

**THE DECOPPERIZATION AND DETINNING
OF IRON AND STEEL BY SULPHIDE TREATMENTS**

A thesis submitted to the University of London
for the Degree of Doctor of Philosophy

by

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December 1986

ABSTRACT

The removal of copper and tin from carbon-saturated and from low carbon content iron by sulphides has been investigated in the present work. The effects of the mode of mixing, compositions of the metal and slag, the weight ratio of the slag to metal, the depth of the crucible and of the metal bath, the area of interfaces and the operating temperature have been tested to study the equilibrium conditions, the rate controlling steps and the mechanisms of the reactions involved.

The composition of 30%FeS-70%Na₂S has been found to be the most suitable slag for copper removal. The transfer of copper from the metal to slag at the initial fast stage is most probably controlled by the transport of copper in the boundary layer of the metal phase when 30%FeS-70%Na₂S is used as the slag and by the removal of sodium vapour when pure Na₂S is used as the slag. In both of these slags, the rate controlling step of copper transfer becomes dominated by the equilibrium of the chemical reaction for the formation and decomposition of Cu₂S after the initial fast stage. Removal of 70% of the initial copper content in iron has been achieved within five minutes at 1523K (1250°C) and inert gas bubbling into the metal. The removal of copper from steel is significantly affected by the carbon content in the metal. A positive interaction coefficient, e_{Cu}^{C} , is calculated.

The detinning process is found to be dependent on the evaporation of SnS from the system. If there is no forced flow of argon within the crucible, the rate of tin removal

is mixedly controlled by the formation of SnS at the metal/gas interface and diffusion of SnS vapour in the gas. A value of $D_{\text{SnS-Ar}}$ equal to $1.51 \text{ cm}^2/\text{sec}$ is obtained from the present study. When argon is bubbled into the metal, the chemical reaction of the formation of SnS reaches its equilibrium and the bubbles are saturated with SnS. The detinning process is then controlled by the equilibrium partial pressure of SnS. It has been found that any change which increases the equilibrium constant and the activities of tin and sulphur in the metal speeds up the removal of tin from iron. The tin removed is proportional to the volume of argon bubbled.

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CHAPTER 1

INTRODUCTION

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INTRODUCTION

One of the principal secondary sources of iron is automobile scrap, but a significant amount of this scrap is not being efficiently recycled into iron and steel products because of the contamination problems caused by non-ferrous impurities, especially by copper and tin. The presence of copper and tin can produce harmful metallurgical effects during steel processing if the concentration is too high in products being made. These tramp elements are difficult to remove in conventional ironmaking and steelmaking processes and have a tendency to build up during scrap recycling⁽¹⁾.

Regarding the formation of product defects, tramp elements generally act by lowering the high temperature ductility via either the presence of liquids or by embrittling precipitates. The accumulation of tin and copper under the oxide layer in surface hot shortness is such an example.

The disadvantages of copper and tin in respect of steel fabrication are of such importance that a method or methods of lowering the copper and tin contents of liquid Fe-C-Cu-Sn alloys have long been investigated. Except by dilution, no industrially acceptable technique for removing copper and tin bearing materials has been found. A wide variety of metallurgical processes could be applied to the removal of tramp elements as shown in Table 1-1⁽⁹¹⁾, but the cost consideration severely limits the range suitable for commercial application.

From the range of physical and chemical techniques

available for refining liquid metals, pyrometallurgy and vacuum/evaporation methods are most applicable to the removal of residuals. One process compatible with current steelmaking operations is to use sodium sulphide and/or sulphate as slagging materials for extracting copper from molten iron. The process is a high temperature liquid-liquid extraction in which copper transfers from the iron phase into the slag phase, displacing sodium, which is reduced and vaporized. Some encouraging results have been obtained by this treatment. However, the thermodynamics, kinetics and mechanisms of reactions involved have received less attention, and no report on the successful removal of tin by a sulphide slag has been found.

As an approach to understanding the process theoretically, the thermodynamic feasibility and rate controlling step in using sodium sulphide and/or iron sulphide to remove copper and tin from high or low carbon content iron have been studied in the present investigation. For convenience the sulphur rich phase is referred to as slag although its constitution more closely approaches that of a matte.

Table 1-1 Possible removal methods

Scrap-metal treatment	Fractional solidification
Magnetic separators	Melt filtration
Heavy-media separators	Volatilization
Electrostatic separators	Vacuum arc refining
Eddy-current separators	Inert gas injection
Hydrometallurgy	Reactive gas injection
Electrochemistry	Pyrometallurgy
Zone refining	Slag-metal reactions
	Powder injection

CHAPTER 2

LITERATURE SURVEY

CHAPTER 2

LITERATURE SURVEY

2-1. ADVERSE EFFECTS ON STEEL PRODUCTS OF USING MODERN SCRAP

A definite disadvantage of copper and tin in steel is that they cause hot shortness during forming by accumulation under the surface oxide⁽²⁾. Melfor⁽³⁾ explained that hot shortness resulted directly from the fact that copper was not oxidized when steel was reheated. Consequently, as iron was removed preferentially in the surface layer, these residual elements were progressively enriched in the subsurface. The copper-enriched alloy had a lower melting point, which, if exceeded, caused the alloy to become molten at the working temperature. The molten alloy penetrated intergranularly, and weakened the steel, thus causing the formation of surface cracks during hot rolling. Tin aggravated this type of hot shortness because of its effect in reducing the solubility of copper in austenite⁽⁴⁾. The concentration of copper in steel should not be greater than 0.1wt% to overcome hot shortness⁽⁵⁾.

Another disadvantage of copper in steel is the decrease of deep drawability of steel sheet. The enrichment of copper (plus Sn and Sb) as a result of scaling leads to fine intergranular surface cracks of the continuously cast product if critical concentration is exceeded⁽⁶⁾.

Although tin increased the strength and hardness of steel, its ductility was decreased, also even very small levels of tin could increase the temper-embrittlement

susceptibility of rotor steels⁽⁷⁾.

In general, the highest toughness and ductility values are associated with the lowest copper and tin contents, these, however, show the lowest strength properties⁽⁶⁸⁾.

Ferrous scrap containing less than 0.2wt% copper, 0.03wt% tin is considered acceptable for virtually all steelmaking processes. Compacted automobile scrap, known as No.2 bundles, has an average value of 0.5wt% for copper and 0.1wt% for tin⁽⁸⁾.

The most effective countermeasure against excessive tramp element content is to dilute the charge with scrap of higher purity, and attempts are also made to give an additional scrap treatment prior to charging. Both methods, however, are costly.

Many steelmakers traditionally use nickel additions to the melt to counteract the deleterious effect of copper, since nickel increases the solubility of copper in austenite. For example, assuming a melt with 0.25%Cu, 0.025%Sn and 0.15%Ni, a Ni addition of 0.12% would be required in order to limit the adverse effects of copper.

If a fine grain surface structure is assured by even shell growth during continuous casting, then a high tolerance for tramp elements will result. Also spray cooling should be optimized so as to ensure minimum scale formation and low thermal stress⁽⁷⁹⁾.

2-2. THEORETICAL BACKGROUND OF PROCESSES FOR REMOVING TRAMP ELEMENTS

2-2-1. General

The refining of iron and steel is an important branch of pyrometallurgy. The process is concerned with at least three phases (gas, slag, metal) in which chemical reactions take place at phase boundaries and reactants as well as products are transported through bulk phases.

Thermodynamics predicts the theoretical extent of spontaneous reactions and the compositions of phases at equilibrium. It can not predict whether reactions will happen or not at a measurable rate. The mechanism and rates of reactions undergone will be determined by chemical and transport kinetics. The combination of both thermodynamics and kinetics can lead to a good understanding of refining processes.

2-2-2. Thermodynamic Properties of Slag/Metal/Gas Systems

The standard free energy changes of some reactions relevant to refining systems have been calculated as a function of temperature and are shown in Fig. 2.1 and 2.2. The calculations are based on the most recently available thermodynamic data⁽⁹⁻¹³⁾. The standard states selected for the various substances are as follows:

Sulphur — diatomic sulphur gas at one atmosphere pressure.

Sulphide — pure stable solids or liquids according to

whether they are above or below their melting points.

Gas — one atmosphere pressure.

Metal — pure stable solids, liquids or gases according to whether they are above or below their melting or boiling points.

Elements dissolved in the iron phase — 1.0wt%.

Cox⁽¹⁴⁾ pointed out that the affinity of sulphur for copper (as measured by the free energy of formation of the sulphide) was considerably greater than that for iron. In the case of tin, this is true at higher temperatures. The use of a sulphide based process for the removal of copper and tin thus appeared attractive and has been investigated in the present work. Sodium sulphide was selected as a possible reagent because although its free energy of formation is more negative than copper or tin sulphides, the volatility of sodium at iron and steelmaking temperatures provides a potential driving force for the formation of the tramp element sulphides.

The positive free energy changes of reactions, as shown in Fig. 2.1 and 2.2 indicate that copper and iron cations will not spontaneously displace sodium cations under standard state conditions. The processes will be favorable only if one of the products of reaction is constantly removed. This can be achieved in an open system due to the evolution of sodium vapour.

Sodium sulphide is readily oxidized at room temperature either dry or in solution. Manufactured sodium sulphide is often discoloured brown by the presence of iron, or yellow by polysulphides. Fused sodium sulphide attacks metals, including silver, gold and platinum, but it does not attack

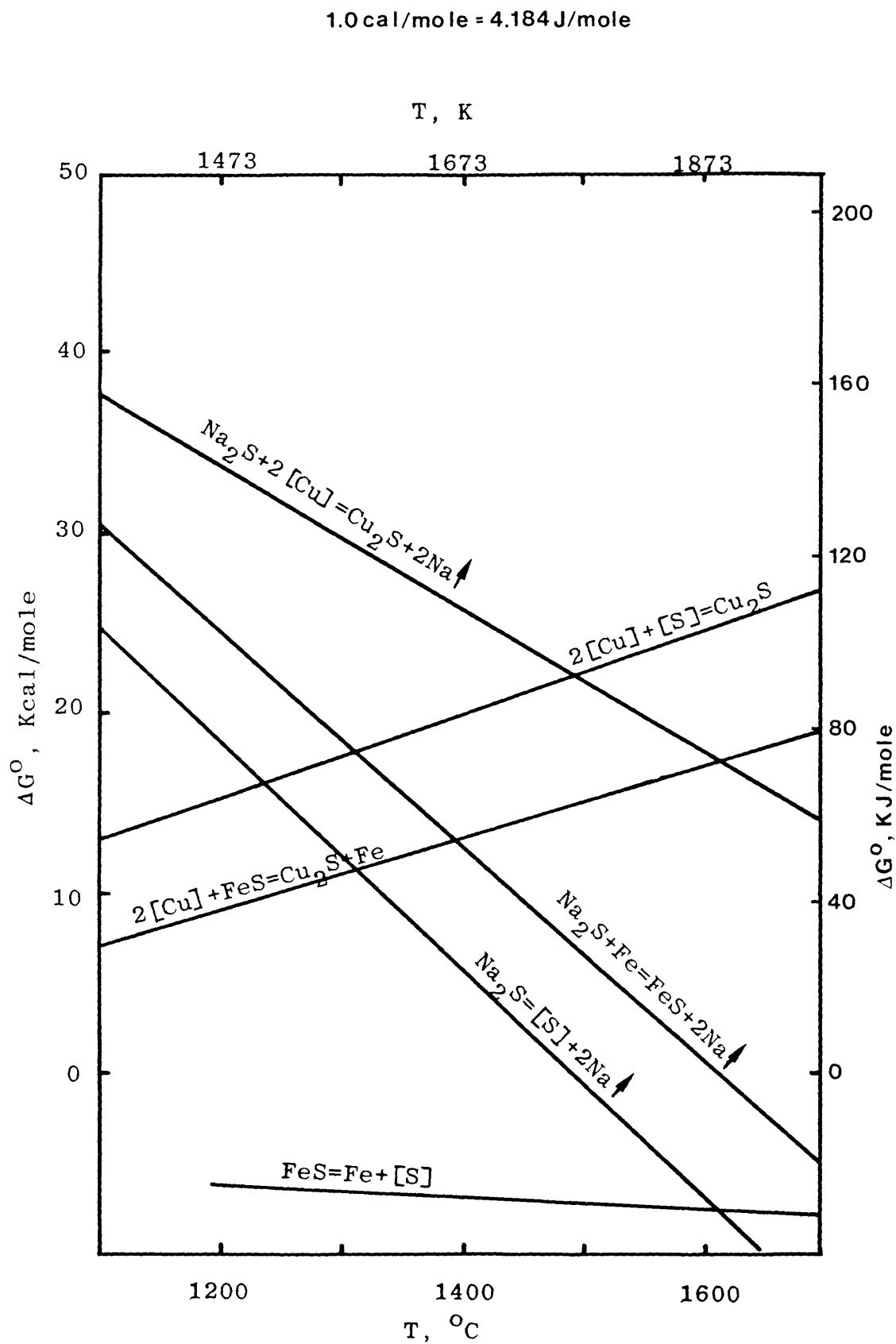


Fig.2.1 Free energy diagram for the reaction of copper

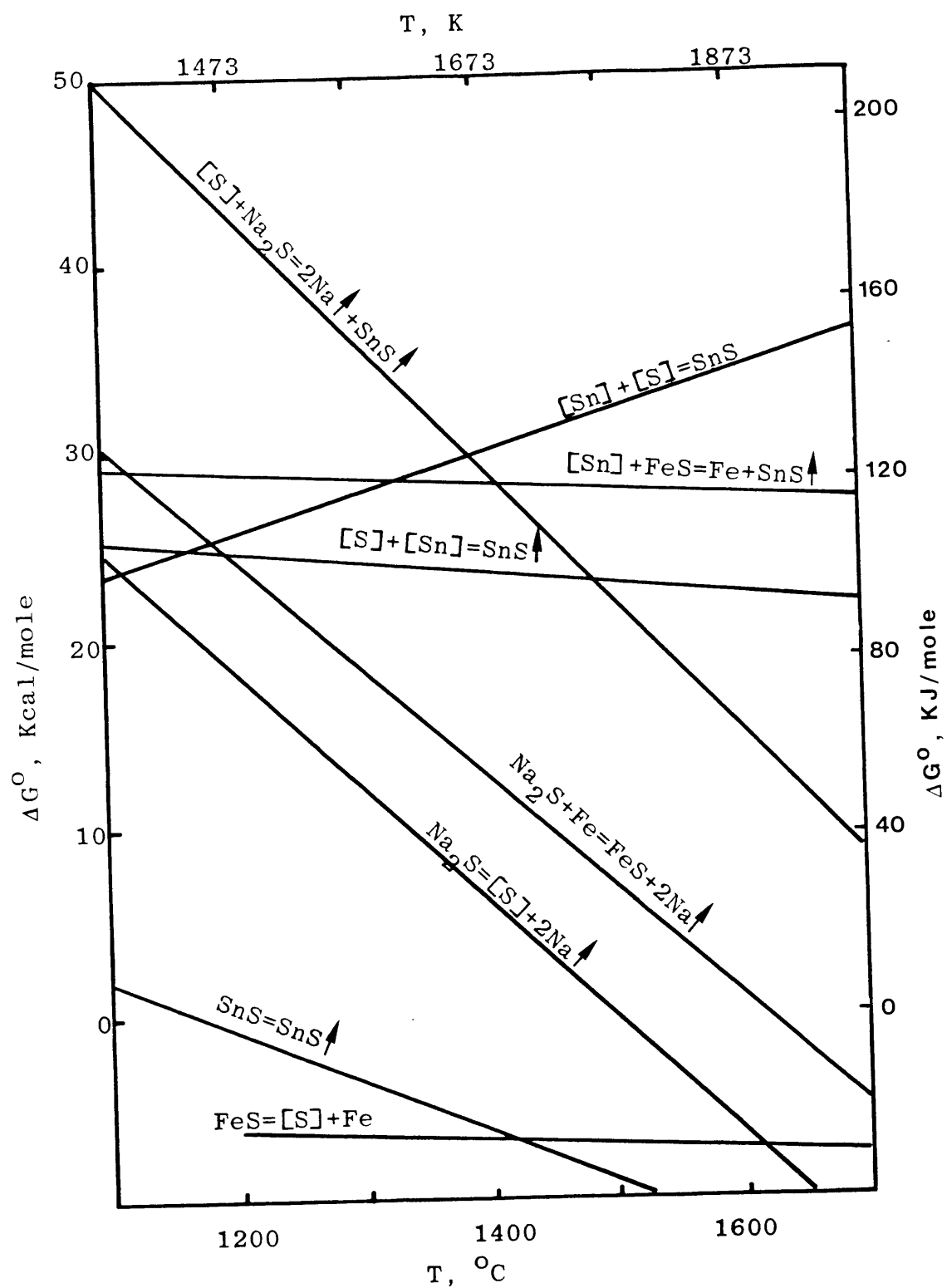


Fig.2.2 Free energy diagram for the reaction of tin

graphite. Al_2O_3 does not react with it⁽¹⁵⁾.

Several compounds of Na and S exist. The monosulphide Na_2S is the most stable sulphide at high temperatures. Sodium sulphide forms liquid mixtures with various other metallic sulphides, such as ferrous and cuprous. With cuprous sulphide, a compound $\text{Cu}_2\text{S} \cdot \text{Na}_2\text{S}$ is formed from the liquid phase with a free energy of formation of -7 Kcal/Mole ⁽¹⁶⁾.

The equilibrium diagrams of $\text{Cu}_2\text{S}-\text{Na}_2\text{S}$, $\text{Cu}_2\text{S}-\text{FeS}$, $\text{Na}_2\text{S}-\text{FeS}$ and $\text{Na}_2\text{S}-\text{Cu}_2\text{S}-\text{FeS}$ were given by Kopylov and Novoselov⁽¹⁷⁾. As shown in Fig. 2.3, there is a wide range miscibility gap in the $\text{Na}_2\text{S}-\text{Cu}_2\text{S}-\text{FeS}$ system at high temperatures. The 'slag' (or matte) phase is a homogeneous electrolyte solution of Fe^{++} , Cu^+ , Na^+ and S^- . Some sodium metal was also present in the slag, but its concentration was much less than that of Na^+ at temperatures of interest in the present work. At these temperatures, any CuS would react almost completely with copper to form Cu_2S . Iron would be present almost entirely in the Fe^{++} state. Thus, there would be one mole of sulphur in the slag for each mole of iron and for every two moles of copper or sodium⁽⁵⁾.

Not much information was found about SnS -containing systems. The reaction between Sn and FeS and sublimation of SnS from $\text{SnS}+\text{FeS}$ melts were reported^(18,19). Some compounds were found in the $\text{SnS}-\text{Na}_2\text{S}$ system at low temperatures⁽²⁰⁾. The boiling point of SnS is 1483K (1210°C)^(11,67).

Kellog⁽²¹⁾ reported that tin sulphide was much more volatile than tin oxide, and this high volatility was maintained over a broad range of sulphur pressures. SnS and Sn_2S_2 were the only species of importance in the vapour of

the Sn-S system, the vapour species having the same valence and compositions as the condensed phase.

The effect of sulphur on the solubility of graphite in

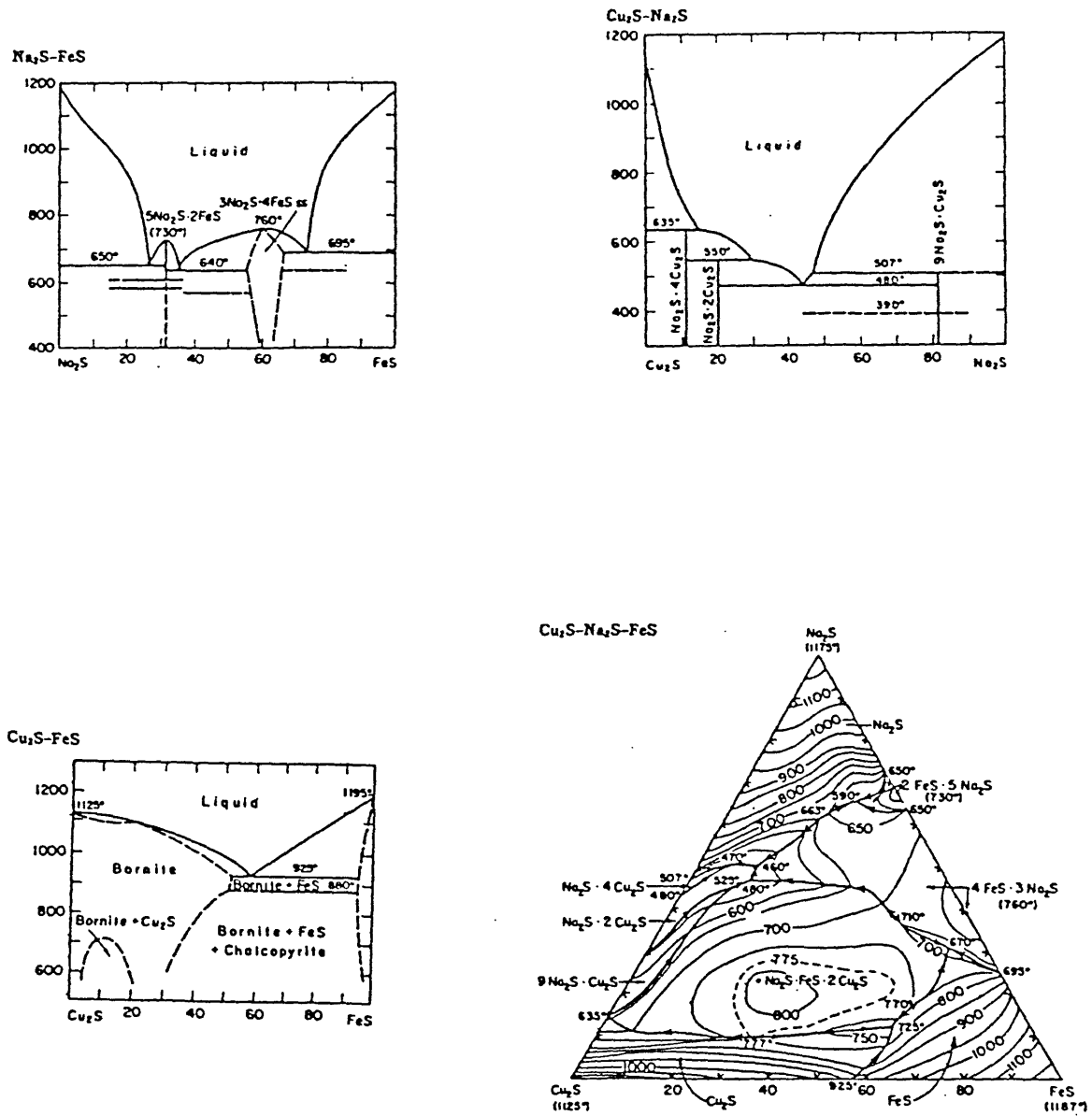


Fig.2.3 Phase diagrams of systems containing Na_2S , Cu_2S and FeS

iron was investigated by Turkdogan and Hancock⁽²²⁾. Their results showed that the solubility of carbon in iron was reduced by dissolved sulphur.

Investigations of the ternary Fe-Cu-C system illustrated that melts in this system separated into two layers over a wide range of compositions. The present studies are related to single liquid phase regions.

Liquid iron may contain several solutes in dilute solution each of which may affect the thermodynamic behaviour of the others as a result of the change in the inter-atomic forces created by the addition of the solutes. This interaction frequently causes marked changes in the solute activities. In a multi-component system, the activity coefficient, f_x , of a solute x is given by⁽⁸⁰⁾

$$\log f_x = \%x e_x^x + \%y e_x^y + \%z e_x^z + \dots$$

where e_x^i is called interaction coefficient and defined as

$$e_x^i = \delta \log f_x / \delta (\text{wt}\%i)$$

A number of compilations have been published of the effects of solute elements on the activity coefficients of certain elements in dilute solution in molten iron.

The activities or activity coefficients of copper, tin and sulphur in liquid iron and steel have been studied by a number of investigators^(12, 23-27). Generally speaking, both Cu-Fe and Sn-Fe system show positive deviation from ideal solution behaviour. Carbon increases the activities of copper and tin, sulphur in molten iron and steel lowers the activity of copper. Adequate information about the activity coefficients in $\text{Cu}_2\text{S-FeS-Na}_2\text{S}$ system is not available, so they are assumed to be unity in some papers. However it can be seen from Fig. 2.4 that $\text{Cu}_2\text{S-Na}_2\text{S}$, $\text{Cu}_2\text{S-FeS}$ and $\text{Na}_2\text{S-FeS}$

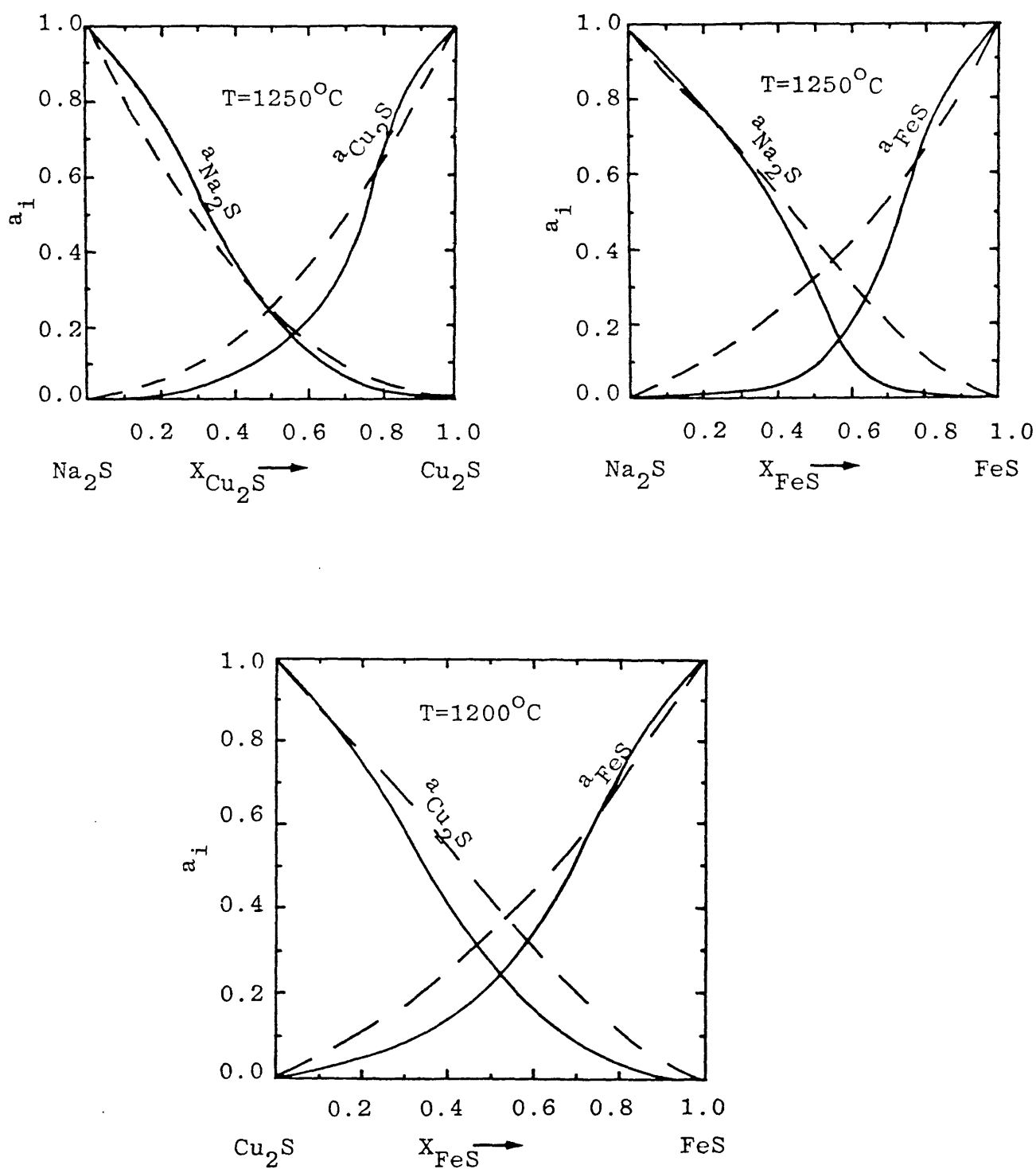
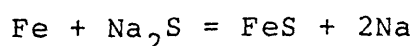


Fig.2.4 Activities of systems of Na_2S - FeS ,
 Cu_2S - Na_2S and Cu_2S - FeS

binary systems show negative deviations from Raoult's law and from Temkin's ideal mixing rule over a wide range of compositions^(28,69).

The extraction of copper was ascribed by Leis⁽⁵⁾ to the reactions



Na_2S , FeS , Cu_2S existed totally as ionic compounds. As iron and copper left the metal phase, they rapidly underwent electrochemical oxidation at the interface between the metal and slag phase. The sodium was reduced as the iron and copper were oxidized. The liberated sodium diffused through the slag phase and evaporated at the slag/gas interface. Sodium boils at 1156K (883°C) at atmospheric pressure. Ferrous sulphide and cuprous sulphide form homogenous solutions with sodium sulphide slag at the temperatures of liquid iron.

The distribution coefficient of copper, defined as the ratio of the weight fraction of the copper in the slag phase divided by that in the metal phase, was equal to 7.7⁽⁴⁹⁾ or 24⁽⁶⁹⁾, but quite scattered results were obtained by Leis⁽⁵⁾. It was not significantly affected by changes in the temperature, initial copper content in the metal or the amount of slag added⁽⁵⁰⁾.

2-2-3. Mechanism and Kinetics of Refining

High temperature metallurgical reactions are usually heterogeneous reactions, involving gas, slag and metal, and consist of three main steps, transport of the reactants to

the interface, chemical reaction in the boundary layer and transport of the products from the interface. Any one or combination of these steps may control or influence the overall reaction rate, but in many cases one particular step is found to be rate controlling. Fig. 2.5 illustrates how those steps can affect a slag/metal reaction⁽²⁹⁾.

The most outstanding contributions in absolute reaction rate theory were made by Eyring⁽³⁰⁾. This theory was based essentially on two principal concepts: (i). the formation of an activated complex in equilibrium with the reactants absorbed on the surface; and (ii). the specific rate for the decomposition of the activated complex.

The dependence of the reaction rate constant, k , on temperature can be related to the energy of activation by the Arrhenius equation $k = Ae^{-E/RT}$, where k is the rate constant, E the activation energy and A a term which is only weakly dependent on temperature. The order of a reaction, determined from studies of its kinetics under various conditions, may also give some insight into its mechanism.

Many pyrometallurgical processes are controlled by the transport of the reacting species to or the products from the interface. Under these conditions, it is assumed that the chemical reactions at the interface are at equilibrium. The rate of mass transfer can be expressed in terms of flux as:

$$J = k(C_b - C_i) \text{ mole/cm s}$$

where J is the flux, k the mass transfer coefficient, C_b and C_i the concentrations of bulk and interface respectively.

Kinetic studies are mainly based on experimental observations, but it is difficult to obtain accurate

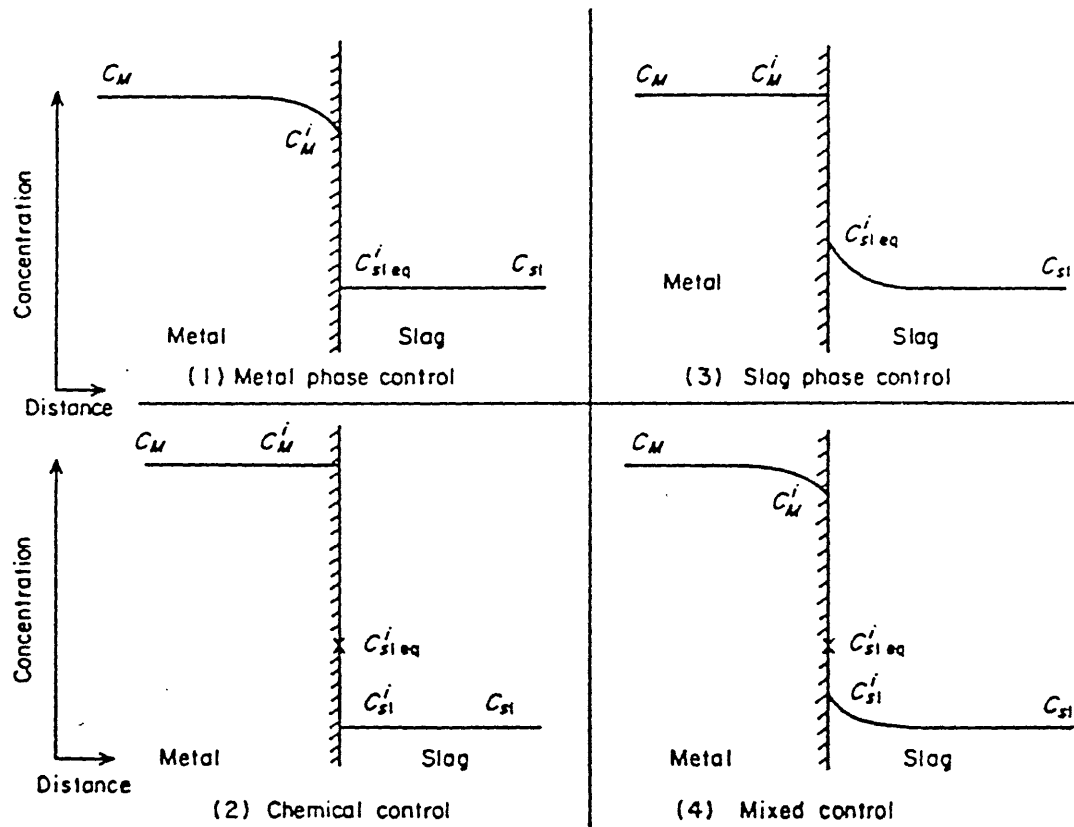


Fig.2.5 Controlling steps for a reaction involving a metal and slag under various conditions

experimental data for high temperature slag-metal systems. The major problems are (a) providing suitable container materials which are inert to both slag and metal, (b) the accurate determination of zero time, (c) the elimination of natural convection, (d) the prevention of side reactions and (e) the determination of reaction area and interfacial concentrations⁽³¹⁾.

Mathematical modelling has recently played an important role in the study of pyrometallurgical processes. Based on a comprehensive reaction model⁽³²⁾, in which the rates were controlled by multi-component transport in the metal and slag phases, Okazaki developed a model to simulate the effect of argon bubbling on the removal of copper and tin from molten iron by Na_2S slag⁽³³⁾. The model, in accordance with the general governing equations, such as chemical equilibria both at the metal/slag and slag/gas interfaces; flux density continuity and mass balance, was constructed under a number of assumptions. For example, only mass transfer in the boundary layers was considered to be a rate controlling step and sodium was vaporised at both metal/slag and slag/gas interfaces. The interfacial activities of all species could be expressed in terms of the bulk activities of which the changes with time were calculated by the model. A simplified version of the mathematical model was also used, namely, a steady-state model in which the final equilibrium was calculated in one step.

Rising bubbles are known to provide a source of mixing in metallurgical systems and at the interface they make for good contact between the phases. The mixing in the bulk liquid occurs by entrainment of liquid in the wake and by

forced convection currents set up by the bubble streams. The mass transfer in bubble stirred two phase system obeys the relation⁽³⁴⁾.

$$k^2 = BDQ/d^2$$

where B is a constant, k the mass transfer coefficient, D the diffusion coefficient, Q the total gas flow rate and d the cell diameter.

The nature of slag-metal interface reactions are electrochemical and similar to corrosion phenomena, the cathodic and anodic reactions occurring over the interface randomly with regard to both space and time⁽³⁵⁾. According to Lu⁽³⁶⁾ and Froberg⁽³⁷⁾, the flux of the species i across the interface, N_i , was related to the chemical and electrical potential difference between the two phases.

The transfer of sulphur between molten iron and slag has received considerable attention⁽³⁸⁻⁴⁰⁾. The rate of desulphurization was significantly increased with an increase in basicity of the slag and by deoxidizers, such as silicon and aluminum. The transfer of sulphur was equivalent to the sum of the transfer of silicon, aluminum, iron and of CO evolution.

2-3. DECOPPERIZATION BY SULPHIDE AND SULPHATE SLAG

The possibility of using a sulphide slag to remove sulphur and copper from molten ferrous metals was proposed by Jordan⁽⁴¹⁾ in 1950. Reagent slag containing either sodium sulphide, potassium sulphide, or aluminum sulphide was used as an extractive in his investigation. Jordan indicated that copper had a greater affinity for sulphur than iron had at

those temperatures where ferrous metals were molten, and that sufficient sulphur present in the ferrous metal enhanced the extraction of copper from metal to slag, the fuming of sodium sulphide was depressed by adding aluminum sulphide. From his results, the copper content of ferrous metals could be reduced to acceptable levels, but the weight ratio of slag to metal was extremely high, equal to one or two.

Langenberg and Lindsay⁽⁴²⁾ studied the decrease of copper content in ferrous alloys by three methods. In their experiments on the treatment of Fe-Cu-C alloys with sodium sulphide or sulphate slags, hydrated sodium sulphide of the approximate composition $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and anhydrous sodium sulphate were used as slag materials. The sulphide slag was formed by several additions. An equivalent slag-metal ratio of about 25wt% in terms of the ratio of dehydrated sodium sulphide to metal was used. Copper contents were reduced from 0.77wt% to 0.1wt% by hydrated sodium sulphide slag at 75wt% of metal weight. An initial sulphur content in the metal was not necessary for copper removal because the sodium sulphide slag supplied sulphur to form a copper-sulphur complex and also acted as a solvent for this complex. Iron sulphide slag was also a solvent for copper sulphide, but it resulted in a high sulphur content in the metal. The copper content appeared to be rapidly lowered immediately following a sulphide slag forming addition. After the copper had quickly reached its new level, it did not change appreciably with time, but the sulphur content of the metal slowly rose with increased slag-metal contact time.

The Bureau of Mines of the United States investigated a refining process that involved adding sodium sulphate to molten iron saturated with carbon, the sulphate being reduced to sulphide in situ by carbon. Subsequent pilot-scale studies established the technical feasibility of reducing the copper content to acceptable levels^(8,43-47).

A lance system was used for intermittent sub-surface injection of sodium sulphate at controlled rates⁽⁴⁵⁾. The rate of copper removal was greater with the initial additions. For each additional increment of slag, the rate gradually decreased as the slag layer accumulated on the surface of the bath.

About 38% of initial copper removal was obtained at all copper levels by minimizing the accumulation of spent slag on the surface of the melt. Thus, effective copper removal was not dependent on copper content in the melt, but was enhanced by slag removal. Their results also showed that copper removal was a function of the total sodium sulphate added rather than the rate of addition. Makar and Punning⁽⁴³⁾ found that the relationship between copper removal and the amount of Na_2SO_4 added could be approximately expressed by the equation

$$Y = 1 - e^{-3.23X}$$

where

Y = Fraction of copper removed

X = The weight ratio of Na_2SO_4 added to metal treated

Initial sulphur contents ranging from 0.1wt% to 0.2wt% were reduced to as low as 0.02wt%. Generally, the Na_2SO_4 treatments were effective up to approximately 1823K (1550°C) with reaction times not exceeding 7 minutes.

Several kinds of sulphate mixtures, including CaSO_4 , K_2SO_4 , MgSO_4 and Na_2SO_4 were tested, but none of them were as effective as Na_2SO_4 alone⁽⁴⁴⁾. Removal of 75wt% of copper (to obtain 0.1wt% or less) requiring about 27wt% sodium sulphate by lance injection with slag removal was observed⁽⁴⁵⁾. Pilot-scale tests demonstrated that effective copper removal, similar to that achieved in the laboratory, could be obtained on the pilot-plant scale⁽⁴⁶⁾.

In a later report⁽⁸⁾, it was shown that there was no significant difference in removal rates using surface additions in gas stirring system as compared with lance injections of the reagents.

Maximum copper removal was achieved in carbon saturated iron at 1573K (1300°C). Temperatures in excess of 1773K (1500°C) would accelerate the loss of sodium sulphide from the slag, sulphur pick up by the metal bath, and reversion of copper. There was no slag on the bath at the end of experiments carried out at 1934K (1670°C)^(48,8).

Topkaya⁽⁷⁷⁾ reduced the copper content in carbon saturated iron from 0.9wt% to 0.19wt% by contacting with pure sodium sulphide slag for 3 hours. The reaction rate, which was sensitive to the interfacial areas, was claimed to be controlled by the chemical reaction at the gas/slag and metal/slag interface and by diffusion of Na vapour in the gas phase. In a closed system of fixed volume, the reaction between slag and metal would stop when sodium vapour pressure was built up to the equilibrium value.

Sulphide slags were not as effective in removing copper from low carbon melts as from high carbon melts, and this was explained by the relative activity of the copper in iron

solution^(5,8,26). There was a definite dependence between copper removal and silicon concentration in the metal, copper removal decreased markedly as silicon content increased⁽⁴⁷⁾. High initial manganese in the metal also significantly lowered the efficiency of copper removal due to its affinity for sulphur.

The removal of copper by sodium sulphide slag was also examined by some other investigators^(49,50).

2-4. DECOPPERIZATION AND DETINNING BY OTHER METHODS

Generally, three main processes have been investigated for treating copper contaminated scrap: (i). selective melting of copper from the scrap at temperatures intermediate between the melting points of copper and iron; (ii). extraction by sulphide or sulphate slag; (iii). vacuum distillation.

Several kinds of melting methods were studied to reduce the contents of copper and tin in auto scrap by Carlson⁽⁵²⁾. Nonconsumable arc and vacuum arc melting did not remove either of these impurities, but electron beam and vacuum induction melting were technically feasible for the removal of copper and tin. Carlson was unsuccessful in developing a slag with the capability of extracting copper, but removed tin by electroslag melting.

Preferential melting techniques were one of the main methods for decopperization of metallic scrap, such as electric motor armature⁽⁵³⁾. The material, pretreated by dipping in sodium sulphate, was placed in a molten salt bath at 1423 to 1523K (1150 to 1250°C). In this process the

molten salt acted only as a protective bath and did not enter into its chemistry. Copper droplets were sweated off the scrap and collected in the bottom of the vessel. In this process, the copper content could be reduced to about 0.3wt%.

Several papers were concerned with decopperization by vacuum treatment⁽⁵⁴⁻⁵⁸⁾. One of the most important investigations was carried out by Harris^(57,58). Although it was confirmed in 1979 that vacuum refining of copper and tin from liquid steel was feasible, refining rates were considerably slower in large systems than those in bench scale systems. It was claimed that this problem had been solved⁽⁵⁸⁾. Impurities, such as copper and tin, were removed to approximately 85% of initial content in liquid iron to produce residual levels less than 0.15wt% Cu and 0.1wt% Sn with the treatment of 50 to 200 tonnes and 20 to 30 minutes in a specific vessel which supplied a high surface area of steel exposed to the vacuum. This system needed high operating temperatures and low pressures. Mn in the molten metal was also completely lost.

From the levitation melting method, Morales and Sano⁽⁵⁹⁾ found that the vaporisation of copper and tin at atmospheric pressure proceeded fast enough for practical applications by using alloying elements instead of vacuum. Carbon, chromium and silicon were found to enhance the vaporisation of both copper and tin. The final contents of copper and tin were reduced from 0.94wt% to less than 0.03wt% after 10 and 6 minutes respectively of levitation at 2073K (1800°C) in a helium atmosphere. In their experiments, the surface/weight ratio was substantially higher than that

of steel in a ladle.

Copper was removed from molten scrap iron by adding sulphur and halide containing compounds to the melt whereby the resultant vaporisation of a halide vapour stripped off a copper-sulphur compound⁽⁵¹⁾. If the halide containing compounds or the sulphur were used alone, only part of the copper was removed.

Makar et al found that tin was not removed by sulphate refining process⁽⁵⁾. Their results, however, showed that chlorination of tin from molten iron using organic solid sources of chlorine was effective, the tin content being reduced from 1.1wt% to 0.17wt% at 1200°C, but between 4 and 9% of the iron was also lost as iron chloride. This process had no effect on the copper content, which remained at the initial value. Tin removal was achieved to a limited extent by co-injection of chlorine or ferrous chloride with sodium sulphate, for example, approximately 20% of tin and copper were removed with a 16% addition of sodium sulphate plus ferrous chloride (50:50 mixture)⁽⁴⁵⁾. Disappointing results of tin removal by sodium sulphide slag were obtained⁽⁶⁰⁾ under the conditions of 0.05-0.1 slag/metal weight ratio, 0.001-0.3wt% initial sulphur content in the metal and refining for one hour in an induction furnace.

Using vacuum induction furnace, under 2-3 μm low pressure, the removal of more than 70% of initial tin in the molten steel containing sulphur was achieved within 30 minutes⁽⁶¹⁾. The rate of tin removal was expressed by a two term equation:

$$-d\text{Sn}/dt = 12 \pm 2 \times 10^{-3} (\% \text{Sn} - 0.15) + 0.5 \pm 0.02 (\% \text{S}) (\% \text{Sn})$$

The former component represented the normal rate of loss of

tin in the absence of sulphur, and the latter the effect of sulphur, which followed second order kinetics and was proportional to the product of the concentration of tin and sulphur in the melt.

Recently, metallurgical possibilities have been studied for the removal of tramp elements, such as Sn, P, As, Sb, Pb and N, from unalloyed and alloyed steel melts under reducing conditions using metallic calcium, calcium dissolved in calcium chloride or fluoride, and calcium carbide⁽⁶²⁻⁶⁶⁾. In the refining treatment, tin formed stable Ca_2Sn with metallic calcium and the product transferred to and dissolved in the calcium compound slag.

As a result of its high vapour pressure, calcium has to be added to the steel melt by special techniques including the application of excess gas pressure⁽⁶³⁾, which is hard to introduce in industrial operation. 67% of initial tin was removed from 18%Cr-8%Ni-Fe alloy at 1873K (1600°C) in 30 minutes by a mixture of CaF_2 -Ca (less than 10%), no removal of tin was achieved when CaF_2 was used alone⁽⁶⁴⁾.

Tin was effectively removed from molten steel by a 3-4% calcium carbide additive when the initial carbon content in steel was low, since the decomposition of CaC_2 was influenced by the activity of carbon in the melt^(65,66). This process was coupled by the increase of final carbon content in the steel up to 1.0-1.5wt%, as shown in Fig.2.6.

Calcium carbide can be used at atmospheric pressure, so that it may have a better future than that of metallic calcium.

Another approach is the chemical fixation of tramp elements by the addition of rare earth metals which also

form stable intermetallic compounds, e.g. $\text{La}_2\text{Sn}^{(78)}$. No practical application has been reported as yet.

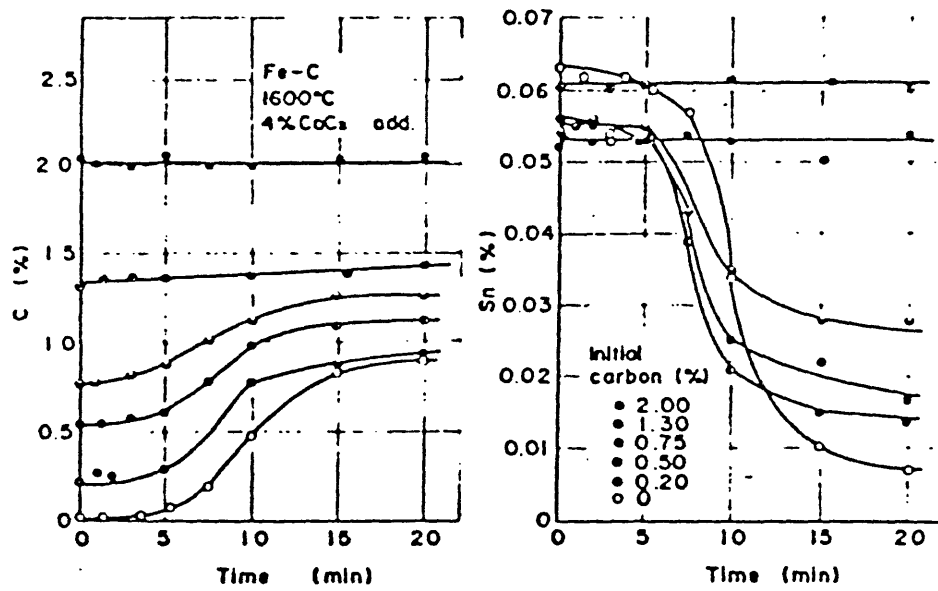


Fig.2.6 Changes in carbon and tin contents after the addition of CaC_2

CHAPTER 3

EXPERIMENTAL

CHAPTER 3

EXPERIMENTAL3-1. INTRODUCTION

The experiments carried out by other workers had been made under a variety of conditions and under various controls and it is difficult to determine what the mechanisms of the reactions were and which the rate determining steps were.

The present series of experiments were designed to provide as much information as possible on the thermodynamics and kinetics of the reactions involved. To this end it was decided to use an electric resistance furnace, whose temperature could be accurately controlled and to contain the metal in crucibles of known dimensions and to vary the degree of metal/slag and liquid/gas agitation by providing a flow of argon gas which could be directed through the furnace from the bottom or from the top, in the latter case through a lance which could be directed at the slag surface from a distance or lowered into the liquid to provide vigorous agitation.

Most of the starting materials used were of AnalaR grade, or prepared on site under carefully regulated conditions. Metallic elements were analyzed by atomic absorption spectrophotometry and sulphur by a combustion/absorption titration method. X-ray diffraction was employed to identify the phases present when necessary.

3-2. APPARATUS

3-2-1. Furnace Assembly

A vertical furnace, as shown in Fig. 3.1, was built for this project. Six lanthanum chromite elements were employed as heaters, which could be heated up to 2073K (1800°C) in air. A 50mm ID X 59mm OD X 825mm long impermeous mullite reaction tube was closed at both ends with water cooled brass heads and located in the centre of the furnace. A 60mm ID X 70mm OD X 425mm long alumina tube was located outside the reaction tube to obtain a more uniform temperature distribution and also to prevent damage to the heating elements in case of fracture of the reaction tube. Ceramic board was used as insulation between heating elements and furnace shell. The top brass head was equipped with a viewing window and two holes for sampling and gas bubbling. Through a hole in the bottom brass head a crucible could be rapidly raised into the hot zone of the furnace or withdrawn by means of a 5.0mm ID X 8.5mm OD X 650mm long closed end mullite tube, which was held in position by rubber O-ring clamping seal. The top gas delivery tube was similarly held in the top brass head.

Temperatures were automatically controlled to set point within $\pm 1^{\circ}\text{C}$ by a three-term Eurotherm Controller connected to a Rh6%-Pt/Rh30%-Pt thermocouple placed adjacent to the alumina tube. The temperature profile of the furnace was periodically checked with a vertical travelling Rh6%-Pt/Rh30%-Pt thermocouple under the experimental conditions, and a typical temperature profile is given in

1. Reaction tube
2. Thermocouple
3. Heating element
4. Brass head
5. Crucible
6. Argon cylinder
7. Blow tube
8. Magnesium perchlorate tower
9. Titanium Furnace
10. Rotameter
11. Needle valve
12. Two way tap valve

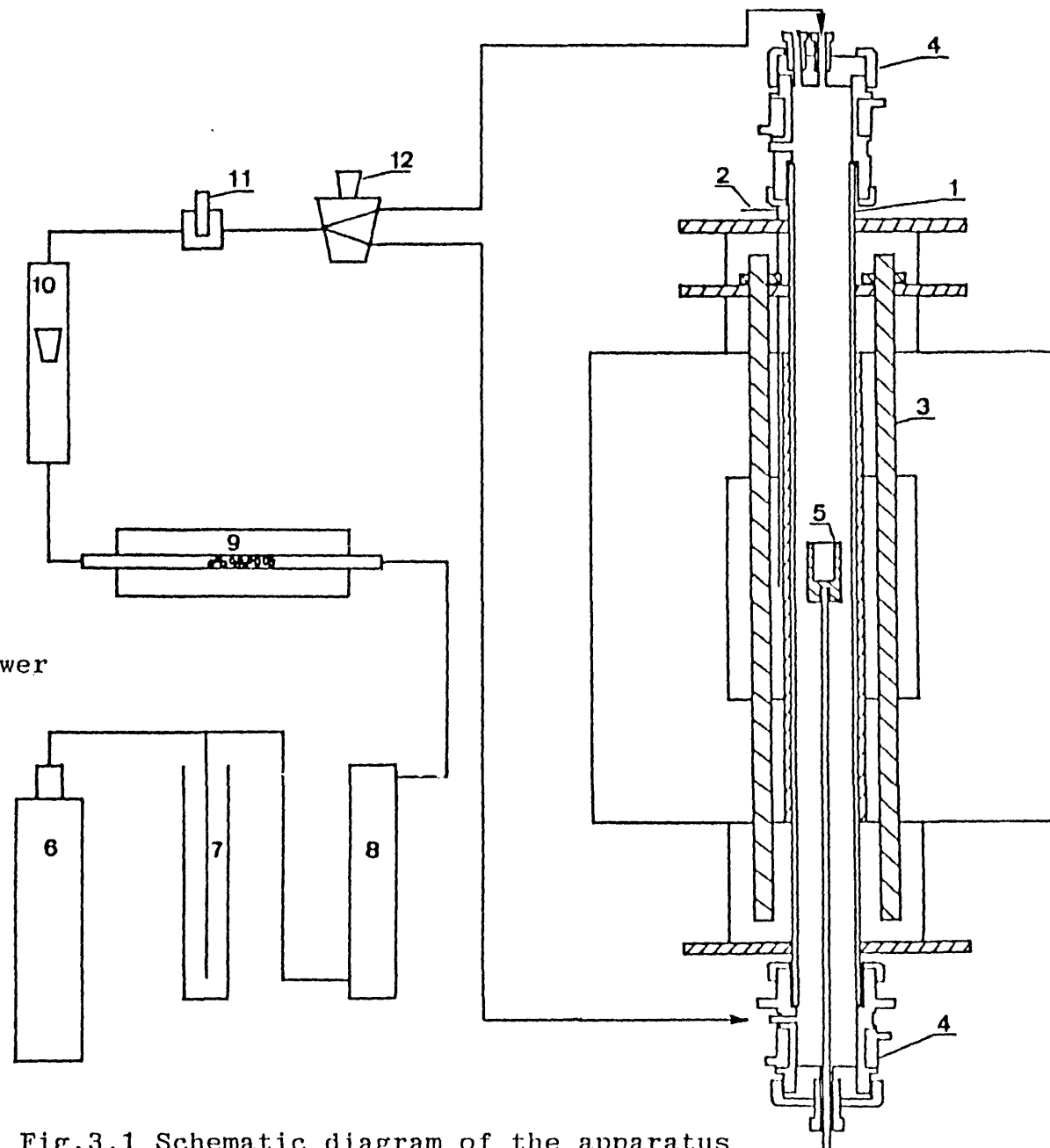


Fig.3.1 Schematic diagram of the apparatus

Fig. 3.2. The temperature variation at the hot zone of the furnace was $\pm 1^{\circ}\text{C}$ over 4cm and $\pm 4^{\circ}\text{C}$ over 7cm.

3-2-2. Gas Supply System

High purity argon was passed through a dibutyl phthalate filled gas blow-off tube to keep a constant pressure as shown in Fig. 3.1, dried through magnesium perchlorate and deoxidized over titanium granules at 1173K (900°C). The flowrate was measured by a rotameter which was calibrated by a soap bubble method. After having been measured, the gas passed through a two-way stopcock which allowed it to be delivered to the furnace either from top or bottom. To control the flowrate accurately, a needle valve was placed as close as possible to the gas inlet of the furnace. A 3.0mm ID X 5.4mm OD X 60mm long recrystallised alumina tube was inserted into the gas inlet on the top brass head, through which purified argon could be directed onto the slag surface or injected into the molten metal bath. Exit gases passed through a short plastic pipe to a fume hood, and also the plastic pipe could be connected to a U tube to check for leakage.

