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COPPER REMOVAL FROM STEEL SCRAP USING A SULFUR MATTE

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FINAL REPORT
TO
DEPARTMENT OF ENERGY

Copper Removal from Solid Ferrous Scrap

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Consolidated Natural Gas
Center for Iron and Steelmaking Research
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Introduction

As discussed in detail in the Appendix, copper is detrimental to the properties of steel. Copper is present in most forms of recycled scrap, such as bundles and shredded scrap. Typical levels of copper in these forms of scrap are 0.2 to 0.4%, whereas critical grades of steel require less than 0.1 and often 0.06% Cu. Therefore, these forms of scrap cannot be used alone to produce quality steels. Steelmakers must dilute the copper from lower quality scrap with expensive high quality scrap or direct reduced iron pellets.

Currently there is no effective method for removing copper from scrap. The only proven method is improved physical separation which is labor intensive, expensive, and only marginally reduces the copper content. Chemical treatments, such as sulfide treatment of liquid metal and vacuum, are not effective as discussed in the Appendix in detail.

Carnegie Mellon University developed a concept for removing copper from solid ferrous scrap at 900-1000°C using a FeS-Na_2S reagent. Small laboratory tests showed 90% of the Cu from simulated solid scrap could be removed. Based on this concept, DOE funded a project to further develop the process with cost sharing from the Center for Metals Production, Consolidated Natural Gas, The Joseph Company and the Center for Iron and Steelmaking Research (CMU).

The major results of this study are summarized in this report. Details are given in the reports in the Appendix.

Scope of Work

Kiln Tests: The major work was run in a large rotary kiln, 0.7 m diameter x 4 m long, using 60-100 kg of scrap. These tests were run to determine the copper removal as a function of time, temperature, matte composition and scrap type.

Basic Laboratory Tests: Laboratory tests were conducted to determine the rate of the reaction and the controlling mechanism, the solubility of Cu_2S in the matte and the wetability of matte on the metal.

Dip Tests: Specific types of scrap, such as motors, were dipped into a bath of matte (10 kg) to see if Cu could be removed.

Drainage and Remelt Tests: Special tests were run in the kiln to determine if the matte could be drained from the kiln. Then a portion of the metal was melted in a 10 kg induction furnace and the sulfur and copper contents were determined.

Environment Report: An expert on copper production (Professor W. Davenport) was retained as a consultant to examine possible environmental problems, such as off-gas and disposal of the matte.

Basic Principle

Copper sulfide (Cu_2S) is thermodynamically more stable than FeS at the temperatures of the process. The basic reaction is,

$$FeS + 2Cu = Cu_2S + Fe$$

The Na_2S, about 15-20%, is present to provide a liquid matte and reduce the activity coefficient of Cu_2S in the matte. If the process is carried out with solid scrap, before the copper is put into solution, the thermodynamics are greatly improved allowing for an economic process. For solid scrap, less than 6 kg of matte per ton of metal is required versus 100 kg for liquid scrap to reduce the copper from 0.2 to 0.1%. Most copper is present in scrap as pure copper (i.e., wires, tubes, etc.) or platted copper.

Experimental and Results

The experimental conditions and results are given in detail in the papers in the Appendix, only the major findings are given below.

Laboratory Studies

As part of the DOE sponsored research a number of fundamental studies of the reaction of solid copper with FeS-Na_2S mattes were carried out. The major findings of this program are as follows:

1. **The equilibrium copper sulphide content in the matte at 1000°C is approximately 50% for a matte with a starting iron sulphide content of 82%.**
2. The equilibrium copper sulphide content in the matte decreases with decreasing temperature and increasing sodium sulphide content in the matte.
3. The rate of the reaction is controlled by liquid phase mass transfer.
4. The rate of the reaction is reduced as the sodium sulphide concentration in the matte is increased due to the formation of a viscous layer at the matte-copper interface.

5. The matte penetrates the grain boundaries of the copper causing small pieces of copper to flake from the whole. In this manner the copper disintegrates as it reacts. The dissolution reaction rate is therefore quite high and the overall reaction rate is limited by transfer of iron sulphide in the matte to the reaction zone. Reaction rates of up to 0.15 grams per minute per cm^2 were measured.

6. The matte wets copper, iron and alumina and contact angles of less than 5 degrees were measured in each case.

7. The reaction should be carried out in a non-oxidizing atmosphere as scale build-up can interfere with the reaction.

These findings indicate that the process should be carried out within a reaction vessel which promotes liquid phase mass transfer and a rotating kiln was chosen as an appropriate vessel. In addition, the 82% FeS - 18% Na_2S matte was chosen as the appropriate starting composition.

Tests were also conducted to determine the composition of any gases coming off the process by analysis with a mass spectrometer. It was found that the sulfur was coming off as SO_2.

To determine the efficiency of matte drainage L angles of steel (40 x 40 x 3 mm), steel plate (40 x 2 mm) and a copper sheet (40 x 2) were dipped into an 18% Na_2S - 82% FeS bath at temperatures of 800, 900 and 1000°C. The samples were emersed for 3 to 5 minutes before being withdrawn from the bath and air cooled.

The copper sheet was completely dissolved at all temperatures. Results of the drainage experiments indicated that the amount of matte adhering to the scrap was minimal at 1000°C; however, significant amounts of matte remained attached to the scrap at lower temperatures. These results suggested that the optimum operating temperature of the kiln would be 1000°C.

Dip Tests

Possible difficult pieces of scrap containing copper were tested by dipping them into a bath (10 kg) of sulfide matte heated in an induction furnace. Of particular interest were electric motors, a major source of copper, which may be expected to give problems for the matte to contact the wires. In these tests virtually all of the copper wires were removed by the matte.

Kiln Experimental Procedures

An externally fired rotary kiln was purchased from CORECO Corp in Milwaukee, Wisconsin. A schematic of the kiln is given in Figure 1.

The kiln and its supporting frame, hydraulic pump mechanism and exhaust system is approximately 15 feet long, 6 feet wide and 9 feet high. the kiln is fired with natural gas and can reach temperatures in excess of 1000°C. The stainless steel cylinder which forms the working area of the kiln is two feet in diameter and twelve feet long. The rotation speed of the kiln can be varied from 1 to 10 rpm. The kiln is set up so that it can be tilted using a hydraulic pump to facilitate drainage of the matte. The heat is transported by conduction through the tube walls into the kiln working area. The hot zone was measured and the experiments carried out within the zone of constant temperature. The steel cylinder surface is therefore the hottest part of the working area of the kiln due to this indirect heating method. In order to contain a pool of matte within the kiln a stainless steel ring was welded into the inside of the kiln as a matte dam. Nitrogen gas was fed into the kiln to provide a protective atmosphere and an extraction fan connected to the kiln chimney to exhaust the kiln.

In each experiment, 40 - 50 kg of matte and 70 - 80 kg of assorted ferrous scrap (rods, pipes, angles, plates, etc.) were placed inside the kiln. The matte amount was determined by the minimum amount necessary to have reasonable matte pool in the kiln. The natural gas was ignited and kiln rotated at 2 rpm. Within 20 minutes a pool of liquid matte had formed and the kiln rotation speed increased to 5 rpm. 30 to 40 minutes later, when the matte has completely melted, and the temperature had reach 1000°C, the rotation speed was increased to 10 rpm.

Once the kiln was at temperature a matte sample was taken. After this sample, additional quantities of scrap were added to the kiln. The second scrap addition was of specially prepared scrap which had a preweighed amount of copper in the form of wire, pipe or tube. In this manner the total amount of copper added to the kiln was determined. Generally 3 to 4 kilograms of copper were added to the kiln during the second scrap addition. The matte was then sampled in 5 minute increments for 30 minutes. After treatment was completed the kiln was hydraulically tilted, the matte drained into a collection ladle and a final sample was taken from the ladle.

Results of Kiln Tests

The results of the kiln trials are described in the Appendix. The major finding were as follows:

1. The process removed over 90% of the copper in less than five minutes.
2. The rate and efficiency of Cu removal was independent of Cu_2S level as long as it was below saturation.
3. At 900°C the process was significantly less effective when using mattes containing up to 25% Na_2S. In these tests large quantities of matte were stuck to the kiln.
4. Motors and other forms of scrap containing copper were successfully treated.

Drainage of Matte

One of the critical concerns was whether the matte would drain effectively from the scrap. A special series of experiments were conducted to determine how much matte stuck to the scrap and how it could be removed. In these tests, scrap which was treated was remelted in 15 kg lots in an induction furnace and the final metal analyzed for S and Cu. The major findings were as follows:

1. The initial Cu and S contents of the bulk scrap increased from 0.04 and 0.043% to 0.05 and 0.159% respectively. The bulk scrap were pieces with no added copper. The increase in copper is tolerable but not for sulfur. The increased sulfur was due to a thin coating of sulfide matte remaining on the scrap.
2. When the scrap was simply washed with water at room temperature and remelted the sulfur content was 0.09% An optimized simple water wash most likely could reduce the sulfur to below 0.05%.
3. Treatment of the scrap with a dilute 8% HCl solution reduced the sulfur content to 0.05%.

Environmental Report

Professor W. Davenport of the University of Arizona who is a leading expert in copper production was retained as a consultant to review the process for any environmental problems associated with the process or disposal of the matte. His report is included and the major findings were as follows:

1. The used matte can be used as a feed material to a conventional copper smelter economically. Treating 1 million tonnes of scrap produces 10^7 kg of matte. After considering refining, grinding and transportation costs, the net value of the copper is $4 million.

2. Using a slightly oxidizing atmosphere in the process will produce SO_2. This was confirmed in the present study; SO_2 can be effectively cleaned from the gas using off the shelf technology.

Conclusions and Recommendations

Copper removal from scrap by the proposed process was proven to be feasible. The major results were as follows:

1. The matte removed copper very quickly, taking less than five minutes to remove 90% of the copper.
2. Based on the results, less than 6 kg of matte per ton of scrap would be required to reduce the copper level from 0.25 to 0.10%.
3. In a commercial process, the production or treatment rate would simply be limited by the rate of heating the scrap.
4. Difficult forms of scrap such as electric motors can be effectively treated.
5. The major problem with the process would be the removal of the matte after treatment. Simple water or dilute acid washing will be effective. However, if this is done the scrap could not be directly charged hot into the electric arc furnace. This reduces the economics of the process but it is still economical.
6. The spent matte can be used in a copper smelter and, therefore, represents a valuable by-product. Technology exists to deal with other environmental considerations.

The next step in the development of the process would be a demonstration plant of about 5-10 tons per hour. This development is beyond the capability of the current reseachers. An industrial partner is required. Very preliminary discussions have been carried out with Linde Division of Union Carbide. Also, Elkem Metals has expressed some interest.

Apparently, at the present time steel and scrap producers do not feel there is an immediate need for the process. The copper problem is solved by dilution with high quality scrap or direct reduced iron. However, as more continuous casting is implemented, steelmaking yields continue to improve, and electric furnace producers continue to produce higher quality steels, there is an inevitable trend for the need for higher quality scrap and a treatment to remove copper from scrap. The present process has proven to be feasible and should be economical. We believe that within the next five to eight years there will be sufficient incentive for a scrap processor to employ this technology. In the short term the potential of the process could keep down the price of high quality scrap by providing a potential alternative.

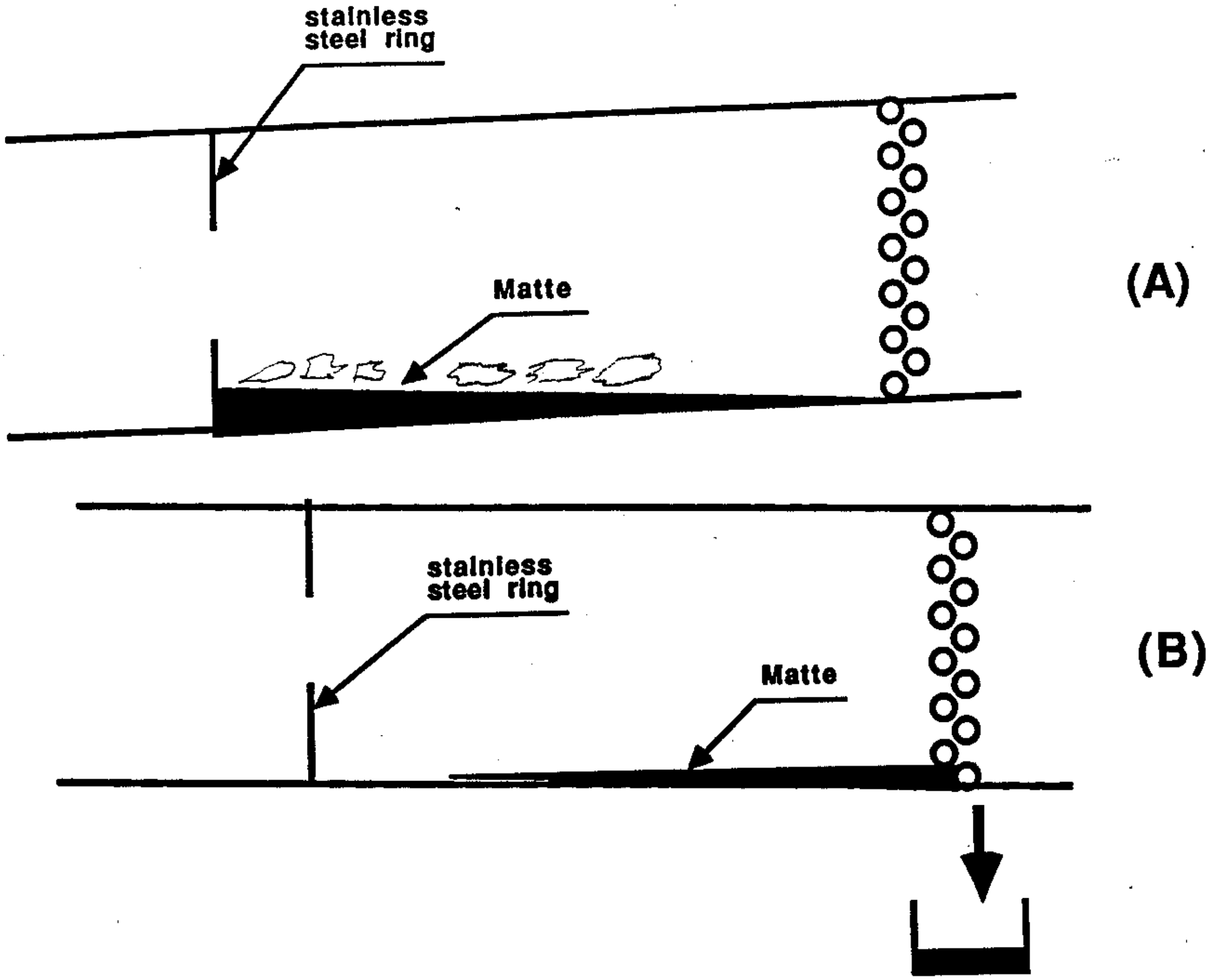

Fig 1: Schematic of (A) Operation Kiln Position and (B) Drainage Kiln Position

Optimum Atmospheric Conditions for Decopperizing Steel with FeS-Na_2S Matte

by

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November 5, 1990

Optimum Atmospheric Conditions for Decopperizing Steel with FeS-Na$_2$S Matte

The proposed steel decopperization process consists of contacting solid steel with liquid FeS-Na$_2$S matte at 900-1000°C. The matte absorbs Cu from the steel until the thermodynamic activity of Cu in steel and matte is nearly the same.

A potential difficulty with the process is sulfur evolution into the workplace and/or environment. However, the equilibrium sulfur pressure of Fe-saturated Cu$_2$S-FeS matte at 1000°C is only 10^{-7} atmospheres(1) so that sulfur evolution should not be rapid.

The question this report addresses is whether the decopperization process should be carried out under:

(a) oxidizing conditions in which case the evolved sulfur will be oxidized and leave the furnace as SO$_2$;

(b) reducing conditions in which case the evolved sulfur will be in the form of gaseous sulfur and H$_2$S.

Industrial contacts indicate that oxidizing conditions would be preferable. The author of this report concurs with their suggestion.

The rationale of the suggestion is that proven off-the-shelf technologies exist for removing SO$_2$ from furnace gases.* Further, it is likely that sulfur and H$_2$S gases (from decopperization under reducing conditions) would most easily be removed by afterburning and SO$_2$ removal. This would seem to be overly complex.

*Depending on the quantity of SO$_2$, sodium or calcium hydroxide solutions are used in the off-the-shelf SO$_2$ absorption systems.

[1] Gaskell, D. R., Palacios, J. and Somsiri, C., "The Physical Chemistry of Copper Mattes," in The Eliott Symposium, Iron and Steel Society (AIME), New York, 1990, pp. 151-162.

Feasibility of Selling Steel-Decopperization Byproduct Matte

by

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Feasibility of Selling Steel-Decopperization Byproduct Matte

The byproduct matte from steel decopperization is similar in composition to the concentrates normally treated by primary copper smelters. Industrial personnel contacted during this study indicate that the byproduct matte could be smelted along with normal copper concentrates. The matte would have to be crushed and ground to -100μm (-150 mesh) for this purpose.

Having concluded that smelting of the matte poses no significant problems, the rest of this report examines the economics of smelting the matte in a primary copper smelter.

1. Decopperization matte production rate

About 10^6 tonnes of steel will be decopperized per year. About 10 kg of byproduct matte (34% Cu_2S, 65% FeS, 1%Na_2S, i.e. 27% Cu) will be generated per tonne of steel. This is equivalent to a production of 10 x 10^6 kg or 10 000 tonnes of byproduct matte per year.

This quantity of matte is equivalent to 1/2 to 1 week's input to a western U.S.A. copper smelter. It is about 100 train-car loads of crushed matte.

2. Prices and costs

Electrolytic copper is currently selling at a spot price of $1.30 per pound (*New York Times*, November 3, 1990).

The cost of smelting the matte and refining and selling the resulting copper will be about $0.50 per pound of copper (industry source). The cost of transporting the matte from the eastern U.S.A. to a western U.S.A. smelter will be about $0.10 per pound of copper. Therefore, the total treatment cost will be about $0.60 per pound of copper.

Smelting the matte will generate a sizeable positive cash flow (please see appendix). There will, of course, be handling costs at the seller's site but these will be incurred whether or not the matte is sold.

3. Crushing and grinding

The matte will have to be crushed and probably ground before smelting. It will probably be crushed to about -2 inch diameter before shipping; then ground at the smelter site. Most smelters have suitable grinding facilities. A small crushing and grinding cost will be incurred.

4. Impurities

This report assumes that the matte contains no impurities except sodium. Normally, there is nothing in steel that should be a problem in a copper smelter. Zinc from galvanizing might be a problem if it is more than 1% in the matte.

5. Conclusion

Smelting of steel-decopperizing matte by primary copper smelters is technically and economically feasible. It will be the best way of dealing with the matte.

Appendix

Calculation of Cash Flow from Treatment of Steel Decopperization Matte

Assumptions:

10 000 tonnes of matte per year, 27% Cu
This is equivalent to 2700 tonnes of Cu per year or:

$$2700 \text{ tonnes Cu per year} \times \frac{2205 \text{ pounds}}{1 \text{ tonne}} = 6 \times 10^6 \text{ pounds Cu per yr.}$$

$$\begin{aligned}\text{Net return \$ per pound of Cu} &= \text{Sales price per pound of Cu - Costs per pound of Cu}\\ &= \$1.30 - \$0.60\\ &= \$0.70\end{aligned}$$

$$\begin{aligned}\textbf{Net cash flow, \$ per year} &= \text{pounds of Cu per year} \times \text{net return, \$ per pound of Cu}\\ &= 6 \times 10^6 \text{ pounds Cu per year} \times \$0.70 \text{ per pound of Cu}\\ &= \mathbf{\$4 \times 10^6 \text{ per year}}\end{aligned}$$

APPENDIX

APPENDIX CONTENTS

A New Process For Copper Removal From Ferrous Scrap

by

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Summary

A new process for the separation of solid copper from solid ferrous scrap has been developed within the Center for Iron and Steel Research at Carnegie Mellon University. The process which uses a liquid iron sulphide - sodium sulphide matte to react with solid copper at 1000°C, has been shown to be technically viable in small scale (100 kg) experiments in a rotary kiln. The process is optimal if run under a non-oxidizing atmosphere and complete separation of the matte from the scrap can be affected by drainage at temperature followed by a hot acid wash. Details of the experimental program and its findings, suggested matte chemistries and potential problems are discussed.

Introduction

The potential build-up of residual elements in steel is a cause for concern within both the steel and the scrap industries. High levels of elements such as copper, nickel, molybdenum, tin and chromium are thought to be deleterious to product consistency and have also been shown to cause problems during casting and subsequent processing.[1] The absolute level at which a residual element becomes deleterious to product quality is dependent upon the application; however, it seems reasonable to assume that, at some time in the future, prudent background levels of residual elements will be exceeded, leading to scrap sorting or pretreatment as a routine operation before charging into an electric arc furnace.

The problem of increasing copper residuals in steel is recognized to be a future problem in the steel industry. The growth of electric arc furnace steelmaking and the decreasing quantities of "home" scrap in the major integrated producers, due to increased use of continuous casters, has lead to a greater demand for quality scrap and increased residual levels in steel products. Large integrated producers can always dilute with hot metal and tolerate higher scrap copper contents; however, even this practice has limits. The problem is more difficult for electric furnace operators who must have an exact scrap analysis in order to meet the maximum allowed residual levels for a certain grade. Dilution, with prereduced iron, is also an option for electric arc furnace operators if it is economically feasible. A simpler solution is to find a method of removing copper from the solid scrap or to remove the copper from liquid steel.

Due to the future importance of this problem, a number of studies have been carried out at Carnegie Mellon University to develop an economical refining process to extract copper from contaminated scrap [2]. The outcome of the initial work was the realization that ladle processes were unlikely to be economical due to low copper distribution ratio's and high reagent or equipment costs. A lower temperature (1000°C) solid scrap treatment process was conceptualized and initial laboratory scale experiments indicated that the process was chemically feasible. As a result, a project was proposed to and accepted by the Department of Energy and, in October of 1988, trials were initiated to determine the technical feasibility of a low temperature matte process for the separation of solid copper from scrap. The purpose of this paper is to report the results of this experimental program which indicates that it is technically feasible to separate solid copper from solid scrap at 1000°C using a liquid $FeS\text{-}Na_2S$ matte.

Background

Copper Induced Defects

The copper residual problem is well recognized in both the solidification and deformation processing of steel. Gross defects have been found during the casting, rolling and welding of steels with significant copper residuals[3-6], while variations in product properties have been correlated to copper variations in the alloy[7].

Casting and rolling defects are caused by embrittlement due to the formation of a liquid copper film which forms when the iron is preferentially oxidized during the formation of scale[4,8]. This preferential oxidation causes an enrichment in copper and other residuals such as nickel, tin and antimony in the grain boundaries. As can be seen in Figure 1, concentration of copper in the grain boundaries leads to the formation of a liquid film at temperatures greater than 1100°C and causes the phenomenon classically known as 'hot shortness', i.e., intergranular decohesion which leads to cracking upon subjecting the casting to a shear stress at high temperatures. This phenomenon of liquid copper film embrittlement of steels in an oxidizing atmosphere is well documented, was originally proposed by Pfeil[10] and was discussed by a number of authors during the sixties[11 - 14]. One suggested method of eliminating this defect is to ensure that a solid intermetallic compound of copper and nickel is formed by setting the copper to nickel ratio in the steel at 3 : 1 or larger[8]; however, at higher copper levels (0.35%) substantial quantities of nickel (0.12%) would have to be intentionally added, or blended by scrap sorting, to ensure avoidance of the defect. An alternative approach is to ensure that copper residual levels are low or that scale formation is minimized during processing.

A copper induced crack which is very common in continuous cast slabs and blooms is the star crack. This crack is caused by localized surface concentrations of copper which are due to wear of the continuous casting mold. Again the cracks are caused by thin liquid copper films which penetrate the grain boundaries leading to embrittlement. This problem is generally countered by coating the molds with a more abrasive resistant material such as chromium or nickel[15,16].

Treatment of Liquid Steel

The copper problem is well recognized in practice and in the literature and has been the subject of a number of studies over the past thirty years. A major goal of a number of researchers was to develop a technique to remove copper from the liquid steel after scrap melting. A review of ladle processes for the removal of copper from liquid steel was recently published by Jimbo et al.[2] and details of the various techniques are given in Table I.

Reagent treatment of liquid steel, either by liquid lead or by a sulphide matte, is practically infeasible due to the low copper distribution ratio's, i.e., the equilibrium ratio of copper in the reagent to copper in the liquid steel at a given temperature, which are found in the current chemical ladle processes. For example, in trials at the Bureau of Mines[17] in a 1.5 ton pilot operation, only 40% of the copper was removed from the liquid steel using 200 lb of an FeS-Na_2S mixture per ton of carbon saturated iron. In both the sulphide slagging and the lead process, reagent costs will be high and results poor. Although technically feasible, these processes are economically infeasible due to equipment and reagent costs.

Vacuum processes for copper removal are kinetically limited and not feasible for large heat sizes. Even for small heat sizes the process would be capitally expensive and time consuming. Therefore, removal of copper from liquid steel in the ladle does not seem a viable alternative at this time.

Treatment of Solid Steel

90% of the copper present in scrap exists primarily as pure copper in the form of wire or platted material. In Table II processes for copper removal from solid scrap such as physical separation, preferential melting, acid treatment and the matte process, which is the subject of this paper, are reviewed.

Currently physical separation and practices of raw material segregation are widespread in the scrap industry[18,19]. In Table III, the benefits of a scrap sorting program are indicated. Although major reductions in scrap copper content can be affected through scrap sorting it is not possible to reduce copper levels to very low levels using this technique. Physical separation and sorting of scrap is time consuming, labor intensive, expensive and cannot reduce the overall copper contents to less than 0.05%; a level necessary for the production of flat products via an electric steelmaking route.

Preferential melting techniques proved unsuccessful due to difficulties in the separation of the liquid copper from the steel[20,21]. If copper can cause hot shortness then liquid copper must be able to penetrate and flow along grain boundaries. Therefore, copper wets solid iron and preferential melting of copper will be unsuccessful as a large portion of the copper will plate the iron surface making separation very difficult. The last two processes: that of a matte treatment at temperatures less than 1000°C and an acid treatment both appear to be conceptually feasible.[1] The dissolution of copper in an acid is chemically feasible therefore such a process could be developed.[2]

The low temperature matte process was invented at Carnegie Mellon University[2] and will be the subject of the remainder of this paper. The process is an extension of the sulphide slagging or matte process that was used in the ladle. The major difference is that the process is carried out at 1000°C while the scrap is solid and the matte is liquid. Clearly the process is also a scrap preheating process which

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[1] A more detailed background discussion and details of some early experimentation is given in reference 22

[2] Such a process was recently announced by Puremet Corp. [25]

means that it may be possible to combine both functions in one process. Due to the economic implications of a preheated scrap source, i.e., it is cost effective to preheat scrap with a cheap energy source such as natural gas before charging to an electric furnace, this process was subjected to an economic analysis which suggested that direct charging of the preheated treated scrap could result in a total process cost savings of $ 20 per ton of steel produced, due to cost savings at the electric arc furnace, if the low copper scrap differential was $40.00 per ton. Due to this overall process potential the matte process was developed at CMU.

Process Principles

This process is based upon two fundamental principles: (1) Copper can be transformed by chemical reaction from the solid state to a liquid, and, (2) The copper containing liquid can be completely separated (by drainage) from the scrap. In this manner solid copper can be completely removed from solid scrap.

Chemistry

The chemistry of the process is based upon the following reaction:

$$2\,Cu + FeS = Cu_2S + Fe \;....\; [1]$$

where solid copper reacts with iron sulphide to form copper sulphide while precipitating solid iron at the temperatures of interest (< 1000°C). This is, of course, the reaction which was the basis for the ladle sulphide slagging process originated by Jordan in 1950[23]; however, in this process, the reaction takes place at a much lower temperature while the scrap and copper are solid and separate.

Reaction 1 proceeds as written at temperatures above 614°C if the products and reactants are solid. At 1000°C the equilibrium constant of reaction 1 has a value of 2.6 and solid copper can reduce iron sulphide. Low temperature solid-solid reactions are generally slow being limited by the rate of diffusion and the contact area. Liquid-solid reactions are usually preferred as there is a larger contact area and the liquid phase diffusivities are much higher than that of the solid. Fortunately, mixtures of sodium sulphide, iron sulphide and copper sulphide have large areas of their phase diagrams which are liquid below

1000°C; thus, the process can be initiated with a liquid matte containing a mixture of iron and sodium sulphide. As can be seen in figure 2, the liquid phase field at 1000°C stretches from approximately 15 to 83% iron sulphide. Sodium sulphide is present only to liquify the matte at treatment temperatures and the reaction of interest is with iron sulphide; therefore, high iron sulphide containing mattes are chosen to initiate the process. Normally the starting matte chemistry for the process was 82% iron sulphide and 18% sodium sulphide for runs at 1000°C and 75% iron sulphide and 25% sodium sulphide for runs at 900°C.

As the reaction proceeds the iron sulphide in the matte is replaced by copper sulphide in an ionic exchange reaction where solid iron is precipitated and copper ions enter the matte phase. Thus the solid copper is transformed into copper ions dissolved in the liquid matte until either the copper sulphide solubility limit in the matte or the equilibrium condition of equation 1 is reached. Fortunately copper sulphide is almost completely miscible in the liquid iron sulphide - sodium sulphide mattes which are appropriate for this process (figure 3) and the matte fluidity increases with quite large additions of copper sulphide. This is important as process success depends upon not only reaction of copper with the matte but subsequent drainage of the matte in order to allow separation of the copper from the scrap. The steps of reaction plus separation are the keys to any successful high temperature process and failure to accomplish both steps will lead to process failure.

Recalculation of the thermodynamics of reaction 1 for the reaction of solid copper with a liquid iron sulphide to form a liquid copper sulphide and solid iron yields a an equilibrium constant at 1000°C of approximately 5 for this thermodynamically favorable reaction. The equilibrium constant for reaction 1 can be written as follows:

$$K = \frac{a_{Fe}\ a_{Cu_2S}}{a_{Cu}^{2}\ a_{FeS}} \qquad [2]$$

Thus to maximize the amount of copper in the matte it is necessary to maximize the activity of copper and iron sulphide and to minimize the activity of copper sulphide in the starting matte. It is also more favorable to treat solid copper ($a_{cu} = 1$) than to treat copper dissolved in liquid iron. In addition, as sodium sulphide reduces the activity of copper sulphide in the matte, it also aids in improving the thermodynamics of copper removal.

Reaction Rate

As part of the DOE sponsored research a number of fundamental studies of the reaction of solid copper with FeS-Na_2S mattes were carried out. The studies will be reported in detail in a subsequent publication [24]. The major findings of this program are as follows:

1. The equilibrium copper sulphide content in the matte at 1000°C is approximately 50% for a matte with a starting iron sulphide content of 82%.
2. The equilibrium copper sulphide content in the matte decreases with decreasing temperature and increasing sodium sulphide content in the matte.
3. The rate of the reaction is controlled by liquid phase mass transfer.
4. The rate of the reaction is reduced as the sodium sulphide concentration in the matte is increased due to the formation of a viscous layer at the matte - copper interface.
5. The matte penetrates the grain boundaries of the copper causing small pieces of copper to flake from the whole. In this manner the copper disintegrates as it reacts. The dissolution reaction rate is therefore quite high and the overall reaction rate is limited by transfer of iron sulphide in the matte to the reaction zone. Reaction rates of up to 0.15 grams per minute per cm^2 were measured.
6. The matte wets copper, iron and alumina and contact angles of less than 5 degrees were measured in each case.
7. The reaction should be carried out in a non-oxidizing atmosphere as scale build-up can interfere with the reaction.

These findings indicate that the process should be carried out within a reaction vessel which promotes liquid phase mass transfer and a rotating kiln was chosen as an appropriate vessel.

Matte Drainage from Scrap

To determine the efficiency of matte drainage L angles of steel (40 x 40 x 3 mm), steel plate (40 x 2 mm) and a copper sheet (40 x 2) were dipped into an 18% Na_2S - 82% FeS bath at temperatures of 800, 900 and 1000 C. The samples were immersed for 3 to 5 minutes before being withdrawn from the bath and air cooled.

The copper sheet was completely dissolved at all temperatures. Results of the drainage experiments are given in Figures 4 and 5, where the ΔM% is the weight gain upon removal from the matte. In both cases the amount of matte adhering to the scrap was minimal at 1000°C; however, significant amounts of matte remained attached to the scrap at lower temperatures. These results suggested that the optimum operating temperature of the kiln would be 1000°C.

Kiln Design

An externally fired rotary kiln was purchased from CORECO, Corp in Milwaukee, Wisconsin. A schematic of the kiln is given in figure 6. The kiln was installed at the USX pilot facility in Universal, PA, where a building was constructed to house the kiln. Electricity and gas hook-ups and supply were supplied by the AISI direct steelmaking task force who were also on-site at the time of the trials.

The kiln and its supporting frame, hydraulic pump mechanism and exhaust system is approximately 15 feet long, 6 feet wide and 9 feet high. The kiln is fired with natural gas and can reach temperatures in excess of 1000°C. The stainless steel cylinder which forms the working area of the kiln is two feet in diameter and twelve feet long. The rotation speed of the kiln can be varied from 1 to 10 rpm. The kiln is set-up so that it can tilted using a hydraulic pump to facilitate drainage of the matte. The heat is transported by conduction through the tube walls into the kiln working area. The hot zone was measured and the experiments carried out within the zone of constant temperature. The steel cylinder surface is therefore the hottest part of the working area of the kiln due to this indirect heating method. In order to contain a pool of matte within the kiln a stainless steel ring was welded into the inside of the kiln as a matte dam. Nitrogen gas was fed into the kiln to provide a protective atmosphere and an extraction fan connected to the kiln chimney to exhaust the kiln. A schematic of the internal configuration of the kiln is given in figure 7 and operational and drainage schematics are given in figure 8.

Experimental Procedure

A typical experimental procedure and schedule of sampling is outlined in figure 9. In each experiment 40 - 50 kg of matte and 70 - 80 kg of assorted ferrous scrap (rods, pipes, angles, plates etc..) were placed inside the kiln. The matte amount was determined by the minimum amount necessary to have reasonable matte pool in the kiln. The natural gas was ignited and the kiln rotated at 2 rpm. Within 20 minutes a pool of liquid matte had formed and the kiln rotation speed increased to 5 rpm. 30 to 40 minutes later, when the matte had completely melted and the temperature had reached 1000°C, the rotation speed was increased to 10 rpm.

The matte, at temperature, was very fluid and could be seen to wet the scrap easily. Generally, the matte was added in its hydrated state. A small amount of fume was given off during initial pool formation but no eruption or excessive amounts of reaction were noted. Apparently, the slow heating rate was sufficient to drive off any water content in the original matte starting materials. A limited amount of gas sampling was carried out to determine the composition of the gaseous species given off from the matte. In an open atmosphere a limited amount of SO_2 could be detected. During kiln operation a small amount of smoke could be seen in the kiln.

Once the kiln was at temperature a matte sample was taken. After this sample additional quantities of scrap were added to the kiln. The second scrap addition was of specially prepared scrap which had a preweighed amount of copper in the form of wire, pipe or tube. In this manner the total amount of copper added to the kiln was determined. Generally 3 to 4 kilograms of copper were added to the kiln during the second scrap addition. The matte was then sampled in 5 minute increments for 30 minutes. After treatment was completed the kiln was hydraulically tilted, the matte drained into a collection ladle and a final sample was taken from the ladle.

After the treatment was complete and the matte drained, only a thin layer of matte was left sticking to the kiln. After the experiment the matte and scrap was carefully examined for the presence of solid copper. In no case was any solid copper discovered in either the matte or the scrap.

Results and Discussion

A number of trials were conducted in the kiln. The major emphasis in the kiln trials were to determine:

1. The viability of the process.
2. The ability of the process to remove copper from electric motors.
3. The temperature range over which the process is applicable.
4. The effectiveness of matte drainage after processing

Chemical analysis of the matte was used to determine the effectiveness of the process and scrap remelting was carried out to determine the detrimental effects of the matte which was left sticking to the scrap.

Initial Experiments

The first series of experiments which were carried out after assembly, set-up and thermal characterization of the kiln were aimed at determining the basic operational viability of the kiln. The temperature was set at 1000°C and the initial matte chemistry was 82% FeS - 18%Na_2S.

Initial experimental results for copper sulphide pick-up and the change in iron sulphide and sodium sulphide contents are given in figures 10 - 12. As can be seen in these figures % Cu_2S increases for the first 7 minutes of the trial, followed by a gradual decrease. Sodium sulphide decreases throughout the experiment while iron sulphide apparently decreases at first and then increases. Theoretical analysis of the reaction assuming a linear reaction rate would give the curve shown in figure 13 and indicates that iron and sodium sulphide contents should decrease in the matte as the copper sulphide content increases. The actual results indicate that something else must be happening during the reaction which affects the matte. In addition to the matte chemical analysis, a mass balance for copper in the process indicated that the maximum recovery of the copper in the matte was 90.2% within 5 minutes of addition and that recovery decreased to 66.6% after 35 minutes. The matte was either increasing in volume as a function of time or the copper was reprecipitating from the matte. The matte was thoroughly examined for any solid copper content and none was found; however, it was noted during the experiments that the ends of the scrap rods were significantly thinner at the end of the experiment than at the beginning. It was postulated that the reoxidation of iron resulted in the formation of FeO which dissolved in the matte. This seemed reasonable as the sodium sulphide content decrease was too large to be accounted for by stoichiometry and that the iron sulphide content decrease was not large enough.

Matte chemical analysis was by a "wet" technique where the matte was first dissolved in acid and the concentrations of iron, sodium and copper determined. In this analysis technique we determine total iron and all graphs are plotted assuming that all iron is present as iron sulphide. Therefore the presence of iron oxide in the matte would appear as increased iron sulphide contents in the matte chemistry.

A second set of experiments were conducted on mattes with higher starting copper sulphide content than the initial experiments (10% vs 2%) and revealed similar results (figures 14 and 15) where the copper sulphide decreased as a function of time after reaching a maximum value. The calculated copper recovery in the matte only reached 85% before decreasing to an apparent 55% after 45 minutes. Again the ends of the scrap rods were significantly thinner at the end of the experiment than at the beginning and the apparent iron sulphide content of the matte increased near the end of the experiment indicating a reoxidation problem.

The atmosphere inside the kiln, although attempts had been made to purge with nitrogen, clearly was not inert due to difficulties in sealing the hot kiln. In addition, due to some smoke problems, an exhaust extraction fan was added to the kiln which caused a draught through the kiln. Thus, the iron oxide which was formed dissolved into the matte, increasing its volume, and accounted for the apparent increase in matte volume. This effect was clearly seen during a trial using a 75% FeS - 25% Na_2S matte at 1000°C. In figure 16 the typical copper sulphide result can be seen where within 7 minutes a maximum is reached which accounts for 95% of the copper added to the kiln. Subsequently the copper sulphide content in the matte decreases. In figure 17 the total matte chemistry change is plotted and the iron sulphide content apparently increases while the sodium sulphide content decreases as a function of time. Due to this problem trial times were reduced to a maximum of 15 minutes.

The major finding from the initial trials was that the process is effective on a larger scale. Copper mixed with scrap reacts with and becomes part of the liquid matte. In the initial experiments at 1000°C both a 75-25 and an 82-18 matte formulation gave similar experimental results and both formulations appear to be appropriate. Trials at higher copper sulphide contents where some of the previous matte had been recycled were also successful; although the time to reaction completion was longer. For fresh matte the reaction was complete by 7 minutes while in trials with 10% initial copper sulphide, the reaction was complete within 12 minutes (by visual observation).

Drainage of the matte from the kiln at 1000°C was straight forward and only a thin layer of matte was left on the kiln surface after reaction. This layer could be simply washed out of the kiln after the kiln had cooled to ambient temperatures. A thin layer of matte could be seen sticking sporadically to the treated scrap.

It was also clear from the initial experiments that reoxidation within the kiln would have to be eliminated in an industrial process.

Treatment of Electric Motors

A series of experiments was conducted to determine if copper windings could be removed from an electric motor in the kiln. The matte pool was formed at 1000°C and the motor added to the pool. The added motor was contained in an aluminum jacket and the copper wires were plastic coated. A photograph of the motor before addition and after addition is given in figures 18 and 19. As can be seen in the figures, the copper was completely separated from the motor. The process is quite smokey as the plastic covering burns off the wires, but the process is effective. Typical matte chemistry changes are given in figure 20. In these trials since the motor is completely immersed there is no oxidation problem and all copper can be accounted for by matte chemistry.

Trials at Lower Temperatures

Experiments were carried out using a matte chemistry of 82% FeS - 18% Na_2S at 900°C. As suggested by the phase diagram, the liquid matte formed a very thick and viscous pool. Upon dissolution of the copper, the matte fuidized and coated the walls of the kiln. It was impossible to drain the matte from the kiln under these conditions. Experiments using a matte of chemistry 75% FeS - 25% Na_2S were also carried out with similar results; although, in this case some of the matte could be drained from the kiln. In both cases a large quantity of matte was left sticking to the scrap making operation at 900°C impractical.

Matte Drainage From Scrap

To determine the effect of the matte left sticking to the scrap a trial was run at 1000°C using the 82% FeS - 18% Na_2S matte where 3.4 kg of copper were added to kiln after it contained 80 kg of scrap. Subsequently, the scrap divided into 15 kg segments. A sample of the treated scrap, in this case all of the initial scrap was cut and sized iron rod of known composition, was then remelted and samples chemically analysed for copper and sulphur contents.

The initial copper content of the selected scrap was approximately 0.04% and the final content was approximately 0.05% indicating that the copper contaminated scrap had been successfully treated by the process. If the process had been unsuccessful the copper content after remelt would have reached 4.12%. In all cases after treatment no significant copper increase could be measured upon remelting treated scrap.

The sulphur content of the remelted scrap increased from 0.043% to 0.159%. Thus, the amount of matte sticking to the scrap is sufficient to significantly increase the remelted scrap sulphur content. 15 Kg of scrap was remelted in this test therefore 17.4 grams of sulphur or approximately 47 grams of matte remained sticking to the scrap. If the matte contained 8% Cu_2S this would be the equivalent of approximately 2.9 g of copper which could only raise the copper content of the scrap by 0.02 % which is within the error of chemical analysis and all of the copper content change in the scrap can be explained solely by the amount of matte sticking to the surface of the scrap.

A second batch of the treated scrap was washed with tap water at room temperature before remelting. Chemical analysis of the remelted scrap revealed no apparent change in copper content but the sulphur content increased from 0.043% to 0.091%. In this case approximately 20 grams of matte was left sticking to the 15 kg of scrap after treatment. Thus a water flushing of the scrap can reduce the amount of matte sticking to the scrap by at least a factor of two. Again if the matte contained 8% Cu_2S there would be approximately 1.2 g of copper which could only increase the copper content of the scrap by 0.008% which is within the accuracy of chemical analysis.

The third batch of treated scrap was placed into a hot (98°C) 8% HCl solution for thirty minutes. Upon remelting no difference in copper content could be measured and the sulphur content increased by only 0.01% indicating only 4 g of matte remained sticking to the scrap. Thus the sulphur pickup problem can be minimized by treatment with a hot acid solution.

The process has been proven to be technically feasible; however, for the scrap to be directly hot charged into an electric furnace after treatment some desulphurization of the melt would be necessary due to excessive sulphur pickup from the small amount of matte left sticking to the scrap. If the scrap was treated off-site from a steelmaker, then, the treated scrap could be washed in a hot acid solution to completely remove the matte from the scrap surface.

This process is more attractive for large scrap pieces which have a large volume to surface area ratio. Due to the large surface area of turnings, etc., it would be difficult to effectively separate the scrap from the matte when treating this material.

It is possible to enhance matte drainage by increasing the drainage temperature. In these experiments the hot zone was small and drainage was carried out within a cold zone in the rotary kiln. Therefore, it is possible that the residual matte problem will be less once the kiln design is optimized. For example, in our laboratory tests the amount of matte left on the dip samples was insignificant; therefore it may be possible to affect a large separation of the matte from the treated scrap in practice.

Conclusions

The process is viable and technically feasible if carried out in a non-oxidizing environment. It is possible to effectively remove copper from solid steel scrap and, with an acid wash, to completely remove the minimal amount of matte which remains sticking to the scrap.

Electrical motors can be effectively treated using the process.

The process is effective when operated at a temperature of 1000°C with a starting matte composition of 82% FeS and 18% Na_2S.

Acknowledgements

Initial studies of the decopperization of solid scrap were funded by the member companies of the Center for Iron and Steelmaking Research at Carnegie Mellon University. The larger scale trials and much of the basic research related to the process was funded by the Department of Energy with cosponsorship by the Center for Metals Production, The David Joseph Company, and Consolidated Natural Gas Service Company. Gene Eckhardt of the DOE was a major driving force in the project adding technical advice, management and encouragement at the appropriate times.

The project could not have continued without the support of the USX Corporation, which allowed us access to their pilot facility, and, the AISI Direct Steelmaking Team who arranged for vital power and gas connections and helped us keep a perspective on the task. In particular we would like to acknowledge the aid of Dr. A. Rathbone and J. Zaranak of USX and Egil Aukrust and Ken Downing of the AISI.

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This is a Center for Iron and Steel Research publication.

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Table I: Ladle Processes for Copper Removal[2]

Process	Comments
Lead Extraction	Low distribution ratio, high amounts of lead.
Vacuum Distillation	Low surface to volume ratio, low volatilization rate
Sulphide Slagging	Low distribution ratio, long reaction times, carbon saturation of melt preferred.

Table II: Processes for Copper Removal from Solid Scrap[2]

Process	Comments
Physical Separation	Labor intensive
Preferential Melting	High fuel cost, metal loss and refractory wear
Matte Treatment	High fuel cost.
Acid Treatment	Disposal Problem?

Table III: Decrease in Average Copper Values Due to Scrap Preparation, After Pflaum[19]

Type	Before	After
Shredded	0.23	0.16
#1 Heavy Melt	0.24	0.19
#2 Heavy Melt	0.46	0.37
Turnings	0.29	0.18
#2 Bundles	0.51	0.42

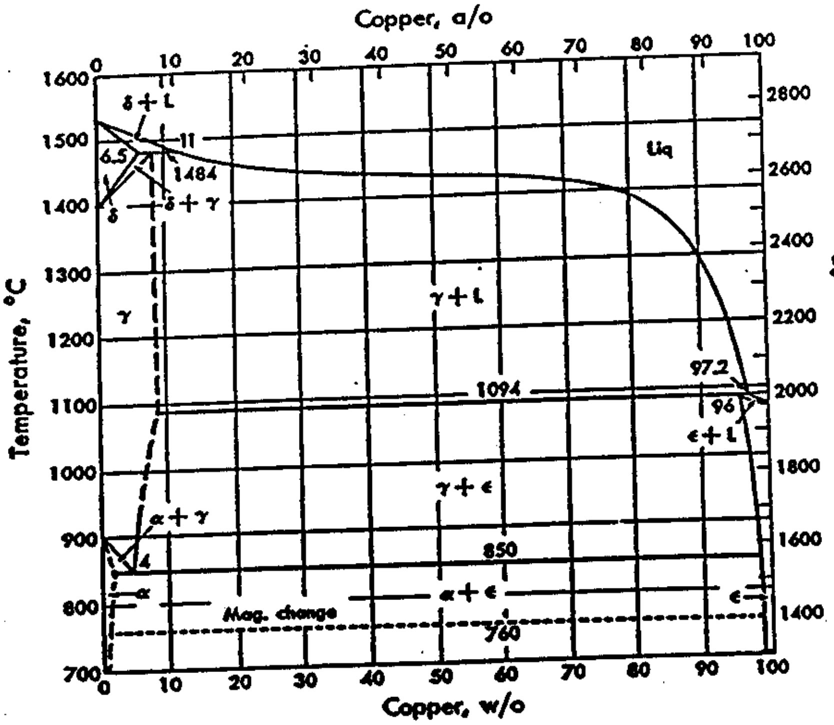

Figure 1: Phase Diagram of Fe-Cu system[9]

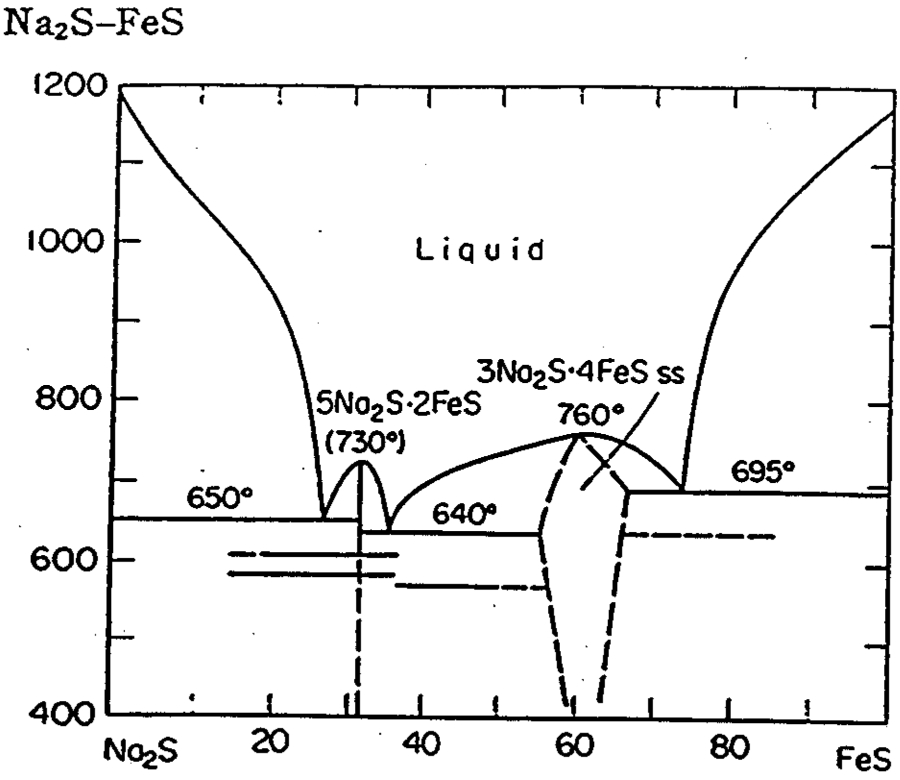

Figure 2: Phase Diagram of Fe-S-Na_2S system.

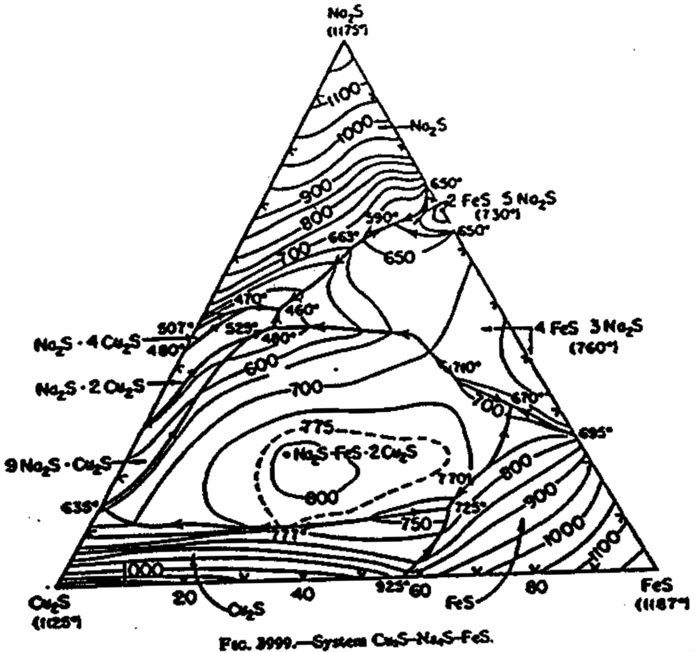

FIG. 3999.—System Cu$_2$S-Na$_2$S-FeS.

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Figure 3: Phase Diagram of the FeS-Na$_2$S-Cu$_2$S system.

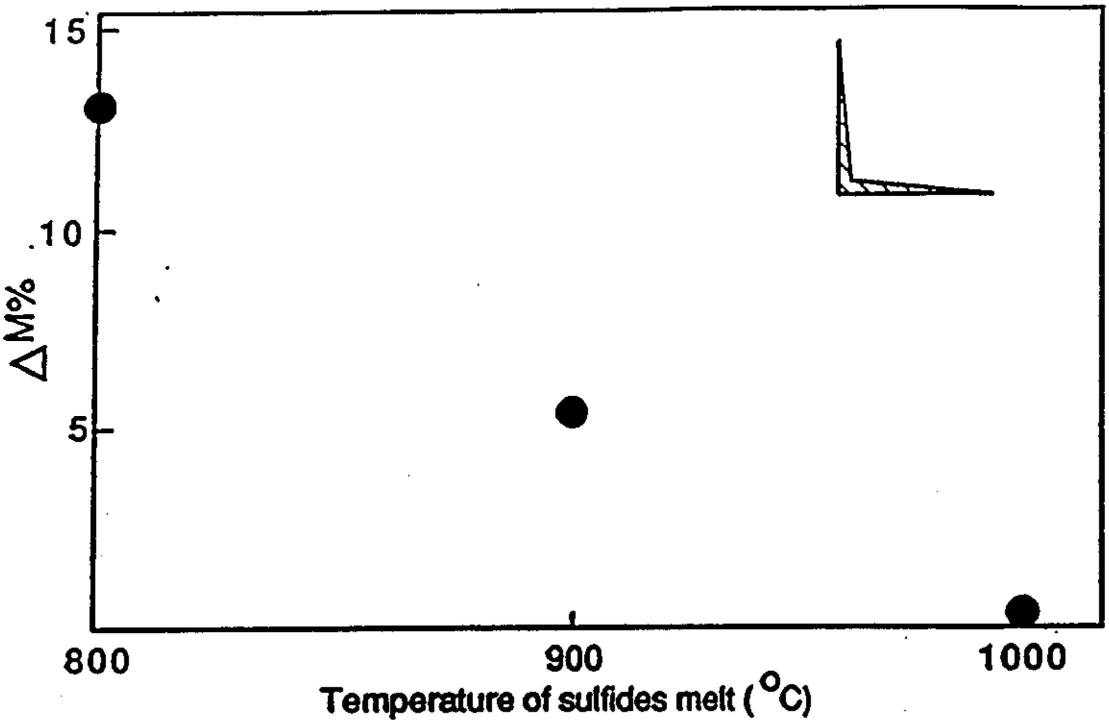

Figure 4: Matte Adherence Trial for Steel L Angle.

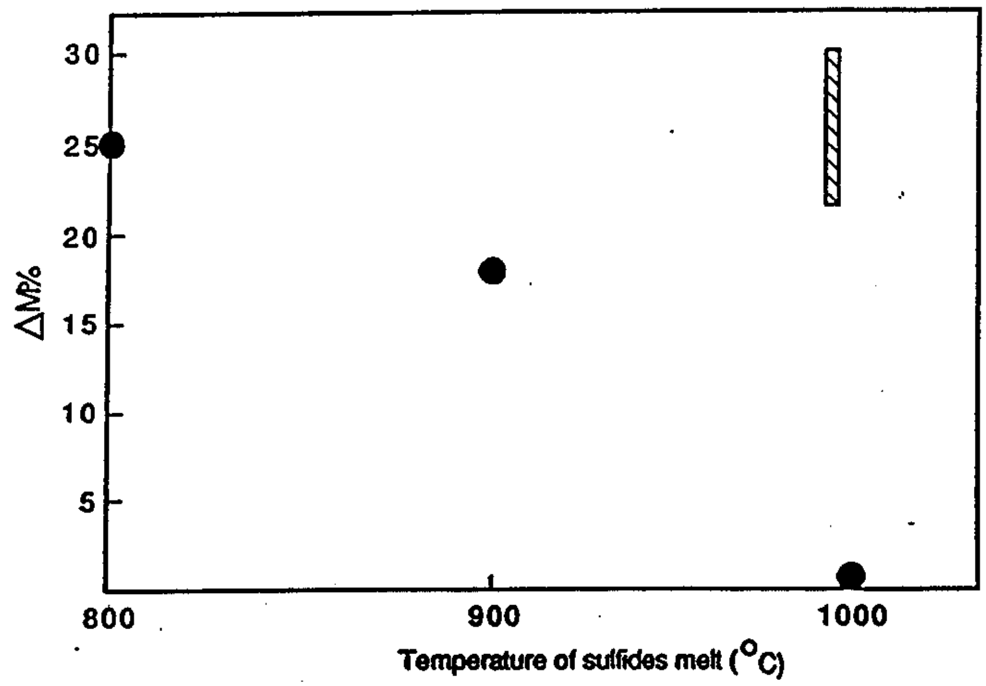

Figure 5: Matte Adherence Trial for Steel Plate.

