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CHEMICAL SULFATIZATION OF CHROME-CONTAINING SLUDGES FROM DUBERSAY TAILING DUMP

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Waste chromium production sludge from the Dubersay tailings dump is present in huge quantities with a magnesium oxide content of up to 40 %. The chrome-containing waste was sintered at 1 100 °C, the resulting sinter was mixed with sulphuric acid when heated to 300 °C. The resulting mixture after heating was leached with water at 90 °C, the solid precipitate was washed and dried to yield a chrome concentrate containing 55,4 % Cr_2O_3, 8,2 % SiO_2. Evaporation of the purified solution produces magnesium sulphate which is a magnesium fertilizer.

Keywords: chromium oxide, sludge tailings, chromium concentrate, sintering, X-ray research

INTRODUCTION

At present, the problem of processing of sludge from gravity concentration of the Dubersay tailings dump located in western Kazakhstan has not been solved. Enrichment of non-ferrous and ferrous metal ores with subsequent hydro- and pyrometallurgical treatment leads to formation of a large number of technogenic mineral formations [1-6].

Chromite ores, unlike sludge, do not have high magnesium oxide content, which in turn is the most refractory and difficult to recover. Therefore, it is reasonable to process the sludge by chemical stripping with removal of magnesium oxide [4, 7- 8].

One of the works [9] applied chromite chlorination at 800-1 000 °C for 2 h removing up to 60 % of iron. Aluminum chloride was used as a chlorinating agent, observing the oxygen pressure in the chlorination reactor. The chemical enrichment by chlorination is suitable for chromite concentrates.

In waste from chrome ore processing the Mg and Cr phases are firmly bonded and chromium is not sufficiently extracted. A method was developed [10] to remove Mg from chrome ore processing waste by roasting with $(NH_4)_2SO_4$ and subsequent leaching with H_2SO_4 80 mmol of $(NH_4)_2SO_4$ was added to the waste and the degree of Mg removal reached 79,55 % during chrome waste roasting.

A number of studies are devoted to the removal of magnesium and calcium oxides from chromites by the action of carbonic acid solutions to form water-soluble MgO and CaO compounds [11].

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The purpose of this paper is to investigate the processing of waste chrome ore by chemical beneficiation to produce a chrome product and magnesium fertilizer.

MATERIALS AND METHODS

The resuting sample of the Donskoy mining and beneficiation plant (DMPP) sludge tailings undergoes preliminary preparation and cutting according to the process flow that includes several processing stages. Raw materials used for the chemical beneficiation process of chromium sludge should be preliminary prepared. All materials are screened, and lumpy materials are first crushed, and then also screened. Chemically pure sulfuric acid 94 % H_2SO_4, chemically pure calcium oxide grade, activated carbon were used.

– Analysis methods-X-ray fluorescence analysis was performed with an Axios PANalytycal wave-dispersive spectrometer (Holland).

The chemical analysis of the samples was performed with an Optima 8300 DV inductively coupled plasma optical emission spectrometer (USA, Perkin Elmer inc).

X-ray experimental data were obtained using a Bruker D8 Advance apparatus from Bruker AXS GmbH (Germany) using Cu-Ka radiation from the International Center for Diffraction Data ICDD (USA) at an accelerating voltage of 36 kV and a current of 25 mA.

RESULTS AND DISCUSSION

X-ray phase analysis of the DMPP sludge tailings from the Dubersay tailing dump showed that there was a significant amount of magnesian chromite $(Fe_{0.51}Mg_{0.49})(Cr_{0.75}Al_{0.26})_2O_4$ – 70,7 %, there was also a significant amount of lizardite -1T $(Mg,Al)_3((Si,Fe)_2O_5)(OH)_4$ – 25,9 %, quartz SiO_2 – 3,4 %. Chemical analysis of