3-2-3. Vacuum Drying System

A low temperature vacuum drying apparatus was constructed to obtain anhydrous sodium sulphide. The system was similar to Kopylov's work⁽⁷⁰⁾. A Pyrex glass tube, Fig. 3.3, was placed in a small resistance furnace, sealed by a rubber bung connected to a mercury manometer and two

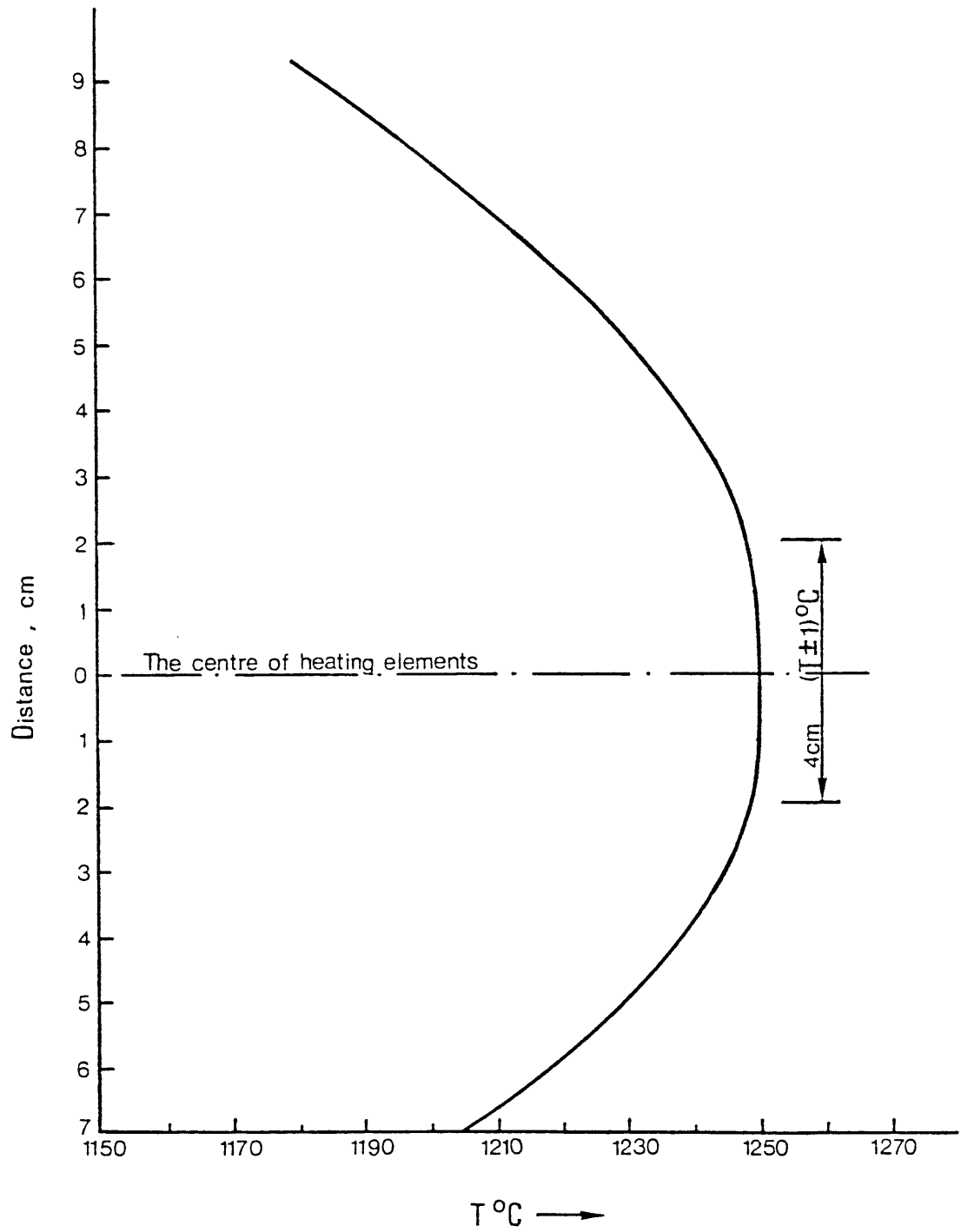


Fig.3.2 Temperature profile of the furnace

1. Furnace 2. Pyrex tube with $\text{Na}_2\text{S} \cdot \text{XH}_2\text{O}$
 3. Mercury manometer 4. Water traps

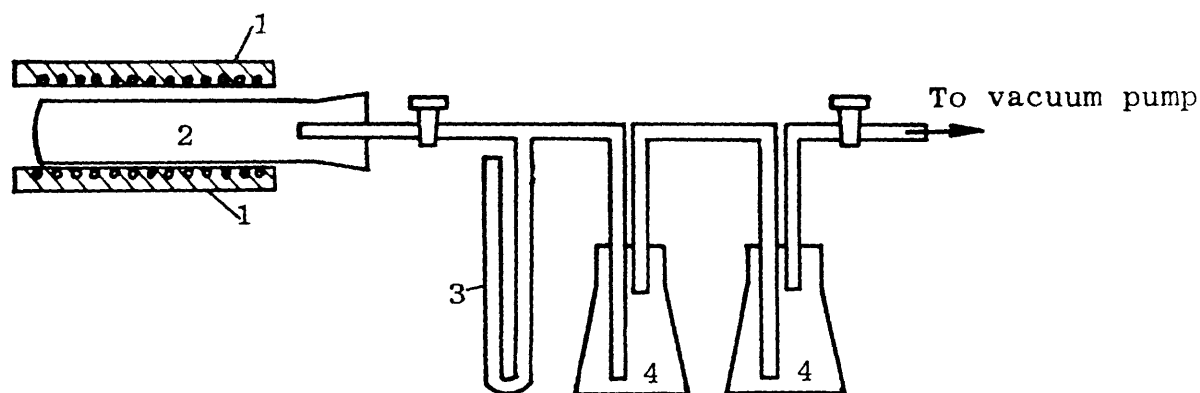


Fig.3.3 Vacuum drying apparatus

moisture traps through a stopcock and a three way glass tap. After the absorption of water, the system was connected to a vacuum pump. Silica gel and concentrated sulphuric acid were used to absorb water.

3-2-4. Sulphur Analysis System

Fig. 3.4 illustrates the sulphur analysis system. A horizontal six-element silicon carbide furnace, with automatic temperature control, and a 38mm ID X 46mm OD X 900mm long gas tight mullite combustion tube fitted with rubber bungs and water cooling coils at either end, was used. The rubber bung of the absorption cell had three holes for the entry of combustion gas, the escape of waste gas and delivery of titrant.

- | | |
|---|--------------------|
| 1. Air cylinder | 6. Furnace |
| 2. $\text{Mg}(\text{ClO}_4)_2$ drying tower | 7. Fireclay boat |
| 3. Rotameter | 8. Absorption cell |
| 4. Rubber bung | 9. Titration tube |
| 5. Water cooling coil | |

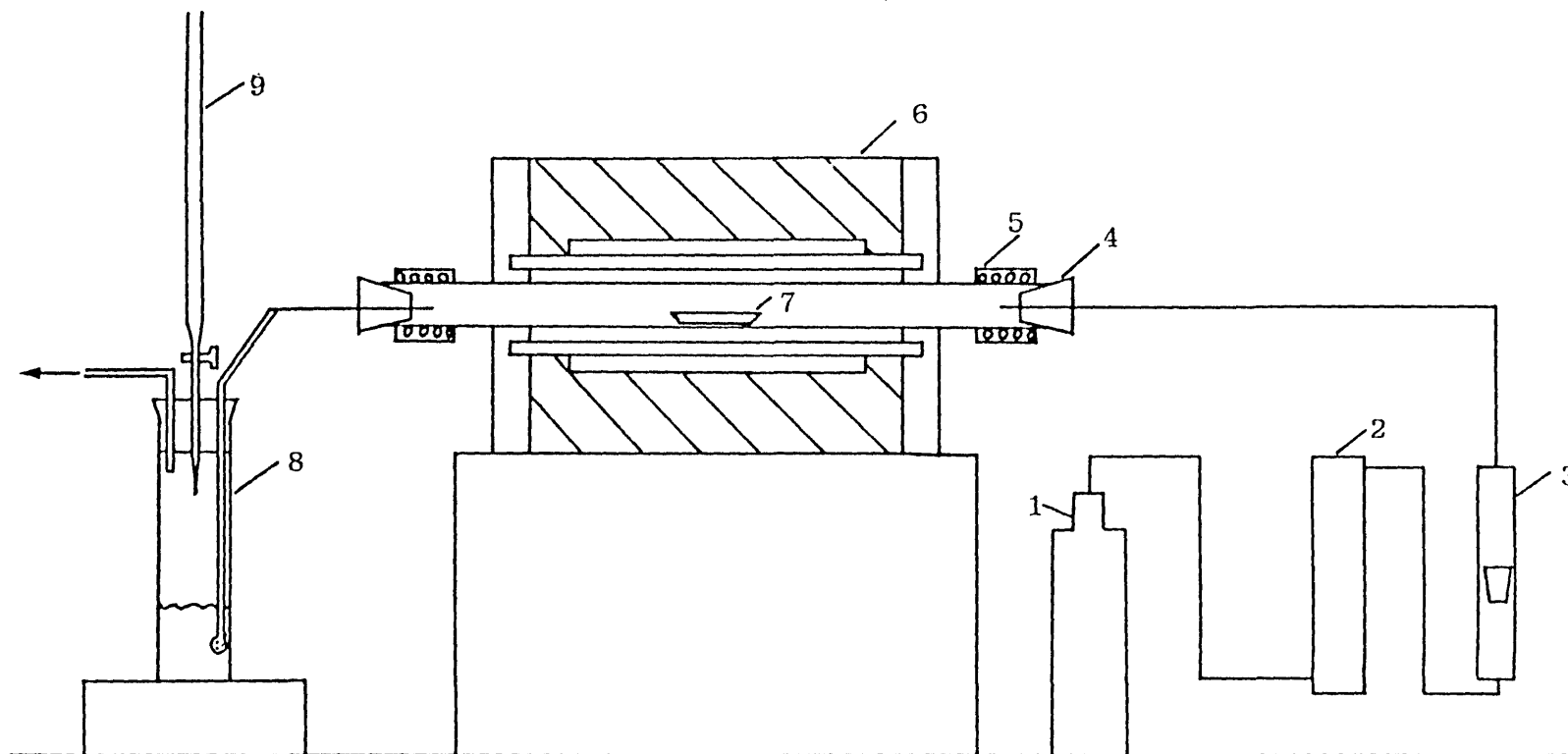


Fig.3.4 Sulphur analysis system

3-3 MATERIALS

3-3-1. Crucibles

High purity electro-graphite rod of EYA9 and EY9 produced by Morganite Carbon Limited was used as a crucible material. It could be machined into convenient shapes and sizes, usually a 20.6mm ID X 28mm OD X 40mm (or 60mm) deep crucible was used in the experiments but sometimes one of 25mm ID X 33mm OD X 40mm (or 60mm) deep was used. The crucibles had a machined 8.7mm diameter X 15mm long hole at the bottom to hold it in a suitable position on a mullite tube.

Recrystallized alumina crucibles were used when the carbon content of the metal phase needed to be controlled. It was placed in a cylindrical support, as illustrated in Fig. 3.5, which was constructed by fastening two different diameter alumina tubes together using alumina cement and firing from room temperature to 1273K (1000°C) slowly.

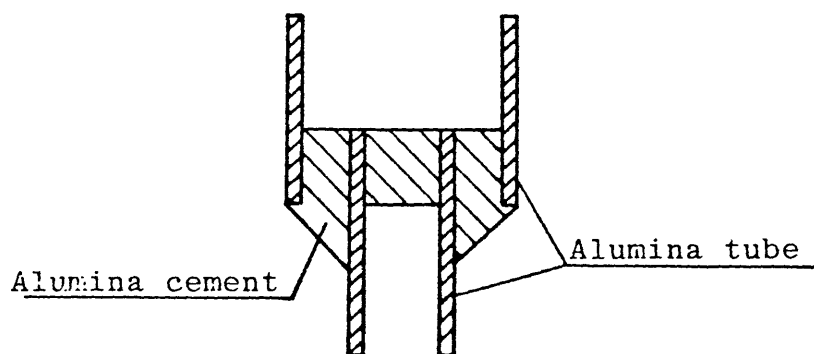


Fig.3.5 Alumina crucible support

3-3-2. Preparation of Alloys

Carbon-saturated master alloys were prepared by melting electrolytic iron powder, high purity graphite powder and

copper foil or tin granule in a graphite crucible. The melting was carried out in a high frequency induction furnace and under an argon atmosphere. Sometimes alloying materials, such as Cu, Sn, FeS, Cu_2S , were added to molten carbon saturated iron. The liquid metal was poured into a graphite mould, and, after cooling, 20mm diameter bars were cut into suitable lengths and kept in a desiccator for later use. Master alloys for steel, usually 1.0wt%Cu-0.5wt%C-Fe and 1.0wt%Sn-0.5wt%C-Fe, were prepared by a similar method as mentioned above but using a recrystallized alumina crucible, a vacuum induction furnace and an iron mould. When only a small amount of material was needed, the alloy was prepared in the furnace used for experiments, in this case, argon was bubbled into the melt to make it homogeneous.

3-3-3. Slag Materials: Preparation of Anhydrous Sodium Sulphide

Several methods for obtaining anhydrous sodium sulphide have been described⁽⁷⁰⁻⁷³⁾. After experimental tests, Kopylov⁽⁷⁰⁾ constructed the equilibrium diagram of $\text{Na}_2\text{S}-\text{H}_2\text{O}$ system as shown in Fig. 3.6 and concluded that pure anhydrous sodium sulphide could be obtained by a single stage drying of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. At a 30-35 mm Hg pressure, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was rapidly heated to 323-333K (50-60°C), then to 423-433K (150-160°C) at 12-15 deg/hour and held at that temperature for 2 hours. This method was employed here after some modifications. AnalaR sodium sulphide $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ produced by BDH Chemicals Limited was used. Minimum assay is 31wt% Na_2S and X was about nine.

In the $\text{Na}_2\text{S}-\text{H}_2\text{O}$ system several crystal hydrates have

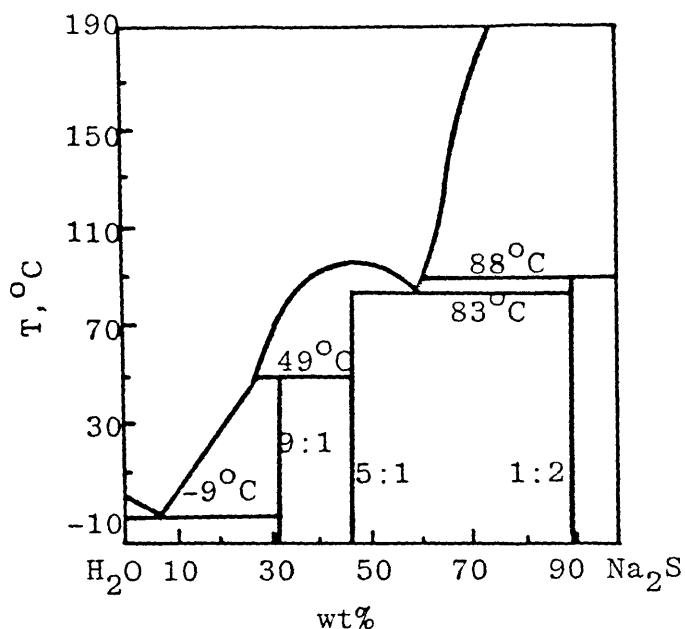


Fig.3.6 Phase diagram of $\text{Na}_2\text{S}-\text{H}_2\text{O}$

been observed as shown in phase diagram. $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$ was heated at a pressure of 5mm Hg to 318-328K ($45-55^\circ\text{C}$), and this temperature maintained for more than 6 hours to remove most of the evolved water by evaporation, because water of decomposition was observed in the tube at above 333K (60°C) when it was heated up continuously. The temperature was then raised at 15-20 deg/hour to 423-433K ($150-160^\circ\text{C}$) and held at that temperature for 2 hours. A residual pressure of 5 mm Hg was employed through out the process. The sulphide was later fired at 1523K (1250°C) in a graphite crucible to reduce any oxide or sulphate that might be present. The final products sucked into 3mm ID silica tubes were kept in a test tube which would be put into a desiccator immediately. The sulphide was taken out of silica tube and put into a glass bottle in a glove-box under argon atmosphere.

Sodium sulphide was observed to be very hygroscopic, it would absorb some water during storage and weighing. Chemical analysis of the sulphide, so produced, showed only slight departure from the stoichiometric composition.

Average composition of the dehydrated sodium sulphide was 40.8wt% S and 57.9wt% Na. Most of the impurities were probably due to the hygroscopicity of sodium sulphide (stoichiometric composition: 41.1wt% S and 58.9wt% Na). The melting point of Na_2S , measured by a Rh6%-Pt/Rh30%-Pt thermocouple which was held in an alumina protection tube, was 1448K (1175°C). This value agreed with Kopylov's work⁽⁷⁰⁾.

3-4. EXPERIMENTAL PROCEDURE

The graphite crucible, containing 20 grams of master alloy and a certain amount of slag usually equal to 3 grams, was placed on top of the bottom brass head and this was fitted into the furnace tube. After having flushed argon through furnace for 15 minutes, the crucible was raised to the place at which the temperature was about 1173K (900°C) by a mullite support tube and held there by a rubber 'O'-ring seal for 5-10 minutes, then raised to the hot zone.

Argon was introduced into the furnace in three ways: 1. purge from the bottom of the furnace; 2. downward from a place 1.0 cm above the slag surface; or 3. by bubbling into the metal bath. In the last case, as soon as the metal was melted, a calibrated alumina tube, held in the central hole of the top brass head, was lowered to touch the bottom of the crucible, then raised about 3-5 mm and held there. The gas needle valve was opened to obtain the required flowrate.

It was difficult to determine the zero time of a reaction accurately. In the present studies, this was chosen as the time at which slag had melted and metal just began to

melt. It usually took about two minutes at 1523K (1250°C), one minute above 1623K (1350°C) from the time of raising the crucible into the hot zone to zero-time. This was checked by lowering the bubbling tube to follow the change of the height of the bottom that tube could touch.

During the experiments samples from metal and/or slag were taken by suction with a 2 mm ID X 4 mm OD silica tube. Metal samples were put into a labeled bottle for later analysis. Slag samples were weighed and dissolved in concentrated nitric acid immediately after being taken out of the furnace to minimise the absorption of water, since it was found that samples absorbed some water if they were not analyzed in time.

After a pre-determined period of reaction time, the crucible was quenched in argon in the lower part of the furnace tube.

For the experiments using alumina crucibles, the support tube was raised to the hot zone in four steps to prevent cracking of the crucible.

3-5. ANALYSIS OF SLAG AND METAL

3-5-1. Atomic Absorption Spectrophotometer

All metallic elements existing in slag and metal were analyzed by an atomic absorption spectrophotometer.

In principle, this method is based on the absorption of radiation by free atoms⁽⁷⁴⁾. A solution of the material to be analyzed is sprayed into a controlled air or nitrous oxide/acetylene flame. A beam of light containing

wavelength characteristic of the element of interest is shone through the flame onto a detector. Absorption of the light by the element in the flame is a function of the amount of that particular element in the flame. The concentration of the element in solution is found by comparing with the standard solutions of known concentrations.

Standard solutions were prepared by mixing stock solution of 1000 ppm, provided by BDH Chemicals Ltd, with appropriate diluents. To eliminate matrix effect, all standard solutions were matched with sample solutions.

3-5-2. Copper and Tin in the Metal

The surface of metal samples were rubbed with a sand paper to remove any oxide or slag attached during sampling. Finely crushed and accurately weighed metal samples were placed in a solvent and heated to dissolve.

For the analysis of copper, about 10 ml of a mixture of concentrated HCl and HNO_3 was used as solvent. After dissolving, the solution was heated to dryness. Doubly distilled water and nitric acid to give a 1.0% concentrated HNO_3 final solution were added to dissolve the remainder, then the solution was diluted into a 100 ml flask. Because usually the concentrations of sample solutions were within the optimum concentration of copper from 2 to 8 ppm

10 ml concentrated HCl was used to dissolve samples containing tin. After dissolving, the solution was heated until the 5ml mark made on the beaker was reached. This was because of the loss of tin found when the solution was

heated to dryness, caused by the evaporation of SnCl_4 , which had a low boiling point of 387K (114°C) ⁽⁷⁵⁾. The remaining solution was diluted into a 50 ml flask and final solution contained 10% concentrated HCl. In an air/acetylene flame many cationic and anionic interferences were observed, so a nitrous oxide/acetylene flame was used for the analysis of tin.

The absolute error of analysis was within $\pm 0.5\%$ of total copper content in the metal and $\pm 1.0\%$ for tin when both concentrations were in the range of 0.2-1.0wt%.

3-5-3. Slag

The preparation of solutions of slag samples were similar to that for metal samples of copper analysis except that they were dissolved in concentrated HNO_3 . To analyze for sodium and iron, exactly 10 ml of the solution for analysis of Cu and Sn was diluted to 100 ml because the concentrations of Na and Fe in Cu analysis solution were higher than the linear range that the instrument could detect. Also this final solution contained 200 ppm potassium chloride to suppress the ionization of sodium, which could happen in an air/acetylene flame.

3-5-4. Sulphur in the Metal

For the analysis of sulphur in metal, the rapid combustion method of Jones ⁽⁷⁶⁾ was used. After being crushed and weighed, the sample was put into a fireclay combustion boat pre-ignited at 1723K (1450°C) for a few minutes. Dried

air was passed into the combustion tube at the rate of 1.0 litre/min, and the exit gases were introduced into 150 ml absorption solution made by adding 30 ml H_2O_2 (20 vols) to distilled water to make up 1.0 litre and 1.0 ml of screened methyl red indicator. The titration of the sulphuric acid produced by N/160 sodium tetraborate was carried out at the end of the combustion period, which lasted about 5 minutes. For a given sulphur content, the sensitivity of the method was found to vary slightly with sample weight. All these factors were taken into account by comparison with British Chemical Standard metal specimens.

CHAPTER 4

RESULTS

CHAPTER 4

RESULTS4-1. DECOPPERIZATION

The removal of copper from carbon-saturated and low carbon iron melts were investigated. Pure Na_2S and 30wt%FeS-70wt% Na_2S slag compositions were used in most of the present experiments, MgS and CaS were added to the slag for the runs of low carbon content in the metal.

The slag and metal samples from the runs were analysed as described in the Chapter 3. The results of these analyses are given below.

The effects of the mode of argon introduction, composition of metal and slag, the weight ratio of slag to metal, the area of interfaces and operating temperature on the decopperization are described here.

Most of experiments were carried out under the following conditons: initial metal charge $W_m=20\text{g}$; initial weight ratio of slag to metal $W_s/W_m=0.15$; $T=1523\text{K}$ (1250°C); initial sulphur in the metal $[\text{Swt}\%]=0$ and inside diameter of the crucibles $C_{id}=20.6\text{mm}$. Three different modes for introducing Ar to the charge were employed; B represents the inlet of Ar gas at the bottom of the furnace, S into the crucible about 1.0 cm above the slag surface and M bubbling through the molten metal phase. Other relevent experimental conditions are illustrated in individual graphs.

4-1-1. Treatment of Analytical Data

Sulphur contents of the slag are calculated from the analytical results of iron, sodium and copper in the slag making the assumption that slag consists entirely of stoichiometric Na_2S , Cu_2S and FeS . Since there is one mole of sulphur for every mole of iron and for every two moles of copper or sodium:

$$W'_S = M_S (W'_{\text{Na}}/2M_{\text{Na}} + W'_{\text{Fe}}/M_{\text{Fe}} + W'_{\text{Cu}}/2M_{\text{Cu}}) \quad (4-1)$$

where

M_i = molecular weight of element i ;

W'_i = uncorrected weight percentage of element i ;

If there is no error in the determination of the weight percentages of the cations, and if the slag sample does consist entirely of Na_2S , FeS and Cu_2S , the summation of W'_{Cu} , W'_S , W'_{Fe} and W'_{Na} will be equal to one hundred. The mass of the slag dissolved for analysis was subject to inaccuracy because of its hygroscopicity. In addition, small amounts of insoluble ceramic and graphite mixed with the slag contributed to errors in the slag weight. These factors made the sum of the components deviate from one hundred.

It is assumed that the deviation is mainly caused by errors in the mass determination of the sample. The corrected weight percent, W , can thus be determined by dividing the experimental weight percent W'_i by $\Sigma W'$. Hence for the three metals:

$$W_i = W'_i / (W'_{\text{Na}} + W'_{\text{Fe}} + W'_{\text{Cu}} + W'_S) \quad (4-2)$$

In this case, the mass ratios of iron, sodium and copper are correct even though their absolute values may be in error. The composition of some typical samples analyzed

is given in Table 4-1 for both uncorrected and corrected weight percentages. The figures representing slag compositions are constructed using the corrected weight percent.

The proportion of reacted copper, represented by R, is plotted versus time or other variables to indicate the efficiency of copper removal, especially when there is a slight difference in the initial copper content between experiments. It is calculated by the equation

$$R = 100\%([Cu\%]_o - [Cu\%]_t)/[Cu\%]_o \quad (4-3)$$

where

$[Cu\%]_o$ = initial copper content of the metal.

$[Cu\%]_t$ = copper content of the metal time t (minute).

The argon flowrates used in all experiments are those measured under normal temperature and pressure (NTP).

4-1-2. Decopperization from carbon saturated iron

Pure Na_2S and 30wt%FeS-70wt% Na_2S slag compositions were those most used in the experiments discussed in this section. Experimental results, in terms of the final copper content in the metal and the proportion of removed copper, are shown in Table 4-2. A graph for each experimental set of conditions is plotted in terms of percentage of copper and/or sulphur in the metal against time.

Typical kinetic curves for both slag and metal composition changes are shown in Fig.4.1 for pure Na_2S and in Fig.4.2 for 30wt%FeS-70wt% Na_2S slag at 1523K (1250°C). There was generally a decrease in sodium and a corresponding increase in iron and copper contents of the slag during the

Table 4-1. Typical Results of Slag Analysis

Run & Sample	Reaction Time Min	Uncorrected Weight Percent %					Corrected Weight Percent %			
		W' _{Na}	W' _{Fe}	W' _{Cu}	W' _S	ΣW'	W _{Na}	W _{Fe}	W _{Cu}	W _S
10-1	22	36.28	18.54	4.81	37.07	96.7	37.52	19.17	4.97	38.34
11-1	7	41.68	17.27	2.61	39.56	100.12	41.40	17.16	2.15	39.29
11-2	20	35.68	17.88	3.86	36.03	93.45	38.18	19.13	4.13	38.56
11-3	34	35.28	20.65	5.05	37.64	98.25	35.91	21.02	5.14	37.93
11-4	60	33.85	23.21	5.38	38.20	100.64	33.63	23.06	5.35	37.96
12-f	60	37.42	22.26	4.56	39.95	104.27	35.89	21.30	4.45	38.36
15-f	60	31.32	18.15	4.12	35.22	86.81	36.10	20.90	4.75	38.30
19-f	61	35.16	21.53	1.06	37.34	95.49	37.2	22.6	1.11	39.10
23-f	61	32.38	22.14	4.98	36.46	95.96	33.7	23.1	5.19	38.0
30-1	4	41.78	14.39	2.72	37.99	96.88	43.1	14.90	2.81	39.2
30-2	18	33.38	16.4	3.94	33.61	87.33	38.2	18.8	4.51	38.5
30-3	32	36.20	19.76	4.98	37.75	98.69	36.7	20.0	5.05	38.3
30-4	64	29.95	22.62	4.94	35.04	92.55	32.4	24.4	5.34	37.9
34-1	5	47.6	6.17	3.14	37.44	94.35	50.5	6.54	3.33	39.7
34-2	12	40.83	9.17	3.16	34.45	87.61	46.6	10.50	3.61	39.3

Table 4-1. (Continued)

Run & Sample	Reaction Time Min	Uncorrected Weight Percent %					Corrected Weight Percent %			
		W' _{Na}	W' _{Fe}	W' _{Cu}	W' _S	ΣW'	W _{Na}	W _{Fe}	W _{Cu}	W _S
34-3	31	35.2	15.40	3.49	34.19	88.28	39.90	17.50	3.95	38.7
34-4	60	32.99	19.8	3.66	35.21	91.66	36.0	21.6	3.99	38.4
50-1	2	38.31	16.99	4.34	37.48	97.12	39.44	17.50	4.47	38.59
50-2	4	40.83	16.98	4.98	39.39	102.18	39.96	16.62	4.88	38.54
50-3	10	39.38	17.52	4.98	38.54	100.15	39.45	17.28	5.00	38.66
50-4	30	35.91	20.25	5.22	37.90	99.18	36.16	20.34	5.27	38.17
52-1	3	38.61	19.07	2.72	38.47	98.87	39.05	19.29	2.75	38.91
52-2	7	37.12	17.63	2.76	36.62	94.13	39.43	18.73	2.93	38.91
52-3	18	37.9	19.03	2.98	38.02	97.93	38.7	19.43	3.04	38.86
52-4	30	37.22	20.27	3.00	38.16	98.75	37.67	20.53	3.04	38.74
58-f	15	33.7	17.7	4.44	34.7	90.54	37.22	19.55	4.90	38.33
59-f	15	36.9	18.2	4.80	37.31	97.2	37.96	18.72	4.94	38.38

Table 4-2. Results of De-Cu from Carbon Saturated Iron

Run No.	Initial Slag $\text{Na}_2\text{S}-\text{FeS}$ wt%	Final [Cu]t wt%	$100(1 - \frac{[\text{Cu}\%]_t}{[\text{Cu}\%]_o})$ %	Remarks
3	100 0	0.034	68.7	Cid=15mm
4	70 30	0.31	69.4	
5	70 30	0.31	69.1	
6	70 30	0.31	69.0	
9	70 30	0.307	69.4	
10	70 30	0.31	69.0	
12	100 0	0.30	70.4	Cid=25mm
13	100 0	0.259	74.2	
15	100 0	0.271	73.0	
17	70 30	0.361	64.0	Cid=25mm 1673K(1400°C)
20	50 50	0.315	68.6	
19	100 0	0.058	71.8	[Swt%] _o =0.19
23	70 30	0.316	68.5	Cid=25mm
24	70 30	0.333	66.8	
26	40 60	0.335	66.6	
30	70 30	0.283	71.8	
31	70 30	0.323	67.8	1573K(1300°C)
32	70 30	0.338	66.3	1623K(1350°C)
34	100 0	0.223	74.1	[Swt%] _o =0.2
35	100 0	0.232	73.0	[Swt%] _o =0.2
36	70 30	0.325	67.6	
37	70 30	0.268	72.5	
38	70 30	0.261	73.2	
39	70 30	0.275	72.0	
49	70 30	0.28	71.3	1473K(1200°C)

Table 4-2. (Continued)

Run No.	Initial Slag $\text{Na}_2\text{S}-\text{FeS}$ wt%	Final [Cu]t wt%	$100(1 - \frac{[\text{Cu}\%]_t}{[\text{Cu}\%]_o})$ %	Remarks
50	70 30	0.279	71.4	
51	70 30	0.293	68.9	
52	70 30	0.171	81.9	Ws/Wm=0.3
53	70 30	0.221	76.6	Ws/Wm=0.2
55	70 30	0.343	64.8	1g CaO Ws=4g
56	70 30	0.292	70.0	
57	70 30	0.304	68.8	
58	70 30	0.276	71.7	
59	70 30	0.299	69.3	
60	60 30	0.364	62.6	10%CaO
61	60 30	0.32	64.4	10%CaO [Swt%]o=0.427
62	60 30	0.33	66.1	10%CaS
63	60 30	0.361	62.9	10%FeO

Note: All runs were carried out under the conditions:

Initial metal charge Wm=20g; Ws/Wm=0.15;

T=1523K(1250°C) and no initial sulphur in the metal.

Inside diameter of the crucibles, Cid=20.6mm,

except where stated in Remarks column.

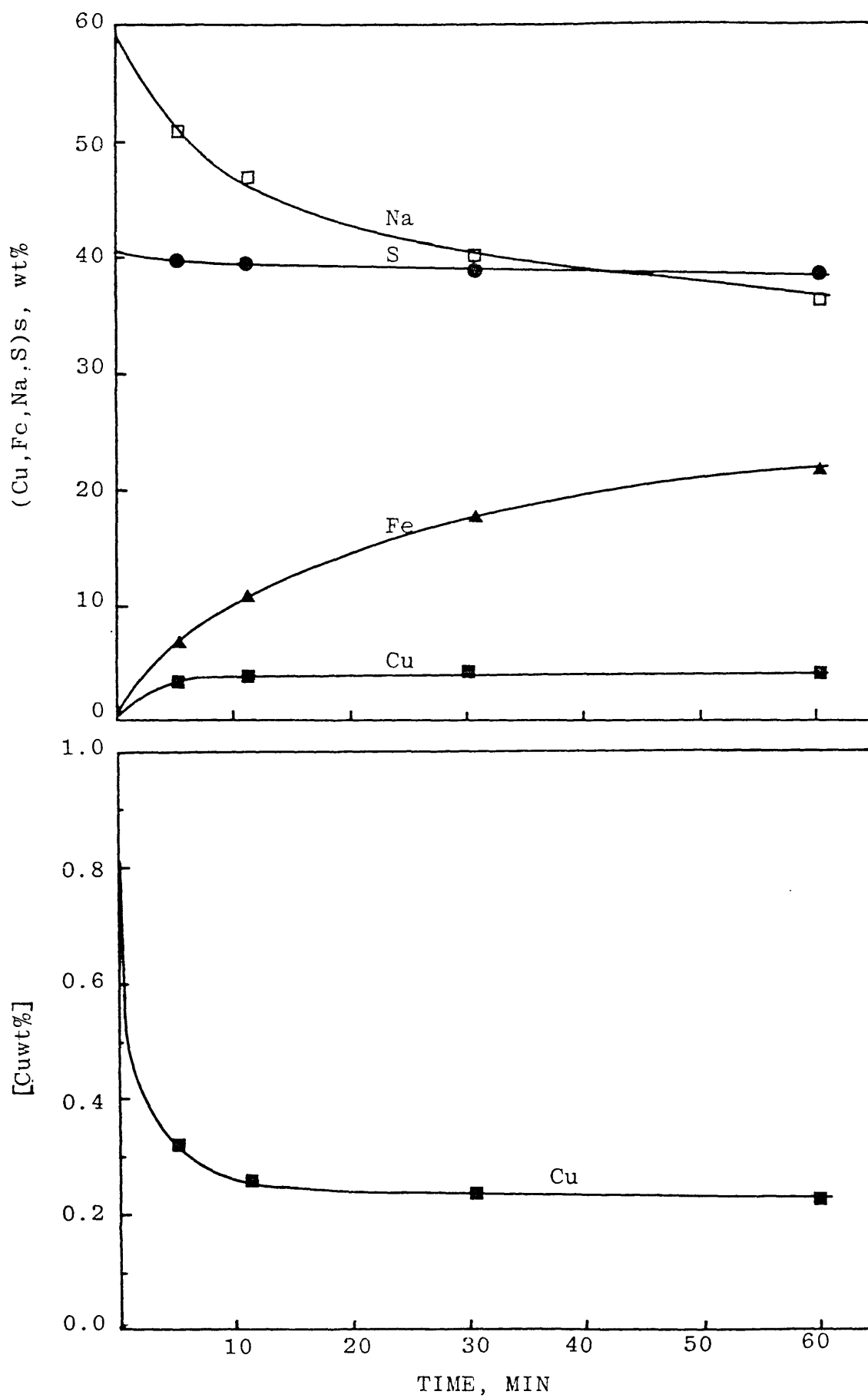


Fig.4.1 Changes of compositions of slag and metal in pure Na_2S slag (Run34)

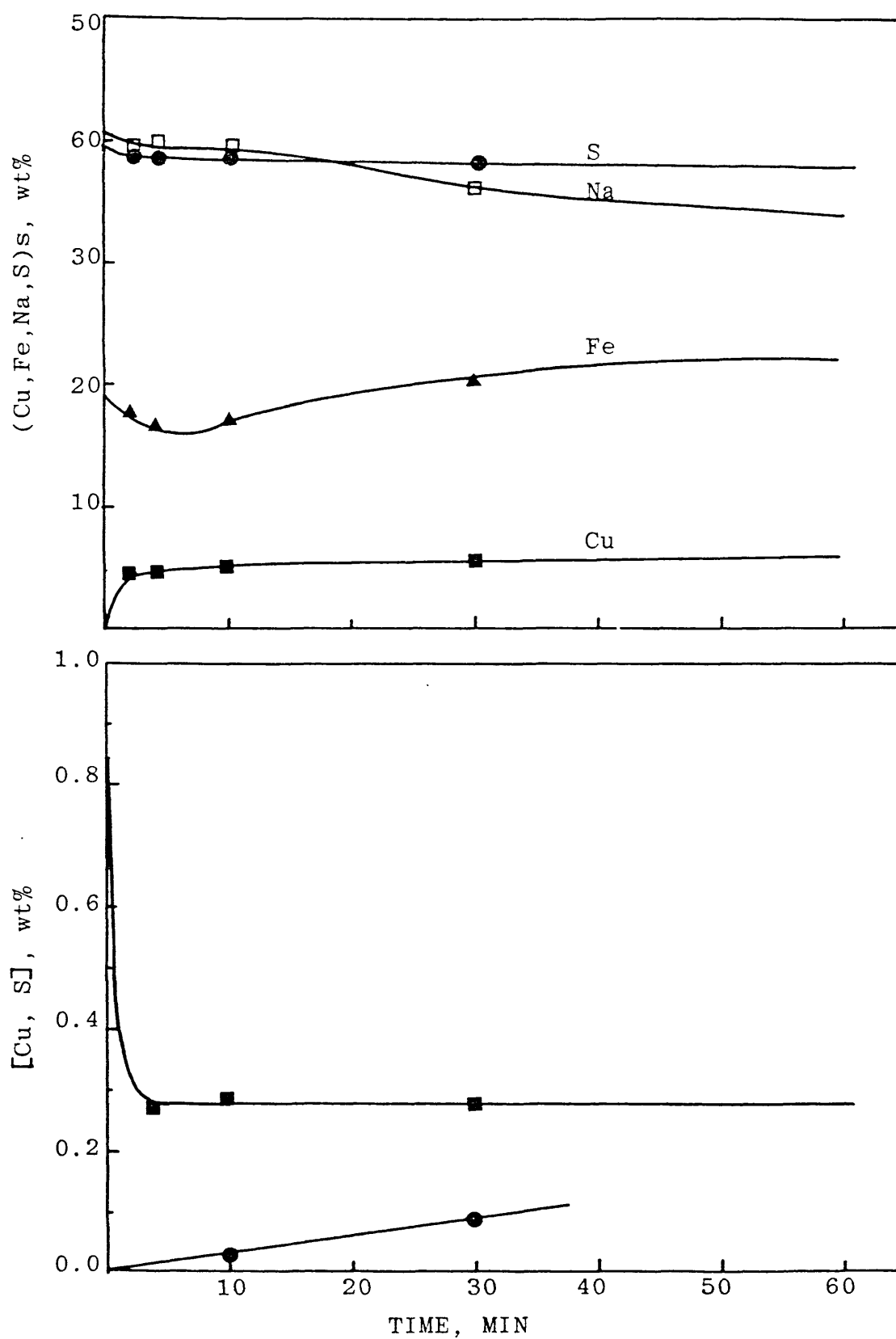
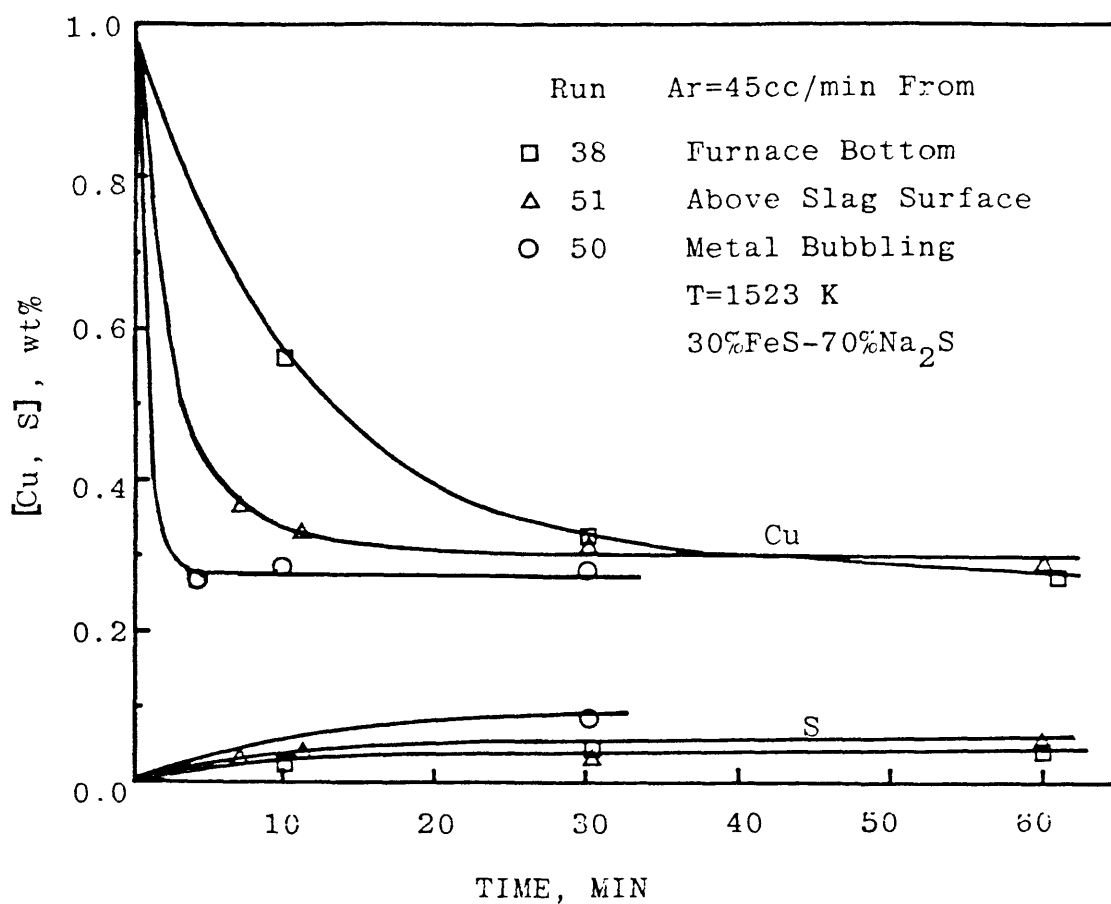
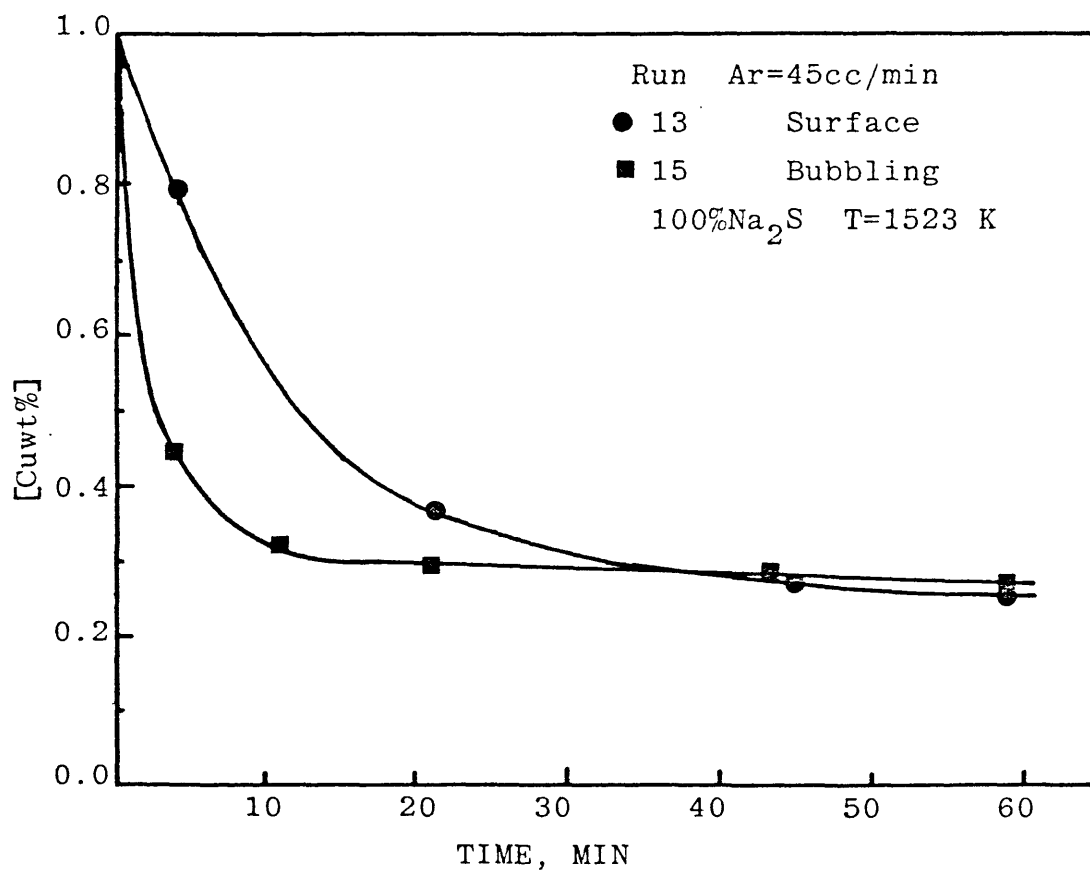


Fig.4.2 Changes of compositions of slag and metal in 30%FeS-70%Na₂S slag (Run50)

course of slag/metal reactions. The initial rate of loss of sodium was relatively high in pure Na_2S slag but decreased later, since, as the transfer of copper reached its quasi-equilibrium value, the driving force for the decomposition reaction of sodium sulphide was reduced. The remarkable differences of the transfer of iron and of sodium observed between runs carried out with pure sodium sulphide and with iron sulphide-containing slags will be discussed in section 5-1-3 on the effect of slag composition.

Run 38, shown in Fig.4.3, was carried out by introducing argon to the system from the bottom of the furnace. Thus there was no forced flow within the crucible and the diffusion of components in the gas, slag and metal could be important factors in the control of the processes. The introduction of argon from about 1.0-2.0 cm above the slag surface in Run 51 enhanced the transport of sodium vapour in the gas phase and components in the slag phase, so that the rate of decopperization was faster than that of Run 38. Argon bubbling into the metal phase caused the process to be completed within 5 minutes in 30wt%FeS-70wt% Na_2S slag by speeding up the mixing of components in the metal and slag phases. Fig.4.4 shows similar effects of the mode of argon introduction with pure Na_2S slag.

Three experiments were carried out using different argon flowrates under conditions of bubbling into the metal phase as shown in Fig.4.5. No large differences were observed when the flowrate was increased from 30 to 105cc/min. The change of the flowrate is not as important as the change of the mode of argon introduction to the decopperization process. However, as shown in Fig.4.6, the

Fig.4.3 Effect of argon introduction mode in FeS-Na₂SFig.4.4 Effect of argon introduction mode in pure Na₂S

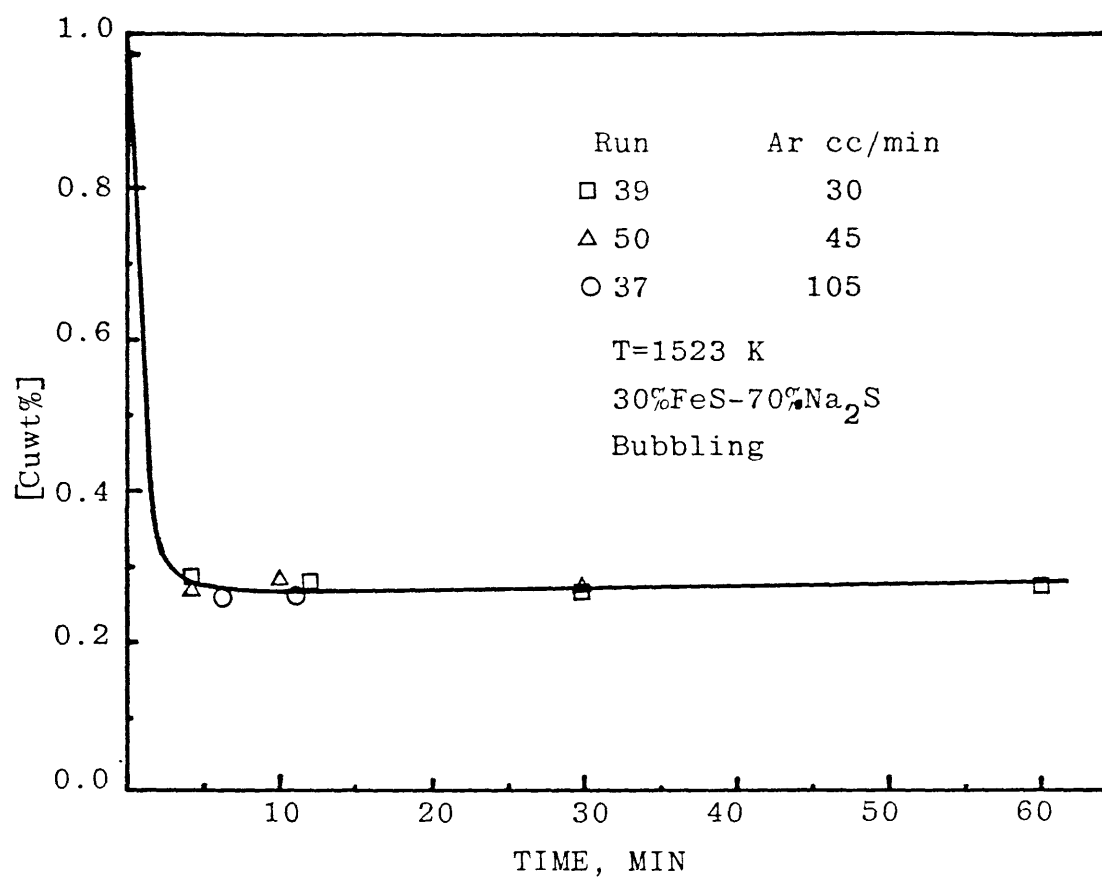


Fig.4.5 Effect of argon flowrate

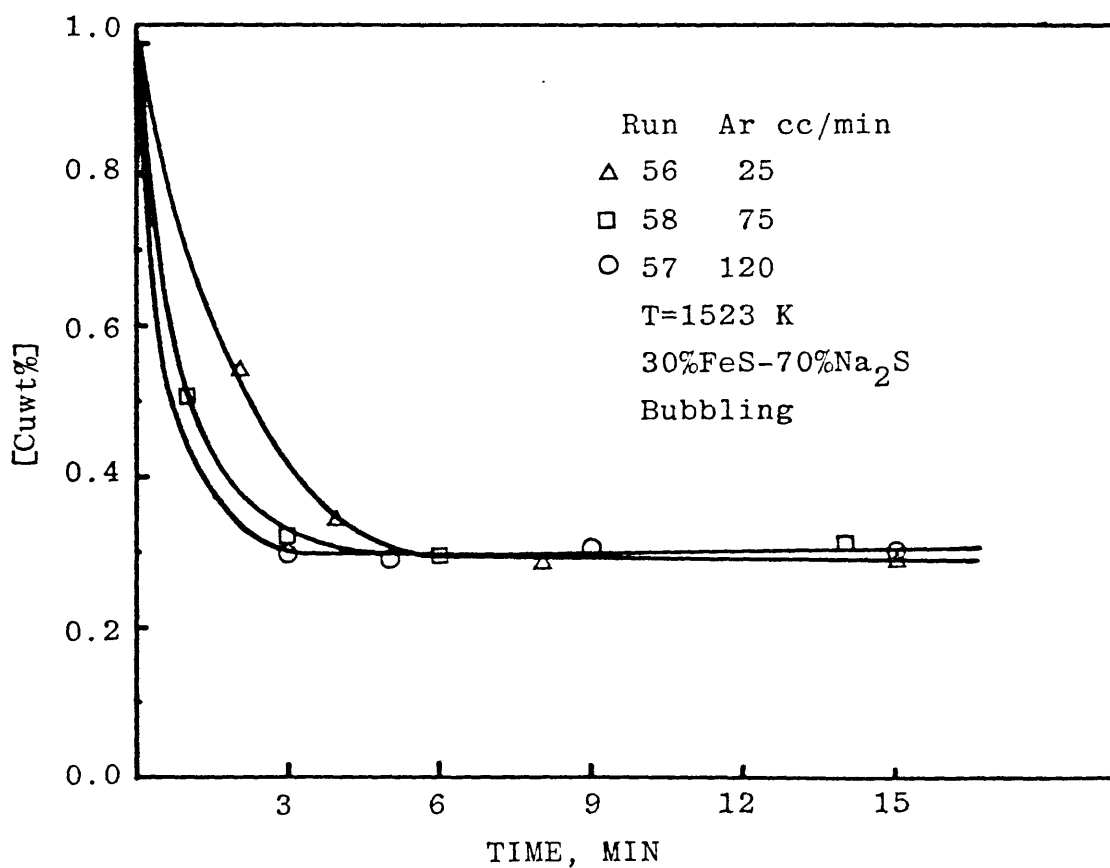


Fig.4.6 Effect of argon flowrate

argon flowrate did affect the rate of copper transfer when considering the early stages of the reaction, that is, during the first four minutes.

Tests in which the initial copper contents were varied, at 1.003, 0.86, 0.206 and 0.108wt% in carbon saturated iron were carried out under conditions of pure Na_2S slag, 1523K (1250°C) and argon bubbling. The results given in Fig.4.7 show generally similar kinetic curves for different initial copper contents.

The proportional and absolute copper reacted, the latter defined as $([\text{Cu}]_0 - [\text{Cu}]_t)W_m/M_{\text{Cu}}$, where W_m is the weight of metal phase and M_{Cu} the atomic weight of copper, are plotted against time in Fig.4.8 to test the effect of the initial copper contents on the rate of reaction.

Initial sulphur contents in Runs 19 and 34 were about 0.2wt% and near zero in Run 15. As shown in Fig.4.8, there is no obvious effect of initial sulphur content on the change of copper content. A slag of 60% Na_2S -30% FeS -10% CaO was used for two experiments with different initial metal sulphur contents as shown in Fig.4.9, 0.427wt% initial sulphur rapidly decreased to less than 0.1wt%, but this did not affect (or slightly accelerated) the transfer of copper in terms of the proportion reacted compared with runs with small initial sulphur contents.

