorption solutions after an extended holding period (~1 hour), confirming that vapourisation of the fluoride melt does not contribute measurably to gaseous fluorides absorbed in the analysis apparatus.

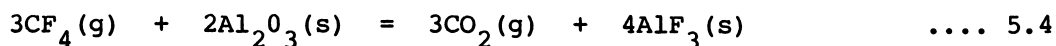
Although the results in Table 5.9 are useful in confirming that the evolution of fluorides occurs during 2.500 V potentiostatic electrolysis, it is unlikely that this analysis technique is

RUN NO.	FARADIC EQUIVALENT OF FLUORIDE ABSORBED (mAh)	TOTAL CURRENT PASSED (mAh)	TOTAL NON-SULPHUR CURRENT THROUGH ANODE (mAh)	RATIO OF FLUORIDE ABSORBED TO NON-SULPHUR ANODIC CURRENT (%)
C1	3.4	43.4	24.7	13.8
D1	1.4	24.8	15.7	8.9
D8	18.6	196.1	137.8	13.5

TABLE 5.9

SUMMARY OF GASEOUS FLUORIDE ANALYSIS DATA

quantitative with respect to CF_4 and any other gaseous carbon-fluorine compounds evolved. The reason is not incomplete absorption, since (as described in Section 4.6.4) a second identical absorption solution in series with the first showed no detectable increase in fluoride concentration. However, it is quite probable that some of the gaseous CF_4 could react with the alumina furnace components at 1423K and thus be consumed prior to reaching the absorption solution. For example, for the reaction:



calculated values for the standard free energy of reaction and equilibrium constant are^{54,55}:

- at 1423K : $\Delta G^\circ_{5.4} = -1099.2\text{kJ}$; $K_{5.4} = 2.23 \times 10^{40}$
- at 1200K : $\Delta G^\circ_{5.4} = -1139.5\text{kJ}$; $K_{5.4} = 4.00 \times 10^{49}$

It is also possible that gaseous carbon-fluorine compounds other than CF_4 could be formed at the anode. Despite CF_4 being the most thermodynamically favourable form at these temperatures, due to kinetic effects associated with the complex carbon-fluorine discharge reaction on the anode surface, some degree of formation of other species such as $\text{CF}_3(\text{g})$, $\text{CF}_2(\text{g})$ could be expected. No information was available on the solubility of these species in water.

Therefore, although the absorption analysis data indicate fluoride evolution accounts for less than 15% of the non-sulphur anodic current, it is quite possible that the actual amount of fluoride evolution was greater than this.

5.3.6 Linear Sweep Voltammetry

In order to further investigate the cell reactions occurring during potentiostatic electrolysis at 2.500 V, linear sweep voltammetry (L.S.V.) techniques were applied using the two-electrode electrolysis cell.

In most cases a sweep rate of 2.0 V/sec. was used to obtain linear sweep voltammograms (from a single-cycle forward/reverse sweep) or cyclic voltammograms (using continuous multiple sweeps). A 'small' type Al anode (true anode area $\sim 0.25 \text{ cm}^2$) was used in most of the L.S.V. investigations, therefore the voltammetry data presented in this section refers to an anode of that size. However, L.S.V. investigations using the two other standard anode sizes ('medium' and 'large') showed that similar behaviour was indicated when the voltammograms were plotted as anode current density versus cell voltage, rather than cell current versus cell voltage (although the short-term current fluctuations were more severe). Therefore, the voltammograms in this section have been plotted showing anode current density and can be considered representative of all three anode size ranges.

A typical linear sweep voltammogram (0-2.50 V) obtained prior to the commencement of 2.500 V potentiostatic electrolysis is shown in Figure 5.12. The main features of this voltammogram are summarised below:

- V_1 - decomposition potential for initial reaction
(0.60-0.70 V)
- I_1 - peak (or limiting) current associated with initial current rise after V_1 ($\sim 300 \text{ mA/cm}^2$). The presence of a peak indicates this current is diffusion-controlled after the peak.
- V_2 - decomposition potential for a second higher voltage reaction (2.05-2.25 V)
- I_2 - current rise associated with the second reaction at V_2 ($250\text{-}350 \text{ mA/cm}^2$); no limiting current was

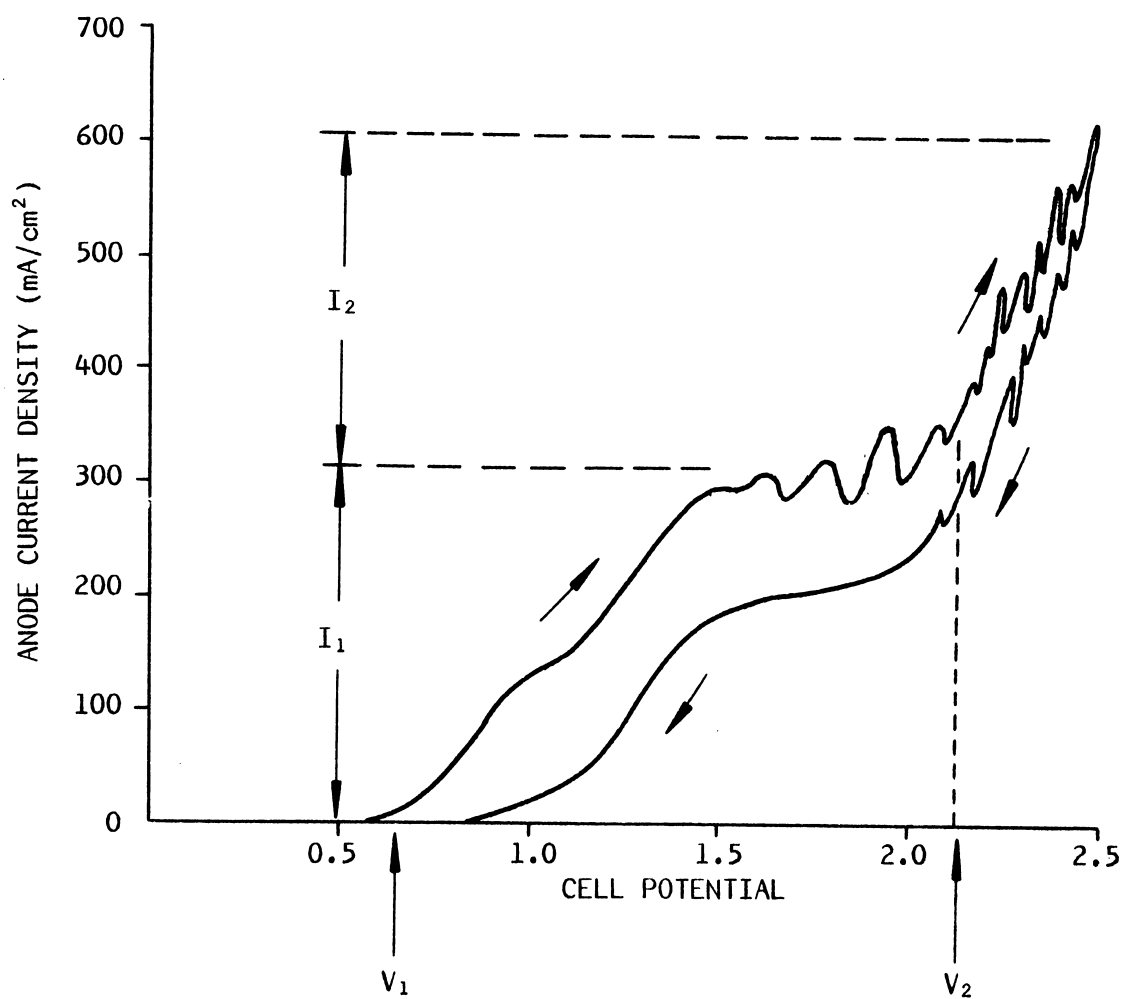


FIGURE 5.12

TYPICAL LINEAR SWEEP VOLTAMMOGRAM TO 2.500V
BEFORE THE COMMENCEMENT OF ELECTROLYSIS

observed at 2.500 V, therefore activation polarization control can be assumed at 2.500 V for this reaction.

A significant amount of short-term current fluctuation was observed after the limiting current I_1 was reached, which increased after the second current rise at V_2 commenced. These effects are indicative of gas evolution at the anode. The nature of the fluctuations made it impossible to determine V_2 with any precision (± 0.1 V was the best achievable) and produced a large variation in the values of I_2 observed.

After commencement of electrolysis and during the progress of electrolysis major changes in the form of the voltammograms were observed, including the appearance of a reverse current peak at low voltages on the return sweep. These are schematically represented in Figure 5.13 which depicts typical cyclic voltammograms obtained at various stages of electrolysis. The actual variations of the potentials V_1 and V_2 and the current components I_1 , I_2 and I_{RP} (the reverse current peak) during electrolysis are summarised graphically in Figure 5.14, along with a typical electrolysis curve for 2.500 V electrolysis with a small anode.

It can be seen from this figure that the electrolysis curve is effectively the sum of the two cell current components I_1 and I_2 . This was confirmed by comparison of the current at the switching potential (2.50 V) in linear sweep voltammograms made during the progress of electrolysis, and the actual electrolysis current observed immediately before the 2.500 V electrolysis was halted to obtain the voltammograms. This showed that the cell current recorded at 2.50 V in the voltammograms was equal to (within $\pm 5\%$) the electrolysis current immediately before the temporary cessation of electrolysis.

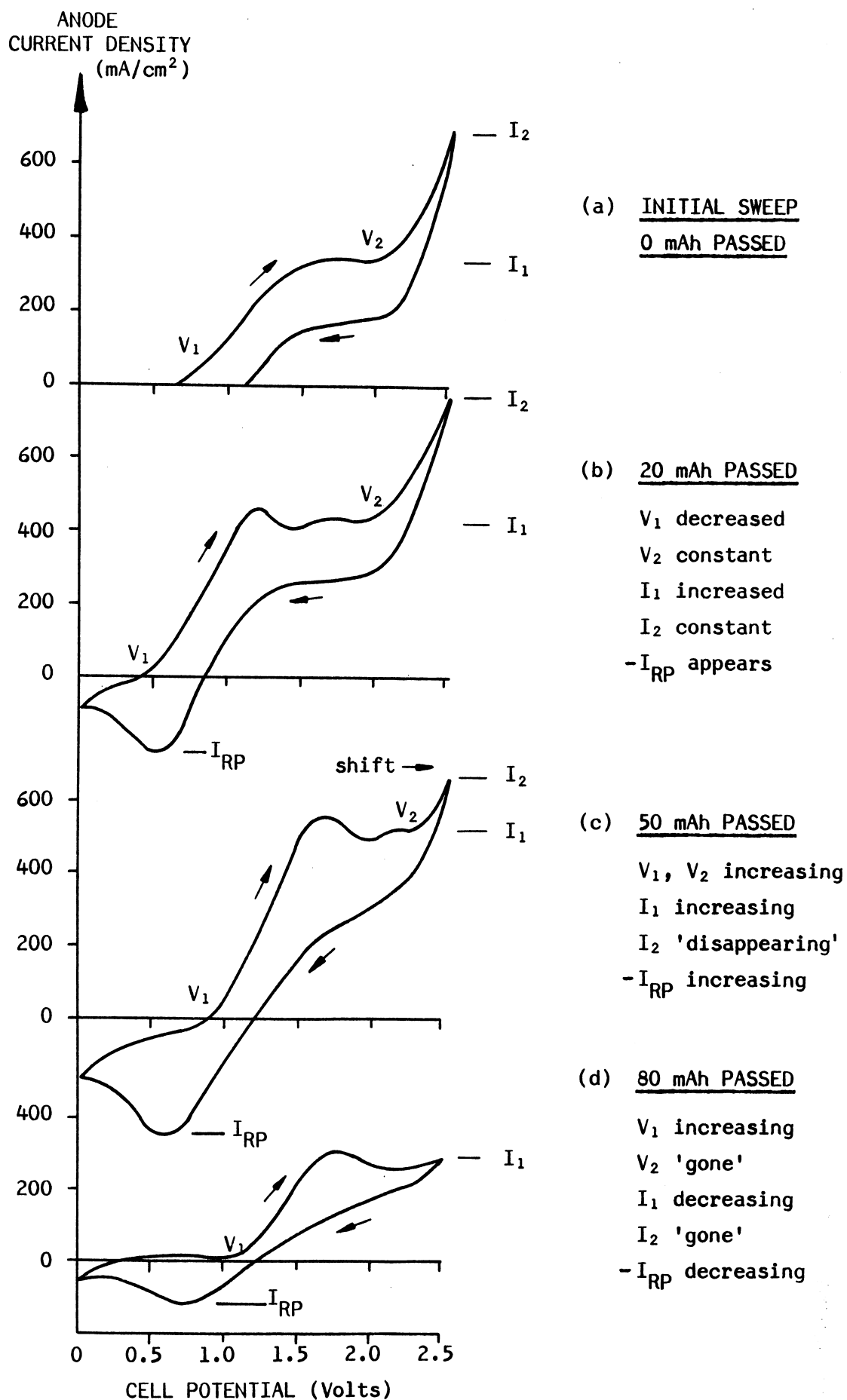


FIGURE 5.13

SCHEMATIC REPRESENTATION OF 0↔2.50 V CYCLIC
VOLTAMMOGRAMS DURING PROGRESS OF 2.500V POTENTIOSTATIC
ELECTROLYSIS

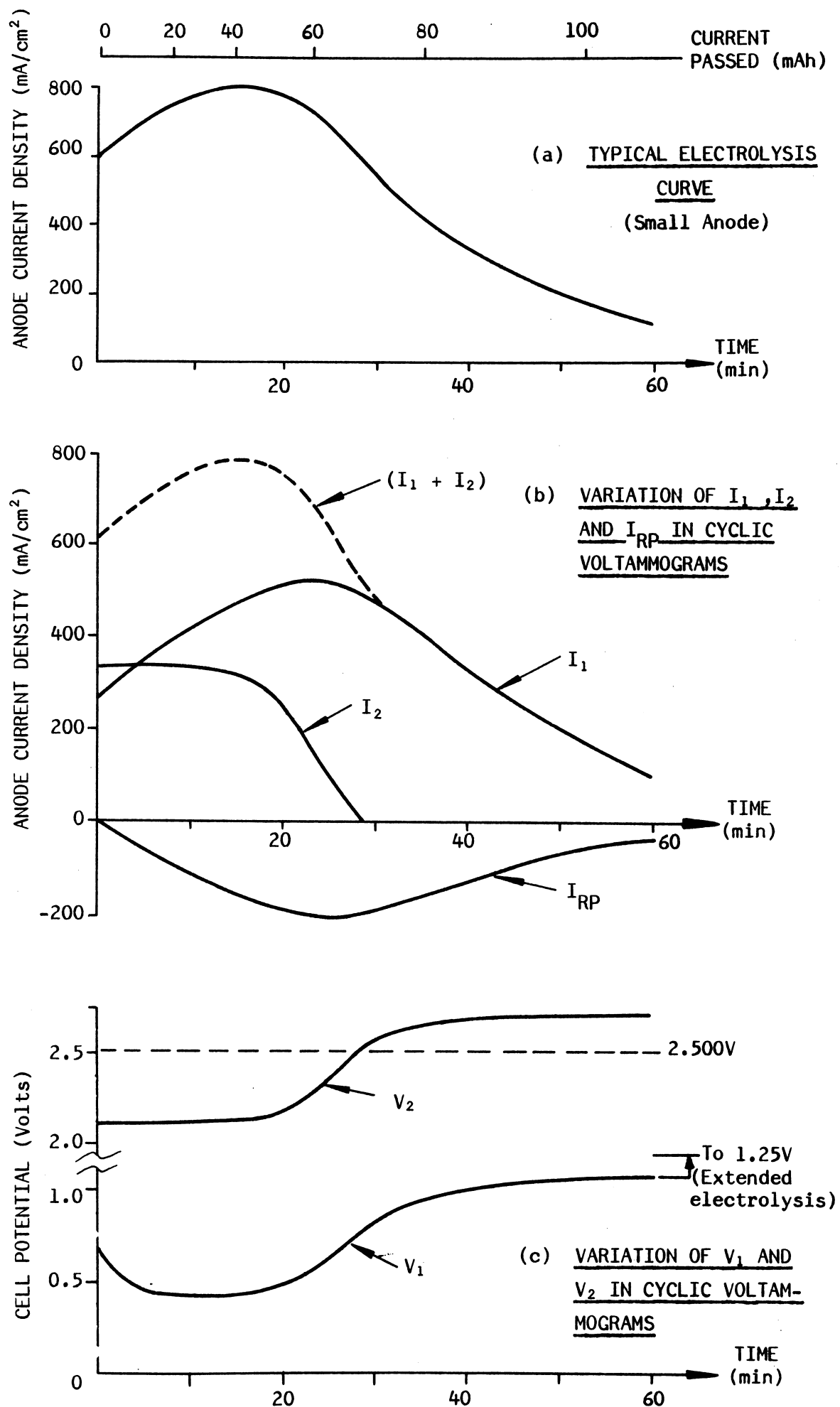


FIGURE 5.14

SUMMARY OF VARIATIONS IN CYCLIC VOLTAMMOGRAMS

Figure 5.15 shows a typical cyclic voltammogram made at an early stage of electrolysis in which the switching potential was raised to 4.00 V in order to further investigate the I_2 current rise commencing at V_2 . It can be seen that the rapid current increase continued until an anode current density of $\sim 1000 \text{ mA/cm}^2$ at a cell potential of 3.1-3.2 V was reached, at which stage a rapid decrease in current to low level was observed. The higher current resumed on the return sweep when the cell potential decreased to 2.7-2.8 V.

As previously described, this behaviour is typical of the 'anode effect' associated with the discharge of gaseous fluorides on carbon, and similar to that observed in the decomposition potential determination work (Section 5.2.1) in sweeps above the decomposition potential.

In experiments in which L.S.V. investigations were done, a final sweep was made immediately before the melt was cooled. The sulphide analysis of the salt phase showed a correlation with the magnitude of the reverse peak current density (I_{RP}), as is shown in Figure 5.16. This suggests that, within the range of sulphide analyses shown on this figure, a qualitative estimate of the sulphide level of the fused salt can be gained from the magnitude of I_{RP} .

It should also be noted from Figure 5.14 that the I_1 current peak is aligned with the I_{RP} peak, and both occur after the passage of approximately 60-70 mAh of current, which is the electrolysis period when the maximum sulphide concentrations in the salt are expected (Section 5.3.2, Figure 5.8).

