

HYDROMETALLURGICAL ROUTE FOR COPPER, ZINC AND CHROMIUM RECOVERY FROM GALVANIC SLUDGE

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HYDROMETALURGICKÉ ZÍSKAVANIE MEDI, ZINKU A CHRÓMU Z GALVANICKÝCH KALOV

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Abstrakt

Galvanický kal patrí do kategórie nebezpečných odpadov, nakoľko obsahuje lúhovateľné nebezpečné zložky ako sú ťažké kovy (napr. Cu, Zn, Cr, Cd), kyanidy, fluoridy, oleje a pod. Ekonomické spracovanie týchto kalov je značne komplikované, najmä kvôli ich komplexnosti a chemickej heterogenite. Táto práca sa zamerala na hydrometalurgické spracovanie kalu s obsahom zložiek ako Cu, Zn, Cr, Cd, Ni, Fe, Si, Ca a iných prvkov s cieľom overiť lúhovateľnosť Cu, Zn a Cr v roztokoch kyseliny sírovej v koncentračnom rozmedzí 0.01-1 M H₂SO₄. Výsledky ukázali, že po 5 minútach lúhovania v roztoku 0.25 M H₂SO₄ a pri pomere kvapalnej ku pevnej fáze 40:1 bola výťažnosť Cu do roztoku 90 % a Zn 85 %. Výťažnosť Cr nepresiahla 25 % bez ohľadu na zvolené podmienky lúhovania. Okrem toho sa zistilo, že výťažnosť Cu sa a ostatných sledovaných kovov sa znižuje so znižovaním pomeru kvapalnej ku pevnej fáze. Najvyššia výťažnosť Cu 95 % do roztoku sa získala pri použití roztoku 0.5 M H₂SO₄. V druhej časti práce sa overila možnosť selektívneho získania medi z komplexného výluhu na železnej platni. Ukázalo sa, že cementácia je vhodnou metódou na získanie Cu z komplexného výluhu. Cementáciou pri teplote 20 °C bez použitia miešania sa z komplexného výluhu získala Cu s účinnosťou viac ako 84 % o čistote 96 %.

Abstract

Galvanic sludge belongs to hazardous waste because of present of various heavy metals like Cu, Zn, Cd, Cr and others substances like cyanides, fluorides etc. The economical treatment is very difficult because of chemical heterogeneity of galvanic sludge. The focus of this investigation was the hydrometallurgical treatment of complex galvanic sludge containing Cu, Zn, Cr, Cd, Ni, Fe, Si, Ca and other elements. The aim of experiments was to verify the leaching behaviour of copper, zinc and chromium in sulphuric acid solution of concentration range of 0.01-1M H₂SO₄. Based on experimental results it was confirmed that maximum copper and zinc extraction 90 % and 85 % could be reached after 5 minutes at room temperature by using of acid concentration of 0.25 M and solid to liquid ratio 1:40. The extraction of chromium did not exceed value of 25 % regardless of leaching conditions. It was also shown that copper and other metals extraction degreased when S:L ratio increased. The highest extraction of Cu 95 % by using of 0.5 M H₂SO₄ was achieved. The second part was focused on recovery of copper from leaching solution by selected separation process- cementation on an iron plate. Cementation

process proved at given conditions as a possible way of how to selectively obtain copper from the complex polymetallic leaching solutions. The product with minimum copper content of 96 % and cementation efficiency more than 84 % at the temperature of 20 °C after 24 hours without stirring was achieved.

Keywords: galvanic sludge, hydrometallurgy, treatment, copper, zinc, chromium, cementation

