

THE REACTION OF SOLID COPPER WITH FeS-Na₂S MATTES

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ABSTRACT

Equilibrium and kinetic studies were carried out to determine the reaction mechanism and rate controlling steps in the reaction of copper with an FeS-Na₂S matte. At matte starting FeS contents greater than 75%, the reaction is controlled by mass transfer of copper in the liquid matte. Equilibrium levels of 50% Cu₂S by weight were measured after reaction of an 82% FeS starting matte composition with solid copper at 1000°C. The matte reacts first along the grain boundaries of the copper causing the release of small particles of copper which subsequently react with the matte. Iron particles precipitate in the matte close to the surface of the reacting copper. At starting matte compositions of 50% FeS and in static experiments, a viscous layer formed against the copper which impeded the reaction. Results of these studies were used to design a larger scale prepilot apparatus for the removal of copper from solid ferrous scrap. Results of these trials are briefly discussed.

Key words: steelmaking, copper, mattes, continuous casting, scrap

1. Introduction

Recently, there has been an interest in the removal of copper from ferrous scrap at low temperatures. Physical separation, acid treatment, dissolution with liquid aluminum and reaction with an FeS-Na₂S matte have all been discussed in the open literature [1-4]. The use of a liquid matte to separate solid copper from solid ferrous scrap was developed at Carnegie Mellon University [4] and the purpose of this paper is to document some fundamental studies on the kinetics of reaction of copper and a FeS-Na₂S matte and to review progress on this development to date.

2. Background

This process is based upon two fundamental principles: (1) copper can be transformed by chemical reaction from the solid state to a liquid sulphide, 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. The chemistry of the process is based upon the following reaction:



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 [5]; however, in this process, the reaction takes place at a much lower temperature while the scrap and copper are solid and separate.

At 1000°C the equilibrium constant of reaction 1 has a value of 5 and solid copper can reduce iron sulphide. The process can be initiated with a liquid matte containing a mixture of iron sulphide and sodium sulphide. As can be seen in Figure 1, the all 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.

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. 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 and the matte fluidity increases with 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 equilibrium constant for reaction 1 can be written as follows:

$$K = \frac{a_{\text{Fe}} a_{\text{Cu}_2\text{S}}}{a_{\text{Cu}}^2 a_{\text{FeS}}} \quad (2)$$

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 ($a_{\text{Cu}} = 1$) 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.

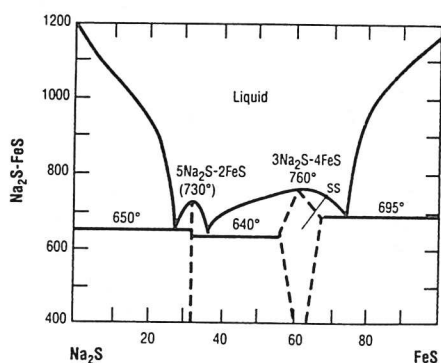


Figure 1: FeS-Na₂S Phase Diagram

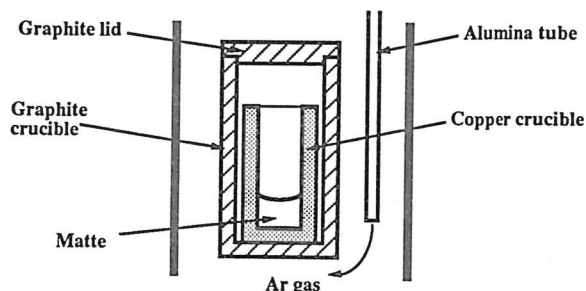


Figure 2: Experimental set-up for equilibrium experiments.

3. Laboratory Scale Experiments

Two laboratory scale experiments were carried out to better understand the reaction of copper with an FeS-Na₂S matte. The first was to determine the equilibrium Cu₂S content for starting matte compositions of 50, 75 and 82 % FeS and the second to determine the rate controlling mechanism in the reaction.

