

Conference Paper

Hydrometallurgical Technology for Processing of Galvanic Sludges

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Ural Federal University named after the first President of Russia B. N. Yeltsin

Abstract

The problem of processing galvanic sludges, formed as a result of neutralization of technological solutions and wastewater containing heavy non-ferrous metals is considered in this study. At present, sludges are transported to disposal area and are not used in any way. Typically, such sludges contain significant amounts of chromium and nickel, which creates environmental hazard. Investigated sludge contains up to 6,6% Ni and up to 7,4% Cr. The hydrometallurgical process to treatment of these sludges is carried out. Solutions of sulfuric acid and ammonia were used as lixivants. It is shown that when using a solution of sulfuric acid with pH=1,5, extraction of up to 93,3% Cu, 70,2 Ni, 90,3 Zn is achieved. For selective nickel recovery sorption concentration by Lewatit TP207 is proposed.

Keywords: Galvanic sludge, hydrometallurgy leaching, nickel, ion-exchange resin

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1. Introduction

Galvanic workshops produce large amounts of waste waters. Solid waste, called galvanic sludge is formed as result of the physicochemical treatment of that waste water. Galvanic sludge is considered to be one of the most highly toxic types of waste and stored mainly in sludge pits. Such practice has not any economic or environmental advantages.

In order to reduce the environmental hazard of galvanic production wastes deposited in the sludge, methods of chemical fixation by means of ferritization of solid phase of wastes, silicification, solidification of wastes with the use of inorganic and organic binders, as well as sintering are used [1–3]. One of the ways of processing of galvanic sludges is their application as filling agents and plasticizers in concretes, asphalt concretes and building mortars [4, 5].

At the same time, the sludge can be considered as a significant source of heavy non-ferrous metals and chromium. Content of copper, chromium, nickel or zinc can reach 30 % of dry weight. Development of alternative and effective ways reducing the impact on the environment and providing extraction of valuable metals contained in these sludges are of paramount importance.

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Considerable variations in sludge composition create additional difficulties for the development of a comprehensive sludge treatment scheme. The most expedient way to process such complex raw material is hydrometallurgical, providing selective extraction of non-ferrous metals.

2. Experimental

Sludge produced by nickel-plating/chrome-plating units has been studied. Sludge samples were taken from different points of the sludge storage facility and have noticeable variations in the composition (Table 1), so the samples taken for the study were averaged. The phase composition of the sludge is represented by the following compounds: $\text{Ni}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, Ca_2SiO_4 , SiO_2 , $\text{Cr}(\text{OH})_3$. The sludge is mixed with sand due to the conditions of its placement in the sludge storage.

TABLE 1: Chemical composition of sludge.

Sample	Content, %						
	Ni	Zn	Cu	Pb	Fe	Ca	Cr
1	3,97	1,26	0,82	0,035	0,58	0,01	4,71
2	6,98	1,43	1,14	0,11	0,64	1,71	8,02
3	3,88	1,73	1,03	0,25	0,81	0,84	2,11
4	3,46	1,65	0,93	0,21	0,74	2,19	1,81
5	7,06	1,94	1,55	0,23	0,98	1,21	7,11
Average sample	6,64	1,33	1,06	0,13	0,58	1,26	7,41

Ammonia leaching of the initial sludge was carried out at pH 8-9, temperature 25 °C, sludge mass 20 g, the volume of the solution 150 cm³, the duration of the process 1,5 hours. The results of the experiment are shown in Figure 1.

As a result of ammonia leaching within 90 minutes, solutions containing about 1 g/dm³ of nickel and 0,628 g/dm³ of copper were obtained. The rate of nickel transfer to the solution reduces at further leaching. The advantage of ammonia leaching is minimal transition of iron to solution and complete absence of chromium in leachate. However, recovery of nickel in the solution does not exceed 50 % of its initial content in the sludge.

Sulphuric acid has proved to be one of the best reagents from previously tested solvents [6, 7]. Therefore, subsequent leaching experiments were carried out using sulfuric acid.

