

Article

Thermodynamic Considerations for a Pyrometallurgical Extraction of Indium and Silver from a Jarosite Residue

Stefan Steinlechner *  and Jürgen Antrekowitsch

Chair of Nonferrous Metallurgy, Montanuniversitaet Leoben, Leoben 8700, Austria;
juergen.antrekowitsch@unileoben.ac.at

* Correspondence: stefan.steinlechner@unileoben.ac.at; Tel.: +43-3842-402-5254

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Abstract: Indium and silver are technologically important, critical metals, and in the majority of cases, they are extracted as a by-product of another carrier metal. The importance of indium has seen recent growth, and for technological reasons, these metals can be found in industrial residues from primary zinc production, such as the iron precipitate—jarosite. To secure the supply of such metals in Europe, and with the idea of a circular economy and the sustainable use of raw materials, the recycling of such industrial residues is coming into focus. Due to the low value of jarosite, the focus must lie simultaneously on the recovery of valuable metals and the production of high-quality products in order to pursue an economical process. The objective of this article is to give the fundamentals for the development of a successful process to extract the minor elements from roasted jarosite. As such, we use thermodynamic calculations to show the behavior of indium and silver, leading to a recommendation for the required conditions for a successful extraction process. In summary, the formation of chlorine compounds shows high potential to meet the challenge of simultaneously recovering these metals together with zinc at the lowest possible energy input.

Keywords: indium; silver; jarosite; recycling; industrial residue; process development; selective extraction; simultaneous recovery; pyrometallurgy

1. Introduction

Recycling rates have increased in recent decades, but this is mainly due to the reutilization of end-of-life products and their better collection logistics. For economic reasons, a decrease in the level of easily minable primary resources, and stricter environmental legislation regulating, for instance, land filling, different industrial residues have also become a focal point of the recycling industry. As the valuable metal content when compared to various end-of-life products or primary ore concentrates is in most cases drastically lower, the requirements of newly-developed recycling processes are more demanding. This results in a strategy to develop concepts capable of the simultaneous extraction of metals and generation of products with an “added value”.

The zinc industry is one of the base metal industries carrying a broad variety of accompanying side elements and is the focus of this research—in particular, its iron precipitate residue. As an example, zinc ore concentrate includes several metals, such as indium, defined as a critical metal by the European Commission [1]. Today, the hydrometallurgical zinc extraction from oxidic or sulfidic zinc concentrates dominates, with a ratio of more than 90% of primary zinc production. Even though several new technologies have been implemented in the last few decades (e.g., direct leaching of sulfidic ore and solvent extraction for solution purification), the typical flow sheet of a hydrometallurgical zinc plant still features the concentration, roasting, neutral- and hot-acid leaching of the zinc ore followed by electrowinning, as shown in Figure 1.

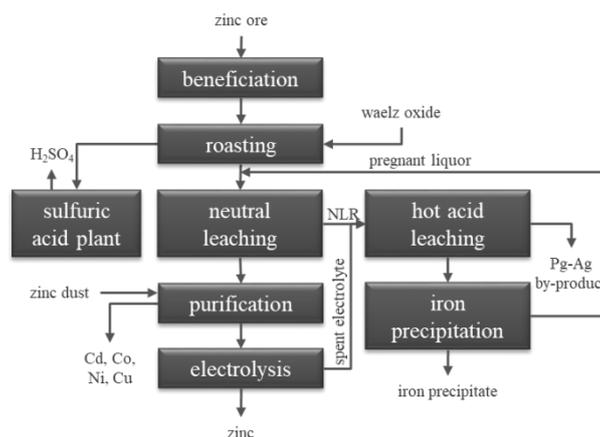


Figure 1. Flow sheet of zinc production by roasting, neutral- and hot-acid leaching, and electrowinning [2, 3]. NLR: neutral leaching residue.

