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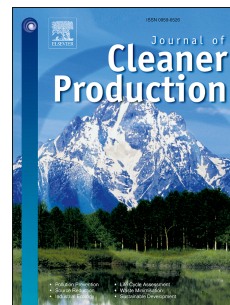
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Thermodynamics data of valuable elements relevant to e-waste processing through primary and secondary copper production – a review

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Abstract

Waste of electronics and electrical equipment (WEEE or e-waste) can be viewed as a resource for metals, as it does not only contain the common metals like iron (Fe), aluminium (Al), lead (Pb) and copper (Cu) but also traces of precious and rare elements such as gold (Au), silver (Ag), tin (Sn), selenium (Se), tellurium (Te), platinum (Pt), palladium (Pd), tantalum (Ta), cobalt (Co) and indium (In). The recovery of these trace elements is vital, not just because it has high commercial values, but also for resources efficiency. One of the existing industrial routes for processing of e-waste is through the primary and secondary Cu smelting processes. During these processes, the trace elements are distributed in different phases, i.e. in metal/matte, slag and gas. Different elements have different thermodynamic properties that govern the partitioning behaviour during the process. There has been a number of studies on the distribution behaviour of the trace elements relevant to primary Cu smelting (extraction of metals from virgin ores). However, there are only limited thermodynamics data relevant to secondary Cu smelting (extraction of metals from secondary/recycled sources). This paper reviews the thermodynamics data relevant for recovering the trace valuable elements from the primary Cu as well as secondary Cu smelting. These data and knowledge provide the basis for determining the optimum conditions favourable for recovering the trace valuable elements in e-waste through the industrial Cu pyrometallurgical processing.

Keywords: Thermodynamics, Precious metals distribution, Valuable metals distribution, Black Copper Smelting, E-waste recycling, WEEE recycling

1. Introduction

Copper is mostly present in the earth's crust as Cu containing minerals and gangue minerals (Davenport et al., 2002). The main route of Cu production from sulphide ores is through pyrometallurgy processes (Cui and Zhang, 2008; Rotuska and Chmielewski, 2008). A continuous depletion of primary resources has diverted us to recycle Cu from non-primary sources such as from industrial wastes, consumer wastes and WEEE (waste of electronics and electrical equipment or e-waste) (Davenport et al., 2002). According to the United State Geological Survey (USGS), around 30% of annual Cu production comes from the recycled sources (Goonan, 2010; Wood et al., 2011).

E-waste is defined as a broad range of electronic devices ranging from refrigerators, air conditioners, personal stereos and consumer electronics to cell phones and computers which have been discarded by their user (Puckett et al., 2002). In addition to the common metals such as Fe, Cu, Al, Ni, e-waste also contains traces of precious and rare elements, like Au, Ag, Pt, Pd, Cd, Se, As, Co, Te, Ta, Ru, Ge, Ga, Rh, Sn, Pb, and Bi (Cui and Zhang, 2008; Lehner, 2003). As, Bi and Pb are considered to be hazardous elements, while Au, Ag, Sn, Pt, Pd, Ge, Rh, Co and other rare elements have high commercial values. To put it in a perspective, one tonne of computer scraps contain more gold than seventeen tonnes of gold ores (Australian Bureau of Statistics, 2013; Doran, 2014). The metals and their concentration vary from one type of e-waste to another and also vary with time as the technology changes.

Recycling and utilisation of e-waste and other urban ores are important for resource efficiency (Reuter and Kojo, 2014; Worrell and Reuter, 2014). Nevertheless, there is still gap in knowledge and there are technical and non-technical challenges that prevent the use of these resources efficiently. There are a number of systematic studies on the analysis of e-waste collection, benefits of e-waste recycling and various proposed solution to e-waste problems (Chi et al., 2014; Menikpura et al., 2014; Nelen et al., 2014; Zeng et al., 2015) which are mainly associated to reduce the environmental challenges. Reuter et al. (2013) described about the opportunities and limits of metal recycling from e-waste. A number of studies have also pointed out that recycling of the rare earth metals from e-waste is important to build a green economy (Binnemans et al., 2013) and reduce the supply chain risk (Binnemans et al., 2015).

Currently, one of the existing industrial routes for processing of e-waste is through metallurgical processes embedded in primary and secondary base metals productions, such as through Cu smelting. It is a great challenge for metal industries to develop and design optimal

smelting processes utilising e-waste (Götze and Rotter, 2012; Khaliq et al., 2014). The elements found (and their concentrations) in e-waste are significantly different than those found in common primary ore concentrates. A large database of information, in particular, the solution thermodynamics data in the primary Cu processing has accumulated over the years but the information is limited to a number of elements (such as In, Te, Se, Co, Pd, Pt and Rh) behaving in Cu/matte/slag systems. There are limited published data available which focus on the trace elements distribution in secondary Cu processing. There is still some gap in the information for the separation of the combination of elements in e-waste particularly in the operating conditions beyond those commonly used in the existing processes. This requires a rethinking of traditional processing techniques, which must be based on knowledge of how these unusual trace elements distribute between phases during smelting.

2. Methods

The current study focuses on a comprehensive and systematic review of thermodynamics data of valuable metals associated with primary and secondary Cu smelting. Particularly, identifying the distribution-ratio data of valuable metals during Cu smelting process relevant to e-waste processing, available in environmental, metallurgical, and chemical literatures. This review paper then highlights the gaps in knowledge required for the improvement and optimisation of current industrial processes. The implication for metal recycling industry as well as the challenges for future research and improvement of industrial processes are also described. It is hoped that the article helps the development of ideas for further research on the thermodynamics behaviour of valuable elements to promote metals resource efficiency and also useful for the industry and scientific community as state of the art reference paper.

3. Thermodynamic Behaviour of Valuable Elements in Cu

The equilibrium reaction of a solute element ' M ' between liquid metal and slag having a valence of 2ν can be described by Equation 1:



The equilibrium constant K for the above reaction is expressed by the activities of metal oxide and metal distribution-ratio as follows

$$K = \frac{a_{MO_v}}{a_M P_{O_2}^{v/2}} \quad (2)$$

The distribution-ratio of 'M' in slag and metal can be defined as

$$L_M^{s/m} = \frac{(pct M)}{[pct M]} \quad (3)$$

Where the parentheses () and [] denote the concentration of the element in slag and metal phases respectively. It was shown that the distribution-ratio can be represented as (Takeda et al., 1983; Yazawa and Takeda, 1982)

$$L_M^{s/m} = \frac{K (n_T) [\gamma_M] P_{O_2}^{v/2}}{[n_T] (\gamma_{MO_v})} \quad (4)$$

Where K is the equilibrium constant for Reaction (1), n_T is the total number of moles in constituents in the relevant phases, γ_M is the activity coefficient of M in the metal, γ_{MO_v} is the activity coefficient of metal oxide MO_v in the slag and P_{O_2} is the oxygen partial pressure. It was reported that monocation form of oxides show constant activity coefficient over a large range of composition (Takeda et al., 1983; Yazawa and Takeda, 1982; Yazawa et al., 1968). As shown in Figure 1, the activity coefficient of oxides in the slag is a function of mole fraction. It can be seen from Figure 1(a) that mono-nuclear atom base oxides such as $CuO_{0.5}$, $AsO_{1.5}$, etc., showing constant activity value throughout the concentration range. However, the activity coefficients of multi-nuclear atom base expression such Cu_2O , As_2O_3 etc., as shown in the Figure 1(b) do not show constant values against the concentration. It was also reported that the value of the total number of moles of species in non-ferrous smelting slag systems (such as in $FeO_{1.5}$ - $CuO_{0.5}$ - CaO - MgO - MO_v/m slag systems) is similar when all the constituents were expressed in mono-nuclear atom base, i.e. the number of moles (n_T) is 1.45 per 100 g of slag phase, and 1.57 per 100g of metal phase (Takeda et al., 1983). For a particular temperature, all the terms on the right side of Equation (4) are constant, with the exception of p_{O_2} . Therefore, the following relationship can be established:

$$\log L_M^{s/m} = \log B + \left(\frac{v}{2}\right) \log P_{O_2} \quad (5)$$

From the slope of the linear relationship between $\log L_M^{s/m}$ and $\log P_{O_2}$, the degree of oxidation of solute element $\frac{v}{2}$ in the slag can be determined. The activity coefficient of MO_v in the slag can be calculated by using Equation (4) if the activity coefficient in of element M in liquid metal phase, γ_M , is known. Takeda et al. (1983) extensively studied the distribution-ratio of selected solute metal elements as a function of p_{O_2} as shown in Figure 2.

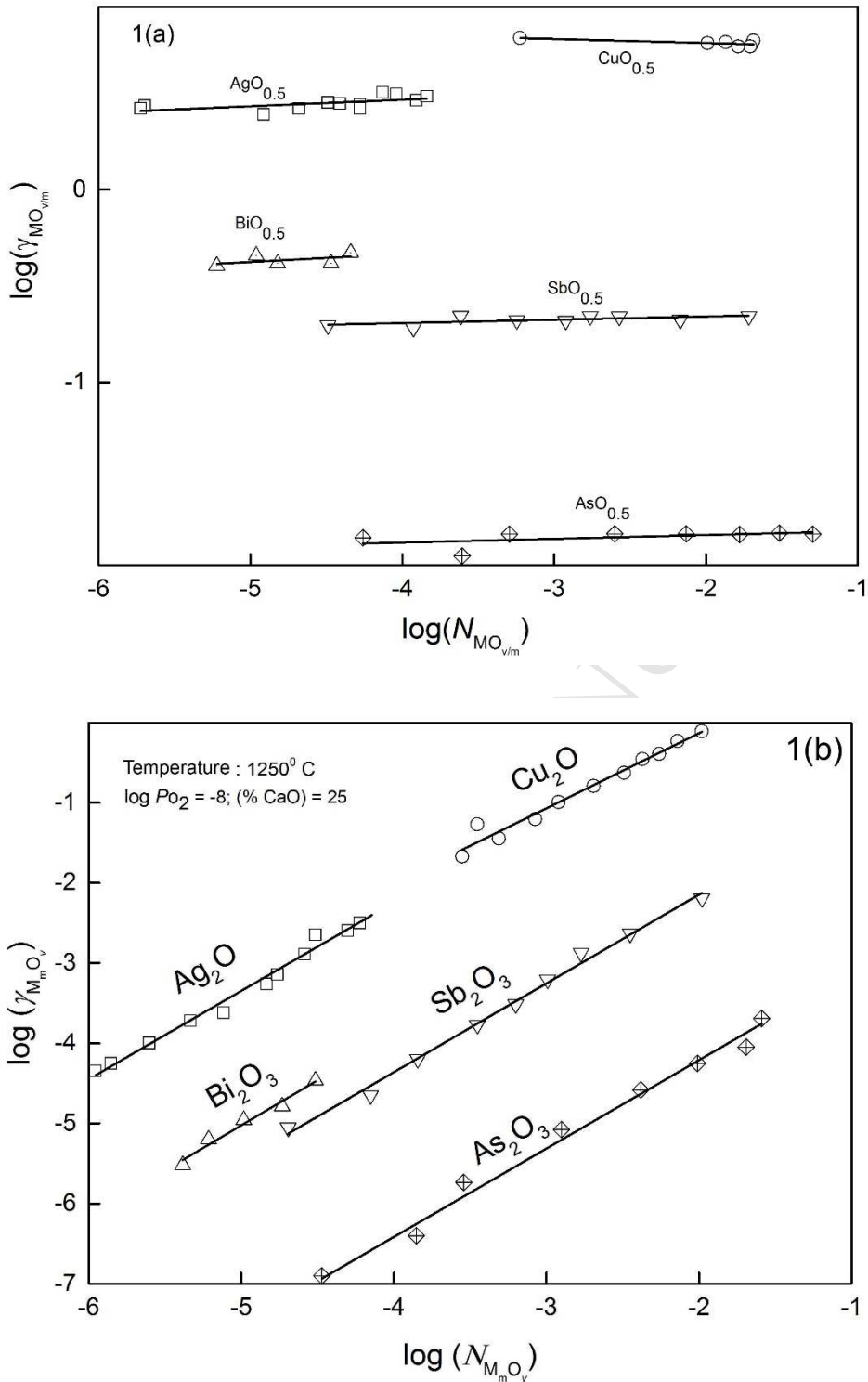


Fig. 1: Relationship between the activity coefficient of oxides and the mole fraction of oxides in FeO_x-CaO slag at 1250°C, reproduced from (Takeda et al., 1983; Yazawa et al., 1968).

