Some Considerations of Copper Removal from Steel by Use of Oxysulfide Systems

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Abstract: It has long been desired to remove tramp elements such as copper and tin from steel, in particular, when ferrous scrap is used for steelmaking. Albeit a number of different approaches have been attempted, however, a satisfactory solution has yet to be found. In the present study a new technology has been investigated, which utilizes a low-melting oxysulfide medium for removal of copper from ferrous scrap. The basic concept of the present approach is that steel scrap containing copper component is melted in the oxysulfide medium, and then metallic iron is induced to precipitate out, leaving most of the copper left in the oxysulfide medium by a proper control of oxygen and sulfur potentials in the system. First, phase equilibria in the Fe-Cu-S ternary system at the Fe-rich corner was experimentally investigated to establish a reliable foundation on fundamental knowledge in the phase relationship of Fe-Cu-S system. Then the two-phase region of solid Fe and liquid solution (Fe-Cu-S) was intensively investigated to quantify the distribution of copper between the phases (L_{Cu} = (mass% Cu)$_{solution}$/[mass% Cu]$_{Fe.}$). Effects of temperature and additional elements such as sodium were also investigated. A typical result is that in the Fe-Cu-S system, L_{Cu} was found to be about 7 at 1,200°C, and sulfur in the steel was about a few hundred ppm level. Addition of sodium in the sulfide markedly increased L_{Cu}, meaning that sodium suppressed copper from moving to the steel. This was attributed to the fact that Na_2S decreases the activity coefficient of Cu_2S in the sulfide solution. The results obtained through the present study warranted further investigation on the oxysulfide system and develop a conceptual process of copper removal from scrap-using steelmaking.

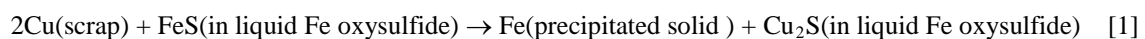**Key words:** Fe-Cu-S Phase equilibria, Cu removal, Ferrous Scrap, Tramp element

1. Introduction

Ferrous scrap consumption has been increasing, due to the limitation of sound iron ore and demand for lowering CO_2 gas emission generated from blast furnace and oxygen steelmaking process. One of the serious problems of the use of ferrous scrap is contamination of steel with tramp elements such as Cu and Sn from the ferrous scrap. Once entered into molten steel, Cu is very difficult to be removed by the conventional route of oxidation refining , mainly due to its oxygen affinity lower than Fe. If the Cu content in steel exceeds a certain limit, it may cause for instance surface defects like hot shortness.

A number of suggestions such as low melting point bath[1], vacuum distillation[2-5], chlorination[6] and sulfide flux refining have been proposed for copper removal process. [7-10] Among those approaches, methods using sulfide flux is worth attracting more attention. The main concept of this method is removal of Cu in carbon saturated liquid iron by reaction with sulfide flux such as FeS, FeS-Na_2S or FeS-Al_2S_3 by which the Cu is removed as Cu2S [7-10] However, requirement of high flux/liquid iron ratio to make the process operative for obtaining reasonable level of Cu content in

the liquid iron and still insufficient level of S content in the liquid iron even after the removal process yet to be resolved.

Elliot [11] suggested a possibility of smelting reduction by using the Fe-O-S oxysulfide melt at low temperatures in the range of 1000 to 1200°C and has attempted to experimentally investigate some fundamentals including reduction rate of FeO dissolved in Fe-O-S oxysulfide melts.[12] The smelting reduction is conducted at the low temperature where Fe is precipitated in solid form. One of the present authors[13] also investigated reduction of Fe oxide in Fe-O-S oxysulfide melts and suggested the smelting reduction mechanism of the Fe-O-S melts, and proposed a possibility of Cu removal in ferrous scrap by melting the scrap in iron oxysulfide followed by the reduction of Fe oxide in the oxysulfide.[14] The basic concept of this approach is that the steel scrap containing Cu component is melted in the oxysulfide solvent at low temperature where the solvent is in liquid state, and then metallic iron which is solid at the temperature is induced to precipitate out, leaving most of the Cu left in the oxysulfide solvent by a proper control of oxygen and sulfur potentials in the system. The main chemical reaction for the process may be written as:

$$2Cu(scrap) + FeS(\text{in liquid Fe oxysulfide}) \rightarrow Fe(\text{precipitated solid}) + Cu_2S(\text{in liquid Fe oxysulfide}) \quad [1]$$

