THE SEPARATION AND ANALYSIS OF TITANIUM AND IRON IN THE MINERAL ILMENITE

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Abstract

Since the location of extensive *ilmenite-bearing beach sands in Australia, and now in Tanzania, the separation and analysis of the mineral has become more important than ever. This is particularly because ilmenite has now become the principal source of rutile, an important product in the manufacture of pigments and ceramic materials.

Ion exchange separation using a mixture of HCl and HF is described in the literature. The method has serious limitations especially when the use of glassware cannot be avoided.

The author has successfully applied exclusively HCl solution for the anion exchange separation. The mineral was first brought in solution by fusion with $KHSO_4$. The excess sulphate was removed in a cation exchange step. In the anion exchange stage carried out in 8.4–8.6 N HCl, the separation of iron from Ti was found to be quantitative.

Introduction

An industrial procedure for recovery of rutile in ilmenite has been reported (Gaskin 1969). Small amounts of coloured oxides V_2O_5, Cr_2O_3 etc are often difficult to remove from rutile. When present they make the material unsuitable for use in the manufacture of pigments. The removal of the coloured oxides may be achieved through suitable separation processes which inevitably increase the production costs. Ilmenite-bearing beach sands are generally found in isolated patches along the coast. Slight variations in composition have been found in samples of different origin.

Therefore accurate analytical data is of great importance when selection of suitable material for pigment manufacture is desired.

Ti may be determined gravimetrically as oxinate, but the results are generally not satisfactory (Vogel 1962). Present investigations however have proved that with some precautions in the working procedure, Ti may be determined with an error not exceeding +0.5%.

Since both Ti and Fe are precipitated by oxine at pH range between 5 and 6, the separation of interfering cations must be first carried out.

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*Ilmenite obtained from Tanzanian beach sands contains up to 0.5% Cr_2O_3.

Ion exchange separation of Fe as $FeCl_4^-$ on an anion exchange resin Amberlite 400 using a solution containing both HCl and HF for elution has been reported (Korkisch 1969). Because of the problems resulting from the undesired action of HF on glass, in the present work only HCl was used.

Fusion of the mineral with $KHSO_4$ has been found by the author to be most effective in converting the mineral in a form which easily dissolves in dilute HCl. This however introduced a large excess of sulphate which reduced the absorption of $FeCl_4^-$ on the anion exchange resin. The sulphate ions were removed in a primary stage by absorption of TiO^{2+} and Fe^{3+} on a cation exchange resin (Dowex 50) and washing the column with 0.2 N HCl. TiO^{2+} and Fe^{3+} were latter removed from the resin with a solution of 2N HCl. The solution containing both TiO^{2+} and Fe^{3+} and free of sulphate was concentrated by evaporation and treated with concentrated HCl to give a solution containing 8.4 N HCl. When this solution was passed in an ion exchange column packed with Amberlite 400, the separation of Ti from Fe was quantitative. In this laboratory, ion exchange methods have been used with great success in metallurgical extractions (Mulokozi 1973) and in analytical separations of elements in important industrial materials (Mulokozi 1972, 1973). The procedure is now described for separation of iron and titanium in ilmenite. The recovery of these elements from titaniferrous iron ore such as the Liganga iron ore has already been described (Mulokozi 1973). A full description of the method, and a discussion of its merit is the subject of this paper.

Materials

(i) Samples of ilmenite were provided by the Mineral Division Dodoma, Tanzania.
(ii) Titanic chloride "not less than 98.5%" of British Drug House Ltd. Poole, England.
(iii) $FeCl_3 . 6H_2O$ and $KHSO_4$, reagent grade chemicals of Merck Darmstadt, W. Germany.
(iv) Conc. HCl, NH_4OH, and 8-Hydroxyquinoline all reagent chemicals of May and Baker Ltd. Dagenham, England.
(v) Cation exchange resin Dowex 50X8 20-50 mesh of Dow Chemicals Co. Midland, Michigan, U.S.A.
(vi) Anion exchange resin Amberlite 400 analytical grade of Rohm & Haas Co. Philadelphia U.S.A.

Apparatus

Ion exchange operations are often time consuming and tedious. In the present work, a simple semi-automatic apparatus capable of ensuring a steady flow rate of solution was used. This make the handling of large volumes of solutions easy. The apparatus used in this work has previously been described (Mulokozi 1972).

Experimental

The mineral sample (500 mg) was fused with (2 g) $KHSO_4$ in a platinum crucible. The procedure is described elsewhere (Jander

& Blasius 1962). The product obtained after 24—40 minutes fusion is soluble in 2N HCl. The solution was evaporated, transferred to a 100 ml volumetric flask, and made exactly to 100 ml with addition of distilled water. Aliquots of this solution (20 ml) were pipetted to 500 ml separation funnel and diluted with 400 ml distilled water. The resulting acid concentration did not exceed 0.2N HC1. The solution was passed through the ion exchange column packed with Dowex 50, which was previously converted to the acid form and washed with distilled water. The flow rate was maintained at 29 drops per minute. Four hours were required to run the funnel empty. Iron and titanium were absorbed on the resin. The resin was washed free of sulphate with 300 ml 0.2N HCl. The cations were removed from the resin with 800 ml 3N HCl.

