ZINC EXTRACTION FROM GHAZOUAT LEACH RESIDUES BY USING JAROSITE METHOD

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Abstract: In this paper, it was aimed to select and propose a feasible as well as an applicable method, for the extraction of zinc that was present in the disposed GHAZOUAT leach residues having 17.82 wt. % Zn and 20.82 wt. % Fe. After the determination of the components of the residue, the acid leaching was performed to reclaim Zn sequentially. The acid leaching experiments were carried out for Zn extraction by controlling acid concentration, reaction duration and temperature. At the optimum conditions, 240 g/L H_2SO_4 at 90 °C for 210 min, 80% of initial iron content was removed, and the resultant overall zinc extraction was usually superior than 96%.

Keywords: *sphalerite, Zn, acid leaching, leaching residue, extraction*

1. INTRODUCTION

Zinc is the third largest non-ferrous metal in the world, and is conventionally produced from sphalerite by roast-leach-electrolysis (RLE) process. Zinc is the most important non-ferrous metal after copper and aluminum. In Algeria, major reserves are composed of sphalerite, and have been used as primary source for Zn production at Ghazouat, plant in Algeria where processing electrowinning route is utilized. During

its operation, Ghazaout, has produced an important quantity of residues with a preliminary chemical composition of 17.82% Zn in mass.
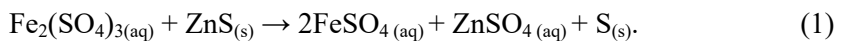
Due to the high metal content and its environmental significance, these residues are regarded as secondary sources rather than wastes for sustainable production. In Ghazouat, the zinc residues typically contain 20.82% iron. The iron commonly associated with zinc concentrates can be present as either a replacement for zinc in sphalerite or marmatite or as separate minerals, such as pyrite, pyrrhotite, or chalcopyrite. Consequently, the disposal of iron residues is an integral part of the design and operation of zinc refineries (Buban 1999).

The hydrometallurgical treatment of sphalerite has always been concerned with the separation of zinc from iron. This arises from the fact that most zinc residus contain iron. Prior to the hydrometallurgical treatment of a sphalerite, it is necessary to utilize a roasting step. During roasting the iron extant in the concentrate combines with ZnO to form $ZnO\text{-}Fe_2O_3$. Neutral leaching of the calcine ends up with the dissolution of free ZnO as ZnSO4, but the zinc trapped in $ZnO\text{-}Fe_2O_3$ will not be leached. Although hot H_2SO_4 leaching can liberate the zinc in the ferrite, iron associated with zinc also dissolves.

The hydrometallurgical recovery of zinc in ferrite became industrially realizable only after the development of effective iron precipitation techniques. Zinc electrolyte contains only very limited amounts of iron. There are several studies on the removal of iron from Zinc electrolytes (Acharya et al. 1992; Principe, Demopoulos 1999; Dutrizac 1999; 2000).

Exact environmental restrictions imposed on sulfide smelters and the necessity of using complex deposits have stimulated the development of alternative process, in particular the hydrometallurgical ones. During the latest years, attention has been granted to leaching of sphalerite concentrates with nitric acid (Bjorling 1954), sulfuric acid (Forward, Veltman 1959; Parker 1961; Begar et al. 2015), hydrochloric acid (Mizoguchi, Habashi 1981; Majima et al. 1981), and solutions containing ferric ions (Bobeck, Su 1985; Begar et al. 2012). Hydrometallurgical pretreatment of sulfides can be performed using different process (Havlik, Kammel 2000; Havlik et al. 2001).

The leaching of sphalerite concentrates with ferric iron under atmospheric pressure has been studied in several studies (Kammel et al. 1987; Crundwell, Verbaan 1987; Suni et al. 1989; Cheng et al. 1994; Lochmann, PedlEFk 1995). As the zinc is leached, the ferric iron is reduced to ferrous iron by the sulphur in the sphalerite according to the following reaction:

$$Fe_2(SO_4)_{3(aq)} + ZnS_{(s)} \rightarrow 2FeSO_{4\,(aq)} + ZnSO_{4\,(aq)} + S_{(s)}. \tag{1}$$

In the case of sphalerite, the effects of temperature, Fe(III) concentration, pH, and particle size on the dissolution kinetics were studied at different levels (Romankiw, de Bruyn 1963; Rimstidt et al. 1994; Olanipekun 1999; De Giudici et al. 2002).