Equilibrium Cu₂S Contents

Equilibrium between solid copper and the liquid FeS-Na₂S-(Cu₂S) matte was investigated in the experimental set-up shown in Figure 2. The required temperature was maintained by a SiC resistance furnace. 8 grams of an FeS-Na₂S powder mixture was melted in a copper crucible (I.D. 1.7 cm, O.D. 2.5 cm and height 5.6 cm) and sealed in a graphite container. Argon gas was introduced into the system at a flow rate of 0.4 l/min. The system was equilibrated for 16-20 hours. Technical grade FeS was used and Na₂S was prepared in the laboratory by dehydration of Na₂S·9H₂O at a temperature of 300°C and under a reduced pressure which was less than 0.05 atm.

The experiments were carried out to obtain the equilibrium Cu₂S concentration in the FeS-Na₂S-Cu₂S melt when the melt was in contact with pure solid copper and pure solid iron at starting binary melt compositions of 82%, 75% and 50% FeS and temperatures varying from 800 to 1050°C. Results are given in Figure 3. Equilibrium Cu₂S concentration increases as the temperature increases and the starting FeS increases. As can be seen high levels of copper sulphide (up to 50%) can be obtained in the matte at 1000°C when the starting matte contained 18% Na₂S-82% FeS.

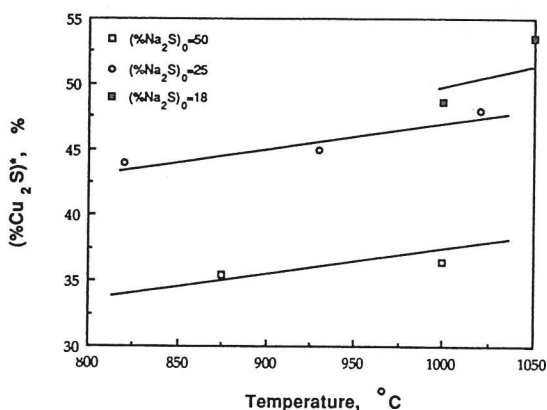


Figure 3: Equilibrium Cu₂S values.

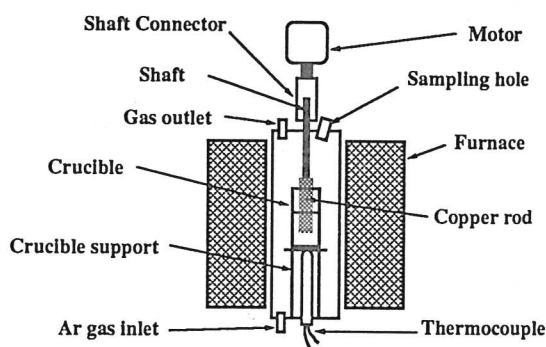


Figure 4: Experimental set-up for kinetic experiments.

Kinetics of Copper Dissolution

In a series of experiments, copper cylinders were reacted with a liquid FeS-Na₂S matte at 900°C. Figure 4 is a schematic of the apparatus. A graphite crucible (I.D. 3 cm and height 9 cm) was placed into the furnace. 100 grams of an FeS-Na₂S mixture were charged into the crucible through a graphite funnel. A speed adjustable motor was mounted above the furnace. A commercial grade solid copper rod, 15 cm in length and 1 cm in diameter, was rotated in the melted matte. 4.5-4.8 cm of the cylinder was in contact with the matte. The shaft connector between the motor and the shaft, which is attached to the copper cylinder, helped lower the copper cylinder and start the reaction precisely at zero time. Argon gas was introduced at a flow rate of 2.5 l/min from the beginning of the experiment. During each run, matte samples were taken as a function of time and subsequently kept in an air-pumped desiccator before being dissolved by

nitric acid (50 percent in volume). Na, Fe and Cu were analyzed by the atomic absorption method and the reacted copper cylinder was examined by both optical and electron microscopes.

Most of the experiments were carried out at an initial Na₂S content of 25%, i.e., the matte is composed of 75 grams FeS and 25 grams Na₂S before the reaction. Rotation speeds of the copper cylinder were chosen at 0, 30, 50, 90, 150 and 200 rpm.