5.4 FURTHER ELECTROLYSIS EXPERIMENTS

In this section the results for electrolyses other than 'standard' potentiostatic electrolysis at 2.500 V (Section 5.3) are

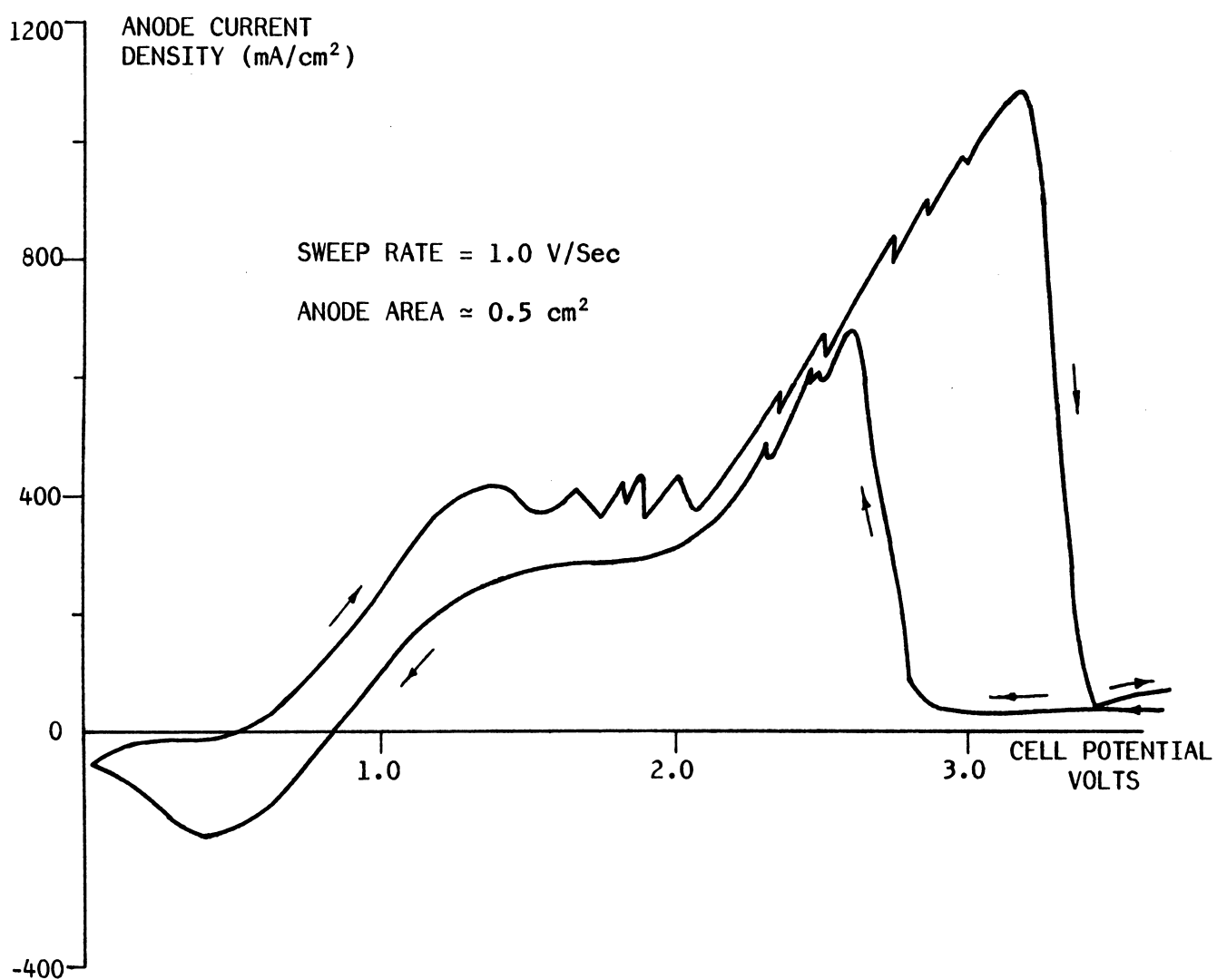


FIGURE 5.15
TYPICAL CYCLIC VOLTAMMOGRAM
T₀ > 2.500V

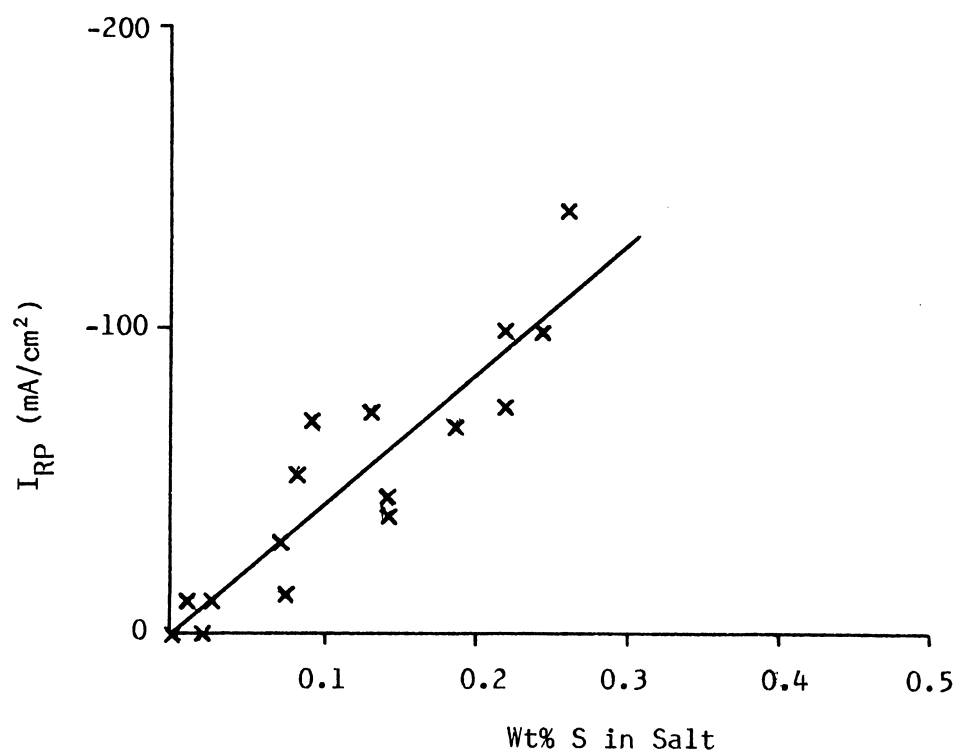


FIGURE 5.16

CORRELATION OF I_{RP} WITH
WT% S IN SALT

Least-squares curve fitting of data :

$$I_{RP} = -0.399 + 455.57 (\text{wt\% S})$$

Correlation coefficient = 0.946

presented. Linear sweep voltammetry data are also presented for runs in which linear sweep voltammograms were obtained during the progress of electrolysis.

5.4.1 Electrolysis with Pre-Doped Salt

In this section the results are presented for four 2.500 V potentiostatic electrolysis experiments in which the fluoride salt was pre-doped to specific levels of anionic impurities. In three of the experiments (Runs F1, F2, F3) sulphide was used as a dopant, while in the fourth (F4) oxide was used.

The sulphur doping was achieved by recycling high-sulphide salt obtained from previous electrolysis runs. This was in the form of a finely ground powder (100% minus 170# mesh, as prepared for analysis) which was blended with pure fluoride salt to give the required sulphide levels. Representative samples for analysis were taken from each batch prior to placing into the crucible.

The oxide doping was achieved by adding an accurately weighed amount of analytical reagent grade magnesium oxide (oven dried at 393K for 24 hours) to a batch of the pure fluoride salt. The salt was doped to an approximate oxide level of 1.0 wt% O^{2-} . The actual doped levels for these four runs and the relevant electrolysis details are given in Table 5.10.

In each of the electrolysis runs an anode in the medium size range ($\sim 0.5 \text{ cm}^2$ true anode area) was used. The copper was doped to normal sulphur levels and standard pre-electrolysis drying and heat-up procedures were applied.

The four electrolysis curves obtained are shown in Figure 5.17(a), together with a typical medium anode undoped 2.500 V potentiostatic electrolysis curve (dashed-line) for comparison, and

RUN	ELECTROLYSIS TIME (min)	ANODE AREA (cm ²)	CURRENT PASSED mAh	COPPER MASS (g)	SALT MASS (g)	COPPER ANALYSIS				SALT ANALYSIS wt% S	
						INITIAL wt% S	FINAL wt% S	FINAL wt% Mg	FINAL wt% Ca	INITIAL	FINAL
F1	40.0	0.54	148.2	43.06	7.83	0.096	N.D.	0.012	N.D.	0.064	0.027
F2	4.5	0.49	48.1	37.97	10.07	0.082	0.016	N.D.	0.0004	0.128	0.218
F3	6.0	0.57	82.7	39.91	9.71	0.088	0.0035	N.D.	N.D.	0.128	0.242
F4	4.5	0.51	69.8	35.16	10.14	0.083	N.D.	0.018	0.0065	(0.990 wt% O) 0.000	0.261

RUN	SULPHUR DISTRIBUTION % TOTAL S					
	INITIAL			FINAL		
	Cu	Salt	Gas	Cu	Salt	Gas
F1	89.2	10.8	0.0	0.0	4.6	95.4
F2	70.7	29.3	0.0	13.8	49.9	36.3
F3	73.9	26.1	0.0	2.9	49.5	47.6
F4	100.0	0.0	0.0	0.0	90.7	9.3

Note:

Run F4: 0.253 g MgO added to 9.889 g of pure fluoride salt, giving nominally 2.49 wt% MgO, or 0.990 wt% O²⁻.

TABLE 5.10
DETAILS OF 2.500 V ELECTROLYSES WITH PRE-DOPED SALT

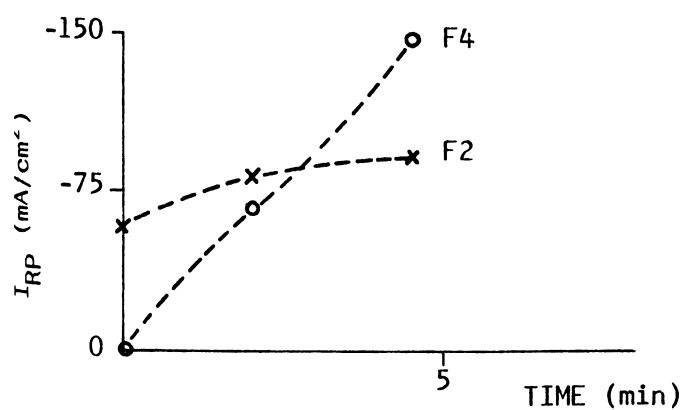
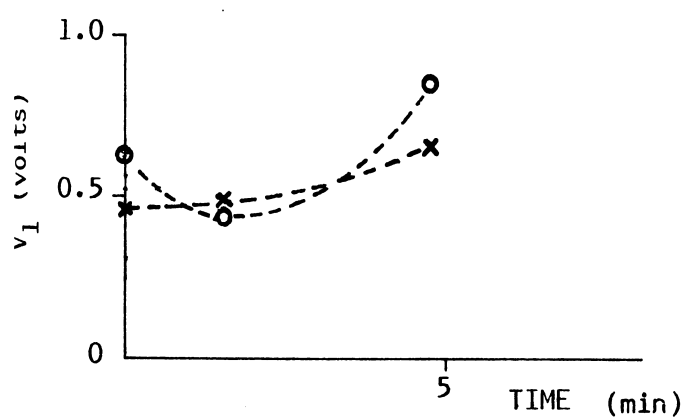
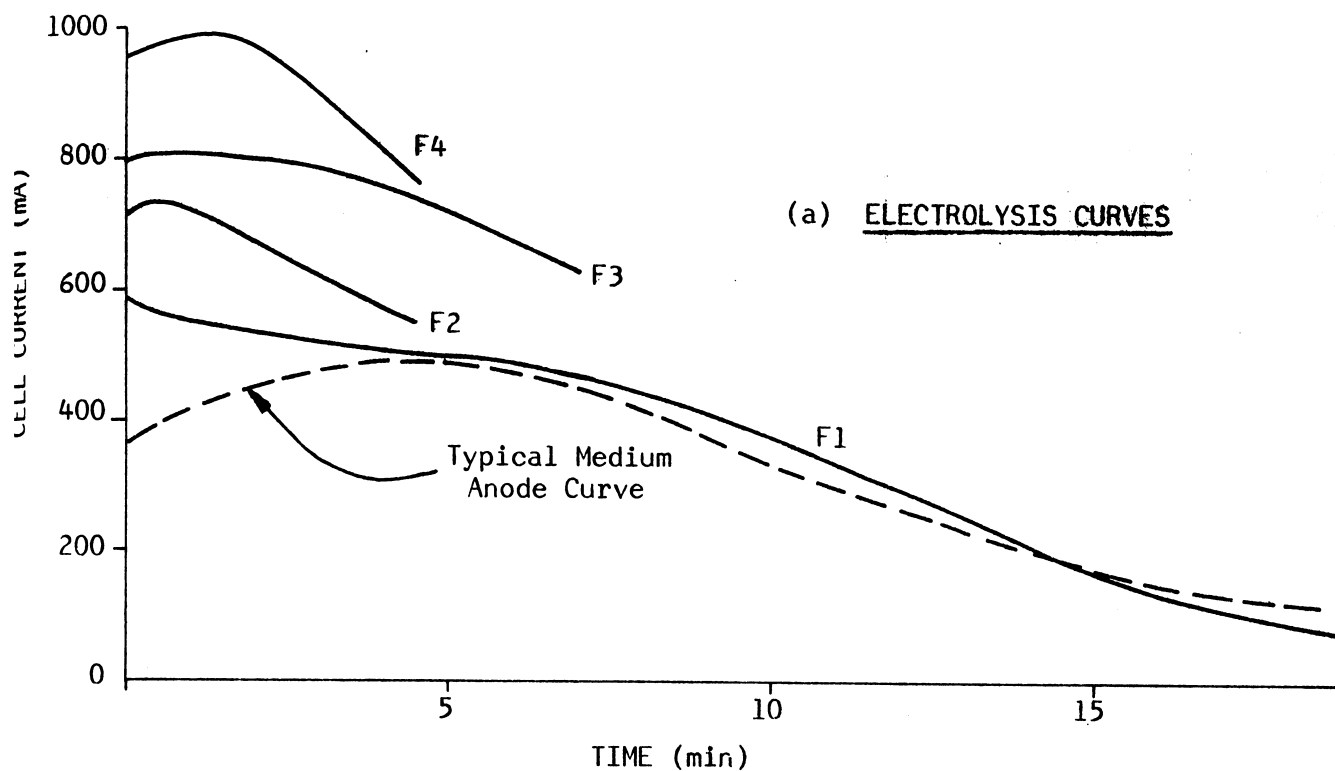


FIGURE 5.17

2.500V POTENTIOSTATIC ELECTROLYSIS WITH
A PRE-DOPED FLUORIDE SALT

data from L.S.V. investigations in runs F2 and F4 (Figures 5.17(b) and 5.17(c)).

The electrolysis curves in Figure 5.17(a) are consistent with anodic control of the electrolysis process, with significantly higher currents observed in the early stages of the electrolysis due to a greater concentration of dissolved anionic species discharging at the lower voltages, i.e. an increased contribution from the I_1 electrolysis current component.

In the sulphide-doped runs the electrolysis current peak is non-existent (F1) or considerably less pronounced (F2, F3) than for the undoped electrolysis, because discharge of sulphide from the fused salt phase at the anode occurs at a significant rate from the time of commencement of electrolysis, thus preventing the rapid initial build-up of sulphide in the salt which normally occurs. However, an increase in sulphide concentration in the salt is still indicated in these runs by the analysis data (F2, F3 - Table 5.10) and the I_{RP} reverse current peak increase shown in Figure 5.17(c) for run F2.

It should be noted that the sulphide build-up in these runs occurred despite the fused salt having a higher initial sulphur concentration than the liquid copper, from which it can be inferred that the initial mass transfer rate of sulphur out of the bulk of the copper is higher than the mass transfer rate of sulphide out of the bulk of the fused salt phase, despite the higher sulphur concentration in the fused salt.

Some further significant aspects of the sulphur-doped electrolyses are:

1. Higher initial electrolysis current for runs F2 and F3 as compared to run F1 due to the higher initial sulphide levels in the fused salt for the former.

2. An initial value of the low-voltage decomposition potential V_1 (Figure 5.17(b)) lower than that normally observed for undoped 2.500 V electrolysis (and similar to that observed after the initial sulphide build-up in the salt - Figure 5.14).

Therefore, this is probably due to the initial sulphide in salt present at the commencement of electrolysis in Run F2 allowing anodic sulphur discharge reactions to take place from the commencement of electrolysis.

3. Significant negative currents are observed in the return sweep of cyclic voltammograms prior to the start of electrolysis (Figure 5.17(c)) due to the presence of initial sulphide in run F2. The initial value of I_{RP} of $\sim (-60) \text{ mA/cm}^2$ is within the range predicted in Figure 5.16 for a sulphide concentration of 0.128 wt%.

The initial electrolysis current for the oxide-doped run F4 was over twice that expected for 'normal' undoped electrolysis and 25-35% higher than that for the two runs doped to 0.128 wt% S (F2, F3). However, the level of oxide doping (1.00 wt% O) was nearly eight times greater than for the sulphide doping in these two runs, and even greater when considered in terms of anion per cent, viz:

F2, F3 - doped to 0.150 anion % S^{2-}

F4 - doped to 2.179 anion % O^{2-}

The cyclic voltammograms in run F4 showed that the increased electrolysis current was due to an increase in the I_1 current component, with initial values of I_1 in the range $1200 - 1500 \text{ mA/cm}^2$ (anode current density) as compared to 'normal' values of $\sim 300 \text{ mA/cm}^2$ for undoped electrolysis. No significant increase in the I_2 current above that expected for 'normal' electrolysis was observed.

The electrolysis current peak in run F4 occurred in the early stages of electrolysis - after the passage of only 19.6 mAh, which represents 41% of the total faradic equivalent of sulphur contained in the copper for this run. This can be compared to a peak after 62% of the total faradic equivalent of sulphur in copper has been passed for the 'typical' medium-anode electrolysis curve shown in Figure 5.5. This indicates that the shift of the higher decomposition potential V_2 to higher values occurs at an earlier stage of electrolysis in the high-current run F4.

The rapid increase in the reverse current component I_{RP} in linear sweep voltammograms for run F4 (Figure 5.17(c)) reflects the rapid increase in sulphide level of the fused salt - reaching 0.261 wt% after 4.5 minutes. This rapid increase in sulphide concentration in the fused salt and the final sulphur distribution data for this run (Table 5.10) which show only 9.3% of total sulphur was anodically discharged from the salt melt suggests that oxide ion discharge was the dominant anode reaction during electrolysis, and hence a very low anodic current efficiency was achieved.

