

Thermodynamic Assessment of Tin-Smelting from Cassiterite Concentrates

Elmira Moosavi-Khoonsari^{1,2*} and Sina Mostaghel³

1. *Department of Mechanical Engineering, École de technologie supérieure, Montreal, QC, Canada*

2. *Department of Materials Science and Engineering, University of Toronto, Toronto, ON, Canada*

2. *SNC-Lavalin, Toronto, ON, Canada*

* Corresponding author: elmira.moosavi@etsmtl.ca

Abstract

Tin is a critical and rare metal produced via carbothermic reduction smelting of upgraded concentrates in two steps, primary and secondary reduction. There is limited literature available on cassiterite smelting and the thermodynamic behavior of Sn during primary and secondary reduction processes. The present work performs a systematic assessment/optimization of smelting parameters of a simplified cassiterite concentrate for the first time. This assessment was carried out with the aid of thermochemical analysis. The effect of process variables including reduction extent, temperature, and flux addition on the outputs of the primary and secondary reduction steps was studied. The effects of temperature and slag composition on slag liquidus temperature and viscosity were determined. The effect of recycling the process by-product, the hard head (HH), on operational parameters and outcomes, especially Sn recovery, was also investigated, and a series of optimum process conditions was proposed.

Keywords: Thermodynamic assessment, Tin-smelting, Critical metal, Process optimization, Cassiterite

1. Introduction

Tin, the Latin name Stanum (Sn), has been an important element since the Bronze Age (i.e., more than 5000 years ago). Tin is a soft metal with a low melting temperature of 232 °C. It is widely used in bronze (Sn-Cu alloy) production, Sn-Pb soft solders, and In-Sn optoelectronic applications. Tin-plating of steel and its application in food packaging and can production is a common practice [1]. It is estimated that the demand for Sn over the next 5-10 years will increase at a rate of 2% per year [2].

Although Sn is found in more than 50 different tin-bearing minerals [3], the major and commercially attractive minerals of Sn are limited. The average concentration of tin in the earth's crust is estimated to be 2-3 ppm [2], therefore, it is considered a rare and critical metal. Almost 75% of global Sn production comes from oxidic ores and 25% from sulfidic primary ores [4]. Cassiterite, a mineral assemblage mainly consisting of stannic oxide (SnO_2), is the most important source of Sn metal. The concentrates typically contain Fe, Nb, and Ta [1]. Cassiterite is chemically stable and does not readily react with acids or bases; hence, reduction smelting is considered the only practical Sn production method [4]. In addition, with the circular economy and multi-metal production strategies adopted by major metal producers, have resulted in the higher recovery of Sn from a number of secondary raw materials such as waste electric and electronic equipment (WEEE), tin-bearing tailings, and tin middlings, which currently account for ~30-50% of the total global tin production [3, 5].

Beneficiation of Sn ores is not straightforward since cassiterite is nonmagnetic, and is also not suitable for flotation. Only gravimetric sorting processes based on relative density separation can be used. Placer-type Sn deposits are less available. Instead, the low-grade/depleted ores that are

fed to smelting processes are vein-type intrusions and have intergrown minerals that do not allow for easy separation of tin-containing fractions. As a result, multistep pyro-/hydro-metallurgical enrichment is necessary before the smelting operation [1]. As an example of multistep operation, during roasting at high temperatures, the sulfides are oxidized, and the major impurities, such as As, are volatilized. During the leaching pre-treatment process, hydrochloric acid dissolves and removes impurities such as Fe, Cu, Pb, and As [1, 6-9]. The upgraded concentrate containing 60-75% Sn can then be sent for the reduction smelting processes in reverberatory, electric, or top-submerged lance furnaces. Reductants reduce the oxides, producing a crude Sn phase, and a Fe-Sn-rich slag. Due to the presence of high quantities of FeO and its high activity in the reaction system, the selective reduction of Sn faces a fundamental challenge. High yield or recovery of Sn from the smelting process (i.e., low Sn loss to slag) is associated with a high reduction of FeO, and high Fe concentration in the metal, which makes the downstream refining process more difficult [1]. Therefore, smelting is carried out in two stages, and an Sn-rich slag from the primary smelting, is fed to a secondary slag reduction process, as illustrated in Figure .

1.1. Primary Reduction

The primary reduction is typically carried out at relatively low temperatures of 1100-1200 °C [3, 10], but higher temperatures of up to 1350 °C were also reported [11], and the reduction extent is strictly controlled to achieve the minimum amount of required Fe in the hard head (HH), mainly FeSn₂, from the second step [11]. Iron oxide and SnO may act as the only fluxes of the system [11], although examples of using lime/limestone as flux were also reported [3]. Tin oxide has a

high saturated vapor pressure (2.07 kPa at 1100 °C), which results in the volatilization of tin, its deposition to the off-gas, and the generation of a fume dust during the smelting process.

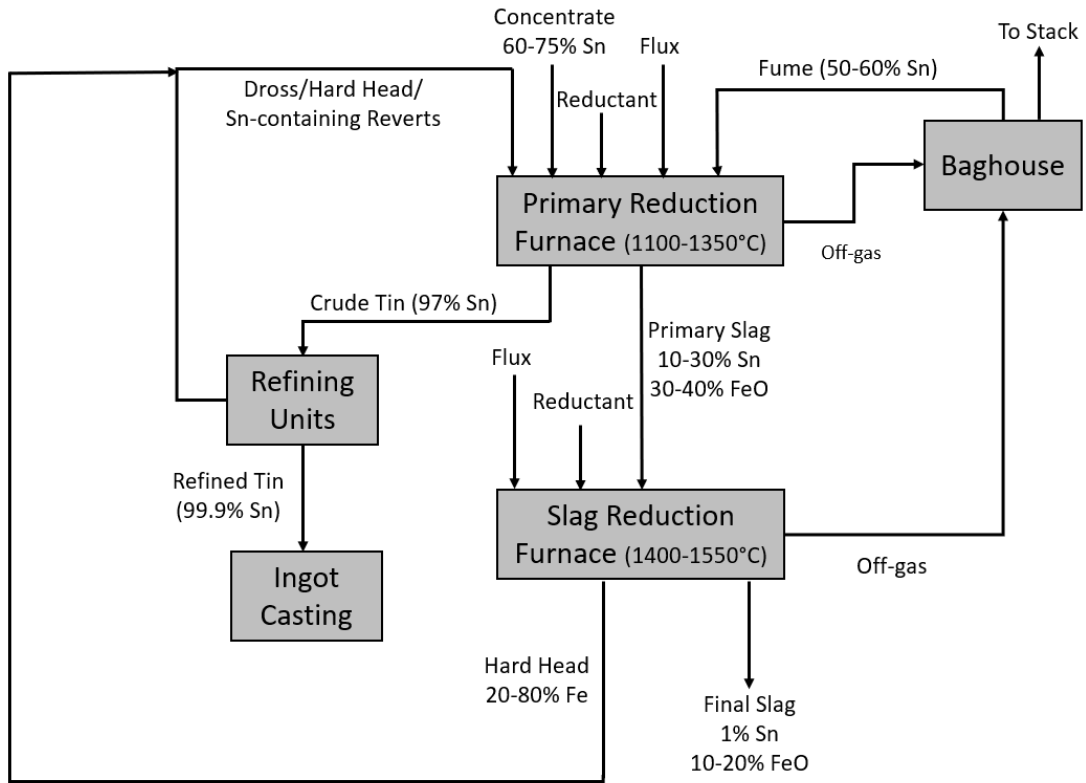


Figure 1: Simplified block flow diagram of the cassiterite smelting operation (adapted from [1, 10, 11]).

The collected dust from the baghouse of the primary smelting is returned to the furnace. After tapping, the crude tin from the primary smelting step is allowed to cool down in the ladle. Most of the dissolved Fe is precipitated as intermetallic phases, as shown in the Fe-Sn binary phase diagram, in Figure 2, and tends to float to the surface to be skimmed off as dross. This process can be repeated by heating the metal just above the melting temperature of Sn and cooling it again (known as the liquation and crystallization process). Typically, further refining in kettles is needed to obtain 99.9% Sn metal. Different techniques have been developed and used for the

refining processes [1], including chlorination and volatilization (e.g., for Pb removal), flux addition and dross/slag formation (e.g., for As removal via Al addition), oxygen injection and selective oxidation in a high basicity slag (e.g., for P removal), and electrorefining [5].

