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RESEARCH ON ACID LEACHING OF Cu, Zn AND In FROM JAROSITE WASTE

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ABSTRACT – The paper presents the results of treatment of technogenic raw materials by the leaching process in order to valorize economically valuable metals and minimize the negative impact of leached residue on the environment. First, the sample was homogenized, and then granulometric, XRD and chemical analysis of the jarosite sample was done. The leaching agents used in experiments were HCl, HNO_3 and H_2SO_4. Investigations have shown that the most acceptable method for the treatment of jarosite is leaching of jarosite using sulfuric acid, where the best leaching of Cu, Zn and In was obtained, namely 93.76%, 91.64% and 97.59%, respectively.

Keywords: Hydrometallurgy, Acid Leaching, Jarosite Treatment, Indium Recovery.

INTRODUCTION

Zinc concentrates, beside zinc, also contain a number of commercially important metals such as copper, lead, silver, germanium, indium, gallium, etc. These metals do not create their own mineral deposits, but as zinc companions, in hydrometallurgical zinc production, by roasting, leaching and electrolytic extraction, they are concentrated in the output waste sludge's of so-called jarosites as by-products [1,2]. By processing by-products, a whole range of metals can be produced, which has a favorable effect on the overall economy of the basic process, because the prices of these metals are relatively high [3,4]. Jarosite, as a newly formed chemical structure, is very stable and poorly soluble in dilute acid [5]. Accompanying zinc metals from jarosite are usually obtained by the Waelz pyrometallurgical process. Pyrometallurgical processes of processing secondary raw materials of zinc and waste sludge from zinc hydrometallurgy are very efficient, but they involve expensive large-capacity industrial plants, in order to be economical. These processes release harmful gases that can have a serious impact on the environment. Some authors have shown that the application of pyrometallurgical processes such as the Waelz and Ausmelt methods consumes a huge amount of coal to provide the power required to achieve a high operating temperature (1100-1300 ^{0}C). These methods are not economically viable, so jarosites are usually deposited.

The aim of this work was to use the hydrometallurgical leaching process to valorize some of the accompanying metals such as Cu and In in addition to Zn. By hydrometallurgical processing of jarosite waste, beside additional recovery of Zn, also Cu and In would be valorized. This would support an integrated approach of metal production in zinc hydrometallurgy.

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EXPERIMENTAL

Characterization of the jarosite

Granulometric composition of the sample

The obtained original jarosite sample was dried and homogenized and then granulometric analysis was done, which is shown in Table 1.

Table 1 Granulometric composition of jarosite sample

Particle size d (mm)	Mass participation m %	Cumulative participation by plus R %	Cumulative participation by minus D %
-0.150+0.106	0.50	0.50	100
-0.106+0.075	0.25	0.75	99.50
-0.075+0.053	0.30	1.05	99.25
-0.053+0.038	0.30	1.35	98.95
-0.038+0.020	0.15	1.50	98.65
-0.020+0.000	98.50	100	98.50

Granulometric analysis showed that the particle size below 38 µm was present in the amount of 98.65%. In order to better extract the metal, the sample was ground to a grain size of 98.50% -20 µm and homogenized again.

Mineralogical analysis of the sample

X-ray diffraction (XRD) analysis was performed on an instrument "Rigaku MiniFlex 600" with "D / teX Ultra 250" with high-speed detector and an X-ray tube with a copper anode. The detection limit of XRD analysis is about 1%. The diffractogram obtained by XRD analysis is shown in Figure 1. The following minerals were present in the jarosite sample: jarosite ($KFe_3(SO_4)_2(OH)_6$), magnetite (Fe_3O_4) and anglesite ($PbSO_4$). Jarosite and magnetite were the most abundant minerals in the sample, while anglesite was less represented.

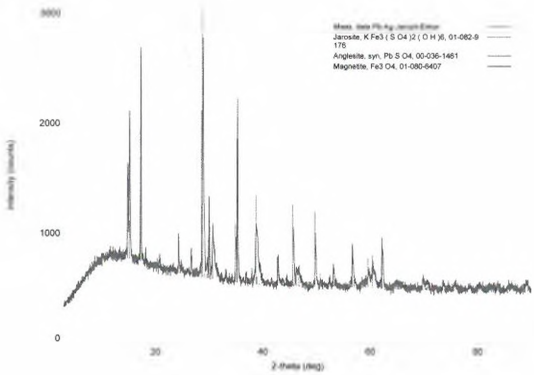

Figure 1 Diffractogram of a jarosite sample

Chemical characterization of jarosite sample

After homogenization, a representative sample was taken and chemical analysis was done. Chemical analysis of the sample is shown in Table 2.

