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Hot Acid Leaching of Vanadium From Western Phosphate Beneficiation Tailings

By D. G. Collins, J. H. Russell, and A. R. Rule



UNITED STATES DEPARTMENT OF THE INTERIOR



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Donald Paul Hodel, Secretary

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Robert C. Horton, Director

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CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Acknowledgments.....	2
Sample description.....	2
Batch tests.....	3
Equipment and procedures.....	3
Results and discussion of bench-scale research.....	4
Continuous circuit tests.....	6
Equipment and procedure.....	6
Results and discussion.....	6
Dissolution with H_2SO_4	6
Excess acid utilization.....	7
Dissolution with H_2SO_4 --recycle H_3PO_4	8
Product acid composition.....	10
Filtration.....	10
Economic evaluation.....	11
Summary and conclusions.....	11
References.....	12
Appendix.--Economic evaluation.....	13

ILLUSTRATIONS

1. Dissolution of tailings A with concentrated H_2SO_4 or H_3PO_4	5
2. Dissolution of tailings A with concentrated H_2SO_4 in combination with H_3PO_4	5
3. Dissolution of tailings B with concentrated H_2SO_4	5
4. Basic flowsheet for continuous-circuit leaching.....	7
5. Flowsheet for tailings dissolution with phosphate concentrate addition..	8
6. Flowsheet for tailings dissolution with concentrated H_2SO_4 and recycle acid.....	9
7. Dissolution of vanadium from tailings B with and without recycle acid...	10
8. Dissolution of vanadium from tailings A with and without recycle acid...	10
9. Effect of recycle acid on vanadium dissolution from tailings A.....	10

TABLES

1. Chemical analyses of Western phosphate tailings samples.....	3
2. Typical size distribution and chemical analyses of Western phosphate tailings.....	3
3. Composition of product acids derived from tailings B.....	10
A-1. Estimated captial cost.....	14
A-2. Equipment cost summary, leach section.....	15
A-3. Equipment cost summary, vanadium recovery section.....	16
A-4. Equipment cost summary, evaporation section.....	17
A-5. Estimated annual operating cost.....	18

UNIT OF MEASURE ABBREVIATION USED IN THIS REPORT

°C	degree Celsius	Mgal	thousand gallon
d/wk	day per week	mL	milliliter
d/yr	day per year	mm	millimeter
diam	diameter	MMBtu	million British thermal unit
gal/(ft ² ·h)	gallon per square foot per hour	min	minute
g	gram	µm	micrometer
g/L	gram per liter	oz/yd ²	ounce per square yard
h	hour	pct	percent
h/d	hour per day	ppm	part per million
kg	kilogram	rpm	revolution per minute
kW·h	kilowatt hour	ton	short ton
L	liter	ton/d	short ton per day
lb	pound	ton/h	short ton per hour
lb/d	pound per day	wt pct	weight percent
lb solids/(ft ² ·d)	pound solids per square foot per day	yr	year

HOT ACID LEACHING OF VANADIUM FROM WESTERN PHOSPHATE BENEFICIATION TAILINGS

By D. G. Collins,¹ J. H. Russell,² and A. R. Rule³

With an Economic Evaluation by Thomas A. Phillips

ABSTRACT

As part of its effort to develop ways to maximize resource recovery, the Bureau of Mines investigated the extraction of vanadium from Western phosphate beneficiation tailings with H_2SO_4 and/or H_3PO_4 . Dissolution of the vanadium was accomplished by digesting a mixture of acid and a 50-pct-solids, tailings-water slurry. In the most effective method investigated, vanadium and phosphorus were leached by digesting the slurry at a constant boiling temperature (100° - 110° C) in a stirred reactor. In batch tests, maximum vanadium dissolution was 95 pct. In continuous-circuit tests designed to further evaluate vanadium dissolution at constant boiling temperature in a continuously stirred reactor, vanadium dissolution ranged from 70 to 85 pct. An economic evaluation of the process demonstrated that H_2SO_4 consumption is the major cost factor. Based on the value of the vanadium product with no allowance for a phosphate product, the cost of producing the V_2O_5 is more than twice its value. The potential for profit would depend upon the value of the phosphate fertilizer produced from the impure H_3PO_4 remaining after vanadium extraction.

¹Chemical engineer.

²Research chemist.

³Metallurgist (group supervisor).

Albany Research Center, Bureau of Mines, Albany, OR.

INTRODUCTION

To further its goal to maintain an adequate supply of critical materials to meet national economic and strategic needs and to maximize resource recovery, the Bureau of Mines conducted research to develop methods for recovery of vanadium from phosphate wastes. Western phosphate ore deposits represent a major potential domestic source of vanadium. The vanadium occurs in the micaceous clay fraction and is concentrated in the slime tailings during beneficiation of the phosphate ore. Based on 1981 production figures (1-2)⁴, about 4.5 million short tons of Western phosphate ore are beneficiated annually and about 1 million tons of tailings are discarded. More recent production figures are atypically low because of the depressed fertilizer market. The tailings contain about 2,500 tons of vanadium and 150,000 tons of phosphate (as P₂O₅) representing an annual value (based on 1983 prices) of \$17 million and \$47 million, respectively. With U.S. vanadium consumption nearing 10,000 tons annually, and predicted to increase to 13,000 tons by 1990, the phosphate beneficiation tailings could supply a significant portion of the Nation's needs (3-4).

Past research for recovery of vanadium from phosphatic materials was thoroughly reviewed by Russell, Collins, and Rule (5). That publication also described

results of bench-scale research to extract vanadium from phosphate tailings using a salt roasting technique. Leaching results showed that H₂SO₄ was the most effective leaching agent for vanadium extraction from roasted and unroasted tailings. Additionally, the gypsum formed improves filtration of the residue, and technology exists for recovery of vanadium from the resulting H₃PO₄. More than 90 pct of the vanadium was dissolved by roasting the tailings at 850° C for 120 min with 8 pct NaCl followed by leaching at 75° C for 120 min with an excess of H₂SO₄. A major problem with this approach was contamination of the most valuable product (H₃PO₄) with NaCl, making the product undesirable for use as fertilizer.

The primary objective of the present research was economic recovery of vanadium by coproduction of a phosphoric acid suitable for off-grade fertilizer production. A method for dissolution of vanadium was devised that avoids the costly drying and high-temperature salt roasting of the tailings, eliminating contamination of the H₃PO₄ with NaCl. Results presented in this report are from 200- to 400-g batch tests and 100-lb/d continuous-circuit studies for dissolution of vanadium from phosphate beneficiation tailings.

ACKNOWLEDGMENTS

The authors would like to thank the J. R. Simplot Co., Conda, ID, for the

samples of beneficiation tailings used in this investigation.

SAMPLE DESCRIPTION

Two tailings samples were obtained for experimental study from the J. R. Simplot Co. phosphate beneficiation plant in southeastern Idaho. The samples were flocculated and decanted at the plant site to 55 pct solids prior to shipment.

Chemical analyses, table 1, show that tailings B contains more CaO and Al₂O₃ than tailings A. A chemical analysis by size fraction of a representative tailings sample (table 2) shows that the vanadium is concentrated in the finest sized fractions. Distribution of uranium, associated with the phosphate-containing apatite mineral, closely follows the phosphate distribution. A

⁴Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

scanning electron microscope (SEM) examination of the tailings indicates that the vanadium is disseminated throughout

the tailings and associated with a mica mineral, most probably roscoelite, $K(V, Al, Mg)_2AlSiO_{10}(OH)_2$.

BATCH TESTS

EQUIPMENT AND PROCEDURES

Two procedures for acid dissolution of the tailings slurry were investigated using 200 to 400 dry grams of tailings solids (TS) per batch test. With the first procedure, concentrated H_2SO_4 or H_3PO_4 and the tailings slurry were mixed, dried, and heat-cured at temperatures ranging from 100° to 300° C. The heat-cured tailings then were leached. The second procedure involved mixing concentrated H_2SO_4 and/or H_3PO_4 with tailings slurry in a stirred reactor and curing

the mixture at the boiling temperature (100° to 110° C).

With the first method, a 50-pct-TS slurry was first mixed with concentrated H_2SO_4 or H_3PO_4 . A low-temperature (100° to 300° C) bake for up to 17 h was used to dry and heat-cure the acid-TS slurry mixture. The heat-cured mixture was then slurried with water or 30 pct H_3PO_4 and leached at 90° C for 1 h before filtration. The dissolution was calculated from the vanadium and phosphate distribution between the filtrate and residue.