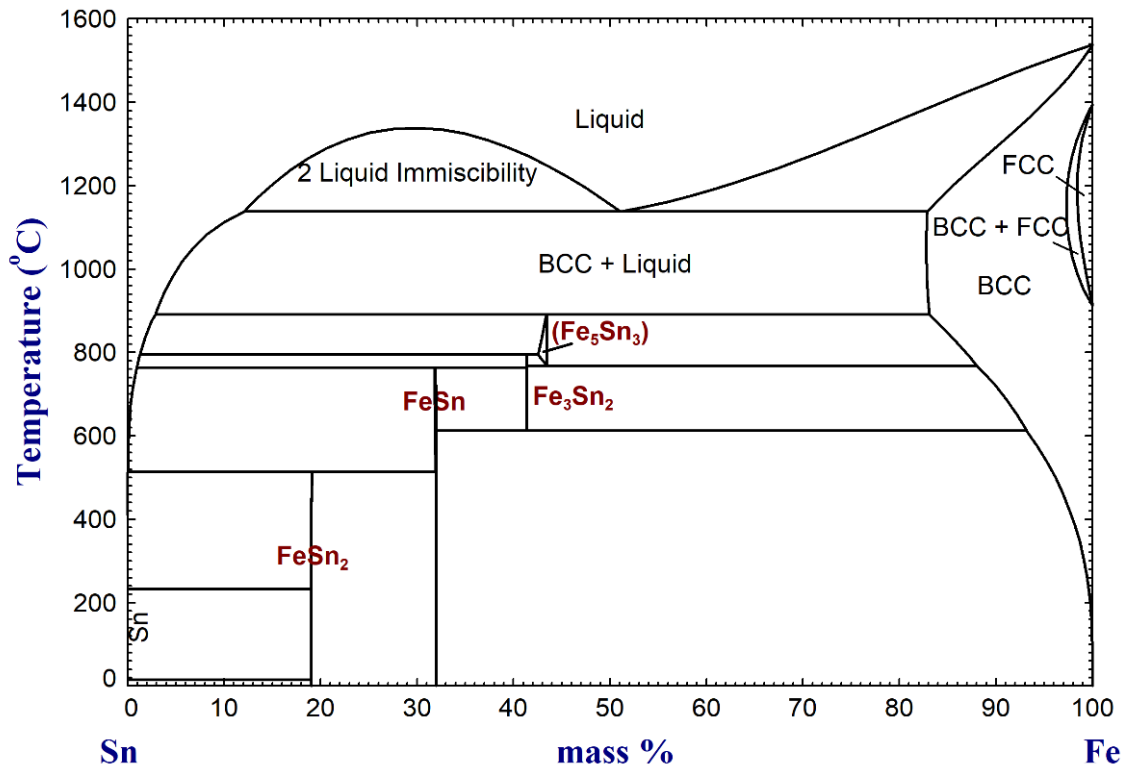


Figure 2: Fe-Sn binary phase diagram calculated using FactSage 8.2 FTlite [12]. (Fe_5Sn_3) is a solution phase. BCC and FCC stand for body-centered cubic and face-centered cubic solid solutions of Fe(Sn), respectively.

1.2. Secondary Reduction

Slag from the primary reduction process contains significant amounts of Sn (typically ~20%), and is fed to the secondary reduction step. Reducing agents (e.g., coal char) and fluxes (burnt lime/limestone or silica) are added to the system. Maximizing the reducing condition in the

second step allows maximum reduction of SnO; i.e., a minimum concentration of Sn is left in the slag from the secondary process. The discharged slag from the secondary step has sufficiently low Sn concentrations that can be discarded. However, in many cases, it contains relatively high Nb and Ta contents. The secondary slag is therefore recycled for Nb/Ta recovery via hydrometallurgical and/or pyrometallurgical processes [11, 13]. It has been reported that a significant portion of Sn loss to slag in the secondary reduction is from the mechanical entrainment of Sn metal in the slag. Therefore, the thermophysical properties of slag, most importantly its viscosity, play a critical role in Sn smelting [11].

Under a strong reducing condition in the secondary reduction, Fe is largely metalized, resulting in the formation of FeSn and FeSn₂ intermetallics known as Hard Head (HH) [14]. Different Fe contents were reported for HH [1, 10, 11]. HH is generally recycled to the primary reduction step. Other methods have also been proposed for Sn recovery from the HH. An example is the use of soda ash (Na₂CO₃) and S to generate a Fe-rich matte and a cleaned Sn metal with less than 0.8% Fe [15]. Other examples are the selective oxidation of Fe to recover a relatively pure Sn metal [16], or oxidation and fusion with sodium hydroxide [17].

1.3. Other Considerations

In general, there is limited literature data on cassiterite smelting and the thermodynamic behavior of Sn during primary and secondary reduction processes. Recently, few studies were carried out on the thermodynamic optimization of SnO_x-containing slags [18, 19]. Some investigations were also performed using hydrogen as the reductant [2] or using sodium carbonate and sodium nitrate

salts as fluxes [20]. However, no systematic assessment/optimization of the smelting operation has been performed so far.

1.4. Objectives

The main objective of the present work is to thermodynamically review cassiterite smelting processes, present some sensitivity analyses, and determine the role of major process parameters such as operating temperature, partial pressure of oxygen, and flux addition on the Sn recovery. A case study was developed for a simplified representative concentrate composition, 60 Sn, 6.5 FeO, ~6 SiO₂, ~1 Al₂O₃ and <1 CaO (in wt%). Only major components of the concentrate were taken into account and valuable metals such as Ta and Nb and other minor impurities (e.g., As, Sb, Cu) were ignored in calculations because of limitations in the chemistry of optimized available thermodynamic databases. Thermodynamic analysis of the system was performed using FactSage 8.2 thermochemical software [12]. Thermodynamic descriptions of the slag and metal phases were taken from the FToxid and FTlite databases, respectively. The thermodynamic behavior of the gas phase was explained using the FactPS database. The viscosity of the slag phase was calculated using the software's viscosity module.

2. Thermodynamic Assessment

In this work, the thermodynamic assessment is divided mainly into three steps of primary reduction, secondary slag reduction, and slag chemistry optimization. The effect of recycling the HH back to the primary smelting furnace is also discussed.

2.1. Primary Reduction

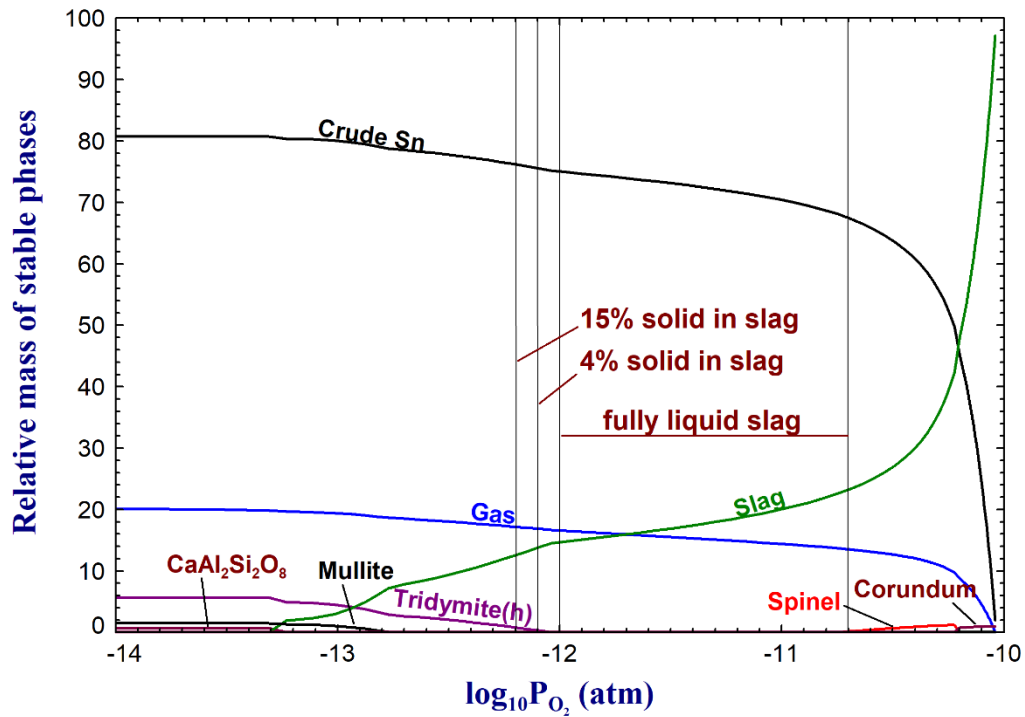
The primary reduction step was optimized in the following order. At first, the effect of reduction extent on smelting outcomes of a typical grade of concentrate, with 60% Sn, at 1200 °C was determined. In the second step, the effect of temperature on the thermodynamic behavior of the system was investigated considering the optimum relative extent of reduction calculated in the first step. In the third stage, the effect of flux addition (lime) on the overall Sn recovery and slag behavior was evaluated. All three steps are explained in detail in the sections 2.1.a to 2.1.c.

There are always inefficiencies associated with reductant addition to the furnaces (i.e., reductant utilization). Some routes for inefficiencies could be short-circuiting of reductant to the off-gas (dragged out by the induced draft fans) and the combustion of a highly gaseous reactive reductant. The level of inefficiencies depends on a number of operational/design parameters, e.g., reductant type, furnace configuration, ingress air, and off-gas handling design. Therefore, it is more reliable to consider the CO/CO₂ ratio in the freeboard off-gas which determines the partial pressure of oxygen (P_{O_2}) as a measure of reduction potential rather than the absolute quantity of the reductant added to the system or the mass ratio of reductant to concentrate.