The necessity for economic ways of removing high concentrations of iron from solution was met by the development of several processes, such as the hematite, goethite, magnetite, and jarosite processes (Brown, 1971; McAndrew et al. 1975; Arregui et al. 1979; 1980).

The jarosite process, which has evinced to be the most widely adopted (Brown 1971; Dutrizac 1980; Kershaw, Pickering 1980; Arauco, Doyle 1986). The simple neutralization of the sulfate solution is not advisable owing to the formation of a gelatinous ferric hydroxide precipitation. The principal advantage of precipitating jarosite--type compounds is comparative ease of settling, filtration, and washing of the residue; iron gels are therefore avoided.

In commercial operations, ferrous iron is reoxidized with oxygen in order to continue the leaching (Svens et al. 2003). The zinc concentrate can successfully be used just as a reducing agent, and is then leached at the same time. This would be a step-in leach process, where jarosite is precipitated without necessity for neutralization with calcine, and thus, the problem with losses of zinc is avert (Fugleberg 2002).

Lochmann and PedlEFk leached sphalerite concentrate in an acidic ferric sulfate solution. It was concluded that a layer of elemental sulfur controlled the dissolution rate (Lochmann, PedlEFk 1995).

Zinc has been recovered from sulphide concentrates by hydrometallurgical routes. The disposal of iron is a major difficulty for the industry, and is directly responsible for low overall zinc recoveries. The introduction of the jarosite process permitted the precipitation of iron in an easily filterable form, thereby growing maximal zinc recovery.

2. EXPERIMENTAL

2.1. MATERIALS AND ANALYSIS

Zinc leaching residue (ZLR) used in this study was obtained from a zinc hydrometallurgical plant in Ghazaouat, Algeria. The samples were dried before grinding and sieving to obtain required fractions. Elemental composition of the residue was determined by volumetric, atomic absorption and spectrophotometry. The various elements in the samples are summarized in Table 1. The crystalline phases of the samples were investigated by X-ray powder diffraction. Examining the natural powder shows that franklinite, anglesite, gypsum, and bianchite are the main crystal mineral phases in the residue. Secondly, the sample was analyzed at 500 °C that was calcined to confirm the presence of gypsum. The main reflection gypsum disappeared; new thinking appears to 504 °C which could be attributed to the anhydrous form a zinc sulphate, zincosite.

Table 1. Chemical composition of residues

Elements	Content [wt. %]	Elements	Content [wt. %]	Elements	Content [wt. %]
Zn (Total)	17.82	Cu	0.24	K	0.281
Zn(H$_2$O)	4.19	Ag	408.75	As	0.051
Zn(H$_2$SO$_4$)	8.33	Ni	0.014	Mg	1.02
Fe	20.82	Co	0.0032	Al	0.505
Ca	2.08	Mn	1.325	Si(SiO$_2$)	8.153
Pb	7.697	Tl	0.0026	S(ZnS)	1.15
Cd	0.177	Na	0.032	Cl	0.0078

Elements composition of the residue after roasting was determined by volumetric, atomic absorption and spectrophotometry. The various elements found are summarized in Table 2.

Table 2. Chemical composition of residues after roasting

Elements	Content [wt. %]	Elements	Content [wt. %]	Elements	Content [wt. %]
Zn (Total)	17.82	Cu	0.24	K	0.281
Zn(H$_2$O)	4.19	Ag	408.75	As	0.051
Zn(H$_2$SO$_4$)	8.33	Ni	0.014	Mg	1.02
Fe	20.82	Co	0.0032	Al	0.505
Ca	2.08	Mn	1.325	Si(SiO$_2$)	8.153
Pb	7.697	Tl	0.0026	S(ZnS)	1.15
Cd	0.177	Na	0.032	Cl	0.0078

2.2. EXPERIMENTAL PROCEDURE

During the leaching experiments hot plate magnetic stirrer and balloons were used as an experimental equipment. Temperature was adjusted and kept controlled by a contact thermometer.

