

Leaching of Polymetallic Cu-Zn-Pb Concentrate with Sodium Nitrate in Sulphuric Acid

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The results of polymetallic sulphide Cu-Zn-Pb concentrate leaching with sulphuric acid in the presence of sodium nitrate as an oxidizing agent, at atmospheric pressure, are presented and discussed. Chemical composition and phase ratio of the starting concentrate and solid residuals after the leaching process are shown. Chemical reactions of leaching and their thermodynamic probabilities are predicted based on the calculated Gibbs energies and analysis of E-pH diagrams. The influence of temperature and time on the leaching degree of the concentrate's components is experimentally determined. It is shown that it is possible to obtain copper, zinc and iron in a solute form, while lead in the anglesite ($PbSO_4$) form remains in the solid residual after the leaching process. The iron is being oxidized to Fe(III)-sulphate, which takes part in a sulphide leached minerals and turns into Fe(II)-sulphate.

Key words: *polymetallic Cu-Zn-Pb concentrate, leaching, sodium nitrate, sulphuric acid*

1. INTRODUCTION

Non-ferrous metals and iron usually appears in a form of sulphide complex ores. Large deposits of complex ores often contain chalcopyrite, sphalerite, galena and pyrite, which are fine-grained structures complexly fused with tailings minerals in complex mineral forms [1]. Sometimes, when it is difficult to prepare flotation concentrates of the individual minerals, then it is easier to prepare bulk concentrates [2]. Although

treatments by pyrometallurgical process are not attractive, because a large amounts of SO_2 is produced, approximately 80-85% of world's total copper is produced pyrometallurgically, and 80% of world's total zinc is produced by roasting-leaching-electrowinning process, and 20% is produced by Imperial Smelting Process [3-4].

Hydrometallurgical processes offer a great potential for treating complex sulphide ores, and it results in increased metal recoveries and reduced air pollution hazards. Recently, an increased interest is remarked related to the possible application of various reagents in a hydrometallurgical processing of sulphide concentrates. Ferric [5-11] and cupric [12, 13] ions, bacteria [14-17], and other oxidants [3, 4, 18-26] were used as oxidative leaching agents of complex sulphides in su-

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lphate and chloride media under atmospheric or extended pressure leaching conditions.

Some of the hydrometallurgical processes developed for copper ores and concentrates treatment can also

be considered for a treatment of complex sulphides. The previous and current developments are discussed in references [5, 14, 15, 18, 23, 24, 27-44]. The main processes and parameters are presented in Table 1.

Table 1. Hydrometallurgical processes for treatment of copper ores and concentrates

Process	Temperature (°C)	Pressure (atm)	Regrind D80 (µm)	Special conditions
Activox (McDonald at al., 2007; Corrans at al., 1993; Streltsova at al., 2003)	100-110	≈12 P(O ₂) ≈10	5-15	Fine grinding combined with high oxygen overpressure overcomes chalcopyrite passivation
Albion (Hourn at al., 1999)	85	1	5-10	Atmospheric ferric leaching of very finely ground concentrate
Anglo-American – University of British Columbia (McDonald at al., 2007; Dreisinger, 2003; Dreisinger at al., 2002)	150	10-12	10-15	Modest regrind combined with surfacants for chalcopyrite leaching
Bactech / Mintek low temperature bioleach (Miller at al., 2006)	35	1	5-10	Low T bioleach (35-50°C) requires very fine grind to overcome chalcopyrite passivation
BIOCOP™ (Dew at al., 2003)	65-80	1	37	High T bioleach (65-80°C) uses thermophilic bacteria
Cymet (Kruesi at al., 1973)	80-100	1	/	Electrochemical dissolution in the presence of ferric chloride, which finally produces copper powder
Cyprus (Anon, 1977))	80-100	1	/	Chalcopyrite concentrate leach in two-stages using a mixed solution of ferric chloride and copper chloride
CESL copper (McDonald at al., 2007; Jones, 1996)	140-150	10-12	37	Chloride catalized leach of chalcopyrite producing basic copper sulphate precipitate in the autoclave
Dynatec (Kofluk at al., 1998; Stiksmas at al., 2000)	150	10-12	37	Chalcopyrite and sphalerite is leached using low grade coal as an additive
Minimet (Demarthe at al., 1976)	90-100	1	/	Atmospheric cupric chloride leaching of complex concentrate. To keep CuCl, PbCl ₂ and AgCl in solution, NaCl was added to the leaching agent.
Mount Gordon (Richmond at al., 2002; Dreisinger at al., 2002)	90	8	100	Pressure oxidation of chalcopyrite/pyrite ore or bulk concentrate in an iron sulfate rich electrolyte
NITROX (Van Weert at al., 1986)	80-100	1	/	Atmospheric leach refractory gold ores and concentrates by hot nitric acid
NSC (Sunshine Mine) (McDonald at al., 2007; Ackerman, 1990; Anderson, 2003; Anderson at al., 1992, 1996)	130-150	7 P(O ₂) ≈ 4	10	Nitrite catalized leach of chalcopyrite by sulphuric acid leaching agent containing cupri and feri chloride with oxygen pressure
PLATSOL (Fleming at al., 2001)	220-230	30-40	15	Total pressure oxidation in the presence of 10-20 g/dm ³ NaCl. Precious metals leached at the same time as base metals
Sepon copper (Baxter at al., 1978)	80-Copper 220-230- Pyrite	Atm 30-40	100 50	Atmospheric ferric leach for copper from chalcocite. Pressure oxidation of pyrite concentrate to make acid and ferric sulphate for copper leach
Sherritt-Cominco (Swinkels at al., 1978)	≈ 150	≈25 P(O ₂) ≈10	/	A two-stage process starting with the removal of sulphur and iron from low grade Cu concentrate. Then a high-grade Cu concentrate leach by sulphuric acid under oxygen pressure
Sherritt-Gordon (Bolton at al., 1979)	150	P(O ₂)≈3.5	44	Oxygen pressure oxidation complex concentrate. Copper and zinc go into solution, lead is transformed into PbSO ₄ and lead jarosite and is retained in the residue
Total pressure oxidation (McDonald at al., 2007; King at al., 1995; Marsden at al., 2003)	200-230	30-40 P(O ₂) ≈ 7	37	Extreme conditions of T and P designed to rapidly destroy refractory gold ores and concentrates in the presence of NaCl in the leaching agent