Figure 5 shows typical results of solid copper dissolution rate as a function of time for a starting FeS content of 75%. The Cu₂S content in matte increases as time increases. The higher the copper cylinder rotation speed, the faster the copper dissolution rate. Figure 6 gives the variation of FeS and Na₂S concentrations in matte as a function of time. FeS content in matte decreases as time increases. According to mass balance, weight percent of Na₂S in matte decreases due to the dilution effect as FeS is replaced by Cu₂S. Results at a starting matte composition of 82% FeS were similar to those of 75% FeS.

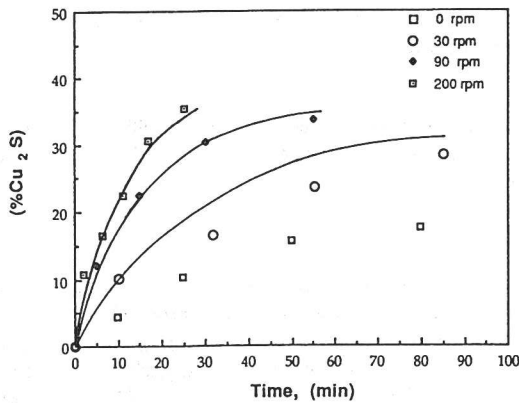


Figure 5: Cu₂S vs time for 75% FeS.

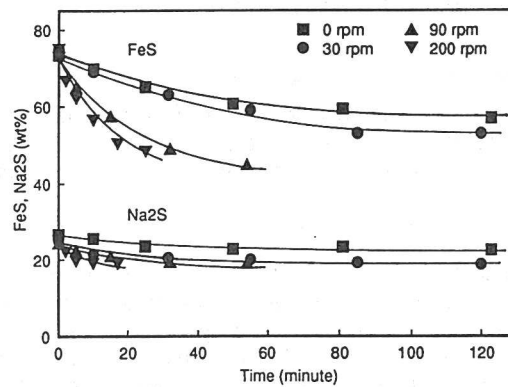


Figure 6: FeS and Na₂S vs time for 75% FeS.

Experiments of 50% initial FeS content were also carried out at 0, 20, 40 and 60 rpm. The results are shown in Figure 7. In this case, the rotation speeds are low, and the results do not indicate that rotating the copper cylinder faster would result in a significantly higher dissolution rate. The copper dissolution rate in this case is affected by factors other than simply the rotation speed.

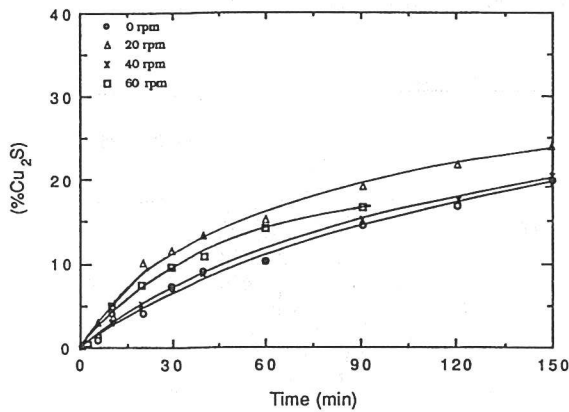


Figure 7: Cu₂S vs time for 50% FeS.

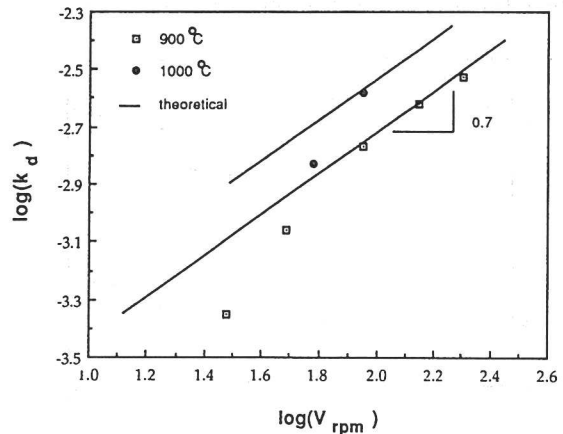


Figure 8: Log K_d vs log ω.