The effect of initial iron sulphide in the slag on the copper removal is shown in Fig.4.10. The curve for 30wt% FeS -70wt% Na_2S is an average of two runs and pure Na_2S of three runs, 50 and 60wt% FeS are represented by one curve in terms of the proportion of reacted copper. 30wt% FeS speeded up the reaction and a similar (or somewhat lower)

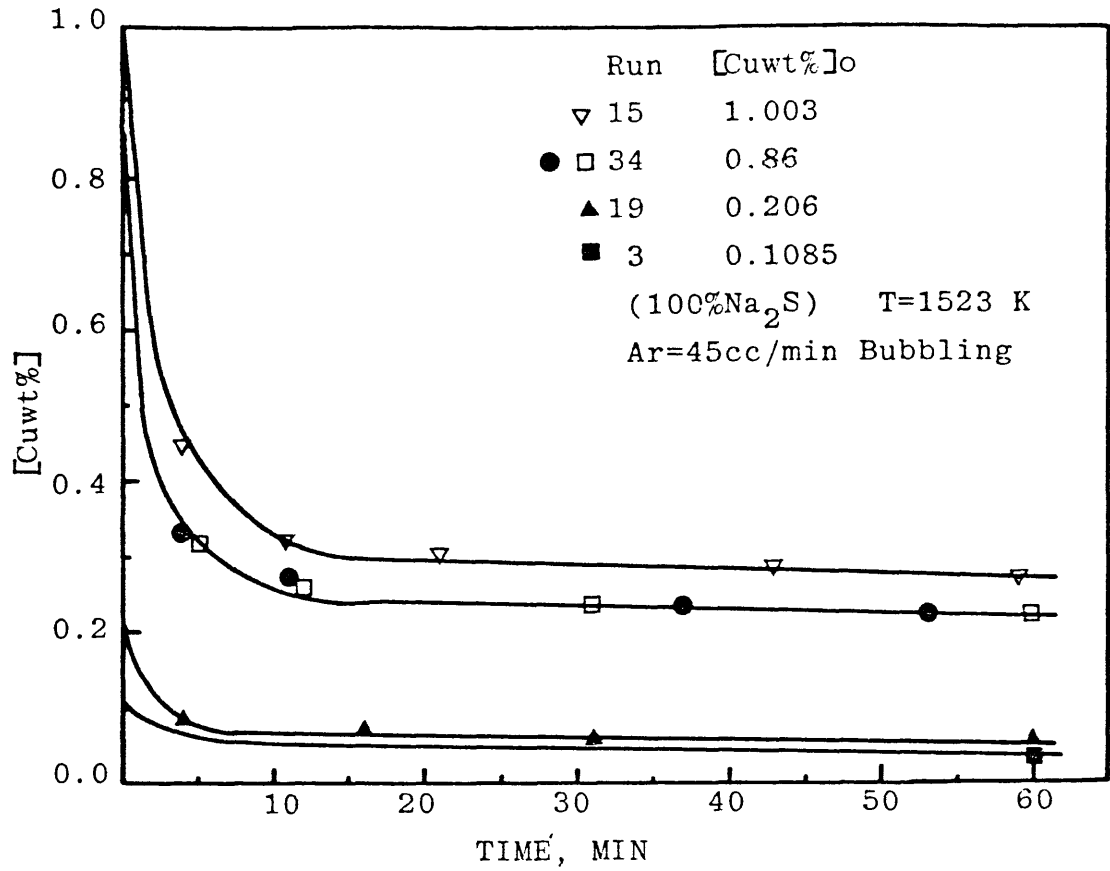


Fig.4.7 Effect of initial copper content in the metal

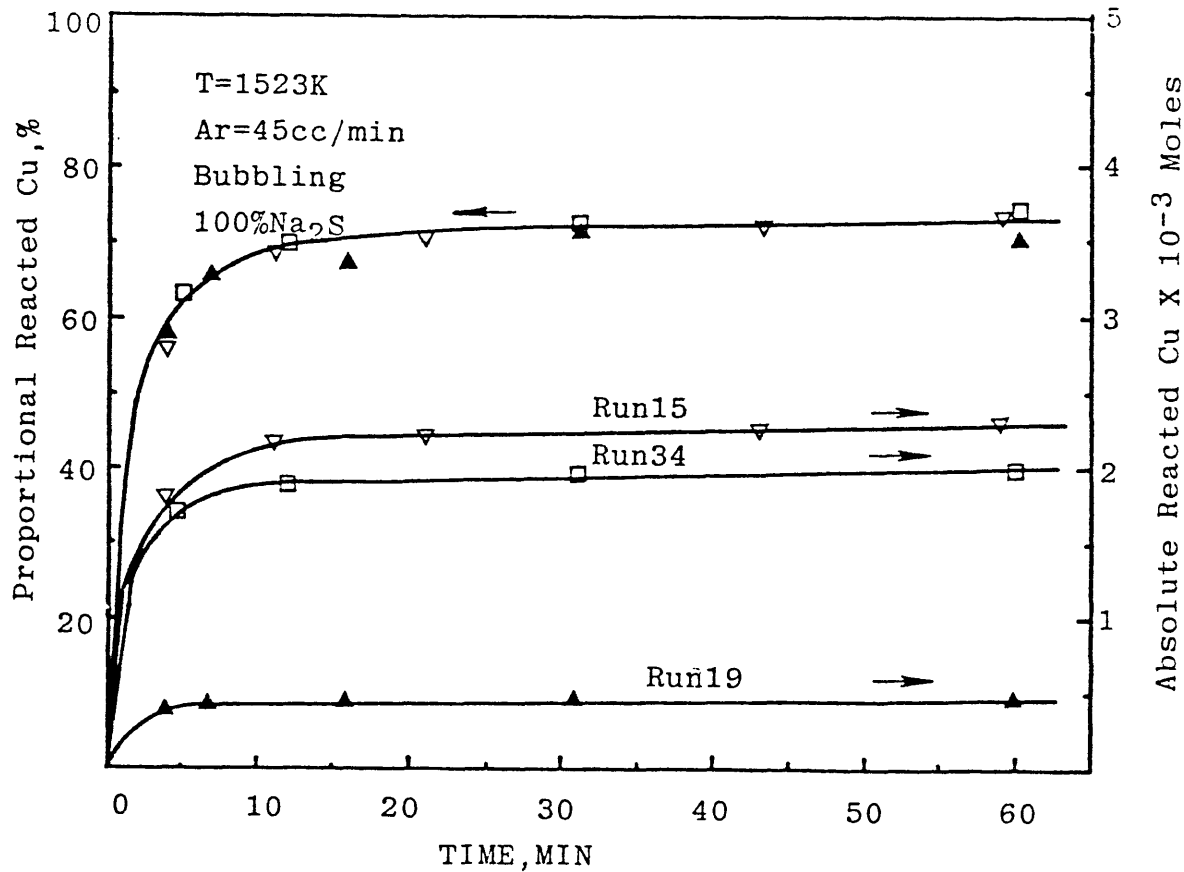


Fig.4.8 Effect of initial copper content in the metal

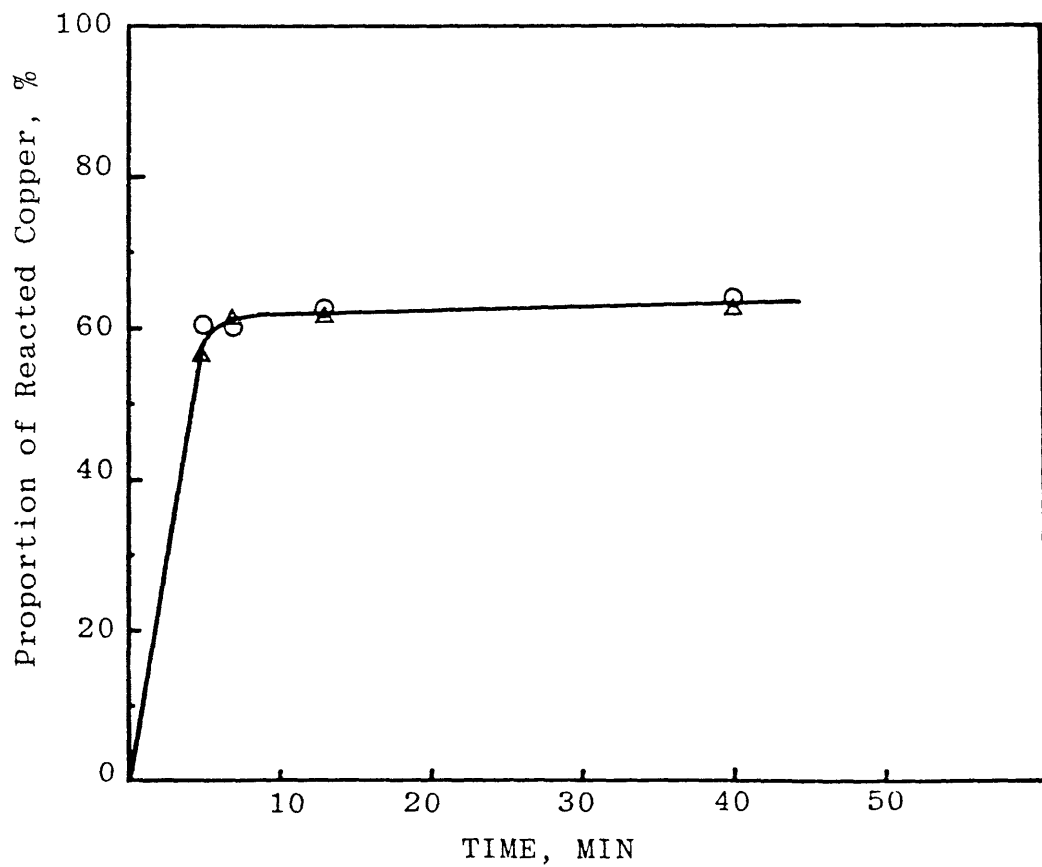
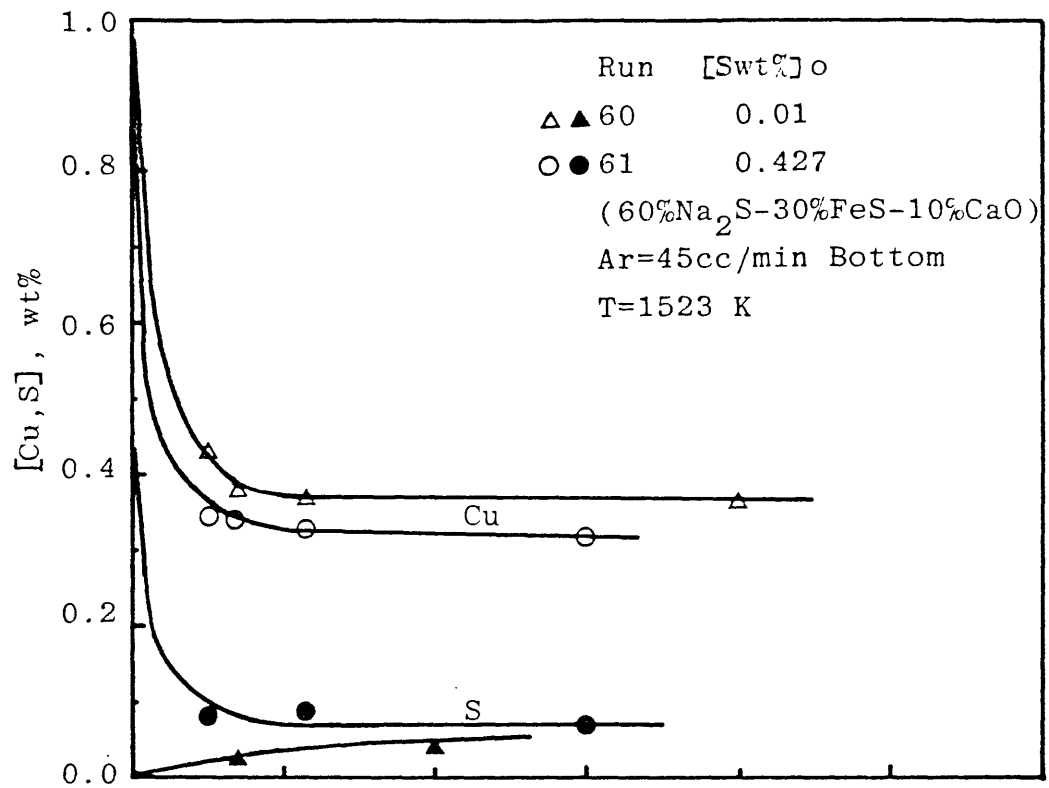


Fig.4.9 Effect of initial sulphur content in the metal

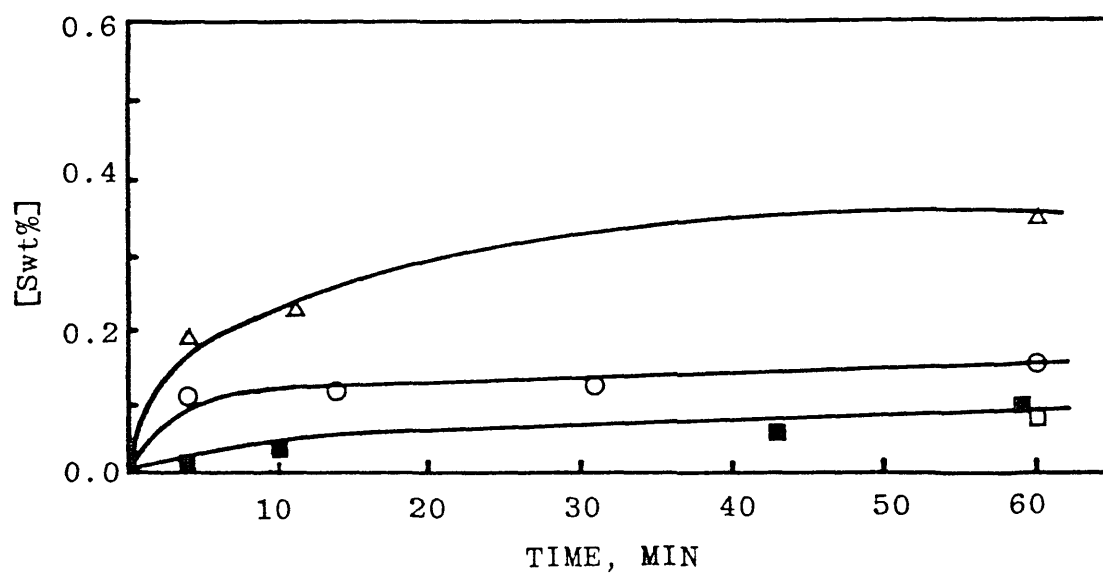
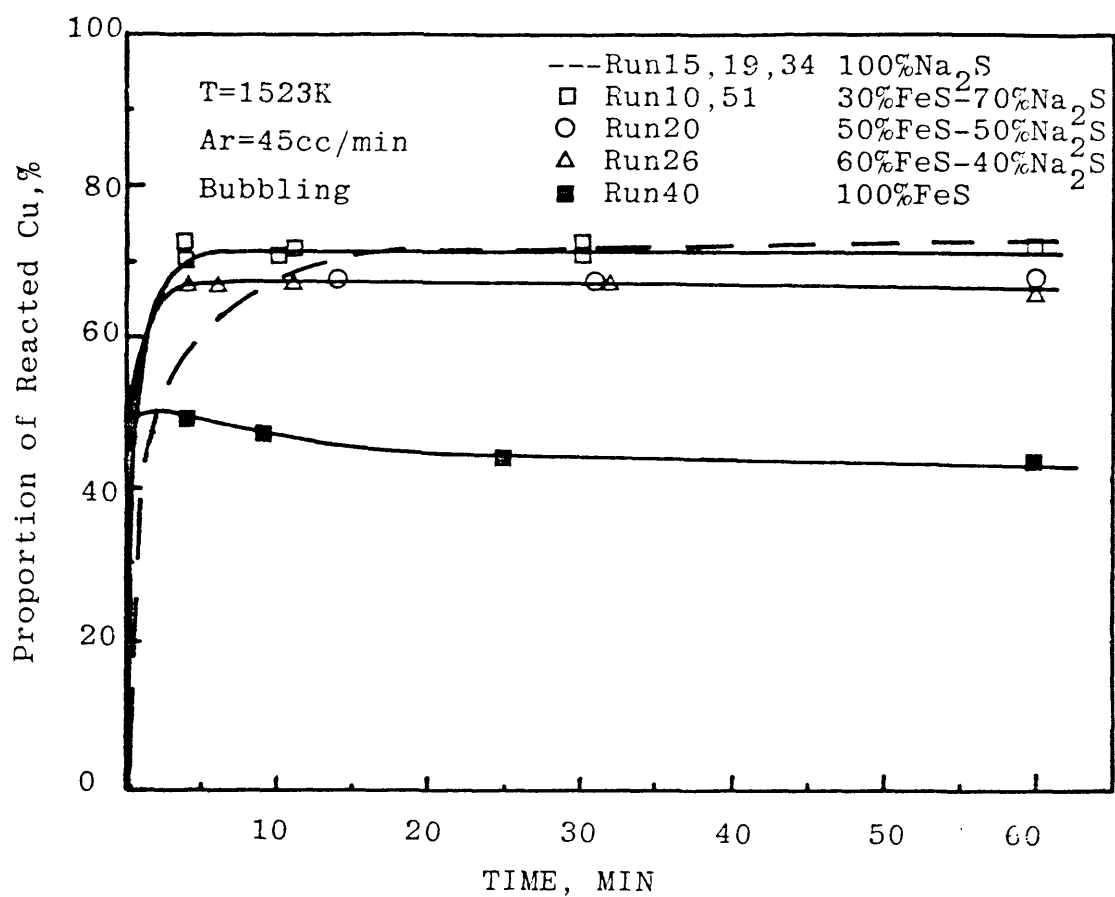


Fig.4.10 Effect of initial FeS in the slag

final result for proportional reacted copper was obtained compared with the values for pure Na_2S . The refining efficiency was decreased significantly with 50 and 60wt%FeS slags. There was no obvious difference in the sulphur contents in the metal between 30wt%FeS-70wt% Na_2S slag and pure Na_2S slag, but the sulphur content of the metal was quite high when the initial slag contained 50 and 60wt%FeS.

If 1 gram CaO was added to 3 grams of the 30%FeS-70% Na_2S initial slag, the reaction of copper was accelerated even under conditions of poor slag/metal agitation. As shown in Fig.4.11, the copper was about 65% removed after 5-10 minutes when the sulphur pick-up by the metal was only 0.013wt%.

Runs 50, 53 and 52 were carried out at the weight ratio of slag to metal equal to 0.15, 0.2 and 0.3 respectively. Comparing Run 50 with 53, Fig.4.12, the proportion of removed copper increases from 71.4% to 76.6% when the ratio is changed from 0.15 to 0.2; a similar increase from 76.6% to 81.9% is obtained as the ratio is changed from 0.2 to 0.3.

It is necessary to study the effect of temperature on the rate of decopperization to assist in the determination of the controlling step of the process. Temperatures were varied between 1473 and 1623K other factors being kept constant. This series of experiments was carried out using 30wt%FeS-70wt% Na_2S slag.

The rate of decopperization was increased when the operating temperature was raised from 1473 to 1523K, but as shown in Fig.4.13, there was only a slight difference in the rate between 1523 and 1623K, the final contents of copper

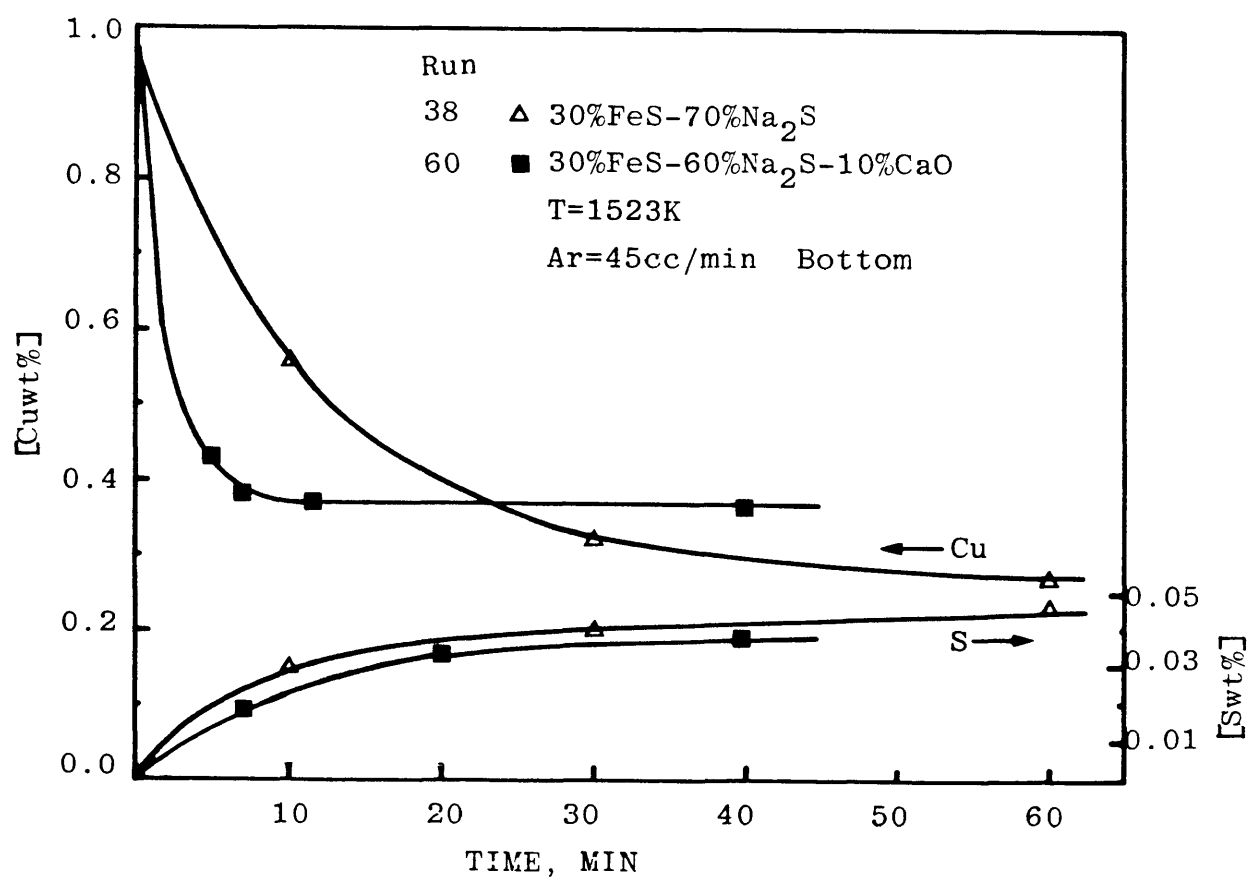
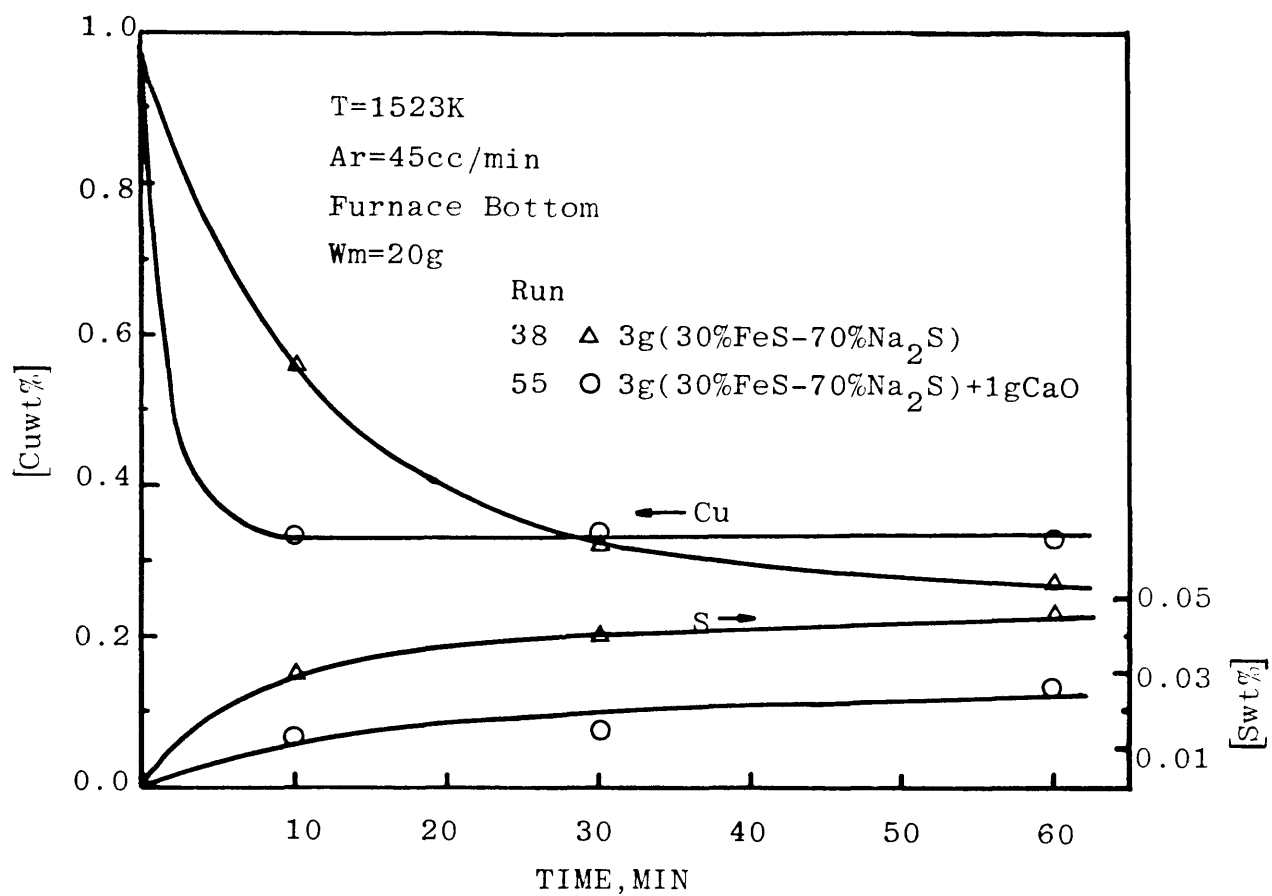
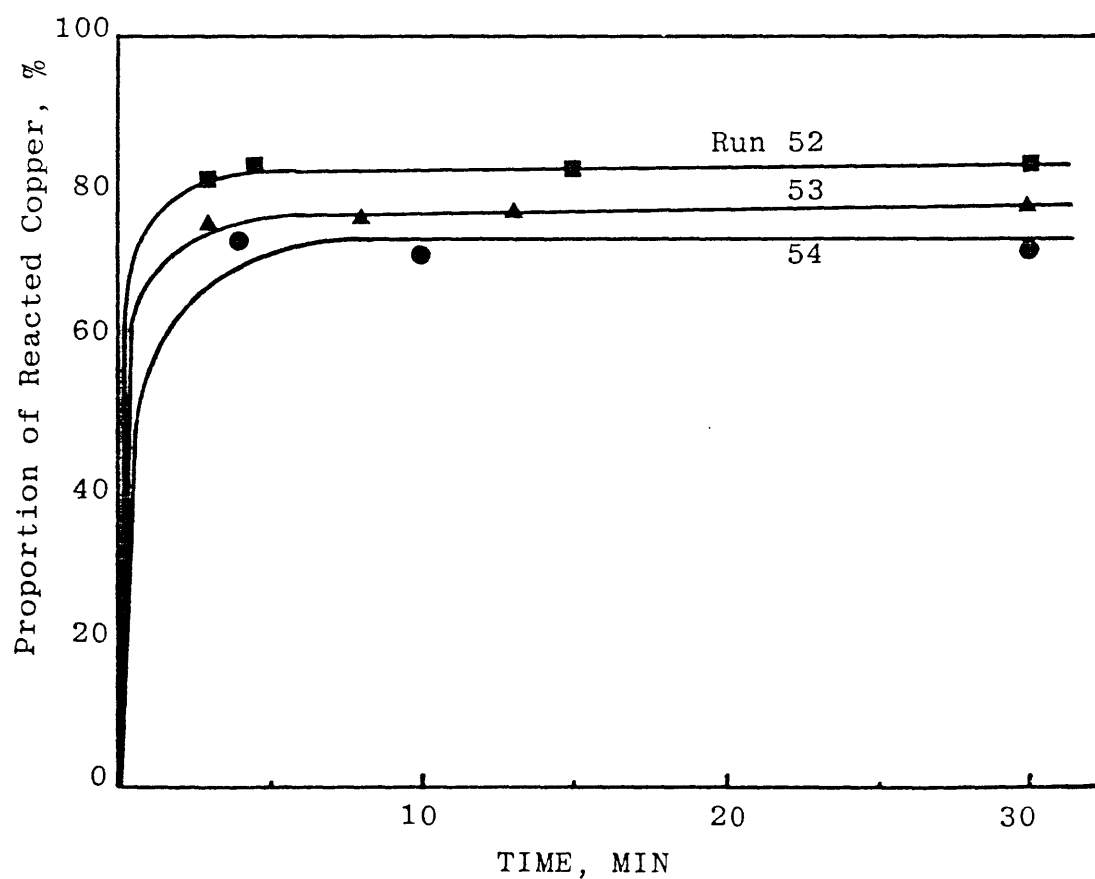
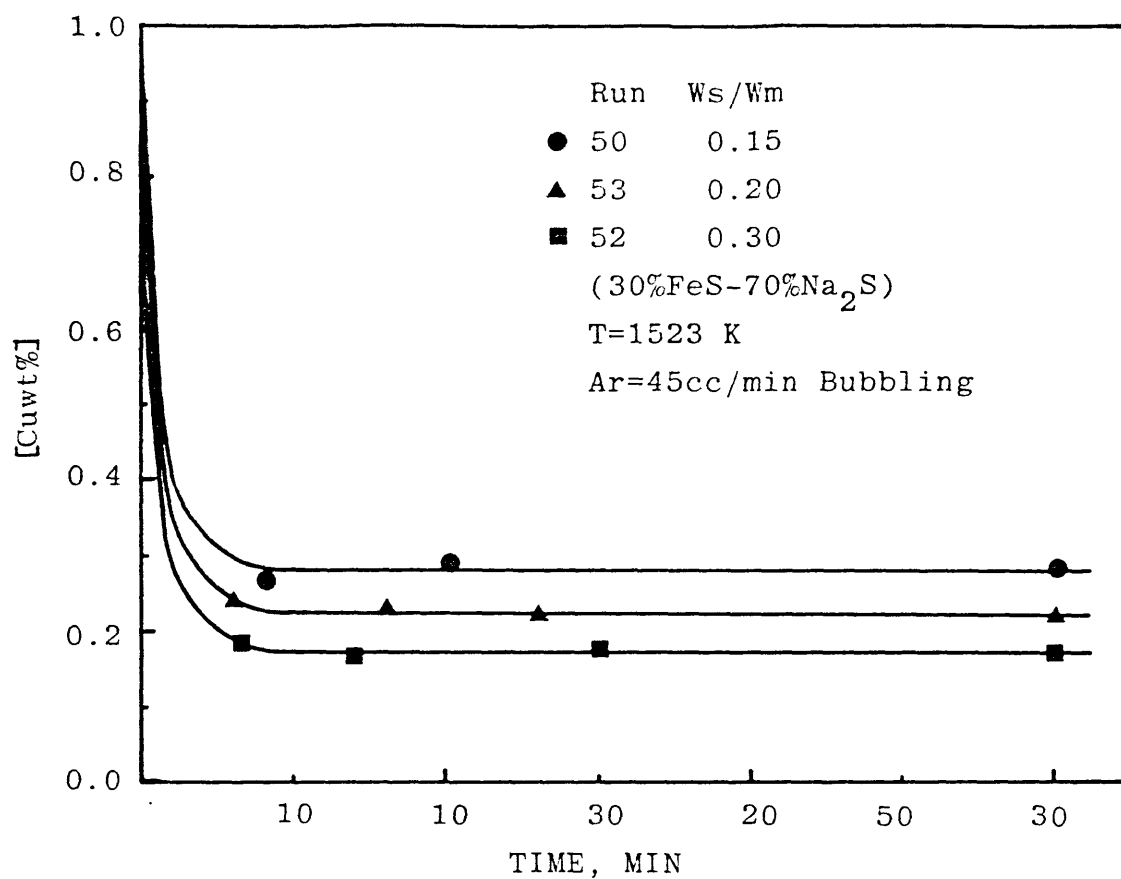


Fig.4.11 Effect of initial CaO in the slag

Fig.4.12 Effect of the W_s/W_m Ratio

and sulphur, however, were definitely higher at a higher temperature.

Run 17 was carried out at 1673K argon being introduced from the bottom of the furnace. From Fig.4.14, the final contents of both Cu and S in the metal are shown to be higher than that at 1623K.

There was no obvious change of the reaction path when the diameter of the crucible was increased from 20.6 mm to 25 mm, that is, the interfacial areas of slag/metal and gas/slag are enlarged 1.47 times, as is shown in Fig.4.15 for argon purge from the bottom of the furnace and Fig.4.16 for argon introduced from 1-2 cm above slag surface. This indicates that the area of the reaction site is not an important factor in the reaction of copper removal by a mixture of FeS- Na_2S .

4-1-3. Decopperization from molten steel

Experiments were carried out at 1873K (1600°C) using alumina crucibles. The initial master alloy usually contained 0.48wt% C, 0.97wt%Cu. The reaction was extremely fast at this temperature. No difference in the reaction rates was noticed when comparing the introduction of argon from the bottom of the furnace with bubbling into the molten metal; the transfer of copper into slag finished within 3 minutes. The variables studied were therefore, the effects of the compositions of slag and metal.

The results of the removal of copper from molten steel are not as satisfactory as those from carbon saturated iron. As shown in Table 4-3, the proportional reacted copper was

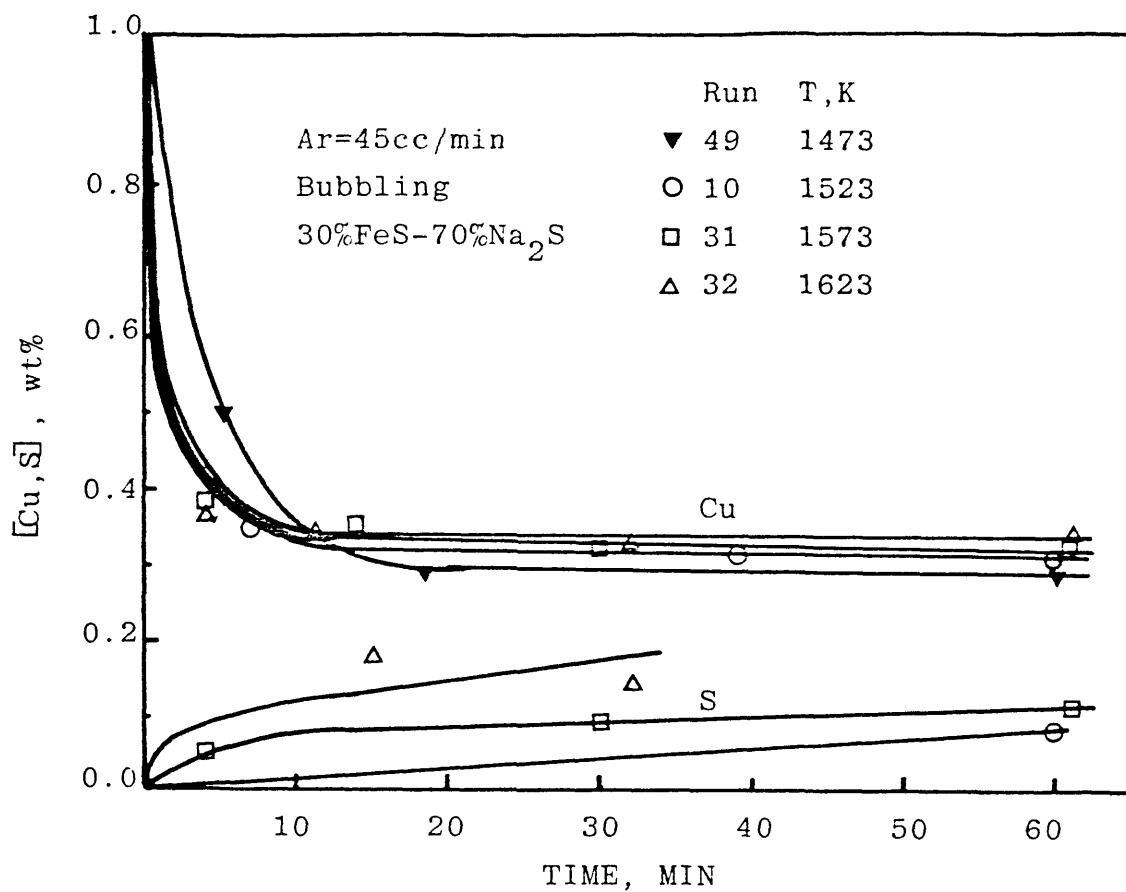


Fig.4.13 Effect of Operating Temperature

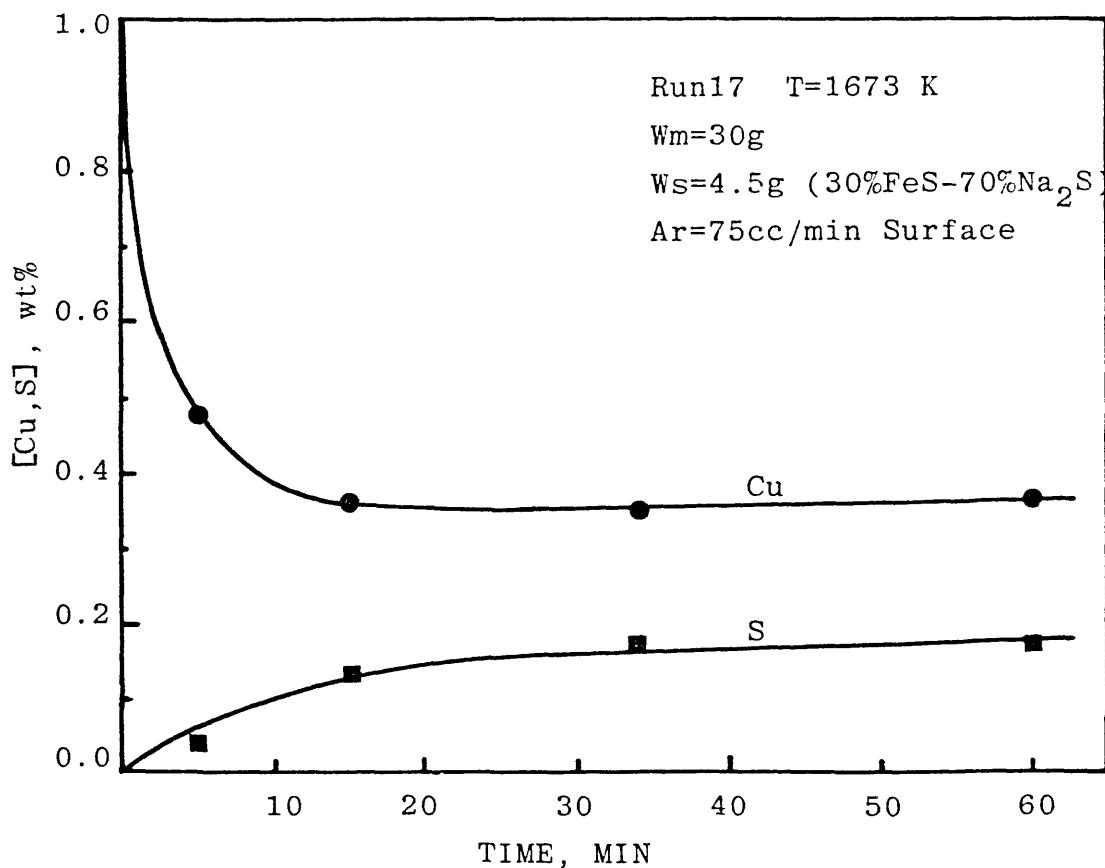


Fig.4.14 Composition changes of metal phase in Run17

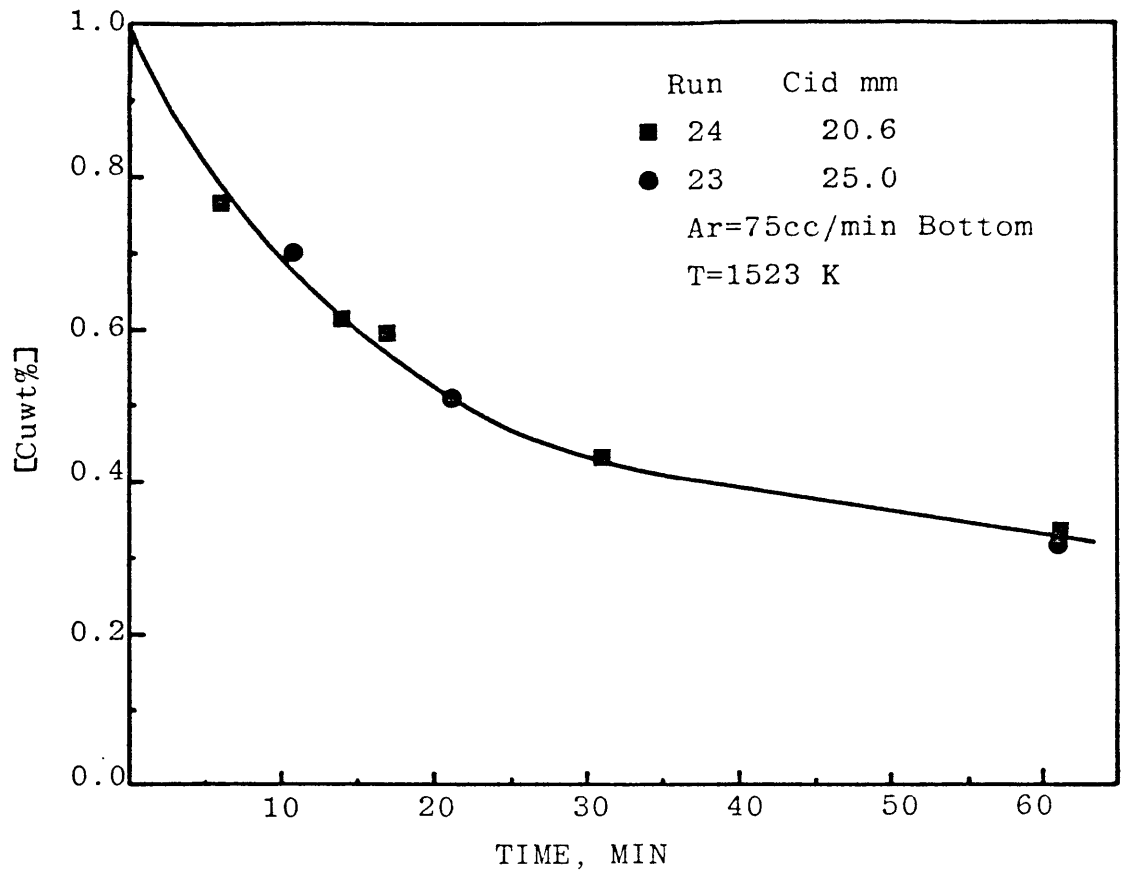


Fig.4.15 Effect of the size of crucible

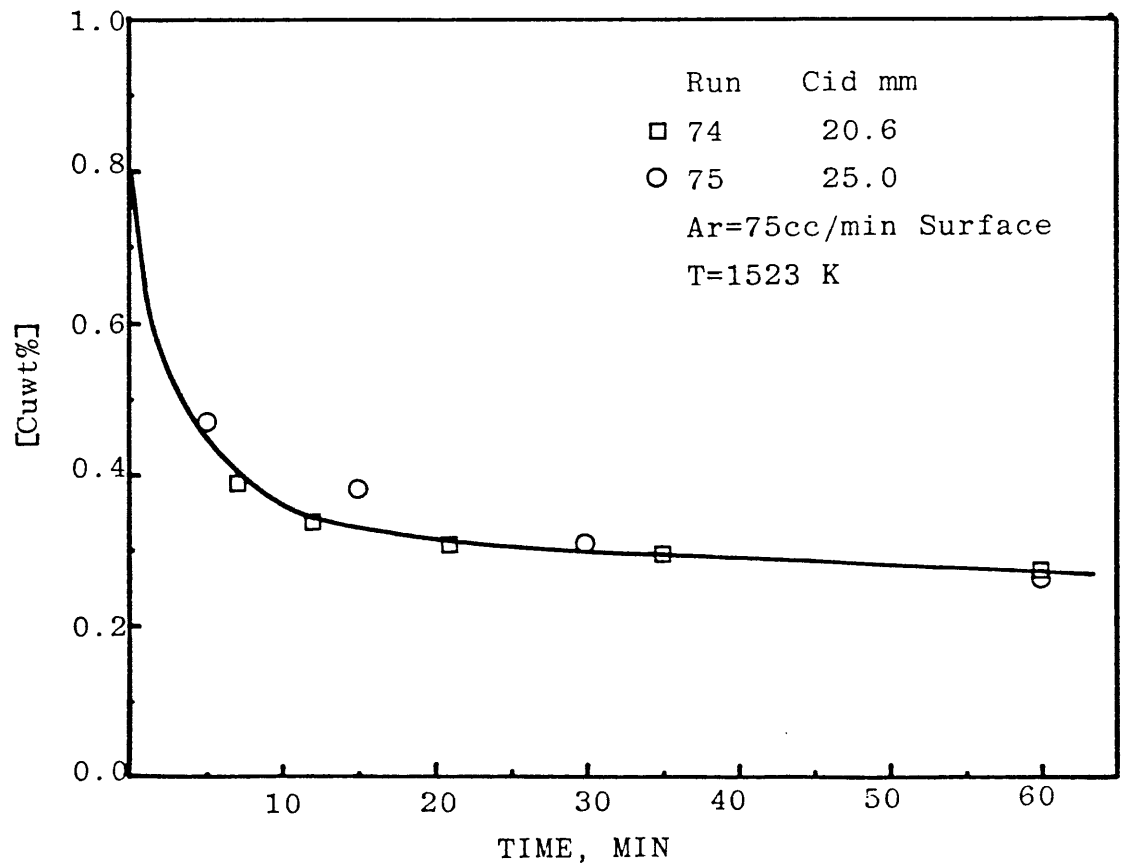


Fig.4.16 Effect of the size of crucible

Table 4-3

The proportion of reacted
copper using different slag compositions

Run No.	Slag Composition wt%	$100(1 - \frac{[Cu\%]_t}{[Cu\%]_o})\%$	Remark
St3	50FeS-50CaS	<5	[Cwt%]=4.3
St4	30CaS-70CaF ₂	<2	
St6	40MgS-40FeS-20Na ₂ S	26	
St7	30CaS-30FeS-40Na ₂ S	25	
St8	40MgS-40FeS-20Na ₂ S	55	
St9	30FeS-70Na ₂ S	35	
St10	30CaO-30FeS-40Na ₂ S	22	
St11	40MgO-40FeS-20Na ₂ S	18	
St12	30CaO-30FeS-40Na ₂ S	25	
St13	40MgO-40FeS-20Na ₂ S	17	
St14	23CaO-37FeS-40Na ₂ S	25	[Swt%]=0.6-0.7
St15	50CaS-50Na ₂ S	28	
St17	37FeS-23CaO-40Na ₂ S	21	

usually lower than 30% and maximum removal of 35% was achieved in 30%FeS-70%Na₂S.

Noticeable reverse transfer of copper occurred in most of the experiments. The amount of slag left in the crucible was found to be less than that in experiments carried out at 1523K (1250°C).

Various slag compositions, consisting mainly of Na₂S, FeS, CaS, CaO, MgS and MgO were tested for the removal of copper from molten steel. The final sulphur content in the metal usually reached about 0.5wt% when the initial FeS in the slag was more than 30wt%.

The results of four typical slag compositions are given in Fig.4.17. 30%FeS-70%Na₂S obtained better decopperization than the other compositions.

Fig.4.18 shows that the removal of copper was about one third less efficient when MgS in slag was replaced by MgO, but the difference between CaS and CaO was rather small as shown in Fig.4.19. The compositions of 40%MgS-40%FeS-20%Na₂S in Run St6 and 30%CaS-30%FeS-40%Na₂S in St7 achieved a similar result as shown in Fig.4.17. However, in both the CaS and the MgS cases, when these were replaced by their oxides, the slag containing CaO showed a greater capacity for removing copper than that of MgO, Fig.4.20.

The effect of initial carbon content of the metal on the process is shown in Fig.4.21 and 4.22, the higher carbon contents clearly promoting a better removal of copper. A set of experiments was carried out to obtain useful data to calculate the interaction coefficient of carbon to copper. Both slag and metal samples were analysed after refining for about 7 minutes and the results are listed in Table 4-4.

