Selective Sulfation of Non-Ferrous Metals in a Salt-Moderated Roast

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ABSTRACT

The chemistry of non-ferrous metals sulfation in the presence of molten mixed alkali sulfate salts has been investigated. The character of the sulfation reactions is changed from gas-solid to gas-liquid-solid with product sulfate formed at less than unit activity. Pyrosulfate is found to contribute to the \( \text{SO}_3 \) activity of the liquid salt. An equilibrium was found to exist between \( \text{CuO} \cdot \text{CuSO}_4 \) and \( \text{CuFe}_2\text{O}_4 \) with the former dissolved in the liquid salt. Similarly, an \( \text{NiSO}_4 \cdot \text{NiFe}_2\text{O}_4 \) equilibrium was observed but \( \text{NiSO}_4 \) was found at unit activity. The results are consistent with earlier studies on sulfide ↔ oxide ↔ sulfate reaction sequences.

INTRODUCTION

Non-ferrous metals frequently occur in nature as complex iron sulfides such as \( \text{CuFeS}_2 \) (chalcopyrite) and \( \text{NiFeS}_2 \) (pentlandite). One method for extracting and separating the metal values is to oxidize the native mineral in such a manner that copper, for example, is converted to \( \text{CuSO}_4 \) while iron becomes \( \text{Fe}_2\text{O}_3 \). The former may then be solubilized in water or dilute acid and recovered by any of several hydrometallurgical techniques.

Oxidation under relatively mild conditions, i.e., at temperatures below 675°C, results in the formation of soluble iron sulfates which can interfere with the recovery of copper in a subsequent process step. On the other hand, oxidation under conditions which are too severe, i.e., at temperatures in excess of 725°C, will result in the loss of copper to insoluble \( \text{CuFe}_2\text{O}_4 \) (copper ferrite). Therefore, the mineral oxidation must be effected in a narrow range of conditions which result in high degrees of copper sulfation but low degrees of iron sulfation.
Using the mineral chalcopyrite as an example, the chemistry of selective sulfation may be summarized in simplified form as follows:

\[
\begin{align*}
\text{CuFeS}_2 + \frac{13}{4} \text{O}_2 & \rightarrow \text{CuO} + \frac{1}{2} \text{Fe}_2\text{O}_3 + 2\text{SO}_2 \quad \ldots \quad (1) \\
\text{SO}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{SO}_3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2) \\
2\text{CuO} + \text{SO}_3 & \rightarrow \text{CuSO}_4 \cdot \text{CuO} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3) \\
\text{CuSO}_4 \cdot \text{CuO} + \text{SO}_3 & \rightarrow 2\text{CuSO}_4 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4) \\
\text{Fe}_2\text{O}_3 + 3\text{SO}_3 & \rightarrow 2\text{Fe}_2(\text{SO}_4)_3 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5) \\
\text{CuO} + \text{Fe}_2\text{O}_3 & \rightarrow \text{CuFe}_2\text{O}_4 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6) \\
\text{CuO} \cdot \text{CuSO}_4 + 2\text{Fe}_2\text{O}_3 & \rightarrow 2\text{CuFe}_2\text{O}_4 + 2\text{SO}_3 \quad \ldots \quad \ldots \quad \ldots \quad (7)
\end{align*}
\]

In a conventional sulfating process, reactions (1)-(7) are gas-solid reactions with the various oxides and sulfides existing at or near unit activity. The copper and iron sulfates formed are mutually miscible and not necessarily present at unit activity. However, a conventional roast will tend to operate under conditions such that:

\[
[\text{CuSO}_4] \gg [\text{Fe}_2(\text{SO}_4)_3] , [\text{FeSO}_4] \quad \ldots \quad \ldots \quad \ldots \quad (8)
\]

so that this miscibility is significant for iron sulfate activity only. CuSO₄ may still be considered to be present near unit activity and literature data on the decomposition pressures of CuSO₄ and CuO·CuSO₄ may be used directly to predict conditions where copper sulfation will be a maximum. The results of studies by several workers on the thermal stability of sulfates have been reviewed by Kellogg [1] and Stern [2].