1. Introduction

Galvanic sludge is formed in electroplating plants as result of precipitation of metals in waste water and from spent electrolyte. The sludge after neutralisation is amorphous and consists mainly of hydroxides and carbonates. Small portion of the sludge form also crystalline substances like CaSO_4 at higher concentration of sulphate ions. Amount of metals present in the sludge varies with galvanising technology applied and with surface area of the sludge. Total volume of the sludge depends on composition of the galvanising baths, on wastewater's concentration and on type of reagents used [1]. This complex sludge belongs to hazardous wastes, but on the other hand they are a valuable source of various metals like copper, zinc, nickel, cadmium, gold, silver etc. The problem of galvanic sludge treatment is very actual and there is a tendency to find the most effective method for treating and utilising each valuable component from it. The economical treatment is very difficult because of complexity of the galvanic sludge. Optimal technique appears to be separating individual wastewater and purifying in particular steps to obtain relatively pure monometallic sludge. This sludge then should be treated very simply. It could be also interesting way to treat individual spent electrolyte in situ by for example solvent extraction, electrolysis, cementation or another process in order to recover present metals. Many plants solve the problem of galvanic sludge by landfill or stabilisation. Intelligent solution from both ecological and economic point of view is given by maximum recovery of valuable components at the lowest possible costs.

2. Theoretical

Galvanic sludge and treatment possibilities

Galvanic sludge consist of metals used for surface treatment like Cu, Ni, Cr, Cd, Sn, Zn, Ag, Au, Pb and bearing metals like Al, Fe, Mn and substances used for precipitation process, as Ca and Na. The galvanic sludge besides heavy metals like copper, zinc and nickel in the form of hydroxides (oxihydroxides) contains also various impurities like CaSO_4 , SiO_2 , CaCO_3 , also cyanides, sulphides, fluorides, tenzides and oils. Moreover, it contains high amount of water and this makes its disposal, transport and landfill difficult. In order to improve recovery of heavy metals form the sludge by leaching or by their interaction with other substances they could spontaneously release and migrate in the environment, mainly in the ground water [2].

Among basic treating possibilities of galvanic sludge are: stabilisation, pyrometallurgical, hydrometallurgical, biohydrometallurgical and combined technologies. It is necessary to note that some technologies are oriented mainly at the disposal and another on recovery of individual substances from sludge. Off course, these latter mentioned methods are energy consuming and therefore less popular among the treating companies.

Stabilizing technologies provide an environmentally friendly solution, but without exploitation of the secondary raw materials potential. Metals present in galvanic sludge, which cannot be recycled or utilised must be immobilised before deposition in the landfill according to

valid regulations of Ministry of Environment of Slovak Republic (ME SR). The purpose of the stabilisation process is immobilisation of contaminants in the solid matrix of stabilised material [3]. Among stabilizing technologies belongs mainly solidification, what means enclosing of waste in solid matrix by using of lime hydrate or cement (bitumenation in solidified melt, cementing, vitrification etc.) [4-5]. Further alternative solidification methods consist of the incorporation of the sludge into the bricks, what it is enabled by zeolitic properties of soils. The problem is chromium, because at its high concentration in the sludge it is present as $\text{Cr}(\text{OH})_3$ and after firing it is converted to CrO_3 , which is soluble and therefore may become a contaminant [6]. Pyrometallurgical methods include melting of galvanic sludge in special reactors producing slag, alloy and ashes with various distributions of heavy metals. Disadvantage of the thermal treatment is the high energy consumption and the costs associated with it and impure products that is often a mixture of oxides and alloys and necessity of drying. According to papers [2,7] roasting of galvanic sludge does not produce adequately pure and marketable product. This product exceeds limits for chromium, copper, nickel and lead.

Hydrometallurgical method for treating galvanic sludge is based on leaching in acid or alkaline solutions followed by selective separation of metals from these solutions by means of solvent extraction methods, electrochemical methods as well as by appropriate precipitation processes. The interesting method for separation of heavy metals from solution is sorption on biological matter. Biosorption of Cu, Cd, Ag, Au, As was studied in works [8-10]. About 90 % of studied metals was taken up from diluted solution (concentration of metal in the solution was about 20 mg.l^{-1}) in dependance of concentration of metal in the solutions. Capacity of the process depends on the biomass origin (biomass originated from algae, moss, fungi and tectrices) and form of the metal.

Hydrometallurgical treatment process is advantageous because of slight leachability of metals precipitates in acid media. On the other hand, it is necessary to test the possibilities of the selective transfer of individual substances into and/or from the solution. It is obvious that the amount of metals and other impurities or substances present in the sludge can affects the leaching process as well as extraction and precipitation processes that will be applied for winning pure metals. It is necessary to look for the optimum leaching and extraction conditions for every sludge.