To begin with, the zinc ore concentrate is oxidized in a roasting step, prior to the leaching of the calcine. During the roasting step, the contained iron reacts with zinc, forming a barely-soluble zinc ferrite spinel, rendering the hot-acid leaching step mandatory. To avoid a high volume of processed solution for the following iron precipitation step, the hot-acid leaching is only carried out for the solid neutral leaching residue (NLR). In the case of iron ores with low iron content, the hot-acid leaching step can be avoided. Over time, various iron removal technologies have evolved. An overview of the three common iron residues (hematite, goethite and jarosite), including the metal contents of iron and zinc, as well as their typical moisture contents, is shown in Table 1.

Table 1. Iron precipitation residues and their characteristics [4,5].

Residue	Content		Quantity Dry (kg/t Zn)	Moisture			Quantity Moist (kg/t Zn)
				Adherent	Chem. Bound	Total	
	Fe (wt. %)	Zn (wt. %)	(kg H ₂ O/t Zn)	(wt. %)	(kg/t Zn)		
Hematite	57–60	1	245	27	0	10	272
Goethite	34–40	8.5–13	370	250	24	43	637
Jarosite	29	2–6	520	350	47	44	907

Furthermore, the typical contents of iron and zinc, and the relative amount of generated residue per ton of produced zinc are given. Since the material is dumped as sludge, the content of H₂O, either chemically bound or adherent to the sludge, is also shown. Although the jarosite precipitate has the lowest iron content and, with this, the highest level of moisture, it is the most commonly used source of iron removal among those listed, and offers the highest possibility of also finding silver and indium in the residue.

Equation (1) is the mineralogical structural formula of jarosite. It shows that it is a basic iron sulfate compound, where R is a placeholder for potential cations like H₃O⁺, Na⁺, K⁺, NH₄⁺, Ag⁺, Li⁺, Ti⁺, Rb⁺, and R₂ for Hg²⁺, Pb²⁺ [2,6]. On an industrial scale, jarosite precipitation is based on the addition of ammonium or sodium for economical and ecological reasons [2,3,7,8].



Moreover, Zn, Cd, Ag, Cu²⁺, and In³⁺ can be assimilated into the jarosite structure [9]. For that reason, this article describes the thermodynamic fundamentals for the extraction of minor elements like silver and indium from industrially generated jarosite over the course of primary zinc production.

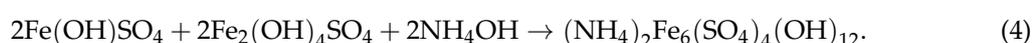
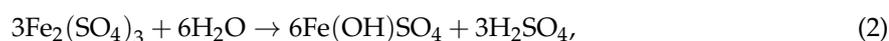
The main focus is placed on the simultaneous extraction of a zinc oxide product also carrying compounds of indium and silver.

This offers the advantage of an easy reutilization of the “added value” product in the primary zinc production industry. The silver and indium form the additional value on top of the zinc oxide, and they can be recovered if the zinc oxide is produced in adequately equipped zinc plants, without further investment in new facilities. Specifically, the simultaneous recovery of an added value product is the basis for the development of an economical and sustainable process for the recycling of jarosite.

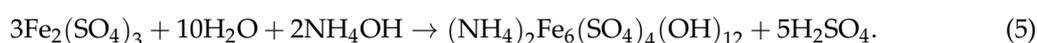
2. Materials and Methods

2.1. Formation of Jarosite

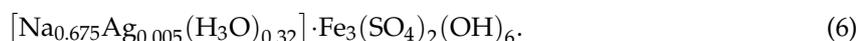
Jarosite precipitation is summarized in Equations (2)–(4), using the case of ammonium jarosite formation:



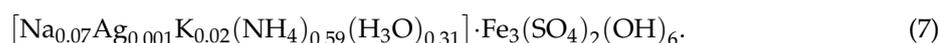
If the above reactions are combined, the overall reaction can be written as in Equation (5):



Although jarosite precipitation is a selective removal process of iron, small losses of other dissolved metals like zinc, lead, or silver cannot be avoided, leading to the aforementioned assimilation into the jarosite structure. Patiño mentioned the substitution of a cation with silver in a sodium jarosite sample in literature [10]—as in Equation (1)—with the ratio of elements as shown in Equation (6):