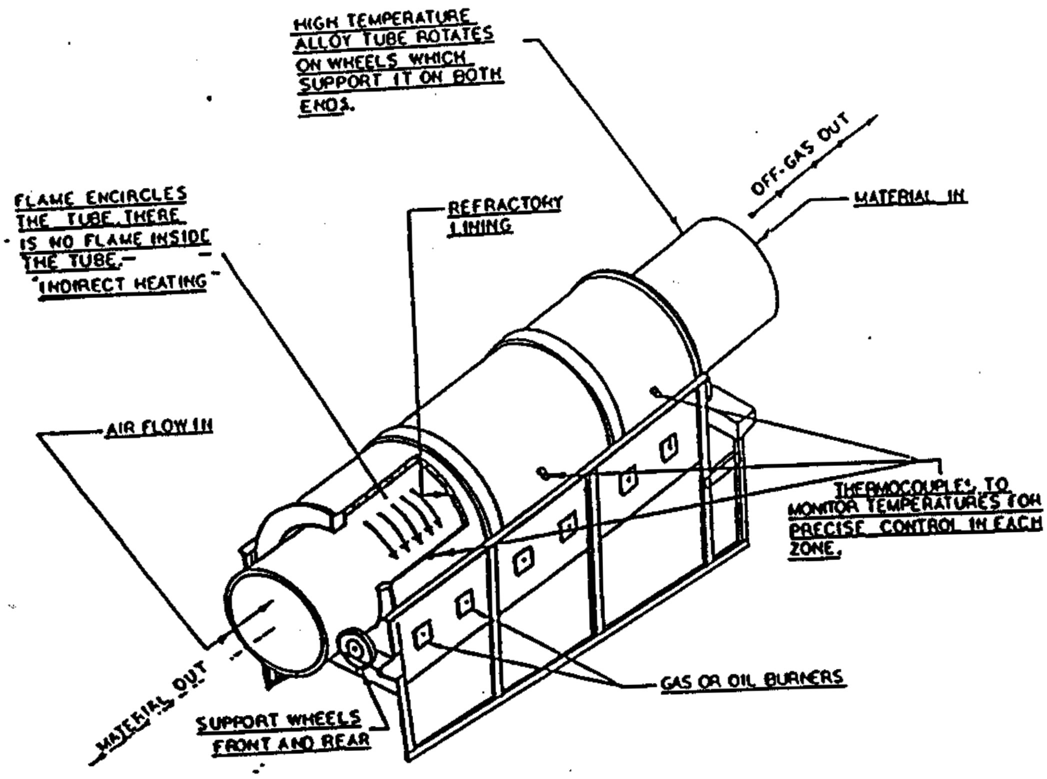

Figure 6: A Schematic of the CORECO Rotary Kiln.

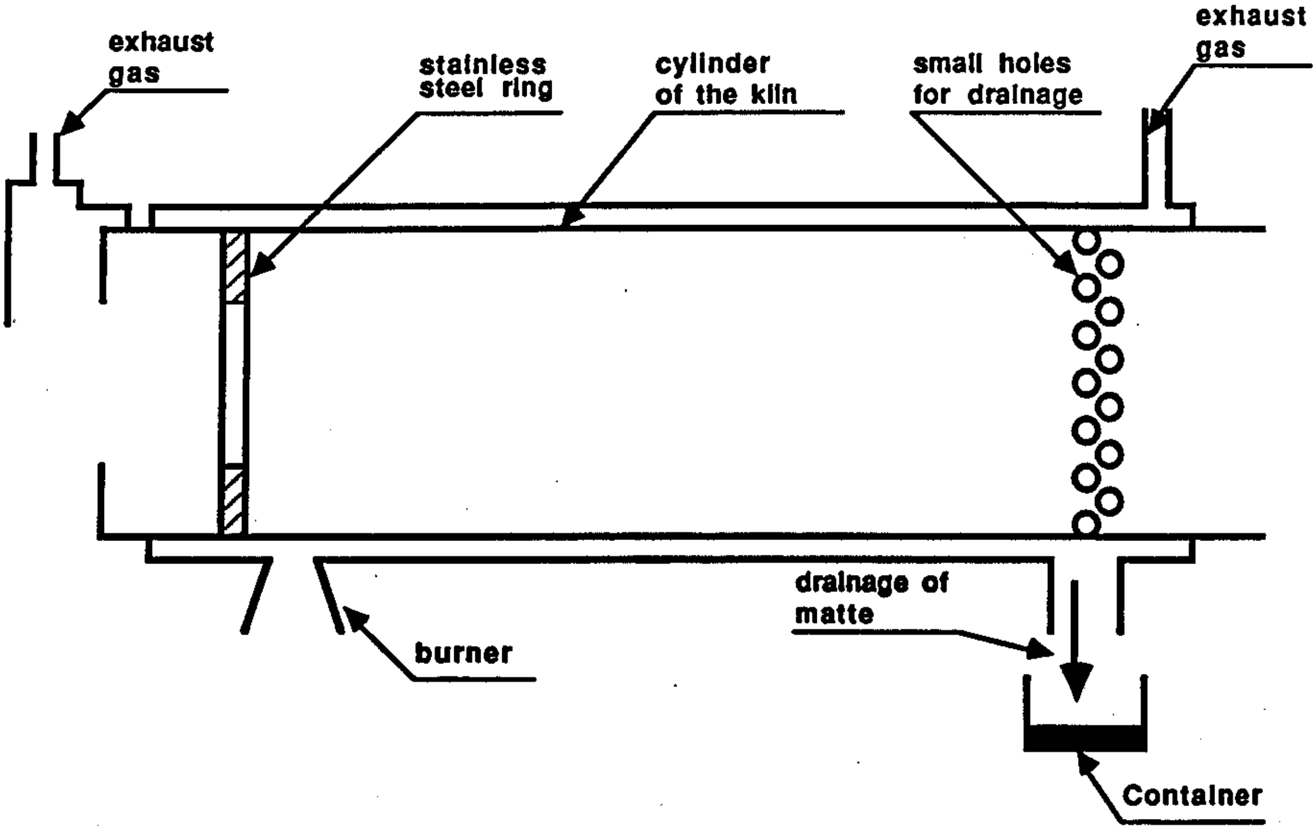

Figure 7: Schematic of the Internal Kiln Configuration

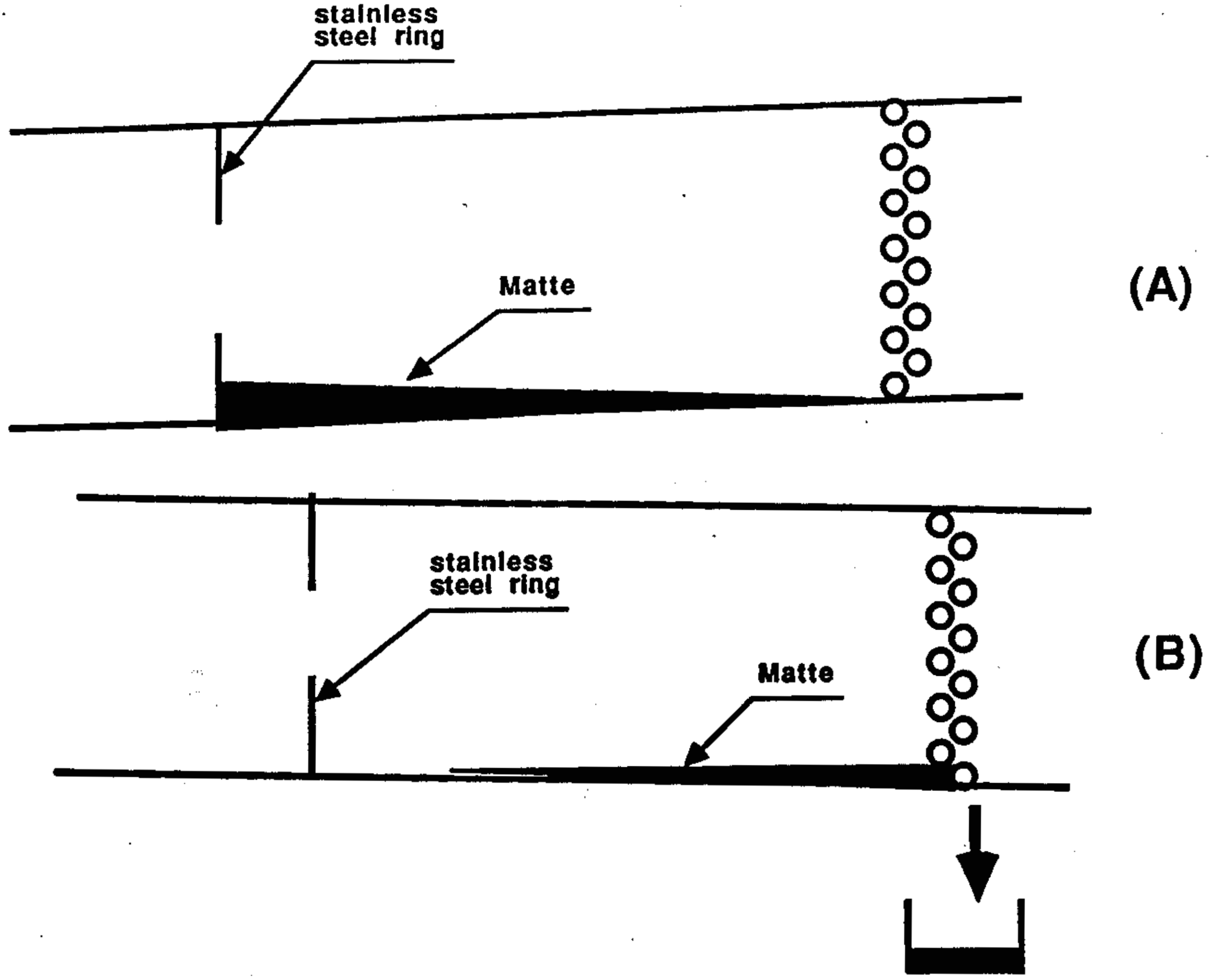

Figure 8: Schematic of (A) Operation Kiln Position and (B) Drainage Kiln Position

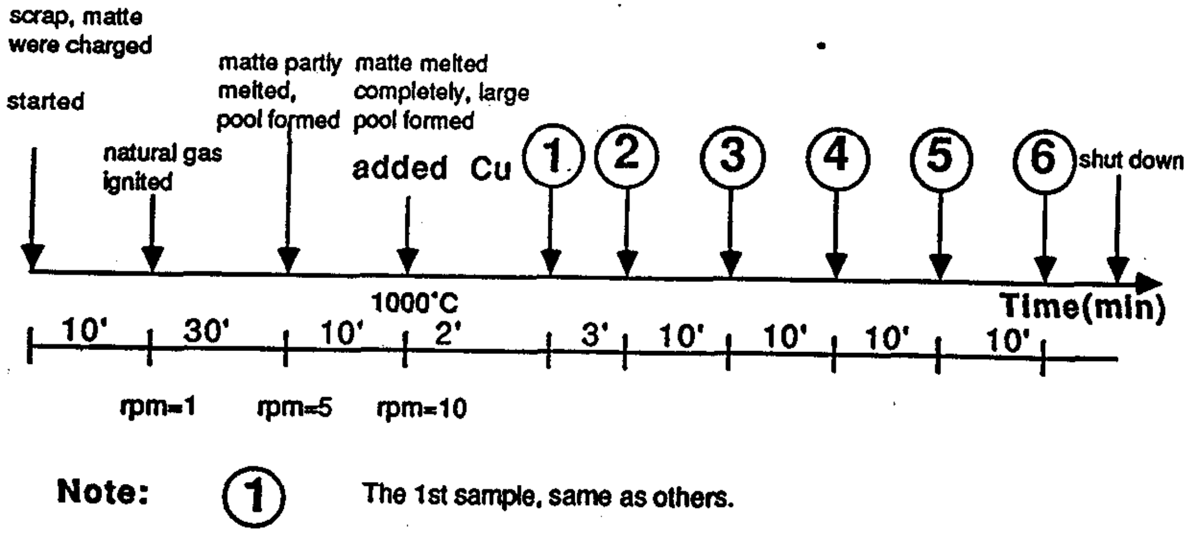

Figure 9: Typical Experimental Procedure

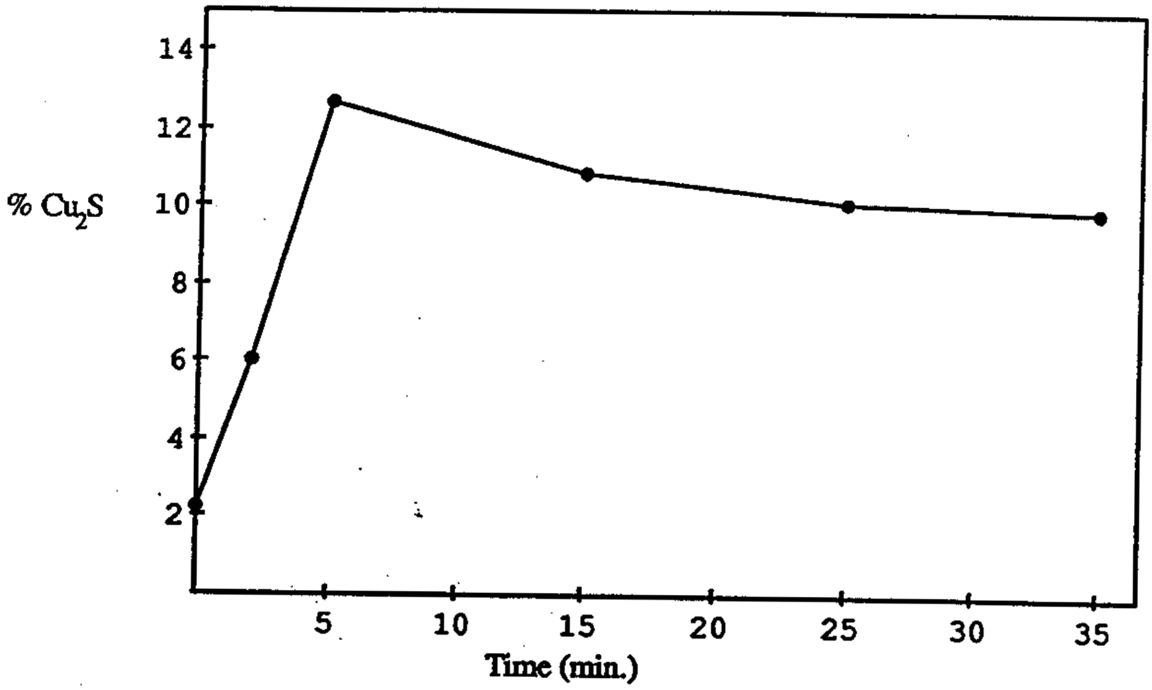

Figure 10: Variation of Copper Sulphide Content in Matte During the Initial Trials

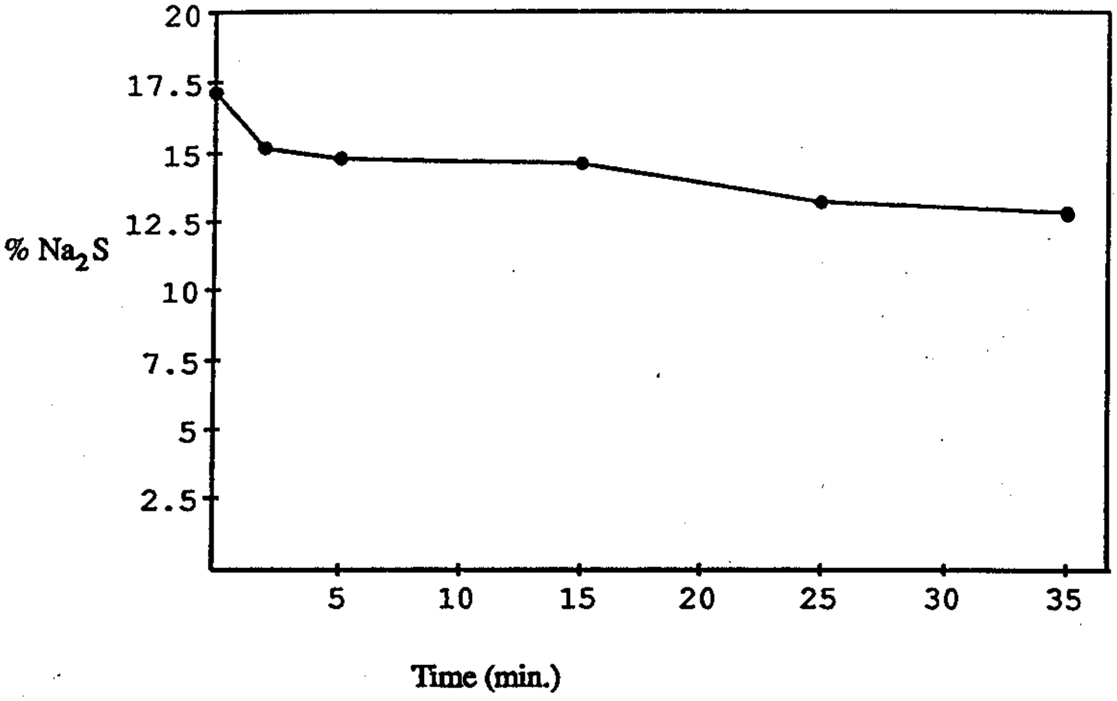

Figure 12: Variation of Sodium Sulphide in Matte During the Initial Trials

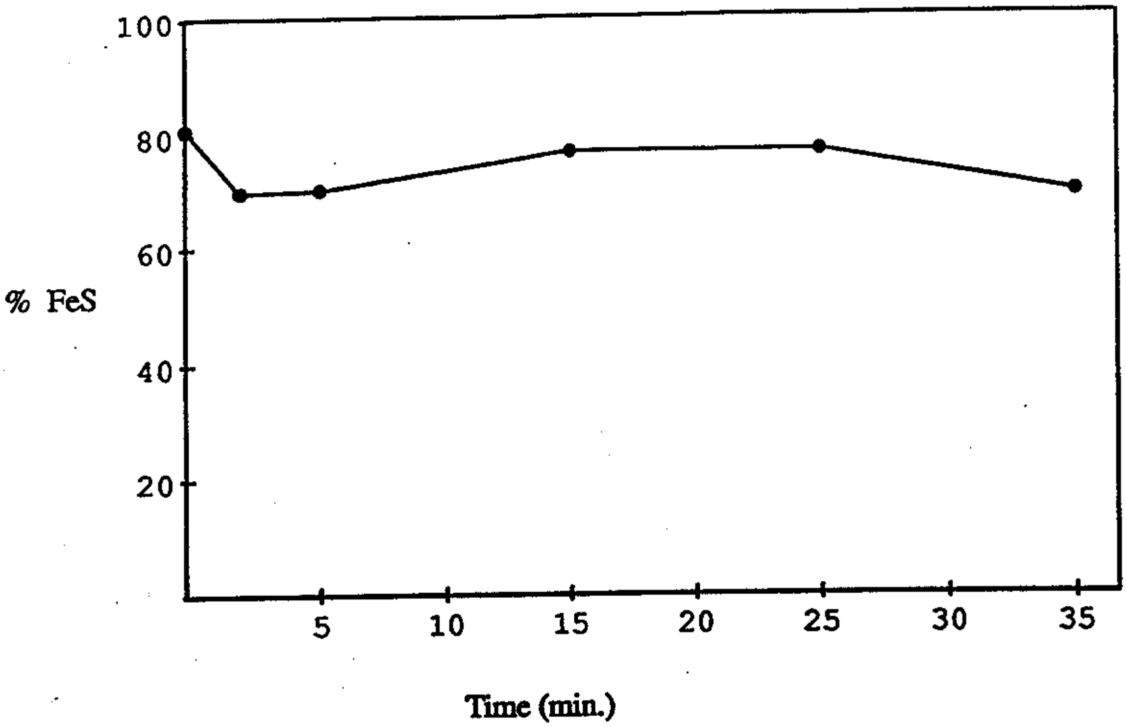

Figure 11: Variation of Iron Sulphide in Matte During the Initial Trials

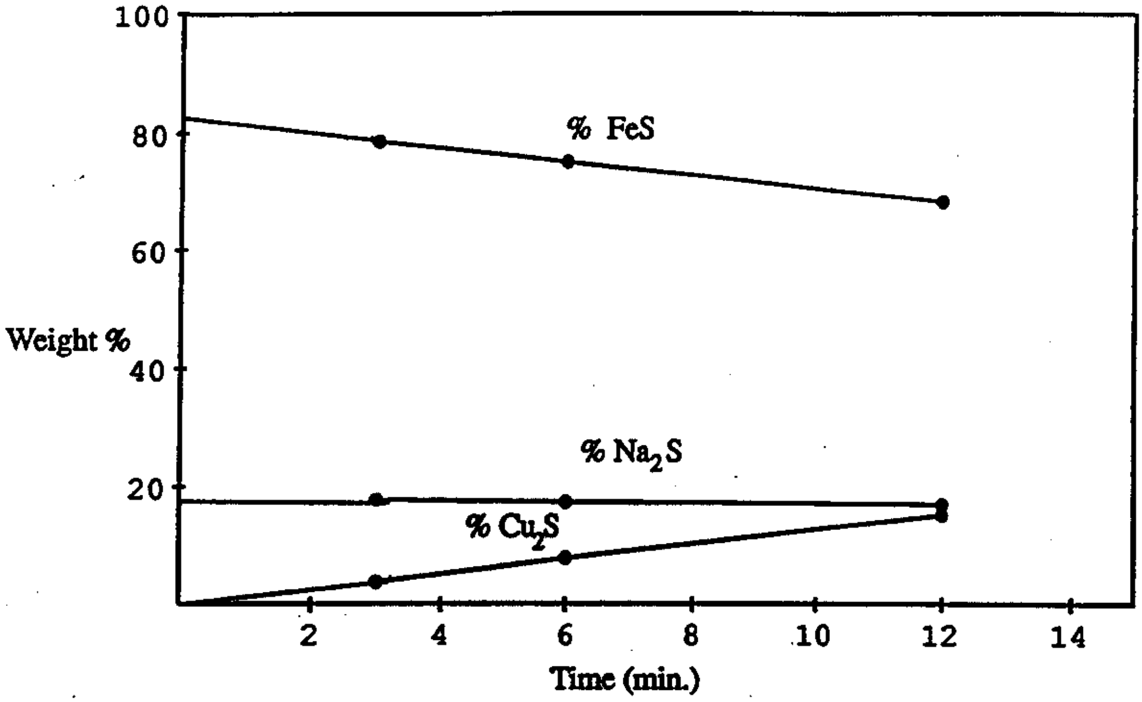

Figure 13: Theoretical Curves Assuming the Rate of Copper Pick-up is Linear

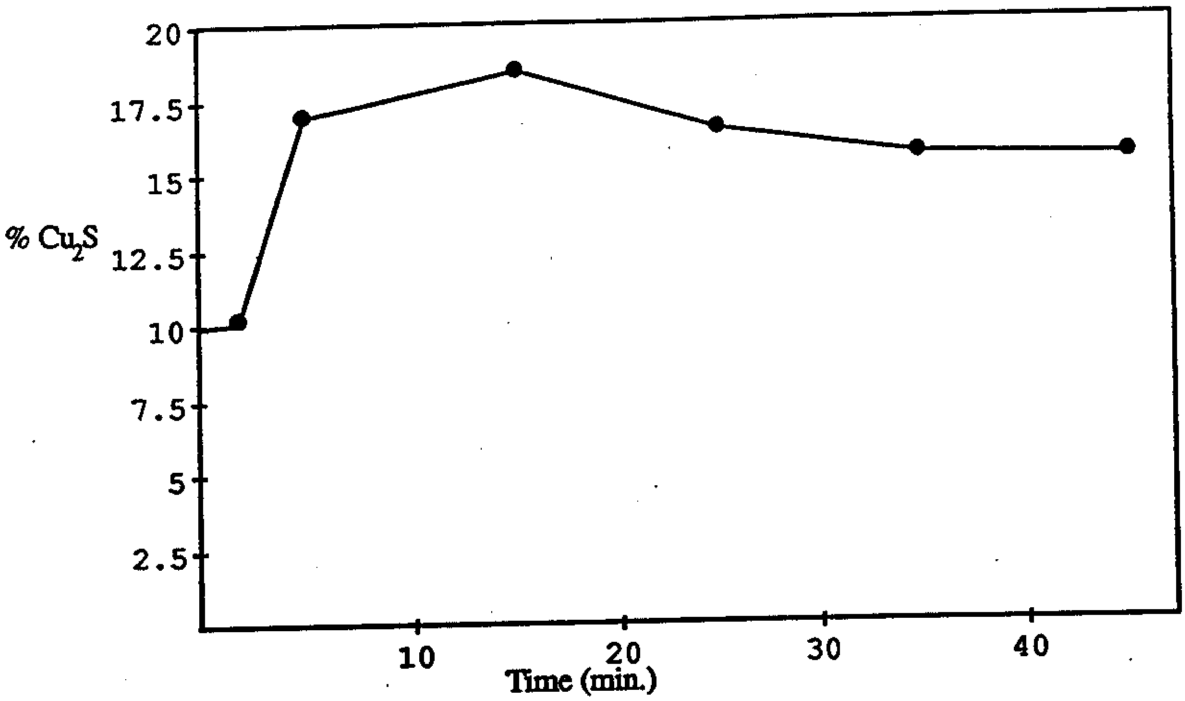

Figure 14: Variation of Copper Sulphide Content for a Matte with a Higher Starting Copper Sulphide Concentration

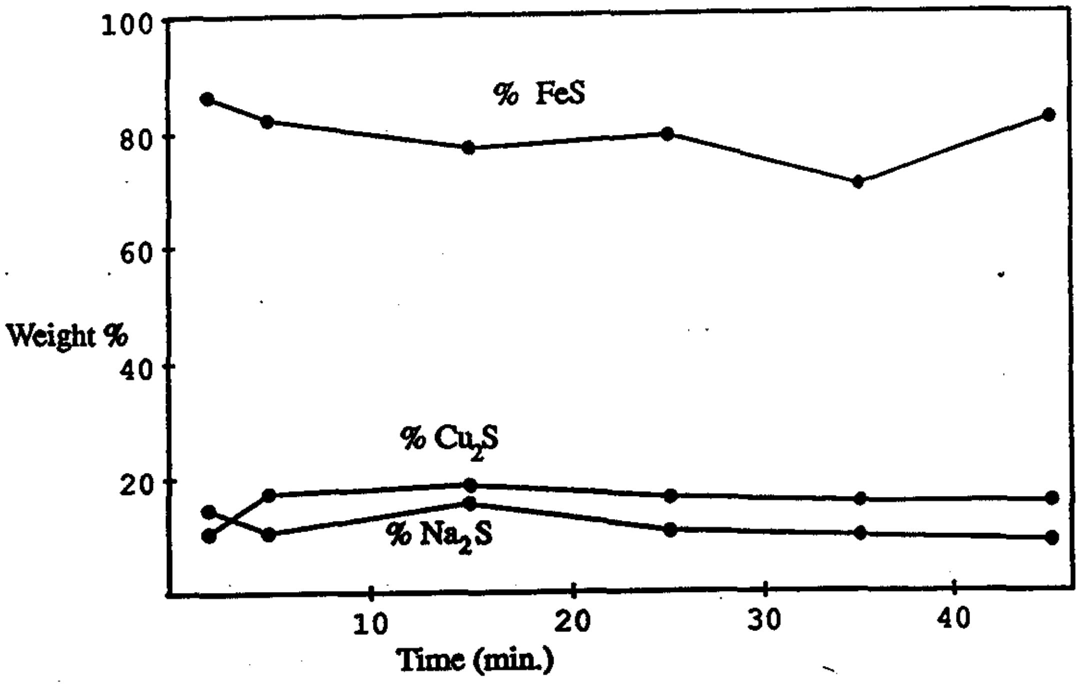

Figure 15: Variation in Matte Chemistries for a Matte of Higher Starting Copper Sulphide Concentration

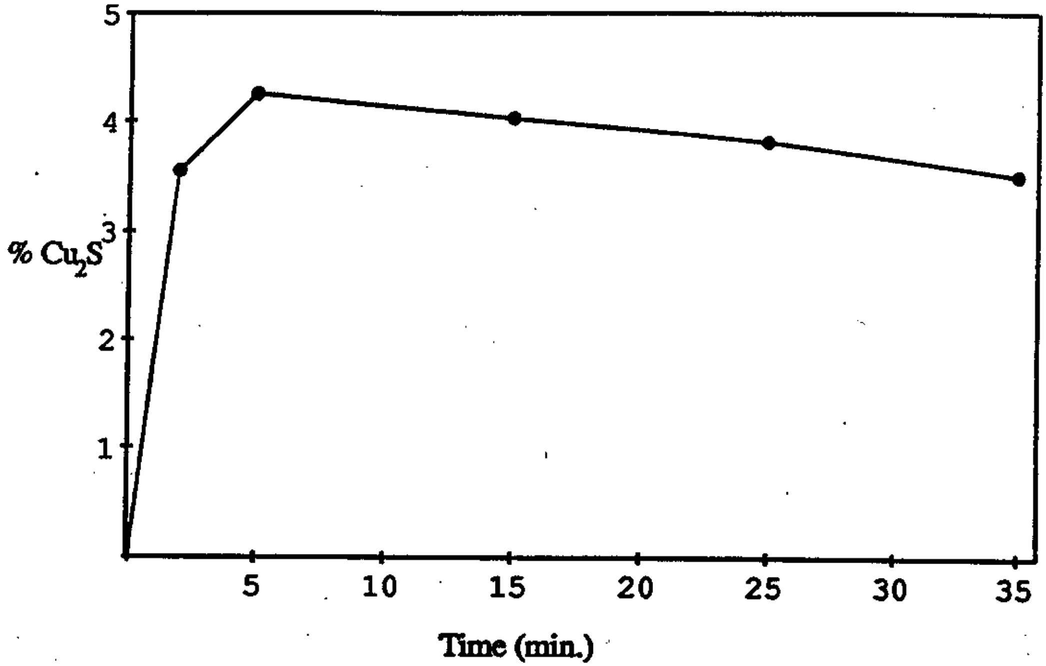

Figure 16: Variation of Copper Sulphide Content during a 75 - 25 Matte Trial.

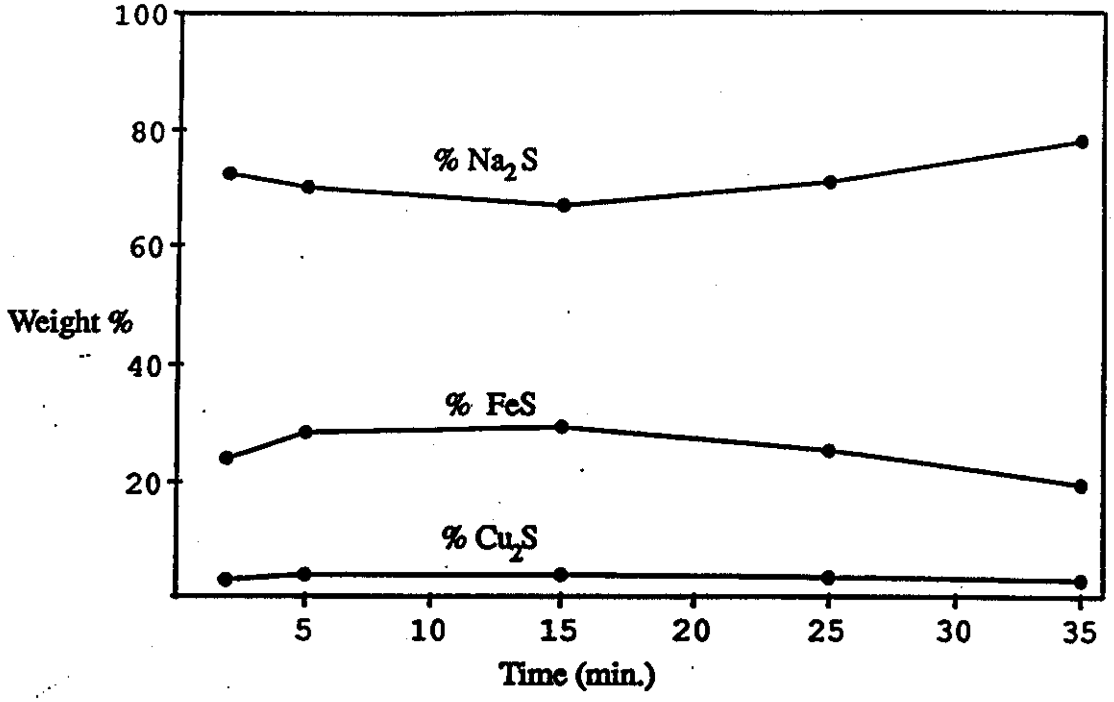

Figure 17: Variation in Matte Chemistries during a 75 - 25 Matte Trial

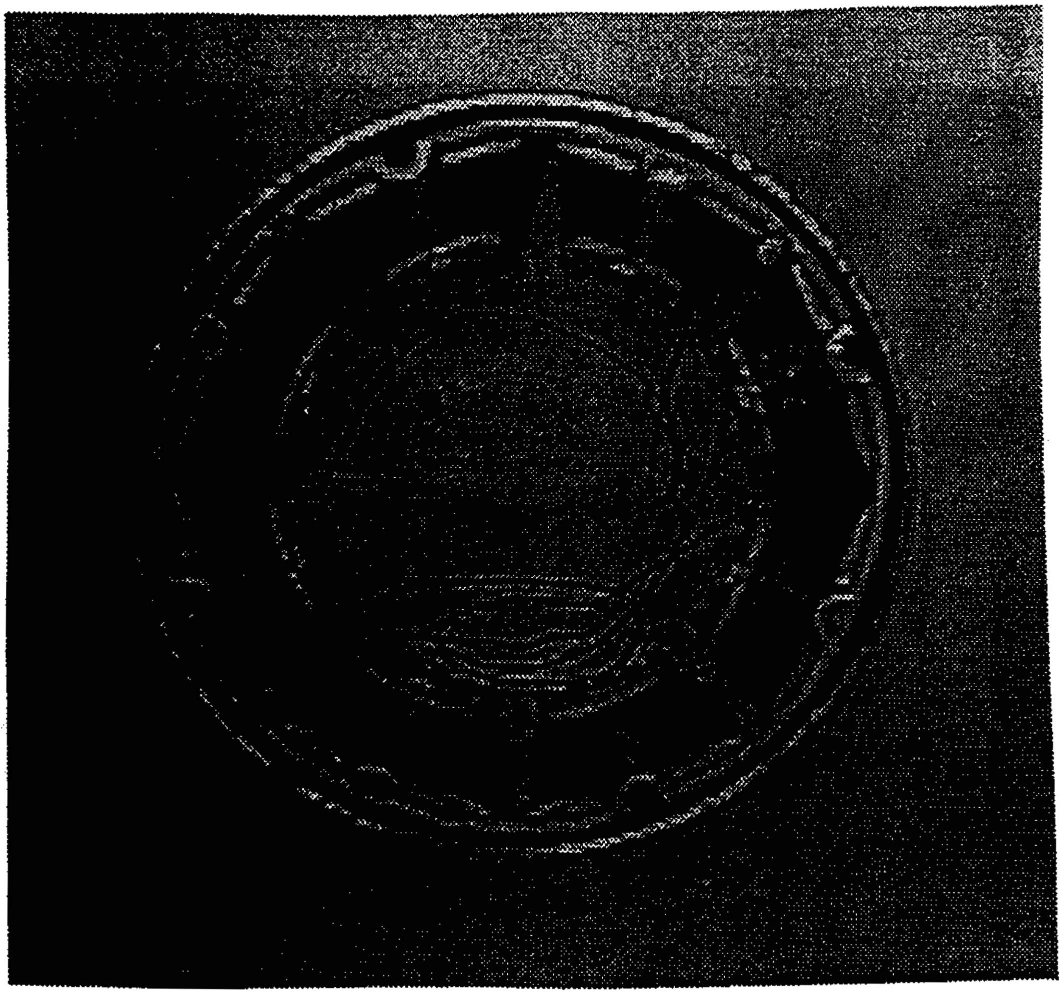

Figure 18: Electric Motor before Addition to Kiln

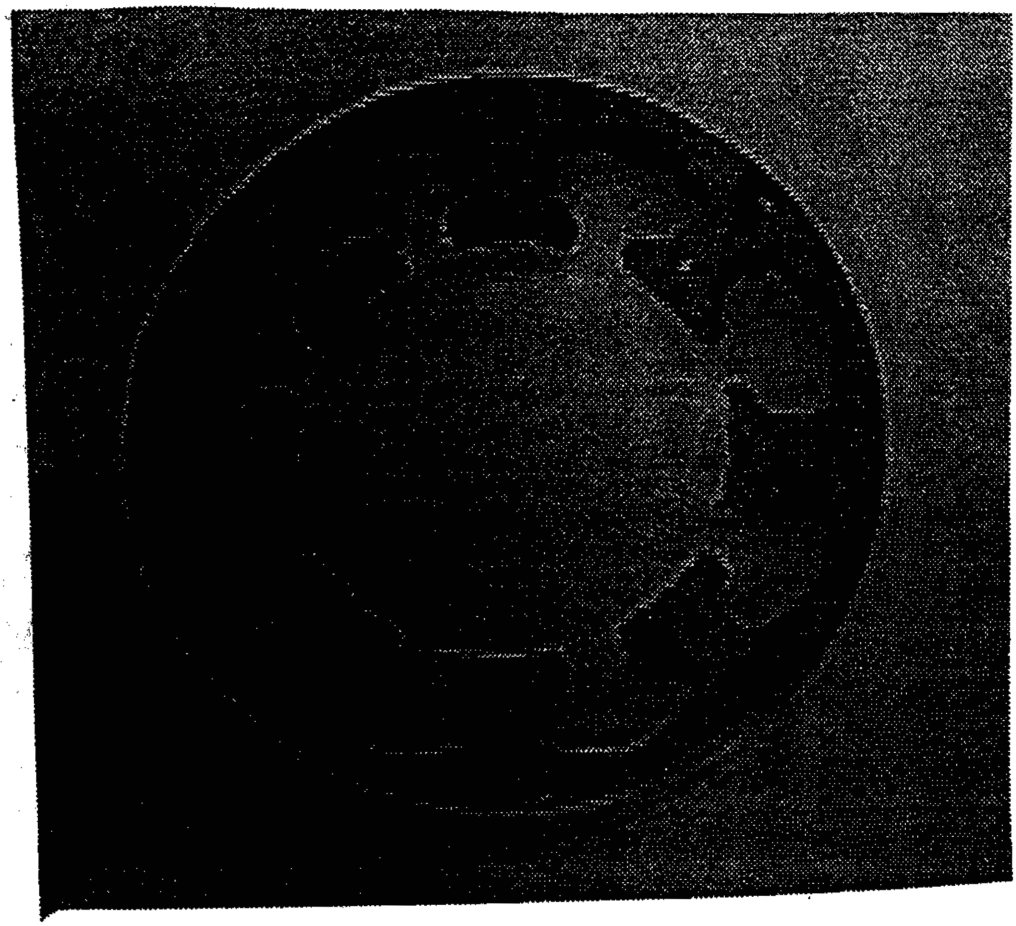

Figure 19: Electric Motor After Addition to Kiln

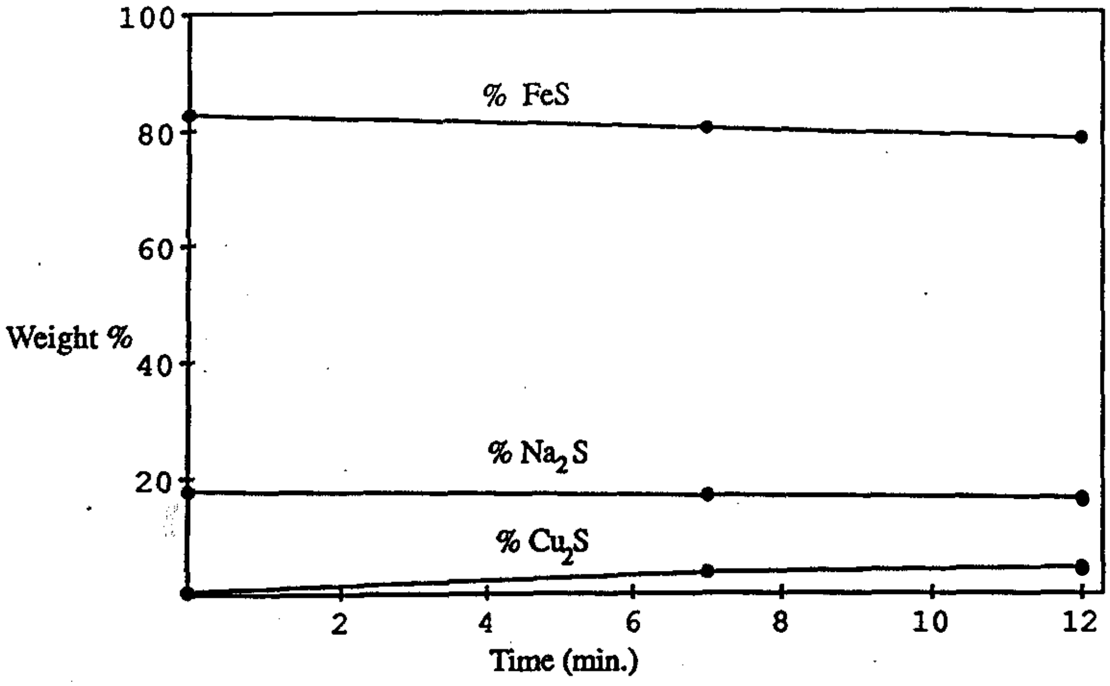

Figure 20: Matte Chemistry Changes during Addition of Electric Motor

RECENT PROGRESS ON FERROUS SCRAP PRETREATMENT

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The potential build-up of residual elements in steel is a cause for concern within both the steel and the scrap industries. High levels of elements such as copper, nickel, molybdenum, tin and chromium are thought to be deleterious to product consistency and have also been shown to cause problems during casting and subsequent processing.[1] The absolute level at which a residual element becomes deleterious to product quality is dependent upon the application; however, it seems reasonable to assume that, at some time in the future, prudent background levels of residual elements will be exceeded, leading to scrap sorting or pretreatment as a routine operation before charging into an electric arc furnace.

In addition to the residual problem, the growth in recycled automotive galvanized sheet scrap has resulted in increasing zinc content in the exhaust dusts of the steelmaking furnaces. This dust is considered hazardous by the EPA and disposal is expensive as it is classified as a hazardous waste. Thus zinc must also be removed from scrap before it is charged into the steelmaking furnace.

The purpose of this article will be to review scrap pretreatment for the removal of copper and zinc from scrap. Some recent efforts at Carnegie Mellon University to develop a method of scrap pretreatment which would allow solid copper to be separated from solid scrap will be highlighted.

The Copper Problem

The United States has a tremendous ferrous scrap surplus. To produce steel from scrap takes less than one third of the energy that it does when starting with ore. In addition, many of the major environmental problems are eliminated, in particular those associated with coke making. However, much of the scrap cannot be used because it contains elements, such as copper and zinc, which are detrimental to the steelmaking process or the properties of the steel produced. If these unwanted elements can be removed, considerably more steel can be recycled and other environmental problems related to steelmaking reduced.

Background

The copper residual problem is well recognized in both the solidification and deformation processing of liquid steel. Gross defects have been found during the casting, rolling and welding of steels with significant copper residuals[2-5], while variations in product properties have been correlated to copper variations in the alloy[6].

Generally copper residual contents are limited to less than 0.35%[1] in most alloy steels with the exception of weathering steels (0.5%) and steels exposed to nuclear radiation (0.1%); however, copper contents of less than 0.25% have been shown to cause fine intergranular cracks on bloom castings[3]. The maximum allowable copper levels for various grades of steel are given in Table I. In general the copper levels in steels produced by integrated producers of flat products are controlled to lower levels than those produced via electric arc furnaces.

Table I: Maximum Allowable Copper Levels

Application	%Cu
Deep Drawing Steel	0.06%
Tin Plate (critical)	0.06%
Drawing Quality	0.10%
Steel Forgings	0.35%
Irradiated Steels	0.10%
Bar Products	0.35%

Casting and rolling defects are caused by embrittlement due to the formation of a liquid copper film which forms when the iron is preferentially oxidized during the formation of scale[3,7]. This preferential oxidation causes an enrichment in copper and other residuals such as nickel, tin and antimony in the grain boundaries. Copper rich phases found in cracks on bloom surfaces at Round Oak Steel Works in England were found to contain 85% Cu, 5% Fe, 5%Sn, 4% Ni and 1% Sb which would be molten

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[1] supplementary requirement S1 of ASTM Specification for Steel Forgings, General Requirements (A 788)

below 1100°C (Figure 1[8]) and give rise to classical 'hot shortness' due to penetration of the liquid film along the grain boundary. This phenomenon of liquid copper film embrittlement of steels in an oxidizing atmosphere is well documented, was originally proposed by Pfeil[9] and was discussed by a number of authors during the sixties[10 - 13]. One suggested method of eliminating this defect is to ensure that a solid intermetallic compound of copper and nickel is formed by ensuring that the copper to nickel ratio in the steel is 3 : 1 or larger[9]; however, at higher copper levels (0.35%) substantial quantities of nickel (0.12%) would have to be intentionally added to ensure avoidance of the defect. A listing of the factors which can favorably affect the hot workability of copper containing steels is given in Table II.

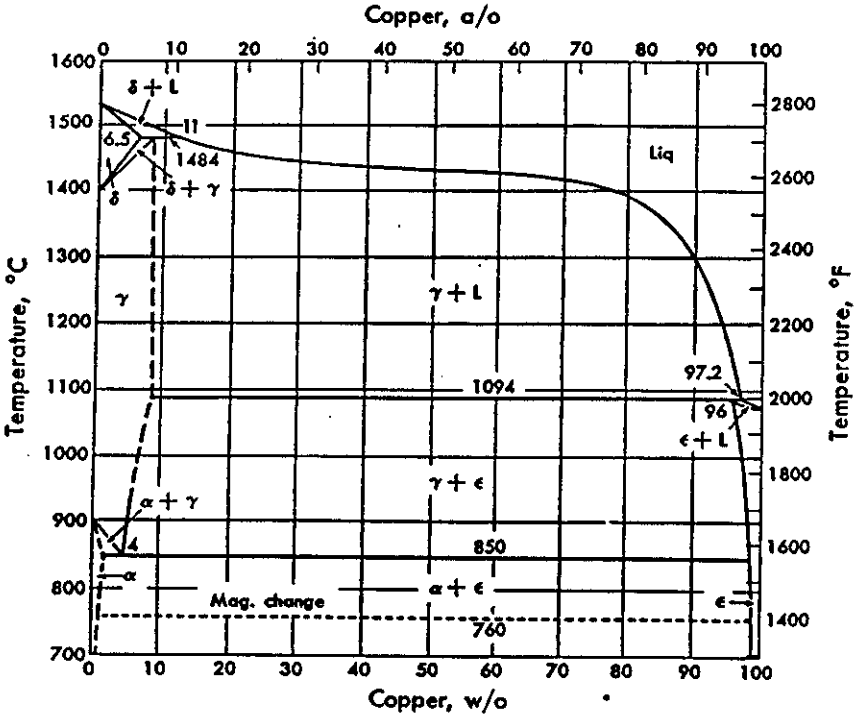

Figure 1: Phase Diagram of Fe-Cu system[8].

Table II: Factors Favorably Affecting the Hot Workability of Copper Containing Steels, after B. F. Glasgal, [1]

- Low Copper Residuals
- Fast Heating Rates
- Reduced Time at Temperature
- Limited Scale Formation
- Nickel:Copper Ratio greater than 1:3

Another copper induced crack which is very common in continuously cast slabs and blooms is the star crack. This crack is caused by localized surface concentrations of copper which are due to wear of the continuous casting mold. Again the cracks are caused by thin liquid copper films which penetrate the grain boundaries leading to embrittlement. This problem is generally countered by coating the molds with a more abrasive resistant material such as chromium or nickel[14,15].

Copper provides a modest degree of solid solution strengthening in ferrite and, as reviewed by Bodnar et al[6], can lead to irradiation and stress relief embrittlement; to reductions in hot tensile strength and creep rupture ductility; and, to temper embrittlement. In addition Bodnar et al. have shown that variations in copper content can lead to gross variations in the yield strength of tubesheet forgings.[6]

Due to the growing body of evidence which suggests that copper levels in steels must be controlled and, due to concerns that the background copper levels in steel scrap are increasing due to increased recycling and decreased production of home scrap, there have been numerous studies over the last forty years to determine an efficient method of copper removal from steel. These studies are based on either the treatment of liquid steel or the treatment of solid scrap.

Treatment of Liquid Steel

A review of the most recent techniques for copper removal from liquid steel was carried out by Jimbo et al[16] and a commentary on liquid and solid techniques is given in Table III. Sulphide slagging has been the most extensively researched method of removing copper from liquid steel. This process, originated by Jordan[17] in 1950, is based upon the following reaction:

$$2\,\underline{Cu} + FeS = Cu_2S + \underline{Fe} \qquad [1]$$

At temperatures above 600°C copper sulphide is more stable than iron sulphide; therefore, solid copper when in contact with a matte containing iron sulphide forms copper sulphide and precipitates iron. In the actual process an ionic exchange reaction occurs:

$$\underline{Cu} + Fe^{2+} = 2\,Cu^{+} + \underline{Fe} \qquad [2]$$

where electrons are transferred from the copper to the iron and the rate of reaction will be determined by liquid phase mass transport of copper in the liquid steel. Sodium sulphide is normally added to iron sulphide to lower the melting point and the viscosity of the matte[18] and carbon is added to the liquid steel to increase the activity coefficient of copper in the liquid steel[19]. Jimbo et al[16] have shown that the optimum copper distribution ratio for FeS-Na_2S mattes at 1600°C is approximately 20. Thus, to reduce liquid steel copper content from 0.3% to 0.1%, 100 kg of matte per 1000 kg of metal would be required. At current prices of iron and sodium sulphide this would make the process prohibitively expensive.

Solid Scrap Treatment

90% of the copper present in scrap exists primarily as pure copper in the form of wire or platted material. This has lead to physical separation as a means of reducing the overall copper content of scrap and to practices of raw material segregation being widespread in the scrap industry[20,21]. In Table IV typical copper levels and standard deviations are given for various scrap types (after Pflaum [21]) and, in Table V, the benefits of a scrap sorting program are indicated. Unfortunately, physical separation and sorting of scrap is time consuming, labor intensive, expensive and cannot reduce the overall copper contents to less than 0.05%; a level necessary for the production of flat products via a

Table III: Processes for Copper Removal from Scrap[17]

Process	Comments
Physical Separation	Labor intensive
Lead Extraction	Low distribution ratio, high amounts of lead.
Preferential Melting	High fuel cost, metal loss and refractory wear
Vacuum Distillation	Low surface to volume ratio, low volatilization rate
Sulphide Slagging	Low distribution ratio, long reaction times, carbon saturation of melt preferred.
Matte Treatment	High fuel cost.
Acid Treatment	Disposal Problem?

steelmaking route that includes scrap remelting.

Table IV: Average Copper Contents, after Pflaum [21]

Type	Average	Standard Error
#1 Bundles	0.021	0.012
Bushelings	0.032	0.014
#2 Steel	0.236	0.115
#1 Steel	0.117	0.005
Turnings	0.063	0.057
Pit Scrap	0.074	0.071
Home Scrap	0.071	0.008

Laboratory Studies

An alternate to scrap sorting was invented by R. J. Fruehan, who combined the preferential melting

Table V: Decrease in Average Copper Values Due to Scrap Preparation, After Pflaum [21]

Type	Before	After
Shredded	0.23	0.16
#1 Heavy Melt	0.24	0.19
#2 Heavy Melt	0.46	0.37
Turnings	0.29	0.18
#2 Bundles	0.51	0.42

technique with sulphide slagging to develop a new technique capable of the removal of solid copper from solid scrap at temperatures lower than the melting point of copper (1083°C). Fruehan's process, which operates at 1000°C or below, is based on an analysis of the chemistry of the system. For example, the equilibrium constant of equation 1 is as follows:

$$K = \frac{a_{Fe}\ a_{Cu_2S}}{a_{Cu}^{2} a_{FeS}} \qquad [3]$$

and,

$$\frac{a_{Fe}\ a_{Cu_2S}}{a_{Cu}^{2} a_{FeS}} = exp\ [\ -\ \frac{\Delta G^o}{R\ T}\ ] \qquad [4]$$

where ΔG^o is the standard free energy of reaction 1. In Fruehan's process solid iron is precipitated upon reaction.

In the above equation ΔG^o is negative (the reaction is spontaneous), and the value for K is approximately 2 at 1000°C[16]. Thus to maximize the amount of copper in the matte one needs a low starting activity of copper sulphide in the matte, a high iron sulphide activity in the matte and a high copper activity. The activity of solid iron is 1.

Thus the starting matte composition should be high in iron sulphide and low in copper sulphide. In addition the matte must be liquid and fluid at treatment temperatures, and sodium sulphide is normally added as the matte's liquidus can be lowered to 700°C by such additions[22] (Figure 2). Sodium sulphide also decreases the activity of copper sulphide in the matte, thus improving the thermodynamics of copper removal. A normal matte starting composition is 82% FeS - 18% Na_2S.

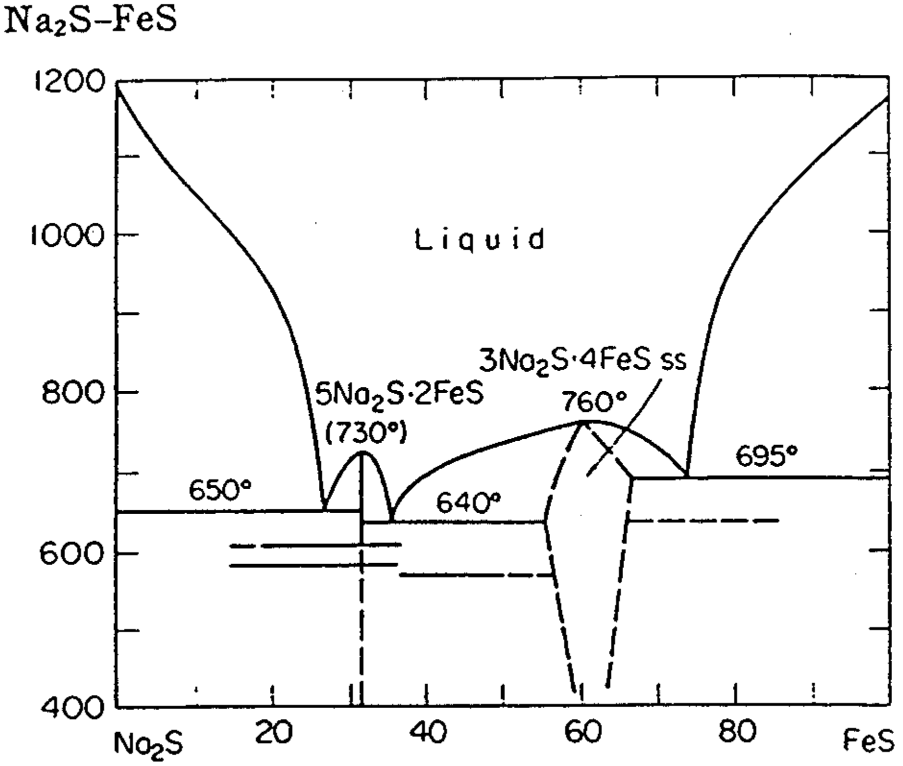

Figure 2: Phase Diagram of Fe-S-Na_2S system.

Melting scrap puts copper into solution in liquid iron and significantly reduces its activity when referred to pure liquid copper. Even in carbon saturated iron, where the copper activity coefficient is high, the activity of copper in solution in liquid iron is reduced by a factor of 25 - 50 as compared with pure copper. Due to the low copper activity in the melt the partition of copper between the matte and the liquid steel is significantly lowered and trials at the Bureau of Mines[22] in a 1.5 ton pilot operation could only remove 40% of the copper from the metal using 200 lb of an FeS-Na_2S mixture per ton of carbon saturated iron. The activity of copper as a pure solid is by definition unity. Thus it is more thermodynamically feasible to remove solid copper from solid scrap than to remove copper from scrap which has been remelted.

The iron sulphide - sodium sulphide matte reacts with solid copper, displaces solid iron and forms a iron sulphide - sodium sulphide - copper sulphide matte which is liquid and fluid at temperature (Figure 3). This matte can then be drained from the scrap.

Initial trials of the concept were carried out by Jimbo et al.[16] on a laboratory scale at Carnegie Mellon University using a matte containing 19 to 25% Na_2S. Simulated scrap consisting of pieces of iron and copper were treated in a rotating crucible with FeS-Na_2S fluxes (Figure 4). Approximately 100 grams of simulated scrap containing from 0.4% to 1% Cu was treated. over 90% of the copper could be removed at 1000 C and nearly 80% at 800 C. Initial trials indicated that only 4 kg of matte per metric ton of scrap would be necessary to treat steel containing up to 1% copper.