Sulphuric acid leaching of the initial sludge was carried out at pH 1,5; temperature 25 °C, sludge mass 10 g, solution volume 100 cm³, pH was regulated by the droplet

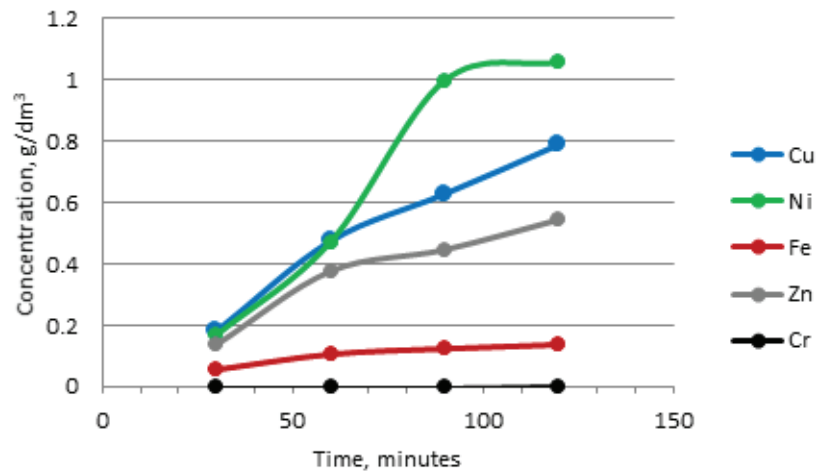


Figure 1: Kinetic of sludge leaching by NH_4OH .

adding of H_2SO_4 (1 M). Dependence of metals concentration in solution and extent of metals extraction in solution from duration of leaching is presented in Figure 2.

Nickel recovery reaches 90 % at leaching by solution of sulfuric acid during 90 minutes. The main disadvantage of sulfuric acid leaching is the lack of selectivity. Up to 80 % of chromium and up to 50 % of the iron contained in the sludge passes into the solution. It is necessary to solve the problem of separation of these elements at further processing of solutions.

Sorption on ion exchange resins was used to extract nickel from sulphuric acid leaching solutions. It is advisable to use a sorbent that preferable absorbs nickel at its joint presence with chromium in the solution. Based on published data, the following sorbents were selected for the tests: KU-2×8, Lewatit TP207, Purolite C104, Purolite S930.

To determine the static exchange capacity, all the ion exchangers were converted to the H^+ -form by washing with 1N H_2SO_4 . A sample of ion exchanger (0,5 g) was brought into contact with 50 cm^3 of nickel (II) solution (1 g/dm^3). To determine the capacity for chromium (III), a solution with concentration of 0,63 g/dm^3 was used. A static exchange capacity was calculated for each ion exchanger; the results are shown in Table 2.

TABLE 2: Ionites static exchange capacity for nickel and chromium.

Ionite	SEC for Ni(II), g/g	SEC for Cr(III), g/g
Purolite S930	0,039245	0,0002
Lewatit TP-207	0,040525	0,0001
KU 2×8	0,043695	0,0266
Purolite C104	0,03046	0,0077