It is important to note that kinetic studies on the oxidation of sulfides [3,4] and on the decomposition of sulfates [2,5] indicate that the formation of a metal oxide is an essential intermediate in the conversion of a sulfide to a sulfate. For copper, the reaction sequence found experimentally is [6]:

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CuS + CuO → CuO·CuSO₄ + CuSO₄

In the presence of Fe₂O₃, however, the reaction

CuO·CuSO₄ + 2CuO + SO₃

no longer adequately describes the oxysulfate decomposition. Equation (7) must then be used and data on the stability of the non-ferrous sulfate in the presence of its ferrite is necessary to thermodynamically describe the reaction system. Such data is available for CuFe₂O₄ [7] and NiFe₂O₄ [8]. The fact that a correct thermodynamic model describing the production of a non-ferrous sulfate in the presence of Fe₂O₃ cannot use the non-ferrous oxide as a final product, if a stable ferrite exists, has been overlooked in previous attempts to describe such systems [9,10].

The equilibrium constant for reaction (7) is:

\[ K_7 = \frac{[\text{CuFe}_2\text{O}_4]^2[\text{SO}_3]}{[\text{CuO}\cdot\text{CuSO}_4][\text{Fe}_2\text{O}_3]} \]  

(9)

In a conventional system consisting only of gases and solids, \([\text{CuFe}_2\text{O}_4] = [\text{Fe}_2\text{O}_3] = [\text{CuO}\cdot\text{CuSO}_4] \approx 1\), and \(K_7\) reduces to the identity

\[ K_7 = [\text{SO}_3] = \text{PSO}_3. \]  

(10)

\(K_7\) is a function of reaction temperature and this represents the only control one has over the sulfation reactions with the constraints of unit product activities. This situation may be altered considerably if a molten salt is added to the reactor which is capable of dissolving CuSO₄ and/or CuO·CuSO₄. Then \([\text{CuO}\cdot\text{CuSO}_4] \neq 1\) and (9) becomes:

\[ K_7 = \frac{[\text{SO}_3]}{[\text{CuO}\cdot\text{CuSO}_4]} \]  

(11)

The presence of the liquid salt introduces an additional control parameter, namely non-ferrous sulfate activity, and significantly increases the thermal stability of the desired product. Ferrous sulfate stability will also be affected, but to a lesser degree since its activity is already low as indicated above.

In our studies we add a sufficient amount of sodium and potassium sulfate to allow the formation of a low melting ternary Cu-K₂Na₂SO₄ salt which coats the reacting particles in our powdered samples. These alkali sulfates react...
with gaseous SO$_3$ to provide additional sulfating activity to the liquid salt in the form of sodium and potassium pyrosulfate.

\[
\text{CuO} \cdot \text{CuSO}_4 + S_2\text{O}_7^2- \rightarrow 2\text{CuSO}_4 + \text{SO}_4^{2-} \quad (12)
\]

Since K$_2$S$_2$O$_7$ is considerably more stable under the conditions of our experiments than is Na$_2$S$_2$O$_7$, for all practical purposes potassium pyrosulfate is the only additional sulfating agent present in the melts. Since the stability of the pyrosulfate anion in a salt melt is affected by the presence of non-alkali cations and our salt melts contain Cu$^{+++}$, Fe$^{+++}$, and sometimes Ni$^{+++}$, it is not possible to predict [S$_2$O$_7$] a priori [11].

The purpose of this study was to gather data on the behavior of sulfating reactions under conditions where the product sulfates were dissolved in a molten salt and not present at unit activity. Evidence was also sought for the sulfating activity of S$_2$O$_7$. This information can be used to calculate conditions under which the copper sulfate/iron sulfate ratio or nickel sulfate/iron sulfate ratio is maximized in a commercial process seeking to selectively recover the non-ferrous metal as a sulfate.