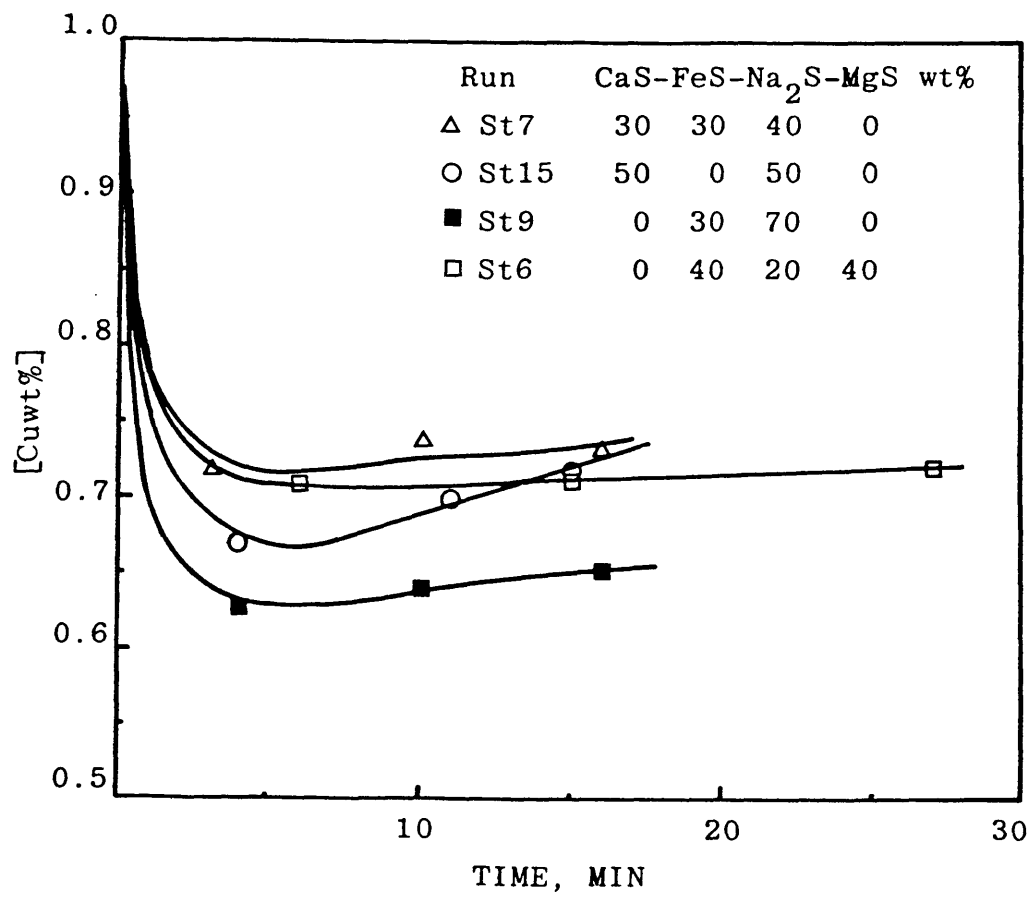


Fig.4.17 Effect of the slag composition

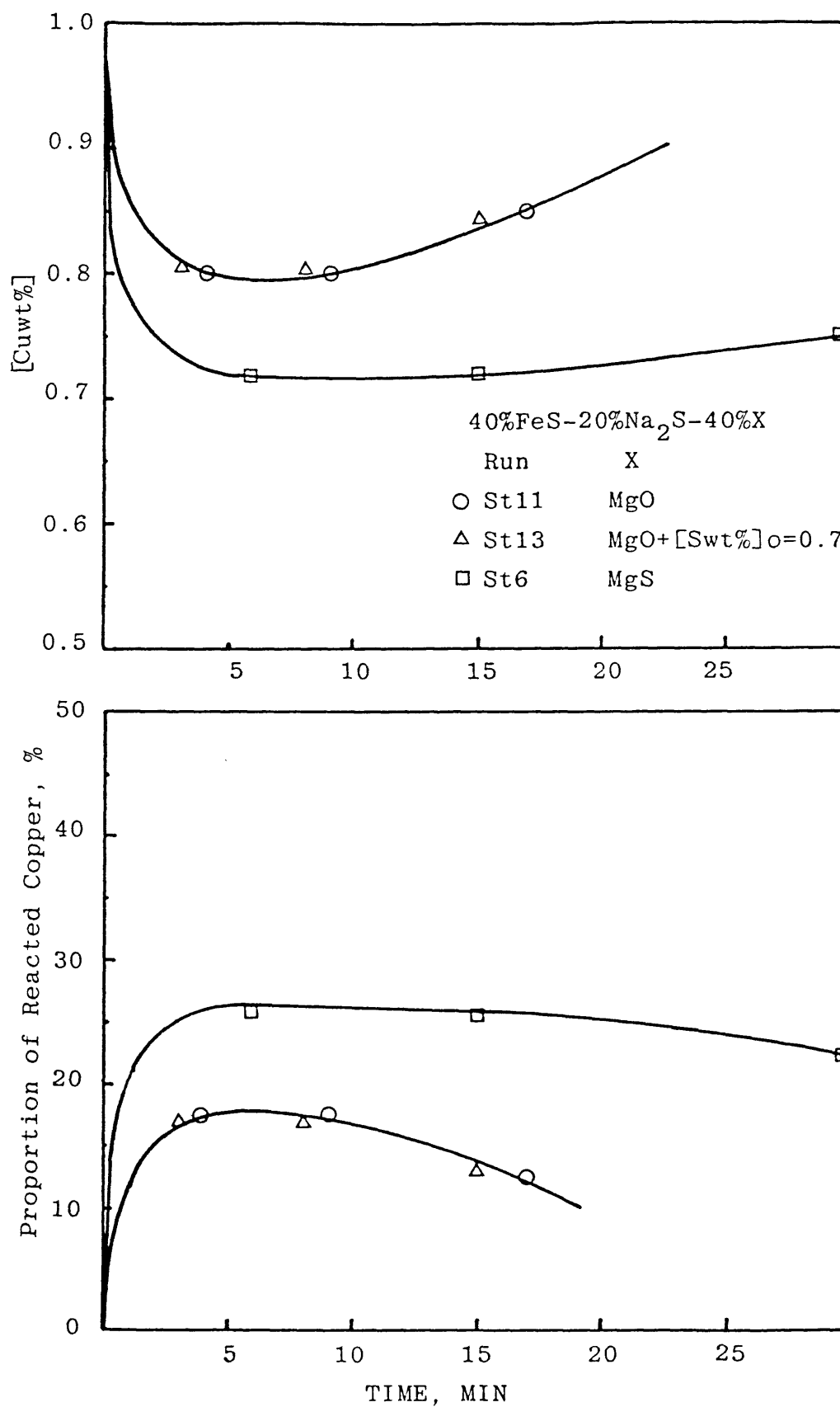


Fig.4.18 Difference between MgS and MgO

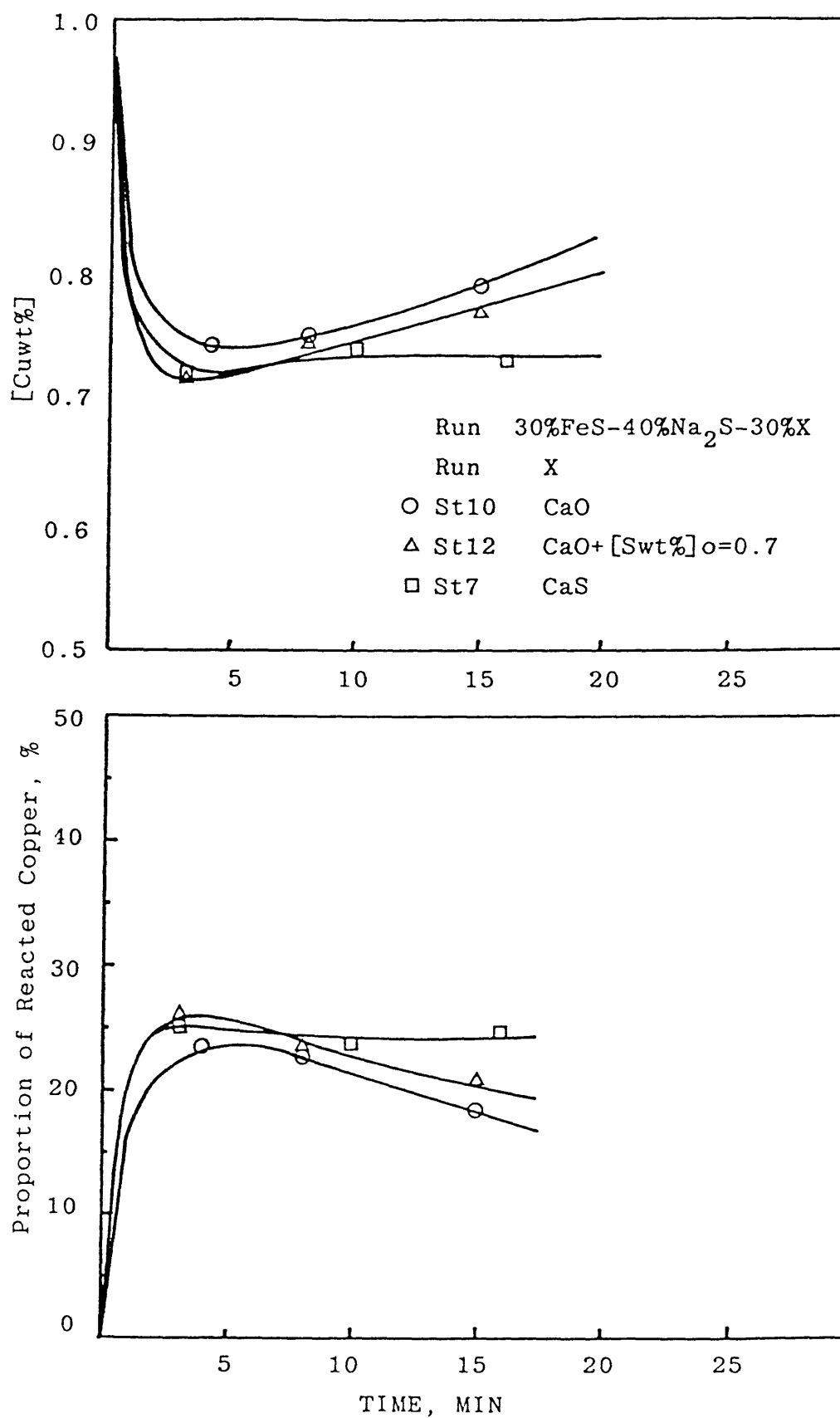


Fig.4.19 Difference between CaS and CaO

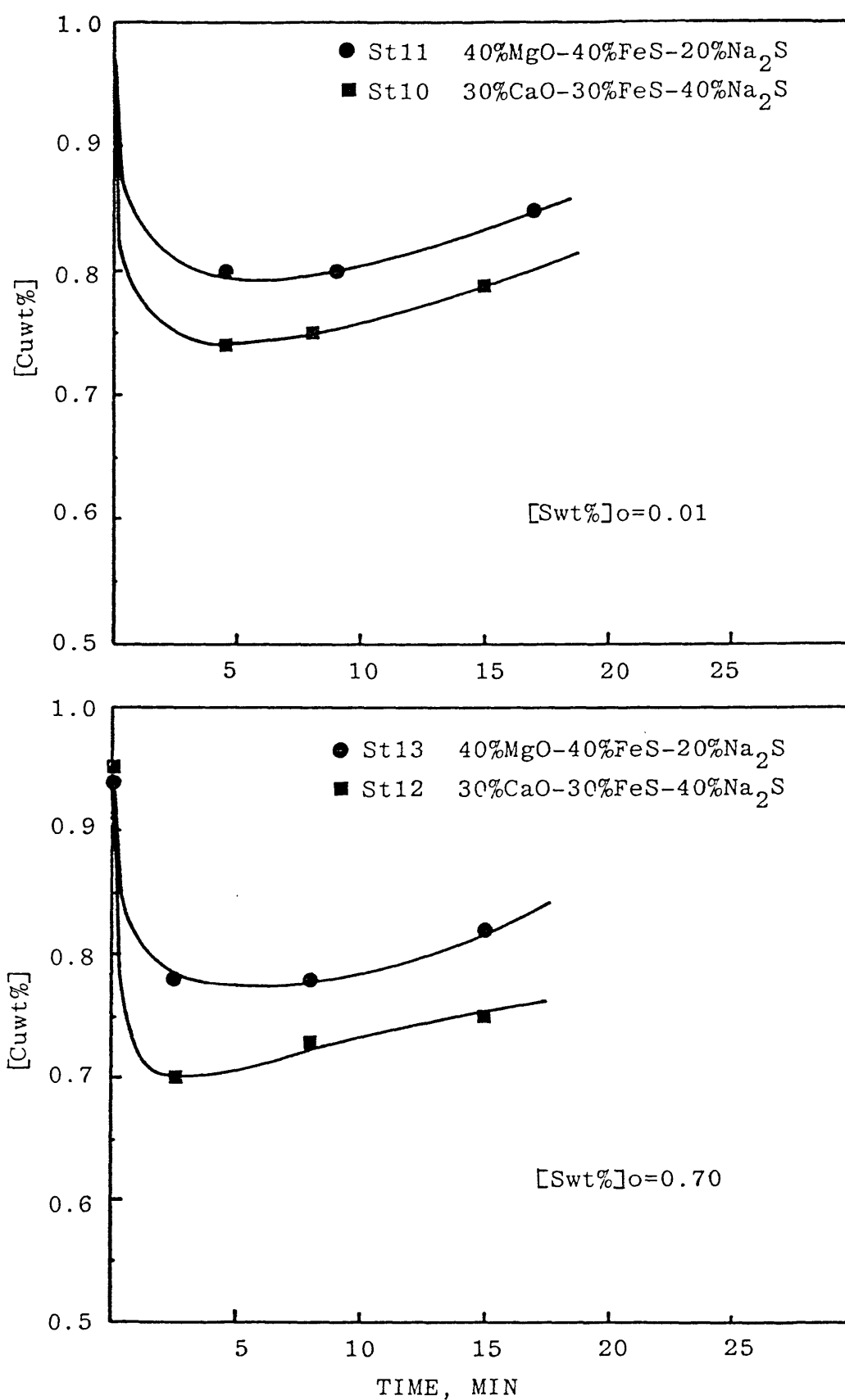


Fig.4.20 Difference between CaO and MgO

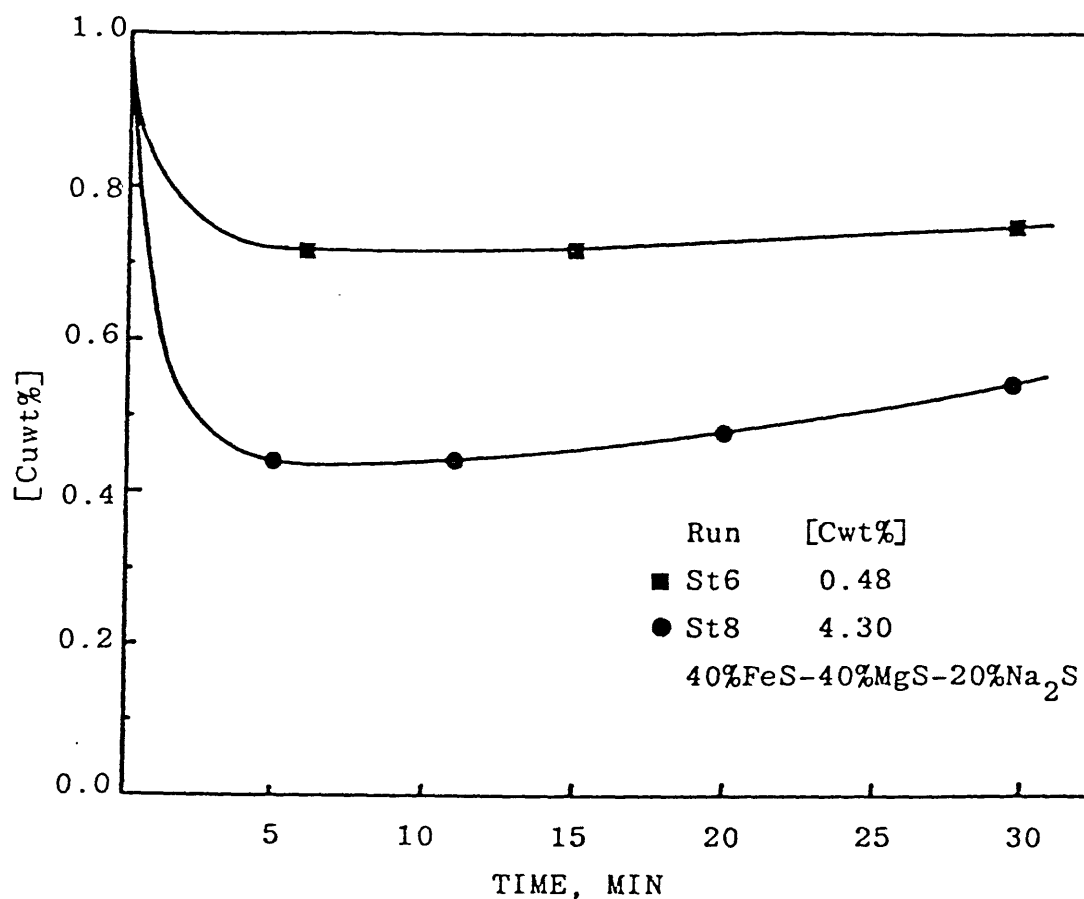


Fig.4.21 Effect of carbon content in iron

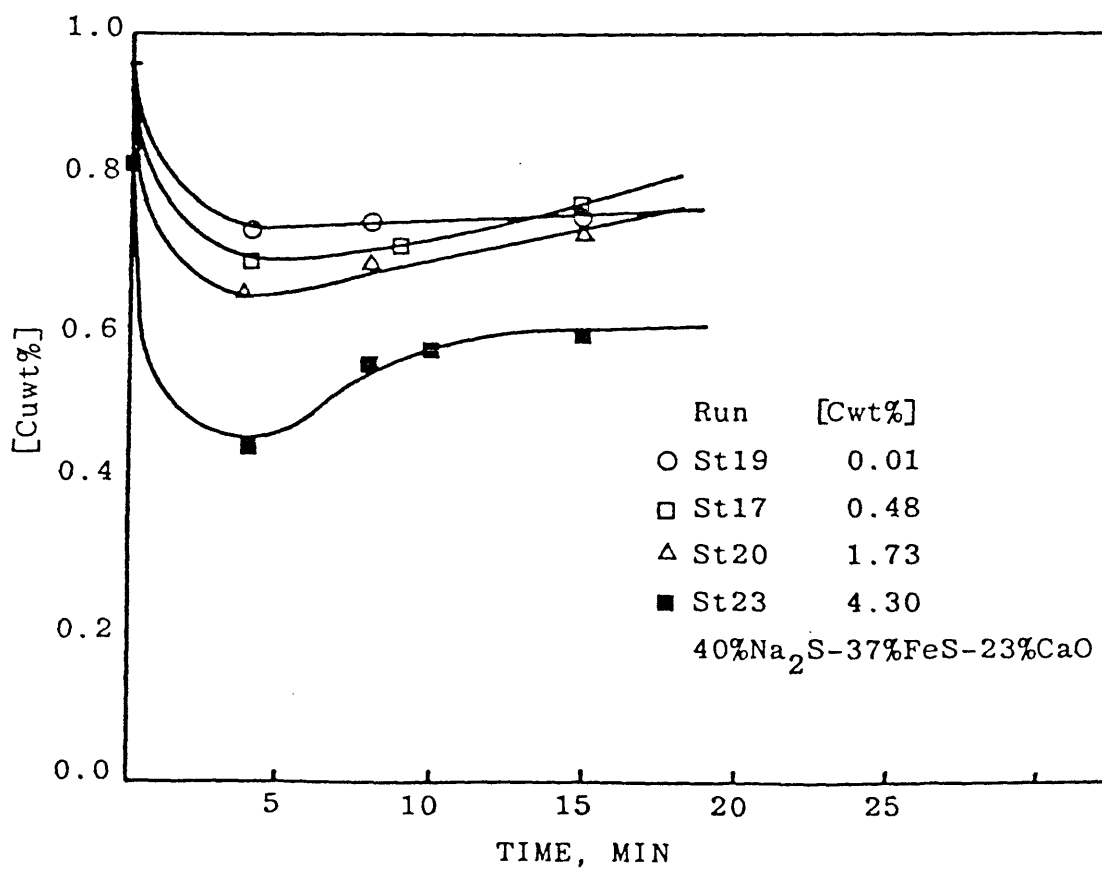


Fig.4.22 Effect of carbon content in iron

Table 4-4

Results of the effect
of initial carbon content

Part A. Metal Phase

Run No.	[Cwt%]o	[Cuwt%]t	[Swt%]t
St27	<0.01	0.639	0.636
St28	0.36	0.583	0.512
St30	1.59	0.515	0.479
St31	3.77	0.396	0.165

Part B. Slag Phase

Run	Cuwt%	Fewt%	Nawt%	Swt%	X_{Cu_2S}	X_{FeS}	X_{Na_2S}
St27	2.65	30.87	28.27	38.09	0.0175	0.4644	0.5182
St28	2.82	27.62	28.27	38.42	0.0185	0.4115	0.5700
St30	3.32	28.32	30.38	37.98	0.0219	0.4249	0.5533
St31	4.10	27.10	30.61	38.19	0.0273	0.4099	0.5628

Part C. Experimental conditions

[Cuwt%]o = 0.98 ; 30wt%FeS-70wt%Na₂S

T = 1873K (1600°C)

Ar = 50cc/min Surface

4-2. DETINNING

No reports of the successful removal of tin from iron or steel by sulphide slags have been found. Preliminary investigations were carried out on the removal of tin from carbon saturated iron by a slag mixture of sodium and iron sulphides with no gas stirring of the liquids. Little removal of tin took place over a period of one hour, but about 98% of the initial tin was removed when the experiments were extended to 60 hours, indicating that detinning by a sulphide slag would be theoretically possible but very slow under these conditions.

Experiments were carried out under conditions of different initial sulphur contents in the metal and, later on, slag additions were discontinued since it was found that tin transferred from the metal did not remain in the slag permanently but evaporated into the gas phase continuously, so that, a slag layer was not necessary to remove tin from molten iron.

The effects of the mode of introduction of argon, the depth of the metal bath, composition of the metal and temperature have been tested to understand the mechanism of the detinning process.

Experimental conditions were similar to those described in section 4-1 for decopperization and some important factors are shown in individual graphs below.

The procedure of determination of sulphur content in the detinning slag is the same as that described in section 4-1-1. It is assumed that tin exists in slag as Sn^{++} , the slag consisting entirely of Na_2S , SnS and FeS .

A few preliminary experiments were carried out at 1250°C, with carbon saturated iron and varying the slag compositions, argon being purged from the bottom of the furnace. As shown in Table 4-5, the proportion of reacted tin was less than 30% after 4 hours refining using any of these slag compositions.

The changes of slag composition are plotted against time in Fig.4.23 for Runs Sn3 and Sn4. The differences between pure Na₂S and FeS-containing slag are similar to those shown in section 4-1-2 for decopperization. It is noticeable that the transfer of tin from metal to slag is extremely slow in pure sodium sulphide slag, it increases continuously and only reaches 0.31wt% in 3 hours reaction.

Changes of metal and slag compositions with reaction time are given in Fig.4.24 for Run Sn6 and Sn7.

Two experiments were carried out at 1350°C, 100 cc/min argon bubbling into metal to test the possibility of simultaneous removal of copper and tin by a FeS-Na₂S and the results are given in Fig.4.25.

Experiments without slag additives were carried out under conditions of varying initial sulphur content in the metal. Effects of mode of argon introduction, depth of molten metal and of temperature were tested with carbon saturated iron and in graphite crucibles. In some cases, alumina crucibles were used when the iron was not saturated with carbon.

Some of the experimental results, in terms of the final content of tin and the proportion of removed tin, are shown in Table 4-6.

Fig.4.26 shows the effect of the position of argon

Table 4-5

Experiments with FeS-Na₂S Slag

Run No.	[Sn] _o wt%	[S] _o	Na ₂ S-FeS wt%	Time Hour	{Sn} _t wt%	[Sn] _t	Removed %
Sn2	0.918	0.22	70 30	4	0.49	0.844	8
Sn3	0.987	0.22	100 0	3	0.31	0.885	10
Sn4	0.92	0.0	50 50	4.5	0.41	0.646	30
Sn6	0.974	0.0	30 70	4	0.44	0.713	27
Sn7	0.968	0.22	30 70	6	0.38	0.667	31

Note -- All runs were carried out under the conditions:

Initial metal charge W_m=20g; T=1250°C (1523K);

W_s/W_m=0.3 (except Sn2 W_s/W_m=0.15); C_{id}=20.6mm;

Ar=75cc/min from the bottom of the furnace;

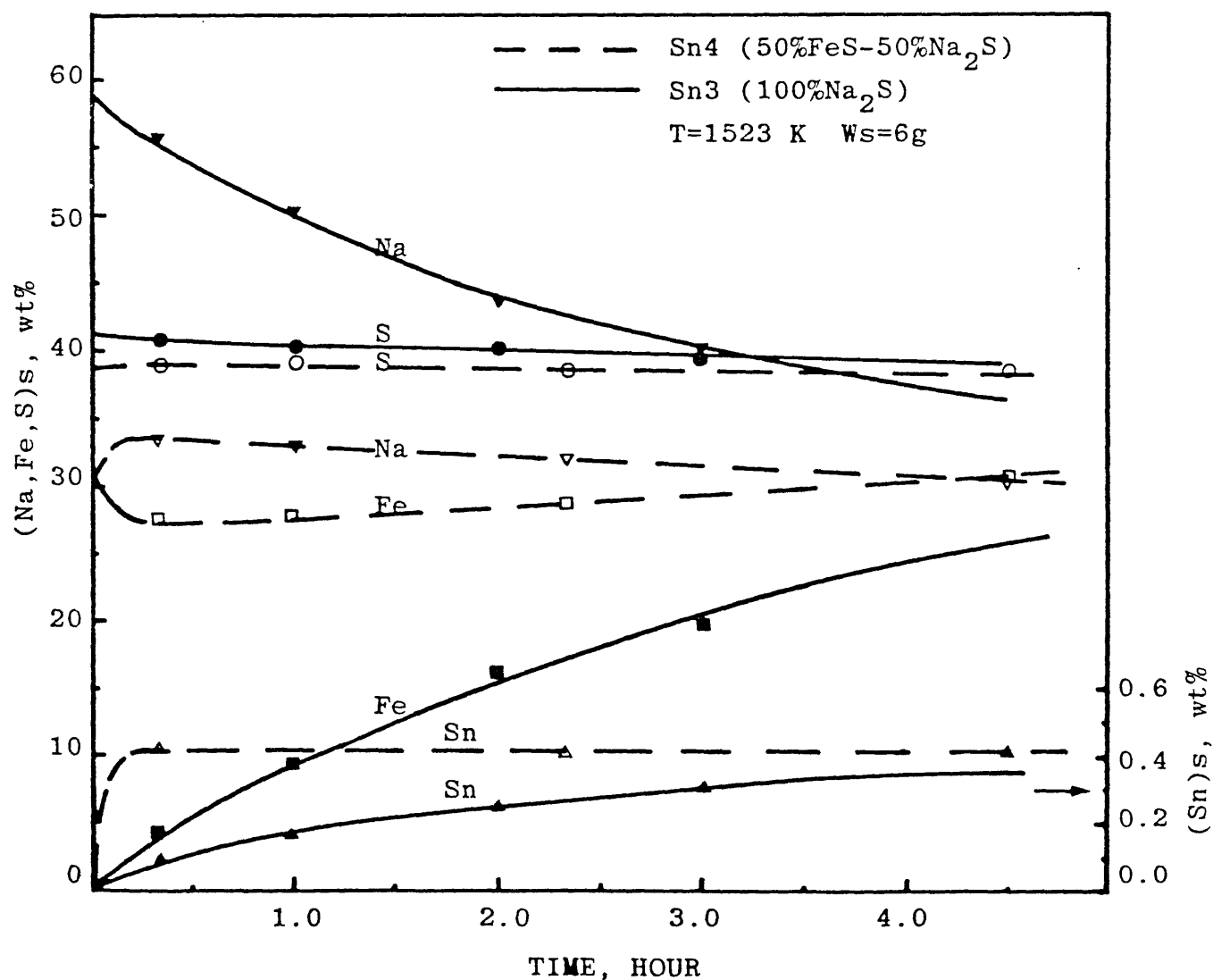


Fig.4.23 Change of Slag Composition

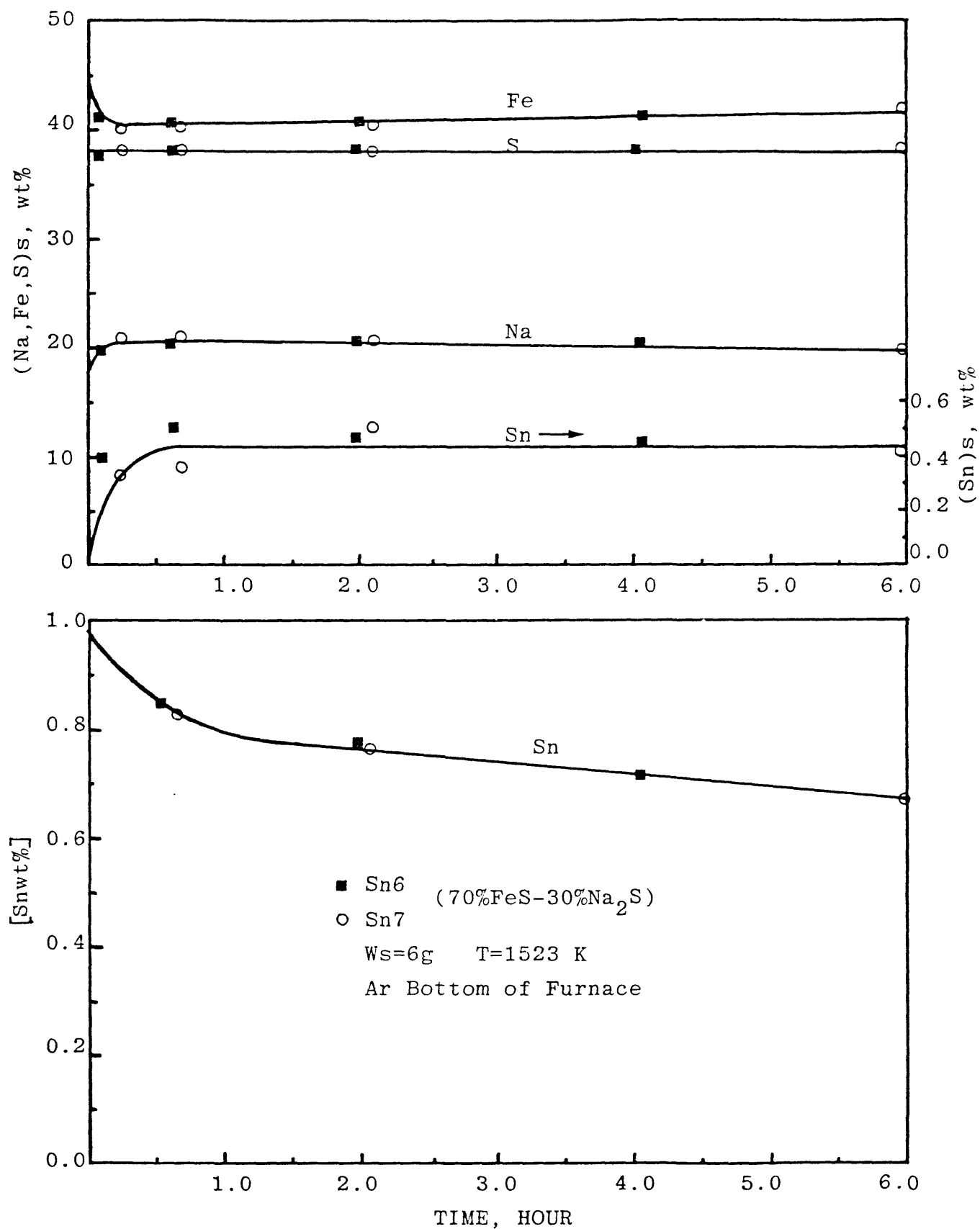


Fig.4.24 Changes of the Slag and Metal Compositons

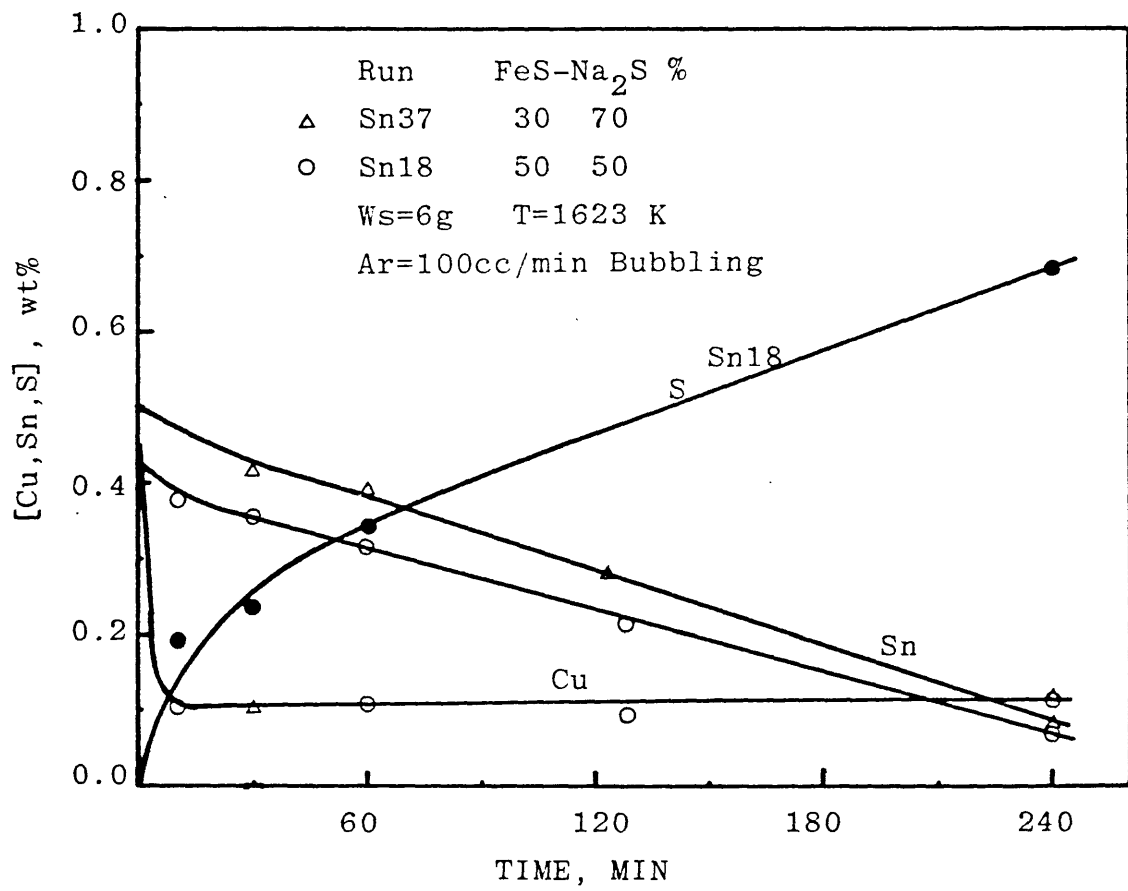


Fig.4.25 Simultaneous Removal of Cu & Sn

Table 4-6
Results of Detinning of Carbon-saturated iron

Run No.	[S]o wt%	Ar cc/min	[Sn]t wt%	$100(1 - \frac{[Sn]t}{[Sn]o})\%$	Remarks
Sn21	0.72	100	0.10	89.8	
Sn22	0.017	100	0.81	4.7	
Sn23	0.22	100	0.64	30.0	
Sn24	0.41	100	0.498	41.8	
Sn25	0.57	100	0.50	43.2	T=1250°C
Sn26	0.57	100	0.305	65.0	
Sn27	0.57	100	0.189	78.5	T=1450°C
Sn28	0.57	50	0.42	52.3	
Sn29	0.57	150	0.145	83.5	
Sn30	0.57	100	0.48	45.5	Ar Surface
Sn31	0.57	150	0.482	45.2	Wm=40g
Sn32	0.55	50	0.63	25.9	Ar Surface Reaction time 210 minutes
Sn33	0.55	100	0.55	35.3	
Sn34	0.55	150	0.39	54.1	
Sn66	0.69	50	0.90	28.4	Ar 2cm above surface#
Sn67	"	"	0.78	31.6	Ar 1cm above #
Sn68	"	"	0.96	15.8	Ar 4cm above #
Sn69	"	"	0.97	14.9	Ar bottom
Sn70	"	"	0.84	26.3	*Ar 2cm above #
Sn71	"	"	0.77	32.5	*Ar 1cm above #
Sn73	"	"	0.96	15.8	*Ar 4cm above #
Sn74	"	"	0.96	15.8	*Ar bottom
Sn76	"	"	0.60	47.4	Ar bubbling

Note: All runs were carried out under conditions:

T=1350°C; Ar bubbling; Reaction time = 240 minutes;

Wm=20g; Carbon-saturated; Graphite crucibles; Cid=20.6mm

& Depth=4cm(*=2cm), except illustrated in Remarks.

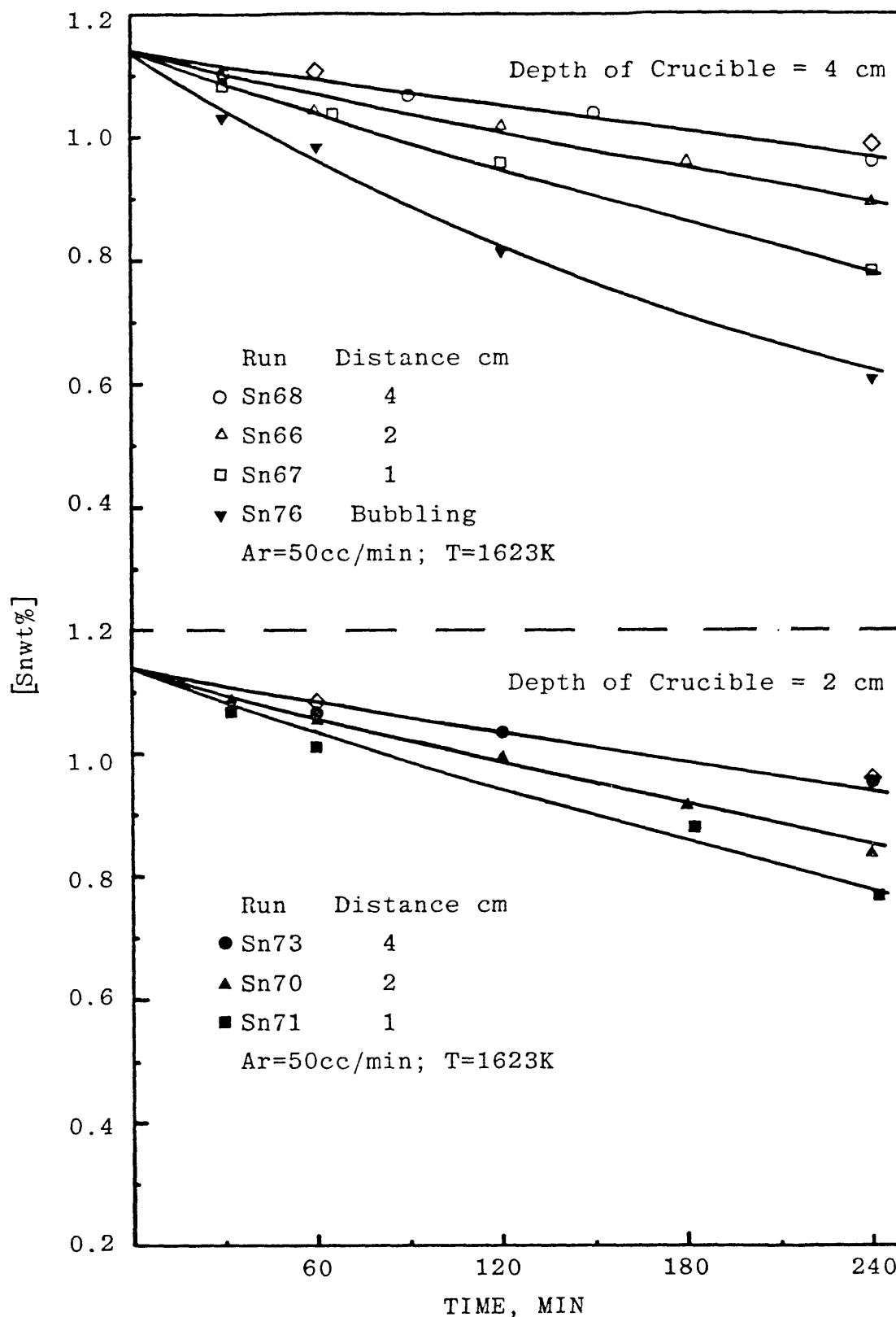


Fig.4.26 Effect of the Distance between the Tip of Argon Tube and the Metal Surface

introduction. Ar was purged from the bottom of the furnace or downwards from 4.0, 2.0 or 1.0 cm above the molten surface to enhance the removal of SnS in the gas phase to a different extent. The bubbling of argon into the metal in Sn76 at the same gas flowrate speeded up the removal of tin due to the stirring of the metal phase and the increase of the free metal/gas interphase surface as the reaction site for the formation of SnS vapour. Fig.4.27 shows similar results by changing argon introduction from surface to bubbling.

Increases of argon flowrate in both surface purge and bubbling accelerated the process as shown in Fig.4.28 and 4.29.

The depth of the crucible obviously affected the rate of removal of SnS vapour as shown in Fig.4.30.

The inner diameter of the crucible was 2.06cm and area 3.33cm^2 in all experiments. The usual metal charge was 20 grams, so that the depth of molten metal was about 0.85cm. Run Sn31 was carried out under the same conditions as Sn29 except for a 40 gram metal charge. As shown in Fig.4.31, the proportion of tin removed in Sn31 was about half as much as in Sn29, the depth of molten metal having been doubled. Although the final concentration was higher in Run Sn31 than that in Sn29, the moles of tin removed was the same within experimental error, which indicates that the reaction rate in terms of mass of tin removed was the same in both runs.

Fig.4.32 shows similar result to Fig.4.31, in which both experiments were carried out at 1600°C , using alumina crucibles, and no carbon addition to the metal.

Experiments in this group were carried out with varying

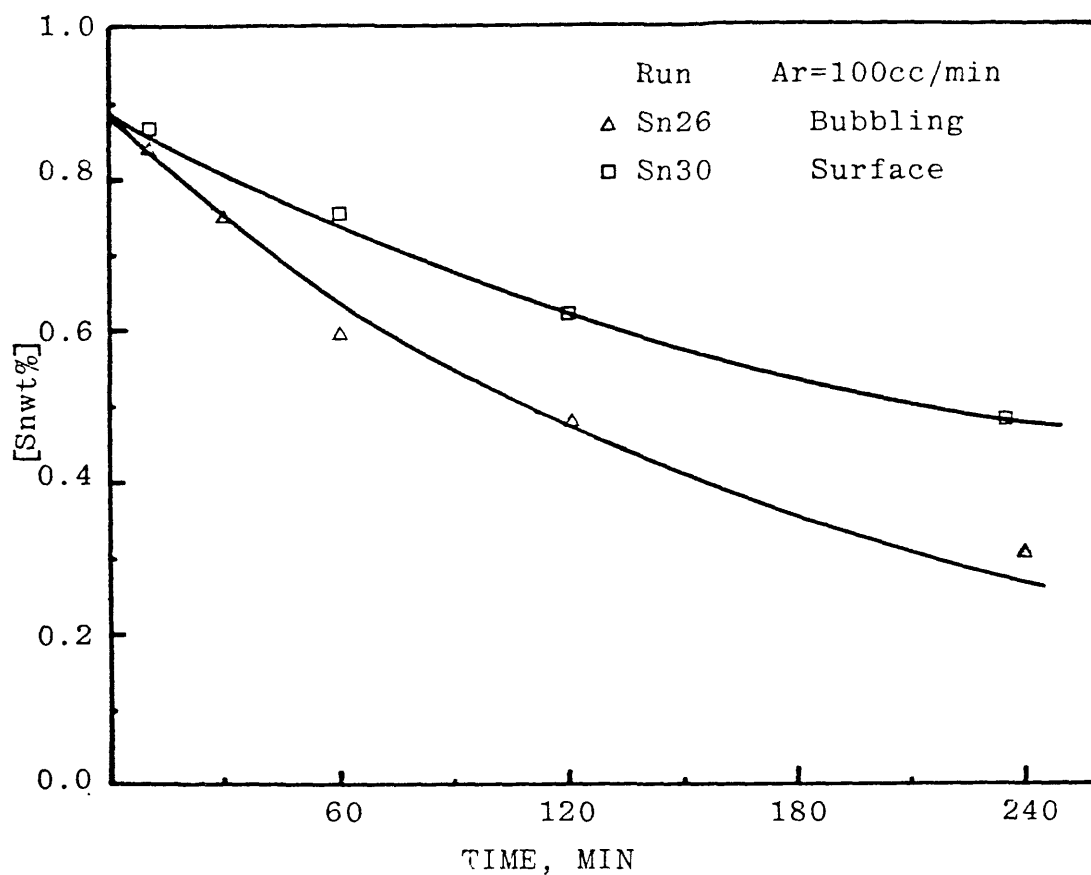


Fig.4.27 Effect of Argon Introduction Mode

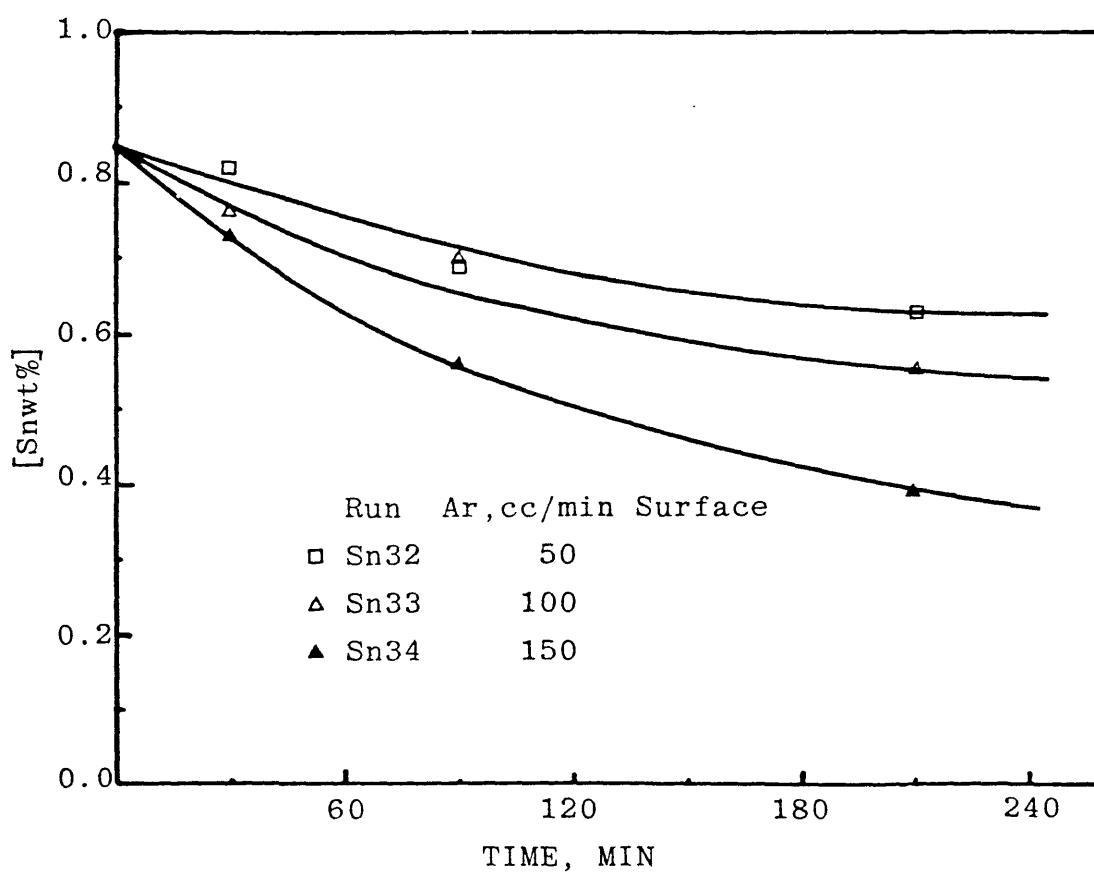


Fig.4.28 Effect of Argon Flowrate

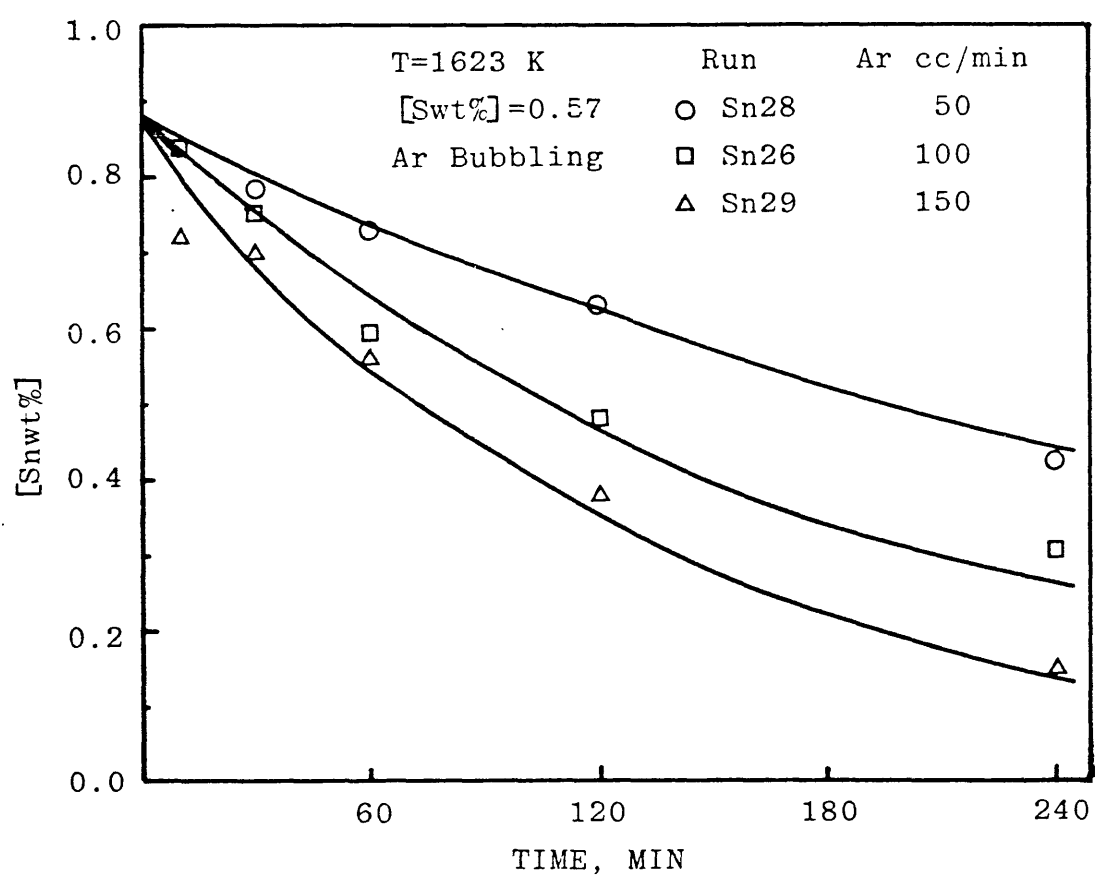


Fig.4.29 Effect of Argon Flowrate

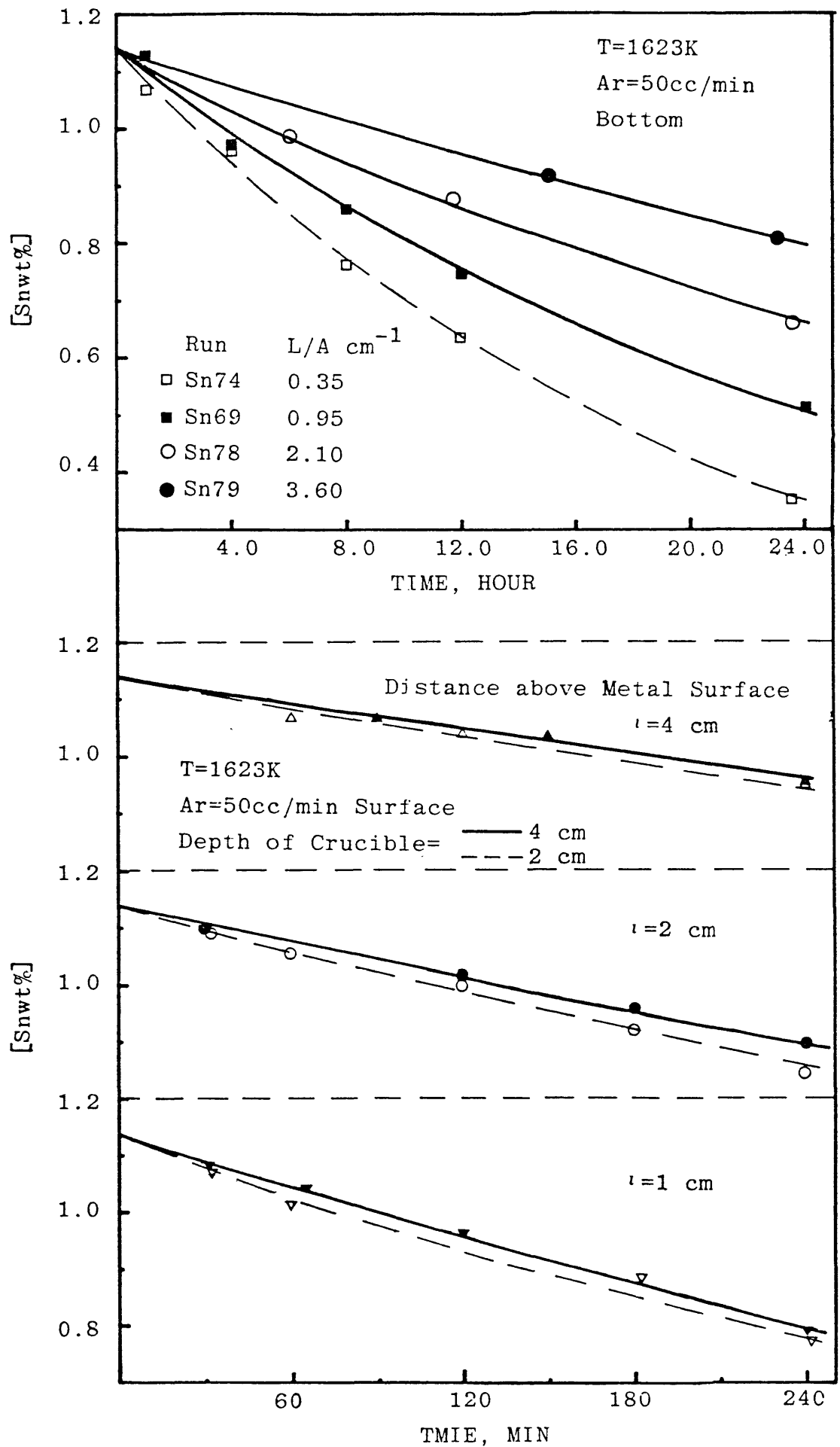


Fig.4.30 Effect of the Depth of Crucible

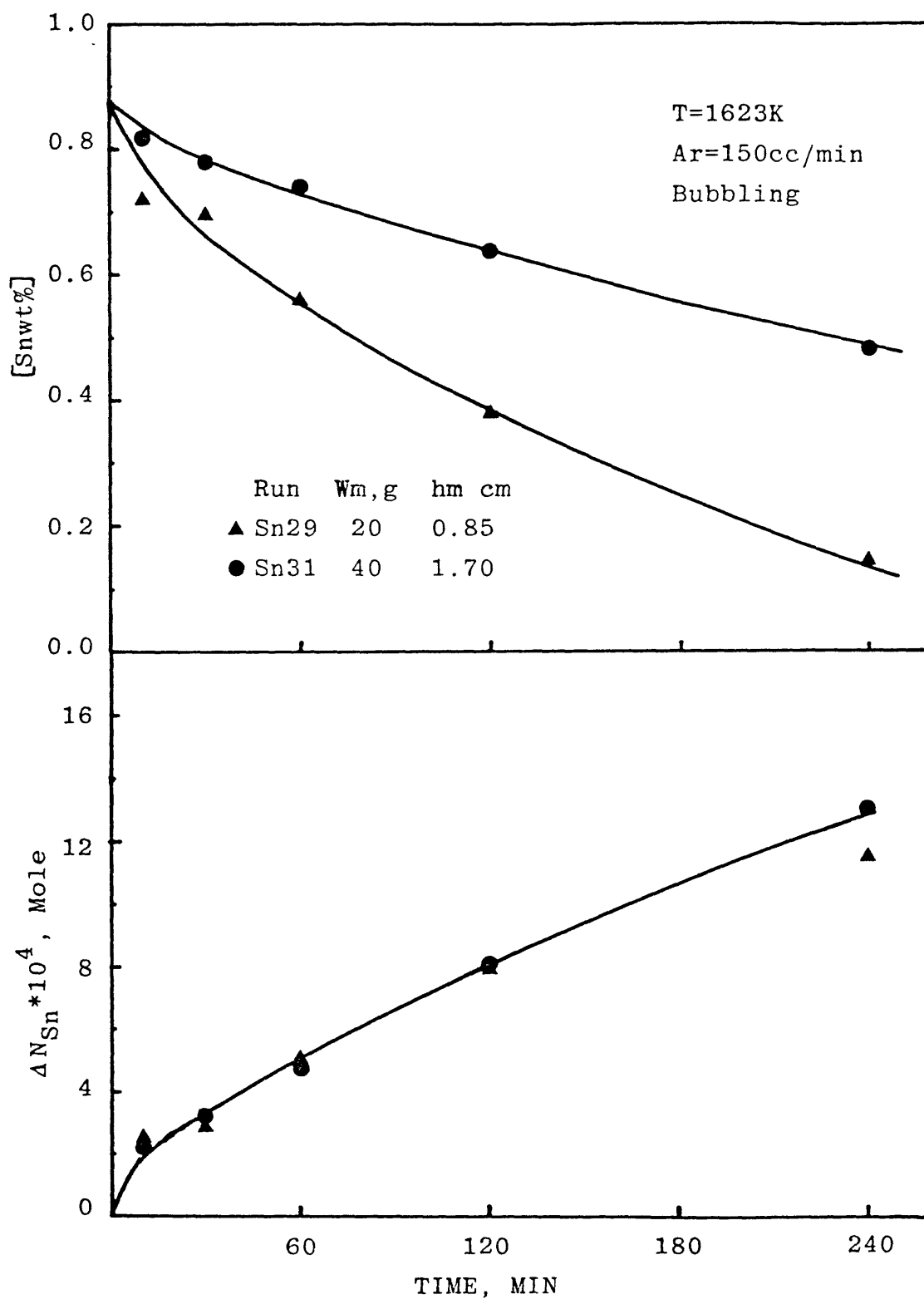


Fig.4.31 Effect of the Depth of Metal Bath

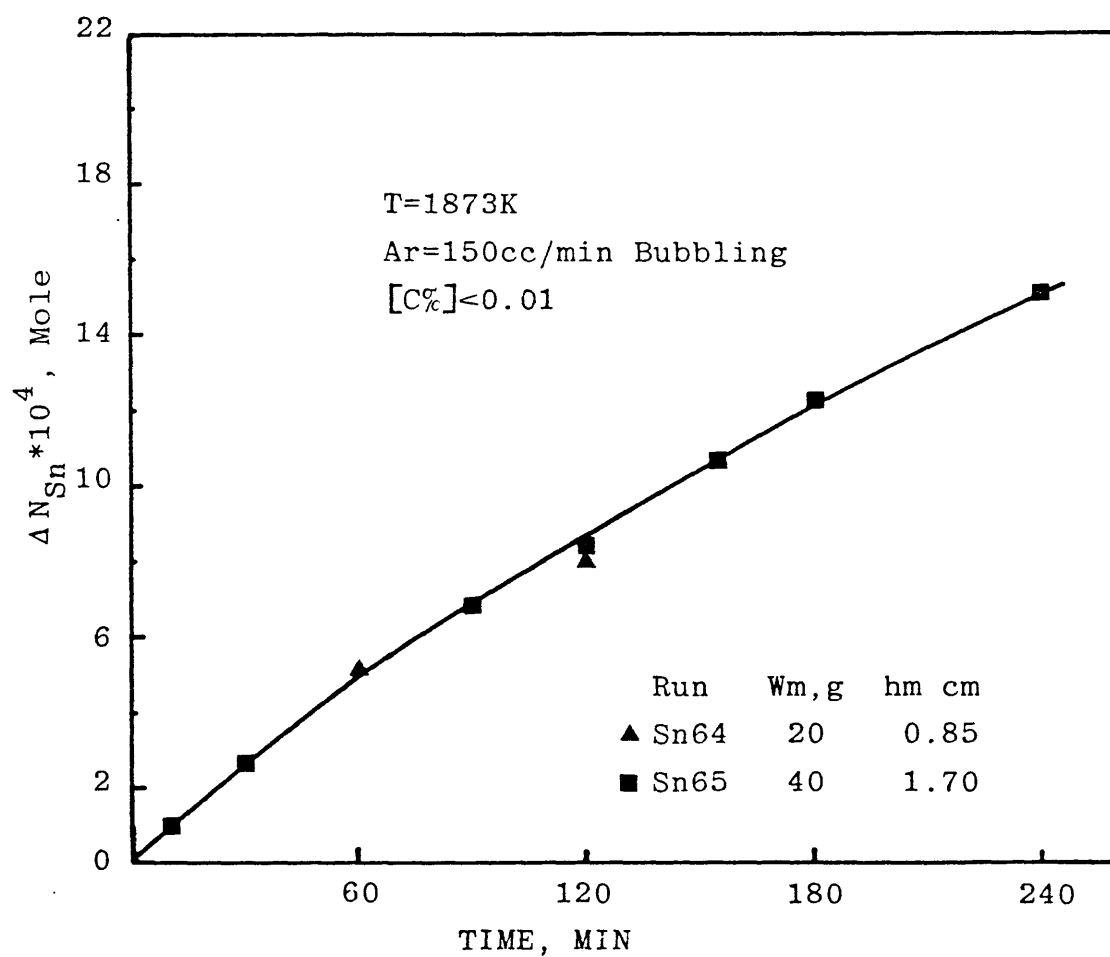


Fig.4.32 Effect of the Depth of Metal Bath

initial sulphur and tin contents. The results are given both as concentration changes and, due to the difference of initial tin content in the metal, as proportion of reacted tin in Fig.4.33 and 4.34. Two grams of FeS were used as slag in RunSn19 and Sn17 to maintain sulphur saturation in the metal and no slag was charged in the other runs.

Two sets of experiments of three runs respectively, were carried out under similar conditions to test the effect of temperature. Alumina crucibles were used for experiments in which the carbon content was fixed at about 3.0wt%.

Temperature obviously affected the process as shown in Fig.4.35. Faster reaction and better final results corresponded to the higher operating temperature. Although the two sets of experiments were carried out under different conditions, the increases of the proportion of reacted tin brought about by 100°C higher were similar to each other as shown in Fig.4.36, An improvement of 13.8% per 100°C was obtained.

Experiments with lower carbon contents, usually less than 0.5wt%, were carried out at 1600°C with argon bubbling into metal phase and using alumina crucibles. As shown in Table 4-7, the removal of tin from iron containing very small amounts of alloying element is not as efficient as that from a high one, the carbon content being particularly important.

