Stability Diagrams for Copper-Sulfide and Copper-Recycle Systems Applied to Extractive Metallurgical Processes

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Copper sulfide from ore deposits and recycled copper from collected wastes are the two main resources for the production of copper metal. Thermodynamic calculations can be used to serve as a guide for characterization of ore deposits and their mineralogy as well as for process development by mineral processing and by waste separation. The concentrated ore and separated waste can then be processed by pyro- and/or by hydro-metallurgical operations. Such operations may be controlled by oxidation-reduction potential, temperature, complexing reagents (gas, solid or dissolved species), oxidant-reductant, and mass of components. Commonly used stability diagrams for aqueous system include speciation (counting alpha) and $E_{0}pH$ (Pourbaix) diagrams and, for non-aqueous systems, are partial pressure (Kellogg), binary and ternary phase, and Ellingham diagrams.

For multicomponent systems, the appropriate approach for the construction of the stability diagram is to use a complete mass balance approach rather than draw the equilibrium line between two adjacent species. Not limited to two variables, a three-dimensional diagram can also be constructed.

This paper illustrates the use of stability diagrams for investigating and interpreting how operation variables are important with a focus on extractive metallurgical operations to produce copper. Industrial operation conditions are marked on the diagrams.

**Keywords**: Thermodynamics copper extraction, Partial pressure diagram, $E_{0}pH$ diagram, Ellingham diagram, Binary and Ternary phase diagrams

1 INTRODUCTION

Sulfides minerals are usually the main feed for the production of non-ferrous metals. Extractive processes involve many unit operations from ore to metal. Each operation has been thoroughly researched and developed not only for the recovery of metals but also for the rejection of the gangue minerals. Because copper is a well-recognized metal processed globally at high tonnages, its extractive metallurgical treatment as various sulfide minerals has been selected as the main focus of this paper.

Not to be ignored, copper is one of the most recycled metals. There is little difference in quality and performance between extracting from ore or recycling materials. Because of tight supply of copper from ore deposits, 34% of global copper produced is from recycled materials. About 60% of recycled copper is primarily from scrap that can be charged directly to the melting furnace for refining. Secondary recycled copper comes from consumer waste and electronic waste (E-waste). It too can be recycled not just for copper but for other valuable metals as well.

Because most of the processing steps involve many critical variables, a simplified overall reaction or list of conditions cannot show the flexibility or the adjustments necessary for changing the materials and operating conditions. Various types of stability diagrams can be used and are thus illustrated based on chemistry and thermodynamics under multi-variable conditions.

Characterization and/or process operations presented in the following discussion include: Copper ore deposit, Mineralogical formation, Flotation chemistry, Smelting and converting by pyrometallurgy, and Leaching processes by hydrometallurgy, both managed and natural.

The authors assume that the reader has basic knowledge about Extractive Metallurgy of Copper which is well presented by the Davenport Ref. [1]. Thus, only crucial processes will be presented. Except ternary phase diagrams, most of the stability diagrams presented herein were constructed by StabCal Ref. [2] with the temperature and composition as close to the actual process as possible. Most of diagrams are also marked with the conditions actually used in plant operations.

2 COPPER ORE DEPOSIT

Copper porphyry ore deposits occur throughout the world and are very important sources of copper, silver, and gold. These deposits initially consist of disseminated sulfide minerals in a rock matrix, but near-surface weathering oxidizes the sulfides and dissolves metals from the residual mass. These leached metals in solution percolate downward and are often precipitated in an enrichment zone overlying unreacted sulfide protore. The near-surface weathered, oxidized portion of the deposit corresponds to the oxidized region (high oxidation potential), while the non-oxidizing reduced enrichment zone corresponds to the reduced...
3 MINERALOGY

3.1 Ternary Diagram of Cu-Fe-S

Copper sulfide minerals are commonly associated with other sulfides, iron sulfides in particular. The mole fraction ternary phase diagram of Cu-Fe-S is shown on Figure 3 which indicates three distinctive zones depending on the Cu/(Cu+Fe) ratio. Using the chemical formula of minerals, Zone 1 has the ratio less than chalcopyrite (CuFeS_2). Zone 2 lies in between chalcopyrite and bornite (Cu_5FeS_4), and Zone 3 has excess copper greater than bornite. All diagrams in this mineralogy section are constructed using species and their free energies of formation re-evaluated from Figure 6.16 of Garrels and Christ Ref. [6].