The stirring rate was kept constant at 250 rpm. All chemicals were of high quality and FNR quality de-ionized water (<10 μs/cm) was used throughout the experiments.

Moreover, a water cooled condenser was attached to the system to avoid evaporation losses at high temperatures.
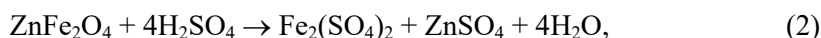
Chemical analyses on undissolved solids were performed by dissolving them in HF added aqua regia at elevated temperatures. Leach liquors and obtained solutions were chemically analyzed using an Atomic Absorption Spectrophotometer (Varian AA 240). X-Ray Diffraction (XRD) analyses of the solids were also done.

3. RESULTS AND DISCUSSION

In the light of the preliminary chemical-physical characterization, the most hopeful leaching agent for zinc was hot H_2SO_4 for zinc. Therefore, the experiments were performed using that aqueous solution under different experimental conditions.

Since water leaching was not yield acceptable values, the experiments were performed in acidic solutions where the individual effects of temperature, acid concentration, and reaction duration were evaluated.

Dissolution reactions for zinc ferrite ($ZnFe_2O_4$) with H_2SO_4 under the optimum conditions as follows:

$$ZnFe_2O_4 + 4H_2SO_4 \rightarrow Fe_2(SO_4)_2 + ZnSO_4 + 4H_2O, \tag{2}$$

$$3Fe_2(SO_4)_3 + 2NH_4OH + 10H_2O \rightarrow (NH_4)_2[Fe_6(OH)_{12}(SO_4)_4] + 5H_2SO_4. \tag{3}$$

3.1. EFFECT OF ACID CONCENTRATION

Among the effective factors, initial sulphuric acid concentration was taken into consideration first while the reaction duration and temperature were kept constant as 4 h, and 95 °C, respectively. These conditions were predefined such that they would be the closest values to the plant's original production line.

The results, which are presented in Fig. 1, simply indicated that when the acid concentration was increased from 200 to 250 g/L, the metal extractions also increased substantially.
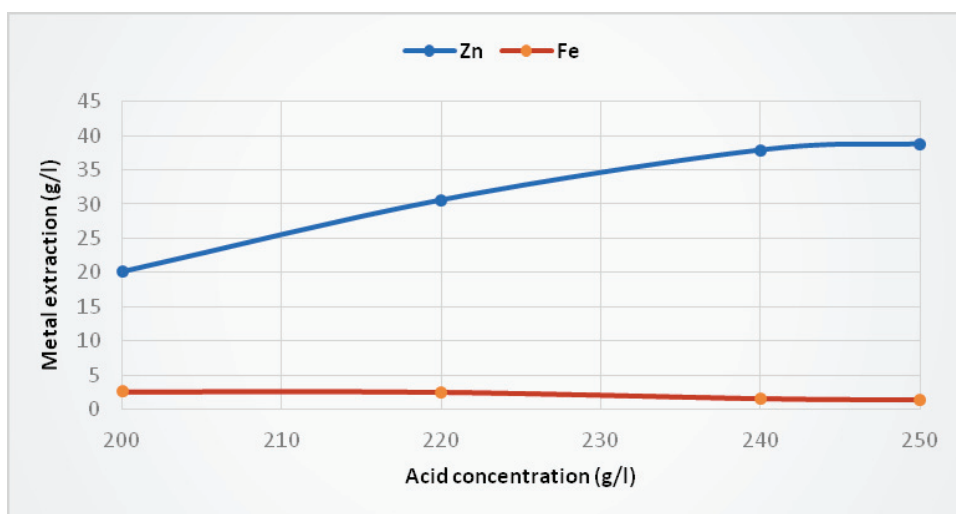

Fig. 1. Effect of acid concentration on metal extraction

However, the leaching trends for Zn and Fe was different considerably such that Zn after 240 g/L limit reached a plateau around 38.75 g/L.

On the contrary, Fe dissolved in concentrated acid solutions, and continued its decreases trend throughout the examined acid concentration range. Such findings were in good agreement with the other researchers (Kahraman 1980; Addemir 1982; Saltoğlu 1988) in terms of acidity, reaction duration and reaction temperature.

