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Physical Beneficiation of Titanium Plant Solid Wastes: Recovery of Titanium Minerals and Coke

By J. I. Paige, R. E. Mussler, and G. W. Elger

UNITED STATES DEPARTMENT OF THE INTERIOR

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PHYSICAL BENEFICIATION OF TITANIUM PLANT SOLID WASTES: RECOVERY OF TITANIUM MINERALS AND COKE

By J. I. Paige,[1] R. E. Mussler,[2] and G. W. Elger[3]

ABSTRACT

The Bureau of Mines studied methods for recovering unreacted titanium minerals and petroleum coke from titanium chlorination plant wastes prior to neutralization treatment with lime. The objective was to recover valuable raw materials and to reduce the amount of waste materials that must be treated for disposal. Samples of solid wastes were physically beneficiated by gravity concentration (tabling) to recover titanium minerals containing 69.0 to 92.4 wt-pct TiO_2 and by selective carbon flotation to recover petroleum coke containing 94.0 to 96.8 wt-pct C. Laboratory data indicate that the recovered titanium mineral would decrease the amount of solid waste to be disposed of from 32.8 to 53.9 wt-pct. The recovery of coke would further decrease the amount by additional 32.9 wt-pct. Preliminary tests conducted on recovering vanadium, chromium, and columbium from liquors obtained by leaching chlorination residues also have shown that (1) 97 pct of the vanadium was extracted from leach liquors in a two-stage solvent extraction procedure and (2) 58 pct of the columbium and 40 pct of the chromium were separated from the leach liquors by an ion exchange technique using a strong acid resin.

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INTRODUCTION

The high cost and future availability of petroleum coke and imported rutile concentrates have prompted the Bureau of Mines to investigate the recovery of unreacted titanium minerals and petroleum coke from the solid waste generated by the chloride process for manufacturing TiO_2 pigments. These chloride wastes represent a domestic resource of titanium minerals and coke. Successful recovery of these constituents would provide a secondary benefit of significantly reducing the volume of material requiring disposal.

Manufacture of TiO_2 pigment accounts for about 95 pct of the titanium raw materials consumed in the United States; the remaining 5 pct is used in making titanium sponge, welding-rod coatings, and carbides and in ceramic and glass formulations. The domestic titanium industry produces 632,500 metric tons (697,000 short tons) (2)[4] [5] of TiO_2 annually by the chloride process. Based on 0.3 t of waste per ton of TiO_2 produced by the chloride process (6), 187,800 t (209,100 tons) of solid waste is produced annually. This waste material contains Cb(Nb), Cr, and V constituents, along with an estimated 74,800 t (82,400 tons) of unreacted titanium minerals and 17,000 t (18,800 tons) of petroleum coke. Presently, these wastes are either disposed of in landfills, deep-well injected, or dumped into the ocean.

Industrial production of $TiCl_4$ for subsequent conversion to TiO_2 or titanium sponge metal consists of the following basic steps: (1) the titanium mineral, mixed with petroleum coke, is reacted with chlorine to form crude $TiCl_4$ and mixed metal chloride impurity gases; (2) condensed impurity metal chlorides and entrained solids (titanium mineral and coke) are separated from the cooled $TiCl_4$ gas stream; (3) $TiCl_4$ is condensed as a liquid; and (4) the condensed $TiCl_4$ is purified. Figure 1 is a composite flowsheet of the steps used to produce $TiCl_4$. The chlorination of TiO_2 is carried out in the presence of a carbonaceous reducing agent, commonly petroleum coke, and may be represented by the following equation:

$$2TiO_2+3C+4Cl_2 \longrightarrow 2TiCl_4+2CO+CO_2 \qquad (1)$$

Most $TiCl_4$ is produced in fluidized-bed reactors operating at 900° to 1,100° C. Solid wastes consisting of metal chloride impurities (high-boiling-point compounds), and insoluble materials are separated and collected in each step of the process.

Previously, the Bureau treated sludge generated by natural rutile chlorination and $TiCl_4$ purification. The sludge contained very fine, unchlorinated rutile, coke, and solid residues from the $TiCl_4$ purification process. This preliminary investigation by Merrill (4) employed a water leach to solubilize about 40 pct of the sludge and over 75 pct of the metallic chloride impurities. The water-insoluble solids (residue from the leach) contained 29.0 wt-pct TiO_2 and 42.8 wt-pct C, with 8 wt-pct SiO_2 as the major impurity. After blending with fresh rutile, its amenability to chlorination was tested in a batch-type 40-mm (1.6-in) diam reactor. Their results indicated the recovered product, representing approximately one-half of the weight of the sludge generated in the industrial production of purified $TiCl_4$, could be recycled to reduce the volume of solid wastes and give more efficient utilization of titanium mineral and coke.

Presently, only one chloride-process TiO_2 pigment producer in the United States chlorinates natural rutile feedstock. Most other domestic chloride processors use a blend of imported titanium

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[5] t = metric ton; ton = short ton throughout this report.

