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Technical Faculty in Bor and
Mining and Metallurgy Institute Bor



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October Conference
on Mining and Metallurgy**

PROCEEDINGS



Editors:

Nada Štrbac

Ivana Marković

Ljubiša Balanović

Bor Lake, Serbia

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CONCEPTUAL STUDY FOR VALORIZATION OF In, Ga AND Ge

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Abstract

European Commission has created a list of Critical Raw Materials (CRMs) including In, Ga and Ge which are important electronic metals. Since their scarce natural abundance and growing demand, nowadays major source of In, Ga and Ge are specific by-products from primary base metals production. Considering the concentration of In, Ga and Ge in solution obtained after hydrometallurgical treatment of Waelz oxide, valorization of these metals could be done by liquid-liquid extraction. The aim of this conceptual study is to propose experimental flow sheet for selective liquid-liquid extraction in order to valorize In, Ga and Ge from the leaching solution.

Keywords: leaching, liquid-liquid extraction, electronic metals

1. INTRODUCTION

In, Ga and Ge do not occur in native state nor has their own ores. As trace metals in Sphalerite, Chalcopyrite and Galena minerals, In, Ga and Ge are obtained as a by-products of primary Zn, Cu and Pb production.

The major end use of In, Ga and Ge are in the fast evolving high-tech industry, including renewable energy, telecommunications and electronics sectors. Following the development trends of this industrial sector, use of In, Ga and Ge is likely to increase in the near future.

Due to natural scarcity, technological and economical importance and high supply risk, In, Ga and Ge are on the list of critical raw materials [1]. So, it is mandatory to provide effective, economically viable and sustainable production of these metals.

Primary zinc production is still based on the traditional methods of roasting-leaching zinc sulfide concentrate. By-product of this treatment is neutral leaching residue – jarosite that contains Fe, Zn and volatile metals such as electronic metals. The Waelz process can be applied for treatment of jarosite and products are clinker and volatile oxides (WO_x) in which zinc and electronic metals are present. One of the methods for obtaining electronic metals from WO_x is hydrometallurgical treatment of oxides in acidic media followed by liquid-liquid extraction.

Liquid-liquid extraction is well known method for recovering In, Ga and Ge. Common organic solvents can be employed as diluents for extractant as organic phase [2] yet kerosene is the most suitable one [3]. Results that can be found in the literature [3, 4, 5] suggesting D2EHPA, Cyanex 272, LIX 984 or IONQUEST 801 as effective electronic metals extractants. Researchers [6, 7] employed LIX 63, N235, TBP or TOA to extract Ge from acidic solution. Above mentioned literature suggested HCl, H₂SO₄, Na₂SO₄ and NaOH as stripping agents and that choice and concentration of these agents is crucial for selective separation of In, Ga and Ge from each other and from co-extracted impurities. So, choice and concentration of the extractant and stripping agent including the volume phase ratio, contact time and number of steps are varied depending

of pH and concentration of metals in feed solution, impurities and metal selected for recovery [6, 8, 9, 10].

This paper presents the results of hydrometallurgical treatment of WO_x in order to obtain solution for valorization of In, Ga and Ge by liquid-liquid extraction. Also, the aim of this conceptual study is to define conditions for liquid-liquid extraction in order to achieve high distribution coefficient and selectivity for electronic metals extraction from real leaching solution.

2. EXPERIMENTAL

2.1 Materials and methods

In this study WO_x is used as raw material. WO_x is a product of Waelz process of primary Zn production waste. Moisture content of WO_x is 0.24%, bulk density is 764g/l, pH=5.37, Eh=84.3mV and particle size composition: 94% of particles are 0.5mm-36µm and rest are particles smaller than 36µm. For obtaining the solution that contains volatile electronic metals In, Ga and Ge hydrometallurgical treatment of WO_x is applied. Leaching experiments were carried out in a glass reactor. First, sample of WO_x was neutral leached in diluted sulfuric acid (pH=4.5) with solid to liquid ratio of 200g/l during 4h at 45°C. After phase separation reductive leaching in 50vol. % sulfuric acid is conducted on solid residue with solid to liquid ratio of 200g/l during 3h at 80°C. One of the products of neutral and reductive leaching is a solution containing In, Ga and Ge among other metals refer to as impurities. Quantitative chemical analysis of raw material and feed solution was done by inductively coupled plasma optical emission spectrometry (ICP-OES). Results are shown in Table 1.