Salinas [11] reports a similar composition of an investigated industrial jarosite sample, with its molar ratio shown in Equation (7):



Furthermore, it can be observed in Equation (5) that H_2SO_4 is formed during this precipitation, which leads to the necessity of the addition of neutralization agents to avoid resolubilization. Commonly, calcined ore from the roasting step is utilized for neutralization during the precipitation of jarosite, leading to a certain amount of impurities not caused by the precipitation itself. Going hand in hand with this, elements or compounds in the ore concentrate are present in the precipitate as well, including lead, silver, zinc-ferrite, and indium, in addition to gangue compounds.

Table 2 shows the elemental analysis of a typical jarosite residue, with 27.1 wt. % of iron, approximately 6.5 wt. % of zinc and lead, and also sulfur, silver, and indium, in concentrations of 8.4 wt. %, 180 ppm, and 230 ppm, respectively.

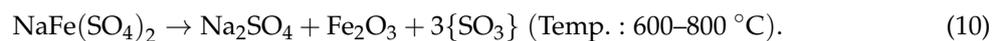
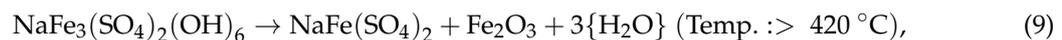
The substitution of the cation placeholder in the jarosite and the utilization of calcine for neutralization are not the only possible sources of side elements in the residue. In some plants, no Pb–Ag–residue separation is performed, due to low contents of those elements in the concentrate. Still, a certain amount of this by-product is always generated, and in such a case, ends up together with the iron in the precipitation residue—jarosite—as well [4]. Aside from that, dissolved silver oxide precipitates to insoluble silver chloride in the presence of chlorine ions in the pregnant solution, resulting in up to 5 wt. % of the silver contained in the residue being present as a chloride compound [13,14].

Table 2. Typical elemental analysis of a jarosite sample [12].

Element	Concentration (wt. %)	Method
Ag	0.018	DIN EN ISO 11885
In	0.023	DIN EN ISO 11885
Fe	27.1	DIN EN ISO 11885
Zn	6.5	DIN EN ISO 11885
Pb	6.2	DIN EN ISO 11885
S	8.4	DIN EN ISO 11885
Cl	<0.1	DIN 38405 D1-2
F	0.01	DIN 38405 part 1

2.2. Behavior of Jarosite during Thermal Treatment

During a pyrometallurgical treatment under oxidizing atmosphere, the jarosite residue decomposes into separate compounds. The splitting of crystal water, the separation of the OH-group, and the separation of the sulfate group can be described for all common types of jarosite in the three characteristic steps shown, respectively, in Equations (8)–(10) for sodium jarosite:

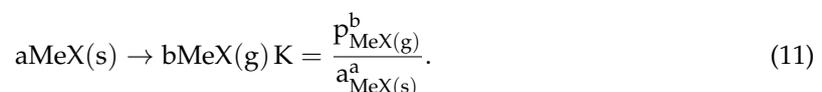


Based on the stoichiometry of the jarosite compounds, a theoretical amount of 35.9 wt. % is separated via the gaseous reaction products, mainly leaving behind iron oxide. In the context of silver and indium, it can be stated that the possibly formed Ag_2O is not stable at an increased temperature, and consequently dissociates to metallic silver. Moreover, stable indium(III)oxide does not show any significant vapor pressure and is therefore also in the calcined residue.

2.3. Thermodynamic Considerations of the Behavior of Indium and Silver

Typically, the volatility of metallic zinc is exploited to extract the valuable zinc from secondary resources, as is done for steel mill dust in Waelz kilns, or for drosses in the French and American processes for the production of high-purity zinc oxide. Based on the previously described idea of an added value zinc oxide for the primary zinc industry, extracted from jarosite, the thermodynamic investigations in this article describe the possibility of forming volatile compounds of silver and indium, resulting in co-evaporation with zinc. To achieve this, the software package HSC Chemistry 8.1.4 (Outotec Oyj., Helsinki, Finland) was used to calculate two kinds of phase stability diagrams. The first module used for calculation showed stability regions (the Tpp diagram module) for the variation of $\text{Cl}_{2(\text{g})}$ partial pressure as a function of temperature at a fixed $\text{O}_{2(\text{g})}$ partial pressure. With this module, the required temperature for a certain reaction could easily be determined. The second module illustrated phase stability boundaries as lines (the Lpp diagram module) for the variation of $\text{Cl}_{2(\text{g})}$ vapor pressure as a function of $\text{O}_{2(\text{g})}$ partial pressure at a fixed temperature.