With the heat-cure processing method, the long time required for drying and curing poses a major handling problem. A rotary kiln was used to determine if continuous agglomeration and heat-curing of the acid-tailings slurry mixture could be accomplished using a shorter retention time and higher temperature. A residence time of 30 min at 300° C furnace temperature produced dry, crumbly pellets which easily disintegrated in 90° C water.

The second procedure employed a stirred reactor for leaching the tailings with concentrated H_2SO_4 and/or H_3PO_4 at a boiling temperature (100° to 110° C). With one technique, the acid-tailings slurry mixture was leached by evaporatively boiling the mixture to a viscous paste. The mixture was then quenched with water or 30 pct H_3PO_4 at 90° C to

TABLE 1. - Chemical analyses of Western phosphate tailings samples

	Tailings	
	A	B
Analysis, pct:		
P ₂ O ₅	13.6	13.6
V ₂ O ₅34	.36
CaO.....	22.6	24.0
SiO ₂	36.9	32.7
Fe ₂ O ₃	2.22	2.67
Al ₂ O ₃	5.69	6.81
MgO.....	1.75	2.16
Na ₂ O.....	.42	.38
K ₂ O.....	2.36	2.06
U ₃ O ₈ppm..	72	68

TABLE 2. - Typical size distribution and chemical analyses of Western phosphate tailings

Particle size, μm	wt pct	Cum. wt pct	Analysis			Distribution, pct		
			P ₂ O ₅ , pct	V, pct	U, ppm	P ₂ O ₅	V	U
+48.....	6.0	6.0	26.0	0.06	99	11.4	1.8	10.6
-48, +34.....	16.7	22.6	15.7	.06	70	19.1	5.1	20.9
-34, +24.....	17.8	40.5	12.8	.09	52	16.6	8.4	16.6
-24, +16.....	11.7	52.1	11.1	.08	45	9.5	4.7	9.4
-16, +12.....	6.6	58.7	10.9	.11	41	5.3	3.7	4.8
-12.....	41.2	100.0	12.7	.35	51	38.1	76.3	37.7
Total or Average...	100.0	100.0	13.7	.19	56	100.0	100.0	100.0

dissolve the vanadium and obtain a filterable slurry. In an alternate technique a constant density was maintained by vapor refluxing to return condensed vapors to the stirred reactor. This technique was used to study the rate and extent of vanadium dissolution. Reaction rate data were obtained by removing and immediately filtering small samples of the acid-tailings slurry mixture from the reactor at timed intervals. The reactor was a round, 5-L flask equipped with several ports and a heating mantle. The 50-pct-TS slurry, containing 400 g of solids, was charged into the flask and agitated. The reaction time was considered to have started when half of the concentrated acid had been added. A pipet was used to withdraw 50-g samples of the reaction mixture at 5, 10, 15, 30, 60, and 90 min reaction time. The samples were immediately filtered, the pipet was rinsed onto the filter cake with 50 g of water, and the residue was then washed with an additional 100 g of distilled water. The dissolution was calculated from the vanadium distribution between the filtrate and residue.

RESULTS AND DISCUSSION OF BENCH-SCALE RESEARCH

Batch-scale research demonstrated that up to 95 pct of the vanadium in these Western phosphate beneficiation tailings would be dissolved by treating a heated 50-pct-TS slurry with acid. Phosphate dissolution was greater than 95 pct for all tests yielding at least 80-pct V extraction.

Vanadium extractions of up to 90 pct were obtained using the heat-curing method of the first procedure. A 50-pct-TS slurry of tailings A was mixed with 0.80 lb H_2SO_4 per pound TS and baked for 6 h at 150° C. Leaching the heat-cured product in water or 30 pct H_3PO_4 at 90° C yielded vanadium extractions up to 90 pct. The H_2SO_4 addition corresponds to approximately 125 pct of the H^+ stoichiometrically required by the acid consumers (CaO , MgO , Al_2O_3 , Fe_2O_3 , K_2O , and Na_2O) in the tailings. Water and 30 pct H_3PO_4 were equally effective in leaching the vanadium from the heat-cured product.

Approximately 30 pct lower vanadium extraction levels were obtained when concentrated H_3PO_4 was substituted for concentrated H_2SO_4 at stoichiometrically equivalent rates in the heat-curing step. Processing tailings A with 0.95 lb H_2SO_4 per pound TS for 30 min in a 300° C rotary kiln resulted in lower vanadium dissolution levels of 80 to 85 pct.

High vanadium dissolution levels also were obtained using the second procedure. After evaporatively boiling tailings A in a stirred reactor with 0.95 lb H_2SO_4 per pound TS, 90 pct of the vanadium was solubilized in water. Vanadium dissolution of 80 pct was obtained at 0.64 lb H_2SO_4 , which corresponds to 100 pct of the stoichiometric H^+ requirement. Treating tailings A with H_3PO_4 during the evaporative boiling step resulted in much lower vanadium dissolution. Only 50-pct extraction was obtained at 0.87 lb H_3PO_4 per pound TS (the stoichiometric equivalent to 0.64 lb H_2SO_4 per pound TS). Addition of H_3PO_4 in combination with H_2SO_4 had little or no effect on vanadium solubility. As with the heat-curing method, no effect was seen from quenching the viscous, acid-tailings mixture with either 90° C water or 30 pct H_3PO_4 . Apparently, acid concentration and type used in the boiling step are the controlling parameters in the dissolution. Once in a soluble state, the mineral values of the tailings appear to remain unaffected by the subsequent quench treatment.

Results from tests with vapor refluxing indicate that vanadium dissolution with H_2SO_4 is relatively fast. Using 1.27 lb H_2SO_4 per pound TS, vanadium dissolution from tailings A was 83 pct at 10 min and 95 pct at 30 min. After 60 min, 84-pct dissolution was obtained with 0.64 lb H_2SO_4 . Results from leaching tailings A at three different H_2SO_4 -TS ratios, shown in figure 1, illustrate the effect of acid-TS ratio on the rate and extent of vanadium extraction. These results show that the reaction rate and extraction level are higher with a higher acid-TS ratio. Also, H_2SO_4 was a more effective leaching agent than H_3PO_4 at equivalent addition ratios (0.95 lb H_2SO_4 and 1.31 lb H_3PO_4 per pound TS correspond to 150 pct of stoichiometric H^+ requirement).

In the stirred reactor with vapor refluxing, slower vanadium dissolution rates were obtained with mixtures of H_2SO_4 and H_3PO_4 than with H_2SO_4 alone. Figure 2 illustrates the slower rate but higher final dissolution level achieved in tests with H_3PO_4 added in addition to 0.64 lb H_2SO_4 . However, for tests run with equivalent stoichiometric amounts of

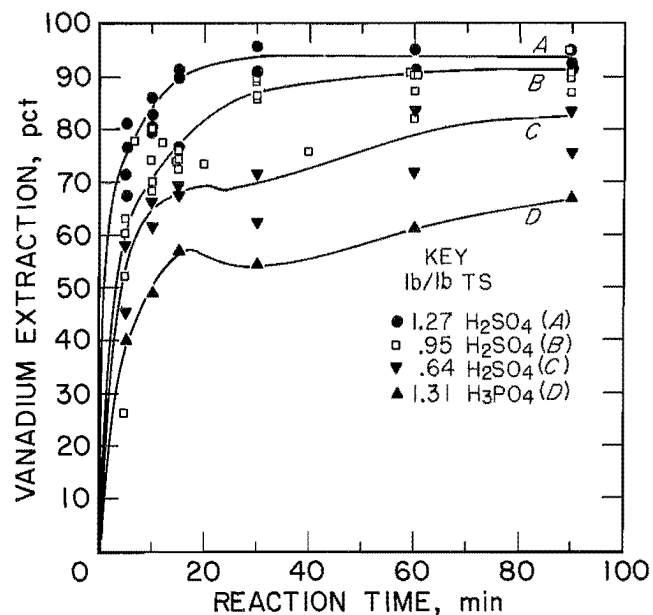


FIGURE 1. - Dissolution of tailings A with concentrated H_2SO_4 or H_3PO_4 .

