Thermodynamics of Gallium (Ga) at Black Copper Smelting Conditions Relevant to E-Waste Processing

MOHAMMAD MEHEDI HASAN, M. AKBAR RHAMDHANI, and GEOFFREY A. BROOKS

Electronic waste (E-waste) is considered as a hazardous material, however, it also contains valuable elements, including gallium (Ga). E-waste can be processed through the black copper smelting to recover these valuable elements. However, the detailed thermodynamics behavior of many of the valuable elements during black copper smelting has not been studied comprehensively. This study aims to investigate the thermodynamics of Ga in copper and slag at black copper smelting conditions. High-temperature equilibrium experiments were carried out to measure the distribution ratio of Ga in Fe₂O₃–CaO–SiO₂ slag and copper at temperature range of 1300 °C to 1450 °C (1573 K to 1723 K) and partial pressure of oxygen (pO₂) of 10⁻⁶ to 10⁻¹¹ atm. The effect of Fe₇/₅SiO₂ ratio and basicity (measured as CaO/SiO₂) of the slag on the distribution ratio of Ga were also investigated. The partitioning of Ga into the copper phase was found to increase with decreasing oxygen partial pressure, and with increasing temperature, Fe₇/₅SiO₂ ratio and basicity. The study revealed that a basic slag at higher temperature and at a reducing atmosphere was favorable to increase Ga partitioning to the copper.

https://doi.org/10.1007/s11663-022-02593-4
© The Author(s) 2022

I. INTRODUCTION

Urban ores are resources already above ground which may consist of electronic waste (E-waste), lower grade copper tailings, spent catalysts, industrial sludge, other low-profile scraps in either metallic or oxide state, end-of-use construction metals, and other resources. Urban ores contain many base metals and valuable elements that potentially can be recovered. For example, e-waste contains gold (Au), silver (Ag), palladium (Pd), ruthenium (Ru), tantalum (Ta), gallium (Ga), indium (In), tin (Sn), bismuth (Bi), antimony (Sb), nickel (Ni), cobalt (Co), titanium (Ti), and other valuable elements. In the context of circular economy and processing of e-waste through black copper smelting, understanding the effect of slag chemistry, temperature, and partial pressure of oxygen during the process is important for maximizing the collection of the valuable elements (including gallium) into the metal phase.

In nature, gallium is found in aluminum ores (bauxite and diaspore) and zinc ores. The oxides of Ga are found in zinc ores when separated from zinc sphalerite. Gallium oxides are also found in chalcopyrite and stannite. Gallium is also found in the industrial wastes or by-products, such as in the caustic liquor produced during Bayer process of bauxite processing, flue dust collected in the fume-collection system in the aluminum production plants, residues obtained in zinc refineries, gallium scraps, and from coal fly ash.¹ High-purity Ga can be recovered from Ga₂O₃ in a caustic solution by a combination of solvent extraction and electrolysis process. Major uses of Ga are for integrated circuits (ICs, accounted for 72 pct of Ga consumption in the USA), light-emitting diodes (LEDs), light amplification by stimulated emission of radiation (LASER), transistors, solar cells, and other electronic devices or components. Therefore, Ga is present in various e-wastes (after these electronics are at their end of life). Approximately 80 pct of Ga is used as GaAs, GaN, and GaP in the USA.² In 2017, 97 pct of the world’s primary gallium was supplied by China. Therefore, USA, EU, and other nations regarded Ga as a critical element which has economic importance and possesses supply risk.³ According to the 2021 US Geological Survey (USGS) report, the global production of Ga was reduced to 300 tons from 351 tons in 2019.⁴ This is largely different from the predicted Ga consumption in 2020, i.e., approximately 420 tons.⁵ The large difference is assumed due to the
COVID effect on the global manufacturing industries. Towards the future, urban ores (particularly e-waste) can play significant role as secondary resources to meet the Ga global demands.

Urban ores, including e-waste, can be processed through black copper smelting route. The processing conditions are vastly different from the typical primary copper smelting. Unfortunately, there are only limited studies available in open literatures on the behavior of valuable elements during black copper smelting, in particular, the thermodynamics and distribution ratio of Ga. Avarmaa et al. measured the distribution ratio of Ga, Ge, In, and Sn in copper and alumina-containing iron silicate slags at 1300 °C (1573 K), at secondary copper smelting conditions. [4] They reported higher partitioning of In and Sn in slag due to the addition of CaO in the slag. Ge was reported to be mostly vaporized during the equilibration and Ga was preferentially distributed into the slag phase. They found the distribution ratio of Ga in metal to slag to vary between 0.5 and 0.0005 when the partial pressure of oxygen was increased from 10^{-10} to 10^{-4} atm. Chernousov et al. studied the Ga partitioning in smelting conditions between pig iron and slag [5] and reported predominant Ga deportment to the pig iron at carbon saturation condition at 1400 °C (1673 K). They reported the distribution ratio of Ga in pig iron and slag to vary between 34 and 257. Sukhominlov et al. studied the distribution of Ga, In, Sn, and tellurium (Te) between copper matte and silica-saturated iron silicate slags at 1300 °C (1573 K). [6] According to their findings, with increasing matte grade from 55 to 75 wt pct copper, the deportment of Te was reported as inconclusive because of the excessive volatilization of Te during equilibration. Yliaho studied the distribution of Ga, Ge, In, and Sn at lead smelting conditions. [7] Experiments were performed at 1150 °C (1423 K) and oxygen partial pressure of 10^{-7} to 10^{-12} atm and the distribution ratio of the elements in lead and slag were reported to be in the range of 0.01 to 0.8 for Ga, 0.1 to 8 for Ge, 0.003 to 11 for In, and 0.002 to 4 for Sn, respectively.