**EXPERIMENTAL**

A schematic diagram of the apparatus used is shown in Figure 1. The reactor is a quartz tube contained within a conventional laboratory furnace whose temperature is controlled to ± 3°C. Gas and mechanical feedthroughs are provided at one end for gas introduction, gas sampling, and sample manipulations. The samples themselves were placed in 15 x 25 x 5 mm alumina trays which can be inserted into or removed from the constant temperature zone of the reactor without physically disturbing those samples previously inserted.

Gas composition in the reactor is controlled by gas flow through calibrated rotameters. SO$_2$ and dried compressed air are metered individually and then mixed. The mixed flow is analyzed using a gas chromatograph with digital integration giving an overall reproducibility of ± 2% of peak area. The chromatograph uses a Poropak-Q, Silica Gel, Molecular Sieve column train with a thermoconductivity detector to record SO$_2$, O$_2$, and N$_2$ concentrations in either input or exhaust gases. An automatic sequential timer allows unattended operation of the gas chromatograph and automatic gas sampling at regular intervals in the course of an experiment.
In some series of experiments, the reactant gas was first placed through a Pt-asbestos catalyst maintained at the same temperature as the sample reactor to bring the SO$_2$-O$_2$ mixture into thermodynamic equilibrium with SO$_3$. With an accurate measure of oxygen and initial SO$_2$ partial pressures, PSO$_3$ at equilibrium in the reactant gas can be calculated from the literature data [1].

\[
PSO_3 = \frac{P}{1 + \frac{K}{(P_{O_2})^{1/2}}} \quad \ldots \ldots (13)
\]

where \( P = PSO_2 + PSO_3 \). \( \ldots \ldots (14) \)

\[
P_{O_2} = .21 - .21P - .5PSO_3 \quad \ldots \ldots (15)
\]

\[
P_{O_2} \approx .21 - .21P \quad \ldots \ldots (16)
\]

and \( \log_{10} K = 8.8557 - \frac{5465.5}{T} - 1.2157 \log_{10} T \quad \ldots \ldots (17) \)

Our experiments were conducted on powdered samples with a particle size of ≤150μ. Two types of samples were used: (1) a commercial powdered mineral sample of CuFeS$_2$ containing about 25% Cu by weight (chalcopyrite concentrate), and (2) a synthetic mix of CuFeS$_2$, NiFeS$_2$, and silicate rock. The mixture contained about 13% Cu and 3% Ni by weight (synthetic concentrate). After reaction, samples were water leached at 50°C to dissolve soluble copper, nickel, and iron. The filtered leach liquor was analyzed using atomic absorption spectroscopy. Overall error limits on the analyses were determined by replicate experiments to be ± 5% of the result obtained.

For each experimental run, a mixture of mineral concentrate and salt was prepared using between 5 and 25 weight percent salt. Up to six equal weight samples were prepared in the alumina trays and placed in a zone of the reactor maintained at room temperature. When the closed reactor was thermally and atmospherically stable, the first sample was mechanically pushed into the constant temperature reaction zone of the furnace. At predetermined times, additional samples were inserted so that time series data could be obtained for each set of conditions studied. Reaction times varied from 2 to 120 minutes, temperatures from 916°K to 1077°K, and total sulfur oxide pressures from 0.008 to 0.130 atm. In addition, we studied the effect of salt composition on the sulfation reactions.
Most variables were studied in conjunction with others using statistically designed factorial sets of experiments. In this manner, information was obtained on the interactions among the parameters as well as on the effects of each parameter separately [12].

