FLOTATION OF CHROMITE ORE IN ACIDIC MEDIA

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Abstract

Chromite is a complex mineral with variable composition and physico-chemical properties and it is the only mineral that is used for chromium production. In Albania, chromium ore is one of the most exploited minerals for trading purposes. In this study is presented the flotation process of the mineral and its efficiency in enriching it. Firstly, the mineral was analysed for its chemical composition and then it was floated. Oleic acid was used as collector, pine oil as foaming agent. The results obtained showed that the flotation process increases the recovery rate of the chromium until 87%

Key words: *flotation, chrome ore, collector, tailings*

Përmbledhje

Kromiti është një mineral kompleks me përbërje dhe veti fiziko-kimike të ndryshueshme dhe është minerali i vetëm nga i cili prodhohet kromi. Në Shqipëri minerali i kromit është një ndër mineralet më të shfrytëzuar për qëllime tregtare. Në këtë studim prezantohet procesi i flotimit të mineralit të kromit dhe efektshmëria e tij në pasurimin e mineralit. Fillimisht minerali u analizua për përbërjen kimike dhe më pas u flotua. Acidi oleik u përdor si mbledhës dhe vaji i pishës u përdor si shkumë formues. Rezultatet e marra treguan që procesi i flotimit rrit shkallën e rikuperimit të kromit deri në 87%.

Fjalë kyçe: *flotim, mineral kromi, mbledhës, sterile*

Introduction

Chromite is a spinel-group mineral and it is the only mineral that is a source of chromium (Imani et.al., 2020; Beklioglu & Arol, 2004). Chromium ore occurs exclusively in ultramafic igneous rocks. Commercial deposits are found in two forms stratiform seams and irregular podiform/lenticular deposits (Murthy et.al., 2011). Chromium is the most versatile and widely used elements. Its main uses in the metallurgical, chemical and refractory industries are known. It is an essential element in the production of a wide variety of stainless steels, tool and allow steels, nickel-chromium heating elements, and plating metals. Its widespread use in the metallurgical industry is attributed to its capacity of enhancing properties such as resistance to corrosion or oxidation, creep, impact strengths and hardenability (Seifelnassr and Tamam, 2011; Hassan Al-Tigani et. al., 2019; Sixhutaet.et.al., 2024).

In Albania, chromite ore deposits occur in the north-east region (ultrabasic masiff of Tropoja and Kukës), central region (ultrabasic masiff of Bulqiza) and south-east region (ultrabasic masiff of Shebenik-Pogradec) (AKBN, 2008). The produced chrome goes for production of high carbon ferro-chrome alloys to metallurgical plant of Elbasan, and most of the chromic ore usually is exported.

Several methods are used for the concentration of chromites such as gravimetric methods, magnetic methods and flotation method (Seifelnassr and Tamam, 2011). The selection of the beneficiation technique depends upon the mineralogical composition and the texture of the ore. Gravity concentration by tabling and spiral is generally employed for chromite ores which are coarsely associated with low specific gravity gangue minerals, whereas for finely disseminated ores, which requires fine grinding for the liberation of chromite mineral, it is technically important to recover the mineral by flotation.

The ores containing gangue minerals possessing densities closer to the chromite are treated by high intensity magnetic separation (Bhatti et. al., 2008; Murthy and Tripathy, 2020; Beklioglu & Arol 2004). Among these methods, flotation is the most promising alternative since it offers an alternative concentration process for the separation of the fine materials and the reduction of chromium losses. A process developed for one ore does not usually yield the optimum results for another ore of different origin. This is thought to happen because of differences in the composition of the gangue materials as well as in the composition of the chromium spinels (Seifelnassr and Tamam, 2011; Ross et. al., 2022). Major associated gangue minerals are talc, quartz, hematite, goethite, limonite, gabbro, serpentine, anorthosite, dunite and pyroxenite (Murthy et. al., 2011).

The aim of this experimental work was to investigate the flotation process of the Albanian chromite ore and to determine the recovery rate of chromite in concentrates and tailings.

Materials and methods

Chromite ore sample

The chromite ore sample was obtained from the central region of Albania (Albanian chrome mine).

Preparation of the material for analysis

The ore was crushed and grinded until 0.07mm fineness was achieved. Jaw crusher, pulverizer and sieves were used to perform these processes. After that the quartile method was used to select the sample for the physical and chemical analysis.