Process Benefits

Due to the success of the small scale tests in proving that Fruehan's concept had potential, a detailed comparison of solid and liquid scrap treatment was made. The advantages of the solid scrap treatment

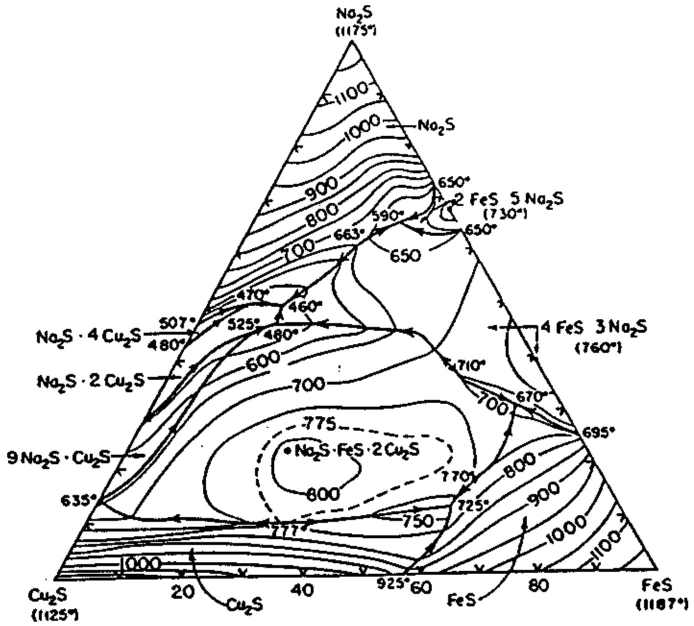

FIG. 3999.—System Cu_2S–Na_2S–FeS.

N. I. Kopylov and S. S. Novoselov, *Zh. Neorgan. Khim.*, 9 [8] 1919 (1964); *Russ. J. Inorg. Chem.* (*English Transl.*), 1042 (1964).

Figure 3: Phase Diagram of the FeS-Na_2S-Cu_2S system.

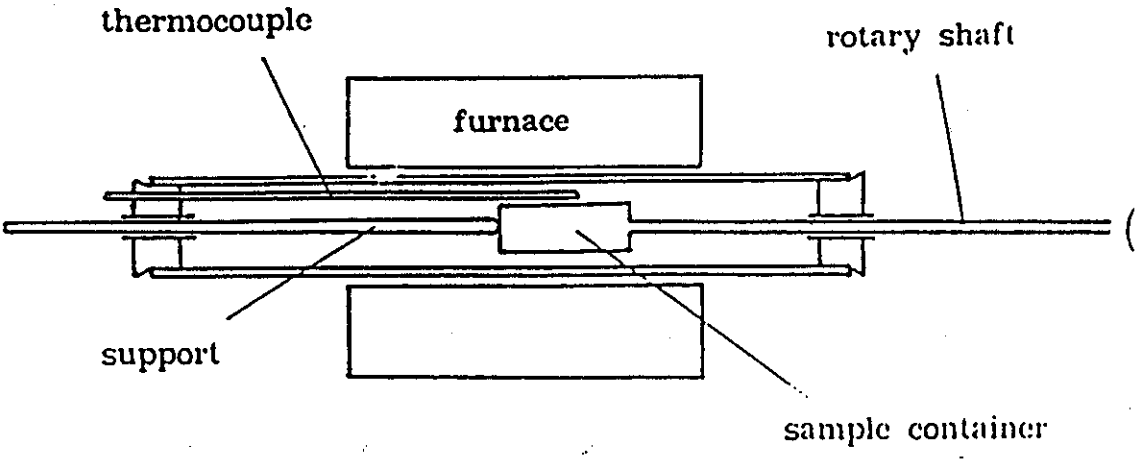

Figure 4: Schematic of Rotary Mixer Used in Initial Tests, after Jimbo[16]

process were as follows:

- Lower Matte Weight. To reduce copper from 0.4 to 0.1% in the scrap less than 10 kg of matte would be thermodynamically necessary via the solid process, while 120 - 200 kg would be needed for liquid processing.

- One Step Process. In the liquid treatment the slag would have to be removed, the matte added and the steel carburized before treatment and decarburized after treatment. In the solid process the matte would mixed with the scrap, and, after reaction, drained.
- Lower Na_2S Loss. Evaporation losses from the matte are much lower at lower temperatures.
- Increased Matte Copper Content. Matte copper content could be as high as 30% in the solid process; therefore, recovery of copper from the matte may be economically feasible.
- Decreased Resulphurization of Metal. In the liquid treatment there will be a significant sulphur pick-up by the liquid steel which would necessitate extensive desulphurization after processing. In the solid scrap process sulphur pick-up would be determined by the amount of matte which did not drain from the scrap.
- Process Flexibility. The solid scrap treatment process could be a stand alone unit off-site from the remelter or an on-site unit supplying preheated low copper scrap to an electric arc furnace. The liquid process would require an advanced ladle metallurgy station, equipped with reheat, slag skimming and injection facilities. The solid treatment would not affect process cycle time after melting, while the liquid treatment stage would have a considerable impact on productivity.

In addition, an economic assessment of the process was made which suggested that the energy cost of treatment would be approximately $5.00 per ton, and the reagent cost approximately $2.00 per ton. If the hot scrap is charged directly into the electric furnace there would be a decrease in electrical energy of approximately 250 kwh\ton and corresponding decreases in heat time and refractory wear which should lead to increased productivity and lower operating costs. Although it is difficult to exactly calculate total cost savings due to variations in raw material prices, we estimate that it may be possible, if there is a $40.00 per ton differential between high copper scrap and low copper scrap, that cost savings of approximately $20.00 per ton for direct electric arc furnace charging and $ 10.00 per ton for a stand alone processor may be possible.

Practical Concerns

The initial small scale experimentation resulted in a number of questions concerning this new process:

- What was the rate controlling step in the reaction?
- Would the matte spread and wet scrap?
- Could the matte be effectively drained from the scrap?
- Could the process be carried out in air?
- Would it be possible to treat electrical motors with this process?

To answer the above questions a number of experiments were carried out before large scale, industrial tests were initiated.

1. Rate Controlling Step.

It was assumed that liquid phase mass transfer would be the rate controlling step in the reaction. Thus, a rotating cylinder experiment was attempted under conditions where the mass transfer was well documented. Typical experimental results from the work of Y. Zhang[2] are given in Figures 5 and 6, where the increase of matte copper sulphide concentration can be seen as a function of time and rotation speed (Figure 4) with the attendant decreases of sodium sulphide and iron sulphide (Figure 5). At higher rotation speeds the reaction was found to be controlled by mass transfer; however, at low rotation speeds the matte formed a viscous layer which impeded mass transfer. Thus it is important to carry out the matte process in an environment, such as rotating kiln, which stimulates matte movement.

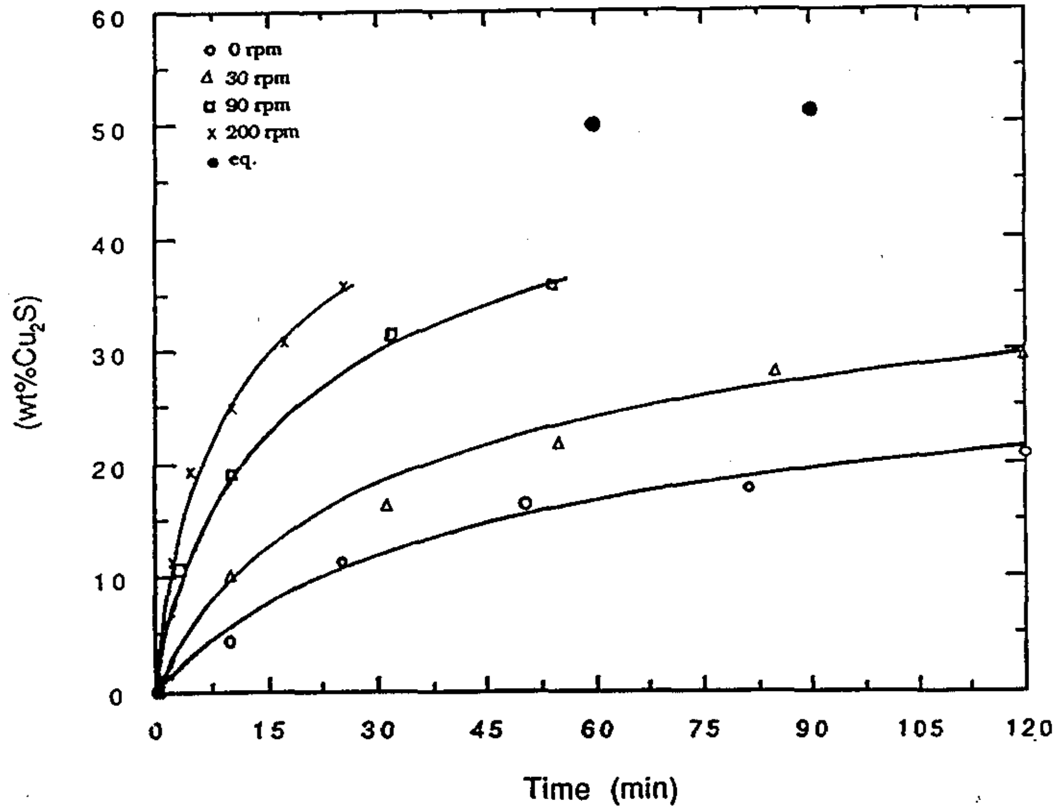

Figure 5: Concentration of Copper Sulphide In Matte as a Function of Time and Rotation Speed.

2. Matte wettability.

Experiments were carried out using an X-Ray Radiographic Technique to determine the contact angle between the matte and iron, copper and an alumina refractory. The results of this study indicated that the matte wet and spread upon iron, copper and the alumina refractory. Contact angles in all experiments were less than 5 degrees.

3. Matte Drainage.

To determine the efficiency of matte drainage L angles of steel (40 x 40 x 3 mm), steel plate (40 x 2 mm) and a copper sheet (40 x 2) were dipped into an 18% Na_2S - 82% FeS bath at temperatures of 800, 900 and 1000 C. The samples were emersed for 3 to 5 minutes before being withdrawn from the bath and air cooled.

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[2] Y. Zhang, A. W. Cramb, and R. J. Fruehan: unpublished research, CISR, Carnegie Mellon University, 1990

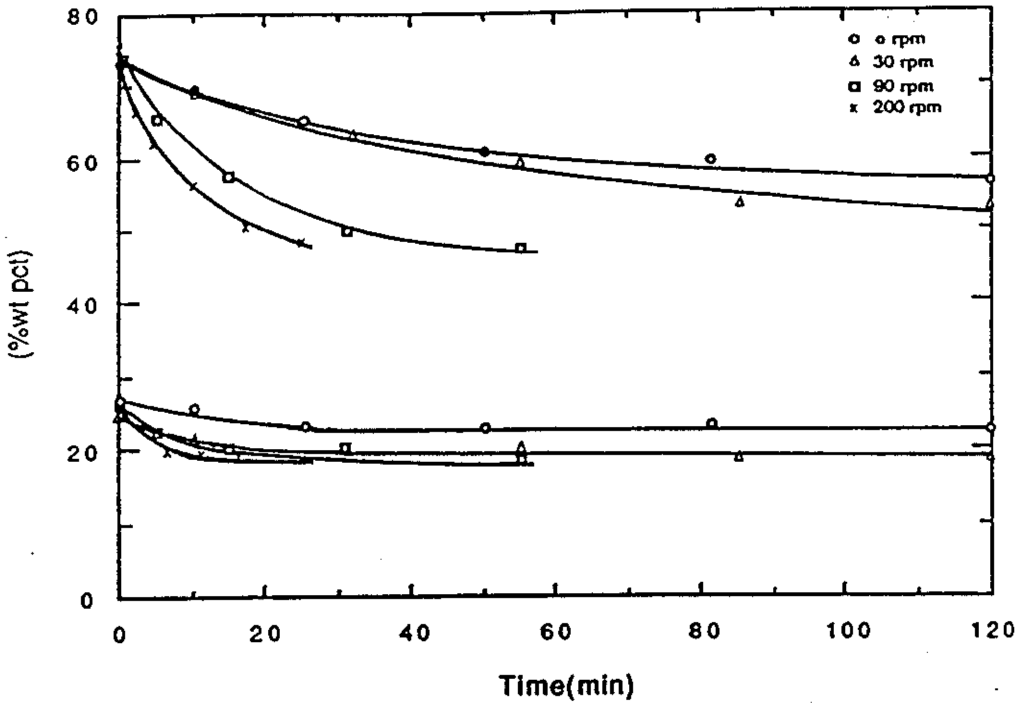

Figure 6: Concentration of Sodium Sulphide and Iron Sulphide in Matte as a Function of Time and Rotation Speed.

The copper sheet was completely dissolved at all temperatures. Results of the drainage experiments are given in Figures 7 and 8, where the ΔM% is the weight gain upon removal from the matte. In both cases the amount of matte adhering to the scrap was minimal at 1000°C; however, significant amounts of matte remained attached to the scrap at lower temperatures.

4. Process Feasibility in Air.

The above dip tests were carried out in air with no apparent deleterious effects; however, the time at temperature was small. Other experiments, carried out over longer time periods, indicated that if the copper was allowed to significantly oxidize, the process efficiency greatly decreased. In addition, if the iron was allowed to significantly oxidize, iron oxide would be picked up in the matte.

5. Removal of Copper from Electrical Motors.

To determine the efficiency of drainage from a copper wound motor, a large bath of matte (40 kg) was melted in an induction furnace using a carbon crucible. The motor was lowered into the matte and slowly rotated. The matte temperature was 1000 C during the experiment. Initially there was a large quantity of smoke as the plastic coverings, etc., on the copper windings burned off. The motor was rotated for 20 minutes and then removed. All copper which was emersed in the matte was removed from the motor.

Larger Scale Trials

In view of the process potential larger scale experiments were proposed to and accepted by the DOE[24]. A rotary kiln was purchased from CORECO, and set-up in the pilot facility of USX Corporation

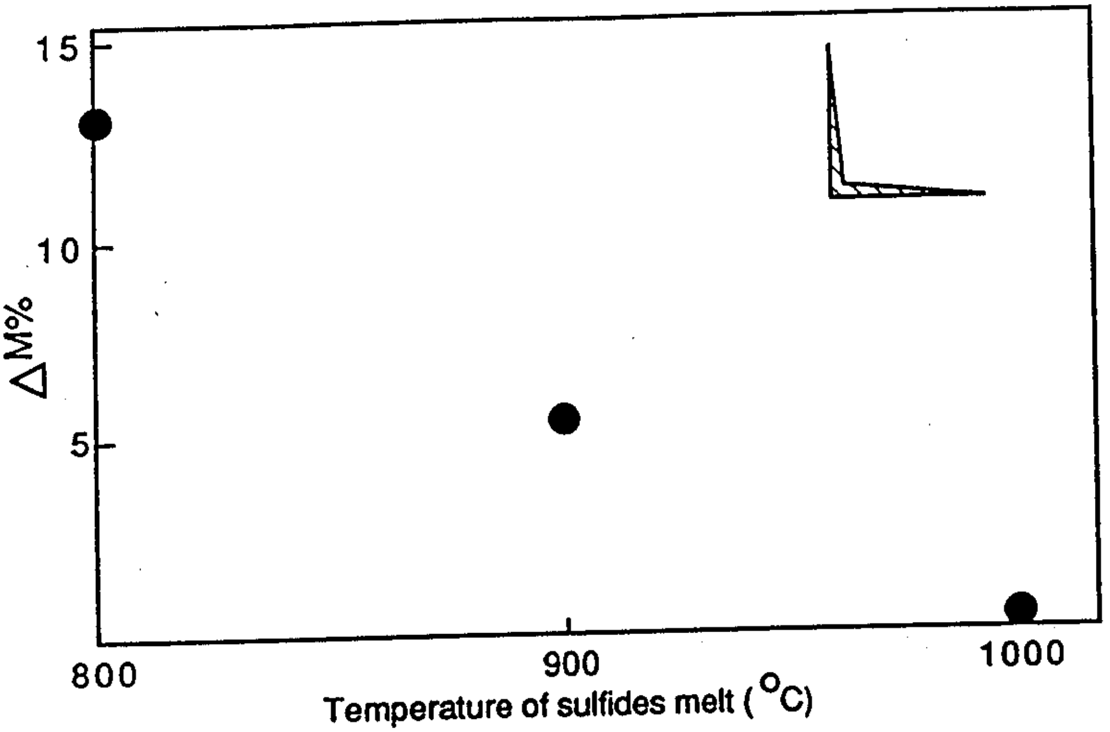

Figure 7: Matte Adherence Trial for Steel L Angle.

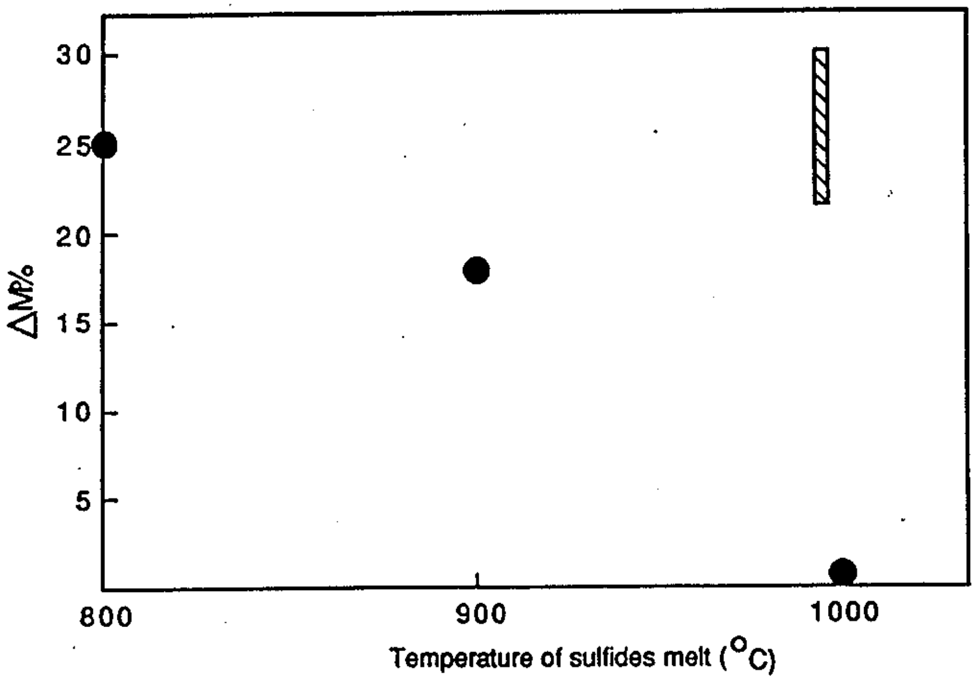

Figure 8: Matte Adherence Trial for Steel Plate.

in Universal, Pa. A schematic of the kiln is given in Figure 9.

To date the kiln has been installed and initial trials conducted. Preliminary results indicate that the process can be used on a larger scale to remove solid copper from scrap. Up to 100 kg of scrap has

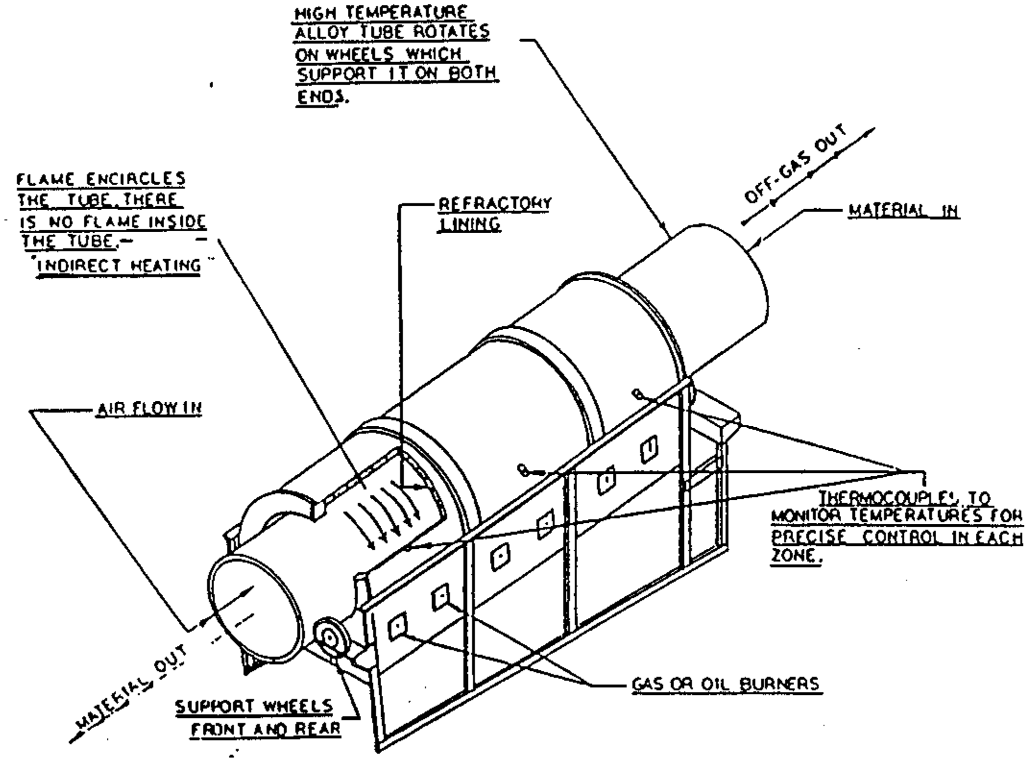

Figure 9: A Schematic of the CORECO Rotary Kiln.

been treated. Copper tubing and wire have been used to simulate the solid copper content of scrap. The process was operated at 1000°C and up to 4 kg of copper was removed from solid scrap in less than 10 minutes. At 1000°C there have been no problems in draining the matte from the kiln and copper removal efficiencies are approximately 90%. An example of the increase in copper sulphide content of the matte during a large scale trial is given in Figure 10. The fast rate of copper pick-up can be seen (4 kg of copper in less than 10 minutes). The copper sulphide content decreases as a function of time due to increasing matte FeO content as a consequence of oxidation of the scrap; therefore, it is best to carry out these experiments in a non-oxidizing atmosphere.

The Zinc Problem

The melting point of zinc under 1 atmosphere pressure is 419.58°C and its boiling point is 907°C. Thus, in any steelmaking process where temperatures can rise to 1600°C, zinc will vaporize, potentially oxidize and be found in the exhaust dust of the process. Electric furnace dusts are considered hazardous by the Environmental Protection Agency[25,26], due to the leachability of the toxic tramp elements of lead, cadmium and chromium and disposal of this dust is expensive. This has lead to numerous attempts to remove the zinc from the scrap before it is charged into the steelmaking vessel[26] in order to produce a material which can be more easily and profitably recycled.

The problem is being exacerbated by the growth in the amount of automotive galvanized sheet steel scrap which was estimated[25] to increase to 1.4 million net tons by 1990 by CMP. Automotive scrap is estimated to be only 10% of the galvanized scrap production, with the remainder joining the scrap problem in future years due to obsolescence of the galvanized part.

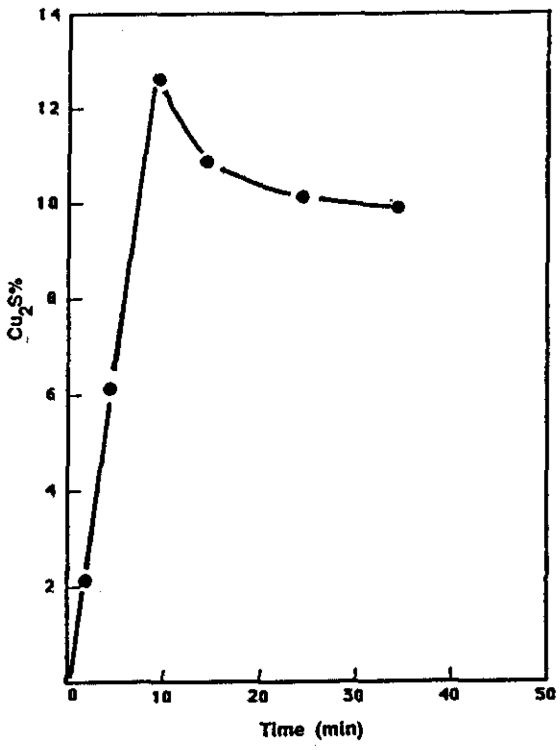

Figure 10: Copper Sulphide Variation In Large Scale Kiln Experiments.

Thus it is of great interest to develop scrap pretreatment processes which will cause separation of the zinc from the scrap before charging into the vessel. Three basic methods of zinc removal have been suggested:

- Chemical Treatment
- Electrochemical Treatment
- Thermal Treatment

A number of the processes are combined chemical and electrochemical where the zinc is dissolved into an acidic or basic solution and electrochemistry is used to accelerate this process[26-29]. A benefit of the chemical processes is that the zinc can be recovered from the liquor.

Thermal treatment methods include plasma processing, induction heating, processing in conventional steelmaking furnaces and high temperature scrap preheating[26].

Plasma processes[30,31] pass a gas through an electric arc between two electrodes to produce an ionized gas which forms the plasma. Temperatures range from 3000 to 5000°C. Major problems in this technology are related to operational cost but the process is feasible[26].

Other thermal treatment methods include induction heating[32], controlled addition to conventional steelmaking to ensure that the average dust content is kept at tolerable levels, and scrap preheating. Of these methods, scrap preheating in a rotary kiln seems advantageous as the energy cost can be alleviated by direct charging into an electric furnace. In fact, the process outlined earlier for copper removal, as it operates above the boiling point of zinc could also be developed to remove zinc from scrap if the vaporized zinc were oxidized and the dust collected[33].

Any scrap preheating system which increases the scrap temperature above the boiling point of zinc will result in zinc removal from the scrap; therefore, processes such as the CONSTEEL Process[34] and KORF's EOF process have the potential to remove zinc from galvanized scrap[35]. However, recondensation of zinc in a commercial vessel can cause a sticking problem in the vessel and it is probably best to remove zinc in a process specifically designed for zinc removal where condensation is strictly controlled or the zinc oxidized to a fine dust for ease of collection[36]. For example, Daido steel has a process where zinc is oxidized in a kiln and the scale is removed in a ball mill.

Conclusions

Scrap pretreatments for the separation of copper and zinc from steel scrap may become commercialized in the next few years due to the need to reduce the copper residuals in melted scrap and to eliminate the furnace dust problem. A number of processes are under development towards this goal and a rotary kiln type of process is technically feasible for both zinc and copper removal from ferrous scrap. A new process, developed at Carnegie Mellon University, allows both scrap preheating and copper removal. A similar type of process could easily be adapted to allow zinc removal as the process temperature is above the boiling point of zinc.

Acknowledgements

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The project could not have continued without the support of the USX Corporation, who allowed us access to their pilot facility, and, the AISI Direct Steelmaking Team who arranged for vital power and gas connections and helped us keep a perspective on the task.

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CISR PROGRESS REPORT

REFINING OF COPPER FROM SOLID FERROUS SCRAP

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Introduction

The United States has a great abundance of ferrous scrap and will have a surplus for the foreseeable future. The American steel industry currently uses more iron units from scrap than from ore for the production of steel.[1] However, scrap often contains detrimental elements which can not be refined in the normal steelmaking operation. The most troublesome of these detrimental elements is copper, which has been identified as a major concern of American steelmakers.[1] An extensive review of the possible pyrometallurgical refining methods of removing Cu was carried out.[3-12] Of all the proposed methods a sulfide treatment appears to be the most promising. There are two options for refining of Cu from ferrous scrap. One is the refining of Cu from liquid ferrous scrap;[4-7,13] another is from solid ferrous scrap.[14] The required quantity of matte for removal of Cu from liquid scrap is too large to lead to an economical refining process, accordingly the refining of Cu from liquid scrap is not practical.

Refining of Cu from solid scrap

A new concept for copper removal from ferrous scrap i.e. a refining of Cu from solid scrap was developed by R.J. Fruehan.[14] Copper is primarily present in ferrous scrap as pure copper, for example, wires and plated metals. The thermodynamics of removing copper before it is put into solution in liquid iron is greatly improved. When the scrap is melted and the copper is in solution in iron, its chemical activity is greatly reduced, even when the effect of carbon, which inceases the activity coefficient of copper, is taken into account. In another words, if the Cu is not put into solution, the reaction for Cu removal will be more favorable. In addition, the treatment of solid scrap has other advantages:

(1) It lends itself to some of the scrap preheating technologies currently under development;

(2) There is no need for desulfurization, carburization and decarburization processes as is the case for treatment of scrap which is melted prior to treatment.

Experiments were performed using a rotating graphite crucible, simulating a rotating kiln with a revolution speed of 20, 40, 60 rpm. In these experiments 100 grams of sythetic scrap containing 0.5 or 1.0% Cu was treated with 8 grams of FeS-Na_2S containing 19 to 25% Na_2S at the temperature of 800 °C, 900°C, and 1000°C. The experimental results showed that over 75% of copper can be removed in duration time of 20 minutes. A crude evaluation indicated that to remove copper level from 0.4 to 0.1% about 10 kg of an 80% FeS-20% Na_2S matte per tonne of scrap is required.

Experiments prior to setting up a kiln

Based on the above experimental results a large scale rotary kiln will be set up for further pre-pilot experiments for removing Cu from solid scrap. Prior to setting up the kiln two types of experiments were planed. The first is a static experiment in a Lindberg horizontal furnace. The purpose of this experiment is to determine the contact angle and wettability between the sulfide melt and the sample and to determine if there is any reaction between the melt and sample at 1000°C in an argon or air atmosphere. The second is a wettability experiment in a Lindberg vertical furnace, in which a metal sample will be inserted into a crucible with sulfide melt in it and then withdrawn out of it to determine rate of matte drainage. An electrobalance above the vertical furnace will be used to determine the change of weight of the sample as a function of time, temperature and at different FeS : Na_2S ratio, at 1000°C and under a controlled atmosphere. Different types of steel e.g. 1008, 4150, 304, 409, 446, 18-8 etc. will be used for the experiments.

To date the static experiment in the horizontal furnace have been completed. Once Lindberg vertical furnace is set up, the experiments to determine matte separation efficiency will be conducted.

Work to Date

(1) Experimental

A Lindberg horizontal furnace capable of temperature exceeding 1000°C was used for experiments. The schematic diagram of the furnace that contains a alumina tube is shown in Figure 1. Inside the furnace tube was put a silica glass tube which is 4 1/2 ' L x 1" D with one end open and another end close and with a gas inlet and a outlet.

The sample with FeS-Na_2S mixture (75:25 or 82:18) was placed in the center part of the silica glass tube (hot zone about 10 cm long) under an argon or air atmosphere at 1000°C for 1, 2, 4 and 20 hrs. The sheets of AISI 1008, AISI 4150, 304, 409, 446, 18-8 and Cu were used as sample for experiments. The chemical composition for above steel is shown in Table 1. After the sample was removed from the silica glass tube and cooled, pictures were taken. Some of those samples were cut, ground, polished, etched. The samples of 1008 and 4150 were etched in a 7% nital solution while the stainless steel 18-8 was etched in a superpicral etchant solution with 0.5% HCl. Finally the polished, etched samples were photographed using SEM to observe the microstructure of the transverse section of the sheet and to determine the depth of attack.

(2) Results and Discussion

After the sample was placed inside the glass tube for 10-15 minutes, the sulfides on the sample began to melt no matter what FeS:Na_2S ratio was used and run all over the surface of the sample. There was no a droplet formation and accordingly no contact angle between melted sulfides and sample could be measured, as shown in Figures 2 and 3. The contact angle is very low (< 5°). The depth of the layer of sulfides which melted on the sample was about 0.1mm .

In an uncontrolled atmosphere (open air) all the steel samples were oxidized with different extent regardless of whether the melted sulfide mixture was 75% FeS:25% Na_2S or 82% FeS:

18% Na_2S. The AISI 4150 steel (containing Cr, Ni, and Mo< 1%) was oxdized most heavily, followed by AISI 1008 (low carbon steel) and finally by 18-8 stainless steel. Figures 4 to 9 show that the unpolished and unetched photographs of the sample and the flake for 4150, 1008, and 18-8 at 1000°C and open air. The longer the time, the deeper the depth attacked, but within 1 hr the sample was slightly oxdized for 4150 & 1008 samples. After 2 or 4 hrs both the 4150 and 1008 were oxidized heavily. The 4150 was oxidized so badly that it was totally encased in the scale with 0.12" thickness, as shown in Figure 10. In contrast with the uncontrolled atmosphere, in argon atmosphere, no matter whether 4150,1008 or stainless steel (e.g. 18-8, 304, 409, 446) samples were used, none of the steel samples were oxidized to any extent as shown in Figure 11,12 and 13. It was noted that a copper sample was totally oxidized and formed a melted mixture of copper oxide and copper sulfides which was brittle, but the copper was not oxidized under argon atmospher, as shown in Figure 14 and 15.

The analysis of the SEM photographs of the unpolished surface reveals essentially the same results as the above Figures. At the uncontrolled atmosphere in all cases of the steel, the surfaces were oxidized so badly that pieces of the scale flaked off. Each of these samples was photographed along with the corresponding flakes. These photographs confirmed the analysis of the visual inspection.

Figures 16 to 21 show that the photographs of the transverse section of each of the samples polished and etched for 4150, 1008 and 18-8. The polished and etched samples might not show a true depth of attack at air atmpsphere. This was due to the fact that it was impossible to polish the samples and retain any of the scale layer. The photographs were analyzed for depth of attack and the results are shown in Table 2. The results show that under an argon atmosphere the surface of the steel samples will not be attacked, while at open air attacked to different extent. The worst case was the 4150 followed by 1008. With the few samples that were attacked under argon atmosphere, it could have been because the argon tank ran out before samples were removed from the furnace. Unfortunately these results are not very accurate due to the large amount of flaking of the scale that occured.

Other experiments were carried out for samples of 304, 409, and 446 under argon or air atmosphere at 1000°C for 1, 2, 4 even 20 hrs in the furnace. All of them were completely wet and no obious attack could be found on the surface of the sample. Thus the higher chromium containing steel appear to be more resistant to both oxidation and attack by the sulfide matte, and these 3 steels are suggested as potential container materials for the kiln. It was also found that the sulfides of 75%FeS : 25%Na_2S melted more easier than that of 82%FeS : 18%Na_2S. That was probably due to the poor uniformity of premelted sulfides melt (82%FeS:18%Na_2S).

(3) Conclusion

1) All types of steel 1008,4150, 304, 409, 446 ,18-8 etc and Cu samples were completely wet. The sulfides on the sample began to melt right after 10--15 minutes heating, and melted sulfides which covered the surface of the sample was about 0.1 mm thin.

2) All types of steel and Cu samples were oxidized and scaled while not under an Ar atmosphere. Therefore, it is favorable to treat the solid ferrous scrap to remove Cu under a controlled argon atmosphere in the furnace, or kiln.

3) Container materials for the kiln shoud be made out of either 304, 409 or 446.

Future work

Based on the results of the above experiments, it is known that the wettability is good enough for treating different types of the metal such as 1008, 4150, 304 400, 446 and Cu. However, a quantative relationship between the sample and the sulfide melt which covers on the the surface of the metal under different conditions must be known. Also, a large scale experiment on a several - kilogram - capacity kiln was planed to be set up to further determine the practical and economical feasibility using the experimental results obtained. So the future work is as follows:

(1) A Lindberg vertical furnace will be set up to do further experiments.

(2) A few specific experiments will be conducted on Lidberg vertical furnace to find out the change of weight of the sample as a function of time , temperature and FeS : Na_2S ratio etc.

(3) A kiln will be set up to do pre-pilot experiments. The kiln will be delievered within 8 weeks. *Drawings of the kiln have been* reviewed and the site is being cleared. attention will also be paid to the following problems:

1) Will the matte make sufficient contact with the scrap ?
2) Can the matte be completely seperated from the scrap ?

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FIGURES

Figure 15. At Ar atmosphere and 1000°C for 20 hrs the Cu sample remained unchanged with no oxidation.

Figure 16 Polished and etched sample for 4150 at open air and 1000°C with $FeS : Na_2S = 75 : 25$ (above), 82 : 18 (below)

Figure 17 Polished and etched sample for 1008 at open air and 1000° C with $FeS : Na_2S = 75 : 25$ (above), 82 : 18 (below)

Figure 18 Polished and etched sample for 18-8 at open air and 1000°C with $FeS : Na_2S = 75 : 25$ (above), 82 : 18 (below)

Figure 19 Polished and etched sample for 4150 at Ar atmosphere and 1000°C with $FeS : Na_2S = 75 : 25$ (above), 82 : 18 (balow)

Figure 20 Polished and etched sample for 1008 at Ar atmosphere and 1000° C with $FeS : Na_2S = 75 : 25$ (above), 82 : 18 (below)

Figure 21 Polished and etched sample for 18-8 at Ar atmosphere and1000°C with $FeS : Na_2S = 75 : 25$ (above), 82 : 18 (below)

Table 1 The chemical composition of steels used for experiments

	C	Mn	Si	Cr	Ni	Mo	Ti
304	0.049	1.09	0.57	18.26	8.45	0.31	
409	0.024	0.26	0.51	11.35	0.23	0.03	0.378
446	0.027	0.33	0.57	27.21	1.93	3.31	0.41
18-8	0.02	0.4	0.6	18	8		
1008	0.05	0.5	0.3				
4150	0.1	0.5	0.3	< 1%	< 1%	< 1%	

Table 2 The depth of attack for 1008, 4150, and 18-8 at 1000 C

sample	FeS : Na_2S ratio	atmosphere	Depth of attack (um)
1008	75 : 25	Air	154
	88 : 12	Air	137
	75 : 25	Argon	no attack
	88 : 12	Argon	no attack
4150	75 : 25	Air	135
	88 : 12	Air	97
	75 : 25	Argon	no attack
	88 : 12	Argon	no attack
18-8	75 : 25	Air	228
	88 : 12	Air	111
	75 : 25	Argon	no attack
	88 : 12	Argon	no attack

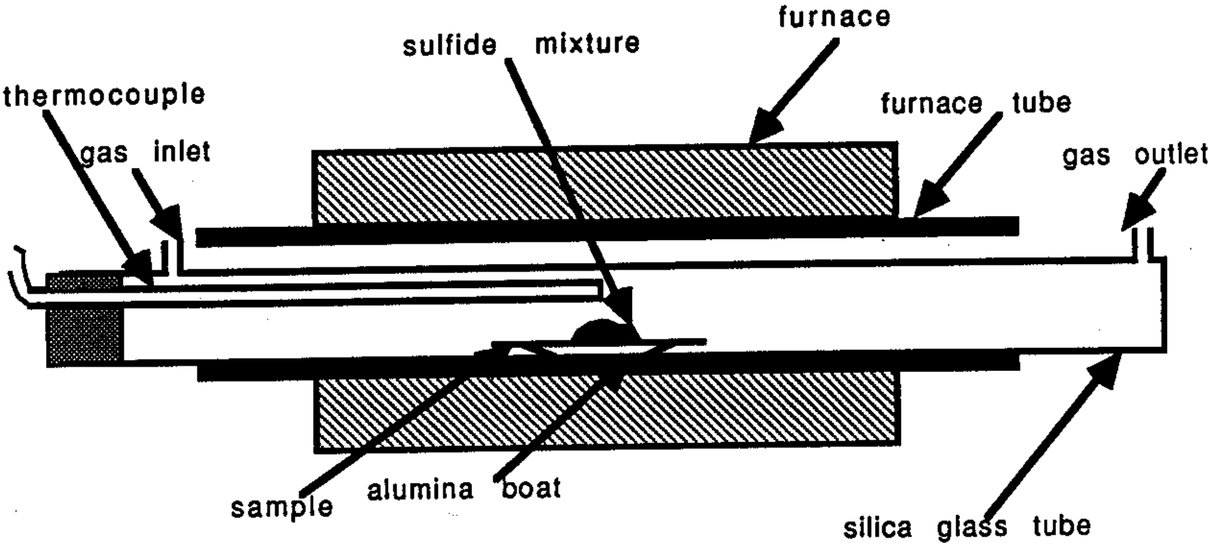


Figure 1 Schematic diagram of Lindberg horizontal furnace used for static experiments.

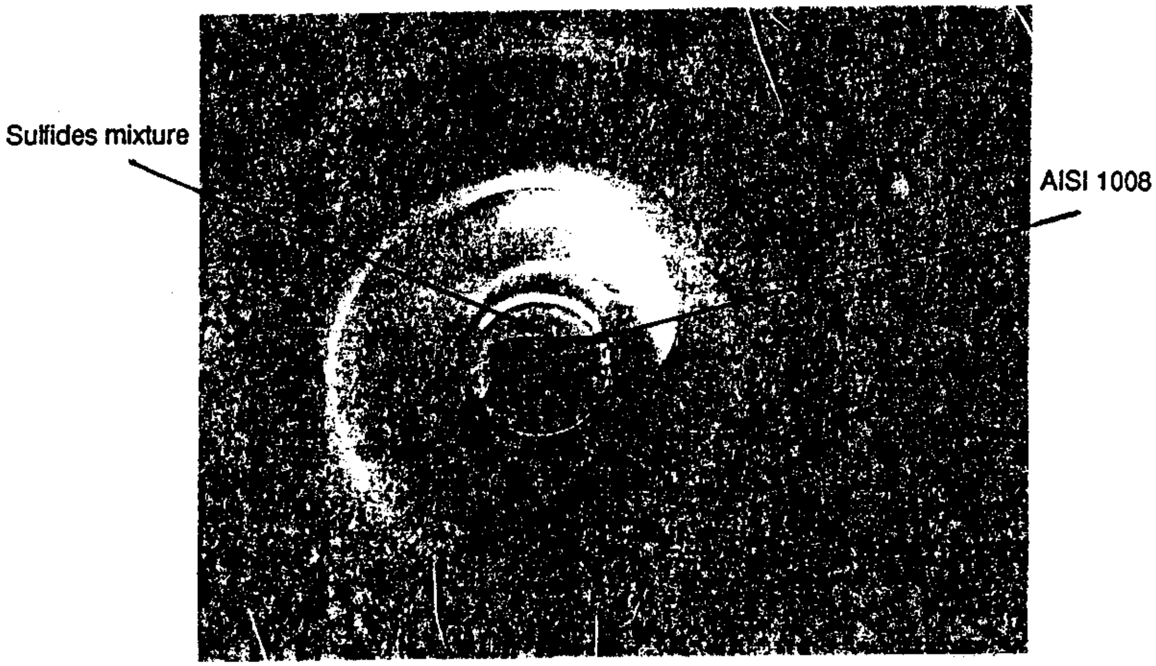


Figure 2. Sulfides mixture on AISI 1008

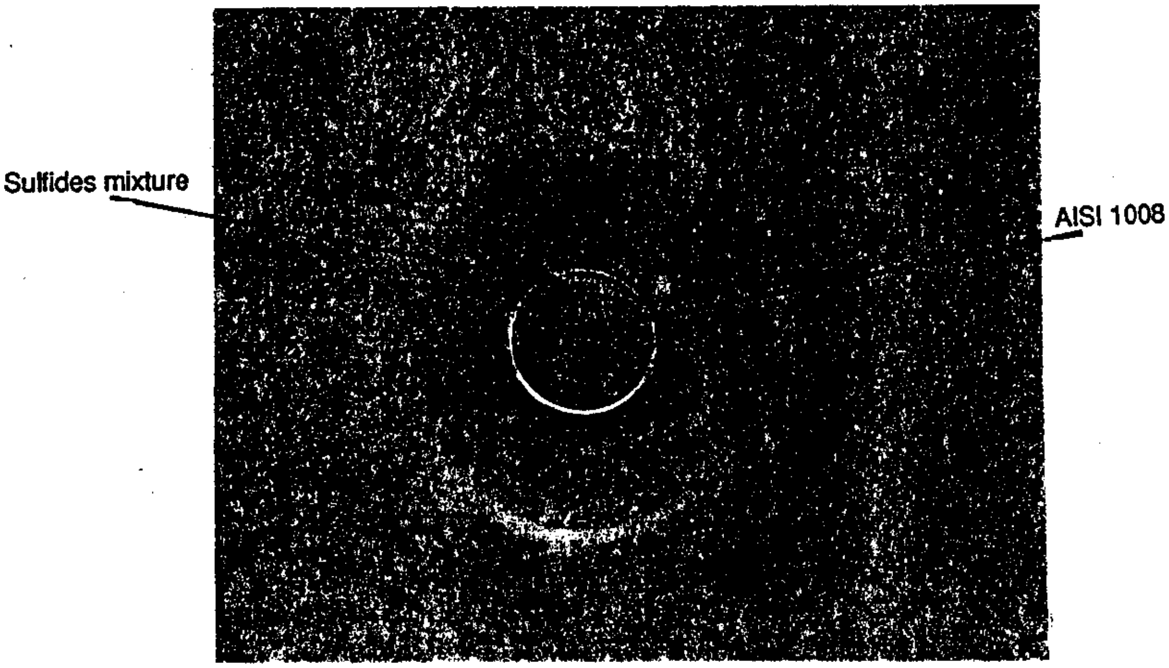


Figure 3. Sulfides mixture on AISI 1008

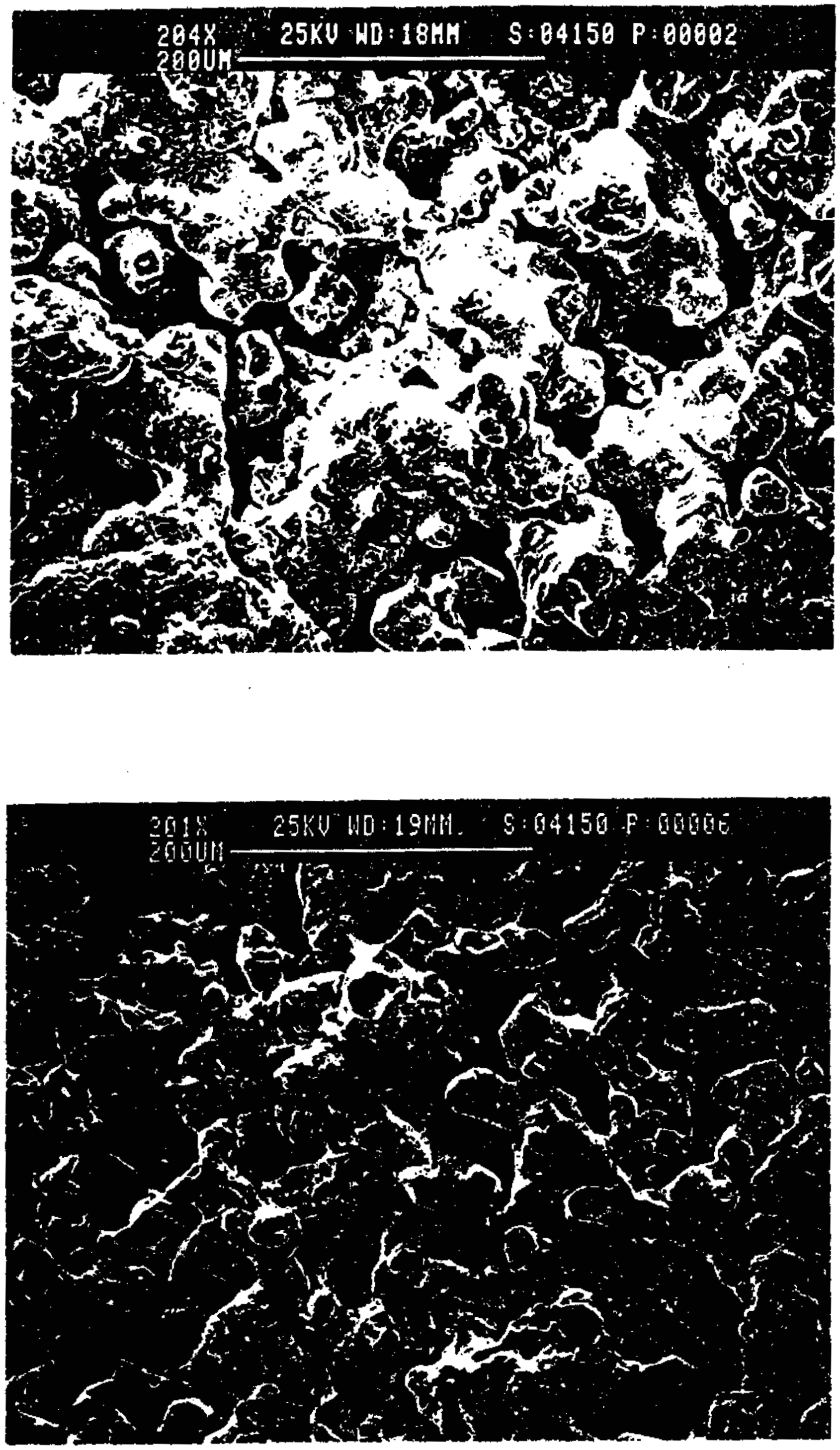


Figure 4. Unpolished sample for 4150 at open air and 1000°C with FeS : Na_2S = 75 : 25 sample (above), flake (below)

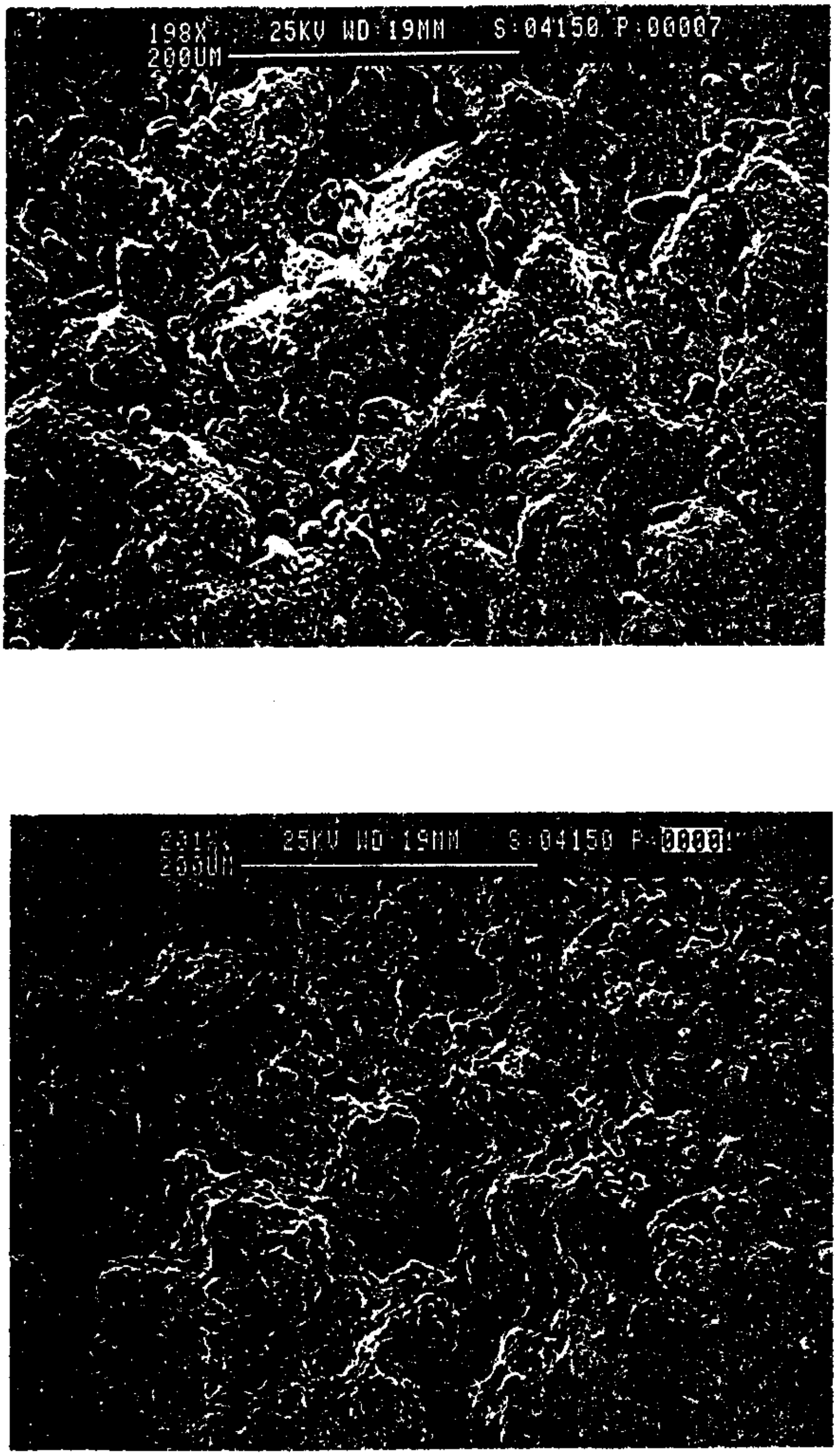
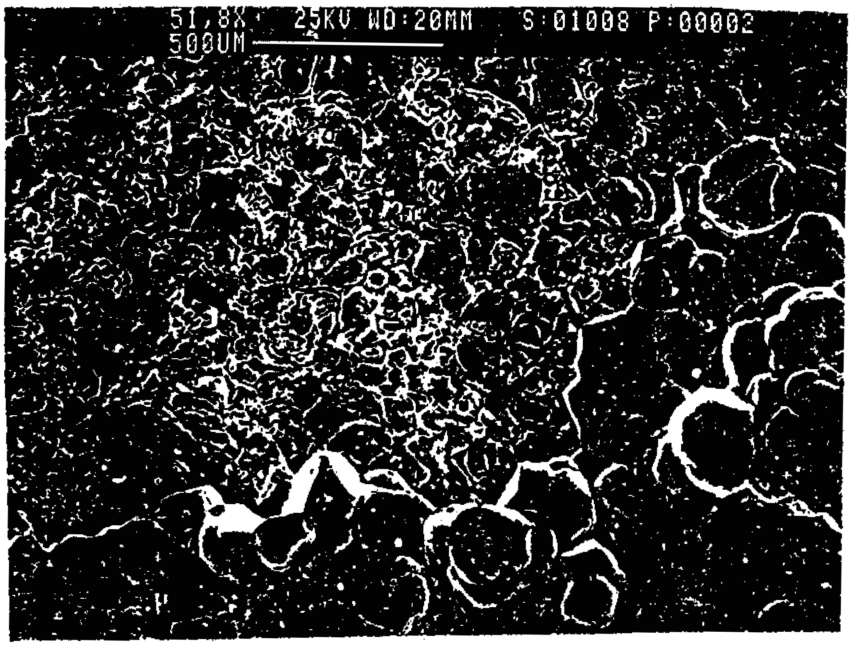


Figure 5. Unpolished sample for 4150 at open air and 1000°C with FeS : Na_2S = 88 : 12 sample (above), flake (below)



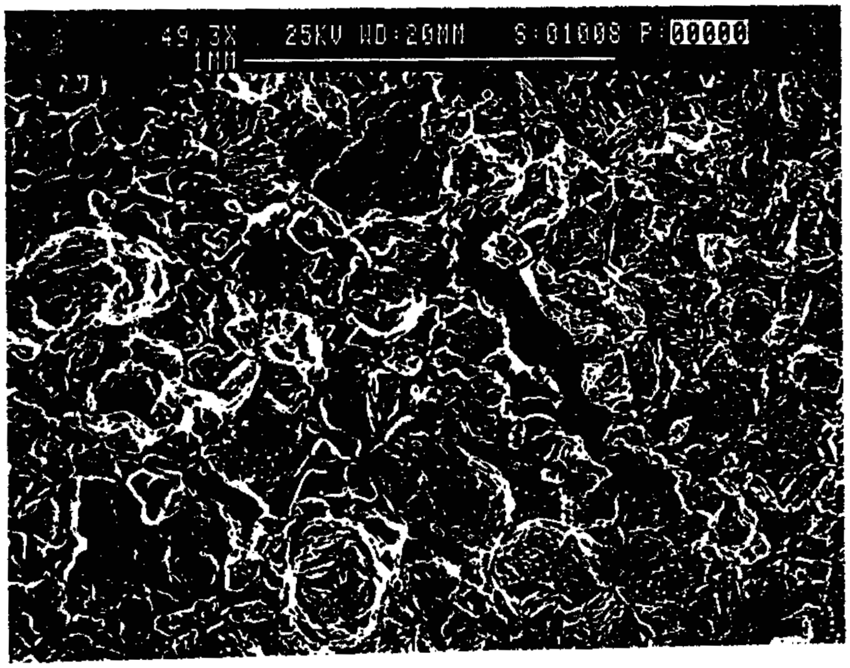


Figure 6. Unpolished sample for 1008 at open air and 1000°C with FeS : Na_2S = 75 : 25 sample (above), flake (below)