Yazawa (1974) described that the trace elements behaviour in primary Cu processing can be represented by the following two reactions:





The logarithmic equilibrium constants, $\log K_1$ and $\log K_2$ of Reactions (6) and (7) were calculated respectively for the various elements found in primary Cu smelting at 1300°C, and shown in Table 1. In addition, the activity coefficient (γ_M^0) at infinite dilute solution of elements and the distribution-ratio coefficient, L_M , in molten Cu and white metal are also given in the table. From Table 1, the stability of various elements during the Cu smelting can be evaluated. Au, Ag, Se and Te are stable among other elements and difficult to be removed by oxidation. Some other elements can be removed in the oxide or sub oxide forms.

Table 1: Thermodynamic data of elements in primary Cu smelting at 1300°C (Yazawa, 1974; Yazawa and Azakami, 1969)

	Cu	Au	Ag	Pb	Bi	As	Sb	Sn	Ni	Co	Fe	Zn	Se	Te
L_M	-	172	2.4	11.5	8.1	9.0	13.6	9.3	3.1	1.12	0.20	0.97	0.074	0.118
γ_M^0	1	0.36	2.9	5.1	2.5	0.0008	0.017	0.13	2.6	8.6	12.6	0.13	0.0034	0.004
$\log K_1$	2.88	-	0.94	1.12	-1.3	-	-0.2	1.35	1.34	1.15	2.39	3.27	-	-
$\log K_2$	2.01	-4.63	-2.23	2.42	1.68	3.525	3.49	4.00	3.18	3.90	5.40	6.16	-1.24	0.04

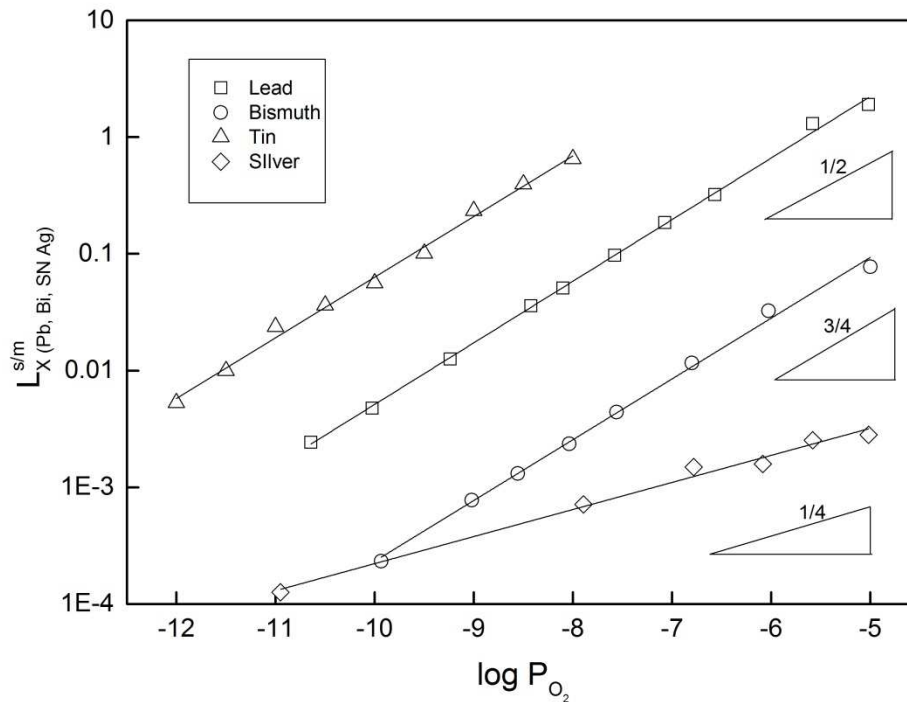


Fig. 2: Distribution-ratios of Pb, Bi, Sn and Ag between slag and liquid Cu systems at 1250°C, reproduced from (Takeda et al., 1983; Yazawa et al., 1968)

Yazawa and Azakami (1969) suggested two mechanisms on handling solute elements during the primary Cu smelting. First is through oxidation immediately after slagging and the second one is through volatilization. They had considered the following Reaction (8) to describe the removal of impurities during the Cu converting:



They utilised available experimental and thermodynamic data of the behaviour of solute elements at 1200°C as listed in Table 2. It was pointed out that Au to Te metals (Group 1) in the Table 2, which have a small K value, are difficult to oxidise. These metals, however, have a high economic value and could be recovered from the anode slime at later stage of the Cu processing. The Group 2 metals cannot be removed by oxidation but can be removed by volatilisation, particularly Zn and Cd because of their high activity coefficient and partial vapour pressure. It should be noted that Se, Te and arsenide have large partial pressure but their activity coefficient are very low. On the contrary, Group 3 metals have large K values and most of them are easily oxidized and very little amount may be found as inclusions. In Cu smelting some impurities have value which can be recovered but deleterious elements which cannot be recovered either in converting or electrolytic refining stages should be removed as much as possible before the smelting process.

Nagamori and Mackey (1978) simplified the distribution-ratio of elements into three feasible models and considered equilibrium systems for high grade matte as well as fayalite slag for all these models. Au, Ag, Bi, Sb and As were categorised in the first model where their distributions depend only on the temperature. The second model represented elements whose distribution varies with temperature and p_{O_2} and p_{S_2} , which include Pb, Zn, Ni, Co and Sn. While, Te and Se were in the third model where their distribution depends on the temperature and p_{O_2} only. The assessment established feasible physicochemical models for different elements in the fayalite slag. Table 3 shows the distribution-ratio of some elements and their relation with p_{O_2} and p_{S_2} at 1250°C and Table 4 shows the Gibbs energy data of elements in Cu.

Nakajima et al. (2011) proposed that precious metals (Au, Pd, Ag, Pt) and other metals (Se, Te, Bi, and Sb) remain in molten metal and can be recovered at later processes. Some elements (In, Ni, Sn and Pb) are distributed in slag and metal. A distribution-ratio chart of different phases in the Cu converting process is shown in Figure 3. It was reported that the distribution of elements largely depends on the operating temperature and p_{O_2} . The effect of temperature and p_{O_2} on In, Ni, Pb, Sn distribution-ratio is shown in Figure 4. In addition, the slag composition also plays an important role to recover or remove elements from the Cu.

Table 2: Thermodynamics data of elements in liquid Cu at 1200°C (Yazawa, 1974; Yazawa and Azakami, 1969)

Element	Content (%)	Equilibrium Constant (K)	γ_M^0	
Au	0.003	1.2×10^{-7}	0.34	
Hg	-	2.5×10^{-5}	-	
Ag	0.1	3.5×10^{-5}	4.8	Group 1 (most stable metals)
Pt	-	5.2×10^{-5}	0.03	
Pd	-	6.2×10^{-4}	0.06	
Se	0.04	5.6×10^{-4}	$\ll 1$	
Te	0.01	7.7×10^{-2}	0.01	
Bi	0.009	0.64	2.7	
Cu	~99	-	1	
Pb	0.2	3.8	5.7	
Ni	0.2	25	2.8	
Cd	-	31	0.73	Group 2 (most volatile metals)
Sb	0.04	50	0.013	
As	0.04	50	0.0005	
Co	0.001	1.4×10^2	10	
Ge	-	3.2×10^2	-	
Sn	0.005	4.4×10^2	0.11	
In	-	8.2×10^2	0.32	
Fe	0.01	4.5×10^3	15	
Zn	0.007	4.7×10^4	0.11	
Na	-	1.1×10^5	-	
Cr	-	5.2×10^6	-	
Mn	-	3.5×10^7	0.80	
Si	0.002	5.6×10^8	0.1	Group 3 (oxidised readily)
Ti	-	5.8×10^9	-	
Al	0.005	8.8×10^{11}	0.008	
Ba	-	3.3×10^{12}	-	
Mg	-	1.4×10^{13}	0.067	
Be	-	5.4×10^{13}	-	
Ca	-	4.3×10^{14}	-	

Table 3: Distribution-ratio value of elements in Cu processing at 1250°C (Nagamori and Mackey, 1978)

Element	Relationship & Dependency	$L_M^{S/m}$ (calculated*)
Ag	1000 (estimated), Independent to P_{O_2} and P_{S_2}	1000
As	30 ± 10 (1200-1300°C), Independent to P_{O_2} and P_{S_2}	30
Au	2.5×10^5 , Independent to P_{O_2} and P_{S_2}	2.5×10^5
Bi	15 ± 5 , Independent to P_{O_2} and P_{S_2}	15
Fe	Dependent on P_{O_2} and P_{S_2}	$\sim 10^{-4}$
Ni	Dependent on P_{O_2} and P_{S_2}	1.38
Pb	Dependent on P_{O_2} and P_{S_2}	0.013
Sb	15 ± 5 , Independent to P_{O_2} and P_{S_2}	15
Se	$\frac{1}{L_{Se}^S} = (7 + 2t) \times 10^{-7} P_{O_2}^{-1/2} + 0.027 + 0.018t$, Independent to P_{S_2} , $t = 0.01(T-1523)$,	35.2
Sn	P_{O_2} and P_{S_2}	1.8
Te	$\frac{1}{L_{Te}^S} = (8 + 4t) \times 10^{-8} P_{O_2}^{-1/2} + 0.029 + 0.006t$, Independent to P_{S_2} , $t = 0.01(T-1523)$	34.2
Zn	Dependent on P_{O_2} and P_{S_2}	6.33×10^{-4}

* $P_{S_2} = 2.22 \times 10^{-6}$ atm, $P_{O_2} = 2.41 \times 10^{-7}$ atm

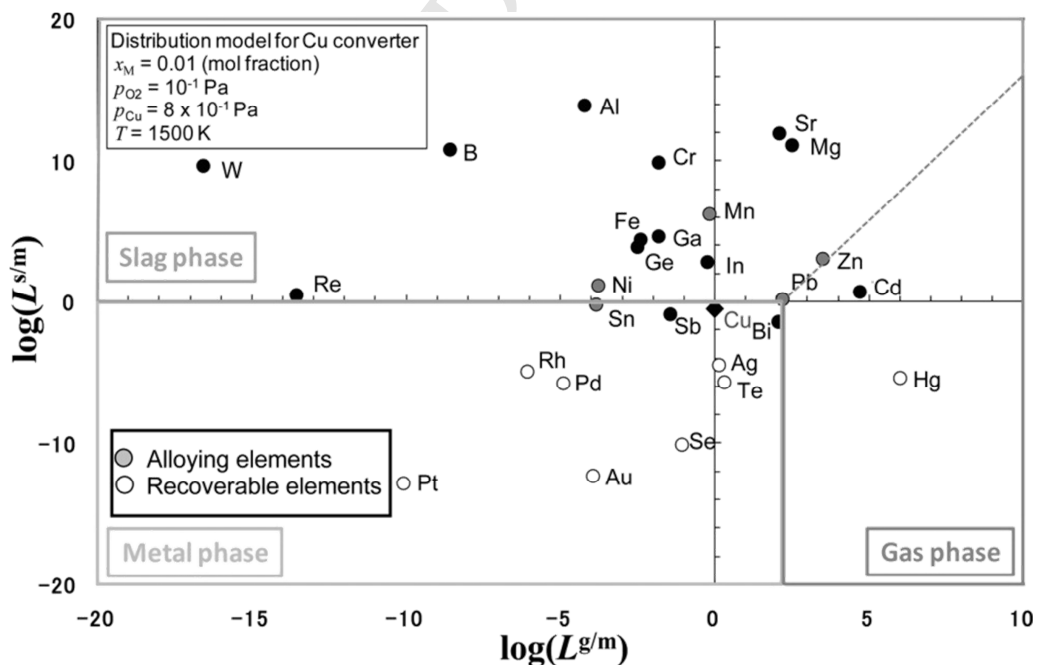
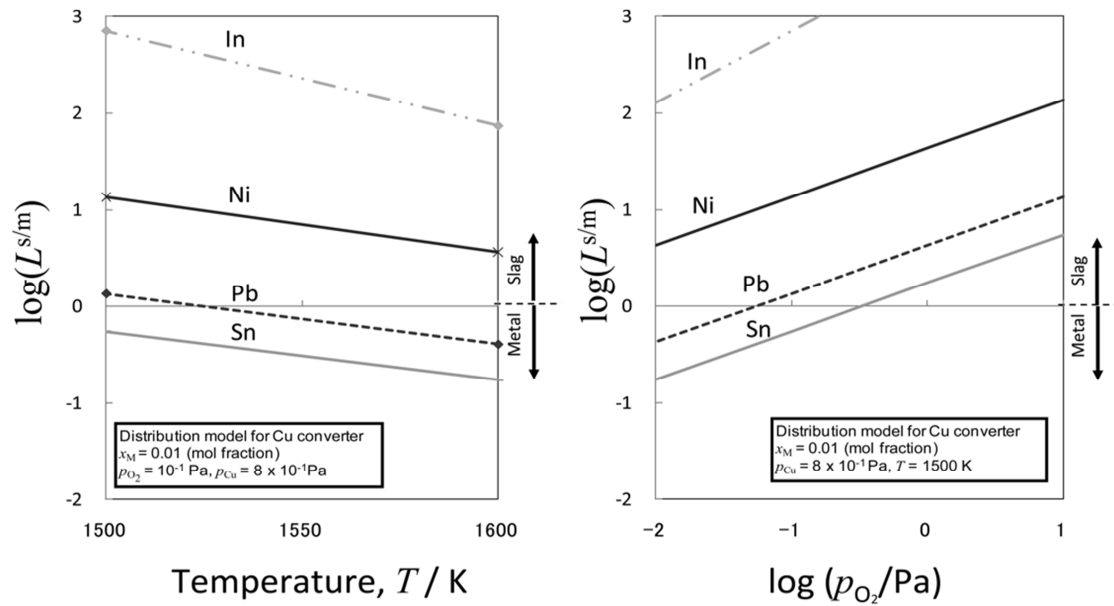