Additionally, vapor pressure curves for different indium and silver compounds were plotted to determine whether they were volatile or stayed in the solid phase. In these cases, the reaction equation module of the HSC software was used to determine the equilibrium constant of the general reaction applied to the relevant compound, as shown in Equation (11):



The formula of the equilibrium constant, K , for the general vaporization reaction above can be transformed according to the vapor pressure, p . Based on the assumption of pure substances, the activity can be set to 1, resulting in the simplified Equation (12) for the vapor pressure of a compound at the temperature assumed for the calculation of the equilibrium constant:

$$P_{\text{MeX}(g)}^b = \sqrt[b]{\left(a_{\text{MeX}(s)}^a \cdot K\right)} \xrightarrow{\text{simplified}} P_{\text{MeX}(g)}^b = \sqrt[b]{(K)}. \quad (12)$$

With a stoichiometric coefficient of 1, the partial pressure becomes equal to the equilibrium constant of the vaporization reaction.

3. Results and Discussion

The results of the thermodynamic investigation concerning the vapor pressure curves plotted with the software package HSC Chemistry 8.1.4 are shown in Figure 2. At a temperature of 900 °C, metallic indium (solid blue line) started to have a slowly-increasing vapor pressure, despite its theoretical boiling point being 2071 °C. In addition, metallic silver (solid red line) first increased in vapor pressure at slightly over 1000 °C, and with this, represented a possible partial transition to the gaseous state. The partial pressures of the metallic forms of indium and silver were very low, and were therefore not suitable for extraction via the vapor phase under moderate temperature regimes.

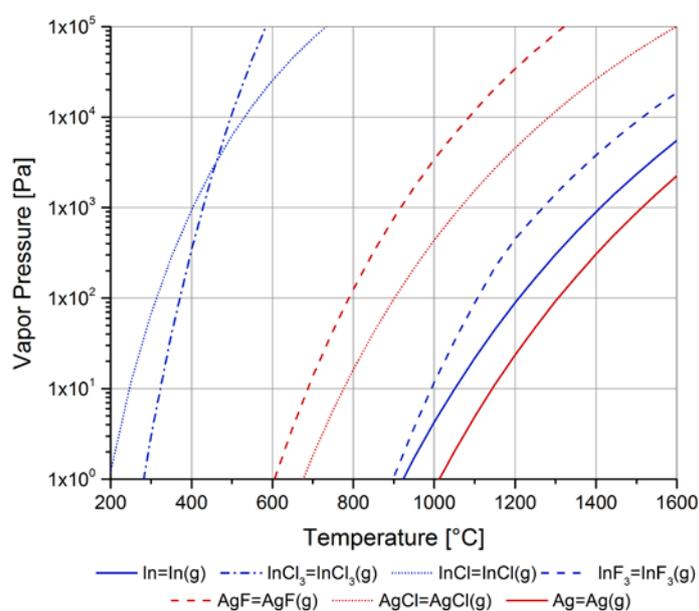


Figure 2. Vapor pressures for selected indium (blue lines) and silver compounds (red lines) as a function of temperature.