Emphasis was put on effects of alloying elements at this temperature. Results similar to those obtained in carbon saturated iron for the effect of initial sulphur content are given in Fig.4.37. The result of Run Sn42 in this figure carried out without initial carbon and sulphur

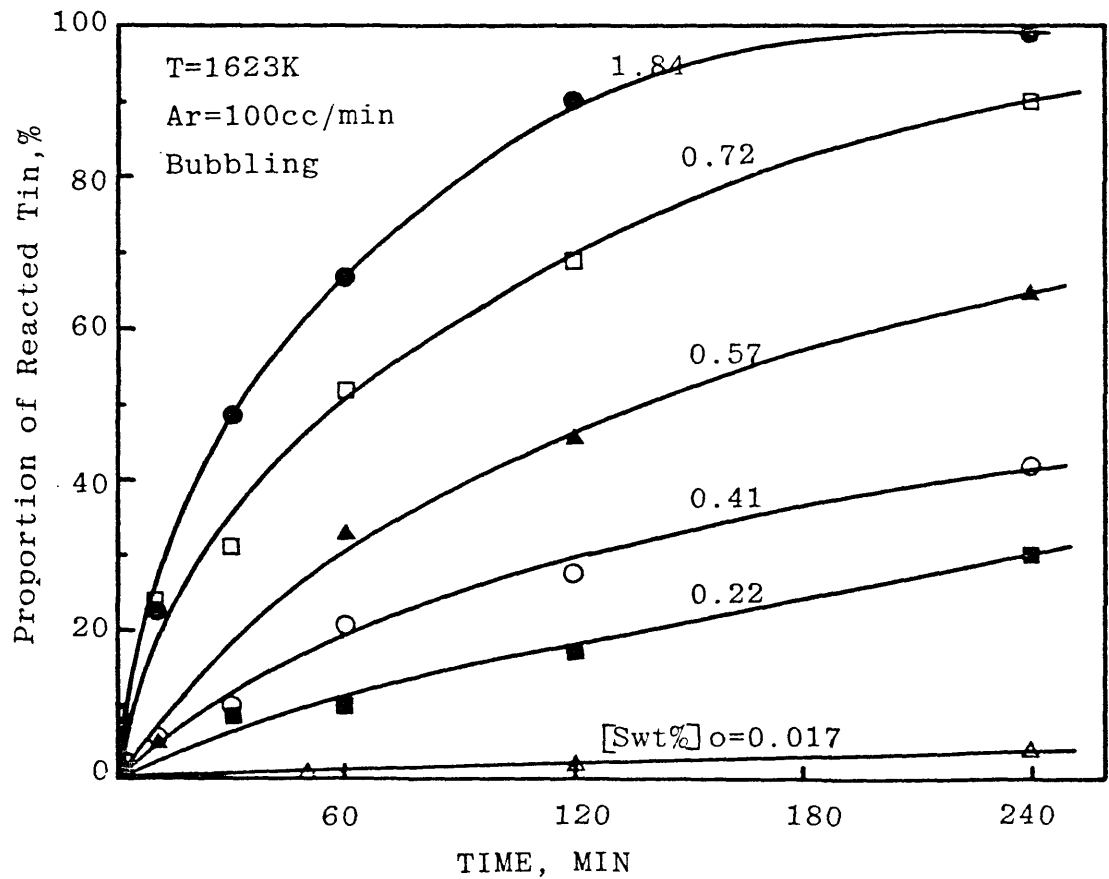
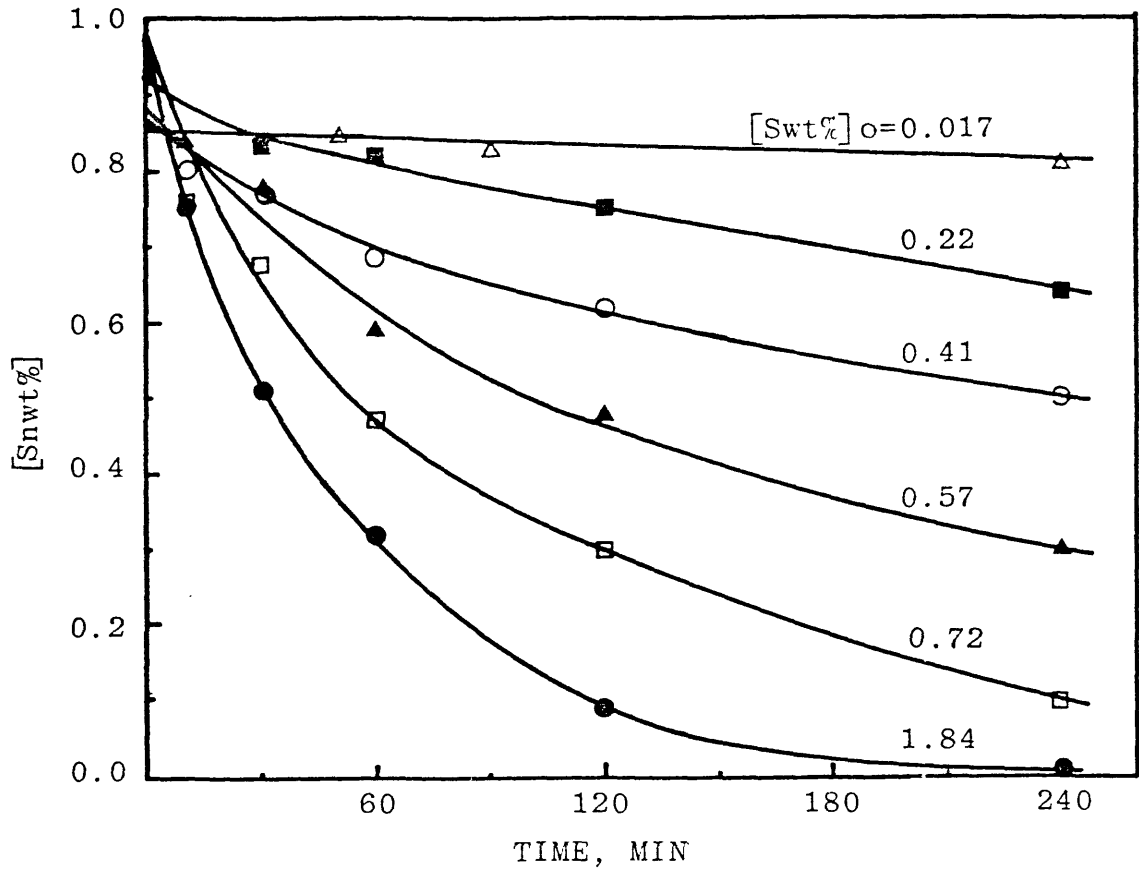


Fig.4.33 Effect of the Initial Sulphur in the Metal

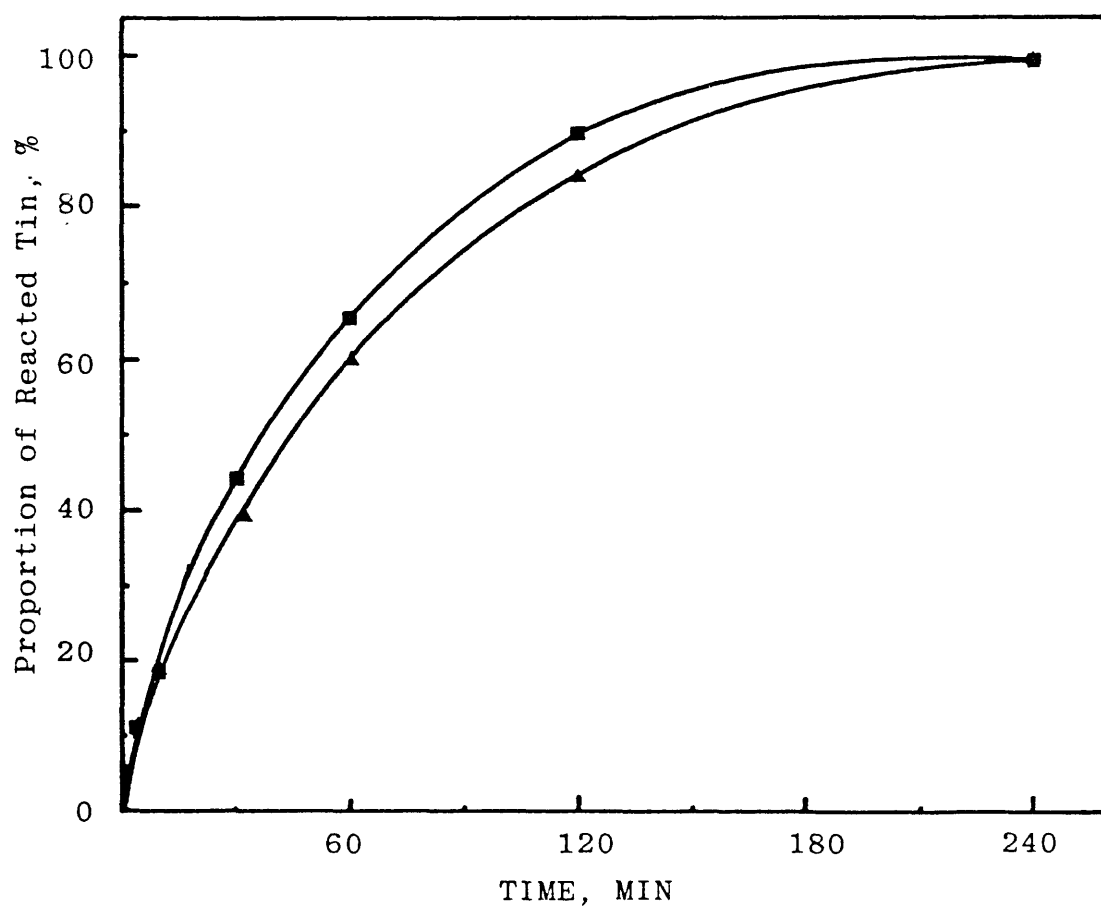
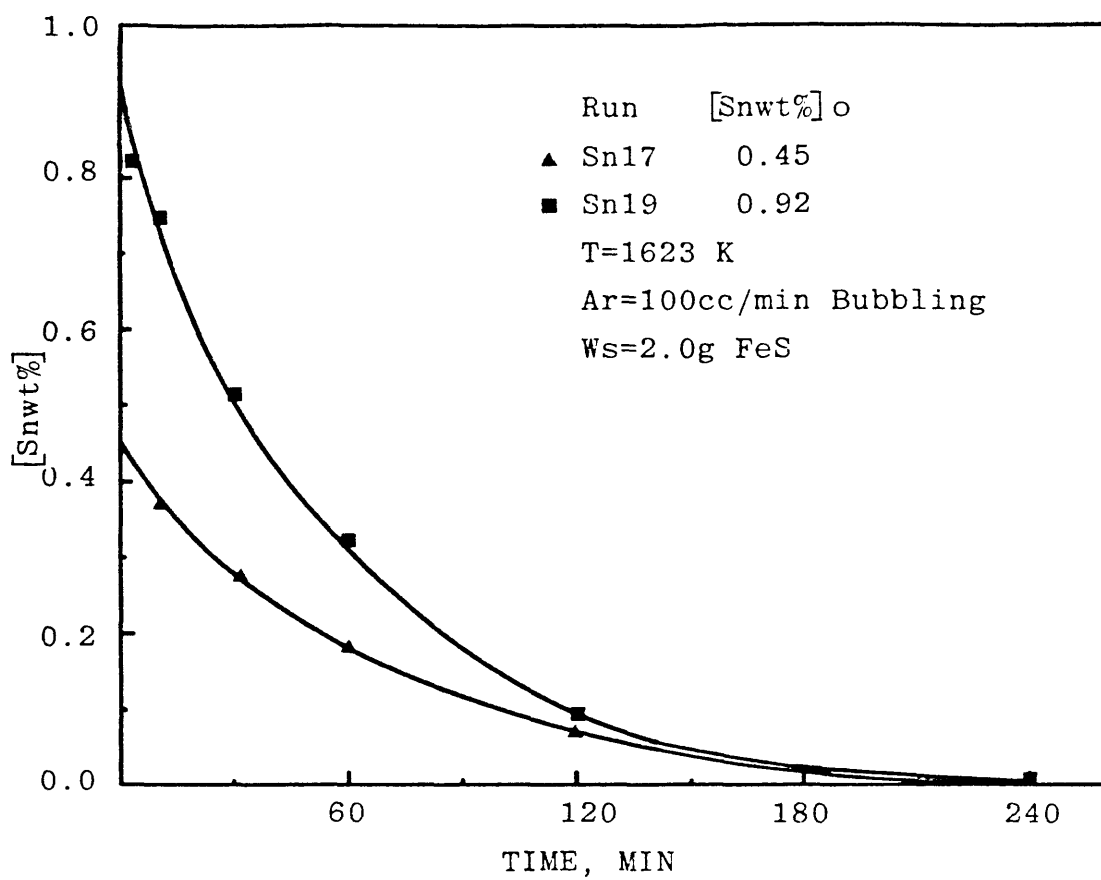


Fig.4.34 Effect of the Initial Tin in the Metal

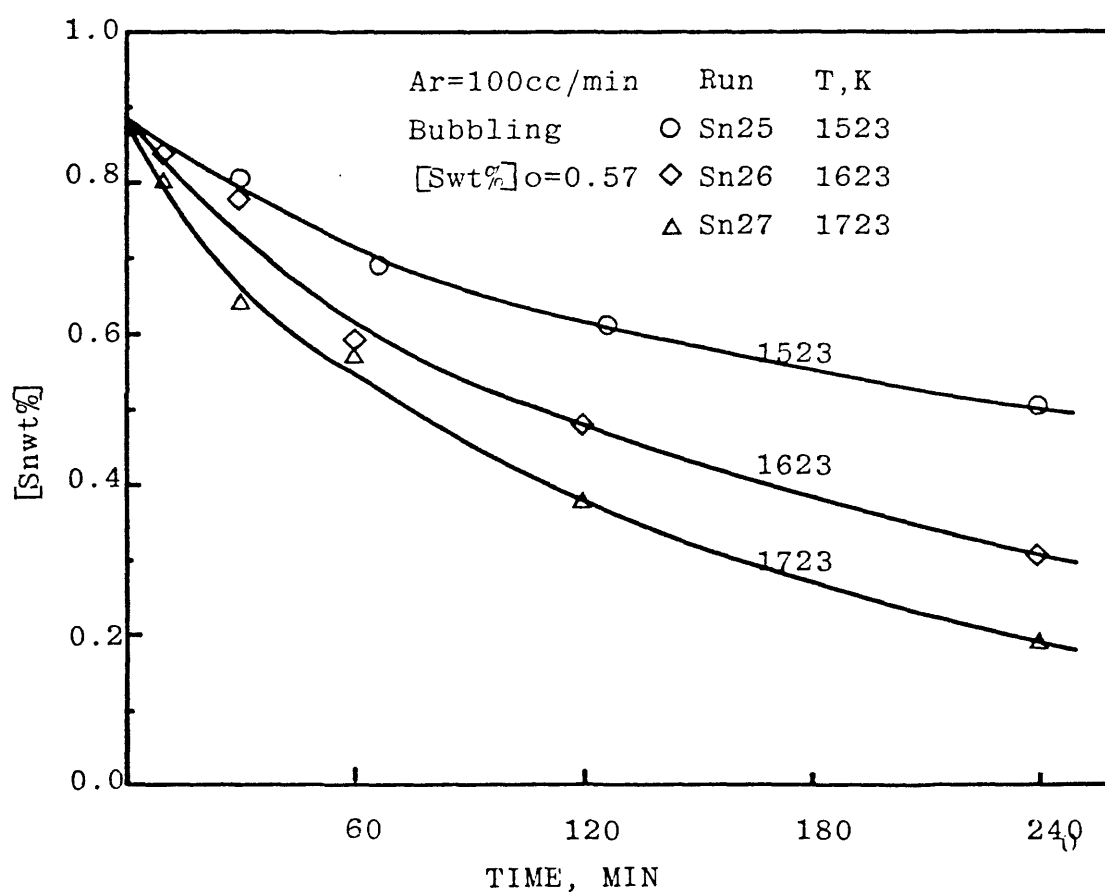
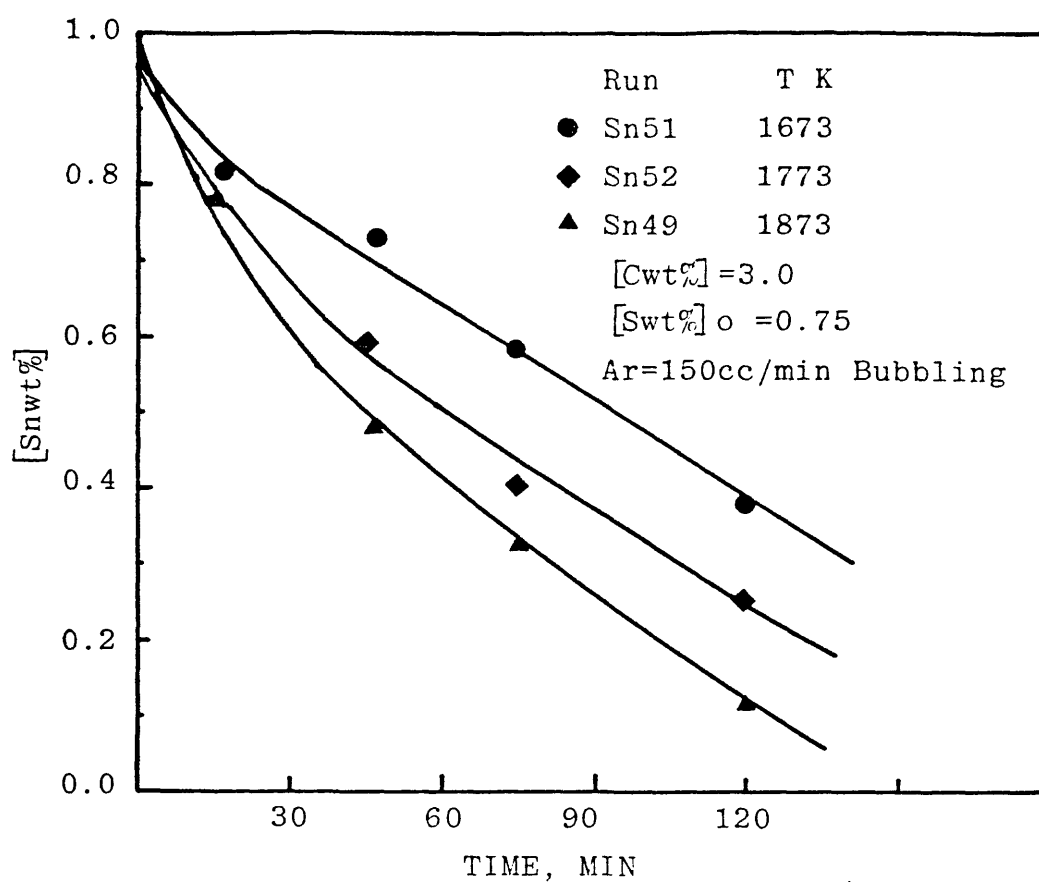


Fig.4.35 Effect of Operating Temperature

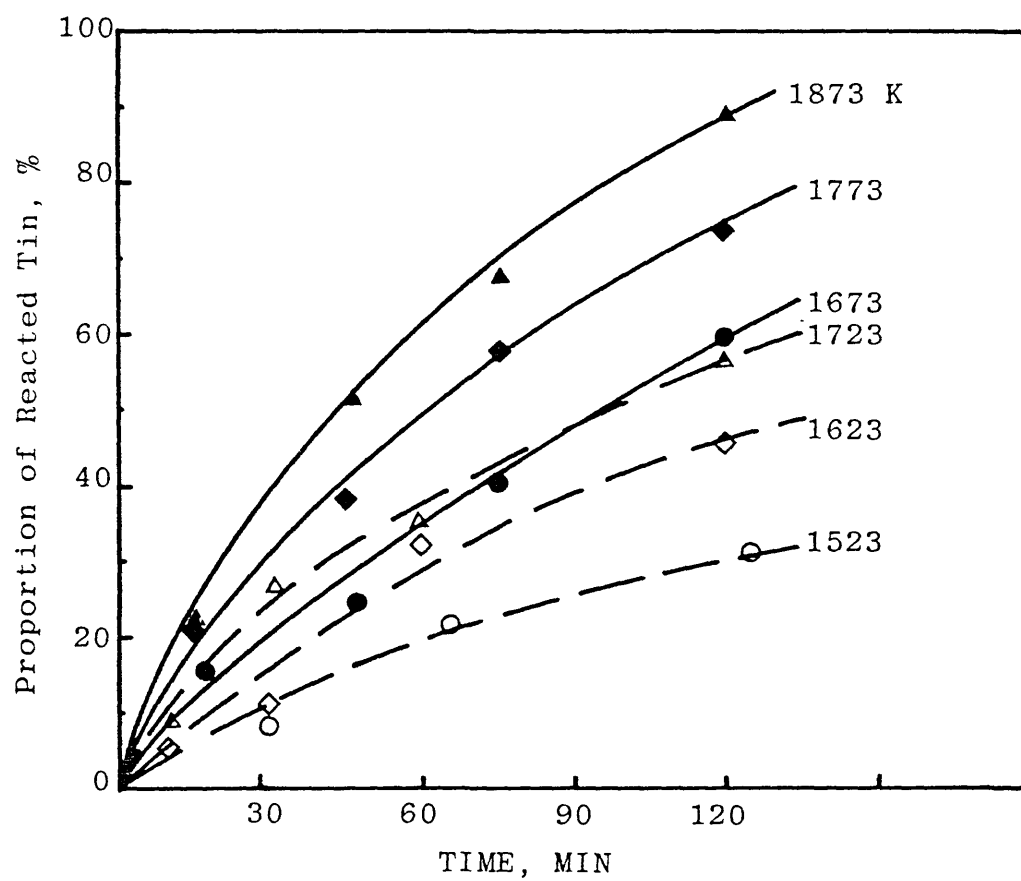


Fig.4.36 Proportion of Reacted Tin
Plot of Fig.4.35

Table 4-7
Results of Detinning of Low Carbon iron

Run No.	[S]o wt%	[C] wt%	[Sn]t wt%	$100(1 - \frac{[Sn]t}{[Sn]o}) \%$	Remarks
Sn38	0.68	0.48	0.70	27.8	
Sn42	<0.01	<0.01	0.973	2.5	
Sn43	0.31	"	0.81	19.8	
Sn44	0.75	"	0.66	36.5	
Sn45	1.10	"	0.53	50.9	
Sn46	1.45	"	0.46	58.9	
Sn51	0.75	3.0	0.38	60.4	T=1400°C
Sn52	0.75	"	0.25	73.7	T=1500°C
Sn49	"	"	0.11	88.8	
Sn47	"	0.50	0.58	42.0	
Sn48	"	1.66	0.39	59.8	
Sn53	"	0.25	0.61	39.0	
Sn54	0.78	<0.01	0.67	34.0	[Si%]=0.5
Sn55	"	"	0.59	41.0	[Si%]=1.0
Sn56	"	"	0.54	46.0	[Si%]=2.0
Sn57	"	"	0.26	66.2	[Si%]=4.0
Sn58	0.65	3.0	0.015	98.0	[Si%]=4.0
Sn59	0.65	3.0	0.027	96.4	[Si%]=4.0
Sn60	0.75	<0.01	0.50	46.0	[B%]=1.0
Sn61	0.75	"	0.03	97.0	[B%]=4.0
Sn62	0.75	"	0.67	34.0	[Cr%]=3.4
Sn64	1.05	"	0.72	40.0	
Sn65	1.05	"	0.902	25.0	Wm=40g

Note: All runs were carried out under conditions:

T=1600°C; Ar=150cc/min bubbling; Cid=20.6mm; Wm=20g;

Reaction time=120 min; Alumina crucibles, except illustrated in Remarks.

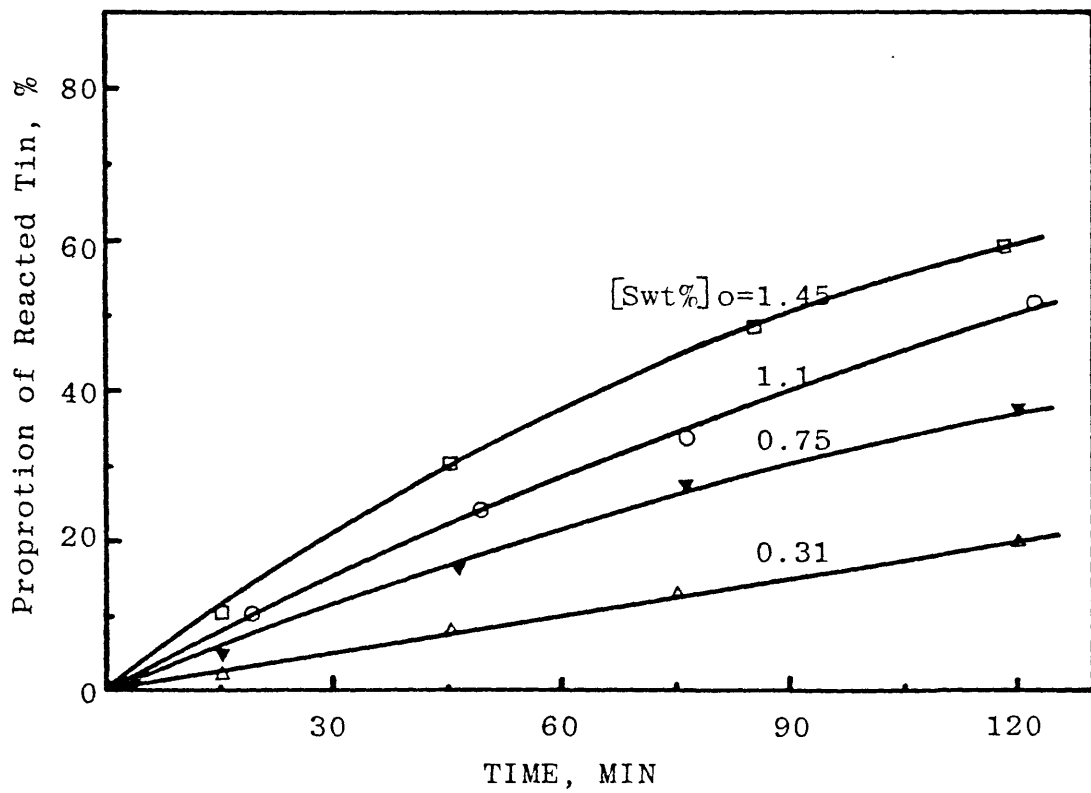
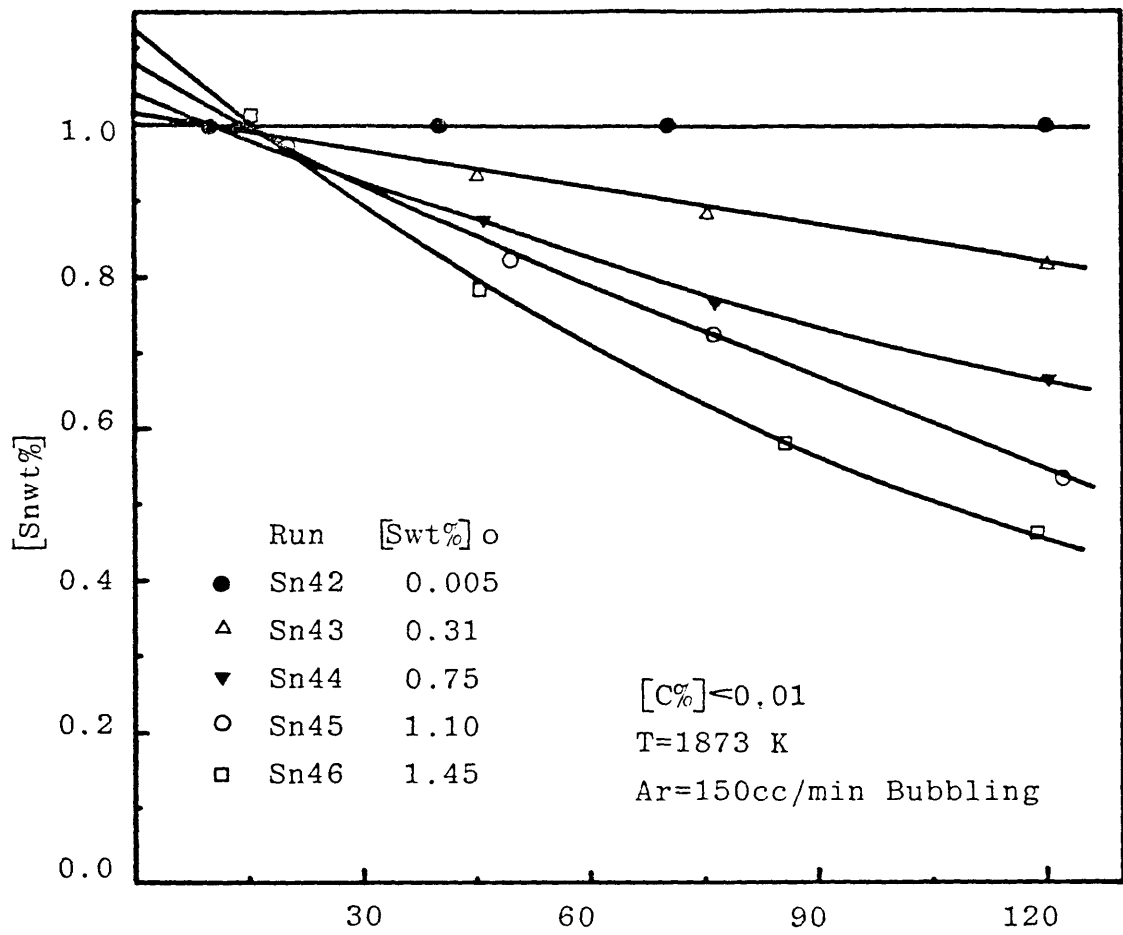


Fig.4.37 Effect of the Initial Sulphur in Metal

confirms that the evaporation of tin from iron in that system was quite insignificant.

The carbon content of the metal, as is the case in decopperization, plays an important role in the detinning process as shown in Fig.4.38. A higher initial carbon content corresponded to faster reaction and better removal of tin .

Experimental results indicated that aluminium did not affect the process. Chromium slightly increased the refining efficiency but not as much as carbon; for example, the effect produced by 3.4%Cr is similar to that by 0.75%C.

Silicon and boron were also tested in experiments. Unfortunately, analytical results for these two elements have not been obtained, so the initial planned concentrations, which probably deviated from actual dissolved content, are quoted in tables and figures. As shown in Fig.4.39, silicon enhances the detinning, but the extent of the effect is smaller than that of carbon. The process is very fast when the metal contains about 3.0% carbon and 4.0% silicon. The effect of boron is compared with the effect of carbon in Fig.4.40. This figure indicates similar results.

Fig.4.41 shows different effects from combined alloying elements. A suitable combination of alloying elements could lead to a detinning process which is fast enough to be applied to industry.

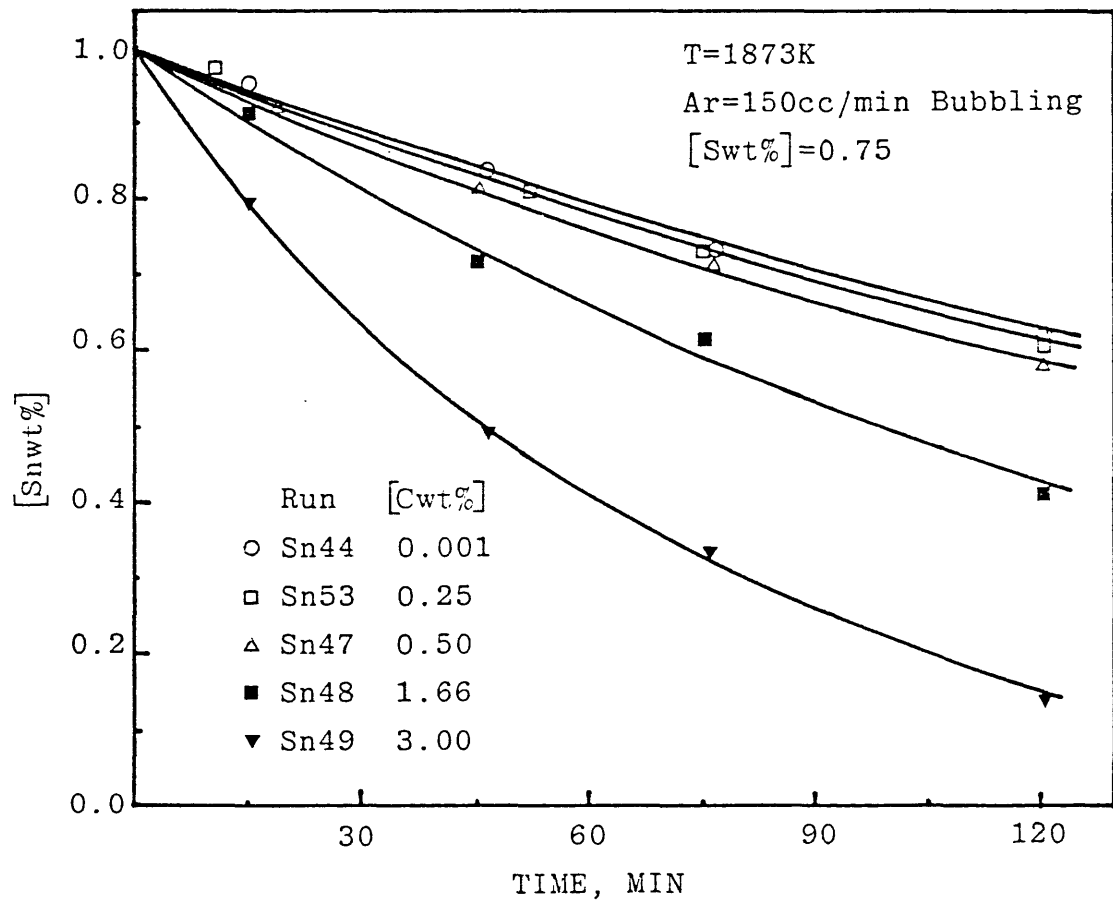


Fig.4.38 Effect of Carbon Content in the Metal

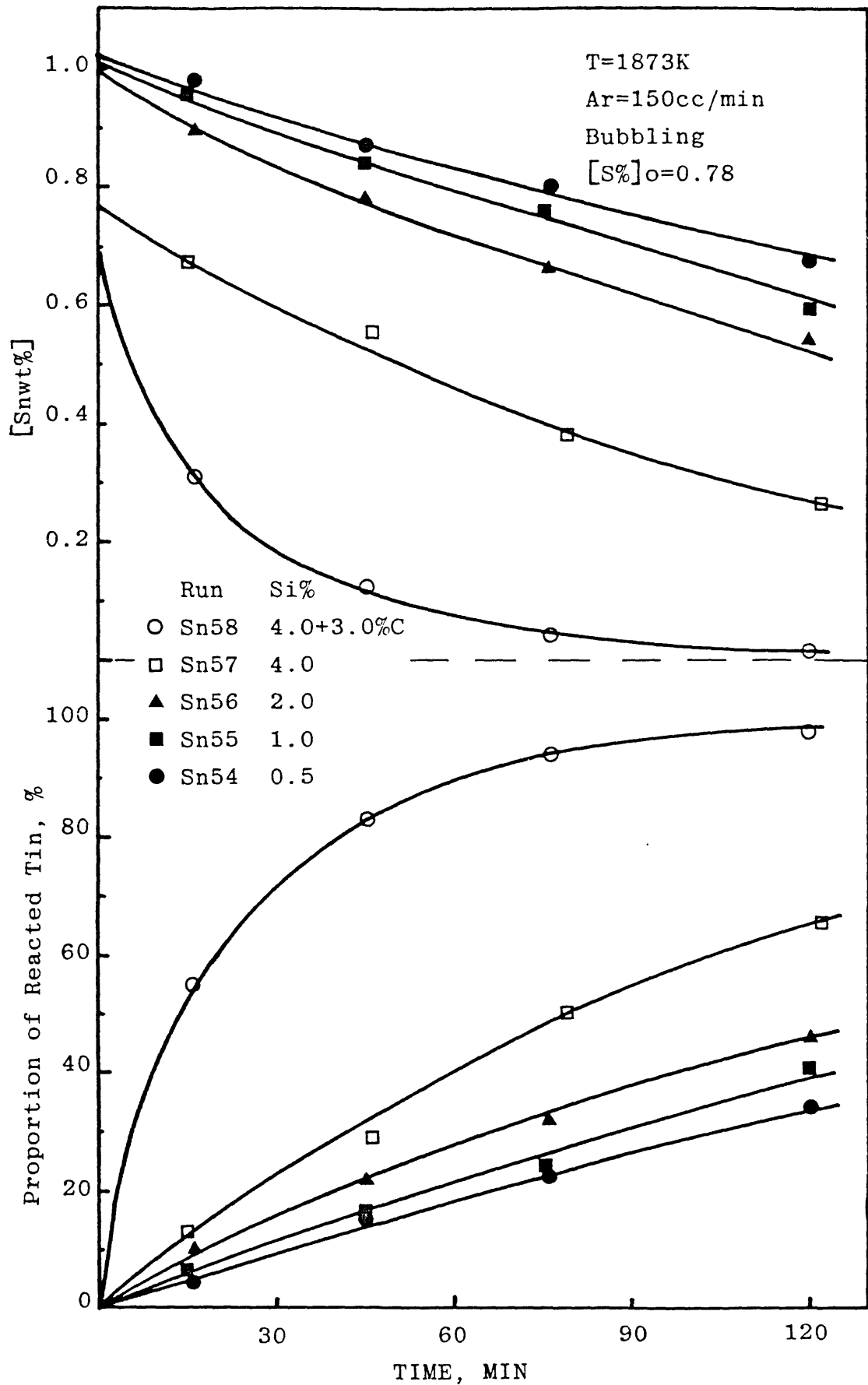


Fig.4.39 Effect of Silicon Content in Metal

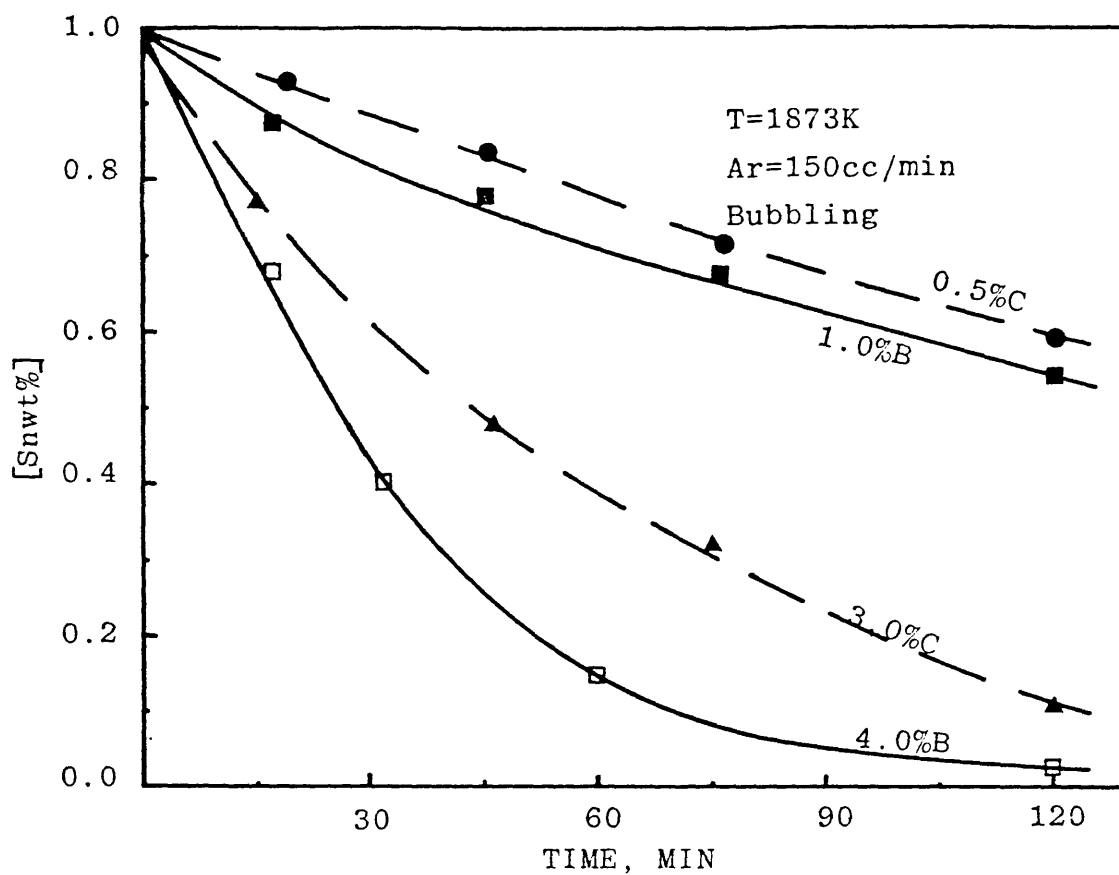


Fig.4.40 Effect of Carbon and Boron in Metal

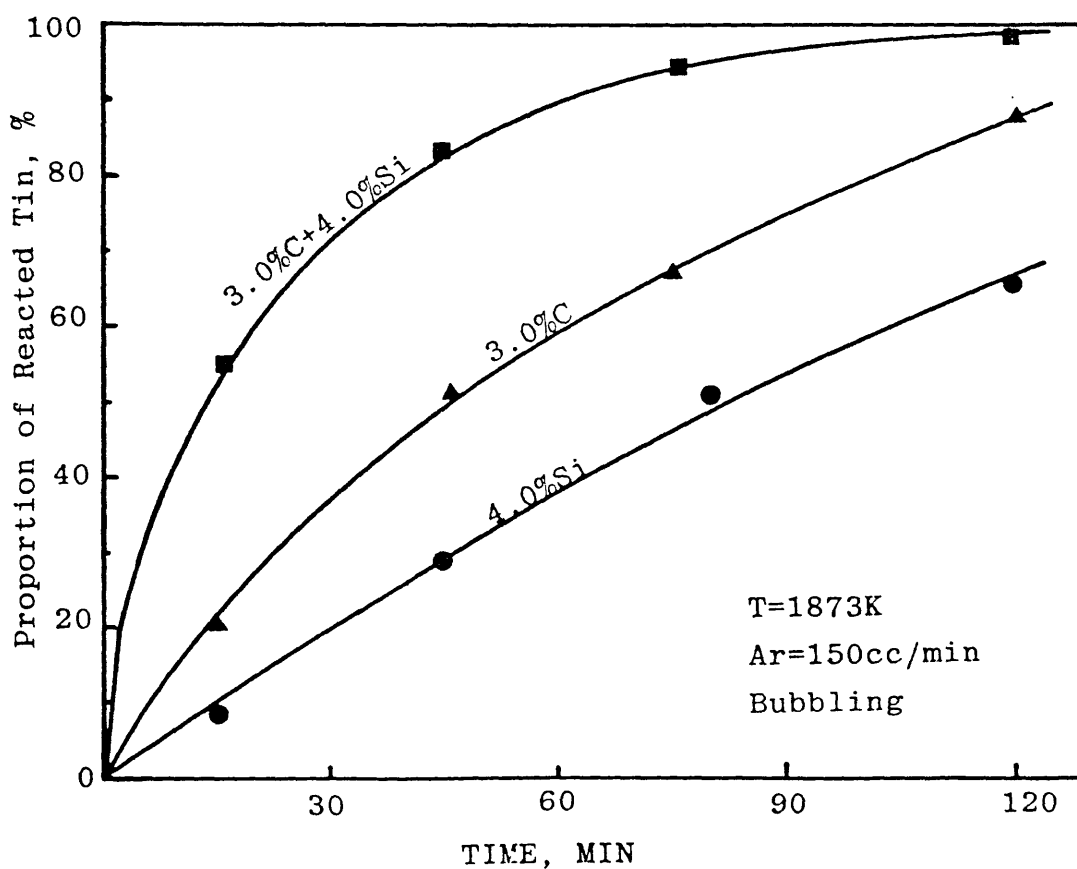


Fig.4.41 Combined Effect of Carbon and Silicon

CHAPTER 5

DISCUSSION OF DECOPPERIZATION

CHAPTER 5

DISCUSSION OF DECOPPERIZATION5-1 DECOPPERIZATION FROM CARBON SATURATED IRON5-1-1. Effect of the mode of introduction of argon

When a reaction occurs locally, the concentrations of reactants are lowered at the site of the reaction and concentration gradients are established with adjacent liquids. The reactants must be supplied to continue the reaction by mass transport caused by diffusion and/or mixing of the system.

The various methods of introducing argon into the apparatus cause changes in the flow conditions of the system studied, and these influence the mass transport processes.

Fig.4.3 and 4.4, page 51, show the variation of copper in the metal with time. Fig.5.1 is the plot of moles of transferred copper from Fig.4.3. If the value of transferred copper at the end of the first minute is taken as the initial rate of the process, top blowing from 1.0cm above the slag results in about a 3.2 fold increase compared with bottom introduction and bubbling through the metal increases the rate by a further factor of 2.8.

The process can be considered as taking place in three separate stages which occur simultaneously:

(i) The continuous supply of copper and sulphur from the bulk metal and slag to the M/S interface.

(ii) Phase boundary processes. These may involve adsorption of reactants, followed by a chemical reaction and

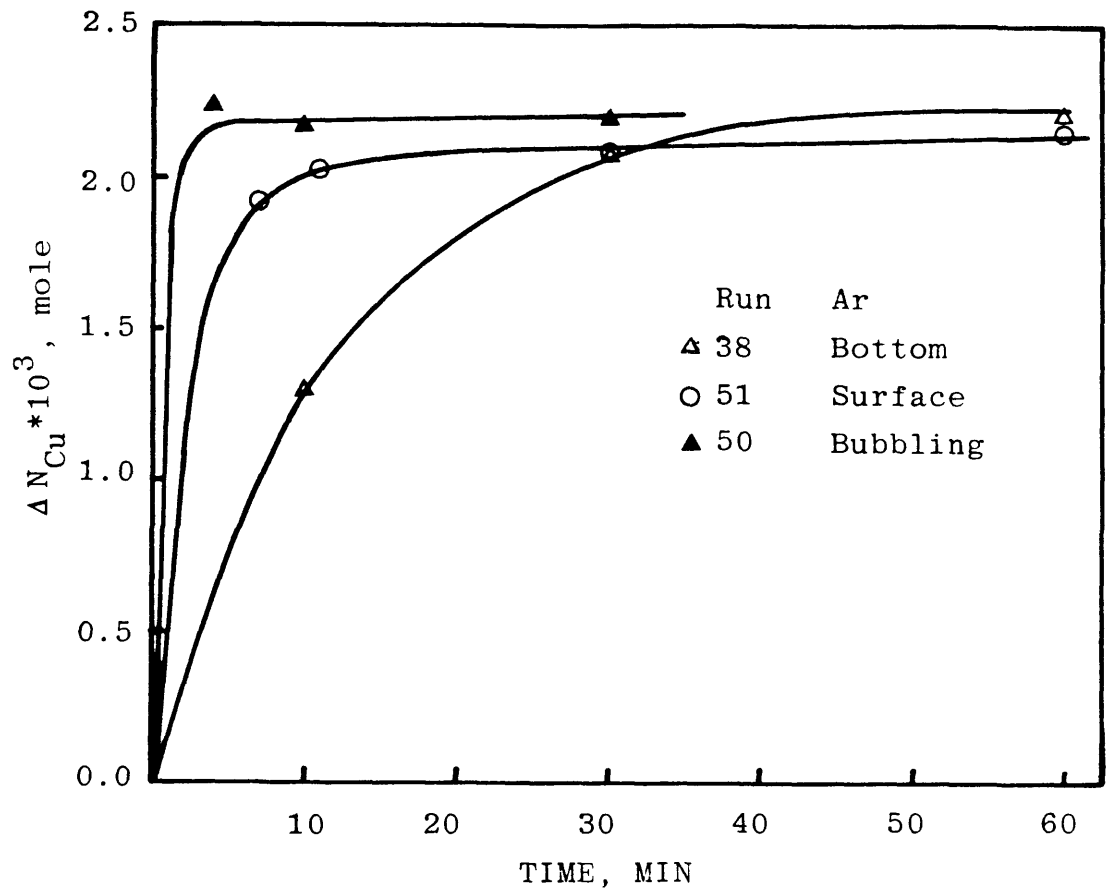


Fig.5.1 Effect of argon introduction mode

then desorption of the reaction products.

(iii) The continuous removal of reaction products from the M/S interface and into the bulk slag.

Steps 1 and 3 involve the transport of some species to or from the site of the reaction and each of these may be controlled by any or a combination of these steps.

The supply of sulphur depends on the decomposition of Na_2S for a pure Na_2S slag and also FeS for a mixture of FeS - Na_2S slag. The decomposition of Na_2S is concerned with the vaporization of sodium, as described by the equation



So step (i) includes the diffusion of sodium vapour in the gas phase which may contribute to the control of the overall reaction rate.

Assuming that interfacial chemical reactions are always at their equilibrium state through the process, the transport of sodium vapour in the gas, and of species in the slag and metal are at their slowest rates under the condition of bottom blowing. The introduction of argon from about 1.0cm above slag surface accelerates the removal of sodium vapour, which in turn, increases the activity of sulphur. It also probably disturbs the slag surface and creates a convective flow in slag bulk which enhances the transport of species in the slag. The difference of overall rate between Run 38 and 51 is due to the elimination of the resistance of diffusion in the gas and slag phases, but present results can not distinguish between these two processes.

The molar flux of diffusion of copper between slag and metal can be expressed as (81)

$$N_{Cu} = ks(C_{s,b} - C_{s,i}) = km(C_{m,i} - C_{m,b}) \quad (5-2)$$

where

ks & km = mass transfer coefficient of Cu in
slag and metal phases respectively.

$C_{s,b}$ & $C_{m,b}$ = Concentration of Cu in the bulk of
slag and metal phases respectively.

$C_{s,i}$ & $C_{m,i}$ = Concentration of Cu at the interface and
in slag and metal phases respectively.

When the interfacial reaction is at equilibrium,

$$K = C_{m,i}/C_{s,i} \quad (5-3)$$

By introducing equation (5-3) into (5-2), the concentrations
at the interface can be eliminated to obtain

$$N_{Cu} = \frac{KC_{s,b} - C_{m,b}}{K/ks + 1/km} \quad (5-4)$$

The numerator in this equation represents the overall
driving force, and the denominator corresponds to the
overall resistance to mass transfer.

In the present system, the distribution of copper
between slag and metal, defined as

$$D = \{Cu_{wt\%}\}/[Cu_{wt\%}] \quad (5-5)$$

has a constant value of between 17 and 18 at equilibrium. A
mean value of 17.88 was obtained from several runs as shown
in Table 5-1.

Table 5-1
Distribution Coefficient of Cu

Run D	3 17.10	7 17.52	15 17.53	19 17.62	30 18.87
Run D	34 17.89	50 18.89	52 17.78	58 17.75	D 17.88

Combining equations (5-3) and (5-5), one can obtain

$$K = [Cu\%]W_{mhs}/\{Cu\% \}W_{shm} = 0.14$$

From equation (5-4) and K equal to 0.14, the respective mass

transfer resistances are

$$0.14/k_s \quad \text{and} \quad 1/k_m$$

If $k_m = 2k_s^{(33)}$, therefore, the resistance in the metal is greater than that in the slag phase.

Under the assumption that the mass transport in the metal controls the process, one can derive

$$\frac{d[Cu\%]}{dt} = \frac{k_m}{h_m} ([Cu\%]_i - [Cu\%]_b) \quad (5-6)$$

where k_m cm/sec is the mass transport coefficient of copper in the metal.

For interfacial equilibrium

$$K_e = \frac{\{Cu_2S\%}}{[Cu\%]_i} = \frac{\{Cu_2S\%}_e}{[Cu\%]_e} \quad (5-7)$$

From the mass balance

$$\{Cu_2S\%} = (159W_m/127W_s) ([Cu\%]_o - [Cu\%]) \quad (5-8)$$

So

$$[Cu\%]_i = ([Cu\%]_o - [Cu\%]) [Cu\%]_e / ([Cu\%]_o - [Cu\%]_e) \quad (5-9)$$

Substituting and rearranging gives

$$\frac{d[Cu\%]}{dt} = \frac{k_m}{h_m} \frac{([Cu\%]_e - [Cu\%])}{([Cu\%]_o - [Cu\%]_e)} \quad (5-10)$$

Upon integration

$$k_m = \frac{h_m ([Cu\%]_o - [Cu\%]_e)}{t [Cu\%]_o} \ln \frac{[Cu\%]_o - [Cu\%]_e}{[Cu\%] - [Cu\%]_e} \quad (5-11)$$

For Run 51, $h_m = 0.82$ cm, $[Cu\%]_o = 0.974$ and $[Cu\%]_e = 0.27$, the calculated values of k_m at different reaction times are shown in Table 5-2.

Table 5-2

k_m for Surface Purge of Argon

Time min	1*	2*	4*	7	11
[Cu%]	0.8	0.65	0.47	0.364	0.33
$k_m \times 10^3$ cm/sec	2.8	3.05	3.11	2.83	2.22

* Estimated values from Fig.4.3, page 51.

If the transport of copper in the metal depends on diffusion,

$$k_m = D/\delta \quad (5-12)$$

where D is the diffusion constant of copper in the metal and δ is the thickness of boundary layer. Usually D has the value between 10^{-4} and 10^{-5} cm^2/sec ⁽⁸¹⁾ and taking the mean of the first four values as k_m , 2.95×10^{-3} cm/sec , equation (5-12) gives δ equal to 0.0034 – 0.034 cm . This value is in agreement with those quoted for similar systems, 0.001 – 0.2 cm , also it is close to the value of 0.03 cm quoted for the sulphur in iron system⁽⁸²⁾. It is possible therefore that the measured copper transfer rate is controlled by the diffusion of copper in the metal.

When argon is bubbled through the metal, the stirring is usually vigorous enough to keep the whole system well mixed, which occurs by entrainment of liquid in the wake and by forced convection currents set up by the bubble streams. Bubbles may also cause the ejection of small drops of one phase into the other, thereby increasing the transfer rate. For Run 50, equation (5-11) gives k_m equal to 1.2×10^{-2} cm/sec .

Robertson and Staples studied mass transfer across metal/slag interface stirred by bubbles⁽³⁴⁾. The mass transfer data available were correlated by the equation

$$k^2 = BDQ/d^2 \quad (5-13)$$

where B is a constant approximately equal to 100 cm^{-1} for the metal phase, D the appropriate diffusivity, Q the total gas flowrate and d the diameter of the cell. In the present case, $B=100$ cm^{-1} , $D=10^{-5}$ to 10^{-4} cm^2/sec , $Q=3.9$ cc/sec at 1523K and $d=2.064$ cm . Equation (5-13) gives k_m ranging

between 3 and 9.6×10^{-2} cm/sec. This estimated value of copper transfer coefficient is about 3-8 times greater than that calculated by equation (5-11) from the present experimental data. Although there is some uncertainty about estimated copper concentration during the first three minutes, the reaction will not reach its equilibrium state before the third minute as shown in Fig.4.6, page 52, which indicates that a value of k_m equal to 1.2×10^{-2} cm/sec for the argon stirred system in the present work is reasonable.

Using a mathematical model, Okazaki⁽³³⁾ calculated a mass transfer coefficient of copper in molten carbon saturated iron equal to 5.2×10^{-2} cm/sec. This value is about 4 times of the present result. This is probably due to the differences of the cell size studied and the flow condition in the system.

The acceleration of the rate of copper transfer following the increases of argon flowrate, as shown in Fig.4.6, page 52, indicates that the process is controlled by mass transport in the system. By substituting the experimental results during the first four minutes into the equation (5-11) and assuming $[Cu\%]_e = 0.29$ from Fig.4.6, the mean value of k_m for different argon flowrates has been calculated and the results are listed in Table 5-3.

Table 5-3

Variations of k_m with Argon Flowrates

Ar cc/min (NTP)	25	75	120
$k_m \times 10^2$ cm/sec	0.56	1.05	1.35
$k_m^2 \times 10^4$	0.31	1.10	1.82

According to Robertson and Staples (equation (5-13)), the plot of km^2 against the gas flowrate should be a straight line. The present experimental results are in good agreement with this statement as shown in Fig.5.2. However, the slope, which is equal to $1.73 \times 10^{-5} \text{ cm}^{-1} \text{ sec}^{-1}$ is much smaller than $2.35 \times (10^{-4} \text{ to } 10^{-3}) \text{ cm}^{-1} \text{ sec}^{-1}$ estimated by equation (5-13). If this difference is accounted for the constant B, in the present system

$$B = 1.73 \times 10^{-5} d^2/D = 0.74-7.4 \text{ cm}^{-1}$$

This is probably caused by the decrease of km in the present system where metal depths were much smaller than those in the Robertson and Staples experiments ⁽³⁴⁾. Presumably, the quantity of liquid entrained in the stream of bubbles is less at shallow depths because the bubble wakes do not become fully developed until the bubbles have travelled a certain height. A value of B equal to 100 cm^{-1} is obtained when the metal depth is greater than 2.5 cm. There is also some uncertainty about the diffusivity of copper in liquid iron.

For the experiments using pure Na_2S , as shown in Fig.4.4, page 51, the rate of copper transfer is smaller than that in the Na_2S -FeS slag under the same flow conditions. The reason will be discussed in the section on the effect of slag composition. The calculated values of km from equation (5-11) are equal to $9 \times 10^{-4} \text{ cm/sec}$ for Run13 and $3.6 \times 10^{-3} \text{ cm/sec}$ for Run15. The difference of km due to the flow condition is the same in pure Na_2S and FeS- Na_2S slag, as shown in Table 5-4. From the discussion above, the conclusion can be drawn that the speeding up of mass transport has a significant effect on the rate of overall reaction.

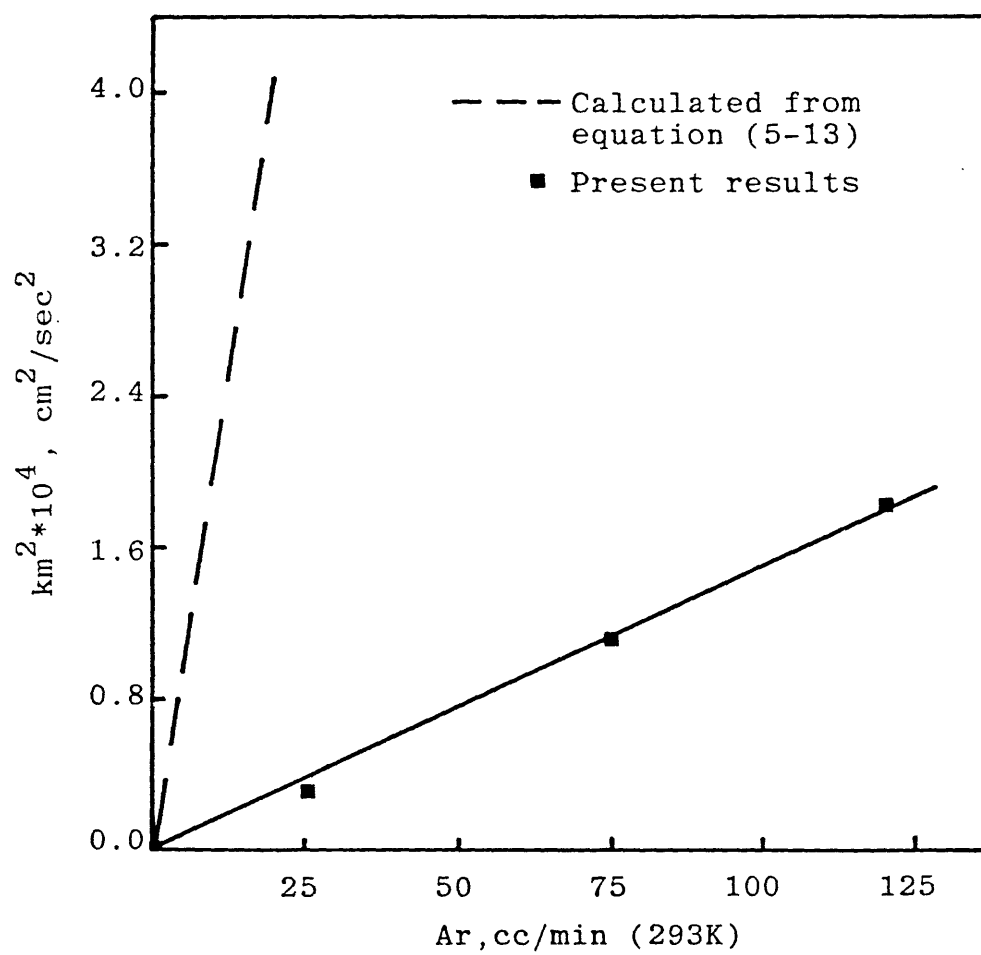


Fig.5.2 Relationship between mass transfer coefficient and gas flowrate

Topkaya⁽⁶⁹⁾ tested the effect of stirring on the reaction of the system which is similar to Run 13 and 15. From an analysis of his results after one hour of reaction, he concluded that there was no significant change in the rate due to speeding up of the mass transport by stirring and that the overall reaction was mainly controlled by interfacial chemical reactions.

Table 5-4

The Similarity of k_m in Different Slags

$k_m \cdot 10^3 \frac{\text{Ar}}{\text{cm/sec}}$ Slag	Surface	Bubbling	$k_m, s/km, b$
S1 Na_2S	0.9	3.6	4.0
S2 30FeS-70 Na_2S	2.95	12	4.07
$k_m, S2/k_m, S1$	3.28	3.33	1.0

From the present results, it is evident that the transfer of copper has reached its partial equilibrium in one hour even when no forced flow was present in the crucible. Topkaya's work was thus concerned with equilibrium conditions rather than reaction rates.

5-1-2. Effect of Initial Copper and Sulphur Content in the Metal

Fig.4.7 and 4.8, page 54, show the experimental results for different initial copper and sulphur contents in the metal. The proportion of reacted copper has a similar value irrespective of the initial copper content throughout the experiments, that is, the rate of reaction and the

refining efficiency represented by the proportion of reacted copper, is not dependent on the initial copper content and 70% of it is removed after 15 minutes under these conditions.