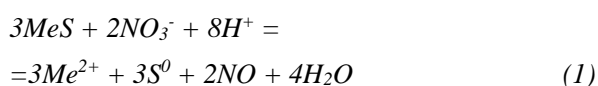
Much attention has been given to the development of nitric acid based processes for sulphide ores and concentrates, e.g. Habashi discuss that metal sulphide oxidation by nitric acid can be achieved in two ways [45]. In the first case, NO_3^- ion is oxidant, and during the reaction it is reduced to NO or NO_2 . In the second case, oxygen which arises from nitric acid decomposition is the oxidant.

Van Weert et al. [46] developed the NITROX process, which utilizes nitric acid to recover gold from refractory pyrite and arsenopyrite ores. They found that sulphide sulphur formed mainly elemental sulphur, while smaller part formed sulphate. The NO gas that is produced is directly oxidized by the air into the NO_2 , which dissolves in the solution and reacts with water to form HNO_3 , thereby completing the NITROX cycle. The most significant problem was high sulphate production. Droppert and Shang [47] showed that sulphate formation could be minimized by addition of a small excess of HNO_3 , followed by slow addition of HNO_3 keeping the acid concentration at a constant low level.

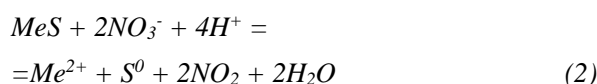
Some industrial operations use the nitric or nitrous acid added in a small concentration to the sulphuric acid, e.g. in oxygen extended pressure leach processes. At Sunshine Precious Metals, silver and copper are recovered from a complex sulphide concentrate at temperatures between 145° and 155°C and at total pressure of 709kPa [24, 39, 48]. In that case, nitrous acid were found to enhance the solubilization of minerals at lower temperatures and pressures, and the nitrous/sulphuric acid leach process is used with success.

Following successful operation in the Sunshine Pressure Leach plant, the catalysis under the extended pressure oxidation, using nitrogen species, is promoted as a nitrogen species catalysed (NSC) technology [23, 48]. It was demonstrated that the addition of nitrite ion in a small amounts catalyses the oxidation of sulfides in the presence of oxygen; recent data show that it is a fast reaction, typically less than 30 min, for slurry containing 100 g/L of solids [23]. The leaching process of metal sulphides by nitric acid as oxidant is more efficient in presence of NO^+ ions. The addition of NO^{2-} ions instead of NO^{3-} ions accelerates the formation of NO^+ ions, which further oxidises sulphide minerals at lower temperatures to the elemental sulfur [40, 48].

Oxidative dissolution of a sulphide concentrate using nitrate as the leaching agent in an acid medium take place with formation of elemental sulphur, and it can be represented by one of the following chemical reactions [20, 21, 49]:



or



Initially the rate of reaction is controlled by a surface chemical reaction and later on changes into a diffusion controlled.