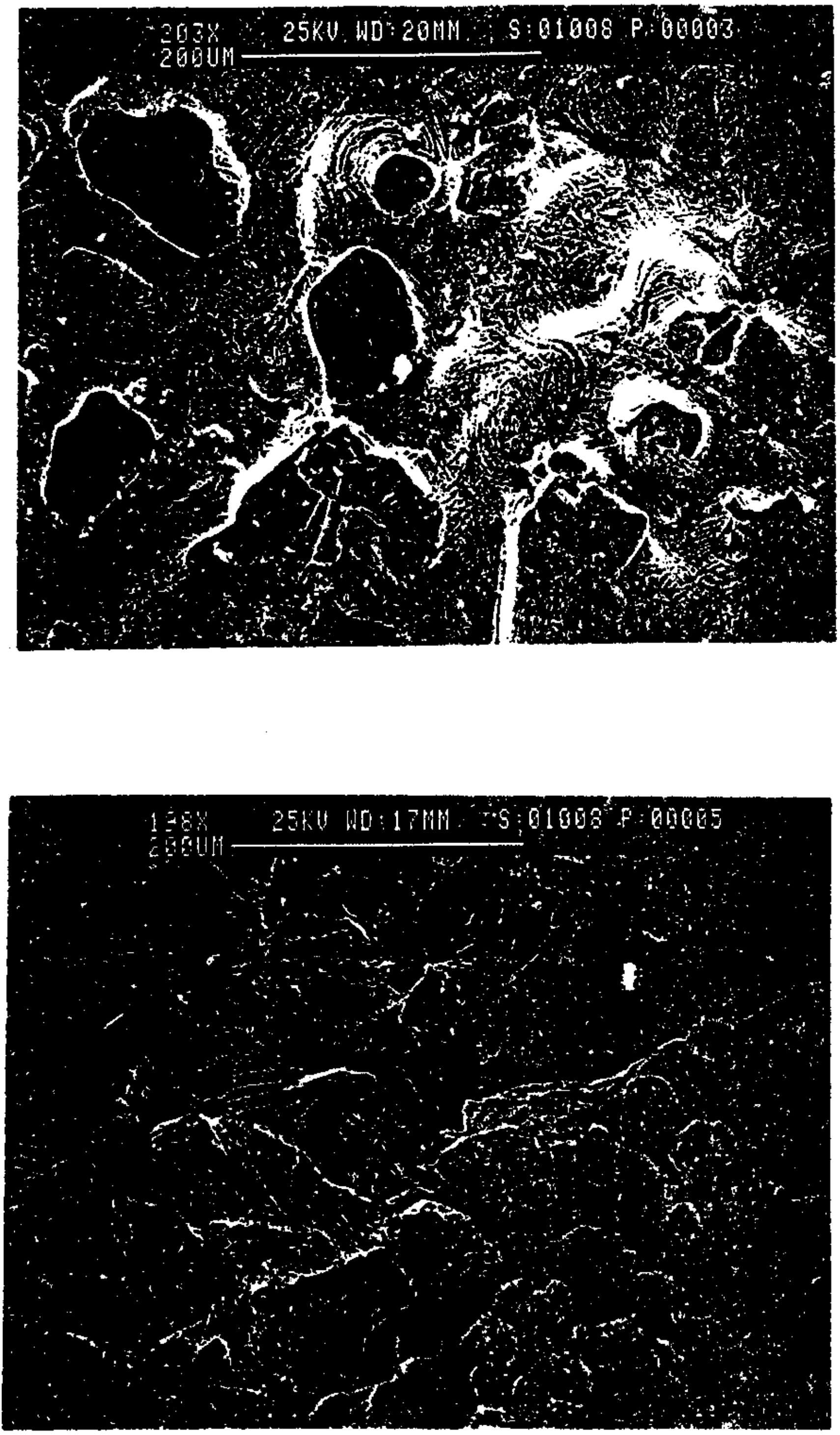


Figure 7. Unpolished sample for 1008 at open air and 1000°C with FeS : Na_2S = 82 : 18 sample (above), flake (below)

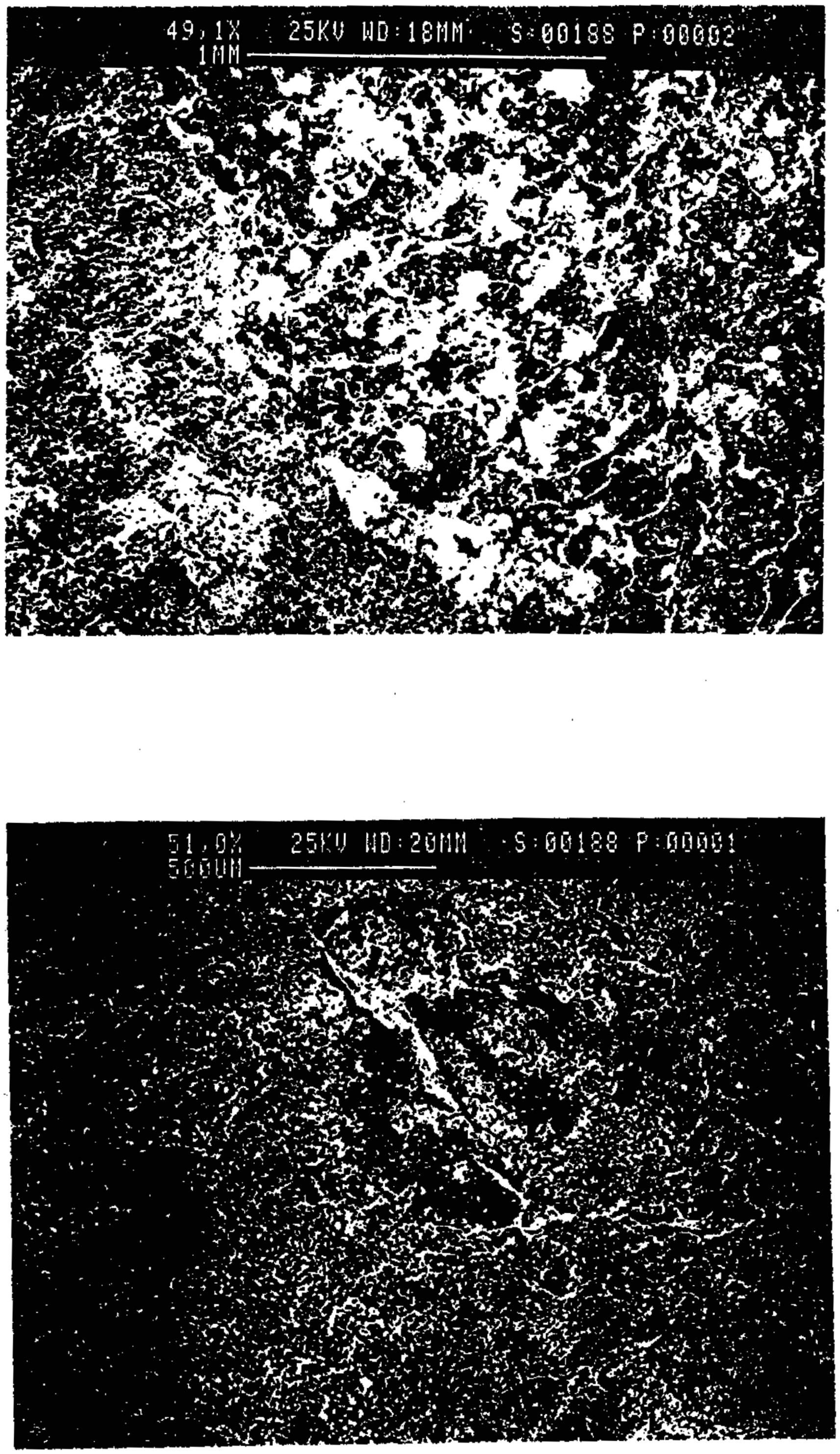


Figure 8. Unpolished sample for 18-8 at open air and 1000°C with FeS : Na_2S = 75 : 25 sample (above), flake (below)

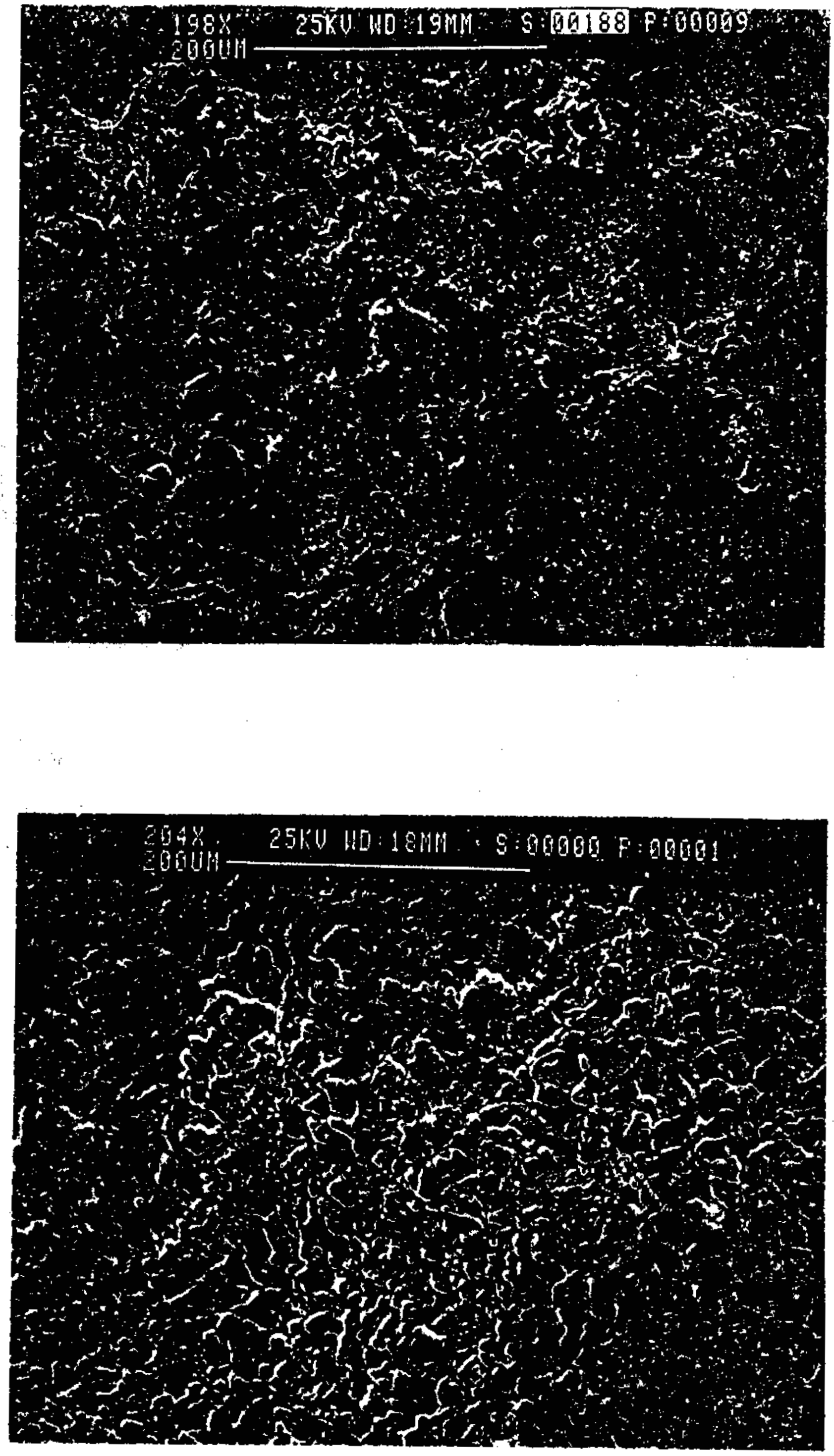


Figure 9. Unpolished sample for 18-8 at open air and 1000°C with FeS : Na_2S = 82 : 18 sample (above), flake (below)

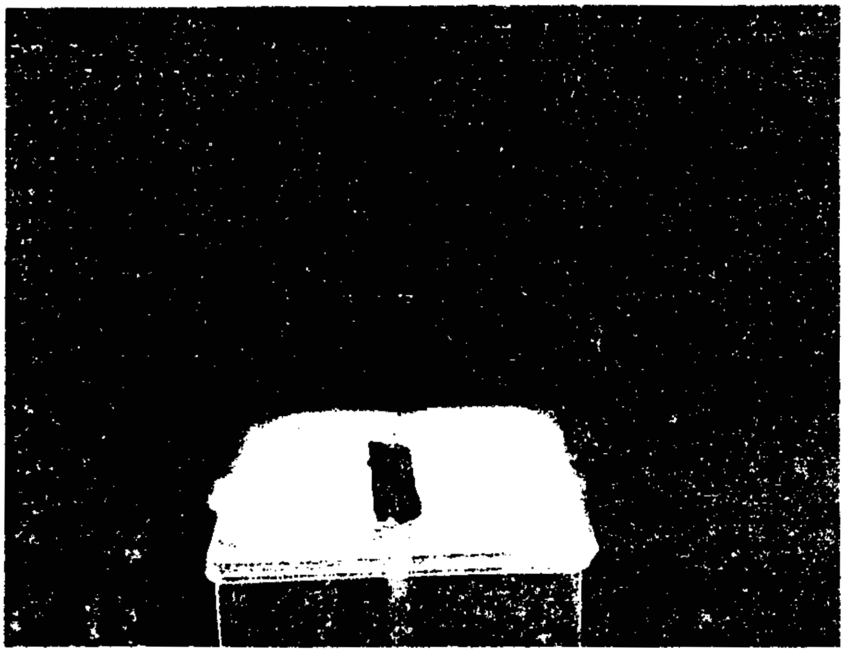


Figure 10. AISI 4150 steel and scale and scale casing at open air and 1000°C

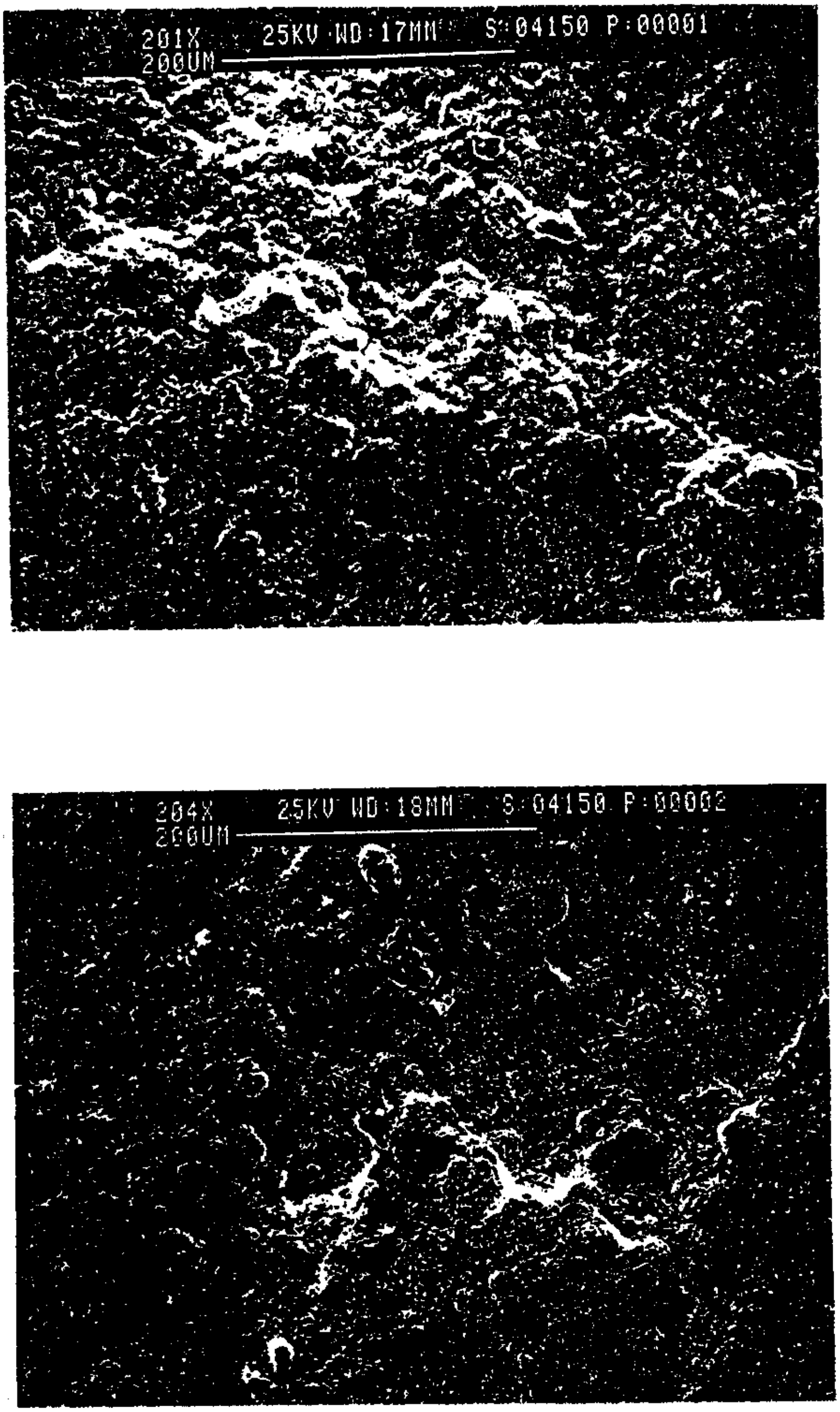
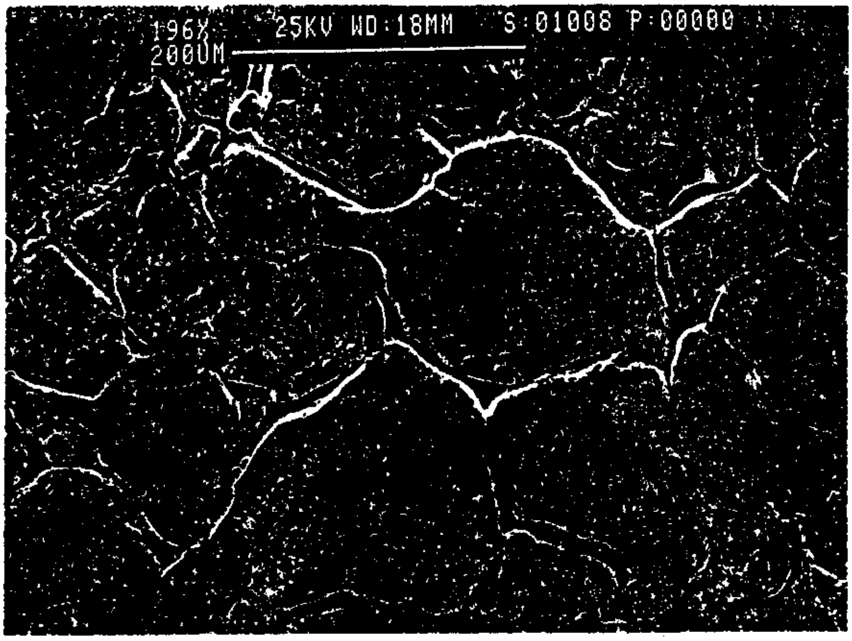


Figure 11. Polished and etched sample for 4150 at Ar atmosphere and 1000°C

FeS : Na_2S = 75 : 25 (above), 82 : 18 (below)



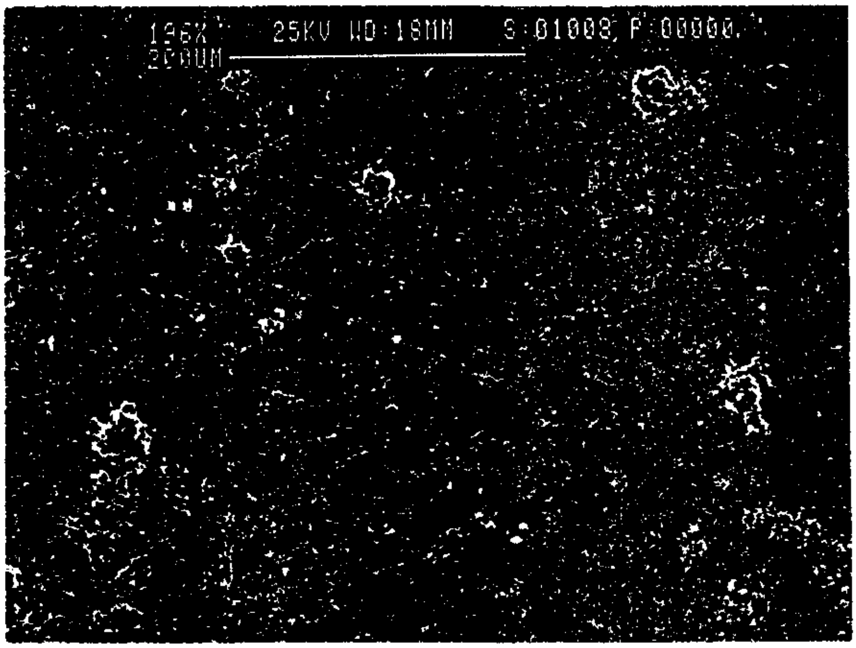


Figure 12. **Polished and etched sample for 1008 at Ar atmosphere and 1000°C**

FeS : Na_2S = 75 : 25 (above), 82 : 18 (below)

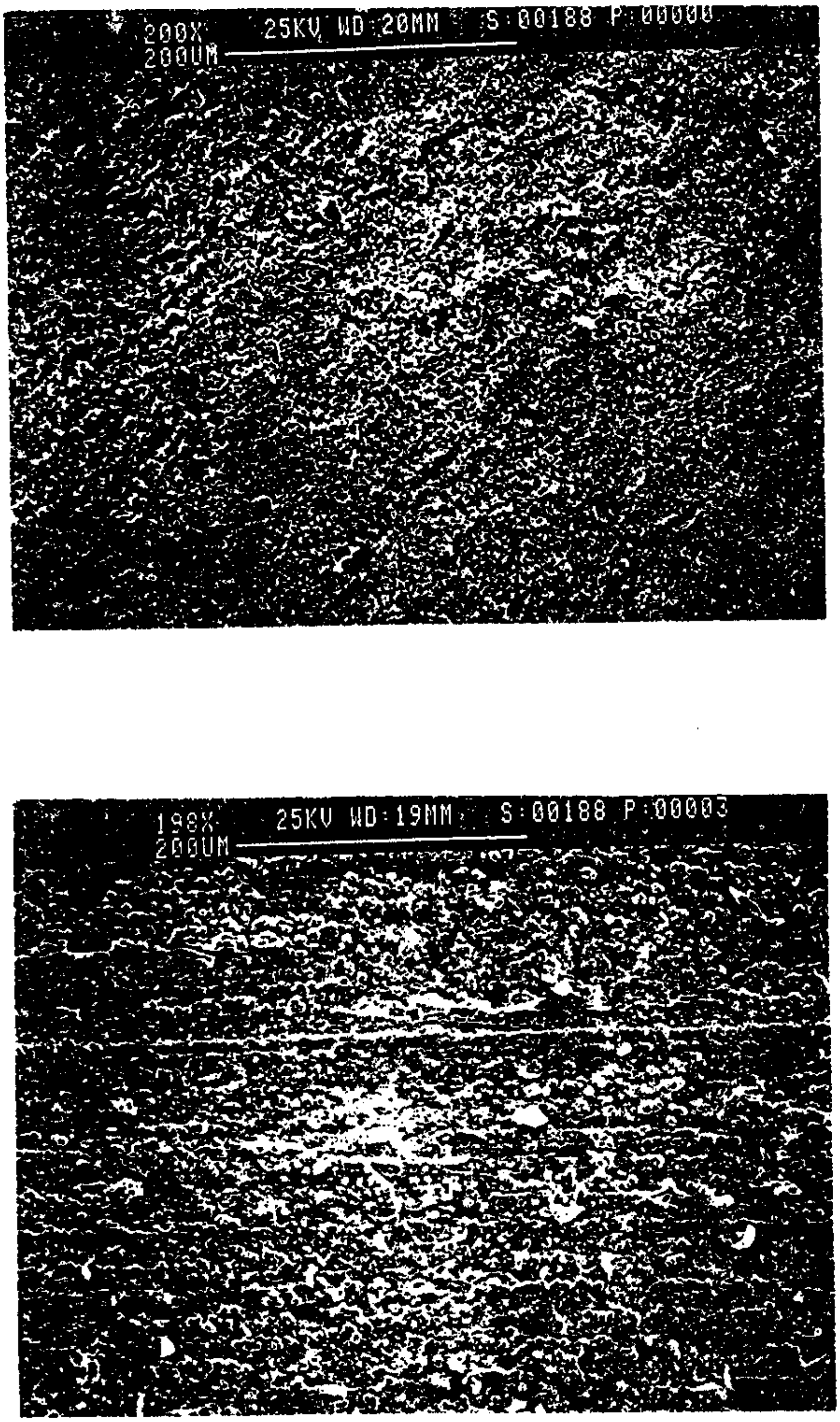


Figure 13. Polished and etched sample for 18-8 at Ar atmosphere and 1000°C

FeS : Na_2S = 75 : 25 (above), 82 : 18 (below)

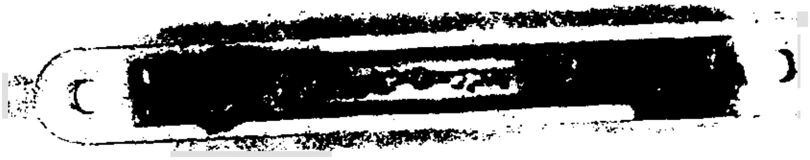


Figure 14 At open air and 1000°C for 20 hrs the Cu sample showed a brittlement with oxidation

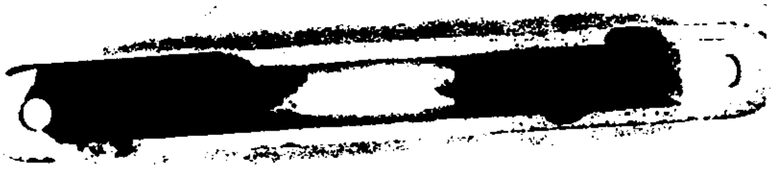


Figure 15 At Ar atmosphere and 1000°C for 20 hrs the Cu sample remained unchanged with no oxidation

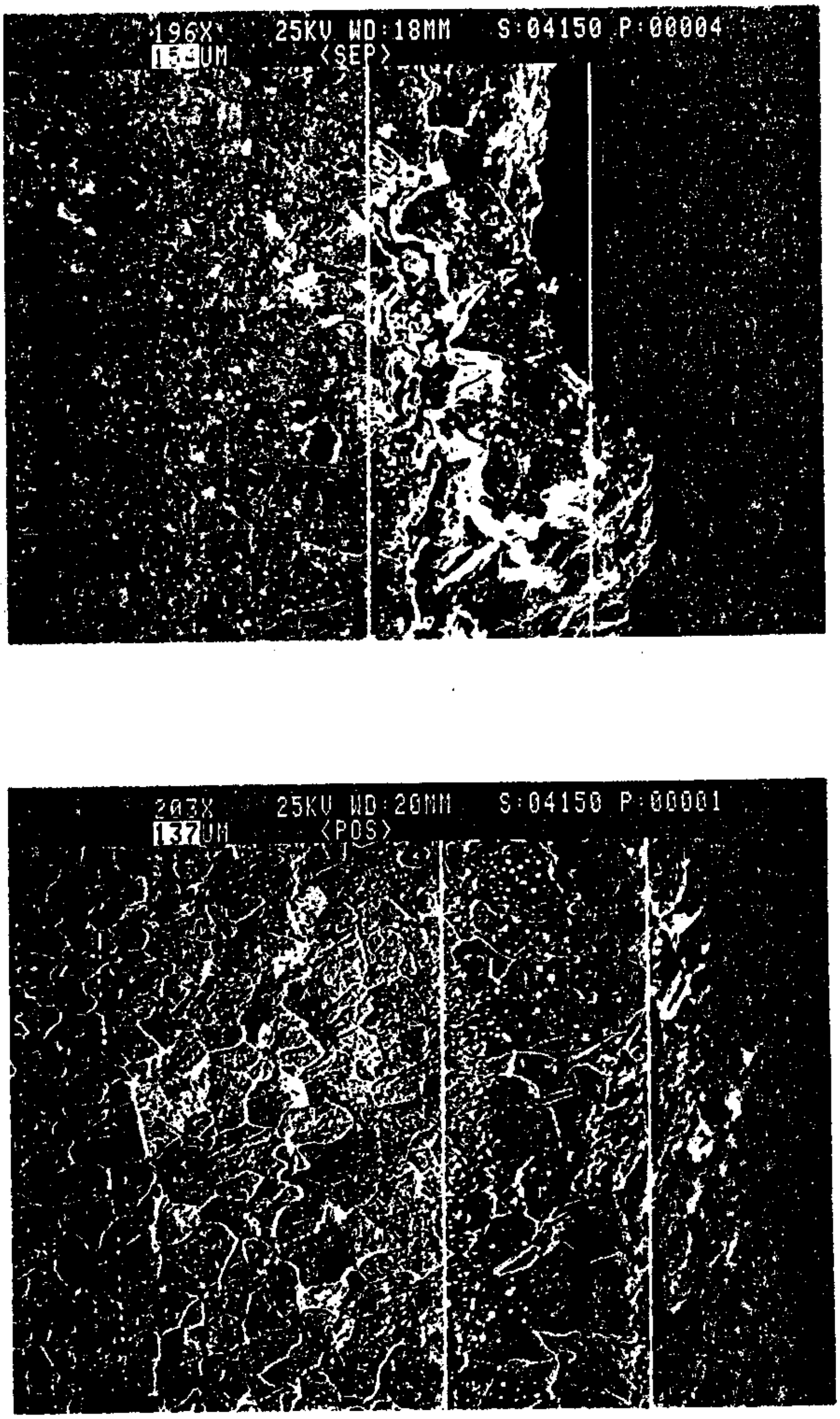


Figure 16 Polished and etched sample for 4150 at open air and 1000°C with

FeS : Na_2S = 75 : 25 (above), 82 : 18 (below)

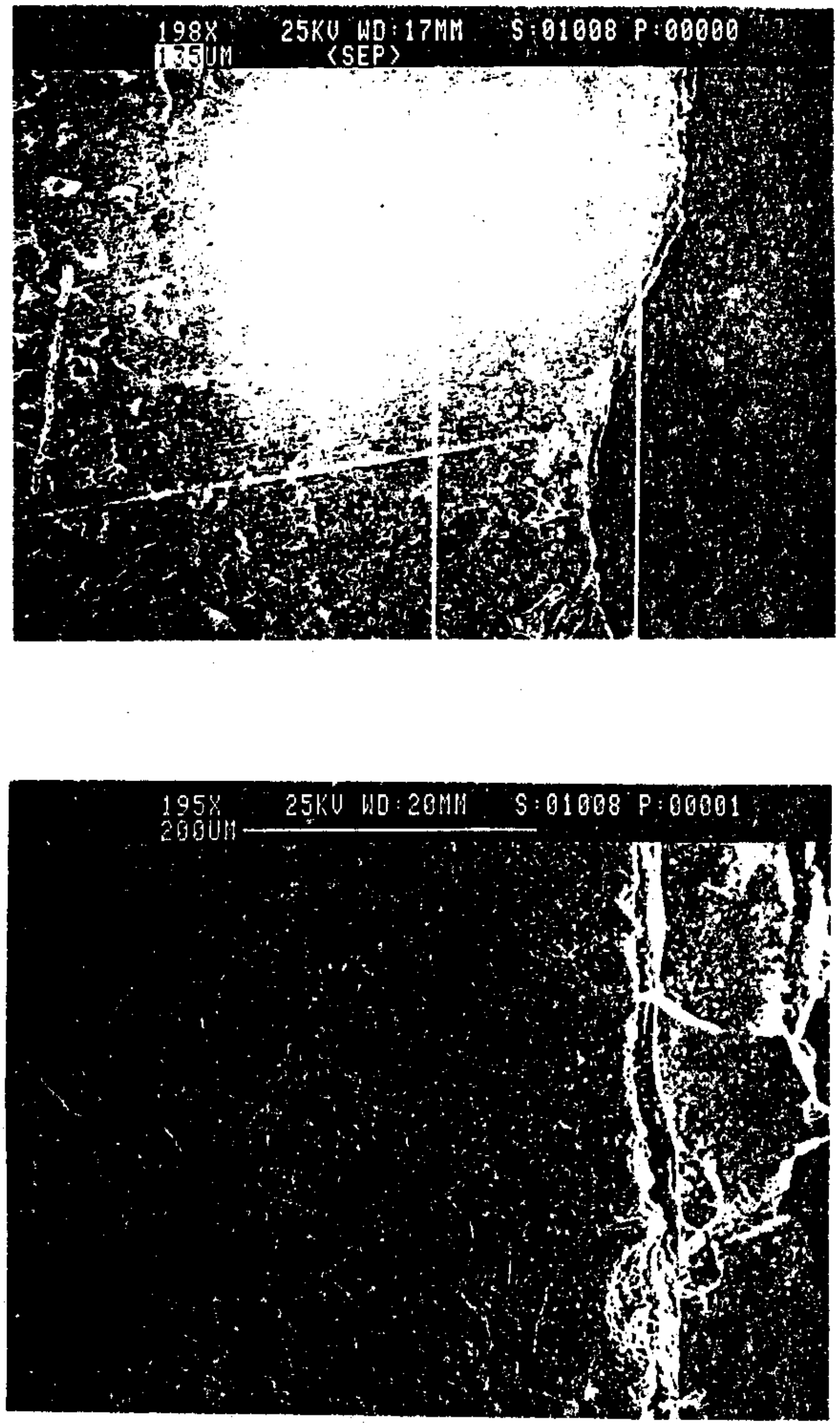


Figure 17 Polished and etched sample for 1008 at open air and 1000° C with FeS : Na_2S = 75 : 25 (above), 82 : 18 (below)

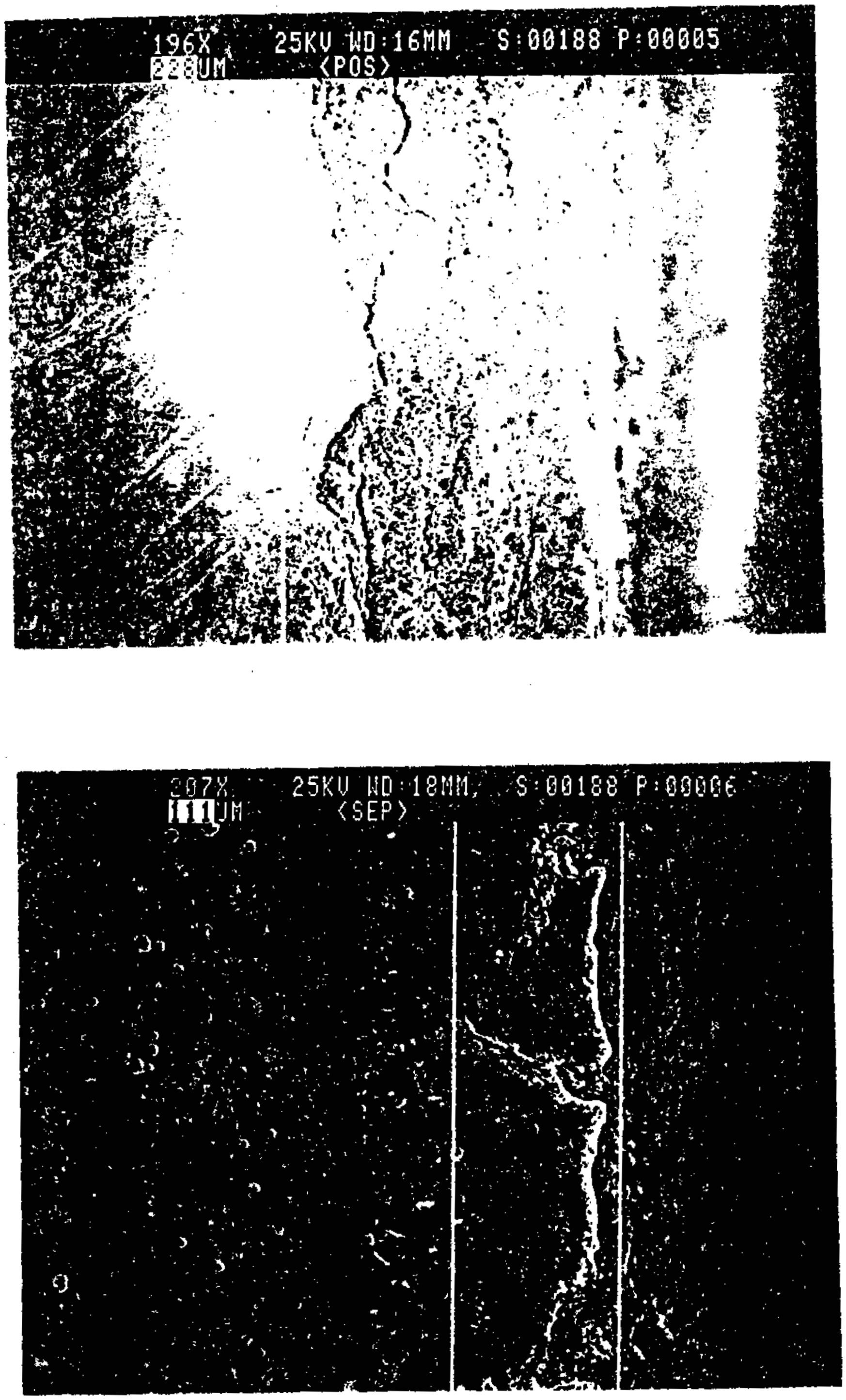


Figure 18 Polished and etched sample for 18-8 at open air and 1000°C with

FeS : Na_2S = 75 : 25 (above), 82 : 18 (below)

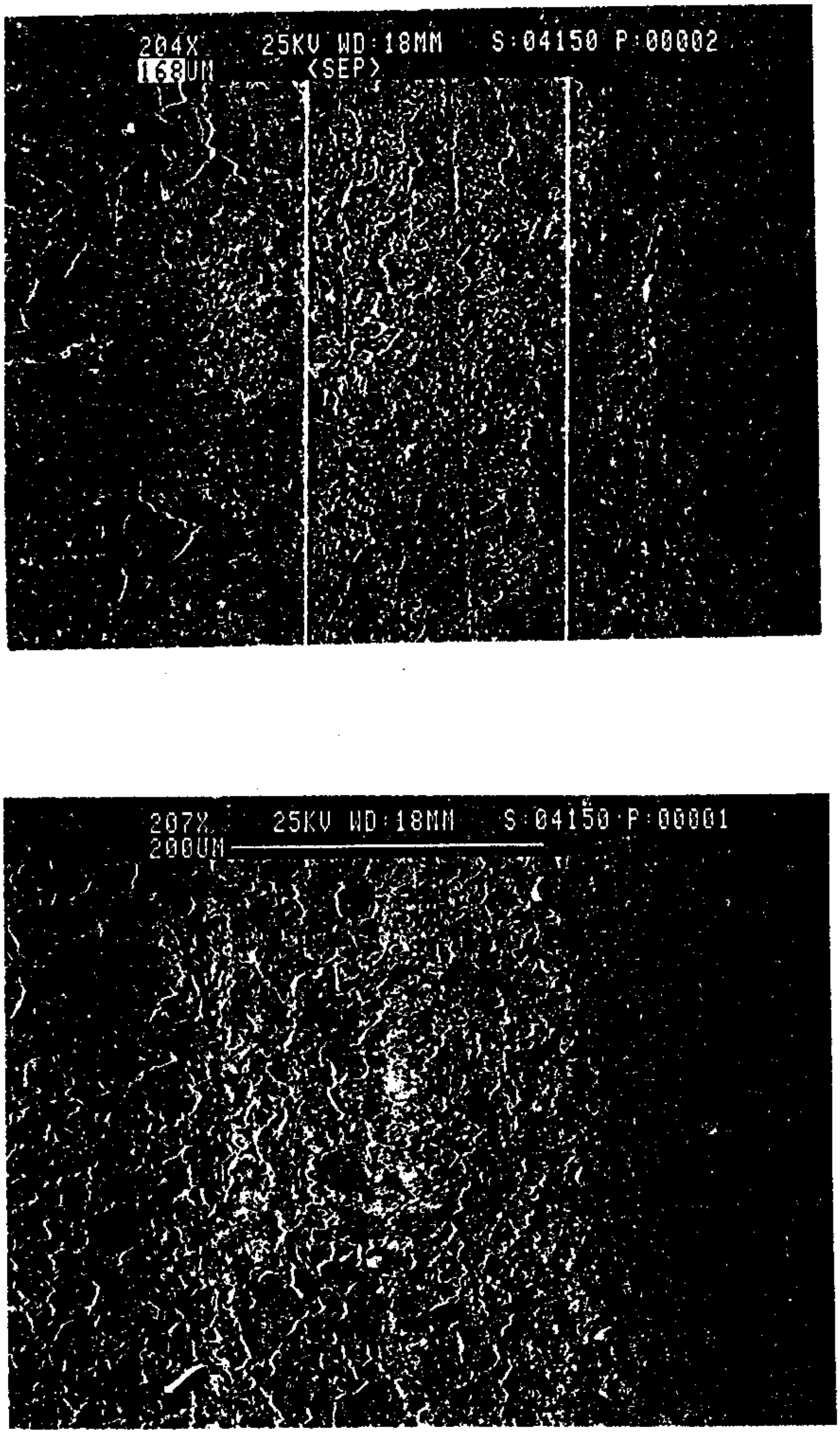


Figure 19 Polished and etched sample for 4150 at Ar atmosphere and 1000°C with FeS : Na_2S = 75 : 25 (above), 82 : 18 (balow)

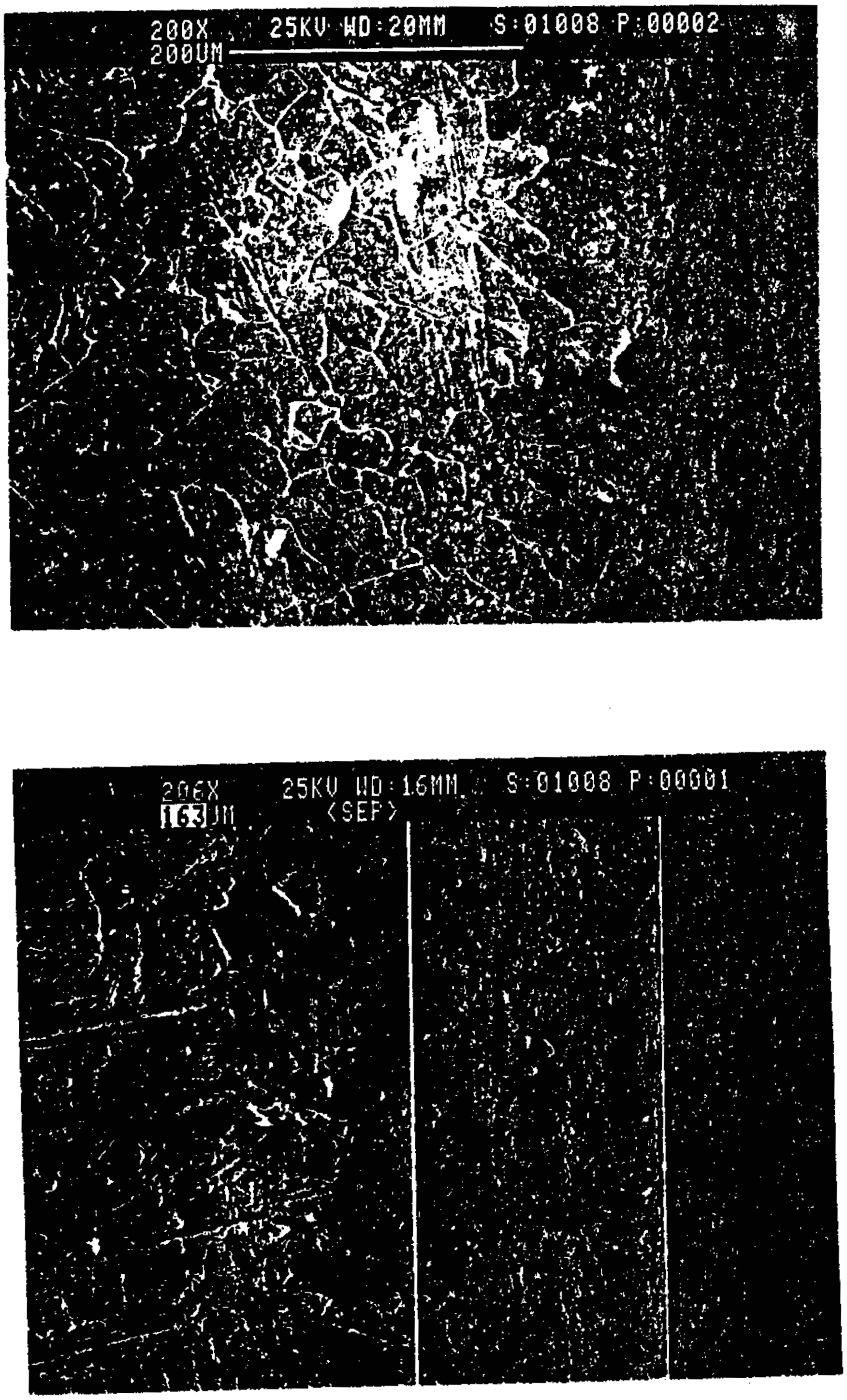


Figure 20 Polished and etched sample for 1008 at Ar atmosphere and 1000° C with FeS : Na_2S = 75 : 25 (above), 82 : 18 (below)

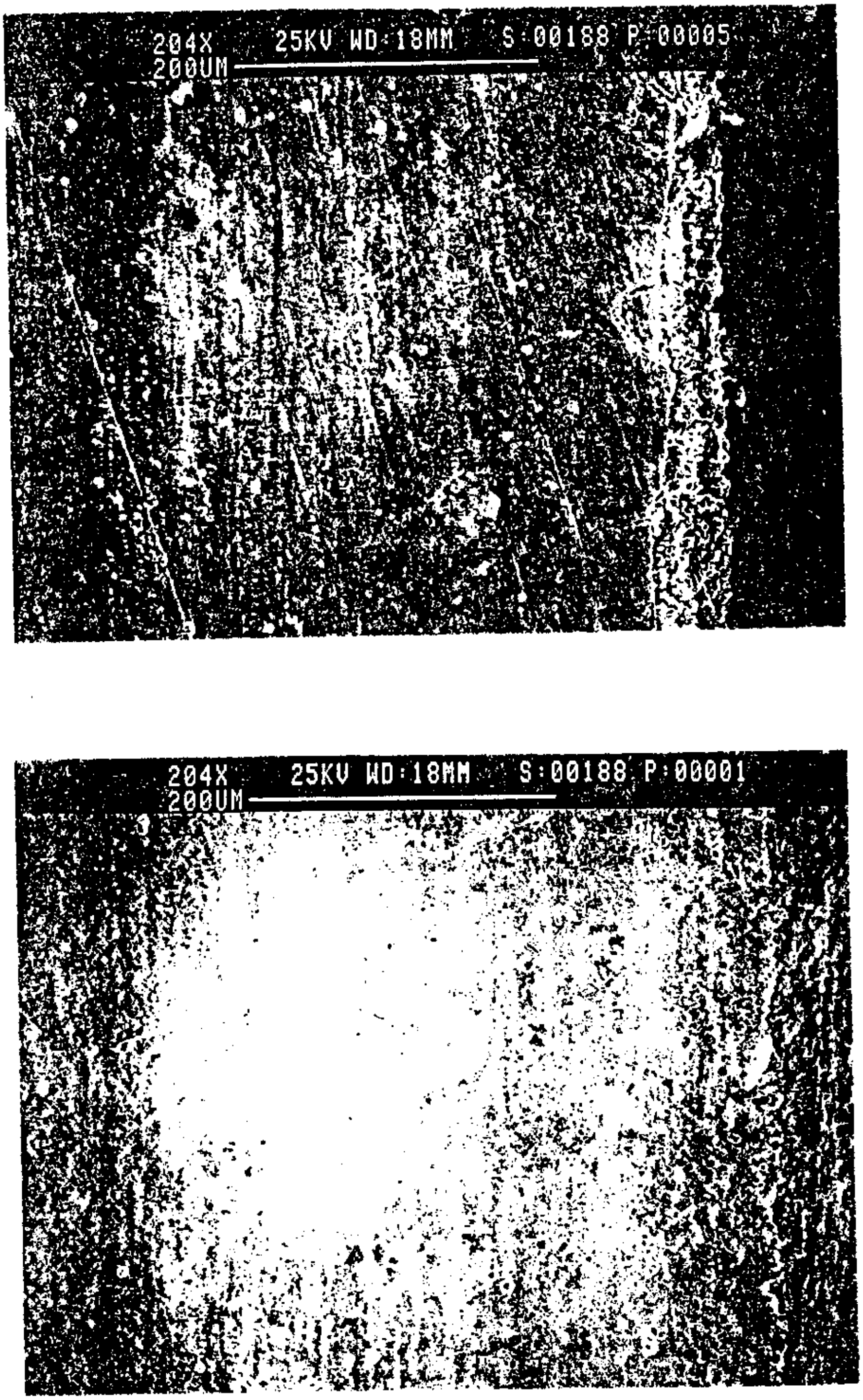


Figure 21 Polished and etched sample for 18-8 at Ar atmosphere and1000°C with $FeS : Na_2S = 75 : 25$ (above), 82 : 18 (below)

Report for Preliminary Experiment: Observation of Interfaces between Solid Copper and Liquid Matte, and between Solid Iron and Liquid Matte

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I. Introduction

As discussed in previous reports [1,2], the authors have found that solid scrap treatment is a promising method to remove solid copper from ferrous scrap. The major merits for this process can be summarized as follows:

1. Lower temperature; below the melting point of copper (1083°C)
2. Very high copper partition ratio; about 500
3. No sulfur pick-up
4. No need to carburize or decarburize the liquid metal

Based on these findings, a large scale experiment using a several-hundred-kilogram-capacity rotary kiln is planned. One of the important factors in this pilot plant scale experiment is to determine the mechanism of drainage of liquid sulfide from solid iron to facilitate the separation of ferrous scrap from liquid matte after refining. In this study, we have measured wettability of liquid sulfide to solid iron and solid copper. This report describes the result of a preliminary experiment to determine the extent of wetting between liquid matte and solid iron and solid copper. In addition, the interfacial reaction was photographed using X-ray radiography.

II. Experimental Procedure

Experiments were carried out to observe the wettability of a liquid FeS/Na_2S sulfide on solid iron and copper using X-ray radiographic technique. The composition of the premelted sulfide mixture was 75 wt% - iron sulfide (FeS) / 25 wt% sodium sulfide (Na_2S). The estimated melting temperature of which is about 810°C. A high purity (99.8%) alumina crucible, which contained a columnar piece of copper (7 mm in diameter, 19 mm long) or iron (15 mm in diameter, 30 mm long) along with the sulfide particles, was charged into the preheated electric furnace. The experimental temperature was 1000°C, and the atmosphere was argon-5% carbon monoxide. The condition for X-ray photography was 50 kVp, 100 mA tube current, and exposure time 0.5 second. A diagram of the experimental apparatus is given in Figure 1.

III. Result and Discussion

(1) Interface between matte and solid copper

Pictures Nos. 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 were taken at 7, 12, 18, 24, 30, 45, 60, 75, 90 and 120 minutes after the crucible was placed onto the pedestal in the preheated furnace. The weights of copper and matte charged were 7.6 and 3.4 grams, respectively.

We can see that the dissolving reaction of copper into matte occurred very quickly in the first 12 minutes and the change after that point is steady but very small. This phenomena observed here is consistent with the previous report [2] in which we found that nearly a 100 percent of solid copper reacted with FeS-Na_2S matte in 10-15 minutes. The reaction can be described in the following:

$$2\,Cu + Na_2S = Cu_2S + 2\,Na$$
$$2\,Cu + FeS = Cu_2S + Fe$$

In the case where the gas is flowing through the system, we should take the first reaction to some extent into account. However, as we discussed in the previous report [2], the activity of FeS is almost equal to unity and the activity of Na_2S is very small. Therefore, the major dissolution reaction for copper is described by the second reaction.

As we can see in the pictures, the copper is completely wet by the matte. The contact angle tends to 0 degrees. It was also observed that the matte also wets the wall of alumina crucible.

Pictures Nos. 11 and 12 are taken during another run. First, a copper piece was dipped in the liquid matte. Then, the piece was drawn upward by about 3 cm using a canthal wire. We can clearly see that a substantial amount of liquid matte is still sticking on the surface of copper. This may point to a significant drainage problem from copper coated surfaces if the matte reaction is not complete. Drainage experiments to determine the drainage of the matte from iron are underway at this time.

(2) Interface between matte and solid iron

Pictures Nos. 13, 14, 15 and 16 were taken 6, 15, 30 and 60 minutes after the crucible was charged into the furnace. We can clearly see the wall of iron piece inside liquid matte. Even after

60 minutes, the iron has not reacted with the matte. The interface remains constant during the experiment. The system is saturated with FeS, and the activity of Na_2S is very small. Therefore, the following reaction

$$Fe + Na_2S = FeS + 2\,Na$$

does not proceed. From the pictures. we can see that the matte wets the iron, although this is not as large an effect as for copper.

IV. Closing Remarks

As expected, $FeS\text{-}Na_2S$ matte showed a significant wetting behavior to solid copper and solid iron. A substantial amount of matte stuck to copper when copper was drawn out of the liquid matte. Future experiments will be conducted to enhance drainage of the matte from steel samples.

V. References

1. I. Jimbo, M. S. Sulsky and R. J. Fruehan: I&S Maker, Vol. 15, No. 8, (1988), pp.20-23.
2. I. Jimbo and R. J. Fruehan: Unpublished Report, Center of Iron and Steelmaking Research, Carnegie Mellon University (1987).