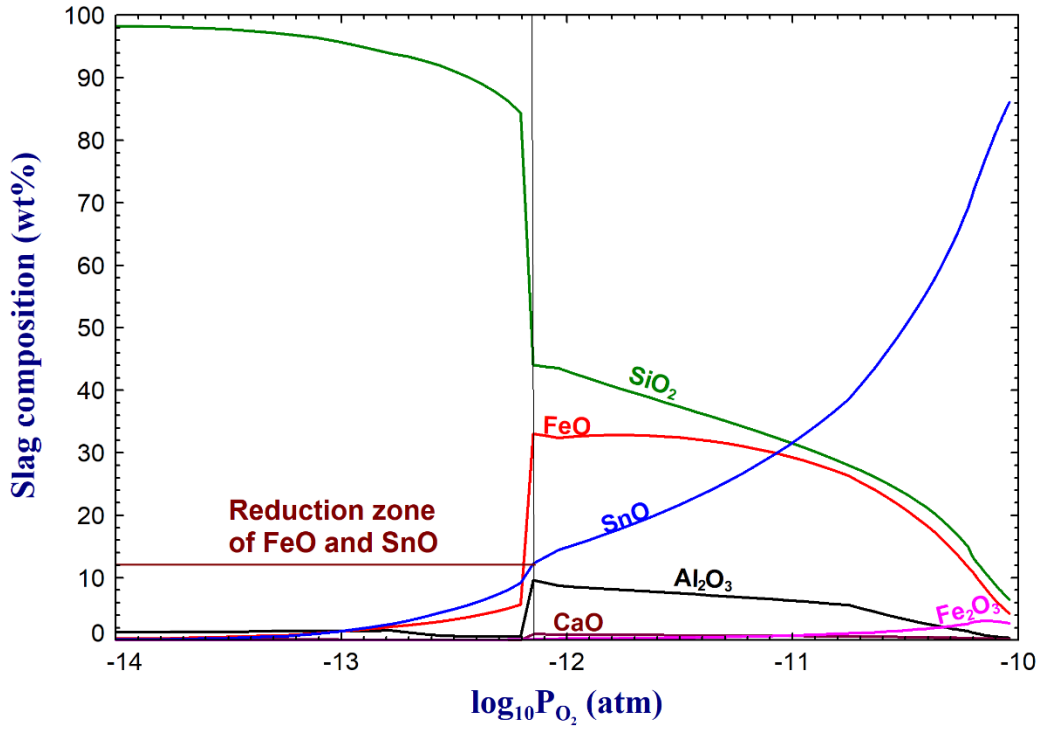
2.1.a. Effect of reduction potential

Figure 3a shows the effect of P_{O_2} on the stable phases forming at equilibrium from the primary smelting of concentrate at 1200 °C. It is clear that with the increase of reduction potential (lowering the P_{O_2}), there is an increase in metallization of oxides, i.e., the mass of crude metal

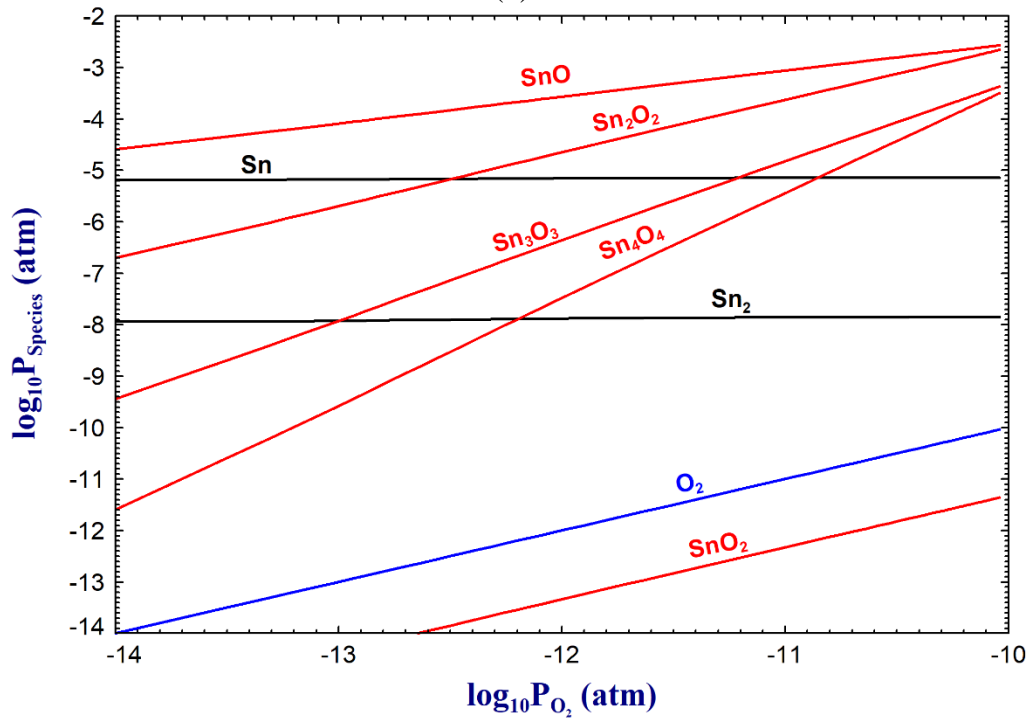
(Sn) steeply increases while the slag mass sharply decreases. At a low reduction potential equivalent to $\log P_{O_2} \sim -10$ atm, slag contains a small amount of corundum solid phase (mainly Al_2O_3 plus some small amounts of Fe_2O_3). With further increasing the reduction potential and for $\log P_{O_2}$ below -10.2 atm, spinel (mainly hercynite, $FeAl_2O_4$) crystallizes in the slag and is stable at $\log P_{O_2}$ above -10.7 atm. With the further addition of reduction potential to $\log P_{O_2}$ between -10.7 and -12.1 atm, the slag is stable in the form of single liquid phase while with further decreasing the $\log P_{O_2}$ to below -12.1 atm, over-reduction occurs and tridymite (SiO_2) starts crystallizing. That is, the liquidus temperature of the slag increases above 1200 °C due to its depletion in SnO and FeO at equilibrium. With slightly increasing the reduction potential and decreasing the $\log P_{O_2}$ from -12.1 to -12.2 atm, the solid/liquid ratio in slag significantly increases from 4% to 15%. That is, the slag liquidus temperature is very sensitive to the reductant amount and P_{O_2} in equilibrium with the system.



(a)



(b)



(c)

Figure 3. Tin smelting - primary reduction as a function of oxygen partial pressure at $T = 1200$ °C; (a) stable phases, (b) slag composition, and (c) gas phase composition.

Figure 3b illustrates the primary slag composition as a function of $\log P_{O_2}$ at 1200 °C. Between $\log P_{O_2}$ of -11.1 and -12.2 atm, the FeO content of slag is maximum and selective reduction of SnO occurs. At the upper range of reduction potential (i.e., $\log P_{O_2}$ of -12.2 atm), SnO in slag decreases to ~12%. Below $\log P_{O_2}$ of -12.1 atm, reduction of FeO and SnO occurs simultaneously which is unfavorable because of a large increase in the Fe content of crude Sn. In addition, significant amounts of solid phases start precipitating out, increasing the slag's apparent viscosity and consequently the metal entrainment. In the literature, a wide range of Sn (10-30%) and FeO (30-40%) in the slag was reported [1-3, 10, 11]. However, according to the present work, the optimum range of reduction potential without any flux addition will be equivalent to $\log P_{O_2}$ of -12.1 atm, resulting in ~11% Sn and ~33% FeO in slag. At this point, the addition of flux may be helpful to lower the slag liquidus temperature and viscosity which will be further discussed in Section 2.1.c.

As a result of the addition of optimum amount of reductant, equivalent to $\log P_{O_2}$ of -12.1 atm, at 1200 °C, the metal contains about 2% Fe and 98% Sn at equilibrium, which is in good agreement with reported concentrations in metal in the literature [1, 10]. This could indicate that Sn smelting furnaces operate quite close to equilibrium conditions and the thermodynamic calculations based on accurately optimized thermodynamic databases can be a cost-effective method to assess process fundamentals and propose potential improvements.

Figure 3c depicts the gas composition from the primary reduction step at 1200 °C as a function of oxygen potential $\log P_{O_2}$. Habashi [1] reported that 20% of the Sn reports to airborne dust. Su et al. [3] also reported the volatilization of Sn and its deportment to the dust during the smelting process. The main gaseous species containing Sn at the optimum $\log P_{O_2}$ of -12.1 atm are SnO

and Sn_2O_2 followed by Sn (the other main gaseous species are CO and CO_2 which are not shown in the figure). Tin reports to the gas phase through the active oxidation and formation of volatile oxide species, indicating that the Sn loss to the gas phase is quite sensitive to P_{O_2} of the system. With the aid of thermodynamic calculations, it is not possible to predict mechanically generated dust. According to the present calculations, with a proper selection of process parameters such as P_{O_2} and temperature, the volatilization of Sn can be minimized, and theoretically, close to 100% of Sn can be recovered in the condensed phases. On the other hand, if the process parameters are not well optimized, the overall Sn in the dust phase (from both mechanical and chemical causes) can reach higher than 20% of the total Sn input to the system. It is calculated that more than 98% of Sn at 1200 °C and $\log P_{\text{O}_2} = -12.1$ atm can be recovered in the metal phase, while less than 2% of Sn in feed reports to the primary slag phase.