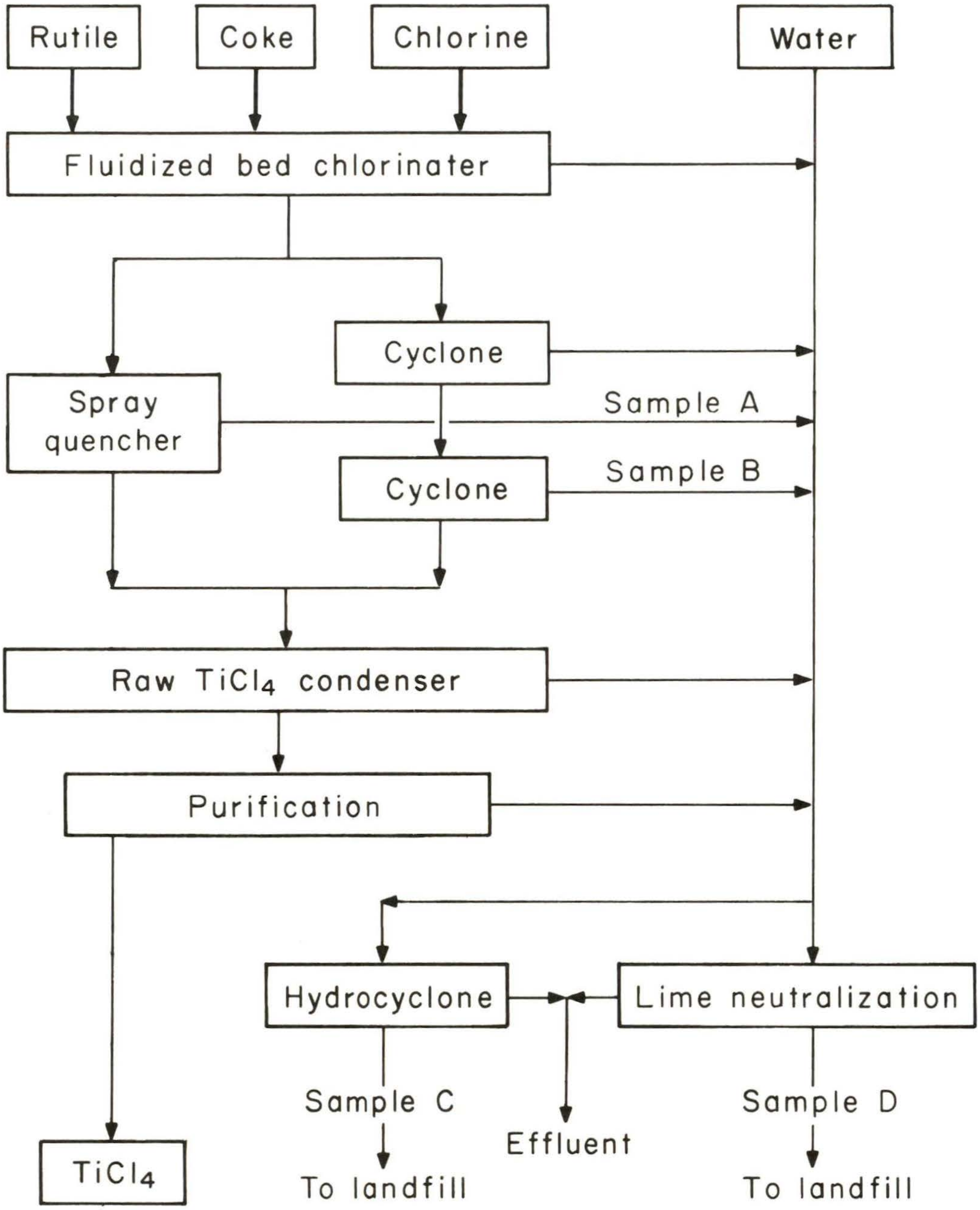

FIGURE 1. - Flowsheet of chloride process.

feedstocks, containing upgraded ilmenite, synthetic rutile, and natural rutile; but one major TiO_2 producer uses mainly ilmenite sand concentrate as a feed. The chloride wastes from these blended feedstocks vary in mineral composition and may require different physical beneficiation procedures to recover the unreacted titanium minerals and coke. A common concern expressed by industrial chloride processors is that the recycled unreacted titanium minerals and coke products could lead to a silica buildup in chlorination reactors unless the grade of the product was better than that achieved in earlier Bureau tests on natural rutile recovery.

Additional work was therefore undertaken by the Bureau to demonstrate that chloride wastes presently generated from a variety of titanium feedstocks could be treated successfully to recover products with low SiO_2 levels. One phase of the investigation involving physical beneficiation was reported at the 4th Recycling World Congress (5). This report discusses the physical beneficiation research in more detail and includes photomicrographs of the beneficiated product. In addition, this report contains the results of a preliminary bench-scale investigation made to recover the valuable Cb, Cr, and V values dissolved in liquors from the leaching of one sample of chloride waste.

DESCRIPTION OF THE SOLID WASTE SAMPLES

Each of the four samples of solid wastes used during this investigation was obtained from a different industrial titanium chlorination plant. The location of each sample in the chloride process flowsheet is indicated in figure 1 and the chemical analyses of the waste samples are shown in table 1.

Sample A (Spray Quencher Waste)

Sample A was obtained from a $TiCl_4$ spray quencher unit used to separate the solids consisting of the higher boiling-point, condensed metal chloride impurities and entrained titanium mineral and coke particles from the $TiCl_4$ in the cooled gas stream from the chlorinator. This sample contained metal chlorides that readily hydrolyze upon exposure to air and therefore required weighing in an inert atmosphere glove box for accuracy before leaching. The waste contained about 10 pct coke. Minerals identified included ilmenite ($FeO\cdot TiO_2$), altered ilmenite, rutile (TiO_2), staurolite [$Fe(OH)_2.2Al_2SiO_5$], quartz (SiO_2), and ferromagnesium silicates. The sample was 53 wt-pct finer than 74 µm (200 mesh).

Sample B (Cold Cyclone Waste)

Sample B was obtained from the second or cold cyclone unit used to separate the higher boiling-point condensed metal chlorides and entrained unreacted solids from the $TiCl_4$ vapors in the cooled gas stream from the chlorinator. Most industrial titanium chlorination plants use either a $TiCl_4$ spray quencher unit or several cyclone units following the chlorination reactor. Because this sample contained metal chlorides, the sample was weighed in an inert atmosphere glove box. The waste material consisted of 19 pct TiO_2 and what appeared to be two types of coke: (1) a black, shiny, reflective material, and (2) a black, dull material. The dull material was determined (spectroscopically) to be a coating of occluded TiO_2 fines on the coke particles. The head material was 75 wt-pct finer than 74 µm (200 mesh).