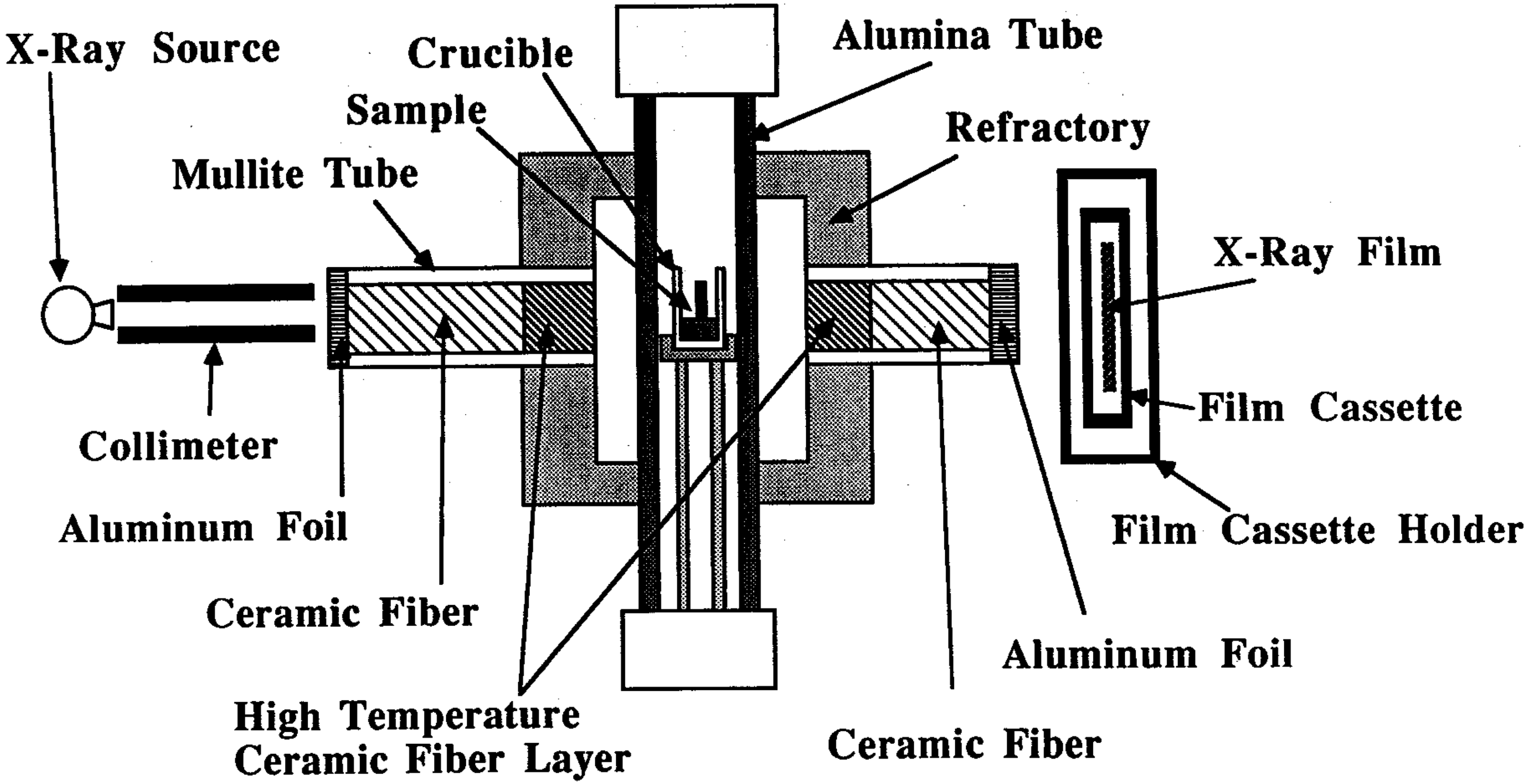
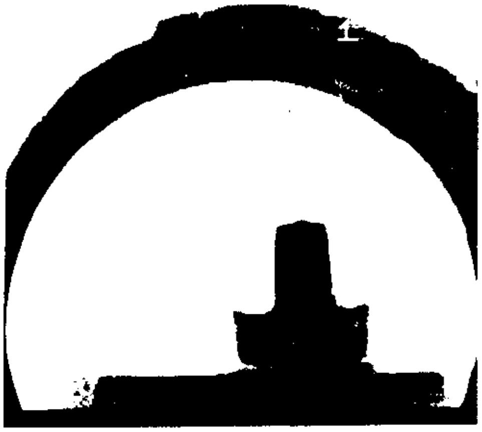
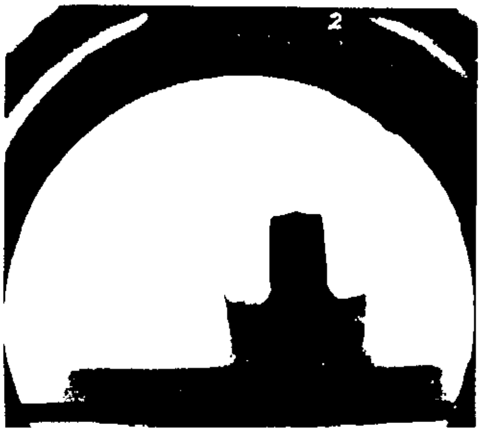


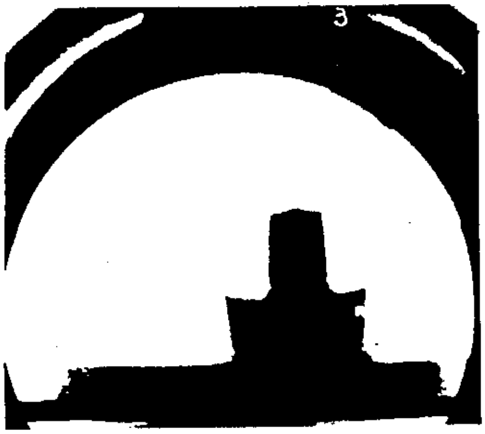
Figure 1. Experimental Apparatus



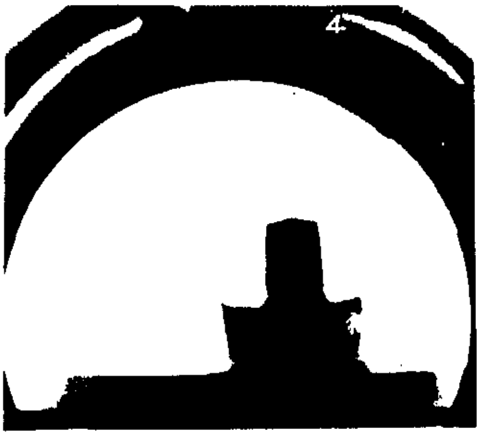
Picture 1: 7 min at 1000°C



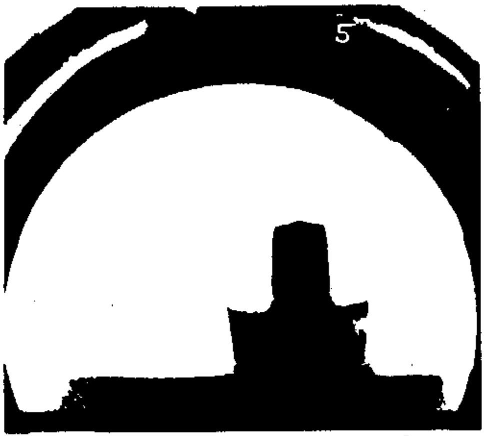
Picture 2: 12 min at 1000°C



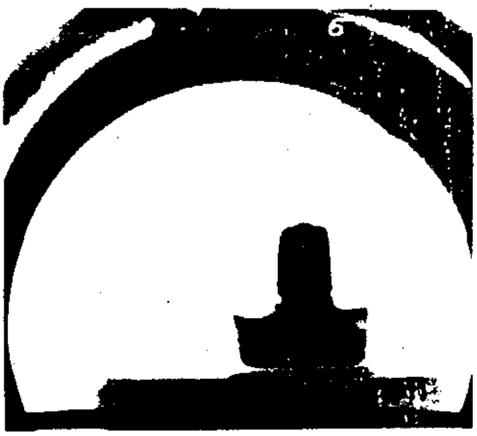
Picture 3: 18 min at 1000°C



Picture 4: 24 min at 1000°C

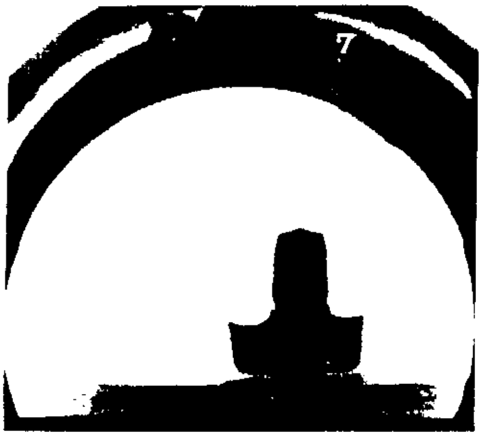


Picture 5: 30 min at 1000°C

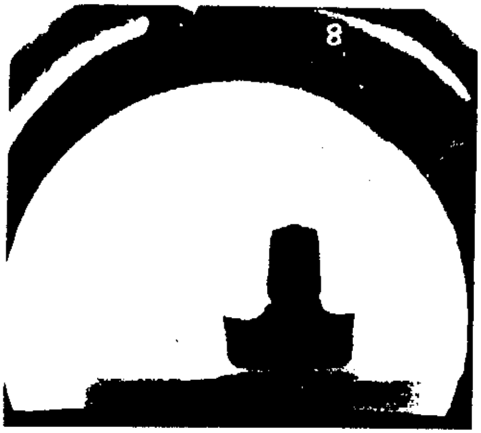


Picture 6: 45 min at 1000°C

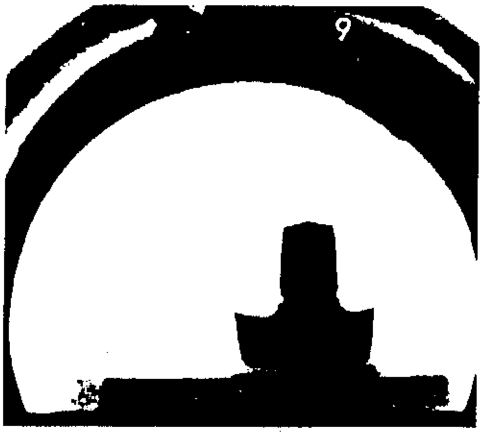
Pictures 1 - 6: Solid copper immersed in FeS-Na_2S matte



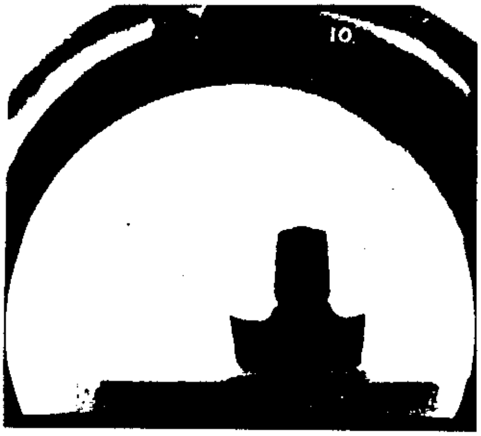
Picture 7: 60 min at 1000°C



Picture 8: 75 min at 1000°C



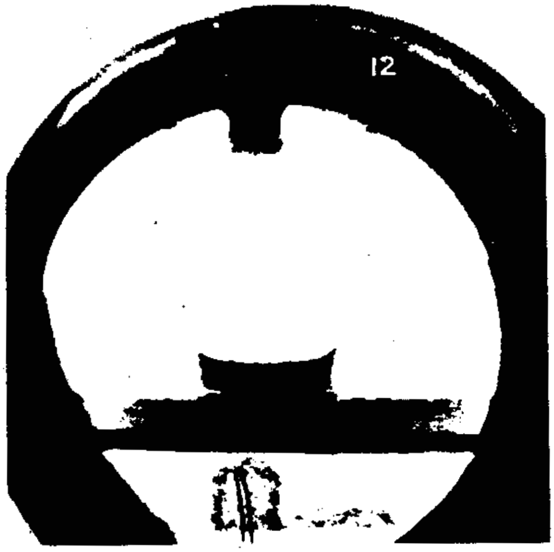
Picture 9: 90 min at 1000°C



Picture 10: 120min at 1000°C

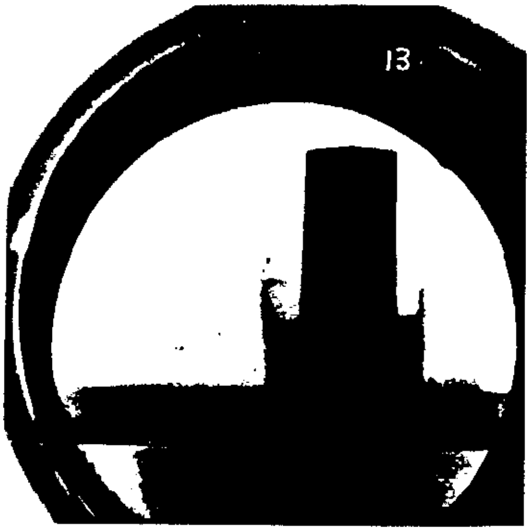
Pictures 7 - 10: Solid copper immersed in FeS-Na_2S matte

Picture 11

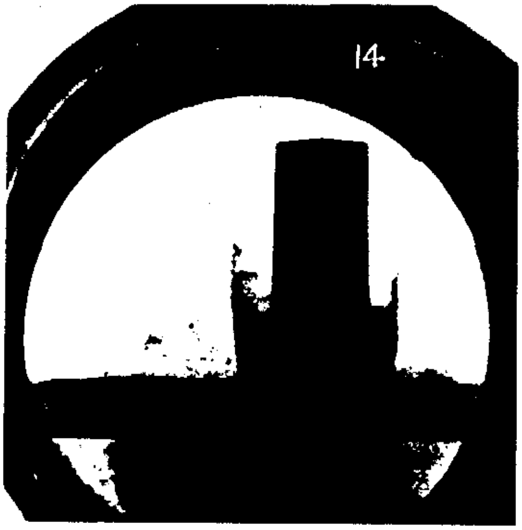


Picture 12

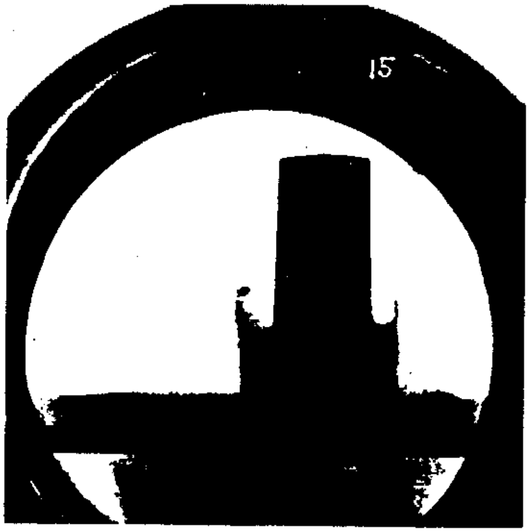
Pictures 11 and 12: Solid copper in contact with FeS-Na_2S matte at 1000°C



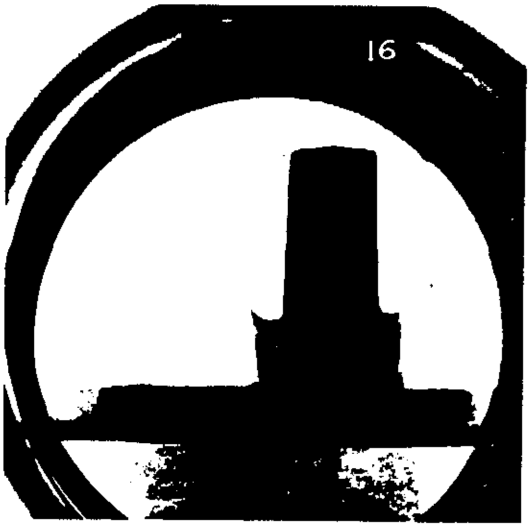
Picture 13: 6 min at 1000°C



Picture 14: 15 min at 1000°C



Picture 15: 30 min at 1000°C



Picture 16: 60 min at 1000°C

Pictures 13 - 16: Solid iron immersed in FeS-Na_2S matte

CISR Progress Report

Preliminary Experiments for Removing Copper from Ferrous Scrap

L. Liao, Research Associate

A. W. Cramb, Associate Professor

R. J. Fruehan, Professor

Prior to setting up the kiln in the pilot plant at Universal, Pa, a number of prelminary experiments were conducted in the experimental melt shop at CMU. The objectives of the experiments were to determine the difficulty of drainage of matte from a sample after reaction; to determine if the matte would easily penetrate motor windings and remove the copper; and, to determine if hydrous sodium sulphide could be used in copper removal experiments. This effort is complimemtary to the efforts previously reported by Mr. Zhang.

Matte Drainage

Small scale experimentation had indicated that the matte wet iron, copper and the alumina crucible materials. This is a necessary first step for copper removal. Reaction of the matte with copper has also been shown. The last step which must be tested, to ensure that the process is viable, is to prove that the reacted matte can be easily seperated from the scrap.

To determine the efficiency of drainage of matte from scrap two seperate experiments were conducted. In the first a rotor and stator of a motor were dipped into a bath of molten matte at 1000C. The experimental set-up is shown in figure 1. After 15 minutes the pieces were removed and the matte was seen to drain freely from the motor, leaving a very thin layer of matte on the motor. In this experiment, as there was significant weight loss of the sample due to copper loss, it was difficult to determine the exact amount of matte left upon the motor.

The second series of experiments were run with a simulated scrap charge. L angles of steel (40 x

40 x 3mm), steel plate (40 x 2 mm) and copper sheet were separately dipped into an 82% Na_2S, 18% FeS bath at temperatures of 800, 900 and 1000 C. Emersion time was from 3 to 5 minutes in each case.

Copper Sheet

At all temperatures the copper sheet was completely dissolved within 3 minutes.

L Angle of Steel

Results of the drainage experiments for L angles of steel are shown in figure 2 where $\Delta M\%$ is the weight gain upon removal from the matte. At 1000C the weight gain was minimal; however, significant amounts of matte were found sticking to the samples as the temperature was lowered.

Steel Plate

Results of the steel plate drainage trials are shown in figure 3. Again the amount of matte adhering to the plate at 1000 C is very small: significant quantities of matte adhered to the plate at lower temperatures.

Motor Dip Tests

As noted earlier the motor dip tests were conducted at 1000 C. The rotor or stator was inserted into the melt and slowly rotated at 22 rpm. After 20 minutes all of the copper windings in the bottom half of the motor windings were gone, as shown schematically in figure 4. Initially there was a quantity of smoke released as the covering on the copper windings burned; however, after this time, fume generation was minimal. In a second set of experiments hydrous sodium sulphide was used. Copper removal results were similar; however, fume generation was greater due to the reaction of H_2O with the matte releasing some SO_2.

Discussion

These preliminary results show that:

1. The matte (Na_2S:FeS = 82:18) is an effective reagent for copper removal from scrap.
2. 1000 C is the best tempertaure of operation to ensure matte drainage from the sample.
3. Hydrous Na_2S can be used to remove copper; however, fume generation is higher than when anhydrous sodium sulphide is used.
4. Copper removal from motors is possible by simply dipping the motor into the matte.

5. Reaction rates for copper removal are high.

Future Work

1. Determine the exact chemical species of off-gases from decopperization experiments.
2. Complete larger scale dip testing.
3. Determine exact quantities of matte sticking to scrap at 1000 C.

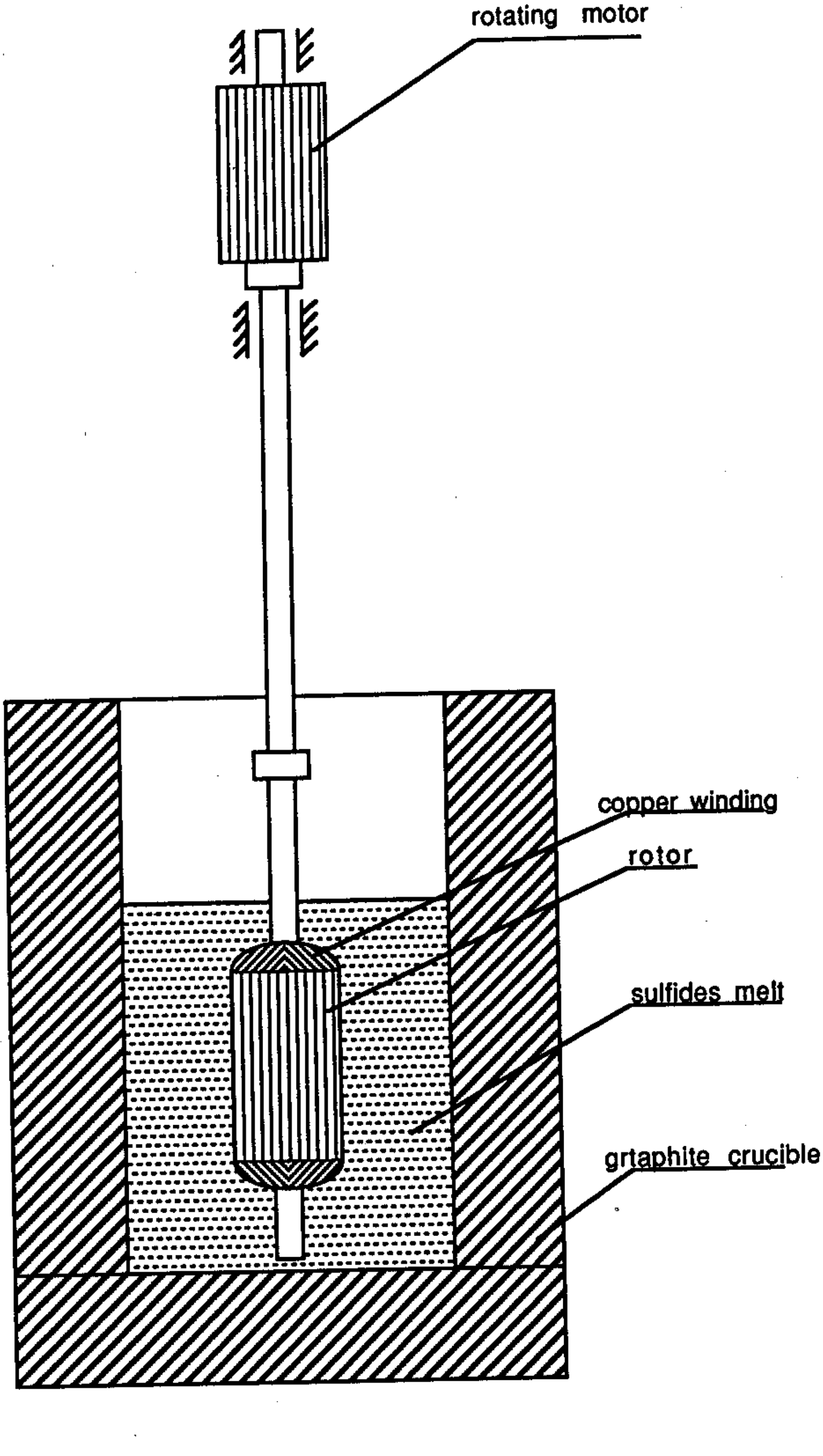


Figure 1 Schematic of experimental arrangement for rotating rotor in sulfides melt at 1000 C

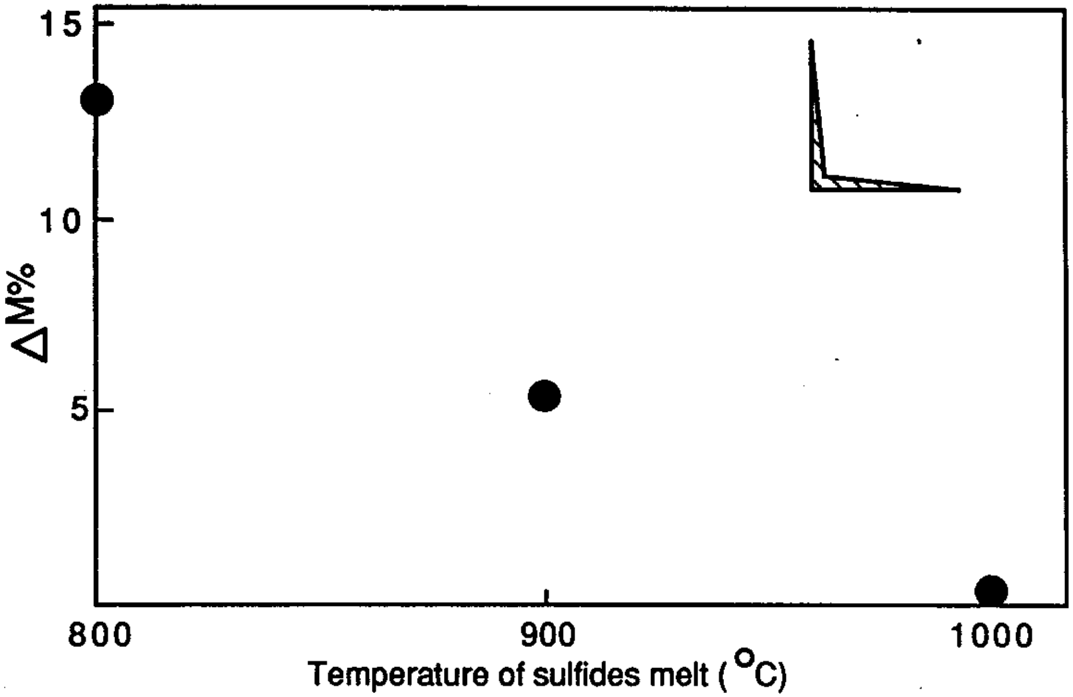


Figure 2 Drainage experiments for L steel angle at different temperatures

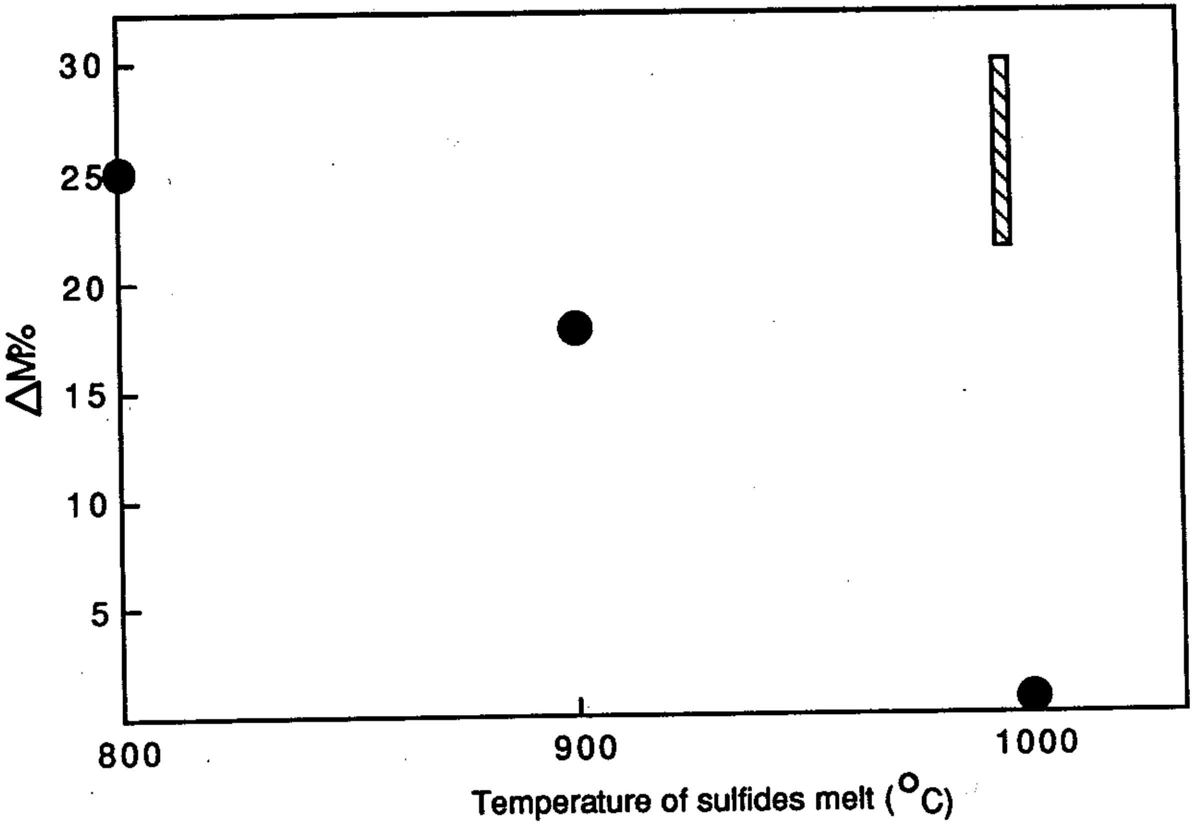


Figure 3 Drainage experiments for steel sheet at diferent temperatures

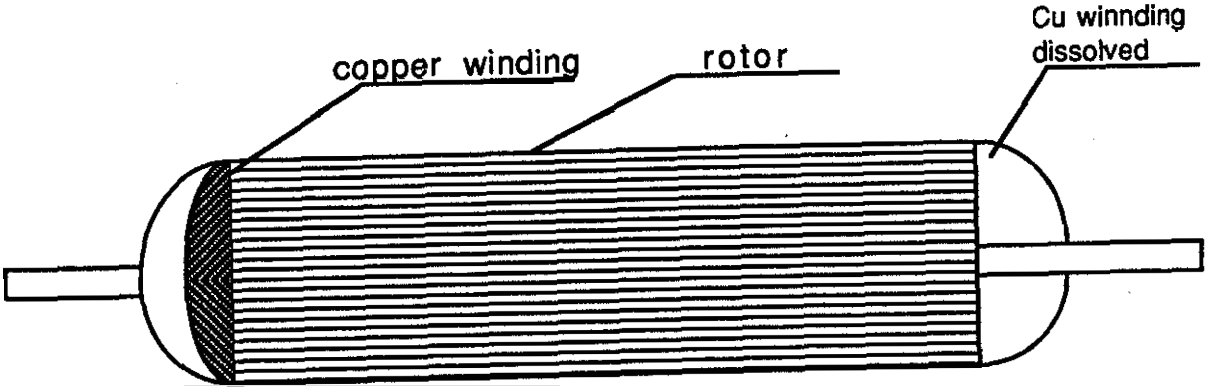


Figure 4 Part of copper winding of rotor of a motor was dissolved by sulfides melt at 1000 C

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PROGRESS REPORT

Removing Solid Copper from Solid Scrap - Initial Kiln Experiments

L. Liao, Research Associate
A. W. Cramb, Associate Professor
R. J. Fruehan, Professor

April 15, 1990

INTRODUCTION

Based upon a series of fundamental studies for removing copper from ferrous scrap, large scale experiments were conducted in a rotary kiln at Universal, Pennsylvania. The objectives of these pre-pilot experiments were to determine the efficiency of the process, to determine if the matte could be drained from the kiln and to determine if the scrap could easily be separated from the matte.

DESCRIPTION OF THE ROTARY KILN

The kiln and its supporting frame, hydraulic pump mechanism and exhaust system etc. is approximately 15 ft long, 6 ft wide and 9 ft high. The gas burner is situated on one end with small holes for matte drainage on the other, as is shown in Figure 1 and 2. The working area of the kiln consists of a stainless steel cylinder which is 2 ft in diameter and 12 ft long. The rotation speed of the kiln can be varied from 1 to 10 rpm. A hydraulic pump was used to tilt the kiln, to hold the liquid matte in the kiln during the experiment and to allow drainage of the liquid matte from the kiln. A stainless steel ring was welded inside the kiln as a matte dam in the high temperature area. Natural gas was used to heat the shell of the kiln and to indirectly heat the matte to the temperature needed for trials. Nitrogen gas was fed into the kiln to provide protective atmosphere.

EXPERIMENTAL

The experimental plan and schedule of sampling are reviewed in Figure 3 and Table 1. For each experiment 40-50 kg of matte was placed inside the kiln. The FeS:Na_2S ratio of the matte was 82:18 at 1000°C or 75:25 at 900°C. 70-80 kg of assorted ferrous scrap (steel rods, pipes, angles, plates etc.) was charged into the kiln. The amount of matte used is more than that needed to remove the copper, but is the minimum necessary to have a liquid matte pool in the kiln.

After the natural gas was ignited the kiln rotation was initiated at 2 rpm. 20 minutes later, the matte was partly melted and liquid matte pool had formed. The kiln rotation speed was then increased to 5 rpm. 35-40 minutes later, when the matte temperature reached 900°C, the rotation speed was increased to 10 rpm. At that time the matte had melted completely and a large liquid pool had formed. The matte was very fluid and wet the scrap. After the first sample was taken, 3.4 kg of copper (tubing wound on steel rods) was added to the kiln to increase the copper content in the scrap to 4%. 2 minutes after adding the copper, a large part of the copper, by visual inspection, had dissolved into the matte. 5 minutes later, a second sample was taken. The copper tubing was found to have completely dissolved into the matte within 6 to 7 minutes after addition at 900°C and within 4 to 5 minutes at 1000°C. Additional samples were taken every 10 minutes, as is shown in Figure 3.

After the treatment, the liquid matte was completely drained into a container by gradually tilting the kiln. Only a thin layer of matte stuck to the inside surface of the kiln and the surface of the ferrous scrap. The drainage of liquid matte was more complete at 1000°C than at 900°C.

After each experiment, the matte and the scrap were carefully examined. No pieces of copper were left in either the matte or the scrap. The copper dissolved completely into the matte. It was also found that the scrap pieces became thinner during the trial, while the amount of matte increased due to the oxidation of iron by air.

RESULTS AND DISCUSSION

Regardless of matte chemistry or kiln temperature, the liquid matte pool was formed within 20 minutes of heating in the kiln. The copper (around 4% in scrap) was completely dissolved within 6-7 minutes after addition at 900°C and within minutes at 1000°C. This shows that the matte process is efficient for removing copper from ferrous scrap and that the solid treatment process could be a successful process technology.

The chemical analyses for a typical experiment is shown in Table 2, Figures 4 to 9. Figure 4 shows that 2 minutes after copper was added, copper content in matte increased to 1.47% and to 8.42% within 5 minutes. In other words, copper was removed by the matte within a very short time. Meanwhile the amount of matte increased almost linearly from 45.4 kg to 61.627 kg (from first sample to sixth), because iron in the scrap was oxidized gradually and continuously dissolved into the matte in the form of iron oxides. 1.578 kg of iron of scrap had dissolved into the matte when third sample was taken; and 7.15 kg of iron of scrap had gone into the matte when sixth sample was taken. Thus the copper in the matte decreased after third sample and the content of Na and Fe in the matte also decreased from the beginning until the end. Figure 5 shows the same results in terms of Cu_2S, Na_2S, FeS. In future experiments, once the copper is removed, it will be appropriate to minimize scrap residence time to minimize iron loss, and to better seal the apparatus to stop oxidation.

FUTURE WORK

1. Determine the effect of increasing matte Cu_2S content.
2. Test the process as a means of recycling of electric motors.
3. Measure accurately the amount of matte sticking on the metal.
4. Carry out continuous experiments in the kiln where scrap containing copper is continuously added into the kiln and the refined product is continuously removed.

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	Matte			Temperature °C	copper	purpose	Results
	FeS%	Na_2S%	Cu_2S%				
1	82	18		1000 °C	wire	To see how the process works	all gone/ 4-5'
2	82	18		1000 °C	tubing	To test if 4% Cu in scrap can be removed	all gone/4-5'
	90		10	1000 °C	tubing	To test initial high Cu content matte	all gone/4-5'
3	82	18					
4	75	25		900 °C	tubing	to test the effect of temperature	all gone/6-7'

Table 1 The experiments performed in the kiln

	1st sample	2nd sample	3rd	4th	5th	6th
Cu%	1.47	4.02	8.42	7.2	6.69	6.6
Na%	10.11	8.92	8.69	8.6	7.77	7.65
Fe%	51.39	44.3	44.77	47.09	48.83	44.1

	1st sample	2nd	3rd	4th	5th	6th
Cu_2S%	2.2	6.03	12.63	10.8	10.04	9.9
Na_2S%	17.14	15.13	14.74	14.58	13.18	12.82
FeS%	80.83	69.68	70..42	74.07	76.81	69.09

Table 2 Chemical analysis results of the matte of a typical experiment in the kiln

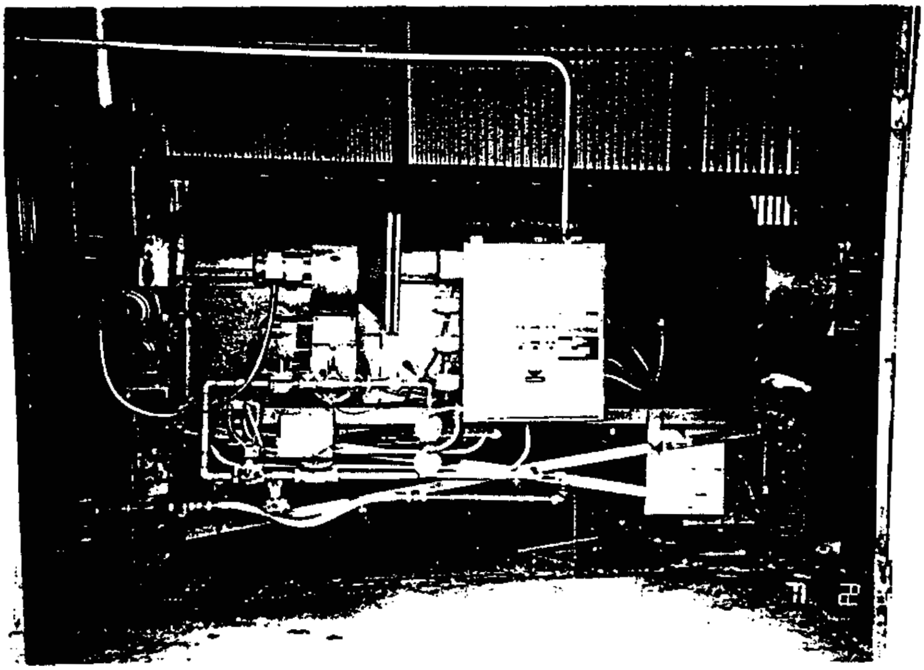


Figure 1 The rotary kiln for large scale experiments at Universal

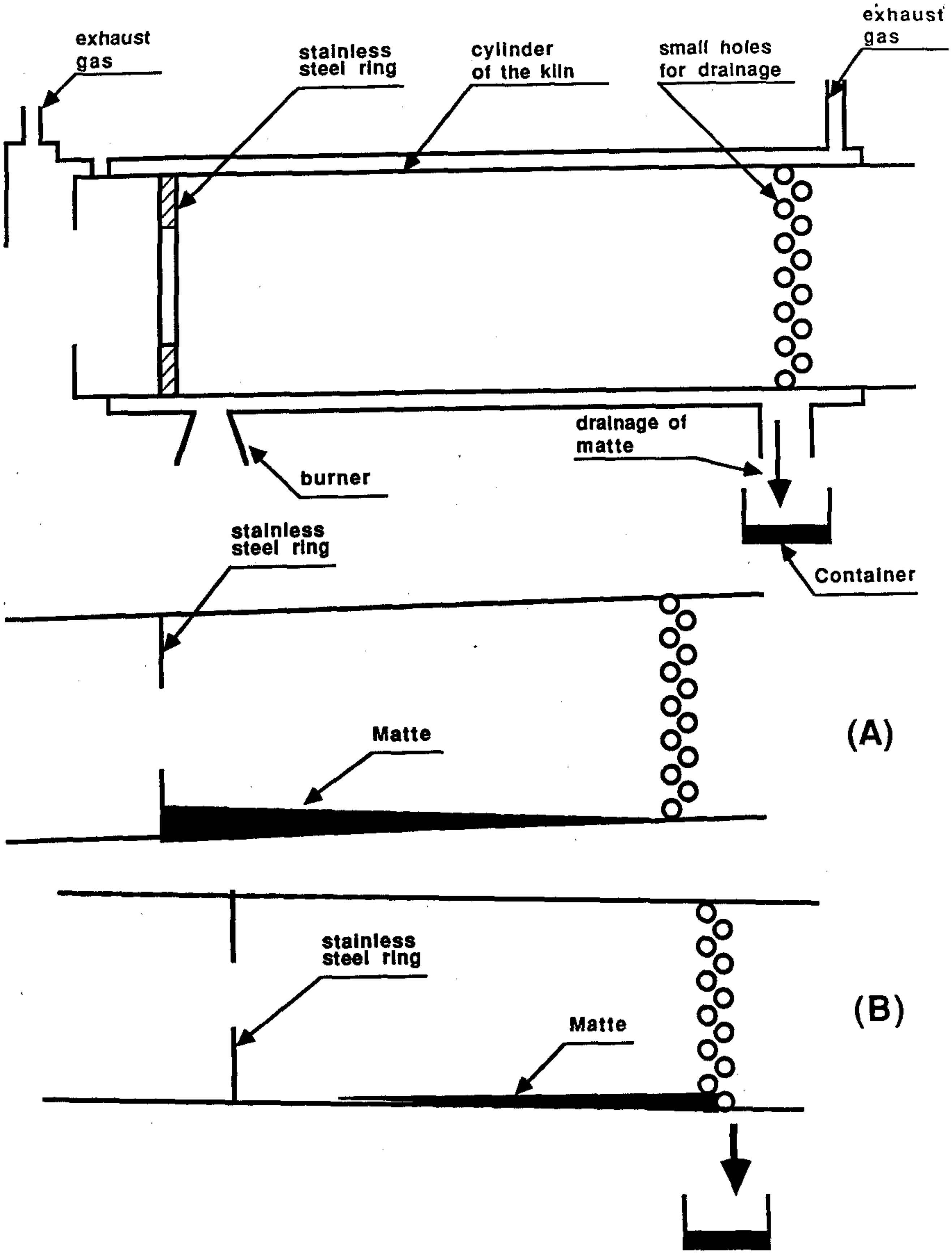


Figure 2 The rotary kiln and (A) the position for refining and (B) the position for drainage of the matte

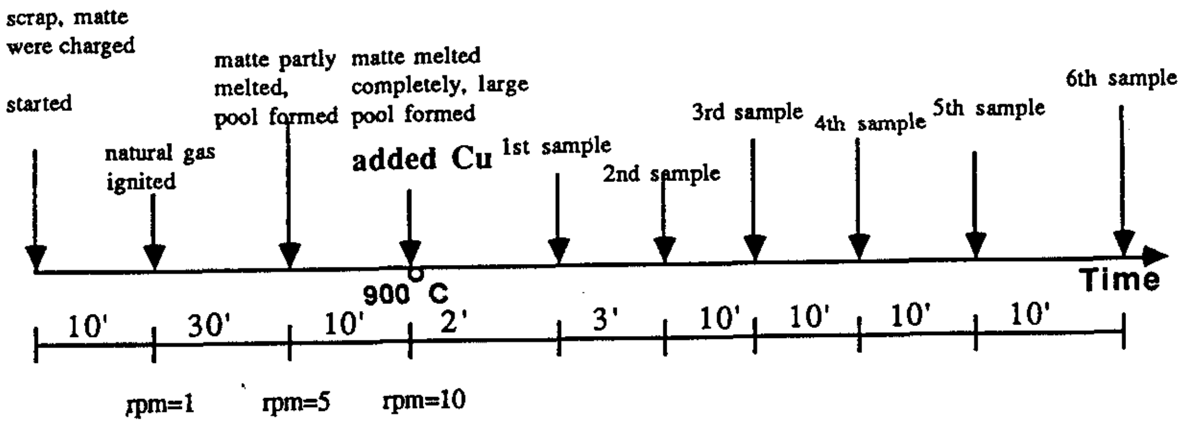


Figure 3 The typical operations of an experiment in the kiln

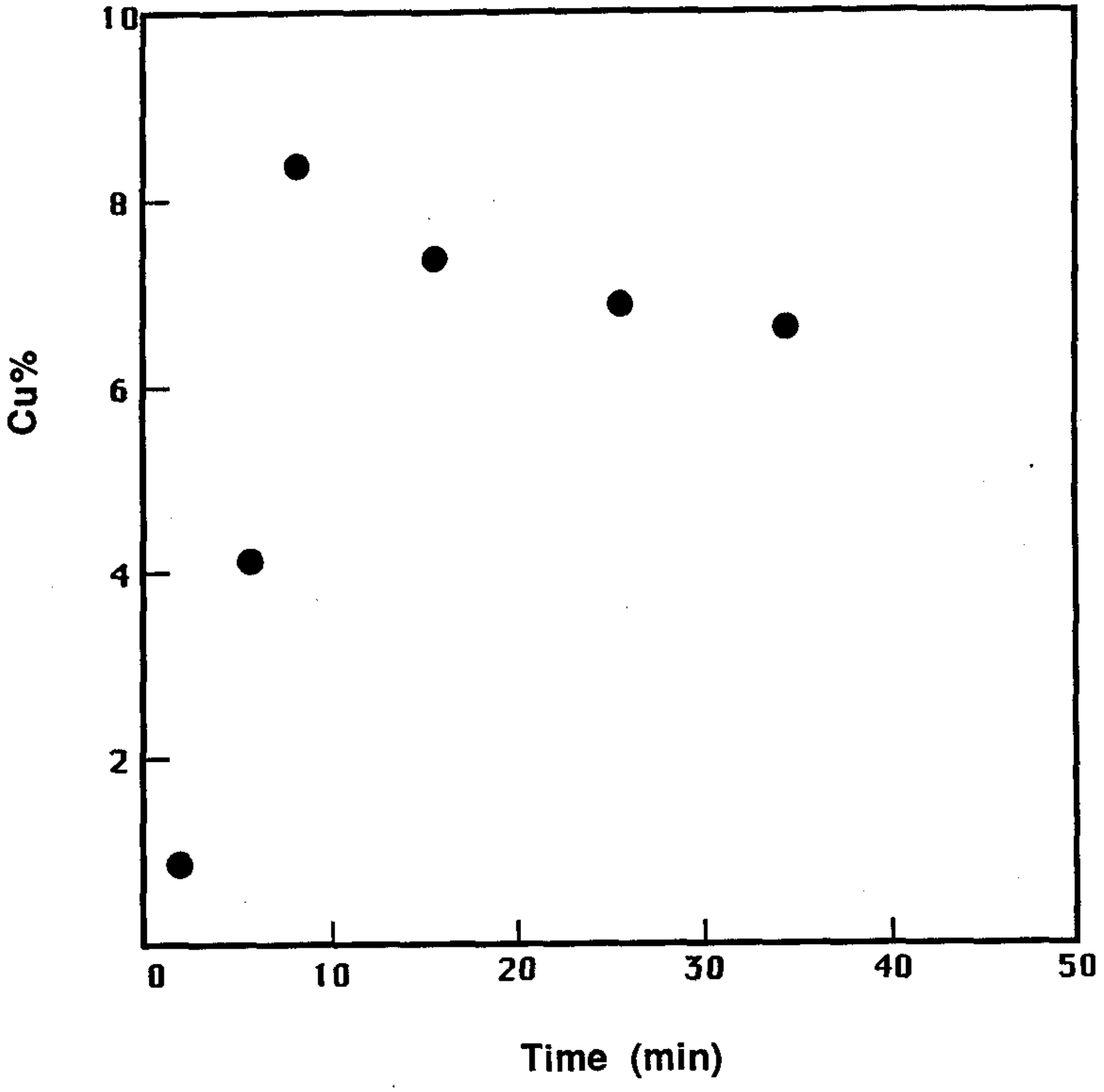


Figure 4 The Change of copper in the matte as a function of time

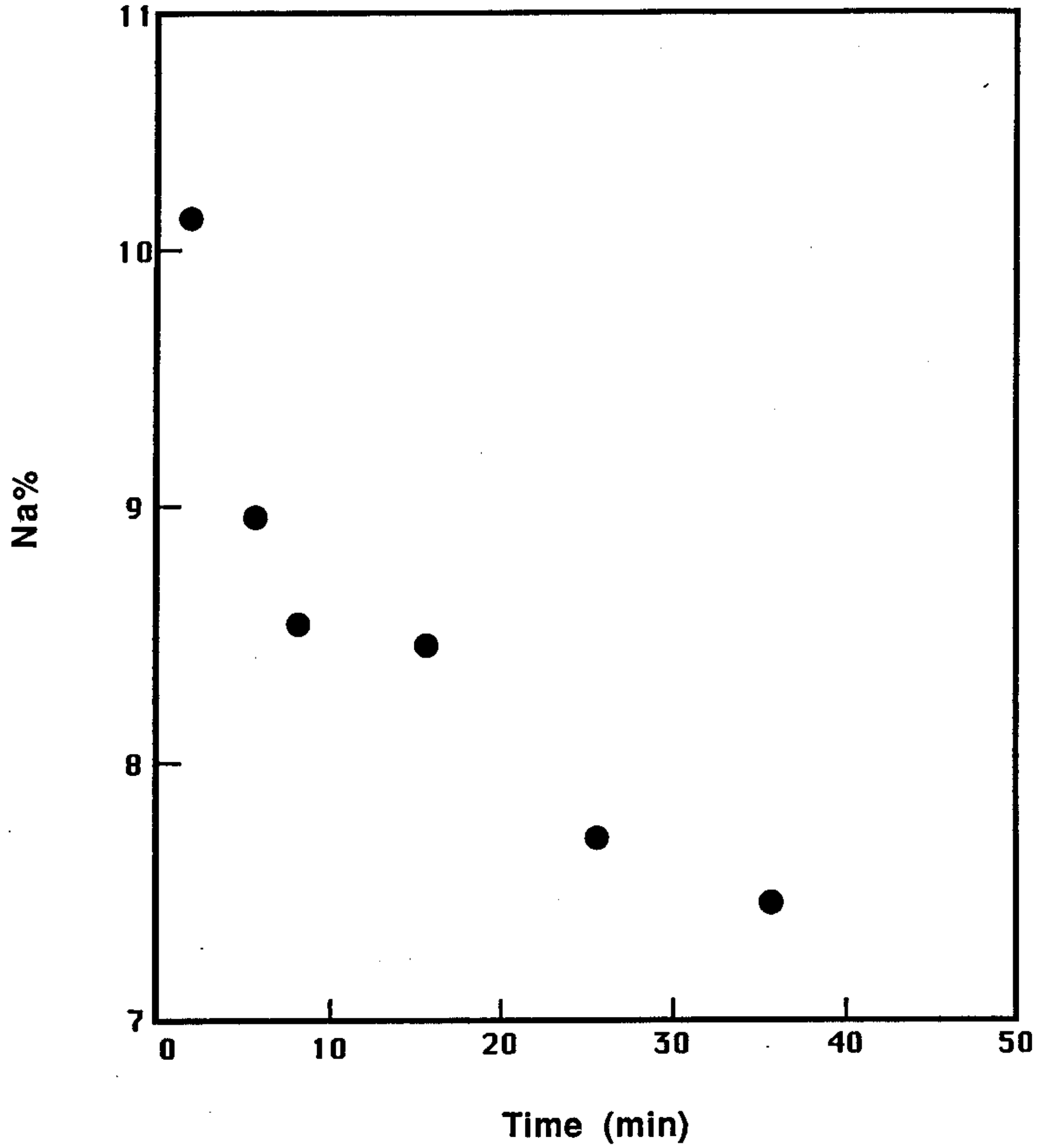


Figure 5 The Change of Na in the matte as a function of time

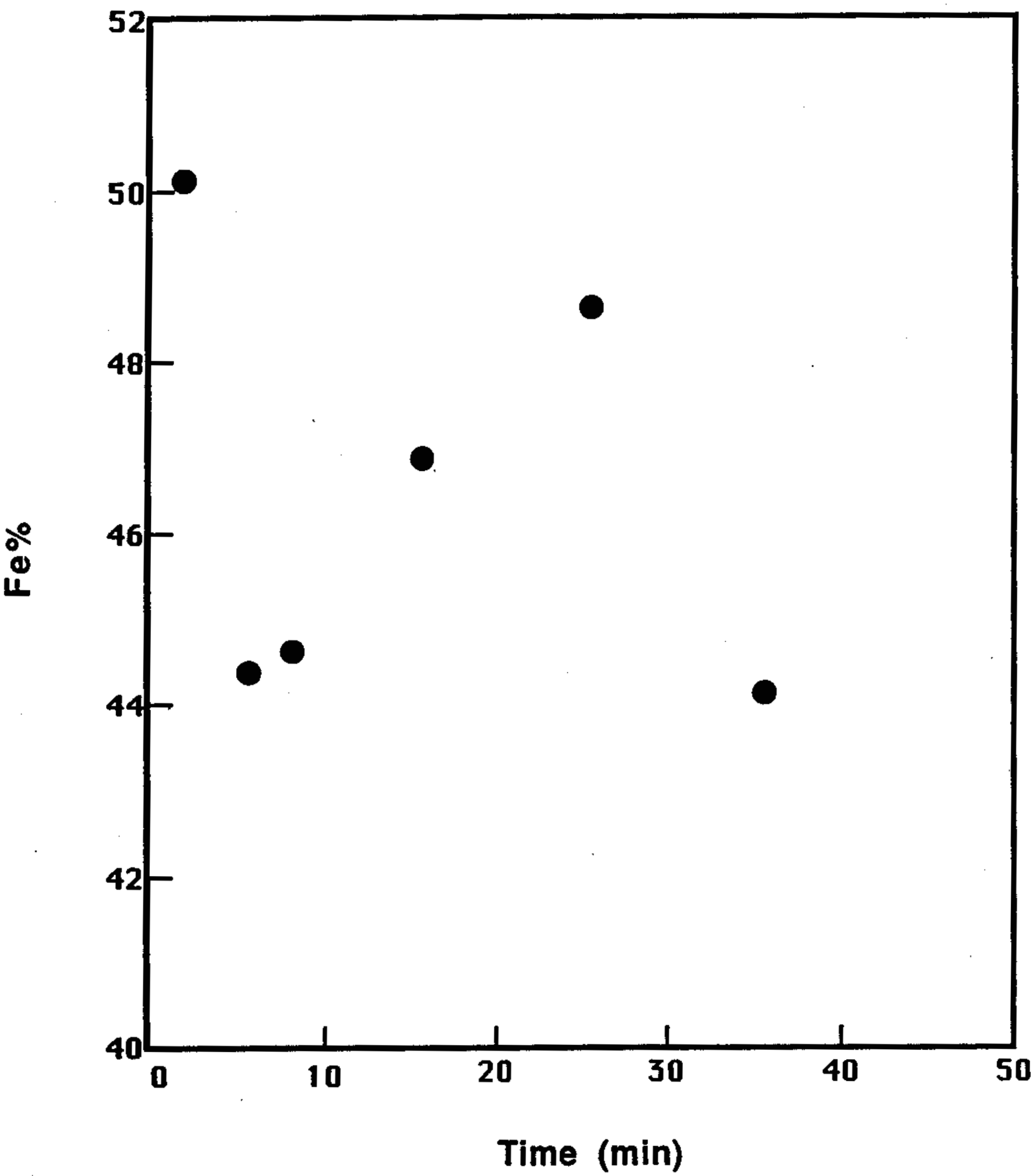


Figure 6 The Change of Fe in the matte as a function of time

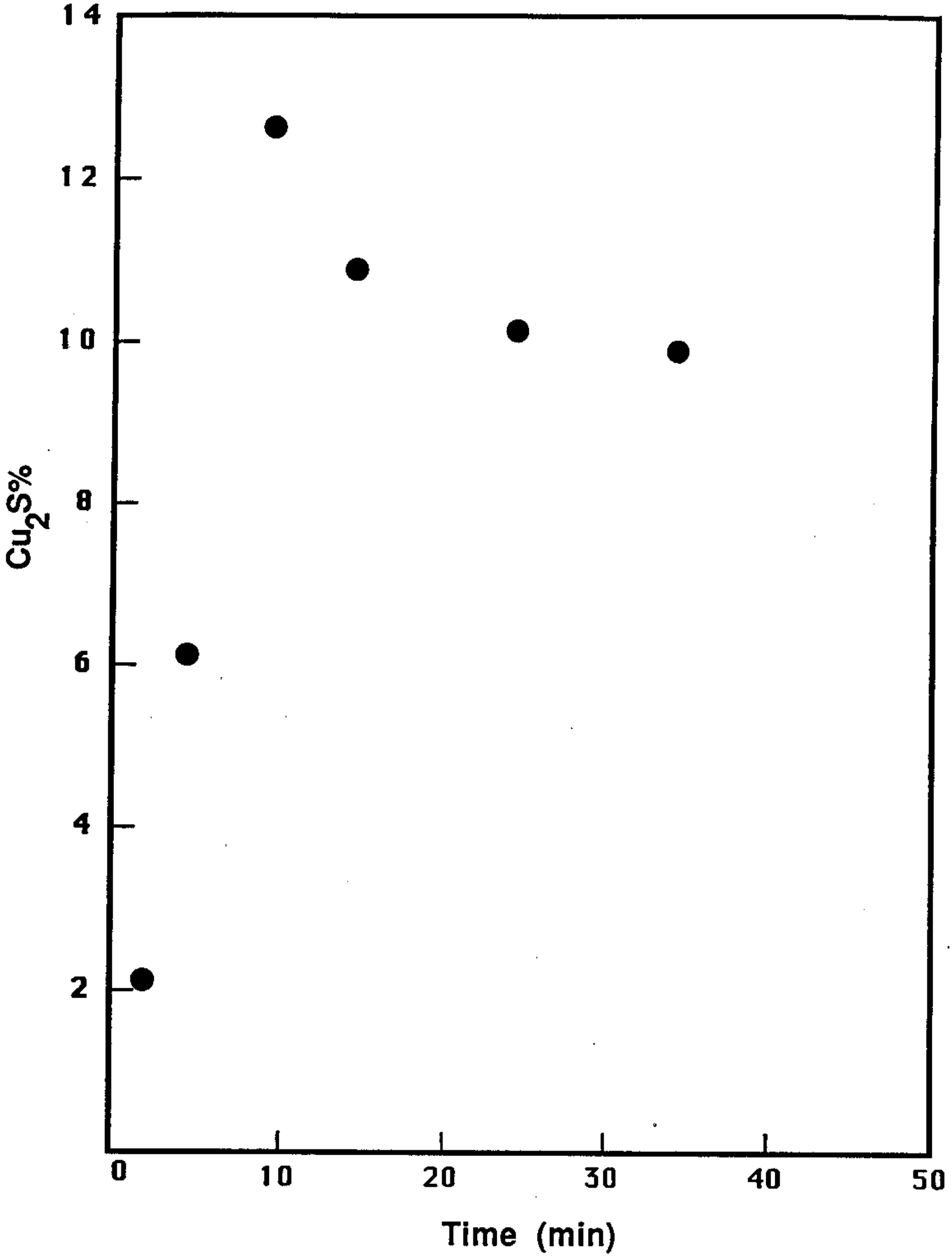


Figure 7 The change of Cu_2S in th matte as a function of time

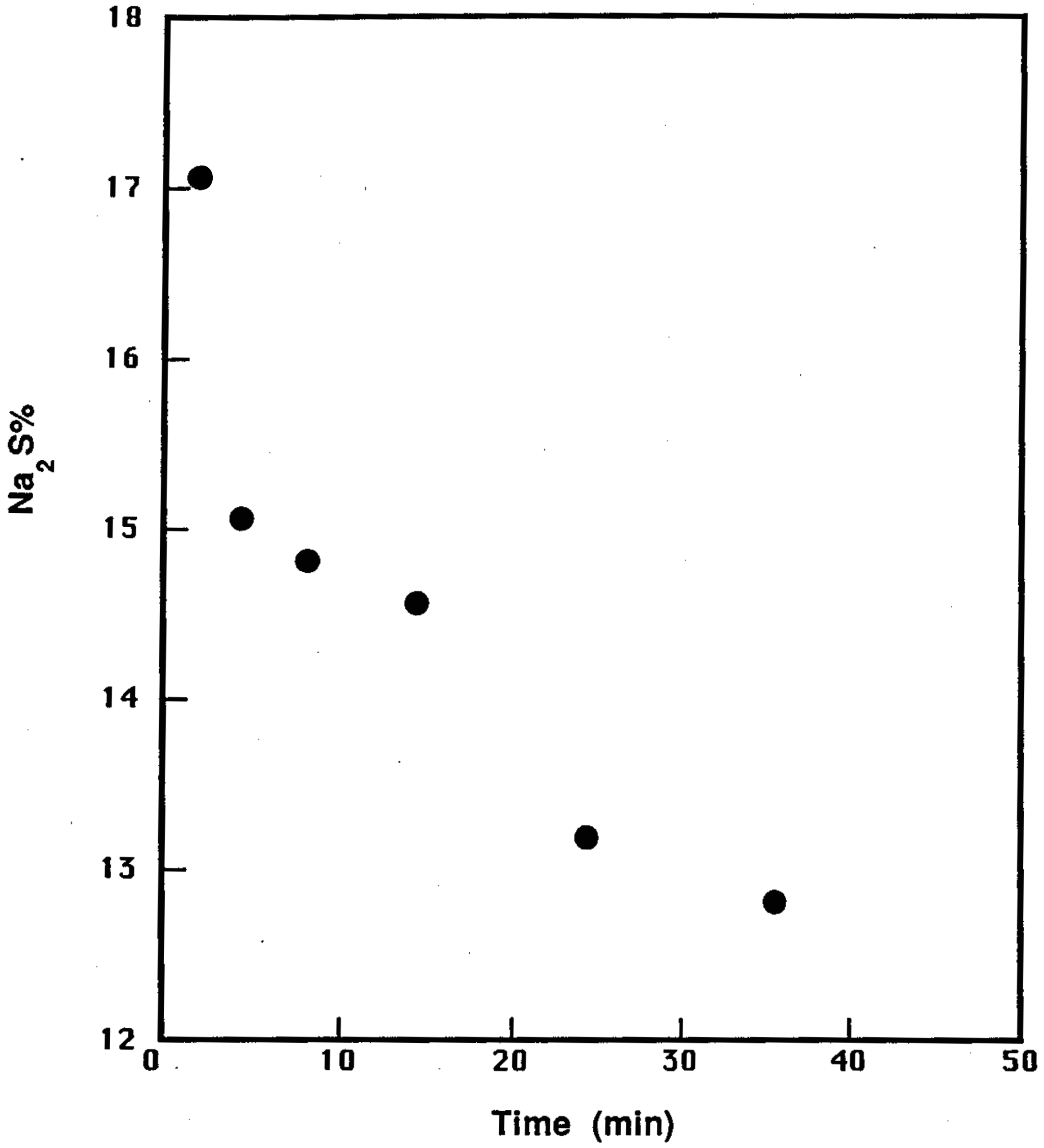


Figure 8 The change of Na_2S in the matte as a function of time

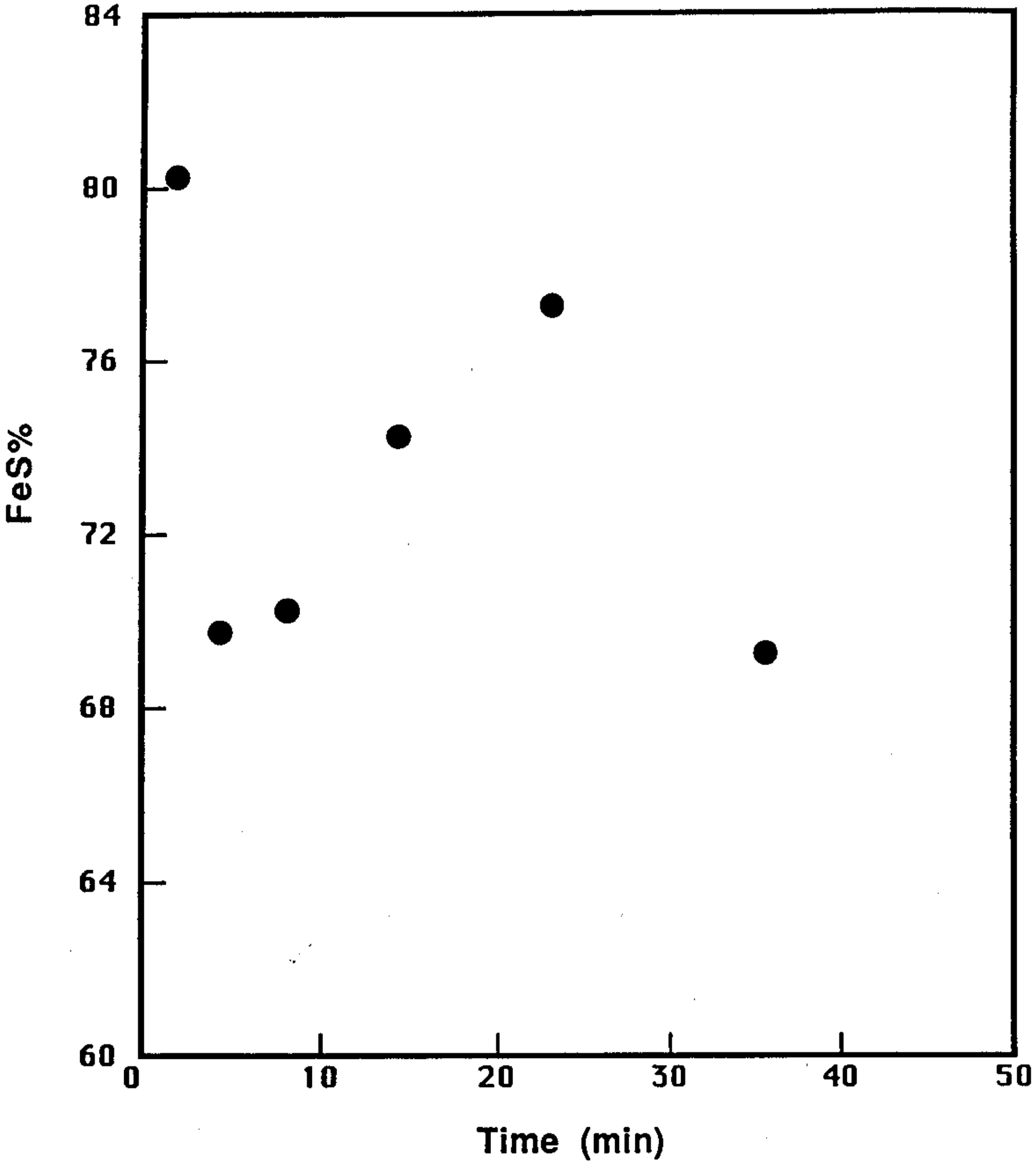


Figure 9 The change of FeS in the matte as a function of time

CISR PROGRESS REPORT

Removing Copper from Ferrous Scrap in a Kiln

L. Liao, Research Associate

A. W. Cramb, Associate Professor

R. J. Fruehan, Professor

September 15, 1990

Introduction

Based upon a series of fundamental studies for removing copper from ferrous scrap, large scale experiments were conducted in a rotating kiln at Universal, Pennsylvania. The objectives of these pre-pilot experiments were to determine the efficiency of the process, to determine if the matte could be drained from the kiln and to determine if the scrap could easily be separated from the matte.