2.1.b. Effect of Temperature

The effect of temperature on the thermodynamic behavior of the primary reduction was studied at the optimum reduction potential determined from the first step i.e., $\log P_{\text{O}_2} = -12.1$ atm. With increasing the temperature from 1200 to 1500 °C, there is an increase (~9%) in the slag mass and a decrease (<2%) in crude metal mass. In addition, with increasing temperature from 1200 to 1500 °C, the partial pressure of Sn in the gas phase increased by minimum 2 orders of magnitude, and Sn loss to the gas phase increased from <<1% to almost 1%. Moreover, with increasing temperature, SnO concentration of slag increased from 12 wt% to 15 wt% and consequently, the Sn loss in the primary slag increased from 2% to 3%. Overall, the Sn recovery in the crude metal decreased from above 98% to about 96% with increasing temperature from

1200 to 1500 °C. That is, increasing the temperature can lead to higher Sn vaporization and lower Sn yield from the primary smelting.

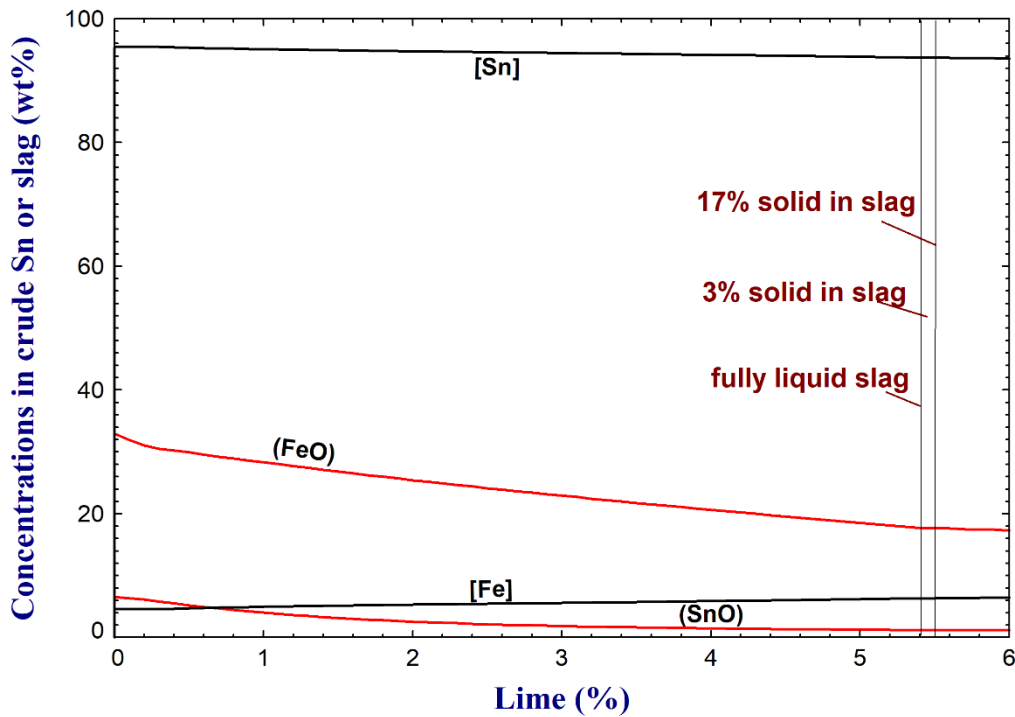
It can be concluded that the lowest end of the temperature range is preferred which has been also favored by others [3, 10]. Operating at the lower end of the temperature helps with fuel/electricity consumption and maximizes the refractory life. On the other hand, the lower temperature could have an indirect effect on metal mechanical (entrainment) loss in slag by increasing the slag viscosity, which could be partly resolved via fluxing the slag. The effect of lime addition and temperature as well as HH recycling on slag viscosity is discussed in Section 2.1.c and Section 4, respectively.

2.1.c. Effect of Flux Addition

Su et al., 2017 [3] reported that flux can be fed into the furnace together with the concentrate and reductant. In this step, the effect of flux addition, in the form of the commonly used burnt lime on the thermodynamic behavior of the primary reduction is studied for the optimized reduction atmosphere and temperature ($\log P_{O_2}$ of -12.1 atm and 1200 °C).

The maximum amount of lime added is around 5-5.5 mass% of the concentrate and reductant. At 5.4% lime addition, the slag is fully liquid. At 5.5% lime addition, a small amount of melilite (about 3% solid fraction) forms in slag. In this chemical system, melilite is a solid solution of several end-members such as $Ca_2FeSi_2O_7$ dissolving some Al in its crystal structure. With the addition of more than 5.5% lime, about 17% solids precipitate (i.e., the liquidus temperature of the slag steeply increases). Up to 5.5% lime, the amount of metal and gas phases slightly increased (by 2%) while slag mass showed comparatively a higher increase (by ~26%).

Figure 4a shows the changes in FeO and SnO concentrations of slag and Fe and Sn concentrations of crude metal as a function of lime addition. The addition of 5.5% lime, FeO concentration of slag largely decreased which is partly due to the dilution effect of lime addition and partly due to an increase in activity coefficient of FeO in the slag ($\gamma_{FeO} = a_{FeO}/x_{FeO}$; where a , x , and γ are activity, mole fraction, and activity coefficient of FeO in slag, respectively). The activity coefficients of FeO and SnO in slag are illustrated in Figure 4b. It is seen that FeO and SnO have close activity coefficients in slag in the absence of CaO. With the lime addition, the activity coefficients of both FeO and SnO increase in the slag with SnO showing a 5-fold increase, and FeO showing a 3-fold increase. That is, simultaneous reduction of SnO and FeO occurs out of the slag phase. Consequently, Fe reports to the metal phase which is consistent with an Fe content increase in the metal phase (from 2 wt% to 3 wt%) with addition of fluxing agent.



(a)

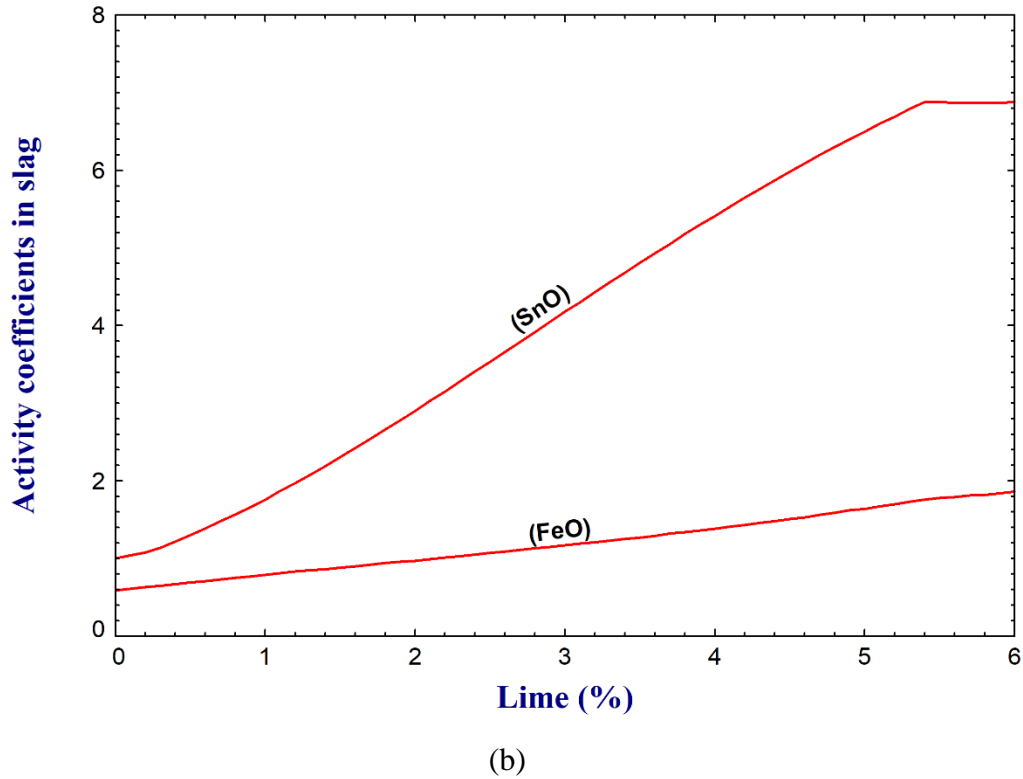


Figure 4. Effect of lime addition on (a) concentrations in crude Sn and slag, and (b) activity coefficients in slag.

Overall, the addition of 5.5% lime improves the Sn recovery in the metal phase, which increases from 98% to close to 99.5%. In addition, a decrease in slag SiO_2 content could lead to a lower slag viscosity and reduce the metal mechanical loss. On the contrary, the slag mass increases by 26% which can lead to increased entrainment loss. A higher mass of slag also requires a higher furnace capacity for secondary slag treatment and higher energy consumption in the second reduction stage. The overall effect of lime addition on metal recovery should be determined on a case-by-case basis and considers all these net effects on Sn recovery. Fluxing the primary slag with lime might not be necessary because the HH recycled from the secondary stage to the primary reduction plays the role of a fluxing agent, which will be discussed in Section 4.

According to the thermodynamic assessment so far, a reducing potential equivalent to $\log P_{O_2} = -12.1$ atm and 1200 °C is recommended for the optimal recovery of Sn in the primary reduction step. No lime addition is necessary during the primary reduction because HH that is recycled from secondary to primary step plays the role of a flux, which will be discussed in Section 4. For that reason, the primary slag produced under this set of operational conditions was taken for thermodynamic assessment of the secondary reduction step.