5.4.2 Blank Electrolyses

The details of two potentiostatic electrolysis experiments using 'pure' undoped copper are given in Table 5.11. It should be noted that the applied cell potential was 2.500 V in run F5, and 1.500 V in run F6.

In each case the copper feed was pre-melted (i.e. deoxidised) and cooled in a graphite crucible, reproducing the temperature cycle experienced in the normal sulphur-doping procedure. A smaller mass of copper was used in run F6 to increase the sensitivity of detection of reduced metallic species in the copper phase in subsequent chemical analysis.

RUN	ELECTROLYSIS TIME (min)	APPLIED POTENTIAL (VOLTS)	ANODE AREA (cm ²)	CURRENT PASSED (mAh)	COPPER MASS (g)	SALT MASS (g)	FINAL COPPER ANALYSIS	
							wt% Mg	wt% Ca
F5	56.0	2.500	0.56	55.6	43.14	9.71	0.033	0.0110
F6	80.0	1.500	0.51	58.2	20.06	9.80	0.037	0.0093

TABLE 5.11

DETAILS OF BLANK ELECTROLYSIS RUNS

The electrolysis curves obtained are shown in Figure 5.18(a) with L.S.V. data (variation of V_1 potential) shown in Figure 5.18(b). In each case electrolysis was continued until low residual currents (~ 2 mA) were obtained.

It can be seen that significant electrolysis currents are observed in the 'pure' systems, as was the case in the preliminary work on determination of the decomposition potential of the fluoride melt (Section 5.2.1) in which electrolyte 'cleaning' at a potential of 1.500 V was necessary. Thus the electrolysis current passed in these runs is impurity-related with decomposition of oxides (MgO, CaO) the most probable reactions.

With no sulphur in the system, no initial current rise is observed because no initial sulphide build-up occurs. Thus a current decay is observed as the impurities are electrolysed out of the melt.

The linear sweep voltammograms and cyclic voltammograms exhibited an initial current-rise at V_1 , but no appearance of a second (I_2) current rise at V_2 or reverse currents (I_{RP}) was evident in 0 - 2.50 V cyclic voltammograms, both of these being sulphur-related. Similarly, there was no evidence of the initial 0.2 V decrease in V_1 which normally is observed during the initial transfer of sulphide into the fused salt (Figure 5.18(b)).

In both cases the final value of V_1 was ~ 1.25 V, which is identical to extended sulphur-doped electrolyses.

If it is assumed that the only impurities present are oxide impurities, then an estimate of the amount of oxide initially in the melt can be made from the amount of current required to electrolyse the impurities out of the salt melt in these runs. For run F5:

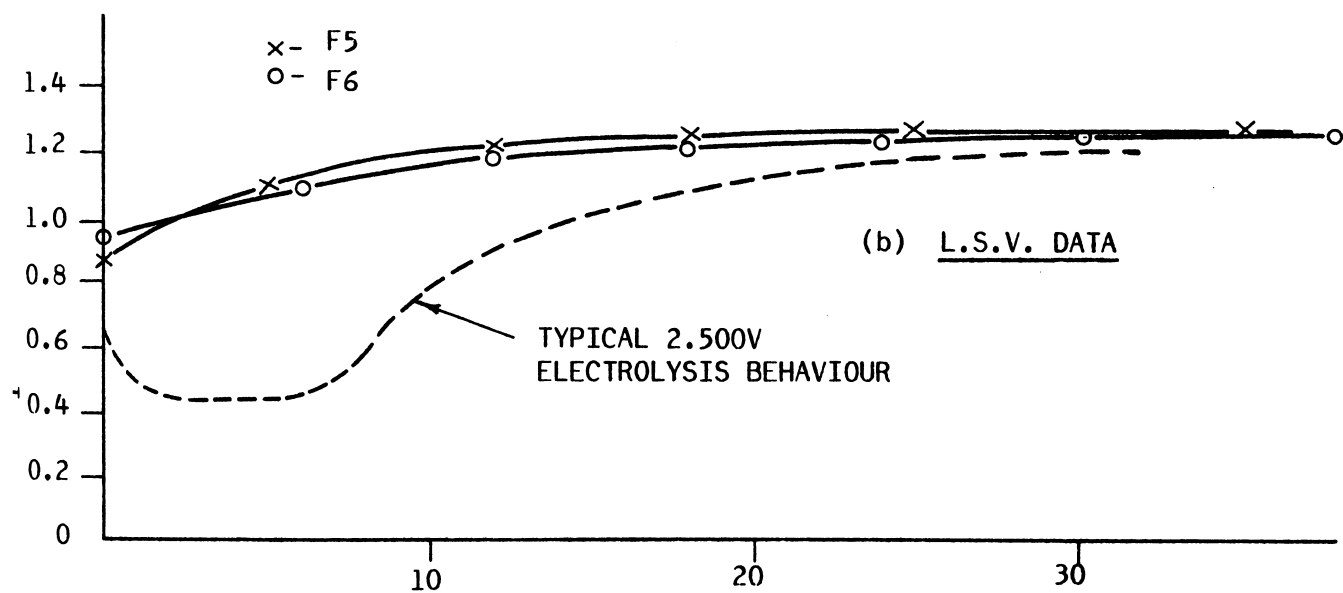
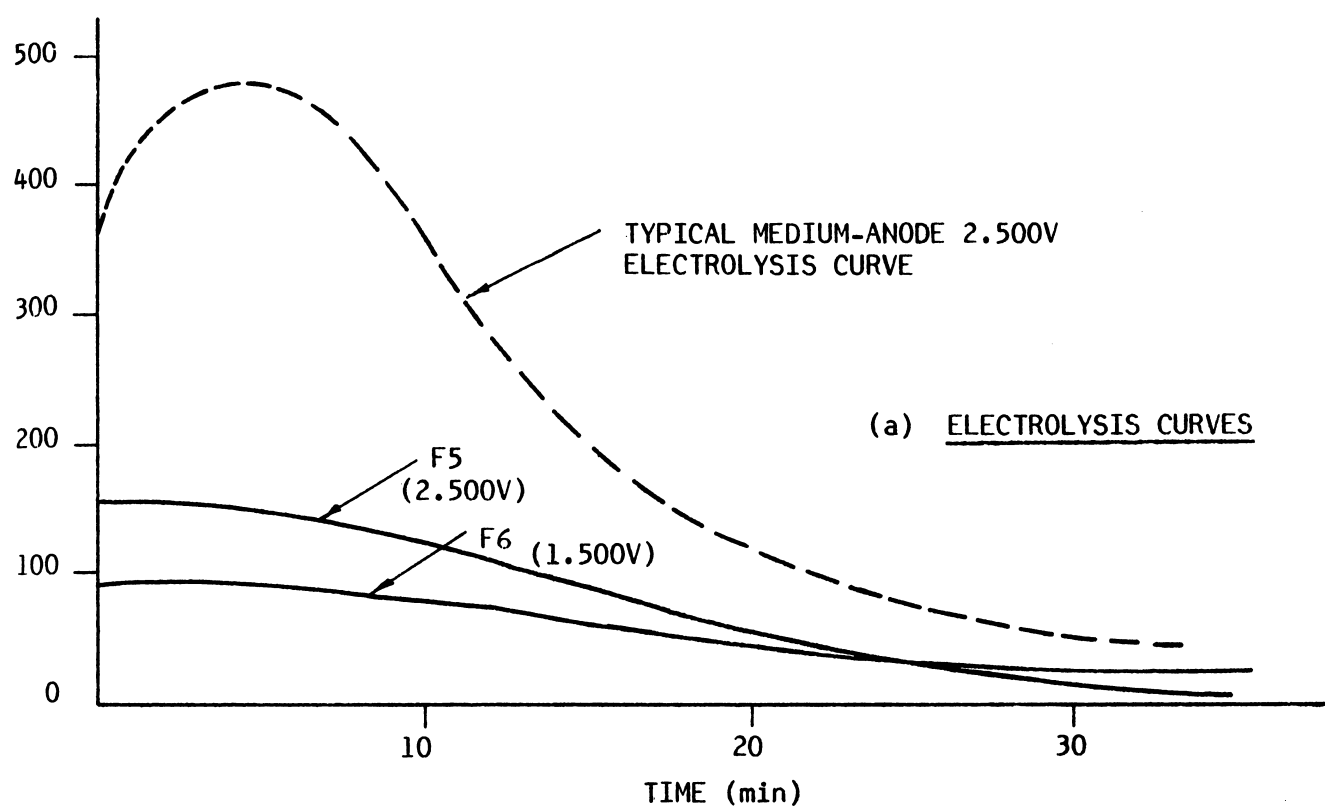


FIGURE 5.18

'BLANK' ELECTROLYSIS RUNS F5 AND F6

$$\begin{aligned}
 55.6 \text{ mAh} &= 0.0166 \text{ g O}^{2-} \quad (n = 2) \\
 &= 0.17 \text{ wt\% O}^{2-} \text{ in } 9.71 \text{ g salt;}
 \end{aligned}$$

and for run F6:

$$\begin{aligned}
 58.2 \text{ mAh} &= 0.0174 \text{ g O}^{2-} \quad (n = 2) \\
 &= 0.18 \text{ wt\% O}^{2-} \text{ in } 9.80 \text{ g salt}
 \end{aligned}$$

Thus significant concentrations of oxide impurities in the fluoride melt are indicated by these data, concentrations that are close to the peak sulphide concentrations normally reached in 2.500 V electrolysis (Section 5.3.2).

The build-up of magnesium and calcium in the copper phase during electrolysis in these experiments represents a faradic equivalent equal to 67.8% and 32.5% of the total current passed for F5 and F6 respectively. The figure for run F5 confirms that Mg^{2+} and Ca^{2+} reduction is the dominant cathode reaction and therefore likely cell reactions in these experiments are decomposition of dissolved MgO and CaO .

5.4.3 High-Sulphur Electrolysis

Table 5.12 summarises the data for two potentiostatic electrolysis runs in which the copper was doped to sulphur levels approximately 6-7 times higher than the 'standard' 2.500 V potentiostatic electrolyses. In Figure 5.19 the electrolysis curve and L.S.V. data for F7 are shown, while the electrolysis curve for the lower voltage electrolysis run (F8 - 1.500 V) is shown in Figure 5.20. No L.S.V. data were obtained for run F8.

The initial current rise to a peak ($418 \text{ mA} = 972 \text{ mA/cm}^2$ anode c.d.) in run F7 is similar to that observed for normal 2.500 V potentiostatic electrolysis. The most obvious effect of the higher sulphur levels is that the subsequent electrolysis current does not

RUN	ELECTROLYSIS TIME (min)	APPLIED POTENTIAL (V)	ANODE AREA (cm ²)	CURRENT PASSED (mAh)	COPPER	SALT
F7	86.0	2.500	0.43	552.0	40.30	9.71
F8	300.0	1.500	0.42	445.0	41.60	7.50

RUN	COPPER ANALYSIS				FINAL SALT ANALYSIS (wt% S)	FINAL SULPHUR DIST. % TOTAL S			ANODE * WT. LOSS (g)
	wt% S		FINAL wt% Mg	FINAL wt% Ca		COPPER	SALT	GAS	
	INITIAL	FINAL							
F7	0.642	N.D.	0.038	N.D.	0.341	0.0	12.8	87.2	0.02120
F8	0.560	0.0054	N.D.	N.D.	0.122	1.0	3.9	95.1	0.01275

TABLE 5.12

DATA FOR HIGH SULPHUR ELECTROLYSES

* Type A3 anodes used

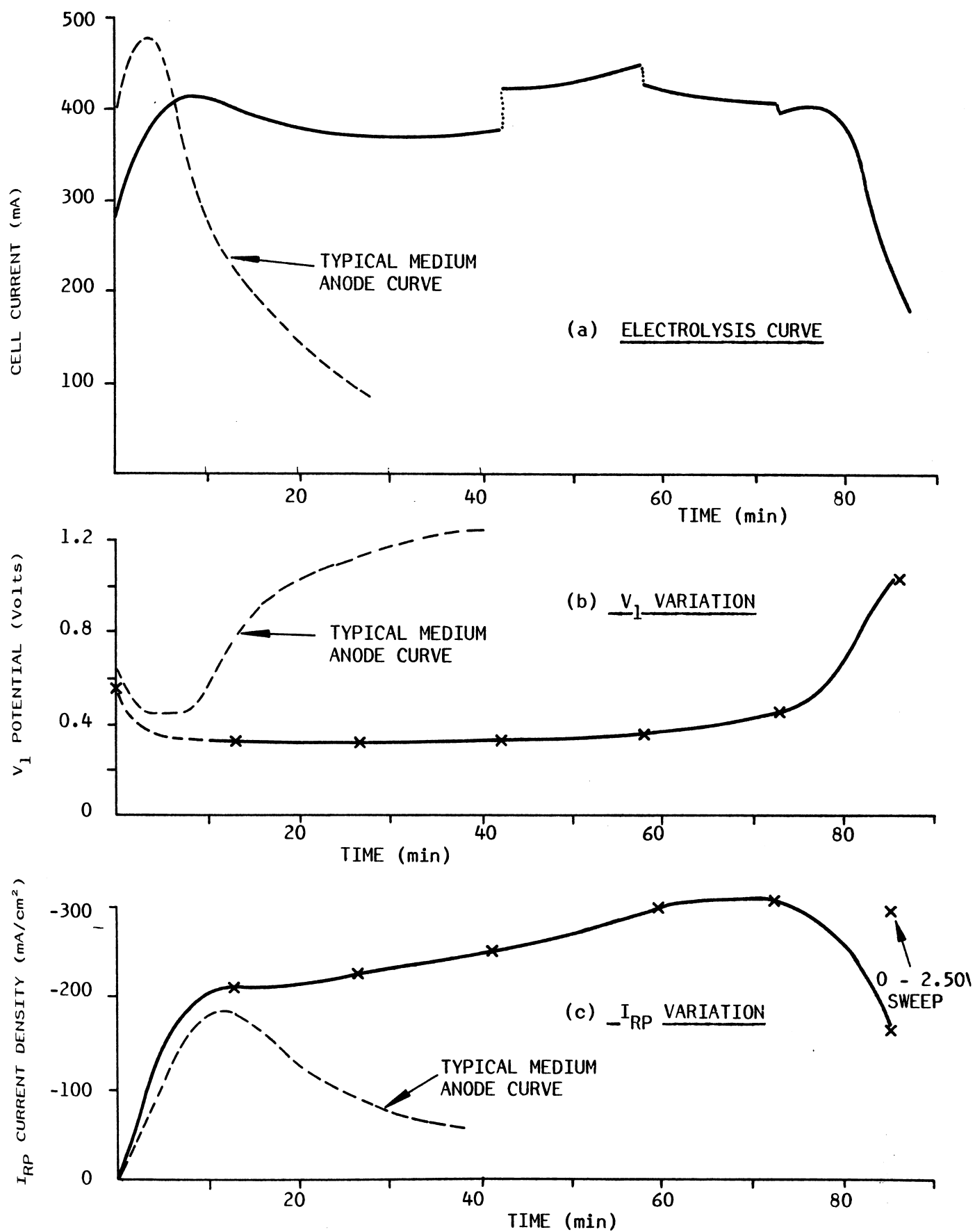


FIGURE 5.19

HIGH-SULPHUR ELECTROLYSIS

RUN F5

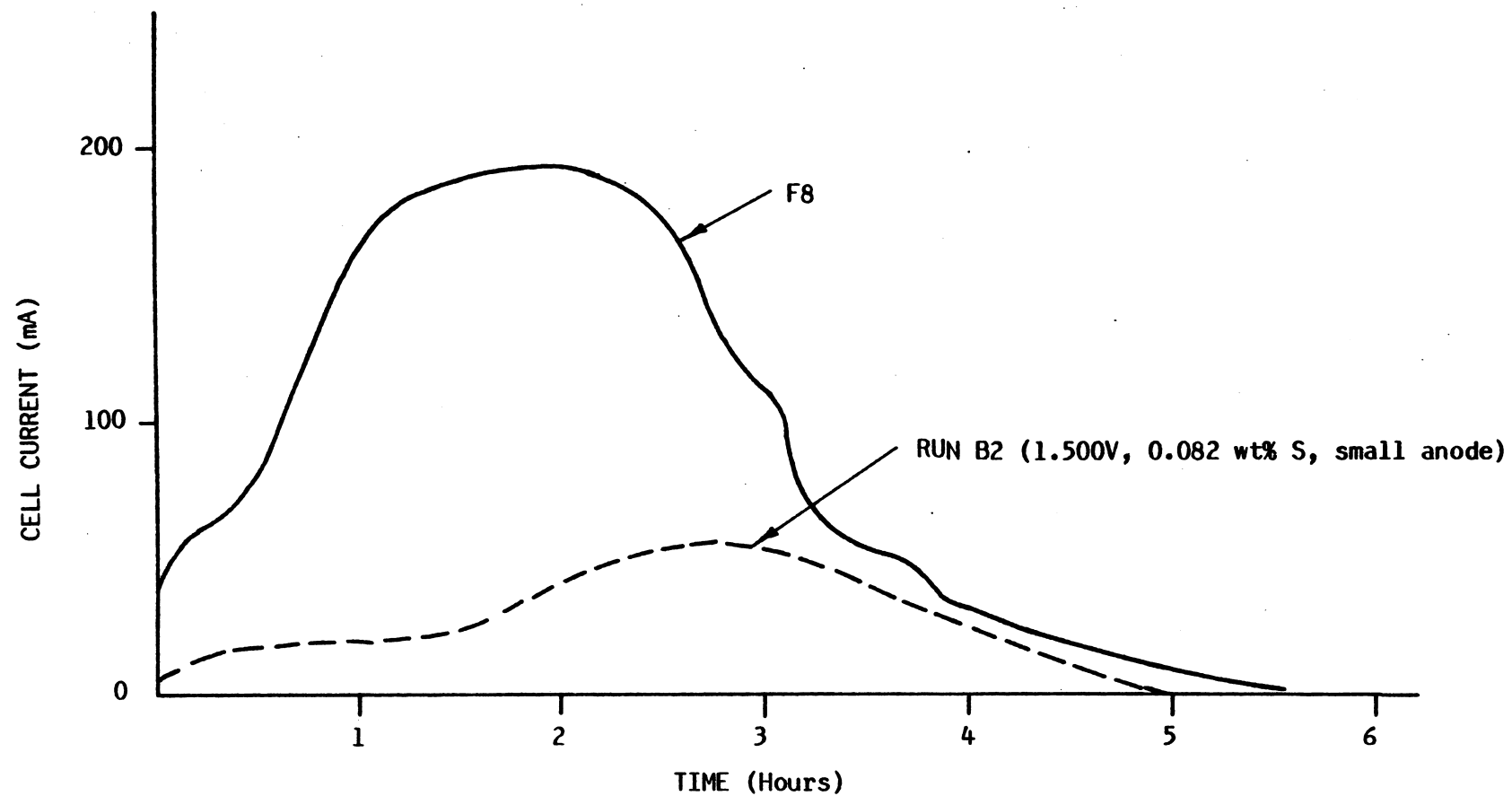


FIGURE 5.20
HIGH-SULPHUR ELECTROLYSIS
RUN F8 : 1.500V

drop rapidly until 75 minutes electrolysis time has elapsed, at which point it is likely that the copper is becoming depleted in sulphur. A rapid drop-off in electrolysis current is observed (similar to the current drop shown on the 'normal' curve) due to the rapid rise in the V_1 (and V_2) decomposition potentials and therefore the loss of the I_2 current component.

