

## Book review

Burkin, A. R. (ed.). *Leaching and reduction in hydro-metallurgy*. London, Institution of Mining and Metallurgy, 1975. £10.

Dr Burkin will be remembered as the author of *The Chemistry of Hydrometallurgical Processes*, published in 1966, in which he successfully bridged the gap between pure and applied science to the benefit of adherents of both branches.

Equally successful in the same objective is the publication now under review, which includes papers prepared under his direction by his research group and which were presented at the Hydrometallurgical Meeting at Imperial College in December 1973. Two papers are on uranium, five on copper, two on nickel, one each on cobalt and chromium, and one on the bacterial leaching of a sulphide concentrate.

The two papers on uranium are from the National Institute for Metallurgy (South Africa) and deal with the fundamentals of acid and of alkaline carbonate leaches. Both conclusively record that uranium dissolution occurs through an electrochemical mechanism.

The paper on chromium covers the kinetics of the

hydroxide leaching of the oxide and of chromite.

The leaching of an auriferous Canadian pyrite-arsenopyrite concentrate with a *Thiobacillus ferro-oxidans* culture isolated from the mine water from the abandoned Ogofau gold mine in Wales is convincingly reported by Mr Anthony Pinches of University College, Swansea.

New and valuable data on the leaching of copper sulphides are recorded under the acidic ferric chloride leaching of chalcocite, ferric sulphate leaching of bornite, acid leaching of chalcopyrite, high temperature E-pH diagrams, which include copper oxides and sulphides, and the reduction of aqueous cupric acetate by hydrogen.

The kinetics of reduction of nickel salts by hydrazine, and of nickel and cobalt in aqueous ammoniacal sulphate solutions by hydrogen, have been studied and recorded in detail.

This volume is worthy of a place on the bookshelves of all extraction metallurgists and in all metallurgical libraries.

H.B.

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## NIM reports

The following reports are available free of charge from the National Institute for Metallurgy, Private Bag 7, Auckland Park, 2006 South Africa.

### Report no. 845

*An electron-microprobe study of the nickel distribution in a serpentinite from Volspruit, Potgietersrus.* (22nd Oct., 1969; re-issued Dec. 1975).

A detailed microscopic and electron-microprobe study of a serpentinite sample showed that most of the minerals vary widely in their nickel content, e.g., serpentine (1 to 8 per cent), magnetite (2 to 5 per cent), and goethite (4 to 14 per cent). The usual nickel-poor minerals, e.g. chromite and martite, show little variation. The darker-coloured serpentines, which accommodate the magnetite that had exuded during serpentinization, appear to have the highest concentrations of nickel.

The sulphide phase in the rock could not be identified beyond doubt, but existing evidence indicates that it may be bravoite.

### Report no. 1546

*Pilot-plant smelting campaign on iron ores from Tete.* (22nd May, 1973; re-issued Jun. 1976).

The objectives of the smelting tests on vanadium-bearing titaniferous iron ore from the Tete area of Mocambique in a 3,6 MVA furnace were to produce a pig iron and a titaniferous slag under conditions that would favour the partitioning of the vanadium to the slag. This slag would then be amenable to pyrometallurgical or hydrometallurgical treatment for the recovery of  $TiO_2$  and vanadium.

A low-carbon pig iron having a low silicon content and a high sulphur content was produced. However, it was shown that the furnace could be operated in such a way that the vanadium would partition to the slag. A pyrometallurgical treatment for the recovery of the vanadium could not be attempted during these tests, but a hydrometallurgical treatment was initiated.

### Report no. 1557

*Cost estimates for the production of pig iron in the Tete district of Mocambique.* (18th Jun., 1973; re-issued Jun. 1976).

Estimates of capital and operating costs are given for the production of 100 000 tonnes of pig iron per annum. The process considered involves the reduction of titaniferous magnetite by smelting in an electric-arc furnace. The capital cost, including fixed and working capital, amounts to R7 781 255, and the total operating cost, including depreciation, is estimated to be R32,25 per tonne of pig iron. Recommendations for future work are given.

### Report no. 1600

*Dilute-acid leaching of slag from Tete ore.* (20th Nov., 1973; re-issued Jun. 1976).