2. Secondary Reduction

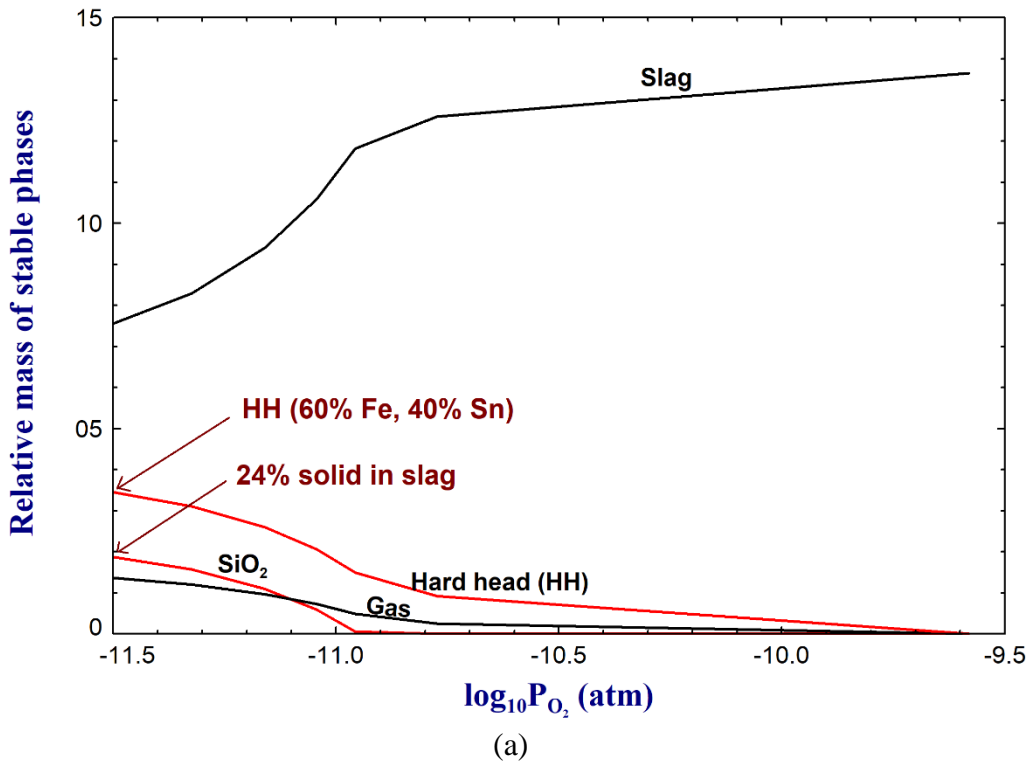
The bulk slag composition from primary smelting mainly contains 44 SiO₂-33 FeO-10 Al₂O₃-12 SnO (11 Sn) in wt%. The effect of reduction potential, temperature and flux addition on Sn recovery from the primary slag was investigated in three steps, which will be discussed in Section 2.1.a to Section 2.1.c.

2.1.a. Effect of Reductant Addition

Figure 5 shows the stable phases precipitating out from the reduction of primary slag and the resulting secondary slag composition, calculated as a function of $\log P_{O_2}$ at 1400 °C. In Figure 5a, the HH phase starts precipitating out from the primary slag first, and at $\log P_{O_2} < -10.9$ atm, SiO₂ also precipitates as a solid in the slag.

In Figure 5b, up to $\log P_{O_2}$ equal to -10.9 atm, the FeO is relatively stable in slag but for a lower oxygen potential of $\log P_{O_2}$ below -10.9 atm, the simultaneous reduction of FeO and SnO occurs.

The reduction extent was optimized to $\log P_{O_2}$ equal to -11.5 atm so minimizing the slag SnO content to less than 1%. With further increasing the reduction potential, a lower Sn concentration of slag could be obtained but at the same time, the resulting Fe content of HH sharply increases above 60%. In the literature [1, 10, 11, 14], a wide range of Fe content (i.e., 20-80 wt%) has been reported for the HH. According to the current calculations, the reduction potential in the secondary stage should be controlled to not only minimize Sn loss in the slag (i.e., (SnO) < 1%) but also maintain a high ratio of FeO/SnO in the secondary slag to avoid the increase of Fe in the primary furnace via HH recycling, Fe should exit the system mostly via the secondary slag.



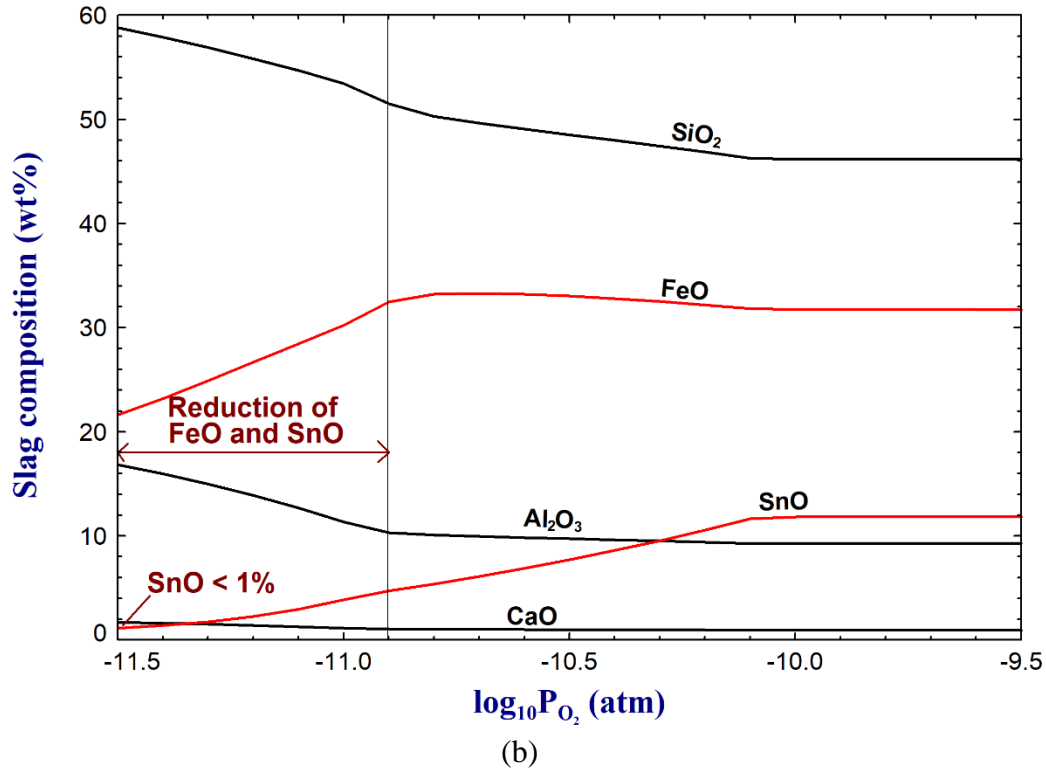


Figure 5. Tin smelting - secondary reduction as a function of oxygen partial pressure; (a) stable phases, (b) and slag composition (at 1400 °C).

Without any flux addition at 1400 °C and $\log P_{O_2}$ equal to -11.5 atm, the amount of Sn chemical loss to the slag reaches about 6%. Under these conditions, slag contains ~24% solid phase (SiO_2 crystals), as shown in Figure 5a, which increases the slag viscosity in the secondary step and Sn entrainment loss, makes the operation difficult to operate, and fluxing becomes essential. The effects of flux addition on lowering the slag liquidus temperature and viscosity are discussed in Section 2.1.c and Section 3.

2.1.b. Effect of Temperature

The effect of temperature on the thermodynamic behavior of system was studied for $\log P_{O_2}$ equal to -11.5 atm, which was an optimum value at 1400 °C obtained from the primary step.

Increasing the temperature from 1400 to 1600 °C, the Sn loss to the gas phase increased from almost 0 % at 1400 °C to ~1% at 1600 °C while the Sn recovery to metal decreased from 94% to 93%.

With increasing the temperature to above 1510 °C, the slag is in a fully liquid state. This leads to a decrease in the overall viscosity and a decrease in Sn entrainment. However, with the flux addition, the liquidus temperature of the slag is lowered to produce a fully molten slag at lower operating temperatures, which will be discussed in Section 2.1.c. It is generally preferable to operate at a lower range of temperature provided that low-viscosity slag can be maintained. This helps with minimizing Sn chemical loss to fume while reducing energy consumption and prolonging the life of the furnace refractory lining.

2.1.c. Effect of Flux Addition

With the addition of ~5% lime with respect to primary slag mass at 1400 °C for $\log P_{O_2}$ equal to -11.5 atm, the slag becomes fully liquid. With further addition of lime to above ~11%, the Sn recovery to metal phase increases from 94% to above 96%, while the HH composition does not significantly change, containing about 60% Fe and 40% Sn. The resultant slag consists of 59 SiO₂-16 FeO-12 CaO-12 Al₂O₃ and <1 SnO in wt%.

Although ~11% of lime with respect to the slag's initial mass leads to a fully liquid slag, a high SiO₂-containing liquid slag is also known to be viscous. Section 3 discusses the effect of lime addition and CaO/SiO₂ ratio on the slag liquidus temperature and viscosity, and whether further adjustment to the secondary step slag composition is necessary.