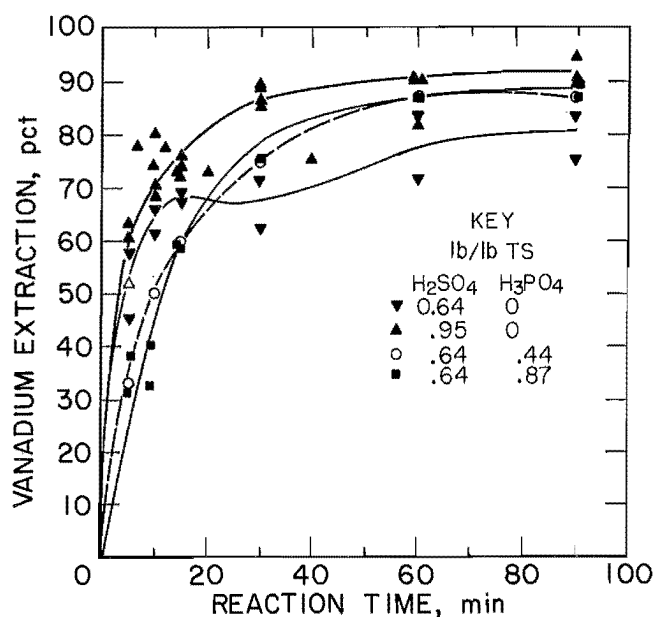


FIGURE 2. - Dissolution of tailings A with concentrated H_2SO_4 in combination with H_3PO_4 .

acid, H_2SO_4 alone was a superior leachant in comparison with a mixture of H_2SO_4 and H_3PO_4 (0.95 lb H_2SO_4 compared with a mixture of 0.64 lb H_2SO_4 and 0.44 lb H_3PO_4 per pound TS).

Additional tests with tailings B showed similar results. The reaction rate curves in figure 3, as compared with those in figure 1, reflect the higher acid-consumer content of these tailings by the slightly slower rate and lower dissolution level obtained for a given acid-TS ratio. Almost 80 pct of the vanadium was dissolved with 0.77 lb H_2SO_4 per pound TS, corresponding to approximately 100-pct acid stoichiometry based on contained acid consumers. Vanadium dissolution reached 90 pct with 1.08 lb H_2SO_4 , which corresponds to approximately 150-pct acid stoichiometry.

With all the leaching methods investigated at the batch scale, dissolution of 80 to 90 pct of the vanadium was achieved from tailings A with 0.95 lb H_2SO_4 per pound TS, an excessive amount. This acid-TS ratio corresponds to approximately 150 pct of the stoichiometric H^+ ion requirement based on the contained acid consumers in the tailings. The reaction rate curves generated from refluxing reactor data also show that an excessive amount of H_2SO_4 is required to achieve

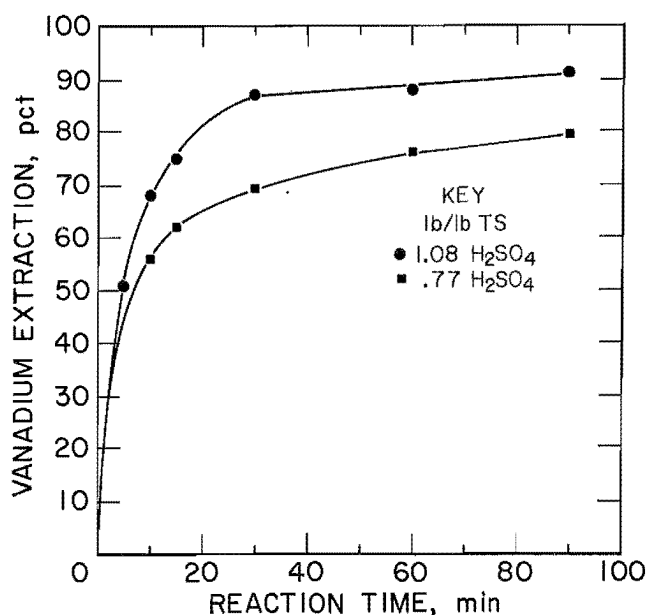


FIGURE 3. - Dissolution of tailings B with concentrated H_2SO_4 .

>90 pct V dissolution. But >80-pct dissolution was attained at 0.64 lb H₂SO₄ per pound TS; therefore, it should be noted that a 50-pct increase in acid addition resulted in only a 10-pct increase in vanadium dissolution.

Since all the treatment methods yield similar extraction results, the process choice for implementation in a larger, continuous system was made on an operational basis. A vapor refluxing reactor with controlled removal of condensed vapors was selected to avoid the difficult

handling problems and higher energy requirements associated with drying the acid-TS mixture to a paste. The drying and heat-curing steps are unnecessary in leaching the tailings slurry with concentrated H₂SO₄. Simply mixing a tailings slurry having a moderately high solids content with (1) at least 100 pct of the stoichiometric amount of acid required by the acid consumers and (2) enough heat to maintain boiling for 60 min dissolves greater than 80 pct of the vanadium and 95 pct of the phosphate.

CONTINUOUS CIRCUIT TESTS

Dissolution of vanadium and phosphate from phosphate beneficiation tailings was demonstrated in a continuous-circuit process. A 50-pct-TS slurry was digested with H₂SO₄ in a stirred-reactor system. Economic evaluation of the leaching process indicates that H₂SO₄ is the major cost factor in the process. Therefore, the continuous-circuit studies focused on optimizing H₂SO₄ usage, either by utilizing the excess H₂SO₄ necessary for >80-pct V dissolution or by reducing the acid requirement for a given dissolution level. Attention was also given to obtaining the most concentrated H₃PO₄ product possible.

EQUIPMENT AND PROCEDURE

The stirred-reactor system included two round glass reactors in series, equipped with heating mantles, condensers, and agitators as shown in figure 4. The tailings slurry, at 50 pct solids, and concentrated H₂SO₄ were fed to the first 5-L stirred reactor. A boiling temperature of 100° to 110° C, depending on the acid-TS ratio, was maintained. The mixture then overflowed to the second stirred reactor (either 5 or 12 L), also operated at boiling, to provide additional retention time. To increase the final product acid concentration, a portion of vapors condensed from the boiling mixture could be removed as shown. The slurry overflow from the second reactor accumulated in an agitated holding tank that was maintained at about 80° C for batch filtration.

Filtration (fig. 4) was carried out in a batch, 340-mm-diam pan filter fitted with a 2-by-2 twill weave, polypropylene filter cloth (59 by 28 count) weighing 9 oz/yd². Vacuum during filtration was maintained at 440 to 490 mm of Hg. A filtration batch consisted of 5 to 8 kg of slurry that yielded filter cakes of 22- to 34-mm thickness. After primary filtration of the accumulated overflow slurry, the cake was displacement washed in three countercurrent stages with solutions from the previous batch and a final 1,750- or 2,000-mL wash with water, depending on batch size. Using a wash water volume approximately equal to the volume of filtrate left in the cake resulted in a first wash filtrate equivalent in concentration to the primary filtrate.

RESULTS AND DISCUSSION

Dissolution With H₂SO₄

Dissolution data obtained in continuous tests using a 50-pct-TS slurry and concentrated H₂SO₄, both fed to the first reactor, are in good agreement with data from batch tests with the vapor refluxing reactor at the same acid-TS ratio. The result was that 91 pct of the vanadium and 97 pct of the phosphate were dissolved from tailings A at feed rates of 100 lb/d TS and 1.19 lb H₂SO₄ per pound TS. Returning all condensed vapors to the reactors produced a product acid containing 7.0 pct P₂O₅ and 2.9 g/L V₂O₅.