In order to confirm the feasibility of the above proposal, it is necessary to confirm whether Cu could be remained in the oxysulfide solvent while the solid Fe is precipitated out of the solvent. It is expected that Cu would stay in the liquid oxysulfide more easily when oxygen potential is low. Therefore, in the present study, phase equilibria in the Fe-Cu-S ternary system at the Fe-rich corner was experimentally investigated to provide a fundamental knowledge relevant to Cu removal into a liquid solvent from which solid Fe is precipitated. Two-phase region of solid Fe and liquid solution (Fe-Cu-S) was intensively investigated to quantify the distribution of copper between the phases (L_{Cu} = (mass% Cu)$_{\text{liquid sulfide}}$/[mass% Cu]$_{\text{solid Fe}(\gamma)}$.). Moreover, addition of sodium in the sulfide is also investigated from very low to relatively high Na$_2$S contents in sulfide.

2. Experimental

The general procedure employed in the present study is that mixtures of sulfide composed of Fe-Cu-S(-Na) were equilibrated in an Fe crucible at desired temperatures where the sulfide melts in order to measure distribution of Cu between solid Fe (the Fe crucible) and liquid sulfide solution. Chemical compositions of each phase in the quenched samples were quantitatively analyzed. The experimental apparatus employed in the present study is schematically shown in Figure 1.

Powder of FeS (99.9mass%, supplied by Strem Chemicals, USA), Cu (99mass%, supplied by Aldrich, USA) and Na$_2$S (99.99mass%, supplied by Aldrich, USA) were used as staring materials. Each mixture was weighed to 5g and placed in a crucible (OD:20mm-ID:15mm-H:60mm) made of electrolytic Fe and pre-melted at 1200°C to quartz sealing. As sulfur in sulfide flux would easily evaporate, the Fe crucible was sealed by a quartz ampule. The assembly was heated in a vertical LaCrO$_3$ resistance furnace at desired temperatures (from 1200 to 1300°C) under an atmosphere of Ar gas purified passing through CaSO$_4$ column, and Mg chip at 450°C.

The furnace temperature was controlled within ± 2 K by a PID controller using a thermocouple (Pt/6%Rh-Pt/30%Rh) in contact with alumina tube. The holding time for equilibration was preliminary determined to be 50 hours. The

establishment of equilibrium was confirmed by observing consistent S and Cu contents in solid Fe phase as time changes. After equilibration, the assembly was quickly withdrawn out of the furnace and cooled down under Ar flow.
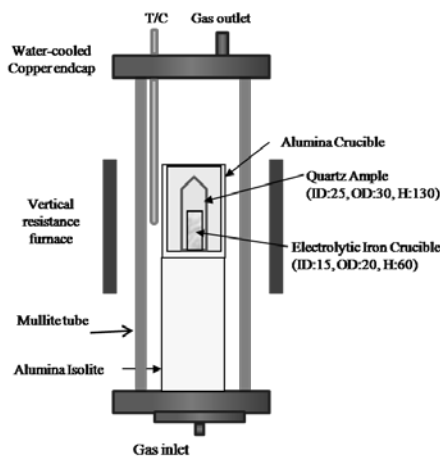

Figure 1. Schematic diagram of experimental apparatus employed in the present study.

For the chemical analysis of the samples, the electron microprobe analysis (EPMA) was carried out for Fe, Cu, S in sulfide and solid Fe, respectively, on a JEOL 8100-JXA (Japan Electron Optics Ltd., Tokyo, Japan) in the WDS mode. When Na_2S was added to the sulfide flux, Na, Fe, Cu contents in the sulfide were analyzed by Inductively Coupled Plasma spectroscopy method (ICP) and S contents in sulfide was analyzed by C/S combustion analysis method. Fe, Cu, S contents in solid Fe were analyzed by the EPMA.

