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Measurement of Non-isothermal Oxygen Potentials In The Cu-Fe-Ca-S-O Liquid During The Reduction of Chalcopyrite, Lime, and Carbon Mixtures

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ABSTRACT

The reduction of Indian chalcopyrite concentrates from the Ghatshila mines with carbon was studied in the presence of lime in the temperature range of 1123K to 1573K. An attempt was made to determine the oxygen potential corresponding to the selective separation of two metals, copper and iron, during the reduction of chalcopyrite by carrying out electro-motive force (emf) measurements under isochronal heating rate conditions using an yttria-stabilised solid electrolyte cell with Cu/Cu₂O as the reference electrode. The isochronal rate data for oxygen potential measurements were analysed by comparing them with the data from isothermal kinetics studies on the reduction of natural and synthetic chalcopyrite minerals in the above temperature range. The analyses of phases formed were carried out using the X-ray powder diffraction and scanning electron microscopic techniques, which showed the presence of a new quinary solid solution C_{III} phase. The solid solution phase, C_{III} forms as a result of mixing between the two rhombohedral lattices: high-temperature form of Cu₂S and C_{II} (FeO.CaS) compounds. The mechanism of reduction of chalcopyrite with carbon in the presence of lime is illustrated by the explanation of the role of the intermediate phases, C_{II}, C_{III} and matte phases.

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1 INTRODUCTION

The production of copper involves three main pyrometallurgical steps for the processing of sulphide concentrates^{1a}. The concentrates are flash-smelted to produce a matte phase, which is converted to further reduce the concentrations of sulphur and iron. The last stage in the production of anode-grade copper having nearly 99% purity is fire refining. Anode copper also consists of all the precious metals, e.g. gold and silver and residual amounts of heavy metal elements: As, Sb, Hg, Cd^{1b}. Pure copper is electrolytically won from the impure anode, and precious metals are reclaimed from the anode mud.

Modern practice utilises one reactor to carry out smelting and converting to save energy and time^{1c}. The oxidation of iron sulphide (FeS) during smelting and converting leads to pyrometallurgical beneficiation of the matte phase rich in copper. The iron silicate slag and SO₂ gas are the two by-products of the oxidation reactions in the flash smelters and converters. The iron silicate slag is discarded, and the SO₂ gas is used either for making sulphuric acid, or for reclaiming sulphur, depending upon the demand for either of the two byproducts in the region where copper is produced. For the manufacture of sulphuric acid, the SO₂ content in the exhaust gas must be more than 5 percent by volume. In the oxidative process, the metallic iron, which constitutes nearly one-third of the total weight of the chalcopyrite mineral concentrates, is irretrievably lost. In previous investigations²⁻⁵ on the reduction of synthetic chalcopyrite, we demonstrated that copper and iron can be separated from a matte phase consisting of Cu₂S, FeS, FeO, CaS and CaO species, provided the oxygen partial pressure is controlled. The phase separation between the metallic copper and iron sulphide-rich matte under the reducing condition is dependent on the equilibrium oxygen potential of the system. It is, therefore, essential to have both equilibrium and non-equilibrium oxygen potential data for understanding the tendency for metallic phase separation.

In the present investigation, an attempt has been made to measure the oxygen potential as a function of temperature to monitor the progress of reduction of natural chalcopyrite (CuFeS₂) concentrates in the presence of lime. The determination of oxygen potential (log P_{O2}) is also important for designing a process for the preferential separation of metallic copper from the matte phase. More recently, the demand for copper metal has increased due to rapid growth in the building construction in the emerging economies of the world, which means there has been a shortage of copper metal in the world market. In this paper we demonstrate by analyzing the oxygen partial dependence of the metallisation

process, from which condition we may be able to better control preferential metallic phase (copper and iron) separation during selective reduction of sulphide mineral concentrates. In this context, some aspects of the heterogeneous phase equilibria in the (Fe,Cu)-Ca-S-O system under low oxygen partial pressures were also reported by Rosenqvist⁶. However, no data on the measurements of oxygen potential in copper-iron-calcium oxysulphide matte under reducing conditions exist. In this study, the onset and progression of the overall reduction reaction is monitored via oxygen potential measurements, using a solid-state emf cell employing yttria-stabilised zirconia solid electrolyte. The measured emf values are related with the phases formed during the reduction process.

In the late seventies and early eighties, many authors studied⁷⁻¹¹ the reduction of sulphide minerals for the extraction of non-ferrous metals because of the growing concern over acid-rain problem in the Northern European countries and North America. In today's world the emission of greenhouse gases remains a major concern, and in this respect the selective reduction under controlled atmosphere also results in the negligible emission of SO₂.

2 *EXPERIMENTAL*

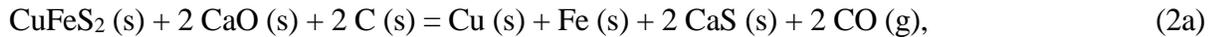
In the present investigation, the chalcopyrite concentrates from the Ghatshila mines in India were used. The chemical analysis of the Ghatshila concentrates is summarised in Table 1. The X-ray diffraction of the concentrates confirms predominantly the presence of CuFeS₂ and some amounts of pyrite (FeS₂) and silica.

The reaction between chalcopyrite and lime was studied by heat treating the powder mixtures (CuFeS₂:CaO=1:2) in an argon atmosphere at selected isotherms chosen between 1173 and 1373K. The duration for each heat treatment was varied between 1 and 4 hours. Pellets from powder mixtures were formed and placed inside an alumina crucible, which was then suspended inside a silica reaction tube. The details of reaction vessel design and apparatus can be found in [ref. \[12\]](#). An inert atmosphere was maintained inside the silica tube by purging with the argon gas at a flow rate of 1000 ml min⁻¹. The silica tube with alumina crucible was lowered inside the constant temperature zone of a MoSi₂ resistance furnace set at a temperature approximately 15-20K above the pre-selected reduction isotherm, which was continuously recorded using a thermocouple.