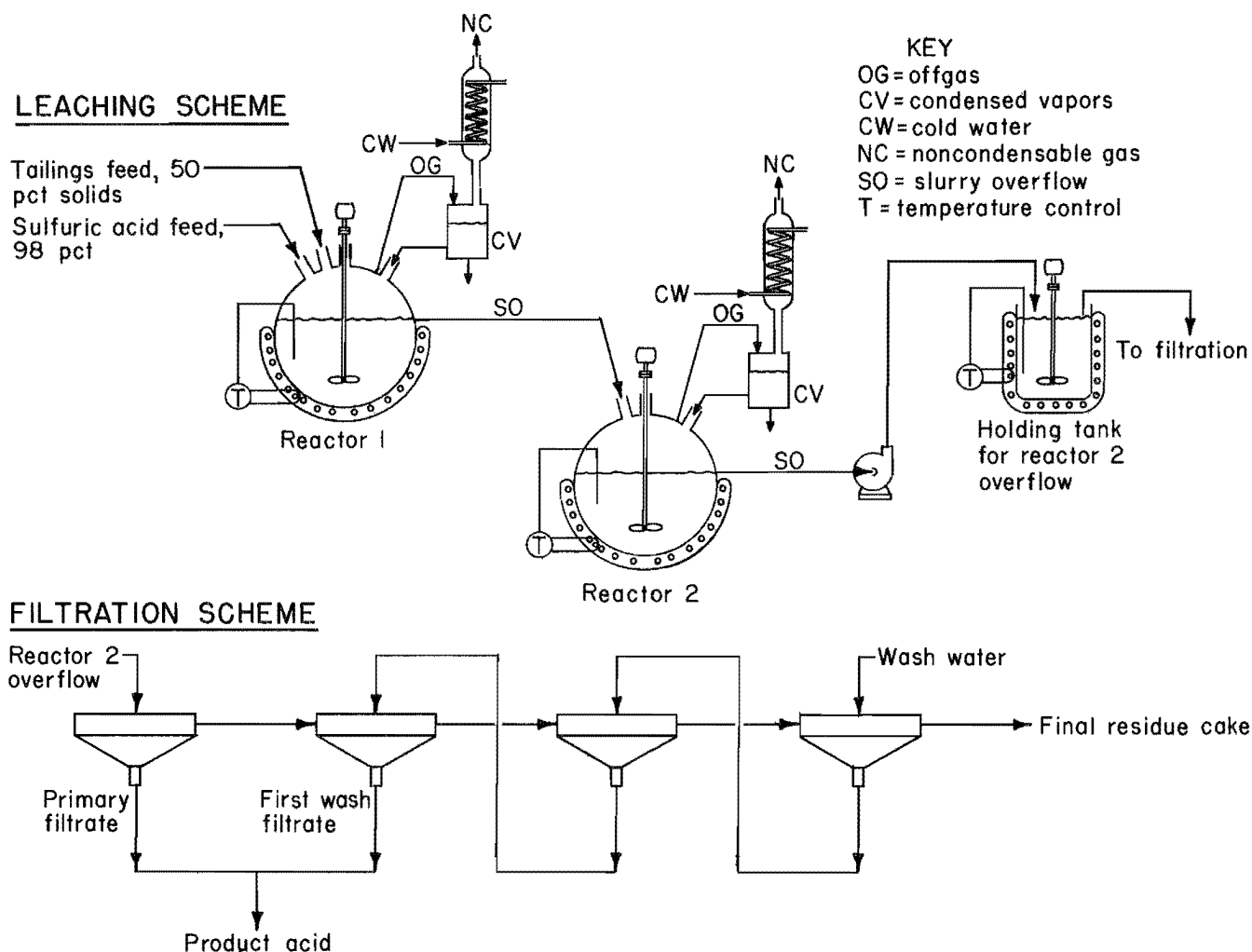


FIGURE 4. - Basic flowsheet for continuous-circuit leaching.

Average total retention time during a 4-h run was 75 min. Leaching tailings B at a lower acid-TS ratio of 0.82 lb H_2SO_4 per pound TS dissolved 79 pct V and 98 pct P_2O_5 . The tailings were fed at 50 lb/d TS for 7 h with an average 200-min total retention time. Product acid concentration was 8.5 pct P_2O_5 and 2.7 g/L V_2O_5 , with 5 wt pct of the feeds removed from the system as condensed vapors.

Excess Acid Utilization

The first series of continuous tests demonstrated the need for a large excess of H_2SO_4 to provide for >80-pct V dissolution. The possibility was investigated of neutralizing the excess H_2SO_4 , which remained after reaction with the tailings, with phosphate rock concentrate to

provide a more concentrated H_3PO_4 product. This approach was investigated using the two-reactor configuration shown in figure 5. After reacting the tailings slurry with excess H_2SO_4 in the first reactor, phosphate rock concentrate mixed with recycled first wash filtrate for dilution was added to the second reactor. About 85 pct of the total vanadium and 90 pct of the total phosphate was dissolved from tailings A and a phosphate concentrate that contained 32.7 pct P_2O_5 and 0.06 pct V. Feed rates were 50 lb/d TS, 1.27 lb H_2SO_4 per pound TS, 33 lb/d concentrate, and 83 lb/d first wash filtrate. The product acid and recycled first wash filtrate contained 27 pct P_2O_5 and 2.2 g/L V_2O_5 . The process scheme successfully dissolves vanadium and phosphate from the phosphate tailings and