3. Results and Discussion

3.1 Distribution of Cu between liquid sulfide flux and solid Fe (γ)

In the present work, distribution of Cu between solid Fe (γ) and liquid sulfide flux composed of Fe-Cu-S at 1200°C at the low Cu contents in sulfide flux was investigated. Equilibrium contents of Cu and S in both phases were obtained and those were plotted in Figure 2 as symbols. A calculated isothermal section of the Fe-Cu-S system at 1200°C using FactSage® thermochemical software and a database for the sulfide system[14,15] is also shown in the figure as full lines. Dashed lines are tie-lines between solid Fe (γ) and liquid sulfide flux, connecting experimentally obtained equilibrium compositions of the two phases in the present study. The measured sulfide compositions in equilibrium with the solid Fe (γ) are in good agreement with the calculated isothermal section. Shown in Figure 3 are the measured Cu and S contents in the solid Fe (γ) and L_{Cu} as functions of Cu contents in the liquid sulfide (all solid symbols). It is seen that L_{Cu} is about 6.5 ~ 7, regardless of Cu_2S content in the liquid sulfide, and Cu content in the solid Fe (γ) increases as the Cu contents in the liquid sulfide increases. This suggests that Cu can be removed into liquid sulfide solution which is in equilibrium with solid Fe, however keeping low Cu contents in the liquid sulfide is necessary to obtain solid Fe with low Cu content.

The obtained Cu distribution ratio L_{Cu} was compared to that obtained in previous investigation employing equilibration between liquid sulfide flux (of the same constitution) and liquid C-saturated Fe by Wang et al.[9] Their

results are also shown in the Figure 3 as open symbols. Although their investigation was carried out at 1300°C, the reported Cu distribution ratio is 7 to 9 which is very close to those of our investigation. However, sulfur contents in solid Fe (γ) obtained in the present study is about 0.03 wt % which is much lower than that of Wang *et al.*'s results (2 ~ 2.5 wt %). Therefore, the proposed process in the present study does not require additional desulfurization process, while Cu removal in liquid Fe using sulfide flux demand very intensive desulfurization process.
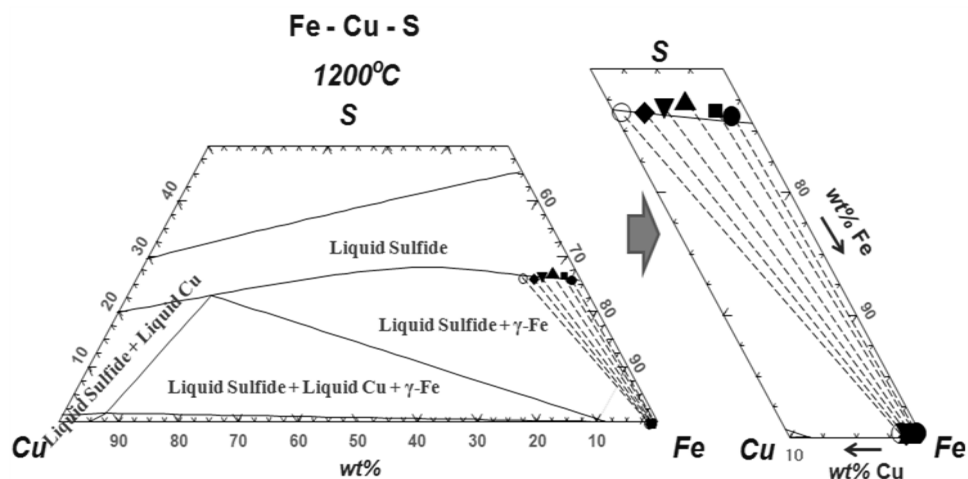
Figure 2. Isothermal section of the Fe-Cu-S system at 1200°C. Lines are calculated using FactSage, and symbols are measured compositions in the present study.
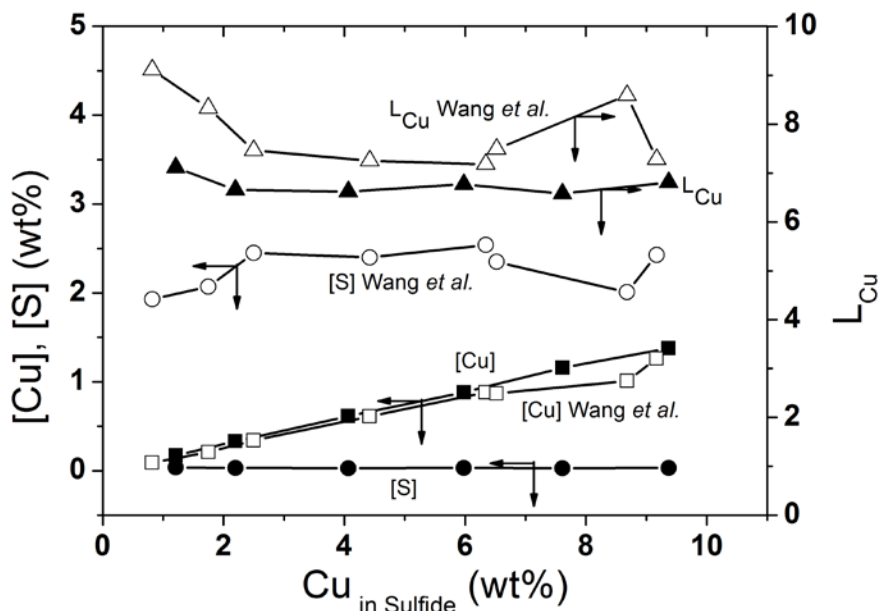