The available acid supply in actual production line, i.e., spent electrolyte had an average acidity of 240–250 g/L. Therefore, 240 g/L initial acid concentration was chosen as the optimum acid concentration for the following experiments.

3.2. EFFECT OF REACTION TEMPERATURE

The reaction temperature was varied in a range from 70 °C to 110 °C while acid concentration, and reaction duration were kept constant at 240 g/L, and 4 h, respectively.

As seen in Fig. 2, along with other elements at different experimental conditions, leach extraction of Zn increased from 18.97 g/L to 32.25 g/L with the increasing temperature, and reached a maximum at between 90 and 95 °C. It is well famous that the rate of zinc ferrite reaction with H_2SO_4 increases with increasing temperature (Jha, Kumar, Singh 2001). At the same time, the dissolution of Fe decreased. This tendency was in good agreement with the previous results, as the amount of dissolved Fe was a function of temperature, acidity, and duration. Therefore, the optimum reaction temperature was chosen as between 90 and 95 °C, as the Zn extraction yielded its maximum value with tolerable Fe content in pregnant leach solution.
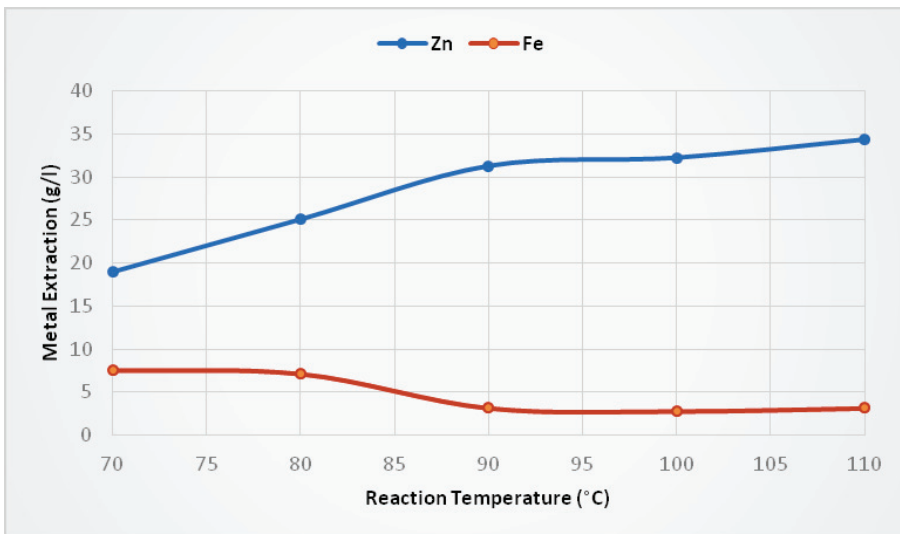

Fig. 2. Effect of reaction temperature on metal extraction

3.3. EFFECT OF REACTION DURATION

Since the extractions of metals can be improved at prolonged periods of leaching, it was intended to find such relations for this residue too.

Thus, the leaching tests were carried out between 3 h and 4.5 h. During these tests, H_2SO_4 concentration, and reaction temperature were maintained at 240 g/L, and 95 °C, respectively.

According to the results of experiments illustrated in Fig. 3, the reaction durations up to 4 h resulted in a steady increase for Zn extraction reaching as high as 35.93 g/L. Meanwhile, the dissolution behaviour of Fe was also investigated, and it was resulted in a decrease in [Fe]. For the optimum leaching conditions between 3.5 h and 4 h of reaction duration was chosen.
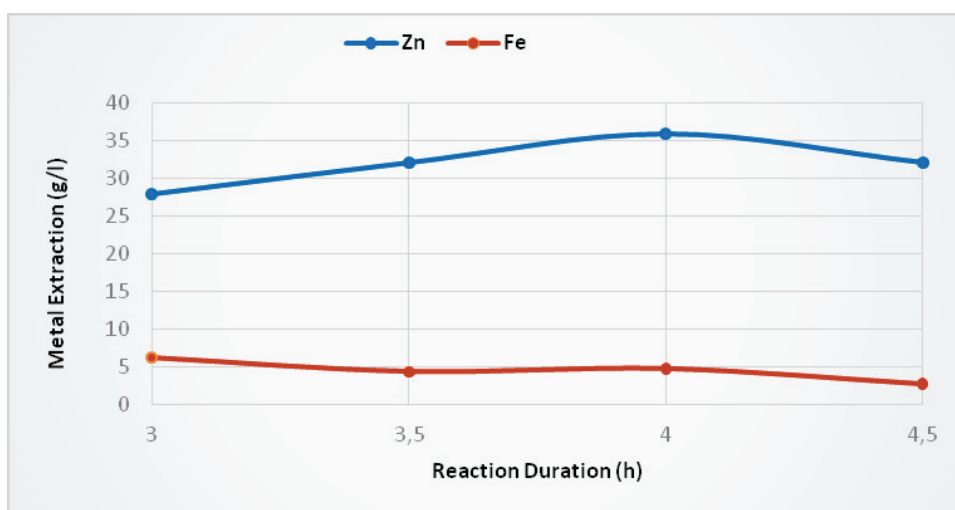