Fig. 3: Metal distribution-ratio in different phases of the converter of the Cu smelting in certain atmosphere. Adapted with permission from Nakajima et al., (2011). Copyright 2011 American Chemical Society



(a) Temperature dependence

(b) Oxygen partial pressure dependence

Fig. 4: Effect of temperature and p_{O_2} on distribution-ratio of elements in a Cu converter. Adapted with permission from Nakajima et al., (2011). Copyright 2011 American Chemical Society

Table 4: Gibbs Energy data and activity coefficient in of elements in Cu

Reaction	ΔG° (J/mole) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K$	γ_M^0	Reference
$Cu(l) + \frac{1}{4}O_2(g) = CuO_{0.5}(l)$	-58800+19.55T	1	(Takeda et al., 1983; Yazawa, 1980)
$Ag(l) + \frac{1}{4}O_2(g) = AgO_{0.5}(s)$	-26020+40.00T	3.1	(Takeda et al., 1983; Yazawa, 1980)
$Co(l) + \frac{1}{2}O_2(g) = CoO(l)$	-235480+71.55T	14	(Azakami and Yazawa, 1976; Takeda et al., 1983; Yazawa, 1980)
$Sn(l) + \frac{1}{2}O_2(g) = SnO(l)$	-262290+86.57T	0.12	(Takeda et al., 1983; Yazawa et al., 1968)
$Sn(l) + \frac{1}{2}O_2(g) = SnO_2(s)$	-584090+212.55T		
$Pb(l) + \frac{1}{2}O_2(g) = PbO(l)$	-195100+77.7T	4.8	(Takeda et al., 1983; Yazawa, 1980)
$As(l) + \frac{3}{4}O_2(g) = AsO_{1.5}(l)$	-330620+115.39T	0.006 ~ 0.06	(Hultgren et al., 1973; Takeda et al., 1983)
$Sb(l) + \frac{3}{4}O_2(g) = SbO_{1.5}(l)$	-334820+114.23T	0.15 ~ 0.6	(Azakami and Yazawa, 1976; Takeda et al., 1983)
$Bi(l) + \frac{3}{4}O_2(g) = BiO_{1.5}(l)$	-284300+133.05T	0.1 ~ 1	(Azakami and Yazawa, 1976; Takeda et al., 1983)
$Te(l) + \frac{1}{2}O_2(g) = TeO_2(l)$	-315470+176.15T	0.033	(Choi and Cho, 1997; Mackey, 1982; Nagamori and Mackey, 1977; Sigworth and Elliott, 1974)
$Fe(\alpha) + \frac{1}{2}Te_2 = FeTe(s)$	-46929+80.79T		
$Se(l) + \frac{1}{2}O_2(g) = SeO_2(s)$	-229870+189.74T	0.002	(Choi and Cho, 1997; Mackey, 1982; Nagamori and Mackey, 1977; Sigworth and Elliott, 1974)
$Fe(\alpha) + \frac{1}{2}Se_2 = FeSe(s)$	-148603+79.95T		

3.1 Distribution of Sn

Sn is relatively scarce element as its average concentration in the earth's crust is about 2 ppm (Emsley, 2001). However, in a personal computer about 1 wt% of Sn is found (Australian Bureau of Statistics, 2013). In Cu smelting, Sn will distribute between gaseous, metal and slag phases. At p_{O_2} between 10^{-9} to 10^{-6} atm, Sn remains as involatile SnO_2 . As the p_{O_2} is decreased, SnO_2 is reduced to a volatile SnO which can segregate to off gas. The distribution-ratio of Sn in different slag system of Cu smelting reported by previous researchers are shown in Figure 5. The activity coefficient of SnO in Cu and various slag systems is presented in Table 5.

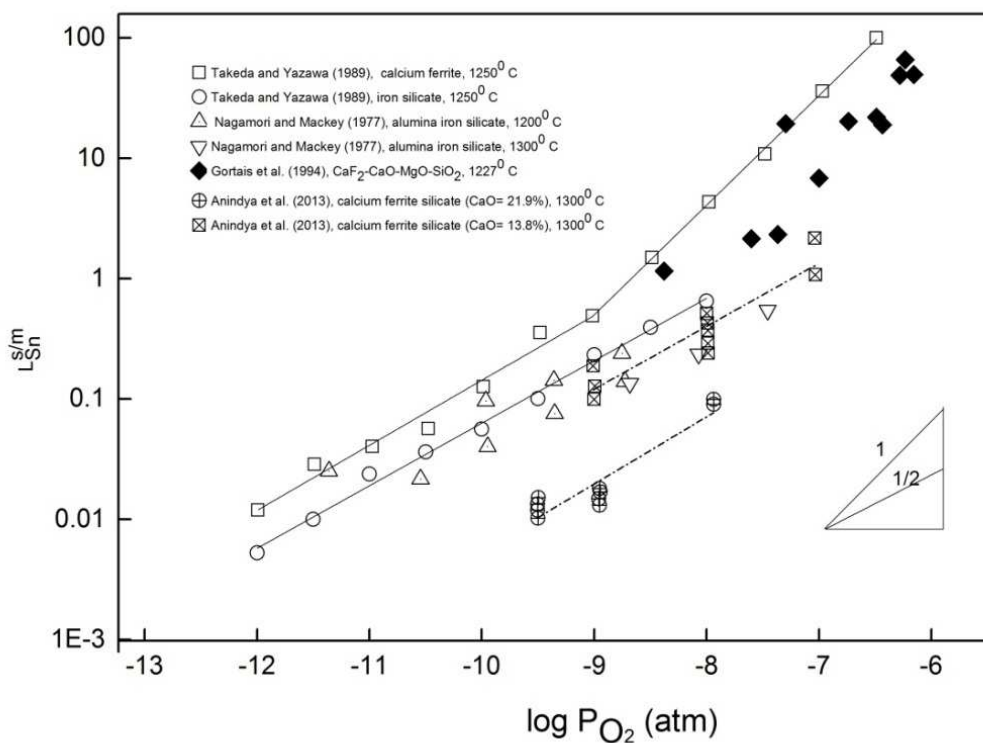


Fig. 5: Sn distribution-ratio as function of p_{O_2} and temperature in different slag systems

Takeda et al. (1983) and Yazawa et al. (1968) described that at high p_{O_2} , Sn was found as a tetra-valent in a FeO_x -CaO slag. Nagamori and Mackey (1977) reported that Sn is present in the slag as SnO at p_{O_2} below 10^{-8} atm. In their work, they used FeO_x - SiO_2 - Al_2O_3 slag and Cu reacted at $1200^\circ C$ and $1300^\circ C$. The presence of alumina in the slag had little effect on the Sn distribution-ratio. Takeda et al. (1983) and Nagamori and Mackey (1977) observed a similar trend of Sn distribution-ratio. Yazawa et al. (1999) investigated distribution-ratio of Sn between Cu and FeO_x -CaO- SiO_2 (FCS) slag at p_{O_2} 10^{-12} to 10^{-9} atm

at 1300°C. They found Sn as SnO in slag and higher SnO activity coefficient in the slag than that in FeO_x-CaO and FeO_x-SiO₂ slags.

Table 5: Activity coefficient of SnO in various slag systems

Investigators	p_{O_2} (atm)	Temperature (°C)	γ_{SnO}
Iron-Silicate Slag			
Nagamori and Mackey (1977)	$10^{-11} - 10^{-6}$	1200	1.9±0.3
		1300	0.8±0.1
Takeda et al. (1983)	10^{-9}	1250	1.5
Takeda and Yazawa (1989)	$10^{-12} - 10^{-9}$	1300	1.8
Louey et al. (1999)	$10^{-11.5}$	1250	-
Calcium-Ferrite Slag			
Takeda et al. (1983)	10^{-9}	1250	0.9
Takeda and Yazawa (1989)	$10^{-12} - 10^{-9}$	1300	1.2
Ferrous-Calcium Slag			
Yazawa et al. (1999)	$10^{-12} - 10^{-9}$	1300	5 – 6.2
Anindya et al. (2013)	$10^{-12} - 10^{-8.5}$	1300	0.9 – 3

Gortais et al. (1994) carried out equilibrium experiments for Sn at 1227°C using CaF₂-CaO-MgO-SiO₂ slag and confirmed that Sn is present as SnO₂ at high p_{O_2} . Louey et al. (1999) investigated the distribution of elements between matte and fayalite slag at 1250°C and at very low p_{O_2} ($10^{-11.5}$ atm) and found that Sn behaved as SnO with the distribution-ratio of Sn of 2.8±0.3, which is close to those reported by Koike and Yazawa (1994) and Yazawa et al. (1968).

Anindya et al. (2013) studied the distribution of Sn between Cu and FCS slag at p_{O_2} below 10^{-9} atm and at 1300°C. The Sn was found in the form of SnO in the slag as confirmed from the slope of the variation of Sn distribution-ratio with p_{O_2} shown in Figure 5. They found much lower the distribution-ratio of Sn in FCS slag and Cu compared to previous studies (Gortais et al., 1994; Nagamori and Mackey, 1977; Takeda et al., 1983; Takeda and Yazawa, 1989; Yazawa et al., 1968). Anindya et al. (2013) reported that the distribution-ratio of Sn and Cu decreases with increasing CaO in the slag and attributed this to the increase of SnO activity coefficient in slag.

Street et al. (2001) investigated the Sn solubility in CaO-Al₂O₃-SiO₂ slag at 1600°C and reported that solubility of Sn is independent of p_{O_2} in the range of $10^{-19.5}$ to $10^{-15.5}$ atm. However, solubility of Sn in slag increases with increasing p_{O_2} in the higher region, because of SnO dissolution in slag. Li et al. (2009) constructed the Cu-Sn phase diagram and Lu et al.

(2012) evaluated existing thermodynamics data and calculated the activity coefficient of Sn in liquid Cu using interaction parameters.

Beyond the Cu system, there are a number of studies on the thermodynamics of Sn removal from steel scrap. Sano et al. (1998) and Kim et al. (2011) studied the recovery of Sn from steel scrap. Wang et al. (1991) determined the activity of Sn in liquid Fe-S alloy saturated with C and Ag.

The relationships of Sn distribution-ratio in different slag systems with p_{O_2} have been investigated by many researchers but the effect of additive like Al_2O_3 , MgO or mix thereof was not extensively studied. The effect of temperature on γ_{SnO} has not been investigated for a wide range of p_{O_2} .

3.2 Distribution of Ag

In FeO_x -CaO slag at 1250°C, Takeda et al. (1983) and Yazawa et al. (1968) showed that the distribution of Ag to the slag is very small because it is difficult to oxidise. The dissolution of Ag in FeO_x -CaO slag did not show any dependency on the content of Ag in Cu. It is seen in Figure 6 that the distribution-ratio of Ag depends on the p_{O_2} . Ag was primarily dissolved as monovalent oxide ($AgO_{0.5}$) at high p_{O_2} . The effect of slag basicity or acidity on Ag distribution-ratio was not reported.

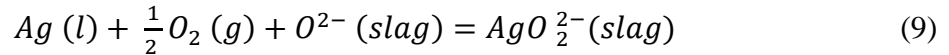
Louey et al. (1999) investigated the distribution-ratio of Ag between Cu-matte and FeO_x - SiO_2 slag at 1250°C at $p_{O_2} = 10^{-11.5}$ atm. The Ag matte/slag distribution-ratio was found to be 120 ± 40 which is in agreement with (Roghani et al., 1997a; 1997b; Takeda and Roghani, 1993). However, they found discrepancy between the measured and the calculated distribution-ratio of Ag, because the Ag was present in slag as oxide rather than Ag metal.

Avarmaa et al. (2015) investigated the equilibrium distribution-ratio of Ag between FeO_x - SiO_2 slag and Cu-matte at 1250-1350°C under controlled p_{O_2} , p_{S_2} and p_{SO_2} . They reported that Ag distribution-ratio slightly increased with increasing grade of Cu-matte. The effect of temperature on the solubility of Ag in slag was found to be large, as volatilisation of Ag occurred at high temperature.