If the aim is to reach high extraction yields for silver and indium via a vaporization process, in addition to the recovery of zinc, the vapor pressure of the compounds should be as high as possible. Typically, zinc is vaporized above 907 °C, but it has significant vapor pressure at even lower temperatures. As such, the aim for silver and indium was to find volatile compounds below 907 °C. Consequently, oxides and halides were also evaluated, as they are typically known to be volatile compounds. Concerning the oxides, it can be stated that silver oxide was not stable and dissociated into its metallic form, while indium(II)oxide was not volatile in the range mentioned. Other indium oxides pointed out in the literature (e.g., In_4O_3 , In_4O_6 , and In_7O_9) could be formed during reduction processes, but reacted under oxidizing conditions once again forming indium(II)oxide. Indium(I)oxide, In_2O , could also be formed during a reduction process, but was only stable in the gaseous phase,

which is the reason why it is not shown in Figure 2. In the case of a reduction potential that was too high, it was further reduced to the metallic state. Thermodynamic calculations also showed that the presence of a chlorine carrier such as ZnCl_2 immediately led to the formation of InCl . It could be seen that InCl and InCl_3 already had significant vapor pressures at very low temperatures ($>300\text{ }^\circ\text{C}$), while AgCl started demonstrating vapor pressure at $>700\text{ }^\circ\text{C}$. The fluorine compounds (dashed lines) of silver (AgF) and indium (InF_3) started showing vapor pressures at $>900\text{ }^\circ\text{C}$ and $>600\text{ }^\circ\text{C}$, respectively.

In summary, the vapor pressure calculations showed that the volatility of halides was higher than that of the oxide compounds or the metallic forms of indium and silver. Moreover, the fact that chlorine compounds are less disturbing in the primary zinc industry than fluorine compounds, and can be removed more easily from a zinc oxide product before utilization, means that they are the preferred compounds for selective extraction via the vapor phase.

To determine the required conditions for the formation of volatile indium and silver compounds, phase stability diagrams of indium and silver, as well as their chlorides and oxides were calculated, as shown in Figure 3.

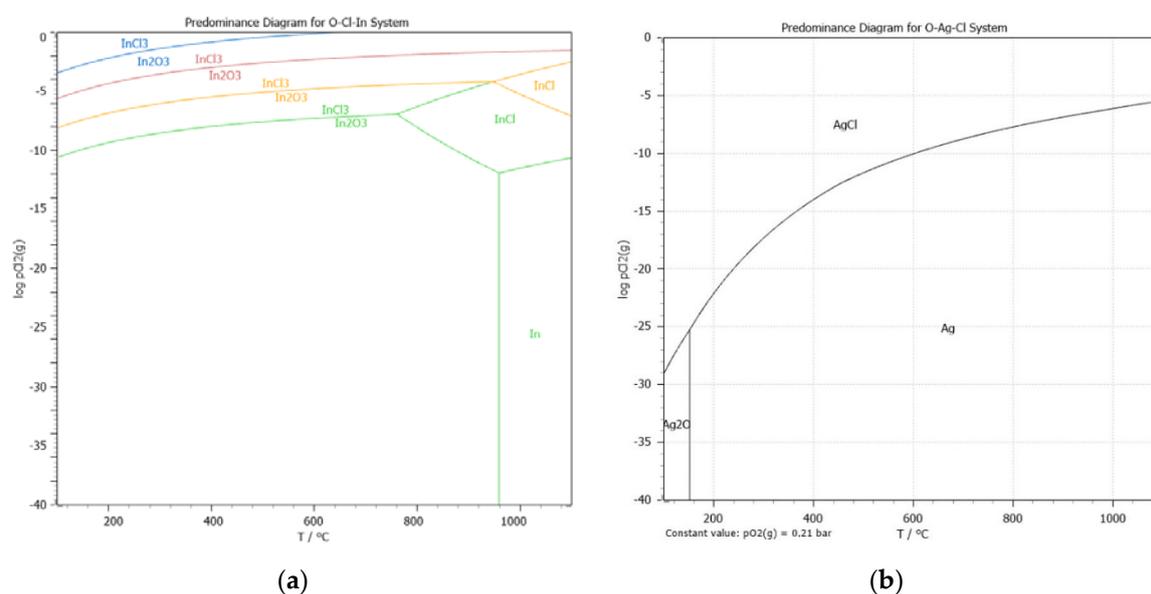


Figure 3. (a) Predominance diagram (Tpp) for the system O-Cl-In at four $\text{O}_2(\text{g})$ partial pressures (green: 1×10^{-15} bar; yellow: 1×10^{-10} bar; red: 1×10^{-5} bar; blue: 0.21 bar;) (b) Predominance diagram (Tpp) for the system O-Cl-Ag at a $\text{O}_2(\text{g})$ partial pressures of 0.21 bar.