For the reduction of natural chalcopyrite concentrates, the stoichiometric amounts of CuFeS₂, CaO and carbon were weighed in a ratio of 1:2:2 and mixed in a ceramic pestle and mortar. The resultant mixture was press-packed inside an alumina crucible. Each sample was weighed accurately before and after the experiment for determining the weight change that took place during the course of the reaction at a preselected isotherm. From the observed weight change, the extent of the reduction reactions (given by percentage reaction, %R) was calculated using the data for stoichiometric weight loss (W_o) and the weight loss given at an instant (W_t) i.e.

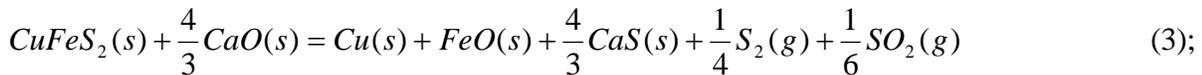
$$\%R = \left(\frac{W_t}{W_o} \right) \cdot 100 \quad (1)$$

Here W_o is the stoichiometric weight loss for the evolution of carbon monoxide gas for the overall reaction shown in eq. 2a, for which the ΔG° function is given by equation 2b¹³:



$$\Delta G^\circ = 234040 - 296.5T \text{ J mol}^{-1} \text{ of Cu.} \quad (2b).$$

Heat treated samples of chalcopyrite minerals with lime in inert atmosphere were also analysed by determining the values of %R as a function of time for the exchange reaction, shown in eq.3.



for which the maximum theoretical weight loss is 10.33 weight percent. At the end of each heat treatment, the silica tube was withdrawn from the hot zone of the furnace. The sample inside was then allowed to cool in an argon atmosphere. The pellet was removed from the alumina crucible and analysed for the phases formed by using the X-ray powder diffraction and scanning electron microscopy, EDX and EPMA techniques. These results together with the results from the reduction reaction of sulphide are shown in **Table 2**. A limited number of thermogravimetric experiments were also carried out using 2 g mixtures of synthetic chalcopyrite with lime and carbon mixed in a ratio of

CuFeS₂:CaO:C=1:2:2 for comparing the results of weight loss (W_t) observed when larger masses of natural chalcopyrite were also reduced, as described below.

Approximately 50 g batch size experiments were also carried out using the above mixture of CuFeS₂, CaO, and C mixed in a ratio of 1:1:2. Each mixture was ground and mixed thoroughly and packed tightly inside a clay graphite (salamander) crucible. A retort furnace was used for heat treating the 50g size mixtures. An inert gas atmosphere inside the furnace chamber was maintained continuously by flowing argon gas at a rate of 3000 ml min⁻¹. Experiments were carried out in the temperature range of 1173K to 1323K for different lengths of time.

The oxygen potential in the molten oxysulphide matte (Cu-Fe-Ca-S-O) was measured by using an yttria-stabilized zirconia solid electrolyte probe. One hundred grams of CuFeS₂ mixed with lime and carbon in a molar ratio of CuFeS₂:CaO:C = 1:2:2 was heated in separate experiments to three different preset temperatures, 1223K, 1473K and 1593K. A heating rate of 10K min⁻¹ was used for all three emf measurements. The cell assembly, as shown in **Figure 1**, was placed inside a resistance furnace, using silicon carbide heating elements. The reaction chamber with oxygen cell was continuously purged with a stream of oxygen-scrubbed high purity argon gas at a rate of 2000 ml min⁻¹. The emf cell can be represented as:

(+) /Pt, /Cu(s)+Cu₂O(s)//(Y₂O₃)ZrO₂//(CuFeS₂+CaO+C), Pt (-).

After the measurements were completed, the furnace power was switched off and the reactor was allowed to cool. The reacted materials were also analysed for phases formed by XRD and SEM-EDAX analysis. It is important to realise that the emf measurements were carried out under isochronal rate of 10 K min⁻¹ and consequently, the phase constitution at the working electrode varies with temperature and the measured oxygen potential corresponds to that of the phase mixture present at that temperature. Furthermore, the measured emf at any temperature during isochronal heating is the instantaneous value at that temperature, and therefore it may not necessarily correspond to the equilibrium value. However, as discussed below, the kinetics of the overall reduction reaction and phase analysis strongly suggest that near equilibrium conditions are attained above 1173K for all natural chalcopyrite samples. From the knowledge of the Gibbs energy of formation of Cu₂O¹³, the oxygen potential in the Cu-Fe-Ca-S-O melt can be expressed in terms of the measured emf, E (mV) of the cell as:

$$\log P(O_2) = -\frac{4FE}{2.303RT} + \log P(O_2)[Cu - Cu_2O] = -\frac{20.157E}{T} - \frac{17590.7}{T} + 7.443(atm) \quad (4)$$

The measured oxygen potential can also be used to construct a $\log P_{(SO_2)}$ versus $1/T$ diagram, by assuming that an equilibrium between CaO and CaS solid phases and O_2 and SO_2 gas mixture coexist, which is shown in equation 5 below.