The solution obtained was evaporated to reduce the volume. Concentrated HCl was added to raise the acid concentration to just above 8.6N. The resulting solution had a volume of about 750 ml. The solution was passed in an anion exchange column (packed with Amberlite 400). Complete retention of iron was achieved. It was necessary to avoid acid dilution in the column. The column was made ready for the experiment by passing through concentrated HCl. The resin was purged of titanium with additional 750 ml 8.6N HCl. Iron was removed from the resin with dilute HCl. The titanium fraction was made to a volume of exactly 100 ml. 50 ml of this solution was taken for gravimetric determination of titanium. To the 50 ml aliquot 400 ml distilled water was added followed by 30 ml 1% alcoholic 8-Hydroxyquinoline. The solution was heated to 60°C. Dilute NH_4OH was added till the pH 5.5 was reached. The solution was boiled for 10 minutes. The yellow precipitate formed was filtered through a pyrex crucible of porosity 4. The precipitate was washed with hot water to remove excess of the reagent, and eventually dried at 110°C. After cooling in a dessicator the precipitate was weighed.

For the titrimetric determination of Ti, 20 ml. portions were taken. The precipitate of the oxinate was dissolved in 100 ml of lN HCl. After cooling to 15°C in an ice bath 1 g KBr was added followed by 20 ml of 0.1N $KBrO_3$. The titration flask was tightly closed with a rubber stopper. The mixture was shaken to allow completion of the reaction. The stopper was removed, 1 g KI was added, and after shaking the solution the liberated iodine was back titrated with 0.1N $Na_2S_2O_3$ solution, using starch as an indicator. The results are shown in table 1.

Iron was eluted with 800 ml lN HCl and determined in the same way as described for titanium. The results are given in table 2.

Discussion

To find the optimum conditions for absorption of iron on Amberlite 400, solutions containing up to 10 mg Fe in 400 ml 6 to 9N HCl were passed in a 30 cm long column of 12 mm diameter, packed with the resin. Complete retention of iron was achieved in solutions of acid concentrations above 8.4 N. At slightly lower acidity retention was increased with decrease of the iron concentration. There are probably two exchangeable species, $[Fe(OH_2)_2Cl_4]^-$ and $[FeCl_4]^-$ with different distribution coefficients. $FeCl_4^-$ is formed at greater HCl concentrations, when water loses its coordinating ability through protonation, and Cl^- has no competitor for the metal ion. Following reaction steps are therefore suggested :

$$[Fe(H_2O)_6]^{3+} + 4HCl \longrightarrow [Fe(H_2O)\ _2Cl_4{}^-] + 4H_3O^+$$

$$[Fe(H_2O)\ _2Cl_4]^- + 2H^+ \longrightarrow FeCl_4{}^- + 2H_3O^+$$

From the reaction equations it is clear, that for the efficient separation of iron from titanium high concentration of HCl is desirable. The high efficiency of the separation was indicated by a clean yellow oxinate obtained from samples of the titanium fraction. Small amounts of iron in the titanium fraction would cause the darkening of the precipitate due to precipitation of iron oxinate.

For iron there was close agreement between the analytical results obtained from weighings of the oxinate and volumetric determination of the oxinate with potassium bromate solution. With titanium however, the results from the gravimetric determination when the oxinate was dried at 110°C were higher by 0.2 to 0.5%. At the temperature mentioned titanyl oxinate did not decompose or sublime as would have happened at higher temperatures. The precipitate still contained water, whose amount depended only on the dehydration conditions (temperature and water vapor pressure). Drying ovens are now available in laboratories which allow close control of temperature and vapour pressure. For moderate accurate results, only the control of temperature is important. With the oxinate dried at 110°C an empirical gravimetric factor 0.2260 was used instead of 0.22685. Good agreement between the results of gravimetric determination of TiO^{2+} and those obtained by titration was found (ref. table 1). The working procedure is one of the few available, which does not require the use of high temperature ovens for drying the precipitate.

Legends to fig. and tables

Table 1 : Analytical data of the titanium fraction. Each 50 ml aliquot used in the gravimetric analysis contained titanium in 50 mg of the mineral. For volumetric analysis the aliquots taken corresponded to 20 mg of the mineral.

Test run No.	$TiO(ox)_2$ mg	TiO_2%	TiO_2% corrected	Vol. of 0.1N $KBrO_3$	TiO_2%
1	122.3	55.50	55.28	11.05	55.21
				11.00	55.10
2	122.5	55.61	55.37	11.10	55.45
				11.05	55.21
3	122.4	55.55	55.32	11.10	55.45
4	122.4	55.55	55.32	11.05	55.21

Table 2 : Analytical data of the iron fraction. Each 20 ml aliquot used in both gravimetric and volumetric analysis corresponded to 20 mg of the mineral.

Test run No.	$Fe(Ox)_3$ mg	Fe mg	Fe%	Vol. of 0.1N $KBrO_3$	Fe mg	Fe%
1	52.8	6.05	30.25	13.00	6.05	30.35
	52.7	6.04	30.20	13.02	6.06	30.30
	53.0	6.07	30.04	13.04	6.07	30.35
2	52.9	6.06	30.12	13.00	6.05	30.25
	52.7	6.04	30.20	13.05	6.08	30.40
	52.8	6.05	30.25	13.05	6.08	30.40
3	52.9	6.06	30.30	13.00	6.05	30.25
	52.8	6.05	30.25	13.05	6.08	30.40
	52.9	6.06	30.30	13.05	6.08	30.40

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