The discontinuities in the electrolysis curve resulted from the interruption of electrolysis to obtain L.S.V. data, and were probably caused by a small change in the true anode area (i.e. a change in the proportion of the anode surface shielded by a stable gas film) during the period when electrolysis was stopped. This is the only run in which this phenomenon was observed, but its occurrence obviously places increased uncertainty on the value of the true anode area used for this run (which was measured as 0.43 cm^2).

The increased sulphur in this run resulted in significantly higher sulphide levels in the fused salt during electrolysis, as is indicated by the greater magnitude of the I_{RP} current and the lower value of the V_1 decomposition potential than is typically observed in normal 2.500 V electrolysis.

It should be noted that the reverse current peak data points in Figure 5.19(c) were obtained with 0-1.50 V voltage sweeps in this case rather than 0-2.50 V sweeps, except at the end of electrolysis where the I_{RP} value for a 0-2.50 V sweep is also shown. The 0-2.50 V sweep gave a significantly higher magnitude of I_{RP} than the 0-1.50 V sweeps, therefore it is likely that all the plotted points would be significantly higher if 0-2.50 V sweeps had been used. It should also be noted that, with the relatively high final sulphur concentration in the salt (0.341 wt%), the value of the I_{RP} anodic current density in

a 0-2.50 V sweep (-290 mA/cm^2) does not show good agreement with the I_{RP} vs. wt% S in salt correlation shown in Figure 5.16, which predicts $I_{\text{RP}} = -140 \text{ mA/cm}^2$ for 0.341 wt% S in salt. It will be assumed, therefore, that the approximately linear relationship between I_{RP} and wt% S in salt only holds for relatively low sulphur levels of less than 0.25 wt%.

Considering the high sulphide concentration in the fused salt reached during electrolysis in run F7, (probably $> 0.5 \text{ wt\%}$ as compared with $\sim 0.2 \text{ wt\%}$ for 'standard' 2.5 V potentiostatic electrolysis), a significantly higher electrolysis current would have been expected for this run. However, the maximum anode current density reached was only 1060 mA/cm^2 (at $t = 56 \text{ mins}$) while the average 'peak' current density (from $t = 8$ to $t = 75 \text{ mins}$) was 930 mA/cm^2 , compared to an average peak anode current density of 981 mA/cm^2 for the 'standard' medium anode electrolyses. In addition, although a rise in the sulphide concentration of this molten salt from $t = 13 \text{ mins}$ to $t = 73 \text{ mins}$ is indicated from the I_{RP} data, the electrolysis current did not show a significant overall rise during this period.

One possible explanation for this behaviour is that the oxide component of the I_1 anode current is less significant in high-sulphur electrolyses, due to the fact that the bulk of the low level oxide impurities would be discharged from the molten salt in the relatively early stages of electrolysis (within 20-30 minutes, from consideration of runs F5 and F6), which could account for the slight drop in electrolysis current observed in this period. Thus the oxide current component would not contribute significantly in the subsequent electrolysis, whereas in normal 'medium' anode 2.500 V electrolyses the bulk of the oxide impurities would still be present in the salt

phase when the peak current is reached, which could produce a significant additional I_1 anode current component above that arising from sulphide ion discharge.

The electrolysis curve for the lower-voltage run F8 (Figure 5.20) shows a maximum cell current of 190 mA (452 mA/cm^2 anode current density) which is less than 50% of the average 'peak' anode current density for F7. At the lower voltage it is likely the cell current is determined only by the rate of diffusion of oxide and sulphide anions through the fused salt to the anode (i.e. I_1 current component) with no I_2 current component possible at this potential. Thus, not only is the electrolysis current significantly lower than for 2.500 V electrolysis but the time required to 'build-up' the current to a maximum is much greater (~ 1.5 hours compared with ~ 8 minutes) because the only source of anode current at the commencement of electrolysis is the discharge of the low-level oxide impurities out of the salt melt, meaning that the initial rate of sulphur transfer from the copper to the fused salt is low. Only when the sulphide level in the salt builds up significantly after 30-40 minutes does the electrolysis current start to increase accordingly.

The rapid reduction in electrolysis current after ~ 2.5 hours occurs when the cathode current efficiency drops (due to depletion of sulphur in the copper). This results in a nett decrease in the sulphide level in the fused salt and therefore the overall electrolysis current decreases.

The peak anode current density for F8 of 452 A/cm^2 was more than twice that of the lower-sulphur 1.500 V run B2 which reached 205 A/cm^2 (see Figure 5.20), indicating a maximum sulphide in salt concentration for F8 approximately 100% greater than for B2 due to the higher total sulphur in the former.

The electrode weight loss data for the runs F7 and F8 give conclusive evidence that the discharge of sulphide at the anode does not result in the formation of CS_2 gas to any significant degree. The calculated values of the electron transfer numbers n_2 and n_1 (as defined in Section 5.3.5) are 3.72 and 11.70 respectively for F7; 2.62 and 15.63 respectively for F8. The values of n_2 are within the expected range of 2-4, while the values of n_1 (calculated assuming sulphur discharge is carbon-consuming) are obviously impossibly high.

The overall current efficiency data for these two runs are summarised below:

	<u>CATHODE C.E. (%)</u>	<u>ANODE C.E. (%)</u>	<u>RATIO: $\frac{\text{ANODE C.E.}}{\text{CATHODE C.E.}}$</u>
F7	78	68	0.87
F8	87	84	0.97

High overall anode current efficiencies can be achieved in high-sulphur electrolyses due to the relatively high levels of sulphide build-up in the fused salt, and the attainment of what is close to 'steady state' conditions.

The anode current efficiency is nearly equal to the cathode current efficiency for the lower voltage run F8, while the difference between the two is significantly greater for run F7, presumably due to the presence of the higher-potential I_2 current component at the higher cell potential.

The total faradic equivalent of magnesium in the final copper for run F7 (no calcium was detected) was 33.8 mAh, which represents only 28% of the total non-sulphur cathode current. If the simple assumption is made that the other 72% of the non-sulphur cathode

current produced cathodic discharge of magnesium vapour which dissolved directly in the fused salt phase then the final level of dissolved magnesium in the salt phase would be 0.40 wt%. The dissolution of reduced metal in the molten salt phase has several implications in terms of a potential continuous fused salt electrorefining process. These are further discussed in Section 5.6.

5.4.4 High Voltage Electrolysis

In run F9 the cell potential was increased in stages up to 3.200 V, which was the maximum that could be sustained without experiencing high resistance fluoride gas filming at the anode and resultant loss of cell current (i.e. the "anode effect"). The data for this run are summarised in Table 5.13 and the electrolysis curve is shown in Figure 5.21.

As expected, the increased potential results in an increased cell current, which can be attributed to a higher I_2 current component. Thus, the cell current is effectively 'climbing up' the steeply rising section of the linear sweep voltammogram above V_2 (Figure 5.15) as the cell potential is increased.

A marked change in the nature of the electrolysis curve is observed when the cell potential is increased from 2.9 V to 3.2 V. Before the increase, the cell current is steadily increasing, with no indication of a current peak being reached at 670 mA. As soon as the cell potential is increased, the cell current rises to 790 mA and begins to drop from this point, indicating the 'peak' has been effectively reached.

When the cell current decreases after the current 'peak', it can be seen that it is still significantly greater than that observed for 'normal' 2.500 V electrolysis with a medium anode, due to the

ELECTROLYSIS TIME (min)	APPLIED POTENTIAL (V)	ANODE AREA (cm ²)	CURRENT PASSED (mAh)	COPPER MASS (g)	SALT MASS (g)
13.0	2.800 -3.200 (varied)	0.56	125.2	39.96	9.71

COPPER ANALYSIS				FINAL SALT ANALYSIS (wt% S)	FINAL SULPHUR DIST. % TOTAL S			ANODE * WT. LOSS (g)
wt% S		FINAL wt% Mg	FINAL wt% Ca		COPPER	SALT	GAS	
INITIAL	FINAL							
0.088	N.D.	0.038	0.0215	0.070	0.0	19.3	80.7	0.01120

TABLE 5.13

DATA FOR POTENTIOSTATIC ELECTROLYSIS

AT HIGH POTENTIAL

*Type A3 anode used

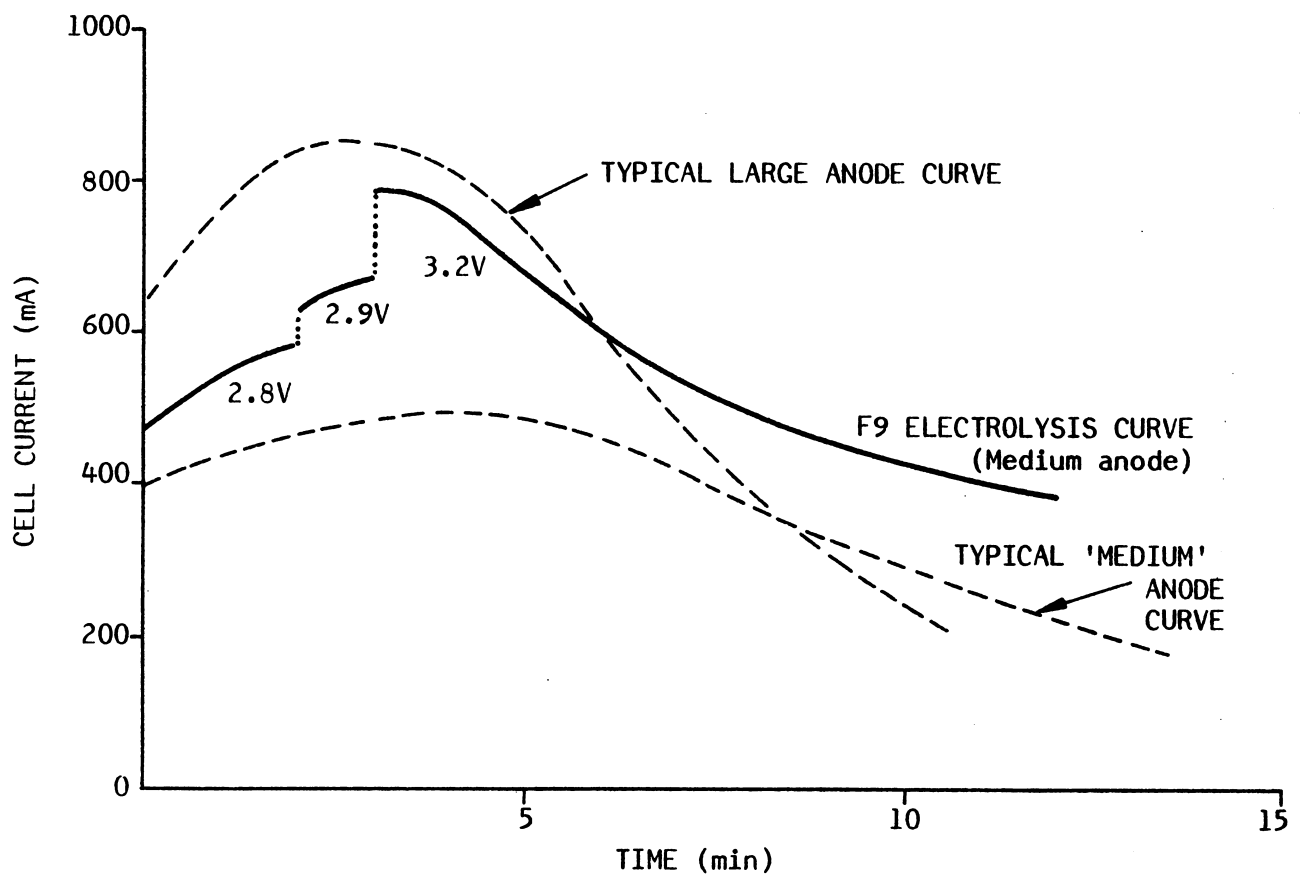


FIGURE 5.21

ELECTROLYSIS CURVE FOR HIGH-VOLTAGE

RUN F9

continued contribution of the I_2 current component in this stage of electrolysis with a cell potential 0.55 V greater than the decomposition potential of the 'pure' fluoride melt (i.e. 2.65 V).

Analysis of the furnace off-gases for gaseous fluoride using the technique described in Section 4.6.4 indicated an amount of fluoride absorbed equivalent to only 8% of the non-sulphur anodic current. This proportion is less than indicated for two of the 'standard' 2.500 V electrolysis runs (see Section 5.3.5) and gives further indication that this analysis technique is not quantitative. The total non-sulphur anode current in this run was 77.5 mAh. If it is assumed that a faradic equivalent of oxide equal to 50 mAh was electrolysed out of the melt in this run (which is probably greater than the actual amount, since a total of less than 60 mAh was electrolysed out of the melt in each of the two extended electrolysis 'blank' runs F5 and F6), this still gives a predicted level of fluoride discharge of 35% of the non-sulphur anodic current, which is over four times greater than the amount detected by the analysis of off-gases.

From the magnesium and calcium analyses for the final copper in run F9, the calculated total faradic equivalent of magnesium and calcium in copper was 45.0 mAh (33.5 mAh Mg, 11.5 mAh Ca), which represents 64% of the total non-sulphur cathodic current. This is significantly higher than the 50% maximum observed for run D6 in the 'standard' 2.500 V electrolyses (see Section 5.3.3), and represents fairly efficient 'collection' of the cathodically discharged magnesium and calcium by the liquid copper.

5.4.5 Galvanostatic Electrolysis

Attempts to complete galvanostatic electrolysis experiments at 'reasonable' current densities were not successful with the

electrolysis cells used in this work due to the repeated occurrence of the "anode effect", resulting in very high cell voltages and almost complete loss of the electrolysis current.

As previously described (Section 5.2.1), the anode effect is commonly observed in the electrolysis of fluoride melts with a carbon anode. Its cause is considered to be the formation of a high resistance gaseous film (e.g. CF_4) which desorbs slowly from the anode surface thereby preventing wetting of the anode by the melt^{47,48,76}. It will occur at a particular 'critical' anode potential and anode current density, which are dependent on the cell conditions prevailing - in particular the concentration of other co-evolving ionic species (i.e. sulphides and oxides in this case) in the melt adjacent to the electrode surface^{47,48,81}. If these species are co-evolving at a sufficiently high rate, then the 'flushing' effect produced will prevent the formation of a stable CF_4 gaseous film.

With a medium type A2 anode and standard electrolysis conditions (i.e. ~ 0.085 wt% S in 40 g copper under a 10 g fluoride melt at 1423K) it was found that the anode effect (A.E.) would occur repeatedly and interrupt electrolysis as summarised below:

Start of electrolysis

A.E. at a critical anode current density of $\sim 550 \text{ mA/cm}^2$ with a cell potential of 2.6 V.

After 'extended' electrolysis (~ 80 mAh passed)

A.E. at a critical anode current density of $\sim 430 \text{ mA/cm}^2$ with a cell potential of ~ 3.1 V.

'Middle' stages of electrolysis

A.E. conditions very variable - critical anode current densities $450\text{--}600 \text{ mA/cm}^2$ at cell potentials of 2.5–3.0 V.

The critical anode current density of 430 mA/cm^2 for the anode effect after 80 mAh 'extended' electrolysis is similar to the anode current density in 2.500 V potentiostatic electrolysis at this period (see Figure 5.6), which is effectively the limiting current for oxide and sulphide anion diffusion to the anode. This is consistent with the critical current density for the anode effect being that at which effective 'flushing' of the CF_4 by the co-evolving gases cannot be sustained.

The range of the critical anode current density for the anode effect during the 'middle' stages of electrolysis when the highest sulphide levels in the salt are expected is not significantly higher (in fact the lower limit is lower) than the critical anode current density levels at the start and towards the 'end' of electrolysis. This would suggest that sulphide ion discharge is not very effective in providing the required 'flushing' action to prevent the occurrence of the anode effect.

When type A1 anodes (with a projecting boron nitride sheath) were used in galvanostatic electrolysis, it was found that the anode effect was repeatedly occurring at anode current densities of the order of 250 mA/cm^2 . This is significantly lower than for the type A2 anode, and presumably due to the stabilising effect the boron nitride sheath provides for the formation of a gaseous CF_4 film.

5.5 SUMMARY OF CURRENT EFFICIENCY DATA

Where data are available, the overall current efficiency has been calculated for the potentiostatic electrolysis experiments detailed in Sections 5.2, 5.3 and 5.4. The calculated values obtained are summarised in Table 5.14.