Table 2 Chemical analysis of jarosite sample

Element	**Cu (%)**	**Zn (%)**	**In (ppm)**
Metal content	0.7	5.39	343.2

Preparation of jarosite sample for leaching experiments

Leaching of jarosites was performed in order metals extraction such as: Cu, Zn and In. Leaching was performed in glass beakers covered with watch glasses on a magnetic stirrer with stirring and heating with the introduction of air for the necessary processes, Figure 2. Three types of leaching were applied:

1. Chloride leaching-using HCl acid solution
2. Leaching in nitric acid solution
3. Leaching in a solution of sulfuric acid

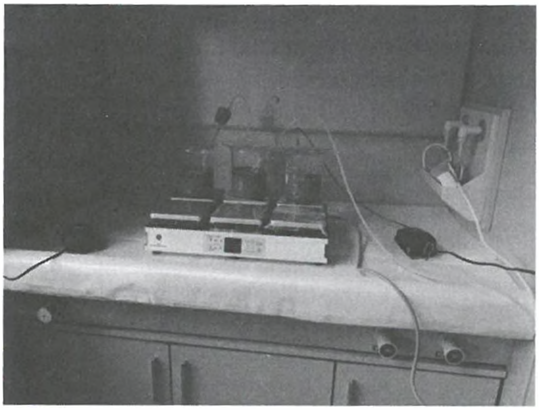

Figure 2 Leaching of jarosite on a magnetic stirrer

After leaching, each sample was filtered and washed. The volume of leach solution together with wash water was measured and 50 mL of the total volume of the solution was weighed in a normal vessel and given for chemical analysis.

RESULTS AND DISCUSSION

Chloride leaching in a solution of hydrochloric acid with air introduction

Leaching in hydrochloric acid was performed by changing the parameters: acid concentration, temperature and leaching time. The results of metals leaching are shown in Table 3.

Table 3 Recovery of metals by HCl leaching

HCl concentration	**Temperature**	**Leaching time**	**Solid: Liquid ratio**	**Metals Recovery**		
				Cu %	**Zn %**	**In %**
10%	room	1h	S:L = 1:4	19.70	14.83	17.02
10%	60 ^{0}C	1h	S:L = 1:4	43.99	35.06	64.03
10%	80 ^{0}C	1h	S:L = 1:4	56.00	52.86	95.06
20%	60 ^{0}C	1h	S:L = 1:4	70.25	92.12	98.00
20%	60 ^{0}C	2h	S:L = 1:4	68.83	57.60	99.12
20%	60 ^{0}C	4h	S:L = 1:4	78.34	70.88	99.01
20%	60 ^{0}C	6h	S:L = 1:4	87.24	95.20	98.50

It can be seen from the Table 3 that, using 20% HCl at a temperature of 60 ^{0}C, for the time of 1h, at a phase ratio of S:L = 1:4 can achieve over 70% recovery of Cu over 90% recovery of Zn and over 90% recovery of In.

Leaching in nitric acid solution

Leaching in nitric acid was performed under the following conditions:

- acid concentration of 20% HNO_3,
- temperature 60 ^{0}C,
- time 6h,
- phase ratio S:L = 1:5.

Metals recoveries are shown in Table 4.

Table 4 Recovery of metals by nitric acid leaching

HNO_3 concentration	**Temperature**	**Leaching time**	**Solid: Liquid ratio**	**Metals Recovery**		
				Cu %	**Zn %**	**In %**
10%	60 ^{0}C	6h	S:L = 1:5	40.25	39.50	63.33
15%	60 ^{0}C	6h	S:L = 1:5	47.39	44.22	68.10
20%	60 ^{0}C	6h	S:L = 1:5	50.79	47.41	71.20

Leaching in nitric acid showed relatively good leaching of Indium but also relatively low leaching of Cu and Zn.

Experimental laboratory tests of the leaching process in sulfuric acid solution with the introduction of air

Leaching with sulfuric acid was done using different acid concentrations of 2%-15%, under different conditions: temperature, leaching time and phase ratio. The results of metals recoveries are shown in Table 5.