The aim of this study is to further investigate the thermodynamics of Ga in copper and slag at black copper smelting conditions. An experimental design was developed for studying the distribution ratio of Ga in Fe_{2}O_{3}-CaO-SiO_{2} (FCS) slag and copper. The studies were carried out at 1300 °C to 1450 °C (1573 K to 1723 K) with varying partial pressure of oxygen (pO_2) from 10^{-6} to 10^{-11}. The effects of variation of Fe_{7}/SiO_{2} ratio and basicity (measured as CaO/SiO_{2}) of the slags on the distribution ratio of Ga were also studied.

II. EXPERIMENTAL METHODOLOGY

The raw materials used in this study are listed in Table I. All the raw materials had a purity greater than 99.5 pct. Mixtures of powders with appropriate composition were weighed and mixed in a ball mill for approximately 12 hours before melting. A vertical resistant-tube furnace (Nabertherm RHTV 120–300/18, Lilienthal, Germany) was used for melting the slags and the copper alloys, as well as for the main equilibration experiments.

A. Minimum Equilibration Time

Preliminary equilibration experiments (approaching equilibrium from both oxidizing and reducing conditions) were carried out to investigate the suitable minimum time for equilibration. For the experiments approaching equilibrium from an oxidizing condition, Ga slag of target composition 51.5 wt pct Fe_{2}O_{3}, 33.4 wt pct SiO_{2}, 10.1 wt pct CaO, 5wt pct Ga_{2}O_{3} was prepared by melting the powder mixture at 1350 °C (1623 K) for 4 hours in an MgO crucible in air. The quenched Ga slag was powdered manually using a stainless-steel mortar and pestle. Approximately 3.5 g of copper powder and 3.5 g of Ga slag were used for these preliminary equilibration experiments.

For preliminary equilibrium experiments approaching from a reducing condition, a Cu–Ga alloy was prepared by melting Cu and 5 wt pct Ga in an alumina crucible in a vertical tube furnace at 1350 °C (1623 K) for 2 hours in Ar gas atmosphere. A similar method to the one used for the Ga-slag preparation was used to prepare a 54.2 wt pct Fe_{2}O_{3}, 35.2 wt pct SiO_{2}, 10.7 wt pct CaO (FCS) slag. Approximately 3.5 g of Cu–Ga alloy and 3.5 g of FCS slag were used for these experiments.

The preliminary equilibrium experiments were carried out using high-density magnesia crucibles at 1350 °C (1623 K) and oxygen partial pressure (pO_2) of 10^{-8} atm. The cylindrical magnesia crucibles (purity 97.4 wt pct MgO with SiO_{2} being the major impurity and minor impurity content of CaO, Fe_{2}O_{3}, and Al_{2}O_{3}) of outside diameter: 18 mm, inside diameter: 14 mm, and height: 30 mm were sourced from Ozark Technical Ceramics, USA. The magnesia crucible was placed on a sample holder that contain a bed of alumina powder. The magnesia crucible was covered with a bigger alumina crucible in an upside-down position to reduce Ga or GaO_{x} losses in vapor. This technique was used successfully by other researchers [8–13] Sample quenching was carried out by quickly lowering the pedestal to cool region in the water-cooled flange of the furnace. The schematic of the furnace arrangement is shown in Fig. 1. A B-type (Pt-30 wt pct Rh/Pt-6 wt pct Rh) reference thermocouple (TC Measurement & Control Pty Ltd, Australia) was used to calibrate the furnace before experiments. The required partial pressure of oxygen was achieved by controlling the flowrate of CO and CO_{2} according to the equation developed by Yazawa and Takeda (Eq. 1). [14]

\[
\log p_{O_2} = 2 \log \left( \frac{R_{CO}}{R_{CO_2}} \right) - \frac{29510}{T} + 9.05
\]  

The CO/CO_{2} gas mixture flow rate was 400 mL/min. To control the CO_{2} and CO gas flow rates into the furnace, digital mass flow controllers (Aalborg, USA) were used. The obtained p_{O_2} inside the furnace was measured and confirmed by ADS-type SIRO2 C700 +
solid zirconia electrolyte oxygen sensor (Ceramic Oxide Fabricators, Australia). Before and after the furnace operations, high-purity argon gas was purged to clean the furnace tube.

B. Ga-Partitioning Study in MgO-saturated FCS Slag and Copper

The effects of temperature, \( p_{O_2} \), \( Fe_{T}/SiO_2 \) ratio, and basicity (measured as \( CaO/SiO_2 \) ratio) on the partitioning of Ga in slag and copper were studied. For this main study, at first, master slags and master alloys were prepared in the vertical tube furnace. The detailed experimental conditions and composition of the master slags are shown in Table II. The powder mixtures of target master slag compositions were melted at 1350 °C (1623 K) for 4 hours in MgO crucibles. For this Ga partitioning study at various process conditions, a 6-hour equilibration time was used. The preliminary equilibration test results are included in the later part of this Section. Approximately 3.5 g of Cu–5 mass pct Ga alloy and 3.5 g of FCS slag were used for the experiments.