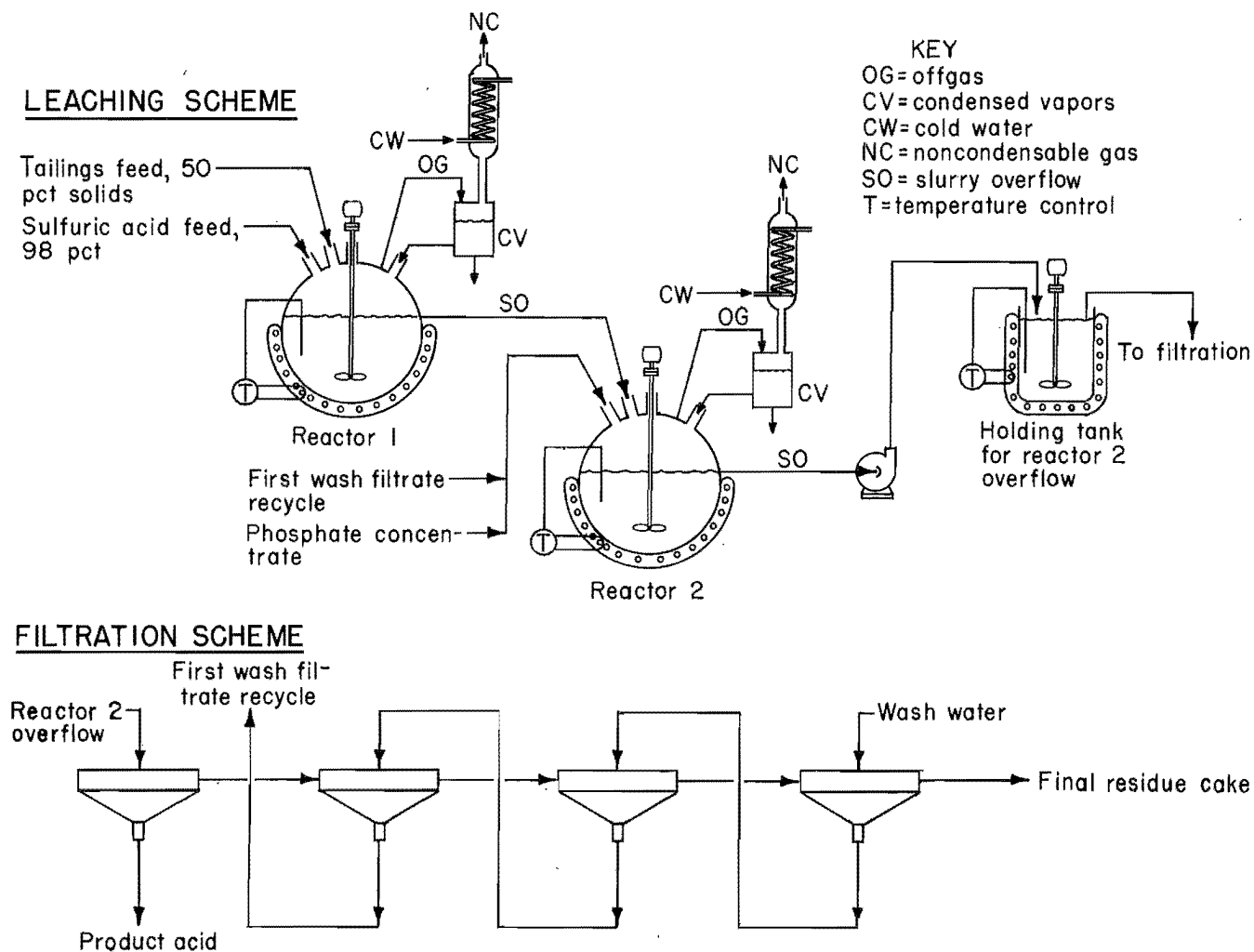


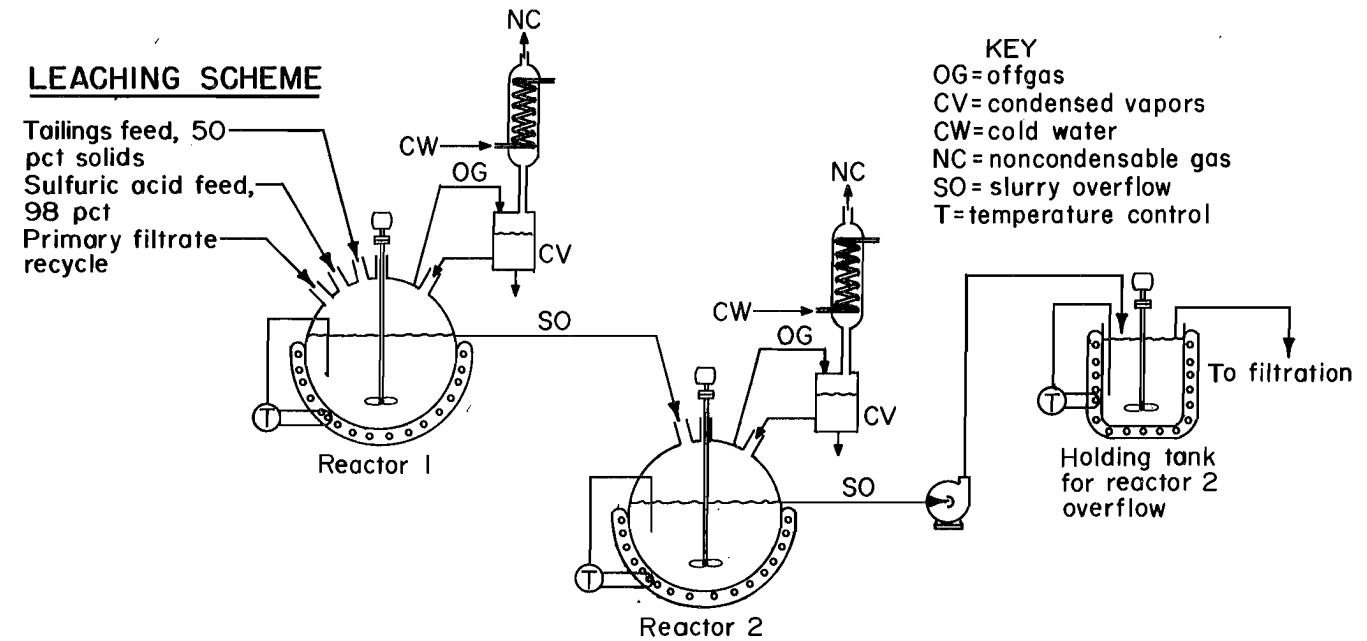
FIGURE 5. - Flowsheet for tailings dissolution with phosphate concentrate addition.

concentrate while utilizing the excess H_2SO_4 . However, the amount of concentrate consumed represents a major portion of a beneficiation plant's output of concentrate. If processed alone, phosphate concentrate would produce a higher grade acid at lower impurity levels with a fast filtering gypsum residue. Consideration of these factors makes this process approach unreasonable.

Dissolution With H_2SO_4 --Recycle H_3PO_4

The effect on the H_2SO_4 requirement of recycling the primary filtrate from the filtration circuit to the first reactor was studied in tests with both tailings materials. Figure 6 shows the leaching and filtration setup for this process.

Results from preliminary refluxing reactor batch tests indicated that H_3PO_4 used in combination with H_2SO_4 could increase vanadium dissolution at lower H_2SO_4 -TS ratios (fig. 2). It was anticipated that recycle acid containing weak H_3PO_4 combined with H_2SO_4 could provide the excess H^+ required for higher levels of vanadium dissolution. In continuous tests to investigate this approach, the primary filtrate was mixed with concentrated H_2SO_4 for metering into the first reactor. The more dilute reaction slurry, in terms of solids to liquor, allowed for a higher removal rate of condensed vapors from the systems and produced more concentrated primary and first wash filtrates. During tests with both tailings materials, removal from the reactor of 12 to 20 wt pct



FILTRATION SCHEME

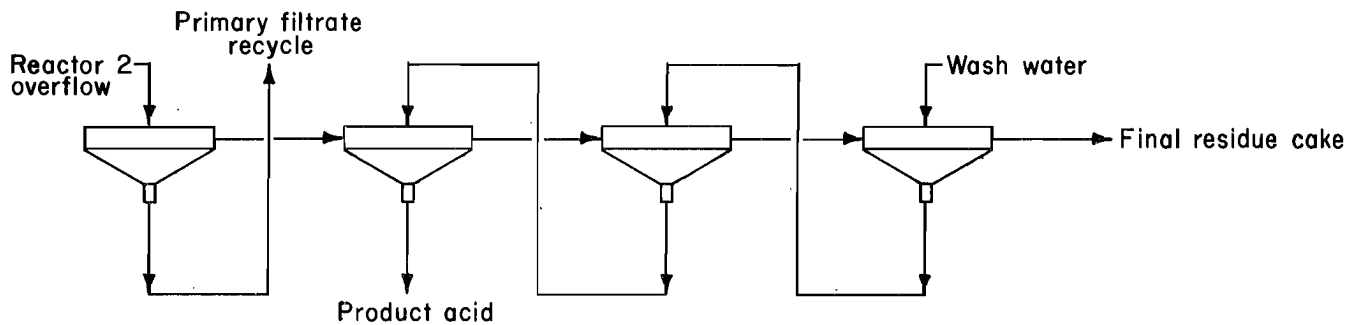


FIGURE 6. - Flowsheet for tailings dissolution with concentrated H_2SO_4 and recycle acid.

as condensed vapors resulted in primary and first wash filtrate concentrations of 9.5 to 11.5 pct P_2O_5 and 2.9 to 3.4 g/L V_2O_5 .

No improvement in vanadium dissolution from either tailings materials was obtained by recycling the primary filtrate acid. In fact, in continuous tests with tailings B, recycle acid addition appears to depress vanadium dissolution at H_2SO_4 -TS ratios greater than 0.76 lb H_2SO_4 per pound TS, presumably an effect of H_2SO_4 dilution. Figure 7 shows the average vanadium extraction levels achieved during continuous leaching tests with tailings B. Conditions included feed rates of 50 to 100 lb/d TS, 0.6 to 0.97 lb H_2SO_4 per pound TS, and 1 lb recycled acid per pound TS. Free H_2SO_4 in the recycle acid

(based on H^+ and SO_4^{2-} concentrations) ranged from 0 to 13 pct, depending on feed conditions. Slurry retention times were varied from 40 to 250 min and showed no statistically significant effect on dissolution. Figure 7 also includes results from a continuous test with only H_2SO_4 and results from two refluxing reactor batch tests.

Similar results were obtained in continuous tests with tailings A. Doubling the recycle acid flow rate to 2 lb per pound TS had no effect on vanadium dissolution, as shown in figure 8. The effect of recycle acid addition on reaction rate was examined by batch leaching tailings A in the refluxing reactor with H_2SO_4 and recycle acid generated from a continuous run at 0.77 lb H_2SO_4 per pound

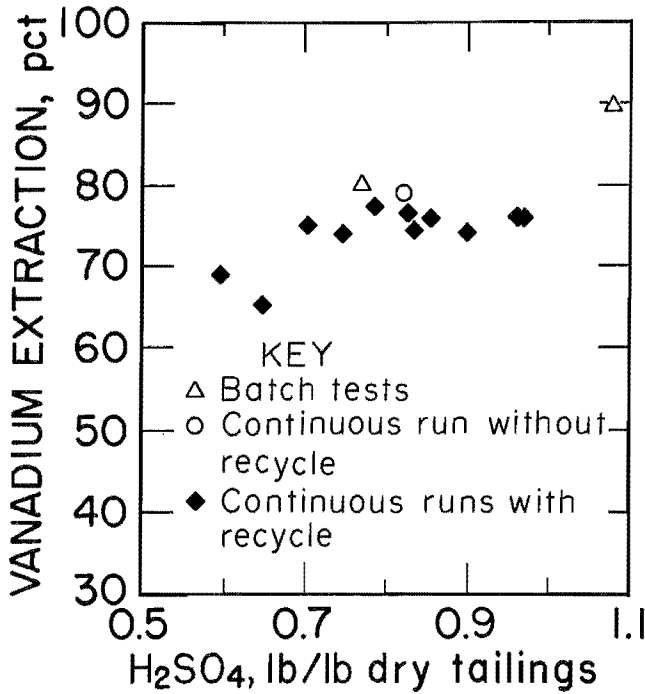


FIGURE 7. - Dissolution of vanadium from tailings B with and without recycle acid.