Schlitt and Richards (1975) determined the Ag distribution in metal and matte systems at 1150 to 1250°C under CO_2 - SO_2 - N_2 atmosphere and found no dependency on temperature, p_{O_2} and p_{SO_2} .

The solubility of Ag in different slags was investigated at high temperature and dissolution mechanism also examined in Na_2O - B_2O_3 , CaO - B_2O_3 and BaO - B_2O_3 slags (Park

and Min, 1999, 2000). It was suggested that solubility of Ag decreased with the increase of basicity. The mechanism of Ag loss in borosilicate slag was studied by Pickles et al. (2011). The ionic reaction of Ag in MO-B₂O₃ (MO=CaO, Na₂O, BaO) slags at higher p_{O_2} is shown in Reaction (9) (Park and Min, 2000):



The partitioning of Ag metal is enhanced with the grade of Cu-matte, but solubility of Ag in slag can be increased with higher temperature and p_{O_2} . Therefore, low temperature is preferable for Ag partitioning during smelting operation. Ag behaviour on other slag systems and the effect of slag additive have not been studied.

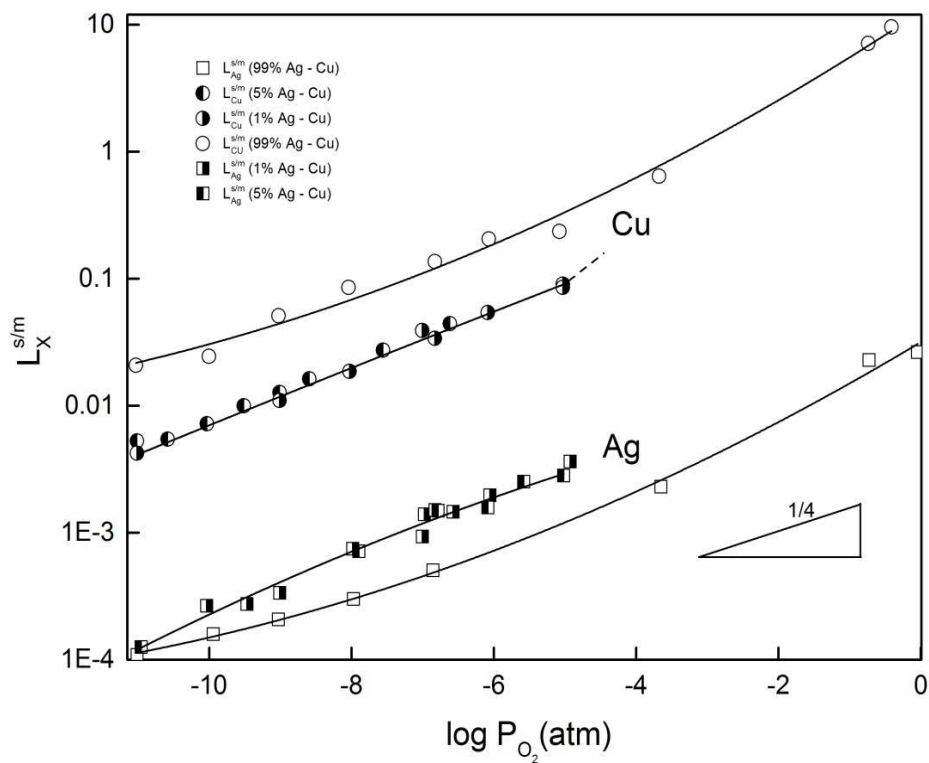


Figure 6: Distribution of Cu and Ag in matte and slag as function of $\log P_{O_2}$, reproduced from (Takeda et al., 1983; Yazawa et al., 1968).

3.3 Distribution of In

Some published data of distribution-ratio of In in between Pb or Cu metal and slag system is shown in Figure 7. Johnson (1983) carried out study on the distribution of In in FeO-SiO₂-Al₂O₃-CaO-MgO-PbO slag and molten Pb at 1200°C and p_{O_2} of 10⁻¹² atm. The oxidation state of In in slag was not assessed in his study. Johnson suggested that In

distribution-ratio was independent of Fe/SiO₂ ratio, and observed a declining trend when slag basicity is increased.

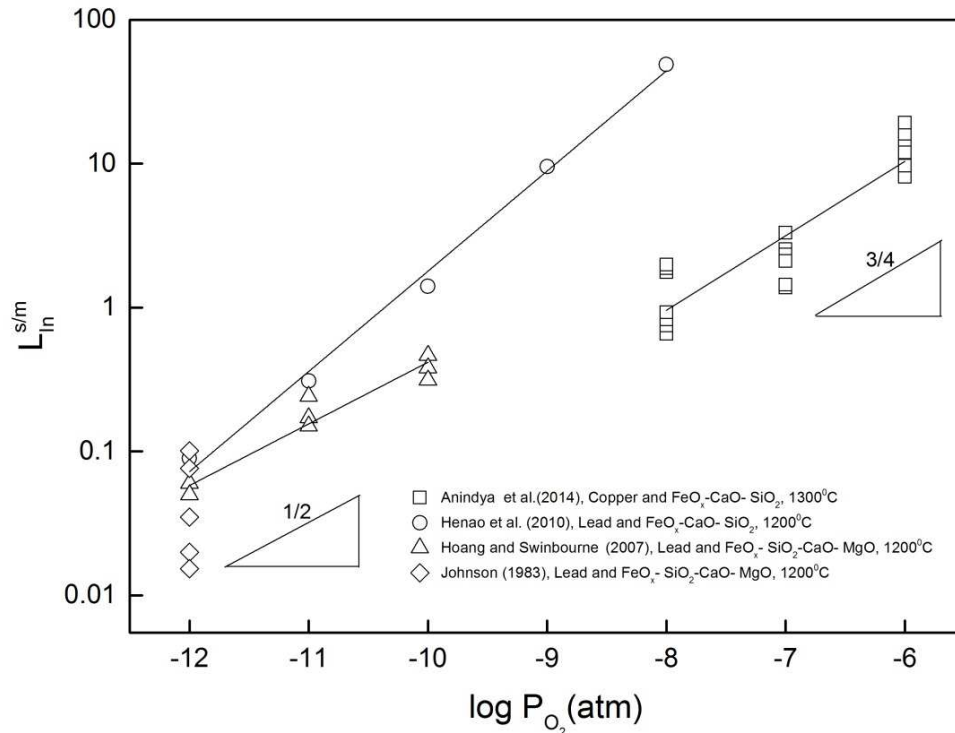
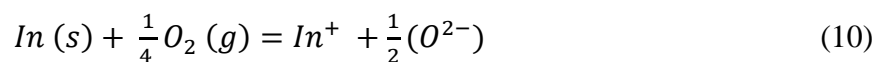


Fig. 7: In distribution-ratio in slag and Cu as a function of p_{O_2}

Hoang and Swinbourne (2007) measured the partitioning of In in Pb and FeO_x-SiO₂-CaO-Al₂O₃ slag at $p_{O_2}=10^{-12}$ – 10^{-10} atm and 1200°C. They found that In distribution-ratio increases with increasing Fe/SiO₂ ratio, but independent of CaO/SiO₂ ratio. Highest distribution-ratio was found at most FeO rich slag. It was reported that In was present in slag as InO. Anindya et al. (2014) determined the In distribution-ratio in Cu and FeO_x-CaO-SiO₂-MgO slag at 1300°C and $p_{O_2}=10^{-6}$ – 10^{-8} atm. In was found to be in the form of InO_{1.5} in slag due to instability of InO. Similar result was also found by Henao et al. (2010), where they used EPMA (Electron probe X-ray microanalysis). Ionic fraction of InO_{1.5} was calculated and it was found that it behaves as neutral oxide in slag. It was reported that distribution-ratio of In in metal increases with increasing of CaO in slag.

Ko and Park (2011, 2012) found that In solubility changes with the slag basicity (In solubility decreases with increasing silica content). The dissolution mechanism of In in CaO-SiO₂-Al₂O₃ slag was constructed in the following reaction:



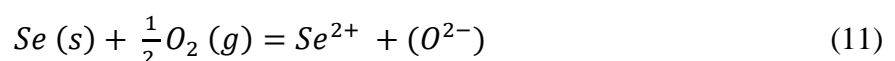
Han and Park (2015) measured In solubility in FeO-SiO₂-Al₂O₃-5CaO-MgO_{sat} slag at 1300°C and $p_{O_2}=10^{-12}$ - 10^{-11} atm and found that In solubility increases with increasing p_{O_2} . The solubility of In was found much lower in CaO-SiO₂-Al₂O₃ compared to FeO-bearing slag. The dissolution of In in FeO-SiO₂-Al₂O₃-5CaO-MgO_{sat} was found to decrease with increasing temperature, which indicates the exothermic nature of In₂O in slag. It was suggested that a high temperature reducing atmosphere with low silica content in calcium-aluminosilicate slags is a conducive condition for pyro-recycling of In bearing materials (Han and Park, 2015). The dissolution mechanism of In oxide in slags is still not fully understood.

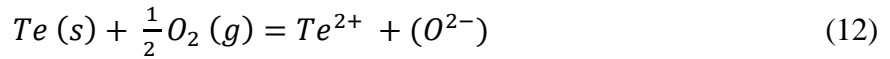
3.4 Distribution of Se and Te

Nagamori and Mackey (1977) measured the solubility of Se and Te in FeO_x-SiO₂-Al₂O₃ slag and Cu at 1200°C to 1300°C in p_{O_2} between 10^{-11} to 10^{-6} atm, where they observed Se distribution-ratio decreases with increasing p_{O_2} . It was reported that Se and Te can dissolve in slag both in elemental (Se⁰, Te⁰) and molecular (SeO, SeO₂, FeSe, TeO, TeO₂, FeTe) form. At low p_{O_2} in addition to atomic dissolution, they are dissolved as stable FeSe and FeTe. The distribution-ratio of Se was found to increase with lowering of p_{O_2} . They found a constant relationship of Te distribution-ratio with p_{O_2} . Alvear et al. (1994) reported that the distribution-ratio of Se and Te decreases with increasing p_{O_2} during reduction and opposite trend was found in oxidation in Na₂CO₃ slag system. The activity of Te oxide and Se oxide were reported to decrease with decreasing of NaO_{0.5} in NaO_{0.5}-CO₂-TeO₂ and NaO_{0.5}-CO₂-SeO₂ systems which is also the indication of high partitioning ratio of Se and Te in metal for Na₂CO₃ slag system.

The behaviour of Se in FeO_x-SiO₂ slag equilibrated with a Cu-Se alloy in N₂ atmosphere was investigated at 1185°C and 1250°C by Fang and Lynch (1987). They found that the nature of Se species in slag is in agreement with Nagamori and Mackey (1977). Fang and Lynch (1987) found that Se solubility is largely affected by Fe²⁺/Fe³⁺ ratio and almost zero at very low ratio.

The distribution-ratios of Se and Te between CaO-FeO_x-MgO slag and Cu in $p_{O_2}=10^{-9}$ to $10^{-0.68}$ atm at 1200°C to 1400°C were investigated by Johnston et al. (2007). The results are shown in Figures 8 and 9 compared with the results of Nagamori and Mackey (1977). Se and Te dissolve into the CaO-FeO_x-MgO slag according to following reactions:





It was found that distribution-ratios of Se and Te are higher in FeO_x -CaO-MgO compared to in FeO_x - SiO_2 - Al_2O_3 slag. This was mainly due to higher activity of Se and Te in FeO_x -CaO-MgO, which also increases with increasing temperature. It was reported that Se and Te enter into slag as complex of calcium ($CaSeO_2$ and $CaTeO_2$) which are more stable with increasing temperature (Johnston et al., 2010; Johnston et al., 2007). Johnston et al. (2007) reported that the partitioning of Se and Te increases with increasing temperature. Swinbourne et al. (1998) investigated Te distribution-ratio in Cu anode slimes smelting at $1100^\circ C$ and found that low temperature and low p_{O_2} are preferable for Te elimination in anode furnace. Zhao and Irons (1997) showed that Se could be reduced using calcium carbide and Na_2CO_3 from molten Cu at $1300^\circ C$.

In summary, the partitioning of Se and Te to slag is enhanced in the presence of lime through formation of complex Ca. In the presence of iron, iron selenide and iron telluride could form and also increase the activity of Te and Se in slag. The effect of additive in FeO_x - SiO_2 slag on the behaviour of Se and Te has not been thoroughly investigated, therefore further study is required.

