Extraction of lanthanons from Egyptian monazite

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The lanthanons have been isolated from monazite as sulphates and converted to hydrous oxides. Thorium and cerium are first separated from the mixed hydrous oxides at pH = 3.5 ± 0.1. The other lanthanons are adsorbed on doves I-XI anion exchanger and eluted.

Monazite sand is one of the most important sources of lanthanon elements besides thorium and cerium. Monazite is found in the Egyptian black sands which are concentrated along the shores of the Nile Delta especially at Rosetta.

Although the separation of lanthanons have been studied quite extensively by several authors1-5, yet the information regarding the composition and processing of Egyptian monazite is inadequate. The lanthanon elements Ce, Nd and Pr have only been determined directly6. Ion exchange technique has also been reported7,8, but this was limited to the separation of Nd and Pr.

The present study deals with a process for monazite breakdown, separation of the light lanthanons as sodium double sulphates, conversion of double sulphate to hydrous oxides, separation of Th and Ce, preparation of the mixed oxides of light lanthanons and finally the elution behaviour of Sm, Nd, Pr and La from ion exchange columns.

Experimental

The principal steps involved in the process are as follows:

Ore breakdown

About 100 gm. of the monazite sand (100-200 mesh) was added gradually to ~ 150-160 ml of H₂SO₄ (96%) previously heated to ~ 150°C, and digestion was carried out at 210°, for ~ 4 h. The cooled pasty mass of anhydrous acid sulphates and excess acid were then poured and dissolved very slowly in one litre of cold water. The temperature was kept below 15°C, by addition of crushed ice to prevent partial precipitation of sparingly soluble sulphates. After complete sedimentation of the unattached sand, the solution was separated by decantation and then by filtration under pressure. The resulting solution containing the lanthanon sulphates and free phosphoric acid will be referred to in the following as monazite sulphate solution.

Separation of the light lanthanon elements as sodium double sulphates

In order to separate the cerium-group or light lanthanons from the yttrium group, a finely divided powder of anhydrous sodium sulphate (44 g) was added to the monazite sulphate solution with constant stirring. The double sodium sulphates of the light lanthanons were then precipitated together with ~ 30% of the thorium content. The heavy lanthanons (yttrium group) form double sulphate and remain in solution. The resulting precipitate was filtered, washed with Na₂SO₄ solution (2%) and dried in an air oven at 110°C, for 24 h.

Conversion of the double sulphates to hydrous oxides

About 100 g of the prepared double sulphates were digested for 1 h with 400 ml of 18% sodium hydroxide solution. The mixed hydroxides, being white in colour, were cooled, filtered and washed with hot distilled water till free from alkali and sulphate and finally dried in an air oven at 110°C overnight and weighed.

The product first assumed a grey-green colour on the surface, but finally changed to bright lemon yellow due to oxidation of cerous hydroxide to yellow ceric hydroxide.

Separation of Th and Ce from the remaining lanthanons

About 50 g of the oven dried hydrous oxides were suspended in water and HCl (2 M) was added dropwise to the mechanically stirred suspension, until the pH was lowered to 3.5 ± 0.1. Under these conditions, the undissolved portion contained all the Th, and 99% of the total Ce and 1% of the total lanthanons, other than Ce.
Preparation of the mixed oxides

The remaining solution after separating Th and Ce, was evaporated nearly to 150 ml and a saturated solution of oxalic acid (25 ml) was added. After digestion and filtration, the oxalates were dried at 110°C and then ignited to the oxides.

The analysis of the mixed oxides was carried out spectrophotometrically using Perkin-Elmer spectracord 4000 A using 1 cm cell, by dissolving a portion of oven dried oxide in the least amount of dilute HCl and the absorbances were measured at 402, 575 and 444 nm for Sm, Nd and Pr, respectively. The percentage of the individual lanthanons in the mixture were computed from calibration curves using 0.025, 0.050, 0.075 and 0.100 solutions of 99.99% pure lanthanon oxides. The lanthanon percentage was calculated by difference and checked volumetrically, using EDTA.

Separation of the remaining lanthanons by ion-exchange

The apparatus used is four-coupled ion-exchange columns which have a diameter of 2 cm and an overall length of 250 cm. The eluent was allowed to flow via a stopcock to a gravity-feed fraction collector.

The resin used was Dowex I-XI anion exchanger, 40-50 mesh, with total exchange capacity 2 me/ml of the wet volume. The resin was initially converted to the nitrate form by treatment with 2M nitrate solution. The excess electrolyte was removed by washing with distilled water.

The load was prepared by dissolving 10 g of the oven dried lanthanon oxides in minimum amount of the solvent. Warming was necessary for complete dissolution. The resultant solution was evaporated gently almost to dryness to remove excess of the acid. Evaporation was carefully controlled to avoid dryness.

The load was adsorbed on the top of the first column and the eluent 6M Li NO₃ − 2 × 10⁻³ M HNO₃ solution was allowed to flow through the columns. Elution was carried out at 25 ± 2°C, at a constant flow rate of 0.25 ml/min. and fractions were collected in 10 ml volumetric flasks. The determination of lanthanons in the eluate fractions involved precipitation of the lanthanon oxalates, ignition to the oxides and dissolution in HCl. The analysis was carried out spectrophotometrically as mentioned above.

Results and discussion

The following data was obtained for the recovery of lanthanons from Egyptian monazite.

Weight of monazite sand = 100 g; weight of double sulphate = 113 g; weight of hydrous oxides = 60 g. Constituents of hydrous oxide: Sm₂O₃ 8.0%; Pr₂O₃ 13.4%; Nd₂O₃ 35.4%; La₂O₃ 43.2%.

For the separation of Ce and Th from the cerite earth, it was necessary to convert the double sulphates to the hydrous oxides and dry the latter at 120°C to convert the cerous to the ceric salt. The separation by selective dissolution in HCl at pH 3.5 was as effective as that described by Pilkington and Wylie¹⁰.

A separation by anion exchange resin using a given chelate ligand, depends on somewhat different factors from one cation exchange using the same chelate ligand, for example, when the complexing agent is EDTA, the order of elution is not the inverse order of the stability constants as it is in cation-exchange.

The results of separation by anion-exchange are shown in Fig. 1 from which it appears that the cations do not elute in the order of its atomic number, but the light cations are strongly adsorbed on the resin than the heavy cations, as observed by Marcus and Nelson¹¹.

References