Makar and Brown⁽⁵⁾ obtained the same result, that the relative amount of removed copper was independent of the initial copper content by treatment with sodium sulphate slag.

The absolute quantity of copper reacted increases when the initial copper content is raised although the relative amount removed does not change much. This is due to the dependence of the reaction rate in terms of the absolute quantity upon the amount of reactant present (the chemical driving force at constant volume).

The majority of reactions in extraction metallurgy have been shown to follow first order reaction kinetics. For a reversible reaction of copper transfer,

$$[\text{Cu}\%] = \{\text{Cu}\% \} \quad (5-16)$$

the rate of change of copper in the metal is given by

$$\frac{d[\text{Cu}\%]}{dt} = k_m[\text{Cu}\%] - k_s\{\text{Cu}\% \} \quad (5-17)$$

where k_m and k_s is the rate constant of copper transfer from metal to slag and slag to metal respectively. From the mass balance and under the condition of initial copper content in the slag equal to zero,

$$W_s\{\text{Cu}\% \} = W_m([\text{Cu}\%]_0 - [\text{Cu}\%]) \quad (5-18)$$

and at equilibrium

$$k_s = k_m \frac{[\text{Cu}\%]_e}{\{\text{Cu}\% \}_e} = \frac{W_s k_m [\text{Cu}\%]_e}{W_m ([\text{Cu}\%]_0 - [\text{Cu}\%]_e)} \quad (5-19)$$

Substituting equation (5-18) and (5-19) into (5-17), one can have

$$-\frac{d[\text{Cu}\%]}{dt} = \frac{k_m [\text{Cu}\%]_o [\text{Cu}\%] - [\text{Cu}\%]_e}{h_m [\text{Cu}\%]_o - [\text{Cu}\%]_e} \quad (5-20)$$

Upon integration

$$-\ln \frac{[\text{Cu}\%] - [\text{Cu}\%]_e}{[\text{Cu}\%]_o - [\text{Cu}\%]_e} = \frac{[\text{Cu}\%]_o}{[\text{Cu}\%]_o - [\text{Cu}\%]_e} \frac{k_m}{h_m} t \quad (5-21)$$

Equation (5-21) is exactly in the same form as equation (5-11), however, the physical meaning of k_m here is the rate constant of the copper transfer reaction and mass transport coefficient of copper in the metal in equation (5-11).

As mentioned before, the proportion of reacted copper has nearly the same value irrespective of initial copper content and reaches about 73% after 60 minutes. Assuming at equilibrium state,

$$([\text{Cu}\%]_o - [\text{Cu}\%]_e)/[\text{Cu}\%]_o = 0.73 \quad (5-22)$$

the equilibrium concentration can be calculated from this equation for different initial copper contents.

Fig.5.3 shows the first order plot of equation 5.21. The reaction is divided into two parts. At the first stage up to about seven minutes, a rate constant of 3.69×10^{-3} cm/sec is independent of the initial copper content in the metal, after this point, lower copper and sulphur contents correspond to a smaller rate constant, k_m values equal to 3.18×10^{-4} , 4.22×10^{-4} and 5.76×10^{-4} cm/sec are obtained for Run19, 15 and 34 respectively from Fig.5.3.

Diffusion in the metal and slag is not usually controlling limitation in a gas stirred system. If the mass transport of copper in the metal is presumed to control the process at the first stage, the value of 3.69×10^{-3} cm/sec is the mass transport coefficient of copper in the metal, which is smaller than that obtained from a $\text{FeS-Na}_2\text{S}$ slag, so the transport of copper in the metal is unlikely to be the

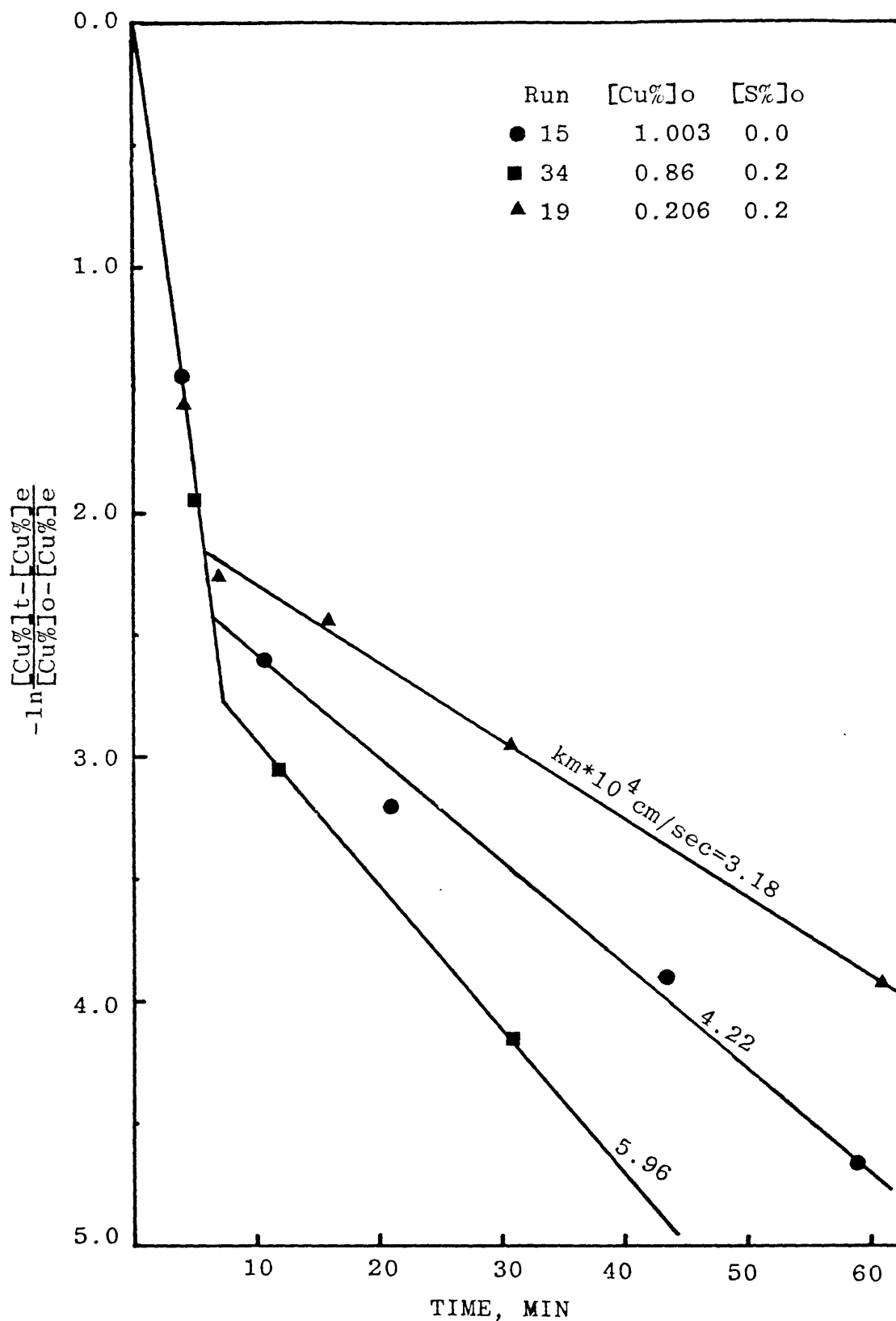
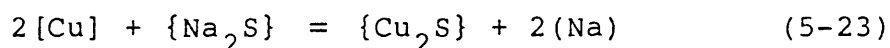


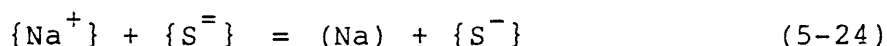
Fig.5.3 First order plot of Fig.4.7 for the effect of [Cuwt%]_o

slowest step.

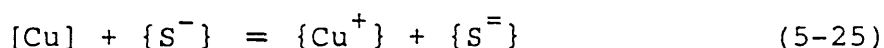
Topkaya and Lu⁽⁷⁷⁾ studied the nature of reactions between sodium sulphide slag and carbon-saturated iron and copper alloys. The reaction



can be expressed more realistically in the following way



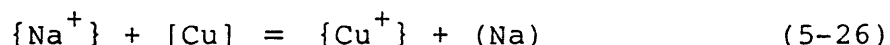
and



The gas/slag reaction (5-24) and slag/metal reaction (5-25) are linked by mass transport processes and electroneutrality conditions for the slag phase. From their results, mass transport processes across slag layer are unlikely to be the slowest ones, as is the case in the present work. They considered that the interfacial reactions (5-24) and (5-25) and diffusion of sodium vapour are the rate controlling steps from their work.

From mathematical modeling studies, Okazaki⁽³³⁾ found that the transport of sodium vapour affected the rate of copper transfer remarkably in the case of pure sodium sulphide slag and it is significantly accelerated by the increase of the flowrate of argon bubbled in.

Reaction (5-24) and (5-25) can be simplified to



During the first stage of reaction, the rate of transfer of copper is dependent on this interfacial reaction which involves the changes of electron and the nucleation and diffusion of sodium vapour. Any of them may contribute to the rate control of the process. As the concentration of copper in the slag becomes bigger, the rate of reverse

reaction of copper, equation (5-27), increases.



then, plays an important role in the process. So the transfer of copper is controlled by the balance of forward and reverse reaction of (5-27) in the second stage.

The point at which the rate constant changes can be judged as the time that the reverse reaction starts to dominate the process. The initial metal contains about 0.2wt% sulphur in both Run19 and 34 and nearly 0.0wt% in Run15. Comparing the three lines, high initial sulphur and copper are not favourable to the reverse reaction, so that it starts to be important later and is less so than with lower initial sulphur and copper contents.

From Fig.4.8, page 54, the proportion of reacted copper under all experimental conditions tested lie close to a single curve and this is explained below.

At the equilibrium of copper transfer the distribution coefficient of copper between slag and metal is constant close to 18.

$$D = \frac{\{Cu\}_e}{[Cu]_e} = \frac{W_m([Cu]_o - [Cu]_e)}{W_s[Cu]_e} = 18 \quad (5-28)$$

Defining $Z = DW_s/W_m$, at present system $Z = 2.7$, and rearranging equation (5-28) gives

$$[Cu]_o = (1 + Z)[Cu]_e \quad (5-29)$$

The proportion of reacted copper, as defined above

$$R = ([Cu]_o - [Cu]_t)/[Cu]_o \quad (5-30)$$

at equilibrium and substituting (5-29) into (5-30),

$$R = \frac{(1+Z)[Cu]_e - [Cu]_e}{(1+Z)[Cu]_e} = \frac{Z}{1+Z} \quad (5-31)$$

Z is a function of thermodynamic properties of the system and the weight ratio of slag to metal and is independent of

the initial copper content. In the present system, R is equal to 0.73, or 73% at final equilibrium of copper transfer.

From equation (5-21), one can express $[Cu\%]_t$ as a function of $[Cu\%]_o$, km and other factors. Substituting this $[Cu\%]_t$ and equation (5-29) into (5-30) gives

$$R = (1 - e^{-Gt})Z/(1+Z) \quad (5-32)$$

where G is equal to $(1+Z)km/Zhm$.

This equation is applicable to those reactions which satisfy a first order plot in the present system, and it is independent of the initial copper content. However, at the second stage, the value of km changes. Similarly, one can derive

$$R = (1 - e^{C-Gt})Z/(1+Z) \quad (5-33)$$

where C is equal to the intercept on the vertical axis in Fig.5.3. Because G and C change with different initial copper contents, in turn, the proportion of reacted copper is actually affected by it. This is shown in Fig.5.4 by comparing experimental results with the plot of equations (5-32) and (5-33) on a large scale.

5-1-3 Effect of Slag Composition

The changes of composition of slag during a run, especially with respect to iron content as shown in Fig.4.1 and 4.2, page 48 and 49, differ radically in pure Na_2S slags and those containing 30%FeS initially.

In pure Na_2S slag, the principal chemical reactions taking place and the corresponding values of ΔG^0 are:

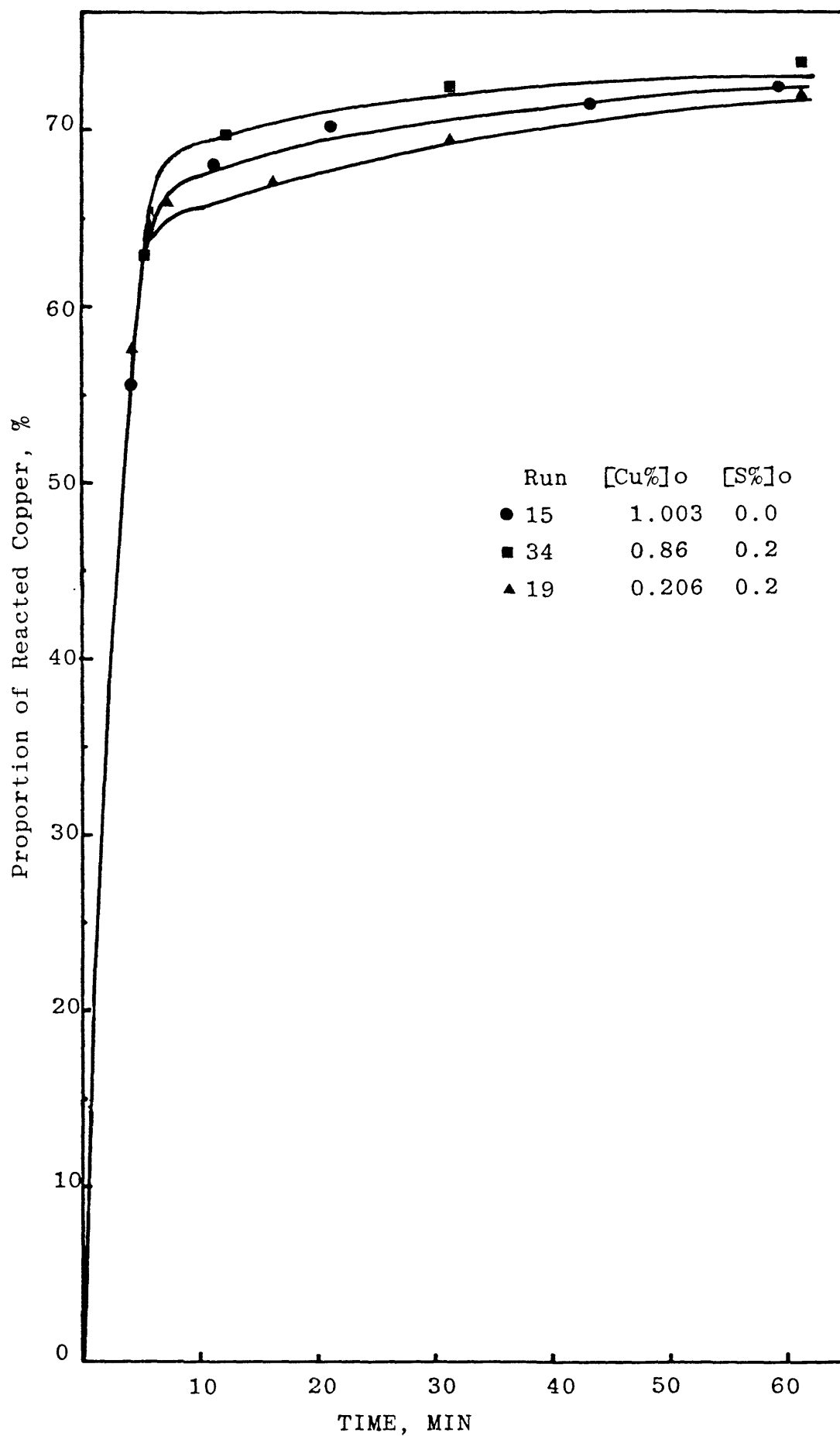
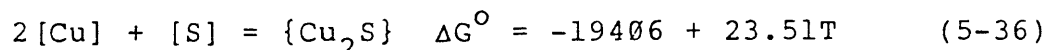
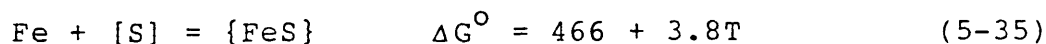
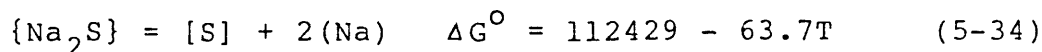
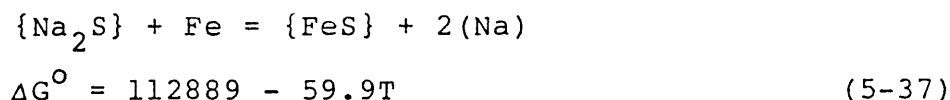


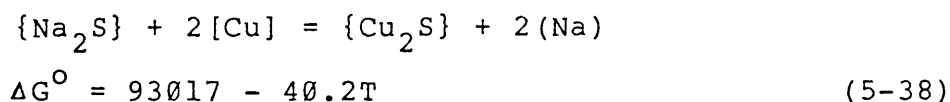
Fig.5.4 Effect of initial Cu and S content



Where the unit of ΔG° is Cal/Mole. Reactions (5-34), (5-35) and (5-36) can be combined as:



and



If the reaction is at equilibrium, the partial pressure of sodium should be in equilibrium with reactions (5-34), (5-37) and (5-38).

For (5-34)

$$p_{\text{Na}}^2 = \frac{K_{34} \gamma_{\text{Na}_2\text{S}} X_{\text{Na}_2\text{S}}}{f_{\text{S}} [\text{S}\%]} \quad (5-39)$$

For (5-37)

$$p_{\text{Na}}^2 = \frac{K_{37} \gamma_{\text{Na}_2\text{S}}^a \gamma_{\text{Fe}} X_{\text{Na}_2\text{S}}}{\gamma_{\text{FeS}} X_{\text{FeS}}} \quad (5-40)$$

For (5-38)

$$p_{\text{Na}}^2 = \frac{K_{38} \gamma_{\text{Na}_2\text{S}}^f \gamma_{\text{Cu}}^2}{\gamma_{\text{Cu}_2\text{S}}} \cdot \frac{X_{\text{Na}_2\text{S}} [\text{Cu}\%]^2}{X_{\text{Cu}_2\text{S}}} \quad (5-41)$$

where

K — equilibrium constant, calculated from

$$\Delta G^\circ = -RT \ln K.$$

X — mole fraction of components in the slag.

γ — activity coefficient of components in the slag.

Topkaya⁽⁶⁹⁾ obtained $\gamma_{\{\text{FeS}\}} = 0.06$, and $\gamma_{\{\text{Na}_2\text{S}\}} = 0.9$ by taking sulphur-saturated iron in equilibrium with pure molten iron sulphide as the reference state, employing pure

sodium sulphide as the initial slag for carbon-saturated iron at 1523K and using equation (5-42).

$$\gamma_{\text{FeS}} X_{\text{FeS}} = \frac{[\text{S}\%]_{(\text{Na}_2\text{S-FeS})}}{[\text{S}\%]_{(\text{FeS})}} \quad (5-42)$$

Substituting Topkaya's data into equation (5-40) and assuming a_{Fe} equal to one, the partial pressure of sodium at different reaction times can be calculated following the change of $X_{\text{Na}_2\text{S}}$ and X_{FeS} based on Run34, and the results are plotted in Fig.5.5 as a solid line. Also plotted in Fig.5.5 the dashed line indicates the measured partial pressure of sodium calculated from the loss of sodium and the argon volume bubbled in. The two sets of values are in good agreement during the period of 10th to 40th minutes and it is difficult to compare them at the initial stages because of experimental errors. From the above calculation, it is clear that pure Na_2S slag produces a lot of sodium fume during the transfer of copper from metal to slag.

At equilibrium, the calculated partial pressure of sodium should also satisfy equation (5-41). Combining equation (5-40) with (5-41), one can derive,

$$\gamma_{\text{Cu}_2\text{S}} = \frac{K_{38} f_{\text{Cu}}^2 \gamma_{\text{FeS}}}{K_{37}} \cdot \frac{[\text{Cu}\%]^2 X_{\text{FeS}}}{X_{\text{Cu}_2\text{S}}} \quad (5-43)$$

The activity coefficient of copper, f_{Cu} , can be calculated from available interaction coefficient data⁽⁸⁰⁾ to be equal to 2.25. γ_{FeS} equal to 0.06 is substituted into equation (5-43). The calculated values of $\gamma_{\text{Cu}_2\text{S}}$ thus obtained from the experimental data of Run34 are shown in Table 5-5.

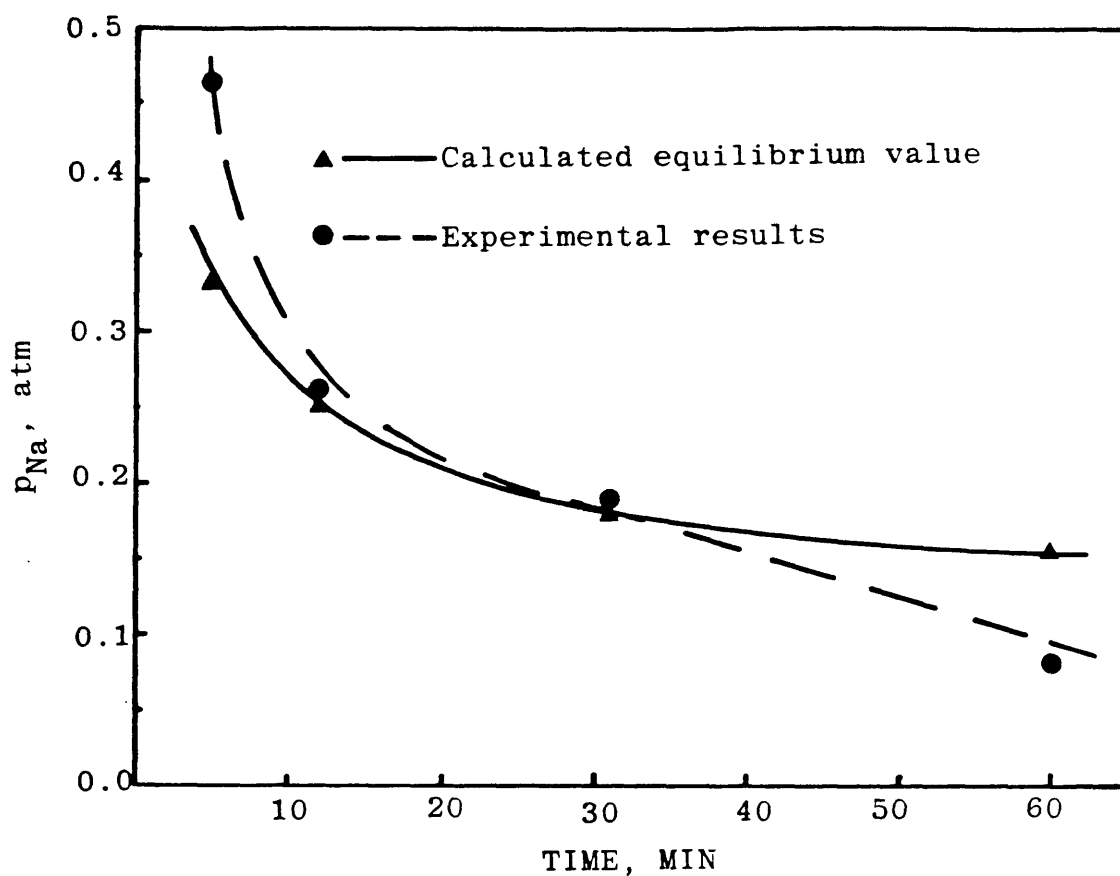


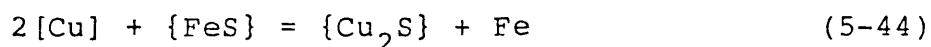
Fig.5.5 Changes of partial pressure of sodium

Table 5-5

The Calculation of $\gamma_{\text{Cu}_2\text{S}}$

Time	5	12	31	60
[Cu%]	0.319	0.26	0.235	0.223
x_{FeS}	0.049	0.152	0.258	0.322
$x_{\text{Cu}_2\text{S}}$	0.021	0.023	0.925	1.026
$\gamma_{\text{Cu}_2\text{S}} \cdot 10^3$	4.8	4.7	6.0	6.5

The mean value obtained for $\gamma_{\text{Cu}_2\text{S}}$ is equal to 0.0055 which shows a strong negative deviation from ideal solution. Topkaya⁽⁶⁹⁾ obtained $\gamma_{\text{Cu}_2\text{S}}$ equal to 0.01 in the ternary FeS-Cu₂S-Na₂S system based on the calculated activity of FeS in the slag and the equilibrium constant of the reaction



His value is greater than that calculated in the present work and this is partly due to the different thermodynamic data chosen to calculate the equilibrium constants.

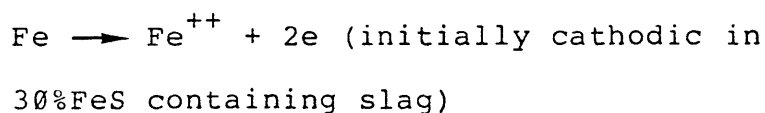
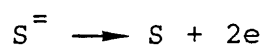
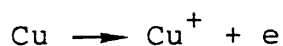
The relationship between the transferred moles of various elements, as shown in Fig.5.6, is satisfied with equation (5-45)

$$n_{\text{Na}} = n_{\text{Cu}} + 2n_{\text{Fe}} + 2n_{\text{S}} \quad (5-45)$$

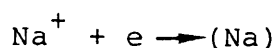
The sum of the equivalents of Fe, Cu and S corresponds closely with the equivalent of sodium lost from the slag throughout. An exact correspondence is not expected in view of experimental and analytical errors, also due to the assumption that the slag contains only Fe^{++} , Cu^+ , Na^+ and $\text{S}^{=}$.

These observations indicate that the transfer reactions in the system can be regarded as electrochemical partial reactions:

Anodic



Cathodic



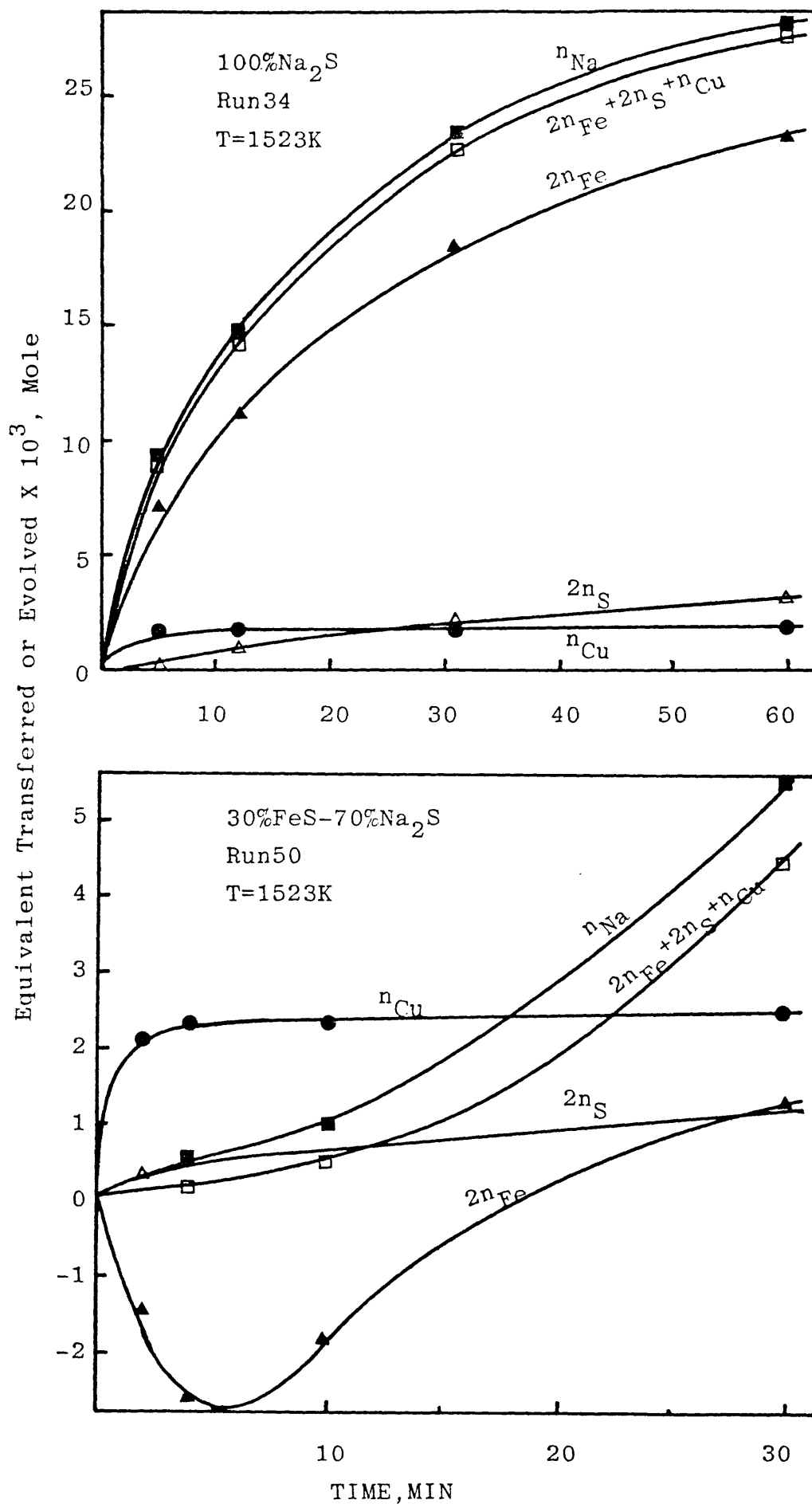
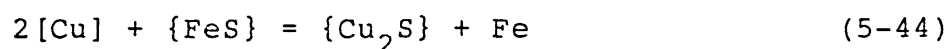


Fig.5.6 Equivalent transferred or evolved moles of elements in the process

Each atom of copper and iron which transfers to the slag must give up its electrons at the phase boundary. To preserve electroneutrality, sodium must pick-up the electrons produced by anodic reactions. Conversely, the loss of sodium from the slag may induce the anodic reactions to take place. In the case of the slag containing FeS initially, the reverse transfer of Fe^{++} into the metal becomes cathodic reaction which neutralizes the process of the transfer of copper and sulphur, and greatly reduces the loss of sodium.

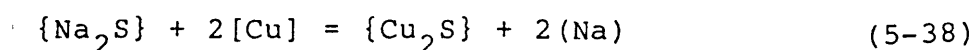
In a pure sodium sulphide slag, the consumption of sulphur due to the transfer of copper and iron depends on the decomposition of sodium sulphide; iron competes with copper for sulphur, accelerating the loss of sodium.

When the initial slag contains 30%FeS, only copper reacts with sulphur and is transferred into slag at the start of the process. The reactions taking place in the system in the first a few minutes are mainly

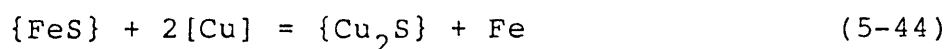


and the transfer of sulphur in the metal. From Fig.5.6, the moles of iron transferred from the slag to metal is not less than that of copper into the slag up to the 4th minute, indicating that the importance of reaction (5-38) is less during this time. The loss of sodium is initially slow and is accelerated by the transfer of iron into the slag. The overall loss of sodium from slag and of iron from the metal are substantially reduced when using a 30%FeS slag.

Comparing the free energy changes and equilibrium constants at 1523K.



$$\Delta G^{\circ} = 93017 - 40.2T ; \quad K = 2.72 \times 10^{-5}$$



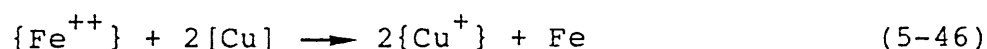
$$\Delta G^{\circ} = -19872 + 19.71T ; \quad K = 3.5 \times 10^{-2}$$

it is clear that the displacement of copper by iron is easier than that by reaction (5-38). When the transfer of copper reaches (or is close to) its partial equilibrium, these two reactions become insignificant and the process is carried out by reactions (5-34) and (5-37). There is not much difference in the composition of the final slags for initially pure Na_2S and 30%FeS-70% Na_2S . The distribution of copper at equilibrium between the slag and metal is the same in both cases, so that as described in equation (5-31) ($R=Z/(1+Z)$), the proportion of reacted copper is the same at the end of the process in both cases.

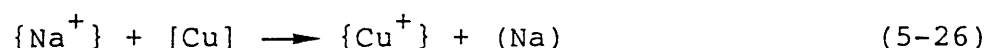
Leis et al⁽⁵⁾ pointed out that for any amount of metal and sodium sulphide at the beginning of an extraction, there was some minimum final concentration of FeS that might be reached in the slag phase. If the initial iron sulphide concentration in the slag phase was more than this, they considered that the slag would not undergo a reverse reaction ($\{\text{FeS}\} = \text{Fe} + [\text{S}]$) since there would not be enough copper to remove a significant amount of iron from the slag. The change of iron content in a Na_2S -FeS slag in their results was thus corrected to a continuous increase or unchanged throughout the experiments, even though the analyzed results showed an initial decrease, followed by an increase. This is not confirmed from the present studies. The importance of reaction (5-44) at the beginning in a FeS containing slag has been neglected in their work.

The transfer of copper into slag is quicker in 30%FeS

slag than that in pure Na_2S slag as shown in Fig.4.10, page 56, The transfer coefficient of copper km is equal to 3.69×10^{-3} and $1.2 \times 10^{-2} \text{ cm/sec}$ for pure Na_2S and 30%FeS slag at the initial stages respectively as calculated above. This indicates that the displacement of copper by iron is faster than that by sodium as expressed below



and



If the reaction (5-46) is controlled by the mass transport of copper in the metal, the reaction (5-26) must be controlled by some other slower steps. Mass transfer of copper is definitely not rate determining as shown in section 5-1-2. Any of the following steps or a combination of them may control the rate of copper transfer: 1. the supply of Na^+ to the reaction site, 2. electrochemical process of (5-26) and 3. the removal of sodium vapour.

The effect of more than 30%FeS in the initial slag on the rate of the copper transfer can not be accurately assessed from the present runs because of the rapidity of the reactions. However, the final refining efficiency, the proportion of reacted copper, is somewhat decreased. Simultaneously, the final sulphur content in the metal is increased with a higher FeS slag, which is due to the easier release of sulphur from FeS than that from Na_2S . One of the reasons of the decrease of reacted copper in a higher FeS slag is probably that the amount of slag is reduced since FeS decomposes into the metal.

It appears that 30%FeS-70% Na_2S slag is the optimum composition used in the present studies, since it reduces

the consumption of sodium sulphide which is more expensive than iron sulphide, minimizes the loss of sodium from the slag (which produces an objectionable sodium fume in the gas phase), increases the recovery of iron in the metal phase, speeds up the transfer of copper and achieves a similar refining efficiency and final sulphur content as is obtained from pure sodium sulphide slag.

The substitution of 10% Na_2S by CaO changes the rate and final state dramatically as shown in Fig.4.11, page 58, A lower final sulphur and higher final copper content in the metal resulted. Fast transfer of copper was observed with the addition of CaO in the initial slag.

Run38 did not obey first order reaction kinetics, but Run60 did, a copper transfer coefficient of k_m equal to $3.5 \times 10^{-3} \text{ cm/sec}$ for the first seven minutes was obtained. This value is a little higher than that for argon surface purge in the same slag composition. At the end of first minute, the copper transferred was 3.15×10^{-6} and $8.47 \times 10^{-7} \text{ mole/cm}^2\text{sec}$ in Runs 60 and 38 respectively, which gives a 3.7 fold increase in the initial rate due to the slag containing 10% CaO .

The reasons for the acceleration of decopperization by CaO are not clear. The agitation by CO bubbles may be a relevant factor. The reactions



can take place in this system.

However, if 10% CaO is replaced by 10% CaS , the transfer of copper is still speeded up. No CO bubbles formed in this case, so the presence of Ca^{++} must have affected the kinetic

process of copper transfer in some unknown way.

At the final equilibrium state, CaO definitely reduces the distribution coefficient of copper. A value of D equal to 12.0 and 11.4 is obtained from the analysis of final copper in the slag and from equation (5-31) respectively.

Considering reaction



its equilibrium constant,

$$K = \frac{a_{\text{Cu}_2\text{S}}}{a_{\text{S}} a_{\text{Cu}}^2} = \frac{\gamma_{\text{Cu}_2\text{S}} X_{\text{Cu}_2\text{S}}}{f_{\text{S}} f_{\text{Cu}}^2 [\text{S}\%] [\text{Cu}\%]^2} \quad (5-49)$$

changing mole fraction of Cu_2S into weight percent concentration of copper in the slag and rearranging (5-49),

$$D = \frac{\{\text{Cu}\% \}}{[\text{Cu}\%]} = \frac{MK f_{\text{S}} f_{\text{Cu}}^2 [\text{S}\%] [\text{Cu}\%]}{\gamma_{\text{Cu}_2\text{S}}} \quad (5-50)$$

where M is a constant introduced by the change of the unit of the concentration.

K decreases with increase of the operating temperature, but it does not change with the composition of the slag and the metal. Oxygen lowers the activity coefficient of copper and sulphur in the metal, however, the concentration of oxygen in the metal is low in a carbon saturated iron. If the effect on f_{S} and f_{Cu} is less significant and $[\text{S}][\text{Cu}]$ is unchanged, CaO could increase $\gamma_{\text{Cu}_2\text{S}}$ resulting in a lower D value, this might be the case. Additionally, CaO is a well known desulphurization agent and it may decrease the $[\text{S}]$ at equilibrium.

Equation (5-50) also explains why D does not change much with the addition of 30%FeS in pure Na_2S , since the final compositions of the slag and metal are similar.

5-1-4. Effect of the Weight Ratio of Slag to Metal

As shown in section 5-1-2, at the final equilibrium of copper transfer the proportion of reacted copper can be expressed by equation

$$R = Z/(1 + Z) \quad (5-31)$$

in which Z is equal to DW_s/W_m . If the weight ratio of W_s/W_m is defined as c , equation (5-31) can be written as

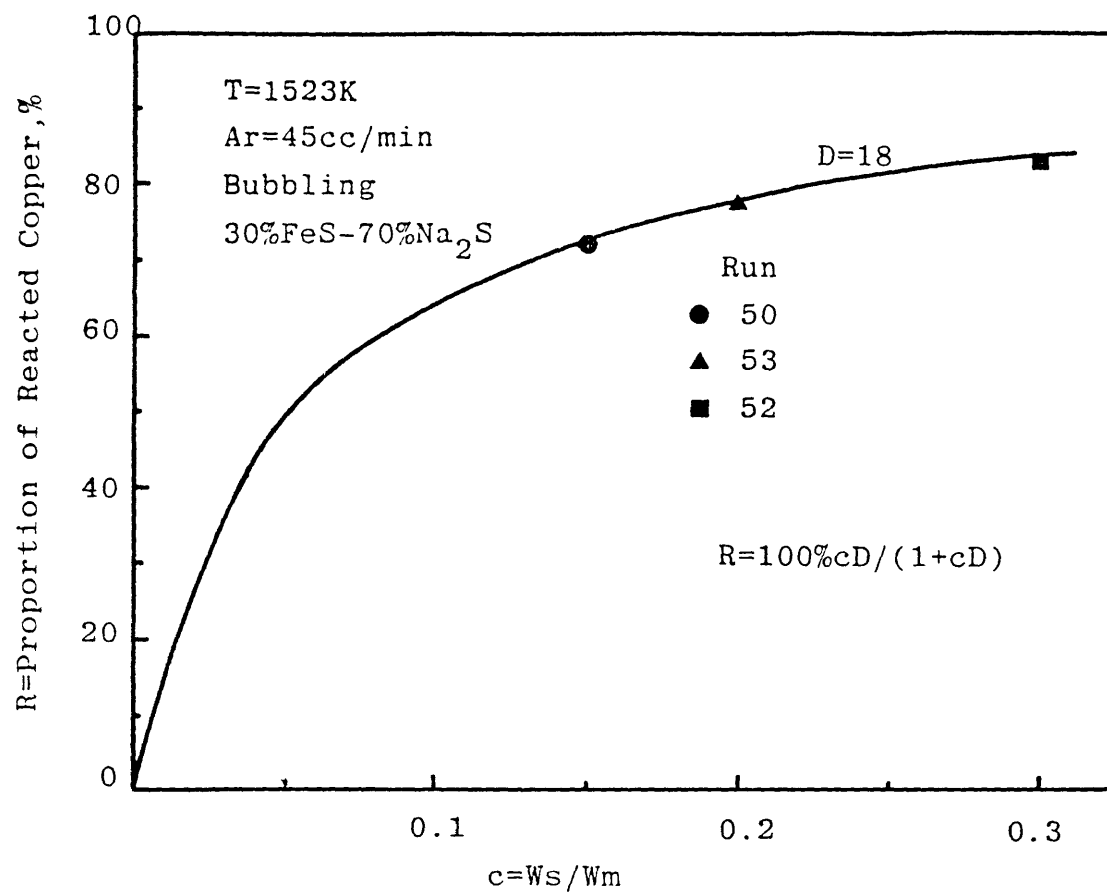
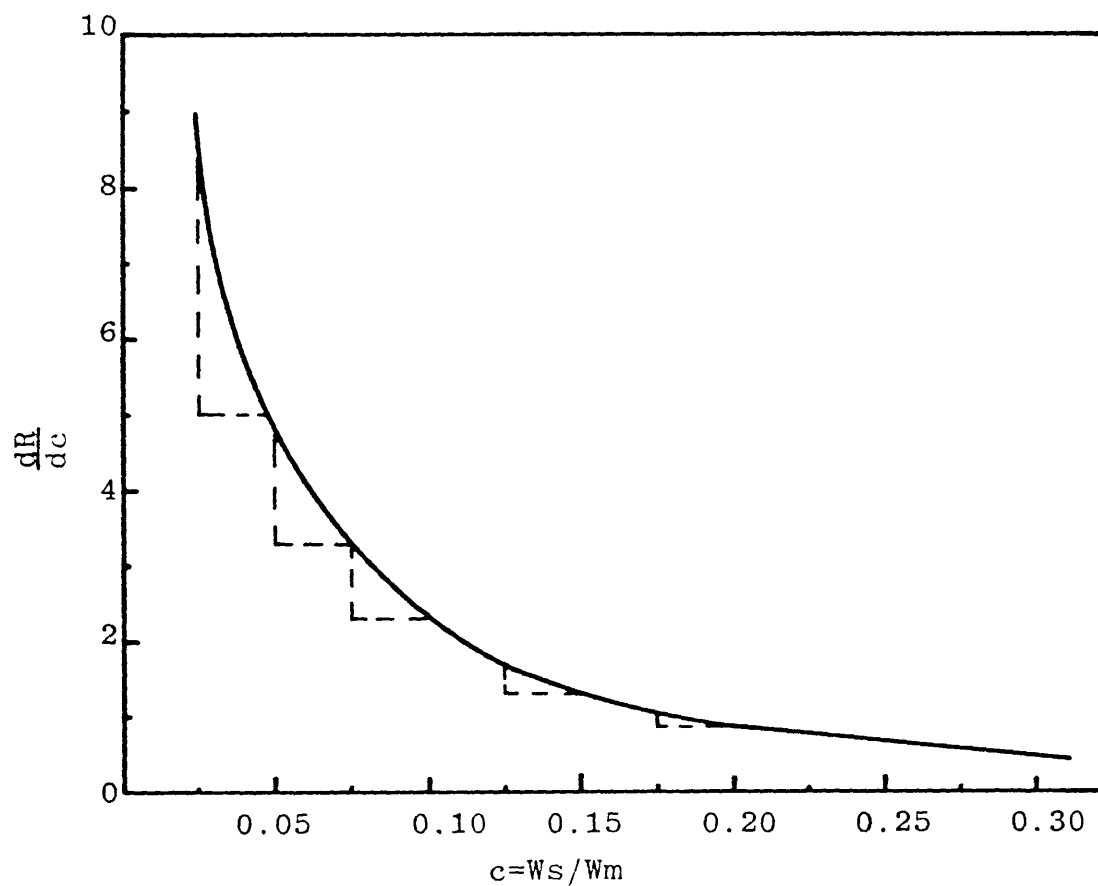
$$R = 100\%cD/(1 + cD) \quad (5-51)$$

A value of $D=18$ is used to test the relationship between c and R at a constant D . Fig.5.7 shows that the experimental results of runs 50, 52 and 53, as shown in Fig.4.12, page 59, are in good agreement with those calculated from equation (5-51), which indicates that the proportion of reacted copper is a function of the weight ratio of slag to metal.

It is not economically worthwhile to increase the refining efficiency by more consumption of slag, especially in W_s/W_m ratio higher than 0.2. This can be explained by differentiating equation 5-51 with respect to c at a constant D .

$$\frac{dR}{dc} = 100\%D/(1+cD)^2 \quad (5-52)$$

Fig.5.8 shows that the slope of the curve in Fig.5.7, dR/dc , falls dramatically as c increases. This is why the proportion of reacted copper is increased in equal steps of 5% from 71.4% to 76.6% and from 76.6% to 81.9% when c is changed in the different ratios of 0.2/0.15 (1.33) and 0.3/0.2 (1.50). If the slag is divided into two refining processes at a total $c=0.3$, which can be achieved in practice by tapping slag, total removal of copper will reach

Fig.5.7 Effect of the Ws/Wm ratioFig.5.8 Effect of the Ws/Wm ratio

92.7% of initial content, compared with 84% obtained by adding $c=0.3$ slag in one operation from equation (5-51).

R value can be increased by increasing the distribution coefficient of copper. If the D value is raised to 25, from equation (5-51) the reacted copper at $c=0.15$ will reach 79% which depends on the slag consumption of 20wt% of the metal weight at $D=18$.

As shown in equation (5-50), D is a thermodynamic characteristic of the system and related to the compositions of the slag and metal and temperature. It can be raised by increasing the activity coefficients of copper and sulphur in the metal and decreasing the activity coefficient of copper sulphide in the slag, also by lowering the operating temperature which gives a greater equilibrium constant for the copper transfer reaction of (5-36).

5-1-5. Effect of Temperature

The reactions are so fast that the copper transfer nearly reaches its equilibrium in ten minutes, as shown in Fig.4.13, page 61. This makes some difficulties in taking enough samples to make an accurate kinetic curve for the determination of the initial rate. A first order of reaction which is usually the case in high temperature metallurgical systems, and an initially irreversible reaction due to absence of copper in slag are assumed. The rate equation

$$kt = -\ln([Cu]_t/[Cu]_o) \quad (5-53)$$

where

$$k = \text{rate constant, min}^{-1}$$

is used to calculate k for first five minutes and the

results are given in Table 5-6.

The dependence of k on temperature can be related to the activation energy by the equation

$$\frac{d \ln k}{d(1/T)} = -\frac{E}{R} \quad (5-54)$$

The activation energy E is obtained by plotting $\ln k$ against $1/T$, as shown in Fig.5.9. The slopes of the lines have the value $-E/R$ giving the apparent energy of activation for decopperization. The calculation gives E equal to 5.9 Kcal/mole (25KJ/mole) between 1523 and 1623K and 41 Kcal/mole (170KJ/mole) between 1473 and 1523K.

From the calculation above, the increase of operating temperature from 1473 to 1523K significantly affects the rate of the process but at higher temperatures the rate increase becomes proportionately less.

However, the higher the operating temperature the final copper and sulphur contents in the metal are greater, that is, faster reaction is accompanied by a lower refining efficiency in terms of the final proportion of reacted copper.

The effect of temperature on the equilibrium constant K can be derived readily from the dependence of standard free energy changes on temperature and expressed as

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^{\circ}}{R} \quad (5-55)$$

Upon integration under the assumption that ΔH° is independent of temperature in the range studied,

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5-56)$$

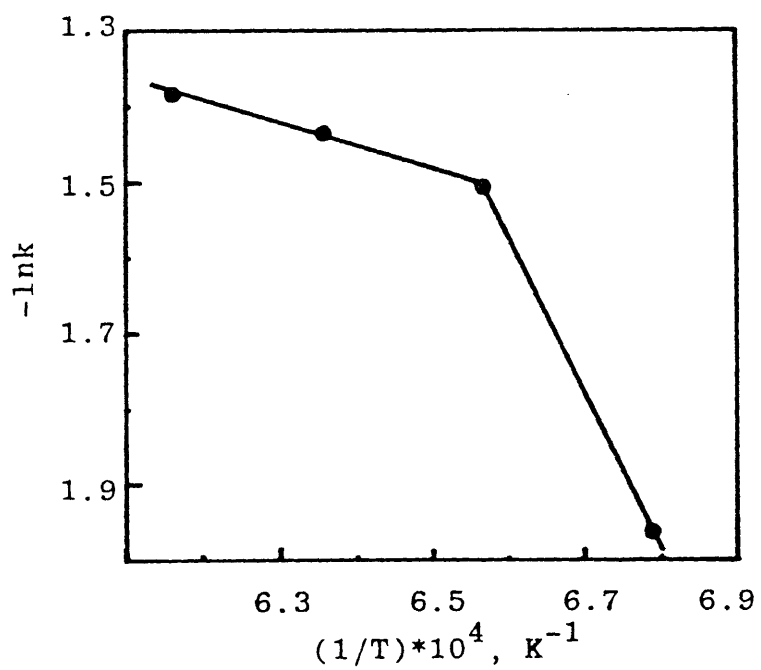
For the reaction,



Table 5-6

Effect of Temperature on Rate Constant

T K	1473	1523	1573	1623
$1/T \times 10^4$	6.79	6.57	6.36	6.16
$k \text{ min}^{-1}$	0.141	0.223	0.239	0.253
$-\ln k$	1.96	1.50	1.43	1.38

Fig.5.9 Plot of $\ln k$ against $1/T$

$$\Delta G^{\circ} = \Delta H^{\circ} - \Delta S^{\circ}T = - 19406 + 23.5T$$

the equilibrium constant is

$$K = \frac{v_{\text{Cu}_2\text{S}}}{f_{\text{S}} f_{\text{Cu}}^2} \cdot \frac{X_{\text{Cu}_2\text{S}}}{[\text{S}\%][\text{Cu}\%]^2} \quad (5-57)$$

In equation (5-56), when T_1 and T_2 are equal to 1523 and 1573K respectively, the change of equilibrium constant of reaction (5-36)

$$K_{1523} = 1.227K_{1573}$$

Usually, $v_{\text{Cu}_2\text{S}}$, f_{S} and f_{Cu} do not greatly change with a small variation of temperature, so the ratio of $X_{\text{Cu}_2\text{S}}$ to $[\text{S}\%][\text{Cu}\%]^2$ should be decreased to produce a lower K value due to the increase of temperature. This results in either increases of the content of copper and sulphur in the metal or the decrease of the concentration of copper sulphide in the slag. Experimental results indicated the former, but unfortunately, no slag analyses were carried out in this series of experiments.

Also greater evolution of sodium at higher temperatures reduces the amount of sodium sulphide in the slag which is a good solvent for copper sulphide. It was found that temperature had a marked effect upon copper removal by a mixture of sodium sulphite and graphite in an air atmosphere⁽⁴⁸⁾. At about 1698K (1425°C) the copper level remained relatively constant after initial removal, however, in the region of 1943K (1670°C), a definitely strong reversion of copper occurred and less slag was left in the crucible. These authors believed that the effects of temperature noted above were related to the evolution of a white fume, which appeared in runs carried out above 1698K (1425°C) and supposed to be principally sodium oxide.

Considering the reaction rate and the control of [Cuwt%] and [Swt%], 1523K appears to be the most suitable operating temperature for decopperization of carbon saturated iron.

5-2 DECOPPERIZATION OF MOLTEN STEEL

5-2-1. Effect of Slag Composition

From the free-energy diagram for sulphides shown in Fig.5.10⁽⁸⁴⁾, at 1833K (1560°C), the free-energy change of the formation (or decomposition) of magnesium sulphide is equal to that of sodium sulphide at 1523K (1250°C), and calcium sulphide is much more stable than either of these. It was expected that magnesium sulphide would have the same effect on the removal of copper at 1873K as that sodium sulphide had at 1523K (1250°C), and that it would decompose less than sodium sulphide because the latter produced a lot of sodium fume at 1873K. However, the experimental results did not agree with this tentative idea. This probably indicates that the activity coefficient of copper sulphide is greater in the system $\text{MgS-FeS-Cu}_2\text{S-Na}_2\text{S}$ than that in $\text{Na}_2\text{S-FeS-Cu}_2\text{S}$.

Table 4-3, page 63, shows that less than 30% of initial copper can be removed in most of slag compositions. This is mainly caused by a higher operating temperature and lower carbon content. Within different compositions of slags, 30%FeS-70%Na₂S still has a greatest capacity for copper sulphide, as shown in Fig.4.17, page 65. Considering the reversion of copper in all these slags, which is due to the reduced amount of slag, the refining period should be controlled to less than ten or even five minutes.

When MgS in the slag 40%MgS-40%FeS-20%Na₂S is replaced by the same amount of MgO, the proportion of reacted copper is decreased to a much lower level as shown in Fig.4.18,

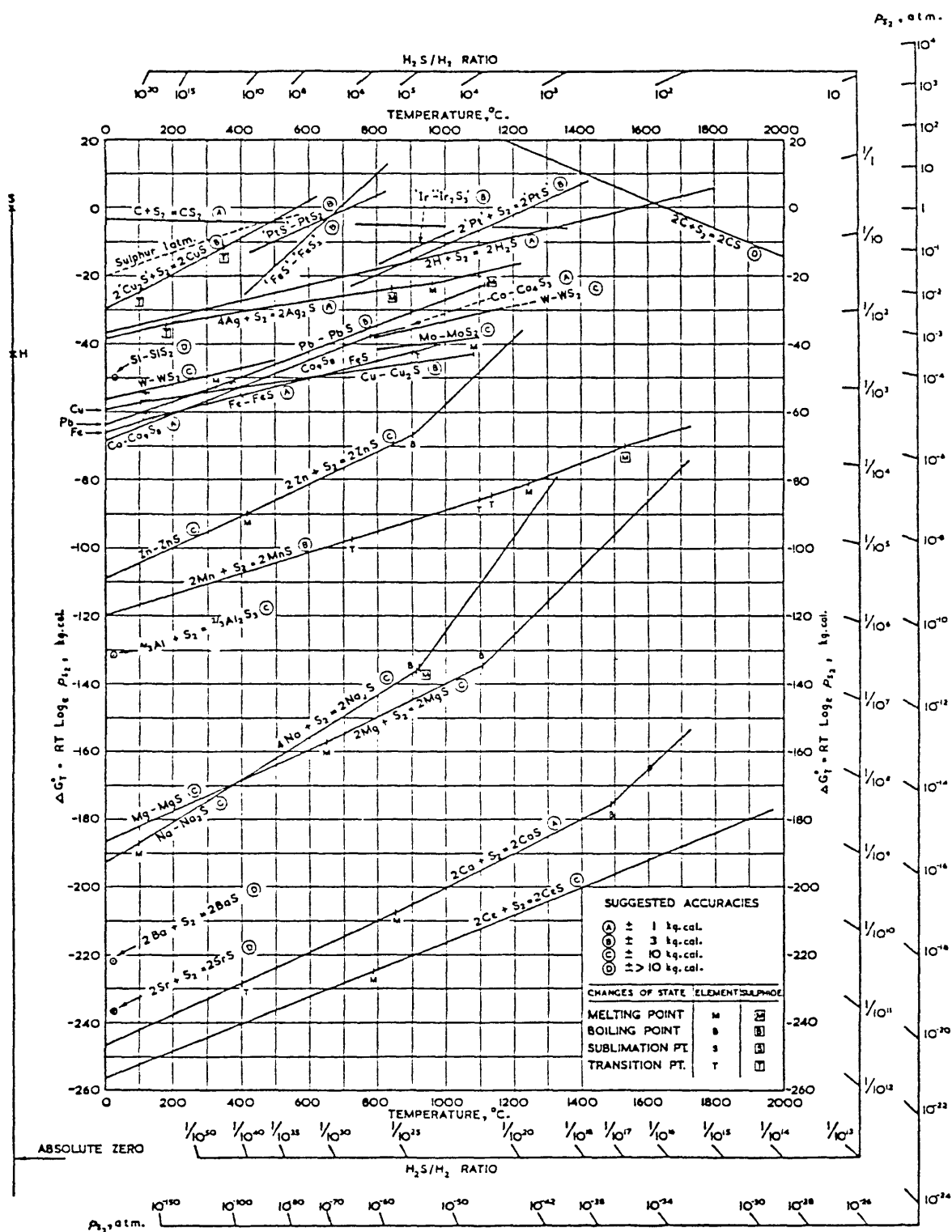
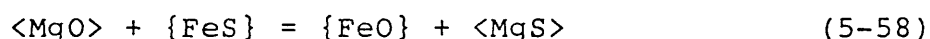


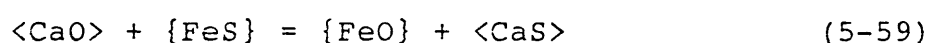
Fig.5.10 Free energy diagram for sulphides of metals

page 66, This indicates that MgO is not a promising component of slags to remove copper from steel. However, the same replacement of CaS by CaO in the slag 30%CaS-30%FeS-40%Na₂S results in only a little reduction of the proportion of reacted copper, Fig.4.19, page 67. As observed in Fig.4.17, slag containing MgS and CaS respectively has a similar potential for the removal of copper, so that CaO and MgO affect the removal of copper from steel by a sulphide mixture slag differently, as shown in Fig.4.20, page 68.

