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THERMODYNAMIC CONSIDERATIONS REGARDING THE VOLATILIZATION BEHAVIOR OF SILVER AND INDIUM FROM JAROSITE BY A PYROMETALLURGICAL TREATMENT

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ABSTRACT

Elements defined as critical by the European Commission, like platinum group metals (PGM), indium, cobalt, gallium, silver, gold, germanium and antimony are often contained in copper-, lead- and zinc-ores. During the metal production process of the above-mentioned base metals different residues accumulate, which can contain these critical elements as well. By depositing thousands of tonnes of these residues from the metallurgical industry, the contained valuable metals are no longer available. Next to that the security of supply in Europe for especially those metals is bad. Due to these problems and an increased environmental awareness, the recovery of critical elements from residues gets more and more important.

Because of carrying high amount of silver and indium, the precipitation residue jarosite or also neutral leaching residue from the hydrometallurgical zinc production are potentially interesting for reprocessing. By adding of different additives and a treatment at higher temperatures, critical elements as well as other valuable metals get vaporized in various chemical compounds. If the mentioned metals are recovered successfully during a recycling process it can contribute to the overall production economy. The paper summarizes carried out thermochemical calculations investigating a possible recovery of silver as well as indium in a pyrometallurgical process by selective vaporization.

INTRODUCTION

Metallic zinc can be produced by two different routes, pyrometallurgically and hydrometallurgically. Nowadays approximately 90 % of the annual primary produced zinc is from the hydrometallurgical way. In this case the ore first of all gets crushed, grinded and enriched by a flotation process to get a zinc concentrate. The oxidic input material required for the leaching process is obtained by roasting the sulfidic ore in a fluidized bed reactor. In the case of higher iron containing ores zinc ferrite builds up during the roasting step. Zinc ferrite is only soluble in strongly acidic solutions, which leads to the necessity of a two-step leaching process as can be seen in Fig. 1 (a). After a neutral leaching step of the calcine a separation of liquid and solid phase is done. The liquid phase gets purified and enters the electrolysis, while the solid phase has to be treated in a hot acid leaching step, where the remaining zinc ferrite is dissolved. In the next step the iron has to be removed by an iron precipitation, within the hardly soluble phase jarosite is formed. Jarosite can contain up to 230 ppm silver and up to 300 ppm indium. Approximately 0.5 t of dry jarosite accumulates in the production of 1 t of zinc by the hydrometallurgical zinc-winning route [1]. Every year about 600.000 t of this residue are produced in the Europe Union [2–4]. The mandatory of getting rid of the iron is because of the fact that it would deposit on the cathode, forming an unwanted impurity in the zinc. The solution from the solid/liquid separation after the iron

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precipitation gets back to the neutral leaching step and passes the purification before entering the electrolysis, where zinc forms a layer on the cathode. [5]

In the case of lower iron containing ore a one-step leaching process is sufficient and leads to a neutral leaching residue (approximately 600-700 kg per ton of zinc), which contains silver up to 0.1 %. The one-step concept flow sheet of the hydrometallurgical zinc production is illustrated in Fig. 1 (b).