RUN NO.	B2	B3	B4	C1	C2	C3	D1	D2	D3	D4	D5	D6
Current Passed (mAh)	127.0	97.5	176.0	38.5	54.0	90.4	24.8	36.2	79.8	68.3	85.0	101.6
Corrected Current Passed (mAh)	119.8	96.9	156.6	34.7	56.2	94.7	25.2	41.0	78.0	63.2	88.4	97.5
Cathode C.E. %	49	60	37	90	87	61	93	90	67	82	63	60
Anode C.E. %	47	47	37	30	39	44	38	26	30	38	42	49

RUN NO.	D7	D8	E1	E2	E3	F1	F2	F3	F4	F7	F8	F9
Current Passed (mAh)	116.4	196.1	38.0	63.3	85.0	148.2	48.1	82.7	69.8	552.5	445	125.2
Corrected Current Passed (mAh)	129.1	186.4	37.0	64.3	89.8	116.5	54.0	82.6	86.1	74.9	66.9	124.7
Cathode C.E. %	44	31	90	78	65	49	87	68	68	78	87	45
Anode C.E. %	36	30	31	28	39	52	60	46	6	68	84	38

TABLE 5.14

SUMMARY OF CURRENT EFFICIENCY DATA

5.5.1 Cathode Current Efficiency

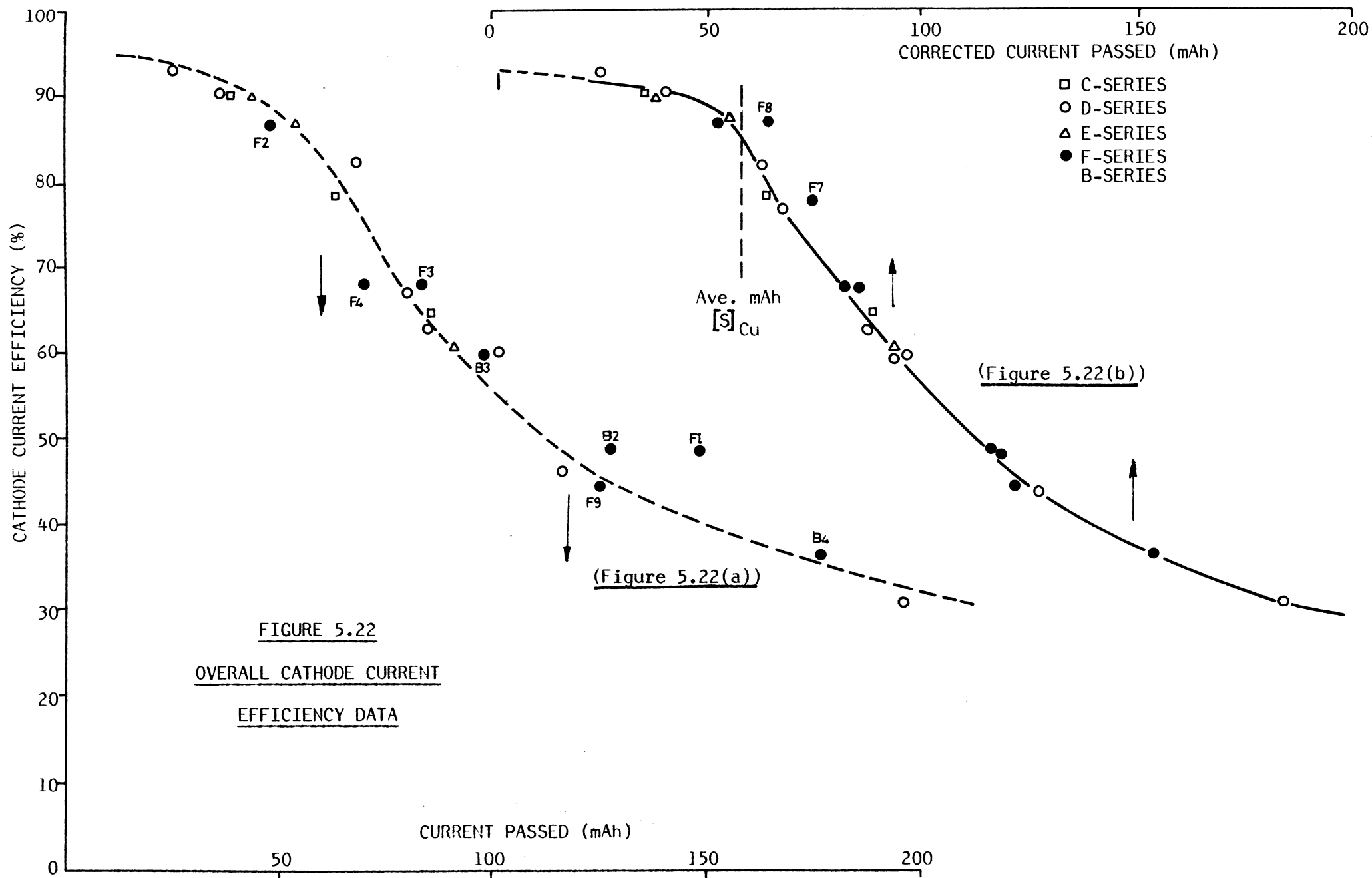
The values of overall cathode current efficiency versus current-passed have been plotted in Figure 5.22(a). The scatter in these points can be considerably reduced if the cathode current efficiency is plotted against "corrected current passed" as shown in Figure 5.22(b). The "corrected current passed" was calculated as defined in Section 5.3.2.

This second plot shows that consistent behaviour is observed in all runs, except the high-sulphur electrolyses (F7, F8) which indicate that higher overall cathode current efficiencies than in the lower sulphur runs (~ 0.085 wt% S) are achieved at the corresponding stage of electrolysis. However, it should be remembered that the amount of current passed in the high sulphur runs was approximately 7-8 times greater, therefore the use of the "corrected current passed" can be misleading with such large differences involved.

At any stage of electrolysis, the instantaneous current efficiency is defined by the equation:

$$\eta_I = \eta_0 + \frac{d\eta_0}{dC} \cdot C \quad \dots 5.5$$

where η_I is the instantaneous current efficiency after the passage of C mAh of current with an overall current efficiency of η_0 . In order to derive instantaneous current efficiency data from Figure 5.22(b) a polynomial curve has been fitted to the data points (excluding F7 and F8) for the period 50-200 mAh using "least squares" curve fitting. In this simple model it has been assumed that the overall cathode current efficiency is constant ($\sim 90\%$) in the 0-50 mAh electrolysis period. A degree 4 polynomial was computed with the following coefficients:



$$\eta_o = 192.51 - 2.19C + 9.18 \times 10^{-3}C^2 - 3.43 \times 10^{-3}C^3 - 4.32 \times 10^{-8}C^4 \quad \dots 5.6$$

The value of $d\eta_o/dC$ at various points on this curve has been calculated and from this data the instantaneous cathode current efficiency versus "corrected current passed" was calculated using (equation 5.5), and is shown in Figure 5.23. This curve indicates a rapid decrease in instantaneous cathode current efficiency occurs during the passage of 30 mAh of current after a total of 50 mAh has passed, such that the instantaneous cathode current efficiency is effectively zero after the passage of 80 mAh.

The indication of negative current efficiencies after $C = 80$ mAh can be attributed to the simplicity of this model and the curve fitting techniques used. At 'high' values of C the computed value of η_I is very sensitive to small changes in the calculated $d\eta_o/dC$ value (equation 5.5) and unrealistic figures can be produced. Negative instantaneous current efficiency values could only result from reversion of sulphur from the salt to the copper phase, and as previously discussed (Section 5.3.2) the experimental evidence indicates this is not occurring.

5.5.2 Anode Current Efficiency

The overall anode current efficiency values for potentiostatic electrolyses have been plotted against "corrected current passed" in Figure 5.24. A large degree of scatter is observed, however the points can be grouped into four regions as defined by the dashed lines in this Figure. The grouping of data points is discussed below:

1. The oxide doped run (F4) exhibited a very low overall anode current efficiency of 6%. All other runs exhibited an overall anode current efficiency which was greater than 25%.

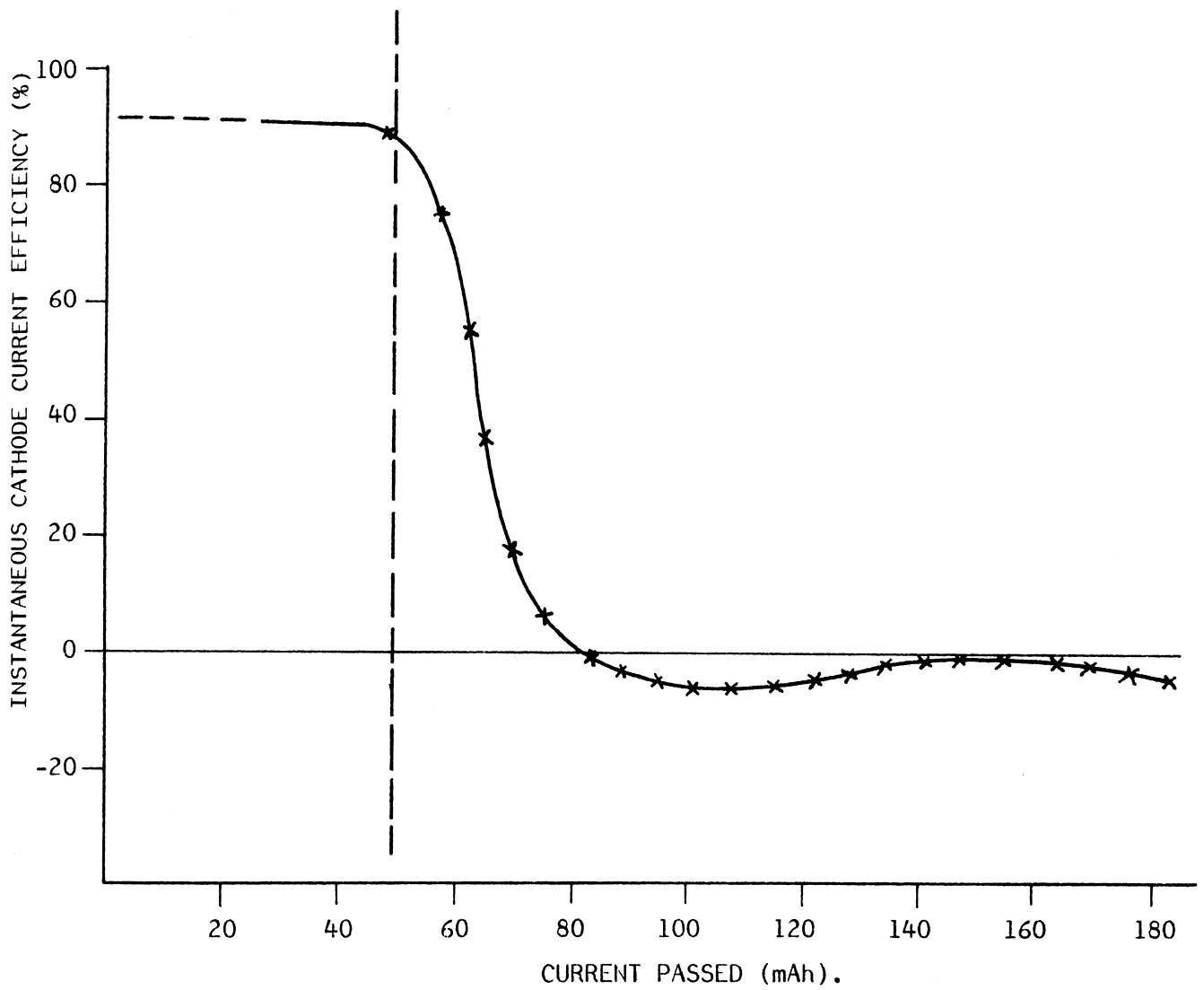
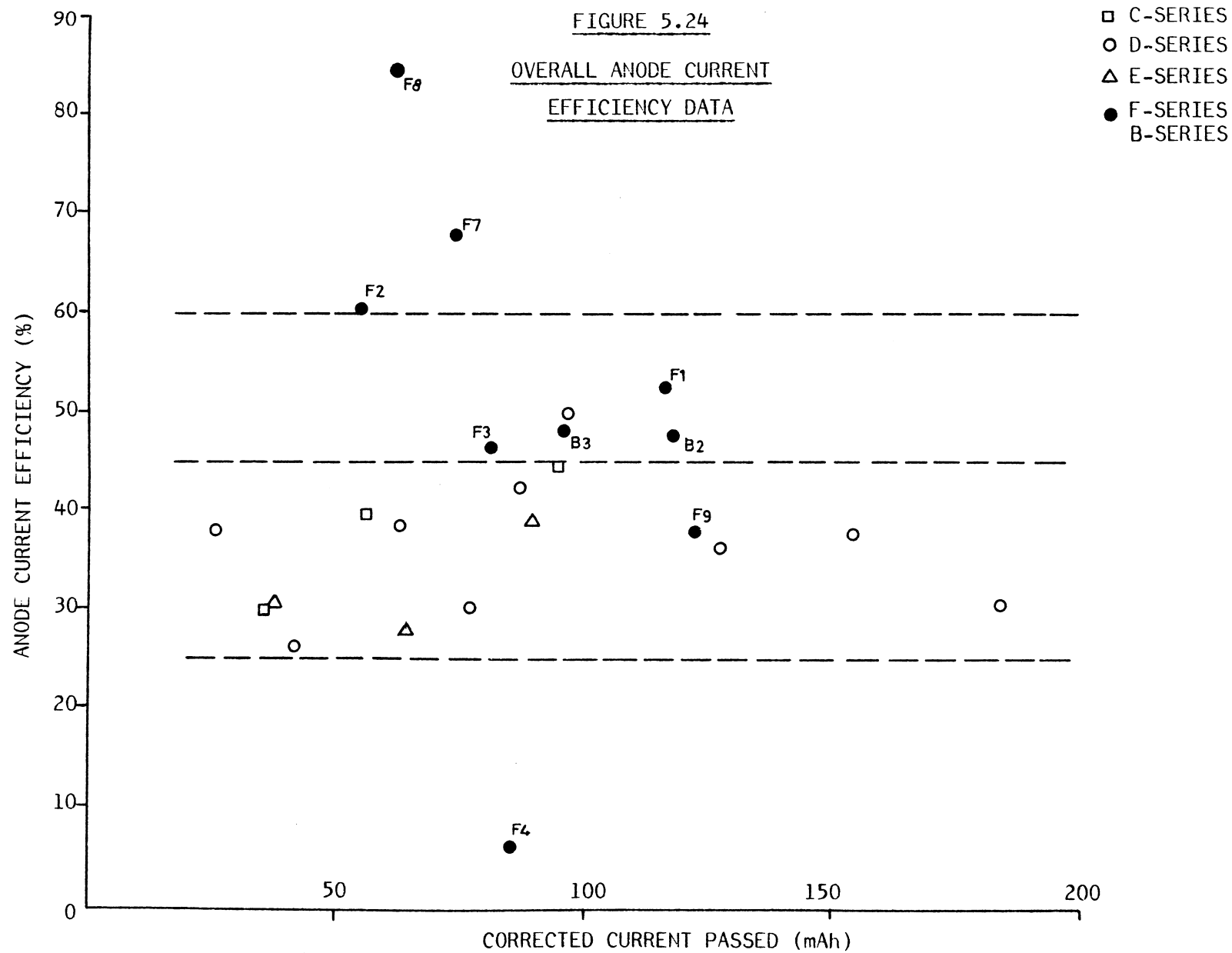


FIGURE 5.23

COMPUTED INSTANTANEOUS CATHODE

CURRENT EFFICIENCY CURVE



2. All of the 'standard' 2.500 V electrolysis runs (with one exception being D6 : C.E. = 49%) showed an overall anode current efficiency in the range 25-45%. The variation in anode area between the C, D and E series runs had no apparent effect on the overall anode current efficiency.
3. The overall anode current efficiency for the high voltage run F9 was in the same range as the 'standard' electrolysis runs.
4. The low-voltage (B2, B3) and sulphide-doped salt runs (F1, F2, F3) exhibited overall anode current efficiencies in the range 45-60%.
5. The two high-sulphur runs (F7, F8) exhibited overall anode current efficiencies in the range 65-85% - significantly higher than those for any other runs.

5.6 DISCUSSION

5.6.1 Impurities in the Melts

Blank electrolyses with 'pure' copper/salt systems (Sections 5.2.1 and 5.2.4) indicated that significant amounts of impurities were present in the melts, with significant electrolysis currents observed at cell potentials of 1.500 V and 2.500 V.

It is likely that the impurity currents observed can be attributed to the presence of oxide anions in the fused salt. The reasons for this are:

1. The deoxidation of the copper in the copper-doping treatment in graphite crucibles was found to be very effective, with test analyses showing less than 15 ppm oxygen in copper after doping. This amount of oxygen in copper represents a maximum faradic equivalent of only 2 mAh. From typical analysis data (Table 4.2) no other copper impurities would be significant.

2. It is recognised that there are two potential sources of oxide contamination of the salt phase, viz:

- . Hydrolysis reactions resulting from the presence of residual moisture in the salt (Equation 4.1, Section 4.5.3).
- . Dissolution of the boric oxide binding agent from the boron nitride crucible sidewalls and boron nitride electrode sheaths.

Both of these sources are likely to be significant contributors to the residual oxides in the fused salt.

Preparation of very pure fluoride melts is difficult⁶⁴, and techniques such as sparging the melt with HF or H_2/HF gas mixtures^{84,85}, or fusing the fluoride with NH_4HF_2 to prevent hydrolysis, combined with pre-electrolysis to discharge oxides⁸⁶ have been employed. It is generally recognised⁶⁴ that simple drying and fusion of fluorides under an inert atmosphere or under high vacuum is not effective in completely removing residual moisture which can result in hydrolysis reactions. The problem of boric oxide contamination arising from the use of hot-pressed boron nitride materials with fluoride melts has been recognised by Castellano et al⁸⁷.

Figures given by the manufacturers (Union Carbide) for the hot-pressed boron nitride used in this work show typical B_2O_3 binding agent contents of 3.9 wt% (maximum) for HBN grade (used for most of this work) and 1.0 wt% (maximum) for HBC grade.

From observations made in this work it is considered more likely that the major source of oxide was from residual moisture in the salt rather than B_2O_3 dissolution. This is because:

1. The use of HBC grade boron nitride components rather than HBN grade components did not give any noticeable increase in anode current efficiencies.
2. Likewise, re-use of boron nitride crucible components did not give any noticeable improvements in anode current efficiency.
3. Electron probe microanalysis of used boron nitride sidewall sections indicated a depth of melt penetration of 0.04 mm for 1 hour of contact with the salt melt at 1423K, and 0.17 mm for 8 hours of contact at 1423K. However, it can be calculated that 'leaching' of the B_2O_3 binding agent from the boron nitride sidewalls to a minimum depth of 0.22 mm for HBN grade boron nitride, and 0.89 mm for HBC grade boron nitride, would be required to produce an oxide concentration of 0.18 wt% in 10 g of salt, which is the level indicated from the electrolysis data in run F6 (blank electrolysis, 80 minutes contact). Thus, a melt penetration depth of ~ 0.05 mm expected for 80 minutes contact should result in an oxide content in the fused salt of ~ 0.04 wt% resulting from leaching of the B_2O_3 binding agent in an HBN crucible, which is less than one-quarter of the estimated oxide content for run F6. If it is assumed the remaining oxide was derived from residual moisture in the melt then this would require a residual moisture content of 0.16 wt% in 10 g of fluoride salt.