General flow sheet for the treatment for the complex Cu-Zn-Pb concentrates is presented in Fig 1.

The objective of this work is performance of the leaching process using the selected complex Cu-Zn-Pb sulphide concentrates, from "Rudnik" flotation plant, by sulphuric acid solution in the presence of sodium nitrate.

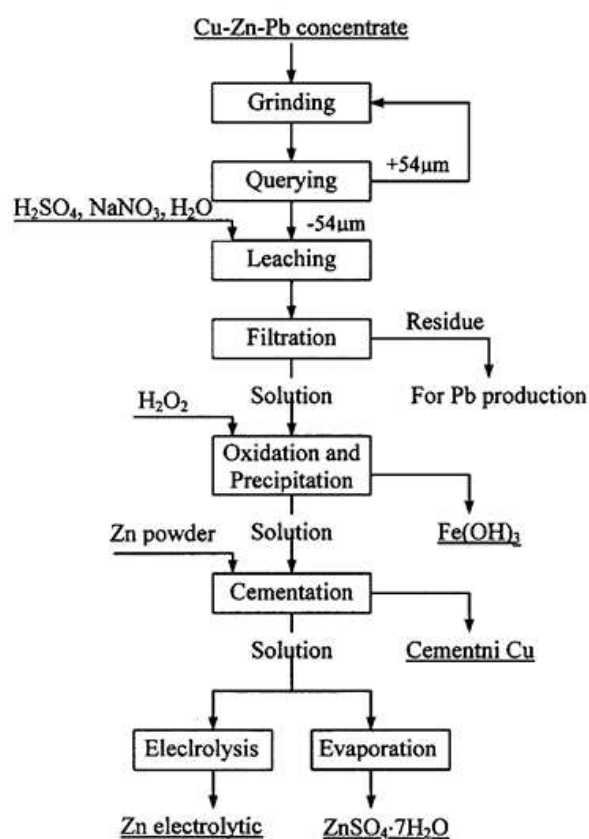
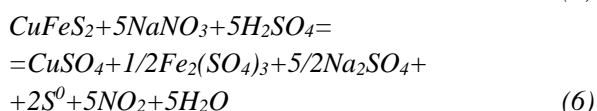
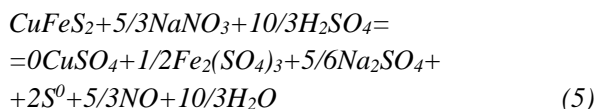
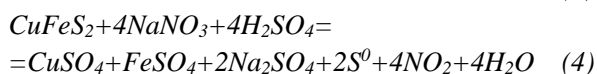
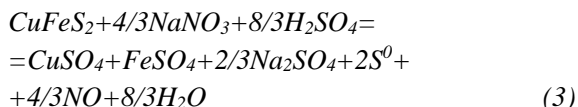


Figure 1 - General flow sheet for the treatment of the complex Cu-Zn-Pb concentrates

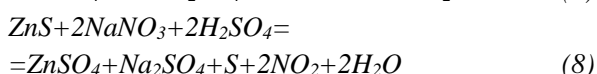
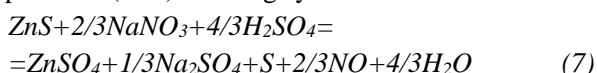
2. CHEMICAL REACTIONS AND THERMODYNAMICS

Based on the literature data and on the characterization of both produced solution and leaching solid residues, obtained by leaching of polymetallic concentrate containing chalcopyrite, sphalerite, galena and pyrrhotite in oxidized acidic medium, following chemical reactions were chosen in this study and then analyzed in the H_2SO_4 - NaNO_3 - H_2O system.

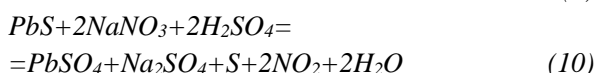
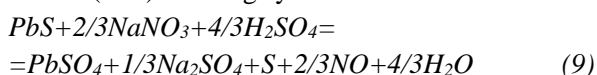
Chalcopyrite (CuFeS_2) leaching system



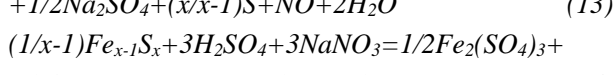
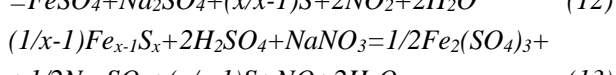
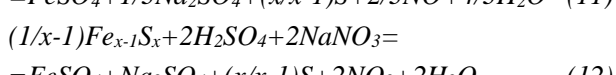
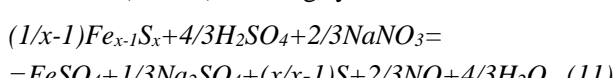
Sphalerite (ZnS) leaching system



Galenite (PbS) leaching system



Pirrotite ($\text{Fe}_{x-1}\text{S}_x$) leaching system



Thermodynamic analysis included calculation of standard Gibbs energy change and E-pH diagrams. In order to clarify the occurrence probability of quoted reactions (3)-(14), Gibbs energy change was calculated within a temperature range of 25 up-to 90 °C and the obtained values are given in Table 2.