Determination of specific weight

The specific weight of the ore was determined using a pycnometer according to ASTM D854-23. The pycnometer was filled with distilled water and weighted together with the lid. After that, 2g of the mineral was added into the pycnometer together with water and left for 4-6 h in desiccator in order to let the water to penetrate into the grains of the mineral. Then the pycnometer was fully filled with water and closed the lid, the excess of water was removed and the pycnometer together with the mineral, water and lid were weighted. The calculations were performed according to the formula:

$$\gamma = \frac{P_m}{P_m - (P_2 - P_1)}$$

Where: P_m is the weight of the material

P_1 – weight of the pycnometer filled with water

P_2 – weight of the pycnometer with water and material

Determination of volumetric weight

The volumetric weight of the mineral was determined in accordance to ASTM D7710. Firstly, the cylinder was weighted empty. Then it was filled until volume of 1liter and weighted again. The calculations were performed according to the formula:

$$P_v = \frac{P_2 - P_1}{V_c}$$

Where: P_1 – weight of the empty cylinder

P_2 – weight of the cylinder filled with the material

V_c – cylinder volume

Analysis of the chromite ore

The chemical analysis of the chromite ore was done following the ISO 6629:1981, ISO 5997:1984B, ISO 5975:1983, ISO 6130:1985 and ISO 6331:1983.

Removal of chrome in the form of chromyl chloride

1g of the mineral was weighted, soaked with several drops of water and treated with 5ml concentrated nitric acid and 30ml perchloric acid 70% in a 250ml beaker. The beaker was covered with glass plate and heated in an electric plate. The heating process was done gradually until the vapors of perchloric acid exit and further for 10-15 minutes at 70-80˚C. Then the beaker was left to cool down. The covering glass plate and the inner parts of the beaker were washed and the beaker was heated again to remove further the vapors of perchloric acid. This process was repeated until the black grains of the mineral are disappeared and the brown-red color was appeared (2-3h). In the beaker are added drops of hydrochloric acid until complete removal of chromyl chloride vapors.

Determination of silica content

The silica content is determined according to ISO 5997:1984B. In the beaker from the removal of chrome was added 100ml of boiled water in order to be sure the salts present in the mineral are dissolved. The beaker left to decantation of the precipitate and filtrated. The filter with the precipitate was washed with diluted (1:100) hydrochloric acid and further with warm water. The filter together with the precipitate was calcined at 950-1000˚C and weighted after it was cooled (P_1). The weighted sample was soaked with water, 3-4 drops of nitric acid and 10ml of hydrofluoric acid 40% are added. The sample was dried and further calcined at 950-1000˚C, cooled in desiccator and weighted again (P_2). The determination of silica content was calculated according to formula:

$$\%SiO_2 = \frac{P_1 - P_2}{P} * 100$$

Where: P_1 – crucible and precipitate weight after the first calcination, g

P_2 – crucible weight after purification, g

P – the initial sample weight taken for analysis, g

The remained filtrate was gradually evaporated to 250ml for further chemical analysis as described in the following procedures.

Determination of calcium oxide

The calcium oxide content is determined according to ISO 5975:1983. From the filtrate solution was pipetted an aliquot of 10ml, 10-12ml solution of triethanolamine (1:3), were added and the solution was neutralized with KOH 5M (pH value must be over 12) in the presence of 2-3 drops of green malachite until whitening. Then the solution was titrated with EDTA 0.05M in the presence of calcein. The calcium oxide content was calculated according to formula:

$$\%CaO = \frac{A * f * K}{P} * 100\%$$

Where: A – volume of EDTA use for titration, ml

f- factor = 1

K – conversion factor (1ml EDTA = 0.001402mg Ca)

P – weight of mineral dissolved in the analyzed aliquot, g

Determination of magnesium oxide

The determination of magnesium oxide is performed in accordance to ISO 5975:1983. For the determination of magnesium oxide, 10ml of the filtrate solution was pipetted into a 250-300ml Erlenmeyer flask, where 10-20ml triethylamine (1:3) and water was added. pH was fixed at 9-11 by adding buffer solution and the titration was performed with EDTA 0.05Min presence of Black Eriochrome.

$$\%MgO = \frac{A * f * K}{P} * 100\% - 71.4\%\ e\ 3.5\%\ CaO$$

Where: A – volume of EDTA used for titration, ml

f- factor = 1

K – conversionfactor (1ml EDTA = 0.001007g)

P – weightof mineral dissolved in the analyzed aliquot, g

Determination of iron

Iron determination was performed in accordance to ISO 6130:1985. For iron determination 50ml of the filtrate solution was added in a 250ml flask, 1-2 ml of hydrogen peroxide and ammonia were added for iron oxidation to oxide form. The flask was heated until formation of iron hydroxide precipitate with brown color. The mixture was filtered and washed several times with warm water. The formed precipitate was treated with hydrochloric acid (1:1) to obtain the ironsalt (III).

