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THE PRODUCTION OF HIGH-PURITY NIOBIUM OXIDE FROM PYROCHLORE-PEROVSKITE CONCENTRATE

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EXTRACTION METALLURGY DIVISION

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The Production of High-Purity Niobium Oxide from Pyrochlore-Perovskite Concentrate*

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ABSTRACT

A chemical process, based on laboratory investigations, is proposed for the production of high-purity niobium oxide from a pyrochlore-perovskite flotation concentrate produced from ore obtained at the Oka, Quebec, property of Columbium Mining Products Limited.

The method developed included the decomposition and dissolution of the flotation concentrate with hot, concentrated sulphuric acid. The dissolved niobium was purified and concentrated by a solvent extraction step, using methyl isobutyl ketone as the extractant. The niobium was recovered from the extractant with ammonium fluoride solution from which niobium oxide was precipitated with ammonia. Finally, the filtered and washed precipitate was calcined. Ninety-six per cent of the niobium was recovered in a product analysing 99.9 per cent Nb_2O_5. The reagent cost was in the range of $1.00 to $1.25 per pound of niobium recovered.

Introduction

OVER the past few years, Columbium Mining Products Limited has been engaged in the development of a niobium-bearing mineral deposit in the vicinity of Oka, Quebec. One phase of this program resulted in a flotation process capable of producing concentrates containing up to 50 per cent Nb_2O_5. Flotation pilot-plant investigations under the direction of the Company's consultant, Mr. H. L. Noblitt, showed that it was not possible to produce concentrates analyzing more than 50 per cent Nb_2O_5 without experiencing a prohibitive drop in recovery. In comparison, niobium-bearing flotation concentrates containing at least 60 per cent Nb_2O_5 are currently available from other world sources. In view of this situation, the Mines Branch was asked by Mr. Noblitt to undertake an investigation directed toward the production, by hydrometallurgical means, of a high-purity niobium salt from the Oka flotation concentrates. If the investigation showed that an operation of this type was economically feasible, the competitive world position of the Oka producers might be improved.

Work done at the Department of Mines and Technical Surveys in 1955 (1), at the Batelle Memorial Institute in 1958 (2) and at the United States Bureau of Mines in 1961 (3) indicated that pyrochlore and perovskite, the ore minerals present in the Oka deposits, could be decomposed and leached with sulphuric acid, and that the dissolved niobium could be recovered from a sulphate system by a solvent extraction process using methyl isobutyl ketone as an extractant. The work reported here was done with a view to determining if these earlier findings could be applied economically to the treatment of the concentrate produced from the Oka deposit of Columbium Mining Products Limited.

Two samples of flotation concentrate were supplied for this work. Mineralogical examination showed that the only niobium-bearing minerals present in these concentrates were pyrochlore and perovskite in a proportion of about three parts pyrochlore to one part perovskite. The chemical analyses of these concentrates are shown in Table I.

Decomposition and Dissolution

Procedure

The general procedure used to effect dissolution of the niobium minerals consisted of two operations which, in this paper, are referred to as the decomposition and dissolution steps. In the decomposition step, the flotation concentrate was contacted with strong, hot, sulphuric acid. After decomposition, the decomposed product was taken up in a more dilute sulphuric acid solution at temperatures of up to 40°C; a procedure referred to as the

*Extraction Metallurgy Division, Internal Report EMA 64-3. ("Crown Copyright Reserved").

Table I—Chemical Analysis of Flotation Concentrate Samples

Sample No.	Nb_2O_5 (%)	Ta_2O_5 (%)	TiO_2 (%)	CaO (%)	Fe (%)	P_2O_5 (%)	SiO_2 (%)	ZrO_2 (%)
1	26.5	0.89	7.41	17.46	—	—	1.75	—
2	48.9	0.28	5.33	19.0	5.47	0.15	0.4	1.33

