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Technical Note

Determining the Correlation of Elements in the Mining Area of Sineqan in Markazi Province in Order to Be Used in the Feasibility Studies of Copper and Rare Earth Elements Processing

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Abstract: Sineqan mine, 25 km away from Delijan city (Markazi province), has shown important evidences of iron oxide ores containing copper, gold and rare earth elements (REE) in the early stages of exploration. In the present study, a low-grade sample of the mine from the albite zone containing 0.69% of copper and 223, 186 and 55 g/t of cerium, lanthanum and neodymium was processed and compared with the results of elements correlation in geochemical samples. Cerium, neodymium and lanthanum showed the highest correlation with each other and with the thorium. The correlation coefficient of light REEs with phosphorus was negative. The results of ammonium sulfate leaching showed that the occurrence of REE in the sample is not as adsorption on clay minerals and the study of the correlation coefficient of REE with aluminum and sodium in geochemical samples also confirmed this result. The results of leaching with H_2SO_4 showed that selective leaching of copper is possible. The low efficiency of leaching with H_2SO_4, HCl and HNO_3 and the higher efficiency of 96% for leaching with cerium and lanthanum under acidic baking conditions showed that a significant part of REEs is in the form of refractory minerals. The concentration ratio of REEs in the magnetic concentrate was close to iron. According to the correlation analysis of elements in geochemical samples, the correlation of calcium with REE was in the range of -0.2to-0.3. In the flotation test, although the grade of calcium increased 3.5 times in the flotation concentrate, this was not the case for REEs. The results of this research can be used in similar cases in the early stages of exploration and processing feasibility studies.

Keywords: Geochemical prospecting, Feasibility study, Rare earth elements, Sineqan mine.

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INTRODUCTION

Rare earth elements (REEs) are a group of 15 lanthanide elements plus yttrium and scandium. The main ores of REEs include monazite and bastnasite minerals, and secondary ores include minerals such as xenotime, apatite, and clays minerals containing REEs, allanite, zircon, eugenite, and loparite[1]. Due to the growing importance of REEs in high-tech industries, different countries have paid special attention to the extraction of REEs from their secondary sources.

Sineqan mine is located in Markazi province (Iran) and 25 km away from Dilijan city. The mine is currently in the early stages of exploration, which has shown significant evidences of iron oxide ores containing copper, gold and rare earth elements. For the first time in Iran, Karimpour introduced iron oxides type deposits containing copper and gold (IOCG) in the Khaf-Kashmar-Bardaskan belt [2].

In this research, the results of initial geochemical studies and the results obtained from processing a low-grade sample of the mine were investigated. In the geochemical studies, the correlation between REEs with other elements was investigated and compared with the results of processing low-grade mine samples by magnetic, flotation and leaching methods with the aim of identifying the behavior of rare earth minerals.

MATERIALS AND METHODS

Preparation of geochemical and mineral processing test samples

The geochemical samples (26 samples) were crushed to -3.34 mm using laboratory jaw and roller crushers and divided using a Jones riffler. Sub-samples were pulverized and analyzed by ICP-MS method.

100 kg of feldspar samples (probably from albitic alteration zone of the mine) was crushed by jaw crusher (two stages in open circuit) and roller crusher (in a closed circuit with 3.34 mm control screen) and ground by using a laboratory ball mill. The results of the chemical analysis of the sample used in the processing tests are shown in Table 1. Results of the semi-quantitative XRD analysis of the feldspar sample showed that the main minerals in the sample are albite (60%), chlorite (19%), quartz (16%) and hematite (3%).

Table 1. Chemical analysis of the sample used in the processing tests

Size fraction (micron)		As	CaO	MgO	Na_2O	Cu	Al_2O_3	Fe_2O_3	Y	Nd	La	Ce
	Wt.%	ppm	ppm	%	%	ppm	%	%	ppm	ppm	ppm	ppm
Feed	100	28	6861	3	7.07	6900	15.06	6.12	28	55	186	223
+150	10.7	28	5000	3.04	6.31	7401	14.18	6.62	22	38	128	163
-150+106	20.4	28	4400	2.58	6.17	4667	13.33	5.87	20	45	158	190
-106+75	7.8	10	8500	2.51	6.16	4519	13.28	5.61	21	50	180	214
-75+38	16.0	34	5800	2.41	6.31	4942	13.49	5.54	24	73	269	317
-38	45.2	30	8500	3.20	7.12	7804	15.56	6.37	35	59	184	221

Mineral procesing tests

Initial processing tests included magnetic concentration, flotation, alkaline and acid leaching, and acid baking (temperatures higher than 100°C) using sulfuric acid. The degree of freedom studies of the sample showed that more than 80% of the iron minerals are free in the +53-75 micron size fraction. For this reason, the sample with d80 of 64 micron was used for preliminary processing tests.