Although, from the above discussion, it is likely that residual moisture is a more significant source of oxide impurities than the B_2O_3 binding agent, the shape of the electrolysis curves in the blank electrolyses, (F5, F6; Section 5.4.2), with a fairly 'flat' region in the first ~ 10 minutes, does indicate that significant

B_2O_3 dissolution is occurring during the initial stages of electrolysis, which is when the maximum rate of 'leaching' would be expected. For the potentiostatic electrolysis of a fixed amount of impurity out of a constant volume of melt, an exponential decay of the electrolysis current from the time of commencement of electrolysis is expected⁹², whereas an approximately constant current would be expected for continuous replacement of the impurity species in the melt as it is electrolytically removed.

The detection of small amounts of MgO in some residues from evolution analysis of salt samples (see Section 4.6.2) gives further evidence that the low-level impurities in the fluoride salt are oxides.

Decomposition of dissolved magnesium and calcium oxides is expected at fairly low potentials when a graphite anode is used. Thompson and Kaye⁹⁷ reported decomposition potentials for saturated solutions of MgO and CaO in a fluoride melt at 1373K using a graphite anode, of 0.82 V and 0.81 V respectively, which, using the temperature coefficients reported by these workers, extrapolate to 0.62 V and 0.64 V at 1423K.

The theoretical decomposition potentials of pure liquid MgO and CaO at 1423K assuming unit activity of decomposition products have been calculated from the data of Barin and Knacke^{54,55} and are summarised below:

<u>Anode Product</u>	<u>MgO</u>	<u>CaO</u>
$O_2(g)$	1.86 volts	2.12 volts
$CO(g)$	0.63 volts	0.90 volts
$CO_2(g)$	0.84 volts	1.10 volts

5.6.2 Proposed Model for Potentiostatic Electrolysis

5.6.2.1. Anode Discharge Reactions

In considering a model for the potentiostatic electrolysis process which is consistent with the experimental results obtained, a 'standard' 2.500 V potentiostatic electrolysis curve will be considered, which is shown schematically in Figure 5.25. This curve has been divided into different regions with the points A, B, C, D, placed on the curve.

The analysis of the form of the electrolysis curves with different anode sizes in Section 5.3.1 showed that the anode reactions were current-limiting at 2.500 V, and therefore determined the overall shape of the electrolysis curve. Thus the regions of the curve in Figure 5.25 can be considered in terms of the probable anode reactions occurring during electrolysis.

Use is made of the distinction between the lower-voltage diffusion-limited cell current component (I_1) and the higher-voltage cell current component (I_2) as described in the section on linear sweep voltammetry work (Section 5.3.6). The results obtained are consistent with the following anodic discharge reactions occurring:

- . I_1 current component - co-discharge of sulphide anions and oxide anions from the salt melt, with the rate of discharge controlled by the effective diffusivity of these 'low level' anionic species from the bulk of the fused salt to the melt adjacent to the anode surface.
- . I_2 current component - discharge of fluoride anions from the salt melt, which will form gaseous species co-evolving with the gaseous species produced in the lower voltage sulphide and oxide discharge reactions. The rate of discharge of fluoride

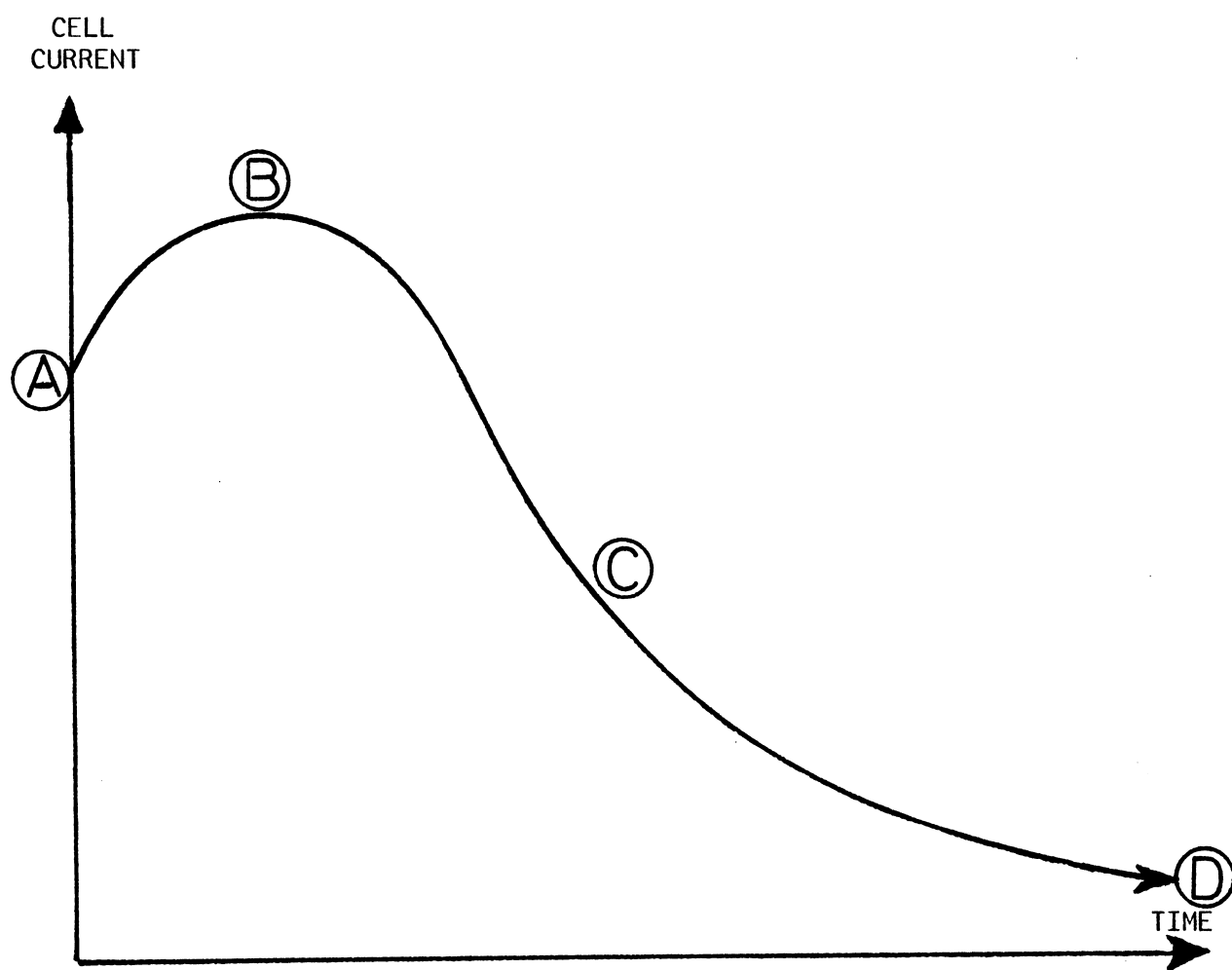


FIGURE 5.25

REGIONS OF TYPICAL ELECTROLYSIS CURVE

ions is not diffusion-controlled due to the high concentration of fluoride anions in the melt. Thus the rate of discharge can be considered 'activation' controlled, and increases with applied potential up to the point where the "anode effect" occurs.

The anode reactions occurring at various stages of electrolysis (see Figure 5.25) are discussed below:

Point A - commencement of electrolysis, 2.500 V applied.

At this point there will be a negligible amount of sulphide present in the fluoride melt, due to the very slow rates of non-electrolytic sulphur transfer from the copper to the salt (Section 5.2.2) and also due to the fact that electrolysis is commenced as soon as possible after the attainment of the cell temperature.

The only anionic species in the melt are therefore low-level oxide ions (I_1) and fluoride ions (I_2). These two initial current components are approximately equal, (see Section 5.3.6).

Region A-B

During this period the sulphide concentration in the fused salt increases rapidly. This results in an overall increase in the I_1 current component, which now comprises oxide and sulphide anion discharge at the anode. The I_2 current component (fluoride ion discharge) remains essentially constant during this period because of an unchanged anode overvoltage, i.e. the higher-voltage decomposition potential V_2 is 'static' during this period (as described in Section 5.3.6).

Region B-C

The rapid decrease in electrolysis current during this period results from the loss of the fluoride ion anode discharge reaction (I_2 current component). This is caused by the 'shift' in the value of the V_2 decomposition potential from ~ 2.1 V to a final value of 2.65 V (Section 5.3.6). During this period the sulphide level in the salt increases and reaches a maximum, hence the I_1 current component reaches a maximum in this period.

Period C-D

Diffusion-controlled sulphide and oxide ion discharge from the fluoride melt continues at the anode. The cell current decays as the concentration of these two species is progressively reduced.

From consideration of the above discussion, the relative contributions of the anionic species in the salt melt to the electrolysis current at the anode during 2.500 V potentiostatic electrolysis can be summarised schematically, as shown in Figure 5.26.

5.6.2.2 Gaseous Species Evolved at the Anode

As discussed above, there are three anionic species discharged on the graphite anode. The gaseous molecular species evolved at the anode cannot be clearly identified from this experimental work, and a mass spectrographic study would be required to obtain more data on the co-evolving species formed under particular conditions of anode electrode potential, current density and anion concentrations in the salt.

Studies of the inherently more simple system of anodic discharge of oxide ions from fluoride melts using graphite anodes in alumina electrolysis⁸², or anodic oxide ion discharge from oxide slags at a

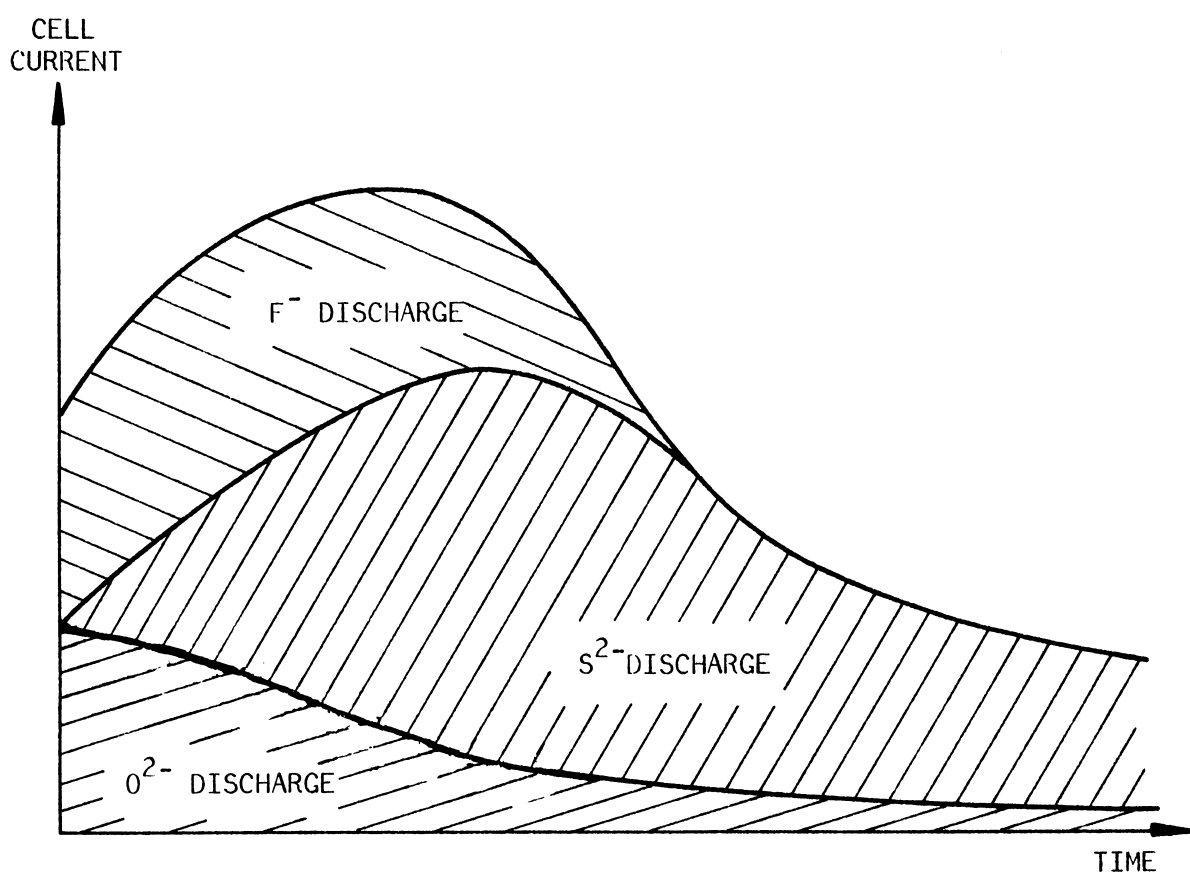
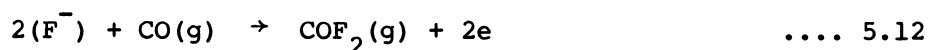
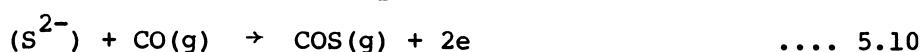
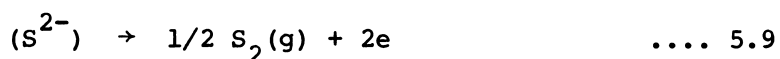


FIGURE 5.26

SCHEMATIC REPRESENTATION OF
THE RELATIVE CONTRIBUTIONS OF
ANIONIC DISCHARGE REACTIONS DURING
2.500V ELECTROLYSIS

graphite anode⁹⁰, clearly show that the nature of the gaseous species evolved at the anode cannot be predicted purely from thermodynamic considerations. The following anode reactions and gaseous species are possibilities:



The relative amounts of any evolved gaseous species will depend on the anion activities in the melt adjacent to the anode, and kinetic considerations associated with the discharge of the anions on the carbon anode.

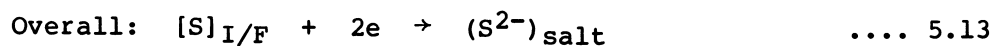
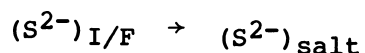
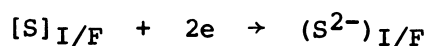
Although a precise understanding of these anodic reactions needs to be established, the present work clearly indicates that co-evolution of sulphide and oxide ions can take place, and hence 'cleaning' of the fused salt is observed.

Further, the anode weight-loss data indicate that under the conditions prevailing in this work, direct electrochemical combination of the discharged sulphide ions and the anode carbon to form CS₂ gas is unlikely. This supports the observations of Eiselev⁹¹ who studied the reaction of graphite with sulphur at high temperatures.

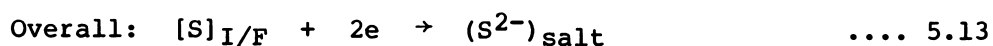
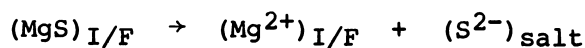
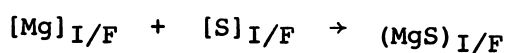
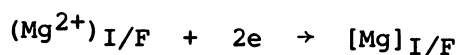
5.6.2.3 Cathode Transfer Reactions

In the early stages of electrolysis, when relatively high levels of sulphur are present in the copper, there are two possible schemes for the cathodic transfer of sulphur from the metal to the fused salt:

1. Direct electrochemical transfer of sulphur:



2. Discharge of reactive metal species (Mg and Ca) and subsequent rapid chemical combination of the reduced metal with dissolved sulphur. Taking magnesium discharge as an example:

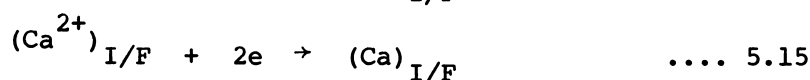
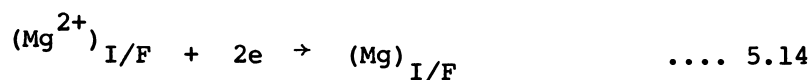


It can be seen that both these possible reaction paths result in the same overall electrode reaction (equation 5.13), which is essentially reduction of dissolved sulphur atoms at the cathode interface to produce sulphide ions dissolved in the salt melt.

An essential feature of these reactions is the necessary presence of sulphur atoms at the metal/salt interface to directly (through scheme (1)) or indirectly (through scheme (2)) participate in the electrochemical reaction. This obviously requires sufficiently high rates of mass transfer of sulphur atoms from the bulk of the liquid copper to the metal/salt interface to sustain these reactions.

When low levels of sulphur in copper are reached, the effects of sulphur depletion will cause a change in the cathode mechanism, with the rate of mass transfer of sulphur atoms to the interface no longer able to maintain the sulphur activity required to sustain the above

reactions. At this stage, direct discharge of reduced metal species (Mg and Ca) will occur; viz:



Obviously once the copper is effectively fully depleted in sulphur these will be the sole cathode reactions occurring.

Clearly, then, two different cathode reaction mechanisms will be observed, viz:

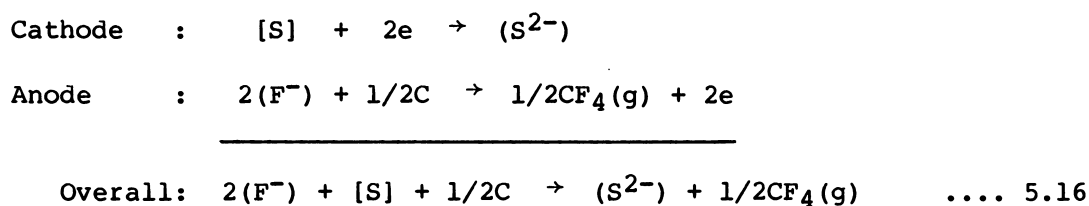
- . Mechanism I : Initial stages of electrolysis - high rate of [S] diffusion - overall cathode reaction is transfer of sulphur according to equation 5.13.
- . Mechanism II : Later stages of electrolysis - low rates of [S] diffusion and depletion of [S] in copper - the overall cathode reaction is discharge of reduced metal species (Mg and Ca) at the cathode interface according to equations 5.14 and 5.15. The reduced metals can subsequently undergo dissolution in both the liquid copper and the fused salt phases, with dissolution in the copper resulting in chemical desulphurisation to very low levels.

A 'transition' period would be expected when the rate of sulphur diffusion in copper drops below a 'critical' level, during which the contribution of Mechanism I decreases and the contribution of Mechanism II increases.