Sample C (Hydrocyclone Waste)

Sample C consisted of the underflow solids from an experimental hydrocyclone unit used by one processor to obtain samples for its own laboratory evaluation program. Combined waste streams from the chlorination and purification sections were slurried in water and pumped through the hydrocyclone unit. The solids in the underflow consisted of 55 pct TiO_2 and what appeared to be two types of coke, very similar to those in sample B (cold cyclone waste). The sample was 51 wt-pct finer than 74-µm (200 mesh).

TABLE 1. - Chemical analyses of titanium plant solid wastes, weight-percent

Sample	Al	C	Ca	Cb	Cl	Cr	Fe	Mg	Mn	SiO_2	TiO_2	V	Zr
A, spray quencher	1.46	9.55	0.51	0.35	14.4	0.28	5.91	0.40	1.08	4.11	54.4	0.18	0.35
B, cold cyclone..	1.27	46.8	.05	1.18	13.1	1.23	2.95	.27	.06	1.26	19.0	1.23	2.51
C, hydrocyclone..	.05	33.8	ND	.05	NA	.23	1.80	.05	.15	5.35	54.8	.04	.20
D, lime-neutralized filter cake.....	2.00	8.99	11.0	.08	NA	.12	1.58	.05	.08	8.30	39.4	.05	.08

NA Not analyzed. ND Not detected.

Sample D (Lime-Neutralized Filter Cake)

Sample D consisted of a filter cake from a rotary vacuum filter following the lime neutralization of the combined chlorination and purification process streams. The filter cake was examined to determine what could be done with several million tons of present land-filled, neutralized waste that represents a potential domestic titanium resource. The material consisted of about 10 pct each of calcium and coke. A technique to remove the calcium impurity such as that described in a patent by Elger (3) probably would be required to make this material acceptable as chlorination feedstock. The minerals identified were similar to those in sample A (spray quencher waste) but with a much smaller proportion of altered ilmenite. Most individual grains were minus 210 µm (65 mesh), with the coarser material containing mostly agglomerates. The sample was 75 wt-pct finer than 74 µm (200 mesh).

PHYSICAL BENEFICIATION

Samples A and B were leached to separate the metal chloride impurities prior to gravity concentration testing. A method similar to that described by Merrill (4) was used. However, the sample was leached with 0.5*N* HCl rather than with water. The acid leach was found desirable because it prevented hydrolysis of $CbCl_2$ to finely divided insoluble oxychloride particles and therefore increased the filterability of the insoluble residue.

The soluble impurity chlorides of Al, Ca, Cb, Cr, Fe, Mg, Mn, Ti, V, and Zr were leached from the insoluble titanium mineral, silica gangue material, and petroleum coke in a 0.5*N* HCl solution. The insoluble fraction of samples A and B amounted to 76 wt-pct and 88 wt-pct, respectively. The unreacted titanium mineral, silica, and petroleum coke were essentially unaffected by the leaching step, with less than 1 wt-pct of these materials solubilized. Samples C and D were slurried in water during the processing cycle and did not require leaching prior to gravity concentration testing.

Bench-Scale Studies

The bench-scale investigation involved treating 10 g (0.03 lb) of the insoluble fraction from each of the four waste materials. Physical beneficiation techniques are generally applied to materials coarser than 74 µm (200 mesh). Since these waste samples were 51 to 78 wt-pct finer than 74 µm (200 mesh), they were first tested on a Haultain Superpanner[6] to determine their amenability to gravity concentration. The superpanner consists of a flat, V-shaped pan 254 mm (10 in) wide, about 25.4 mm (1 in) deep at the head motion end, and 50.8 mm (2 in) deep at the other end. The superpanner requires samples ranging from 10 to 15 g (0.02 to 0.03 lb) and performs efficiently on closely sized fractions as coarse as 210 µm (65 mesh) and as fine as 14 µm.

Samples of each waste were separated on the superpanner into five products including (1) titanium mineral concentrate, (2) middling, (3) low-middling, (4) tailing, and (5) slimes. All the particles of sample D (lime-neutralized filter cake) were brown in color; visual separations between products based on differences in color bands were more difficult to make. Therefore, only four products were obtained on this sample. The products were examined and analyzed for nine elements by a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray detector. Semiquantitative analyses (table 2) were obtained on individual particles in each product. The SEM counts the number of X-rays in each element channel, subtracts out a background count, adds these values for all the selected elements, and computes

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[6] Reference to specific equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 2. - Normalized semiquantitative analysis (SEM) of waste products (superpanner), weight-percent

Sample and product	Distribution	Al	Ca	Cl	Cr	Fe	S	Si	Ti	Zr
A, spray quencher:										
Concentrate.............	4	ND	NA	ND	ND	0.6	0.2	3.6	95.3	0.4
Middling................	74	1.0	NA	ND	ND	.8	ND	5.1	93.9	ND
Low-middling............	6	6.6	NA	3.8	ND	6.5	18.0	31.1	27.5	6.3
Tailings................	2	2.3	NA	.2	ND	.1	ND	19.5	77.9	ND
Slimes..................	14	7.4	ND	3.7	0.9	1.9	11.2	31.3	42.7	.6
B, cold cyclone:										
Concentrate.............	21	1.6	NA	ND	.5	1.6	.7	1.9	93.1	1.0
Middling................	4	.6	NA	ND	.5	2.7	1.9	9.7	84.8	ND
Low-middling............	2	3.5	NA	2.6	7.5	20.4	37.9	6.0	21.1	.9
Tailings................	1	6.1	NA	1.5	4.7	6.1	9.6	5.1	57.2	9.5
Slimes..................	72	9.1	NA	3.6	3.4	18.2	35.8	2.8	25.4	1.4
C, hydrocyclone:										
Concentrate.............	15	1.5	NA	ND	ND	.3	ND	1.2	97.2	ND
Middling................	26	1.0	NA	ND	ND	.9	.4	1.9	95.5	.4
Low-middling............	3	ND	NA	ND	ND	2.4	4.1	68.7	26.8	ND
Tailings................	5	1.7	NA	ND	ND	19.0	24.0	37.4	19.9	ND
Slimes..................	51	11.8	NA	ND	ND	38.0	37.5	4.9	10.7	ND
D, lime-neutralized filter cake:										
Concentrate.............	8	.9	1.7	.3	ND	1.6	ND	.9	95.7	ND
Middling................	28	1.6	16.3	.2	.3	4.1	ND	3.2	74.8	ND
Tailings................	6	4.0	26.3	ND	ND	20.1	1.1	.2	49.8	ND
Slimes..................	58	5.4	39.1	ND	1.4	14.6	9.1	6.0	25.0	ND