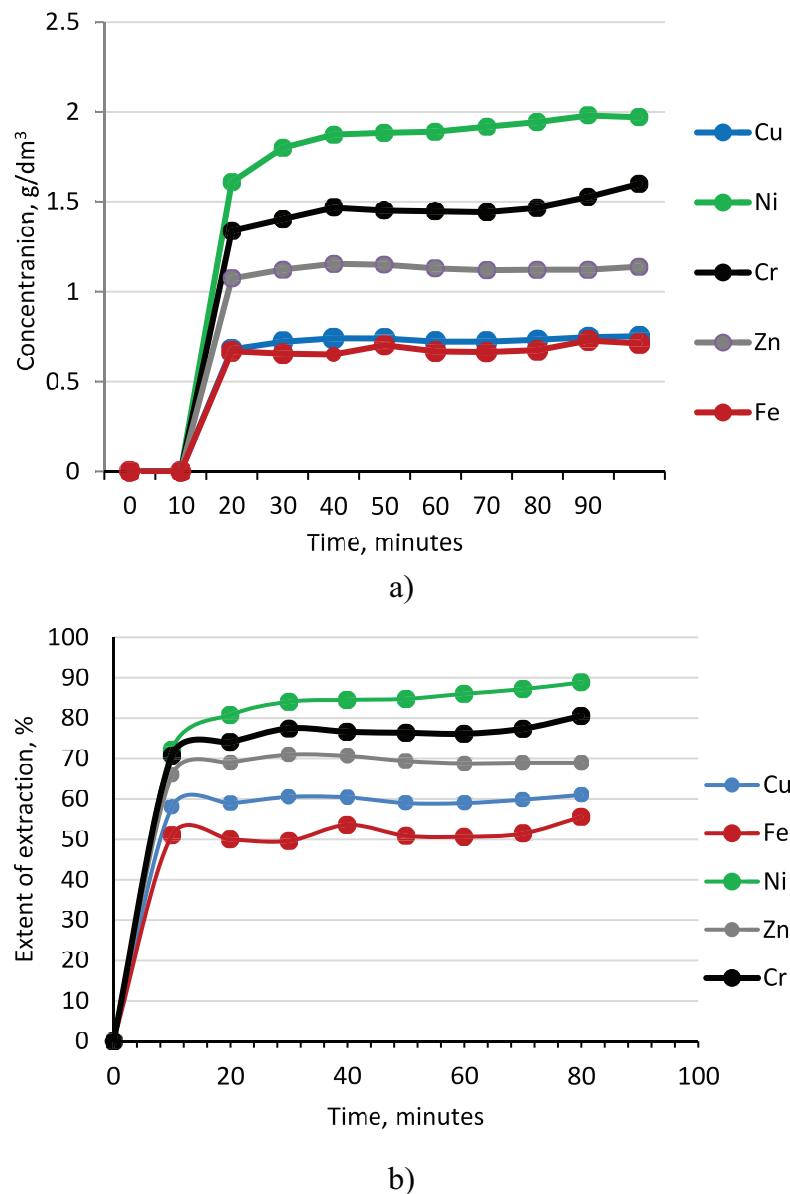


Figure 2: Dependence of metals concentration in solution (a) and extent of metals extraction in solution (b) from duration of leaching.

Based on the obtained data, Lewatit TP-207 was selected as having the best indices for metal selection. Ionite Lewatit TP-207 is a weakly basic macroporous cation exchange resin with chelate groups of iminodiacetic acid. Ionite is intended for the selective removal of heavy non-ferrous metal ions from weakly acidic and slightly alkaline solutions. This ion exchanger showed a high sorption capacity with respect to nickel, but insignificant sorption of chromium when they collectively presence in solution.

The effectiveness of the sorption process strongly depends on the pH value; therefore, an experiment to study the effect of pH on the nickel sorption process was

conducted. At pH=2, the concentration of H^+ ions in the functional groups is high and pushes metal cations into the solution due to the high degree of protonation of the functional groups, i.e. competition between H^+ ions and metal cations is observed. At pH 2-4, H^+ ions and metal cations still completely fill the functional groups, but the latter begin to be deprotonated. At pH 7, the carboxylic acid residue of the functional group is deprotonated, and at pH 12 the iminodiacetate group is completely deprotonated (Figure 3).

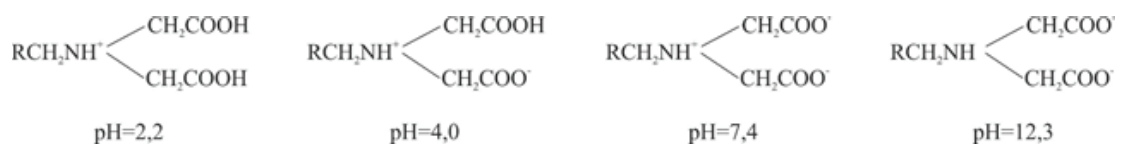


Figure 3: Influence of pH on iminodiacetate functional groups.

