Crossref
DOI: 10.31643/2022/6445.39

Promising methods for hydrometallurgical processing of copper slag

[1*]Kurmangaliyev D.B., [1]Abdulina S.A., [2] Mamyachenkov S.V.

[1] D.Serikbayev East Kazakhstan technical university, Ust-Kamenogorsk, Kazakhstan
[2]Federal State Autonomous Educational Institution of Higher Education «Ural Federal University named after the first President of Russia B.N.Yeltsin», Ekaterinburg, Russia

* Corresponding author email: kurmangaliyev_d@mail.ru

Received: *January 28, 2022*
Peer-reviewed: *March 18, 2022*
Accepted: *May 04, 2022*

ABSTRACT

Metals are important in many modern industries. Due to the depletion of their natural resource base, it is necessary to adapt, which means developing new and optimizing existing methods of extraction of valuable components from ore materials. Only comprehensive processing of copper metallurgical slags will solve the problem of resource recovery and the creation of low-waste technology, which has great economic, environmental, and social importance. Hydrometallurgical technologies take into account the specific conditions of the system and the physical and chemical properties of metals when developing and selecting the method of extraction. This article provides a review of the current state and prospects of development technologies used for base metal extraction by leaching with the use of inorganic acids and environmentally safe reagents, the methods are conditionally divided into two groups. The listed studies have made a significant contribution to solving the problem of processing metallurgical slags, however, none of the technologies has gone beyond the scope of laboratory and semi-industrial tests. Noted a tendency to reduce the concentrations of leaching agents by certain pre-treatment of raw material, as well as the transition to ubiquitously use "green technologies": such as bioleaching and organic acid leaching. Directions are suggested to solve the problem of rational use of raw materials and increase the sustainability of the future material cycle.

Keywords: hydrometallurgy, metallurgical slag, leaching, organic acid, bioleaching.

Information about authors:

Kurmangaliyev Damir Bolatovich	*Ph.D. student of School of Metallurgy and Mineral Processing, D. Serikbayev East Kazakhstan technical university, Ust-Kamenogorsk, Kazakhstan. Email: kurmangaliyev_d@mail.ru, ORCID ID: 0000-0002-5022-696X*
Abdulina Saule Amangeldyevna	*Ph.D., Assistant professor of School of Metallurgy and Mineral Processing, D. Serikbayev East Kazakhstan technical university, Ust-Kamenogorsk, Kazakhstan. Email: abdulina.saule@mail.ru, ORCID ID: 0000-0001-6328-8652*
Mamyachenkov Sergey Vladimirovich	*Doctor of Technical Sciences, Senior Researcher of Federal State Autonomous Educational Institution of Higher Education «Ural Federal University named after the first President of Russia B.N.Yeltsin», Ekaterinburg, Russia. Email: s.v.mamiachenkov@urfu.ru, Scopus Author ID 6507625972*

Introduction

The problem of processing mining and metallurgical slag dumps is one of the most complicated and unresolved problems in modern nonferrous metallurgy. These wastes occupy a large territory and have a negative impact on the environment. Each ton of copper produced about 2.2 tons of copper slag [1]. On average, the annual production of copper-melting slags in the world is about 25 million tons, which usually contain a significant amount of valuable components, the concentration of which often far exceeds their concentration in the extracted raw materials. The growing value of non-ferrous metals and reduction of the mineral resource base do not allow their irretrievable losses and make the processing of such material economically attractive.

Copper smelting slags of different enterprises vary in their chemical composition and structure and usually contain about 1% of copper and 40% of iron, depending on the type of processing and elemental composition of ores, concentrates, and fluxes. Significant amounts of oxides of aluminum, magnesium, calcium, barium, etc., and minor amounts of other elements (e.g., zinc, titanium, and lead) are also associated with copper slag. The main components of copper slag are iron oxide and SiO_2, which are present in copper slag mainly in the form of fayalite ($2FeO - SiO_2$).

