GOCE DELCEV UNIVERSITY

FACULTY OF NATURAL AND TECHNICAL SCIENCES

NATURAL RESOURCES AND TECHNOLOGY

ISSN: 1857-6966
DOI: 10.46763/NRT

No 1 Volume XVII

JUNE 2023

UNIVERSITY "GOCE DELCEV" – STIP
FACULTY OF NATURAL AND TECHNICAL SCIENCES

Natural Resources and Technology

JUNE 2023

VOLUME: XVII **NO. 1**

ISSN 1857-6966

NATURAL RESOURCES AND TECHNOLOGY

Editorial Office
Goce Delcev University - Stip
Faculty of Natural and Technical Sciences

Contents

Manuscript received: 12.03.2023
Accepted: 03.05.2023

Natural Resources and Technology
Vol 17, No. 1, pp. 21- 25 (2023)
ISSN 1857-6966
UDC: 622.342:622.75/.77]:628.16.08(497.741)
DOI: https://doi.org/10.46763/NRT23171021t
Original research paper

HEAVY METALS REMOVAL FROM WASTEWATER FROM THE LEACHING PROCESS BY NEUTRALIZATION

Adrijana Trajanova[1], Afrodita Zendelska[2], Blagoj Golomeov[2], Dejan Mirakovski[2], Nikolinka Doneva[2], Marija Hadzi-Nikolova[2]
[1]*Mine Buhcim, Radovis, North Macedonia*
[2]*Faculty of Natural and Technical Sciences, Goce Delcev University, Stip, North Macedonia*

**Corresponding author: anen.trajanova@yahoo.com*

Abstract

The leaching process has been successfully used in the mining industry for a hundred years. Nowadays, technologies are developed in order to prevent harmful effects of the leaching process on the environment. The aim of this paper was to investigate the possibility of neutralizing and removing heavy metals from the water that circulates in the leaching process. Usually, no waste water is generated in the leaching process, that is, the leaching solution is not thrown out, but reused in a closed cycle. However, in the event of an accident, i.e., if these waters are spilled, the neutralization process can be applied in order to raise the pH value of the water and help in the precipitation of heavy metals. This paper presents the results of the studied potassium hydroxide, which proved to be a very effective neutralizer that successfully removes heavy metals.

Key words: *potassium hydroxide, mine Buchim, copper, zinc, iron, manganese, lead*

INTRODUCTION

Leaching is a hydrometallurgical process which is still the only method for recovering precious metals from the ores. In this process of solubilization through cyanidation, fine particles of metal are taken into solution in the complex ion. In other words, the metal is taken into the liquid phase and then it is precipitated from the solution [1].

Compared to pyrometallurgy, leaching is easier to perform, requires less energy and is potentially less harmful as no gaseous pollution occurs. Drawbacks of leaching include its lower efficiency and the often significant quantities of waste effluent and tailings produced, which are usually either highly acidic or alkali as well as toxic (e.g., bauxite tailings).

Precious metals such as gold are extracted from their ores by a cyanide or ozone leaching process. Radioactive metals such as uranium are extracted by the process of acid leaching. Choosing the appropriate leaching method for metal extraction is done based on economic and environmental viability. The two main types of leaching are heap and *in situ* leaching. Heap leaching is also known as acid leaching. This method is most effective for the extraction of metals from difficult ores and is one of the most tried and tested methods. The pre-processing of ore before leaching involves the grinding and roasting of the ore. Roasting is done to remove the carbonaceous elements trapped inside the ore. After pre-processing, the ore is leached with acid of alkali solutions to extract the metal. Heap leaching is carried out in the extraction of copper, nickel, uranium, and precious metals. *In situ* leaching is also known as *in situ* recovery, or solution mining. This is especially used to extract copper and uranium. In this process, holes are drilled into the ore deposit by explosive or hydraulic fracturing methods. The leaching solution is then pumped through these channels. The solution that dissolves the ore is then pumped out and processed.