Species and their individual masses in Zone 1 were simulated by titration. Total mass of Cu-Fe-S components were 0.1-0.2-0.15 moles, respectively. By keeping Cu and Fe amounts constant, S was incrementally added from 0 to 0.4. The simulation path is shown on Figure 3 using a long arrow labelled with the area from A to I. The results of equilibrium calculation are shown in Figure 4 with the same labels and are noted to satisfy Gibbs Phase Rule under all conditions such that no more than three solids are simultaneously stable although their amounts can change depending on the amount of sulfur titrated. For instance, in area E, three stable species are observed (CuFeS_2, FeS_2, and FeS) with their respective masses.

Figure 1 Illustrated copper ore deposit (Dudas et al. Ref. [3]) for comparison to the Eh-pH diagram in Figure 2.

Figure 2 Eh-pH diagram for Cu-CO_2-Fe-S in water. pCO_2 = 0.1 atm, [S] = 0.01 M, [Fe] = [Cu] = 0.001 M. Species and their free energies of formation were taken from the LLnl database Ref. [5]. In reference to Figure 1, light gray represents the oxidized/leached zone (solid and soluble species) whereas moderate gray illustrates the enriched zone, and dark gray shows the primary sulfide zone.

Figure 3 Ternary Cu-Fe-S mole fraction phase diagram. This figure is copied and edited from Figure 6.15 in Garrels and Christ Ref. [6].

Figure 4 Species and their mass from Zone 1 of Figure 3 along the path from A to I in Figure 3.

3.2 Partial Pressure Diagram–Equilibrium Line versus Mass-balanced Method

The partial pressure diagram, aka Kellogg diagram, can be constructed either by the equilibrium line or by mass-balanced methods. The line method is used to calculate and draws equilibrium boundaries between two adjacent species. The mass-balanced method solves equilibria from all species and balances specified for all components together for each location on the diagram. For a multicomponent system, the line method suffers the lack of controlling individual mass. Huang and Young Ref. [7] presented more detailed comparison between these two methods.

3.2.1 Line method diagram—Suitable only for Zone 1 from Cu-Fe-O-S system: The log pS_2 vs log pO_2 partial pressure diagram was originally presented by Garrels and Christ Ref. [6] and has
been recalculated using StabCal. The new result is presented in Figure 5 where Cu is the main component and Fe serves as the ligand. Without specifying the mass of each component, this type of diagram always assumes that the mass of ligand to be greater than or equal to the mass main component. In other words, it represents only Zone 1 on the ternary diagram shown in Figure 3.

### 3.2.2 Mass-balanced diagram – Suitable for All Zones from Cu-Fe-O-S system

By comparison to Zone 1, the other Zones requires Cu/(Fe+Cu) to be greater than 0.5 and have to be constructed by the mass-balanced method. Figure 6 shows the diagram for Zone 3 using Cu/(Cu+Fe) = 0.9. As indicated on the ternary diagram, Figure 6 illustrates that chalcopyrite is not present in Zone 3.

### 3.2.3 3-D diagram – Combine all 3 zones into one diagram

The best way to show all 3 Zones for a partial pressure diagram is to include an additional variable of the mass ratio Cu/(Cu+Fe). Results from this mass-balanced calculation are shown in Figure 7 and Figure 8 after importing StabCal results into Paraview 3-D software Ref. [8].

Even though the diagram can be animated by rotation, clipping and slicing, only still pictures can be presented in this paper.

### 4 FLOTATION

#### 4.1 Frumkin Adsorption

During froth flotation, some minerals absorb collector and change their hydrophilic surfaces to hydrophobic. Resulting minerals will attach to air bubbles injected into the slurry to rise and form a froth at the top of the pulp. A separation is made when the froth is removed by scraping into a launder thereby forming a concentrate. Non-adsorbing minerals remain in the pulp and are removed as tailings at the bottom of the cell.