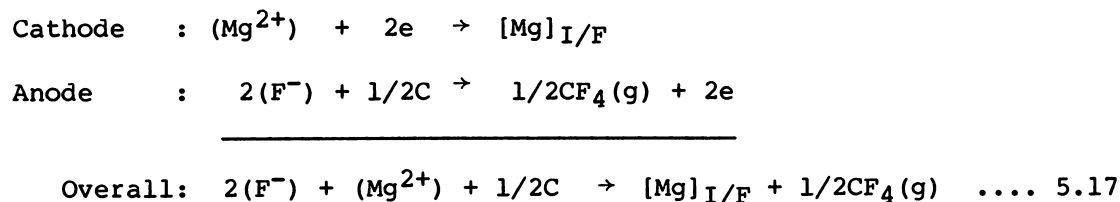
During this transition period, the cathode potential will increase as the mechanism changes from 'low-voltage' discharge of sulphur, to 'high voltage' discharge of magnesium and calcium ions. This is manifested in the observed upwards shift in the V_1 and V_2

potentials of approximately 0.5 V (Section 5.3.6) as the effects of depletion of sulphur in the copper become predominant.

Thus, it can be seen then that, although the overall current magnitude at any stage of electrolysis is effectively controlled by the anode reactions, the reason for the rapid decrease in current observed after the current peak (i.e. the loss of I_2 current) is the change in cathode discharge mechanism. The presence of sulphur at the cathode in the initial stages of electrolysis can be considered as a 'depolarizing' effect, which allows discharge of fluoride at the anode to occur at a cell potential as low as ~ 2.10 V, through the reaction:



As the cathode reaction changes towards Mechanism II, obviously fluoride ion discharge will no longer be possible at 2.500 V, since that would require the overall decomposition of the fluoride melt according to equation 5.17 below:



which requires a minimum cell potential of 2.65 V (see Section 5.2.1).

The relative shifts in the 'internal' current-voltage curves (i.e. polarization curves) for each electrode which result from the change in the reaction mechanism at the cathode have been summarised schematically in Figure 5.27.

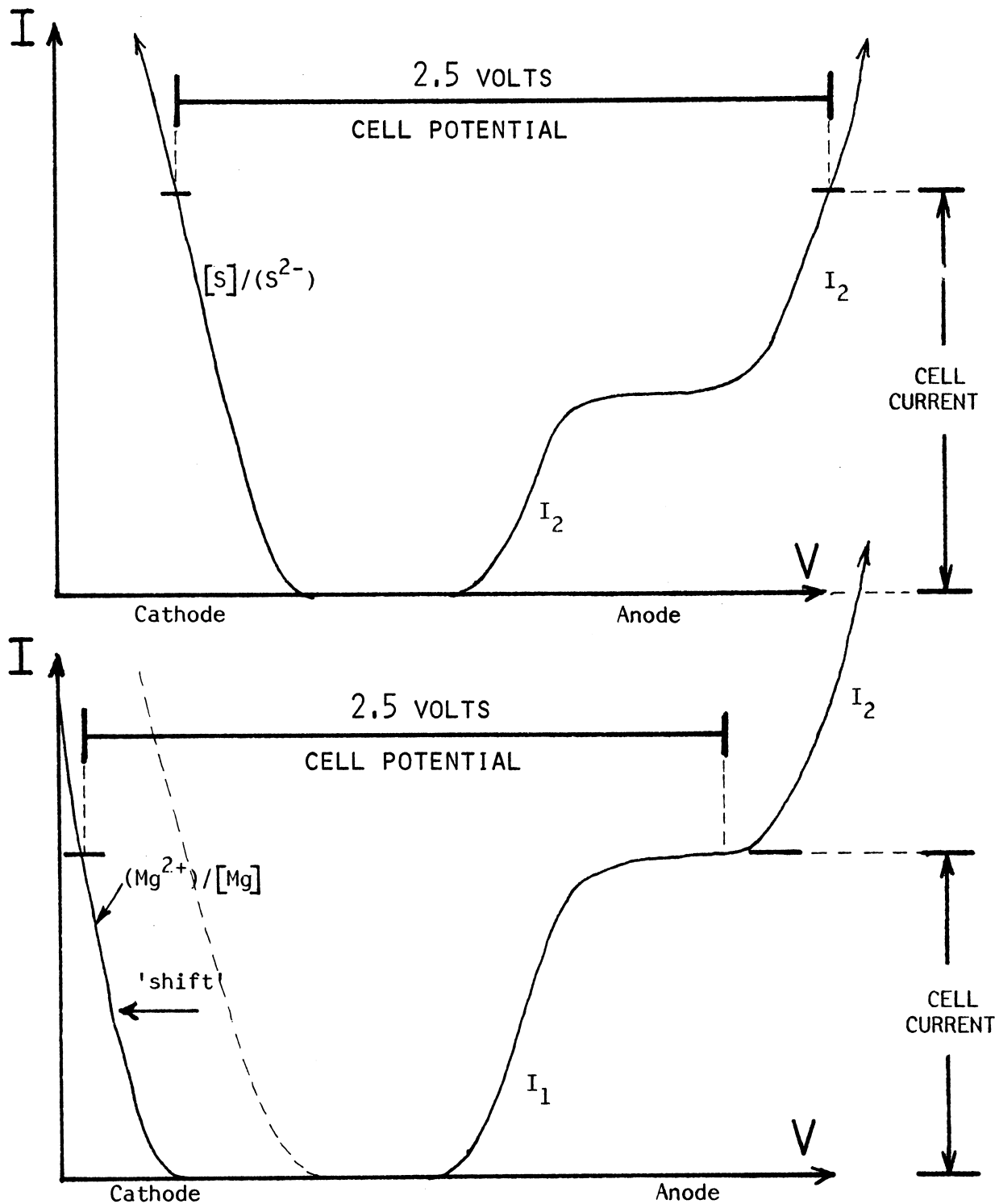


FIGURE 5.27

SCHEMATIC REPRESENTATION OF CHANGES IN
THE ELECTRODE POLARIZATION CURVES DURING 2.500V
ELECTROLYSIS

Top Diagram - 'early' stages of electrolysis (eg., 10 mAh passed)

Lower Diagram - 'later' stages of electrolysis (eg., 80 mAh passed)

5.6.3 Kinetics of Sulphur Transfer

5.6.3.1 Cathodic Transfer

As described in the previous section, a change in the cathode reaction mechanism occurs when the amount of sulphur in the copper is reduced to a level where the rate of mass transfer of sulphur atoms from the bulk to the cathode interface can no longer 'keep up' with the anode-controlled electrolysis current. This change in mechanism results in a subsequent drop in electrolysis current due to the loss of fluoride discharge, and thus a current peak is observed.

Therefore, the peak cathode current density for potentiostatic electrolysis at 2.500 V (or greater) can be considered a 'critical' cathode current density at which the mass transfer of sulphur in the copper becomes rate-limiting for cathodic sulphur transfer, at the bulk sulphur concentration that exists in the liquid copper at that time.

An estimate of the expected bulk sulphur concentration in the liquid copper when the current peak occurs has been derived for the three 'typical' 2.500 V potentiostatic electrolysis curves (small, medium and large anode curves - see Figure 5.5) and the high voltage electrolysis run F9 (see Figure 5.21), with the data summarised in Table 5.15. Values of the expected sulphur concentration in the copper at the current peak have been calculated, assuming 90% overall cathode current efficiency up to that point.

The data derived in this table have been plotted in Figure 5.28 as wt% S in copper versus critical cathode current density.

From theoretical considerations the limiting current density (i.e. 'critical' current density) for mass transfer of an electroactive species to an electrode⁹³ is given by:

RUN	AVE. MASS Cu (g)	AVE. TOTAL mAh [S]	AVE. mAh TO PEAK	AVE. INITIAL wt% S IN Cu	EXPECTED wt% S in Cu AT CURRENT PEAK	PEAK CATHODE CURRENT DENSITY (mA/cm ²)
C-Series	41.23	59.0	43.4	0.0856	0.029	51.1
D-Series	39.73	58.1	35.8	0.0883	0.039	132.9
E-Series	40.48	57.8	31.0	0.0854	0.044	237.8
F9	39.96	57.9	29.0	0.0925	0.055	218.0

TABLE 5.15PREDICTED BULK CONCENTRATION OF SULPHUR IN COPPERWHEN THE ELECTROLYSIS CURRENT PEAK IS REACHED

- NOTE: 1. Ave. mAh[S] and mAh to peak data for C, D and E-Series taken from Figure 5.6.
2. 90% overall cathode current efficiency has been assumed for the electrolysis period from commencement to attainment of the current peak.
3. Peak cathode current density is based on a nominal cathode area of 3.62 cm².

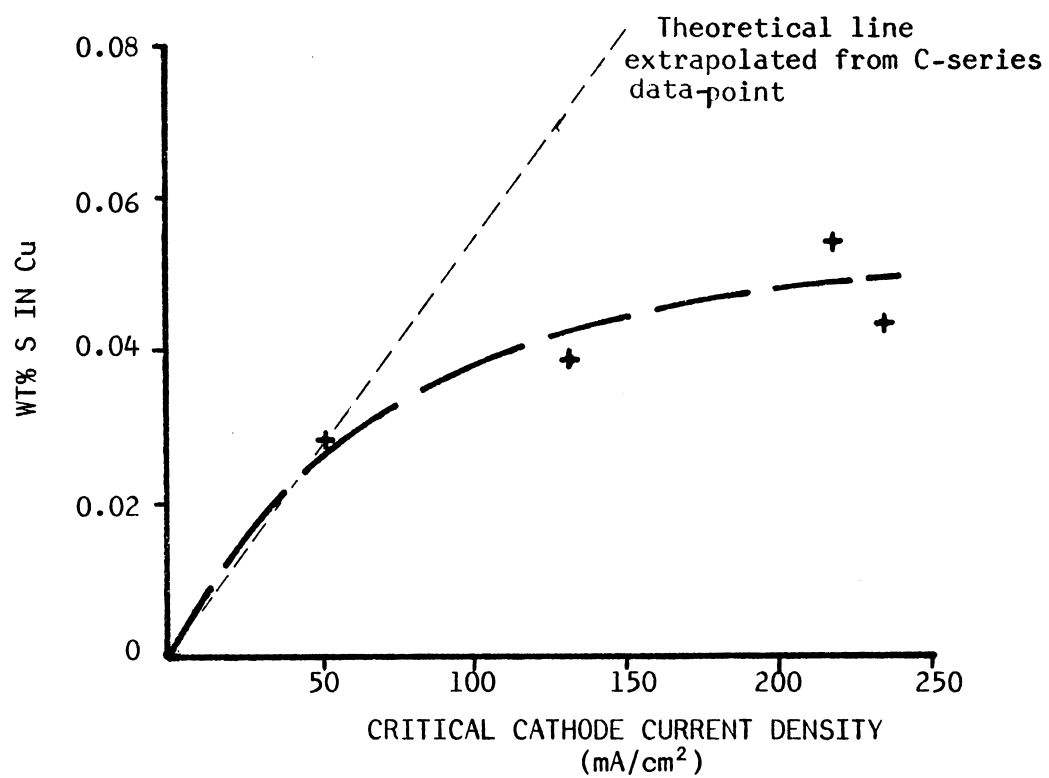


FIGURE 5.28

CALCULATED WT% S IN COPPER VERSUS CRITICAL
CATHODE CURRENT DENSITY

(Data from Table 5.15)

$$I_{lim} = nkAFC_b \quad \dots 5.18$$

where: I_{lim} = critical or limiting current
 A = electrode area
 k = mass transfer coefficient
 n = electron transfer number
 C_b = bulk concentration of the species
 F = Faraday's constant

Thus, if the electrode area, electron transfer number and mass transfer coefficient remain effectively constant, then a plot of critical current density versus bulk concentration should be linear. The straight dashed line shown in Figure 5.28 gives theoretical values for the critical current density, assuming the values of k , A and n remain unchanged and equal to those for the small anode (C-Series) electrolyses. As can be seen in this figure, the departures from this theoretical line are quite pronounced, with the observed values of the critical cathode current density significantly higher than those predicted from extrapolation from C-Series data.

This type of behaviour can be attributed to two possible phenomena in this system:

1. An increase in the effective cathode area with increased anode size and increased cell current.
2. An increase in the mass transfer coefficient for sulphur transfer from the bulk of the liquid copper to the copper/salt interface with increased bulk sulphur concentration.

The first phenomenon could be a consequence of the cell configuration used in this work, with an anode area significantly less than the cathode area, and a small anode/cathode separation, producing

a non-uniform current density distribution over the surface of the cathode that would change significantly with increased cell current or increased anode area. These effects would be further exaggerated by the shielding of the lower anode surface observed in these electrolyses (see Section 4.5.7).

The second phenomenon is likely to be significant in this system due to the high surface activity of dissolved sulphur in liquid copper⁹⁴, which can result in interfacial turbulence⁹⁵ and surface tension-driven flow (the Marangoni effect⁹⁶). These can produce greatly enhanced values of the effective mass transfer coefficient for transport of sulphur atoms from the bulk to an interface, when sulphur is being continuously removed at the interface. It should also be noted that interfacial turbulence effects could account for the detection of calcium (presumably as entrained calcium sulphide precipitates) in relatively 'high' sulphur copper samples from electrolysis (see Section 5.3.3), although if this were the case the reason why no entrainment of magnesium sulphide precipitates was detected in these cases is not clear.

Insufficient information is available on the enhancement of mass transfer rates through the surfactant properties of sulphur in liquid copper to allow any quantitative analysis of this phenomenon, but its potential significance is recognised in this type of system, particularly at the 'higher' sulphur levels.

From the L.S.V. work (Figure 5.14, Section 5.2.6) it is apparent that the shift in the V_2 potential to higher values is complete after approximately 35 minutes electrolysis at 2.500 V with a small anode, or more generally, after the passage of approximately 75 mAh of current in 2.500 V electrolysis. From consideration of the sulphur

distribution curves, at this stage of electrolysis a level of sulphur in copper in the range 0.005-0.01 wt% would be expected. Thus it can be assumed that when these levels are reached, the sole cathodic reactions are discharge of reduced magnesium and calcium. It is likely that the rate of desulphurisation of the copper in this period will obey first order kinetics, with the rate controlled by diffusion of sulphur from the bulk to the cathode interface where heterogeneous nucleation of magnesium or calcium sulphides will take place. Homogeneous nucleation of these compounds in the bulk of the liquid copper is unlikely.

In summary, in the initial stages of 'standard' 2.500 V electrolysis the rate of desulphurisation is limited by anodic discharge reactions, and an approximately linear rate of decrease of sulphur in copper is observed. When sulphur levels are reduced to $\sim 0.03-0.05$ wt% (dependent on anode size) the nature of the cathode reactions will begin to change, with a transition from 'direct' sulphur transfer (Mechanism I) to reduced Mg/Ca discharge (Mechanism II) occurring. Once levels of 0.005-0.01 wt% are reached the sole cathode reactions will be discharge of reduced Mg/Ca, and the rate of desulphurisation will obey first order kinetics with diffusion of sulphur from the bulk of the liquid copper to the cathode interface likely to be rate-controlling.

5.6.3.2 Anodic Discharge

The L.S.V. studies in this work indicated that the rate of discharge of sulphide from the fused salt phase at the anode is controlled by the rate of diffusion of the sulphide from the salt in the region of the cathode interface to the anode. That is, a diffusion-limited sulphide current is observed (see equation 5.18).

The only exceptions to this are the low-voltage electrolyses (e.g. B1 ; 0.600 V electrolysis) in which the rate of sulphide discharge is controlled by activation polarization at low anodic over-voltages.

The sulphur-doped electrolyses (F1, F2, F3) produced higher electrolysis currents due to the increased rates of sulphur diffusion to the anode, and as expected the higher sulphur-doped electrolysis runs (F2, F3) gave a proportionally greater initial current than F1. However, it is interesting to note that in the oxide-doped electrolysis (F4), in which the doping level was more than ten times that of the sulphide-doped electrolyses, an initial electrolysis current only 25-35% higher was observed, which suggests that the oxide discharge rate could be controlled by the charge transfer or chemical reaction steps in that regime.

5.6.4 Current Efficiencies

The analysis of cathode current efficiency data in Sections 5.3.2 and 5.5 shows that consistent cathode current efficiency behaviour is observed in most potentiostatic electrolysis experiments, with high cathode current efficiencies of the order of 90% maintained until the passage of approximately 50 mAh (~ 0.015 wt% S in Cu) when a rapid decrease is observed, as the bulk of the remaining sulphur is eliminated by chemical reaction with reduced magnesium and calcium. The low cathode current efficiencies in this latter stage of electrolysis indicate that the bulk of these reactive metal species generated at the cathode interface are not utilised in desulphurising the copper.

However, possible reasons for 'wastage' of approximately 10% of the cathode current during the early stages of electrolysis when sulphur levels are high are not so clear.

The cathodic discharge of boric ions in the fused salt according to the equation:



is a possibility. For example, the 'leaching' of B_2O_3 from an HBN crucible sidewall in contact with the salt to a depth of ~ 0.05 mm (see Section 5.6.1) would produce a faradic equivalent of boron in the salt melt of approximately 13 mAh. However, it is unlikely that the presence of boric ions in the salt melt is the major cause of reduced cathode current efficiency because:

1. The rate of leaching of B_2O_3 from the boron nitride is time-dependent. Therefore, lower cathode current efficiencies would be expected for the small anode electrolyses as compared to the large anode electrolyses if boric ion discharge was the major reason for reduced cathode current efficiency, due to the significantly longer duration of the latter electrolyses. This was not observed in practice.
2. The relatively long duration high-sulphur electrolysis (F7 - cathode C.E. = 78%) did not show a cathode current efficiency significantly higher than comparable 'low'-sulphur electrolyses, which were stopped at a similar stage, i.e. when depletion of sulphur was indicated by a rapid drop in the electrolysis current. Further, the amount of non-sulphur cathode current passed in run F7 was 119.4 mAh, which, if predominantly due to boric ion discharge, would require the dissolution of 0.052 g of B_2O_3 in the fluoride melt, that is, 'leaching' of the HBN sidewalls to a depth of 0.4 mm. This depth is approximately ten times greater than the measured melt penetration depths for electrolysis runs of this duration.

Chemical Analysis of electrolysed copper samples for boron was attempted using an emission spectrograph, and an optical spectrographic technique described by Elwell and Scholes⁶⁸. However, in both cases the boron assays obtained were not reproduceable, and apparently erroneous values were obtained, with 'pure' copper samples giving significant boron assays. The likely reasons for this are, in the case of the emission spectrographic work, boron is a common impurity present in the carbon electrodes, while in the optical spectrographic work, normal pyrex glassware was used in the preparation of the complexed solutions. Pyrex glassware is a source of boron contamination using these techniques, and pure silica-glass apparatus only should be used.