Cyanidation is the dominant leaching technique due to its simple process and low cost [2]. However, unfortunately, cyanide is very toxic and there have been several serious environmental accidents worldwide caused by cyanide leakage from metallurgical plants [2-4]. Due to environmental concerns, cyanide leaching is currently banned in many regions. Alternative reagents have received increasing attention in recent years. Among them, chloride, thiourea and thiosulfate have the most attention. The development of chloride leaching has been hindered due to its hazardous working environment, poor reaction selectivity and high requirements for equipment corrosion protection [5-7]. The future of thiourea leaching was not attractive because the consumption and cost of thiourea are high and, in addition, it is a suspected carcinogen [8-11]. Leaching with thiosulfate is considered the most promising alternative method due to its reduced risk to the environment, high selectivity of reactions, low corrosiveness of the leaching solution, cheap reagents, etc. [12-17]. Thiosulfate leaching is a promising alternative to cyanidation, and the main obstacles to its wide commercial application are the high consumption of thiosulfate and the difficulty of obtaining the dissolved gold.

North Macedonia is one of the countries where procedures with leaching or flotation of metallic mineral resources with cyanides or with sulfuric acid in open pit mines are prohibited, but the exception are the existing mines.

In the Buchim mine, the leaching process is carried out in piles near the mine and is a closed system, where after separating the useful metal, the leaching solution (diluted sulfuric acid) is regenerated and used again for leaching new quantities of ore. The extraction of pure metal, i.e., pure copper, is by means of electrolysis. The purity of Cu is 99.99%. Although it does not generate wastewater, i.e., throws out the leaching solution, the goal of this study was to investigate the possibility of neutralizing and removing heavy metals from the water that circulates in the leaching process. In case there was an accident, that is, if there was a spill of those waters, how to be able to apply the neutralization process on them.

The neutralization process is commonly used for acid mine drainage treatment. Acid mine drainage has high acidity and large amounts of dissolved heavy metals such as copper, zinc, manganese, iron, arsenic, and lead [18]. The acid mine drainage has similar content with the leaching water. Generally, metals can be removed from acid water by precipitation and sorption. Fe precipitates as hydroxides, whereas Mn is removed by a combination of oxidation and precipitation. Some divalent metals (e.g., Fe, Zn, Pb) can be removed by precipitation as sulfide minerals. Sorption, coprecipitation, and exchange to precipitated Fe and Mn, organic materials, and soil-like materials are additional mechanisms for metal removal. Sorption to organic materials is important for Al and divalent transition metals and Pb, while sorption to precipitated Fe and Mn and even limestone surfaces can contribute to trace metal removal [19].

MATERIAL AND METHODS

The water from the leaching process in mine Buchim was used for the investigation of the possibility of application the neutralizing process for heavy metal removal. The initial pH value of the water was 2.12 and the initial concentration of the studied metals Cu, Fe, Mn, Zn and Pb were 15.8, 49.8, 136.0, 5.75 and 0.83mg/L respectively. To control and monitor pH pH 1000L VWR was used, which is combined with electrode pHenomenal 221 (ecn: 662-1161). The measurement of metal concentration was performed using atomic absorption spectroscopy. The instrumental technique used was AAnalyst 400 Perkin Elmer atomic absorber.

Analyses were also made of the total dry residue at 105°C, total dry residue from filtrate, suspended substances, sulfates (SO_4^{2-}) and organic substances (determination of oxygen with consumption of $KMnO_4$).

The used neutralizing agent in the experiments was KOH. According to Zendelska et al. (2022), potassium hydroxide was selected as the most effective of the eight studied neutralizing agents [20]. Neutralizing agents prepared in concentrations of 0.025 mol/L were added with a 10 ml A class pipette in a 100 ml of the leach water solution using 300 ml glass. The neutralizing agents were loaded continuously, adding 10 ml at a time until the constant pH was achieved in the leach water solution. The solution was mixed using a magnetic stirrer, model: As One HS-4DC /1-262-01 Battery Operated Starler.

RESULTS AND DISCUSSION

To investigate the possibility of neutralizing and removing heavy metals from the water that circulates in the leaching process, experiments were performed using KOH with a concentration of 0.025mol/L as a neutralyzing agent.