Xanthate, represented by X, is a common collector that has been used and studied often for the flotation of copper ores. Species HX, X⁻, X₂ (aqueous and liquid), and CuX₅ and FeX₅ all have been identified. In addition, Woods Ref. [9] also reported that electrochemically adsorbed X(chem) occurs by the surfaces of chalcocite and Cu metal. Even though the adsorption is independent of pH, surface coverage depends not only on collector concentration but also the potential of the minerals. The Frumkin isotherm was modified to formulate this type of adsorption.
where, $\theta$ is fraction of surface coverage, $a_\lambda$ is collector concentration, and $E$ is potential. Constants $g$, $K$ and $\gamma$ can be estimated by regression from experimental data. The final equation for Ethyl Xanthate (EtX) chemisorption by chalcocite is:

$$\left(\frac{\theta}{1-\theta}\right) \exp \left(\frac{g \theta}{1-\theta}\right) = K a_\lambda \exp \frac{\gamma FE}{RT}$$

(1)

$$\left(\frac{\theta}{1-\theta}\right) \exp \left(40\right) = 8.4 \times 10^9 X^{-\gamma} \exp \left(-\frac{E}{0.016}\right)$$

(2)

4.2 $E_\text{th}$-pH Diagram of Flotation Chemistry

By combining all the Ethyl Xanthate (EtX) species for the Cu-Fe-S system, the $E_\text{th}$-pH diagram was constructed and is shown on Figure 9 using free energy ies reported by Forssberg Ref. [10]. The diagram shows not only the predominant area of Cu plus xanthates species: EtX, CuEtX, EtX, and EtX(chem). The shaded area on the diagram indicates where EtX(chem) can cover over 90% of CuS. The diagram also indicate the $E_\text{th}$ and pH from some discharged tailings from industrial flotation reported by Forssberg Ref. [10]. For clarity, the extremely small areas are not labeled with species on the diagram. Bowden and Young Ref. [11] used voltammetry to verify the diagram under alkaline conditions.

5. PYROMETALLURGY

About 80% of primary copper concentrate is treated by pyrometallurgical operations. It starts by smelting copper concentrate into matte and slag, then converting matte to blister copper (98.5 to 99.5% Cu) which is then electrorefined to make high purity copper. Gold and other precious metals are recovered as copper (98.5 to 99.5% Cu) which is then electrorefined to make concentrate into matte and slag, then converting matte to blister copper.

5.1 Smelter Operation

5.1.1 $\text{SiO}_2$ Separates Slag from Matte: Excluding data from Russia, a survey of 43 major copper smelting operations Ref. [12] shows that the average copper concentrates is CuFe$_{0.23}$S$_{0.69}$ which is a stoichiometry that closely matches chalcopyrite. During the smelting operation, iron is partially oxidized to FeO and Fe$_2$O$_3$ with $O_2$. These oxides are then converted at high temperature into a liquid phase (slag) using $\text{SiO}_2$ and possibly other fluxes.

$$\text{CuFe}_S + O_2 + \text{SiO}_2 \rightarrow \text{Slag (CuFeSulfides)} + \text{FeS(oxides)} + \text{SO}_2 (g)$$

(3)

The sulfides remain as liquid matte. Using data from Figure 2 of Yazawa Ref. [13], the partial ternary diagram FeO-FeS-$\text{SiO}_2$ in Figure 10 was constructed. It shows how FeS-rich matte and FeS-lean slag become two immiscible liquids by $\text{SiO}_2$ addition. After point A, shown on the diagram, the two phases begin to separate.

5.1.2 Matte Grade: The average matte grade from the survey Ref. [12] is CuFe$_{0.99}$S$_{2.07}$. The Cu-Fe-S ternary diagram shown in Figure 11, originated from Schuhmann Ref. [14] and was redrawn by Davenport Ref. [1]. It is used to show the thermodynamic basis for matte composition. The symbol * on the diagram is from the survey Ref. [12] and clearly shows that the composition of matte is nearly saturated with liquid copper or solid iron.