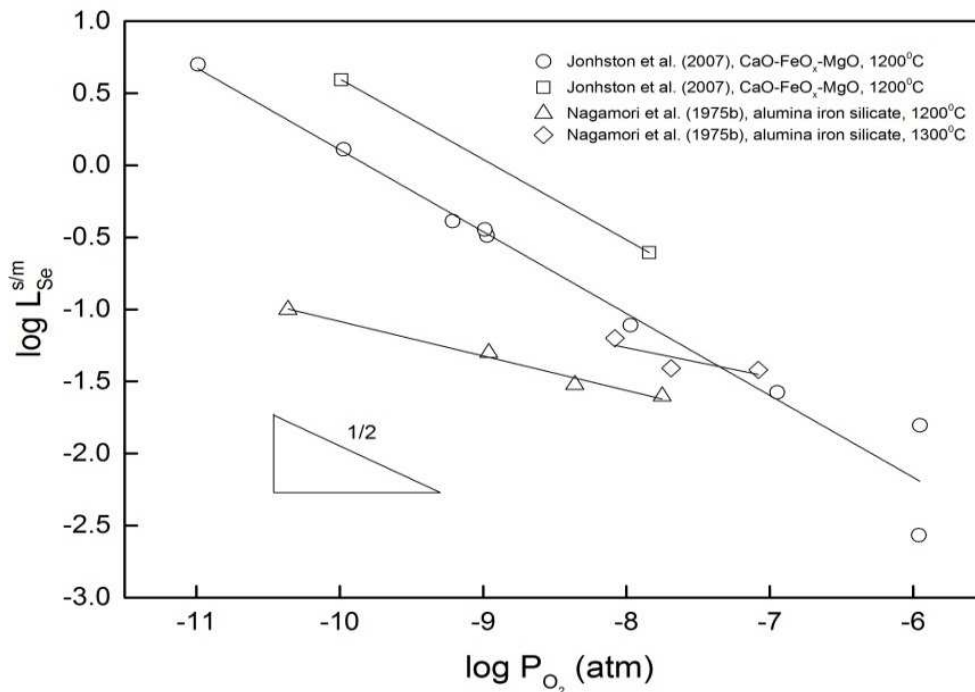


Fig. 8: Se distribution-ratio in the slag and Cu as a function of P_{O_2} and temperature

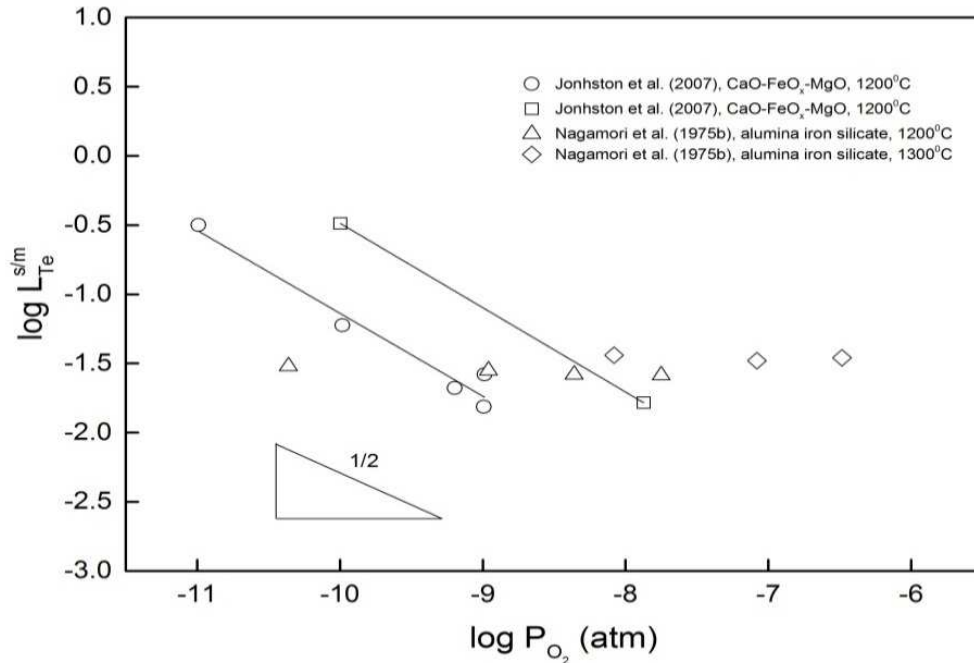


Fig. 9: Te distribution-ratio in the slag and Cu as a function of P_{O_2} and temperature

3.5 Distribution of Pt, Pd, Au and Rh

The concentration of Pt group metals (PGM) in the virgin ore is low (3-20 ppm), therefore most of them are recovered as by-products during Ni and Cu smelting (Cabri, 1992; Graedel et al., 2002; Saurat and Bringezu, 2008). The trace concentration of Pt in e-waste is 0.1-5 ppm. The PGM are favourably recovered using current Cu production circuits (Reuter and Kojo, 2014).

Yamaguchi (2010, 2013) determined the distribution-ratio of Pt and Pd in Cu alloy and FeO_x -CaO slag at $1300^\circ C$ and $p_{O_2}=10^{-9}$ - 10^{-5} atm and reported that the distribution-ratios of Pt and Pd were increased with increasing p_{O_2} (shown in Figure 10). Henao et al. (2006) measured the distribution-ratio of Pt, Pd and Rh between Cu-matte and FeO_x - SiO_2 slag at $1300^\circ C$ under fixed p_{SO_2} . It was found that distribution-ratio is constant up to 60% Cu in matte and then increases with increasing matte grade. Henao et al. (2006) reported the $L_x^{Matte/Slag}$ of 1000 for Pd and 100 for Pt, respectively.

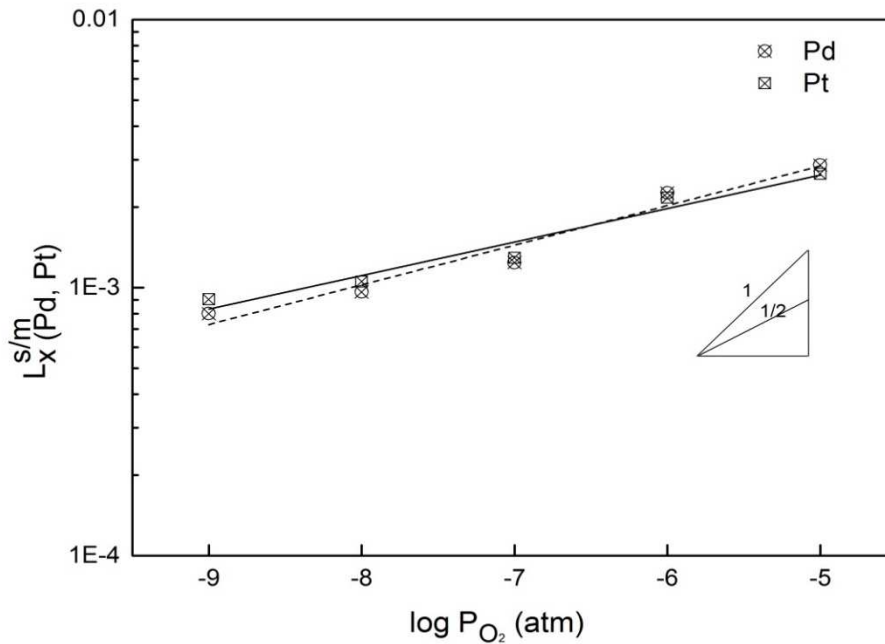
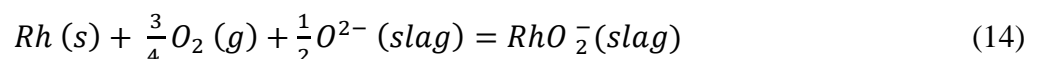
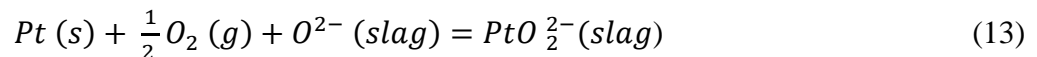
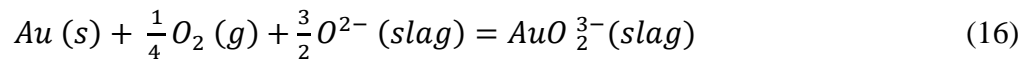
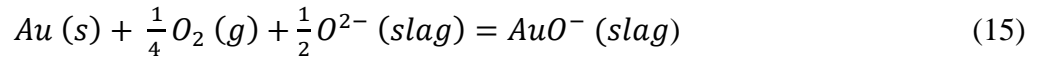


Fig. 10: Distribution-ratio of Pt and Pd between FeO_x-CaO slag and Cu alloy at 1300°C, reproduced from (Yamaguchi, 2013).

Avarmaa et al. (2015) investigated the distribution of Pt, Pd and Rh between FeO_x-SiO₂ slag and Cu-matte at 1250 to 1350°C and reported an increase in $L_x^{Matte/Slag}$ of Pt, Pd and Rh with increasing matte grade. The $L_x^{Matte/Slag}$ were 3000 for Pd, 6000 for Pt, and 10000 for Rh in a matte grade of 65% Cu, respectively. They also reported that the effect of temperature was very small. The solubility of Pt and Pd was increased with increasing matte grade, temperature and p_{O_2} (Avarmaa et al., 2015; Yamaguchi, 2010), as both Pt and Pd exhibit deviation from Raoultian behaviour in the dilute Cu-Pd and Cu-Pt systems (Abe et al., 2006; Li et al., 2008).

Swinbourne et al. (2005) investigated Au solubility in slag and found that solubility of Au in Pb-slag is higher compared to in FeO_x-SiO₂ and CaO-SiO₂ slag. The dissolution behaviour of Pt (Nakamura et al., 1998; Nakamura and Sano, 1997; Wiraseranee et al., 2014), Rh (Wiraseranee et al., 2013a; Wiraseranee et al., 2013b) and Au (Han et al., 2015; Schlitt and Richards, 1975; Swinbourne et al., 2005) have been studied to understand the dissolution reaction in slags. The ionic reactions of Pt in CaO-Al₂O₃ slag (Nakamura and Sano, 1997), Au in CaO-SiO₂-Al₂O₃-MgO_{sat} slag (Han et al., 2015) and Rh in CaO-SiO₂ slag (Wiraseranee et al., 2013a) were suggested to follow these reactions:





3.6 Distribution of Pb

The summary of published data of Pb distribution-ratio in Cu and different slags is shown in Figure 11. Takeda et al. (1983) and Yazawa et al. (1968) measured the Pb partitioning between FeO_x -CaO and FeO_x - SiO_2 slags and liquid Cu at 1250°C. It was reported that Pb exists in slag as PbO and partitioning to slag is higher in FeO_x - SiO_2 slag compared to FeO_x -CaO slag. The activity coefficient of PbO was found to increase with increasing of CaO. Takeda et al. (1983) reported the stability of PbO in slag increases with decreasing temperature.

Nagamori et al. (1975a) investigated the equilibrium of Pb in FeO_x - SiO_2 - Al_2O_3 - $CuO_{0.5}$ slag and metallic Cu at 1200°C and 1300°C at $p_{O_2}=10^{-11}$ - 10^{-6} atm and found that distribution-ratio of Pb depends on p_{O_2} , and γ_{PbO} increases with increasing Al_2O_3 content in the slag. The activity of PbO in slag was found to be 0.07, which was independent of p_{O_2} and temperature.

Kim and Sohn (1998) measured the distribution-ratio of Pb in Cu and FeO_x - SiO_2 slag at 1250°C and $p_{O_2}=10^{-12}$ - 10^{-6} atm. It was found that the distribution behaviour depends on p_{O_2} , basicity and FeO_n/SiO_2 ratio. They also found that the activity coefficient of PbO and the distribution-ratio of Pb are not remarkably affected by the addition of Al_2O_3 , CaO, MgO or a mixture thereof. Due to the addition of additive in slag, Pb^{2+} was replaced to decrease its proportion in slag by Ca^{2+} , Mg^{2+} and Al^{3+} .

It was proposed by Acuna and Yazawa (1987) that the distribution-ratio of Pb is highest for FeO_x - SiO_2 slag, followed by FeO_x -BaO and FeO_x -CaO slags. Matsuzaki et al. (2000) measured the distribution-ratio of Pb between CaO - SiO_2 - Al_2O_3 and liquid Cu at 1350°C and reported that the partitioning of Pb is affected by p_{O_2} , temperature and slag basicity. The slag system was considered as a regular solution by Matsuzaki et al. (2000) to calculate γ_{PbO} and they found similar results indicated by (Takeda and Yazawa, 1989). It was also mentioned by Matsuzaki et al. (2000) that γ_{PbO} was decreased, as CaO was replaced with SiO_2 at a fixed Al_2O_3 . In the study of Kim and Sohn (1998), it was also found that γ_{PbO} has a linear correlation with p_{O_2} .