Calculation of correlation coefficient of elements in geochemical samples

Pearson's linear correlation coefficient method was used to check the correlation of elements in the geochemical samples. Pearson's linear correlation coefficient is the most common method for determining the correlation coefficient. In this method, the following averages are calculated for Xa column in X matrix and Yb column in Y matrix[3].

$$\bar{X}_a = \sum_{i=1}^{n} (X_{a,i})/n \qquad (1)$$

$$\bar{Y}_b = \sum_{j=1}^{n} (X_{b,j})/n \quad (2)$$

Pearson's linear correlation coefficient (rho(a,b)) is defined as follows:

$$rho(a,b) = \frac{\sum_{i=1}^{n}(X_{a,i} - \bar{X}_a)(Y_{b,i} - \bar{Y}_b)}{\left\{\sum_{i=1}^{n}(X_{a,i} - \bar{X}_a)^2 \sum_{i=1}^{n}(Y_{b,i} - \bar{Y}_b)^2\right\}^{1/2}} \quad (3)$$

Where:

n: is the length of each column.

The correlation coefficient values obtained from this method are in the range of +1 to -1. A value of -1 indicates a completely negative correlation and a value of +1 indicates a completely positive correlation. *A* value of 0 indicates that there is no correlation among the columns [3].

RESULTS AND DISCUSSION

The results of preliminary exploration studies (mineralogy of the trench samples) of the sineqan mine

Preliminary mineralogical studies of the trench samples indicated that the host rocks of the area are andesite (basaltic andesite) and tuff. About 15-20% of the rock volume is in the form of coarse crystals, of which 70-75% of the coarse crystals belong to plagioclase, 15-20% to pyroxene, and about 5-10% to hornblende. Metalic minerals make up about 4-5% of the rock volume and are often seen in the form of fine crystals in the rock background.

Investigating the correlation of elements in geochemical samples

In 26 geochemical samples taken from Sineqan mine, Al_2O_3 grades range from 5.98 to 16.24%, Fe_2O_3 grades range from 0.97 to 42.79%, copper grades range from 22 ppm to 2.29%, and the range of total REEs is from 70 to 1600 ppm. Results of the correlation studies showed that the cerium, neodymium and lanthanum light REEs have the highest correlation with each other and with the thorium element with a correlation coefficient of about 1. A noteworthy point is the low correlation coefficient of the cerium, lanthanum and neodymium with the yttrium as a heavy REE.

PROCESSING TESTS RESULTS

Leaching

The results of ammonium sulfate leaching of the sample showed that the occurrence of elements in the examined sample is not in the form of absorption on clay minerals. On the other hand, investigating the correlation coefficient of rare earth elements with aluminum and sodium in geochemical samples also confirmed this issue and the correlation coefficient of aluminum with cerium and lanthanum elements was obtained as -0.6 and -0.5, respectively.

Considering that sulfuric acid is a common acid for the leaching of copper minerals, the sulfuric acid leaching behaviors of copper, iron and REEs were investigated. Increasing the concentration of sulfuric acid from 1 to 2 M increased the copper leaching efficiency from 65 to 89%. The maximum leaching efficiency of cerium and lanthanum elements was 10 and 14%, respectively, which shows that some of the minerals containing REEs are not refractory in nature (such as apatite).

The possibility of the sample leaching with hydrochloric acid and nitric acid at a temperature of 70°C and for 60 minutes was studied. The results showed that the leaching efficiency of cerium and lanthanum elements with hydrochloric acid was 22.6 and 23%, respectively, and with nitric acid was 18.6 and 22.7%, respectively. The maximum leaching efficiency of iron and copper was 85.4% and 95% using hydrochloric acid and 70.6% and 97% using nitric acid, respectively.

Finally, in order to confirm the presence of rare earth elements in the refractory minerals such as monazite [4] and sphene, acid baking tests were performed. By performing an acid baking test at 250°C and 120 minutes and then leaching the resulting paste with water for 60 minutes at room temperature, it is possible to leach 96% of cerium and lanthanum and all the iron and copper. This result confirms the presence of a significant part of rare earth elements in the form of refractory minerals.

Magnetic concentration and flotation

The purpose of the flotation test was to concentrate the rare earth minerals with calcium (such as apatite and sphene). The concentration ratio of cerium, lanthanum and neodymium in magnetic separation concentrate was very close to iron. This trend was also been observed in the flotation test. According to the correlation analysis of elements in geochemical samples, the correlation of calcium with rare earth elements cerium, lanthanum and neodymium was in the range of -0.2 to -0.3. In the flotation test, despite the fact that calcium increased 3.5 times in the concentrate, this increase was less for REEs.

CONCLUSIONS

Correlation analysis of the elements in geochemical samples showed that, unlike other deposits of the Iran that are usually associated with phosphorus, REEs in Sineqan mine do not have a significant positive correlation with phosphorus element. The results of leaching with ammonium sulfate showed that the occurrence of REEs in the sample is not in the form of absorption on clay minerals, and the correlation coefficient of the occurrence of REEs with aluminium and sodium in geochemical samples also confirmed this issue. The results of leaching with H_2SO_4 showed that there is a possibility of selective leaching of copper compared to REEs. The leaching efficiency of 96% of cerium and lanthanum under acidic baking conditions showed that a significant part of REEs is in the form of refractory minerals. The concentration ratio of REEs in magnetic concentrate was close to iron. According to the correlation analysis of elements in geochemical samples, the correlation of calcium with REE was in the range of -0.2 to -0.3. In the flotation test, despite the fact that calcium increased 3.5 times in the concentrate, this increase was less for REEs.

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