For reactions of CaO and MgO with FeS and their free energy changes⁽¹⁰⁾,



$$\Delta G^{\circ} = 15234 + 1.135T$$



$$\Delta G^{\circ} = -8146 + 2.635T$$

where bracket $\langle \rangle$ denotes solid and $\{ \}$ liquid. The equilibrium constant at 1873K (1600°C) is equal to 9.42×10^{-3} for reaction (5-58) and 2.37 for (5-59). Turkdogan⁽¹⁰⁾ also explained why CaO was easier to react with sulphur to form CaS than MgO to form MgS in the case of desulphurization. His examples are given in Fig.5.11 for the reaction



The higher the equilibrium ratio $a_{\text{O}}/a_{\text{S}}$, the easier the formation of sulphide. The products of the reaction (5-59) formed a melt above 1108K (835°C)⁽⁸³⁾.

In the present system, the metal phase contains about 0.48%C and is nearly free of oxygen. As FeO forms in the slag, it will decompose into the metal to establish a equilibrium with oxygen in the slag and also some of it

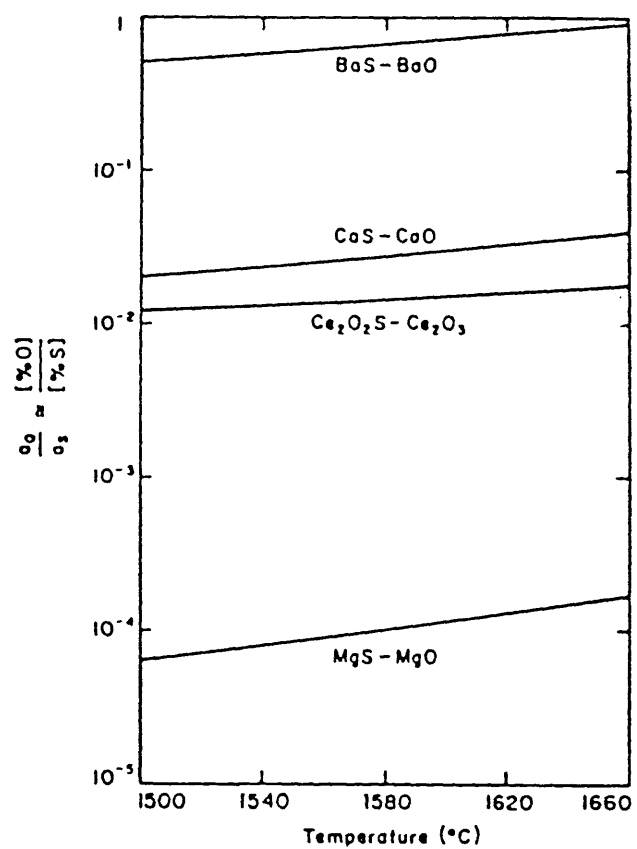


Fig.5.11 a_O/a_S ratio in liquid iron for the indicated sulphide-oxide equilibrium

reacts with carbon. This makes reaction (5-59) more favourable towards the right hand side and produces more CaS in the slag. These reactions change the composition of the slag into a mixture of Na_2S -FeS-CaS-CaO-FeO. If the concentration of $\text{O}^{=}$ in the slag is much lower than the initial slag due to their transfer into the metal and possible evolution of CO, the final composition of slag is probably similar to those initially containing Na_2S , CaS and FeS.

In MgO containing slag, if reaction (5-58) does not take place or only a small amount of MgS is produced, the concentration of MgO in the final slag will not be reduced. The concentration ratio of oxygen to sulphur in the final slag is greater in MgO containing slags than that of CaO containing slags. Steel making slags, as is the case with known oxide slags, have no capability to remove copper, so it is probable that the more the oxide in the slag, the less efficient the removal of copper.

5-2-2 Effect of Carbon Content in the Metal

The removal of copper from iron with a low carbon content is not as good as that obtained in carbon-saturated iron as shown in Fig.4.21 and 4.22, page 69. Fig.5.12 shows the relationship between the proportion of reacted copper and initial carbon content in the metal. To explain this effect, the thermodynamic properties of the liquid metal solutions must be considered.

Investigations of the ternary iron-copper-carbon

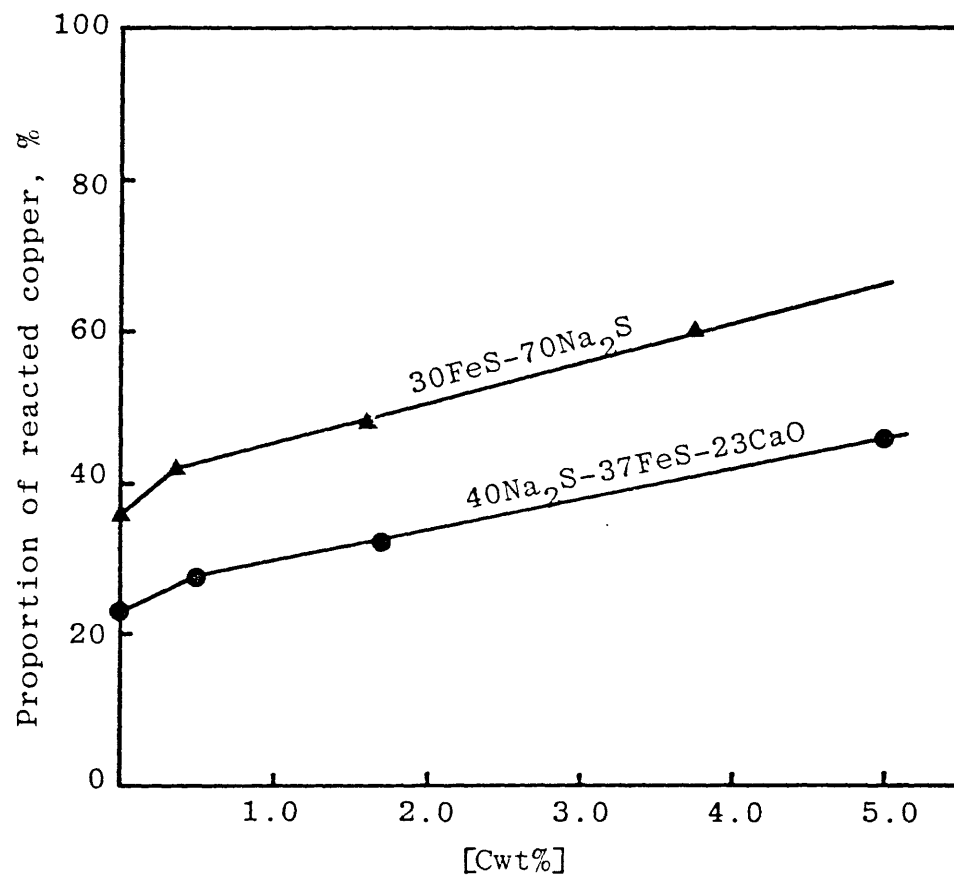


Fig.5.12 Effect of carbon content in the metal

system⁽⁸⁵⁾ have shown an increasing tendency for immiscibility in the system as the content of either copper or carbon increases, from which it is anticipated that the activity of copper in iron will be raised by the addition of carbon.

The transfer of copper expressed by the reaction,



is extremely fast at 1873K (1600°C) and reaches equilibrium in five minutes. The equilibrium constant of reaction (5-36)

$$K = a\{\text{Cu}_2\text{S}\} / a^2[\text{Cu}] a[\text{S}] \quad (5-61)$$

Standard states are selected as:

$\{\text{Cu}_2\text{S}\}$ — pure liquid.

$[\text{Cu}]$ and $[\text{S}]$ — 1.0wt%.

when melt is carbon free,

$$K = \frac{\gamma_X}{(f_{\text{Cu}}^{\text{S}} f_{\text{Cu}}^{\text{Cu}} [\text{Cu}\%])^2 f_{\text{S}}^{\text{S}} f_{\text{S}}^{\text{Cu}} [\text{S}\%]} \quad (5-62)$$

and when it contains a certain amount of carbon

$$K_{\text{C}} = \frac{\gamma_{\text{X}_\text{C}}}{(f_{\text{Cu}}^{\text{C}} f_{\text{Cu}}^{\text{S}} f_{\text{Cu}}^{\text{Cu}} [\text{Cu}\%]_{\text{C}})^2 f_{\text{S}}^{\text{C}} f_{\text{S}}^{\text{S}} f_{\text{S}}^{\text{Cu}} [\text{S}\%]_{\text{C}}} \quad (5-63)$$

where

X — mole fraction of Cu_2S in slag

γ — activity coefficient of Cu_2S

f_{Cu}^i — the effect of element i upon the activity coefficient of Cu

f_{S}^i — the effect of element i upon the activity coefficient of S

Subscript C — denote property belong to the system containing carbon

At equilibrium state and at the same operating

temperature

$$K = K_C \quad (5-64)$$

Assuming that f_{Cu}^{Cu} , f_{Cu}^S , f_S^{Cu} , f_S^S and γ do not change with different carbon content in the metal in the present system, or that the change is very small and can be neglected, then,

$$\frac{X}{[Cu\%]^2 [S\%]} = \frac{X_C}{([Cu\%]_C f_{Cu}^C)^2 f_S^C [S\%]_C} \quad (5-65)$$

rearranging;

$$f_S^C (f_{Cu}^C)^2 = \frac{X_C [Cu\%]^2 [S\%]}{X [Cu\%]_C^2 [S\%]_C} \quad (5-66)$$

If values of X , $[Cu\%]$ and $[S\%]$ are measured experimentally and f_S^C is known, f_{Cu}^C can be calculated from equation (5-66).

The results of experiments with different initial carbon contents in the metal are shown in Table 4-4, page 70. Taking Run St27 as the carbon free case, then, three values of $f_S^C (f_{Cu}^C)^2$, corresponding to different initial carbon contents are calculated. Since also

$$\log f_S^C (f_{Cu}^C)^2 = \log f_S^C + 2 \log f_{Cu}^C \quad (5-67)$$

and (80)

$$\log f_S^C = [wt\%C] e_S^C \quad (5-68)$$

$$\log f_{Cu}^C = [wt\%C] e_{Cu}^C \quad (5-69)$$

where e_j^C is called the interaction coefficient of carbon to j , combining equation 5-67, 68 and 69, one can derive

$$2e_{Cu}^C + e_S^C = \frac{1}{[wt\%C]} \log f_S^C (f_{Cu}^C)^2 \quad (5-70)$$

and

$$e_{\text{Cu}}^{\text{C}} = \frac{1}{2} \left(\frac{1}{[\text{wt}\% \text{C}]} \log f_{\text{S}} (f_{\text{Cu}})^2 - e_{\text{S}}^{\text{C}} \right) \quad (5-71)$$

As shown in Table 5-7, there is a poor agreement among the values given for e_{S}^{C} obtained by different investigators from the compilation of Bodsworth and Bell⁽⁸⁰⁾. A value of 0.114 obtained from the study of equilibrium in the reaction $[\text{S}] + \text{H}_2 = \text{H}_2\text{S}$ at 1823K (1550°C), is most generally used. e_{S}^{C} equal to 0.114 is substituted into equation (5-71) to calculate e_{Cu}^{C} in the present study.

All calculated results are given in Table 5-8 and $\log f_{\text{Cu}}^{\text{C}}$ is plotted against [C%] in Fig.5.13.

The results from the present work can be compared with those obtained by other investigators as shown in Table 5-9.

Koros and Chipman⁽²⁴⁾ calculated the activity coefficient of copper in liquid iron by the distribution of copper between liquid silver and iron under the condition of known activity coefficient of copper in liquid silver. The interaction coefficient of carbon to copper was determined from its effect on the distribution. It was found that γ_{Cu} was independent of copper concentration and $\log \gamma_{\text{Cu}}^{\text{C}}$ was approximately a linear function of carbon concentration as shown in Fig.5.14. Safiah and Sale⁽²⁶⁾ used these γ_{Cu} data to calculate the activity of copper in liquid iron treated with sodium sulphate. Their results gave a_{Cu} equal to 0.085 and 0.0101 (pure liquid as standard state) for low carbon and saturated carbon respectively.

Morales and Sano⁽⁵⁹⁾ obtained e_{Cu}^{C} equal to 5.4 from the effect of carbon on the vaporization of copper using the levitation melting technique at 2073K (1800°C) under a

Table 5-7
Different ϵ_S^C and e_S^C

No.	1	2	3	4
ϵ_S^C	15.2	12.4	6.4	6.2
e_S^C	0.29	0.23	0.114	0.11

Table 5-8
Results of Calculation of e_{Cu}^C

Run	[Cwt%]o	$f_S^C (f_{Cu}^C)^2$	$e_S^C + 2e_{Cu}^C$	e_{Cu}^C	$\log f_{Cu}^C$
St27	0.46	1.578	0.4304	0.158	0.073
St30	1.59	2.557	0.2564	0.0712	0.113
St31	3.77	15.66	0.3169	0.1014	0.382

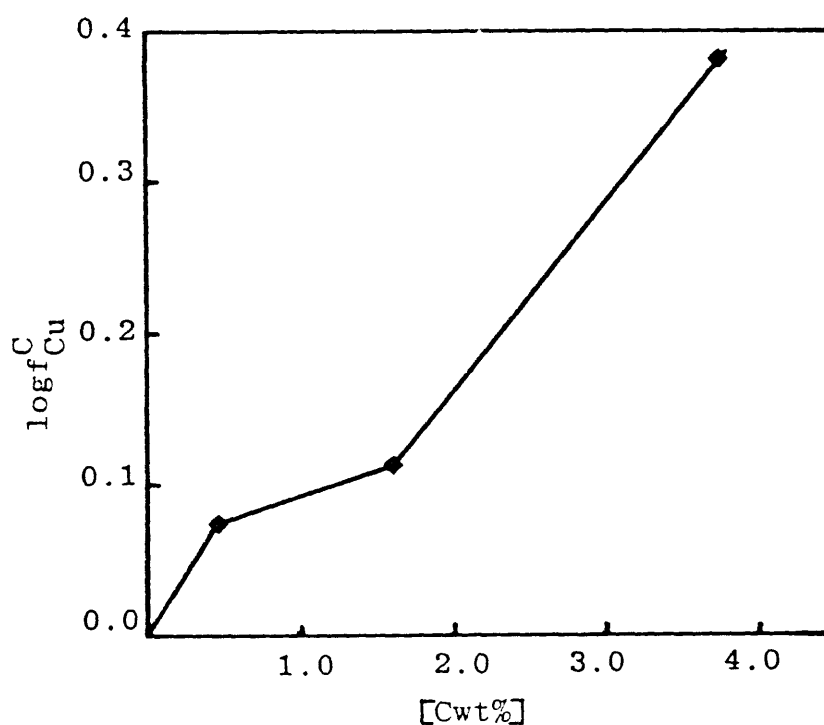


Fig.5.13 The influence of carbon on the activity coefficient of copper

Table 5-9
Different $\epsilon_{\text{Cu}}^{\text{C}}$ and e_{Cu}^{C}

Reference No.	24	59	87
$\epsilon_{\text{Cu}}^{\text{C}}$	4.2	5.4	4.8
* e_{Cu}^{C}	0.069	0.093	0.082

* Calculated by equation (5-74) (88)

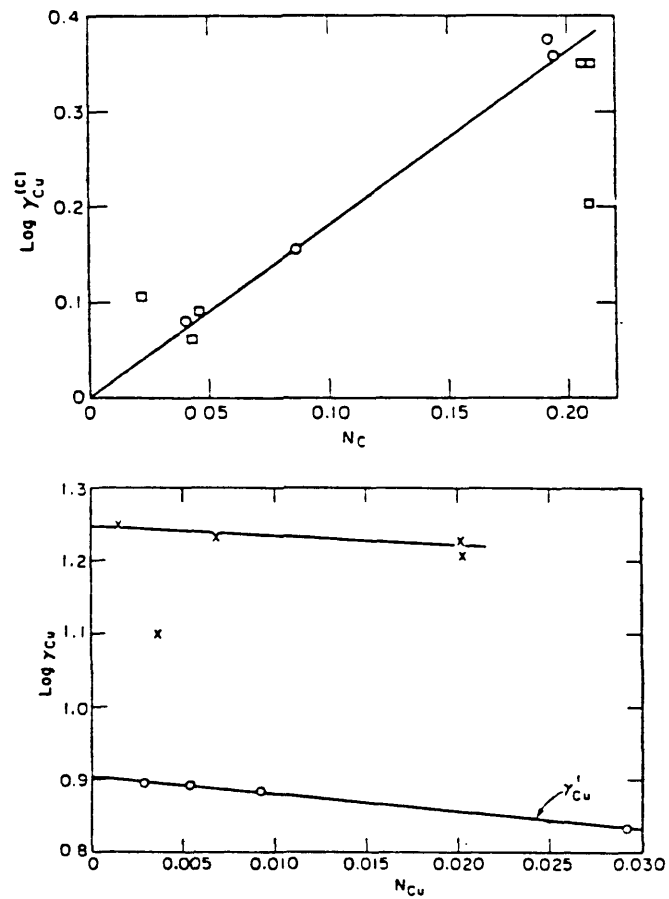


Fig.5.14 Relationships between activity coefficient of copper and concentration of Cu and C

helium atmosphere. Mori et al⁽⁸⁷⁾ measured the equilibrium of the reaction



and the effect of alloy elements on it, then, calculated ϵ_{Cu}^C equal to 4.8 in their system.

e_{Cu}^C equal to 0.158 for 0.46%C calculated in the present work is much greater than those obtained by others, but 0.0712 and 0.1014 for higher carbon contents are in reasonable agreement with them. Using equation⁽⁸⁸⁾

$$\epsilon_{Cu}^C = (230M_C/M_{Fe})e_{Cu}^C + (M_{Fe} - M_C)/M_{Fe} \quad (5-73)$$

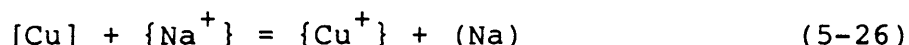
and e_{Cu}^C equal to 0.0712 and 0.1014, ϵ_{Cu}^C equal to 4.3 and 5.8 respectively is obtained for the present work.

A positive interaction coefficient of carbon to copper in iron shows that iron has a stronger tendency to form a stable carbide or a more tightly bound clusters than that of copper, so that copper atoms are rejected from liquid iron and makes the Fe-Cu bonding less firm. So the addition of carbon to an iron-copper melt increases the activity of copper in it and makes the removal of copper from the metal easier.

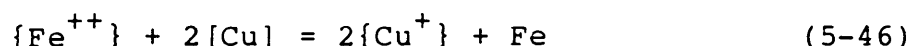
The results in Table 4-4 show that a marked sulphurization of the metal occurs, and the level of sulphur pick-up depends on the carbon content of the bath. Carbon significantly increases the activity of sulphur in iron as shown in Table 5-7 so that it is apparent that a given sulphur potential above liquid iron melts would result in a higher sulphur pick-up in low carbon melts than in carbon saturated ones.

5-3 SUMMARY AND CONCLUSIONS OF DECOPPERIZATION

The transfer of copper from metal to slag involves a number of secondary reactions necessitated by the need to maintain electroneutrality. These can be simply expressed as



or



depending on the composition of the slag. These reactions involve the transport of reactants to the interface, adsorption of reactants and the formation of the products by way of an activated complex at the interface, followed by the desorption and transport of products into the bulk phases. Any of these steps or their sub-processes may be slow enough to control the overall transfer of copper. When argon is bubbled through the metal, the possible concentration gradients in phases are destroyed and the bulk diffusion of species does not control the process. Details of reactions will be discussed under the condition of argon bubbling.

In pure sodium sulphide slag, the transfer of copper into slag is accompanied by transfer of iron and their combination with sulphur is responsible for the vaporization of sodium. The rate of transfer of copper at the initial fast stage is not controlled by the transport of species in the metal and slag since iron sulphide containing initial slag speeds up the rate. The independence of the initial rate on the initial copper and sulphur contents in the metal indicates that the slowest step of the process expressed as reaction (5-26) is not directly concerned with those steps

involving copper. Therefore, the reaction



must play an important role in rate controlling of the copper transfer.

The measured partial pressure of sodium is quite close to the calculated equilibrium value, so the removal of sodium vapour is most probably the controlling step for the initial stage of overall reaction.

The supply of sulphur for the transfer of copper into slag does not depend on the evaporation of sodium in a slag containing 30%FeS. The reaction (5-46) involves only slag and metal phases instead of the three phases in reaction (5-26). Iron releases sulphur and enters into the metal at the initial stage. The transfer of copper during this period is most probably controlled by the transport of copper in the boundary layer of the metal phase. The calculated copper transfer coefficient, k_m , is increased with the argon flowrate. The initial rate is not sensitive to greater additions of iron sulphide in the slag, the change of the operating temperature and the interfacial area.

In both pure sodium sulphide slag and iron sulphide containing slag, the rate controlling step is changed after the initial fast stage, which usually lasts less than seven minutes. As the transfer of copper into the slag and sulphur into the metal reach a certain degree, the reversibility of the reaction



plays an important role in the process and the equilibrium of the forward and reverse reactions dominates the transfer of copper. Higher initial sulphur and copper in the metal

delay the change of controlling step and have a greater rate constant in the second stage. Higher operating temperature gives a greater final copper and sulphur content in the metal through the decrease of the equilibrium constant of the reaction (5-36).

The removal of copper from steel is significantly affected by the carbon content in the metal. Positive interaction coefficients indicate that the addition of carbon increases the activities of copper and sulphur, and as a result, the equilibrium distribution of copper between slag and metal is raised, so a better removal of copper and lower final sulphur in the metal are achieved.

The following conclusions are drawn from the discussion.

Mass Transport is an important controlling step in the removal of copper by either sodium sulphide or its mixture with iron sulphide. Inert gas stirring makes the transfer of copper into the slag nearly reach equilibrium in five minutes.

The composition of $30\% \text{FeS}-70\% \text{Na}_2\text{S}$ can be regarded as the most suitable slag for copper removal since it achieves a similar efficiency of copper removal and sulphur control, faster reaction, less sodium fume and iron loss than that in pure sodium sulphide slag. Higher carbon content in the metal is more favourable for the removal of copper.

The operating temperature is best controlled in the range of 1523-1573K for high carbon content melts. The proportion of copper removed is a function of the amount of slag added. A better removal will be obtained if the same amount of slag is divided into two refining processes, which

can be achieved by intermediate tapping of slag, compared with a single addition.

CHAPTER 6

DISCUSSION OF DETINNING

CHAPTER 6

DISCUSSION OF DETINNING6-1. EXPERIMENTS WITH $\text{FeS-Na}_2\text{S}$ SLAG

It has been proved that $\text{FeS-Na}_2\text{S}$ slag can remove copper from molten iron rapidly. The same experimental conditions were applied to the removal of tin from carbon saturated iron. As shown in Table 4-5, page 73, only a small amount of tin can be removed after four hours refining when no direct gas purging of the metal was used.

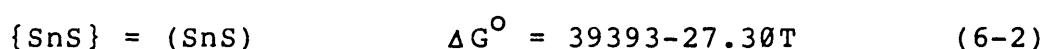
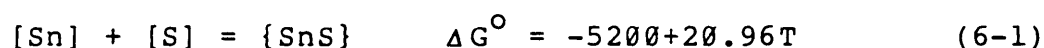
A rather fast decrease of tin content in the metal at initial stage, Fig.4.24, page 74, corresponded to the increase of tin in the slag. After this period, the content of tin in the slag did not change very much and the removal of tin from the metal was slowed down and followed a zero order reaction model.

It was found that the content of tin in the metal decreased continuously, but the content of tin in the slag nearly kept constant at 0.4-0.5wt% throughout the process as shown in Table 4-5 and Fig.4.23, page 73. The results shown in Table 6-1 illustrate that the amount of tin accumulating in the slag was less than that transferred from the metal, which indicates that some volatile species such as SnS evaporated into the gas phase.

As shown in Fig.4.25, page 75, the presence of tin causes no detectable difference in the removal of copper. The latter reaction was still fast and about 76% of the initial concentration was removed in both runs. The results show that $\text{FeS-Na}_2\text{S}$ slag is capable of removing both tin and

copper when a gas purge of the metal is used, but that the removal of tin takes rather a long time compared with copper. The changes of tin content with time followed a straight line relationship except at the very beginning stage, which agreed with the results in Fig.4.24 obtained in the absence of copper in the metal.

For FeS containing slag, the content of tin in the slag rapidly reached a partial equilibrium value. This value was so low that it is unlikely that it was the solubility limit of SnS. Three experiments were carried out by contacting pure tin with pure sodium sulphide, pure iron sulphide and a mixture of 70%Na₂S-30%FeS. The concentration of tin reached 27wt% and 13wt% in sodium sulphide and its mixture with iron sulphide respectively while FeS-Sn became one phase. The distribution of tin is concerned with the three phase metal, slag and gas equilibrium. So the constant content of tin in the slag is probably a partial equilibrium value satisfying both equations (6-1) and (6-2)



SnS is very volatile⁽²¹⁾ and its boiling point is 1483K (1210°C)^(11,67). At 1523K, the equilibrium constant of reaction (6-2) is equal to 2.06. As a result, tin sulphide

Table 6-1

Mass Balance of Tin in the Process

Run No.	Sn in slag, g	Sn from metal, g	ΔSn, g
Sn2	0.0147	0.0173	0.0026
Sn3	0.0186	0.0194	0.0008
Sn4	0.0246	0.0512	0.0275
Sn6	0.0264	0.0496	0.0232
Sn7	0.0228	0.0572	0.0344

continuously evaporates into the gas phase, which, in turn, pushes the reaction (6-1) towards the right hand side.

A dark gray material condensed on the surface of the furnace cap during those experiments without using Na_2S was collected and analysed by X-ray diffraction. Tin sulphide, SnS , was observed as the main phase. It is concluded from these facts that tin is removed by evaporation of SnS and that the function of the slag is mainly to supply sulphur. If this is so, a slag phase is no longer necessary when initial sulphur is added to the metal phase. All experiments concerned in the following sections were carried out under the conditions that no slag addition was made but that the metal contained sulphur initially.

Also, the calculations of mass balance for several runs, in which no slag was added but the initial metal contained a certain amount of sulphur, showed that the loss of tin and sulphur from the metal during the same period were equimolar as shown in Table 6-2.

Table 6-2
Reacted Moles of Tin & Sulphur

Run No.	$N_{\text{Sn}} \cdot 10^3$ Mole	$N_{\text{S}} \cdot 10^3$ Mole	$N_{\text{S}}/N_{\text{Sn}}$
Sn21	1.41	1.324	0.94
Sn25	0.6087	0.5094	0.84
Sn27	1.107	1.392	1.257
Sn26	0.9212	1.0842	1.18
Sn28	0.7369	0.744	1.01
Sn29	1.177	1.2469	1.059
Sn30	0.6408	0.6122	0.9553
Mean			1.0345

6-2. MASS TRANSPORT PROCESSES IN THE VAPORIZATION OF TIN SULPHIDE

6-2-1. Effect of the Mode of Argon Introduction

Mass transport usually plays an important role in vaporization processes. This was observed in the present studies. As shown in Fig.4.26 and 27, page 77 and 79, the rate of the removal of tin from iron was greater the closer the tip of the argon tube was to the surface of the metal. The fastest rate corresponded to argon bubbling into the metal and the slowest rate corresponded to no convective flow of argon within the crucible. These results give a positive indication that the diffusion of tin sulphide vapour in the gas affects the removal of tin significantly.

When the tip of the argon tube was located 4.0 cm above the metal surface, the rate of tin removal was nearly the same as when argon was purged from the bottom of the furnace when the depth of the crucible H was equal to 2.0cm, and a little faster when H was equal to 4.0cm. This indicates that the argon flow penetrating into the deeper crucible caused the deeper stagnant layer of gas above the metal to be stirred with a detectable effect.

When $\ln([Sn]_t/[Sn]_0)$ is plotted against time in Fig.6.1 for all the results shown in Fig.4.26, straight lines are observed. The transfer coefficient of tin, k , is calculated from the slope of these lines. Fig.6.2 shows how k changes with the distance between the tip of argon tube and the metal surface at a constant argon flowrate. The argon stream probably touched the metal surface when it was purged from

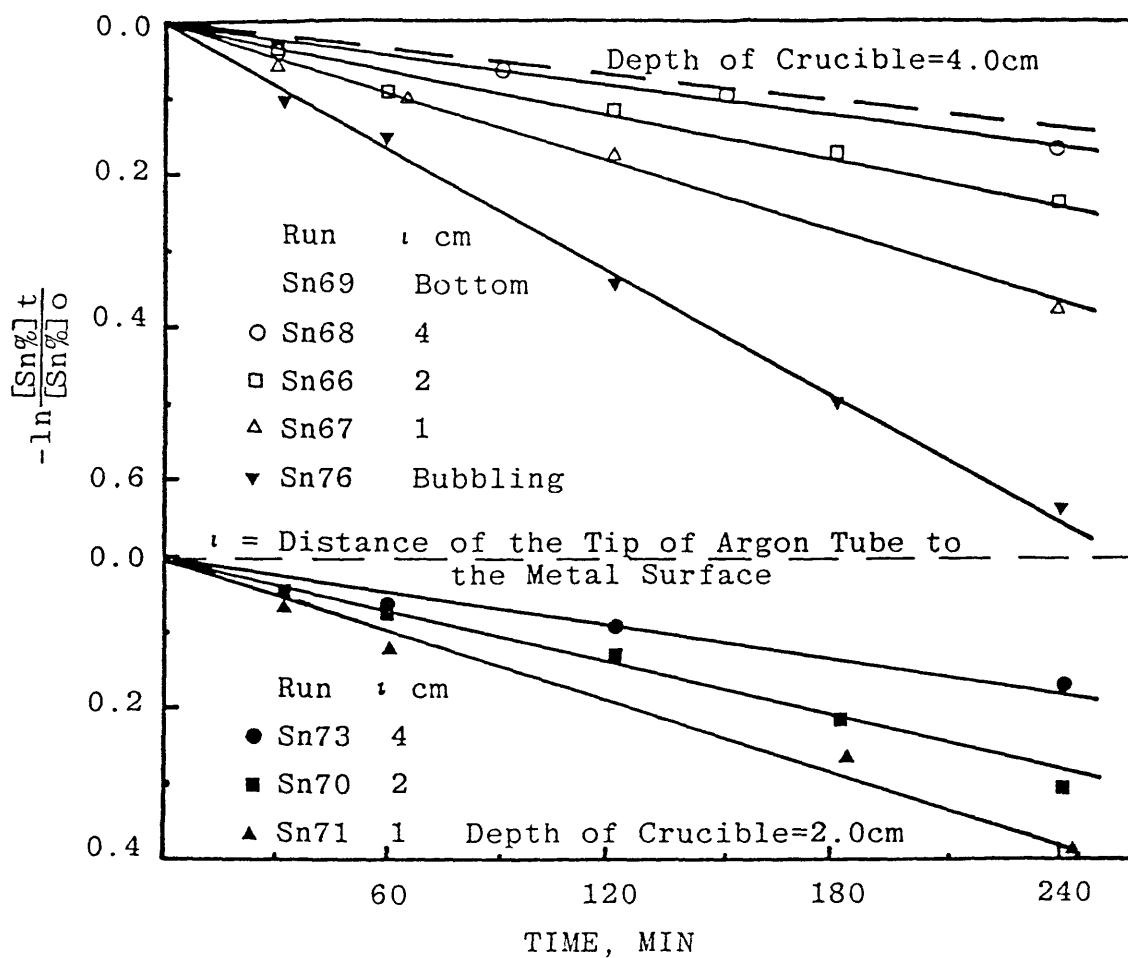
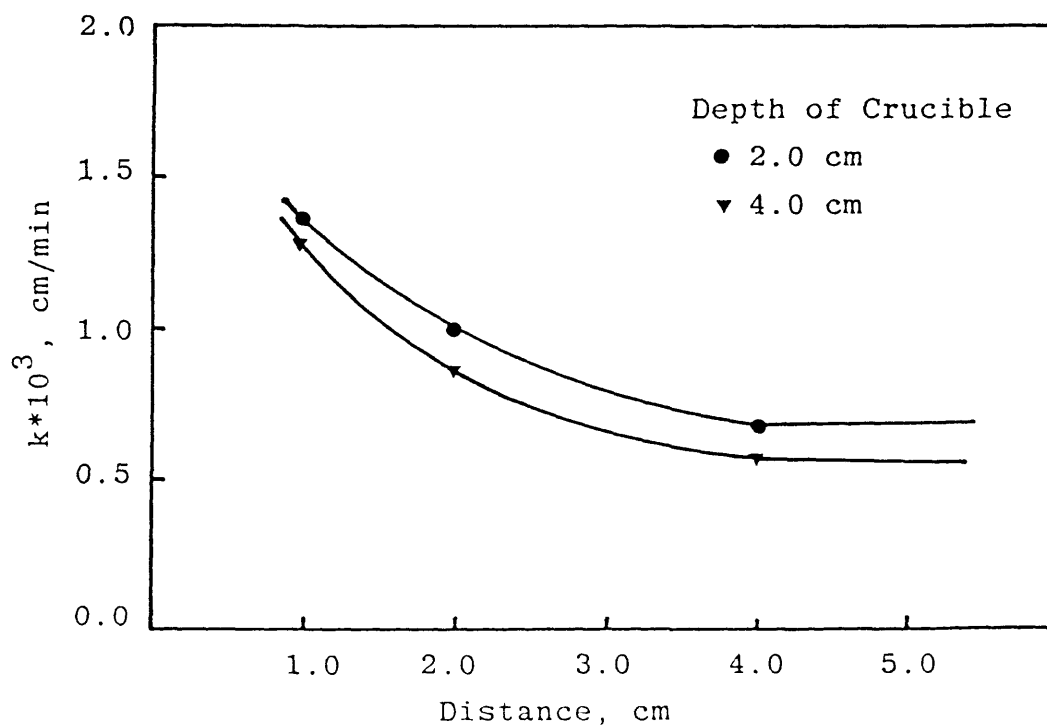
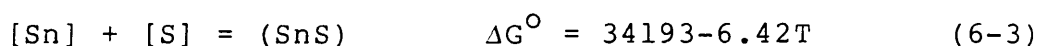


Fig.6.1 First Order Plot of Fig.4.26

Fig.6.2 Changes of k with the Distance Between the Tip of Argon Tube & Metal Surface

1.0cm above it, so that tin sulphide vapour could be immediately swept away from the surface where the chemical reaction took place. The acceleration of the tin removal when argon was bubbled into the metal bath indicates that some factors other than diffusion of SnS vapour in the bulk gas phase controlled the rate of the process when the molten metal was not disturbed. Assuming that the chemical reaction



is always at its equilibrium state (this will be discussed later), the controlling factor could be mass transport in the metal phase. When the liquid is stagnant, the transfer of tin to the surface takes place by diffusion. In such a case, the mass transfer coefficient of tin can be expressed as

$$k = D_m / \delta \quad (6-4)$$

where D_m is the diffusivity of tin in molten iron and δ is the boundary layer thickness which is usually in the range 0.001-0.2 cm⁽⁸¹⁾. From Fig.6.3. a value of k equal to 2.27×10^{-3} cm/min for Run Sn30 was calculated from the equation

$$k = -\frac{hm}{t} \ln \frac{[\text{Sn}\%]_t}{[\text{Sn}\%]_o} \quad (6-5)$$

Substituting this value and δ equal to 0.001 or 0.2 cm into equation (6-4), D_m values of 3.78×10^{-8} or 7.56×10^{-6} cm²/sec are obtained. These values are lower than usual range of diffusivities of solute in molten iron which are normally in the range of 10^{-5} - 10^{-4} cm²/sec. It seems reasonable to conclude that the measured tin transfer rate is too slow to be accounted for only by diffusion in the metal.

The increases of argon flowrate in the surface purge condition as shown in Fig.4.28, page 79, accelerated the

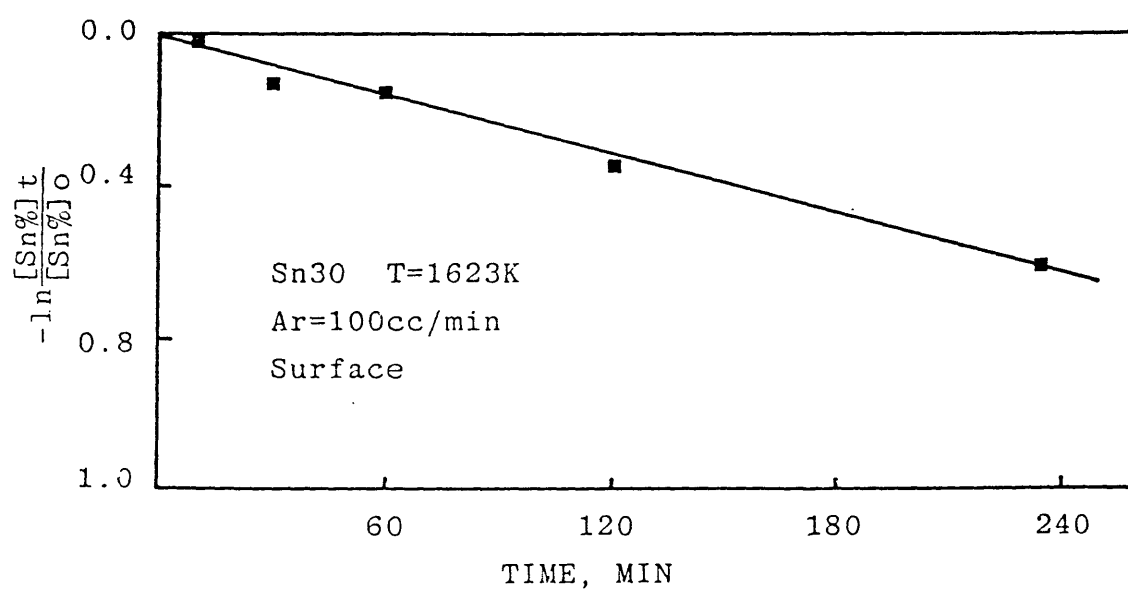


Fig.6.3 First Order Plot of Run Sn30

mass transport of SnS in the gas, and also decreased the partial pressure of SnS in the argon, which in turn was favourable to the formation of SnS by chemical reaction.

6-2-2. Effect of the Depth of the crucible

As shown in Fig.4.30, page 81, faster detinning occurred in a shallow crucible or in one with a small ratio of depth to area. For those results obtained under the condition of argon being purged from the bottom of the furnace, the rate of tin removal was mainly controlled by the diffusion of SnS vapour in the bulk gas phase. All those results satisfy a first order reaction model as plotted in Fig.6.4 and their tin transfer coefficients, k , which are equal to the rate constant of a first order reaction, are given in Table 6-3.

This process could be considered as a case of vaporization of SnS from metal contained in the bottom of a narrow tube and the entrainment of the vapour in an argon gas flow over the upper end of the tube. The system is isothermal and it may be assumed that convection in the tube is negligible; all mass transport from the surface of the metal to the gas stream must therefore take place by diffusion. Under the assumption of zero accumulation of diffusing substance in any volume, Fick's first law can be written as

$$J_{\text{SnS}} = D_{\text{SnS}} \frac{dC}{dy} \quad (6-6)$$

for the diffusion of SnS vapour from the surface of the metal to the open end of the crucible, where J_{SnS} is the

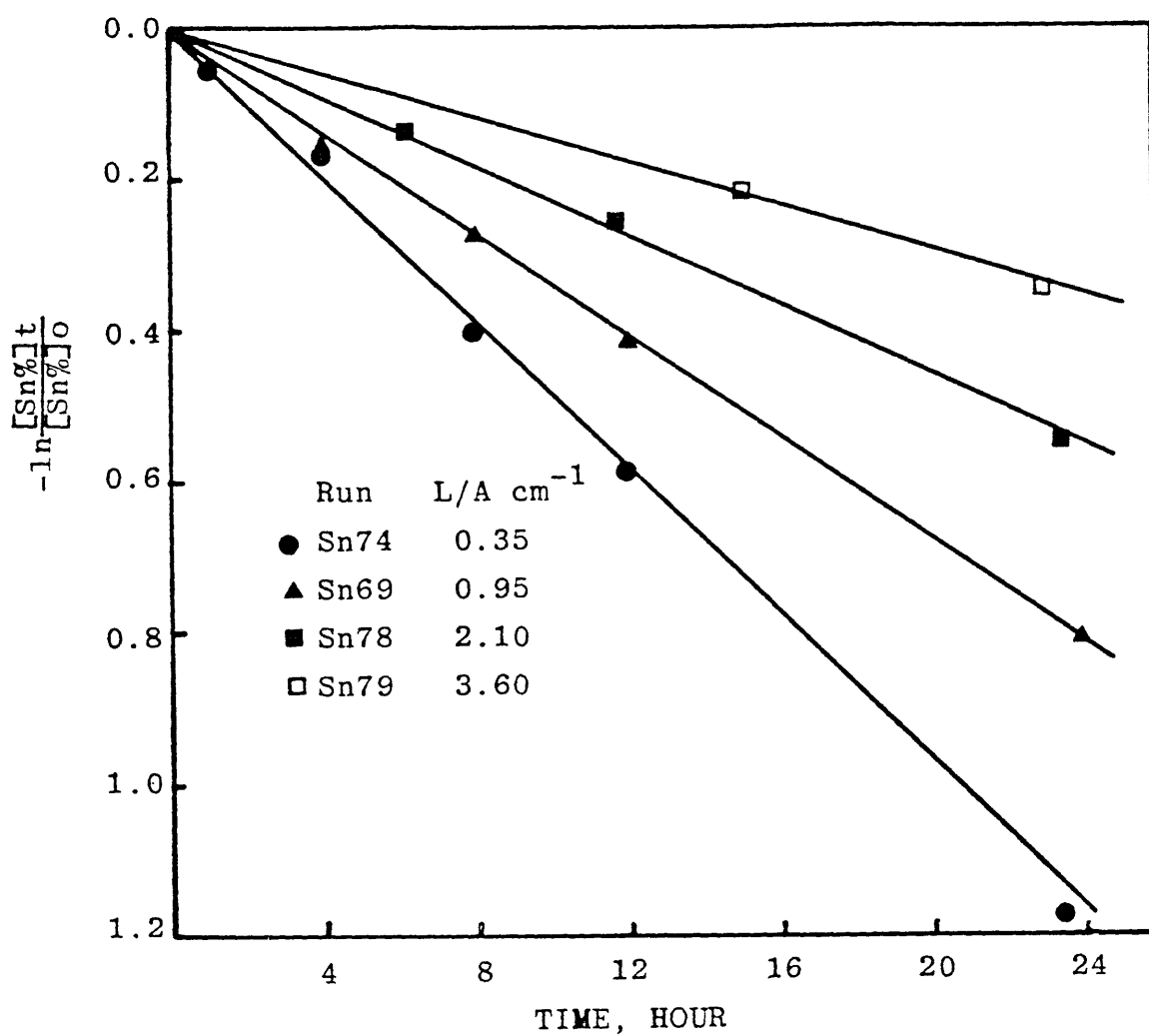


Fig.6.4 First Order Plot of Fig.4.30 for Effect of L/A

Table 6-3

Changes of tin transfer coefficient with L/A

Run	L cm	L/A cm^{-1}	$k \cdot 10^4 \text{ cm/min}$
Sn74	1.15	0.35	8.17
Sn68	3.15	0.95	5.69
Sn78	7.00	2.10	3.82
Sn79	6.00	3.60	2.35

flux of SnS, D_{SnS} the diffusivity of SnS in argon and dc/dy the concentration gradient of SnS along the y direction as shown in Fig.6.5.

It has been determined experimentally that for ideal gases, when the diffusing component is at relatively low concentration a linear concentration profile will be established under steady state conditions⁽⁸¹⁾. Assuming that SnS vapour is an ideal gas and satisfies the equation $PV=nRT$, the diffusion of SnS in the present system can be derived from (6-6) as

$$J_{\text{SnS}} = \frac{D_{\text{SnS}} p^0}{RT L} \quad (6-7)$$

or

$$D_{\text{SnS}} = RTL \frac{J_{\text{SnS}}}{p^0} \quad (6-8)$$

where L is the distance between the surface of the metal and the open end of the crucible, p^0 is the partial pressure of SnS in argon gas at the surface of the metal. The partial pressure of SnS in the open end of a narrow tube is quite low and assumed equal to zero.

If the chemical reaction is at equilibrium, the equilibrium partial pressure of SnS can be calculated from the loss of tin from the metal and the volume of argon bubbled through the metal. The change of p^0 with the concentration of tin in the metal has been calculated from the results of Run Sn76 which was carried out under the same conditions as the experiments discussed above except that argon was being bubbled through the metal. The method of calculation of p^0 and J_{SnS} is given in Appendix I and the calculated results are shown in Table 6-4 where D_{SnS} is obtained from the equation (6-8).

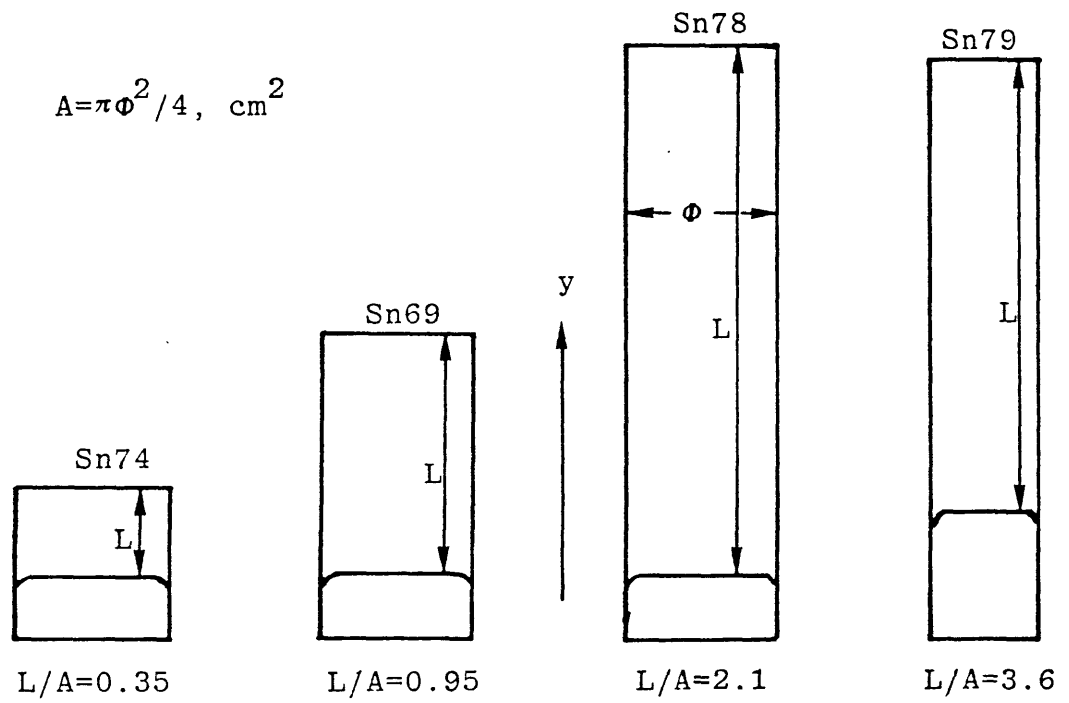


Fig.6.5 The Size of Crucibles

Table 6-4

Calculated results of J_{Sn} , p° and D_{SnS}

Run Sn76						
[Sn%]t	1.10	1.05	1.00	0.90	0.80	0.60
$p^{\circ} \cdot 10^3$	2.18	2.08	1.98	1.78	1.59	1.19
Run Sn74						
$J \cdot 10^7$	4.31	4.11	3.92	3.53	3.13	2.35
D_{SnS}	0.51	0.50	0.51	0.51	0.50	0.50
Run Sn69						
$J \cdot 10^7$	3.00	2.86	2.73	2.46	2.18	1.64
D_{SnS}	0.96	0.96	0.96	0.97	0.96	0.96
Run Sn78						
$J \cdot 10^7$	2.02	1.92	1.83	1.65	1.47	1.10
D_{SnS}	1.44	1.43	1.44	1.44	1.44	1.44
Run Sn79						
$J \cdot 10^7$	2.48	2.37	2.25	2.03	1.80	1.35
D_{SnS}	1.51	1.52	1.51	1.52	1.51	1.51

Note: The unit for J is mole $\text{cm}^{-2} \text{min}^{-1}$, D_{SnS} $\text{cm}^2 \text{sec}^{-1}$ and p° atm.

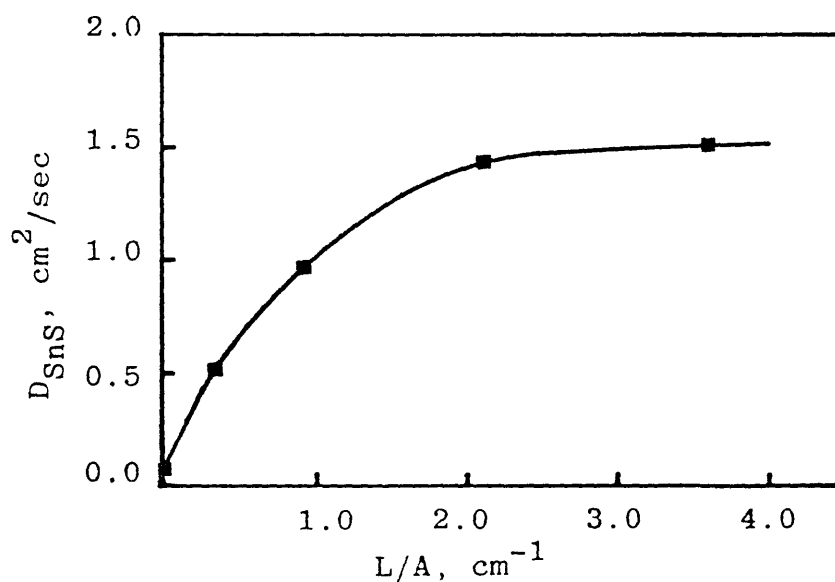


Fig.6.6 Calculated Diffusion Coefficient of SnS

As shown in Fig.6.6, D_{SnS} substantially changes with the ratio L/A when the latter is smaller than 2.1. At larger values of L/A the slope $dD_{\text{SnS}}/d(L/A)$ is reduced to less than 0.047, which indicates that the value of D_{SnS} is close to the true diffusivity constant of SnS. From this it appears that the diffusivity of SnS vapour in argon would probably not exceed $1.60 \text{ cm}^2/\text{sec}$ in the present system.

Turkdogan⁽¹⁰⁾ reviewed transport properties of gases. The coefficient of diffusion in binary nonpolar gas mixtures can be derived from the kinetic theory of gases.

$$D_{12} = 1.858 \cdot 10^{-3} (T^{1.5} P \delta_{12} \Omega^{(1,1)*}) (1/M_1 + 1/M_2)^{1/2} \quad (6-9)$$

where P is the pressure in atm, M_1 and M_2 molecular weights, δ_{12} collision diameter equal to $1/2(\delta_1 + \delta_2)$ in Å and $\Omega^{(1,1)*}$ the collision integral for mixtures of 1 and 2 at a given reduced temperature T_{12} ; $T_{12} = (\epsilon/\kappa)T$, where ϵ/κ is the force constant and can be estimated from $\epsilon/\kappa = 1.15T_b$, where T_b is the boiling temperature in K. $\Omega^{(1,1)*}$ equal to 1.476 and δ_{Ar} 3.418 Å are used⁽¹⁰⁾ for the present system, and δ_{SnS} equal to 2.44 Å is estimated from the values obtained for some metal vapours⁽⁸⁹⁾. Substituting all these data into the equation (6-9), $D_{\text{SnS-Ar}}$ equal to $1.71 \text{ cm}^2/\text{sec}$ is obtained. This value is a little higher than that observed from experiments but is in reasonable agreement.

In Fig.6.6 when L/A is close to zero, say 0.03, D_{SnS} equal to $0.08 \text{ cm}^2/\text{sec}$ is obtained from Run Sn67 where the argon tube was located 1.0 cm above the metal surface. As discussed above, fresh argon gas most probably arrived at the metal surface, so SnS vapour would be swept away as it formed and the diffusion of SnS in argon would not then

control the process.

D_{SnS} equal to $1.51 \text{ cm}^2/\text{sec}$ from Run Sn79 is taken as the diffusivity of SnS vapour in argon in the present system. Substituting this value into equation (6-9), J_{SnS} , for which process is only controlled by the diffusion of SnS vapour in argon, is calculated and compared with the experimental results in Fig.6.7. A similar comparison of the total loss of moles of tin after 24 hours refining is shown in Fig.6.8. The process is clearly not only controlled by the diffusion of SnS vapour in argon when the L/A ratio is less than 2.1, but also retarded by resistances coming from either the chemical reaction at the interface or the mass transport in the metal. A tin transfer coefficient, k , equal to $2.13 \times 10^{-5} \text{ cm/sec}$ is obtained from Run Sn67 in which fresh argon arrived at the metal surface. If the process were controlled by mass transport in the metal, this value of k would be the mass transport coefficient of tin in the metal. However, it is much lower than the usual values 10^{-3} - 10^{-2} cm/sec , and also lower than the value of $2.95 \times 10^{-3} \text{ cm/sec}$ obtained in section 5-1-1 in an unstirred metal bath for copper transfer in the molten iron. Even under bubbling conditions, in Run Sn76, k is only equal to $3.93 \times 10^{-5} \text{ cm/sec}$. Mass transport in the metal phase is thus unlikely to contribute to the rate control of the process.

The chemical reaction process will be discussed in detail in the following section, but it can be said now that the evaporation of SnS from the molten iron is mixedly controlled by the diffusion of SnS vapour in argon and the chemical reaction at the gas/metal interface when there is no convective argon flow in the crucible.