The initial pH of the leaching water was 2.12, and after neutralization we got a final pH of 10.73. This pH was achieved with the addition of 600 ml of the KOH for the time of around 30 minutes. According to the results obtained by Zendelska et al. (2022), it was expected that the final pH (11.67) would be obtained by adding 250 mL, but with the fact that this study was done using real water from the leaching process, it was expected that the neutralizing agent consumption would be higher. The results of the analyzed parameters of leaching water are given in Table 1.

Table 1. Results of the chemical analysis of the leaching water

Parameter	Concentration (mg/L)
Total dry residue of 105°C	36685.0
Total dry filtrate residue	35197.0
Suspended substances	1488.0
Sulfates - SO_4^{2-}	4568.1
Organic matter (Determination of oxygen consumption by KMnO4)	3168.5

Also, it was expected that the removal of heavy metal should be around 72%, but in this study a bigger percentage of removal was obtained. More precisely, the removal of heavy metals is quite efficient after neutralization, such as Cu has a removal of 96.7%, Fe - 98.07%, Mn - 86.99%, Zn - 91.83% and Pb - 80.72%. The results of the initial metal concentration, metal concentration after the process of neutralization and the percentage of the removal of heavy metals are presented in Table 2 and Figure 1.

After neutralization, a flocculant was added to aid and accelerate the precipitation process of the heavy metals. The settling time was less than 1 hour. From the obtained results shown in Figure 1, it can be seen that all metals were removed by 100%, except for Mn - 99.93%.

The results show that satisfactory concentrations are obtained only during the neutralization process, which means that flocculation is desirable, but in some situations it can be omitted.

Table 2. Concentration of heavy metals before, after neutralization and after flocculation

Metal	Initial metal concentration (mg/L)	Metal concentration after neutralization (mg/L)	Removal of metal (%)
Cu	15,8	0,52	96,7
Fe	49,8	0,96	98,1
Mn	136,0	17,69	87,0
Zn	5,75	0,47	91,8
Pb	0,83	0,16	80,7