Paper [11] describes the recovery of copper from galvanic sludge by hydrometallurgical method. The process comprises leaching of sludge in $0.5 \text{ M H}_2\text{SO}_4$, precipitation of impure copper hydroxides, calcination of these precipitates at he temperatures of $800\text{-}900 \text{ }^\circ\text{C}$ during 2 hours and final leaching the resulting oxides in $1 \text{ M H}_2\text{SO}_4$ at $60 \text{ }^\circ\text{C}$. The highest copper recovery, 84 % was achieved after leaching in $0.5 \text{ M H}_2\text{SO}_4$ at pH between 0.9 and 1. During calcination step the mixtures containing metals Fe, Cr, Al, Zn, Ni and Si were transformed in less soluble oxides, which were separated in the following leaching stage.

Biohydrometallurgical recovery of non-ferrous metals is based on utilisation of bacteria in bioleaching process [12]. The authors [13] describe process, in which the beneficial substances are recovered by bacterial leaching using IBES method (Indirect Bioleaching with Effects Separation). This method combines oxidation effect of trivalent Fe in sulphuric acid and biooxidation of bivalent Fe by the action of bacteria *Thiobacillus ferrooxidans* during leaching process. Two samples with various contents of metals Cu, Zn, Ni, Cd and Cr were subjected to bioleaching. By using this method, the total extraction 93 % of all metals into the solution was achieved. In case of another sample the recovery was 94 % of Zn and Ni and 65 % of Cu and Cd. Plant using the IBES technology have to be very flexible to allow for the change of parameters according to type of treated waste, its density, temperature and leaching time.

There are several processes for treating galvanic sludge. Stabilising technologies provide an environmentally friendly solution although without recovering valuable substances. Moreover, they contribute to increasing amounts of stabilised waste. Pyrometallurgical routes are energy demanding processes and achieved products of melting are not usable for next treatment. Hydrometallurgy enables (bioleaching, various leaching agents, and extractive, sorption and precipitating steps) to recover valuable or contaminating substances from the sludge. On the other hand the complexity of the sludge often requires higher costs as consequence of number of operating steps and amounts of used reagents. In spite of some disadvantages, big attention is being paid to solving the problem of galvanic sludge and to looking for optimum process for recovery substances from this sludge with the highest possible purity. There are also some technologies used in the practice, which are treating this sludge: e.i. MAX-Process, TNO-Process and Goldschmidt-Process [14].

The focus of this investigation is the hydrometallurgical treatment of galvanic sludge. The aim of experiments was to verify the leaching behaviour of copper or zinc and chromium in acidic solution. As suitable leaching medium, the diluted solution of sulphuric acid was chosen because the sludge consists mainly of metals hydroxides. Experiments were carried out at room temperature. The second part was focused on recovery of copper from leaching solution by selected separation process- cementation on an iron plate. The purity of achieved products and efficiency of copper extraction were also determined.

3. Experimental

Input material

The sludge sample from galvanising plant was used. This sludge was formed in the process of neutralising of rinse wastewater from surface electrotechnical material make-up.

In neutralising station the acidified water is treated with chromic one and alkaline water with cyanide. The mixing of chromic with cyanide is impossible because of generation of toxic hydrocyanic acid.

In order to determine cyanides in alkaline waste waters the methods of cyanides oxidation by gaseous chlorine or by mixture of sodium hypochlorite and soda or chlorinated lime is used.

Waste chromium-containing waters disposal means the reduction of Cr(VI) to Cr(III) by reducing agent like for example ferrous sulphate. Reaction of waters with reducing agent requires acidic environment with initial pH values in the range of 2-3. The binding of free mineral acids as well as precipitation of Fe, Ni, Zn in the form of hydrated insoluble hydroxides is achieved by neutralisation process. Oxidation of Fe is achieved by using chlorine residue from alkaline wastewater without cyanides. Using oxygen from air in neutralising step carries out further oxidation of Fe. When chromium is neutralised, it is necessary to ensure pH in the range of 7.5-8 by use of soda before it is siphoned. After treatment, the water is poured in the transfer tank and alkaline and acid waters are stirred by air. Then the water is poured into the sedimentation tank and keep to settle during 2-3 hours. In the next step, the settled sludge is transferred in the sludge field.