Recently, scientists around the world have paid special attention to hydrometallurgical processes for the extraction of valuable components from metallurgical slags, and many technologies have been developed. In these studies, the efforts were mainly focused on leaching processes with the use of inorganic acids and environmentally safe reagents (organic acids and microorganisms), according to the same principle the methods have been classified in this review, but it should be noted that this division is conventional.

The first group includes technologies of leaching with the use of inorganic acids.

In the work, Banza A.N. et al [2] performed an extraction of non-ferrous metals using three different methods (sulfuric acid leaching, leaching at a constant hydrogen peroxide flow rate, and leaching at a constant Eh potential) with samples of milled slag from Lubumbashi, Democratic Republic of Congo. Metal recoveries of about 60% Cu, 90% Co, 90% Zn, and 90% Fe were obtained after 2 hours using only H_2SO_4. Using a combination of H_2SO_4 and H_2O_2, resulted in better metal recovery: 80% Cu, 90% Co, 90% Zn, and 5% Fe.

Yang, Z. et al [3] investigated the leaching of copper smelting slag from Guangdong province in China using the same acid (H_2SO_4) with $NaClO_3$ oxidizer and $Ca(OH)_2$ neutralization to accelerate sludge filtration. The overall leaching and selective precipitation process recovered about 98% Co, 97% Zn, and 89% Cu from this slag, with only 3.2% Si and 0.02% Fe dissolved.

By another technology [4] the authors studied the extraction of copper and cobalt from converter slag obtained at Zhongtiaoshan Nonferrous Complex metallurgical plant, China. Pre-dried slag was treated with H_2O_2 and H_2SO_4 (120% stoichiometric amount), and then solidified slag was leached with water, and as a result, was extracted more than 95% Co and up to 90% Cu.

In the method developed at Firat University, Turkey [5] was shown that roasting with $Fe_2(SO_4)_3$ at 500°C, duration of 120 minutes and ratio ($Fe_2(SO_4)_3{\cdot}xH_2O$: slag = 1: 1) followed by water leaching resulted in copper, cobalt, nickel and zinc recovery respectively: 93%; 38%; 13% и 59%. Copper converter slag from Ergani Copper Plant, Maden, Elazig, Turkey was investigated.

In the work of the previously mentioned university [6], the extraction characteristics of copper, cobalt, zinc, and iron from converter slag obtained at Ergani Copper Plant, Maden, Elazig, Turkey were investigated. Studies were carried out by oxidative leaching with a leaching agent based on potassium dichromate ($K_2Cr_2O_7$) and sulfuric acid (H_2SO_4). Experimental results showed that the presence of dichromate has a great influence on the extraction of base metals. The process extracted 81.15% Cu, 12.0% Co, 3.15% Fe and 10.27% Zn.

Arslan and Arslan [7] focused on the recovery of copper, cobalt, and zinc from smelter and converter slags by sulfuric acid roasting. This study used leaching experiments to investigate the effect of firing time, acid: slag ratio, and firing temperature on the degree of metal dissolution. In 2 hours of firing at 150°C and acid: slag ratio = 3: 1, the metals recovered were: 88% Cu, 87% Co, 93% Zn and 83% Fe. Moreover, increasing the firing time to 4 hours increased the copper recovery to 95%.

In work [8] the influence of the degree of grinding of copper smelting slags Kazakhmys Smelting, Balkhash, Kazakhstan on the degree of extraction of non-ferrous metals by sulfuric acid at room temperature in the presence of potassium dichromate was studied. Grinding in a planetary ball mill and an abrasion mill was used for mechanical activation of copper extraction. Figure 1 compares SEM images of slag subjected to dry grinding in a planetary (Fig. 1a) and an abrasion mill (Fig. 1b) for 20 minutes at 600 rpm, a ball : powder ratio = 20 : 1. The figure shows that the planetary grinding produces finer particles.