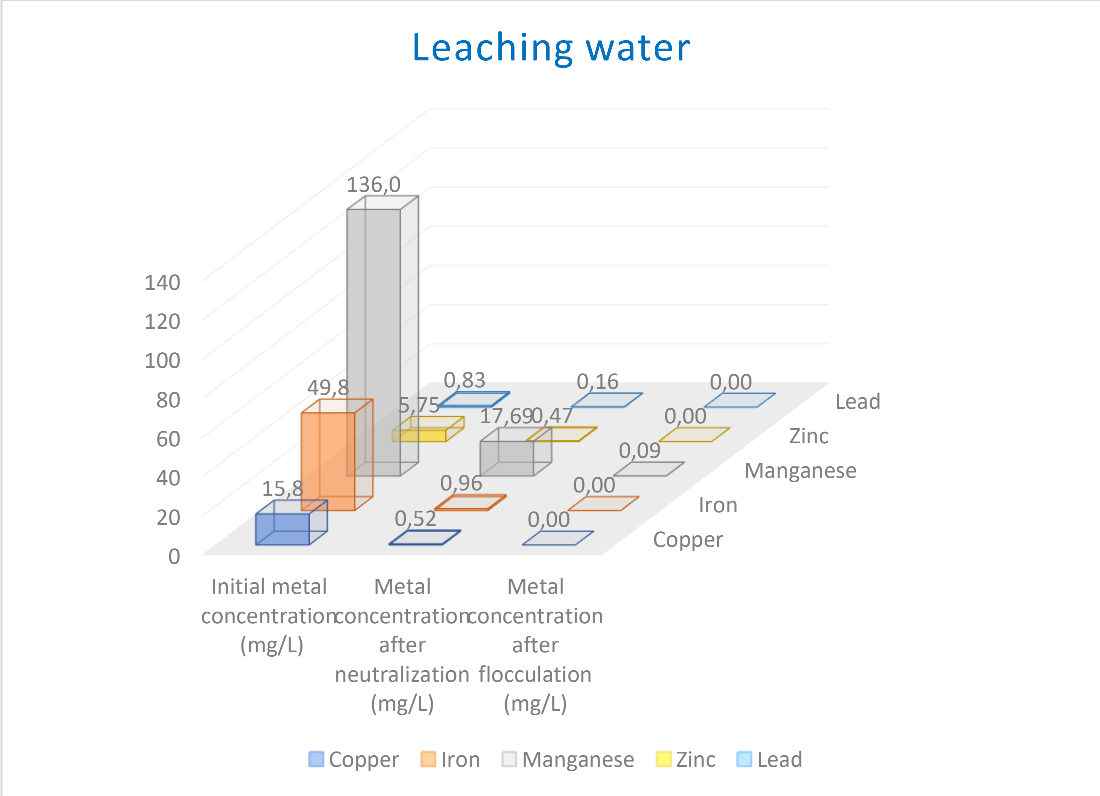

Figure 1. Concentration of metals before and after treatment with a KOH

CONCLUSION

Leaching is a very important operation in the mining industry. Extraction of metals from ore is carried out by using different solvents. Leaching can sometimes adversely affect the fertility of land as many important minerals may be leached away with water.

The possibility of neutralizing and removing heavy metals from the water that circulates in the leaching process was studied. The obtained results show that after neutralization with 0.025 mol/L KOH, a successful removal of metals was achieved, with a removal percentage of 96.7, 98.1, 87.0, 91.8, 80.7 for Cu, Fe, Mn, Zn and Pb respectively and raising the pH value was from 2.12 to 10.73. Therefore, KOH as well as other neutralizing agents can find application in the case of wastewater generation from the leaching process.

REFERENCES

1. A. Ekrem Yuce, Şeref Girgin, Güven Önal, M. Zeki Dogan, The truth about cyanidation process and its environmental effects on gold mining, The Criton Curi Int.Symp. on Environmental Management in the Mediterranean Region
2. Hilson, G.; Monhemius, A.J. Alternatives to cyanide in the gold mining industry: What prospects for the future? *J. Clean. Prod.* **2006**, *14,* 1158-1167.
3. Muir, D.M. A review of the selective leaching of gold from oxidised copper-gold ores with ammonia-cyanide and new insights for plant control and operation. *Miner. Eng.* **2011**, *24,* 576-582.
4. Jiang, T. *Chemistry of Extractive Metallurgy of Gold;* Hunan Science and Technology Press: Changsha, China, 1998.
5. Hasab, M.G.; Rashchi, F.; Raygan, S. Chloride-hypochlorite leaching and hydrochloric acid washing in multi-stages for extraction of gold from a refractory concentrate. *Hydrometallurgy* **2014**, *142,* 56-59.
6. Hasab, M.G.; Raygan, S.; Rashchi, F. Chloride-hypochlorite leaching of gold from a mechanically activated refractory sulfide concentrate. *Hydrometallurgy* **2013**, *138,* 59-64.
7. Xu, B.; Yang, Y.; Li, Q.; Li, G.; Jiang, T. Fluidized roasting-stage leaching of a silver and gold bearing polymetallic sulfide concentrate. *Hydrometallurgy* **2014**, *147,* 79-82.
8. Chen, X. Associated Sulfide Minerals in Thiosulfate Leaching of Gold: Problems and Solutions.