The smelting of titaniferous iron ore from the Tete district results in a by-product slag having a  $TiO_2$  content of about 50 per cent. For this slag to be salable, the  $TiO_2$  content should be increased to at least 56 per cent. Laboratory tests showed that the slag can be upgraded by 20 to 25 per cent if it is leached with dilute

sulphuric acid (100 g/l) at a liquid-to-solid ratio of between 8 and 10 for 4 hours at 70 to 90°C. The loss of  $TiO_2$  by dissolution is about 1 per cent. Leaching with stronger sulphuric acid (200 g/l) does not improve the upgrading much, and increases the dissolution of  $TiO_2$  to 5 per cent. A disadvantage of the process is its requirement of large volumes of dilute acid and water to ensure good filtration and washing.

Leaching with dilute hydrochloric acid produced an upgraded slag having a  $TiO_2$  content of up to 60 per cent, but appears to have no advantages over leaching with dilute sulphuric acid.

The  $V_2O_5$  content of the Tete slag is 1,3 per cent.  $V_2O_5$  is not recovered normally in the process of pigment manufacture, but it may be possible to treat the slag for the recovery of both the  $TiO_2$  and the  $V_2O_5$ . It is therefore of interest to note that less than 5 per cent of the  $V_2O_5$  is dissolved in the weak-acid leach.

### Report no. 1602

*The roasting of Tete slag for the extraction of vanadium.* (20th Nov., 1973; re-issued Jun. 1976).

The recovery of vanadium from Tete slag by a sodium carbonate roast and a leach with water was studied. The best result was a recovery of 80 per cent, achieved when a sodium carbonate addition of 20 per cent was made and roasting continued for 3 hours at 1000°C. In normal practice, only 3 to 7 per cent sodium carbonate is used, but this amount resulted in very poor extraction with Tete slag, probably because of the high silica and lime contents of the slag.

A roasting temperature of 1000 to 1100°C should be used. Roasting in a shallow vessel with efficient rabbling (to permit access to the air required for oxidation) is most important for efficient recovery.

### Report no. 1635

*Magnetic separation tests on Tete slag and ore.* (30th Apr., 1974; re-issued Jun. 1976).

Low-intensity magnetic separation of the slag yielded a small fraction (8 per cent) of substantially reduced  $TiO_2$  content, so that the bulk of the material was slightly enriched in  $TiO_2$ . High-intensity magnetic separation of this enriched material once again yielded a small fraction (12 per cent) of reduced  $TiO_2$  content and a large fraction slightly enriched in  $TiO_2$ . The total enrichment obtained by a combination of low-intensity and high-intensity magnetic separation appears to be too small to be of practical value.

Magnetic separation of the ore yielded fractions in which the  $TiO_2$  content ranged from 19 to 45 per cent. However, theoretical calculations show that, if these fractions were smelted under the conditions that gave slag 1A, there would be no great difference in the  $TiO_2$  content of the slags because the ratio of  $TiO_2$  to total non-ferrous material does not vary greatly.

### Report no. 1671

*Pyrometallurgical retreatment of a slag for the recovery of vanadium.* (11th Oct., 1974; re-issued Jun. 1976).

Attempts were made to extract the vanadium remaining in a slag produced as a result of the electric smelting of a titaniferous magnetite. Additions of char

equivalent to 100 per cent, 125 per cent, and 150 per cent of the carbon requirement for complete reduction were made, but only a maximum of 27 per cent of the vanadium present in the slag could be recovered as a low-grade ferrovanadium. Use was also made of ferro-silicon in addition to carbon, but there was no improvement in the recovery.

#### Report no. 1785

*Some thermodynamic aspects of systems relevant to the flotation of sphalerite.*

Calculations of the distribution of species in systems relevant to the flotation of sphalerite are described.

The following aspects of the investigation are discussed.

- (i) The effect of carbonate and calcium on the species present in the diluted  $\text{ZnSO}_4\text{-NaCN-CaO}$  slurry used at the Prieska Copper Mine to depress sphalerite.
- (ii) Recalculation of the species present during the deactivation of copper-activated sphalerite with cyanide and comparison with the calculations and experimental results reported previously.
- (iii) Calculations concerning the efficiency of ammonia, ethylenediamine, propylenediamine, and cyanide as deactivating agents for copper-activated sphalerite.
- (iv) A calculation of the species present in the sphalerite-copper-xanthate system at pH values around 7.

The results for (iii) and (iv) are discussed in the light of experimental results reported in the literature.