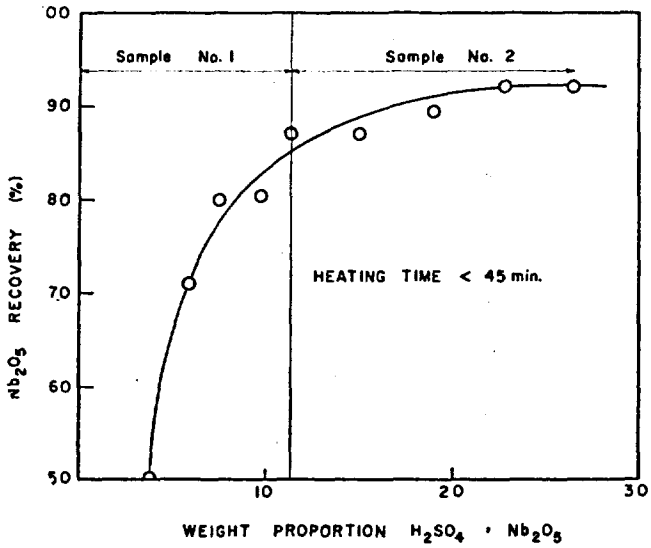

Figure 1.—Effect of the Acid: Nb_2O_5 Weight Proportion Used in Decomposition on the Niobium Recovery in Solution.

dissolution step. In most of the tests, the dry, ground concentrate was mixed with 93 per cent sulphuric acid in the decomposition step. However, in this paper, weight proportions of sulphuric acid to niobium oxide or sulphuric acid to concentrate are expressed in terms of 100 per cent H_2SO_4.

In the decomposition tests in which the acid to concentrate weight ratio was 3:1 or less, the mixture was heated in porcelain crucibles in a muffle furnace. In these tests, prior to heating, the mixture had the consistency of paste and the decomposed product, after heating, was dry or only slightly moist. In the tests in which the acid to concentrate weight ratio was 4:1 or greater, the mixture, being a fluid slurry, was heated in a glass reaction vessel and stirred continuously during the heating period.

The two samples, being flotation concentrates, were about 70 per cent minus 325 mesh. Consequently, the samples were not subjected to any additional grinding prior to decomposition.

The procedure employed in the dissolution step depended on the procedure followed in the decomposition step. Where the concentrate had been decomposed in the muffle furnace with low acid to concentrate weight ratios, the dry or almost dry decomposed product was taken up in 65 per cent sulphuric acid solution. Where the concentrate had been decomposed in the glass reaction vessel at high acid to concentrate weight ratios, the slurry, on completion of the heating period, was cooled to room temperature and gradually diluted with water or melting ice until the acid concentration of the solution was reduced to 40-45 per cent H_2SO_4. The slurry was stirred continuously during the cooling and dilution steps and for a period following dilution during which the niobium was taken up in solution.

After the dissolution step, the slurries were filtered and the filter cakes washed twice; once with 35 per cent H_2SO_4 solution and then with water. The primary and wash filtrates were combined for the liquid-liquid extraction test work.

Results

The first tests were done using Sample No. 1, containing 26.5 per cent Nb_2O_5, as feed material; they had the objective of determining the effects of the H_2SO_4:Nb_2O_5 weight ratio and of retention time on the decomposition of the niobium-bearing minerals. In these tests, mixtures of 93 per cent H_2SO_4 and concentrate in proportions ranging from 3.8 to 26.4 weight parts of acid per part of Nb_2O_5 were used, with retention times of from 0.5 to 3.0 hours. The temperature during decomposition was controlled at about 205°C in all the tests. Where the acid to Nb_2O_5 weight ratio was 11.3 or less, the decomposed product, in the form of a dry or almost dry cake, was taken up in 65 per cent sulphuric acid solution and stirred for a 3-hour period at room temperature to obtain maximum dissolution of the niobium. With acid to Nb_2O_5 weight ratios of 15.1 or higher, the decomposed product, which was in the form of a slurry, was cooled and diluted with water to an acid concentration of 35 per cent H_2SO_4 and stirred for a 3-hour period. In all tests, the slurry was finally filtered and the residue, after washing, analyzed for Nb_2O_5.

The results of some of these tests, given graphically in Figure 1, show that the Nb_2O_5 extraction increased from 50 to 92 per cent as the weight ratio of sulphuric acid to Nb_2O_5 increased from 3.8 to 22.6, at which level the extraction curve reached a maximum. The data shown in Figure 1 were obtained from the tests using retention times of 0.5 to 0.75 hr. in the decomposition step. The results of tests in which the retention time in decomposition was greater than 0.75 hr. indicated that prolonged heating was detrimental to the subsequent dissolution of niobium.