If it is assumed that the the dissolution rate of solid copper is controlled by mass transfer in the liquid matte phase and that the copper concentration at the interface is considered equal to the copper concentration in liquid matte at equilibrium (%Cu_{*}), the following expression results:

$$\frac{d(\%Cu)}{dt} = \frac{2 \pi r l}{V} k_d [(\%Cu)^* - (\%Cu)] \quad (3)$$

At zero time, copper content in liquid matte phase (%Cu) is zero and the mass transfer coefficient k_d can be derived from the instantaneous rate at zero time.

$$\left[\frac{d(\%Cu)}{dt} \right]_{t=0} = \frac{2 \pi r_0 l}{V} k_d (\%Cu)^* \quad (4)$$

Alternatively, k_d can be calculated by the integral method. Both techniques gave similar values for the mass transfer coefficient.

Mass transfer phenomenon during the rotation of a cylinder in a liquid phase was studied by Eisenberg and a relationship between the mass transfer coefficient and other transport variables was established [6]:

$$St = 0.0791 (Re)^{-0.30} (Sc)^{-0.644} \quad (5)$$

where St is the Stanton number, Re is the Reynolds Number and Sc is the Schmidt number. In this case, $Re = 2r_0 u/v$ where Re is the Reynolds number related to the initial diameter of the copper cylinder; $Sc = \nu/D_{Cu}$ where Sc is the Schmidt number; and, $St = k_d/u$ where St is the Stanton number and u is the peripheral linear velocity of the cylinder and k_d is the mass transfer coefficient.

With changing rotation speed of the cylinder and that the other conditions such as initial diameter of the cylinder and liquid melt physical properties are the same during each experiment, equation (5) can be simplified as:

$$k_d = A \cdot u^{0.7} \quad (6)$$

where A is a constant,

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

This implies that a plot of $\log k_d$ against $\log u$ or $\log \omega$ has a slope of 0.7 and k_d can be calculated from a knowledge of the physical properties in the system.

Diffusivity of copper in molten FeS-Na₂S-(Cu₂S) mattes at 900°C was calculated by Sutherland equation [7]:

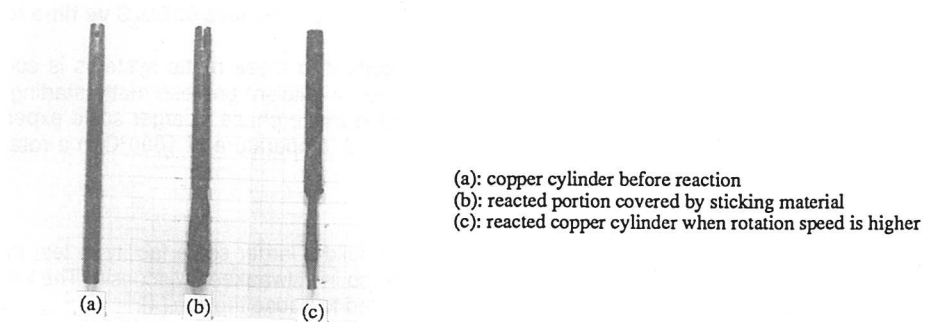
$$D = \frac{KT}{4\pi r_i \mu} \quad (7)$$

where the ionic copper (Cu⁺) radius was $r_i = 0.96 \text{ \AA}$, and the viscosity of FeS-Na₂S-(Cu₂S) mattes at 1000°C was estimated from available matte data [8]. k_d values in equation (6) were then calculated for these experimental conditions.

$\log k_d$ is plotted against $\log \omega$ in Figure 8 and compared with the theoretical relationship of liquid phase Cu mass transfer control mechanism as calculated by Equation (6) for starting matte compositions of 75% FeS at 900°C and 82% FeS at 1000°C. As can be seen, these results fit Eisenberg's predictions. The lines drawn in Figure 5 are also from Eisenberg's correlation showing that a liquid phase mass transfer argument can be used to explain these experimental results.

Results of the case with a starting composition of 50% FeS were also compared with the same theoretical relationship. At lower rotation speeds (<90 rpm), the dissolution rate was less than that predicted by the mechanism of mass transfer in liquid matte phase. Therefore, mass transfer of copper in liquid phase is not the rate controlling step in this case.