RESULTS

The first set of experiments was conducted to investigate the effect of mixed vs. pure salt additives on the formation of non-ferrous sulfates during the oxidation of the sulfide minerals described above. The experiments were conducted at 975°K under an atmosphere of air + 0.05 atm SO$_2$. The degree of non-ferrous conversion to sulfate at equilibrium was taken as the independent variable. The results are summarized in Table I. Reaction times were 120 minutes but little or no change in the degree of sulfate formation was detected after 90 minutes.

| Concentrate       | Salt Added      | Cu   | Ni   | Fe   |
|-------------------|-----------------|------|------|------|
| Chalcopyrite      | 15% (Na,K)$_2$SO$_4$ | 0.98 | --   | 0.033 |
| Chalcopyrite      | 15% $K_2$SO$_4$  | 0.87 | --   | 0.035 |
| Synthetic         | 30% (Na,K)$_2$SO$_4$ | 0.97 | 0.95 | 0.018 |
| Synthetic         | 50% $Na_2$SO$_4$ | 0.70 | 0.40 | 0.027 |
| Chalcopyrite      | 15% (Na,K)Cl    | 0.96 | --   | 0.041 |
| Chalcopyrite      | No salt         | 0.83 | --   | 0.01  |

The second set of experiments sought to determine the identity of copper containing species as a function of reaction time. Here, 0.50 g samples of CuFeS$_2$ containing 15% by weight (Na,K)$_2$SO$_4$ were placed into the reactor at 1000°K under a controlled air + 5% SO$_2$ atmosphere. Absolute levels of CuFeS$_2$ and CuFe$_2$O$_4$ were determined by x-ray diffraction using an inert SiO$_2$ contaminant as an internal calibration standard. Copper found to be water soluble is termed CuSO$_4$ in this series even though some may have been present as oxy-sulfate. Material balances closed within experimental error on all but the 6 min. sample. The difficulty of accurately measuring the residual CuFeS$_2$ makes the measurement on this species most likely to be in error at low concentrations. The results are shown in Figure 2.
The next experimental set was a 3-factorial statistical design series of experiments using 3 levels for each variable. The independent variables were reaction temperature \( \text{P}_\text{SO}_2 \), and salt additive level. The degrees of copper, nickel, and iron sulfation were used as dependent variables. Fixed parameters were 0.500 g sample size, 1000 ml/min total gas flow, and a Na/K ratio of 0.30 in the salt additive. In this series, the air/SO\(_2\) mixture was first passed over a Pt-asbestos catalyst maintained at the same temperature as the reactor to assure \( \text{SO}_2 - \text{SO}_3 \) equilibrium in the reaction atmosphere. The design parameters and experimental results are summarized in Table II. Replicate and supplementary experiments were conducted for this set. Each experiment consisted of a time series of samples to assure that results were obtained at a point reasonably close to equilibrium. Results at 1.25 hrs and 6.00 hrs were not detectably different.

The bottom section of Table II shows how the degree of sulfation varies with each of the independent variables. For example, as temperature increases, the fraction of copper, nickel, and iron found as sulfates decreases. However, an increase in \( \text{P}_\text{SO}_2 \) or in salt additive level can overcome the negative temperature effects. Variable interactions were also determined from the data listed and found to be strong among all three of the independent variables.
### TABLE II

**Face-Centered Cube Response Surface Design**

| Expt | Temp | % SO₂ | % Salt | Cu  | Ni  | Fe  |
|------|------|-------|--------|-----|-----|-----|
| 1    | -    | -     | -      | 100.0 | 54.0 | 7.5  |
| 2    | +    | -     | -      | 30.0  | 2.4  | 0.8  |
| 3    | -    | +     | -      | 98.0  | 52.0 | 18.0 |
| 4    | +    | +     | -      | 48.0  | 12.0 | 3.5  |
| 5    | -    | -     | +      | 100.0 | 89.0 | 20.0 |
| 6    | +    | -     | +      | 57.0  | 5.8  | 1.5  |
| 7    | -    | +     | +      | 100.0 | 92.0 | 42.0 |
| 8    | +    | +     | +      | 90.0  | 27.0 | 5.0  |
| 9    | +    | 0     | 0      | 67.0  | 20.0 | 7.0  |
| 10   | -    | 0     | 0      | 98.0  | 94.0 | 26.0 |
| 11   | 0    | +     | 0      | 96.0  | 46.0 | 8.0  |
| 12   | 0    | -     | 0      | 82.0  | 15.0 | 2.8  |
| 13   | 0    | 0     | +      | 100.0 | 71.0 | 6.0  |
| 14   | 0    | 0     | -      | 93.0  | 65.0 | 5.5  |
| 15   | 0    | 0     | 0      | 94.0  | 31.0 | 5.5  |