Table 2. The calculated values of standard Gibbs energy change at temperatures 298 and 363 K (HSC) of the analysed reactions in the polymetallic concentrate-H₂SO₄-NaNO₃-H₂O system

Eq. no.	ΔG_{298}^0 (kJ/mol)	ΔG_{363}^0 (kJ/mol)	Eq. no.	ΔG_{298}^0 (kJ/mol)	ΔG_{363}^0 (kJ/mol)
(3)	-330.978	-341.369	(9)	-236.464	-241.964
(4)	-352.302	-391.600	(10)	-247.126	-267.079
(5)	-396.085	-408.423	(11)	-235.312	-240.721
(6)	-422.741	-471.211	(12)	-245.974	-265.836
(7)	-191.784	-196.993	(13)	-300.420	-307.775
(8)	-202.446	-222.108	(14)	-316.413	-345.448

HSC Chemistry software and its data base of the thermodynamic values of reaction participants were used in calculations.

The negative values of Gibbs energy change ΔG_T for reactions (3)-(14) show that they are all thermodynamically feasible at standard pressure and temperature range of 30-100°C. Higher negative ΔG_T value of the reaction (4) than that of the reaction (3) suggests its occurrence with higher thermodynamic probability. NO and NO₂ ratio in gaseous products and elemental sulphur and sulphate ratio after leaching depend on concentration of nitrate ion (Droppert et al. 1995). E-pH diagrams show the thermodynamic stability of water solution components and the correlations electrochemical potential - pH values. E-pH diagrams for the behavior of copper, zinc, lead and iron in Cu-Zn-Pb-Fe-S-H₂O system are presented in Fig. 2.

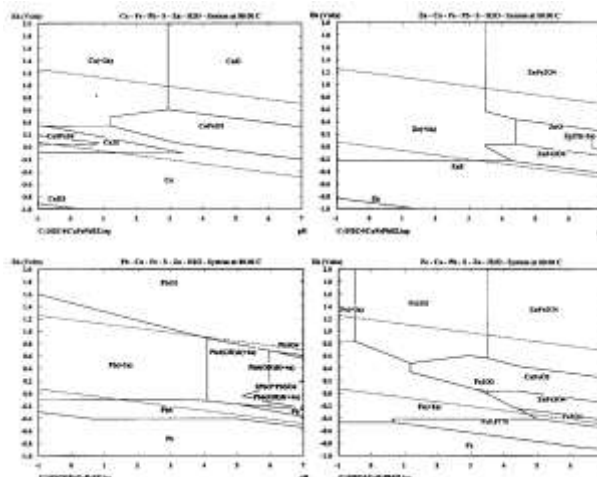


Figure 2 - E-pH diagrams for Cu-Zn-Pb-Fe-S-H₂O system at 80°C

From Fig. 2 it can be concluded that copper, zinc, lead and iron leach from their minerals at low pH values and under the given oxidizing conditions. Under these oxidizing conditions at high electrode potential and low pH values, Cu²⁺, Zn²⁺, Fe²⁺ and Fe³⁺ ions exist in water solutions, while Pb²⁺ exists in sulphate form in the resi-due. The increase of temperature lowers the possibility of Fe³⁺ ion existence in the system.

3. EXPERIMENTAL

The concentrate enriched during the flotation of a CuFeS₂-PbS-ZnS polymetallic ore in the "Rudnik" flotation plant (Rudnik – Serbia) was used. All leaching experiments of polymetallic concentrate at atmospheric pressure and temperatures up-to 90°C were carried out using experimental set-up, which provides the stable hermetic conditions and allow the heating at constant temperature.

The liquid volume was kept constant during the experiments. The calculated volumes of H₂SO₄ and

NaNO_3 solutions were put into the glass reactor and heated-up to the selected temperature. When the temperature was reached, the solid concentrate was added and that moment is taken for the beginning of reaction.

After finite time intervals, during the leaching process, the solution samples were taken for chemical analysis which was carried out with AAS (Perkin Elmer).

The solid residues were carefully filtered out, washed with distilled water, dried and their phase content was determined by AAS, X-ray analysis using diffractometer (Siemens D500), light microscopy (Carl Zeiss-Jena JENAPOL-U) and thermal DTA / TG analysis on a NETZSH 409 Ep.