The quenched samples after experiments were mechanically broken into pieces. The metal and slag portions were physically separated from the crucible. The metal samples were cut to small pieces and then dissolved in nitric acid (0.01 g metal in 1 ml of conc. HNO\(_3\)). The diluted solutions were tested in ICP-AES (inductively coupled plasma-atomic emission spectrometry) against the standard solutions of Cu and Ga. The ICP standards were 1000 mg/L of Cu and Ga solutions in nitric acid from Sigma-Aldrich. Selected slag samples were separated manually after equilibration experiments and ground to fine powder. The powdered slag samples were fused using sodium peroxide and dissolved in the mixture of hydrochloric and nitric acids. The chemical analysis of the solutions was carried out using ICP-AES technique (Varian 730 ES: ICP-AES). For the rest of the slag samples, mass balance was carried out to calculate the partitioning of Ga in slag phase.

The partitioning of Ga in slag and copper phase was recorded at different equilibration times (from 2 to 18 h) as shown in Fig. 2. A 6-hour equilibration time was found to be sufficient to achieve the equilibrium. Therefore, 6-hour equilibration time was used for all the equilibrium experiments. Chemical composition of the slags after equilibrium experiments were measured using XRF and are provided in Table A1 in the Appendix.

III. RESULTS AND DISCUSSIONS

A. Thermodynamics of Ga Partitioning in Cu metal and MgO-saturated FeO\(_x\)-CaO–SiO\(_2\) Slags

The basics of thermodynamics of elements during copper processing are discussed briefly below. The distribution ratio of Ga in slag phase and metal phase can be defined as given in Eq. (2).

\[
L_{Ga}^{Cu} = \frac{\text{pct Ga in metal phase}}{\text{pct Ga in slag phase}} = \frac{[\text{Ga}]}{[\text{Ga}]} \tag{2}
\]

The oxidation reaction of Ga is given by Eq. (3) considering the valency of Ga is \( 2v \).

\[
[Ga] + \frac{v}{2} O_2 = (GaO_v), \tag{3}
\]

where \([\ )\) indicates Ga in solution in Cu and ( ) indicates Ga in solution in the slag. The corresponding reaction constant (K) is given by Eq. (4),

\[
K = \frac{a(GaO_v)}{a([Ga]) \cdot p_{O_2}^{v/2}} \tag{4}
\]

Here, \( a(GaO_v) \) and \( a([Ga]) \) are the activity of Ga in metal and GaO\(_v\) in slag, and \( p_{O_2} \) is partial pressure of oxygen. Activity of any species is dependent on the mole fraction and the activity coefficient (\( \gamma \)) of that species in that solution and is given in Eq. (5).
Considering the difference of molar weights of Ga and GaO₃, the distribution ratio of Ga (L₉/Cu) can be written as given in Eq. 6 (from Eq. (2) to Eq. (5)),

\[ L_{\text{Ga}}^\text{Cu} \approx \frac{K(n_T)^{\gamma_{\text{Ga}}}p_{O_2}^{2/3}}{N_T^{\gamma_{\text{Ga}}}} \]  

Here, \((n_T)\) is the total number of moles in 100 g of slag and \(N_T\) is the total number of moles in 100 g of copper which is 1.57.

At a specified temperature, except partial pressure of oxygen, all terms on the right side of Eq. 6 are fixed. Therefore, we can rearrange the equation into Eq. (7):

\[ \log L_{\text{Ga}}^\text{Cu} = \log B + \left( \frac{V}{2} \right) \log p_{O_2}. \]  

From the experimental data of the distribution ratio of Ga in slag and metal at a varied oxygen partial pressure, the log–log plot should yield a linear relationship. The slope of the straight line multiplied by two is the valence of the metal in slag.

The effect of processing condition (temperature and partial pressure of oxygen, \(p_{O_2}\)) and slag composition (variation of Fe₅/SiO₂ ratio and slag basicity) on the partitioning of Ga in MgO-saturated FeO–CaO–SiO₂ (FCS) slag and copper metal were investigated. In the following subsections, the details of result and analysis are given. The distribution data of Ga in different phases at different processing conditions are listed in Appendix in Table A2.

1. Effect of Temperature

The effect of temperature on the distribution of Ga in copper and MgO-saturated FeO₉–CaO–SiO₂ slag is shown in Fig. 3. The experiments were carried out at fixed Fe₅/SiO₂ ratio and slag basicity of 1 and 0.3, respectively. The oxygen partial pressure was fixed at 10⁻⁸ atm while the temperature was varied from 1300 °C (1573 K) to 1450 °C (1723 K) to study the effect of temperature on the partitioning of Ga. It was found that Ga prefers to distribute to the slag phase below 1450 °C. With increasing temperature from 1300 °C (1573 K) to 1450 °C (1723 K), the partitioning of Ga to copper was found to increase.

The free energy of formation of Ga₂O₃ (oxidation reaction of Ga) found in the literature is shown in Eq. (8).\(^{[15,16]}\)

\[ 2\text{Ga(l)} + 3/2 \text{O}_2(g) \rightarrow \text{Ga}_2\text{O}_3(s) \quad \Delta G^\circ = -718392 - 212T(J/mol). \]  

The equilibrium constant of Ga oxidation was also calculated using the “Reaction” module of FactSage 7.2 thermochemical software for temperatures 1300 °C (1573 K), 1350 °C (1623 K), 1400 °C (1673 K), and 1450 °C (1723 K) and the values are shown in Table III. It was observed that the equilibrium is shifted to the left side of the reaction with increasing temperature. Therefore, higher amount of Ga reports to copper at higher temperatures. The viscosity of the slags is also expected to decrease with increasing temperature which would be beneficial for slag tapping.