**Symbol**

| (+)  | 1073°CK | 10% | 25% |
| (0)  | 1000°CK  | 5%  | 15% |
| (-)  | 923°CK   | 1%  | 5%  |

**Effect Summary**

- Temp: † † † † †
- % SO₂: † † † † †
- % Salt: † † † † †

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Separate experiments were conducted to study the effect of adding Cl\textsubscript{2} to the reaction atmosphere. Those results showed that 0.6% Cl\textsubscript{2} in the gas flow did not affect sulfation yields. Thus reactions of the type:

$$2\text{NaCl} + \text{SO}_2 + \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{Cl}_2.$$  

(18)
do not contribute to the enhanced sulfation rates observed in the presence of molten chloride salts.

**DISCUSSION**

The melting point of an equimolar mixture of NaCl-KCl is about 935°K. Since this is below the reaction temperature for those experiments listed in Table I, it is reasonable to expect that a molten liquid would form very early in the reaction. The mixture of Na\textsubscript{2}SO\textsubscript{4}-K\textsubscript{2}SO\textsubscript{4} used has a melting point of 1135°K and cannot form a binary liquid in these experiments. However, if CuSO\textsubscript{4} is added, then a liquid ternary melt can form at a 20-40-40 mixture of Cu, Na\textsubscript{2}, and K\textsubscript{2} sulfates. The phase diagram for the system, Figure 3, shows that even more CuSO\textsubscript{4} must mix with pure Na\textsubscript{2}SO\textsubscript{4} or pure K\textsubscript{2}SO\textsubscript{4} to achieve melting [13]. From the results in Figure 2, it can be seen that ferrites form very early in a sulfating system (probably due to local overheating) and, therefore, an early formation of the salt melt is necessary to achieve high degrees of sulfation at short reaction times. Since mixed salts will tend to melt earlier in the reaction sequence, it is reasonable to expect them to be more effective at enhancing the degree of sulfate formation achieved, just as is observed.

The extent to which the product sulfates are mixed with the alkali salt additive can be determined by measuring their equilibrium decomposition pressures in the mixed salt system formed during the sulfide oxidation. Since PSO\textsubscript{3} is held fixed in these experiments, the ferrite-sulfate equilibria are used:

$$\text{CuO} \cdot \text{CuSO}_4 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{CuFe}_2\text{O}_4 + \text{SO}_3.$$  

(7)

Since $[\text{Fe}_2\text{O}_3] = [\text{CuFe}_2\text{O}_4] = 1$  

(19)

$$K_7 = \frac{[\text{SO}_3]}{[\text{CuO} \cdot \text{CuSO}_4]}$$  

(20)

Where $[\text{SO}_3] = [\text{S}_2\text{O}_7^\text{m-}]$ and $[\text{S}_2\text{O}_7^\text{7-}] \ll \text{PSO}_3$  

(21)
We calculated [SO₃] based upon a direct reaction of 
CuSO₄ with hematite:

\[ \text{CuSO}_4 + \text{Fe}_2\text{O}_3 \rightleftharpoons \text{CuFe}_2\text{O}_4 + \text{SO}_3 \]  
\( (22) \)

for reaction (7) with \([\text{CuO-CuSO}_4] < 1\) and for reaction (7) 
with \([\text{CuO-CuSO}_4] = 1\). The latter calculation was made since 
it is not clear a priori that the copper basic sulfate is 
soluble in the molten salt solution coating the product particles.