Table 1 - Chemical analysis of WO_x and leaching solution

Element	In	Ga	Ge	Fe	Zn
WO _x , %	0.07	0.01	0.007	1.68	46.79
Leaching solution, g/l	0.1914	0.0030	0.001	2.7930	10.7800

In feed solution Ag, Ca, Cd, Cl, Cu, F, Pb and Si are also found in small quantities: 0.0010, 0.0917, 0.0697, 0.1606, 0.1391, 0.1271, 0.0030 and 0.0021, respectively, expressed in g/l. These elements are leached from WO_x in less than 2%, except for Cu and F ions for which leaching percentage was higher.

3. CONCEPTUAL STUDY FOR ELECTRONIC METALS VALORISATION

According to literature results conceptual study for liquid-liquid extraction is made. The most suitable extracting agent as organic phase is di-(2-ethylhexyl) phosphoric acid (D2EHPA) diluted in kerosene. In optimal conditions D2EHPA is selective for In, Ga and Ge extraction although some amount of Fe³⁺ is also extracted. One way to prevent co-extraction of ferric ions is to reduce them with Zn powder in stoichiometric amount. If not so, separation of electronic metals from ferric ions could be done in stripping stage of liquid-liquid extraction.

So, in order to achieve high distribution coefficient for In, Ga and Ge it is necessary to optimize extraction conditions like pH of feed solution, organic phase concentration, volume phase ratio, extracting contact time and number of extracting stages. Also, optimization of the stripping stage must be done to achieve best separation of In, Ga and Ge from each other and from possible extracted impurities like ferric ions.

Due to its dielectric constant and loading capacity, kerosene is the most appropriate diluent for D2EHPA. Appropriate volume ratio of D2EHPA and kerosene is 4:6 but ratios 2:8, 3:7 also

should be examined. Feed solution obtained by neutral and reductive leaching of WO_x has $pH = -1$. Extraction from this feed solution is possible but there should be examined extraction from feed solution after its neutralization by mean of ZnO or washed WO_x . Aqueous to organic phase ratio (A/O) is in range of 2 to 4 to provide enough extractant to quantitatively extract all In , Ga and Ge present in feed solution. Contact time in one extracting stage to reach equilibrium with minimum co-extraction of impurities should not exceed 10min. Also, more than one stage could give efficient extracting rate.

After extraction in separatory funnel and separation of phases by gravitation stripping of metal-loaded organic phase should be done in order to concentrate In , Ga and Ge in strip solution. Each of these metals requires different stripping conditions in order to selectively separate them from each other and from impurities loaded in organic phase, primarily Fe^{3+} . Conceptual flow sheet of electronic metals extraction and stripping is given in Figure 1.

