

Note

Determination of the tetrathionate content of an anion-exchange resin

Gy. NOVÁK and M. ERDÉLYI

Mecsek Ore-mining Company, Pécs (Hungary)

and

M. VIGVÁRI*

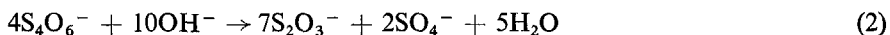
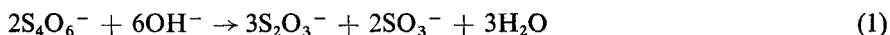
Research, Engineering and Prime Contracting Centre of the Hungarian Aluminium Corporation, Budapest (Hungary)

The capacity of the anion-exchange resins in uranium-ore processing plants using sulphuric acid for leaching decreases during the operations. This is mainly due to the accumulation of resin poisons. One such poison is tetrathionate formed from the sulphides in the ore during leaching under oxidizing conditions^{1,2}.

Robinson³ reported on a process to determine tetrathionate sorbed on an anion-exchange resin in which the resin was eluted at room temperature using a 10% sodium hydroxide solution. The thiosulphate content of the eluate was then determined by iodometric titration, while the sulphite ions were masked with formaldehyde. The decomposition of the tetrathionate was assumed to occur as in eqn. 1. The reproducibility of the measurements made in this way was poor. Therefore a new process was developed.

Methods for determining tetrathionate

Tetrathionate is usually determined by measuring its decomposition products. The breakdown of polythionates, such as tetrathionate, in alkaline solution is a slow, rather complicated process that takes place in more than one step⁴. The rate of decomposition, the nature and the quantity of the products at a given time depend on a number of different factors such as the hydroxide ion concentration of the solution, temperature, time passed from the moment of resolution, etc. The two reactions by which the decomposition takes place can be described as follows^{3,5-7}:



In the present work two methods of analysis were applied. One was iodometric determination, the other was the method reported by Solymosy and Varga⁷. In the latter the products of decomposition are titrated in sodium hydroxide solution at 50–70°C with potassium ferricyanide in the presence of osmium tetroxide catalyst using “dead stop” end-point indication. The advantage of this method is that the titrating solution measures the same sulphur content from tetrathionate regardless of the mode of decomposition of the tetrathionate.

EXPERIMENTAL

For studying the decomposition of tetrathionate, equal quantities of tetrathionate⁸ were added to sodium hydroxide solutions of different concentrations. The samples were kept at different temperature (25–90°C) and from time to time aliquots were withdrawn and titrated to determine their thiosulphate content. It was found that the total decomposition of tetrathionate requires at least 20% sodium hydroxide and 5 h at 90°C.

In further work, 20% sodium hydroxide solution was used to elute tetrathionate from Varion AP anion-exchange resin, which had been partly saturated with tetrathionate. A 5-ml volume of anion exchanger was placed into flasks with reflux condensers containing 20–100 ml of alkali solution. The flasks were then heated on a water-bath. Samples were withdrawn from the solutions at different times and the eluted decomposition products of tetrathionate were determined by the two methods mentioned. To improve the efficiency of the elution process, a steam-heated ion-exchange column was constructed in which the sodium hydroxide solution flowed continuously through the resin. The eluate fractions were analysed as before.

Determination of the tetrathionate content of anion-exchange resin

A 10-cm³ volume of anion-exchange resin was placed in the steam-heated column, and eluted with 20% sodium hydroxide solution at a rate of 50 cm³/h. The total volume of eluate was 250 cm³. A suitable volume of this solution, according to the expected tetrathionate concentration was made up to 50 cm³ with 20% sodium hydroxide solution. The resulting solution was heated to 50–70°C and, after the addition of 2–3 drops of osmium tetroxide catalyst it was titrated by 0.1 *N* potassium ferricyanide solution. The end-point was determined by the “dead stop” method⁷. A 1-cm³ volume of 0.1 *N* potassium ferricyanide solution is equivalent to 0.916 mg sulphur in tetrathionate. Reproducibility was $\pm 3\%$.

DISCUSSION

The experiments showed that tetrathionate can be broken down and eluted in a reproducible way only by 20% sodium hydroxide solution and at a temperature near 100°C. Even under such conditions, acceptable results, *i.e.*, total elution in a reasonable time, can only be achieved by using an ion-exchange column.

An unexpected result was the systematic difference obtained between the tetrathionate concentration of the resin determined by the two different titration methods despite the fact that both solutions were generated by the same thiosulphate solution, and in contrast to the earlier experiments where the two methods had given the same result for the decomposition of tetrathionate in concentrated alkali solution at 90°C. From this we conclude that the mode of decomposition of tetrathionate on the ion exchanger is different from that in solution. The average difference in concentrations measured by the two methods was *ca.* 16%, which seems to suggest that eqn. 2 describes the actual decomposition mode and that the ferricyanide analysis method is suitable.

ACKNOWLEDGEMENT

The authors wish to acknowledge the valuable contribution of Mispál Valéria and Papp Sándorné to this work.

REFERENCES

- 1 N. Clegg and J. Foley, *Uranium Ores Processing*, Elsevier, New York, 1958.
- 2 E. Szabó, *Bevezetés az urán kémiai technológiába*, Tankönyvkiadó, Budapest, 1962.
- 3 R. B. Robinson, *Leaching Report No. 173*, Government Metallurgical Laboratory, Johannesburg, 1953.
- 4 M. Goehring, *Fortschr. Chem. Forsch.*, 2 (1952) 444.
- 5 M. Great-Cabande, *Bull. Soc. Chim. Fr.*, (1952) 784.
- 6 R. C. Brasted, *Comprehensive Inorganic Chemistry, Vol. 8, Sulfur, Selenium, Tellurium, Polonium and Oxygen*, Van Nostrand, New York, 1961.
- 7 F. Solymosi and A. Varga, *Magy. Kem. Foly.*, 64, No. 11 (1958) 443.
- 8 F. Martin and H. Metz, *Z. Anorg. Allg. Chem.*, 127 (1923) 83.