NA Not analyzed. ND Not detected.

their relative percentages. This procedure is referred to as normalizing. Photomicrographs of the concentrate, middling, tailing, and slime products of sample C (hydrocyclone waste) are shown in figure 2. The concentrate product consisted of approximately 50 pct each of unreacted and partially reacted titanium minerals. The middling product is composed mainly of partially reacted titanium minerals and only about 10 pct unreacted titanium mineral. The low-middling product was mainly composed of silica gangue, and no photomicrograph is shown. The tailing product is mainly composed of petroleum coke and about 10 pct silica gangue. The slimes product contained about 99 pct petroleum coke.

Because it would be desirable to decrease the amount of material to be treated, the products from the superpanner were further examined by screen sizing. Each waste sample was separated into a combined concentrate product and a combined tailing product. The combined concentrate was composed of the concentrate product, the middling product, and the low-middling product. The combined tailing was composed of the tailing product and the slimes product. These recombined products were size-analyzed using standard Tyler testing sieves in a geometric progression with the multiplier $\sqrt{2}$. The cumulative weight-percent retained versus the Tyler sieve size curves for the combined concentrate and tailing products are shown in figure 3. These diagrams may be used as an aid in screen selection to decrease the amount of material to be treated by gravity concentration. For example, screening sample B or C on a 105-μm (150-mesh) sieve will give an oversize fraction which contains 33 to 41 wt-pct of the tailings but

Concentrate, x 200 **Middling, x 200**

Tailing, x 100 **Slime, x 100**

FIGURE 2. - Scanning electron microscope photomicrographs of sample C (hydrocyclone waste).

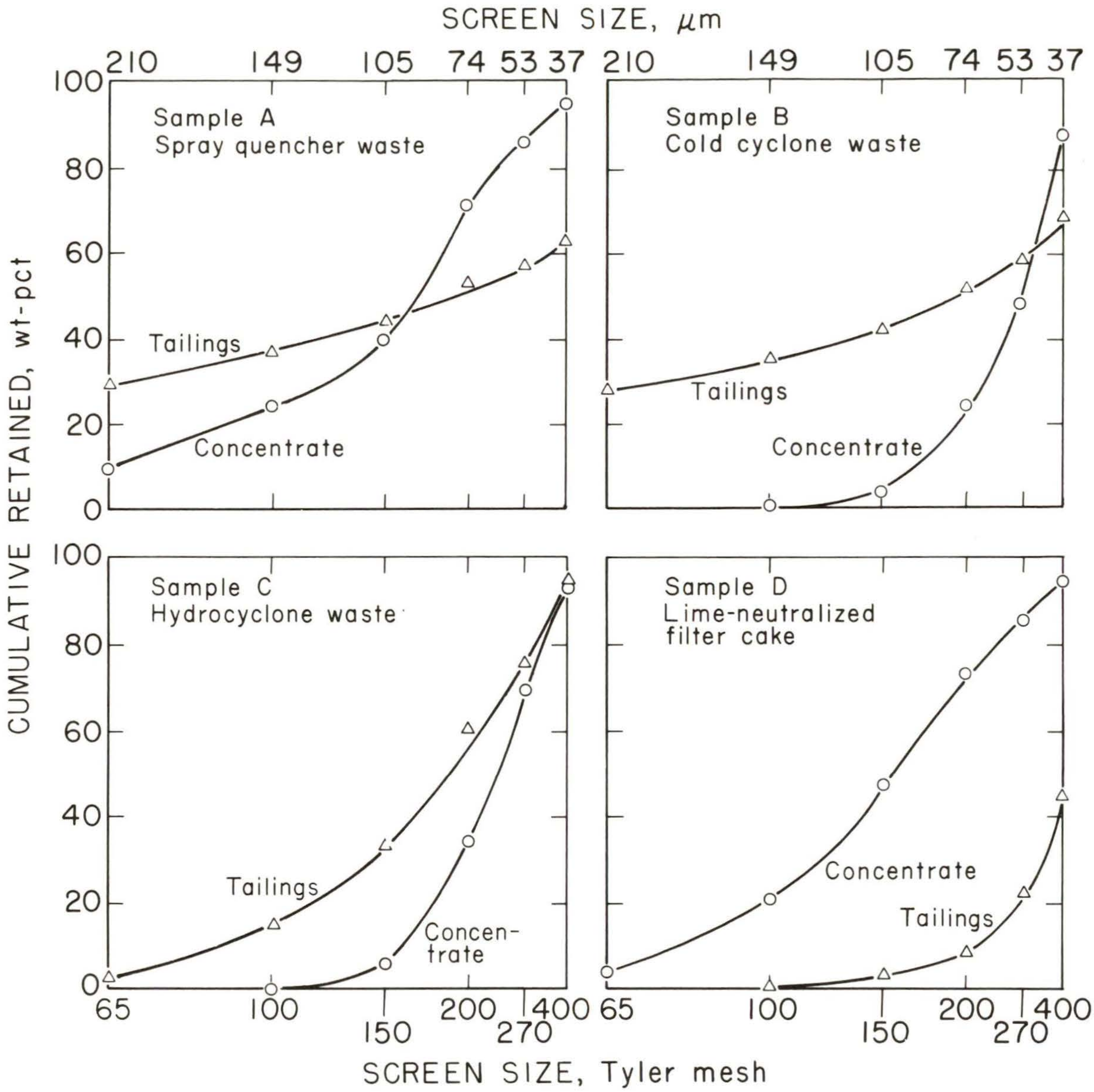


FIGURE 3. - Size distribution diagrams.

only 4 to 6 wt-pct of the titanium concentrate. The undersize fraction then may be treated to produce the desired concentrate. Screening of samples A and D would be done on a 53-µm (270-mesh) sieve, and the oversize fraction would be treated.