Figure 3a shows, for four selected $\text{O}_2(\text{g})$ partial pressures ranging from 0.21 bar (blue line) to 1×10^{-15} bar (green line), the predominance diagrams for metallic indium, In_2O_3 , InCl , and InCl_3 . Indium oxide had a wide range of stability in all cases, but was a non-volatile compound in the temperature range considered. It was also determined that a certain $\text{Cl}_2(\text{g})$ partial pressure or any chlorine source was required, which could be ensured by, for instance, the addition of less-stable chlorine compounds, forming indium chloride. The stability region of In_2O_3 could be decreased by lowering the $\text{O}_2(\text{g})$ partial pressure, which could be realized by purging with an inert gas or through the addition of reducing agents like carbon. Furthermore, it could be seen that at increased temperatures ($>800\text{ }^\circ\text{C}$) and adequate $\text{O}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ partial pressures, InCl showed a more stable region. The advantage of InCl when compared to InCl_3 is the ratio of indium to the consumed chlorine carrier for the formation of volatile indium chloride, which is one-third of its molar ratio in InCl_3 . The predominantly-formed compound at lower $\text{Cl}_2(\text{g})$ partial pressure in the temperature range considered was InCl_3 .

As mentioned before, silver oxide was not stable when the temperature was increased above 180 °C, and reacted to form metallic silver. Figure 3b illustrates this fact on the left side of the diagram. The influence of $O_{2(g)}$ partial pressure on the stability regions concerning AgCl and Ag was not significant; the only change upon decrease was that the silver oxide already dissociated at a lower temperature. This was why only one $O_{2(g)}$ partial pressure is shown in the diagram. It can also be stated that, over the complete investigated temperature range, silver(I)chloride was formed so long as a source for chlorine was available, which was less stable than AgCl. As exhibited in Figure 2, silver(I)chloride had a higher vapor pressure than metallic silver, which positively influenced a targeted recovery.

Figure 4 shows the phase stability boundaries calculated for three temperatures, ranging from 700 °C (green line) to 1100 °C (red line), for indium and silver, and their chlorides and oxides.