3 RESULTS

3.1 The Analysis of Phases Formed

The new phases formed after the exchange reaction between chalcopyrite and lime (CaO:CuFeS₂ = 2:1) were analysed by X-ray powder diffraction technique and these results are summarised in **Table 2**. At 1123K, for time less than 120 minutes, the major phases identified after the heat treatment of lime and chalcopyrite mixture (2:1) were calcium sulphide together with the unreacted lime. The observations from X-ray diffraction patterns indicate that the reaction does not reach completion at 1123K. Although the complex quaternary and quinary oxysulphide phases, C_I, C_{II} and C_{III}, were also identified at 1123K, the phases C_I and C_{III} were found to be less prevalent at temperatures higher than 1173K for longer periods of time. In our previous investigations³, we reported the measured hexagonal lattice parameters of compound C_{II}, which is an approximant of a rhombohedral structure with $\alpha=120^\circ$, are **a** = 0.652 nm and **c** = 0.374 nm, whereas the high-temperature hexagonal form of β -Cu₂S has larger **a** (= 0.677 nm), and **c** (= 0.396 nm)^{2-4,14} dimensions. A preliminary crystal structure analysis of the quinary C_{III} phase reveals that it is analogous with the C_{II} phase, described elsewhere^{3,4}, having a rhombohedral approximant, for which the values of the lattice parameters fall between those of β -Cu₂S and C_{II} phases.

3.2 *Heat treatment and reduction of natural chalcopyrite minerals in an inert atmosphere*

In **Figure 2**, the values of percentage weight loss (ΔW_T) are plotted against time, t for the reduction reaction occurring at 1173K and 1273K. In Tables 2a and 2b, we compare the percentage reduction (%R) versus time (t) in hours data for 1173 K and 1273 K. By contrast, the heat treatment of mineral sulphide with lime was carried out only at 1123K, in a stream of argon atmosphere (500 ml min^{-1}). The total weight loss sustained over a period of 2 hours is less than 1 wt%, which corresponds to a value of %R less than 10%. Once the initial period of rapid reaction elapsed, the overall reaction virtually ceased after 30 minutes and resumed very slowly after 75 minutes. The observed weight loss in **Figure 2** is due to the evolution of gaseous species, S_2 and SO_2 , as described in eq.3. At the end of the reaction, the phases formed were analysed, and these were identified as CaS, C_I , C_{II} , C_{III} , and alongside the unreacted lime. No significant evidence for the presence of metallic copper was found at this stage. When the heat treatment temperature was raised to 1223K, significantly more reaction took place, which is apparent from the observed percentage weight loss data in Table 2a. The microstructures of reacted pellet with carbon are shown in **Figure 3a and 3b**. In Fig.3a the bright regions are rich in metal sulphide. By comparison, the light grey phase is rich in calcium ions. The phases present in the microstructure were also verified by X-ray powder diffraction and the data for the chemical reactions with and without carbon are summarized in Tables 2a and 2b, respectively. We point out in Table 2b that the values of percentage reduction exceeded more than 100% which was due to the loss of matte phase from the alumina crucible during higher temperature reduction of pellets. In **Figure 3b** we see copious nucleation of copper within the iron-calcium-copper rich matte, which has been discussed extensively, in previously reported investigations^{2,3}. Large particles of CaO appear to have reacted by forming a thin layer of CaS.

3.3 *Phase analysis of reaction products from heat treatment and reduction reactions of chalcopyrite with carbon in the presence of lime*

The weight loss (W_t), shown above in eq.1, is due to the evolution of CO gas during reaction. The values for the percentage reduction are compared in **Table 2b** together with the phase analysis data, obtained from X-ray powder diffraction. In this table, the relative proportions of phases are arranged in the descending order of their abundance, which was determined by the strength of the relative intensities of the diffraction peaks in the powder pattern. A complete reduction of the mineral phases

to metals was attained by increasing the temperature to 1223K, and holding the sample for two hours in an atmosphere of argon gas. In **Figures 4a-4c**, the elemental analysis of metallized region is shown by comparing with the distribution of copper and iron. Only a small trace of sulphur (not included) was observed with no trace of calcium, suggesting that the metallic copper must have aggregated with help of ambient liquid matte phase. We also compared the measured % R versus time data for synthetic chalcopyrite against the natural chalcopyrite and found that the synthetic chalcopyrite reacted more slowly than the natural chalcopyrite concentrates. For example, at 1173K the natural chalcopyrite nearly reduces to 90%R in less than 90 minutes, which when compared with the synthetic CuFeS_2 reaches just over 70%R in 8 hours. The reaction rates for natural chalcopyrite at temperatures lower than 1173K are also found to be significantly higher than that for synthetic chalcopyrite. The apparent difference in the reduction rates between natural and synthetic chalcopyrite is attributed to their differences in the crystal chemistry and the concentrations of defects present in the structure.

3.4 *Medium scale trials*

From the results of the reduction reaction in the smaller samples of 1 to 2 g, it was observed that the reduction reaction nearly completed at 1223K. Experiments using 50 g samples of chalcopyrite, lime, and graphite mixtures, prepared in the ratio of 1:2:2, were undertaken at 1223K. The results from the X-ray analysis of medium-scale sample were found to be consistent with the phases formed in the small-scale trials. When the temperature was raised from 1223K to 1333K, which is near the melting point of copper and the products were analyzed by X-ray powder diffraction, the relative intensities of diffraction peaks for metallic iron and copper, and calcium sulphide increased with temperature. A similar trend was also observed at 1423K, where copper was expected to be completely molten. The spherulites of metallic iron and copper, as shown in Figure 4a, were found to have dispersed in the matrix of copper as a solute, which appear to be consistent with the Fe-Cu binary phase equilibria. The reacted material was also analysed for phase analysis. It was found that the majority of copper had segregated in the bottom half of the reacted mixture leading to an extensive clustering of molten copper at 1423K. It was also noticed that the matte phase, produced during the course of reduction reaction at 1223K, was partly absorbed by the crucible wall. As a result, the observed weight loss was greater than the stoichiometric weight loss, as shown in Table 2.