3) Sensitivity Analysis of Secondary Slag Composition

Figure 6 shows the sensitivity of slag liquidus temperature to changes in CaO and Al₂O₃ concentrations. The FeO and SnO concentrations were kept constant for all cases, at 20% and 1%, respectively, and the calculations were carried out at $\log P_{O_2}$ equal to -12 atm. The respective primary crystallization phase fields are also marked for each composition region. Depending on Al₂O₃ concentration, which is expected to typically lie between 10 and 15 wt% [10], up to ~15%, and 10% total CaO, respectively, in the system reduces the liquidus temperature. Above these limits, CaO increases the liquidus temperature to some extent, especially for high concentrations of Al₂O₃ in slag, above 10 wt%.

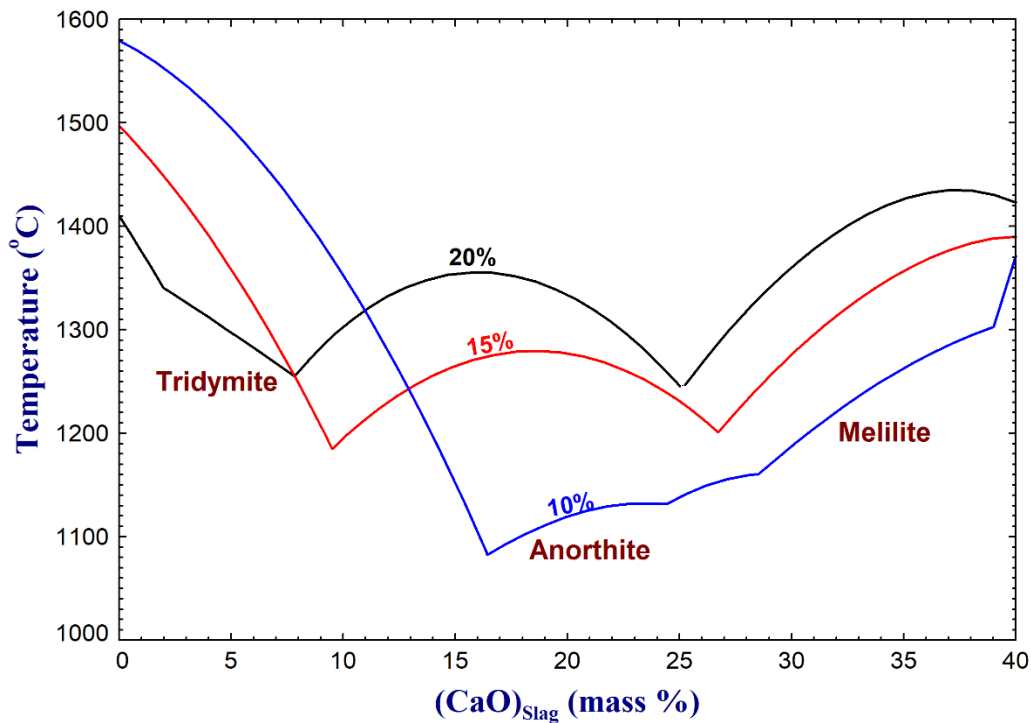


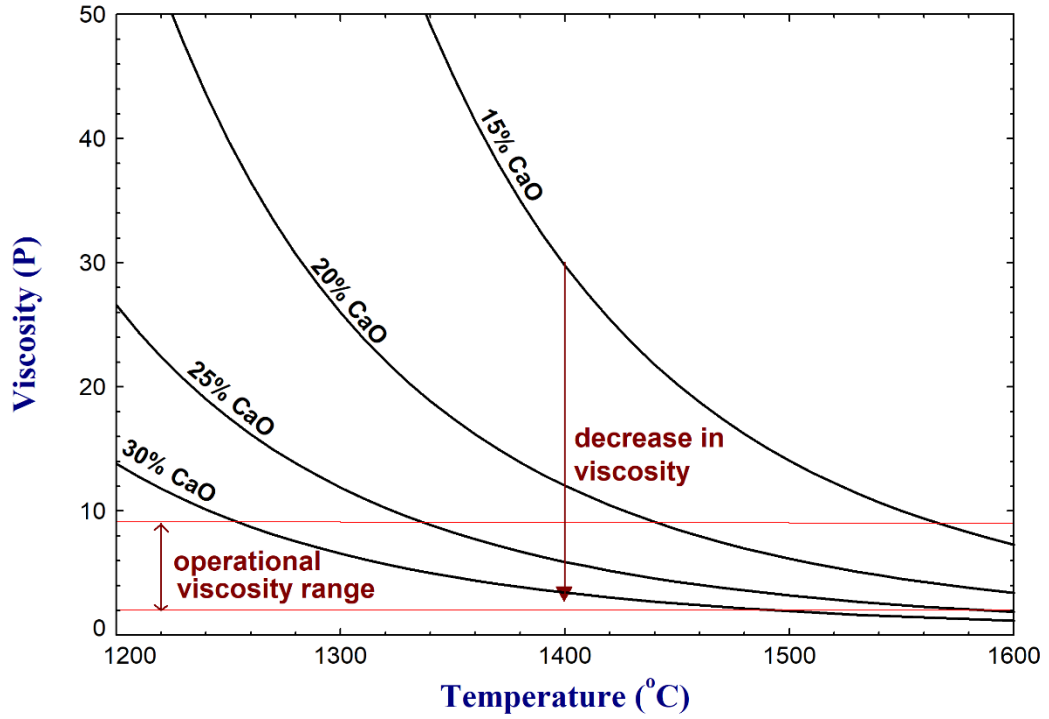
Figure 6. Liquidus temperature of slag as a function of CaO and Al₂O₃ concentrations (for 20% FeO and 1% SnO).

Maintaining the operating temperature at 1400°C, requires (CaO) content of at least 10 wt% to generate a fully liquid slag for a composition with ~10% (Al₂O₃), as in the case of calculated

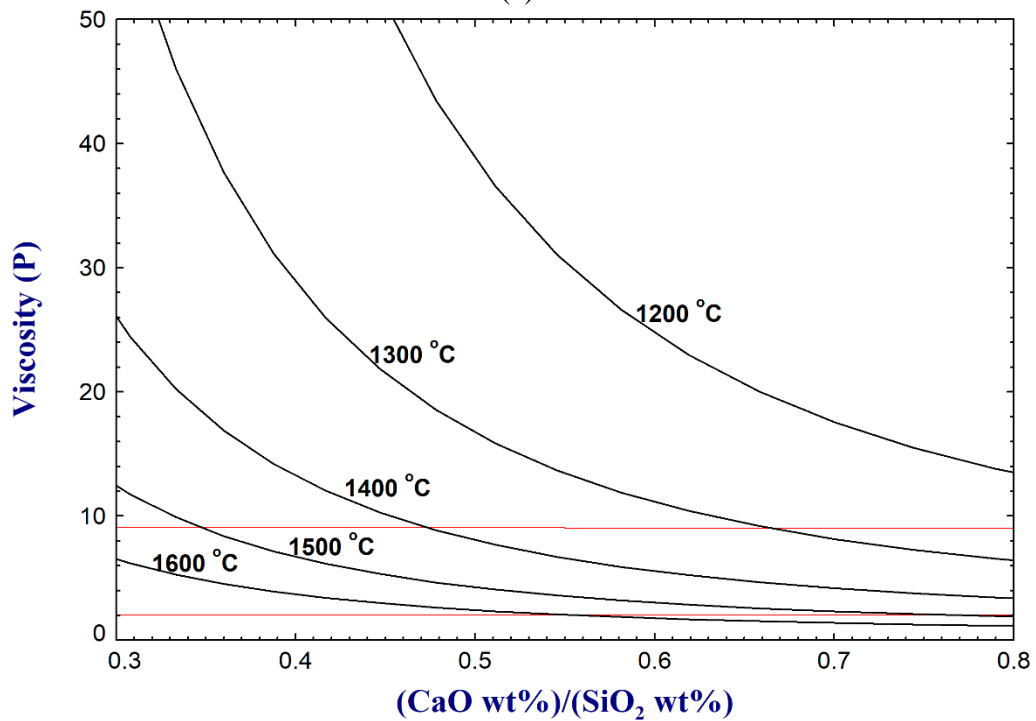
secondary slag. Figure 6 shows that depending on slag composition and concentration of different components, a trade-off exists between raising the operating temperature to e.g., 1450 °C or 1500 °C and increasing the CaO concentration. An optimization needs to be carried out for any operation.

Another significant factor to be considered while determining the operating parameters is the resulting slag viscosity. As mentioned earlier, slag viscosity and mechanical entrainment of Sn in the slag is a major consideration for cassiterite smelting, and slag viscosities between 2 and 9 Poise (P) were reported. Several empirical models were reviewed for slag viscosity effect and none of them have any parameters for the effect of SnO in the slags. Sn and Fe charges and their cationic radii (0.83Å and 0.81Å, respectively) are very similar, and FeO and SnO show similar behaviors in silicate melts [4]. Hence for viscosity calculation, all SnO in the slag was replaced by FeO on a molar basis. The calculations were carried out using the viscosity module of FactSage, assuming fully liquid slag. Slag containing any solid particles, shows higher viscosities than the calculated values for a fully liquid slag.