Laboratory-Scale Studies

The laboratory-scale studies involved treating 6.0 to 8.3 kg (13.2 to 18.3 lb) of the insoluble material from each of the four wastes on a diagonal-deck concentration table equipped with a slime deck. The difference in color of the minerals of interest was used to obtain the desired products from the concentrate end of the table.

Ten-kilogram (22-lb) feed samples each of sample A (spray quencher waste) and sample B (cold cyclone waste) were used for the tests. After leaching, they yielded about 7.5 kg (16.5 lb) and 8.3 kg (18.3 lb), respectively, of insoluble material for gravity concentration testing. Six-kilogram (13.2-lb) samples each of sample C (hydrocyclone waste) and sample D (lime-neutralized filter cake) were used for gravity concentration testing. During preliminary testing, the waste samples were subjected to elutriation in a flowing water column to yield an overflow stream high in coke fines and an underflow containing the titanium mineral, along with some coke and silica gangue. The elutriation underflow then was tabled to remove additional coke and silica gangue from the titanium mineral concentrate. It was also found that the addition of a sizing step following the first (rougher) tabling removed most of the lighter density (larger particle size) silica gangue in the screen oversize fraction. A 210-µm (65-mesh) screen was used to size samples A and D, and a 105-µm (150-mesh) screen was used to size samples B and C. This step was significant, since all of the commercial producers expressed concern about the silica content of potential recycle concentrates. The screen underflow was tabled (cleaner) to separate out the desired titanium mineral concentrate. Further testing showed that the slime fraction of the wastes readily washed over the tailing (lower edge) of the rougher table. This procedure was adopted and the elutriation step was eliminated.

RESULTS

Following preliminary gravity concentration testing, the basic scheme shown in figure 4 was adopted for the laboratory-scale study. Samples were attrition scrubbed to separate the particles, and the slurry was pumped onto the table at a rate of 8.2 to 9.1 kg/hr (18 to 20 lb/hr). The water flow across

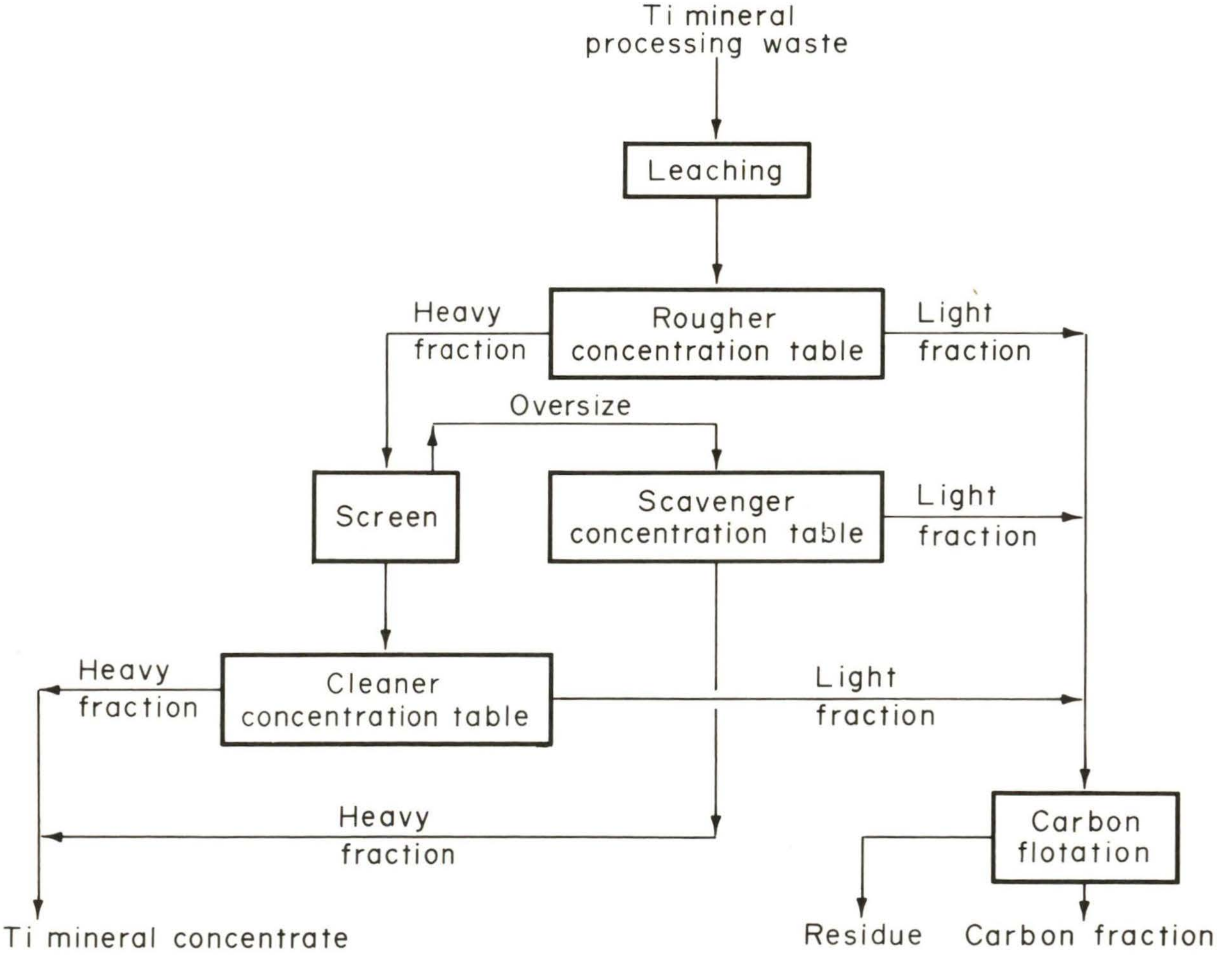


FIGURE 4. - Gravity concentration scheme.