Figure3. Equilibrium contents of Cu and S in solid Fe (γ), and Cu distribution ratio between the solid Fe (γ) and liquid sulfide flux obtained in the present study (solid symbols). Open symbols are Equilibrium contents of Cu and S in liquid C-saturated Fe, and Cu distribution ratio between the liquid Fe and liquid sulfide flux reported by Wang *et al.*[9]

3.2 Effect of Temperature on Copper Distribution

In order to investigate the effect of temperature on the Cu distribution between solid Fe (γ) and liquid sulfide flux composed of Fe-Cu-S, additional experiments were conducted for the same initial flux composition at 1200, 1250 and 1300°C.   Obtained results are shown in Figure 4.   While no significant changes of Cu and S contents in solid Fe (γ) (denoted as [Cu] and [S] in the figure) phase were observed, Cu content in the liquid sulfide phase (denoted as (Cu) in the figure) decreases about 25% when temperature increases as much as 100°C.
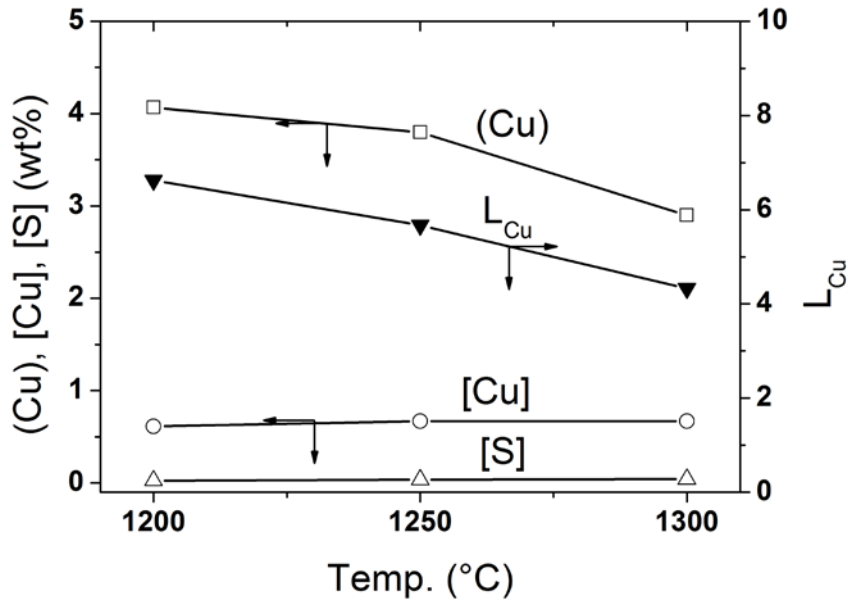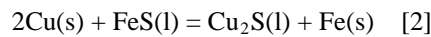

Figure 4. Effect of temperature on Cu contents in sulfide and Cu, S contents in solid Fe (γ) and Cu distribution ratio between the solid Fe (γ) and liquid sulfide flux.