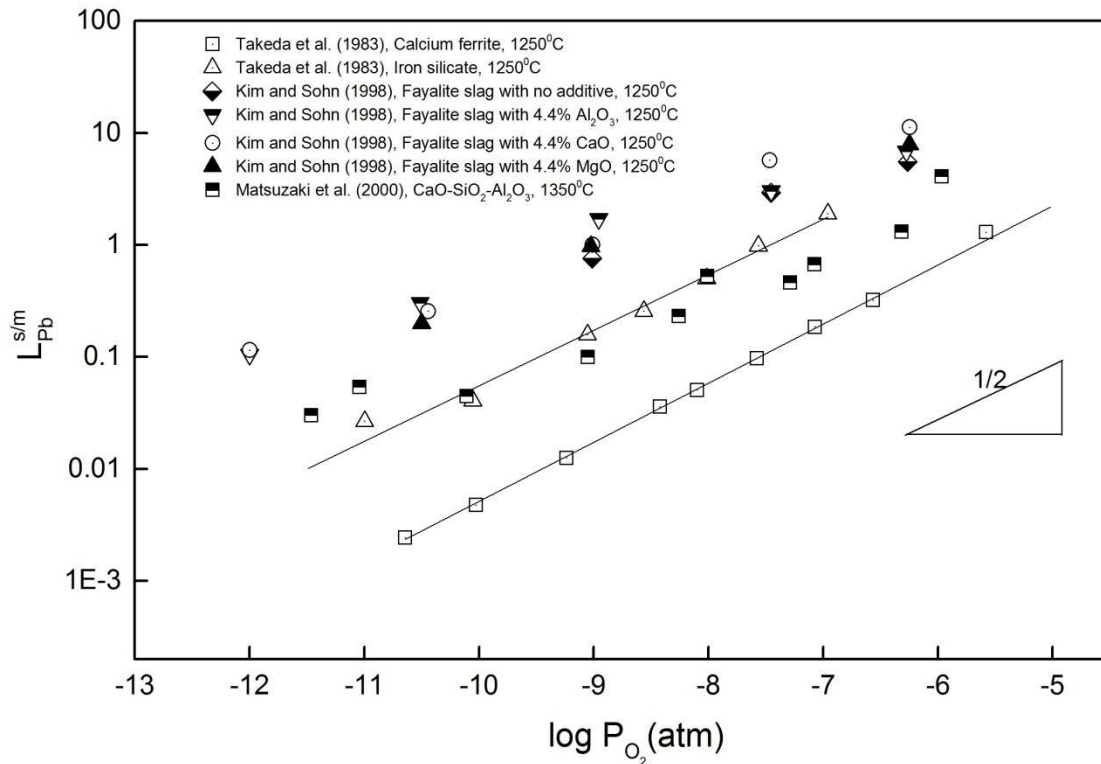


Fig. 11: Pb distribution-ratio as function of p_{O_2} and temperature in different slag systems

Heo et al. (2012) investigated the distribution-ratio of Pb between FeO_x - SiO_2 -(CaO, Al_2O_3) and molten Cu at $1200^\circ C$ and 10^{-10} atm. They found that Pb distribution-ratio decreases with increasing of CaO and Al_2O_3 in the slag. Heo et al. (2012) proposed that due to the increase of alumina content, the activity of FeO decreases from about 0.45 to 0.25 which promotes the dissolution of Pb into the slag.

Kaur et al. (2009) measured the Pb distribution-ratio between Cu and FeO_x -CaO- SiO_2 slag at $1300^\circ C$ and $p_{O_2}=10^{-6}$ atm; and indicated that Pb partitioning in FCS slag is better compared to in FeO_x - SiO_2 slag. Degterov and Pelton (1999) optimised the thermodynamics database for equilibrium calculation of Pb which relates to the Cu production at temperature range 1150 to $1350^\circ C$ and p_{O_2} 10^{-10} to 10^{-6} atm; and reported that the distribution-ratio of Pb is affected by slag basicity and Fe/ SiO_2 ratio. PbO behaves as a strong basic oxide at the conditions of Cu processing (Heo et al., 2012; Kim and Sohn, 1998; Matsuzaki et al., 2000).

3.7 Distribution of Co

The distribution-ratio of Co was investigated by Yazawa et al. (1968) between liquid Cu and FeO_x -CaO or FeO_x - SiO_2 slag at $1250^\circ C$ and the result is shown in Figure 12. It was

found that the distribution-ratio decreases with lowering p_{O_2} . It was also reported that under oxidative smelting condition Co goes to slag and is difficult to recover for a matte grade approximately above 80% Cu. Kho et al. (2006) measured the Co distribution-ratio in synthetic Cu-matte and FeO_x-SiO_2-MgO slag at $1250^\circ C$ to be 4.3 ± 0.9 , which is in a good agreement with results of Mwema et al. (1995) but is higher than the finding of Yazawa et al. (1968).

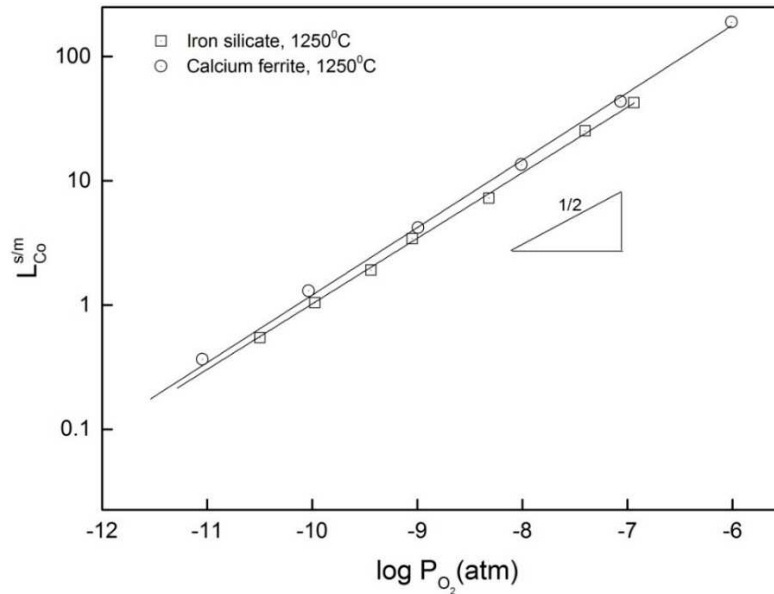


Fig. 12: Co distribution-ratio as function of p_{O_2} in different slag systems, reproduced from (Takeda et al., 1983; Yazawa et al., 1968).

Derin and Yücel (2002) studied the solubility of Co between Co-Cu and $Al_2O_3-FeO-Fe_2O_3-SiO_2$ slag at $1350^\circ C$ and p_{O_2} 10^{-10} to 10^{-8} atm. They found that γ_{CoO} increases with decreasing p_{O_2} . The Equation (17) shows the activity coefficient of CoO in silica saturated fayalite slag as a function of Co solubility. It shows that γ_{CoO} increases with Co solubility in slag (Grimsey and Toguri, 1988).

$$\gamma_{CoO} = 1.94 + 0.123 [\text{wt\% Co}] \quad (17)$$

Reddy and Healy (1981) investigated the distribution-ratio of Co in Cu-Co alloy and $Cu_2O-CoO-SiO_2$ slag at $1200^\circ C$ to $1300^\circ C$ under argon atmosphere, where they found that distribution-ratio of Co increases with decreasing temperature. They proposed a relationship of distribution-ratio of Co as a function of temperature as shown in Equation (18).

$$\log L_{Co}^{S/M} = 2090/T + 1.26 \quad (18)$$

Grimsey and Liu (1997) measured the effect of additive in FeO_x-SiO_2 slag on the activity coefficient of Co oxide at p_{O_2} of 10^{-9} to 10^{-10} at $1200^\circ C$. They found that γ_{CoO}

increases with increasing of Al_2O_3 , MgO and CaO and decreases with increasing of SiO_2 of slag. According to Teague et al. (2001), γ_{CoO} increases with SiO_2 content in the slag, but above 4% SiO_2 it decreases due to precipitation of spinel crystals from the slag. Chen et al. (2004) reproduced the experimental data by model calculation for silica content up to 20% in slag and found that the presence of silica in FeO_x - CaO slag induces a strong interaction between CaO and SiO_2 , thus lowering the interaction between CoO and CaO and resulting in the decrease of γ_{CoO} in slag.

Kubišta and Vřešt'ál (2000) determined the thermodynamic properties of Co-Cu system and calculated the phase diagram. Later, (Lu et al., 2012) calculated the activity coefficient of Co in liquid Cu using interaction parameter determined by Kubišta and Vřešt'ál. The partitioning of Co to slag is enhanced in the presence of lime, magnesia or alumina in slag, as these increase the CoO activity in slag and the p_{O_2} also plays important role in term of Co recovery (Eerola et al., 1984; Grimsey and Liu, 1997).

3.8 Distribution of As, Bi and Sb

The summary of published data of distribution-ratio of As, Bi and Sb in different slag system is shown in Figures 13, 14, 15 respectively and dissolution form of these metals in various slag systems is shown in Table 6.

Nagamori et al. (1975b) studied the distribution-ratio of As, Bi and Sb between FeO_x - SiO_2 - Al_2O_3 - $\text{CuO}_{0.5}$ slag and metallic Cu at 1200°C and 1300°C at p_{O_2} 10^{-11} to 10^{-6} atm. It was found that distribution-ratio of Sb and Bi decreases with increasing temperature but independent of p_{O_2} . It was suggested that Bi and Sb dissolved as atomic form in slag. This was in good agreement with (Jimbo et al., 1984).

Yazawa et al. (1968) and Takeda et al. (1983) measured the As, Bi and Sb partitioning between FeO_x - CaO and FeO_x - SiO_2 slags and liquid Cu at 1250°C . It was reported that Bi, As, Sb dissolve through oxidic dissolution such as $\text{BiO}_{1.5}$, $\text{AsO}_{1.5}$, $\text{SbO}_{1.5}$ respectively; which was in contrary to Nagamori et al. (1975b). Takeda et al. (1983) found a linear relationship between these metals partitioning and p_{O_2} in FeO_x - SiO_2 slag. It was also found that partitioning of As and Sb was lower in FeO_x - SiO_2 slag compared to FeO_x - CaO slag. Sb and As oxide are acidic which tend to form oxide with basic flux. Thus the activity coefficient of $\gamma_{\text{AsO}_{1.5}}$ and $\gamma_{\text{SbO}_{1.5}}$ decrease with the increasing of CaO , which was also the reason of higher distribution-ratio of As and Sb in FeO_x - CaO slag.

Table 6: Dissolution form of Bi, Sb and As

Investigators	p_{O_2} (atm)	Temperature ($^{\circ}$ C)	Results
Iron-Silicate Slag			
Nagamori et al. (1975b)	10^{-11} - 10^{-6}	1200 and 1300	atomic dissolution (Bi,Sb,As)
Takeda et al. (1983)	10^{-11} - 10^{-6}	1250	oxidic dissolution (BiO _{1.5} , SbO _{1.5} , AsO _{1.5})
Jimbo et al. (1984)	10^{-11} - 10^{-7}	1200 and 1300	oxidic dissolution (BiO, SbO, AsO)
Kim and Sohn (1998)	10^{-11} - 10^{-6}	1250	atomic dissolution (Bi,Sb,As)
Chen and Jahanshahi (2010)	10^{-11} - 10^{-6}	1300	oxidic dissolution (AsO _{1.5})
Calcium-Ferrite Slag			
Takeda et al. (1983)	10^{-11} - 10^{-6}	1250	oxidic dissolution (BiO _{1.5} , SbO _{1.5} , AsO _{1.5})
Eerola et al. (1984)	10^{-11} - 10^{-5}	1250	oxidic dissolution (BiO _{1.5} , SbO _{1.5} , AsO _{1.5})
Chen and Jahanshahi (2010)	10^{-11} - 10^{-6}	1300	oxidic dissolution (AsO _{1.5})
Ferrous-Calcium Slag			
Paulina et al. (2013)	10^{-6}	1300	oxidic dissolution (BiO _{1.5})
Chen and Jahanshahi (2010)	10^{-11} - 10^{-6}	1300	oxidic dissolution (AsO _{1.5})
Kaur et al. (2011)	10^{-6}	1300	oxidic dissolution (SbO _{1.5})

Kim and Sohn (1998) examined the distribution-ratio of Bi, Sb and As in Cu and FeO_x-SiO₂ slag at 1250 $^{\circ}$ C and p_{O_2} of 10^{-12} to 10^{-6} atm. It was reported that their distribution behaviour is independent of p_{O_2} . They found very small effect of Al₂O₃, CaO, MgO or a mixture thereof on the distribution.