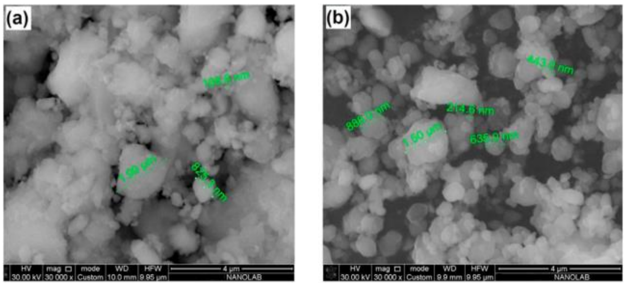

Figure 1 - SEM images of crushed slag samples [8]

When conducting leaching experiments under optimal conditions for milled slag, and with optimal parameters for copper extraction and copper selectivity, the maximum copper extraction was 87.3%, and the maximum copper selectivity was 97.9%.

The second group includes technologies using environmentally safe reagents.

Sukla et al [9], described a leaching process, using a strain of Aspergillus niger, copper converter slag from M/S Hindustan Copper Limited, Gatsila, India, isolated from Sukinda laterite nickel ore. The bacteria were pre-enriched with 2% - potato dextrose broth and the pulp density was varied by dextrose concentration from 2 to 10%. At the same time, good results were obtained by trial experiments with oxalic, acetic, and succinic acids (1M) for 72 hours on a rotary vibrator at 37°C. The maximum recoveries of copper, cobalt, and nickel were 47%, 50%, and 23%, respectively.

Mehta et al [10] investigated the recovery of copper, cobalt, and nickel from converter slag at room temperature by biological leaching using Thiobacillus ferrooxidans, and iron-oxidizing bacteria from two copper converter slag samples from the Indian Copper Complex (ICC) in Gatsil, India on a laboratory scale. The slag treatment optimized parameters such as the degree of grinding of the material, acidity of the medium, solid: liquid ratio, Fe(II)/Fe(III) ratio, and the amount of Fe(II) and additives. Metal recovery from slag under sterile and biological leaching conditions was 80.0% and 99.0% Cu (80 days), 18.0% and 22.0% Ni (70 days), and 16.0% and 30.0% Co (50 days).

Selective leaching of lead and copper by citric acid solutions from the slag of suspended copper smelting was proposed in the work [11]. In the work, the optimal conditions for the transition of lead into solution (85%) were determined, while the leaching of copper into solution was minimal (26%). In the next step, the solid residue could be treated using H_2SO_4 solutions to extract the copper.

In another paper [12], an environmentally friendly hydrometallurgical process for the recovery of copper, nickel, and cobalt from copper-enriched converter slag using organic acids was proposed. In order to optimize copper leaching, the authors of the work varied such parameters as acid concentration, slurry density, temperature, and process time. Optimal extraction of 99.1% Cu, 89.2% Ni, 94% Co and 99.2% Fe was achieved in 9-10 hours at 35°C, pulp density 15% using 2N citric acid, and particle size <45 µm.

The authors of [13] studied the characteristics of Cu, Co, Zn, and Fe extraction from Küre-Kastamonu Historical Copper Slag (KHS) by oxidative leaching under pressure using a sulfuric acid-based leaching additive. The samples used in the leaching tests averaged 0.84% Cu, 0.34% Co, 0.23% Zn, 2.90% Al, 0.70% Ca, 1.30% S and 42.80% Fe. It was found that metal recovery increased with increasing temperature and sulfuric acid concentration. However, high acid concentrations led to gel formation, which caused filtration problems. Under optimal conditions, the recovery efficiency of cobalt, copper, and zinc from KHS was 96.82, 92.85, and 93.44%, respectively.

S.N. Vinogradov Institute of Microbiology of the Russian Academy of Sciences proposed the process of non-ferrous metals leaching [14] from slag by trivalent iron sulfate obtained with the help of iron-oxidizing chemolithotrophic bacteria, which allowed fully enough convert non-ferrous metals to the liquid phase for 1.0 hour at 70°C. At the same time extraction of copper in the solution reached 90%, nickel - 88%, cobalt - 67%, and extraction of iron in the solution was only about 30%.