the table was maintained at 5.7 L/min (1.5 gal/min). The distribution of the three major minerals of interest (rutile, quartz, petroleum coke) was calculated on the basis of the head sample being equal to 100 pct. The distribution was determined by comparing the amount contained in each product to the amount contained in the head sample. The handling losses due to spillage, fines washing through filters, and weighing errors are shown in tables 3 through 6 for each waste sample.

TABLE 3. - Analysis and distribution of table products, spray quencher waste

Product	Wt-pct	Analysis, wt-pct			Distribution, wt-pct		
		TiO_2	SiO_2	C	TiO_2	SiO_2	C
Cleaner concentrate[1]	51.8	88.7	4.71	1.07	69.2	21.6	2.6
Concentrate[2]	9.6	36.1	28.2	22.9	5.2	23.9	10.4
Tailings[2]	5.2	10.3	16.7	62.8	.8	7.8	15.3
Tailings[1]	28.3	44.3	13.0	36.5	18.9	32.7	48.7
Handling loss	5.1	NAp	NAp	NAp	5.9	14.0	23.0
Head sample total or composite.	100.0	66.5	11.3	21.2	100.0	100.0	100.0

NAp Not applicable. [1]Minus 65 mesh (210 μm). [2]Plus 65 mesh (210 μm).

TABLE 4. - Analysis and distribution of table products, cold cyclone waste

Product	Wt-pct	Analysis, wt-pct			Distribution, wt-pct		
		TiO_2	SiO_2	C	TiO_2	SiO_2	C
Cleaner concentrate[1]	21.9	90.5	1.31	3.53	48.8	7.6	1.5
Scavenger concentrate[2]	10.9	90.8	4.79	2.17	24.3	13.8	.5
Scavenger tailings[2]	14.7	8.32	2.10	78.5	3.0	8.3	22.9
Tailing[1]	49.2	10.6	5.69	77.6	12.9	75.2	76.0
Handling loss	3.3	NAp	NAp	NAp	11.0	[3]4.8	[3]1.0
Head sample total or composite.	100.0	40.6	3.75	50.2	100.0	100.0	100.0

NAp Not applicable. [1]Minus 150 mesh (105 μm). [2]Plus 150 mesh (105 μm).
[3]Amount in excess of 100 pct.

TABLE 5. - Analysis and distribution of table products, hydrocyclone waste

Product	Wt-pct	Analysis, wt-pct			Distribution, wt-pct		
		TiO_2	SiO_2	C	TiO_2	SiO_2	C
Cleaner concentrate[1]	34.1	89.5	1.93	5.89	55.7	12.0	5.9
Scavenger concentrate[2]	19.8	92.4	3.32	1.49	33.3	12.0	.9
Scavenger middling[2]	10.4	27.4	24.8	41.0	5.2	48.0	12.6
Scavenger tailings[2]	19.8	1.24	4.84	94.4	.5	18.0	55.3
Tailing[1]	16.2	11.8	3.79	70.7	3.5	11.3	34.0
Handling loss	[3].3	NAp	NAp	NAp	1.8	[3]1.3	[3]8.7
Head sample total or composite.	100.0	54.3	5.35	33.8	100.0	100.0	100.0

NAp Not applicable. [1]Minus 150 mesh (105 μm). [2]Plus 150 mesh (105 μm).
[3]Amount in excess of 100 pct.

TABLE 6. - Analysis and distribution of table products, lime-neutralized filter cake

Product	Wt-pct	Analysis, wt-pct			Distribution, wt-pct		
		TiO_2	SiO_2	C	TiO_2	SiO_2	C
Cleaner concentrate[1]...............	43.0	69.0	6.48	3.65	75.2	33.5	17.4
Concentrate[2]......................	4.7	23.2	32.1	26.7	2.8	18.0	13.7
Tailings...........................	52.7	19.9	8.88	11.5	25.7	56.2	67.3
Handling loss......................	[3].3	NAp	NAp	NAp	[3]3.7	[3]7.7	[3]1.5
Head sample total or composite..	100.0	39.4	8.30	8.99	100.0	100.0	100.0

NAp Not applicable. [1]Minus 150 mesh (105 µm). [2]Plus 150 mesh (105 µm).
[3]Amount in excess of 100 pct.

Sample A (Spray Quencher Waste)

The gravity concentration procedure yielded a minus 210-µm (65-mesh) cleaner concentrate that contained 88.7 wt-pct TiO_2 and 4.71 wt-pct SiO_2, representing 69.2 wt-pct recovery of TiO_2 from the waste. This concentrate product represents a 51.8-wt-pct reduction in the amount of waste. The results are shown in table 3. This waste contains approximately 50 pct minus 53-µm (270-mesh) material in the tailings (fig. 3). The low accountabilities of the silica and carbon are due to the finer sized particles passing through the pressure filters. The waste also contains a large quantity (18.9 wt-pct TiO_2, table 3) of unreacted mineral, minus 210 µm (65 mesh), that reported to the tailing product and was not recovered during these tests. Although it was not done during these tests because there was not enough feed material present to establish steady-state conditions on the table, it should be possible to recover these fines by tabling the nonfloat fraction following the selective carbon flotation step. It should also be possible to increase the titanium recovery about 5 wt-pct by an additonal tabling step (scavenger) on the plus 210-µm (65-mesh) concentrate product.