5.1.3 Slag Composition: The ternary diagram of FeO-Fe$_2$O$_3$-$\text{SiO}_2$ in Figure 12, shows the thermodynamics of slag composition during the smelting operation. Indicated on the diagram, from the same survey Ref. [12], is the label “A” indicating the average smelting temperature of 1242°C at an average composition 30.5% $\text{SiO}_2$. Under this average condition, according to Figure 12, FeO and Fe$_2$O$_3$ will be 51.5% and 18.0%, respectively.

5.2 Converter Operation

Remaining sulfides in the matte are further treated in the converter by blowing air to form $\text{SO}_2$ and produce blister copper. From the survey Ref. [12], the average converter temperature is 1223°C, the S content in the feed materials is 22.41%, and the purity of blister copper produced is 98.55%. The cutout Cu-S phase diagram, shown Figure 13, indicates the direction of the reaction of the matte to form blister copper and is marked with * for the temperatures and starting matte grades from the survey Ref. [12].

5.3 Pyrometallurgical Operation for Recycling Copper

Copper smelting is the most important step for treating secondary source of copper for recycling. In order recover most

![Figure 9](image9.png)  Mass-balanced $E_\text{th}$-pH diagram of Cu sulfides under flotation conditions. Mass of Cu-Fe-S-EtX are 2.91-2.91-5.82-1x10^-4 mole/L, respectively. The gray area indicates the predominance of EtX(chem). Symbol * represents the $E_\text{th}$ and pH of tailings from flotation operations taken from Forssberg Ref. [10].

![Figure 10](image10.png)  Partial ternary phase diagram of FeS-FeO-$\text{SiO}_2$ at 1200°C. Composition of matte (o) and slag (*) under the influence of $\text{SiO}_2$ addition. Experimental points were taken from Yazawa Ref. [13].
valuable metal, the smelting technology has to be adapted and evolved from conventional method of treating sulfide minerals.

The new “black copper” route that is commonly used consists of both reduction and oxidation steps Ref. [15]. The combined steps produce three output streams: liquid copper metal, slag and exhaust gas that likely contain dust. The purpose of the operation is to recover as much valuable metals as possible.

Due to the high investment required, only a handful of companies are actually processing secondary recycle copper Ref. [15]. The flowsheet of the Kosaka (Japan) operation is shown on Figure 14 Ref. [16]. The smelting furnace is an Ausmelt that runs under the multiple-stage batch cycled between oxidation and reduction Ref. [17]. Three output streams are: slag to be discarded, exhaust gas and dust which contains volatile Zn, Pb, Sn and Bi, and molten Cu which also contains precious metals as well as Ni and Co. All mixture of metals are treated and recovered as individually.

5.3.1 Iron Slag: Unlike copper from sulfide concentrates, iron is only a minor constituent in recycled copper. This unwanted element is best rejected as a slag with proper flux using the phase diagram of CaO-“FeO”-SiO2 Ref. [18]. Formation of an olivine slag is the best choice, due to its low melting temperature, low viscosity and low copper solubility Ref. [19]. The cut out diagram with additional log pO2(g) in the area of olivine and its adjacent minerals (Temperature ≤ 1200°C) are shown in Figure 15. Partial oxygen pressures were calculated based on the measured Fe2O3 content (less than 4%) and free energies provided for the reaction Ref. [20]. Below the temperature of 1200°C on the liquidus surface, the values of log pO2(g) are between -12 to -14, but, as the temperature increases to 1500°C, these log pO2(g) values can increase to between -5.5 and -8.5.

5.3.2 Non-Ferrous Slag: To reject undesirable, non-ferrous types of materials, the ternary phase diagram of Al2O3-CaO-SiO2 with 10% MgO system is deemed the most suitable. In this case, the target temperature is in the area below 1200°C Ref. [21]. The percent compositions of SiO2-CaO-Al2O3-MgO at the center of these areas are 53-23-14-10, respectively.