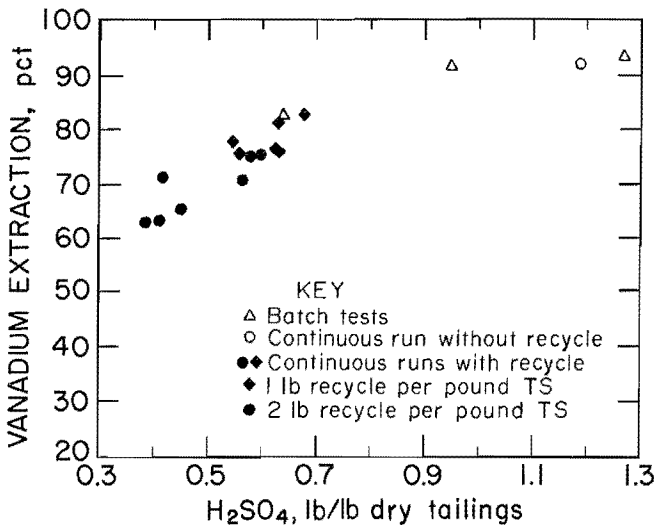


FIGURE 8. - Dissolution of vanadium from tailings A with and without recycle acid.

TS. The rate data obtained, plotted in figure 9 along with rate curves from figure 1, illustrate the recycle acid's dampening effect on the reaction rate.

Product Acid Composition

Typical compositions of product acids from continuous-circuit digestion of

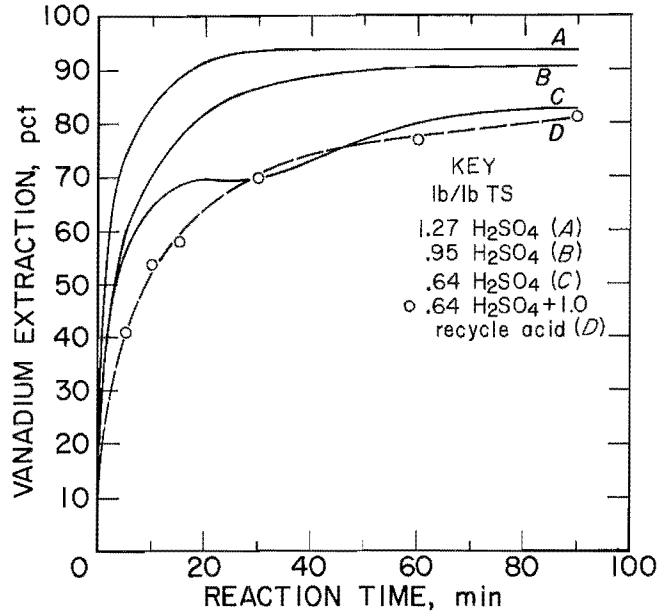


FIGURE 9. - Effect of recycle acid on vanadium dissolution from tailings A. Curves A, B, and C correspond to curves A, B, and C in figure 1.

tailings B with 0.83 lb H₂SO₄ per pound TS, with and without recycle addition, are shown in table 3. Acid derived from the tailings material is relatively high in iron, aluminum, and magnesium impurities, limiting the choice of processing alternatives for utilizing the phosphate values. Ammoniating the acid to produce an off-grade solid fertilizer product after removal of the vanadium is one possibility.

TABLE 3. - Composition of product acids derived from tailings B

	Acid sample	
	No recycle	With recycle
Analysis, g/L:		
P ₂ O ₅	113	140
V ₂ O ₅	2.7	3.0
Fe ₂ O ₃	21.0	26.0
Al ₂ O ₃	35.3	35.5
MgO.....	17.2	16.0
U ₃ O ₈ppm..	44	46

Filtration

Digestion of phosphate tailings under conditions necessary for vanadium dissolution results in a residue of small,

irregular gypsum crystals and very fine unreacted silica. Filtration rates obtained during continuous runs ranged up to 13 gal/(ft²·h) and 600 lb solids/(ft²·d). Unlike wet-process phosphoric acid processing, which controls digestion conditions for optimum filtration rates, filtration characteristics of the acid-TS residue appear unaffected by digestion conditions. In batch studies no correlation was found between filtration rate

and acid concentration, reaction mixture density, temperature, or retention time in the reactor. However, a limited screening of commercial flocculants showed a nonionic polyacrylamide to be effective in improving rates approximately 25 pct at dosages >75 ppm on a solids basis. During continuous runs, 80 to 120 ppm of Superfloc 127⁵ was added to each batch of slurry immediately prior to filtration.

ECONOMIC EVALUATION

The process selected for economic evaluation included H₂SO₄ leaching of the tailings with recycle acid addition as shown in figure 6. Although not improving vanadium dissolution, the higher removal rate of condensed vapors obtained using recycle acid produced a more concentrated product acid. Cost estimates for the proposed process to recover vanadium and phosphate indicate that economic viability depends on the market value of the recovered phosphate. Capital and operating cost estimates, detailed in the appendix, are based on a plant designed to process 50 ton/h (dry basis) of tailings. The estimated operating cost of \$7.78 per pound V₂O₅ produced is more than twice the current market value of V₂O₅. The 45 lb of phosphate recovered

per pound V₂O₅ coproduced is worth \$6.95 as 54 pct merchant-grade H₃PO₄. Although the impurity level of the acid product would prevent concentration to 54 pct P₂O₅, the potential value of the recovered phosphate illustrates its importance.

Capital and operating costs are dominated by the cost of the equipment and sulfur required to produce H₂SO₄. The construction of an H₂SO₄ plant represents 41 pct of the estimated fixed capital cost of \$45.5 million. Locating a plant in conjunction with an existing H₃PO₄ plant could reduce the capital and operating costs. Furthermore, an adjacent H₃PO₄ plant could more readily incorporate the impure H₃PO₄ product with minimal refining.

SUMMARY AND CONCLUSIONS

Hot acid digestion of vanadium from Western phosphate beneficiation tailings with H₂SO₄ was demonstrated in both batch and continuous-circuit tests. In batch studies using a constant boiling temperature (100° to 110° C) and vapor refluxing, >90 pct of the vanadium was dissolved from a 50-pct-TS slurry with 1.27 lb H₂SO₄ per pound TS. Also, >80-pct V dissolution was achieved at 0.64 lb H₂SO₄ per pound TS, corresponding to 100 pct of the stoichiometric acid requirement based on acid consumers.

In continuous-circuit leaching tests 75 to 80 pct of the vanadium and >92 pct of the phosphate were dissolved using 100 pct of the H₂SO₄ stoichiometrically required. This corresponds to 0.64 lb H₂SO₄ per pound TS for tailings A and

0.76 lb H₂SO₄ per pound TS for tailings B. Also, >90-pct V dissolution was obtained from tailings A with 185 pct of the stoichiometric H₂SO₄ requirement. Efforts to increase the vanadium dissolution obtained at lower acid-TS ratios by recycling the weak H₃PO₄ primary filtrate proved ineffective. Utilization of the excess H₂SO₄, required for >80-pct V dissolution, by digestion with phosphate rock concentrate was found to be uneconomical in terms of the low product acid concentration and product purity.

⁵Reference to specific tradenames or manufacturers is only for identification and does not imply endorsement by the Bureau of Mines.

The acid digestion of tailings produces a weak (8 to 11.5 pct) H_3PO_4 , inherently inferior to that prepared from commercial-grade phosphate rock concentrate. Since economics necessitates the

recovery of the phosphate value, the process's profit potential depends upon the value of the phosphate fertilizer that could be made from the impure H_3PO_4 .

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APPENDIX.--ECONOMIC EVALUATION

By Thomas A. Phillips¹

Data obtained in the continuous tests have been used as the basis for designing a full-scale plant to extract vanadium from Western phosphate tailings. Capital and operating cost estimates based on this design are presented. The plant, based on the continuous setup shown in figure 6, is designed to process 50 ton/h (dry basis) of beneficiation tailings for 24 h/d, 330 d/yr.

PLANT DESCRIPTION

The plant has been divided into four sections: Leaching, solvent extraction and vanadium recovery, evaporation, and H₂SO₄ production. It is assumed that the plant is located adjacent to a Western phosphate concentrator and receives feed directly from that plant. It should also be possible to reclaim tailings from existing tailings ponds; however, this option was not considered in this study. Tailings are received as a 50-pct-TS slurry.

Leaching Section

As-received tailings, recycle acid, and 98 pct H₂SO₄ are fed directly to a stirred reactor. About 80 pct of the vanadium and 95 pct of the phosphate react with the H₂SO₄ and dissolve. The reactor design is based on a 30-min retention time, and the temperature is maintained at the slurry boiling point, about 105° C. Vapor from the reactor is condensed and may need additional treatment to remove elements such as fluorine. No equipment is included to treat this stream, because data are not available for equipment sizing.