At this point in the program, Sample No. 2, containing 48.9 per cent Nb_2O_5, became available, and the investigation was continued using this more representative concentrate sample. It was shown that the optimum conditions for decomposition and dissolution determined from the work with the lower grade Sample No. 1 were applicable to the higher grade sample. The results showed that at an H_2SO_4:Nb_2O_5 weight ratio of 22.7:1, and with a decomposition retention time of 40 minutes at 205°C, the niobium extraction levelled off at about 97 per cent; a recovery in solution 5 per cent higher than that obtained from Sample No. 1. It was also observed, as with Sample No. 1, that prolonged retention time in the decomposition step resulted in lower recoveries of Nb_2O_5 in solution. Further study showed that when retention time in the decomposition step was more than 40 minutes, the decomposition products underwent a change which, in some way, made them less soluble in the subsequent dissolution step.

In all the test work described, commercial grade (93 per cent H_2SO_4) had been used for decomposition of the minerals. To determine the importance of high acid concentration in the decomposition step, tests were done in which the starting concentration of the acid used for decomposition ranged from 80 to 93 per cent H_2SO_4. The results showed that with a starting concentration of 85 per cent H_2SO_4, the extraction dropped 20 per cent from the extraction obtained when the starting acid concentration was 93 per cent H_2SO_4. When the acid used for decomposition was 80 per cent H_2SO_4, the

extraction dropped an additional 10 to 15 per cent. These results indicate that very high acid concentrations are required in the decomposition step if the extraction of niobium is to be satisfactory. In connection with this, it was observed that the acid concentration of the solutions at the end of the decomposition of Sample No. 1 was 83 per cent H_2SO_4 compared to an 87 per cent H_2SO_4 concentration in the solutions after the decomposition of Sample No. 2. This difference in acid concentrations during decomposition may explain why niobium extractions were higher from the higher grade concentrate, and why undecomposed perovskite was found in the residues from Sample 1.

The importance and operating characteristics of the dissolution step were indicated by the test work. The results showed that on completion of the decomposition step only two-thirds of the niobium was in solution, and that a 2- to 3-hour retention time in the dissolution step was shown to be effective in allowing time for the precipitation of the calcium sulphate which had been taken into solution during decomposition. Tests also showed that extension of the dissolution retention time beyond 3 hours was of no advantage. The most critical operation in the dissolution step was the control of the pulp temperature while diluting the pulp after decomposition. If the dilution was done too quickly the pulp temperature rose rapidly, and there was visible evidence of niobium re-precipitation if the temperature rose much above 40°C. The use of melting ice as the diluent in this step provided an effective means of temperature control in these small-scale tests.

After completion of the dilution step, the niobium-bearing solution was recovered by filtration. The filter cake was washed with 35 per cent sulphuric acid, using about 3 ml. wash solution per gram of dry filter cake. Finally, the cake was washed with a similar volume of water. It was observed that, in the initial pulp filtration and in the subsequent washing operations, filtration was rapid.

Liquid-Liquid Extraction and Precipitation

Procedure

The general procedure followed in the solvent extraction and precipitation operations was composed of five steps. First, hydrofluoric acid was added to the combined niobium-bearing dissolution filtrate and wash solutions to a concentration of 5 per cent HF. After addition of the hydrofluoric acid, the acid solution and methyl isobutyl ketone (MIBK) were shaken together. On standing for a short period, the aqueous and organic phases separated cleanly and the niobium-barren aqueous phase could then be drawn off from the bottom of the funnel. The niobium was stripped from the organic phase by shaking the MIBK with an equal volume of 5 per cent aqueous ammonium fluoride solution. After allowing the mixture to settle, the NH_4F solution, now containing the niobium, was drawn from the bottom of the funnel and treated to precipitate the niobium. In most tests, the now-barren MIBK from the stripping operation was contacted with an equal volume of 4.75 per cent H_2SO_4 solution and recycled to the subsequent extraction step. The Nb_2O_5-NH_4F solution from stripping was neutralized with ammonia to precipitate the purified Nb_2O_5, which was then filtered, washed, dried and calcined. The barren solution from precipitation was re-acidified with hydrofluoric acid and recycled to subsequent stripping operations. In this work, polyethylene equipment was used throughout.