Table 5 Recovery of metals by sulfuric acid leaching

Experiment No.	H_2SO_4 conc.	Temp.	Leaching time	Solid:Liquid ratio	Metals Recovery		
					Cu %	Zn %	In %
1.	2%	60 ^{0}C	6h	S:L = 1:4	7.87	13.22	6.50
2.	5%	60 ^{0}C	6h	S:L = 1:4	23.25	31.20	19.70
3.	10%	60 ^{0}C	6h	S:L = 1:4	46.98	47.49	42.70
4.	15%	60 ^{0}C	6h	S:L = 1:4	44.87	67.93	70.04
5.	2%	90 ^{0}C	6h	S:L = 1:4	10.15	17.81	5.13
6.	5%	90 ^{0}C	6h	S:L = 1:4	29.47	51.28	18.95
7.	10%	90 ^{0}C	6h	S:L = 1:4	54.15	82.97	37.10
8.	15%	90 ^{0}C	6h	S:L = 1:4	55.31	76.19	52.75
9.	2%	90 ^{0}C	1h	S:L = 1:4	12.10	22.02	6.63
10.	5%	90 ^{0}C	1h	S:L = 1:4	23.46	33.87	14.91
11.	10%	90 ^{0}C	1h	S:L = 1:4	44.09	30.19	37.80
12.	10%	90 ^{0}C	6h	S:L = 1:5	53.17	61.46	42.96
13.	10%	90 ^{0}C	6h	S:L = 1:10	75.80	84.96	77.50
14.	10%	90 ^{0}C	6h	S:L = 1:15	87.85	72.08	96.80
15.	15%	60 ^{0}C	1h	S:L = 1:4	54.54	51.18	59.90
16.	15%	90 ^{0}C	1h	S:L = 1:4	54.85	63.96	56.12
17.	15%	90 ^{0}C	6h	S:L = 1:5	68.68	73.02	68.50
18.	15%	90 ^{0}C	6h	S:L = 1:10	93.76	91.64	97.59
19.	15%	90 ^{0}C	6h	S:L = 1:15	93.48	80.04	98.74
20.	20%	90 ^{0}C	6h	S:L = 1:5	93.34	90.88	99.07
21.	30%	90 ^{0}C	6h	S:L = 1:5	93.39	88.36	98.80

Table 5 shows the different leaching conditions, under which different metal recovery occur. It can be seen from the table that using 15% H_2SO_4, at a temperature of 90 ^{0}C, leaching time 6h, with phase ratio S:L = 1:10, by introducing air, recovery of Cu and Zn were over 90% individually, and recovery of In was 97.59%. Under these conditions, one experiment was performed without the introduction of air. The results showed that the percentage of metal leaching is the same, which means that the process is possible without the introduction of air. Research by some authors has shown that by treating similar material under almost the same conditions (experiment no. 18), a high recovery of Zn and In can be achieved [6].

The solution obtained under the leaching conditions shown in experiment no.18 is acceptable for further treatment. Considering the price of sulfuric acid in relation to others that were used for leaching and working conditions that are not rigorous, it is considered that the choice of this acid is profitable. The resulting solution under these conditions can be further treated in order to selectively separations of the metals from the solution.

CONCLUSION

For the treatment of jarosite waste different kind of acids are used. The obtained metals recoveries under accepted leaching conditions are shown in order:

-20% HCl	(600C, 1h, S:L = 1:4)	70.25% Cu	92.12% Zn	98.00 %In,
-20% HNO_3	(600C, 6h, S:L = 1:5)	50.79% Cu	47.41% Zn	71.20 %In,
-15% H_2SO_4	(900C, 6h, S:L = 1:10)	93.76% Cu	91.64% Zn	97.59 %In.

It can be seen that leaching of jarosite using HCl acid under the most aggressive conditions results in high recovery of Cu, Zn and In, while leaching of jarosite in nitric acid yields relatively good recovery of In but also low recovery of Cu and Zn. Leaching in sulfuric acid yields the best recovery of all considered metals. Leaching with hydrochloric acid under selected conditions would not be safe due to the aggressive environment. Leaching with nitric acid releases a large amount of aggressive nitrogen oxides. Considering the price of sulfuric acid in relation to others that were used for leaching and working conditions that are not rigorous, it is considered that the choice of this acid is justified. The solution obtained using sulfuric acid would be further treated in order to selectively separations of the metals.

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REFERENCES

1. Yong-xing, Z., Jin-fang, L.V., Wei, L., Wen-qing, Q., Shu-ming, W. (2016) An innovative technology for recovery of zinc, lead and silver from zinc leaching residue. Physicochem. Probl. Miner. Process., 52 (2) 943–954.
2. Yayun, W., Huifen, Y., Weihao, Z., Ronglong, S., Bo, J. (2018) Study on recovery of lead, zinc, iron from jarosite residues and simultaneous sulfur fixation by direct reduction. Physicochem. Probl. Miner. Process., 54 (2) 517-526.
3. Stanojević, D., Filipović-Petrović, L. (2014) Doprinos integrisanoj valorizaciji metala u hidrometalurgiji cink. Zaštita materijala, 55 (1) 25-35.
4. Stanojević, D., Todorović, M. (1998) Valorisation of useful metals from by-products of hydrometallurgical manufacturing of zinc. 1st International Conference of Chemical Societies of the South-East European Countries: "Chemical Sciences and Industry", 1.-4. June, Solun, Greece, Vol II, PO 729.
5. Stanojevic, D., Rajkovic, M.B., Toskovic, D. (2006) Extraction of useful metals from lead-silver cake in the process of hydrometallurgical zinc production by leaching in calcium-chloride solution. Buletin of Electrochemistry, Karaikudi (India), 22, 337-341.
6. Deng, Z. (2016) Acid Leaching Zinc and Indium with Reduction Ferric Simultaneously From Marmatite and High Iron Neutral Leaching Residue. Rare metal technology, First published: 22 January, Chapter 6.