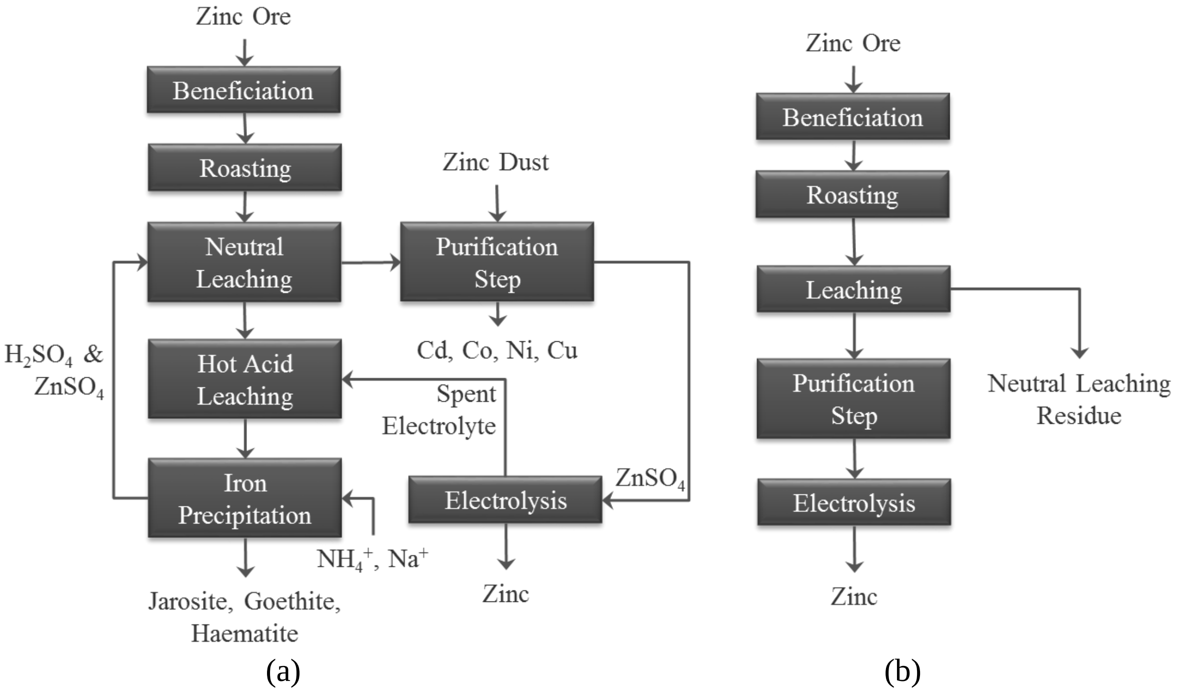

Fig. 1–Flow sheet of the hydrometallurgical zinc production, two-step concept (a) and one-step concept (b)

Although there is a possibility of high content of valuable metals in this residue beside iron, huge amounts of precipitate gets landfilled due to inefficient recycling processes. The accumulation of these residues causes a series of environmental problems in ecosystems on the one hand but also takes up massive land on the other. Moreover, arsenic and cadmium can be diluted by rainwater and are harmful to the health of the aquatic systems due to their toxicity. [6; 7]

Nevertheless, future investigations should enable the recovery of critical metals such as silver and indium out of residues from the zinc industry next to the often solely focused base metals.

Typically, thermodynamic calculations form the basis for process development and were therefore carried out for the selective vaporization of indium and silver out of jarosite.

THERMODYNAMIC CONSIDERATIONS

In order to investigate which phases are stable or unstable at certain temperatures, vapor pressure curves of pure metals as well as possible compounds were calculated. The calculation of the vapor pressure is carried out by using the equilibrium constant of the various volatilization reactions as can be seen in formula (1), (2), and (3).

$$aMeX(s) \rightarrow bMeX(g) \tag{1}$$

$$K = \frac{p_{MeX(g)}^{b}}{a_{MeX(s)}^{a}} \tag{2}$$

$$p_{MeX(g)} = \sqrt[b]{\left(K * a_{MeX(s)}^{a}\right)} \tag{3}$$

Assuming that various metal compounds have an activity of 1, following simplification can be done (see formula 4):

$$p_{MeX(g)} = \sqrt[b]{K} \tag{4}$$

With the Software HSC Chemistry 8.1 and the corresponding database for calculating the equilibrium constants, it is possible to calculate the theoretical volatilization behavior of silver as well as indium and the influence of zinc and lead as well as chlorine and fluorine.

First of all the vapor pressure of pure metals are illustrated in Fig. 2. In the defined boarders every metallic element shows a significant vapor pressure. Elements like indium, silver and iron show a low vapor pressure, which means they do not change the solid state if they occur in their metallic form and are therefore not available for recovering. Zinc for example starts to have a relevant vapor pressure above 350 °C and is highly volatile above 900 °C, if it is in metallic form. Lead in contrast is located between zinc and the other elements.