The chemical reaction involved in the Cu removal may be written as:

$$2Cu(s) + FeS(l) = Cu_2S(l) + Fe(s) \quad [2]$$

$$K = \frac{a_{Fe} \cdot a_{Cu_2S}}{a_{FeS} \cdot a_{Cu}^2} = \frac{a_{Fe} \cdot a_{Cu_2S}}{a_{FeS} \cdot \left(\gamma_{Cu} X_{Cu}\right)^2} \quad [3]$$

$$\gamma_{Cu} = \sqrt{\frac{a_{Fe} a_{Cu_2S}}{K a_{FeS} X_{Cu}^2}} \quad [4]$$

The above reaction is a weak exothermic reaction, resulting in moderate change of Cu concentration change as temperature varies.   Figure 5 shows equilibrium constant K of the above reaction [2], obtained from FactSage software and database for the liquid sulfide phase.[14,15]   The equilibrium constant is insensitive to the temperature.   On the other hand, the activity coefficient of Cu in the solid Fe phase was calculated using Eq. [4] and is shown in the Figure 5. In order to utilize the Eq. [4], activity of Fe in the solid Fe (γ) phase was assumed to follow Raoult's law, activities of

FeS and Cu_2S in the liquid sulfide were calculated from FactSage software and database for the liquid sulfide phase. Compositions in both phases were obtained in the present study. Under the given condition (equilibrium between solid Fe (γ) phase and liquid oxysulfide phase), the activity coefficient of Cu in the solid Fe (γ) phase significantly decreases as temperature increases. Therefore, increasing temperature will results in increasing Cu content in the solid Fe (γ) phase, resulting in decreasing Cu distribution ratio for a given flux composition.
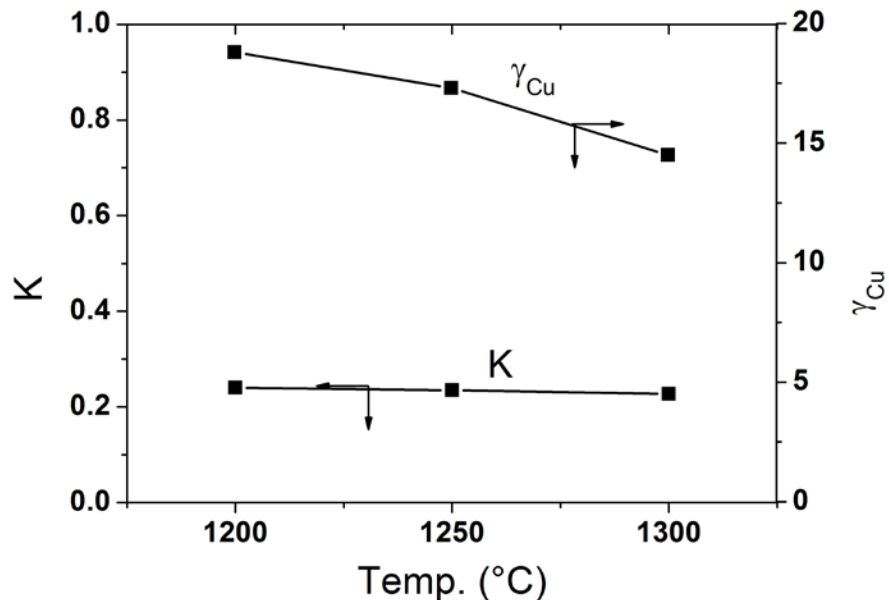

Figure 5. Effect of temperature on equilibrium constant and activity coefficient of Cu in the solid Fe (γ).

From the results obtained in the present study, it appears that low temperature is more appropriate for the decopperization by the reaction between solid Fe (γ) phase and liquid oxysulfide phase from the thermodynamic point of view. This is also desirable in the view of environmental issues. However, low temperature would retard overall chemical reaction as well as mass transfer in phases involved. This requires further investigations 1) thermodynamically to increase the Cu distribution ratio by adding appropriate flux, and 2) kinetically to increase reaction rate.