As a result of the analysis of studies in the field of technologies aimed at extraction of valuable components from copper production slags by hydrometallurgical methods the following was revealed:

– in recent years, domestic and foreign scientists have proposed a large number of promising methods for extracting valuable components from copper slag, but none of them has gone beyond the laboratory and semi-industrial tests;

– the main trend in the processing of copper slag with inorganic acids is a certain pretreatment of the material, which will ensure the use of low concentrations of leaching agents, which is intended to make the process more environmentally friendly;

– much emphasis is now being placed on introducing "green technologies" into production: this is an environmentally safe and economically competitive approach to the extraction of non-ferrous metals from copper slag, in which organic acids and microorganisms are preferred to inorganic acids.

Conflict of interest

The correspondent author declares that there is no conflict of interest on behalf of all authors.

Cite this article as: Kurmangaliyev DB, Abdulina SA, Mamyachenkov SV. Perspektivnyye metody gidrometallurgicheskoy pererabotki mednykh shlakov. Kompleksnoe Ispol’zovanie Mineral’nogo Syr’a = Complex Use of Mineral Resources. 2022; 4(323):46-50. https://doi.org/10.31643/2022/6445.39

Мыс қождарын гидрометаллургиялық өңдеудің перспективті әдістері

[1] Курмангалиев Д. Б., [1] Абдулина С.А., [2] Мамяченков С.В.

[1] Д. Серікбаев атындағы Шығыс Қазақстан техникалық университеті, Өскемен қ, Қазақстан
[2] Ресейдің тұңғыш президенті Б.Н. Ельцин атындағы Орал федералдық университеті, Екатеринбург, Ресей

Мақала келді: *28 қаңтар 2022*
Сараптамадан өтті: *18 наурыз 2022*
Қабылданды: *04 мамыр 2022*

ТҮЙІНДЕМЕ

Қазіргі замандағы барлық салаларда металдардың маңызы өте зор. Минералдық-шикізат базасының сарқылуына байланысты кендерден құнды компоненттерді алудың жаңа әдістерін әзірлеу және қолданыстағы әдістерді оңтайландыру қажет. Мыстың металлургиялық қождарын кешенді қайта өңдеу ғана ресурстарды қалпына келтіру және қалдығы аз технологиялар жасауға мүмкіндік береді, бұның орасан зор экономикалық, экологиялық және әлеуметтік маңызы бар. Гидрометаллургиялық технологиялар металды өндіру әдісін әзірлеу және таңдау кезінде жүйенің ерекше жағдайларын және металдардың физика-химиялық қасиеттерін ескереді. Бұл мақалада бейорганикалық қышқылдар мен экологиялық таза реагенттерді қолдана отырып, ерітінділеу (шаймалау) арқылы мыс алу үшін қолданылатын технологиялардың қазіргі жағдайы мен даму перспективаларына шолу жасалады. Әдістер шартты түрде екі топқа бөлінген. Айтылған зерттеулер металлургиялық қожды өңдеу мәселесін шешуге айтарлықтай үлес қосты, дегенмен технологиялардың ешқайсысы зертханалық және жартылай өнеркәсіптік сынақтар шеңберінен шыққан жоқ. Қазіргі кезде материалды алдын ала белгілі бір өңдеу кезінде қолданылатын ерітінділеу агенттерін пайдалануының төмендеу үрдісі, сонымен қатар "жасыл технологияларды" кең түрде пайдалану байқалады. Мұның бәрі кен шикізатын ұтымды пайдалану проблемасын шешуге және материалдардың айналымының тұрақтылығын арттыруға бағытталған.