The galvanic sludge for the experiments was taken off from sludge field in Slovak Company. The sludge was washed, filtered and finally dried at the temperature of 110 °C. Table 1 gives the chemical analysis of this sludge.

Table 1 Chemical analysis of galvanic sludge

Substance	Al ₂ O ₃	CaO	SiO ₂	Cu	Zn	Fe	Ni	Cr	Pb	Cd	Ag	LOI
[%]	5.52	9.79	15.83	11.30	3.75	12.13	0.15	0.14	0.097	1.05	0.20	29.5

The particle size of the sludge is 97 % below 50 µm was determined by using of rastersedigraph FRITSCHE. Density of the sludge determined by pycnometer was 2.17 g.cm⁻³. X-ray diffraction analysis shows presence of only crystalline phases like limestone CaCO₃ and quartz SiO₂. These phases come from neutralising or degreasing reagents. Because the sludge consists mainly of amorphous precipitates (hydroxides), the presence of other phases was not expected and not even confirmed. X-ray diffraction analysis was realised with diffractometer DRON 2.0 (ZSSR) and diffraction pattern was analysed by RIFRAN software [15].

Leaching experiments

Before sample was subjected to leaching, the dried sludge was homogenised in mortar. The leaching apparatus was constructed and the layout of this apparatus is illustrated in figure 1.

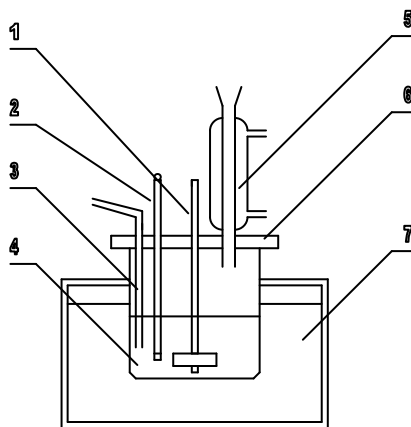


Fig.1 Schematic representation of the laboratory apparatus: 1- glass blender, 2- thermometer, 3- samples offtake, 4- glass beaker, 5-cooler, 6-lid, 7-thermostat

The charge of the sludge for leaching experiments was 10 grams and volume of leaching medium 400 ml. As leaching medium the solution of diluted sulphuric acid was used in range of concentration of 0.01-0.5 M. Moreover, the leachability of copper in distilled water was studied. In individual experiments the sample of 15 ml was taken from leaching solution in time intervals of 2, 5, 10, 20, 40, 60 minutes and analysed by AAS method. After leaching the residual sludge was filtered followed by volume measuring of final leachate in order to correct achieved extraction results.

The effect of leaching time, concentration of sulphuric acid as well as solid liquid ratio (S:L) at room temperature (approximately in range of 18-20 °C) on copper zinc and chromium extraction, at changed solid/ liquid ratios was also studied in this part of experimental work. Proposed reactions of the sludge substances with sulphuric acid in leaching step:





Cementation experiments

For cementation experiments two achieved final filtrates after leaching were used. The experiments were oriented at cementation of important metal - copper because it is the main component of the sludge as well as of leachate. The cementation was realised with two iron-plates with dimensions of 70x26x0.5 mm and weight of 22.35 g and of 22.39 g, respectively. Glass beakers with leachates were introduced to magnetic stirrer and Fe-plates were immersed into deep 47 mm or 50 mm into the leachate. Cementation process runs at room temperature. The leachates were stirred for 8 minutes and then Fe plates remained in leachate during 24 hours without stirring. After this time the copper was present in solution as powder or in compact pieces. Cementates were filtered, dried and weighed as well as subjected to chemical analysis and X-ray diffraction phase analysis.