However, with increasing temperature the total copper loss to the slag was observed to decrease as shown in Fig. 4. The total copper loss to the slag was decreased from 1.45 to 1.18 wt pct with increasing temperature at a fixed oxygen partial pressure of 10⁻⁸. The loss of copper to the FCS slag was found to be higher (but comparable) than that from the previous studies.\(^{[10,12,14,17]}\)

A semi-empirical relation of temperature and \(p_{O_2}\) with total copper loss to the iron silicate and calcium silicate slags was developed by Yazawa and Takeda and is provided in Eq. 9.\(^{[14]}\) The data from the current study were compared to the total copper loss to the slag calculated from their model and are presented in Fig. 4.

A slightly higher total copper loss to the slag was observed in this study compared to Yazawa and Takeda model, however, a similar trend of total copper loss to the slag with temperature was observed.

\[ \log (\text{wt.pct Cu in slag}) = 0.221 \log (p_{O_2}) + 2490/T + 0.455 \]  

2. Effect of \(p_{O_2}\)

The effect of oxygen partial pressure on the partitioning of Ga in copper and MgO-saturated FeO₉–CaO–SiO₂ slag was investigated in the oxygen partial pressure range between 10⁻⁸ atm and 10⁻¹ atm at 1350 °C (1623 K). The Fe₅/SiO₂ ratio and the basicity of the slag were kept fixed at 0.1 and 0.3, respectively, for this series of experiments.

The distribution ratio of Ga in FCS slag and copper was plotted against partial pressure of oxygen in a log–log scale in Fig. 5. Ga was preferably distributed to the slag phase for the whole \(p_{O_2}\) range, from 10⁻¹ atm to 10⁻⁸ atm. However, in the highly reducing condition (\(p_{O_2}\) of 10⁻¹ atm and 10⁻⁸ atm) the distribution of Ga in the metal phase was quite significant. Here, it is to be noted that at highly oxidizing condition (very low concentration of Ga), the measurement of Ga concentration in the metal phase is prone to error due to the instrumental detection limit of Ga. At extreme condition of very low oxygen potential (\(p_{O_2}\) of 10⁻¹ atm at 1350 °C, for example), the formation of FeO alloy could also happen, which may affect the measurement of Ga concentration in the Cu phase, hence, the results at these extreme conditions should be taken carefully.

The slope of the curve was found to be 0.45 in the current study. This may indicate that the major oxide species of Ga in slag had a + 2 valence (from Eq. 3 and Eq. 7). Considering this, the oxidation reaction of Ga can be written as

\[ [\text{Ga}] + \frac{1}{2} \text{O}_2 = (\text{GaO}). \]  

The published data for Ga distribution during black copper smelting by Avarmaa et al.\(^{[4,18]}\) are also included in Fig. 5 for comparison. Their data, corresponding to the Ga distribution in FeO₉–SiO₂–5 wt pct Al₂O₃ and...
FeOₓ–SiO₂–5 wt pct Al₂O₃–5 wt pct CaO slags, provide linear fittings with slope of 0.35 and 0.42, respectively. This is similar to the slope obtained from the current study. This may also support the idea that the majority of Ga present in these slag systems in the form of divalent gallium oxide, i.e., GaO. It should be noted, however, previous old studies in the 1960s in CaO–Ga₂O₃,[19] Fe₂O₃–FeO–Ga₂O₃[20] and Ga₂O₃–SiO₂ systems[21] only referred to the existence of Ga³⁺ (Ga₂O₃) species. These works, however, were carried out in the system at oxidizing conditions (ambient atmosphere and pO₂ of 1 to 10 atm). It is plausible that in the reducing condition (like in the present study), the majority of Ga could be present as Ga²⁺ (GaO). Zinkevich et al. reported the instability of solid GaO phase as previous attempts to synthesize solid GaO was a failure.[22] It is clear that further studies will be needed to clarify this matter.

Sukhomlinov et al. reported the variation of Ga distribution with changing matte grade and changing partial pressure of oxygen. They reported that the Ga distribution ratio in iron silicate slag and copper matte is increased from 57 to 505 with increasing oxygen partial pressure from 10⁻⁸.1 atm to 10⁻⁷.6 atm keeping the sulfur dioxide partial pressure constant at 0.1 atm. Yliaho[7] studied the distribution of Ga in lead bullion and lead slag. Yliaho reported the distribution ratio of Ga in lead to slag varied little from 0.01–0.8 with decreasing the oxygen partial pressure from 10⁻⁶.5 atm to 10⁻¹² atm.

| Temperature °C (K) | log(pO₂) atm | Fe₂O₃ | SiO₂ | CaO | Fe₁/SiO₂ | Basicity (CaO/SiO₂) |
|--------------------|--------------|-------|------|-----|----------|--------------------|
| 1350 (1623)        | – 8          | 41.49 | 44.90| 13.61| 0.60     | 0.30               |
|                     |              | 48.60 | 39.45| 11.95| 0.80     | 0.30               |
|                     |              | 58.65 | 31.74| 9.62 | 1.20     | 0.30               |
|                     |              | 57.22 | 37.15| 5.63 | 1.00     | 0.15               |
|                     |              | **54.17** | **35.17** | **10.66** | **1.00** | **0.30** |
| 1450 (1723)        | – 8          | 51.43 | 33.39| 15.18| 1.00     | 0.45               |
| 1400 (1673)        |              | 48.95 | 31.79| 19.26| 1.00     | 0.61               |
| 1350 (1623)        | – 6          | 54.17 | 35.17| 10.66| 1.00     | 0.30               |
| 1300 (1573)        |              | – 8   |      |      |          |                    |
| 1350 (1623)        | – 10         |       |      |      |          |                    |
| 1350 (1623)        | – 11         |       |      |      |          |                    |

Bold values indicate the key data points
This indicates that gallium deported to the lead slag phase in oxidizing conditions. All these results support and are in line with the current findings.