3.5 *The measurements of oxygen potential during the reduction of chalcopyrite*

The oxygen partial pressure in the matte phase was measured using an yttria-stabilised zirconia solid electrolyte and Cu+Cu₂O reference electrode, as discussed above. The measured values of P(O₂) on a logarithmic scale have been plotted as a function of reciprocal of the absolute temperature (1/T) in **Figure 5**. For determining the regions of phase stability as a function of temperature and oxygen partial pressure, a logP(O₂) versus 1/T plot was constructed and compared with the results of measured isochronal oxygen potential and phase analysis using X-ray powder diffraction. The powder diffraction analysis points out to the coexistence of the intermediate compound phases, C_I (4FeO.3CaS), C_{II} (FeO.CaS), and C_{III} (β-Cu₂S/C_{II}) solid solution with CaS and metallic phases, Cu and Fe at various stages of reduction reaction. As the thermodynamic properties of the intermediate compound phases are not known, the measured oxygen potential can only be compared with reference to the pure solids and liquids as the standard states. The standard states for the relevant reactions, considered in the ternary and quaternary systems, are defined in Table 3.

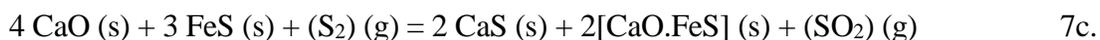
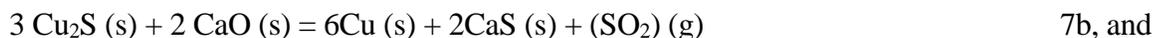
The equilibrium reactions considered for comparing the measured P(O₂) data are summarised in Table 3 along with their corresponding log P(O₂) equations, derived from the Gibbs energy data given in **reference 12**. In the Cu-Ca-S-O and Fe-Ca-S-O systems, we have considered equilibrium between Cu and Cu₂S, and Fe and FeS, respectively. The consideration for metal-metal sulphide and metal-metal oxide equilibrium conditions described in Table 3 for the two quaternary systems means that the values of oxygen potential, given by logP(O₂) plotted against 1/T, represents a univariant only when one of the condensed phases coexist in a solution or compound form. The univariant phase relationship is discussed in detail below. In Figure 5, the measured data sets (runs 1, 2, and 3) are compared with the equilibrium conditions defined by reactions in Table 3. The univariant 6e is plotted for P(SO₂) = 0.1 atm, since such a comparison may be useful to relate with the measured P(O₂) data under reducing condition and with the oxidising conditions maintained during various stages of conventional copper making. Similarly the univariant 6d is plotted using the value of P(S₂) defined by Cu/Cu₂S equilibrium. The condensed phases, defined in Table 3, are those phases which are likely to co-exist with metallic Cu and Fe at a unique oxygen partial pressure for an isothermal condition. By considering the Gibbs phase rule (P+F=C+1) for a constant total pressure condition, it is apparent that the reactions 6a, 6b and 6c have zero degree of freedom (F) for the number of constituents, C = 4. In each reaction, there are 4 condensed phases (P) present, which establish an equilibrium with a gas

phase having predominant constituent species, such as SO₂, O₂, and S₂. Other species in the gas phase have insignificant partial pressures under the inert atmosphere conditions considered in reactions 6a to 6d, 6g, and 6h. The univariant log P(O₂) vs 1/T relationship for reactions 6a, 6b, 6c, 6f, and 6g in the quaternary systems will only be permissible from the Gibbs phase rule, when a liquid or a solid-solution phase may co-exist with the condensed phases defined in these reactions, which means the formation of either a solution or a compound phase will allow the system to have an additional degree of freedom. Previous investigations in the related areas²⁻⁵ have confirmed the presence of a matte and intermediate crystalline phases, C_I, C_{II}, and C_{III}. The stabilities of crystalline phases C_I and C_{II} are consistent with the phase diagram in the FeO-CaS system, reported by Koch and Tromel¹⁵.

In **Figure 5**, the univariant plots are compared with the measured values of logP(O₂), which linearly increases with the decreasing values of 1/T. The measured values of P(O₂) abruptly change slope and again follow a linear relationship. The comparison of measured data with the computed univariants clearly indicate that at low temperature the oxygen potential data follow the univariant corresponding to reaction 6g, and gradually drift towards the equilibrium conditions defined by reaction 6b with the increasing temperature. Above the melting point of copper, the oxygen potential drifts towards 6g and eventually towards 6a.

4. DISCUSSION

The observed weight loss during the calcination-roasting of chalcopyrite in the presence of lime in an argon gas atmosphere above 1123K confirms the formation of metallic copper via the reactions:



The weight loss is primarily due to the evolution of SO₂ above 1123K. Any unreacted Cu₂S thus combines with C_{II} [FeO.CaS] phase and forms a solid solution phase, C_{III} (C_{II}-Cu₂S mixture), in which

the concentrations of Cu^{1+} ions determine the cell dimension. It is therefore expected that the extent of reaction, attained at a given temperature during the reduction and calcination with lime, determines the composition of the solid solution C_{III} phase.

The microstructural evidences from the reduced chalcopyrite (see Figures 3 and 4) point out to a strong tendency for metallic phase separation between copper and iron. Above the melting point of copper, liquid copper gradually drains away through the pore channels and segregates at the bottom part of the reduced material in the crucible. It is due to this reason that the intensity of copper in the powder diffraction pattern reduced significantly with increasing temperature. The melting point of iron is at 1808K, and the metallic copper has a higher solubility in the γ -Fe phase¹⁶ than in α -Fe. Also the γ -Fe solid solution phase is in equilibrium with copper-rich liquid¹⁴, which explains the segregation of copper around the spherulitic iron produced from chalcopyrite reduction in Figures 4a-4c. The presence of encapsulated iron around copper exhibits that it is unable to separate away completely from the γ -iron solid-solution as it cools down from 1173K to lower temperatures after the reduction reaction. Below 573 K, less than 0.02 weight percent copper can dissolve in α -iron. As a result of the reduced mutual solid solubility of copper and iron in the terminal region at low temperatures and due to the non-wettable iron-copper interface, metallic iron segregates as globules within molten copper. During the reduction reaction, copper and iron however appear to form in the following stages:

i) Below 1173K, the extent of reduction reaction is less than 80% R in the first 80 minutes, as can be seen in Table 2b. At this stage copper metallises first, followed by iron in the latter stages of reduction reaction. This is consistent with the observations made earlier for the reduction of synthetic chalcopyrite under similar conditions². Copper formed at this stage does not appear to have any metallic iron. Most of the copper and iron, after the initial stage, are present in their ionic forms in the C_{III} (FeO.CaS-Cu₂S solid solution) and C_{II} (FeO.CaS) lattices, and are essentially reduced from these two phases and the liquid matte (Cu-Fe-Ca-S-O).