4. Results and discussion

Leaching results

In respect of quantity of present important substances in the sludge, the analysis was oriented mainly on copper extraction. Moreover, in one case the comparison of zinc and chromium extraction at chosen conditions and possibility of their selective extraction was studied. Results achieved from kinetic study of leachability of copper and selected metals into the solution and effect of concentration and S:L ratio on copper leachability are shown in the Figs 2-7.

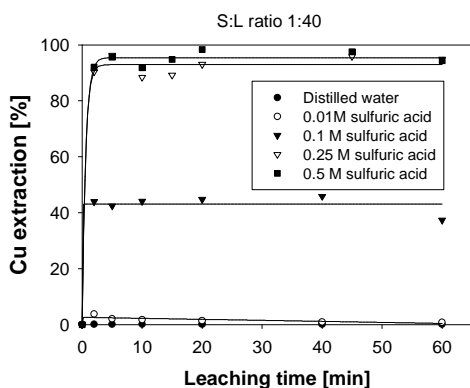


Fig.2 Effect of $c_{\text{H}_2\text{SO}_4}$ on Cu extraction

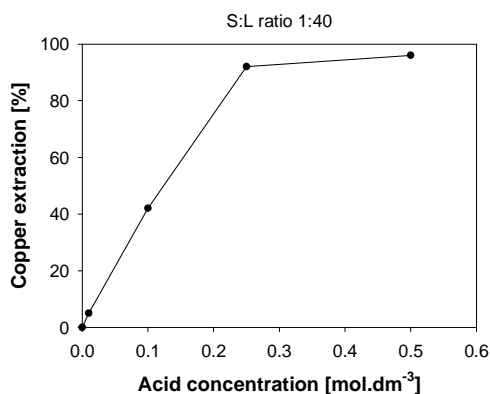


Fig.3 Effect of $c_{\text{H}_2\text{SO}_4}$ on Cu extraction (extraction value after 5 min. of leaching)

From the figure 2 it follows that with increasing concentration of acid at the room temperature and S:L ratio 1:40 the extraction of copper into the solution is increased, too. Copper practically does not dissolve in distilled water. From this picture it is obvious that there are significant differences in copper extraction efficiency when different concentrations of acid

(0.01, 0.1 and 0.25 M) were used. After 2 minutes of leaching the copper extraction of about 5 % was reached by using of acid concentration of 0.01 M. It was shown that this concentration is not sufficient and even not acceptable at these conditions. The copper extraction value of 43 % at acid concentration of 0.1 M was achieved what means 10-times higher acid concentration used caused about 9-times higher copper extraction. From figure 3 it follows that up to the acid concentration of 0.25 M the copper extraction is fast and rather linearly increasing and then it does not increase so much. The maximum copper extraction of about 95 % after 2 minutes of leaching process was achieved by using of 0.5 M sulphuric acid. The difference between extraction values reached by using 0.25 M and 0.5 M was very small and represents 5 %. It means that further increase of acid concentration over 0.25 M is ineffective. From the fig.2 it follows that approximately after 2 minutes of leaching the maximum copper extraction is achieved without further increasing tendency. This fact indicates that metals in the sludge are in the form of highly soluble compounds such as hydroxides, oxides or oxihydroxides. Due to this fact, it is advantageous to use weak concentrated sulphuric acid solution up to the 0.25 M.