3.3 Effect of Na$_2$S in Sulfide Flux on Copper Distribution

It is well known that Na_2S forms numerous solid compounds with Cu_2S and FeS[16]. This suggests that the Na_2S in liquid sulfide solution strongly attracts Cu, resulting in decrease of activity coefficient of Cu_2S. Therefore, equilibrium relation in copper removal by FeS-Na_2S flux has been investigated by Imai and Sano[7], Jimbo *et al.*[8] and Wang *et al.*[9], confirming effectiveness of the use of Na_2S for increasing Cu distribution ratio between the liquid sulfide flux and liquid C-saturated liquid Fe. In the present study, it was also attempted to investigate the effect of Na_2S on the Cu distribution between the liquid sulfide flux and solid Fe, as a function of Na content in the liquid sulfide flux.

Figure 6 shows the equilibrium contents of Cu and S in solid Fe (γ) equilibrated with liquid sulfide flux, and L_{Cu}, as functions of Na content in the liquid sulfide flux. As a comparison, L_{Cu} reported by Wang *et al.*[9] in which liquid

metal phase (C-saturated liquid Fe) was used is also shown. Cu contents in the solid Fe (γ) is rapidly decreasing as Na_2S contents in sulfide increases and as the results the maximum L_{Cu} becomes 25 ~ 30.   A similar Cu distribution ratio was observed by Wang *et al.*,[9] and this suggests that decreasing activity coefficient of Cu_2S enhances removal of Cu in solid Fe (γ) similar to that happens between the liquid sulfide flux and liquid Fe.
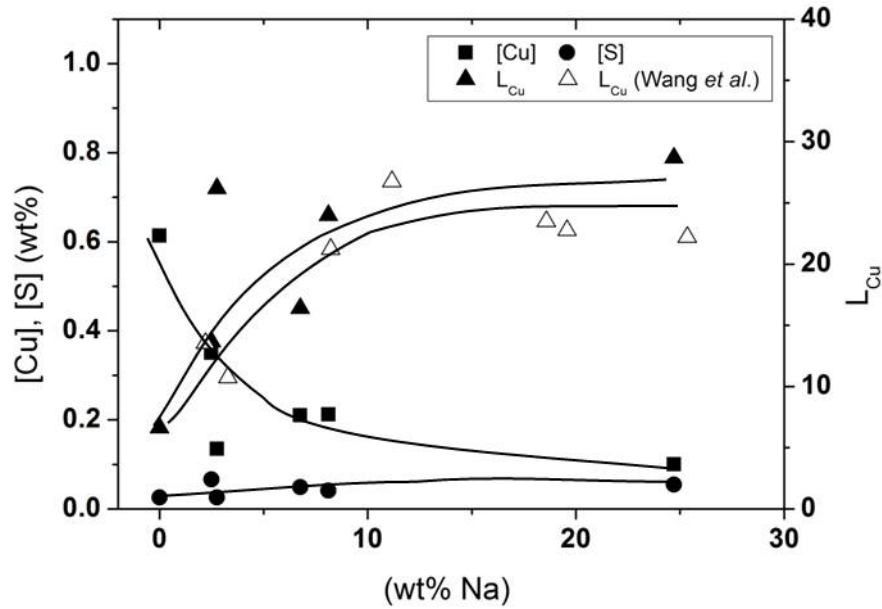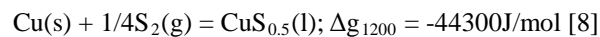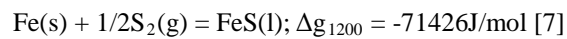

Figure 6. Effect of Na contents in liquid sulfide on Cu and S contents solid Fe (γ) and Cu distribution ratio between the solid Fe (γ) and liquid sulfide flux.