As shown in Figure 7, to obtain operable viscosities (less than ~9 P), it is necessary to adjust both the CaO concentration, and the operating temperature. Decreasing the temperature from 1600 to 1300 °C, the required CaO content of slag increases from about 15% to 27%. Although low-viscosity slag is essential to minimize Sn mechanical loss to the slag, excessively superheated slag also needs to be avoided. In addition to important Sn loss to the fume, the high silicate slags can be very aggressive toward furnace refractory lining, especially if operated at temperatures significantly above their liquidus. That is, excessive superheating of slag can cause severe damage to the furnace lining due to two mechanisms of penetration into bricks and dissolution of bricks having basic compositional properties.



(a)



(b)

Figure 7. Viscosity of slag as a function of (a) temperature for different CaO concentrations, and (b) CaO/SiO₂ mass ratio for a range of temperature. The slag contains 11% Al₂O₃, 20% FeO, and 1% SnO.

Figure 8 illustrates that Al_2O_3 increases the slag viscosity. As shown in Figure 6, for (CaO) concentrations of slag >15%, alumina addition increases the slag liquidus temperatures. Hence, Al_2O_3 concentration in the feed material should be limited if blending and upstream processes allow.

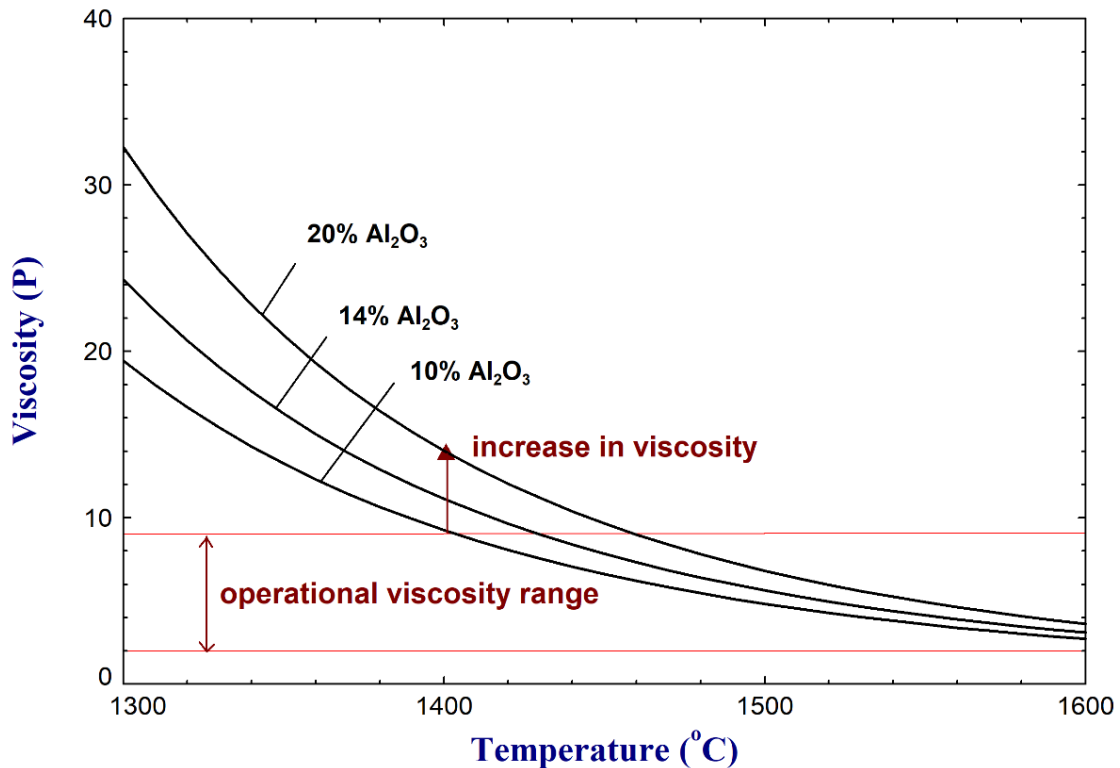


Figure 8. Slag viscosity as a function of temperature and Al_2O_3 concentration at the basicity $\text{CaO}(\text{wt}\%)/\text{SiO}_2(\text{wt}\%)$ of 0.57 and $\text{FeO}+\text{SnO}$ equal to 16%.

Considering liquidus temperatures and viscosities and the need to obtain a controllable superheat, the most suitable operating condition for the targeted secondary slag is the operation with ~25% CaO at 1400°C. These conditions result in a slag superheat of ~200°C, and viscosity of ~7 P. It should be noted that with the addition of lime, the slag liquidus temperature decreases relative to the slag Al_2O_3 content, the slag mass increases. This, in turn, will increase

Sn entrainment. Additionally, this increase in slag mass is not environmentally friendly because the secondary slag is sent to slag dump.

4. Effect of Recycling Hard Head on Sn Smelting Steps

The HH produced from the secondary reduction is recycled back to the primary smelting, where it is treated together with the fresh concentrate and reductant to produce primary slag and crude Sn.

Recycling HH back to the primary step provides additional metallic iron to the system, which can act as a reductant and fluxing agent upon converting to FeO in slag. The increase in (FeO) content of the slag decreases its liquidus temperature and solid fraction from 4% to 0% in the primary reduction step, leading to lower viscosity and lower entrainment loss. With recycling HH, the viscosity of the resulting slag was calculated to considerably decrease to ~10 P (at 1200 °C and $\log P_{O_2}$ equal to -12.2 atm) while the Sn recovery in metal stayed almost unchanged at ~98%. To maintain the slag viscosity within the reported operational range (i.e., < 9 P), it is required to increase the temperature to 1300 °C and simultaneously adjust the reduction potential ($\log P_{O_2}$ to -11.1 atm) to obtain the FeO and SnO of slag at ~48 wt%. To lower viscosity and entrainment loss and have an easier operation during tapping (e.g., no clogging and accretion build-up), higher temperature is desirable. However, this comes at the expense of higher chemical loss as well as faster refractory deterioration, and high energy consumption, and should be optimized case by case. That is, there is a trade-off between the Sn chemical loss and mechanical loss in slag, both of which affect the overall Sn recovery, making the cassiterite smelting rather a complex process. This further indicates that lime addition during the primary

step might not be necessary since recirculated HH behaves as the slag liquifying agent. As also mentioned in Section 2.1.c, to minimize the slag mass from the primary smelting, and consequently minimize the energy consumption and maximize the furnace capacity in secondary reduction, it is important to keep the lime consumption to a minimum.

The effect of HH recycling further on secondary smelting was also evaluated in this work.

Considering both chemical and mechanical loss of Sn in slag, an optimum set of operational variables of $\log P_{O_2} = -11.3$ atm, 1400 °C, and 24% lime addition with respect to primary slag mass, are suggested for the secondary step. As a result, Sn recovery of ~97% and HH composition with 65% Fe could be obtained. At 1400 °C, the secondary slag contains about 28% CaO (with a CaO/SiO₂ mass ratio of ~0.59) reducing the slag viscosity to ~8 P. That is, it would be desirable to flux the secondary slag well to minimize Sn losses.

Based on the present step-by-step thermodynamic assessment, an example of the optimized process variables for primary and secondary steps of cassiterite concentrate smelting (60 Sn-6.5 FeO~6 SiO₂~1 Al₂O₃ and <1 CaO in wt%) is provided in Table 1. It should be noted that the effect of HH recycling on the process inputs (i.e, reduction extent, temperature, and flux addition) and outputs (i.e., crude metal/HH composition, bulk slag composition, and Sn recovery rate) has been also considered. According to this investigation, there is an optimum compositional range for the HH (i.e., 60-70% Fe) to maximize the Sn recovery rate, and simultaneously prevent excessive Fe accumulation in the system. Lower Fe content of HH could be obtained but at the expense of higher Sn loss to the slag. Figure 9 depicts the direct correlation between the Sn recovery and Fe recovery in the crude Sn and HH. It is clear that with increasing the Sn recovery in the metallic phases, either crude Sn or HH, the Fe recovery in metal also increases. It could be said that the Sn recovery rate in the second step is more sensitive to the Fe

recovery than the first step. Equations (1) and (2) show the Sn recovery as a function of Fe recovery in crude Sn and HH, respectively, fitted to the present calculations under the operational parameters, provided in Table 1:

$$R_{Sn} = 109.6 - 0.04579R_{Fe} - \frac{53.74}{R_{Fe}^{-0.5}} - \frac{6.984}{R_{Fe}} + \frac{3.877}{R_{Fe}^2} - \frac{0.274}{R_{Fe}^3} \quad (1)$$

$$R_{Sn} = -102.8R_{Fe}^{-0.1239} + 158 \quad (2)$$

where R_{Sn} and R_{Fe} are the recovery of Sn and Fe in the metal phase, respectively.