ii) Above 1173K, a quinary liquid composed of elemental components Cu, Fe, Ca, S and O forms. This liquid is a derivative of the reaction between decomposed chalcopyrite (Cu₂S/FeS solid solution) and lime. The liquid on cooling yields CaS, C_{II} and C_{III} phases. The reduction of the quinary liquid, which is in equilibrium with C_{II} and C_{III} phases, yields copper and iron together.

iii) From the apparent changes in the slopes of the oxygen potential data in Figure 5, it is evident that the overall reduction reaction encounters two other lower oxygen potential states, one of which, the region I, may correspond to oxygen potential states similar to univariant 6b. The second intermediate oxygen potential region II can be comparable with the oxygen potential defined by univariant 6c. The linear regimes, I and II, may correspond to the equilibrium between the quinary liquid matte of compositions I and II in equilibrium with metallic copper. The complex phases, C_{II} and C_{III} observed at the room temperature with calcium sulphide are the product of crystallisation from the quinary liquids I and II.

iv) From **Figure 5**, the two linear regimes appear to have an identical slope, which may also suggest that the enthalpy of the reaction, representing the corresponding equilibrium states, may not change when the transition between the regions I and II takes place.

v) The measured emf at higher temperatures (>1323K) drifts towards the univariants 6a and 6g, and appear to follow these two equilibria, which correspond to equilibrium between (Cu/Cu₂S and CaO/CaSO₄) and (Cu/Cu₂S and CaS/CaSO₄) phases. Previous investigation on the reduction of copper sulphide^[16] demonstrated that when the rate of reduction by carbon was slower than the exchange reaction between lime and sulphide phase, the oxygen potential at the reduction interface increased to a limit, at which CaS oxidised to CaSO₄. The period of CaSO₄/CaS equilibrium appeared as a plateau on the rate of reduction versus time curves. Similar observations were made when graphite was used as an inert reducing agent (Cu₂S:CaO:C=1:1:2) in stoichiometric amount to sustain the overall reduction reaction. The transient equilibrium states, indicated by the sharp changes in slopes between the regions I, II, and univariant 6g might therefore correspond to redox states of CaSO₄, which changes during the oxygen potential measurements between univariants 6b and 6g. However, unlike previous observation, we were unable to identify the presence of CaSO₄ from the emf data because the size of sample was too large and the sampling of matte was too difficult.

5. CONCLUSIONS

a) Chalcopyrite minerals can be directly reduced to form copper and iron metals in the powder form below 1273 K. The tendency for metallic phase separation between copper and iron during the

reduction can be controlled by maintaining oxygen potentials, shown in Figure 5.

b) A complex solid solution (C_{III}) phase exists between the compositions of β - Cu_2S and C_{II} . The lattice parameters of C_{III} is dependent on the concentrations of Cu^{1+} ions dissolved in the C_{II} phase, which may vary between the cell sizes of C_{II} and β - Cu_2S crystals, e.g $c = 0.396$ nm, $a = 0.677$ nm in Cu_2S and $c = 0.374$ nm and $a = 0.652$ nm in C_{II} . Consequently, the cell dimension of C_{III} phase is also expected to change as a function of reduction condition.

c) The isochornal measurements of oxygen potential during the course of the reaction in the presence of lime identified the conditions for a selective separation of two metallic phases by following univariants 6a, 6b and 6g. The emf measured by the oxygen cell at any temperature is the instantaneous value and corresponds to the conditions, which are determined by the two boundary equilibrium conditions defined by reactions 6a and 6b in Table 3.

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Table 1: Composition of Ghatshila mineral concentrates (weight percent)

Elements/oxides analyzed	Weight percent (wt %) or in ppm
Cu	25.20
Fe	28.28
S	31.60
Ni	0.43
Co	0.17
Mo	0.09
loss on ignition	2.31
Al ₂ O ₃	4.44
SiO ₂	7.04
MgO	0.50
Ag	20 parts per million (ppm)
Au	1.5 ppm

Table 2: A comparison of phases formed and %R data for various conditions of heat treatment of chalcopyrite, lime, and carbon. "AC" designates the activated charcoal, "50 g size" designates experiments in a retort furnace with 50 g size of the mixture trials in a clay/graphite (salamander) crucible. The identified phases are arranged in the descending order of the relative intensity of the powder diffraction pattern. The flow rate of argon gas through the retort furnace was 3000 ml min⁻¹.

a) Heat treatment of chalcopyrite in an inert atmosphere of argon (flow rate = 1000 ml min⁻¹).