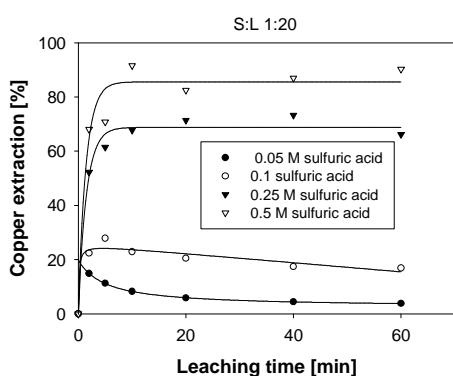
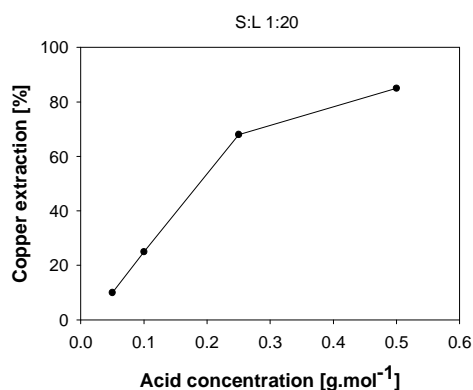
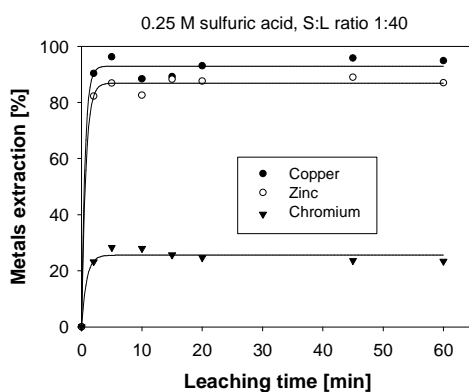
Fig.4 Effect of $c_{\text{H}_2\text{SO}_4}$ on Cu extraction (S:L ratio 1:20)Fig.5 Effect of $c_{\text{H}_2\text{SO}_4}$ on Cu extraction (extraction value after 5 minutes of leaching)

Fig.6 Leachability of metals at 20 °C/S:L ratio 1:40

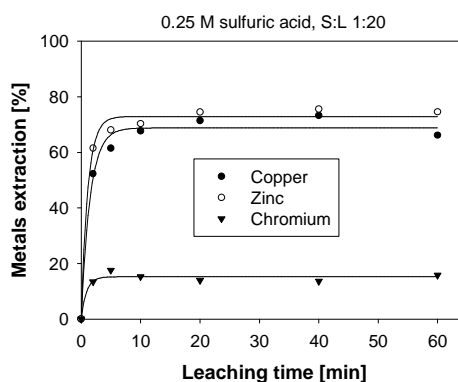


Fig.7 Leachability of metals at 20 °C/S:L ratio 1:20

Fig.4 and 5 show that at the changed S:L ratio to 1:20 the increase of copper extraction with concentration of acid is not so dramatic as it was in case of S:L ratio 1:40.

Providing S:L ratio 1:20 the copper extraction was lower at each concentration used and maximum value of 86 % at acid concentration 0.5 M was achieved. It is obvious that low concentrations of sulphuric acid under 0.1 M at higher S:L ratios are inconvenient. In the leaching process of the complex sludge the individual substances could react with each other in different ways as well as they could change ions activities during leaching following precipitation of Cu compounds or other substances. Moreover, the red spots observed in some leaching residues probably belong to Fe-hydroxide. For more precise determination it would be necessary to use the X-ray diffraction phase analysis. During leaching process the formation of white precipitate in removed samples especially at the beginning of leaching and at lower acid concentration was observed. Precipitates were subjected to the X-ray phase analysis and the presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) was confirmed. In the sludge, the calcium as CaO or CaCO_3 is present originating from neutralizing step. These substances react with sulphuric acid to form calcium sulphates and CO_2 (g). By using of concentrated acid solutions the foaming of suspension was observed due to release of the gas:



After finishing of the leaching process the variety of colours of the filtrates could be observed: transparent, soft blue, soft green, yellow-green, dark-green, brown.

In the fig.5 and 6, it is shown that at the acid concentration of 0.25 M the S.L ratio has significant effect on the leachability of metals. The maximum copper and zinc extraction at S:L 1:40 of 90 % and 85 %, respectively was achieved compared with values of 70 % and 75 % for copper and zinc achieved at lower S:L ratio 1:40, respectively.

These results are interesting from the point of view of process selectivity. Based on achieved results we can propose an optimum methods of sludge leaching in order to obtain in stages important metals by means of suitable precipitation or extraction techniques. On the other hand, the strategy of waste process plays an important role, too. One effective way for sludge leaching is to use diluted sulphuric acid. Copper could be gradually leached from the sludge and chromium should mostly remain in the sludge. The leachate containing zinc then could be subjected to cementation of copper and after this step the remaining solution with zinc could be subjected to electrolysis of zinc. Moreover, the calcium sulphate it is possible to separate from the leachate spontaneously. For this purpose the spent electrolytic baths from electroplating processes could be used. Of course, it is necessary to realise that the galvanic sludge is mostly polymetallic waste with many substances. Due to this fact, it will be beneficial to study the leachability of other metals.