The solution further was treated with 10ml hydrochloric acid and heated until 80-90˚C and stannous chloride was introduced to obtain the iron (II) salt. The beaker was cooled very quickly to avoid the oxidation of iron (II) to iron (III). Then 10ml mercuric chloride was added and left for 5-7 minutes. 100ml of water was added and the mixture of acids was added (H_2SO_4:H_3PO_4; 1:1). The titration was performed in presence of 2-3 drops of sodium diphenylamine sulfonate with potassium bichromate 0.01N solution.

$$\%Fe = \frac{A * 0.005585}{P} * 100\%$$

Where: A – volume of titration solution, ml

P – weight of mineral dissolved in aliquot, g

Determination of Cr_2O_3

The content of Cr_2O_3 is determined according to ISO 6331:1983. 0.2g of the mineral was added in a 500ml Erlenmeyer and wetted with water dots and then 10ml of concentrated sulfuric acid was added. After that 8ml of concentrated phosphoric acid was added and the Erlenmeyer was closed with a funnel and heated until 400˚C for 25 minutes.

The beaker was removed from the heater and distilled water was added with portions until 250ml. 5ml of silver nitrate 1% was added as catalyst for oxidation of chromium (III) to chromium (VI), 0.5-1ml manganese sulfate 0.1% as indicator and 30ml ammonium persulphate 15%, and was heated again for 15-20 minutes (reddish color was appeared). After that the beaker was removed from the heater and 15ml of hydrochloric acid (1:3) was added and heated again for 20 minutes (white precipitate was formed), and then was cooled down. Further, the titration was performed according to Mohr method and the calculations are done according to the formula:

$$\%Cr_2O_3 = \frac{(V_1 * f - V_2) * K}{P} * 100\%$$

Where: V_1 – amount of Mohr salt 0.1N used for reduction of chromium from (VI) to (III), ml

V_2 – amount of potassium bichromate 0.1 N used for titration of Mohr salt excess, ml

f- factor =0.96

K – conversion factor (1ml bichromate = 0.002533g Cr (III))

Flotation of the mineral

500g of the mineral was floated in the flotation machine. The flotation was done for 3-5 min. Firstly, 5-6ml of sulfuric acid was added to create an acid environment (pH 4-5), after that 0.05ml of oleic acid was added as collector and 0.0005g of pine oil was added as foaming agent. The mixture was mixed in the flotation machine and the concentrate was collected, dried and further analyzedfor chromium content.The flotation process was repeated twice in order to increase the recovery rate of Cr_2O_3. The amount of $Cr_2O_3$was determined also in the sterile fraction of the flotation process.

Figure 1. Flotation machine during the process

Yield of the process was calculated according to the formula:

$$Y = \frac{A - S}{C - S} * 100\%$$

Where: Y – is the yield of the flotation process

A – Cr_2O_3 percentage in mineral

S – Cr_2O_3 percentage in sterile

C – Cr_2O_3 percentage in concentrate

The recovery rate of the $Cr_2O_3$was calculated according to the formula:

$$\varepsilon = \frac{Y * C}{A}$$

Where: Ɛ – is the recovery rate

Y – Yield of the flotation process

C – Cr_2O_3 percentage in concentrate

A – Cr_2O_3 percentage in mineral

Results and discussions

Specific weight and volumetric weight of chrome mineral

The specific weight of the chrome mineral resulted to be 5.75g/ml, whereas the volumetric weight of chrome mineral resulted to be1.02kg/L.

Chemical composition of the chromium mineral

The chemical composition of the chromium mineral is presented in table 1.

Table 1. Chemical composition of the chromium mineral before the flotation process

Element	SiO_2	CaO	MgO	Fe_2O_3	Cr_2O_3
Content (%)	21.8	3.4	10.015	12.57	33.93

Results of the flotation process

After the first step of flotation, the concentrate and sterile obtained were analyzed for Cr_2O_3 content. The results are shown in table 2.

Table 2. Results of the first flotation process

Parameter	%Cr_2O_3 in concentrate	%Cr_2O_3 in sterile	Yield (%)	Recovery rate (%)
Percentage	49	14.42	56.41	81.46

The first step flotation is successfully performed. Since the content of Cr_2O_3 in the sterile from the first flotation is considered relatively high, and to increase the recovery rate of the Cr_2O_3, a second flotation was performed for the sterile obtained from the first step of the flotation. The results of the second flotation are shown in table 3.

Table 3. Results of the second flotation process

Parameter	%Cr_2O_3 in concentrate	%Cr_2O_3 in sterile	Yield (%)	Recovery rate (%)
Percentage	42	6	71	87

The flotation process is successfully realized. The content of Cr_2O_3 remained in the sterile is very low (6%) and the recovery rate for Cr_2O_3 is increased up to 87%.

Conclusions

Flotation is a physico-chemical process used for mineral enrichment. In this experimental work the chrome mineral was obtained from Albanian chrome mines and was analyzed for its chemical composition. The flotation of the chromic mineral was successful. It was performed in two steps in order to increase the recovery rate of the Cr_2O_3. The recovery rate achieved was 87%.

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