Acuna and Yazawa (1987) studied the distribution of As and Sb between matte and FeO_x-BaO slag at 1300 $^{\circ}$ C and FeO_x-CaO slag at 1250 $^{\circ}$ C. They found that distribution-ratio of As and Sb decreases with increasing matte grade up to 70%. The distribution-ratio of As and Sb were the highest for FeO_x-BaO and followed by FeO_x-CaO and FeO_x-SiO₂ slag. Roghani et al. (1996) investigated the distribution-ratio of As, Bi and Sb between FeO_x-CaO slag and Cu matte at 1250 $^{\circ}$ C under high p_{SO_2} and found that the distribution-ratio decreases with increasing p_{SO_2} . According to Roghani et al. (1996), As and Sb were stable in matte phase, therefore constant ratio of $L_{As}^{s/m}$ and $L_{Bi}^{s/m}$ were found against matte grade in low region. However, $L_{As}^{s/m}$ and $L_{Sb}^{s/m}$ were found to increase with increasing CaO in the slag, whereas $L_{Bi}^{s/m}$ showed constant value.

Riveros et al. (1987) determined the distribution-ratio of As and Sb between Na₂CO₃-Na₂O-SiO₂ and molten Cu at 1250 $^{\circ}$ C. They found that higher valence specie are more stable with increasing of p_{O_2} and basicity. The most stable oxide species of As was found to be

AsO_{2.5} which was in disagreement with (Kim and Sohn, 1998; Roghani et al., 1996; Takeda et al., 1983).

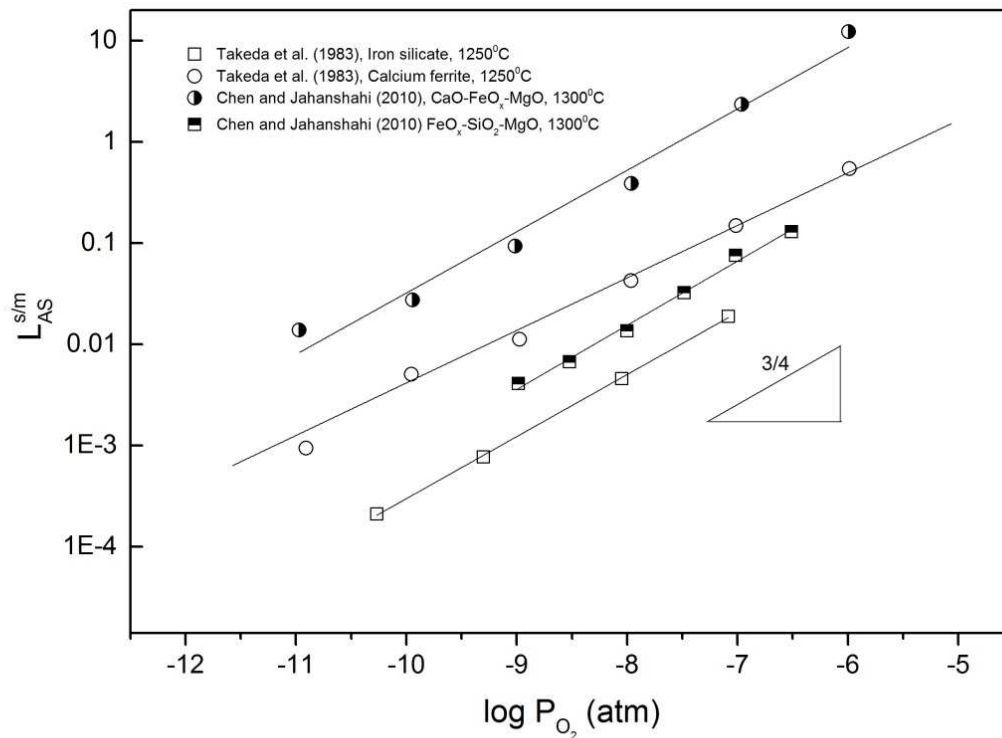


Fig. 13: As distribution-ratio as function of p_{O_2} in different slag systems

Kaur et al. (2011), Chen and Jahanshahi (2010) and Paulina et al. (2013) studied the distribution-ratio of Sb, As and Bi in FeO_x-CaO-SiO₂ (FCS) slag and molten metal (Cu or Ag) at 1300°C. It was proposed by Kaur et al. (2011) that Sb dissolves in FeO_x-CaO-SiO₂ slag as SbO_{1.5} at $p_{O_2}=10^{-6}$ atm. The distribution-ratio of As in FCS was reported to be lower than the FeO_x-CaO slag. Paulina et al. (2013) determined the distribution-ratio of Bi in FCS slag and Cu at $p_{O_2}=10^{-6}$ atm. The distribution-ratio of Bi was affected by the CaO content in slag, but independent to Fe/SiO₂ ratio. Paulina et al. (2013) compared the distribution-ratio of Bi with previous results (Gortais et al., 1994; Takeda et al., 1983) and proposed that Bi dissolves in FCS slag as BiO_{1.5}. Furthermore, it has been also shown using previous data (Nagamori et al., 1975b; Teppo et al., 1990) that activity coefficient of Bi in liquid Cu decreases with increasing of temperature.

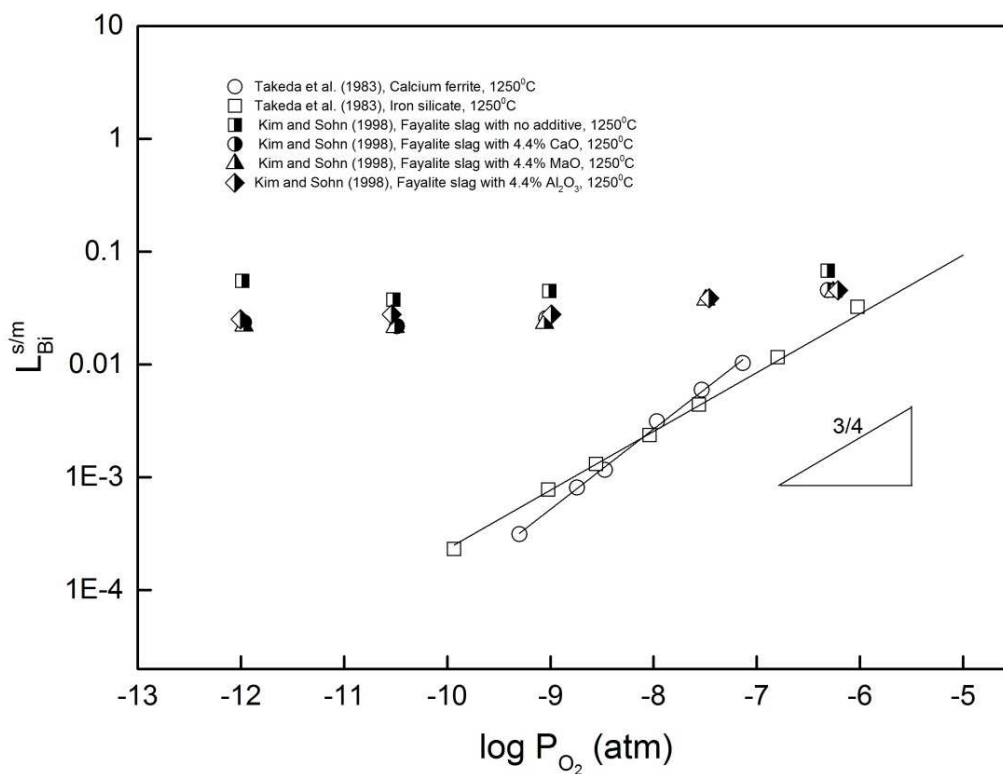


Fig. 14: Bi distribution-ratio as function of p_{O_2} in different slag systems

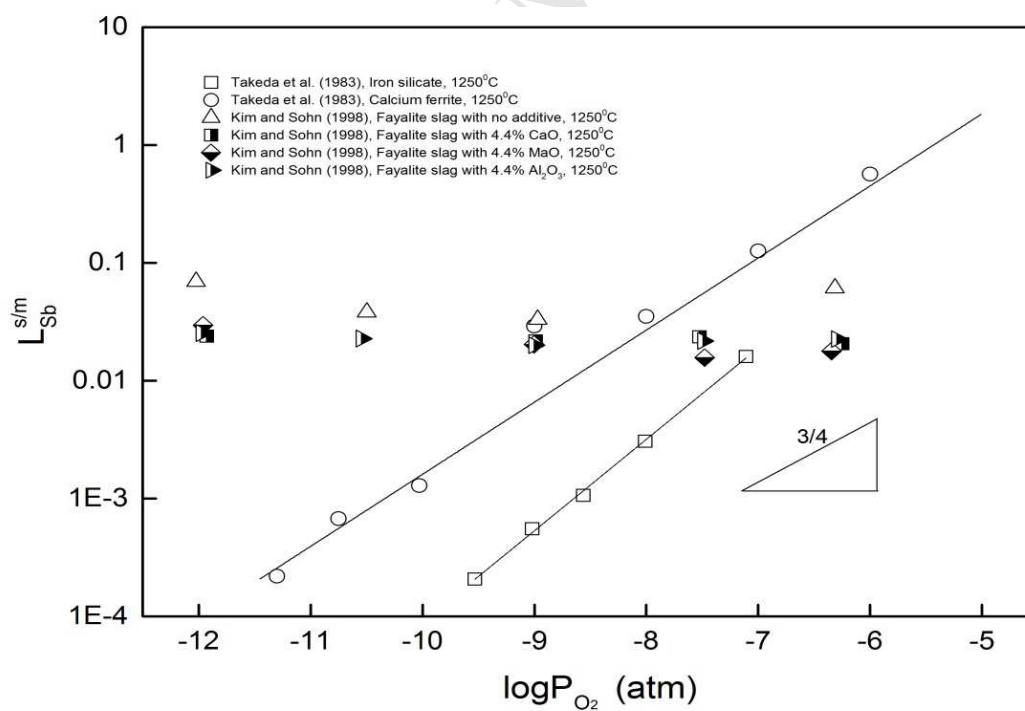


Fig. 15: Sb distribution-ratio as function of p_{O_2} in different slag systems

Chen and Jahanshahi (2010) measured the distribution-ratio of As between FeO_x -CaO-SiO₂-MgO and Ag at 1300°C and $p_{\text{O}_2}=10^{-11}$ – 10^{-6} atm. Ag-As alloys were used in their experiment, where they found that $L_{\text{As}}^{S/M}$ was strongly affected by p_{O_2} , and it was considered that As dissolves in slag as $\text{AsO}_{1.5}$. Distribution-ratio of As in FeO_x -CaO slag was one magnitude higher than in FeO_x -SiO₂ slag. They also studied the effect of slag composition on distribution of As, where they found that $L_{\text{As}}^{S/M}$ decreases with increasing silica content in the slag. According to them, p_{O_2} also affected the activity coefficient of $\text{AsO}_{1.5}$ ($\gamma_{\text{AsO}_{1.5}}$) and it was found that $\gamma_{\text{AsO}_{1.5}}$ in FeO_x -SiO₂ slag was 40 times higher than that in FeO_x -CaO slag.

Wypartowicz (1995) re-examined thermodynamics properties of Cu-As liquid solution at temperatures 950°C to 1175°C, where they found that the activity of As in Cu decreases with increasing of temperature. Relation of the activity coefficient of As and As oxide with temperature has not been studied extensively. There is gap in knowledge regarding the effect of temperature and slag composition on the distribution behaviour of Sb, As and Bi in FCS slag.

4. Gaps in Knowledge

The distribution and partitioning behaviour of common elements such as, Au, Ag, Se, Te, Sn, Pb, Bi, As, and Sb in the conditions relevant to primary Cu processing have been studied by a number of researchers. However, limited data were found for the elements like Pt, Pd, Rh, In and Co and no data were found for Ge and Ga. The information on the distribution behaviour of valuable elements in the conditions relevant to secondary Cu processing is not available except for Sn and In. The summary of previous studies of valuable elements distribution-ratio shown in Table 8 indicate that the majority of the thermodynamic data existed are relevant to primary rather than secondary Cu processing.

The presence of multi-solute elements in a solution can affect each other's thermodynamic behaviour. One important aspect that needs to be mentioned is the fact that the majority of the previous partitioning behaviour studies focused on selected individual elements and assuming that the influence of one element in Cu on the activity of other is negligible. In real systems where there is more than one solute element, such as in processing of e-waste via Cu smelting, it is necessary to consider the elements confluence effect, which usually represented by interaction parameters (Sigworth and Elliott, 1974). To fully understand the distribution behaviour, the interaction parameters will need to be taken into consideration for complex systems.