Slurry from the leach tank is pumped to a thickener. Acid overflow is pumped back to the leach reactor, and underflow, at about 45 pct solids, is pumped to a belt filter. After filtering off the

product acid, the solids, including the byproduct gypsum, are dewatered and washed on the filter and then conveyed to a disposal site. The filtration rate is assumed to be 13 gal/(ft²·h).

Solvent Extraction and Vanadium Recovery Section

Product acid filtrate from the belt filter is pumped to a series of three mixer-settlers and contacted with an organic extractant. A suitable organic is assumed to be available commercially, such as those used to recover uranium at Florida operations. The organic extracts vanadium and any uranium present from the acid filtrate. The vanadium is stripped from the organic in two stages using a sodium carbonate solution. Stripped organic is recycled to load additional vanadium.

The loaded strip solution is fed to an agitated tank and mixed with ammonium chloride, then fed to a reactor. Ammonium metavanadate precipitates over a 6-h period. The resulting slurry is pumped to a vacuum filter, where the solids are dewatered and washed. Filtrate and washings are pumped to a disposal pond. The vanadium precipitate is dried to 400° C. At this temperature the ammonium metavanadate decomposes to V₂O₅ and ammonia vapor. The ammonia is collected and can be used in making an ammonium phosphate fertilizer. The V₂O₅ is fed to a fusion furnace to form a fused flake product. Separate recovery of the small amount of uranium present will be possible by conventional means; however, no equipment for this is included in this plant design.

Evaporation Section

Raffinate acid from the solvent extraction section contains about 10 pct P₂O₅. For the purposes of this evaluation, it is assumed that this acid will be fed to a multieffect evaporator and concentrated

¹Chemical engineer, Process Evaluation Group, Bureau of Mines, Avondale, MD.

to 54 pct P_2O_5 . Although it is common industrial practice, impurities in this product will probably make handling in this manner impractical. It is likely that this product can be concentrated to some degree, then ammoniated to produce an off-grade fertilizer product at the plant site. Additional process development is needed to determine what products can be made.

Sulfuric Acid Production

The sulfuric acid needed for this process is provided by a standard contact acid plant. For this evaluation the cost for an 800 ton/d acid plant is used. Surplus steam and electricity will be available for use elsewhere at the plant site or for sale.

CAPITAL COSTS

The capital cost estimates are of the general type called a study estimate by Weaver and Bauman (6). This type of estimate, prepared from a flowsheet and a minimum of equipment data, can be expected to be within 30 pct of the actual cost for the plant described. The estimated fixed capital cost on a second quarter 1984 basis (Marshall and Swift (M and S) index of 781.7) for the proposed plant is \$45.5 million as shown in table A-1. Operating 3 shifts per day, 7 d/wk, 330 d/yr the plant can recover 2,150,000 lb/yr V_2O_5 . A breakdown of the sectional costs is shown in tables A-2 through A-4.

Equipment costs for the proposed process are based on cost-capacity data and manufacturers' cost quotations. Cost data are brought up to date by the use of inflation indexes. In developing the plant capital costs, corrosion-resistant materials of construction were used where appropriate. For example, the leach tank is mild steel lined with rubber and acid-resistant brick.

Factor for piping, etc., except for the foundation and electrical factors, are assigned to each section, using as a basis the effect that fluids, solids, or a combination of fluids and solids may have on the process equipment. The foundation factor is estimated for each piece

of equipment individually, and a factor for the entire section is calculated from the totals. The electrical factor is based on the motor horsepower requirements for each section. A factor of 10 pct, referred to as miscellaneous, is added to each section to cover minor equipment and construction costs not shown with the equipment listed.

For each section, the field indirect cost, which covers field supervision, inspection, temporary construction, equipment rental, and payroll overhead, is estimated at 10 pct of the direct cost.

TABLE A-1. - Estimated capital cost¹

Fixed capital:	
Leach section.....	\$8,416,200
Vanadium recovery section..	2,972,400
Evaporation section.....	4,801,000
Acid plant.....	<u>18,591,500</u>
Subtotal.....	34,781,100
Plant facilities, 10 pct of above subtotal.....	
	3,478,100
Plant utilities, 12 pct of above subtotal.....	
	<u>4,173,700</u>
Basic plant cost.....	<u>42,432,900</u>
Escalation costs during construction.....	
	<u>1,048,600</u>
Total plant cost.....	<u>43,481,500</u>
Land cost.....	0
Subtotal.....	<u>43,481,500</u>
Interest during construction period.....	
	<u>2,039,000</u>
Fixed capital cost.....	<u><u>45,520,500</u></u>
Working capital:	
Raw material and supplies..	750,100
Product and in-process inventory.....	1,364,000
Accounts receivable.....	1,364,000
Available cash.....	<u>993,200</u>
Working capital cost....	<u><u>4,426,300</u></u>
Total capital cost.....	49,946,800

¹Basis: M and S equipment cost index of 781.7.

TABLE A-2. - Equipment cost summary,
leach section

<u>Item</u>	<u>Equipment</u> ¹	<u>Labor</u>	<u>Total</u>
Holding tank	\$105,900	\$24,500	\$130,400
Pumps.....	15,900	2,600	18,500
Leach tank..	174,200	10,200	184,400
Condenser...	17,800	1,000	18,800
Condensate receiver...	6,500	2,100	8,600
Thickeners..	937,600	110,600	1,048,200
Pumps.....	29,700	5,400	35,100
Pumps.....	23,500	4,300	27,800
Horizontal-belt filters....	1,790,200	85,400	1,875,600
Sump.....	20,400	4,000	24,400
Pump.....	3,600	1,200	4,800
Reslurry tank.....	33,400	10,300	43,700
Total..	<u>3,158,700</u>	<u>261,600</u>	<u>3,420,300</u>
Total equipment cost × factor indicated:			
Foundations, × 0.153.....			483,900
Structures, × 0.080.....			252,700
Insulation, × 0.050.....			157,900
Instrumentation, × 0.100.....			315,900
Electrical, × 0.020.....			64,700
Piping, × 0.300.....			947,600
Painting, × 0.020.....			63,200
Miscellaneous, × 0.100.....			315,900
Total.....			<u>2,601,800</u>
Total direct cost.....			<u>6,022,100</u>
Field indirect, 10 pct of total direct cost.....			602,200
Total construction cost...			<u>6,624,300</u>
Engineering, 5 pct of total construction cost.....			331,200
Administration and overhead, 5 pct of total construction cost			331,200
Subtotal.....			<u>7,286,700</u>
Contingency, 10 pct of above subtotal.....			728,700
Subtotal.....			<u>8,015,400</u>
Contractor's fee, 5 pct of above subtotal.....			400,800
Section cost.....			<u>8,416,200</u>

¹Basis: M and S equipment cost index of 781.7.

Engineering cost is estimated at 10 pct, and administration and overhead cost is estimated at 5 pct of the construction cost. A contingency allowance of 10 pct and a contractor's fee of 5 pct are included in the section costs.

The costs of plant facilities and plant utilities are estimated as 10 and 12 pct, respectively, of the total process section costs and include the same field indirect costs, engineering, administration and overhead, contingency allowance, and contractor's fee as are included in the section costs. Included under plant facilities are the proportional cost of material and labor for auxiliary buildings such as offices, shops, laboratories, and cafeterias, the cost of nonprocess equipment such as office furniture, and the cost of safety, shop, and laboratory equipment. Also included are labor and material costs for site preparation such as clearing, grading, drainage, roads, and fences. The costs of water, power, and steam distribution systems are included under plant utilities.

The cost for interest on the capital borrowed for construction is included as interest during construction, assuming an interest rate of 12 pct. To determine the interest cost during construction, the total plant cost is factored by an adjusted interest rate, which depends upon the length of the construction period and the interest rate at which the money is borrowed. Cost for the plant owner's supervision is not included in the capital cost of the proposed plant.