5.3.3 Ellingham Diagram: Ellingham diagrams involving oxides are a popular source to show oxidation-reduction reactions between a metal and its oxide. Figure 16 shows some of selected metals related to the copper recycling process. Assuming log pO2
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can be operated from -6 to -10 atm at temperature ranges from 1500 to 1700K, the diagram indicates:

- Cu, Co and Ni will report to the stable molten metal; whereas, Pb, Zn, Bi and Cd will vaporize into the exhaust.
- Fe can easily be oxidized but cannot be reduced; hence it would stay as the slag to be discharged.
- Sn can be easily converted to SnO₂ by changing the oxygen pressure and temperature. It can also be vaporized as SnO(g) as shown in Figure 17.

5.3.4 Partial Pressure of a Minor on a Predominance Diagram:
For vaporization purposes, it is crucial to indicate the partial pressure of their gaseous species. The log pO₂(g) versus Temperature diagram for Sn is shown on Figure 17 in which the dominant species are Sn(l), SnO(l) and SnO₂. In this regard, the pressures contours of SnO(g) are also plotted in light gray.

6 HYDROMETALLURGY

6.1 Chloride Elevated Temperature Leach
Secondary copper sulfides such as Cu₂S and their oxidized products are suitable for leaching with dilute sulfuric acid at ambient temperature. The processes can be chosen from dump to agitation leaching. The more refractory type of primary sulfides such as chalcopyrite requires fine grinding to particles < 15 μm and

a much more aggressive lixiviant under elevated pressure and temperature conditions. Many processes have been proposed and developed, but only a few were successful Ref. [1]. Currently, one of the prominent processes is chloride acid leaching Refs [23, 24]. According to the literature, there are 3 major groups of reactions to the process.

Group 1. Oxygen can leach chalcopyrite to form soluble Cu(II) chloride and solid elemental S and Fe₂O₃:

$$4\text{CuFeS}_2 + 5\text{O}_2 + 8\text{HCl} \rightarrow 4\text{CuCl}_2 (a) + 8\text{S} + 2\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{O}$$

Group 2. Cu(II) and Fe(III) chlorides can leach chalcopyrite to form soluble Cu(I) and Fe(II) chlorides and solid elemental S:

$$\text{CuFeS}_2 + 3\text{CuCl}_2 (a) + 10\text{Cl}^- \rightarrow 4\text{CuCl}_2^{2-} + \text{FeCl}_4^{2-} + 2\text{S}$$

Group 3. Depending on the leaching pH, two solid phases can form such that Fe(III) chloride precipitates as Fe₂O₃ (hematite) when pH > 0.5, and Cu(II) chloride precipitates as Cu₂Cl(OH)₃ (atacamite) when pH > 2.5.

$$2\text{FeCl}_2^{2-} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 (s) + 4\text{Cl}^- + 6\text{H}^+$$

$$2\text{CuCl}_2 (a) + 3\text{H}_2\text{O} \rightarrow \text{Cu}_2\text{Cl}_3(\text{OH})_3 (s) + 3\text{Cl}^- + 3\text{H}^+$$

The Eh-pH diagram for the Cu-Fe-S-Cl system shown in Figure 14 is presented to illustrate the basis reactions for the chloride leach. The area of chalcopyrite is painted in light gray, and elemental S is in darker gray. The diagram indicates the reactions by drawing directional arrows from reactant to product with their group numbers as described from Equations 4 to 6-2.

6.2 Hydrometallurgy for Secondary Recycle Copper
Most of investigations on direct leaching of secondary recycled copper utilize traditional hydrometallurgical technology from leaching, and purification to metal recovery. More specific, small
scale, and highly profitable material such as printed circuit board (PCB) for recovering Cu, precious metals, Zn, Ni, Sn and Pb have been investigated with hydrochloric acid Ref. [15] and ammonia Ref. [25] as the two leaching reagents most considered.