Table 8: Summary of previous work of trace valuable elements distribution in primary and secondary Cu smelting

Metal	Primary Copper Processing	Ref.	Secondary Copper Processing	Ref.
Ag	Data available	(Avarmaa et al., 2015; Fountain et al., 1991; Gortais et al., 1994; Kashima et al., 1978; Louey et al., 1999; Mackey, 1982; Nagamori and Mackey, 1978; Schlitt and Richards, 1975; Takeda et al., 1983; Takeda and Roghani, 1993; Yazawa, 1974; Yazawa and Takeda, 1982; Yazawa et al., 1968)	No data available	-
Au	Limited data available	(Han et al., 2015; Nagamori and Mackey, 1978; Schlitt and Richards, 1975; Swinbourne et al., 2005)	No data available	-
Pt	Limited data available (matte-slag system)	(Avarmaa et al., 2015; Henao et al., 2006; Schlitt and Richards, 1975; Yamaguchi, 2010, 2013)	No data available	-
Pd				
Rh	Limited data available (matte-slag system)	(Avarmaa et al., 2015; Henao et al., 2006)	No data available	-
Se	Data available	(Alvear et al., 1994; Choi and Cho, 1997; Fang and Lynch, 1987; Johnston et al., 2010; Johnston et al., 2007; Nagamori et al., 1975b; Nagamori and Mackey, 1977; Nagamori and Mackey, 1978; Swinbourne et al., 1998; Zhao and Irons, 1997)	No data available	-
Te				
Sn	Data available	(Fountain et al., 1991; Gortais et al., 1994; Louey et al., 1999; Mackey, 1982; Nagamori and Mackey, 1977; Nakazawa and Takeda, 1983; Roghani et al., 1997a; Roghani et al., 1997b; Takeda et al., 1983; Takeda and Yazawa, 1989; Yazawa and Takeda, 1982; Yazawa et al., 1968)	One data available	(Anindya et al., 2013)
In	Very limited data available	Nakajima et al. (2011)	Two data available	(Anindya et al., 2014; Han and Park, 2015)
Pb	Data available	(Acuna and Yazawa, 1987; Degterov and Pelton, 1999; Kaur et al., 2009; Kim and Sohn, 1998; Matsuzaki et al., 2000; Nagamori et al., 1975a; Nagamori and Mackey, 1978; Nakazawa and Takeda, 1983; Takeda et al., 1983; Takeda and Yazawa, 1989; Yazawa et al., 1968, 1999)	No data available	-
Bi	Data available	(Chen and Jahanshahi, 2010; Jimbo et al., 1984; Kaur et al., 2009; Kaur et al., 2011; Kim and Sohn, 1998; Mackey, 1982; Nagamori et al., 1975a, b; Nagamori and Mackey, 1978; Nakazawa and Takeda, 1983; Paulina et al., 2013; Riveros et al., 1987; Roghani et al., 1996; Takeda et al., 1983; Yazawa and Takeda, 1982; Yazawa et al., 1968)	No data available	-
As				

Sb				
Co	Data available	(Choi and Cho, 1997; Derin and Yücel, 2002; Grimsey and Toguri, 1988; Kho et al., 2006; Mwema et al., 1995; Teague et al., 2001)	No data available	-
Ge	No data available	-	No data available	-
Ga	No data available	-	No data available	-

5. Implication for Metal Recycling Industry

The valuable elements found in e-waste could be considered as resources as opposed to waste in the overall materials flow if these can be recovered using feasible routes. It may be possible to recover most of these valuable elements if the conditions favourable for partitioning them into appropriate phases are identified. For this thermodynamics data and their understanding are essential. It can be seen from the present review study that most researchers have conducted their study in the temperature range 1250-1350°C which is mainly driven by the current industrial practice in Cu processing. There are also other parameters such as p_{O_2} , activity of these valuable metals in slag and metal and the composition of slag (which relates to slag physicochemical properties favourable for operation) to consider for the control of the distribution of valuable elements in different phases. The information on the existing thermodynamic data and distribution behaviour of the valuable elements in the literature have been collected; and listed and classified by operating parameters (temperature and p_{O_2}) and slag systems as shown in Table 9. The table provides information about the typical slags, temperatures and p_{O_2} range previously investigated to understand the behaviour of valuable elements distribution in industrial Cu smelting processes.

A systematic research is required to understand and determine the thermodynamics data, particularly the interaction parameters and partitioning of valuable metals in wider conditions relevant to both primary and secondary Cu processing. On the basis of more comprehensive thermodynamic information, further optimisation and improvement of the existing processes can be carried out to maximise recovery of most if not all the valuable metals. These can also induce the development of novel processes for better recovery of the metals from other urban ores or wastes.

Table 9: Different experimental conditions in various slag systems for elements distribution in molten metal

Equilibrium System	Slag System	p_{O_2} (atm)	Temperature (°C)	Minor Elements	Ref.
<i>Iron-silicate slag</i>					
Slag – Cu alloy	FeO _x -SiO ₂	10 ⁻¹² – 10 ⁻⁶	1250	Ag, Sn, Pb, As, Sb, Bi, Co	(Nakazawa and Takeda, 1983; Takeda et al., 1983; Yazawa et al., 1968, 1999)
Slag – Cu alloy	FeO-Fe ₂ O ₃ -SiO ₂ -Al ₂ O ₃	10 ⁻¹¹ – 10 ⁻⁶	1200 and 1300	Sn, Te, Se, Bi, As, Pb, Sb,Co	(Derin and Yücel, 2002; Nagamori et al., 1975a, b; Nagamori and Mackey, 1977)
Slag – Cu matte	FeO _x -SiO ₂	10 ^{-11.5}	1250	Ag, Sn	(Louey et al., 1999)
Slag – Cu matte	FeO _x -SiO ₂	–	1250 and 1300	Ag, Pb, Bi,Sb	(Kashima et al., 1978; Roghani et al., 1997a; Roghani et al., 1997b; Takeda and Roghani, 1993)
Slag – Cu matte	FeO _x -SiO ₂	10 ^{-8.4} – 10 ^{-7.3}	1250 to 1350	Au, Ag, Pt, Pd,Rh	(Avarmaa et al., 2015)
Matte – Cu alloy	–	–	1150 to 1250	Ag, Au, Pd, Pt	(Schlitt and Richards, 1975)
Slag – Cu alloy	FeO _x -SiO ₂ -(CaO, MgO, Al ₂ O ₃)	10 ⁻¹² – 10 ⁻⁶	1200	Pb, Bi, As, Sb	(Heo et al., 2012; Kim and Sohn, 1998)
Slag – Cu matte	FeO _x -SiO ₂ -MgO	–	1250	Co	(Choi and Cho, 1997; Kho et al., 2006)
Slag – Cu alloy	FeO-Fe ₂ O ₃ -SiO ₂ -Al ₂ O ₃	10 ⁻¹⁰ – 10 ⁻⁸	1350	Co	(Derin and Yücel, 2002)]
Slag – Cu alloy	FeO _x -SiO ₂ -MgO	10 ⁻¹¹ – 10 ⁻⁶	1300	As	(Chen and Jahanshahi, 2010)
Slag – Cu alloy	FeO _x -SiO ₂	10 ⁻⁹ – 10 ⁻⁵	1300	Pt, Pd	(Henao et al., 2006; Yamaguchi, 2013)

<i>Calcium-ferrite slag</i>					
Slag – Cu alloy	FeO _x -CaO	10 ⁻¹² – 10 ⁻⁶	1250	Ag, Sn, Pb, As, Sb, Bi, Co	(Nakazawa and Takeda, 1983; Takeda et al., 1983; Yazawa et al., 1968, 1999)
Slag – Cu alloy	CaO-FeO-Fe ₂ O ₃ -MgO	10 ⁻¹² – 10 ^{-6.8}	1185 and 1250	Se, Te	(Johnston et al., 2010)
Slag – Cu matte	FeO _x -CaO	–	1250	Ag, Pb, Bi, Sb	(Roghani et al., 1996)
Slag – Cu alloy	FeO _x -CaO-MgO	10 ⁻¹¹ – 10 ⁻⁶	1300	As	(Acuna and Yazawa, 1987)
<i>Ferrous-calcium-silicate slag</i>					
Slag – Cu alloy	FeO _x -CaO-SiO ₂	10 ⁻⁶ – 10 ⁻⁸	1300	Sn, In	(Anindya et al., 2013, 2014)
Slag – Pb alloy	FeO _x -CaO-SiO ₂	10 ⁻¹² – 10 ⁻¹⁰	1200	In,	(Hoang and Swinbourne, 2007)
Slag – Cu alloy	FeO _x -CaO-SiO ₂	10 ⁻⁶	1300	Sb, Bi, Pb	(Kaur et al., 2009)
Slag – Ag alloy	FeO _x -CaO-SiO ₂ -MgO	10 ⁻¹¹ – 10 ⁻⁶	1300	As	(Chen and Jahanshahi, 2010)
<i>Others slag system</i>					
Slag – Cu alloy	CaF ₂ -CaO-MgO-SiO ₂	–	1227	Sn, Sb	(Gortais et al., 1994)
Slag – Cu alloy	CaO-SiO ₂ -Al ₂ O ₃	–	1350	Pb	(Heo et al., 2012; Matsuzaki et al., 2000)
Slag – Cu alloy	Cu ₂ O-CoO-SiO ₂	–	1200 to 1300	Co	(Reddy and Healy, 1981)
Slag – Cu alloy	Na ₂ O ₃ -Na ₂ O-SiO ₂	–	1250	As, Sb	(Riveros et al., 1987)

6. State of the Art Research Tools and Future Challenges

Accurate measurement and meaningful data of elements distribution in phases rely on good experimental, characterisation and measurement techniques. Recent studies on the area emphasised on the use of equilibration and quenching technique to measure the distribution of valuable metals and understand their thermodynamic behaviour. During the equilibration, the multi-components in the system are let to equilibrate at certain conditions (e.g. p_{O_2} and temperature). It is important for the system to reach the true equilibrium. The checking of the true equilibrium condition can be done by carrying out experiments approaching equilibrium from different directions, for example from reducing and oxidising conditions.

Once the true equilibrium is achieved, a quenching of the sample is then carried out to preserve the conditions at high temperature and allow the analysis at room temperature. It is important to carry out the quenching carefully as not to shift the equilibrium. The sample is then characterised and the elements distributions are then measured using different analysis methods, including XRD (X-Ray Diffraction), ICP-AES (Inductively Coupled Plasma-Optical Emission Spectroscopy), EPMA as well as wet chemical analyses. EPMA measurement provides an accurate measurement of phases at microscopic level. EPMA analysis, however, is not able to accurately measure concentration below 1 wt%. It cannot also be used to quantify accurately composition of sample with multivalent cation simultaneously exist, e.g. differing Fe_2O_3 and FeO , unless other techniques (such as wet chemical analysis) is used in conjunction.

The challenges for future research include the understanding of the behaviour of volatile valuable metals, e.g. In, Ge and Sn. A novel experimental technique to limit the evaporation during equilibration is required. The choice of material for containing the sample is also a challenge as there may be a possibility of reaction between the sample and the material of the container. Some of the valuable metals have different state of valency; therefore oxidation state of metal in slag is another challenge to identify. Sometimes it is difficult to determine the slag composition using a single technique only, rather a multiple approach and techniques are required.

7. Concluding Remarks

This paper has highlighted the thermodynamics data of valuable trace elements in Cu and slag systems to understand their partitioning behaviour in different phases in relation to p_{O_2} , temperature and slag composition. Thermodynamics data of valuable elements in ferrous

calcium silicate (FCS), which is relevant to secondary Cu processing, is limited. Only data for Sn, In, Sb, Bi and As in selected operating conditions are available. Extending the thermodynamics knowledge in FCS slag to understand the behaviour of remaining valuable trace elements such as Au, Ag, Pd, Te, Pd, Rh, Ru, Ge, In, Ga, Co and Ta would provide a more comprehensive information that can be used to develop more economical and eco-efficient high temperature routes for the recovery of all valuable metals and for an improved control of hazardous emission during the e-waste processing through primary and secondary Cu production. There is still a lot of gap in the information and understanding, which requires further systematic research to develop, measure and generate a more comprehensive thermodynamics information.

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Highlights:

- The paper collates and systematically reviews the thermodynamic data of valuable metals relevant to e-waste processing through primary and secondary copper processing.
- Thermodynamics data of valuable elements in ferrous calcium silicate (FCS) slag, which is relevant to secondary copper processing, is limited. Only data for Sn, In, Sb, Bi and As in selected operating conditions are available.
- There is a need in extending the thermodynamics knowledge in FCS slag to valuable trace elements of Au, Ag, Pd, Te, Pd, Rh, Ru, Ge, In, Ga, Co and Ta.
- A more comprehensive thermodynamic information is vital to develop more economical and eco-efficient high temperature routes for the recovery of all valuable metals and for an improved control of hazardous emission during the e-waste processing through primary and secondary copper production.