Description of the Rotary Kiln

The kiln and its supporting frame, hydraulic pump mechanism, and exhaust system etc. is approximately 15 ft long, 6 ft wide and 9 ft high. The gas burner is situated on one end with small holes for matte drainage on the other, as is shown in Figures 1 and 2. The working area of the kiln consists of a stainless steel cylinder which is 2 ft in diameter and 12 ft long. The rotation speed of the kiln can be varied from 1 to 10 rpm. A hydraulic pump was used to tilt the kiln to hold the liquid matte in the kiln during the experiment and to allow drainage of the matte from the kiln. A stainless steel ring was welded inside the kiln as a matte dam in the high temperature area. Natural gas was used to heat the shell of the kiln and to indirectly heat the matte to the temperature needed for trials. Nitrogen gas was fed into the kiln to provide a protective atmosphere.

Experimental

The experimental plan and schedule of sampling are reviewed in Figure 3 and Table 1. For each experiment 40-50 kg of matte was placed inside the kiln. The FeS:Na_2S ratio of the matte was 82:18 at 1000°C or 75:25 at 900°C. 70-80 kg of assorted ferrous scrap (steel rods, pipes, angles, plates etc.) was charged into the kiln. The amount of matte used is more than that needed to remove the copper, but is the minimum necessary to have a liquid matte pool in the kiln. The natural gas was then ignited and the kiln rotated at 2 rpm. 20 minutes later, the matte was partly melted a liquid matte pool had formed. The kiln rotation was then increased to 5 rpm. 35-40 minutes later, when the matte temperature reached 900°C, the rotation speed was increased to 10 rpm. At that time the matte had melted completely and a large liquid matte pool was formed. The matte was very fluid and wet the scrap. After the first sample was taken, 3.4 kg of copper (tubing wound on steel rods) was added to the kiln to increase the copper content in the scrap to 4%. 2 minutes after adding the copper, a large part of the copper, by visual inspection, had dissolved into the matte. 5 minutes later, a second sample was taken. The copper tubing was found to have completely dissolved into the matte within 6 to 7 minutes after addition at 900°C and within 4 to 5 minutes at 1000°C. Additional samples were taken every 10 minutes, as is shown in Figure 3.

After the treatment process was finished, the liquid matte was completely drained through the small holes into a container by gradually tilting the kiln. Only a thin layer of matte stuck to the inside surface of the kiln and the surface of the ferrous scrap. The drainage of liquid matte was more complete at 1000°C than at 900°C.

After each experiment, the matte and the scrap were carefully examined. No pieces of copper were left in either the matte or the scrap. The copper was dissolved completely into the matte. It was also found that the scrap pieces became thinner during the trial, while the amount of matte increased due to the oxidation of iron by air.

Results and Discussion

Regardless of matte chemistry or kiln temperature, the liquid matte pool was formed within 20 minutes of heating in the kiln. The copper (around 4% in scrap) was completely dissolved within 6-7 minutes after addition at 900°C and within 4-5 minutes at 1000°C. This shows that the matte process is efficient for removing copper from ferrous scrap and that the solid treatment process could be a successful process technology.

The chemical analysis for a typical experiment are shown in Table 2, Figures 4 to 9. Figure 4 shows that 2 minutes after copper was added, copper content in matte increased to 1.47% and to 8.42% within 5 minutes. In other words, copper was removed by the matte within a very short time. Meanwhile the amount of matte increased almost linearly from 45.4 kg to 61.627 kg (from first sample to sixth), because iron in the scrap was oxidized gradually and continuously dissolved into the matte in the form of iron oxides. 1.578 kg of iron of scrap had dissolved into the matte when third sample was taken; and, 7.15 kg of iron of scrap had gone into the matte when sixth sample was taken. Thus, the copper in the matte decreased after third sample and the content of Na and Fe in the matte also decreased from the beginning until the end. Figure 5 shows the same results in terms of Cu_2S, Na_2S and FeS. In future experiments, once the copper is removed, it will be appropriate to minimize scrap residence time to minimize iron loss, and to better seal the apparatus to stop oxidation.

No matter what ratio ($FeS:Na_2S=82:18$ or 75:25) was used in experiments, even when the matte with 9.35% Cu_2S content was used, the copper in scrap was dissolved within 4-5 minutes at 1000°C, and it was dissolved within 6-7 minutes at 900°C. The matte could be drained easily out of the kiln at 1000°C, while at 900°C the matte could hardly be drained out of the kiln but stuck to the wall of the kiln.

In order to examine the change of the sulfur and copper content of the scrap before and after experiment, the scrap with sticking matte was remelted in the induction furnace and cast into a ingot mold. Three samples were taken and analyzed for sulfur and copper contents. The analysis shows that the copper content remained almost the same (0.5%), the sulfur content after experiment (0.159%) was three times higher than the original sulfur content (0.043%). However, after the scrap was washing using water, remelted and analyzed, the sulfur content of the scrap decreased from 0.159% to 0.095%. Furthermore, the scrap was placed into the 8% HCl solution for washing and cleaning the sticking matte at 102°C for 30 minutes, then it was rinsed in the water and analyzed, the sulfur content of the scrap decreased again from 0.095% to 0.053%. That means the problem with increased sulfur content after experiment can be solved by the above measures.

Summary

1. The process is effective to remove copper from scrap and from electric motors at 1000°C.
2. The matte can be reused.
3. The problem of increasing sulfur content of the scrap after experiment can be solved by using water and 8% diluted HCl solution to wash and clean the sticking matte.

	Matte			Temperature ^0C	tested object	objectives for experiment	Results
	FeS%	Na_2S%	Cu_2S%				
1	82	18		1000 °C	Cu wire	To see how the process works	The copper dissolved within 4-5'
2	82	18		1000 °C	Cu tubing	To test if 4% Cu in scrap can be removed	The copper dissolved within 4-5'
	90 (82:18)		10	1000 °C	Cu tubing	To test initial high Cu content matte	The copper dissolved within 4-5'
3	82	18					
4	75	25		900 °C	Cu tubing	To test the effect of lower temperature	The copper dissolved within 6-7'
5	82	18		1000°C	motor	To test Cu winding in motor	The copper dissolved within 4-5'
6	82	18		1000°C	Cu tubing and motor	Same as above	The copper dissolved within 4-5'
7	82	18		900°C	Cu tubing	*To test 82:18 ratio and 900°C*	The copper dissolved *within 7'*, the matte was very thick .

Table 1 The experiments performed in the rotary kiln

	1st sample	2nd	3rd	4th	5th	6th
Cu%	1.47	4.02	8.42	7.2	6.69	6.6
Na%	10.11	8.92	8.69	8.6	7.77	7.65
Fe%	51.39	44.3	44.77	47.09	48.83	44.1

	1st sample	2nd	3rd	4th	5th	6th
Cu_2S%	2.2	6.03	12.63	10.8	10.04	9.9
Na_2S%	17.14	15.13	14.74	14.58	13.18	12.82
FeS%	80.83	69.68	70. 42	74.07	76.81	69.09

Table 2 Chemical analysis results of the matte of a typical experiment in the kiln

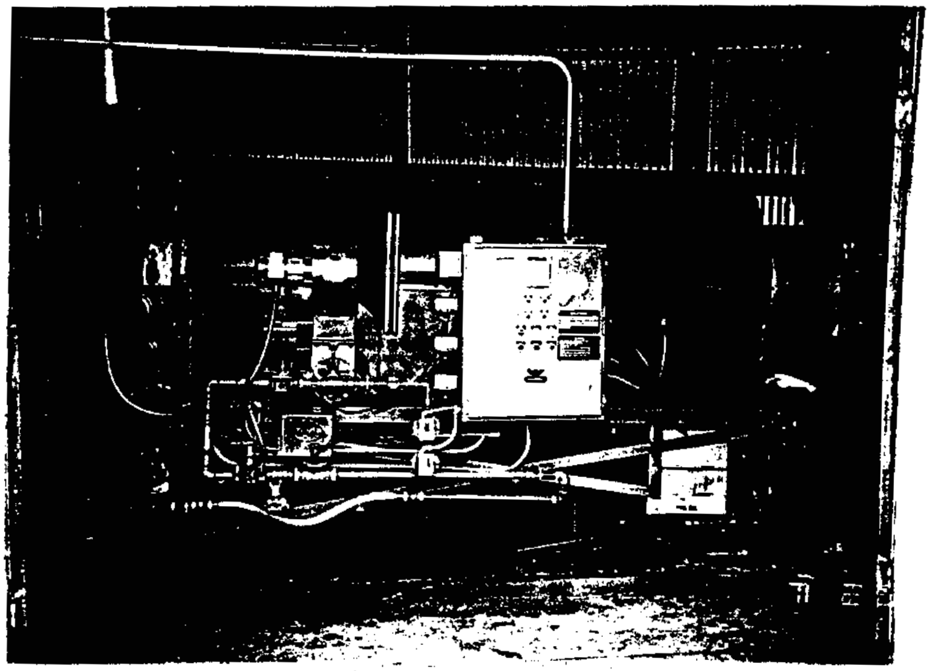


Figure 1 The rotary kiln for large scale experiments at Universal

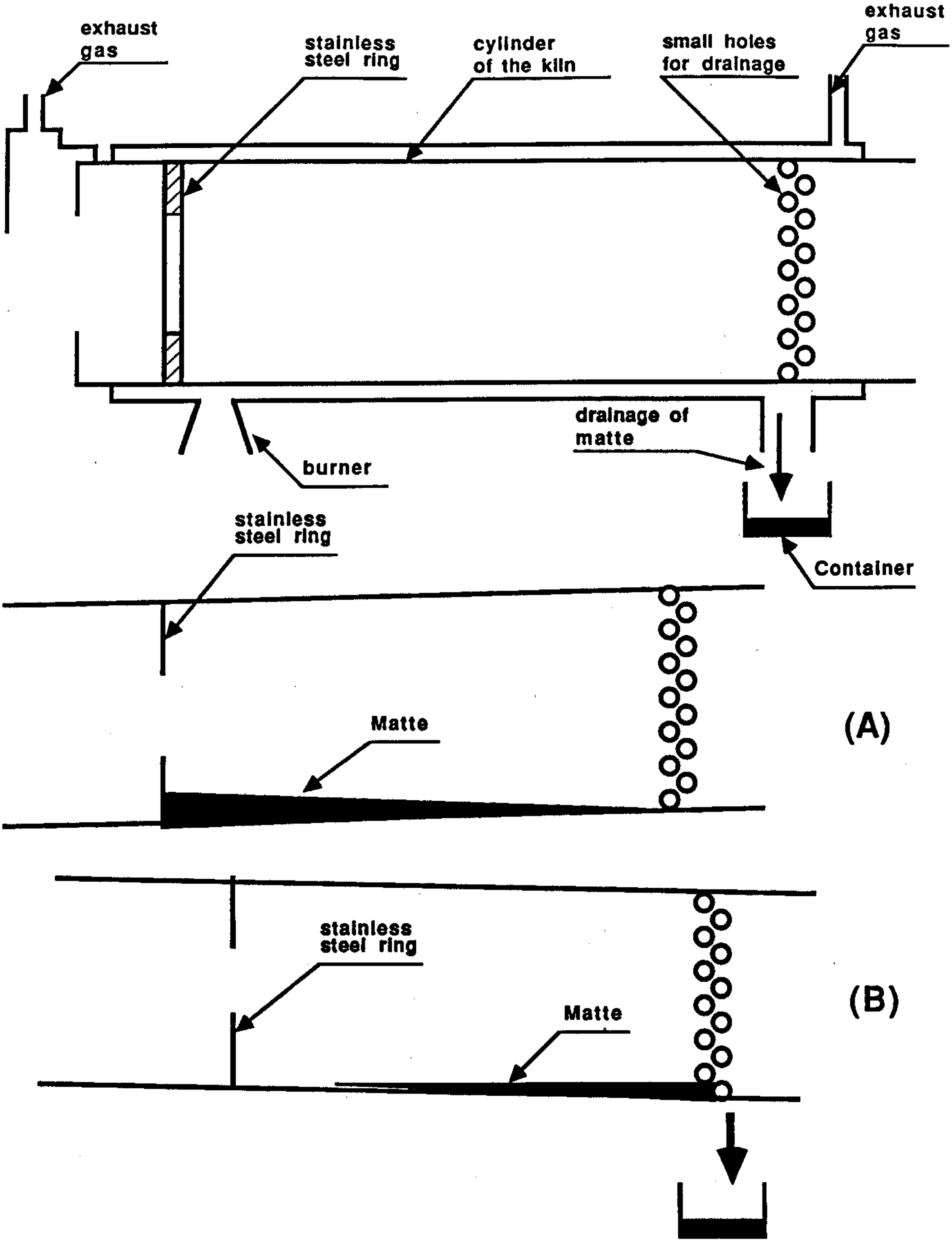


Figure 2 The rotary kiln and (A) the position for refining and (B) the position for drainage of the matte

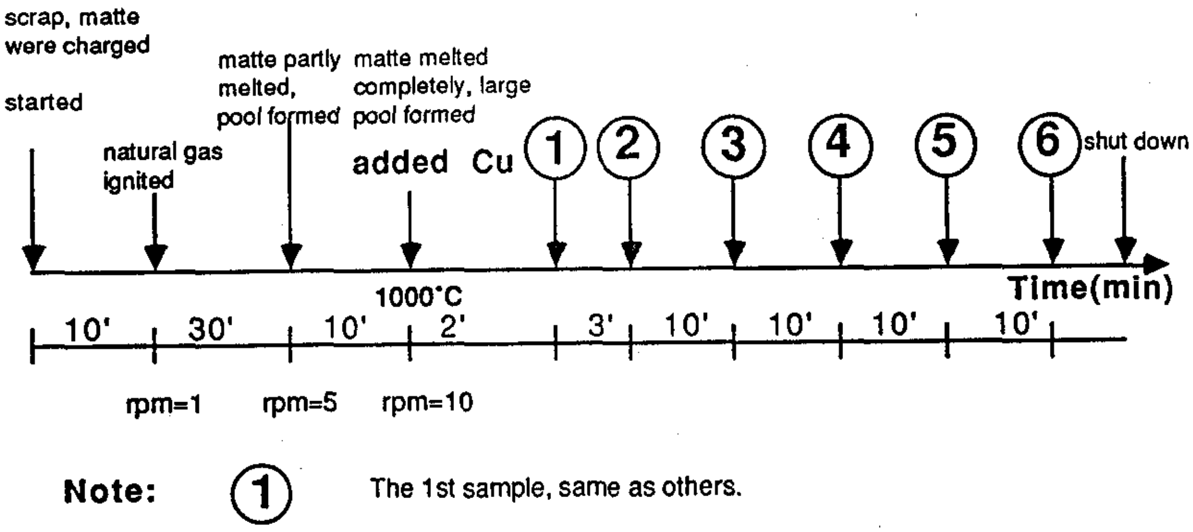


Figure 3 The typical operations of an experiment in the kiln

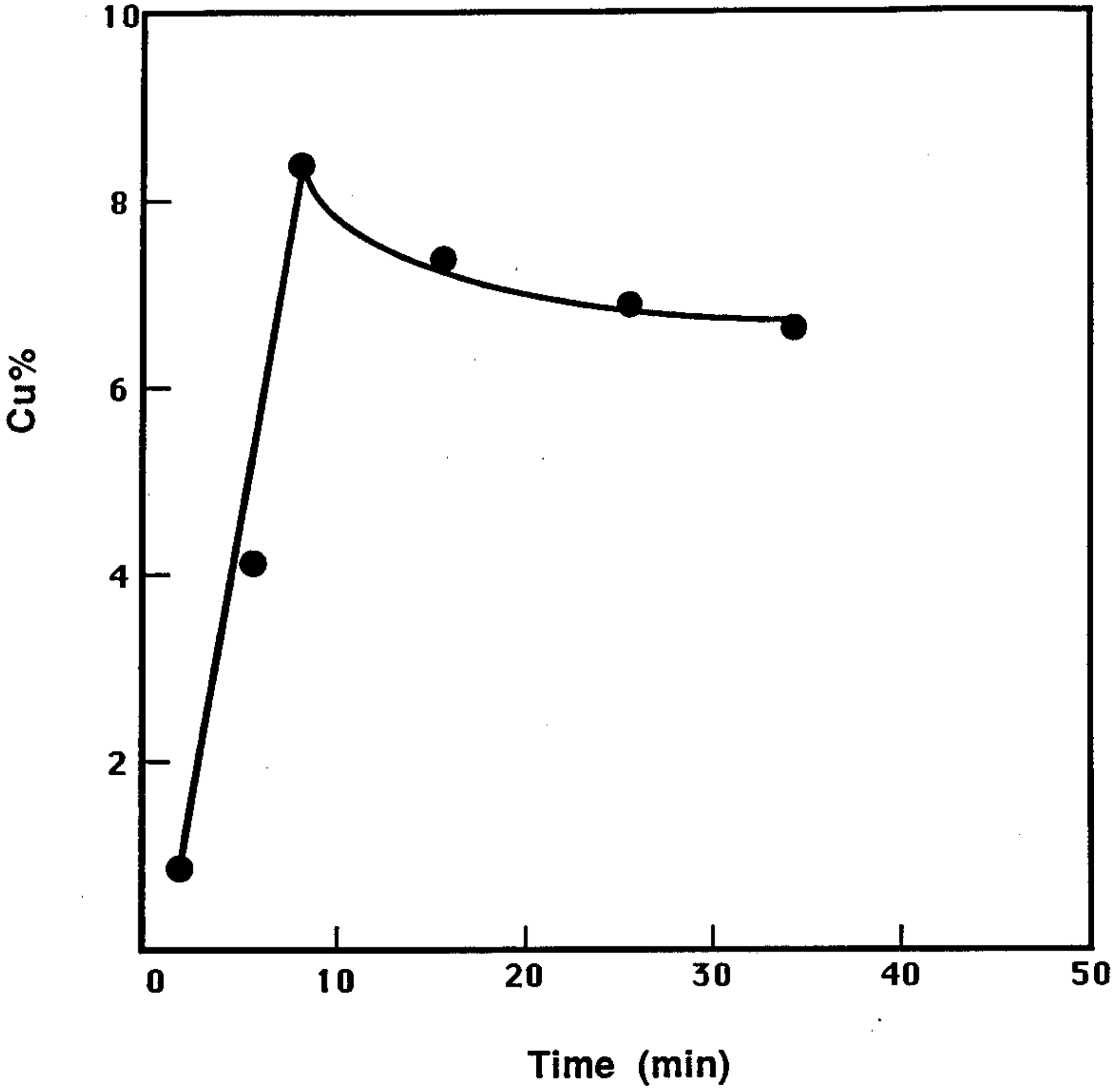


Figure 4 The change of copper in the matte as a function of time

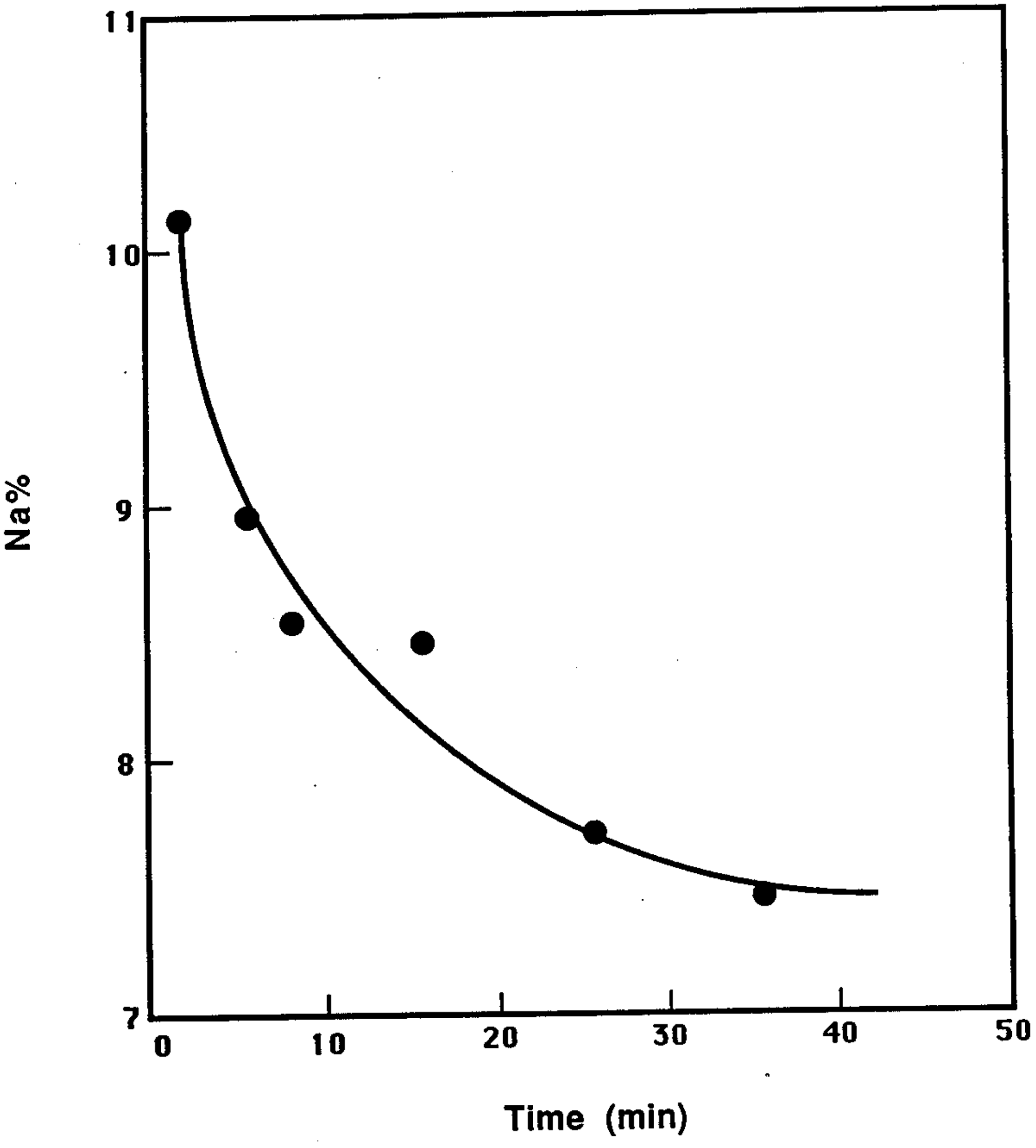


Figure 5 The change of Na in the matte as a function of time

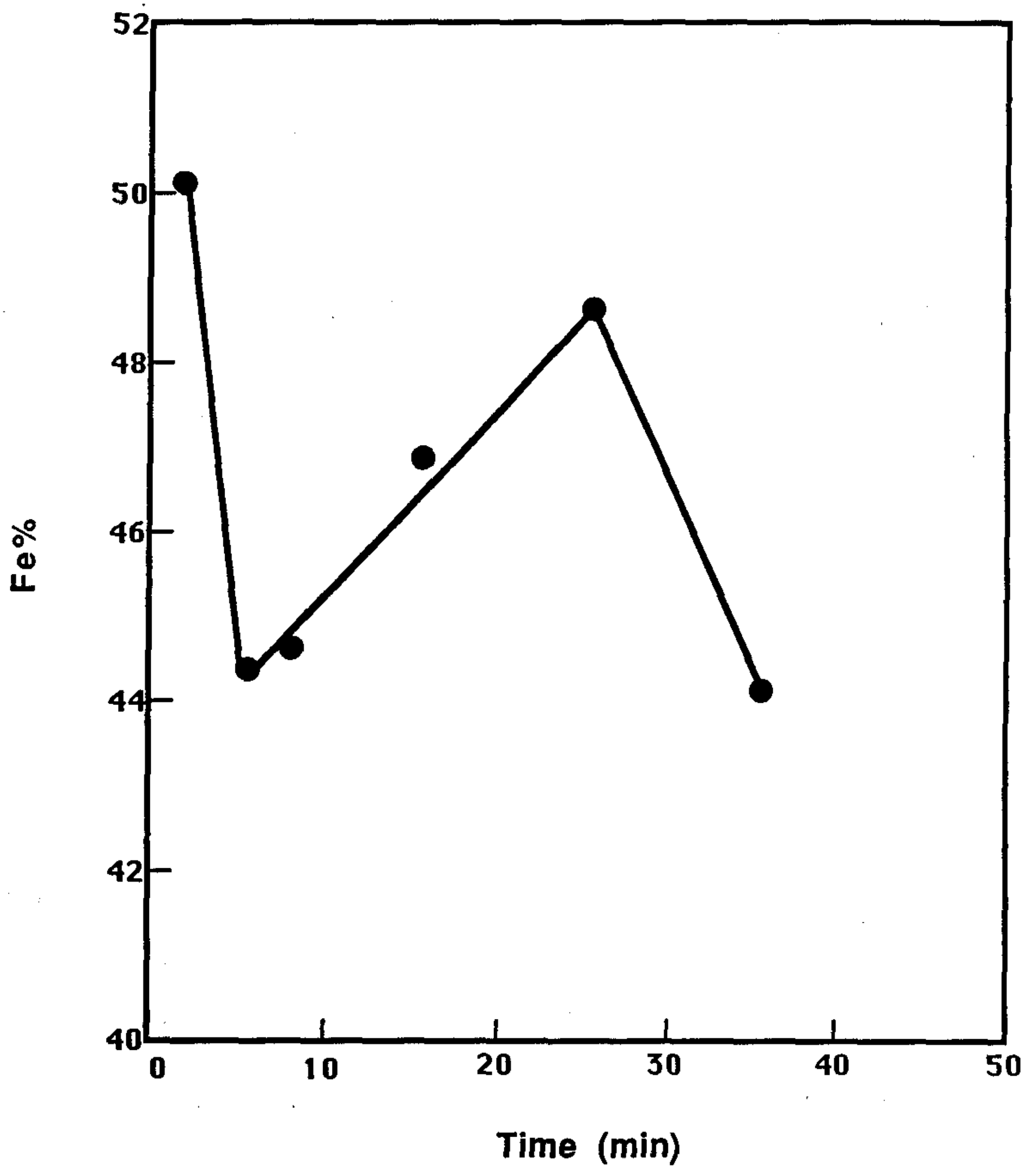


Figure 6 The change of Fe in the matte as a function of time

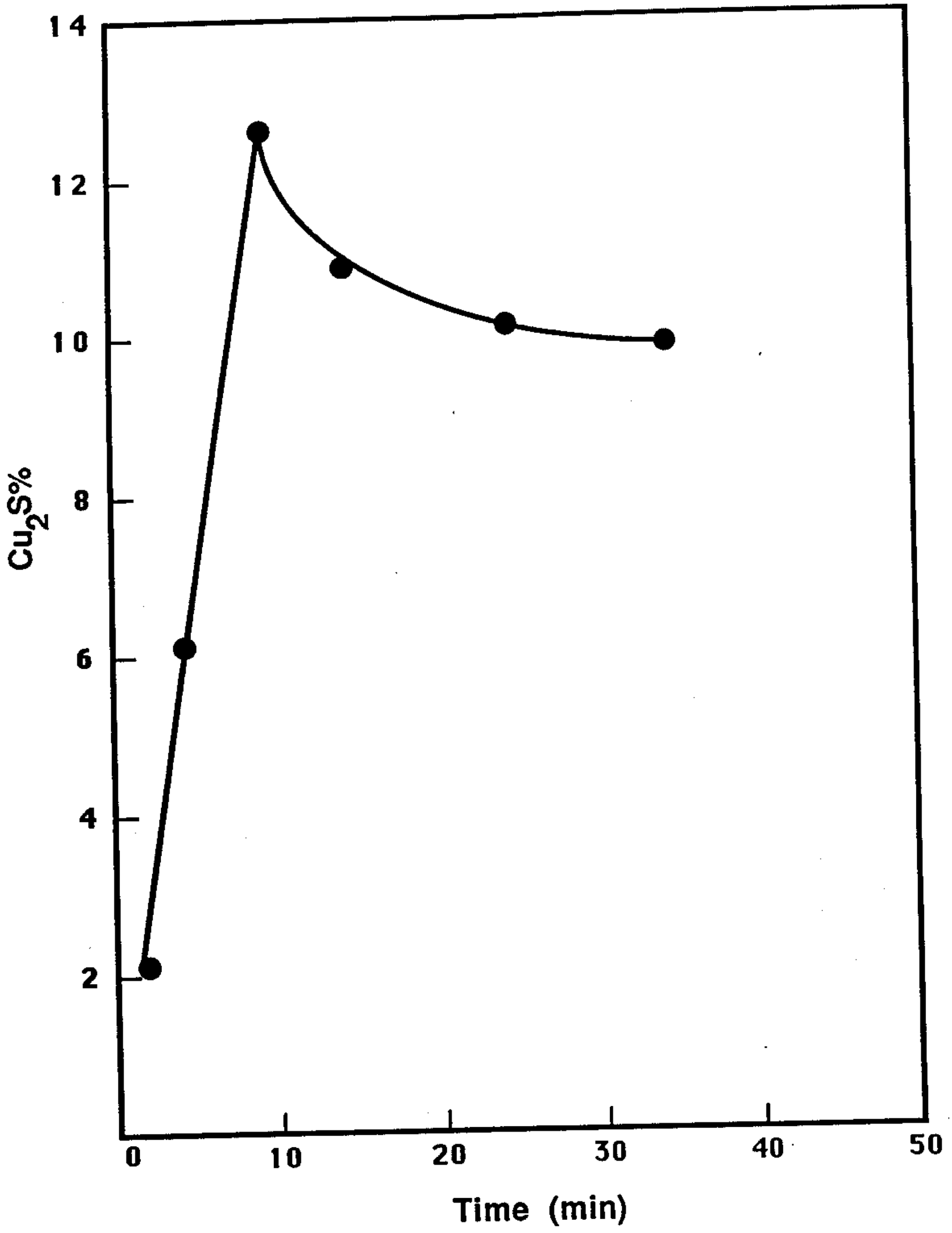


Figure 7 The change of Cu_2S in the matte as a function of time

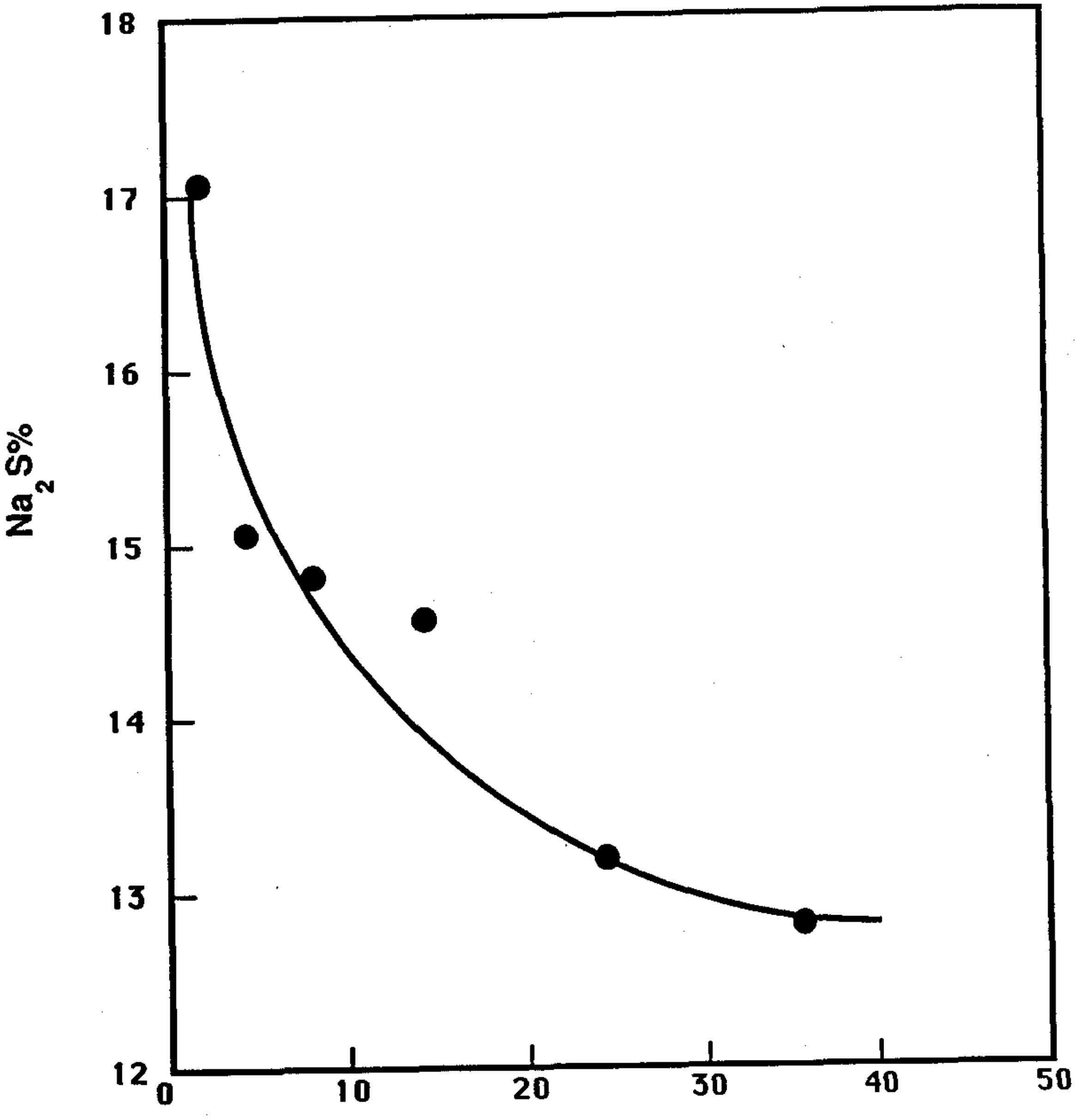
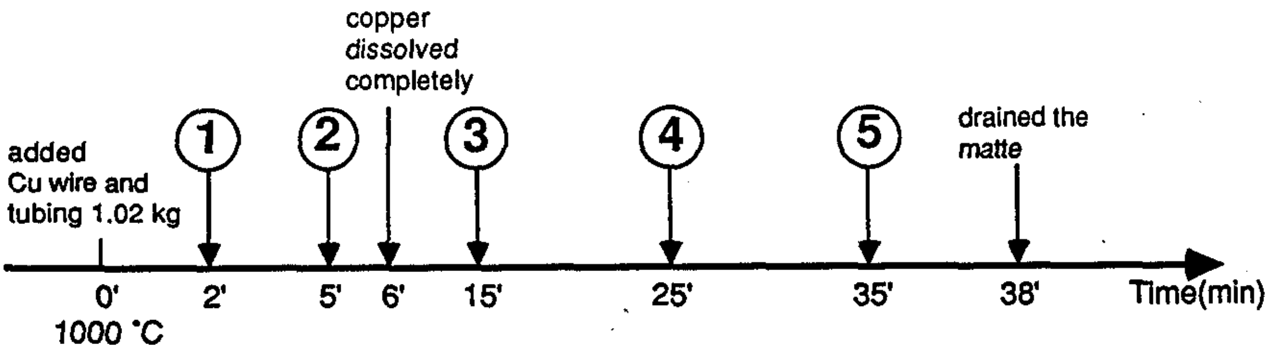


Figure 8 The change of Na_2S in the matte as a function of time

Experiment 1

1. Objective: To see how the process works.
2. Matte: 31.3 kg
   FeS 20 kg
   Na_2S(60%) 7.5 kg (82:18)
3. Ferrous scrap: 66 kg (steel rods, iron angles, steel pipes and steel sheets)
   copper (tubing) 1.02 kg
4. Temperature: 1000 °C
5. Experimental:



6. Chemical analysis results:

% \ Time (min) after 1000 °C	2'	5'	15'	25'	35'
Cu	2.84	3.4	3.21	3.1	2.8
Fe	46.4	44.5	42.5	45.2	49.78
Na	14.24	16.7	17.3	14.86	11.6

% \ Time (min) after 1000 °C	2'	5'	15'	25'	35'
Cu_2S	3.55	4.26	4.03	3.81	3.51
FeS	72.1	69.99	66.85	71.07	78.03
Na_2S	24.15	28.32	29.33	25.2	19.66

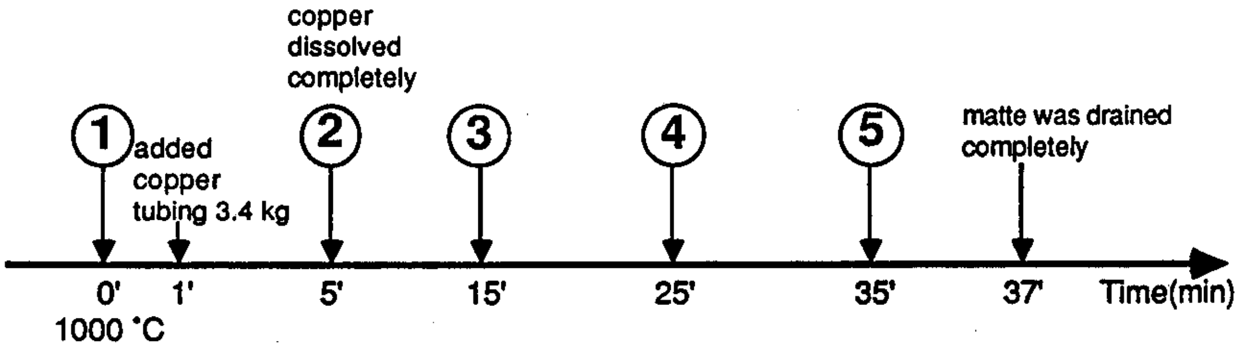
Experiment 2

1. Objective: To see if more Cu tubing in scrap (Cu=4.08%) can be removed.
2. Matte: 50.5 kg
   FeS 37 kg
   Na_2S(60%) 13.5 kg (82:18)

3. Ferrous scrap: 79 kg
   copper (tubing) 3.4 kg (Cu=4.08%)

4. Temperature: 1000 °C

5. Experimental:



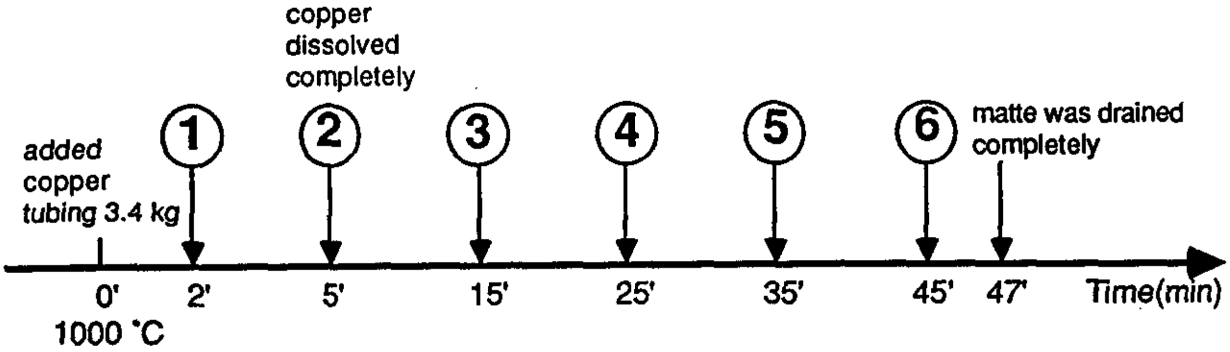
6. Chemical analysis results:

% / Time (min) after 1000 °C	2'	5'	15'	25'	35'
Cu	0.36	1.66	3.73	3.98	4.02
Fe	57.04	55.77	52.67	51.46	50.2
Na	5.76	4.92	4.47	3.86	3.7

% / Time (min) after 1000 °C	2'	5'	15'	25'	35'
Cu_2S	0.45	2.07	4.67	4.98	5.03
FeS	89.7	87.7	82.84	80.94	78.97
Na_2S	9.77	8.34	7.51	6.55	6.27

Experiment 3

1. Objective: To do experiment using high Cu_2S content matte.
2. Matte: 41.66 kg
   FeS 31.7 kg
   Na_2S(60%) 11.6 kg (82:18)
   Cu_2S 4 kg (Cu S=9.38 %)
3. Ferrous scrap: 80 kg
   copper (tubing) 3.4 kg (Cu=4.08%)
4. Temperature: 1000 °C
5. Experimental:



6. Chemical analysis results:

% \ Time (min) after 1000 °C	2'	5'	15'	25'	35'	45'
Cu	8.12	13.55	14.7	13.01	12.41	12.35
Fe	54.8	52.3	49.1	50.22	44.6	51.8
Na	8.47	5.98	5.89	6.22	5.89	4.97

% \ Time (min) after 1000 °C	2'	5'	15'	25'	35'	45'
Cu_2S	10.17	16.97	18.4	16.4	15.54	15.46
FeS	86.2	82.26	77.23	78.99	70.15	81.48
Na_2S	14.36	10.14	15.51	10.54	9.54	8.43

Experiment 4

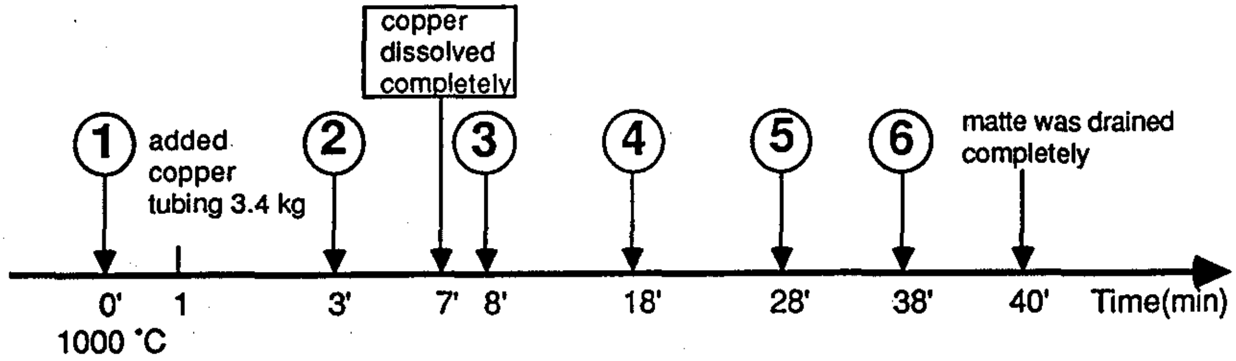
1. Objective: To test the matte with FeS/Na_2 S=75:25.

2. Matte: 42 kg
   FeS 31.5 kg
   Na_2S(60%) 17.5 kg (75:25)

3. Ferrous scrap: 81 kg,
   copper (tubing) 3.4 kg (Cu=4.04%)

4. Temperature: 1000 °C

5. Experimental:



6. Chemical analysis results:

% \ Time (min) after 1000 °C	0	2'	5'	15'	25'	35'
Cu	1.47	4.02	8.42	7.2	6.99	6.6
Fe	51.39	44.3	44.77	47.09	48.83	44.1
Na	10.11	8.92	8.69	8.6	7.77	7.56

% \ Time (min) after 1000 °C	0	2'	5'	15'	25'	35'
Cu_2S	2.2	6.03	12.63	10.8	10.04	9.9
FeS	80.83	69.68	70..42	74.07	76.81	69.37
Na_2S	17.14	15.13	14.74	14.58	13.18	12.82

Note: Before the matte was drained, it was very thick. The Cu tubing dissolved into the matte within 7'.

Experiment 5

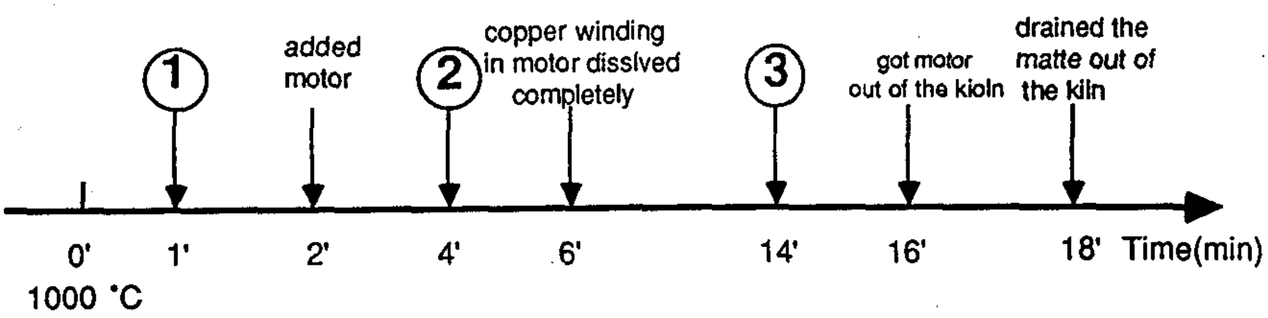
1. Objective: To test if the winding in the motor dissolves into the matte.

2. Matte: 23.4 kg
   FeS 19.2 kg
   Na_2S(60%) 7 kg (82:18)

3. A motor was added (no ferrous scrap)

4. *Temperature: 1000 °C*

5. *Experimental:*



6. Chemical analysis results:

% \ Time (min) after 1000 C	1'	4'	14'	
Cu	0.32	0.35	2.31	
Fe	51.94	51.2	50.03	
Na	10.55	9.84	9.81	

% \ Time (min) after 1000 C	1'	4'	14'	
Cu_2S	0.41	0.44	2.89	
FeS	81.37	80.67	78.69	
Na_2S	17.89	16.69	16.63	

Experiment 6

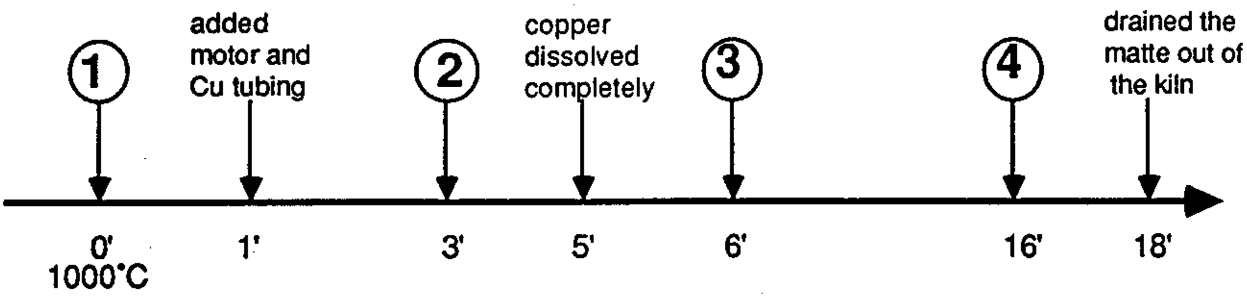
1. Objective: A demonstration. To test using both the motor and the Cu tubing.

2. Matte: 36.6 kg
   FeS 30 kg
   Na_2S(60%) 11 kg (82:18)

3. Ferrous scrap: 60 kg
   a motor
   copper (tubing) 3.8 kg

4. Temperature: 1000°C

5. Experimental::



6. Chemical analysis results:

% \ Time(min) after 1000°C	0'	3'	6'	16'
Cu	0.124	0.184	4.02	6.11
Fe	53.1	52.95	50.46	48.59
Na	9.7	8.27	8.16	6.94

% \ Time(min) after 1000°C	0'	3'	6'	16'
Cu_2S	0.14	0.23	5.03	7.64
FeS	83.61	83.25	79.33	76.39
Na_2S	16.54	14.03	13.84	11.76

Experiment 7

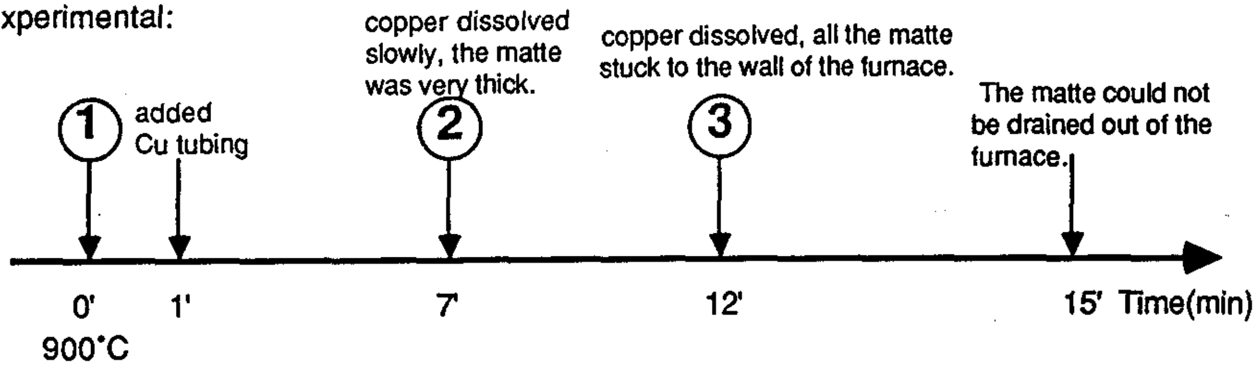
1. Objective: To test how the process works under the conditions of:
   (1) 900°C, (2) FeS:Na_2S=82:18.