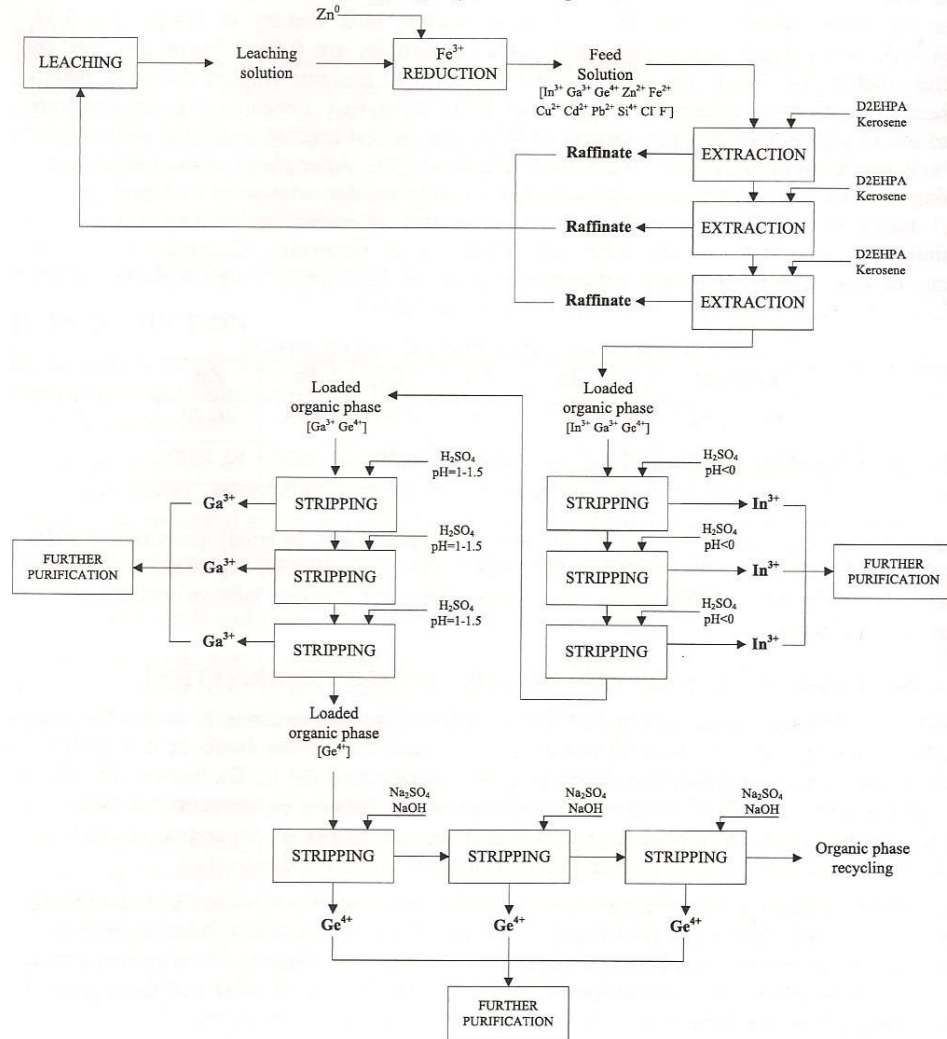


Figure 1 – Conceptual flow sheet for liquid-liquid extraction of electronic metals

Selective stripping of In from loaded organic phase could be achieved using 180g/l sulfuric acid solution. Equilibrating contact time is no more than 10min so co-stripping of Fe³⁺ is negligible. Three to five stages of stripping for A/O range of 1 to 3 should give satisfactory results. Less acidic sulfuric acid solution with pH=1-1.5 should be applied for Ga stripping with all other conditions remained the same. Ge could be stripped from loaded organic phase from which In and Ga are already removed. In order to achieve this, 140g/l Na₂SO₄ and 20g/l NaOH solution is used as a stripping agent. Ratio of loaded organic phase to aqueous phase is between 2 and 4. Recommended equilibrating contact time is no more than 10min in each of three to five stripping stages.

After collecting raffinate and strip solutions from extracting and stripping of In, Ga and Ge, results of quantitative chemical analysis should be used to characterize liquid-liquid extraction efficiency (Equations 1-4) in mean of distribution coefficient (D), extraction percentage (E), separation factor (β), and stripping efficiency (S).

$$D = (M(C_0) - M(C_{AQ})) / M(C_{AQ}) \quad (1)$$

$$\%E = (D / D + (V_{AF} / V_{OF})) \times 100 \quad (2)$$

$$\beta = D_A / D_B \quad (3)$$

$$\%S = (M(C_{RE}) / M(C_{OF})) \times 100 \quad (4)$$

where M(C₀) and M(C_{AQ}) represent the initial and final concentrations of metal ions in the feed solution and raffinate, V_{AF} and V_{OF} are the volumes of the aqueous and organic phases, D_A and D_B are distribution coefficients of two metals, M(C_{RE}) is the equilibrium concentration of metal ions in the stripping solution, and M(C_{OF}) is the concentration of metal ions in the loaded organic phase.

4. CONCLUSION

This conceptual study is made in order to propose conditions for valorization of In, Ga and Ge from real leaching solution by liquid-liquid extraction. D2EHPA diluted in kerosene is considered as extractant. At A/O=3, temperature of 25°C, contact time less than 10min and more than one extracting stages, extraction of electronic metals should be efficient with minimum co-extraction of impurities present in feed solution. For preventing co-extraction of Fe³⁺ as the main impurity it is need to reduce it beforehand liquid-liquid extraction. Also, separation of electronic metals from ferric ions can be achieved in stripping stage. Further, selective separation of In and Ga could be done by stripping them with sulfuric acid solution of pH<0 and pH=1-1.5, respectively, while Ge could be selectively stripped with less acidic solution.

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