Although the latter case is more favorable for the sorption of cations due to the absence of hydrogen ions in the functional groups, maximum of metal cations sorption occurs at a pH value about 5.

To study the effect of pH on the sorption of nickel (II), model solutions of nickel with different pH were prepared. Samples of ion exchanger weighing 1 g in H^+ -form were brought into contact with the solution. Duration of sorption was 24 hours; the results are shown in Figure 4.

Obtained data shows that ion-exchange resin Lewatit TP207 has the maximum capacity for Ni (II) at pH=4-4,5. Thus, during the leaching operation, obtaining of solutions with a pH close to this value is preferable or the pH of the leachate should be adjusted.

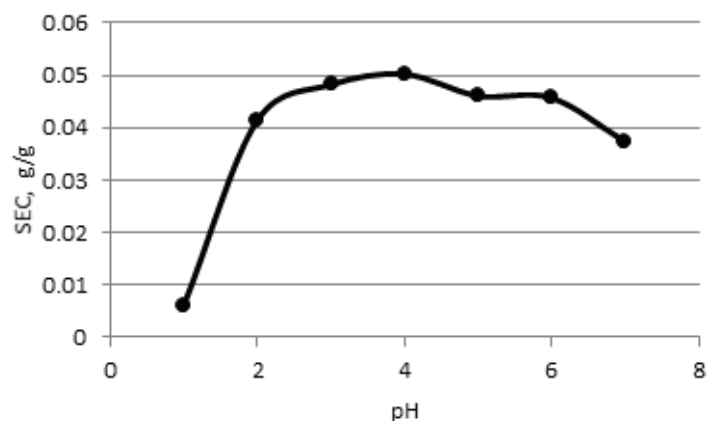


Figure 4: Dependence of SEC for from pH value.

3. Conclusions

Thus, for the processing of nickel-chromium galvanic sludges hydrometallurgical technology can be used. The proposed scheme includes steps of sludge leaching with sulfuric acid solutions, pH correction and selective sorption of nickel by synthetic ion-exchange resin Lewatit TP207.

References

- [1] Pérez-Villarejo, L., *et al.* (2015). Valorization and Inertization of Galvanic Sludge Waste in Clay Bricks. *Applied Clay Science*, vol. 105-106, pp. 89-99.
- [2] Stanisavljevic, M., Krstic, I. and Zec, S. (2010). Eco-technological Process of Glass-ceramic Production from Galvanic Sludge and Aluminium Slag. *Science of Sintering*, vol. 42, issue 1, pp. 125-130.
- [3] Ozdemir, O. D., Figen, A. K. and Piskin, S. (2011). Utilization of Galvanic Sludge as Raw Material for Production of Glass. Presented at *International Conference on Chemistry and Chemical Process*, IPCBEE.
- [4] Stepanov, S., *et al.* (2016). Efficiency of Use of Galvanic Sludge in Cement Systems. *Procedia Engineering*, vol. 165, pp.1112-1117.
- [5] Bednarik, V., Vondruska, M. and Koutny, M. (2005). Stabilization/solidification of Galvanic Sludges by Asphalt Emulsions. *Journal of Hazardous Materials*, vol. 122, issue 1-2, pp. 139-45.
- [6] Makovskaya, O. Y. and Kostromin, K. S. (2019). Leaching of Non-ferrous Metals from Galvanic Sludges. *Materials Science Forum*, vol. 946, pp. 591-595.
- [7] Silva, J. E., *et al.* (2005). Leaching Behaviour of a Galvanic Sludge in Sulphuric Acid and Ammoniacal Media. *Journal of Hazardous Materials*, vol. B 121, pp. 195-202.