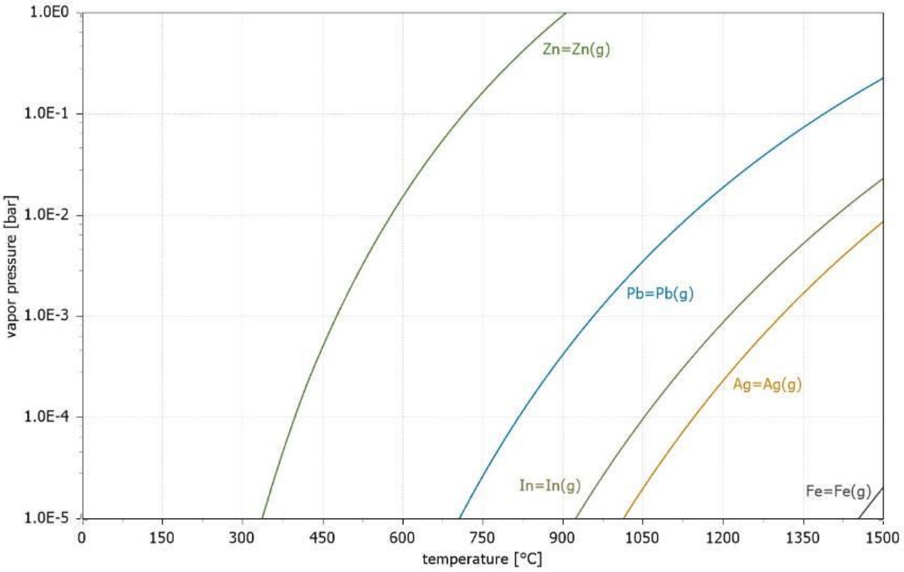

Fig. 2–Vapor pressures of selected metals

If we take a look on the the vapor pressures of selected metal oxides, shown in Fig. 3, only lead (II) oxide shows an elevated vapor pressure at a temperature of about 1100 °C. Zinc (II) oxide is more or less not volatile. Other oxidic compounds in the jarosite such as silver (II) oxide are not stable at higher temperatures, respectively do not show any volatile behavior within the defined boarders.

A result of these two calculations is that both critical elements, silver and indium are not recoverable by volatilization neither in metallic nor in oxidic form. This means that just oxidizing or reducing conditions do not lead to a satisfying result.

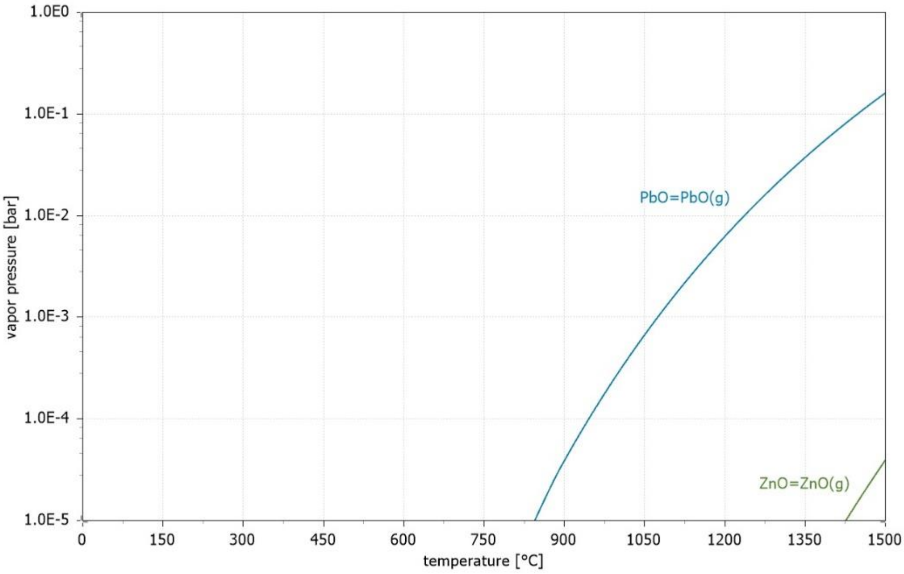

Fig. 3–Vapor pressures of selected metal oxides

The vapor pressure curves of chloride compounds shown in Fig. 4 are more interesting. Silver (I) chloride is the most stable compound in this graph, but still shows a tendency to volatilize at higher temperatures. At a temperature lower than 1050 °C, lead (II) chloride vaporizes, while zinc (II) chloride, iron (III) chloride as well as indium (III) chloride reach their boiling point at a temperature even below 800 °C.