Other possible reasons for less than 100% cathode current efficiency during the early stages of electrolysis when sulphur levels are high could be:

- (1) Dissolution in the fused salt of small amounts of 'excess' reduced magnesium and calcium generated at the cathode interface during this period via scheme (2) proposed for desulphurisation (see Section 5.6.2.2).
- (2) A significant component of electronic conduction through the fused salt.
- (3) 'Short-circuiting' of the current through the crucible sidewalls.

The likelihood of (2) and (3) being major contributors to the reduced cathode current efficiency would appear remote. Appreciable dissolution of metallic species in the salt melt would be required to give a significant electronic conduction component, while conduction through the boron nitride sidewalls (volume resistivity = 1×10^{15} ohm-cm, surface resistivity = 1×10^{12} ohm-cm) is unlikely. Even with

significant melt penetration this would be a very high resistance path compared with direct conduction through the fused salt.

The anode current efficiency data (Section 5.3.2, Figure 5.10; Section 5.5.2, Figure 5.2.4) show that relatively high anode current efficiencies ($> 70\%$) can be achieved for discharge of sulphide from the fluoride melt. Clearly, the anode current density is dependent on the sulphide concentration of the salt melt, which should produce efficient 'self-cleaning' of the electrolyte. Sulphide build-up in the electrolyte will result in an increase in the anode current efficiency until effectively a 'steady state' situation is reached. This work clearly demonstrates that sulphide build-up to fairly 'modest' levels ($< 0.5 \text{ wt}\%$) will result in high anode current efficiencies at anode current densities in the range $500\text{--}1000 \text{ mA/cm}^2$.

Apart from sulphide concentration in the melt, the anode current density is also dependent on the concentration of co-evolving oxide species in the melt, and the extent to which fluoride anion discharge can occur at the anode. Thus, a relatively 'high' oxide concentration of $0.99 \text{ wt}\%$ in the fused salt in run F4 resulted in an overall anode current efficiency of only 9% for that run, compared to the $30\text{--}40\%$ overall anode current efficiencies achieved for 'standard' potentiostatic electrolyses of similar duration (in terms of current passed). And in the case of the low-voltage high-sulphur run F8 (1.500 V applied), a very high overall anode current efficiency of 84% was achieved (with no fluoride discharge possible) compared to 68% for the high-sulphur run F7 (2.500 V applied) in which continuous discharge of fluoride was occurring.

The low current anode efficiency for the oxide-doped run F4 is consistent with the observations of other workers (Section 2.1.1) who

found very low anode current efficiencies were achieved for discharge of sulphide from oxide systems.

Very low levels of sulphur in copper can only be achieved with the generation of a considerable amount of excess magnesium and calcium at the copper/salt interface, (see following section), as is evidenced by the low cathode current efficiencies at this stage of electrolysis. Partial dissolution of these reduced metal species in the fused salt will result in reduced anode current efficiencies due to recombination of the dissolved metal with anodically liberated sulphur.

Evidence for this occurring can be gained from the extended potentiostatic electrolyses done in this work. The indicated anode current efficiencies after the virtually complete elimination of sulphur from copper are quite low (Figure 5.10), due presumably to the steady dissolution of reduced magnesium and calcium in the fused salt occurring at the cathode interface. Thus, even when electrolysis was continued until very low residual currents were achieved (Section 5.2.3) significant amounts of sulphide still remained in the salt phase due to the continuous recombination reaction.

5.6.5 Dissolution of Cathodic Magnesium and Calcium

Both the liquid copper and the fused salt phases are expected to have a high capacity for dissolution of 'excess' magnesium and calcium metal generated at the metal/salt interface. Magnesium and calcium are soluble in liquid copper in all proportions at 1423K⁶³ and should have a high solubility in the fused salt phase (Section 3.2.3).

Therefore, it is reasonable to expect a distribution of these reduced metal species between the liquid metal and salt phases, which will be dependent on the relative affinity of each phase for the

dissolved metals, and the physical nature of their discharge at the metal/salt or metal/salt/boron nitride interface, which includes possible surface tension effects and interfacial turbulence.

With regard to the results obtained in this work, it is clear that the copper/salt distribution of these reduced metal species exhibits a high degree of variability, with no specific correlation evident to relate the relative degree of dissolution of magnesium and calcium in the liquid copper phase with variations in cathode current density, cell potential or sulphur content of the system.

However, the results obtained do show clearly that once levels of sulphur in copper of the order of 0.01 wt% are reached (from Figure 5.11 - after the passage of 60-70 mAh), a steady build-up of magnesium and to a lesser extent calcium in the liquid copper phase will occur. Thus very low levels of sulphur in copper (< 5 ppm) can only be achieved at the expense of contamination of the copper phase with these dissolved metals, to a combined (Mg + Ca) level of the order of 0.01-0.02 wt% indicated by this work.

5.6.6 Linear Sweep Voltammetry

The use of L.S.V. techniques in a simple two-electrode cell has proved to be quite useful in this work to help delineate the cell reactions occurring. The use of a three-electrode cell (i.e. with a reference electrode) is an inherently more powerful technique which allows the reactions at a single electrode to be studied in detail. Some experimental work was carried out in this research using the three-electrode cell assembly, with a graphite 'quasi-reference' electrode⁶⁴ immersed in the fused salt. Unfortunately, however, reproduceable and consistent results were not obtained and that work has not been reported here.

Some further aspects of L.S.V. work are briefly discussed below.

No correction for 'IR' drop through the melt was made for the reported value of the V_2 decomposition potential in Section 5.3.6. Typically, with a small electrode used, cell currents of the order of 50-150 mA were flowing prior to the onset of the V_2 decomposition reaction. With such low currents, and considering the uncertainty in determining the V_2 potential from linear extrapolation techniques, it was not expected that the 'IR' drop correction would be significant in this case. Confirmation of this was gained from measurement of the V_2 potential after the passage of approximately 85 mAh when its upwards 'shift' was complete. A value of 2.65 V (± 0.10 V) was indicated, which is the same as the decomposition potential of the 'pure' system determined with no cell current flowing prior to the onset of decomposition (Section 5.2.1). If the 'IR' drop were significant, the former value would be expected to be significantly greater than 2.65 V.

Calculation of the expected 'IR' drop in this work is difficult because the effective cross sectional area for current is hard to estimate with such a non-uniform current path, and virtually no information on the specific conductance of alkaline earth fluoride melts is available in literature, although it is generally recognised that fluoride melts have 'high' conductivities with specific conductances in the range $1-6 \text{ ohm}^{-1} \text{ cm}^{-1}$ likely^{56,98,99}.

As discussed in Section 5.3.6, the appearance of a reverse current peak in linear sweep voltammograms when sulphide enters the fused salt phase is potentially a useful tool for qualitative analysis of sulphide levels in the fused salt. The occurrence of this peak is indicative of redissolution in the salt melt of gaseous sulphur

species adsorbed on the surface of the anode, and does not occur when no sulphide is present in the salt due to the irreversibility of the chemical reaction of discharged oxide and fluoride species with the anode carbon.

The corresponding reverse-current reaction at the cathode is likely to be re-oxidation of sulphide ions present in the fused salt adjacent to the metal/salt interface.

5.6.7 Practical Considerations

With the experimental conditions in this work, it is clear that electrorefining to very low levels of sulphur (e.g. < 5 ppm) can only be achieved with the penalty of reduced current efficiency and significant contamination of the liquid copper by calcium and magnesium. The extent of this contamination (and the minimum sulphur levels attainable before it becomes significant) will, for any one system, depend on the kinetics of sulphur transfer from the bulk of the liquid copper to the cathode interface, with higher rates of sulphur transfer allowing lower sulphur levels to be achieved before these effects become significant.

On the other hand, electrorefining to more 'modest' sulphur levels (e.g. 0.005-0.01 wt%) can be achieved at a high cathode current efficiency and without significant metallic contamination.

'Self-cleaning' of the fluoride electrolyte can be expected with anodic discharge of sulphide ions at high current efficiencies obtained. The effectiveness of the 'self-cleaning' is reduced by the presence of significant concentrations of co-evolving oxide ions in the salt melt, the discharge of fluoride ions at the anode or the dissolution of cathodically generated reduced metal in the fused salt. Thus, to prevent 'fouling' of the electrolyte due to build-up

of sulphide in a continuous electrorefining process, it would be necessary to prevent excessive oxide contamination of the salt melt and to operate at a low cell potential (<2.1 V) to avoid significant anodic fluoride discharge (which is obviously undesirable from environmental considerations).

The restriction of the cell potential to less than 2.1 V (for 'high' sulphur levels in copper) or 2.65 V (for 'low' sulphur levels in copper) in order to avoid fluoride discharge at the anode means that careful control of current density in an electrorefining process would be required. Basically, fluoride ion discharge can be avoided if the anode current density is maintained below the limiting current density for diffusion of dissolved anionic species to the anode.

CHAPTER 6

CONCLUSIONS

Under typical conditions of potentiostatic electrolysis at 2.500 V, with 'high' sulphur levels in copper (> 0.05 wt%), desulphurisation of the liquid copper occurs essentially via direct electrochemical transfer of sulphur from the liquid copper to the salt phase, with a high cathode current efficiency for sulphur transfer ($\sim 90\%$). The rate of sulphur transfer is controlled by the combined rate of the ionic discharge reactions at the anode.

With 'low' levels of sulphur in copper (< 0.01 wt%), desulphurisation of the liquid copper occurs with a low current efficiency ($< 20\%$) via chemical reaction of dissolved sulphur atoms with reduced metallic species (magnesium and calcium) that are electrochemically discharged at the cathode interface. The rate of sulphur transfer in the low sulphur regime is controlled by mass transfer of sulphur from the liquid copper bulk to the cathode interface. A low current efficiency for sulphur transfer results from the cathodic generation of excess magnesium and calcium which subsequently undergo dissolution in the liquid copper and fused salt phases.

With intermediate sulphur levels between the two above-mentioned regimes, a region of 'mixed control' exists with the transfer mechanism and resultant cathode current efficiency for sulphur transfer undergoing a transition from 'high' sulphur behaviour to 'low' sulphur behaviour.

The particular sulphur levels in copper at which the transition from the direct sulphur transfer mechanism to the 'chemical' desulphurisation mechanism will occur are dependent on the kinetics of

sulphur transfer from the liquid copper bulk to the cathode interface, and the cathode current density, and therefore will be mainly dependent on the physical nature of any one system (e.g. convective conditions, interfacial properties, cell geometry) and the cathode current density applied.

The discharge of dissolved sulphide out of the fused salt at the anode is diffusion-controlled (except at low cell potentials) and occurs with a current efficiency for sulphur transfer which is dependent on:

- (1) The concentration of sulphide ions in the melt.
- (2) The concentration of co-evolving oxide ions in the melt.
- (3) The degree of discharge of fluoride ions.
- (4) The amount of reduced magnesium and calcium dissolved in the fused salt.

The high anodic current efficiencies for sulphur transfer of 70-80% obtained in this work with concentrations of sulphide in the fused salt of ~ 0.5 wt% or less confirm that 'self-cleaning' of the electrolytes does occur.

Fluoride ion discharge at the anode will occur at a minimum cell potential of (2.1 ± 0.1) V in the high sulphur-in-copper regime, which increases to (2.65 ± 0.04) V in the low sulphur-in-copper regime, the difference being due to the 'depolarizing' effect of sulphur atoms present at the cathode interface.

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APPENDIX ITHERMODYNAMIC CALCULATIONSAl.1 The Use of β -functions

Standard free energies of formation and values of equilibrium constants for chemical reactions have been calculated in this work using the " β -functions" tabulated in the compilations by Barin and Knacke^{54,55}. The dimensionless β -function is defined as follows:

$$\beta_i(T) = \frac{-G_i^O(T)}{RT \ln 10} \quad \dots \text{Al.1}$$

where:

$\beta_i(T)$ = β -function of a pure substance i at 1 atmosphere pressure and temperature T

G_i^O = molar Gibbs free energy of i at 1 atmosphere pressure and temperature T (kJ/mole)

R = gas constant (8.3143 J/mole K)

T = temperature (K)

Thus, for chemical equilibrium at temperature T for reaction between components, B_i , of the reaction with mole numbers ν_i ,

$$\nu_1 B_1 + \nu_2 B_2 + \dots = \nu_j B_j + \dots \quad \dots \text{Al.2}$$

the equilibrium constant is defined by:

$$\log K(T) = \sum_i \nu_i \beta_i(T) \quad \dots \text{Al.3}$$

that is, $\log K(T)$ is derived from a simple summation of the

β -functions : (products)-(reactants). Standard free-energies of

formation can thus be derived using:

$$\Delta G^O(T) = -RT \ln 10 \cdot \log K(T) \quad \dots \text{Al.4}$$

Al.2 Extrapolation of Thermodynamic Data to Metastable Standard States

In Section 3.2.2 the theoretical decomposition potentials for supercooled liquid CaF_2 , MgF_2 and BaF_2 at 1423K were calculated by extrapolation of liquid phase values of β -functions for these pure compounds to 1423K:

$$\text{CaF}_2 : \beta(T) = 13.81449 + 52889.46/T \quad \dots \text{Al.5}$$

$$(\text{correlation coefficient} = 0.999896)$$

$$\text{MgF}_2 : \beta(T) = 12.80214 + 48345.49/T \quad \dots \text{Al.6}$$

$$(\text{correlation coefficient} = 0.99989)$$

$$\text{BaF}_2 : \beta(T) = 13.79698 + 55061.17/T \quad \dots \text{Al.7}$$

$$(\text{correlation coefficient} = 0.99999)$$

Al.3 Interpolation of β -functions at 1423K

Values of β -functions at 1423K were calculated from interpolation of the tabulated values at 1400K and 1500K assuming linearity between $\beta(T)$ and $1/T$. The values so derived and used in this work are listed below:

$\text{AlF}_3(\text{s}) : 61.849$	$\text{CO}_2(\text{g}) : 27.444$	$\text{Mg}(\text{g}) : 3.162$
$\text{Al}_2\text{O}_3(\text{s}) : 68.484$	$\text{Ca}(\text{l}) : 3.485$	$\text{MgF}_2(\text{s}) : 47.170$
$\text{Ba}(\text{l}) : 5.184$	$\text{CaF}_2(\text{s}) : 51.562$	$\text{MgCl}_2(\text{l}) : 32.120$
$\text{BaF}_2(\text{s}) : 52.504$	$\text{CaCl}_2(\text{l}) : 38.913$	$\text{MgO}(\text{s}) : 25.322$
$\text{BaCl}_2(\text{l}) : 41.433$	$\text{CaO}(\text{s}) : 27.344$	$\text{MgC}_3(\text{s}) : 7.065$
$\text{C}(\text{gr}) : 0.912$	$\text{Cl}_2(\text{g}) : 13.094$	$\text{MgC}_2(\text{s}) : 2.365$
$\text{CF}_4(\text{g}) : 50.804$	$\text{F}_2(\text{g}) : 11.983$	$\text{O}_2(\text{g}) : 11.988$
$\text{CO}(\text{g}) : 15.612$	$\text{H}_2\text{O}(\text{g}) : 20.227$	$\text{S}_2(\text{g}) : 8.587$

APPENDIX II

FUSION ANALYSIS OF SULPHUR IN THE FLUORIDE SALT

Analysis of total sulphur in finely powdered (100% < 170#mesh) fluoride salt samples was carried out using a sodium peroxide-sodium carbonate fusion/oxidation technique followed by determination as barium sulphate; as described by Vogel⁸⁸.

Good agreement was obtained using this technique and the evolution technique described in Section 4.6.3. As an example, the results for analysis of powdered fluoride salt from run F7 are summarised below:

• Fusion analysis:

- ```

- ~ 2.5 g samples weighed to ± 0.1 mg

- Results of three analyses : total sulphur = 0.337 wt%
 0.329 wt%
 0.343 wt%

Ave : 0.336 wt%

uncertainty = ± 0.007 wt%

```

- Evolution analysis:

- ```

-    ~ 0.3 g samples weighed to  $\pm 0.1$  mg

-    Results of five analyses : sulphur      =    0.328 wt%
                                           0.347 wt%
                                           0.353 wt%
                                           0.331 wt%
                                           0.347 wt%
                                           0.347 wt%
                                           Ave   : 0.341 wt%
uncertainty =  $\pm 0.013$  wt%

```

APPENDIX III

X-RAY POWDER DIFFRACTION ANALYSIS OF
YELLOW CONDENSATE IN LOWER REGION
OF REACTION TUBE

. Details of Analysis:

Radiation : Cu K_α

Observed Diffraction Lines:

<u>Line No.</u>	<u>Calculated d (Å)</u>	<u>Estimated I/I₁</u>
1	5.720	30
2	3.840	100
3	3.455	40
4	3.325	20
5	3.160	50
6	3.090	20
7	2.840	20
8	2.610	10
9	2.495	10
10	2.420	10
11	2.108	20
12	1.903	20

All the above lines can be attributed to the orthorhombic sulphur diffraction pattern (see Figure A1.1).

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d	3.85	3.21	3.44	7.69	S
I/I ₁	100	60	40	6	SULFUR
Rad. CuK λ 1.5405 Filter Dia. 114.6mm Cut off 50A I/I ₁ PHOTOMETER GUINIER CAMERA Ref. DEWOLFF, TECHN. PHYS. DIENST, DELFT, HOLLAND					
Sys. ORTHORHOMBIC S.G. D _{2h} ²⁴ - FDD (B.P.) a ₀ 10.45 b ₀ 12.84 c ₀ 24.46 A C e B Y Z D ₂ Ref. IBID.					
f ₄ D n = s f ₇ Color Sign 2V Ref.					
SEE FOLLOWING CARD					
d Å	I/I ₁	hkl	d Å	I/I ₁	hkl
7.69	6	111	2.614	4	400
5.76	14	113	2.569	8	333
5.68	5	022	2.501	7	244
4.80	2	202	2.424	13	317
4.19	2	151	2.404	2	404
4.06	11	220	2.375	4	422
3.91	12	131	2.366	4	335
3.85	100	222	2.288	6	0.2.10
3.57	8	133	2.215	2	048,2.0.10
3.44	40	026	2.146	4	1.1.11
3.38	3	224	2.112	10	319,0.2
3.33	25	311	2.098	2	2.2.10
3.21	60	206	2.057	1	511
3.11	25	313	2.041	1	0.0.12,248
3.08	17	135	2.003	2	359
3.06	1	008	1.998	4	408
2.842	18	044	1.957	2	262
2.688	2	331	1.926	1	444
2.673	1	242	1.900	7	355,066,515
2.621	13	137	1.856	1	3.1.11

FIGURE A1.1

ORTHORHOMBIC SULPHUR POWDER DIFFRACTION DATA ⁸⁹