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Technical note

Processing of the xenotime concentrate of Southwestern Sinai via alkali fusion and solvent extraction

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ABSTRACT

A xenotime flotation concentrate prepared from Sarabit El Khadem ferruginous sandstone of Southwestern Sinai (55.4% RE2O3 and 0.9% U3O8) is subjected to processing via alkali fusion using NaOH under different conditions. The obtained oxide cake of REEs and U was dissolved in sulfuric acid followed by separation of REEs as oxalates. Extraction of uranium from the REE-free sulfate solution was then studied using trioctylamine in kerosene. The relevant conditions of both the alkali fusion of the concentrate as well as those of uranium recovery through the tertiary octylamine have been optimized. Highly pure products of the REEs and U have been prepared and subjected to an ESEM qualitative analysis.

1. Introduction

Xenotime is a REE (rare earth elements) phosphate mineral and represents one of the three principal REE minerals together with monazite and bastnasite (Jordens et al., 2013).These minerals contain indeed about 98% of the world reserves of these elements and are therefore the principal ore minerals for their extraction. Xenotime may or may not contain uranium or thorium and its REEs belong mainly to the heavy elements (Gd to Lu together with Y that could attain up to 63% as oxide) contrary to the two other minerals (Zhu et al., 2015).

On the other hand, while bastnasite and monazite are abundantly available in nature in almost equal quantities, xenotime occurrence and availability is very small. Xenotime is actually a minor constituent of granite or gneiss rocks. Having undergone a weathering, transportation, and concentration process similar to that of monazite, xenotime co-occurs with it in placer deposits, but such deposits are relatively few. Usually the content of xenotime may range from 0.5 to about 5% of the monazite present (Gupta and Krishnamurthy, 1992).

Yttrium and the heavy rare earths are actually used in a growing number of applications and at the forefront of this wave of discovery are new technologies being developed for computer science uses, industrial engineering, renewable energy sciences and military applications. In electronics, the heavy rare earths are used in television screens, computers, cell phones, silicon chips, monitor displays, long-life rechargeable batteries and camera lenses besides high strength magnets, alloys, stress gauges, ceramic pigments, colorants in glassware, chemical oxidizing agent and as additives for strengthening other metals in addition to several medical applications. In technology, the heavy rare earths are used in the manufacture of lasers, optical glass, fiber optics, masers, radar detection devices, nuclear fuel rods and batteries together with high temperature superconductors and renewable energy devices (Bannerjee et al., 1995).

According to Gupta and Krishnamurthy (1992), xenotime concentrate is generally treated using three breakdown processes; namely a direct sulfuric acid treatment or fusion with caustic soda or else an alkali roasting with sodium carbonate. In 1st process, the xenotime concentrate is attacked using concentrated H_2SO_4 (98%) at 250 to 300 °C for 1 to 2 h (Viyayalakshmi et al., 2001) where about >80–90% of the rare earths are solubilised. Due to the high solubility of the yttrium and heavy rare earths double sulfates, their sulfate solution is thus directly taken for separation using oxalic acid. In 2nd process, the finely ground xenotime concentrate is processed by fusion with molten caustic soda at 400 °C (Alex et al., 1998) while in 3rd process, the xenotime concentrate is roasted with Na_2CO_3 at 900 °C for several hours (Lever and Payne, 1968). After leaching out the phosphates from the latter two processes, the REE hydroxide residue is dissolved in the minimum amount of HCl acid and after filtration; the rare earths are recovered by precipitation as oxalates.

The present work is concerned with the processing of the xenotime mineral concentrate that has been physically upgraded through froth flotation from its occurrences in Sarabit El Khadem area of Southwestern Sinai. While the purity of the latter attains up to 82.8% RE phosphates, it was also found to assay up to 0.9% U_3O_8. The alkali fusion with soda procedure has thus been found adequately convenient for the working xenotime concentrate in order to economically recover

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its constituents. The relevant factors of the alkali soda fusion step have first been studied and after water washing of the phosphate values, both the REE and U values have been dissolved by sulfuric acid. From the latter, the REEs have been precipitated as their oxalates while recovery of the U value left behind has properly been studied via solvent extraction technique using trioctylamine in kerosene.

2. Experimental

2.1. Material characterization

The working xenotime concentrate has indeed been prepared from the ferruginous sandstone of Sarabit El Khadem area of Southwestern Sinai through froth flotation as mentioned above. A representative sample has first been subjected to complete chemical analysis of its major oxides of SiO_2, Al_2O_3, P_2O_5 and Fe_2O_3 using the conventional wet procedure of Shapiro and Brannock (1962). For analysis of REEs, the spectrophotometer has been used to measure their concentration with Arsenazo-III as the chromogenic reagent (Merczenko and Balcerzak, 2000) while uranium analysis was performed by the oxidimetric titration procedure using ammonium metavanadate (Davies and Gray, 1964).