The loss of copper to the FCS slag with varying $pO_2$ was also tracked in this study. Total copper loss to the slag at 1350 °C (1623 K) as function of oxygen partial pressure is shown in Fig. 6. It was observed that with increasing $pO_2$, the copper content of the slag was also increased. Increasing $pO_2$ above 10$^{-10}$ atm resulted in dramatic increase of copper loss to the slag. The obtained total copper loss to the slag was compared to the values calculated from Yazawa and Takeda model[14] and are also presented in Fig. 6. A slightly higher total copper loss to the slag was observed in this study compared to their model, however, similar trend of total copper loss to the slag with $pO_2$ was observed.

### 3. Effect of FeT/SiO2 ratio

The effect of FeT/SiO2 ratio on the Ga distribution ratio at 1350 °C (1623 K) and partial pressure of oxygen of 10$^{-8}$ atm is shown in Fig. 7(a). In general, Ga preferred to deport to the slag phase in the range of FeT/SiO2 ratio studied. The results show that the Ga partitioning in the MgO-saturated FCS slag decreases with increasing FeT/SiO2 ratio from 0.6 to 1.2. In other words, increasing the total iron content (i.e., high FeT/SiO2 ratio) resulted in more Ga partitioning to the copper phase.
The effect of Fe\textsubscript{T}/SiO\textsubscript{2} ratio on the total copper loss to the MgO-saturated FCS slag is shown in Fig. 7(b). Increasing Fe\textsubscript{T}/SiO\textsubscript{2} ratio from 0.6 to 1.0 at a fixed temperature of 1350 °C (1623 K) and fixed partial pressure of oxygen of 10\textsuperscript{-8} atm reduced the total copper loss to the slag phase. However, increasing Fe\textsubscript{T}/SiO\textsubscript{2} ratio further to 1.2 did not result in significant change in the copper loss, identifying the deportment of copper to the slag phase being less dependent on Fe\textsubscript{T}/SiO\textsubscript{2} ratio when Fe\textsubscript{T}/SiO\textsubscript{2} ratio is higher than 1. The total copper loss to the slag was found to be in the range of 1.2–1.4 wt pct which is similar to the total copper loss to the slag reported by Yazawa and Takeda\textsuperscript{[14]} and Shuva et al.\textsuperscript{[10,12]}

Fig. 7—Effect of Fe\textsubscript{T}/SiO\textsubscript{2} ratio on the (a) partitioning of Ga in MgO-saturated FeO\textsubscript{x}–CaO–SiO\textsubscript{2} slag and copper and (b) loss of copper to the slag at fixed temperature of 1350 °C and fixed partial pressure of oxygen of 10\textsuperscript{-8} atm.

The effect of Fe\textsubscript{T}/SiO\textsubscript{2} ratio on the total copper loss to the MgO-saturated FCS slag is shown in Fig. 7(b).

4. Effect of Basicity

The basicity of the oxide slag can be represented by the mass ratio of basic components to the acidic components of the slag. In this study, slag basicity was calculated in terms of the mass ratio of CaO to SiO\textsubscript{2}. The effect of slag basicity on the distribution ratio Ga in MgO-saturated FCS slag and copper was investigated and is shown in Fig. 8(a). Gallium preferred to deport to the FCS slag throughout the basicity range studied. However, it can be seen that increasing slag basicity favored Ga partitioning to the copper. About three-fold increase of \( L\textsubscript{Ga/Cu} \) was observed when basicity of the FCS slags was increased from 0.15 to 0.6. It is observed that

Fig. 8—Effect of slag basicity (measured as CaO/SiO\textsubscript{2} ratio) on the (a) partitioning of Ga in MgO-saturated FeO\textsubscript{x}–CaO–SiO\textsubscript{2} slag and copper and (b) loss of copper to the slag at fixed temperature of 1350 °C (1623 K) and fixed partial pressure of oxygen of 10\textsuperscript{-8} atm.
Ga₂O₃ behaves as basic oxide in the FCS slag at the given conditions. This was supported by the observation of the effect of Fe₇/ΣSi₂ ratio on the partitioning of Ga as is shown in Fig. 7(a).