L_{Cu} can be calculated for the reaction Equations [3] and [5]:

$$L_{Cu} = \frac{(wt\%Cu)}{[wt\%Cu]} = K' a_{FeS}^{1/2} \left(\frac{\gamma_{Cu}}{\gamma_{CuS0.5}} \right) \quad [6]$$

where K' is the equilibrium constant of the reaction [2] after conversion of concentration from mole fraction to weight %.   Therefore, L_{Cu} can be increased by increasing activity of FeS, and decreasing activity coefficient of $CuS_{0.5}$. Activity of FeS and activity coefficient of $CuS_{0.5}$ can be obtained from the following reactions along with concentrations of S in solid Fe (γ), Cu_2S in liquid sulfide and the obtained results are presented in Figure 7.

$$Fe(s) + 1/2S_2(g) = FeS(l); \Delta g_{1200} = -71426 J/mol \quad [7]$$

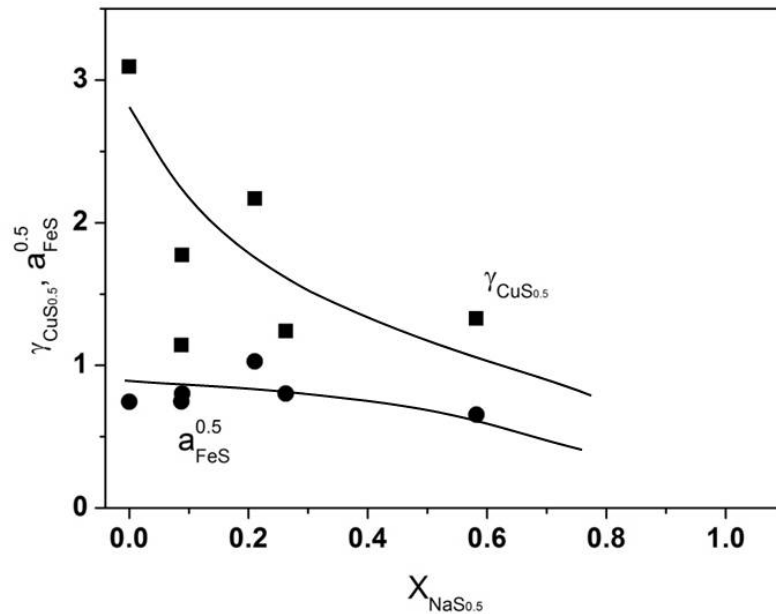$$Cu(s) + 1/4S_2(g) = CuS_{0.5}(l); \Delta g_{1200} = -44300 J/mol \quad [8]$$

Figure 7. Relation of $NaS_{0.5}$ contents in sulfide with activity coefficient of $CuS_{0.5}$ and activity of FeS

Partial pressure of $S_2(g)$ over solid metallic Fe phase was obtained by FactSage thermochemical software and the database for the sulfide system[14,16] which was based on earlier experimental measurements.[17] Activity of Cu and Fe were evaluated by thermodynamic information of Fe-Cu binary alloys[18] and Raoult's law respectively. Activity coefficient of $CuS_{0.5}$ decreases rapidly as Na_2S in sulfide increases, but activity of FeS does not decrease severely. Therefore, it is concluded that Cu distribution ratio can be increased by the addition of Na_2S in sulfide flux, as was observed by Wang et al.[9] This suggests that the effect of addition of other flux components reported by previous investigations may be similarly utilized.[19]

4. Conclusions

Distribution of Cu between FeS, $FeS-Na_2S$ sulfide flux and solid austenite iron has been observed mainly at 1200°C. Conclusions may drawn from the results obtained in the present study as follows.

(1) Cu may be removed by utilizing sulfide flux decopperization, because of strong affinity of Cu with S.

(2) Copper distribution ratio at 1200°C was investigated experimentally and L_{Cu} was confirmed as around 7 with 300 ppm of sulfur contents in austenite iron.

(3) L_{Cu} between liquid sulfide flux and solid Fe phase increases as temperature decreases, because activity coefficient of Cu in the solid Fe phase increases as temperature decreases.

(4) L_{Cu} may be raised up to about 26 by applying Na_2S. The main reason responsible for increasing L_{Cu} is decrease of activity coefficient of Cu_2S in the liquid sulfide flux.

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