#### Report no. 1808

*Spectrophotometric determination (with pyrocatechol violet as chromogenic agent) of aluminium in zirconium metal and in the residue from anode sludges.*

A method is described for the determination of aluminium within the ranges 40 to 1000 p.p.m. in residues from anode sludges and 10 to 10 000 p.p.m. in zirconium metal.

Aluminium is separated from major amounts of antimony, lead, copper, nickel, silver, and bismuth by extraction of its complex with N-benzoyl-N-phenylhydroxylamine into benzene at a pH value of 8 in the presence of masking agents, and by back-extraction into 0,2 N hydrochloric acid. Since the extraction of aluminium by this reagent is unsuccessful in the presence of large amounts of zirconium, an alternative separation step is described, in which depolymerized zirconium in 1 N sulphuric acid is separated from aluminium by liquid-liquid extraction of its cupferron complex into chloroform. In both instances, aluminium is determined spectrophotometrically with pyrocatechol violet as the chromogenic agent.

The coefficient of variation for the determination of zirconium metal is 10 per cent at an aluminium concentration of 44 p.p.m.

#### Report no. 1813

*The economic potential of some pegmatites from the Kenhardt area in relation to the trace-element content of their border zones.*

Forty-one samples collected from the border zones of pegmatites were analysed for their lithium, beryllium, niobium, tantalum, uranium, thorium, bismuth, and tin contents. A technique developed previously was used in an attempt to classify the pegmatites as containing economically significant quantities of these rare elements or as barren.

Twenty-one of the samples were collected from pegma-

tites that were known (from previous attempts to mine them) to be either economically significant or barren, and were used as a control group; 75 per cent of these samples were classified correctly.

Of twenty samples from pegmatites of unknown economic potential, two were classified as economically significant. However, in view of the low rate of success of classification of the control group, it is considered that further refinement of the technique is necessary before classification of a pegmatite as containing economically significant amounts of minerals can be considered to be conclusive.

#### Report no. 1817

*The rapid determination by X-ray-fluorescence spectrometry of tungsten in tungsten ores and concentrates.*

A method is presented that is applicable to tungsten concentrations above about 0,1 per cent. Matrix variations are suppressed by a tenfold to fiftyfold dilution of the sample material during fusion, which eliminates any mineralogical effects and produces a clear glass disc that is used direct for intensity measurements. Residual matrix variations are compensated for by application of the background-ratio technique, and the intensity measurements are evaluated by comparison with synthetic standards, the calculation being done on-line by use of an Olivetti Programma 602 desk-top computer. An annotated computer programme is provided for calculation of the curve of the calibration graph and evaluation of the sample intensities.

The method is rapid and has a coefficient of variation of 1,5 per cent at a level of 50 per cent tungsten when used under routine conditions. Comparison with the results of a wet-chemical method showed the proposed method to have no bias.

#### Report no. 1820

*The thermodynamics of the formation of chlorocomplexes of iron (III), cobalt (II), iron (II), manganese (II), and copper (II) in perchlorate medium.*

In this investigation, the programme for the determination of the thermodynamic properties of complexes in aqueous solution for conditions encountered in hydrometallurgical processes was extended to the chlorocomplexes of iron(III), cobalt(II), and manganese(II).

Thermodynamic data derived from the stability constants and characteristics of the absorption spectra allow the complex species to be classified as inner sphere or outer sphere. The classification provides an understanding of the response of the systems to changes in medium, acid strength, and temperature.

The highly charged iron(III) ion forms the inner-sphere complexes  $\text{FeCl}^{2+}$  and  $\text{FeCl}_2^+$ , whereas the divalent ions form the outer-sphere complexes  $\text{FeCl}^+$  and  $\text{MnCl}^+$ . Contradictory evidence regarding  $\text{CoCl}^+$  prevented classification of this complex.  $\text{CuCl}^+$  appears to exist in both the inner-sphere and outer-sphere forms.

Distribution diagrams show that, at 25°C, half of the total metal is in the complexed form in the iron(III), cobalt(II), iron(II), and manganese(II) systems at free chloride concentrations of 0,1 M, 1,9 M, 2,4 M, and 5,2 M respectively.

The importance of thermodynamic data to extractive metallurgy is discussed. There are often no data available for hot concentrated systems, and it is shown that recognition of chlorocomplexes as outer-sphere species allows data available for dilute solutions at 25°C to be applied to these systems.