4. RESULTS AND DISCUSSION

4.1. Characterization of Polymetallic Concentrate

Chemical composition of the polymetallic concentrate, which was used in the leaching process, is presented in Table 3.

Table 3. Chemical composition of polymetallic concentrate from "Rudnik" flotation plant [50]

Cu	Zn	Pb	Fe	S	Bi
8.92%	8.79%	12.66%	19.07%	21.02%	0.083%
Sb	Cd	As	Ag	Au	
0.012%	0.065%	0.034%	0.021%	0.0006%	

X-ray diffraction (XRD) analysis was used for the phase fraction determination in the polymetallic concentrate; the result is shown in Figure 3.

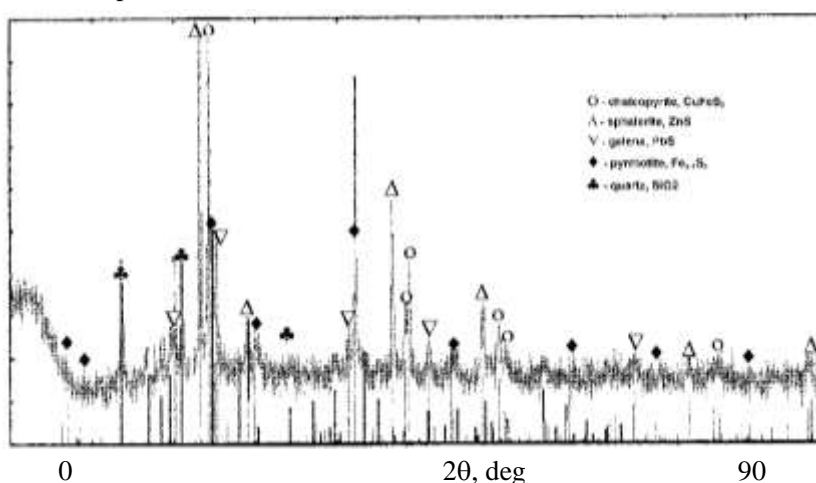


Figure 3 - X-ray diffraction (XRD) analysis of the polymetallic concentrate from "Rudnik" flotation plant [20]

The presence of chalcopyrite, sphalerite, galena, pyrrhotite and quartz is registered. Prepared sample

microphotograph of polymetallic concentrate from „Rudnik“ flotation plant is presented in Figure 4.

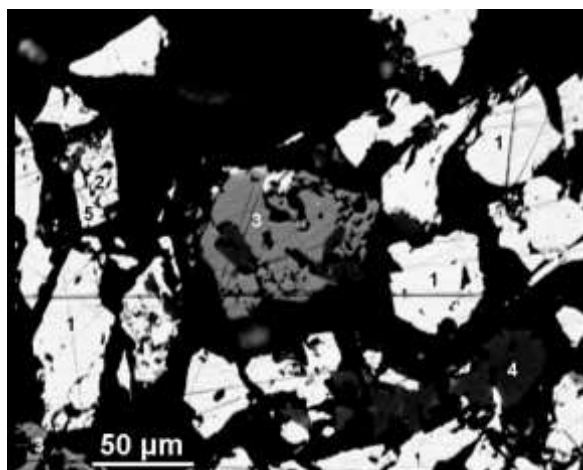


Figure 4 - Microphotograph of the polymetallic sulphide concentrate: 1-chalcopyrite, 2-pyrrhotite, 3-sphalerite, 4-quartz and 5-galena

Sulphide monominerals are predominantly irregular in shape, with dimensions in the range 10-100 μm . Besides, there can be observed simple and complex adherent minerals, with different combinations; mu-

tually adhered beneficial minerals or minerals adhered with gangue minerals, predominantly quartz. Thermogram of polymetallic concentrate obtained at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in air and shown in Figure 5.

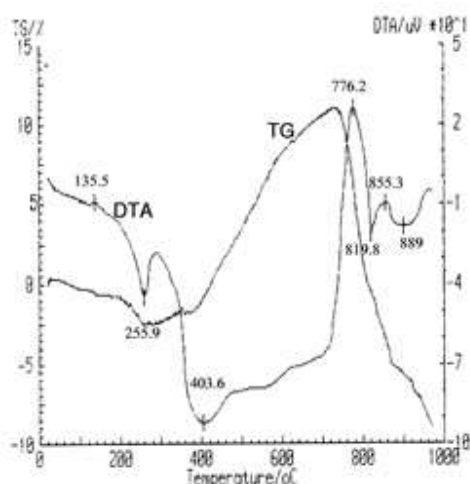


Figure 5 - DTA/TG analysis of polymetallic concentrate

When the concentrate is heated, there is an increase in mass, which is accompanied by more or less pronounced exothermic effects (up to 730°C), which are the result of the presence of several types of sul-

fides that oxidize differently. Further heating leads to a sudden loss of mass, which also occurs in several stages, which indicates that more different sulfates are present. These mass losses are accompanied by endothermic effects, of which they are clearly expressed at 776°C (CuSO_4 dissociation) and 855°C ($\text{CuSO}_4 \cdot \text{CuO}$ dissociation).