Table III shows the total moles of soluble copper, 
nickel, and iron found in several experiments in our series. 
PSO₃ and reaction temperatures are also shown. Since activity 
coefficient data is not available, we used mole fractions 
for calculating the \([\text{SO}_3]\) required to stabilize the observed 
sulfates. Table IV shows the results of these calculations 
under several sets of assumptions. The first assumes all 
soluble copper was present in the salt as CuSO₄. The next 
columns are calculated assuming all soluble copper was as 
\(\text{Cu}_0\text{CuS}_04\) dissolved in salt. The calculations for 
\([\text{CuO-CuSO}_4] = 1\) are not shown. Finally, \([\text{SO}_3]\) was calculated 
over NiSO₄ under the assumptions of \([\text{NiSO}_4]\) equal to the 
observed mole fraction and for \([\text{NiSO}_4] = 1\). The equilibrium 
constants used were obtained from literature data on the 
species involved in the reactions \([7,8]\). For the two possible 
decomposition paths of copper sulfate,

\[ \ln K_7 = \frac{24.160}{T} - 76.6 + 0.0488T \]  
\( (23) \)

\[ \ln K_{22} = \frac{-1520}{T} - 25.13 + 0.0233T \]  
\( (24) \)

and for

\[ \text{NiSO}_4 + \text{Fe}_2\text{O}_3 \rightleftharpoons \text{NiFe}_2\text{O}_4 + \text{SO}_3 \]  
\( (25) \)

\[ \ln K_{25} = 21.08 - \frac{26.010}{T} \]  
\( (26) \)

The data in the tables is split into three groups for 
illustrative purposes. In the first group, PSO₃ exceeds the 
\([\text{SO}_3]\) needed to stabilize all the copper as either sulfate or 
oxysulfate and all the nickel as sulfate even at unit activity. 
Perrite formation was not observed here. In the second 
group a similar situation appears to exist, but nickel sulfate 
formation is not complete. Finally, in the third group 
PSO₃ is less than the \([\text{SO}_3]\) required to stabilize copper 
oxysulfate at reduced activity or the nickel sulfate at unit 
activity. However, uniformly across all conditions, the
[SO₃] required to stabilize CuO•CuSO₄ in the salt and NiSO₄ at unit activity were found to be very close.

TABLE III
Soluble Salts Recovered in Various Experiments
(Moles x 10⁴)

| Expt | Temp  | Cu   | Ni   | Fe   | Salt Additive | PSO₃  |
|------|-------|------|------|------|---------------|-------|
|      |       |      |      |      | Complete Cu & Ni Sulfation |       |
| 10   | 920°K | 9.14 | 1.97 | 6.53 | 4.49          | 0.029 atm |
| 22   | 951   | 8.96 | 2.21 | 5.78 | 4.49          | 0.030   |
| 23   | 970   | 8.87 | 2.12 | 2.01 | 4.49          | 0.031   |
|      |       |      |      |      | Complete Cu, Incomplete Ni Sulfation |       |
| 1    | 918°K | 10.2 | 1.38 | 1.95 | 1.50          | 0.0083  |
| 3    | 918   | 10.0 | 1.33 | 5.02 | 1.50          | 0.071   |
| 21   | 951   | 9.8  | 1.73 | 3.07 | 1.50          | 0.030   |
|      |       |      |      |      | Incomplete Cu, Incomplete Ni Sulfation |       |
| 2    | 1077°K| 3.06 | 0.074| 0.28 | 1.50          | 0.0021  |
| 29   | 1077  | 6.76 | 0.35 | 0.88 | 4.49          | 0.015   |

From the observations made, a model of the sulfation reaction sequence in the molten salt can be derived. First it seems very unlikely that pyrosulfate can supply [SO₃] at any level near that required to stabilize CuSO₄ in preference to CuO•CuSO₄ in experiments 2 and 29. Therefore, we conclude that equation (7) remains correct for the molten salt system and that the oxysulfate is present at less than unit activity. Next, it appears that NiSO₄ and NiFe₂O₄ exist in equilibrium, that both species are at unit activity, and that the [SO₃] required to stabilize the NiSO₄ comes from the salt melt rather than the atmosphere over the melt.