Fig. 3. Effect of reaction duration on metal extraction

After the sulphuric acid leaching experiments, in order to minimize Fe removal expenses at solution purification stage, acid concentration and reaction duration had to be limited by compromising with Zn extractions. Therefore, it can be claimed that the optimum conditions for the leaching, were obtained as 240 g/L H_2SO_4 concentration, between 90 and 95 °C reaction temperature, and between 3.5 h and 4 h reaction duration.

3.4. SIMPLIFIED PROCESS FLOW

After the experimental study that showed encouraging results, it was necessary to incorporate the jarosite process in the leach circuit while avoiding major changes.
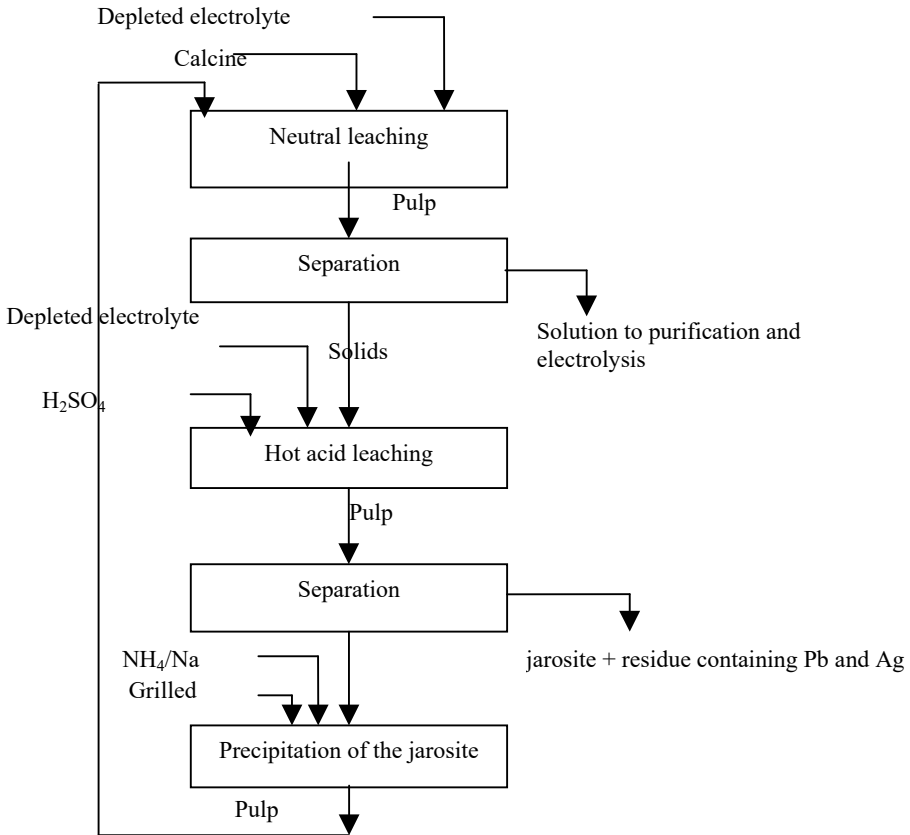
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Depleted electrolyte

Calcine

Neutral leaching

Pulp

Separation

Solution to purification and electrolysis

Depleted electrolyte

Solids

H_2SO_4

Hot acid leaching

Pulp

Separation

jarosite + residue containing Pb and Ag

NH_4/Na
Grilled

Precipitation of the jarosite

Pulp

Fig. 4. Simplified process flow sheet

3.5. ADVANTAGES OF SUCH A PROCESS

The pulp of the jarosite precipitation containing the zinc in the form of ferrous or oxide put to excess upon neutralization is recycled, and therefore, the Zn can be recovered during the hot acid leaching.