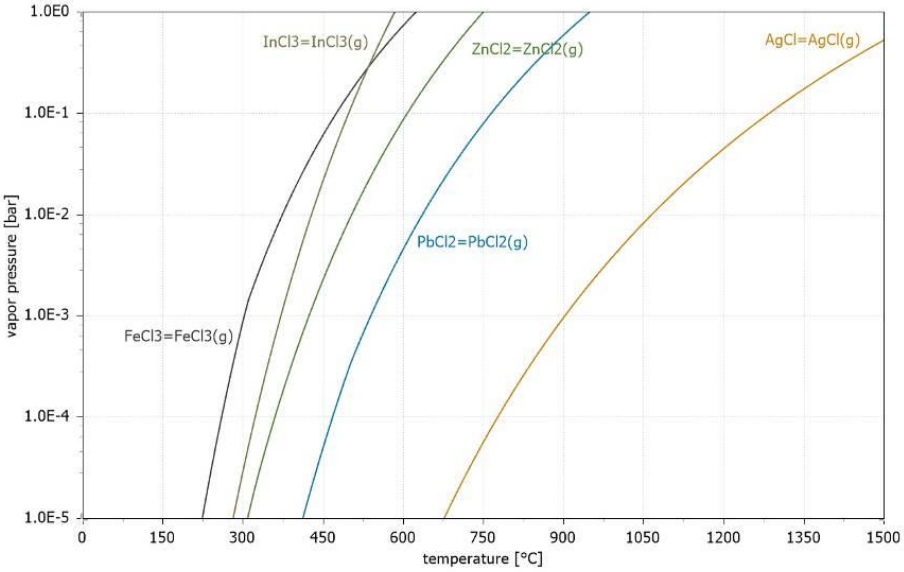

Fig. 4–Vapor pressures of selected metal chlorides

Fig. 5 displays the vapor pressure curves of selected metal fluorides. Also fluoride compounds lead to a volatile behavior. Lead (II) and silver (I) fluoride show a vapor pressure of 0.1 bar at about 1100 °C, zinc (II) fluoride is a little bit beneath these two curves. Moreover, indium forms volatile compounds with fluorine as well but in general with lower vapor pressure.

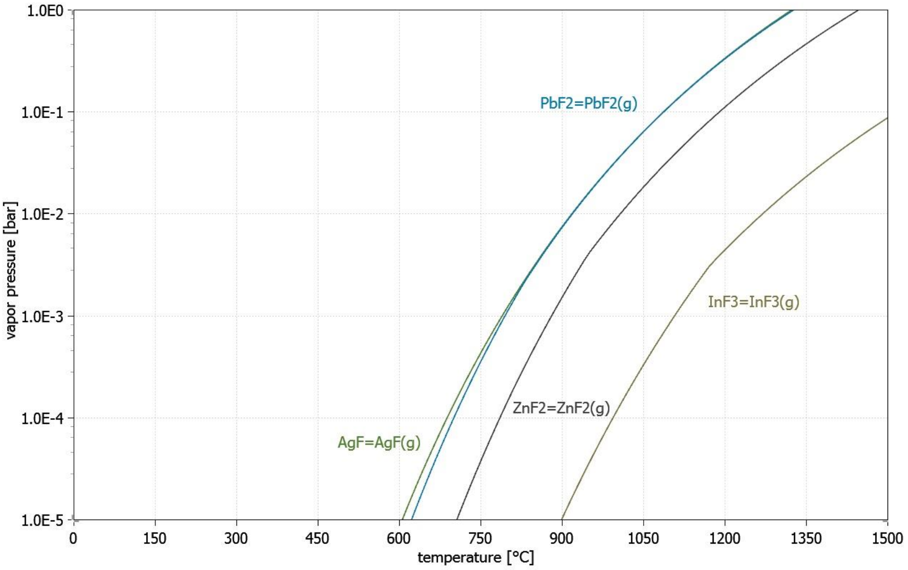

Fig. 5–Vapor pressures of selected metal fluorides

The outcome of these calculations is, that additives are necessary to get volatile compounds at relatively low temperatures, respectively to transform indium and silver contained in jarosite into volatile chlorides and/or fluorides.

Next to vapor pressure curves, predominance diagrams are an excellent tool to display the stability regions of chloride compounds depending on the partial pressure of different gases at a certain temperature.

In Fig. 6 the behavior of silver in a gaseous chlorine atmosphere can be seen. At a temperature of 1100 °C silver (I) chloride is stable up to a chlorine partial pressure of lower than 10^{-5} bar. That means if there is a source of chlorine, silver can react to silver (I) chloride at this temperatures. As described in the vapor pressure diagrams previously silver (I) chloride shows a tendency to volatilize at higher temperatures and can therefore be recovered by vaporization.