Typical observations of reacted cylinders are shown in Photograph 1. At lower rotation speeds and starting FeS contents of 50%, the reacted portion of the copper cylinder was covered by a layer of a viscous molten material (Photograph 1.(b)).

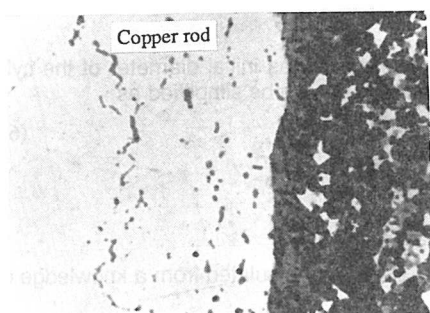


Photograph 1: Reacted cylinders.

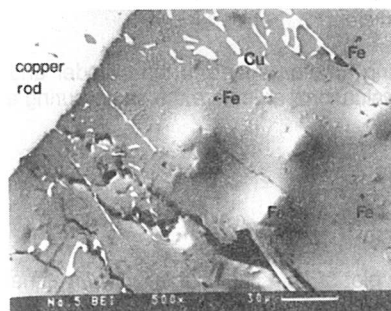
This apparently formed a barrier to mass transfer and thus hindered the reaction. When both the rotation speeds were greater than 30 rpm and the starting FeS contents was higher than 75%, the sticking layer did not form around the copper cylinder but was found to settle to the bottom of the crucible. Thus, under these conditions, there exists a very clear interface between the liquid matte and the solid copper (Photograph 1.(c)), and the dissolution rate of copper is

controlled by mass transfer of copper in the liquid matte phase. At starting FeS contents of 50%, the sticking layer could not be removed by higher rotation speeds and the reaction rate is governed by transport through the sticking layer.

As mentioned above, when the rotation speed of the copper cylinder is low, a layer of material forms around it. As this layer is important in determining the dissolution rate and the reaction mechanism under static conditions, samples were taken from a quenched copper cylinder which was reacted with a matte for two hours under a static condition (rotation speed = 0 rpm). Photograph 2 shows a general view of a cross-section of the reacted copper cylinder with the material formed around it. The sticking material is about 2 mm thick. It is composed of the stratified precipitate and sulfide matte.

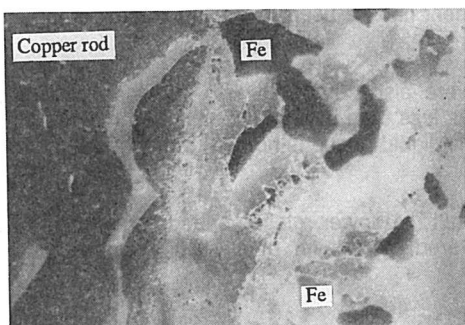


Photograph 2: Cross section of a reacted cylinder



Photograph 3: Copper fragmentation.

Analysis by SEM of the reacted copper rods allowed a better understanding of the details of the reaction mechanism. The liquid matte penetrates along the grain boundaries of the copper rod causing the rod to slowly fragment and free particles of copper, which subsequently react, into the melt (Photograph 3). Iron particles precipitate in the matte phase near the surface of the copper rod (Photograph 4) causing a three phase slurry of iron, copper and matte near the interface of the reacting rod. At low rotation speeds this slurry impedes transport of copper into the matte.



Photograph 4: Iron particles in matte phase.

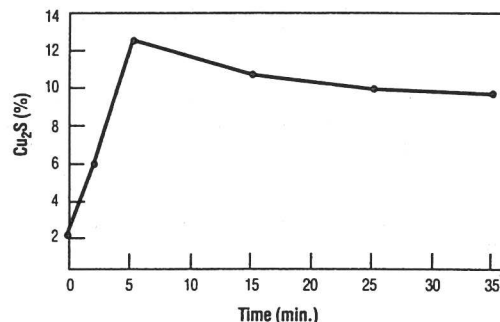


Figure 9: Cu₂S vs time for kiln trial.