Results

The feed solution to the MIBK extraction step analyzed about 23 g.Nb_2O_5/l. and 40 per cent H_2SO_4. The principal impurities and their approximate concentrations were Fe-4.0 g./l., Ca-0.2 g./l., TiO_2-0.05 g./l., P_2O_5-0.5 g./l., ZrO_2-0.5 g./l., F-0.8 g./l., Ta-0.03 g./l. and SiO_2-0.05 g./l. When Hydrofluoric acid was added to this solution to a concentration of 5 per cent HF, a white precipitate formed. About 2 g. of precipitate was produced per litre of solution. On analysis, the precipitate was found to contain about 13 per cent ZrO_2, 0.1 per cent HfO_2 and 3 per cent Nb_2O_5. This represented less than 0.5 per cent of the niobium in the feed solution. The precipitate, being difficult to filter, was recovered by centrifuging, and the clarified solution extracted with MIBK. Adjustment of the feed solution to 5 per cent HF required 2.5 lbs. HF/lb. Nb_2O_5.

The test work done on the MIBK extraction step covered MIBK to aqueous volume ratios of 1:1 and 2:1, contact times of 2 and 4 minutes, recycling of the MIBK after stripping and a consideration of whether two contact stages were necessary. The results showed that an MIBK to aqueous volume ratio of 1:1 was sufficient to recover 99.95 per cent of the niobium with a high degree of selectivity from an aqueous solution analyzing about 21 g./l. Nb_2O_5. About half of the tantalum present in the feed solution was extracted with the niobium. These results were obtained with a 4-minute contact time, and were slightly better than those obtained with a 2-minute contact time. The tests to investigate the effect on extraction of recycling the MIBK showed that the extraction of niobium levelled off at 99 per cent by the fifth cycle. Organic solvent losses are difficult to estimate from small-scale tests, as the measured loss is usually much higher than that experienced in larger scale continuous operations. The measured loss in these tests was in the order of 0.5 lb. MIBK per lb. Nb_2O_5.

The test work done to investigate the removal of niobium from the MIBK with 5 per cent NH_4F solution showed that with an organic to aqueous volume proportion of 1:1, 99.9 per cent of the niobium was transferred to the aqueous phase in 4 minutes. The ammonium fluoride solution from this step was prepared by acidifying the ammonium hydroxide barren from the precipitation operation in the previous cycle with hydrofluoric acid to a pH of about 3.5. The amount of HF required for this was 1.0 lb. per lb. Nb_2O_5 produced.

After the niobium was removed from the organic phase, the MIBK was scrubbed with a 4.75 per cent H_2SO_4 aqueous solution using volume proportions of MIBK to aqueous of 1:1. This procedure is necessary to remove, from the MIBK, ammonium salts which would interfere with the extraction operation when the MIBK was recycled. This step also removed tantalum, which was present in a concentration of 0.02 g./l. The sulphuric acid used in preparing the scrub solution amounted to 2 lbs. H_2SO_4 per lb. Nb_2O_5. The scrubbed MIBK was re-used for subsequent extraction of feed solution.