Table 1. Optimized process conditions for primary and secondary reduction steps according to thermodynamic assessment for concentrate with 60% Sn (including HH recirculation)

	T (°C)	$\log P_{O_2}$ (atm)	Lime*	Distribution			Crude Sn or HH (wt%)	
				[Sn] _{metal}	(Sn) _{slag}	Sn _{gas}	Sn	Fe
Primary	1300	-11.1	-	98%	2%	~0%	96	4
Secondary	1400	-11.3	24%	97%	3%	~0%	35	65

* with respect to primary slag mass

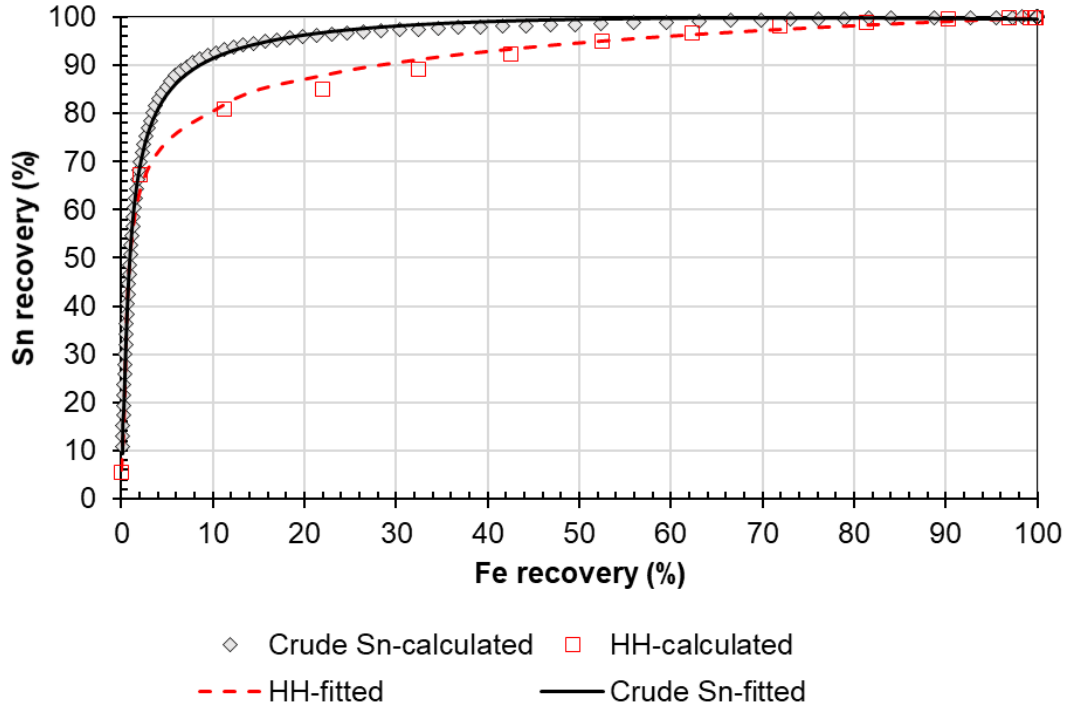


Figure 9. Calculated Sn recovery versus calculated Fe recovery in the metallic phases (from the optimized parameters in Table 1).

Table 2 lists the equilibrium bulk slag compositions, and their physicochemical properties produced from primary and secondary smelting, including the HH recirculation. In theory, the yield of Sn is very sensitive to variations in P_{O_2} and temperature hence, these parameters need to be carefully examined and adjusted in practice.

Table 2. Equilibrium bulk slag physical and chemical properties calculated from the optimized primary and secondary reduction of Sn smelting

	Slag composition (wt%)								Liquidus temperature (°C)	Viscosity (P)
	Al ₂ O ₃	SiO ₂	CaO	FeO	Fe ₂ O ₃	SnO	CaO/SiO ₂	Fe _{Total} /SiO ₂		
Primary slag	9	42	<1	37	<1	11	~0	0.66	1166	~7 @ 1300 °C
Secondary slag	9	47	28	16	<<1	0.4	0.59	0.25	1217	~8 @ 1400 °C

Conclusions

In this work, the Sn smelting process (both primary and secondary reduction steps) was thermodynamically assessed for a cassiterite concentrate with the composition (60 Sn-6.5 FeO ~6 SiO₂~1 Al₂O₃ and <1 CaO in wt%). A comparison of the calculation equilibrium results and operational outcomes from the literature implied that Sn smelting furnaces could operate quite close to equilibrium conditions. Therefore, thermodynamic calculations based on accurately optimized thermodynamic databases can be a cost-effective method to assess process fundamentals and propose potential improvements.

Optimum calculated conditions for primary reduction to maximize the Sn recovery rate included the temperature of 1300 °C and reduction potential $\log P_{O_2}$ equal to -11.1 atm (which can be converted to the required amount of reductant). It was demonstrated that no lime is necessary as flux because hard head, recycled from the secondary step, plays the role of a fluxing agent in the primary step.

Optimum conditions calculated for the secondary reduction included 1400 °C, $\log P_{O_2}$ equal to -11.3 atm, and 24% lime (with respect to the primary slag mass) as a fluxing agent. It was shown that this amount of lime is required to decrease the slag viscosity below an operational level, i.e., 9 P, and minimize the Sn entrainment loss.

There is a trade-off between the chemical loss and entrainment loss of Sn in slag. The chemical loss can be minimized via maintaining the lower operational temperature range and proper adjustment of reduction potential to maintain low SnO in slag and simultaneously avoid FeO over reduction. The entrainment loss can be minimized by upholding low slag viscosity which can be obtained by controlling the reduction potential (affecting the slag composition), and/or

increasing the operational temperature. Particularly, the primary slag viscosity seems to be very sensitive to P_{O_2} control and the SnO+FeO content of slag, where no lime is added, and the (FeO+SnO)/SiO₂ ratio controls the slag viscosity.

Currently, there is no optimization concerning the Ta and Nb solubility in the oxide phase in FactSage FToxid database. It would be useful to model the thermodynamic behavior of Ta and Nb in the slag to predict their distribution between two phases of metal and slag in the future.

References

- [1] F. Habashi, "Handbook of extractive metallurgy," WILEY, 1997. pp.688-702.
- [2] W. K. M. Kalenga, "Review of key parameters during carbothermic reduction of tin from cassiterite," *Metal*, 2021, 26-28.
- [3] Z. Su, Y. Zhang, B. Liu, M. Lu, G. Li, and T. Jiang, "Extraction and separation of tin from tin-bearing secondary resources: A review," *JOM*, 69, 2017, 2364–2372.
- [4] S. R. Chandrashehar, "The recovery of tin from slags by gaseous reduction and fuming," University of London, 1977.
- [5] F.A. López, I. García-Díaz, O. Rodríguez Largo, F.G. Polonio, T. Llorens, "Recovery and purification of tin from tailings from the Penouta Sn-Ta-Nb deposit," *Minerals*, 8(1), 2018, 20.
- [6] P. A. Wright, "Extractive Metallurgy of Tin." 2nd ed. New York: Elsevier Scientific Publishing Company Press, 1982.
- [7] W. S. Huang, "Stannum." Beijing, China: Metallurgical Industry Press, 2000.
- [8] H. Louis, "Metallurgy of Tin." New York: McGraw-Hill Book Company, 1911.
- [9] Z. Wen, "Method for removing arsenic and sulfur from tin concentrate." Chinese Patent, CN103725900A, 2013.
- [10] T. Wakamatsu, "Recent aspects of cassiterite processing and tin smelting in malaysia and indonesia".

- [11] H. A. Uys, "The metallurgy of tin smelting arc furnace," Journal of South African Institute of Mining and Metallurgy, 1977, 121-125.
- [12] C.W. Bale, E. Bélisle, P.Chartrand, S.A.Decterov, G. Eriksson, A.E. Gheribi, K.Hack, I.H. Jung, Y.B. Kang, J. Melançon, et al. "FactSage thermochemical software and databases, 2010–2016." Calphad, 54, 2016, 35–53.
- [13] F. D. N. Kanari, "Development of a process for the concentration of the strategic tantalum and niobium oxides from tin slags," Minerals Engineering, 134, 2019, 97-103.
- [14] S. H. D. Miller, "Rooiberg revisited – the analysis of tin and copper smelting debris," Historical Metallurgy, 42 (1), 2008, 23-38.
- [15] C. B. Porter, "Method of treating tin hardhead to recover tin". USA Patent 2,364,815, 1944.
- [16] P. S. D.A. Wilson, "Recovering tin from hard head by selective oxidation of iron," University of Michigan, 1961.
- [17] C. J. A. Bunnakkha, "Extraction of tin from hardhead by oxidation and fusion with sodium hydroxide," Journal of Metals, Materials, and Minerals, 22(1), 2012, 1-6.
- [18] T. Yin, J. Lee, E. Moosavi-Khoonsari, I.-H. Jung, "Critical evaluation and the thermodynamic optimization of the Sn-O system," Ceramics International, 47, 2021, 29267-29276.
- [19] J. Lee, T. Yin, P. Hudon, I.-H. Jung, "Phase diagram study of the SnO₂-SiO₂ system and thermodynamic optimization of the SnO-SnO₂-SiO₂ system," Ceramics International, 48(3), 2022, 4141-4152.

[20] A. B. El Deeb, I. M. Morsi, A. A. Atlam, A. A. Omar, W. M. Fathy, "Pyrometallurgical extraction of tin metal from the egyptian cassiterite concentrate," International Journal of Scientific and Engineering Research, 6(3), 2015, 54-60.

Disclosure statement

The authors report there are no competing interests to declare.