These results indicate that the dissolution of copper in these matte systems is controlled by transport of copper away from the dissolving piece. Thus, in order to have an efficient process matte starting chemistries should be high in FeS and efforts must be made to increase mixing in the matte phase. Larger scale experiments were conducted with a matte starting chemistry of 82% FeS and 18% Na₂S at a temperature of 1000°C in a rotary kiln to facilitate liquid phase mass transfer.

4. Larger Scale Trials

After these bench scale tests it was decided to build a larger scale facility to test the practicality of this approach. An externally fired rotary kiln was purchased from Coreco in Milwaukee, Wisconsin. The kiln was installed at the USX pilot facility in Universal, PA, where a building was constructed to house the kiln [4].

The kiln and its supporting frame, hydraulic pump mechanism and exhaust system is approximately 5 meters long, 2 meters wide and 3 meters 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 61 cm in diameter and 4 meters long. The rotation speed of the kiln can be varied from 1 to 10 rpm.

The first 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%Na₂S.

Initial experimental results for copper sulphide pick-up are given in Figure 9. As can be seen in these figures, the % Cu₂S increases for the first 7 minutes of the trial, followed by a gradual decrease. Sodium sulphide decreased throughout the experiment while iron sulphide apparently decreased at first and then increased. 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.

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. Details of this larger scale experimental program are given in reference 4.

5. Conclusions

Reaction between copper and an FeS-Na₂S matte results in a high equilibrium Cu₂S content which increases with temperature and starting FeS content. For an 82% FeS starting matte the equilibrium copper sulphide content is approximately 50% at 1000°C. Reaction kinetics were found to be controlled by liquid phase mass transfer in the matte at high starting FeS content; however, at lower rotation speeds, and, lower starting matte FeS contents, the reaction kinetics were lower than that predicted by a simple liquid phase mass transfer model due to the presence of a thick viscous slurry which became attached to the rod.

Larger scale experiments were carried out in a rotary kiln to avoid problems with viscous film formation. Larger scale experimentation revealed that copper could be effectively removed from ferrous scrap by this technique.

Major Symbols

(%Cu), (%Cu)^{*}: copper content and equilibrium copper content in matte, wt%
D: diffusivity of copper element in liquid matte phase, cm²/s
l: length of copper cylinder immersed into the liquid matte, cm
*r*₀: radius of the original copper cylinder before reaction, cm
t: time, s
V: total volume of liquid matte phase, cm³
μ: viscosity of liquid matte, g/cm·s

(%Cu₂S), (%Cu₂S)^{*}: copper sulfide content and equilibrium copper sulfide content in matte, wt%
K: Boltzmann's constant
*k*_d: mass transfer coefficient, cm/s
(%Na₂S)₀: initial sodium sulfide concentration in matte, wt%
r: radius of the copper cylinder, cm
*r*_i: radius of the Cu⁺ ion, Å
T: temperature, K
u: peripheral linear velocity of copper cylinder, cm/s
ω: rotation speed of copper cylinder, rpm
v: dynamic viscosity of liquid matte, cm²/s

References

1. J. Peace and D. Engledow: "Developments of Scrap Beneficiation by the British Steel Corporation," *Ironmaking and Steelmaking*, Vol.14, No.5, (1987), pp.248-52.
2. R. J. Schmidt: "Automotive Shredder Residue - The Problem and Potential Solutions," *Recycling of Metals and Engineered Materials*, TMS, (1990), pp.315-32.
3. M. Iwase and K. Tokinori: "A Feasibility Study for the Removal of Copper from Solid Ferrous Scrap," *Steel Research*, Vol.62, No.6, (1991), pp.235-39.
4. A. W. Cramb and R. J. Fruehan: "A New Low Temperature Process for Copper Removal From Ferrous Scrap," *Iron and Steelmaker*, Vol.18, No.11, (1991), pp.61-68.
5. J. F. Jordan: US Patent 2,512,578, (1950).
6. M. Eisenberg, C.W. Tobias and C. R. Wilke: *Chem. Eng. Prog. Symp.*, No.16, (1955), p.1.
7. W. Sutherland: *Phil. Mag.*, Vol.9, (1905), pp.781-85.
8. N. Nagamori and A. Yazawa: *Japan Inst. of Metals J.(in Japanese)*, Vol.14, (1975), pp.163-72.