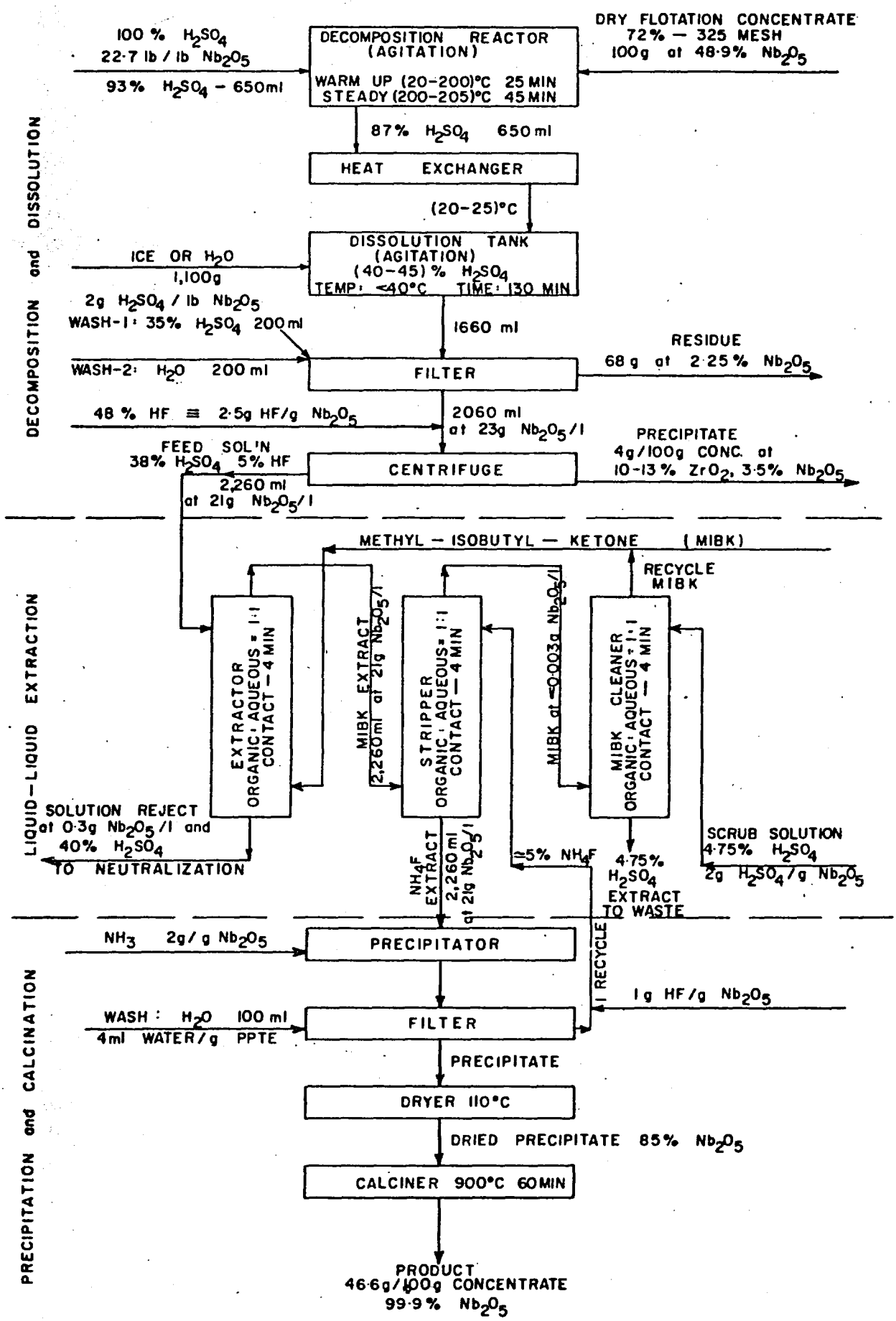

Figure 2.—Schematic Presentation of the Laboratory Procedure Used to Produce Nb_2O_5 from Flotation Concentrate.

After it had been used to recover the niobium from the MIBK, the ammonium fluoride solution had a pH value of about 3.5. When anhydrous ammonia was added to raise the pH to 8.0, 99.9 per cent of the contained niobium precipitated. About 2 lbs. NH_3 per lb. of Nb_2O_5 recovered was required for this pH adjustment. The precipitate was recovered by vacuum filtration using a Buchner funnel. It was observed that the precipitate filtered rapidly. The barren filtrate was acidified to a pH of 3.5 with hydrofluoric acid and re-used to recover the niobium from the MIBK extract of the subsequent test. The filtered precipitate was washed with a volume of water equivalent to about 4 mls. water per gram of precipitate and then dried at 100°C.