Table 1 **Content and recovery of target components into the cake**

Product name	Content of MgO/wt. %	Recovery of MgO/%	Content of Cr_2O_3/wt. %	Recovery of Cr_2O_3/%	Content of Fe_2O_3/wt. %	Recovery of Fe_2O_3/%
Cake from leaching with 3 % solution H_2SO_4	26,4	80,6	39,3	93,9	10,2	99,6
Cake from leaching with 5 % solution H_2SO_4	26,1	78,4	38,2	88,4	10,1	97,9
Cake from leaching with 10 % solution H_2SO_4	23,8	69,4	39,2	93,1	10,5	97,9

sludge tailings, wt. %: 39,9 Cr_2O_3, 31,4 MgO, 9,8 Fe_2O_3, 2,7 Al_2O_3, 26,3 SiO_2, 0,51 CaO.

Dubersay sludges were preliminarily leached with 3, 5 and 10 % sulfuric acid solutions. 100 g of sludge were taken and leached with these solutions at 90 ^oC at a ratio of S:L=1:3 for 60 min, then they were filtered. The cake was washed with hot water on the filter at S:L=1:2. The dried cake and filtrates were submitted for analysis. Cake yield during leaching with 3 % H_2SO_4 solution was 96 %, 5 % H_2SO_4 solution - 94 %, 10 % H_2SO_4 solution-91 %. As the concentration increased, the cake yield decreased. Table 1 presents the results of leaching with sulfuric acid solutions.

There is a marked decrease in the magnesium oxide content with an increase in the sulfuric acid concentration under the results in Table 1. The recovery of chromium and iron oxides into the cake remains at the same level.

When sedimentation analysis was performed with tailings samples, it was determined that the DMPP tailings received for the study were treated with a large amount of organic flocculants, which were very strongly adsorbed on the surface of mineral particles. The original Dubersay sludge was fired at a temperature of 1 100 ^oC for 60 min to remove flocculant residues, weaken the bonds of magnesium with serpentinites in chromium sludge, and the sinter yield was 92,4 % of the initial one. An average sample of sludge tailings was roasted in a ST-1400 GX-V1 (China) high-temperature rotary kiln. Weight loss of tailings was 5,3 % after sintering, and product yield - sintered product was 94,7 %. Figure 2 shows an X-ray fluorescence analysis of the sludge sinter. Chemical analysis of sludge tailings cake, wt. %: 43,3 Cr_2O_3, 33,6 MgO, 10,6 Fe_2O_3, 2,86 Al_2O_3, 28,4 SiO_2, 0,54 CaO.

Figure 1 shows that lizardite has passed into forsterite, and a part of the magnesian chromite has passed into the alumina-magnesian ferruginous spinel.

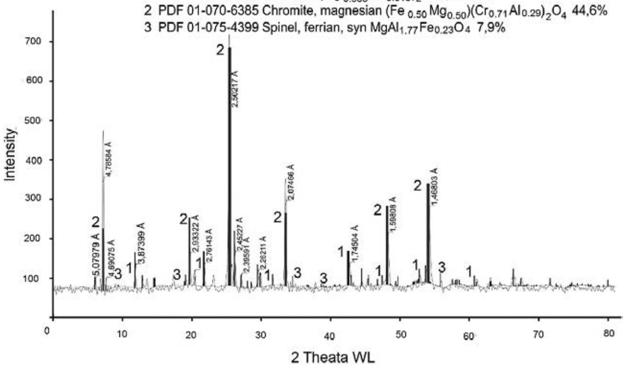

Figure 1 X-ray phase analysis of the sintered sludge

It was decided to execute thermal sulfatization of sludge with concentrated sulfuric acid, by analogy with ammonium sulfate [12].

A mixture was prepared from 462 g of Dubersay sludge cake, 235 ml of concentrated sulfuric acid and 46 ml of water. The mixture was placed in a BML-2 Daihan laboratory ball mill (South Korea) for mixing and averaging the composition of the mixture.

A product to be leached was obtained after thermal sulfatization in a furnace, in the amount of 153,7 % of the original tailings. Weight loss was 24,70 %. Chemical analysis of the mixture with chromium sludge wt. %: 25,7 Cr_2O_3, 20,2 MgO, 6,3 Fe_2O_3, 17,0 SiO_2, 0,32 CaO.