In an attempt to understand the odd behavior of the nickel, we examined partially oxidized NiFeS₂ under an electron microprobe. An example of what is found is seen in Figure 4 which shows Ni₂S₃ remaining with the iron having been oxidized out of the NiFeS₂ particle. It appears that NiSO₄ does not form until late in the oxidation and not until after the reacting particles are well coated with molten salt. It further implies that NiSO₄ is rather slow to mix with the molten salt, possibly because of the formation of a complex Ni-Cu-Na-K sulfate coating which is a solid at reaction temperatures.
| Expt | PSO₃ | Cu₆⁺Ni Sulfation | Cu⁺Ni Sulfation | Cu⁺Ni Sulfation |
|------|------|------------------|------------------|------------------|
|      |      |                  |                  |                  |
| 10   | .029 | .41              | .0020            | .0020            |
| 22   | .030 | .42              | .0041            | .0041            |
| 23   | .031 | .51              | .0083            | .0083            |
| 1    | .083 | .68              | .0029            | .0029            |
| 3    | .071 | .56              | .0024            | .0024            |
| 21   | .030 | .61              | .0060            | .0060            |
| 2    | .021 | .62              | .0075            | .0075            |
| 54   | .015 | .54              | .0035            | .0035            |
| 12   | .015 | .54              | .0035            | .0035            |

Calculated [SO₃] Required to Stabilize Copper and Nickel Sulfates at the Observed Mole Fractions

Calc [SO₃]

| for NiSO₄=1 |
|------------|
| .007       |
| .0019      |
| .0035      |
| .0007      |
| .0007      |
| .0019      |
| .0044      |
| .0012      |

TABLE IV
It should also be noted that Ni$_2$S$_3$ can liquify at the reaction temperatures. This could result in the production of NiO in good contact with Fe$_2$O$_3$ and allow the rapid formation of NiFe$_2$O$_4$ as sulfide oxidation proceeds. With NiSO$_4$ remaining at unit activity, the system is at equilibrium and very little driving force exists for breaking down the ferrite which does form. The presence of a salt coating on the Fe$_2$O$_3$ would interfere with the NiO-Fe$_2$O$_3$ contact and therefore allow time for an increased degree of nickel sulfation. In this manner, the salt modifies the reaction kinetics as well as the thermodynamics. The postulated behavior is consistent with an earlier micrographic study of sulfide oxidation by Thornhill [14] and explains why previous attempts to quantitatively sulfate pentlandite have not been successful [15].

In summary, the presence of alkali sulfate salts during mineral sulfide oxidation modifies both the kinetics and the thermodynamics of the reactions which occur. The reaction mechanisms in the molten salt appear to be unchanged from those observed in the corresponding gas-solid reactions. Care must be used in determining which species are participating in the reactions, however, since salts not stable at unit activity under reaction conditions will nevertheless be stable at reduced activities. This increased stability of species such as CuSO$_4$, CuO·CuSO$_4$ and FeSO$_4$ must be taken into account if a correct thermodynamic model of a reaction sequence is to be constructed.

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Figure 1  APPARATUS FOR THE STUDY OF SULFATION REACTIONS.

Figure 2  FRACTION OF COPPER IN VARIOUS PHASES DURING CHALCPOYRITE SULFATION

Figure 3  PHASE DIAGRAM FOR K₂SO₄ · Na₂SO₄ · CuSO₄