Түйін сөздер: гидрометаллургия, металлургиялық қож, сілтілеу, органикалық қышқыл, биосілтілеу

Авторлар туралы ақпарат:

Курмангалиев Дамир Болатович — *Докторант, Металлургия және пайдалы қазбаларды байыту мектебі, Д. Серікбаев атындағы Шығыс Қазақстан техникалық университеті, Өскемен қ., Қазақстан. Электрондық пошта: kurmangaliyev_d@mail.ru, ORCID ID: 0000-0002-5022-696X*

Абдулина Сауле Амангельдыевна — *PhD, Металлургия және пайдалы қазбаларды байыту мектебі Металлургия және пайдалы қазбаларды байыту мектебің қауымдастырылған профессоры, Д. Серікбаев атындағы Шығыс Қазақстан техникалық университеті, Өскемен қ., Қазақстан. Электрондық пошта: abdulina.saule@mail.ru, ORCID ID: 0000-0001-6328-8652*

Мамяченков Сергей Владимирович — *Техникалық ғылымдар докторы, Ресейдің тұңғыш президенті Б.Н. Ельцин атындағы Орал федералдық университетінің аға ғылыми қызметкері, Электрондық пошта: s.v.mamiachenkov@urfu.ru, Scopus Author ID 6507625972*

Перспективные методы гидрометаллургической переработки медных шлаков

[1]Курмангалиев Д. Б., [1] Абдулина С.А., [2] Мамяченков С.В.

[1] Восточно-Казахстанский технический университет им. Д. Серикбаева, Усть-Каменогорск, Казахстан
[2] Уральский федеральный университет имени первого Президента России Б.Н. Ельцина, Екатеринбург, Россия

Поступила: *14 января 2022*
Рецензирование: *18 марта 2022*
Принята в печать: *04 мая 2022*

АННОТАЦИЯ

Металлы важны во многих современных отраслях. По причине истощения их минерально-сырьевой базы, необходимо адаптироваться, значит разрабатывать новые и оптимизировать существующие методы извлечения ценных компонентов из рудных материалов. Только комплексная переработка медных металлургических шлаков позволит решить задачу восстановления ресурсов и создания малоотходных технологий, имеющую огромное экономическое, экологическое и социальное значение. Гидрометаллургические технологии, при разработке и выборе метода извлечения, учитывают специфические условия системы и физико-химические свойства металлов. В данной статье представлен обзор современного состояния и перспектив развития технологий, используемых для извлечения меди выщелачиванием с применением неорганических кислот и экологически безопасных реагентов, методы условно поделены на две группы. Перечисленные исследования внесли серьезный вклад в решение проблемы перерабоки металлургических шлаков, однако ни одна из технологий не вышла за рамки лабораторных и полупромышленных испытаний. Отмечается тенденция снижения концентраций применяемых выщелачивающих агентов, путём определенной предварительной обработки материала, а также повсеместное внедрение «зеленых технологий». Всё это направлено на решение проблемы рационального использования рудного сырья и повышения устойчивости будущего круговорота материалов.

Ключевые слова: гидрометаллургия, металлургический шлак, выщелачивание, органическая кислота, биовыщелачивание

Информация об авторах:

Курмангалиев Дамир Болатович	*Докторант, Школа металлургии и обогащение полезных ископаемых, Восточно-Казахстанский технический университет им. Д. Серикбаева, Усть-Каменогорск, Казахстан. Email: kurmangaliyev_d@mail.ru, ORCID ID: 0000-0002-5022-696X*
Абдулина Сауле Амангельдыевна	*PhD, Ассоциированный профессор Школы металлургии и обогащение полезных ископаемых, Восточно-Казахстанский технический университет им. Д. Серикбаева, Усть-Каменогорск, Казахстан. Email: abdulina.saule@mail.ru, ORCID ID: 0000-0001-6328-8652*
Мамяченков Сергей Владимирович	*Доктор технических наук, Старший научный сотрудник Уральский федеральный университет имени первого Президента России Б.Н. Ельцина, Екатеринбург, Россия. Email: s.v.mamiachenkov@urfu.ru, Scopus Author ID 6507625972*

Reference

[1] Gorai B, Jana RK. Premchand. Characteristics and utilisation of copper slag - A review. Resour. Conserv. Recycl. 2003;39: 299-313. DOI: 10.1016/S0921-3449(02)00171-4.