2.2. Experimental procedures

2.2.1. Alkali fusion of the xenotime concentrate

Several fusion experiments have been performed upon the working xenotime concentrate using NaOH. In these experiments, different amounts of NaOH were mixed with fixed weight sample portions (2 g) of the xenotime concentrate in a porcelain crucible for different time periods and at different temperatures. The obtained melt was then cooled and washed with 200 ml of hot distilled water, filtered and made up to volume (250 ml) for P_2O_5 analysis and from which the xenotime dissolution efficiency was calculated.

2.2.2. Recovery of REEs and U

To study the recovery of both REEs and U, a 50 g sample portion of the working xenotime concentrate was subjected to alkali fusion under the optimum conditions of alkali fusion and after cooling and proper washing of the melt to remove the phosphate values, the oxide cake was dissolved in 50 ml concentrated sulfuric acid at 100 °C for 2 h.

2.2.2.1. Recovery of REEs. From the obtained sulfate leach liquor, the REEs were recovered by their direct precipitation as oxalates using oxalic acid while U was left behind in the solution.

2.2.2.2. Recovery of U. In order to obtain an adequately pure uranium concentrate, it was found necessary to study the U extraction from the REE-free sulfate leach liquor using the synergistic system of TOA/Octanol in kerosene as diluent to prepare different concentrations thereof. Octanol ($C_8H_{18}O$) was used as modifier (0.06 M) to prevent the third phase formation during the alkaline stripping of U. In each extraction experiment, the organic phase was shaken with the uranyl sulfate aqueous phase in a separating funnel for the desired time. The two phases were then allowed to settle, separate and an aliquot sample of the aqueous phase was analyzed for its remaining metal content in order to calculate the extraction efficiency. The relevant solvent extraction factors have thus been studied; namely the solvent concentration, the contact time and the pH of the leach liquor as well as the aqueous/organic phase ratio (A/O). On the other hand, a loaded solvent sample was prepared for studying the stripping behavior of the extracted uranium metal value using sodium carbonate. The relevant factors thereof have also been studied; namely the contact time and the alkali concentration.

2.3. Control analysis

For the control analysis of all the performed experiments, both the REE and U have been analyzed in all the working stream solutions via the above mentioned procedures; viz spectrophotometric and titrimetric respectively. On the other hand, the two highly pure products of both the REEs and U were analyzed in the labs of the Chemical Warefare by ESEM qualitative analysis using EWAR Model FEI Inspect S (Hollanda-USA).

3. Results and discussion

3.1. Chemical composition of xenotime concentrate

As previously mentioned, the xenotime concentrate has completely been analyzed by the relevant methods for its major constituents. From the obtained results as shown in Table 1, it is clearly evident that the working xenotime concentrate is mainly composed of RE_2O_3 (55.4%) and P_2O_5 (27.7%) (xenotime constituents) and to a much lesser extent of Fe_2O_3 (7.4%), SiO_2 (6.7%) and Al_2O_3 (1.8%). On the other hand, the associated U content was found to assay 0.9% as U_3O_8.

3.2. Processing of xenotime concentrate

As previously mentioned, the alkali fusion using caustic soda has been used for the breakdown of the xenotime mineral and the relevant factors of this procedure have been optimized; namely the fusion time and temperature as well as the xenotime concentrate/alkali ratio. After water leaching of the melt, the dissolved P_2O_5 was taken as a measure of the mineral breakdown whereas the insoluble oxide cake of uranium and the rare earths was subsequently dissolved in sulfuric acid for their recovery.

3.2.1. Optimization of the relevant factors of alkali fusion

3.2.1.1. Effect of the fusion time. The effect of the fusion time upon the breakdown of the working xenotime concentrate was studied in the range of 1 to 4 h with the other fusion conditions were fixed at a xenotime concentrate/NaOH ratio of 1:3 and a fusion temperature of 300 °C. From the obtained results given in Fig. 1, it is clearly evident that increasing the fusion time from 1 to 3 h has increased the dissolution efficiency of P_2O_5 where it reached 54% at 3 h. Further increasing the fusion time to 3.5 h and 4 h has not shown any perceptible increase in phosphorus dissolution thereafter. At 3 h, sodium hydroxide reacted with the xenotime concentrate forming sodium phosphates solution while uranium and rare earths are liberated from the concentrate as hydoxides [$UO_2(OH)_2$, $RE(OH)_3$].

3.2.1.2. Effect of the fusion temperature. A series of experiments has been performed to study the effect of temperatures upon the breakdown of the working xenotime concentrate in the range from 300 to 600 °C. In these experiments, the other fusion conditions were fixed at a xenotime concentrate/NaOH ratio of 1:3 for 3 h as the fusion time. The dissolution efficiency of P_2O_5 given in Fig. 2, was found to gradually increase by increasing the fusion temperature from 300 to 500 °C where it attained 74.3% at 500 °C. Further increase in the fusion temperature and at the

Table 1
Chemical analysis of the working xenotime concentrate.

Component	Weight percent, %
RE_2O_3	55.4
P_2O_5	27.7
Fe_2O_3	7.4
SiO_2	6.7
U_3O_8	0.9
Al_2O_3	1.8