It also makes it possible to have a single residue.

The residue obtained may contain a great deal of Pb and Ag which can be recovered.

4. CONCLUSION

In the light of physical, chemical, and mineralogical investigations and general literature survey, the leach residue of Ghazaouat (Algeria) displayed a complex nature, and

contained 17.82% Zn and 20.82% Fe. Having defined the characteristics, as the process economy is the basic limitation for production, hydrometallurgical treatment methods were assessed in order to find the optimum extraction conditions of zinc.

Water leaching experiments were ended with insufficient zinc extractions at different duration and temperature which led to hot sulphuric acid treatment of leach residue. By hot acid leaching 32.25 g/L of Zn was taken into solution at the optimum conditions of 240 g/L H_2SO_4, between 3 h 30 min and 4 h 00 min, between 90 and 95 °C.

The simplified process flow, given in Fig. 4, can be proposed by considering the above-mentioned optimum conditions. After successive treatment of the residues under the optimum conditions, in the acid leaching step.

REFERENCES

BEGAR A., DJEGHLAL M., OULD HAMOU M., Sep 2015, *Study of the reaction of dissolution of Sphalerite in the absence of oxygen*, Russian Journal of Non-Ferrous Metals,

BEGAR A., DJEGHLAL M., Jun 2012, *Recovery process of the mineral Sphalerite of Chaabet El Hamra's deposit (Algeria)*, The European Physical Journal Conferences.

ACHARYA S., ANAND S., DAS R.P., 1992, *Iron Rejection through Jarosite Precipitation during Acid Pressure Leaching of Zinc Leach Residue*, Hydrometallurgy, 31, 10–110.

ARAUCO H., DOYLE F.M., 1986, *Hydrolysis and Precipitation of Iron during Pressure Leaching of Zinc Sulphide Materials*, Hydrometallurgical Reactor Design and Kinetics, R.G. Bautista, R.J. Wesely, G.W. Warren (Eds.), TMS, 187–207.

ARREGUI V., GORDON A.R., STEINTVEIT G., 1979, *The Jarosite Process –Past, Present and Future*, LeadZinc-Tin '80, J.M. Cigan, T.S. Mackey, T.J. O'Keefe (Eds.), TMS of AIME, 97–123.

BJORLING G., 1954, *Lixiviation of sulphidic minerals under oxygen pressure*, Metallurgie, 8, 781–784.

BOBECK G.E., SU H., 1985, *The kinetics of dissolution of Sphalerite in ferric chloride solutions*, Metall. Trans., 16B, 413–424.

BROWN J.B., 1971, *Jarosite-Goethite Stabilities at 25 °C, 1 atm*, Mineral Deposita (Berl.), 6, 245–252.

BUBAN K.R., COLLINS M.J., MASTERS I.M., 1999, *Iron control in zinc pressure leach processes*, Journal of Metallurgy, 51, 23–25.

CHENG C.Y., CLARKSON C.J., MANLAPIG E.V., 1994, *The leaching of zinc sulphide concentrates in sulphate–chloride solutions with ferric ions*, The AusIMM Proceedings, 2, 57–62.

CRUNDWELL F.K., VERBAAN B., 1987, *Kinetics and mechanisms of the non-oxidative dissolution of Sphalerite (zinc sulphide)*, Hydrometallurgy, 17, 369–384.

DE GIUDICI G., VOLTOLINI M., MORET M., 2002, *Microscopic surface processes observed during the oxidative dissolution of Sphalerite*, Eur. J. Mineral., 14, 757–762.

DUTRIZAC J.E., 1999, *The Effectiveness of Jarosite Species for Precipitating Jarosite*, Journal of Metals, 51, 12.