Working capital is defined as the funds in addition to fixed capital, land investment, and startup costs that must be provided to operate the plant. Working capital, also shown in table A-1, is estimated from the following items: (1) Raw material and supplied inventory (cost of raw material and operating supplies for 30 days), (2) product and in-process inventory (total operating cost for 30 days), (3) accounts receivable (total operating costs for 30 days), and (4)

TABLE A-3. - Equipment cost summary, vanadium recovery section

Item	Equipment ¹	Labor	Total
Mixer-settlers.....	\$538,100	\$8,500	\$546,600
Motors.....	7,900	1,700	9,600
Pumps.....	5,100	2,400	7,500
Pump.....	3,600	1,200	4,800
Pump.....	1,000	400	1,400
Sump.....	1,700	2,000	3,700
Vibrating feeder.....	1,300	200	1,500
Belt conveyor	18,900	5,300	24,200
Storage bin..	4,800	1,600	6,400
Screw feeder.	2,300	400	2,700
Mixing tank..	2,800	1,200	4,000
Pump.....	1,000	400	1,400
Sump.....	100	300	400
Pump.....	1,100	400	1,500
Mixing tank..	2,000	800	2,800
Reactors.....	12,000	5,800	17,800
Storage bin.	5,600	2,000	7,600
Screw feeder.	2,300	400	2,700
Pumps.....	8,300	800	9,100
Rotary-vacuum drum filter.	51,000	6,100	57,100
Filtrate receiver.....	100	400	500
Pump.....	1,200	400	1,600
Belt conveyor	8,700	2,200	10,900
Belt conveyor	22,600	6,100	28,700
Storage bin..	5,900	2,100	8,000
Turbo-tray dryer.....	154,700	4,300	159,000
Fusion furnace.....	177,800	17,000	194,800
Total...	1,041,900	74,400	1,116,300
Unloading hopper.....			<u>218,600</u>
Total equipment cost x factor indicated:			
Foundations, x 0.116.....			121,000
Buildings, x 0.120.....			125,000
Structures, x 0.080.....			83,400
Insulation, x 0.050.....			52,100
Instrumentation, x 0.100....			104,200
Electrical, x 0.066.....			68,600
Piping, x 0.300.....			312,600
Painting, x 0.020.....			20,800
Miscellaneous, x 0.100.....			104,200
Total.....			<u>991,900</u>
Total direct cost.....			<u>2,126,800</u>

TABLE A-3. - Equipment cost summary, vanadium recovery section--Cont.

	Total
Field indirect, 10 pct of total direct cost.....	212,700
Total construction cost...	<u>2,339,500</u>
Engineering, 5 pct of total construction cost.....	117,000
Administration and overhead, 5 pct of total construction cost	117,000
Subtotal.....	<u>2,573,500</u>
Contingency, 10 pct of above subtotal.....	257,400
Subtotal.....	<u>2,830,900</u>
Contractor's fee, 5 pct of above subtotal.....	141,500
Section cost.....	<u>2,972,400</u>

¹Basis: M and S equipment cost index of 781.7.

²Installed cost.

available cash (direct expenses for 30 days).

Capitalized startup costs are estimated as 1 pct of the fixed capital cost, which is shown in table A-1.

OPERATING COSTS

The estimated operating costs are based on the average of 330 d/yr of operation over the life of the plant. This allows 35 d/yr downtime for inspection, maintenance, and unscheduled interruptions. The operating costs are divided into direct, indirect, and fixed costs.

Direct costs include raw materials, utilities, direct labor, plant maintenance, payroll overhead, and operating supplies. The raw material costs do not include transportation costs because a particular plant site has not been selected. Electricity, water, natural gas, and steam are purchased utilities. The water temperature from local wells is assumed to be 10° C.

The direct labor cost is estimated on the basis of assigning 4.2 employees to each position that operates 24 h/d, 7 d/wk. The cost of labor supervision is estimated as 15 pct of the labor cost.

TABLE A-4. - Equipment cost summary, evaporation section

<u>Item</u>	<u>Equipment</u> ¹	<u>Labor</u>	<u>Total</u>
Evaporator.....	\$1,701,000	\$304,500	\$2,005,500
Total.....	1,701,000	304,500	2,005,500
Cooling tower.....			² 128,400
Total equipment cost x factor indicated:			
Foundations, x 0.110.....			187,800
Structures, x 0.080.....			136,100
Insulation, x 0.050.....			85,100
Instrumentation, x 0.100.....			170,100
Electrical, x 0.005.....			8,000
Piping, x 0.300.....			510,300
Painting, x 0.020.....			34,000
Miscellaneous, x 0.100.....			170,100
Total.....			1,301,500
Total direct cost.....			3,435,400
Field indirect, 10 pct of total direct cost.....			343,500
Total construction cost.....			3,778,900
Engineering, 5 pct of total construction cost.....			188,900
Administration and overhead, 5 pct of total construction cost.....			188,900
Subtotal.....			4,156,700
Contingency, 10 pct of above subtotal.....			415,700
Subtotal.....			4,572,400
Contractor's fee, 5 pct of above subtotal.....			228,600
Section cost.....			4,801,000

¹Basis: M and S equipment cost index of 781.7.

²Installed cost.

Plant maintenance is separately estimated for each piece of equipment and for the buildings, electrical system, piping, plant utility distribution systems, and plant facilities.

Payroll overhead, estimated as 35 pct of direct labor and maintenance labor, includes vacation, sick leave, social security, and fringe benefits. The cost of operating supplies is estimated as 20 pct of the cost of plant maintenance.

Indirect costs are estimated as 40 pct of the direct labor and maintenance costs. The indirect costs include the expenses of operating control laboratories, accounting, plant protection and safety, plant administration, and marketing. Research and overall company administrative costs outside the plant are not included.

Fixed costs include the cost of taxes (excluding income taxes), insurance, and depreciation. The annual costs of taxes and insurance are each estimated as 1 pct

of the plant construction cost. Depreciation is based on a straight-line, 20-yr period.

The estimated annual operating cost for the proposed plant is \$16.6 million and is presented in table A-5. Included is a credit for the surplus electricity, which will be generated by the sulfuric acid plant. Although the acid plant also produces excess steam, no credit has been given for its potential sale. The estimated operating cost is equivalent to \$7.78 per pound V₂O₅ recovered.

PRODUCT VALUE

The published price for V₂O₅ (fused or flaked) is \$3.35/lb as of November 1984 (7). The estimated operating cost, \$7.78/lb, is more than double the value of the V₂O₅. At present, this process will not be economically viable based on the vanadium's value alone.

TABLE A-5. - Estimated annual operating cost

	Annual	Per pound vanadium pentoxide
Direct cost:		
Raw materials:		
Sulfur at \$90/ton.....	\$7,425,000	\$3.46
Sodium carbonate at \$90/ton.....	96,800	.05
Ammonium chloride at \$360/ton.....	464,500	.22
Total.....	7,986,300	3.73
Utilities:		
Electric power at \$0.05/kW·h.....	-651,000	-.30
Process water at \$0.25/Mgal.....	10,600	.01
Raw water at \$0.05/Mgal.....	500	.01
Natural gas at \$5.50/MMBtu.....	7,300	.01
Total.....	-632,600	-.27
Direct labor:		
Labor at \$9/hr.....	393,100	.18
Supervision, 15 pct of labor.....	59,000	.03
Total.....	452,100	.21
Plant maintenance:		
Labor.....	1,346,300	.63
Supervision, 20 pct of maintenance labor.....	269,300	.13
Materials.....	1,346,400	.63
Total.....	2,962,000	1.39
Payroll overhead, 35 pct of above payroll.....	723,700	.34
Operating supplies, 20 pct of plant maintenance.....	592,400	.28
Total direct cost.....	12,083,900	5.68
Indirect cost, 40 pct of direct labor and maintenance.....	1,365,600	.64
Fixed cost:		
Taxes, 1 pct of total plant cost.....	434,800	.20
Insurance, 1 pct of total plant cost.....	434,800	.20
Depreciation, 20-yr life.....	2,276,000	1.06
Total operating cost.....	16,595,100	7.78

In addition to the V_2O_5 , 146 ton/d of P_2O_5 as phosphoric acid are produced. The dilute phosphoric acid product is not equal in quality to commercial wet-process phosphoric acid. Impurities including high levels of iron, aluminum, and magnesium will make the acid unmarketable as is. Some additional processing will be needed to convert this product to a form suitable for use in fertilizer. Therefore, the value of this product is not known.

The present published price for 54-pct- P_2O_5 phosphoric acid is \$3.10 per unit-ton (8) (a unit-ton is 1 pct of 2,000 lb of the basic component, in this case P_2O_5). If impurities are ignored, the maximum value for this product is about \$15 million annually or \$6.95/lb of coproduced V_2O_5 . This is more than twice the V_2O_5 's value. About 60 pct of this maximum value will have to be obtained to equal the estimated operating costs in addition to the V_2O_5 's value.