Ph.D. Thesis, Queen's University, Kingston, ON, Canada, September 2008.
9. Oncel, M.S.; Ince, M.; Bayramoglu, M. Leaching of silver from solid waste using ultrasound assisted thiourea method. *Ultrason. Sonochem.* **2005**, *12,* 237-242.
10. Orgul, S.; Atalay, U. Reaction chemistry of gold leaching in thiourea solution for a Turkish gold ore. *Hydrometallurgy* **2002**, 67, 71-77.
11. Zheng, S.; Wang, Y.; Chai, L. Research status and prospect of gold leaching in alkaline thiourea solution. *Miner. Eng.* **2006**, *19,* 1301-1306.
12. Feng, D.; Van Deventer, J.S.J. Thiosulphate leaching of gold in the presence of carboxymethyl cellulose (CMC). *Miner. Eng.* **2011**, *24,* 115-121.
13. Jeffrey, M.I.; Breuer, P.L.; Chu, C.K. The importance of controlling oxygen addition during the thiosulfate leaching of gold ores. *Int. J. Miner. Process.* **2003**, *72*, 323-330.
14. Lampinen, M.; Laari, A.; Turunen, I. Ammoniacal thiosulfate leaching of pressure oxidized sulfide gold concentrate with low reagent consumption. *Hydrometallurgy* **2015**, *151,* 1-9.
15. Xu, B.; Yang, Y.; Li, Q.; Jiang, T.; Li, G. Stage leaching of a complex polymetallic sulfide concentrate: A focus on the extractions of Ag and Au. *Hydrometallurgy* **2016**, *159,* 87-94.
16. Xu, B.; Yang, Y.; Li, Q.; Yin, W.; Jiang, T.; Li, G. Thiosulfate leaching of Au, Ag and Pd from a high Sn, Pb and Sb bearing decopperized anode slime. *Hydrometallurgy* **2016**, *164,* 278-287.
17. Xu, B.; Kong, W.; Li, Q.; Yang, Y.; Jiang, T.; Liu, X. A Review of Thiosulfate Leaching of Gold: Focus on Thiosulfate Consumption and Gold Recovery from Pregnant Solution. *Metals* 2017, *7*, 222. https://doi.org/10.3390/met7060222
18. Penreath, R.J. (1994). The discharge of waters from active and abandoned mines. In: Hester, R.E. and Harrison, R.M. (Editors.) Mining and its environmental impact. Issues in Environmental Science and Technology No. 1. Royal Society of Chemistry, Herts, UK, 121-132.
19. Skousen, J., Zipper, C.E., Rose, A., Ziemkiewicz, P.F., Nairn, R., McDonald, L.M., and Kleinmann R.L. (2017). Review of Passive Systems for Acid Mine Drainage Treatment, Mine Water Environ (2017) 36:133–153, DOI 10.1007/s10230-016-0417-1
20. A. Zendelska, A. Trajanova, M. Golomeova, B. Golomeov, D. Mirakovski, N. Doneva, M. Hadzi-Nikolova (2022) Comparison of Efficiencies of Neutralizing Agents for Heavy Metal Removal from Acid Mine Drainage. Journal of Mining and Environment, 13 (3). pp. 679-691. https://doi.org/10.22044/jme.2022.12090.2205

ОТСТРАНУВАЊЕ НА ТЕШКИТЕ МЕТАЛИ ОД ОТПАДНА ВОДА ПОСЛЕ ПРОЦЕСОТ НА ЛУЖЕЊЕ СО НЕУТРАЛИЗАЦИЈА

Адријана Трајанова[1*], Афродита Зенделска[2], Благој Голомеов[2], Дејан Мираковски[2], Николинка Донева[2], Марија Хаџи-Николова[2]
[1]Рудник Бучим, Радовиш, Северна Македонија
[2]Факултет за природни и технички науки, Универзитет „Гоце Делчев“, Штип, Северна Македонија

**Контакт автор: anen.trajanova@yahoo.com*

Резиме

Процесот на лужење успешно се користи во рударската индустрија веќе 100 години. Во денешно време се развиваат технологии со цел да се спречат штетните ефекти од процесот на лужење врз животната средина. Целта на овој труд беше да се истражи можноста за неутрализирање и отстранување на тешките метали од водата што циркулира во процесот на лужење. Обично во процесот на лужење не се создава отпадна вода, односно растворот за лужење не се исфрла, туку повторно се користи во затворен циклус. Меѓутоа, во случај на несреќа, односно ако овие води се излеат, може да се примени процесот на неутрализација со цел да се подигне pH вредноста на водата и да се помогне во таложење на тешки метали. Во овој труд се прикажани резултати од испитувањето на калиум хидроксидот кој се покажа како доста ефикасен неутрализатор со кој успешно се отстрануваат тешките метали.

Клучни зборови: *калиум хидроксид, рудник Бучим, бакар, цинк, железо, манган, олово*