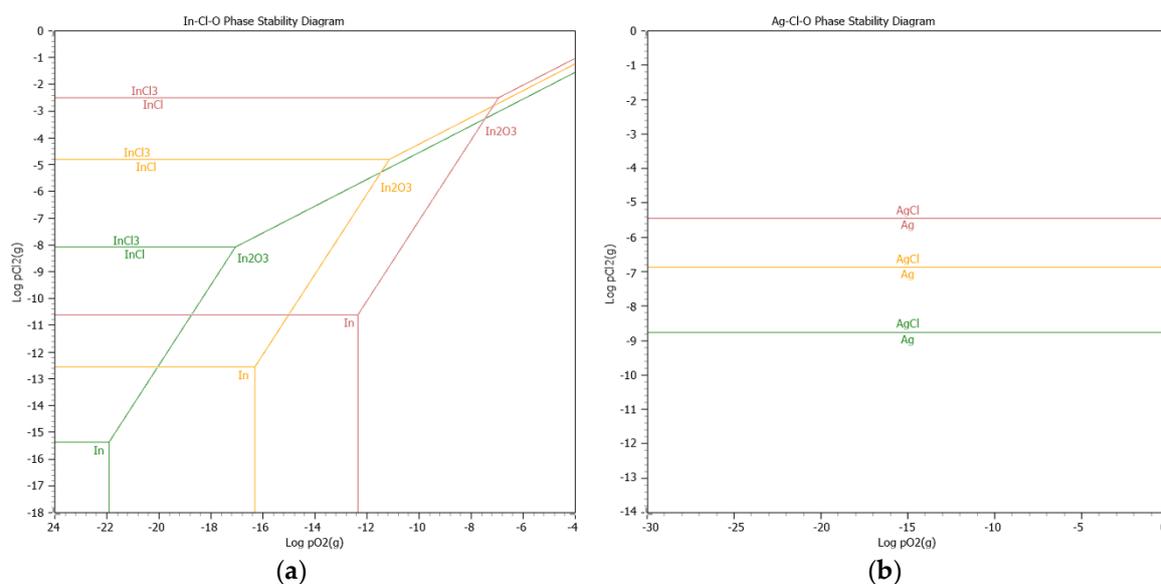


Figure 4. (a) Predominance diagram (Lpp) for the system O-Cl-In at three temperatures (green: 700 °C; yellow: 900 °C; red: 1100 °C) (b) Predominance diagram (Lpp) for the system O-Cl-Ag at three temperatures (green: 700 °C; yellow: 900 °C; red: 1100 °C).

Figure 4a shows again that the indium oxide was stable so long as the partial pressure of oxygen was high enough and the $Cl_{2(g)}$ partial pressure was low. In the case of decreased $O_{2(g)}$ partial pressure, metallic indium could be formed. The lower the temperature, the lower the partial pressure of $O_{2(g)}$ had to be to form metallic indium. If the $Cl_{2(g)}$ partial pressure was also taken into account, the diagram shows that the partial pressure itself had the main influence on $InCl_3$ formation, instead of temperature variation. For the formation of InCl from In_2O_3 , the temperature could also significantly move the stability boundaries, but as described in the preliminary paragraph, the formation of InCl₃ was more likely in the investigated temperature region due to a requirement for lower $Cl_{2(g)}$ partial pressure, combined with an acceptably high $O_{2(g)}$ partial pressure. The increase in temperature shifted the stability region of InCl to a lower $Cl_{2(g)}$ partial pressure, and at a temperature of 1415 °C (not shown in Figure 4a), indium(I)chloride was formed instead of $InCl_3$.

The predominance diagram for silver shown in Figure 4b illustrates the $Cl_{2(g)}$ partial pressure as a function of the $O_{2(g)}$ partial pressure at constant temperatures. The horizontal lines for all three investigated temperatures highlight the aforementioned fact that the $O_{2(g)}$ partial pressure had no significant influence on the stability boundary of $AgCl_{(g)}$ and Ag. Silver(I)oxide was not stable at the investigated temperatures between 700 to 1100 °C, and therefore does not appear in the diagram.

In summary, it can be said that the volatilization of silver could be positively influenced by the presence of a chlorine carrier, leading to the formation of silver(I)chloride at any $O_{2(g)}$ partial pressure in the investigated range (below 1 bar) and with this, the required temperature shifted to lower values.

Regarding indium oxide, reducing conditions were required to bind the oxygen and reduce the $O_{2(g)}$ partial pressure, supporting the formation of $InCl_{3(g)}$ or $InCl_{(g)}$ for successful volatilization.

4. Conclusions

For the development of an economical and ecological process, the target is the simultaneous recovery of product with optimized quality. Especially in the case of industrial residues such as the iron precipitate of the zinc industry (which is typically low in value), elements like indium and silver contribute significantly to the overall economy of a potential recycling process if they are recovered in a meaningful way. Therefore, the investigated extraction method by the formation of volatile chlorine compounds of indium and silver supports the idea of generating an “added value” product through the simultaneous recovery of the elements zinc, indium, and silver in one metallurgical step. The fact that indium oxide requires a reducing agent is not a disadvantage, as it goes hand-in-hand with a potential reduction of zinc oxide for its vaporization as metallic zinc. Furthermore, this does not influence the silver extraction, where the oxygen partial pressure is of minor significance.

In the context of minimizing the operational costs of the process, the substitution of required additives (e.g., chlorine carriers in this case) is also a factor. This was investigated in [11], describing a possible combined treatment of two residues, one of them carrying chlorine as a constituent, along with electric arc furnace dust.

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