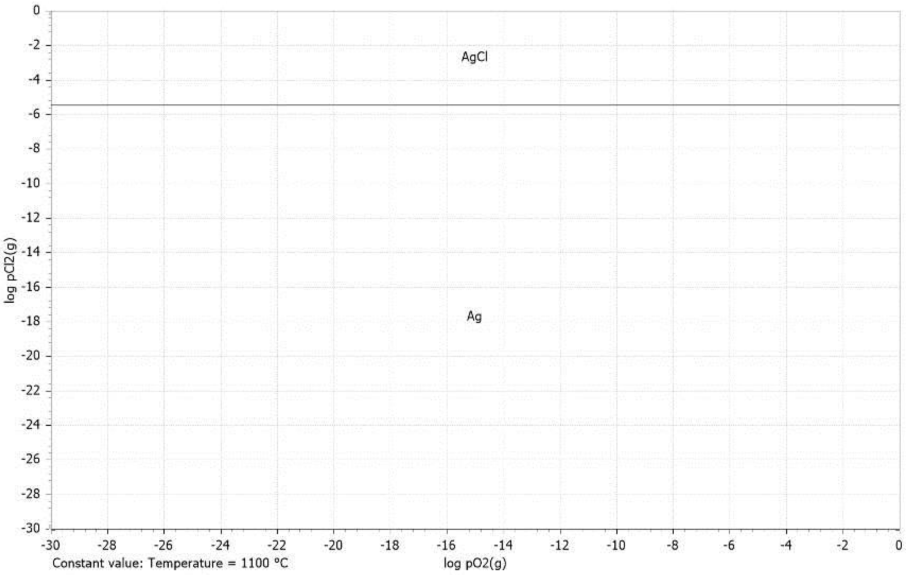

Fig. 6–Predominance diagram for Ag-O-Cl system (1100 °C)

The predominance diagram for the In-O-Cl system at 1100 °C is displayed in Fig. 7. Indium oxide is stable over a wide range. Nevertheless, it is no volatile compound. Therefore it has to be changed into indium (III) chloride to get a volatile behaviour as shown in the vapor pressure graphs before. The stability of indium oxide can be lowered by reducing conditions. By adding a reducing agent it is possible to generate indium (III) chloride up to a chlorine partial pressure of lower than 10^{-2} bar, because indium (III) chloride is only stable within a small range.

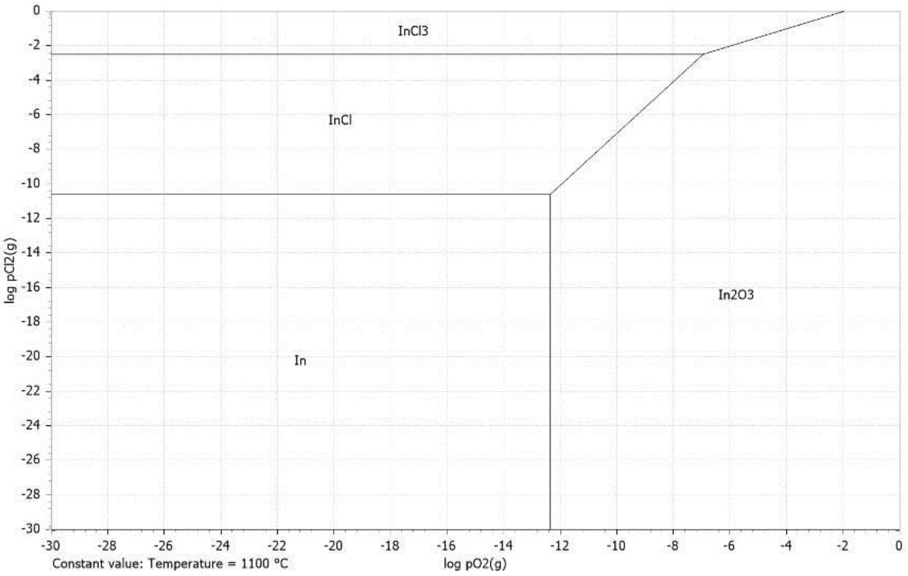

Fig. 7–Predominance diagram for In-O-Cl system (1100 °C)

To sum up, if there is enough chlorine available, silver should be vaporized at a temperature of 1100 °C. To recover indium it is necessary to add a reducing agent and to provide enough chlorine. In general it is necessary to keep in mind that also other elements like lead and zinc form stable chlorides and are easy to volatilize. Nevertheless, all these diagrams and graphs only provide considerations of the equilibrium and do not include any statements about the kinetics, respectively the necessary activation energy.

CONCLUSION

Due to the supply risk of critical elements in Europe and an increased environmental awareness, the recovery of currently dumped material gets more and more important. Valuable side metals such as silver and indium in residues like jarosite from the hydrometallurgical zinc winning route represent a high economical potential for new recycling concepts. In order to get an idea on how to recover these elements, thermodynamic calculations form the base to develop new recovery processes.

Based on the thermodynamic calculations it should be possible to volatilize silver as well as indium from jarosite. The vapor pressure curves show that it is necessary to create chloride and fluoride compounds by adding chlorine and fluorine for the volatilization. In general the indium oxide is in comparison to the indium chloride more stable. To recover the indium as chloride reducing conditions are also mandatory as illustrated in the predominance diagram.

The next logical step is to verify these theoretical findings by performing a pyrometallurgical test series under these given conditions.

ACKNOWLEDGMENTS

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