Compositions	T,(K)	t,(mins)	% R	Phases Identified
1:2	1123	5	7.57	CaS, CaO,
1:2	1123	30	8.66	CaS, CaO, C _{II}
1:2	1123	60	7.69	CaS, CaO, C _{II}
1:2	1123	90	9.917	CaS, CaO, C _{III}
1:2	1123	120	9.78	CaS, CaO, C _{III} , C _{II} , C _I
1:2	1223	60	10.55	CaS, C _{II} , C _{III} , C _I

Table 2 (continued)

b) Reduction of chalcopyrite

Compositions CuFeS ₂ :CaO:C=	T, K	Time, minutes	%R	Phases identified
1:2:2	1123	5	41.1	CaS, CaO, C _I
1:2:2	1123	30	42.0	CaS, CaO, C _{III} , C _{II} , C _I
1:2:2	1173	5	41.3	CaS, CaO, C _{III} , C _{II}
1:2:2	1173	120	95.9	CaS, Cu, C _{III} , C _{II}
1:2:2	1223	120	145.5	CaS, Cu, Fe
1:2:2 50 g size	1223	120	144.0	CaS, Fe, Cu
---	1273	180	150.4	CaS, Fe, Cu
1:2:2	1273	120	119.5	CaS, Cu, Fe
1:2:2 (AC)	1123	60	70.4	CaS, Fe, Cu
1:2:2 (AC)	1173	60	106.1	CaS, Fe, Cu
1:2:2 (AC)	1223	60	126.2	CaS, Fe, Cu
1:2:2 (AC)	1273	60	159.9	CaS, Fe, Cu
1:2:2 (AC)	1323	60	154.1	CaS, Fe, Cu

Table 3: The equilibrium conditions considered for drawing a plot of $\log P(O_2)$ against $1/T$ in Figure 7. $\log P(S_2)$ is fixed with respect to Cu/Cu₂S equilibrium at a given T.

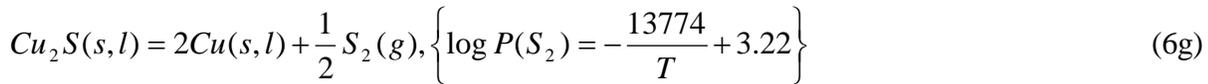
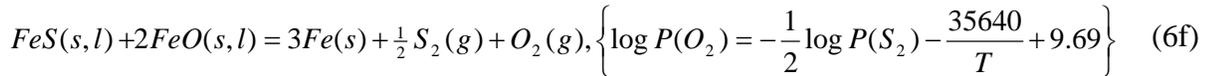
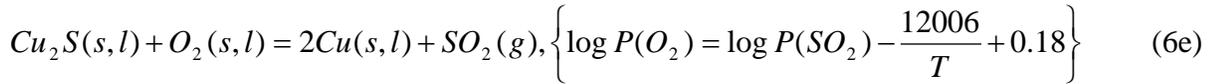
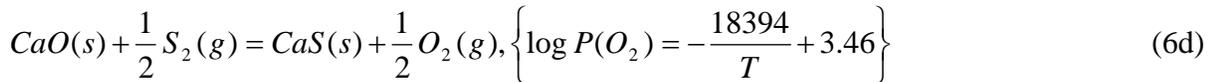
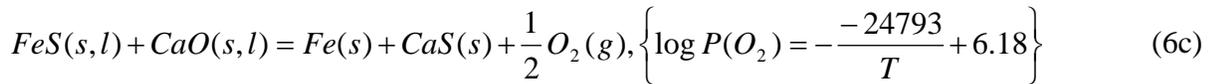
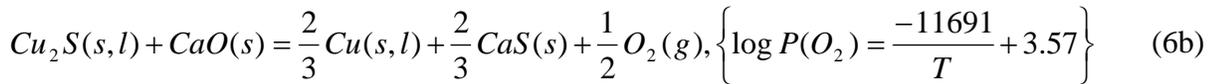
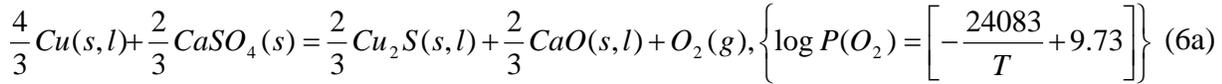
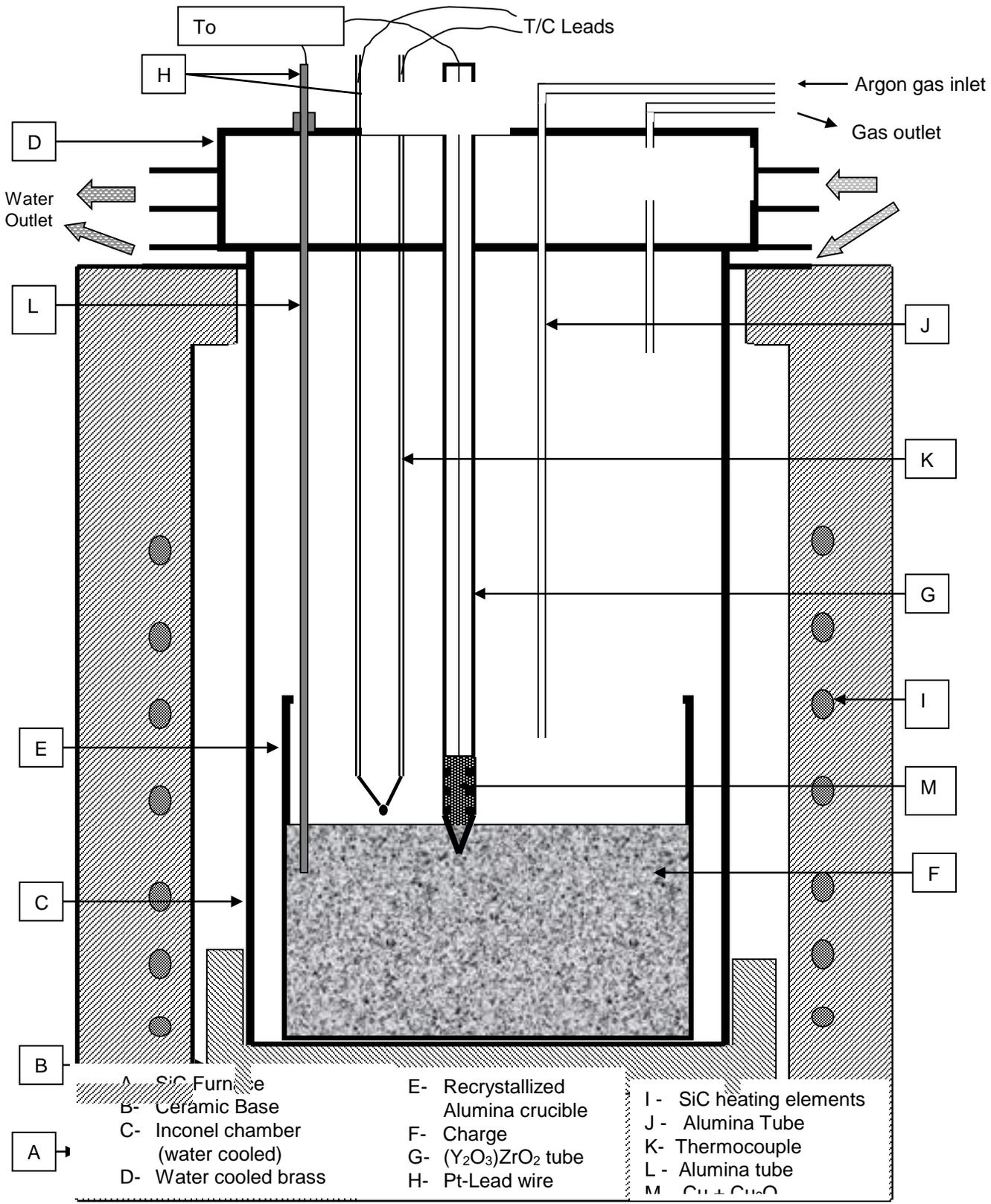