The $E_{H-PH}$ diagram of copper associated with HCl at low pH and NH$_4$OH at high pH is shown on Figure 19. Both reagents have the capability to leach metal and be regenerated by O$_2$(gas). The chloride is represented by Equations 5-1 and 6-2; whereas, the ammonia system is represented by Equations 6-3:

Table 1 lists reactions and equilibrium potential for chloride leaching of important metals from PCB as well as the potentially useful oxidants. The mixture of HCl with HNO$_3$, even aqua regia, is sometimes suggested. Nitric acid will serve not only as an oxidant and also to ensure the dissolution of all metal chlorides.

Hydrometallurgical processes should not be ignored for recycling processes. For example, as shown by the flowsheet for the Kosaka smelting in Figure 14, except for two pyro-furnaces, almost all subsequent processes involve hydrometallurgical separation and recovery of individual metals.

6.3 Bacterial Oxidation of Metal Sulfides

The mechanism of bioleaching from metal sulfides in aerobic environments has been subjected to investigation for many years.

The latest report from Sand et al. Ref. [27] proposed two different paths for biooxidation: (a) thiosulfate mechanism for acid-insoluble

![Figure 18](image1.png)

**Figure 18** $E_{H-PH}$ diagram for the Cu-Fe-S-Cl system to illustrate the chloride leaching reactions at 100°C. The equilibrium line method was used with the LLnL database Ref. [5] at concentrations of $[Cu] = [Fe] = 1$, $[S] = 2$ and $[Cl] = 5$ moles/L. Arrows indicate the direction of reaction, and numerical numbers indicated the reaction groups described in the text.

![Figure 19](image2.png)

**Figure 19** $E_{H-PH}$ diagram of Cu influenced by ammonia and by chloride at 25°C. Concentrations of NH$_3$:Cl:Cu are 2:1:0.01 mole/L, respectively. NBS database Ref. [26] was used.

| 8 | Equilibrium Half Cell Reaction | Potential $V$ |
|---|--------------------------------|--------------|
| O | $H_2O + O_2(g) + 2H^+ + 2e^-$ | 1.2288 |
| O | $2H_2O \leftrightarrow 2H^+ + H_2O_2(a) + 2e^-$ | 1.8340 |
| N | $NO_2^- + H_2O(l) \leftrightarrow NO_3^- + 2H^+ + 2e^-$ | 0.8192 |
| Cu | $CuCl^2+ \leftrightarrow Cu^{2+} + 2Cl^- + e^-$ | 0.4224 |

| Leaching of Metal to Metal Chlorides | $E_n$ nonStd. |
|--------------------------------------|---------------|
| Au | Au + 4Cl$^-$ $\leftrightarrow$ AuCl$_4^{3-}$ + 3e$^-$ | 0.9616 |
| Pd | Pd + 4Cl$^-$ $\leftrightarrow$ PdCl$_4^{2-}$ + 2e$^-$ | 0.4995 |
| Ag | Ag + Cl$^-$ $\leftrightarrow$ AgCl(s) + e$^-$ | 0.2222 |
| Cu | Cu + 2Cl$^-$ $\leftrightarrow$ CuCl$_2^-$ + e$^-$ | 0.0649 |
| Sn | Sn + 2Cl$^-$ $\leftrightarrow$ SnCl$_2$(s) + 2e$^-$ | -0.2311 |
| Pb | Pb + 2Cl$^-$ $\leftrightarrow$ PbCl$_2$(s) + 2e$^-$ | -0.2678 |
| Ni | Ni + Cl$^-$ $\leftrightarrow$ NiCl$^-$ + e$^-$ | -0.2971 |
| Fe | Fe + Cl$^-$ $\leftrightarrow$ FeCl$^-$ + e$^-$ | -0.5289 |
| Zn | Zn + 2Cl$^-$ $\leftrightarrow$ ZnCl$_2$(s) + 2e$^-$ | -0.8296 |

| Non-standard potential: Dissolved Metal Chloride ~ 0.01, and Chloride ion ~ 1 moles/L Activity of solid = 1 |

![Figure 20](image3.png)

**Figure 20** Bioleaching of metal sulfides proposed by Sand Ref. [19] has two different indirect mechanisms: (a) thiosulfate path for acid-insoluble sulfides such as pyrite and (b) polysulfide path for acid soluble sul fixtures such as chalcopyrite.