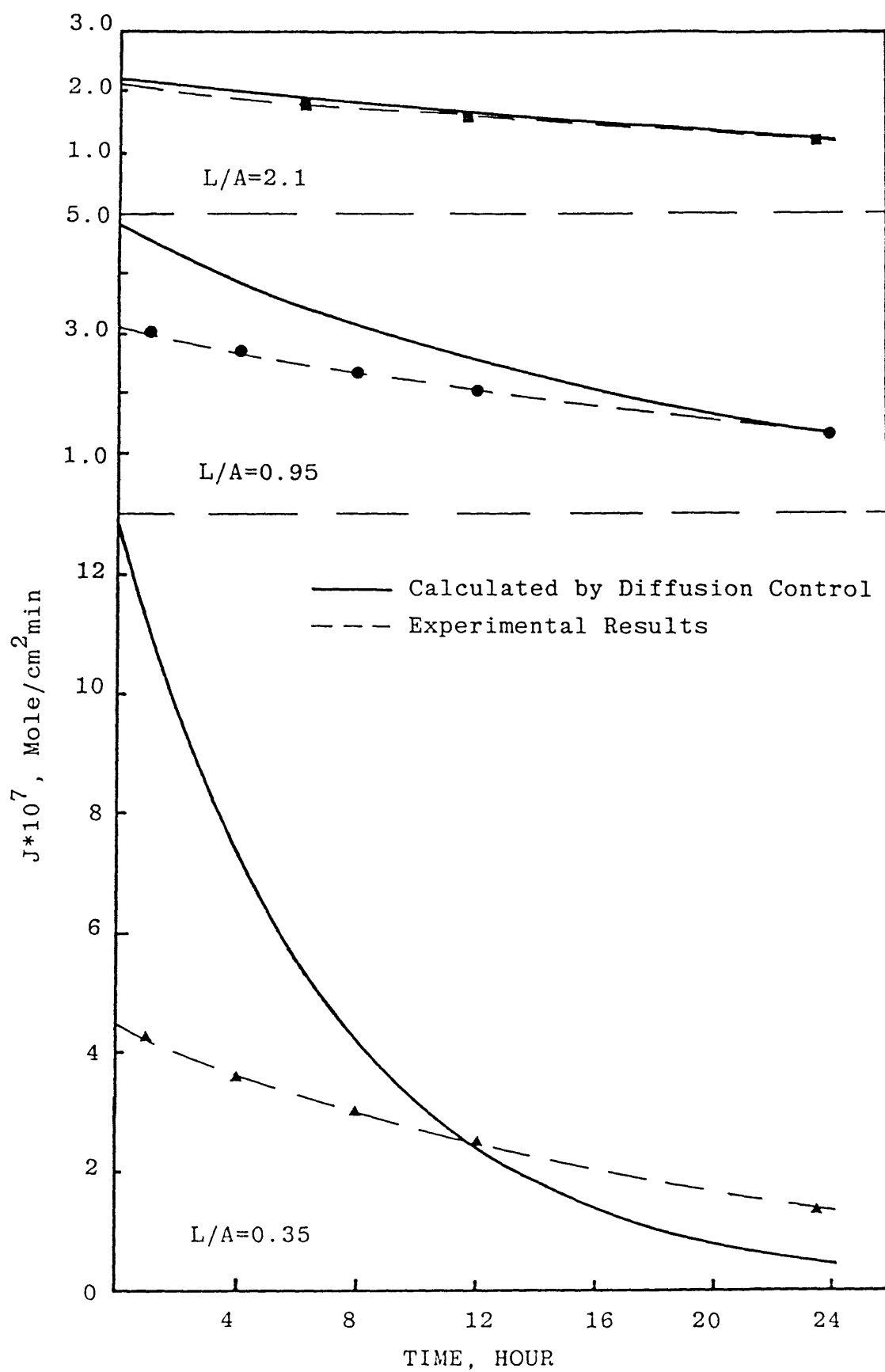


Fig.6.7 Calculated Rate of Mass Transfer of Sn by Diffusion Control & Experimental Results

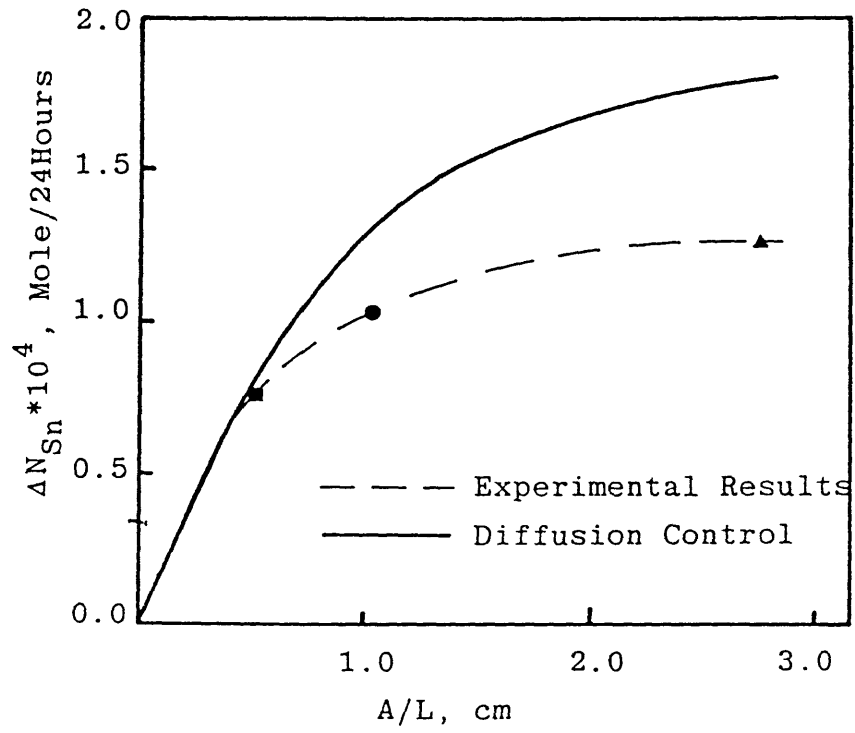


Fig.6.8 Calculated Mass Transfer of Sn by Diffusion Control & Experimental Results

6-3. CHEMICAL REACTION PROCESS OF THE VAPORIZATION OF TIN SULPHIDE

6-3-1. Effect of the Interfacial Area of Metal/Gas

The change of argon introduction from surface purge to bubbling into the metal and increase of argon flowrate usually speeds the rate of a reaction if mass transport in the metal is a rate determining factor. As discussed above, all k values obtained are the range of 10^{-5} - 10^{-4} cm/sec, which is too small to represent simply the mass transfer coefficient of tin in the metal. Mass transport in the metal is therefore fast enough to be neglected in consideration of the rate controlling step.

The chemical reaction involving in the system is



which takes place at the metal/gas interface, so that any change of the interfacial area should affect the rate of the process if it is controlled by chemical reaction. Bubbling argon into the metal and increasing its flowrate both enlarge the area of the metal/gas interface. The experimental results of this effect are shown in Fig.4.26, 27 and 29, page 77, 79 and 80. A clear acceleration is perceived following each increase of the interfacial area.

This can also be explained in terms of the decrease of the partial pressure of SnS by large argon volumes pushing the reaction (6-3) towards the right hand side to establish a new equilibrium. If the reaction is always at its equilibrium state, the mass of tin removed should change in the same ratio as the volume of argon bubbling, that is, the

rate of tin removal will be doubled as the argon flowrate is increased from 50 to 100 cc/min under the bubbling condition.

Three straight lines are plotted in Fig.6.9 under this assumption, k equal to 2.30×10^{-3} , 4.59×10^{-3} and 6.9×10^{-3} cm/min corresponding to argon flowrates of 50, 100 and 150 cc/min respectively. Also shown in this figure, the experimental results from Fig.4.29 are in reasonable agreement with these values in view of experimental errors, especially during the first two hours.

The interfacial area created by argon bubbles has been calculated under the assumption that it exists as 0.3 cm diameter semi-spherical bubble and rises through the metal phase in 0.05 second (about 17 cm/sec), and the results are given in the Table 6-5.

Table 6-5

Surface Area of Metal/Gas				
Ar cc/min	0	50	100	150
Area cm ²	3.33	6.93	13.85	20.78

As argon is bubbled into the metal, the superficial area of the metal surface is not thought to be important in the chemical reaction, since the gas phase will have already been saturated with SnS when the bubbles reach the surface as is discussed in the following section. Only the surface area created by the argon bubbles is thus considered as the reaction site in the bubbling condition.

The relationship between the area of the reaction site and the rate constant is shown in Fig.6.10. k equal to 1.1×10^{-3} cm/min when argon was only blown onto the surface

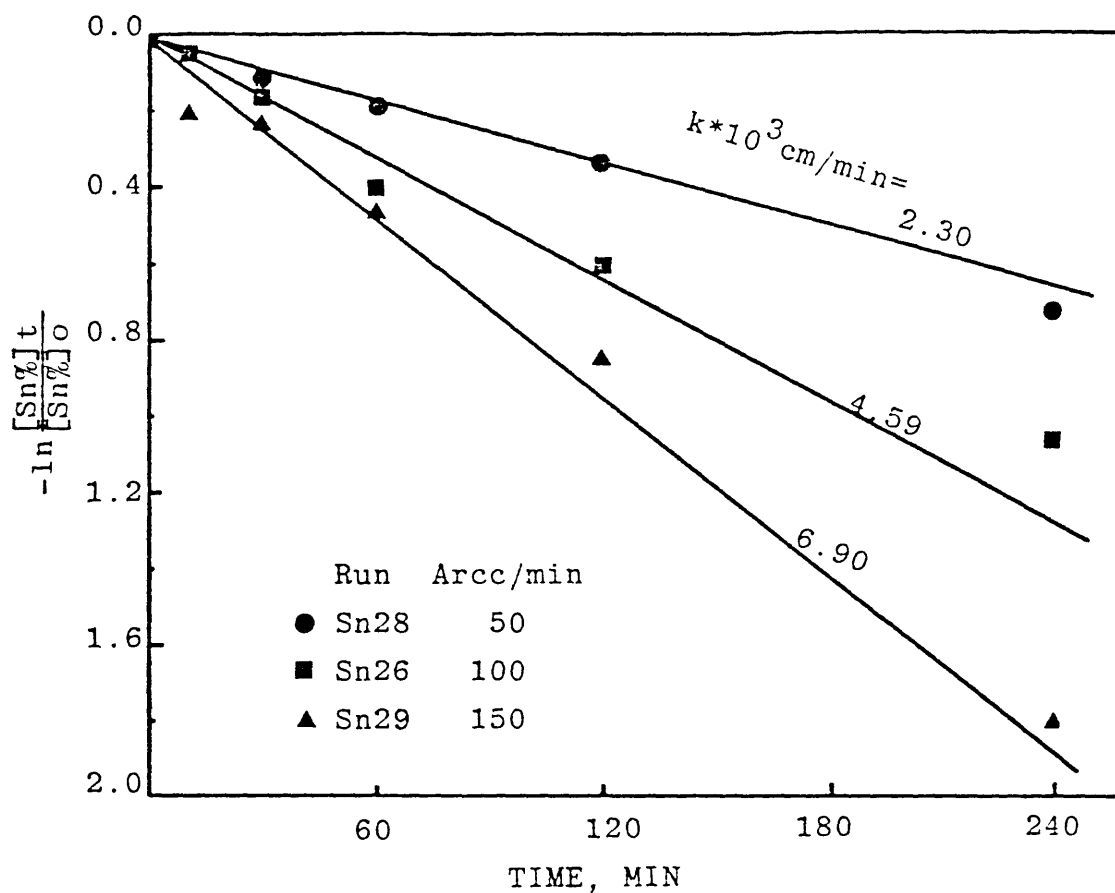


Fig. 6.9 First Order Plot of Fig. 4.29 for Effect of Argon Flowrate

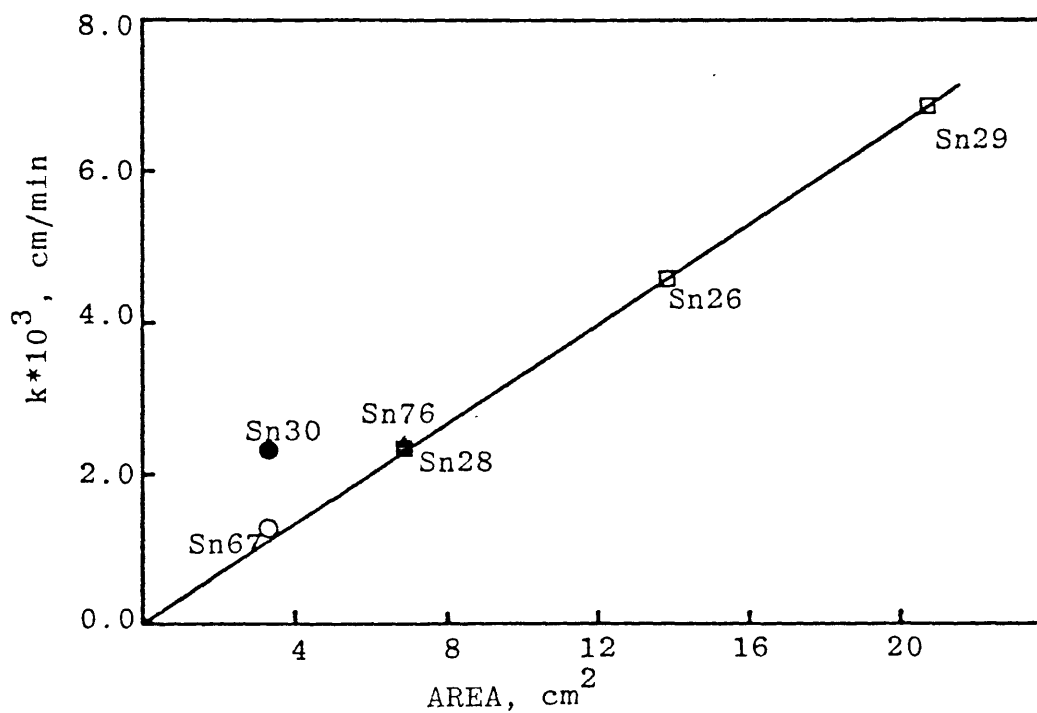


Fig. 6.10 Effect of the Area of Reaction Site on Rate Constant

was the smallest rate constant of the chemically controlled reaction (6-3) in the present system. If k is higher than this value, the process is controlled by chemical reaction, otherwise, there must be some other slower step in the process.

The position of the k value of Run Sn30 in Fig.6.10 should be noted. Taking the flowrate v and the area A of Run Sn30 as a base, a comparison is made with the rest of the runs and shown in Table 6-6.

Table 6-6

Changes of k with Surface Area & Ar Flowrate

k/k_{30} Area Flowrate	A	2A	4A	6A
0.5v	0.5 (Sn67)	1 (Sn76)		
v			2 (Sn26)	
1.5v				3 (Sn29)

k is positively proportional to v and to A . It is noticeable that k does not change in the same proportion as the increase of the area. This may possibly be caused by the saturation of SnS in the bubbles.

The relationship between the tin transfer coefficient k and the argon flowrate v under bubbling condition is established as

$$k = Uv \quad (6-10)$$

where U is a constant concerned with thermodynamic properties of the system studied and equal to $4.6 \times 10^{-5} \text{ cm}^{-2}$ for the experiments shown in Fig.4.29. For more practical application, the proportion of tin removed can be expressed as a function of the volume of argon bubbles, which is related to the metal/gas surface area, from equation (6-5)

and (6-10), that is,

$$\begin{aligned} R &= ([\text{Sn}\%]_o - [\text{Sn}\%]_t) / [\text{Sn}\%]_o \\ &= 1 - e^{-(U/hm)vt} \end{aligned} \quad (6-11)$$

6-3-2. Effect of the Depth of Metal Bath

If the charge of metal is doubled, the depth of the metal bath is also doubled as the diameter of the crucible is unchanged. This affects the detinning process since the amount of reactants is changed. As shown in Fig.4.31 and 32, page 82 and 83, when the depth of molten metal was doubled, the proportion of tin removed was decreased by half, but the moles of tin removed, ΔN_{Sn} , were nearly the same, especially during first two hours. As tin is removed by argon bubble carrying SnS vapour, this unchanged rate of removal indicates that argon bubbles have been saturated with SnS vapour after they passed through the 0.85 cm depth of the metal corresponding to the smaller metal charge. Otherwise, the moles of tin removed in a doubled depth of molten bath should be more than those using the lesser charge since the amount of reactants has been doubled and the area of reaction site per mole of reactant is still the same. The results also show that the volume flowrate of argon, is more important than the area of reaction sites generated under argon bubbling conditions. The chemical reaction at the metal/gas interface is fast enough to saturate the gas with SnS vapour at the partial pressure in equilibrium with the metal at the interface. The increase in argon flowrate decreases the partial pressure of SnS in the argon bubbles, which pushes the chemical reaction taking place to reach new

saturation.

6-3-3. Effect of Initial Sulphur and Tin Contents

It is clear that higher initial sulphur and tin in the metal enhance the removal of tin markedly as shown in Fig.4.33 and 4.34, page 85 and 86. The process satisfies a first order reaction model and straight lines with different slopes are plotted in Fig.6.11.

For the reaction



the sulphur required to combine with 1.0wt% Sn in the metal to form SnS is equal to 0.27wt%. If this detinning process is controlled by chemical reaction, the increase of the concentration of either tin or sulphur will speed up the process. As expressed by the equilibrium constant

$$K = p_{SnS} / a_S a_{Sn} \quad (6-11)$$

or

$$p_{SnS} = K f_S f_{Sn} [S] [Sn] \quad (6-12)$$

and a higher initial sulphur or tin content results in a new equilibrium state with higher partial pressure of SnS, that is, more tin and sulphur react to reach a new equilibrium in the same period. The moles of tin removed as a function of different initial tin contents in the metal are shown in Fig.6.12. The reaction rate is doubled as the amount of reactant present (the chemical driving force) is doubled. The above discussion shows that the effects of initial sulphur and tin satisfy the equation (6-12), which, in turn, indicates that the chemical reaction is always at its equilibrium state.

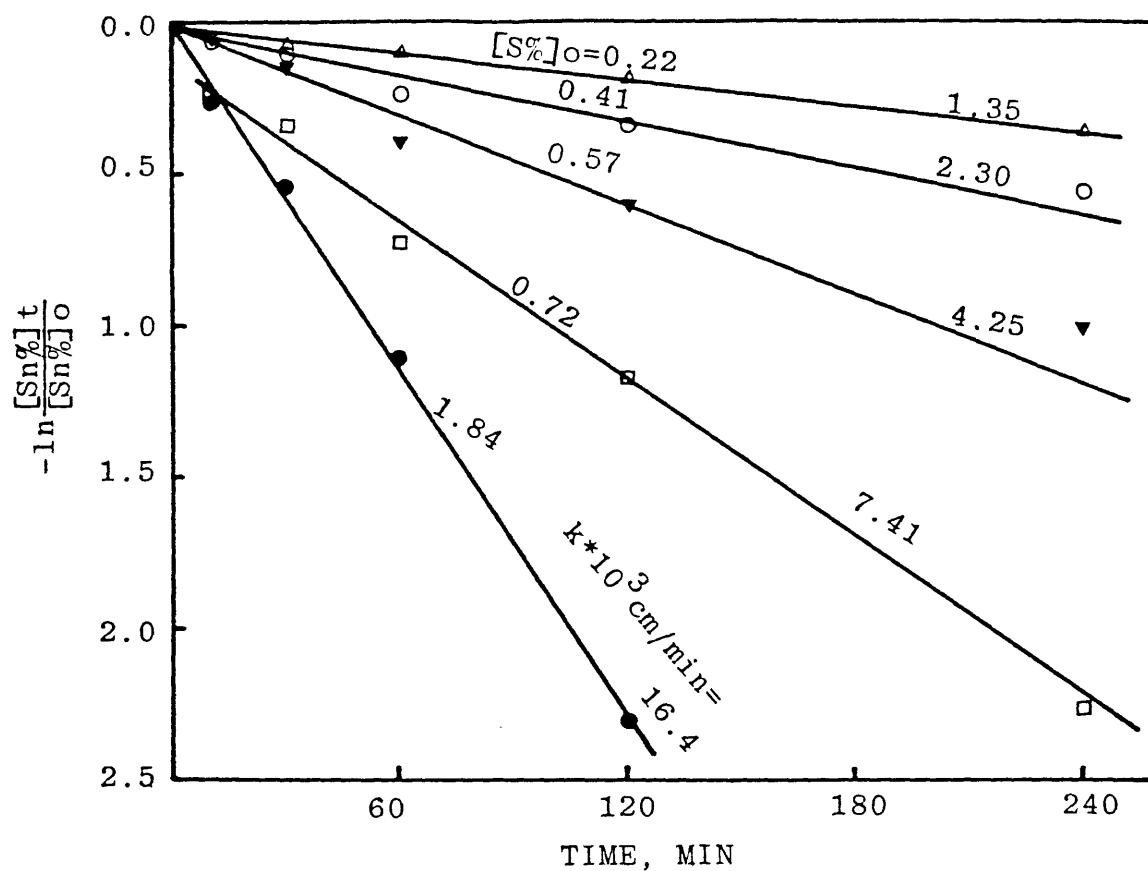


Fig.6.11 First Order Plot of Fig.4.33 for the Effect of Initial Sulphur Content

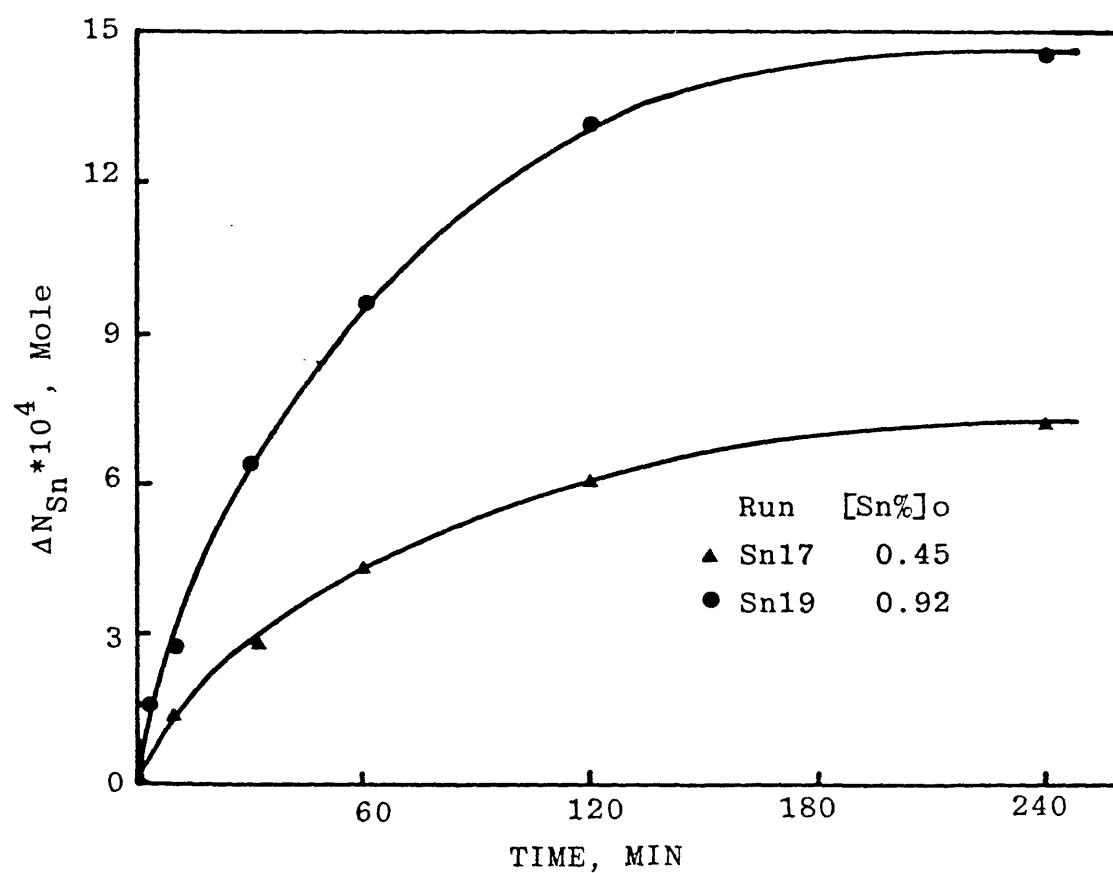


Fig.6.12 Effect of $[\text{S}\%]_o$ on Transferred Moles of Sn

6-3-4. Effect of Temperature

Higher operating temperature is usually favourable to a volatilization process. As shown in Fig.4.35 and 36, page 87 and 88, there was marked acceleration of tin removal with the increase of temperature.

Straight lines with different slopes were obtained in Fig.6.13 by a first order reaction model. The corresponding reaction rate constants are indicated. A mean apparent activation energy of 25 KCal/mole for the process is obtained from a plot of $\ln k$ against $1/T$ as shown in Fig.6.14.

Temperature influences the rate of a process by its effects on the equilibrium constant K and rate constant k , which can be expressed as

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^{\circ}}{R} \quad (6-13)$$

and

$$\frac{d \ln k}{d(1/T)} = -\frac{E}{R} \quad (6-14)$$

For the reaction



$$\Delta G^{\circ} = -RT \ln K = 34193 - 6.34T ; \quad K = p_{SnS}/a_S a_{Sn}$$

Using this value of ΔH° , equation (6-13) becomes

$$\frac{d \ln K}{d(1/T)} = -17.21 \text{ KCal/mole}$$

Using the value of 25 KCal derived from the temperature dependence of the reaction rate equation (6-14) becomes,

$$\frac{d \ln k}{d(1/T)} = -12.58 \text{ KCal/mole}$$

K varies with temperature more than does k , however, it is difficult to make an exact comparison due to errors

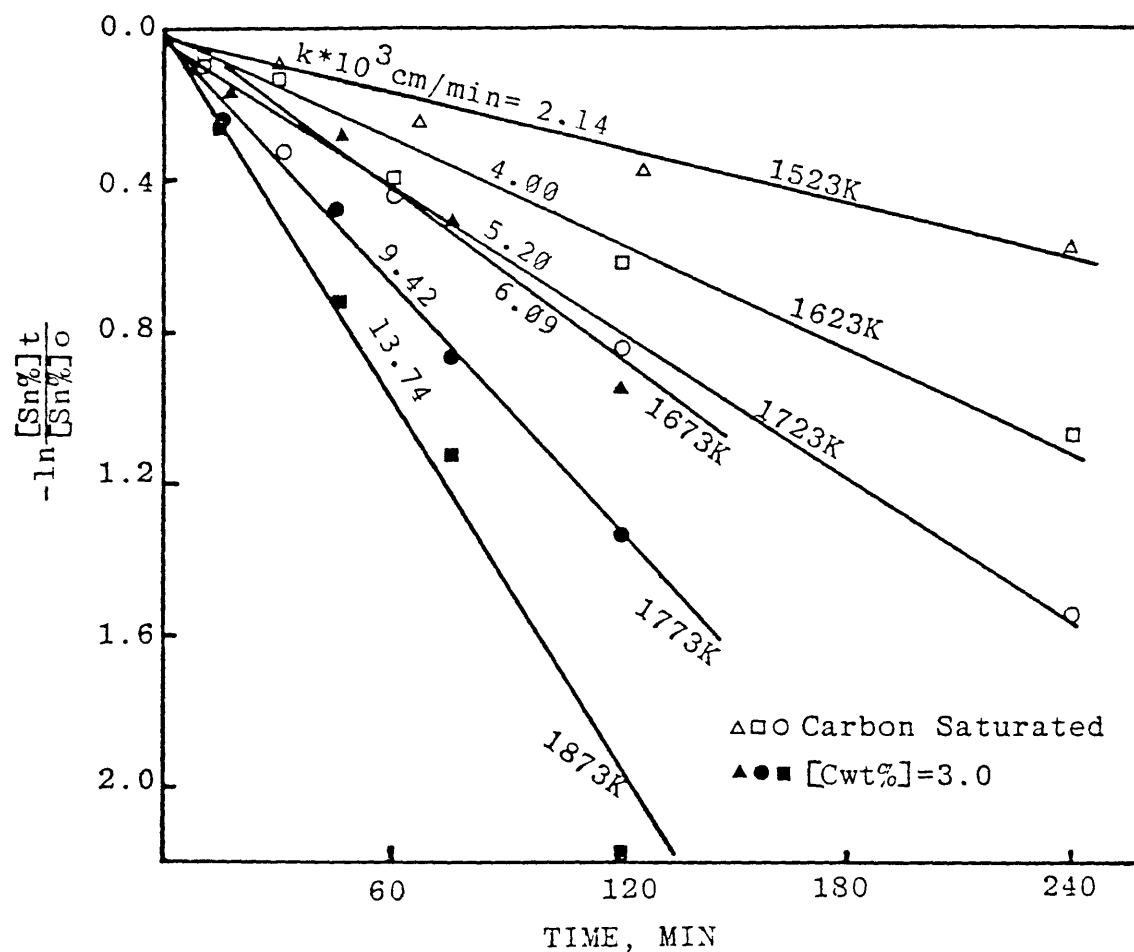


Fig.6.13 First Order Plot of Fig.4.36 for the Effect of Temperature

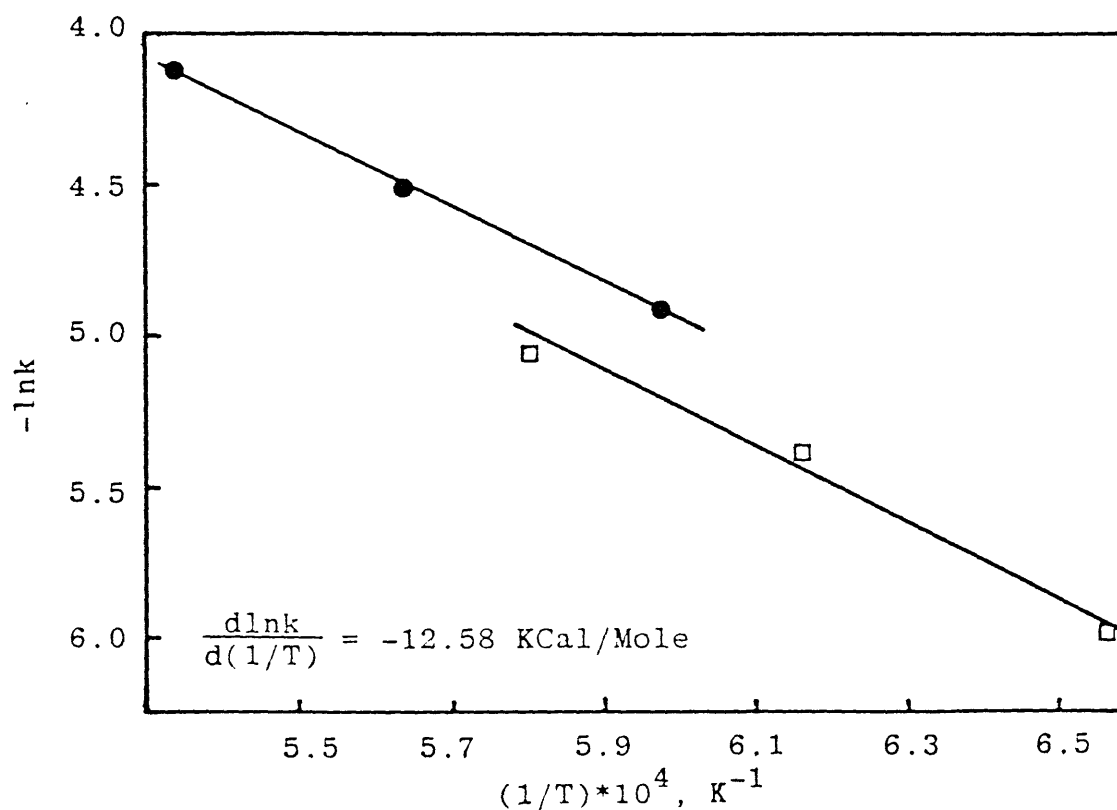


Fig.6.14 Plot of $\ln k$ against $1/T$

induced by thermodynamic and experimental data. The dependence of the rate constant on the temperature in the present system is most probably due to the increase of equilibrium constant with temperature. This gives a greater equilibrium partial pressure of SnS when activities of tin and sulphur in the metal are unchanged. Since this is an irreversible reaction and argon bubbles supply enough interfacial area, more dissolved tin and sulphur react producing a greater partial pressure of SnS to match the new equilibrium state. If the increase of the rate is entirely due to the change of equilibrium state, ΔH° in the range of 1523-1873K can be estimated as 25 KCal/mole for this reaction.

6-4. DETINNING FROM LOW CARBON IRON

6-4-1. Effect of Carbon on the Activity Coefficient of Tin

The results of the removal of tin from low carbon iron are not as satisfactory as those from carbon saturated iron as shown in Table 4-7, page 89. This lower refining efficiency arises from the effect of carbon on the activity coefficients of tin and sulphur in the iron.

For the reaction



the equilibrium constant can be expressed as

$$K = \frac{P_{\text{SnS}}}{[\text{Sn}][\text{S}]f_{\text{Sn}}f_{\text{S}}} \quad (6-15)$$

for a carbon free melt, and

$$K^C = \frac{P_{\text{SnS}}^C}{[\text{Sn}][\text{S}]f_{\text{Sn}}^C f_{\text{S}}^C f_{\text{S}}^C f_{\text{Sn}}^C} \quad (6-16)$$

for a carbon containing melt. At the equilibrium state and at constant concentrations of Sn and S,

$$K = K^C$$

that is

$$f_{\text{S}}^C f_{\text{Sn}}^C = P_{\text{SnS}}^C / P_{\text{SnS}} \quad (6-17)$$

where f_{S}^C and f_{Sn}^C represents the effect of carbon on the activity coefficient of sulphur and tin respectively, and is related to interaction coefficients e_{S}^C and e_{Sn}^C by equations $e_{\text{Sn}}^C = (1/[\text{C}\%]) \log f_{\text{Sn}}^C$ and $e_{\text{S}}^C = (1/[\text{C}\%]) \log f_{\text{S}}^C$. P_{SnS}^C and P_{SnS} can be calculated from equation (A-8) in Appendix I and the experimental results given in Fig.4.38, page 92. Fig.6.15 shows the first order plot of the results given in Fig.4.38. To obtain P_{SnS} the appropriate k value

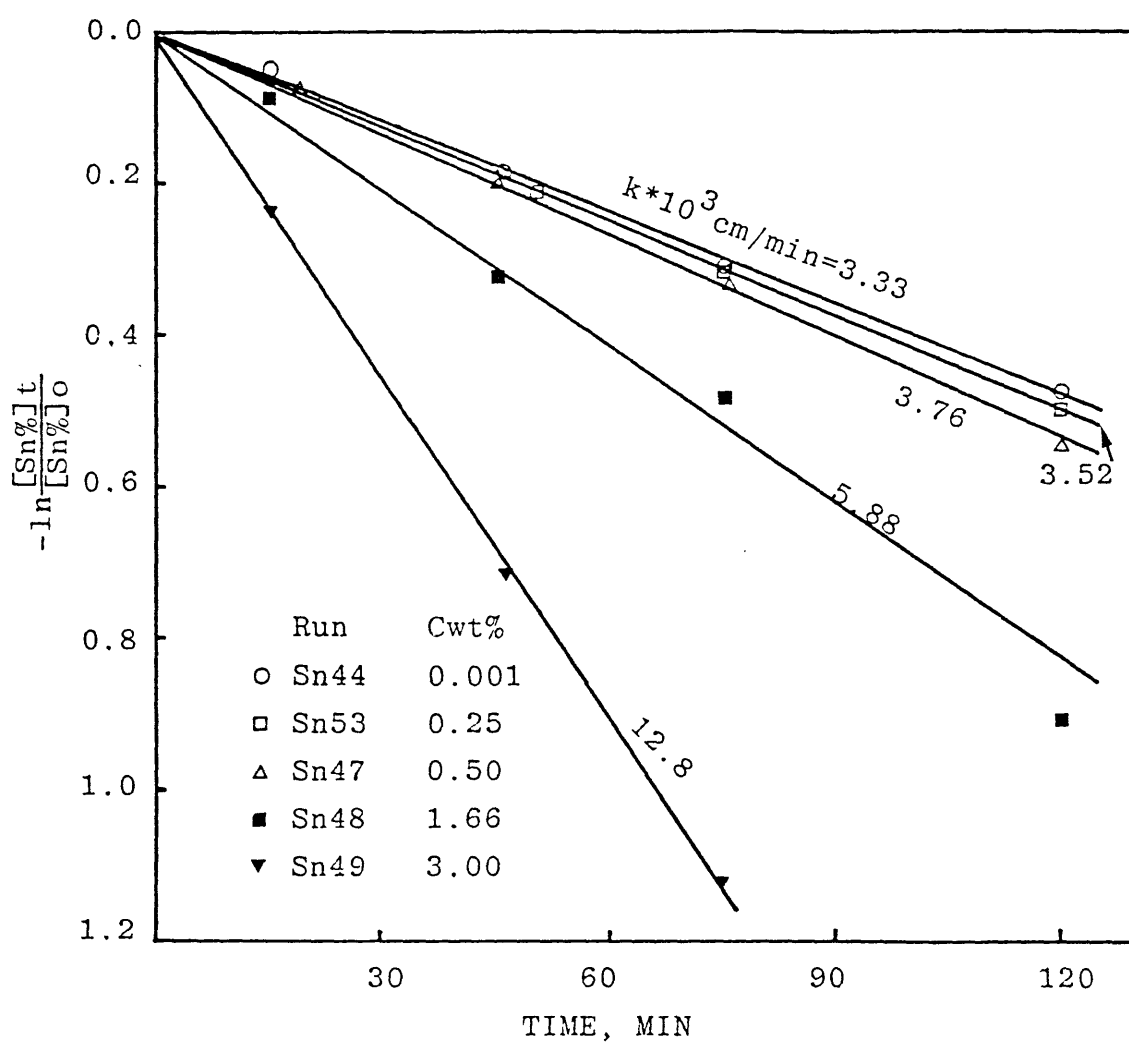


Fig.6.15 First Order Plot of Fig.4.38 for
the Effect of Carbon Content

from this figure is substituted into the equation (A-8)

$$P_{SnS} = \frac{b[Sn]_t(e^{k'}-1)}{b[Sn]_t(e^{k'}-1)+v} \quad (A-8)$$

where $k'=k/hm$ and $b=224.14Wm/M_{Sn}=35.8$ for the present system. Following a similar procedure described in the section 5-2-2 for the calculation of e_{Cu}^C , e_S^C equal to 0.114 is used as a base to calculate e_{Sn}^C in the present system. The calculated results are given in Table 6-7 and $\log f_{Sn}^C$ is plotted against [C%] in Fig.6.16.

The values of the interaction coefficient of carbon to tin obtained by other investigators are quite scattered as listed in Table 6-8.

Table 6-8

Interaction Coefficient of Carbon to Tin

Reference	13	59	27	90	87
e_{Sn}^C	0.28	0.18	0.06	0.0	0.0

Schenk and Froberg⁽²⁷⁾ estimated the interaction coefficient from the position of the element in the periodic system. The periodicity was explained in terms of the electronic states of the metal solutions. Alloying elements brought into metallic solutions are ionized from the unexcited atomic state by giving off or taking up electrons. Tin dissolves in iron and gives off electrons. If a third element, for example carbon, which gives off electrons, is brought into solution, tin should be driven out, which increases the activity of tin. Since the periodic system is based implicitly on the electronic states of atoms, the connection with solubility and activity changes is reasonable. Estimated value of e_{Sn}^C equal to 0.06 is the

Table 6-7 Results of calculation of e_{Sn}^{C}

Run	Sn44	Sn53	Sn47	Sn48	Sn49
[Cwt%]	0.001	0.25	0.50	1.66	3.00
$k' \cdot 10^3 \text{ min}^{-1}$	3.92	4.14	4.42	6.92	15.06
$p_{\text{SnS}} \cdot 10^4 \text{ atm}$ [Sn%] $t=0.99$	9.27	9.79	10.46	16.38	35.72
$f_{\text{S}}^{\text{C}} f_{\text{Sn}}^{\text{C}}$		1.056	1.128	1.767	3.852
$e_{\text{S}}^{\text{C}} + e_{\text{Sn}}^{\text{C}}$		0.095	0.1046	0.1489	0.1952
e_{Sn}^{C}		-0.019	-0.009	0.035	0.081
$\log f_{\text{Sn}}^{\text{C}}$		-0.005	-0.005	0.058	0.243

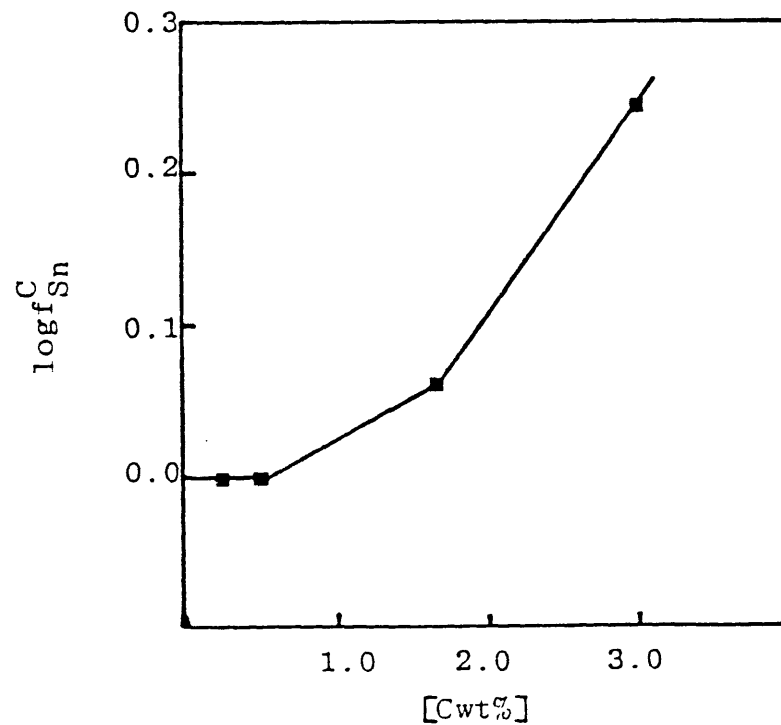


Fig.6.16 The Influence of Cwt% on the Activity Coefficient of Tin

closest to the present calculations in Table 6-8.

A value of e_{Sn}^{C} equal to 0.18⁽⁵⁹⁾ was obtained from a study of the effect of carbon on the vaporization of tin at 2073K using the levitation melting technique. Chipman and Fuwa⁽⁹⁰⁾ measured the equilibrium of the reaction $[\text{C}] + \text{CO}_2 = 2\text{CO}$ by passing CO/CO_2 gas mixture over the surface of the liquid iron, in which the carbon content usually did not exceed 0.3%. From the effect of alloying elements, they found that the effect of tin on the activity coefficient of carbon seemed to be negligible until the concentration of tin in the iron exceeded 10%. Mori et al⁽⁸⁷⁾ repeated this investigation and obtained a similar result. In the present study, the effect of carbon on the activity coefficient of tin is also extremely small when carbon content is not more than 0.5%.

6-4-2. Effect of Other Alloying Elements

When argon is bubbled into the metal phase, mass transport processes both in the metal and gas are comparatively fast. It also has been found that the chemical reaction is at equilibrium. A method of speeding up this kind of process would be to change the equilibrium state and result in a greater thermodynamic driving force for the reaction. The removal of tin would then be faster if the equilibrium partial pressure of SnS were raised since the chemical reaction is fast enough to be at equilibrium. From the equation (6-12)

$$p_{\text{SnS}} = K_f f_{\text{Sn}} [\text{Sn}] [\text{S}] \quad (6-12)$$

p_{SnS} can be raised by increasing either or both of the

activity coefficients of tin and sulphur, which can be achieved by adding alloying elements that have a positive interaction coefficient on tin.

Carbon, of course, has a great effect on the activity coefficient of tin as calculated above. Elements close to it in the periodic table, silicon and boron, were tested and the results are shown in Fig.4.39 and 4.40, page 93 and 94. Since the contents of silicon and boron have not been confirmed by analysis, quantitative explanation of the interaction coefficients can not be made for these two elements. However, qualitatively, both of them promote the vaporization of SnS from iron melts.

The effect of silicon on the tin removal is not as good as that of carbon. $\epsilon_{\text{Sn}}^{\text{C}}$ equal to 9.6 and $\epsilon_{\text{Sn}}^{\text{Si}}$ 4.0 were obtained⁽⁵⁹⁾ by studying the effect of alloying element on the vaporization of tin at 2073K. Both indicate that silicon increases the activities of tin and sulphur in the iron but the extent of the effect is less than that of carbon. The present results are in agreement. There is another possible coupled reaction taking place in the system,



$$\Delta G^{\circ} = 63240 - 13.48T; \quad K = 3.7 \times 10^{-5} \text{ at } 1873\text{K}$$

The equilibrium constant is about 70 times smaller than that of the formation reaction of SnS. If this reaction occurs, silicon will compete for sulphur with tin and it is not favourable to the detinning.

Boron markedly enhances the vaporization of SnS, at least as well as carbon or better as shown in Fig.4.40, page 94. It has been reported⁽⁸⁶⁾ that boron has a similar effect on the activity coefficient of sulphur as on that of carbon.

If this is true, boron also increases the activity coefficient of tin as carbon does or even better in the present system.

As shown in Fig.4.41, page 94, when the metal contains about 4.0%Si and 3.0%C, the removal of tin is very fast and 50% of initial tin can be removed in 15 minutes. It is noticeable that the combined effect on the rate is greater than the sum of separate effects of 3.0%C and 4.0%Si. This also can be seen from the differences of rate constants as shown in Fig.6.17.

Chromium slightly speeds up the detinning process but the effect is not as good as those discussed above. Morales and Sano⁽⁵⁹⁾ also found that chromium promoted the vaporization of tin from iron at 2073K a quarter as well as did carbon.

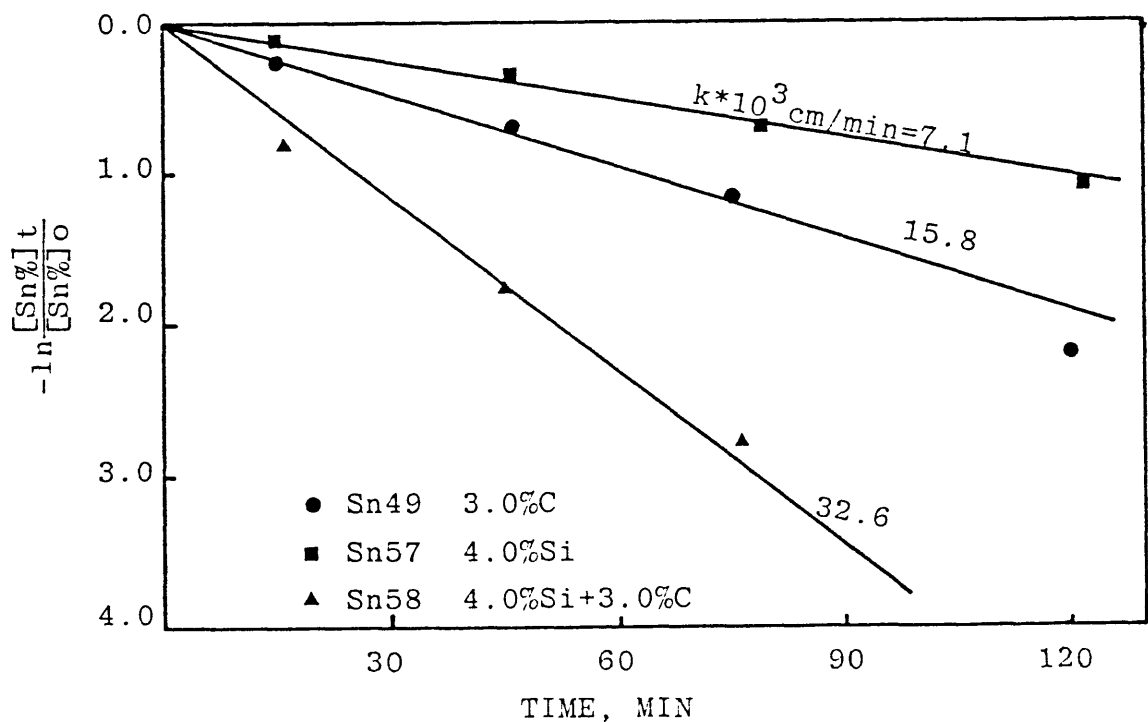


Fig. 6.17 The Influence of Carbon and Silicon on the Rate Constant

6-5 SUMMARY AND CONCLUSIONS OF DETINNING

In the study of kinetics of high temperature reactions, one of the possible rate-controlling processes is the transport of reactants and products to or from the reaction interface. For the system studied in the present work, mass transport processes include the transfer of tin and sulphur in the bulk metal phase to the metal/gas interface and the removal of the product, SnS vapour, from the reaction surface to bulk gas phase.

If there is no forced flow of argon within the crucible, the removal of the product of reaction depends upon the diffusion of SnS vapour in argon gas. A value for the diffusivity, $D_{\text{SnS-Ar}}$, equal to $1.51 \text{ cm}^2/\text{sec}$ is obtained from the present experimental results. This value is close to that of $1.71 \text{ cm}^2/\text{sec}$ which is calculated by the equation based on the kinetic theory of gases⁽¹⁰⁾. From the changes of the mass of tin removed with the depth of the crucible, it can be concluded that the diffusion of SnS vapour in argon takes part in the rate control but the process does not depend only on it. The removal of tin is mixedly controlled by the diffusion of SnS in the gas and the chemical reaction at the interface under these conditions.

When argon is bubbled into the metal, the stirring is usually vigorous enough to keep the bulk concentration uniform. The resistance of mass transport exists only near the interface. Mass transfer coefficients for from surface to the inside of a rising bubble can be estimated to be in the range of $10-10^2 \text{ cm/sec}$ from the value of k_g , which is theoretically derived gas mass transfer coefficient on the

basis of steady state gas circulation within the bubble⁽²⁹⁾. Usually k_m is of magnitude of 10^{-2} for a bubble stirred system. The calculated tin transfer coefficient k cm/sec is always in the range of 10^{-5} - 10^{-4} even in a vigorous bubbling condition. This low value indicates that the process is unlikely to be controlled by mass transport in the metal in the bubbling condition. Otherwise, the rate of the removal of tin should be greater.

All parameters which affect p_{SnS} influence the apparent rate of the process. The reaction (6-3) is an endothermic one, and its equilibrium constant K increases with operating temperature. Initial sulphur and tin contents represent the chemical driving force which directly control the value of p_{SnS} . Alloying elements, carbon, silicon, boron and chromium, increase either or both activity coefficients of tin and sulphur in the iron, which, in turn, speeds up the removal of tin via a greater p_{SnS} in the argon bubbles.

The equilibrium partial pressure of SnS is calculated from equation (6-12) by choosing $e_S^C = 0.114$ and $e_{\text{Sn}}^C = 0.06$ or 0.081 . The change of equilibrium partial pressure following tin content in the metal is compared with the experimental results of Sn28 and Sn76 which are calculated from the equation (A-8). As shown in Fig.6.18, experimental results are quite close to the equilibrium value.

The mechanism of the removal of tin is clear so far. The following conclusions may be drawn from the above discussion.

As argon is bubbled into the metal, the apparent rate of tin removal is controlled by the magnitude of the equilibrium partial pressure of SnS, that is, the chemical

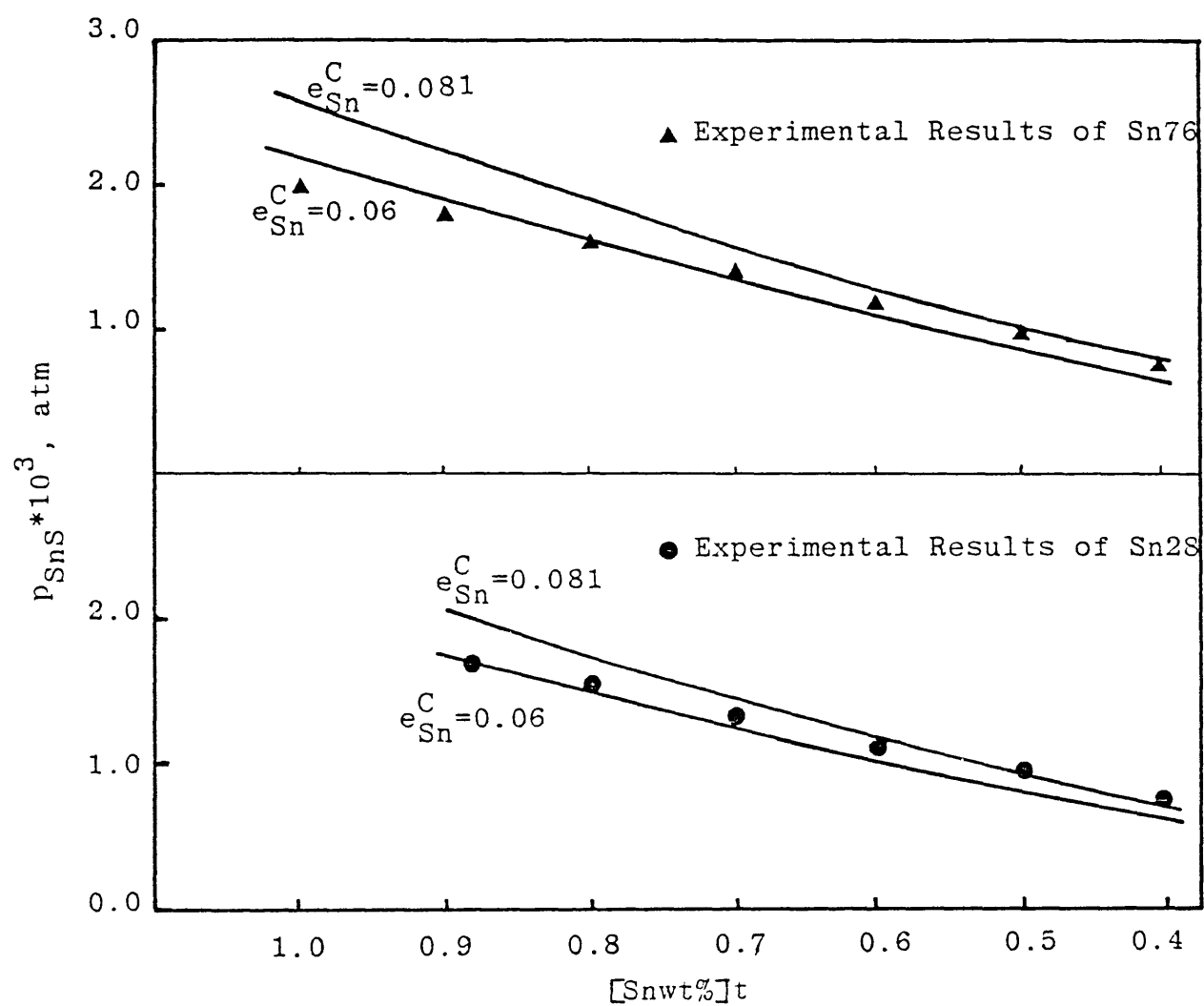


Fig.6.18 The Change of Partial Pressure of SnS with $[Snwt\%]t$

reaction is at equilibrium. Any improvement to increase activities of tin and sulphur in the metal and to remove SnS vapour away from the reaction site will speed up the detinning process. Carbon, silicon and boron promote the equilibrium partial pressure of SnS by increasing activity coefficients of either or both tin and sulphur in the metal. For iron melts containing about 0.65%S, 0.7%Sn, 4.0%Si and 3.0%C , 50% of the initial tin can be removed within 15 minutes at 1873K under inert gas bubbling conditions.

Argon bubbles not only reduce mass transport resistance, they also affect the chemical reaction process in the present system. A greater argon volume provides a bigger area of metal/gas interface at which SnS vapour forms and lowers the partial pressure of SnS in the gas which pushes the chemical reaction taking place. The removed tin is proportional to the volume of argon bubbled.

Tin is removed from iron melts by the evaporation of SnS. Higher operating temperature and greater inert gas stirring are favourable for the process.

APPENDIX I

The Calculations of J_{SnS} and p_{SnS}

As the evaporation of SnS is irreversible and follows a first order reaction model, the rate equation of the process can be expressed as

$$\ln \frac{[\text{Sn}\%]_t}{[\text{Sn}\%]_0} = -\frac{k}{hm}t \quad (\text{A-1})$$

or

$$[\text{Sn}\%]_t = [\text{Sn}\%]_0 e^{-k't} \quad (\text{A-2})$$

where $[\text{Sn}\%]_t$ and $[\text{Sn}\%]_0$ are the concentrations of tin in the metal after being refined for t minutes and at the beginning of the refining respectively; hm (cm) the depth of the metal bath, k (cm/min) the rate constant, k' (min^{-1}) equal to k/hm and t (min) the refining time.

The loss of moles of tin per minute after t minutes refining can be written as

$$\Delta N_{\text{Sn}} = ([\text{Sn}\%]_{(t-1)} - [\text{Sn}\%]_t) W_m / 100 M_{\text{Sn}} \quad (\text{A-3})$$

According to equation (A-2),

$$[\text{Sn}\%]_{(t-1)} = [\text{Sn}\%]_0 e^{-k'(t-1)}$$

$$[\text{Sn}\%]_t = [\text{Sn}\%]_0 e^{-k't}$$

Substituting $[\text{Sn}\%]_{(t-1)}$ and $[\text{Sn}\%]_t$ into equation (A-3) and rearranging:

$$\begin{aligned} \Delta N_{\text{Sn}} &= (W_m / 100 M_{\text{Sn}}) [\text{Sn}\%]_0 e^{-k't} (e^{k'} - 1) \\ &= (W_m / 100 M_{\text{Sn}}) [\text{Sn}\%]_t (e^{k'} - 1) \end{aligned} \quad (\text{A-4})$$

As the loss of moles of tin and sulphur is equal, the flux of SnS across the surface of the metal of which the area is equal to A can be calculated by the equation

$$\begin{aligned}
 J_{\text{SnS}} &= \Delta N_{\text{Sn}} / A \text{ mole cm}^{-2} \text{ min}^{-1} \\
 &= (Wm / 100 A M_{\text{Sn}}) [\text{Sn}\%]_t (e^{k'} - 1)
 \end{aligned}
 \tag{A-5}$$

In a similar way and under the assumption that SnS vapour is an ideal gas, the volume of SnS vapour produced, V_{SnS} , can be expressed as

$$\begin{aligned}
 V_{\text{SnS}} &= 22414 \Delta N_{\text{Sn}} \text{ cc/min} \\
 &= (224.14 Wm / M_{\text{Sn}}) [\text{Sn}\%]_t (e^{k'} - 1)
 \end{aligned}
 \tag{A-6}$$

The partial pressure of SnS in one atmosphere of argon at time t , in turn, can be derived as

$$P_{\text{SnS}} = V_{\text{SnS}} / (V_{\text{SnS}} + V_{\text{Ar}}) \tag{A-7}$$

where V_{Ar} , the volume of argon being bubbled into the metal every minute, is equal to the argon flowrate v (cc/min). Substituting V_{Ar} and V_{SnS} into the equation (A-7),

$$P_{\text{SnS}} = \frac{b [\text{Sn}\%]_t (e^{k'} - 1)}{b [\text{Sn}\%]_t (e^{k'} - 1) + v} \tag{A-8}$$

where

$$b = 224.14 Wm / M_{\text{Sn}}$$

The results of J_{SnS} shown in section 6-2-2 are calculated by equation (A-5) for those experiments in which argon was purged from the bottom of the furnace, and p^0 from equation (A-8) and experimental data of Run Sn76 in which argon was bubbled into the metal.

ACKNOWLEDGEMENTS

I would like to express my profound gratitude here to Professor J.H.E. Jeffes for his helpful supervision and unforgettable kindness throughout the past three years.

Also, I am deeply grateful to Professor P. Grieveson for valuable suggestions and discussions.

Thanks are due to those members of the Department of Metallurgy and Materials Science at Imperial College who offered their assistance and friendship to me during the course of this study. Special recognition is due to M. Haddon and A. Chrysanthou.

I am indebted to the Chinese Government and Stephen-Anna Hui Fellowship for their financial support.

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