The effect of slag basicity on the percent of total copper that loss to the MgO-saturated FCS slag is shown in Fig. 8(b). Increasing slag basicity from 0.15 to 0.3 reduced the loss of copper to the slag, however, any further increase in slag basicity appeared not to change the weight percentage of copper to the FCS slag. Therefore, it can be deduced that the oxide of copper behaves in basic way in the FCS slag system at lower basicity range. The loss of copper was in the range of 1.3 to 1.6 wt pct which is aligned to the previous studies of Yazawa and Takeda[14] and Shuva et al.[10,12]

### B. Slag Design Criteria for Ga Recovery

In order to design a slag system to recover the valuable metals during copper processing, the acidic–basic nature of the valuable metal oxides is important to know. According to the ionic theory of melts a basic slag has free oxygen (O²⁻), which can easily react with acidic elements in the system. Acid slags on the other hand are highly active to capture basic elements. Gilchrist[23] categorized the elements according to their acidic–basic nature in terms of the term Ion-Oxygen Attraction, which is measured as z/a². Here, z is the charge of the cation and a is the sum of ionic radius of cation and oxygen (oxygen ion radius is 1.4 Å)[24,25]. Oxides falling in the ranges of z/a² value of 0.1–0.35 were described as basic oxides, 0.35–0.9 as intermediate oxides, and greater than 0.9 as acidic oxides. The z/a² value of the oxides of different valuable elements present in E-waste (i.e., Au, Ag, Pd, Ru, Ga, In, Sn, Ta, and Ge) are calculated and listed in Table IV. The z/a² value of Ag₂O was found in the acidic range; PdO, GaO, Au₂O₃, GeO₂, and In₂O₃ were found to be in the intermediate range; and for SnO₂, RuO₂, Ta₂O₅, and GeO₂ were found in the acidic range. Holistically, from the Ion-Oxygen Attraction (z/a²) analysis it can be summarized that acidic slag and acidic refractory materials are suggested to design for the recovery of Sn, Ru, Ta, and Ge. However, basic slags with basic refractories are suggested to design for the recovery of Ag. The suitability of acid–base slag for the oxides in the intermediate z²/a² range (Pd, Au, Ga, and In) are assessed based on the behavior of the elements and their oxides at various experimental processing conditions.

The ionic bond fraction of the oxides was also calculated from the electronegativities of the cation and oxygen (x_M and x_O, respectively) using the relation I = 1 − e⁻0.25(x_M−x_O)[26]. The results of the calculation showed that about 50 pct bond fraction are ionic for the Au–O, Sn–O, Ga–O, and In–O bonds but for Au–O, Pd–O, Ru–O, and Ge–O bond the ionic bond fraction is pretty low in 20–40 pct range (40 pct for Si–O bonds). The bond fraction value suggests the covalent-type behavior of Au₂O₃, PdO, RuO₂, and GeO₂ and its probability to act as an acid oxide in the molten slag. This gives the hints for designing an acidic slag for recovering Au, Pd, Ru, and Ge during black copper smelting. From the ionic bond fraction analysis of Ag–O, Sn–O, Ga–O, and In–O, their acidic–basic behavior/classification is not clear.

It is to be noted that the acid–base behavior of the elements largely depends on the experimental condition and slag composition and could be different from simple ion oxygen attraction (z/a²) assessments. The data of minor element distributions at conditions suitable for black copper smelting are compiled from literatures and are listed in Table V. A multistage slag treatment (i.e., treating the molten metal subsequently with acidic slag and basic slag or vice versa) can be incorporated to recover all the valuable elements from E-waste[27].

From the current research it was found that Ga prefers to partition to the slag phase. However, higher temperature, Fe₇/ΣSi₂ ratio, and slag basicity and lower P₀₂ favors Ga distribution to the metal phase. Therefore, high iron-containing basic slags are suggested to collect Ga in liquid copper during black copper smelting.

### Table IV. Ion-Oxygen Attraction (z²/a²) and the Ionic Bond Fraction for the Most Stable Oxides of Some of the Valuable Materials in E-Waste[9,24,25]

| Oxide   | Cation Charge, z | Ionic Radius of Cation, Å | Electronegativity (3.44 for Oxygen) | Ionic Bond Fraction of the Oxides | Ion-Oxygen Attraction, z²/a² | Nature of Oxide   |
|---------|------------------|---------------------------|-------------------------------------|-----------------------------------|-----------------------------|----------------------|
| Ag₂O   | 1                | 1.14                      | 1.9                                 | 0.45                              | 0.16                        | basic               |
| PdO    | 2                | 0.78                      | 2.2                                 | 0.32                              | 0.420                       | intermediary        |
| GaO    | 2                | 0.74                      | 1.81                                | 0.49                              | 0.44                        | intermediary        |
| Au₂O₃  | 3                | 0.88                      | 2.5                                 | 0.20                              | 0.58                        | intermediary        |
| In₂O₃  | 3                | 0.8                       | 1.78                                | 0.50                              | 0.62                        | intermediary        |
| Ga₂O₃  | 3                | 0.62                      | 1.81                                | 0.49                              | 0.74                        | intermediary        |
| SnO₂   | 4                | 0.69                      | 1.8                                 | 0.49                              | 0.92                        | acidic              |
| RuO₂   | 4                | 0.62                      | 2.2                                 | 0.32                              | 0.98                        | intermediary        |
| Ta₂O₅  | 5                | 0.78                      | 1.5                                 | 0.61                              | 1.05                        | intermediary        |
| GeO₂   | 4                | 0.53                      | 2                                   | 0.40                              | 1.07                        | intermediary        |

Bold values indicate the key data points.
IV. CONCLUSIONS

The thermodynamic behavior of Ga has been investigated under the conditions relevant to e-waste processing through the black copper smelting. The effect of temperature, partial pressure of oxygen, $Fe_T/SiO_2$ ratio, and slag basicity ($CaO/SiO_2$ ratio) on the partitioning of Ga in MgO-saturated $FeO_x$–$CaO$–$SiO_2$ slag and molten copper was studied. The key findings of this study are summarized below:

- Higher partitioning of Ga in copper was observed with decreasing oxygen partial pressure from $10^{-6}$ to $10^{-11}$ atm at $1350 \, ^\circ C$ (1623 K) for a fixed slag composition ($Fe_T/SiO_2$ ratio of 1.0 and slag basicity of 0.3).
- Increasing temperature from $1300 \, ^\circ C$ (1573 K) to $1450 \, ^\circ C$ (1723 K) at fixed slag composition and fixed oxygen partial pressure of $10^{-8}$ atm, increased Ga partitioning to the copper phase. The increase of temperature and decrease of oxygen partial pressure also reduced weight percentage of copper to the slag.
- At $1350 \, ^\circ C$ (1623 K) and $pO_2$ of $10^{-8}$ atm, the Ga partitioning was affected by the $Fe_T/SiO_2$ ratio and slag basicity ($CaO/SiO_2$ ratio). Partitioning of Ga in copper was increased with increasing both $Fe_T/SiO_2$ ratio and slag basicity. Increasing $Fe_T/SiO_2$ ratio and slag basicity also resulted lower loss of copper in the slag, however, this was observed for a limiting value of $Fe_T/SiO_2$ ratio of 1.0 and slag basicity of 0.3.
- The current results may suggest that Ga in the MgO-saturated $FeO_x$–$CaO$–$SiO_2$ slag under reducing condition was in the form of GaO (determined using a graphical approach considering simple oxidation reaction of Ga). It is noted that previous works under oxidizing conditions reported the presence of Ga$_2$O$_3$ only.
- Basic slags at higher temperature with a reducing atmosphere are recommended to increase the Ga collection in copper. However, at higher temperature the basic slag is expected to be less viscous or highly fluid and can aggressively react with the refractory linings.

ACKNOWLEDGMENTS

The authors are grateful to Swinburne University of Technology for providing the research facilities and Swinburne University Postgraduate Research Award (SUPRA) to conduct this study.

FUNDING

Open Access funding enabled and organized by CAUL and its Member Institutions.
Table A1. Chemical Composition of the Slags After Equilibrium Experiments were Measured Using XRF in this Study

| Temperature °C (K) | log($p_{O_2}$) atm | FeOx | CaO | SiO₂ | MgO | Cu₂O | Fe₂O₃/FeO | Basicity (CaO/SiO₂) |
|-------------------|-----------------------|------|-----|------|-----|------|------------|---------------------|
| 1350 (1623)       | -8                    | 42.25| 12.81| 33.90| 9.56| 1.49 | 0.60       | 0.30                |
|                   | 37.75                 | 11.74| 40.03| 9.04 | 1.44| 0.80 | 1.20       | 0.30                |
|                   | 31.14                 | 9.97 | 48.71| 8.89 | 1.29| 1.20 | 0.15       | 0.30                |
|                   | 33.98                 | 5.57 | 45.69| 13.21| 1.55| 1.00 | 0.45       | 0.30                |
|                   | 34.05                 | 10.81| 44.85| 8.82 | 1.47| 1.00 | 0.45       | 0.30                |
|                   | 33.47                 | 15.22| 42.22| 7.63 | 1.45| 1.00 | 0.45       | 0.30                |
|                   | 32.82                 | 19.88| 40.15| 5.79 | 1.35| 1.00 | 0.45       | 0.30                |
| 1450 (1723)       | -8                    | 33.83| 10.25| 44.96| 9.75| 1.20 | 1.00       | 0.30                |
| 1400 (1673)       |                       | 33.97| 10.30| 44.59| 9.80| 1.35 |            |                     |
| 1350 (1623)       |                       | 34.05| 10.81| 44.85| 8.82| 1.47 |            |                     |
| 1300 (1573)       |                       | 34.18| 12.01| 45.36| 6.86| 1.47 |            |                     |
| 1350 (1623)       | -6                    | 36.05| 10.94| 40.19| 10.49| 1.33 |            |                     |
|                   | -8                    | 34.05| 10.81| 44.85| 8.82| 1.47 |            |                     |
|                   | -10                   | 33.45| 10.86| 46.58| 8.17| 0.95 |            |                     |
|                   | -11                   | 38.22| 12.78| 39.76| 8.49| 0.75 |            |                     |

Bold values indicate the key data points.

Table A2. The Distribution Data of Ga in Different Phases at Different Processing Conditions