During the time period of this investigation, the metal chlorides contained in this head sample continually hydrolyzed, and filtration following leaching became more difficult with each batch treated. This problem should be minimized in a plant situation since the material would be treated soon after it was generated.

Sample B (Cold Cyclone Waste)

The gravity separation scheme yielded a minus 105-µm (150-mesh) cleaner concentrate that contained 90.5 wt-pct TiO_2 and 1.31 wt-pct SiO_2, representing 48.8-wt-pct recovery of TiO_2 from the waste. The results are shown in table 4. Sufficient quantities of plus 105-µm (150-mesh) concentrate product was available to establish steady-state conditions, and a scavenger tabling was done on this waste. The additional step recovered 24.3 wt-pct TiO_2, which increased titanium recovery to 73.1 wt-pct. The composited cleaner and scavenger concentrate products contained 90.6 wt-pct TiO_2 on a weighted average basis and represented a 32.8-wt-pct reduction in the amount of waste.

The concentrate product of this waste was much finer than the concentrate product of sample A, and the accountability of the TiO_2 was always lower with this waste material. In general, the accountability of both samples A and B, which required leaching, always were lower than that in samples C and D, which did not require leaching prior to physical beneficiation. The exact reasons for this observation are not known.

Sample C (Hydrocyclone Waste)

The gravity separation scheme yielded a minus 105-µm (150-mesh) cleaner concentrate that contained 89.5 wt-pct TiO_2 and 1.93 wt-pct SiO_2, representing 55.7-wt-pct recovery of TiO_2 from the waste. The results are shown in table 5.

Sufficient quantities of plus 105-µm (150-mesh) concentrate product also were available to establish steady-state conditions, and a scavenger tabling was done on this waste. The scavenger table on this sample was unique with respect to the formation of a silica band located in the middle of the concentrate product. This band was easily separated as a middling product. The scavenger tabling step recovered 33.3 wt-pct TiO_2, which increased titanium recovery up to 89.0 wt-pct. The composited cleaner and scavenger concentrate products contained 90.7 wt-pct TiO_2 on a weighted average basis and represented a 53.9-wt-pct reduction in the amount of waste requiring disposal.

The cleaner concentrate products from samples A, B, and C ranged from 88.7 to 90.5 wt-pct TiO_2 and contained 1.31 to 4.71 wt-pct SiO_2. The concentrate product from sample C (89.5 wt-pct TiO_2 and 1.93 wt-pct SiO_2) was the nearest to a median and was examined by X-ray diffraction to determine the minerals present. Figure 5 is a stick diagram of the X-ray diffraction trace. Trace A is the diagram for the cleaner concentrate (sample C). Trace B and C are diagrams from the Joint Committee on Powder Diffraction Standards (JCPDS) file. By comparison of the traces from the JCPDS file cards with the concentrate trace, the primary phase was found to be rutile with a trace (<1 pct) of alpha-quartz.

Sample D (Lime-Neutralized Filter Cake)

The lime-neutralized waste material was brown in color, and most of the titanium mineral and petroleum coke particles also were coated with the brown material.