4.2. Influence of the Operating Parameters

The experimental results on determination of leaching parameters of polymetallic concentrate from „Rudnik“ flotation plant with sulphuric acid in the presence of sodium nitrate were performed in the temperature range of 20-90°C and during the time intervals 60-240min. Further, the optimum values were: the phase ratio solid/liquid (S:L) = 1:5, the starting sulphuric acid concentration 225g/dm³, the sodium nitrate content exceeds 30% of the stoichiometric calculated value.

The influences of temperature and time on the leaching degrees of the zinc, copper and iron are presented in Figure 6.

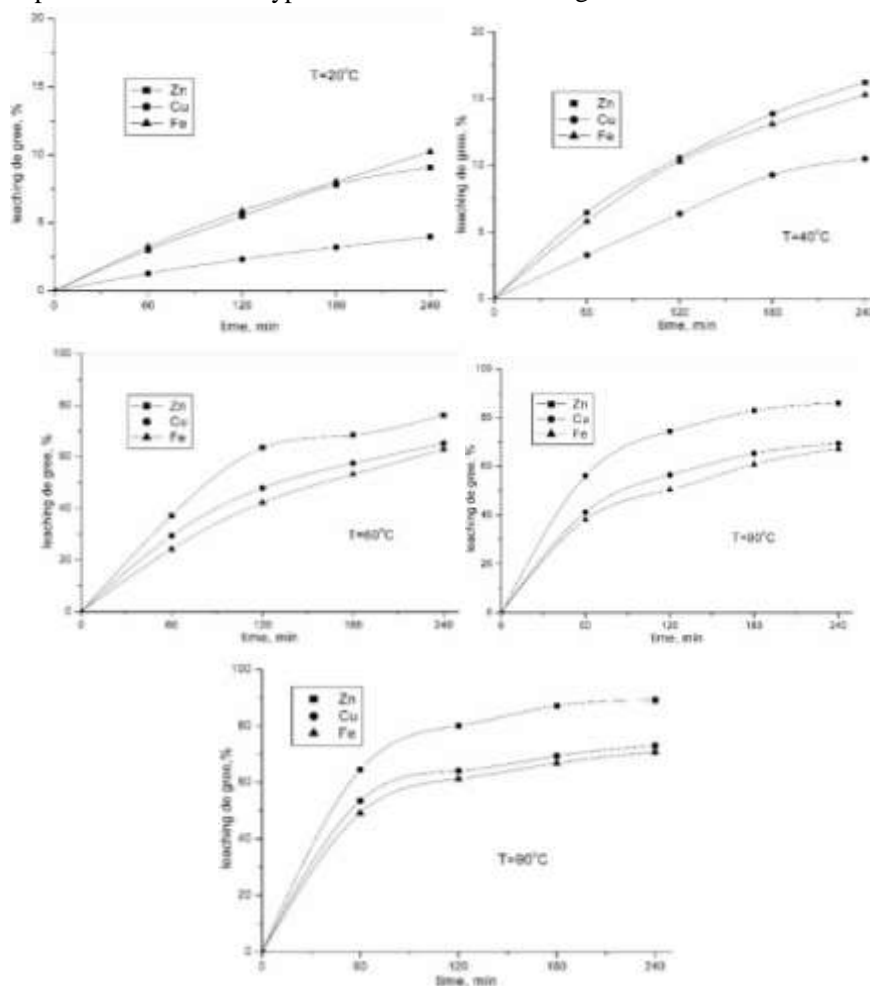


Figure 6 - Temperature and the leaching time influence on the leaching degrees: S:L=1:5, the starting concentration of $\text{H}_2\text{SO}_4=225\text{g/dm}^3$, NaNO_3 content 30% above the stoichiometrically needed, the stirring speed 300r/min

It is well known that the oxidative dis-solution of galena produces insoluble $PbSO_4$ in the sulphuric acid leaching medium [51]. Low leaching degree is obvious for all three metals, but for copper it is extremely low (Fig. 6.a). The similar situation occurs for the influence of time on the leaching degrees at the temperature of 40°C (Fig. 6.b).