| Temperature °C (K) | log($p_{O_2}$) atm | Fe₂O₃/FeO | Basicity (CaO/SiO₂) | L₆Ga | Wt Pct of Ga in Copper | Wt Pct of Ga in Slag Phase | Wt. pct of Ga in Gas Phase |
|-------------------|---------------------|------------|---------------------|------|------------------------|-----------------------------|-----------------------------|
| 1350 (1623)       | -8                  | 0.60       | 0.30                | 81.19| 1.16                   | 94.38                       | 4.46                        |
|                   | 0.80                | 0.30       | 73.10               | 1.30 | 95.30*                 | 4.46                        | 3.40                        |
|                   | 1.00                | 0.30       | 49.10               | 1.91 | 93.63                  | 4.46                        | 3.40                        |
|                   | 1.00                | 0.15       | 107.01              | 0.88 | 94.66                  | 4.46                        | 3.40                        |
|                   | 1.00                | 0.30       | 64.26               | 1.47 | 94.31*                 | 4.46                        | 3.40                        |
|                   | 1.00                | 0.45       | 48.34               | 1.94 | 93.54*                 | 4.46                        | 3.40                        |
|                   | 1.00                | 0.61       | 36.94               | 2.52 | 93.02                  | 4.46                        | 3.40                        |
| 1450 (1723)       | -8                  | 1.00       | 0.30                | 12.90| 6.87                   | 88.67                       | 4.46                        |
| 1400 (1673)       |                    | 1.00       |                     | 42.27| 2.18                   | 92.19*                      | 5.63                        |
| 1350 (1623)       |                    |           |                     | 64.26| 1.47                   | 94.31*                      | 4.22                        |
| 1300 (1573)       |                    |           |                     | 98.07| 0.96                   | 94.58                       | 4.46                        |
| 1350 (1623)       | -6                  |           |                     | 495.00| 0.19                   | 95.35                       | 4.46                        |
|                   | -8                  |           |                     | 64.26| 1.47                   | 94.31*                      | 4.22                        |
|                   | -10                 |           |                     | 8.01 | 10.59                  | 84.80*                      | 4.61                        |
|                   | -11                 |           |                     | 2.90 | 24.50                  | 71.04                       | 4.46                        |

Slag sample compositions that are directly measured by ICP-AES technique are indicated by the symbol (*).
REFERENCES

1. R.G. Bautista: JOM, 2003, vol. 55, pp. 23–6.
2. B. Jaskula: U.S. Geological Survey, Mineral Commodity Summaries, accessed 15th January 2021, https://pubs.usgs.gov/periodicals/mcs2021/mcs2021-gallium.pdf.
3. Gallium, Outlook to 2030, 10th Edition, Roskill Information Services Ltd., accessed on 17th December 2020, https://roskill.com/market-report/gallium/.
4. K. Avarmaa, S. Yliaho, and P. Taskinen: Waste Manag., 2018, vol. 71, pp. 400–10.
5. P.I. Chernousov, O.V. Golubev, and A.L. Petelin: Metallurgist, 2010, vol. 54, pp. 285–90.
6. D. Sukhomlinov, L. Klemettinen, H. O’Brien, P. Taskinen, and A. Jokilaakso: Metall. Mater. Trans. B, 2019, vol. 50B, pp. 2723–732.
7. S. Yliaho: Master’s thesis, Materials Science and Engineering, Aalto University, 2016.
8. A. Anindya, D.R. Swinbourne, M.A. Reuter, and R.W. Matuszewicz: Miner. Process. Extr. Metall., 2013, vol. 122, pp. 165–73.
9. A. Anindya, D.R. Swinbourne, M.A. Reuter, and R.W. Matuszewicz: Miner. Process. Extr. Metall., 2014, vol. 123, pp. 43–52.
10. M.A.H. Shuva, M.A. Rhamdhani, G.A. Brooks, S.H. Masood, and M.A. Reuter: Metall. Mater. Trans. B, 2016, vol. 47B, pp. 2889–903.
11. M.A.H. Shuva: PhD Thesis, Swinburne University of Technology, 2017.
12. M.A.H. Shuva, M.A. Rhamdhani, G.A. Brooks, S.H. Masood, and M.A. Reuter: Metall. Mater. Trans. B, 2017, vol. 48B, pp. 317–27.
13. M.M. Hasan, M.A. Rhamdhani, M.A.H. Shuva, and G.A. Brooks: Metals, 2020, vol. 10, pp. 1–23.
14. A. Yazawa and Y. Takeda: Trans. Jpn. Inst. Met., 1982, vol. 23, pp. 328–33.
15. S.M. Howard: South Dakota School of Mines and Technology, accessed on 2nd February 2022, http://showard.sdsmt.edu/ME T320/Handouts/EllinghamDiagrams/Ellingham_v22_Macro.pdf.
16. G.K. Sigworth and J.F. Elliott: Can. Metall. Q., 1974, vol. 13, pp. 455–61.
17. M.D. Johnston, S. Jahanshahi, and F.J. Lincoln: Metall. Mater. Trans. B, 2007, vol. 38B, pp. 433–42.
18. K. Avarmaa, L. Klemettinen, H. O’Brien, P. Taskinen, and A. Jokilaakso: Minerals, 2019, vol. 9, p. 367.
19. J. Jeevaratnam and F. Glasser: J. Am. Ceram. Soc., 1961, vol. 44, pp. 563–66.
20. H.V. Hook: J. Am. Ceram. Soc., 1965, vol. 48, pp. 470–72.
21. F. Glasser: J. Phys. Chem., 1959, vol. 63, pp. 2085–086.
22. M. Zinkevich and F. Aldinger: J. Am. Ceram. Soc., 2004, vol. 87, pp. 683–91.
23. J.D. Gilchrist: Extractive Metallurgy, 2nd ed. Pergamon Press plc, Oxford, 1989, p. 431.
24. W.M. Haynes: CRC handbook of chemistry and physics, CRC Press, Florida, 2014.
25. R.D. Shannon: Acta Crystallogr. A, 1976, vol. 32, pp. 751–67.
26. L. Pauling: The nature of the chemical bond and the structure of molecules and crystals, 3rd ed. Cornell University Press, Ithaca, NY, 1965.
27. M. Shuva, M.A. Rhamdhani, G.A. Brooks, S. Masood, M. Reuter, and M. Firdaus: 8th International Symposium on High-Temperature Metallurgical Processing, 2017, Springer.

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.