2. Matte: 25 kg
   FeS 20.5 kg
   Na_2S(60%) 7.5 kg (82:18)

3. Cubing 1.7 kg, stainless steel rod.

4. Temperature: 900 °C

5. Experimental:



6. *Chemical analysis results:*

Time (min) after 900 °C %	0'	7'	12'	
Cu	0.32	2.85	3.42	
Fe	52.65	50.75	49.7	
Na	10.36	9.91	9.46	

Time (min) after 900 °C %	0'	7'	12'	
Cu_2S	0.32	3.57	4.28	
FeS	82.81	79.83	78.25	
Na_2S	17.57	16.81	16.04	

Note: The amount of the matte sticking to the rod/ the weight of stainless steel rod=1.94%

The change of S% and Cu% for the scrap before and after experiment

experiment order	S%(original) before experiment	S% after experiment	Description of experimental condition
1	0.033	0.079 0.075 0.078	After experiment, three sections of steel rod, which weight were 27.8g, 28.7g and 28.8g, were put inside three small alumina crucibles separately. All the three alumina crucibles were put inside a graphite crucible which was placed in an induction furnace. After all the three samples were remelted, chemical analysis was done using Gravimetric Method.
2	0.032	0.053 0.051 0.048	Same as above(except samples weight).
3	0.043 Cu: ~0.05	0.159 0.157 0.161 Cu: ~0.05	After demonstration experiment,15 kg of steel rods were cut into small sections, then remelted in an induction furnace and cast into an ingot mold. Samples were taken by drilling the ingot and analyzed for Cu and S content, while the original sample without experiment was also analyzed. It was found that: (1) the sulfur content increased almost four times after remelting in the induction furnace; (2) there was no obvious change for Cu content after remelting and the Cu contents were very low.
4	0.043	0.091 0.096 0.095	After being washed the scrap was remelted and then analyzed. It was found that the surfur content increased by two times, but the surfur content increased by four times if the scrap was not washed.
5	0.043	0.054 0.053 0.044	The scrap was placed into the 8% HCl solution for washing and cleaning the sticking matte at 102°C for 30 minutes, then it was rinsed in the water and cut into three sections. The three sections of steel rod were remelted in the induction furnace and then analyzed. The analysis results show that by using 8% HCl solution to clean the sticking matte the sulfur content increased from the original S content 0.043% to 0.054%, 0.053% and 0.044% only, which are better(lower) than using water.

Work Report

DECOPPERIZATION OF FERROUS SCRAP

Yuting Zhang
April 3, 1989

Introduction

Removal of copper from scrap has been receiving great attention widely by the metallurgists because of the increase of the scrap usage in steelmaking processes. As a common knowledge, copper, the major source of which in the steelmaking process is recycled scrap, causes great problems in steel quality and processing. Therefore, various kinds of method have been studied to try to extract copper out of the contaminated scrap before using. Particularly, a new suggestion for copper removal from scrap by solid state treatment with $FeS\text{-}NaS_{0.5}$ flux seems much more economical, although further work of verification needs to be done.[1,2]

1. An Overview of the Potential Techniques

(i) ***Physical beneficiation*** methods may not be satisfactory because of its economics and difficulty to achieve high copper removal efficiency. Some of the recent works of this kind have been done by British Steel Corporation[3] and P. Vejnar etal.[4]

(ii) ***Lead extraction*** has not been found after the works of Ogawa[5], Langenberg etal[6], Oelsen etal[7] and Schenck etal.[8,9]

(iii) ***Preferential smelting*** is of minor interests nowadays. However, a patent publication in Czechoslovakia in 1987[10] adopted this method for copper recovery from iron scrap. According to the abstract description, *Cu* is melted selectively in an electric furnace and separated from *Fe* in a layer of $CaO\text{-}FeO\text{-}SiO_2$ based slag by vibration and gravitation and collected at bath bottom. Separation in the molten slag prevents oxidization and contact of *Fe* with *Cu*. The recovered products contained *Cu* 98-99 and *Fe* 0.4-0.8%.

(iv) ***Vacuum distillation*** is still interesting to a number of researchers [11] and some improvements have been proposed. T. Matsuo[12] investigated the copper and tin removal in a laboratory scale plasma furnace using argon-hydrogen and argon gas. *Cu* and *Sn* removal was much accelerated. Degrees of *Cu* and *Sn* removal reached 90 and 60% respectively in 2 hours. It was concluded that a high H_2 content in plasma gas and a high initial carbon content were favorable. Effective removal of these elements could be obtained at pressures of 1.3×10^4~2.0×10^4Pa (0.12atm~0.20atm). C.N. Esimai[13] also suggested that addition of silicon to the molten metal enhances the vaporization of copper and tin. And tin evaporates even faster than copper does. When add 10wt% *Si*, copper was removed from 1wt% to a final 0.06wt% and tin from 1wt% to 0.045wt%. Unfortunately, the high *Si* content in the product may limit the range of usage of the reclaimed scrap.

(v) ***Slag refining*** of copper from liquid scrap has been attracting the most attention of the researchers, since this technique is relatively cheap and may be used in either furnace or ladle. Major problems are that it requires carbon saturation of liquid metal and a relatively high temperature which may cause vaporization of Na_2S. Also resulphurization was found after the treatment which is unfavorable for the afterward steel refining. Attempts to find the slagging agents other than Na_2S (or Na_2SO_4) or methods to reduce its vaporization have been made, but there are no achievements yet without sacrificing the decopperization efficiency. Major works reviewed are listed in Table I.

(vi) A ***low temperature oxidization*** method was revealed by C.J. Herter.[26] In this process, a kiln is maintained at an oxidizing atmosphere at about 1700F(927°C). As charges move through the kiln, the atomsphere changes from oxidizing to neutral and reducing, kiln temperature rises to 1900F(1038°C) at the discharge end. *Cu* may be removed as *CuO* dust from the oxidizing part of the rotary kiln as a metallic brittle scale. Test results showed that the method could be viable. However no detailed publication related to this kind of technique could be found.

2. Physical Chemistry of Fluxing Mattes

As the above indicated, $FeS\text{-}NaS_{0.5}$ system has been approved to be the only reliable fluxing agent for copper removal from the liquid ferrous scrap. Accordingly, Fruehan etal[1,2] also chose $FeS\text{-}NaS_{0.5}$ for their low temperature solid state treatment method. The principle of this method then relies on that the affinity of *S* for *Cu* is greater than that for *Fe*. Thus,

$$Cu_{(s)} + \frac{1}{2}(FeS)_{matte} = (CuS_{0.5})_{matte} + \frac{1}{2}Fe_{(s)} \qquad \text{———— (1)}$$

While $NaS_{0.5}$ serves as a solute to reduce the melting temperatures of the matte.

T.Imai etal[23] obtained the iso-activity coefficient contours of $CuS_{0.5}$ amd FeS for $NaS_{0.5}$-FeS-$CuS_{0.5}$ ternary system at 1200°C and showed that the activity coefficients of both components decrease with increasing (%$NaS_{0.5}$). They explained that Na_2S forming many compounds with Cu_2S and FeS might be the reason for the decrease in $\gamma_{CuS_{0.5}}$ and γ_{FeS} with increasing (%$NaS_{0.5}$). See Fig.1 and 2.

I. Jimbo etal[24] also plotted their experimentally obtained Raoultian activities at 1400°C of $CuS_{0.5}$ and FeS in the $NaS_{0.5}$-FeS-$CuS_{0.5}$ triangle. But their data were too scattered fo form the isopleth (Fig.3,4). However, they reasonably concluded that (Fig.5,6 and 7):

- At lower sodium sulfide concentrations ($NaS_{0.5}$<25%mole) the activity coefficient of $CuS_{0.5}$ decreases faster than the square root of the activity of FeS does.
- At higher sodium sulfide concentrations, the activity of FeS is decreasing, while the activity of $CuS_{0.5}$ is almost constant or decreasing slightly with increasing copper sulfide content in this range.

Another study on the thermodynamic of melts of sufides of copper, iron and sodium is in Russian language and the journal *Tsvetnaya Metallurgiya*, [1988(5),pp28-30] is very rare in this country.

Accordingly, it is almost impossible to obtain any data from present publications of the thermodynamic properties of $NaS_{0.5}$-FeS-$CuS_{0.5}$ ternary matte at relatively low temperatures 800-1000° C, in which solid state decopperization of ferrous scrap may be conducted.

Nevertheless, some knowledge on the thermodynamics of binary systems such as Cu-Fe[27-30], Cu-S[31,32], Fe-S[31,33] and binary mattes $CuS_{0.5}$-FeS[31,34-39], $CuS_{0.5}$-$NaS_{0.5}$[21] has been learned.

3. A Brief Consideration of the Solid State Decopperization of Ferrous Scrap

According to the CISR work plan on this project, the major task will be setting up a pilot scale rotary kiln and testing the concept on this unit process. And some preliminary tests concerning the kiln operation efficiency are currently carried out.[40]

(i) Following is a calculation on the minimum amounts of matte and FeS required for solid state decopperization which shows a minor difference from that by I. Jimbo.[2] Assuming W^0_{matte} kilograms initial matte is required for extracting ΔW_{Cu} kilograms copper from solid scrap. After treatment completed, the amount of matte becomes

$$W_{matte} = W^{0}_{matte} + \frac{\Delta W_{Cu}}{M_{Cu}} M_{CuS_{0.5}} - \frac{0.5 \Delta W_{Cu}}{M_{Cu}} M_{FeS} \qquad \text{———(2)}$$

where M_{Cu}, $M_{CuS_{0.5}}$ and M_{FeS} are kg-mole weight of *Cu*, $CuS_{0.5}$ and *FeS* (kg/kg-mole). Then, the final copper content $(\%Cu)_f$ in matte is given by

$$(\%Cu)_f = \frac{\Delta W_{Cu}}{W^{0}_{matte} + 0.5605\ \Delta W_{Cu}} \qquad \text{———(3)}$$

or,

$$W^{0}_{matte} = \frac{1-0.5605\,(\%Cu)_f}{(\%Cu)_f} \Delta W_{Cu} \qquad \text{———(4)}$$

After equilibrium, the saturated copper content in matte is denoted as $(\%Cu)_{sat}$

$$(\%Cu)_{sat} = \frac{M_{CuS_{0.5}}}{M_{Cu}} (\%CuS_{0.5})_{sat} \qquad \text{———(5)}$$

Therefore, the minimum matte requirement is

$$W^{0}_{matte} = \frac{1-0.5606\,(\%Cu)_{sat}}{(\%Cu)_{sat}} \Delta W_{Cu} = \frac{1-0.4478\,(\%CuS_{0.5})_{sat}}{0.7988\,(\%CuS_{0.5})_{sat}} \Delta W_{Cu} \qquad \text{———(6)}$$

According to Jimbo, the $NaS_{0.5}$-*FeS*-$CuS_{0.5}$-*Cu* system can contain $CuS_{0.5}$ up to 36wt% at 1000° C. Then if the initial and final contents of copper in scrap during treatment are 0.3wt% and 0.1wt% (the same condition as Jimbo's), the amount of copper removed

$$\Delta W_{Cu} = 0.2\%\ W_{scrap} \qquad \text{———(7)}$$

Treating 1000kg scrap (W_{scrap}=1000kg), the minimum amount matte required

$$W^{0}_{matte} = \frac{1-0.4478\times 36\%}{0.7988\times 36\%} \times 0.2\% \times 1000 = 5.834\ kg \qquad \text{———(8)}$$

which is a little higher than Jimbo's result 4kg/1000kg.

FeS usage ΔW_{FeS} results from

$$\Delta W_{FeS} = \frac{1}{2}\frac{\Delta W_{Cu}}{M_{Cu}} M_{FeS} = 0.6913\,\Delta W_{Cu} = \frac{0.5522\,(\%CuS_{0.5})_{sat}}{1-0.4478\,(\%CuS_{0.5})_{sat}} W^{0}_{matte} \qquad \text{———(9)}$$

In the above case,

$$\Delta W_{FeS} = \frac{0.5522\times 36\%}{1-0.4478\times 36\%} W^0{}_{matte} = 23.7\% W^0{}_{matte} = 1.383\,kg \tag{10}$$

Consequently, the amount of *FeS* needed in the initial matte flux $W^0{}_{FeS}$ would be

$$W^0{}_{FeS} = 23.7\% W^0{}_{matte} + (\%FeS)_{eq} W_{matte} \tag{11}$$

where, $(\%FeS)_{eq}$ is the finial *FeS* content in matte equilibrated with solid scrap.

(ii) The following are problems of major concern:

- ensuring a good mixing of copper inclusions in scrap with the liquid matte and a higher rate of copper dissolution into the liquid matte
- eliminating adhesion of matte onto the ferrous element.

4. Work Interests

(i) Thermodynamic properties and fluidity of ternary $NaS_{0.5}$-FeS-$CuS_{0.5}$ liquid matte at temperatures of 700-1000°C.

(ii) Dissolvability of copper in the liquid $NaS_{0.5}$-FeS melt.

(iii) Dissolving rate of solid copper in $NaS_{0.5}$-FeS-$CuS_{0.5}$ liquid melt (mass transfer coefficient of *Cu* in liquid matte.

5. References

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Table I: Slag refining of copper from liquid scrap

Flux system	De-*Cu* efficiency	Work done	References
Na_2S	L_{Cu}=7~8(1260~1550°C)*	•mechanism of reaction •observed sulfur content in metal	[14,15]
Na_2SO_4	Y=1-exp(-3.23x)**; L_{Cu}=1.2~7.9	effect of lump versus powder Na_2SO_4	[16]
Li_2SO_4-Na_2SO_4-K_2SO_4 K_2SO_4	Y=20% (1354~1649°C)	•recycling of used slag •and use of the recycled slag	[17]
Na_2SO_4	1550 ± 20°C [0.01%*C*]: [%*Cu*]1.5 → 1.4 [2%*C*]: 1.5 → 1.22 *C*-sat.: 1.5 → 0.8	•mechanism of *Cu* removal •effect of *C* content •sulfur pick-up and *Na* vaporization	[18]
Na_2S FeS-Na_2S	1200~1350°C Y=70%	•best slag composition for *Cu*-removal & *S*-control: 30%FeS-70%Na_2S •iron recovery and minimum *Na* fume •mass transport is an important controlling step •CaO accelerates de-*Cu*	[19]
Na_2S	L_{Cu}=24	•kinetics of the process: rate controlled by chemical reactions at gas/slag and metal/slag interface & diffusion of *Na* in gas phase •thermodynamics of Na_2S-Cu_2S system studied •suggested closed system as for reducing *Fe* loss & *S* pick-up	[20]
FeS-$NaS_{0.5}$	Y=80~90% using 19wt% slag L_{Cu}=25 at 1250°C	math-modelling of de-*Cu* process assuming mass transfer in boundary layer to be rate controlling step	[21]
$NaS_{0.5}$-FeS CaS-FeS-(FeO)	Y=55% using 10wt% slag L_{Cu}=16~20 low de-*Cu* observed FeO has bad effect	•20%FeS-80%$NaS_{0.5}$ has maximum copper removal •thermodynamics of FeS-$CuS_{0.5}$ system •evaporization of *Na*	[22]

Table I: Slag refining of copper from liquid scrap (continued)

Flux system	De-*Cu* efficiency	Work done	References
CaF_2-FeS	poor de-*Cu* due to high m.p. of CaF_2	•[S] content in metal phase •reaction kinetics examined	
$NaS_{0.5}$-FeS-CaS	moderate between 37~50%		
$NaS_{0.5}$-FeS	L_{Cu}=17~21.5 as (%$NaS_{0.5}$) decreased from 95 to 13%	•*Cu* capacity C_{Cu} defined as $\frac{(\%CuS_{0.5})}{a_{[Cu]} \cdot P_{S_2}{}^{1/4}}$ $logC_{Cu}=\frac{5640}{T}+0.213$ •examined the effect of other alkali/ alkali earth sulfides, found the order of being favorable to de-*Cu* is $Na_2S>Li_2S>BaS>K_2S>CaS$ •activities of $NaS_{0.5}$-FeS-$CuS_{0.5}$ system are given at 1200°C	[23]
FeS-$NaS_{0.5}$	L_{Cu}=20 at 1400°C minimum 10wt% slag needed for the removal of *Cu* from [0.3%] to [0.1%]	•optimum composition of slag was 30%($NaS_{0.5}$)-70%(FeS) •effect of MnS,PbS & Al_2S_3 additions •activities of FeS and $CuS_{0.5}$ in ternary $NaS_{0.5}$-FeS-$CuS_{0.5}$ system	[2,24]
Na_2S-FeS-K_2O (CaO-SiO_2)	unsatisfactory *Cu* recovery 0.3%	large scale tests by the slagging agent injection	[25]

* L_{Cu}: *Cu* partition ratio

** Y: percentage of *Cu* removal; x: weight ratio of slag to scrap

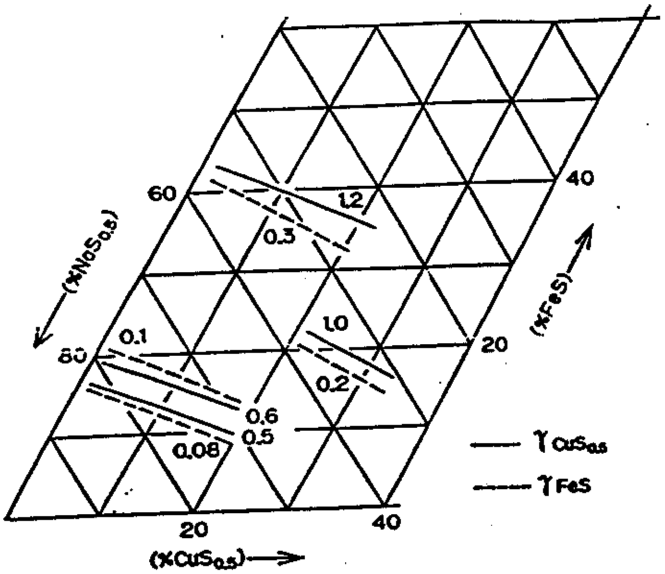

Fig. 1 Iso-activity coefficient contours of $CuS_{0.5}(l)$ and $FeS(l)$ for the $NaS_{0.5}$–FeS–$CuS_{0.5}$ system at 1 473 K.

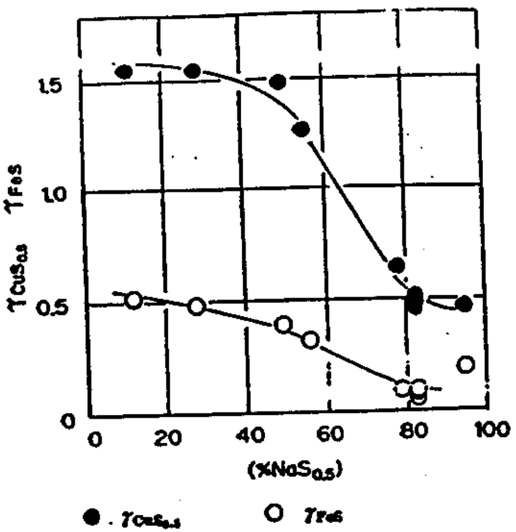

Fig 2 Variations in the activity coefficients of $CuS_{0.5}(l)$ and $FeS(l)$ with ($\%NaS_{0.5}$) in the $NaS_{0.5}$–FeS system at 1 473 K.

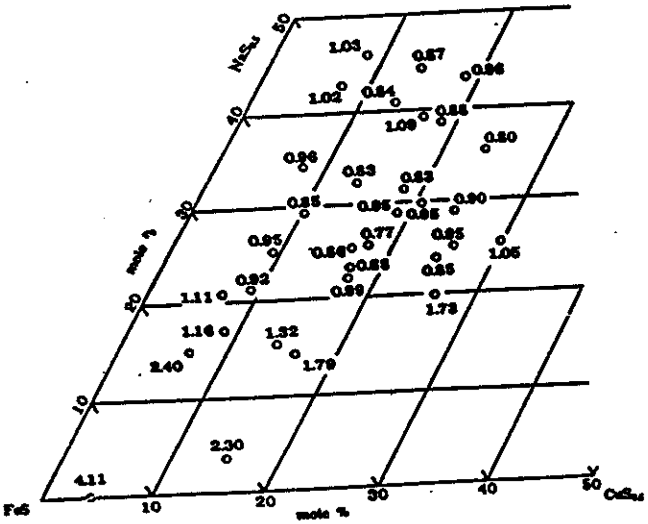

Figure 3 - Effect of matte composition on activity coefficient of copper sulfide

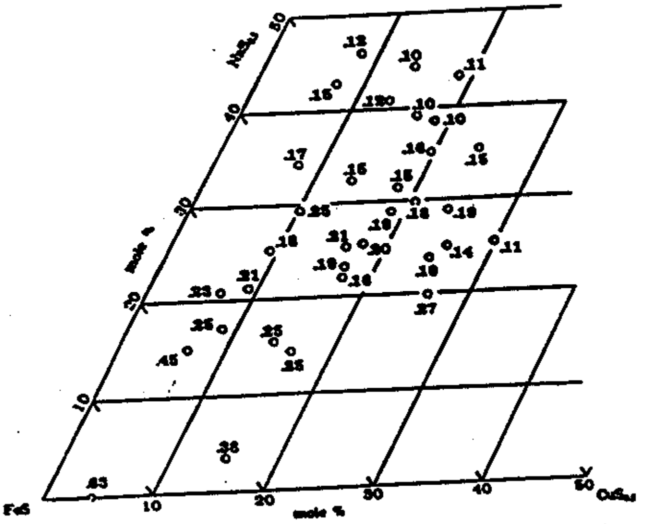

Figure 4 - Effect of matte composition on activity of iron sulfide

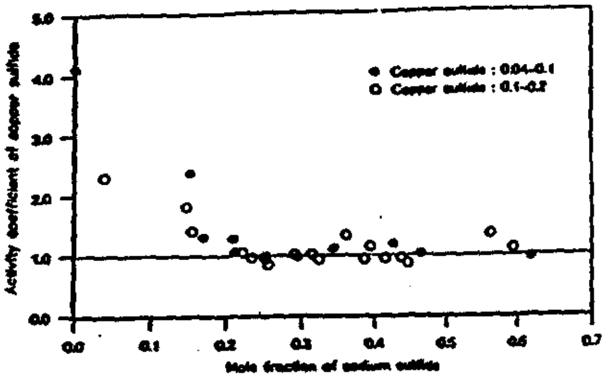

Figure 5 - Effect of sodium sulfide content on activity coefficient of copper sulfide

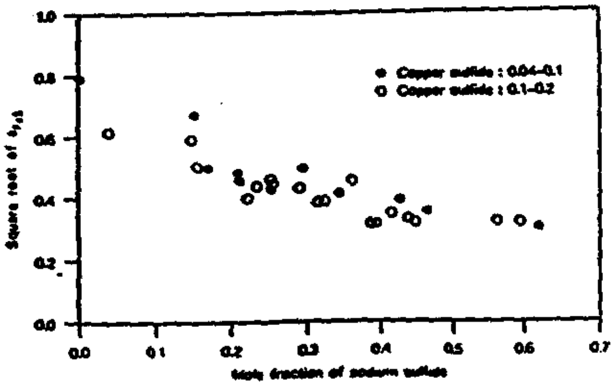

Figure 6 - Effect of sodium sulfide content on the square root of activity of iron sulfide

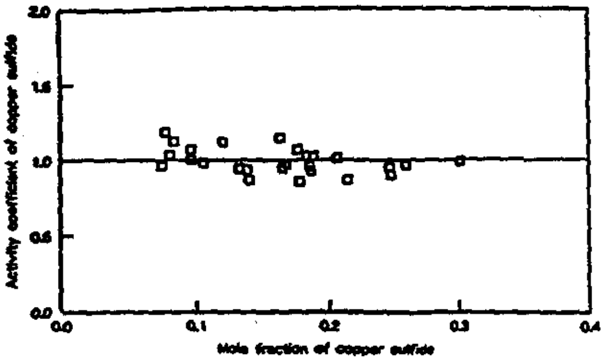

Figure 7 - Effect of copper sulfide content on activity coefficient of copper sulfide

CISR PROGRESS REPORT

Fundamentals of Decopperization from Solid Scrap

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R. J. Fruehan, Professor

September 22, 1989

INTRODUCTION

Steel can become contaminated by a number of non-ferrous metals which are present in the various forms of scraps. Copper is a common contaminant and causes deleterious effects on certain steel product properties. As conventional steelmaking processes cannot remove copper, researchers, worldwide, are seeking a process to remove copper from steel scrap. At CMU, a process by which the steel scrap is treated at 1000°C with a FeS-Na_2S matte to remove copper is under investigation.

Previous studies of the mechanism of removing copper from solid scrap using FeS-Na_2S sulfide matte[1,2,3] have highlighted the following facts:

- only about 10 kilograms of matte are needed to treat one ton of scrap, which is advantageous economically.
- there is no need for carburization-decarburization or extensive desulfurization.
- the treatment may not be conducted under an oxidizing atmosphere.

The concept of the method is that the affinity of S for Cu is greater that that for Fe at temperatures higher that about 670°C. Therefore,

$$FeS + 2Cu = Cu_2S + Fe$$

While the addition of Na_2S serves to make a liquid matte with FeS at temperatures even as low as 700°C and improve the thermodynamics of copper removal by decreasing the activity coefficient of Cu_2S in the matte.

CURRENT WORK

The objective of this study is to investigate the solid copper dissolution rate in the liquid sulfide matte. This should help improve understanding of solid scrap decopperization and enhance large scale experimental optimization.

To date, the following work has been accomplished:

- The experimental apparatus has been set up and initial experiments accomplished.
- A method of preparing anhydrous Na_2S by $Na_2S{\cdot}9H_2O$ dehydration has been successfully developed.
- Experiments on the dissolution rate as a function of copper cylinder rotation speed has been completed.
- As the experimental study being in progress, the mechanism of the solid copper being dissolved by the liquid matte is under investigation.

EXPERIMENTAL

Fig.1 shows the experimental set-up. A carbon crucible 3cm in inner diameter and 9cm in height is placed into the furnace. About 100 grams of $FeS\text{-}Na_2S$ mixture were charged into the crucible through a carbon funnel. A speed adjustable motor was mounted above the furnace. The commercial grade copper cylinder, 15cm in length and of varying diameter, is rotated in the melted matte by the motor. The shaft connector between motor and the shaft which is attached to the copper cylinder also helps lower the copper cylinder so as to start the reaction precisely at zero time. Argon gas is introduced at a flow rate of 2.5l/min from the beginning of the experiment. During each run, matte samples are taken as a function of time. Then they are kept in an air-pumped desiccator before being dissolved by nitric acid(50 percent in volume). *Na, Fe* and *Cu* are analyzed by the atomic absorption method.

RESULTS

1. Dehydration of $Na_2S{\cdot}9H_2O$

Anhydrous Na_2S was prepared by dehydration of $Na_2S{\cdot}9H_2O$ at temperatures below 300°C and pressures between 3-3.5 mmHg. Efforts were made to avoid the hydrolysis reaction of the dried Na_2S and the decomposition of Na_2S was prevented by an adequate vacuum and by reducing the temperature of the system to 200°C after about three hours. Fig.2 illustrates the operation pattern for *$Na_2S{\cdot}9H_2O$* dehydration. At late stages, the weight of the sample has been checked to determine the stoichiometry.

2. Solid copper dissolution rate in matte

As a preliminary step of study, the following conditions were set:

(1)*FeS/Na_2S=50g/50g*; (2)Copper cylinder diameter=10mm;

(3)Temperature=900°C; (4)Rotation speed of copper cylinder=0, 20, 40 and 60rpm.

Liquid *FeS-Na_2S* matte had a height of 5.5cm in the crucible after melting. Its density was 3g/cm^3. The copper cylinder immersion depth was 4.5cm.

A typical result of solid copper dissolution rate in the liquid matte as a function of time is shown in Fig.3. Copper cylinder rotation speed was 20rpm. After about two and half hours, *Cu_2S* content in matte reached 30wt%. This is considered as approaching the equilibrium as predicted by I. Jimbo et al[4] at 32wt%. Ratio between the weight of initial *FeS-Na_2S* matte and the weight of removed copper(copper in the matte phase) is about 4.17. *FeS* content in matte reduced almost constantly as a function of time. At the meantime, *Na_2S* behaved quite differently at different stages during the experiment. The extent of decomposition of *Na_2S* at the beginning of the experiment accounted for the majority of the copper dissolution. After about 30 minutes, *Na_2S* concentration was constant. The overall reduction of the *Na_2S* content in matte is about 12wt%.

The effect of copper cylinder rotation speed on the dissolution rate is shown in Fig.4. It does not indicate that rotating the copper cylinder faster would result in a higher dissolution rate of copper. The highest rate was obtained when the copper cylinder was rotated at 20rpm. Increasing the rotation speed to 40rpm and 60rpm resulted in a decrease of the copper dissolution rate, however, *FeS* and *Na_2S* initial concentrations in the case of rotation at 60rpm were not controlled accurately at 50wt% each. The dissolution rate of copper into the liquid matte under the static condition (rotation speed=0) was almost the same as that at 40rpm rotation speed. It is thus concluded that,

- relative velocity between solid copper and liquid matte does not have significant influence on the dissolution rate of copper into the *FeS-Na_2S* matte.
- the reaction between the liquid *FeS-Na_2S* matte and solid copper is quite complicated and

cannot be interpreted as simple mass transfer control and topo-chemical reaction control mechanism.

3. Preliminary observations on the reaction mechanism

After experimental runs, it was found that the part of copper cylinder that was immersed into the matte was fully covered by a half-molten material, which could be dropped back to the crucible by pulling the cylinder out of the vessel and rotating it faster. Fig.5(a) shows an original copper cylinder and Fig.5(b) shows the half-molten material.

The sticking materials obtained after the experiments at static condition and when rotation was at 20rpm speed have been analyzed for the average contents of *Na, Fe* and *Cu* elements. The table below gives this result,

	wt%Na	*wt%Fe*	*wt%Cu*
0 rpm:	11.69	49.67	10.37
20 rpm:	10.58	48.22	20.17

It is quite obvious that this material sticking to the copper cylinder contains mainly iron. But *Na* and *Cu* contents are less that those in the matte phase. This suggests that the sticking material hindered the reaction by resisting the mass transfer of *FeS* from liquid phase to the vicinity of the unreacted solid copper, and may explain that the rotation speed of copper cylinder has no significant effect on the dissolution rate.

Attempts are underway to determine the concentration profiles of *S, Na, Fe* and *Cu* along the radius direction from the boundary of the unreacted solid copper to the edge of the sticking material by SEM.

In addition, Fig.5(c) shows clearly a quite uniform erosion of solid copper cylinder when it is rotated during the experiments. Under the static condition, there is less dissolution of copper at the bottom which suggests non-uniform distribution of the liquid matte composition along the copper cylinder.

FUTURE WORK

Future work will be concentrated on the following experiments:

- dissolution rate as a function of initial matte composition;
- dissolution rate and the equilibrium Cu_2S concentration in matte as a function of temperature;
- understand the reaction mechanism better and solve relevant problems.

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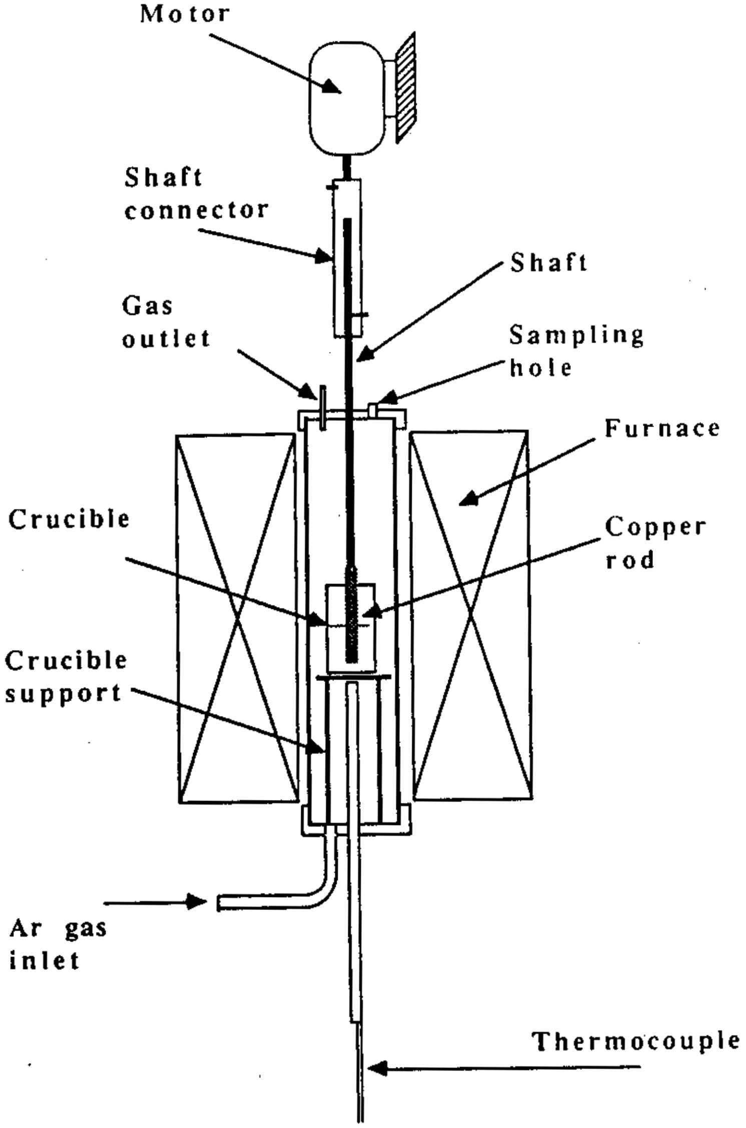


Fig.1 Experimental apparatus for testing the dissolution rate of solid copper into liquid FeS-Na_2S matte

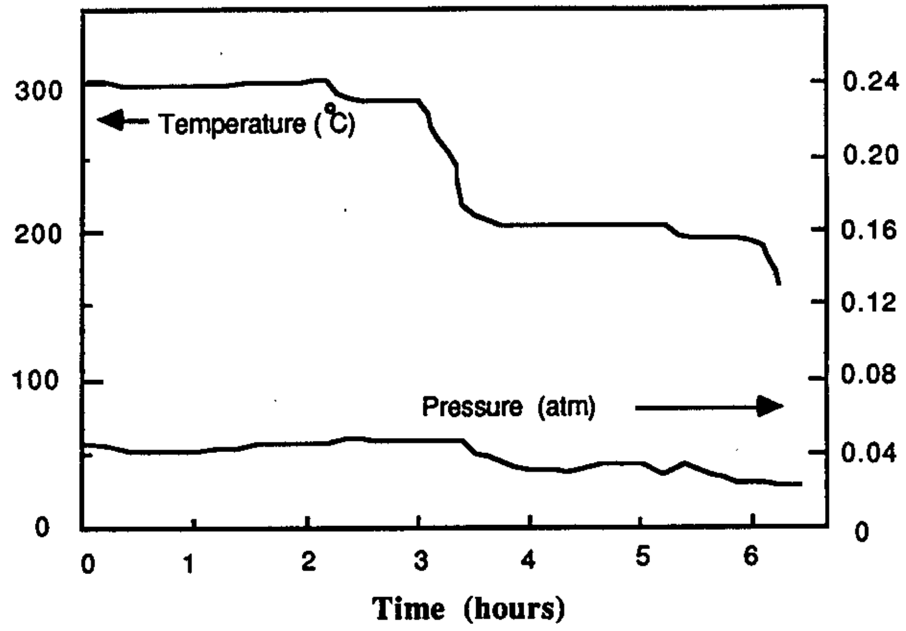


Fig.2 Operation parameters for Na_2S dehydration

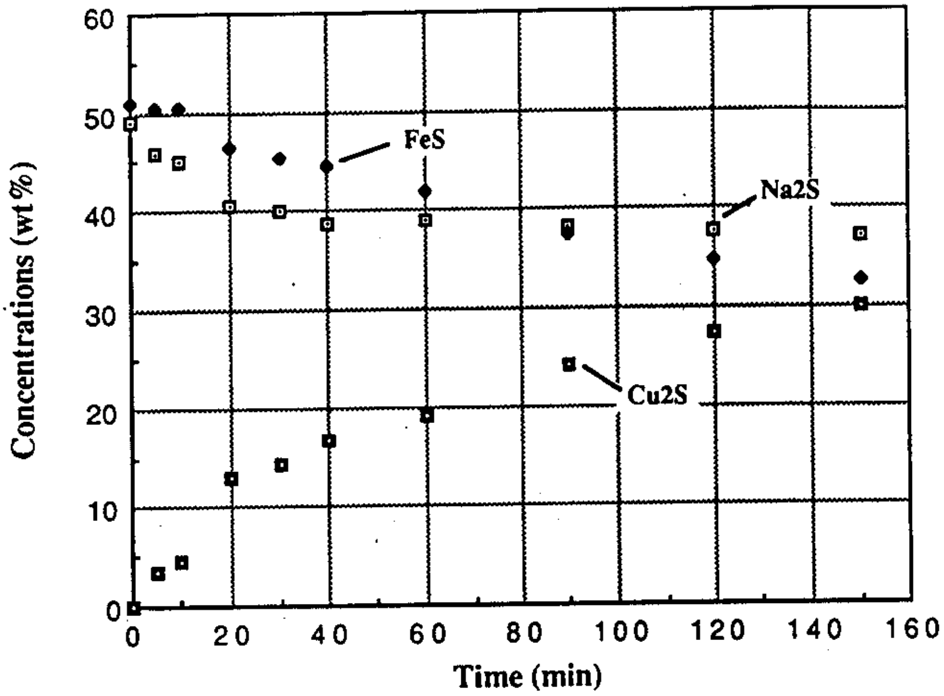


Fig.3 Solid copper dissolution rate as a function of time

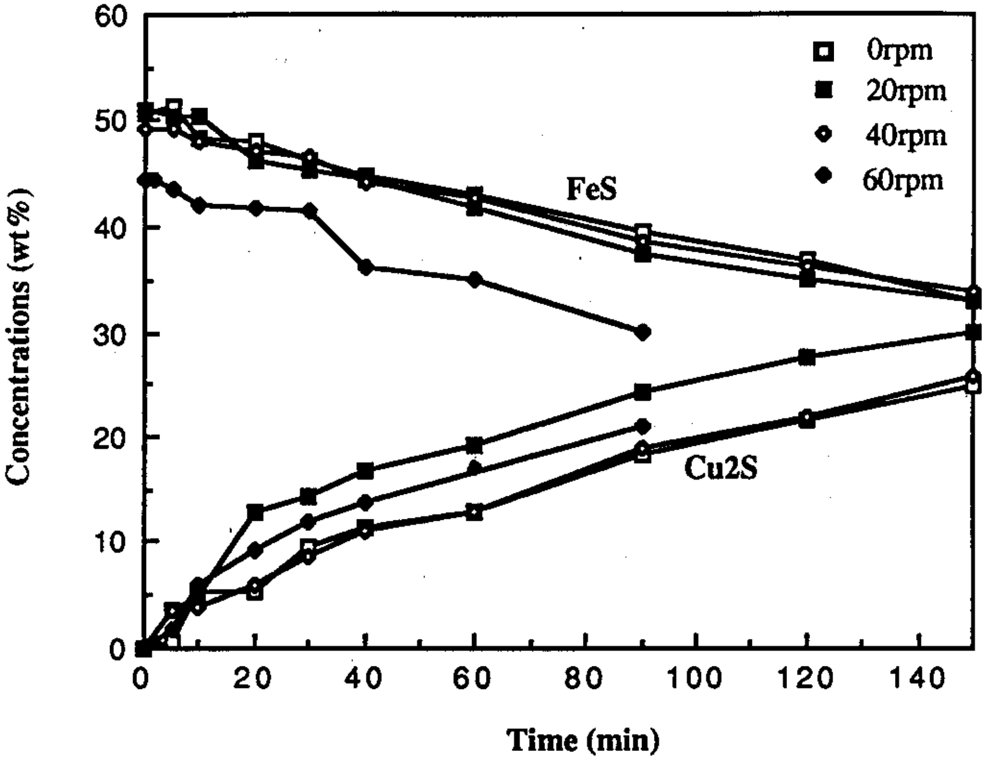
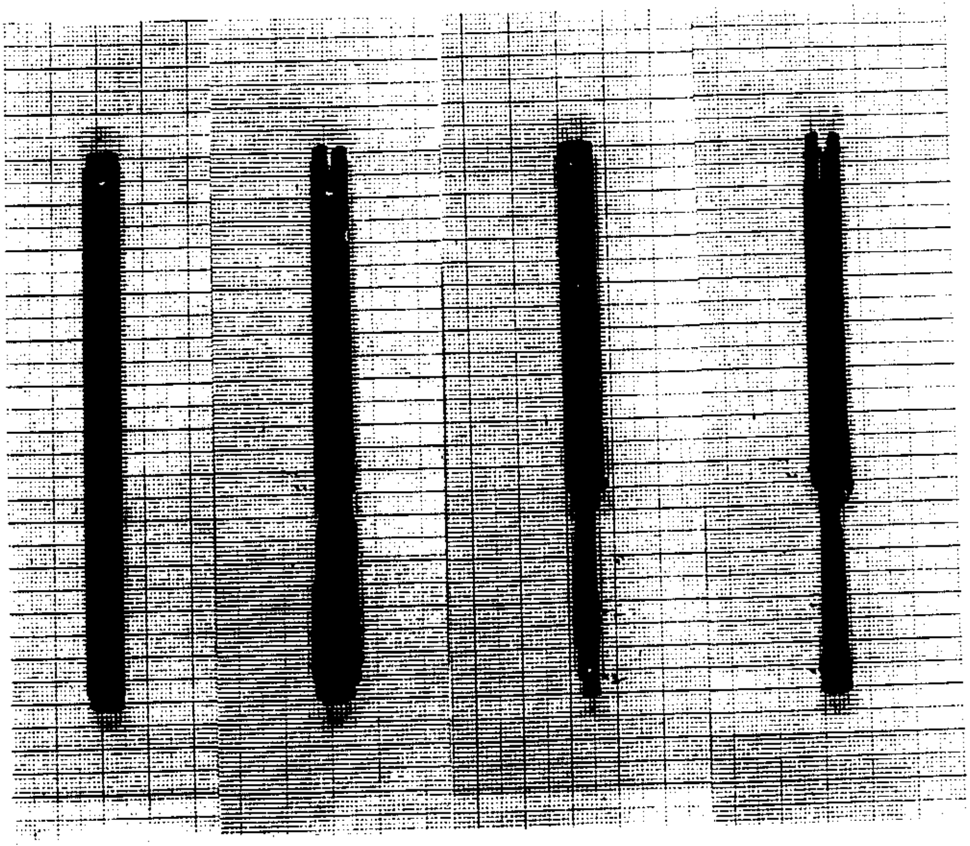


Fig.4 Effect of copper cylinder rotation speed on reaction rate



(a) (b) (c) (d)

a: copper cylinder before reaction

b: reacted portion covered by a half-molten material

c: quite uniform erosion of copper along the reacted region

d: reacted under static condition

Fig.5 Preliminary observations on the reaction mechanism

CISR PROGRESS REPORT

Fundamentals of Decopperization from Solid Scrap

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R. J. Fruehan, Professor

April 10, 1990

INTRODUCTION

Steel can become contaminated by a number of non-ferrous metals which are present in the various forms of scraps. Copper is a common contaminant and causes detrimental effects on certain steel product properties. As conventional steelmaking processes cannot remove copper, researchers, worldwide, are seeking a process to remove copper from steel scrap. At CMU, a process by which the steel scrap is treated at 1000°C with a FeS-Na_2S matte to remove copper is under investigation.

Previous studies of the mechanism of removing copper from solid scrap using FeS-Na_2S sulfide matte[1,2,3] have highlighted the following facts:

- only about 10 kilograms of matte are needed to treat one tonne of scrap, which is advantageous economically.
- there is no need for carburization-decarburization or extensive desulfurization.

At temperatures greater than 670°C, Cu_2S is more stable that FeS. Thus copper will exchange with iron if in contact with iron sulfide. The addition of Na_2S to FeS forms a liquid matte at temperatures even as low as 700°C and improves the thermodynamics of copper removal by decreasing the activity coefficient of Cu_2S in the matte. Thus FeS-Na_2S mattes should react with solid copper.

The objective of this study is to investigate the kinetics and mechanism of the dissolution of solid copper into a liquid FeS-Na_2S sulfide mattes and therefore improve understanding of solid scrap decoppperization and enhance large scale experimental optimization.

WORK TO DATE

To date the following work has been accomplished:

- Initial experiments were carried out using FeS-Na_2S (50g:50g) matte[4].
- A method of preparing anhydrous Na_2S by $Na_2S \cdot 9H_2O$ dehydration has been successfully developed.
- A preliminary study on the kinetics of the dissolution of solid copper into a liquid FeS-Na_2S matte has been completed. This includes the development of a theoretical model and experiments of the dissolution rate as a function of copper rotation speed.
- Experiments on the equilibrium concentration of copper in the FeS-Na_2S(75g:25g) matte have been carried out.
- SEM and microscopic observations have been used to study the mechanism of the process of solid copper dissolution into liquid matte.

EXPERIMENTAL

Fig.1 shows the experimental set-up. A graphite crucible 3*cm* in inner diameter and 9*cm* in height is placed into the furnace. 100 grams of FeS-Na_2S mixture are charged into the crucible through a graphite funnel. A speed adjustable motor is mounted above the furnace. The commercial grade copper cylinder, 15*cm* in length and about 1*cm* inner diameter, is rotated in the melted matte by a motor. The shaft connector between the motor and the shaft, which is attached to the copper cylinder, helps lower the copper cylinder and start the reaction precisely at zero time. Argon gas is introduced at a flow rate of 2.5*l/min* from the beginning of the experiment. During each run, matte samples are taken as a function of time. Then they are kept in an air-pumped desiccator before being dissolved by nitric acid (50 percent in volume). *Na*, *Fe* and *Cu* are analyzed by the atomic absorption method.

RESULTS AND DISCUSSIONS

1. Kinetics of copper dissolution in matte

Conditions of the experiments are as follows:

- FeS-Na_2S=75g:25g
- copper cylinder diameter=10*mm*
- temperature=900°*C*

- rotation speed of copper cylinder=0, 30, 50, 60, 90, 150, 200*rpm*

The depth of liquid *FeS*-Na_2S was 5.5 cm in the crucible. Its density was approximately $3g/cm^3$. The copper cylinder was immersed into the liquid, or that 4.5-4.8 *cm* of the cylinder was in contact with the melt.

Fig.2 shows typical results of solid copper dissolution rate in the liquid matte *FeS*-Na_2S(75*g*:25*g*) as a function of time. Cu_2S content in matte increases as time increases. The higher the copper cylinder rotation speed, the faster the copper dissolution rate. Copper has a very high solubility in the liquid *FeS*-Na_2S matte. By rotating two pieces of copper cylinder (changing a second one after the first copper cylinder has worn out), the *Cu* concentration in matte was found to be 40%, which is equivalent to a 50% Cu_2S content in matte in case that there is minimal solubility in matte. In another experiment, *FeS*-Na_2S (6*g*:2*g*) matte was melted in a copper crucible at 900°C for 16 hours. Final *Cu* content in liquid matte phase was 37%, which corresponds to a Cu_2S content of about 46%.

Fig.3 gives the variation of *FeS* and Na_2S concentrations in matte as a function of time. *FeS* content in matte decreases as time increases. According to mass balance, weight percent of Na_2S in matte decreases mainly because the dilution effect as *FeS* is replaced by Cu_2S in matte.

Theoretically, supposing that the dissolution rate of solid copper is controlled by mass transfer of *Cu* in liquid matte phase, we would have the following expression:

$$\frac{d[\%Cu]}{dt} = \frac{2\pi rl}{V} k_d ([\%Cu]^* - [\%Cu]) \qquad (1)$$

At zero time, copper content in liquid matte phase is zero and the mass transfer coefficient k_d can be solved by

$$\left.\frac{d[\%Cu]}{dt}\right|_{t=0} = \frac{2\pi r_0 l}{V} k_d [\%Cu]^* \qquad (2)$$

If copper dissolution is controlled by mass transfer of *Cu* in liquid matte phase, k_d calculated above should obey the relationship that[5]

$$k_d = 0.0791 (Re)^{-0.30} (Sc)^{-0.644} \qquad (3)$$

In case that the initial diameter of the copper cylinder is the same in each experiment,

$$k_d = A \cdot u^{0.7} \qquad (4)$$

where A is a constant,

$$A = 0.0791 \left[\frac{2r_0}{\nu}\right]^{-0.30} (Sc)^{-0.644}$$

Fig.4 shows the relationship of the calculated k_d from Eq.(2) with the rotation speed of the copper cylinder assuming mass transfer control mechanism. Thus this relationship is consistent with the theoretical relationship of mass transfer control mechanism when the rotation speed is greater that 90 *rpm*. At lower rotation speeds, mass transfer of *Cu* in liquid matte is not the rate limiting step. When using higher Na_2S content (50%) in matte, the results of low rotation speed (even at 60*rpm*) were observed to have even larger deviation from mass transfer control mechanism as shown in Fig.5.

Fig.6 shows the typical observations of the reacted copper cylinder. At lower rotation speeds, the reacted portion of the copper cylinder was covered by a layer of half-molten material (Fig.6b), this formed a barrier for mass transfer and thus hindered the reaction. But at higher rotation speed, the sticking layer did not form around the copper cylinder and was found to settle to the bottom of the crucible. Thus under high rotation speeds, there exists a very clear interface between the liquid matte and the solid copper (Fig.6c). In addition, when a higher Na_2S content is used, a more stable sticking layer around the copper cylinder is formed and thus retards the reaction rate.

Eq(1) can also be integrated over time. From mass balance, it can be estimated that,

$$r^2 = r_0^2 - \frac{[\%Cu]\ W_{matte}}{\pi\ \rho_{Cu}\ l} \tag{5}$$

Then we have,

$$-\frac{V}{\pi l\sqrt{a - r_0^2}}\ arctg\left[\frac{\sqrt{r_0^2 - aX}}{\sqrt{a - r_0^2}}\right] = k_d t + C \tag{6}$$

where,

$$X = \frac{[\%Cu]}{[\%Cu]^*}\ ;$$

$$a \doteq \frac{W_{matte}[\%Cu]^*}{\pi\ \rho_{Cu}\ l}\ ;$$

$$C = -\frac{V}{\pi l\sqrt{a - r_0^2}}$$

Fig.7 and Fig.8 show the plots of the left hand side (LHS) of Eq.(6) as the function of time. It is obvious that at higher rotation speed, good linear relationship holds between LHS and time. The slop of each line is the value of k_d. Table.1 compares the mass transfer coefficient of *Cu* in liquid matte phase estimated by Eq.(2), Eq.(6) and the theoretical value. The theoretical k_d was calculated by Eq.(3), where the diffusivity of *Cu* in matte was estimated by Sutherland equation,

$$D = \frac{KT}{4\pi r_i \mu} \tag{7}$$

Fig.9 shows the comparison of experimental and the calculated *Cu* content in matte as a function of time. They agree well at higher rotation speeds and the data can be calculated for alter conditions, if necessary.

2. Investigation on Reaction Mechanism

In large scale decopperization operation, scrap and liquid matte are rotated together in a kiln. The relative velocity between liquid and solid phases is low. Therefore, an understanding of the reaction mechanism at low copper cylinder rotation speed will aid in the understanding of the exact mechanism of decopperization of scrap.

Phase analyses by SEM, microscopic observation and X-ray diffraction have been carried out to determine where the various phases occur in the matte and at the matte/copper interface.

Fig.10 shows a general view of a cross-section of the sticking material formed around the copper cylinder in a static experiment (rotation speed = 0*rpm*). The unreacted copper cylinder has a very smooth surface. The sticking material is about 2*mm* thick. It is composed of the stratified precipitate and sulfide matte which was enclosed within layers of the precipitate. As the copper cylinder being dissolved, the sticking material gets thicker but does not grow outwards.

Fig.11(a) is a back-scattered electron image of a magnified field showing the precipitate phase. Distributions of *Fe, S, Cu* and *Na* elements were examined by X-ray mapping [Fig.11(b,c,d and e)]. The precipitate was found to be metallic iron.

Small pieces of copper were found in the vicinity of the copper cylinder. Fig.12(a) shows a very small copper piece with an irregular shape which was found in the matte phase of the sticking material. Fig.12(b) and (c) show the distribution of *Cu* and *S* in the field of observation.

It was also found that inside the solid copper cylinder, a thin layer of copper sulfide was formed (about 0.5*mm* from the interface). Fig.11(a) shows the foreign phase inside the near-interface region of the solid copper cylinder. Fig.13(b) and (c) show distributions of *S* and *Cu* elements. This suggests that sulfur may have diffused into the solid copper cylinder, although the details of this need further investigation.

Once the major phases in the system were identified, optical observations were made. Special efforts were taken during preparation of the specimen to prevent sample degradation as the sulfide absorbs water from the atmosphere.

From Fig.14 it can be seen that Fe^0 did not nucleate very close to the copper cylinder, but at a small distance (about 0.2-0.3*mm*) away from it. Close to the cylinder, there is much less *Fe* nucleation, while copper with a relatively small size distribution can be found. Fig.15 shows some detailed observations at the interface between the copper cylinder and the matte phase in the sticking material. There is evidence that small copper pieces break off from the copper cylinder in these observations.

Fig.16(a) and (b) show the morphology of the copper sulfide phase in the copper cylinder in two dimensions. Its shape is much like that of a thin scale. It is believed that the formation of this copper sulfide phase inside the copper cylinder caused small copper pieces break off from it.

Fig.17 shows the observations on the matte phase (cooled in air) at a horizontal cross-section of the crucible. Fig.17(a) shows the matte phase, its morphology was formed depending on the cooling direction. Fig.17(b) was taken at a higher magnification. Metallic iron inclusions were scattered in the matte. These Fe^0 inclusions are considered to precipitate during solidification or as a result of reaction in solid state[6]. Therefore it is reasonable to assume that there is no Fe^0 or Cu^0 in bulk matte phase in chemical analysis.

SUMMARY

1. At low copper cylinder rotation speed, a layer of half-molten sticking material was formed around

the unreacted copper rod in place of the reacted copper. In this case, reaction mechanism was found to be complicated. At high copper cylinder rotation speed, the precipitate settled to the bottom of the crucible and there existed a clear interface between solid copper and liquid matte. It has been found that the mass transfer of *Cu* in matte phase (from interface to bulk region) is the rate-controlling step. Mass transfer coefficient of *Cu* in matte was evaluated.

2. At 900°C, equilibrium content of *Cu* in liquid $FeS\text{-}Na_2S\text{-}(Cu_2S)$ phase would be up to 37-40%. Equilibrium experiments showed no significant *Na* evaporation.

3. A theoretical expression for copper dissolution from a rotating copper cylinder into the liquid matte was proposed based on that mass transfer of *Cu* in liquid matte is the rate-controlling step. The calculated results can explain the experimental ones of higher copper cylinder rotation speed.

4. SEM X-ray mapping method was used and metallic *Fe, Cu* phases in the sticking material and copper sulfide phase in the solid copper cylinder have been identified.

At the static condition, layers of solid metallic iron precipitates around the copper rod and encloses very thin layers of sulfide matte, and therefore sticks to the copper cylinder firmly and forms a barrier for mass transfer.

Reaction mechanism is very complicated. Interfacial reaction between solid copper and matte needs further study. And it is obvious that *S* diffuses into the solid *Cu* forming copper sulfide and breaks small pieces of solid copper into matte so that the kinetics of the process is enhanced.

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APPENDIX

Derivation of Eq.(6)

In Eq.(1) the radius of the copper cylinder is also a function of time as it is being dissolved. Eq.(5) gives the estimation of r related to the copper content in matte $[\%Cu]$, while assuming that the total matte weight and the immersion depth of the cylinder do not change. Let

$$X = \frac{[\%Cu]}{[\%Cu]^*} ; \tag{8}$$

$$a = \frac{W_{matte}[\%Cu]^*}{\pi\ \rho_{Cu}\ l} \tag{9}$$

Then,

$$r = \sqrt{r_0^2 - aX} \tag{10}$$

Substituting Eq.(8) and Eq.(10) to Eq.(1), it is obtained that

$$\frac{dX}{dt} = \frac{2\pi l}{V}\ k_d\ (1 - X)\ \sqrt{r_0^2 - aX} \tag{11}$$

By separating variables and integrating both sides of Eq.(11) with the assumption that V,l and a are constants, Eq.(6) can be obtained.

MAJOR SYMBOLS

$[\%Cu]$,$[\%Cu]^*$: copper content in matte and equilibrium copper content in matte;

D: diffusivity of copper element in liquid matte phase, cm^2/s;

K: Boltzmann's constant;

k_d: Mass transfer coefficient, cm/s;

l: length of copper cylinder immersed into the liquid matte, cm;

r: radius of the copper cylinder, cm;

r_0: radius of the original copper cylinder before reaction, cm;

r_i: radius of the Cu^+ ion, $\mathring{A}$;

T: temperature, K;

t: time, s;

u: linear velocity of copper cylinder, cm/s;

V: total volume of liquid matte phase, cm^3;

W_{matte}: weight of liquid matte, g;

μ: viscosity of liquid matte, $g/cm{\cdot}s$;

ν: dynamic viscosity of liquid matte, cm^2/s;

ρ_{Cu}: density of solid copper, g/cm^3.