Onset of leaching degrees is noticeable at the temperature of 60°C (Fig. 6.c), where the zinc leaching degree is the highest. Further temperature increasing contributes that all three metals leaching degrees increase (Fig. 6.d), and finally reaching the temperature of 90°C at time of 240min (Fig. 6.e). It is

important to notice that in contrast to the lower temperatures, when the process goes on above 50°C the zinc leaching degree is higher than that for iron.

4.3. Characterization of the Solid Residuals

Characterization of the solid residuals after the leaching process included chemical and mineralogical analyses. The samples were chosen to be representative regarding a wide range of possible leaching products. Chemical analysis of the solid residual after the leaching is presented in Table 4, as well as the overall mass of the solid residual after the leaching process.

Table 4. Chemical analysis of the solid residual: $t=90^\circ\text{C}$, $\tau=240$ min, $S:L=1:5$, the starting concentration of $H_2SO_4=225\text{g/dm}^3$, $NaNO_3$ content 30% above the stoichiometrically needed, the stirring speed 300r/min

Mass of the concentrate (g)	Mass of the solid residual (g)	Composition of solid residual (%)			
		Zn	Cu	Fe	Pb
100.00	59.90	1.41	3.88	8.97	20.93

X-ray diffraction (XRD) analysis, presented in Fig. 7, was used for determination of the mineral

composition of the solid residual after the leaching process.

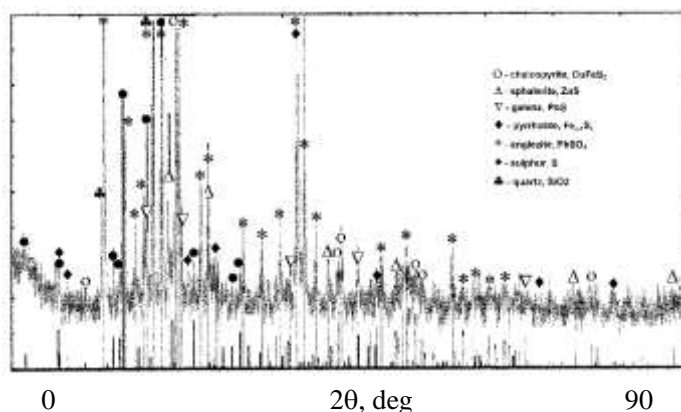


Figure 7 - X-ray diffraction (XRD) analysis of the solid residual after the leaching: $t=90^\circ\text{C}$, $\tau=240$ min, $S:L=1:5$, the starting concentration of $H_2SO_4=225\text{g/dm}^3$, $NaNO_3$ content 30% above the stoichiometrically needed, stirring speed 300r/min [20]

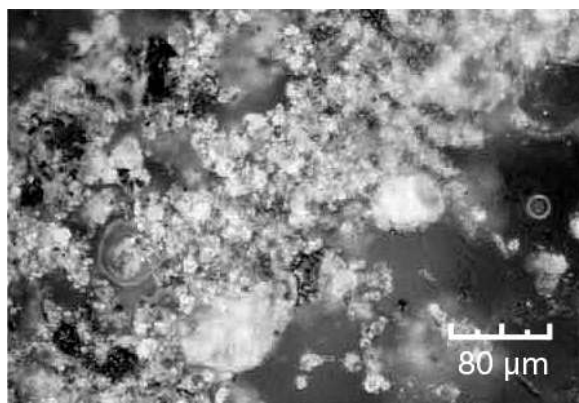


Figure 8 - Microphotograph of the solid residual after leaching (X Nicols, in oil): $t=90^\circ\text{C}$, $\tau=240$ min, $S:L=1:5$, the starting concentration of $H_2SO_4=225\text{g/dm}^3$, $NaNO_3$ content 30% above the stoichiometrically needed, stirring speed 300r/min

Microphotographs were taken on a prepared sample of the solid residuals after the leaching process for detection of the present phases. A microphotograph of a selected sample is shown in Fig. 8. For the reason of better phases recognition, the cedar oil was used.

The presence of sulphur and greater amount of anglesite, which shines milky white, is evident in Fig. 8, and corroded chalcopyrite and pyrrhotite are situated next to the right figure's margin. Thermogram of the solid residual after leaching obtained at a heating rate of 10 °C/min in air and shown in Figure 9.