![Figure 21](image4.png)

**Figure 21** Speciation diagram of S versus $E_{H}$ for pyrite (FeS$_2$) that follows the thiosulfate path of bioleaching. $S = 0.0001$ moles/L at 25°C and pH 1.5.

The mechanism of bioleaching from metal sulfides in aerobic environments has been subjected to investigation for many years.
sulfides such as pyrite and MoS₂, and (b) polysulfide mechanism for acid soluble sulfides such as chalcopyrite and other copper sulfides. Their reaction paths are presented on Figure 20.

These two oxidation paths can be seen from their speciation versus EH diagrams. Figure 21 is for the thiosulfate path and Figure 22 is for the polysulfide path. Both diagrams used dGs from Forssberg Ref. [10] but required additional thiosulfate species were taken from HSC Ref. [22], and additional polysulfide species were taken from Rickard Ref. [28]. These additional species were made consistent to insure there were no errors from mixing data from different sources.

Summary

Stability diagrams for several unit operations utilized in the extractive metallurgy of copper sulfides and recycled materials have been presented. The diagrams based on thermodynamic calculations allow the effects of several variables to be predicted. A summary of the topics covered in this paper and their associated diagrams are:

1. Copper ore deposit: Eₜₜₜ-pH diagrams for the Cu-CO₂-Fe-S system to relate the depth of the deposit to the EH of the diagram.
2. Mineralogy: (a) Ternary phase diagram for the Cu-Fe-S system; (b) Speciation by titration of Cu-Fe with S; (c) the log p₅ₒ₂-log p₅ₛ₂ diagram of Cu-Fe from three different zones shown on the ternary diagram; (d) the multicomponent diagram by mass-balanced calculations; and (e) the 3-dimensional diagram for log p₅ₒ₂-log p₅ₛ₂-Cu/(Cu+Fe) mass ratios.
3. Flotation chemistry: Frumkin adsorption and the EH-pH diagram for the Cu-Fe-S with ethyl xanthate. Xanthate species X₂, CuX₂ and X(chem) adsorbed by Cu₂S were also shown.
4. Pyrometallurgy: Smelter operation includes three ternary diagrams to illustrate how SiO₂ separates slag from matte, as well as matte grade and slag composition; and converter operation uses the Cu-S binary phase diagram to show how smelter matte becomes blister copper.
5. Hydrometallurgy: Eₜₜₜ-pH diagram for the Cu-Fe-S-Cl system at 100°C to explain the major reactions occurring in a chloride leach operation.
6. Bioleaching under aerobic conditions: Sulfur speciation versus Eₜₜₜ illustrating the thiosulfate path and the polysulfide path.
7. Secondary recycle copper: pyrometallurgy and hydrometallurgy unit operations are needed to additionally recover precious metals and other base metals. Thermodynamic calculations for processing these valuable metals are critical:
   a. Pyrometallurgy–Phase diagrams for slag formation, predominance diagrams of Sn-O and for vaporization of SnO₂ gas, and Ellingham diagram for interaction between metal and their oxides.
   b. Hydrometallurgy–Eₜₜₜ-pH diagrams for leaching of Cu using chloride and ammonia. The tabulated equilibrium potentials for oxidants and dissolution of metals in chloride system.

Acknowledgements

The authors would like to thank the Montana Tech Library for their collections, and librarians for their help obtaining valuable references. The authors would like to thank Dr. Yasushi Takasaki of Akita University for providing papers covering the Fundamental Studies on Copper Smelting Reports published by Professor Yazawa when he was at Tohoku University. Particular thanks to ICMR 2017 Akita Organization for their invitation and financial support for hosting Dr. Hsin-Hsiung Huang when he lectured and presented at the conference (October 25-27 2017) and attended the field trip to the Kosaka Smelter (October 23-24 2017). Dr. Huang personally thanks faculties and staff at Akita University while in Japan, particularly Dr. Kazutoshi Haga for his translations, and Dr. Yasushi Takasaki for his hospitality and guidance.

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