The mixture after sulfation was leached with water. During leaching, magnesium from sludge goes into solution in the form of soluble magnesium sulfate according to the reaction:

$$MgO + H_2SO_4 = MgSO_4 + H_2O \tag{1}$$

The product after sulfatization was leached in water at 90 oC. After clarification of the pulp, the solution was decanted, and the solid part was washed with hot water in the ratio S:W = 1:2.

The filtrate contained 1,6 g/dm^3 Cr, 6,0 g/dm3 Fe and 37,4 g/dm^3 Mg. Water-soluble chromium and iron may appear during thermal sulfatization with the magnesium sulfate formation. They go into solution practically little.

The yield was 81,52 % of the original tailings after solid part separation and drying. The cake was obtained with the following chemical composition wt. %: 55,4 Cr_2O_3, 10,6 MgO, 7,6 Fe_2O_3, 8,2 SiO_2, 0,4 CaO, 3,0 Al_2O_3, 0,8 SO_3. X-ray phase analysis of the cake showed $(Al_{0.32}\ Cr_{1.68})MgO_4$,- 78,1 %, Cr_2O_3 – 11,2 %, $Ca_3(Fe_{0.34}\ Al_{1.58})(SiO_4)_3$ – 10,7 %.

The ferrous sulfate present in acidic solutions converts most of the hexavalent chromium to trivalent form. And milk of lime was added when the solution was cleaned from iron to pH 4-6. The solution was filtered to obtain a purified filtrate from iron and chromium, and a precipitate was obtained. The purified solution was passed through an activated carbon column to remove chromium residues, then the solution was sent to evaporation at 100 °C to obtain magnesium sulfate heptahydrate. Magnesium sulfate hemihydrate was calcined in a muffle furnace at 300 °C for 120 min to obtain magnesium sulfate with the yield of 81,89 % from the original tailings. X-ray phase analysis of magnesium sulfate showed, Hexahydrite, syn $Mg(SO_4)(H_2O)_6$ – 85,8 %, Ferrobustamite $(Ca_{0.79}Fe_{0.21})SiO_3$ – 14,2 %. Evaporated water can be returned to wash the cake.

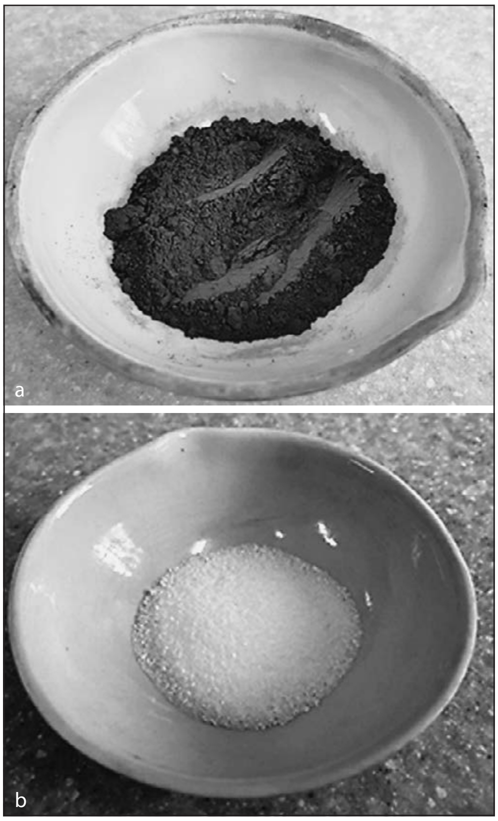

Figure 2 Photographs of products – (a) chromium-containing cake and (b) magnesium sulfate obtained during chemical beneficiation of the DMPP sludge tailings

Figure 2 shows photographs of the products obtained during laboratory studies of the chemical beneficiation of the DMPP sludge tailings from the Dubersay tailings.