DUTRIZAC J.E., 1980, *The Physical Chemistry of Iron Precipitation in the Zinc Industry*, Lead-Zinc-Tin '80, J.M. Cigan, T.S. Mackey, T.J. O'Keefe (Eds.), AIME, New York, 532–564.

DUTRIZAC J.E., CHEN T.T., 2000, *The Behaviour of Gallium During Jarosite Precipitation*, Mineral Processing and Extractive Metallurgy Review, 21, 16.

FORWARD F.A., VELTMAN H., 1959, *Direct leaching of zinc sulphide concentrate by Sherrit Gordon*. J. Met., 11, 836–840.

FUGLEBERG S., 2002, *Method for the hydrolytic precipitation of iron*, Patent No. WO0246481.

HAVLIK T., KAMMEL R., 2000, *Procedure for selective copper recovery from tetraedrite*, Metall., 54, 26–29.

HAVLIK T., MIŠKUFOVÁ A., TATARKA P., 2001, *Modern methods of oxidative chalcopyrite leaching*, Acta Metall. Slovaca, 4, 62–68.

HAVLIK T., POPOVIČOVÁ M., UKAŠÍK M., 2001, *Use of microwave energy for chalcopyrite leaching*, Metall., 55, 332–335.

JHA M.K., KUMAR V., SINGH R.J., 2001, *Review of hydrometallurgical recovery of zinc from industrial wastes*, Resources, Conservation and Recycling, 33, 1–22.

KAMMEL R., PAWLEK F., SIMON M., XI-MING L., 1987, *Oxidizing leaching of Sphalerite under atmospheric pressure*, Metall., 41, 158–161.

KERSHAW M.G., PICKERING R.W., 1980, *The Jarosite Process – Phase Equilibria*, Lead-Zinc-Tin '80, J.M. Cigan, T.S. Mackey, T.J. O'Keefe (Eds.), AIME, New York, 565–580.

LOCHMANN J., PEDLEFK M., 1995, *Kinetic anomalies of dissolution of Sphalerite in ferric sulfate solution*, Hydrometallurgy, 37, 89–96.

MAJIMA H., AWAKAURA Y., MISAKI N., 1981, *A kinetic study on nonoxidative dissolution of Sphalerite in aqueous hydrochloric acid solution*, Metall. Trans., 12B, 645–649.

MCANDREW R.T., WANG S.S., BROWN W.R., January 1975, *Precipitation of Iron Compounds from Sulphuric Acid Leach Solutions*, CIM Bulletin, 101–110.

MIZOGUCHI T., HABASHI F., 1981, *The aqueous oxidation of complex sulfide concentrates in hydrochloric acid*, Int. J. Miner. Process., 8, 177–193.

OLANIPEKUN E., 1999, *Kinetics of Sphalerite leaching in acidic ferric chloride solutions*, Trans. Indian Inst. Metals, 52, 81–86.

PARKER E.G., 1961, *Oxidative pressure leaching of zinc concentrate*, CIM Bull., 74 (5), 145–150.

PRINCIPE F.T., DEMOPOULOS G.P., 1999, *The Separation and Concentration of Iron from Zinc Process Solutions*, Journal of Metals, 51, 12.

RIMSTIDT J.D., CHERMAK J.A., GAGEN P.M., 1994, *Rates of reaction of galena, Sphalerite, chalcopyrite and arsenopyrite with Fe (III) in acidic solutions*. In: C.N. Alpers, D.W. Blowes (Eds.), *Environmental Geochemistry of Sulphide Oxidation*, Am. Chem. Soc. Symp. Series, 550, Washington, DC, pp. 2–13.

ROMANKIW L.T., DE BRUYN P.L., 1963, *Kinetics of dissolution of zinc sulphide in aqueous sulphuric acid*. In: M.E. Wadsworth, E.T. Davis (Eds.), Unit Processes in Hydrometallurgy, Vol. 24, Gordon and Breach Science Publishing, pp. 45–66.

SUNI J., HENEIN H., WARREN G.W., REDDY D., *Modelling the leaching kinetics of a Sphalerite concentrate size distribution in ferric chloride solution*, Hydrometallurgy, 22, 25–38.

SVENS K., KERSTIENS K., RUNKEL M., 2003, *Recent experiences with modern zinc processing technology*, Erzmetall., 56, 94–103.