Figure 1: The drawing of the emf cell for the measurement of oxygen partial pressure during the reduction of chalcopyrite and lime mixture with carbon.



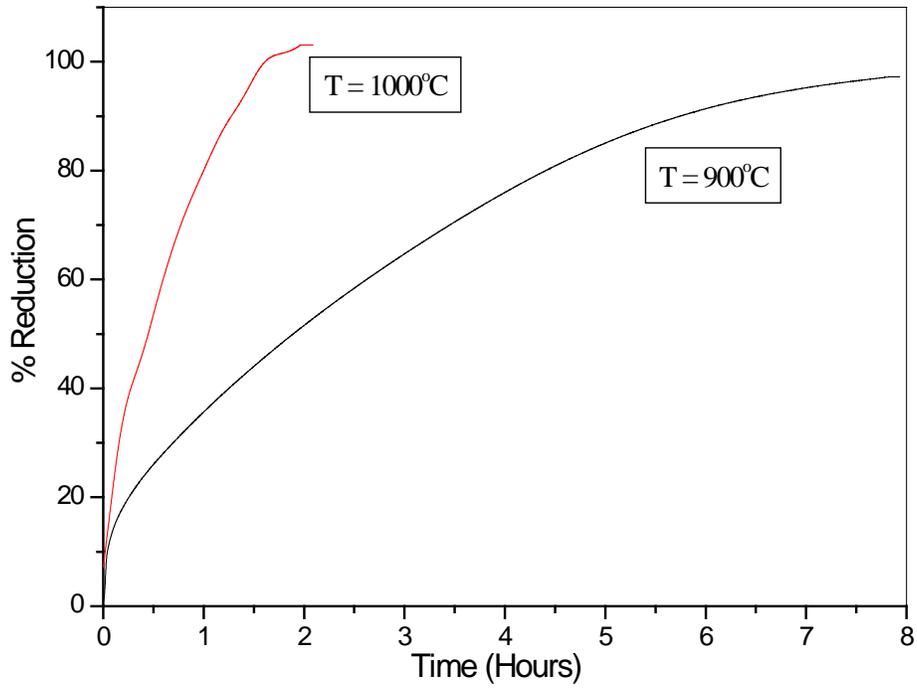


Figure 2: A comparison of the kinetics of reduction of chalcopyrite concentrates mixed with lime and carbon in the ratio of $\text{CuFeS}_2:\text{CaO}:\text{C}=1:2:2$ in argon atmosphere, maintained at a rate of 1000 ml min^{-1} at 1173 K and 1273K.

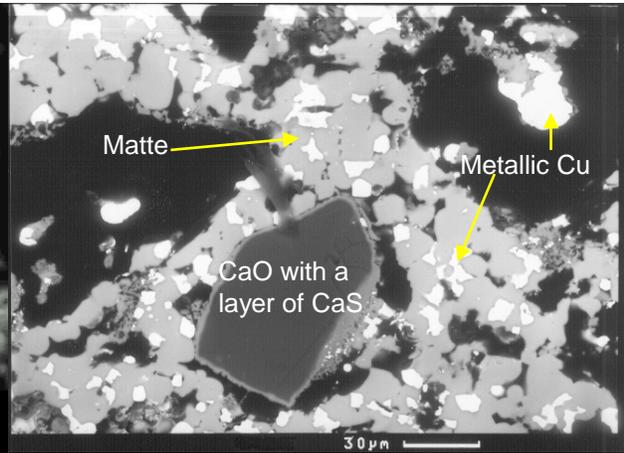
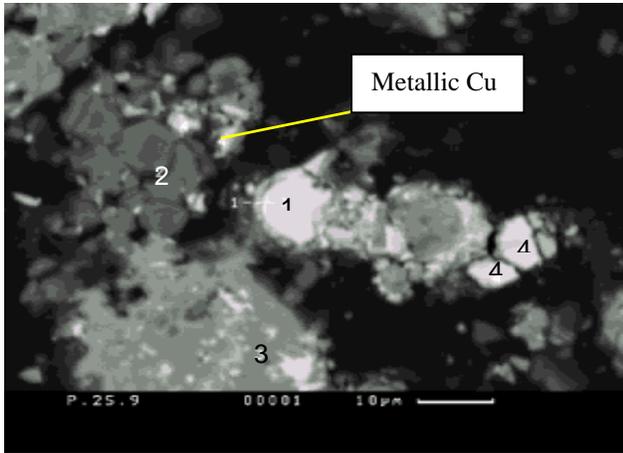