Table.1 comparison of mass transfer coefficients by different estimations

exp. no.	rev. speed (rpm)	eq.(2) kd ($\times 10^{-3}$)	eq.(6) kd ($\times 10^{-3}$)	eq.(3) kd ($\times 10^{-3}$)
1	30	0.449	0.352	0.781
2	90	1.683	1.489	1.686
3	150	2.412	2.134	2.410
4	200	3.002	2.947	2.948

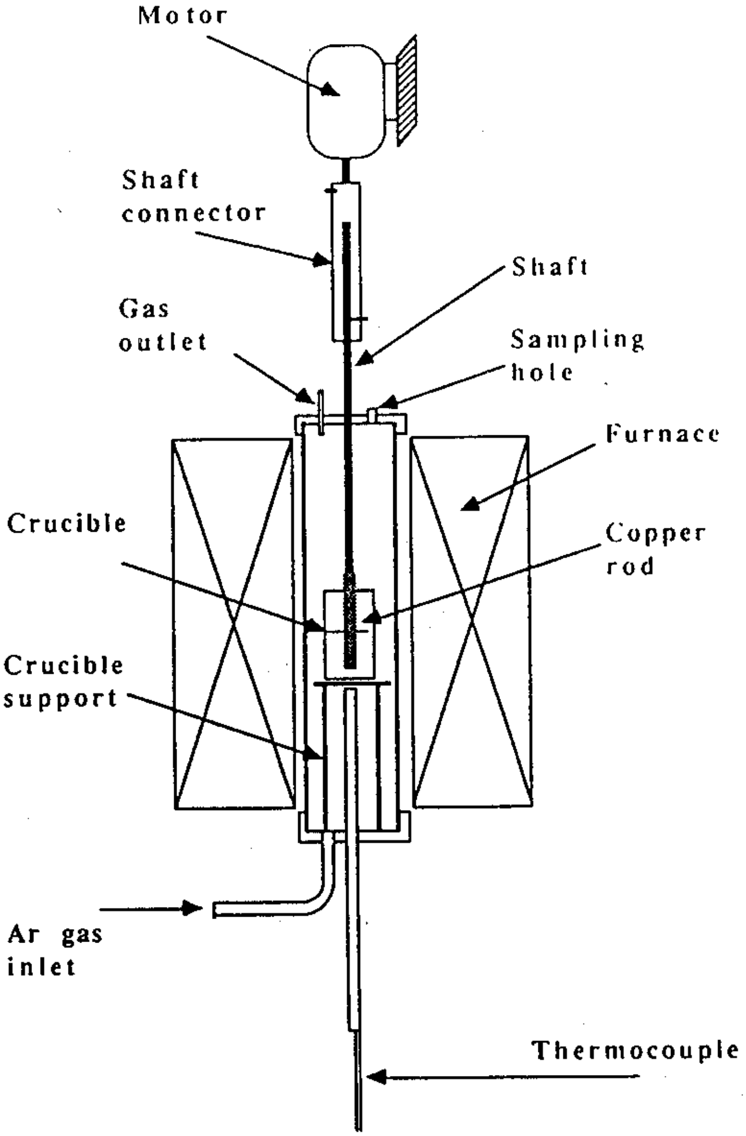


Fig.1 Experimental apparatus for testing the dissolution rate of solid copper into liquid $FeS-Na_2S$ matte

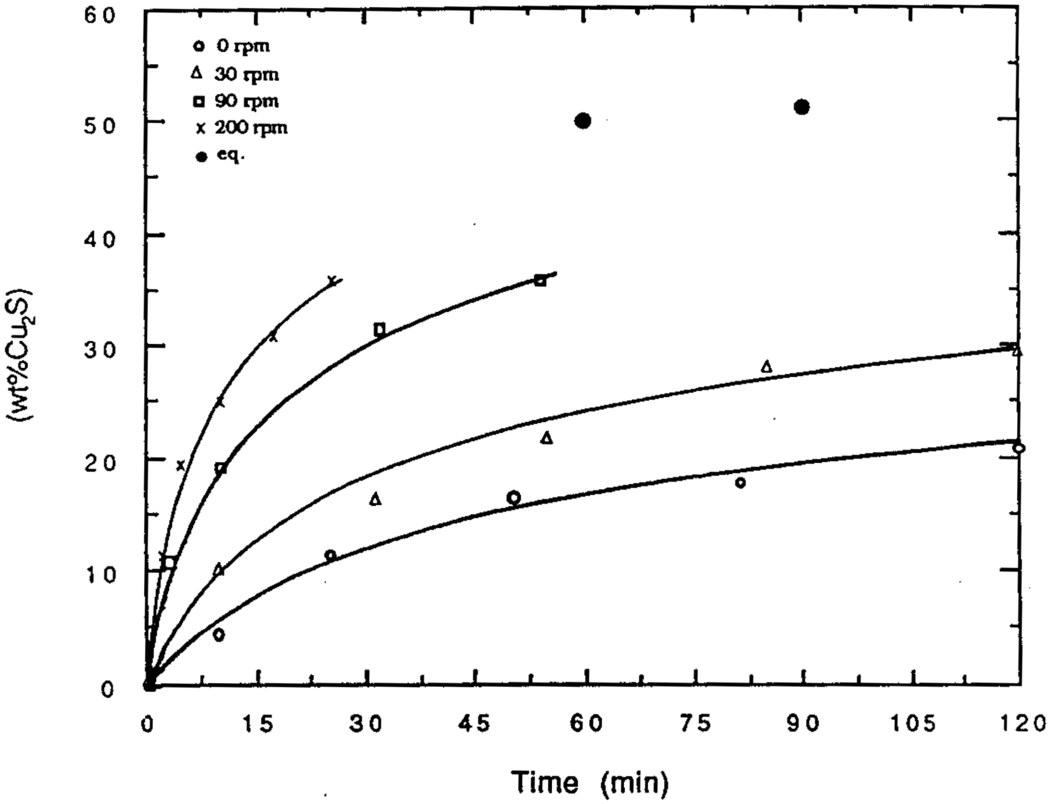


Fig.2 Concentration of Cu_2S in matte as a function of time.

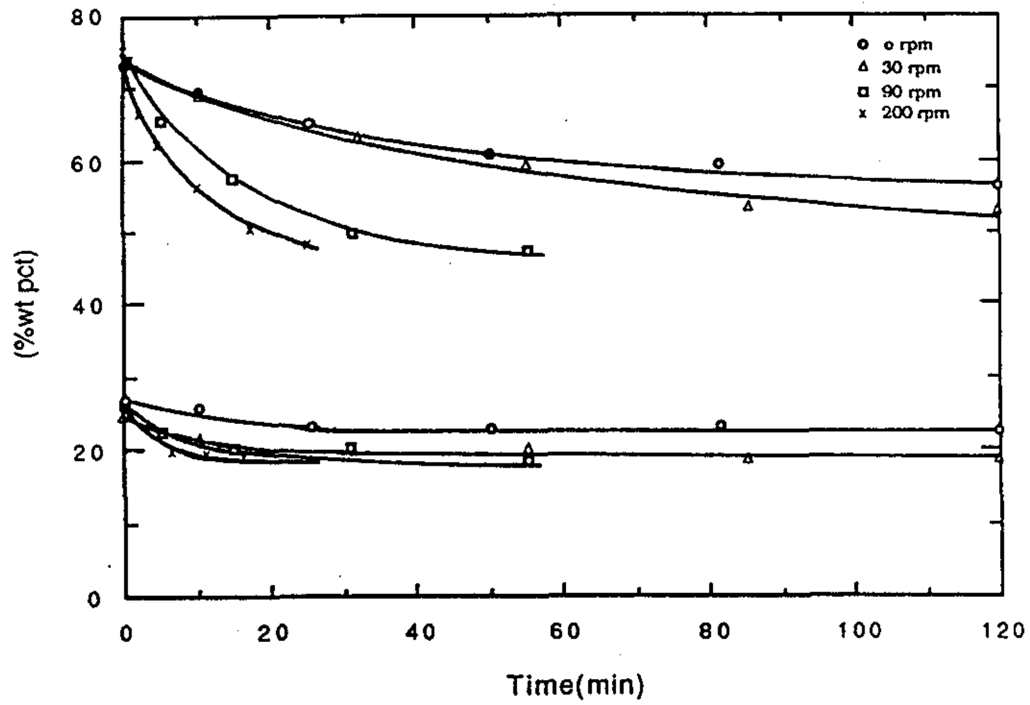


Fig.3 Concentrations of FeS and Na_2S in matte as a function of time.

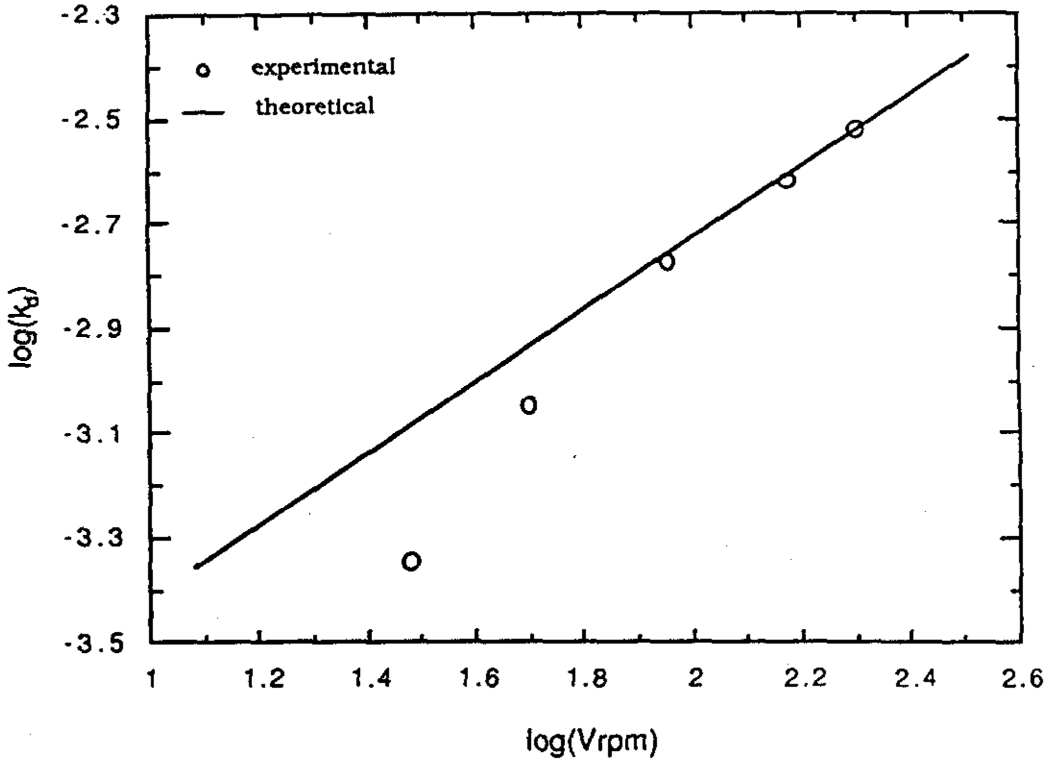


Fig.4 Comparison of the experimental results of the coefficient k_d assuming mass transfer control mechanism with the theoretical relationship $k_d = A \cdot u^{0.7}$.

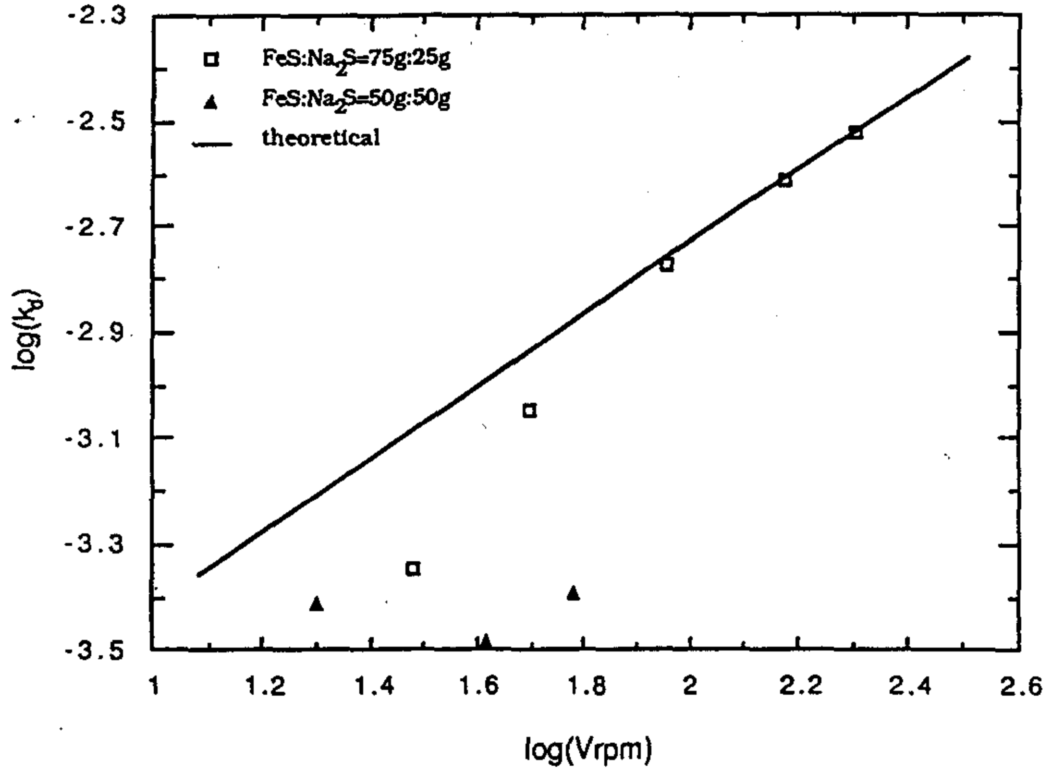
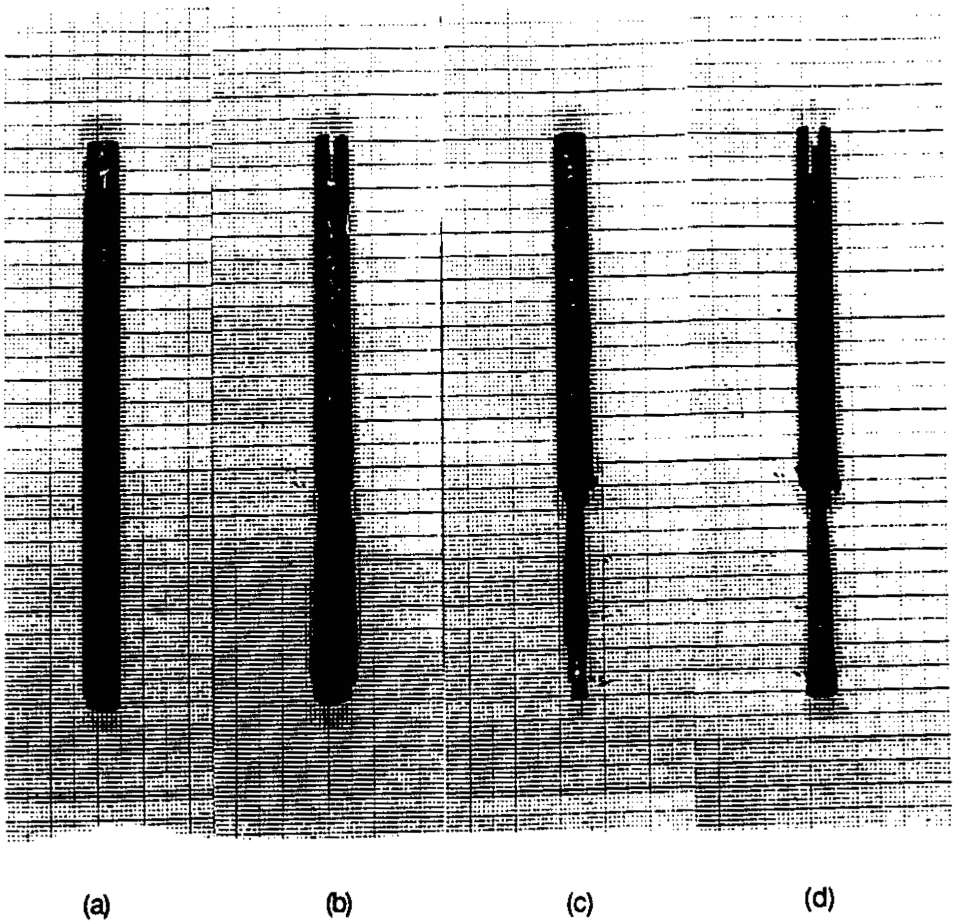


Fig.5 Observation on the reaction mechanism when using the matte with higher Na_2S content.



a: copper cylinder before reaction

b: reacted portion covered by a half-molten material

c: quite uniform erosion of copper along the reacted region

d: reacted under static condition

Fig.6 Preliminary observations on the reaction mechanism

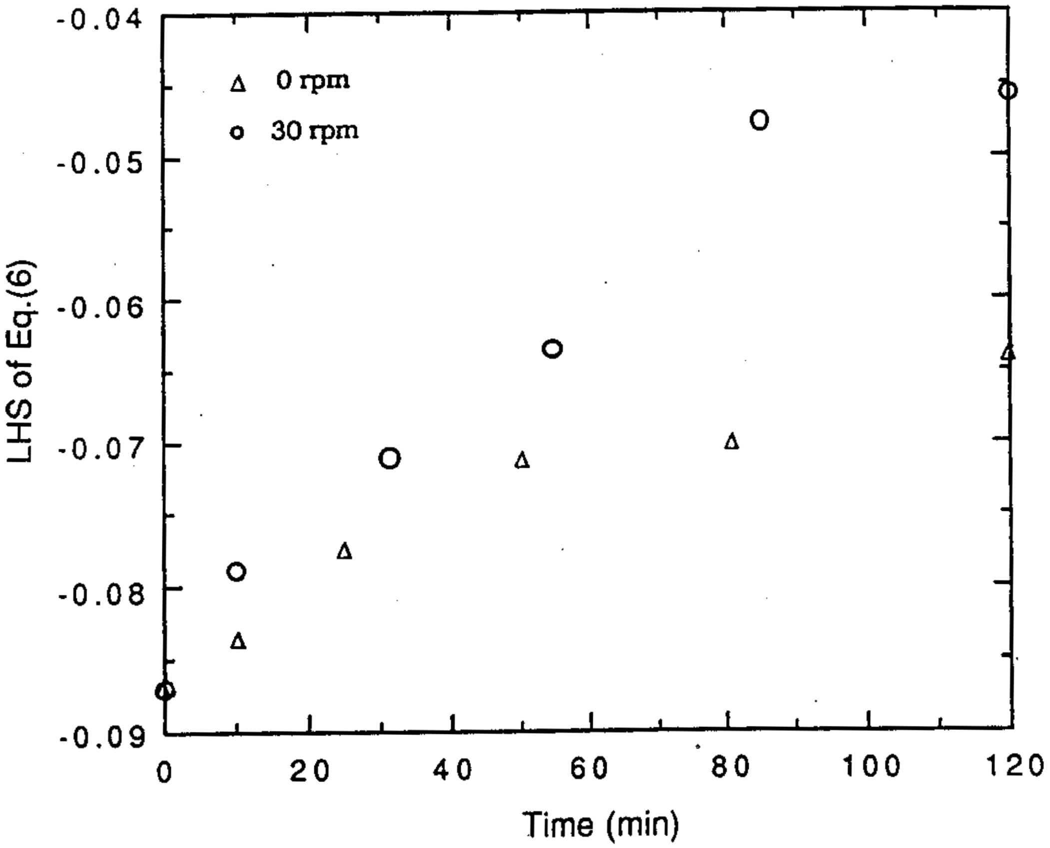


Fig.7 Plot of the left-hand side of eq.(6) as a function of time on the data of low revolution speed.

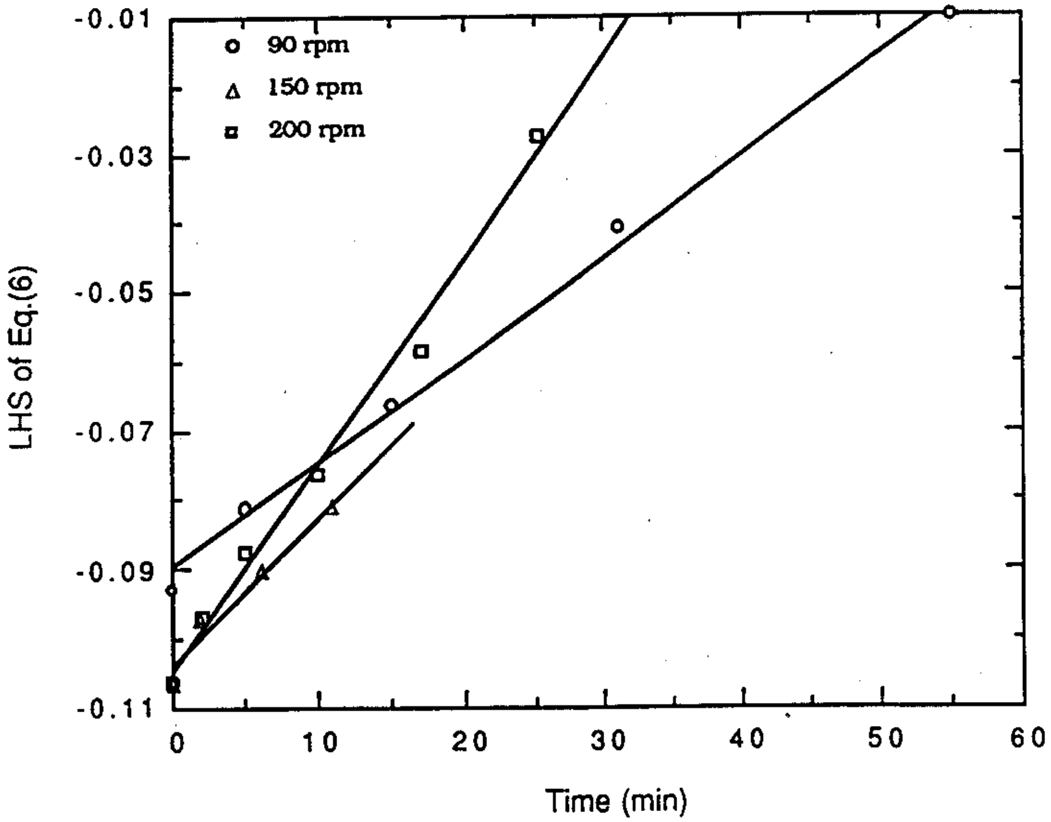


Fig.8 Plot of the left-hand side of eq.(6) as a function of time on the data of high revolution speed.

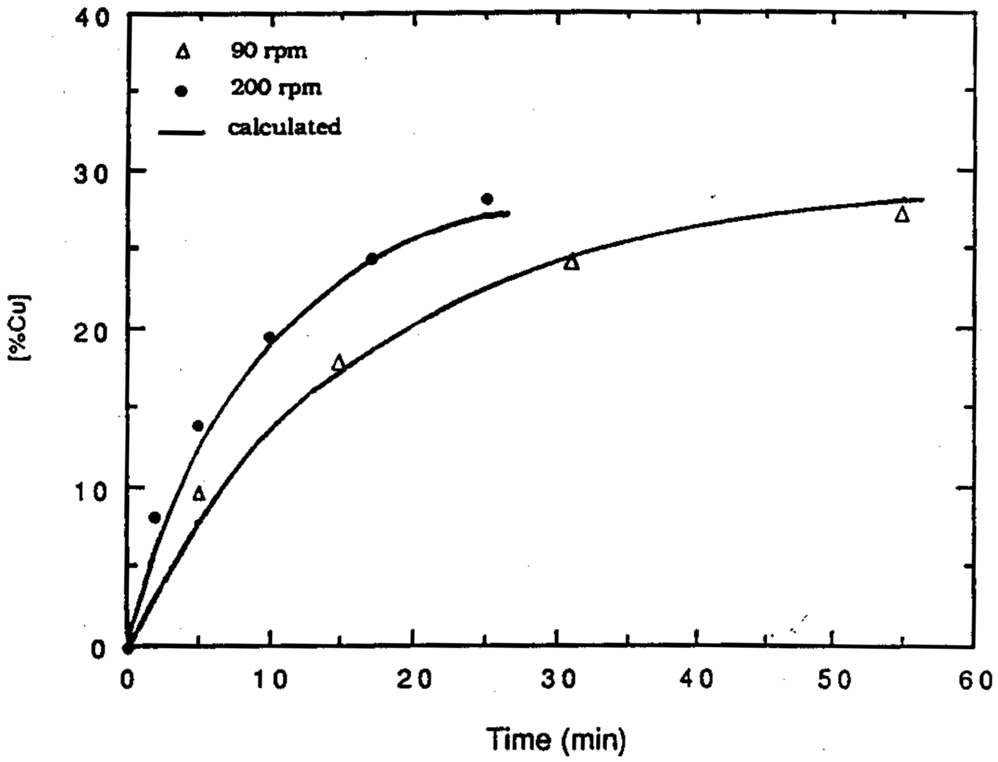


Fig.9 Comparison of experimental data with the calculated values.

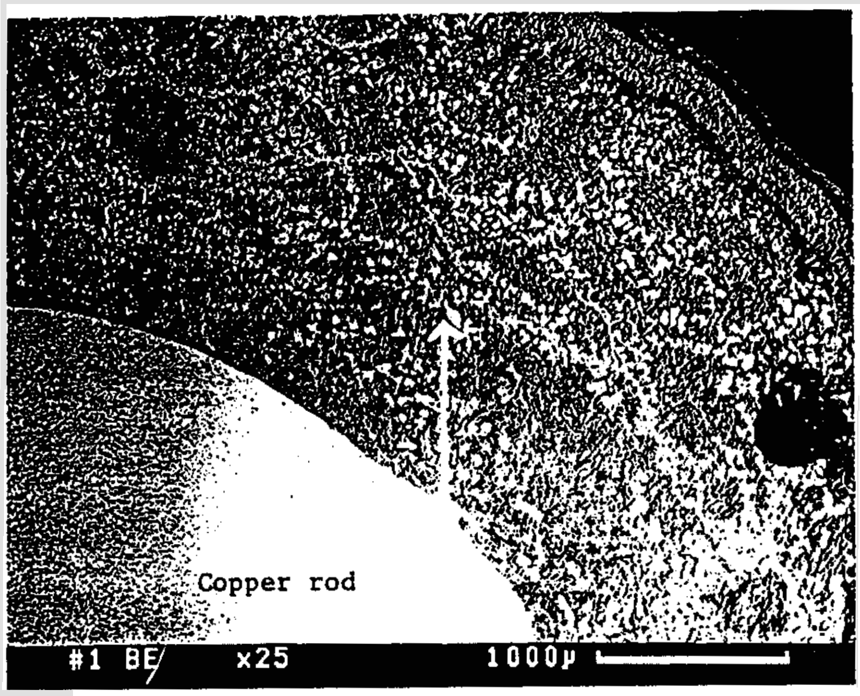


Fig.10 Sticking material around the unreacted copper cylinder
(the arrow points where the magnification of Fig.9 was taken)

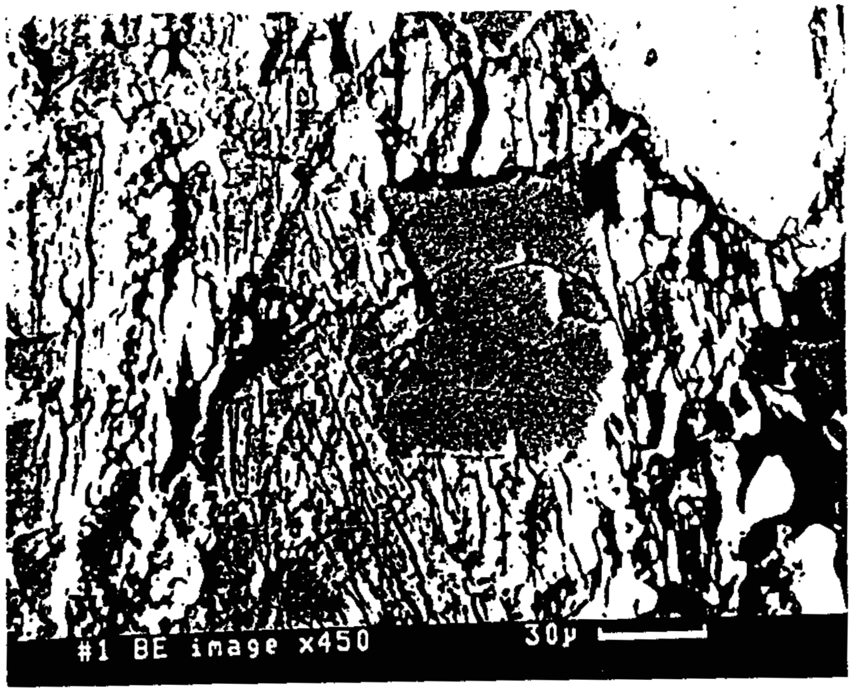


Fig.11(a) Back-scattered Electron image of a maginified field showing the precipitate phase

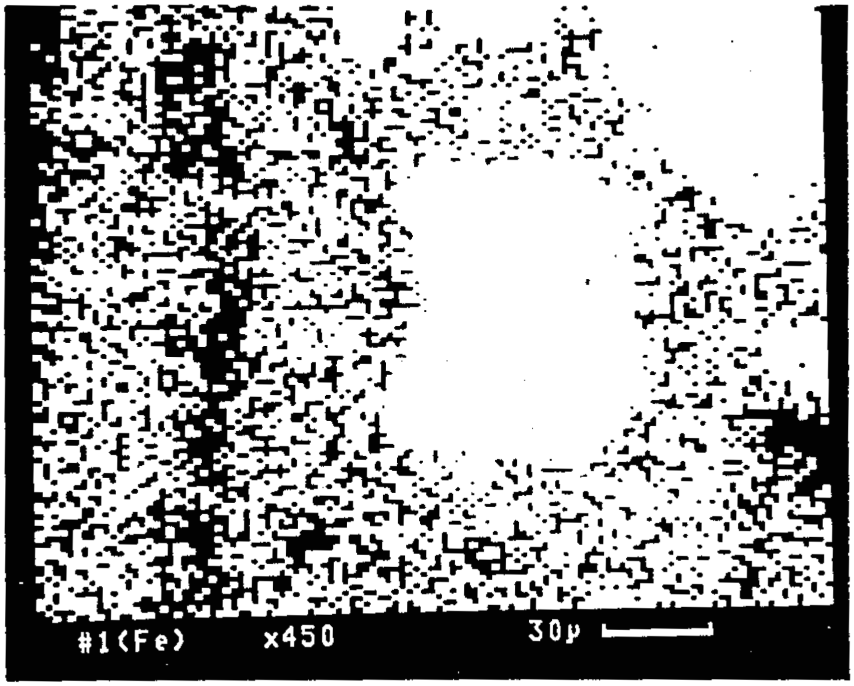


Fig.11(b) Distribution of Fe element by X-ray mapping

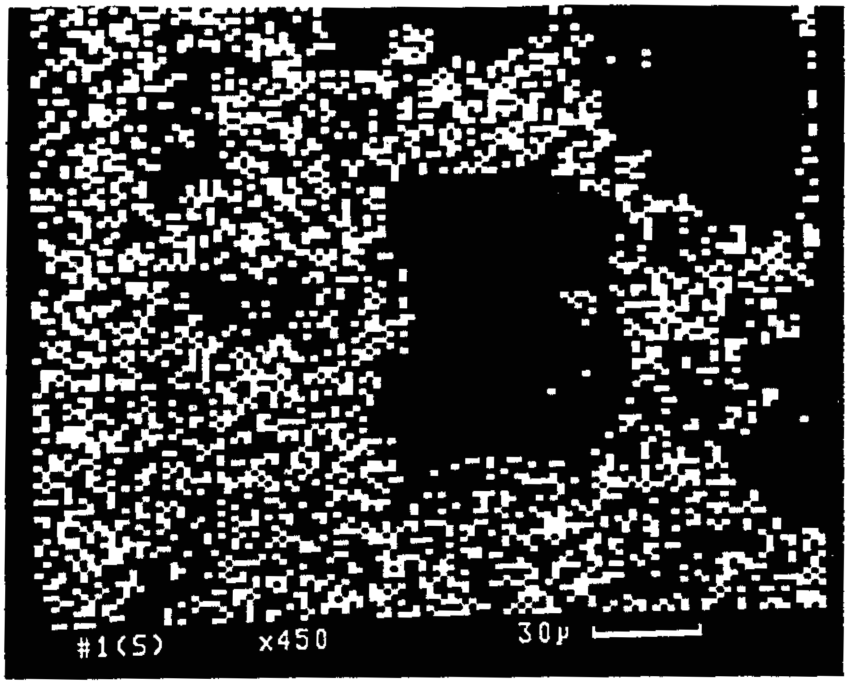


Fig.11(c) Distribution of S element by X-ray mapping

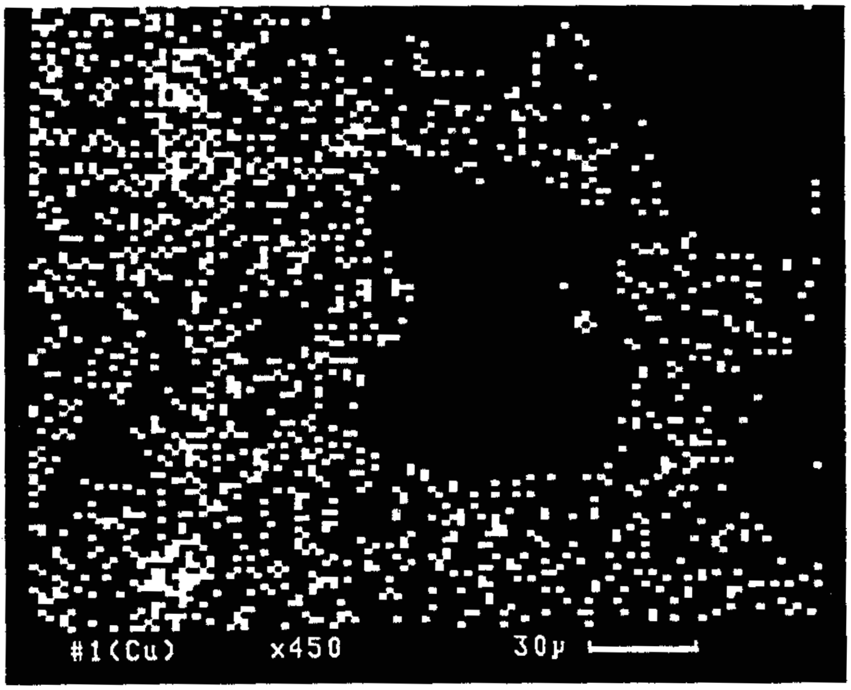


Fig.11(d) Distribution of Cu element by X-ray mapping

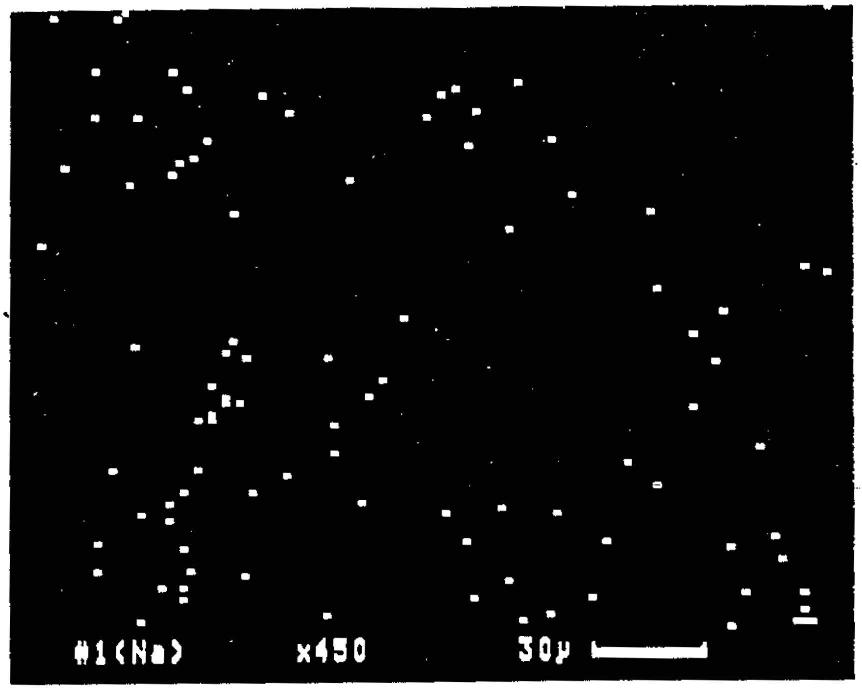


Fig11(e) Distribution of Na element by X-ray mapping

Fig. 12(a) Back-scattered Electron image of a piece of copper in the sticking material near the copper rod

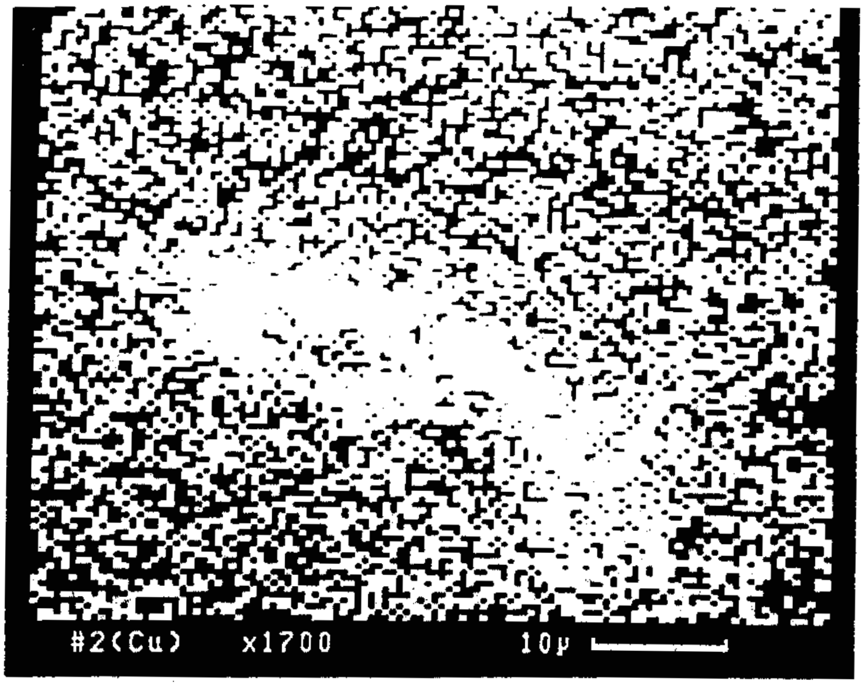


Fig.12(b) Distribution of Cu element by X-ray mapping

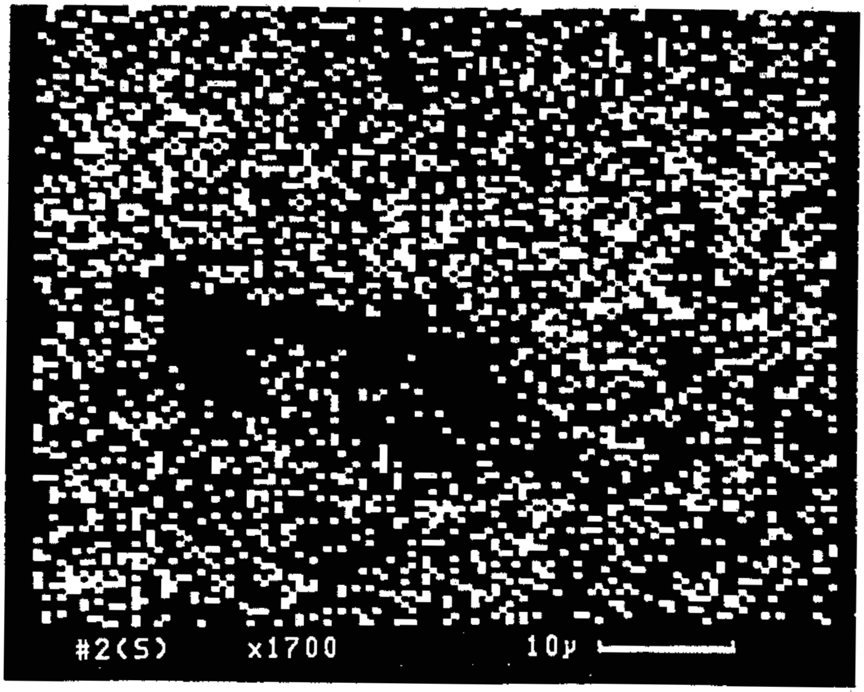


Fig.12(c) Distribution of S element by X-ray mapping

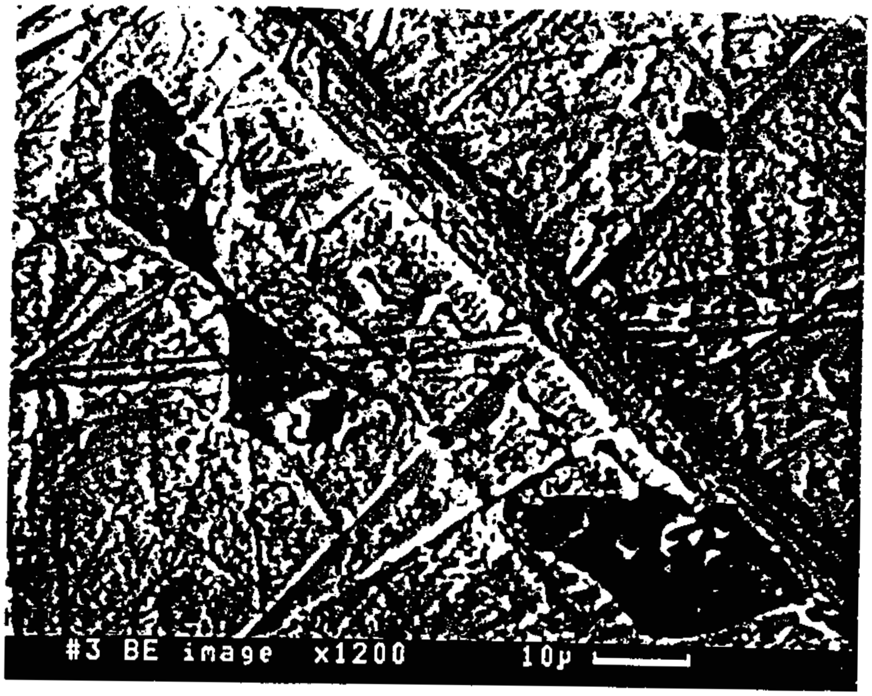


Fig.13(a) Back-scattered Electron image of copper sulfide phase in the boundary layer of copper rod

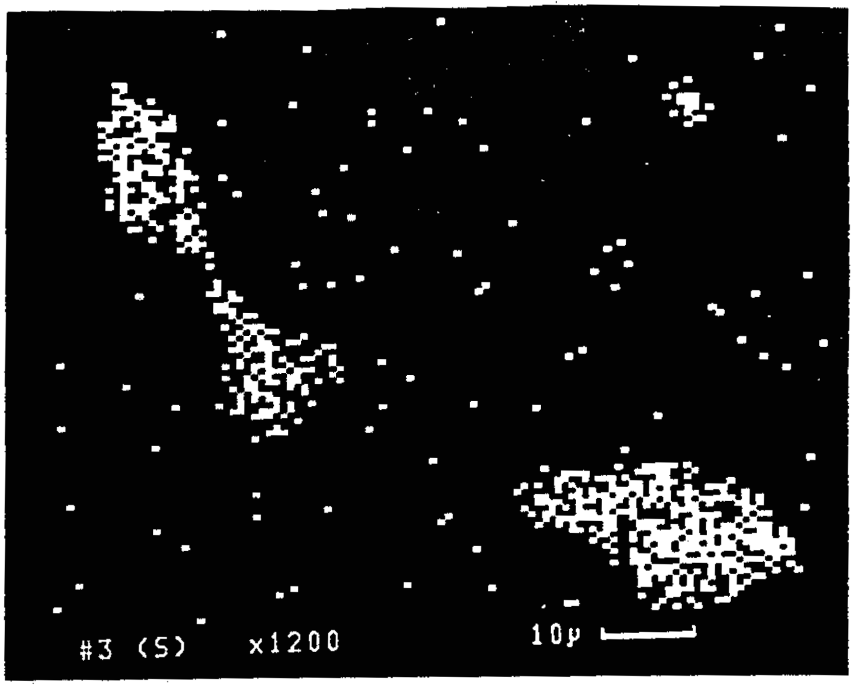


Fig.13(b) Distribution of S element by X-ray mapping

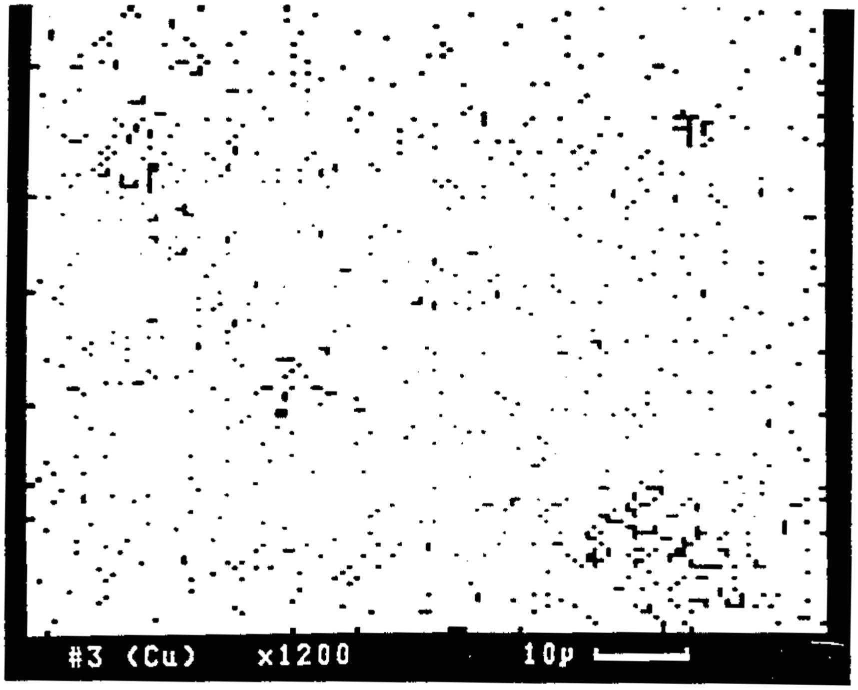
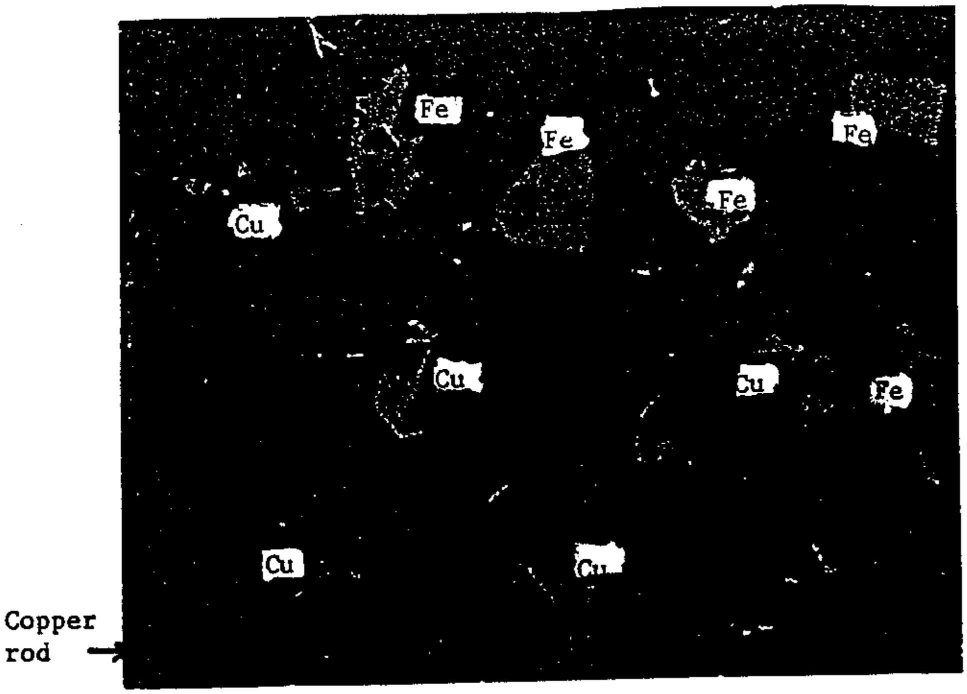
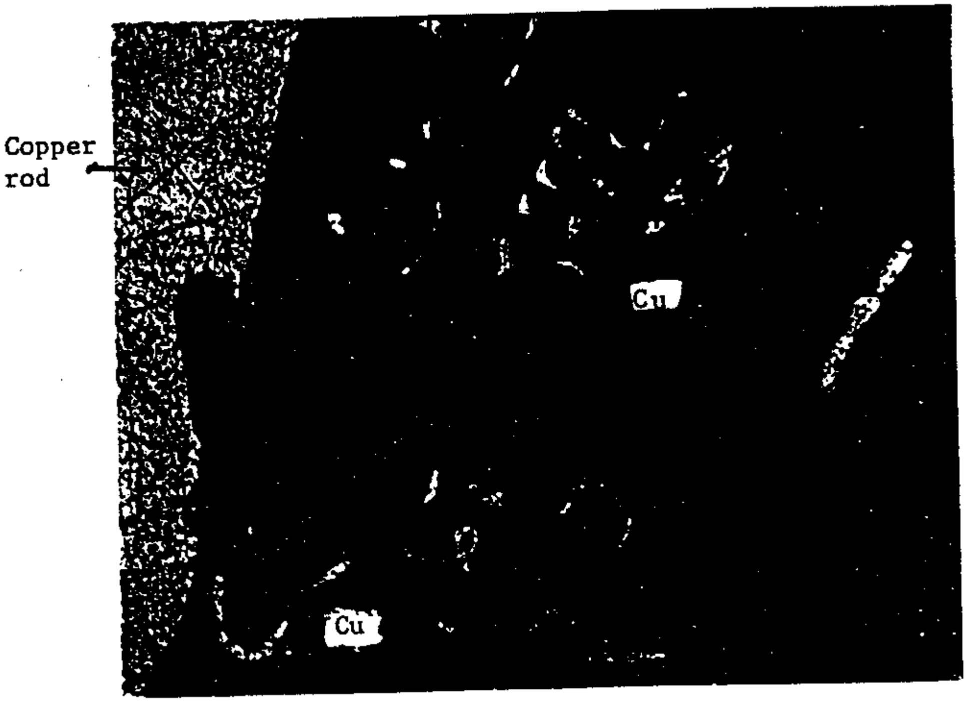


Fig.13(c) Distribution of Cu element by X-ray mapping

Fig.14 Fe nucleation around the copper cylinder (magnification 200x)



(a)



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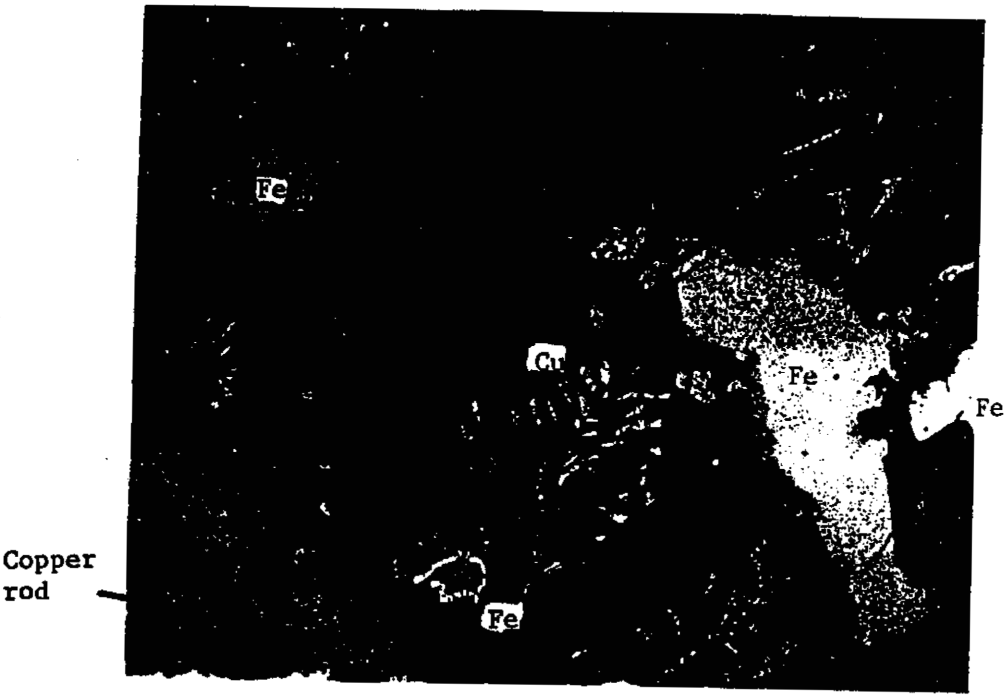


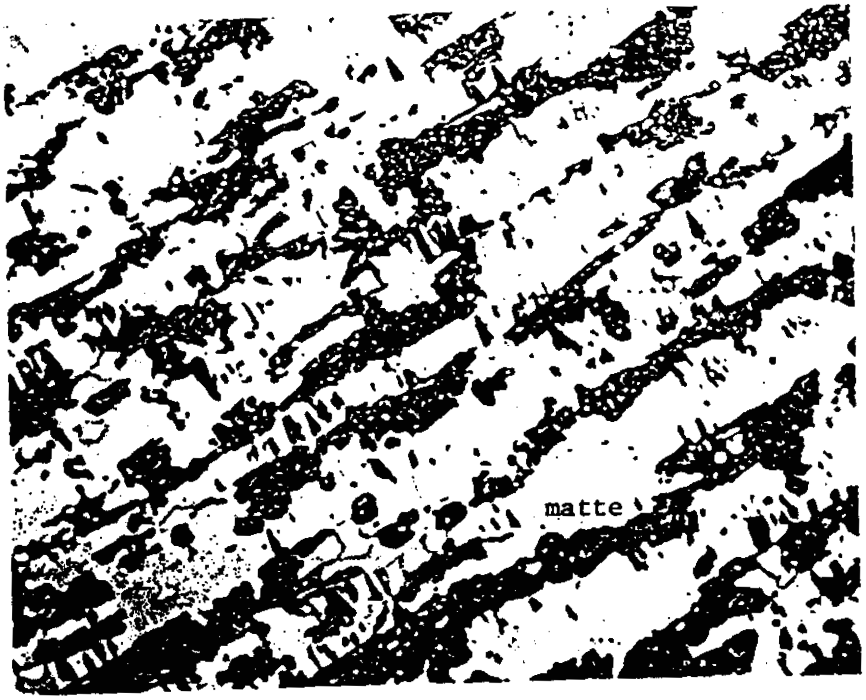
(c)

Fig.15 Typical conditions at the interface between the copper rod and the matte in the sticking material
(a) 500x (b) 1000x (c)500x

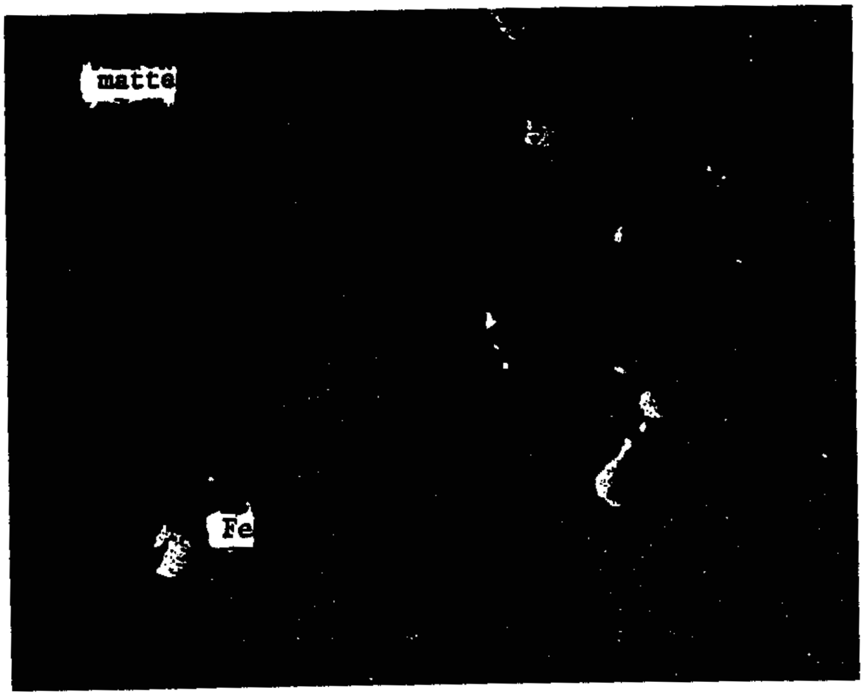
(a)

(b)

Fig.16 Formation of copper sulfide phase in the boundary layer of copper rod
(a) horizontal cross-section; 100x
(b) longitudinal cross-section; 200x



(a)



(b)

Fig.17 Microscopic observation on the matte phase
(a) horizontal cross-section of crucible;200x
(b) scattered small iron phase; 1000x