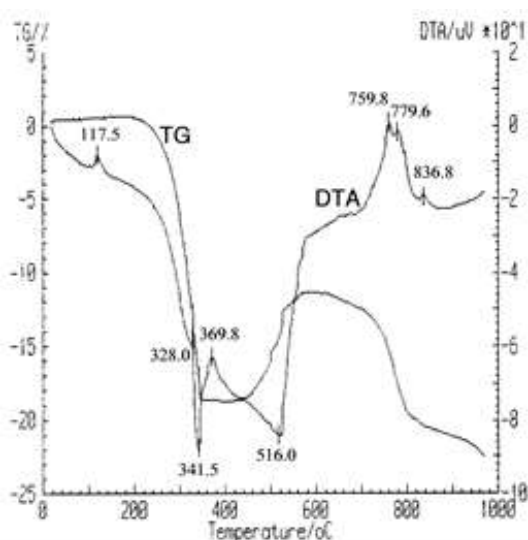


Figure 9 - DTA/TG analysis of polymetallic concentrate

When the sample is heated, an endothermic peak characteristic of elemental sulfur is observed at a temperature of 118°C. After that, there is a large loss of mass in the range of 250-350°C, which is a consequence of the oxidation of a large amount of sulfur to SO₂. The increase in mass followed by exo-thermic effects takes place in the range of 350-600°C and is much smaller than the increase in mass in polymetallic concentrate, which indicates the presence of a small amount of unleaded sulfides. The mass loss above 700°C is the result of the dissociation of the present sulphates (mainly anglesites) and is much smaller in relation to the analogous mass loss in concentrates before leaching.

5. CONCLUSION

Based on the chosen leaching chemism of the polymetallic sulphide Zn-Pb-Cu concentrate and its thermodynamical analysis, the assumed chemical reactions mechanism for zinc, copper and iron leaching is confirmed.

The phases detection in both, the starting concentrate and the products after the leaching process with

H₂SO₄ and NaNO₃, were performed for better understanding of the chemical reactions that took place in the system.

The presence of the anglesite, elemental sulphur, gangue and unleached sulphide minerals, was registered using X-ray diffraction (XRD) analysis of the solid residual. This fact points out that leaching product of any sulphide mineral is elemental sulphur, which does not oxidize to sulphate in the temperature range (20-90°C) and the time interval (60-240 min).

After the leaching process, copper and zinc are in the form of copper(II) sulphate and zinc(II) sulphate. Iron is being oxidized to form iron(III) sulphate, which then acts as a leaching agent for the present sulphide minerals, and at the same time become reduced to iron(II) sulphate. Lead from the galena reacts to form the lead sulphate (anglesite), which is insoluble and remains in the precipitate.

Detailed mineralogical investigations indicate a polymetallic concentrate complexity and explain weak leaching effect of sulphide minerals in the final leaching stage. The main reasons for that are:

- elemental sulphur and anglesite, formed during the process and precipitate at the grain boundaries, fine grained mineral structure and complex mutual inter-growth of chalcopyrite, sphalerite, galena and pyrrhotite (inclusion, impregnation, simple and complex inter-growth),
- complex adhered beneficial sulphide minerals with gangue minerals (predominantly quartz).

The accomplished leaching degrees under the given conditions (temperature of 90°C, time of 4 hours, phase ratio S:L=1:5, the starting H₂SO₄ concentration of 225g/dm³, with sodium nitrate addition in the content of 30% above the stoichiometric needed) are as follow: Zn – 89.25%, Cu – 73.08% and Fe – 70.80%.

6. ACKNOWLEDGEMENTS

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REZIME**LUŽENJE POLIMETALNOG CU-ZN-PB KONCENTRATA NATRIJUM-NITRATOM I SUMPORNOM KISELINOM**

U radu su prikazani i diskutovani rezultati luženja polimetalnog sulfidnog Cu-Zn-Pb koncentrata rastvorom natrijum-nitrata i sumporne kiseline pri atmosferskom pritisku. Prikazan je hemijski i mineraloški sastav polaznog koncentrata i čvrstih ostataka nakon procesa luženja. Hemijske reakcije luženja i mogućnosti njihovog odvijanja analizirane su primenom termodinamičke analize na osnovu izračunatih Gibbsovih energija i analize E-pH dijagrama. Eksperimentalno je analiziran uticaj temperature i vremena na stepen izluženja korisnih metala iz sulfidnog koncentrata. Pokazano je da je moguće dobiti bakar, cink i železo u rastvoru u obliku sulfata, dok olovo u obliku anglesita (PbSO₄) ostaje u čvrstom ostatku nakon procesa luženja. Železo se oksidiše u Fe (III) -sulfat, koji učestvuje u luženju sulfidnih minerala i prelazi u Fe (II) -sulfat.

Ključne reči: polimetalni Cu-Zn-Pb koncentrat, luženje, natrijum-nitrat, sumporna kiselina