Figure 3a

Figure 3b

- Figure 3: a) An SEM microstructure of reduced chalcopyrite from Ghatshila mines (T=1173K)
 Composition $\text{CuFeS}_2:\text{CaO}:\text{C} = 1:2:2$. Area 1 – sulphur and copper phase, Area 2 – sulphur, iron, calcium, and copper matte phases, Area 3 – calcium, iron and oxygen phase, Area 4 – CaS. The metallic copper is dispersed with CaS phase.
- b) The microstructure shows the presence of metallic Cu (Bright white) dispersed in the matrix of iron-copper-CaO-rich matte (grey in colour). The lime-rich particle (dark grey in colour) has a thin layer of CaS.

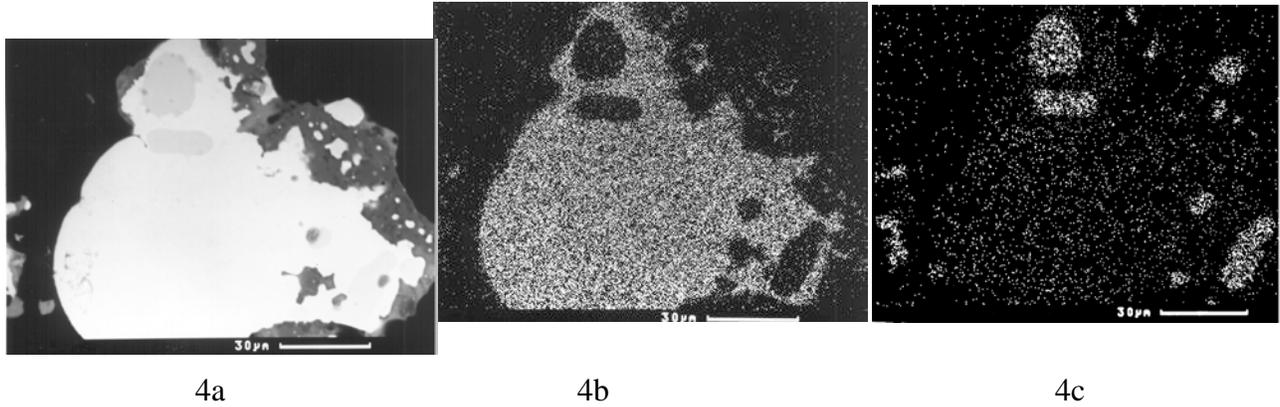


Figure 4: A high-magnification secondary electron image of metallized area: a) Metallic copper (bright) with iron copper alloy dispersed within, b) copper elemental map and c) iron elemental map. The mineral concentrate was reduced at 1273K for 2 hours. Mixture ratio was chalcopyrite: CaO: C=1:2:2. The reduced solubility of γ -Fe in copper at low temperature yields a trapped iron, shown as a light gray phase within copper (shown bright).

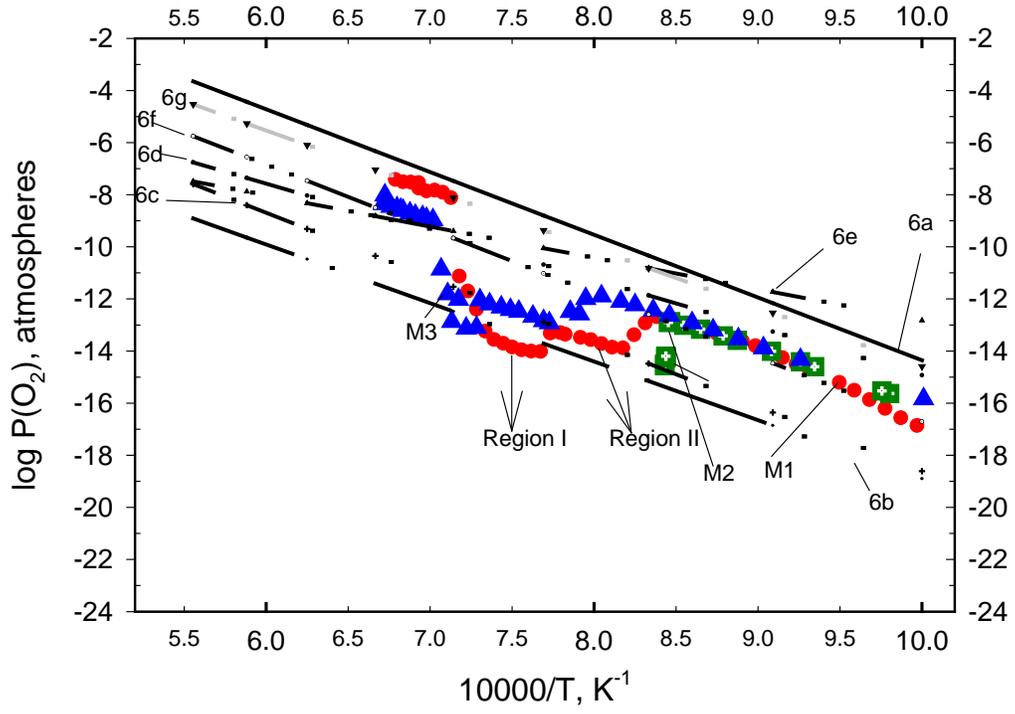


Figure 5: A comparison of the measured P_{SO_2} with the calculated equilibrium values of P_{SO_2} determined from the Gibbs free energy changes for the reactions tabulated in Table 3, which represent the likely reactions during the reduction of a Cu-Fe-Ca-S-O matte.