Besides these facts, there is one possible way how to reduce the amount of galvanic sludge. The solution consist in direct separation of metals or their compounds from the spent electrolytic or pickling baths as well as waste waters by using liquid extraction, ion exchange or precipitation.

Cementation results

For purpose of copper cementation experiments at room temperature (20 °C) two solutions were chosen. First solution was filtrate with copper concentration of $5145 \mu\text{g} \cdot \text{ml}^{-1}$ and the second one with copper concentration $5720 \mu\text{g} \cdot \text{ml}^{-1}$. The observed parameters were the purity of cementation products, phase composition and cementation efficiency. During experiments, the flaking-off the cementation coating after first or fourth minute in stirred

solution was observed. After finishing cementation experiments, the solution was filtered and cemented metal was separated, dried and weighed. The weight of cementate in first case was 430 mg and in the second one 500 mg. X-ray diffraction phase analysis of obtained cemented precipitates in both cases showed the presence of main phase copper, index 4-836 JCPDS and small amount of Cu_2O , index 5-667 JCPDS due to air oxidation.

Chemical analysis of these products in tab.2 confirmed dominant copper and small amount of impurities.

With regard to low contents of both oxide and impurities, their presence was ignored in calculations of the efficiency of cementation. The calculated cementation efficiencies for copper by use of Fe-plate at room temperature were in first case 83.58 % and in second one 87.41 %.

Based on cementation results it follows that by using polymetallic leachates it is possible to obtain by cementation on Fe-plate at room temperature without mixing powdered copper with high efficiency and satisfactory purity. It is also possible to use Zn powder as cementing agent instead of Fe-plate or powder.

Table 2 Chemical analysis of cementates for both cases

Metal [%]	Cu	Zn	Ni	Cr	Cd	Pb
1. experiment	96.34	0.021	0	0	0.03	0.09
2. experiment	96.44	0	0	0	0.03	0.10

5. Conclusion

The hydrometallurgical route for galvanic sludge treatment was verified in this work. The aim was to obtain information about optimum conditions for selective leaching of copper, zinc and chromium in diluted sulphuric acid solutions. Besides this, the possibility of copper cementation on Fe-plate was tested. Based on experimental results it was confirmed that maximum copper and zinc extraction 90 % and 85 % could be reached at room temperature by using acid concentration 0.25 M and S:L ratio 1:40. It was shown that using higher acid concentrations is not necessary. The copper and other metals extraction decreased when S:L ratio increased. It is clear that with a tendency to increase the S:L ratio also higher acid concentration above 0.25 M would be needed for higher extraction rates. Zinc shows good leachability in selected media compared to copper leachability. The extraction of chromium did not exceed value of 25 % regardless of leaching conditions. In most cases the metals are leached into the solution with maximum extraction value, which is then stable during leaching. That is an economically viable because it is not necessary to leach during long period but few minutes.

Cementation proved at given conditions as a possible way how to selectively obtain copper from the complex polymetallic leaching solutions. In the first case, the product with copper content of 96.34 % and cementation efficiency of 84 % at the room temperature after 24 hours without stirring was achieved. In second case at the same conditions, the product with copper content of 96.44 % and cementation efficiency of 87.41 % was achieved.

The proposed method for treating the galvanic sludge consists in leaching with sulphuric acid of concentration of 0.25 M at room temperature during max.10 minutes at S:L ratio 1:40 following recovery of copper powder by cementation on Fe-plate at room temperature during 24 hours without stirring. The recovered cementation product is relatively pure and suitable as a secondary raw material for remelting. Selective leaching of copper and zinc without chromium at room temperature requires low concentration of sulphuric acid under 0.25 M and

S:L ratio 1:40. On the other hand, we should be aware of precipitation of some metal compounds from the solution.

Acknowledgements

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