Thus, a product beneficiated in chromium with a content of 55,4 % Cr_2O_3 was obtained based on laboratory studies for chemical beneficiation. The throughout recovery of chromium oxide into the chromium-containing cake was 97,6 % during chemical beneficiation. This cake was a conditioned chromium concentrate for the production of ferrochromium. Besides, magnesium sulfate was obtained with the content of impurity components - Cr_2O_3 - not detected, Fe_2O_3 – 0,001 %, SiO_2 - 0.003 %, which is a magnesium fertilizer.

CONCLUSION

A high recovery of Cr_2O_3 was achieved asa result of laboratory tests intended to beneficiate chromium waste chemically – 98,1 % with the production of a conditioned chromium concentrate containing 55,4 % Cr_2O_3. The throughout recovery of chromium oxide from waste sludge tailings into substandard chromium concentrate was 976 %, and magnesium sulfate that is magnesium fertilizer. The waste used during the processing of dump tailings of the DMPP beneficiation plants occupies huge areas of tailings adversely affecting the environment.

Acknowledgments

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REFERENCES

[1] Fursenko A.F. Benefication of stale tailings from Factory 1 of Donskoy GOK, Mining Journal (2008) 5, 11-14. http://www.rudmet.ru/journal /729/article/ 15807
[2] Ralph H. Nafziger. A review of the deposits and beneficiation of lower-grade chromite, Journal of the South African Institute of mining and metallurgy (1982) 205-226. https://www.saimm.co.za/Journal/v082n08p205.pdf
[3] Master plan for the development of the mining and metallurgical industry of the Republic of Kazakhstan until 2030. Astana (2012).
[4] Bespaev H. A., Kayupov S. K., Parilov Yu. S. Technogenic mineral raw materials of ore deposits of Kazakhstan: reference book, Information and Analytical Center of Geology and Mineral Resources of the Republic of Kazakhstan. (2000) 122.
[5] Ultarakova, A.A., Karshigina, Z.B., Lokhova, N. G., Yessengaziyev, A.M., Kassymzhanov, K.K., Tolegenova, S.S. Extraction of amorphous silica from waste dust of electrowinning of ilmenite concentrate, Metalurgija 61 (2022) 2, 377–380. https://hrcak.srce.hr/265927
[6] Nicholas P. Cheremisinoff. Handbook of Solid Waste Management and Waste Minimization Technologies, Chapter 7 - Industry Practices (2003) 188-290. https://doi.org/10.1016/B978-075067507-9/50008-5
[7] Rama Murthy, Sunil Kumar Tripathy, C. Raghu Kumar. Chrome ore beneficiation challenges & opportunities – A review, Minerals Engineering 24 (2011) 5, 375-380. https://doi.org/10.1016/j.mineng.2010.12.001
[8] Guney A., Onal G., and Atmaca T. New Aspect of Chromite Gravity Tailingss Re-Processing, Minerals Engineering 14 (2001) 11, 1527-1530 https://doi.org/10.1016/S0892-6875(01)00165-0
[9] N. Kanaria, I. Gaballaha, E. Allainb. Use of chlorination for chromite upgrading, Thermochimica Acta 351 (2000) 109-117.
[10] J.Zhang, W. Xie, Sh. Chu, Zh. Liu, Zh. Wu, Y. Lan, V. Galvita, L. Zhang, X. Su. Sufficient extraction of Cr from chromium ore processing residue (COPR) by selective Mg removal, Journal of Hazardous Materials Volume 440 (2022) 129754. https://doi.org/ 10.1016/j.jhazmat. 2022. 129754
[11] Patent RU(51) IPC B01D53/62 (2006.01) Removal of carbon dioxide from waste streams by combined production and/or carbonate and bicarbonate minerals,by Joe David Jones (US)
[12] I. Bondarenko, N. Serzhanova, Y. Kuldeyev, N. Sadykov, A. Tastanova Beneficiation of chrome slurry tailings at donskoy mining and beneficiation plant (DMBP) JSC to produce hard pellets, Metalurgija 61 (2022) 3-4, 767–770. https://hrcak.srce.hr/file/397149

Note: The responsible for English language is A. Kurash, Almaty, Kazakhstan