After being dried, the precipitate analyzed 85 per cent Nb_2O_5. Spectrographic analysis of the precipitate showed that it contained about 0.10 per cent impurities in the form of metals and silica. In addition, it was apparent that the fluorine and ammonia consumed in the precipitation operations were contributing to the impurity of the precipitate. On the presumption that these latter impurities could be driven off with heat, the precipitate was calcined at 900°C for one hour. After calcination, the precipitate analyzed 99.9 per cent Nb_2O_5. Table II is a spectrographic analysis of the high-grade precipitate. It is shown that the total impurity level was about 0.10 per cent.

Discussion

The test work has defined a procedure for the production of high-purity niobium oxide from pyrochlore-perovskite flotation concentrate. In the work done, the over-all recovery of niobium from the flotation concentrate was 95.2 per cent in a product containing 99.9 per cent Nb_2O_5. Figure 2 is a schematic presentation of the laboratory procedures used, along with material balances and reagent consumptions. This schematic diagram and the procedural details and results described in the preceding sections serve as a basis for discussion.

The test work in this investigation was limited to small-scale laboratory studies in which the many variables, particularly those related to the liquid-liquid extraction operation, were not exhaustively investigated. However, the scope of the work was such that it is possible to assess the applicability of the process to a specific operation. Sufficient information was obtained on reagent consumptions, retention times, solution balances, compositions of solutions, recovery and grade of final product to provide data for an economic feasibility study to determine if further process development is warranted.

Table II—Semi-Quantitative Spectrographic Analysis of the Calcined Precipitate

	%
Nb_2O_5	99.9 (chemical analysis)
Si	0.005
Mg	0.05
Fe	0.01
Al	0.01
Ti	trace
Ta	trace
Mn	0.003
Ca	0.03

Table III—Breakdown of Reagent Costs

	lb./lb. Nb_2O_5	$/lb. reagent	$/lb. Nb_2O_5
93% H_2SO_4 for decomposition	24.4	.011	0.263
93% H_2SO_4 for res. washing	2.0		0.022
93% H_2SO_4 for MIBK scrub	2.2		0.024
70% HF to liquid-liquid ext. feed	3.6	0.11	0.396
70% HF to precipitation barren	1.5	0.11	0.165
Anhydrous ammonia to pptn.	2.0	0.05	0.100
MIBK loss	0.5	0.17	0.085
Lime to neutralize acid wastes	25.0	0.07	0.175
Total			1.230

The indicated cost of reagents, based on the laboratory results, is in the order of $1.25 per pound of Nb_2O_5 recovered. Table III gives a breakdown of this figure. It is thought that this reagent cost is probably a maximum figure, and that further investigation would show ways in which it could be reduced. There is reason to believe that the HF concentration in the aqueous feed to liquid-liquid extraction could be lowered below the 5 per cent level used in this work. Each 1 per cent reduction in the HF concentration at this point would reduce the cost by $0.08/lb. Nb_2O_5. As the aqueous feed to liquid-liquid extraction contains only 20 g. Nb_2O_5/l., it might be possible to reduce the organic to aqueous volume ratio below 1:1, the minimum used in this investigation. A reduction in the organic to aqueous ratio would, in turn, reduce the volumes of ammonium fluoride and sulphuric acid solutions required to recover niobium from the MIBK and to scrub the MIBK prior to recycling. Possibly a part of the aqueous barren solution from the MIBK extraction step could be used to wash the residue. The MIBK loss experienced with laboratory testing would almost certainly be reduced considerably in a larger scale operation.

The ZrO_2 precipitate formed when HF is added to the combined dissolution and wash filtrates is not economically significant, because the ZrO_2 recovered amounts to only 0.001 lb. ZrO_2 per lb. Nb_2O_5 recovered. In practice, it might be more economical to add the HF to the dissolution slurry and thus discard the ZrO_2 precipitate with the leach residue. This would eliminate the relatively costly centrifuging step shown in the schematic representation.

The liquid-liquid extraction operation is highly selective for niobium, and through its use a premium-grade niobium oxide was produced. The final product analyzed 99.9 per cent Nb_2O_5 by chemical analysis, and this was confirmed by spectrographic analysis. The purity of this product is as good or better than that of the currently available analytical-grade Nb_2O_5 and would make it ideally suited for feed material in niobium metal production (4). Consequently, this process would be particularly useful if an integrated process going from concentrate to metal were to be considered.

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