[2] Banza AN, Gock E, Kongolo K. Base metals recovery from copper smelter slag by oxidising leaching and solvent extraction. Hydrometallurgy 2002;67:63-69. https://doi.org/10.1016/S0304-386X(02)00138-X

[3] Yang Z, Rui-lin M, Wang-dong N, Hui W. Selective leaching of base metals from copper smelter slag. Hydrometallurgy 2010;103:25-29. DOI: 10.1016/j.hydromet.2010.02.009

[4] Deng T, Ling Y. Processing of copper converter slag for metal reclamation: Part I: Extraction and recovery of copper and cobalt. Waste Manag. Res. 2007;25:440-448. https://doi.org/10.1177/0734242X07077613

[5] Altundogan HS, Tumen F. Metal recovery from copper converter slag by roasting with ferric sulphate. Hydrometallurgy 1997;44:261-267. DOI: 10.1179/cmq.2006.45.2.145

[6] Altundogan HS, Boyrazli M, Tumen F. A study on the sulphuric acid leaching of copper converter slag in the presence of dichromate. Miner. 2004;17:465-467. DOI: 10.1016/j.mineng.2003.11.002

[7] Arslan C and Arslan F. "Recovery of copper, cobalt, and zinc from the copper smelter and converter slags. Hydrometallurgy. 2002;67(1-3):1-7. DOI: 10.1016/S0304-386X(02)00139-1

[8] Mussapyrova L, Nadirova R, Balaz P, Rajnak M, Bures R. Matej Balaz Selective room-temperature leaching of copper from mechanically activated copper smelter slag Elsevier B.V. 2021;2011-2025. https://doi.org/10.1016/j.jmrt.2021.03.090

[9] Sukla LB, Kar RN, Panchanadikar VV. Bioleaching of copper converter slag using Aspergillus niger isolated from lateritic nickel ore. Int. J. Environ. Stud. 1995;47:81-86. https://doi.org/10.1080/00207239508710947

[10] Mehta KD, Pandey BD. Premchand. Bio-leaching of copper, nickel, and cobalt from copper converter slag by Thiobacillus ferrooxidans. NML Tech. J. 1997;39:59-70. http://www.jstage.jst.go.jp/article/isijinternational/45/1/45_127/_article/10.2355/isijinternational.45.127

[11] Gargul K, Jarosz P, Małecki S. Leaching of Lead and Copper by Citric Acid from Direct-to-Blister Copper Flash Smelting Slag. Preprints 2018, 2018110209. DOI: 10.20944/preprints201811.0209.v1

[12] Pratima Meshram, Uday Prakash, Lalit Bhagat, Abhilash, Hongbo Zhao and Eric D. van Hullebusch , Processing of Waste Copper Converter Slag Using Organic Acids for Extraction of Copper, Nickel and Cobalt, 2020. DOI:10.3390/min10030290

[13] Abdullah Seyrankaya, Mehmet Canbazoğlu, Recovery of Cobalt, Copper and Zinc from Küre-Kastamonu Historical Copper Slag by High-Pressure Oxidative Acid Leaching, Russian Journal of Non-Ferrous Metals. July. 2021;62(4):390-402. DOI: 10.3103/S1067821221040131

[14] Fomchenko NV, Kajnova AA, Murav'ev MI. Vyshchelachivanie cvetnyh metallov iz metallurgicheskih shlakov sernokislymi rastvorami trekhvalentnogo zheleza, poluchennymi putem biookisleniya [Leaching of non-ferrous metals from metallurgical slags with ferric sulfate solutions obtained by bio-oxidation]. Izvestiya MGTU «MAMI», 2013;119-123. (in Russ.). https://doi.org/10.17816/2074-0530-67838