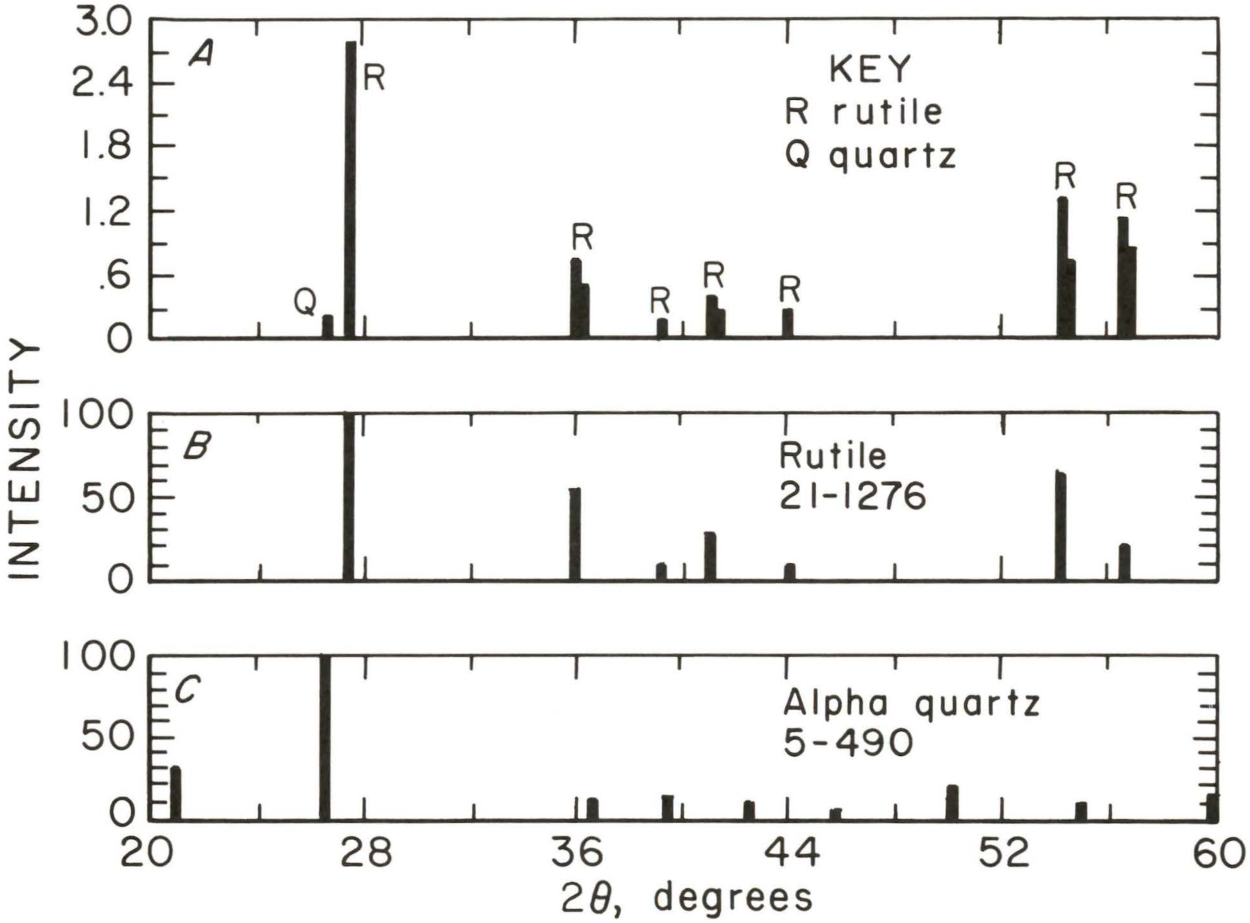


FIGURE 5. - Stick diagrams of X-ray diffraction patterns.

Because of the lack of color differences for the minerals present, it was very difficult to separate the products on the concentration table.

Tabling yielded a minus 210-µm (65-mesh) cleaner concentrate that contained 69.0 wt-pct TiO_2 and 6.48 wt-pct SiO_2, representing 75.2-wt-pct recovery of the TiO_2 from the waste. This concentrate product represents a 43.0-wt-pct reduction in the amount of waste. The results are shown in table 6. The cleaner concentrate also contained 7.70 wt-pct CaO. Another test was made to obtain a higher grade of TiO_2 in the concentrate product by taking a narrower band on the table. The test yielded a minus 210-µm (65 mesh) cleaner concentrate that contained 93.2 wt-pct TiO_2 and 2.12 wt-pct SiO_2, but it contained only 23 wt-pct of the TiO_2 in the waste. This concentrate also contained 2.1 wt-pct CaO. Since calcium is a troublesome impurity because it forms a high-boiling-point liquid chloride that accumulates and causes plugging in a fluidized bed chlorination reactor, these concentrates would not be suitable for direct recycle. A sulfation process for removing impurities from titanium-bearing materials such as the one described by Elger (3) might be effective in reducing the calcium impurities to an acceptable level (<0.2 pct).

Flotation

A selective carbon flotation scheme was tested to recover the coke contained in the tailing products from both the rougher and cleaner tabling and the oversize product from the screen sizing. The initial flotation tests were done in a 1-kg (2.2-lb) rotor-stator, batch-type flotation cell. These tests were made with a pulp consisting of 25 pct solids. Pine oil was added as a frother, and number 2 diesel oil was added as a collector for the carbon. After the addition of reagents, the cell was allowed to condition for 5 min before air was introduced. Samples A and B were found to produce very little froth. This was initially attributed to their low pH (2.5 to 3.5). Adjusting the pH up to 7.0 and 9.0 by lime neutralization did not improve frothing. Frothing was accomplished by the addition of a surfactant, sodium di-(2-ethylhexyl) phosphate. The amount of reagents required for each sample is shown in table 7. The amount of surfactant required to float samples A and B would be considered high. The amount of pine oil (frother) appears high compared with the amount required for flotation of sulfide minerals or oxides [0.02 kg/t (0.05 lb/ton)], but not excessive. The amount of number 2 diesel oil (collector) required is considered to be in the normal range.

Chemical analyses for the three major elements of interest are shown in table 8 for the initial selective carbon flotation tests. Head analyses were not made on the feed materials for these initial tests and therefore, only the chemical compositions of the product are shown. The best separation of coke was obtained with the tailings and screen oversize products from sample C (hydrocyclone waste). The coke product (float) contained 96.8 wt-pct C and the nonfloat

TABLE 7. - Reagent requirements for selective carbon flotation

Sample[1]	Surfactant		Pine oil		No. 2 diesel oil	
	kg/t	lb/ton	kg/t	lb/ton	kg/t	lb/ton
A, spray quencher..............	0.94	1.88	0.10	0.20	0.11	0.21
B, cold cyclone................	.94	1.88	.10	.20	.25	.50
C, hydrocyclone................	None	None	.10	.20	.17	.34
D, lime-neutralized filter cake	None	None	.10	.20	[2].23	[2].46

[1] Combined tailings and screen sizing oversize.

[2] Total, added in stages--first stage, 0.17 kg/t (0.34 lb/ton); second stage, 0.03 kg/t (0.96 lb/ton); third stage, 0.03 kg/t (0.06 lb/ton).

product only 1.30 wt-pct C. The tailings and screen oversize from samples A and B did not separate as well in a single application of reagents in the cell. These samples would require two or three cells connected in series to recover most of the coke remaining in the nonfloat fraction. The tailing from sample D (lime-neutralized filter cake) did not respond well to selective carbon flotation. After two additional conditioning periods with additional collector added, the grade of the float fraction was only 59.2 wt-pct C. The carbon particles also were coated with a brown substance and would require additional cleaner flotation stages to obtain a useful coke product.

TABLE 8. - Analysis of carbon flotation product, 1-kg (2.2-lb) cell

Source	Wt-pct	Analysis, wt-pct		
		C	Si	Ti
Tailings A:				
Float........	15	96.5	0.62	0.98
Nonfloat.....	85	10.6	15.5	25.3
Tailings B:				
Float........	76	94.0	.98	1.36
Nonfloat.....	24	35.0	14.1	21.0
Tailings C:				
Float........	64	96.8	NA	NA
Nonfloat.....	36	1.30	37.6	12.0
Tailings D:				
Float........	5	59.2	NA	NA
Nonfloat.....	95	7.82	4.34	22.4

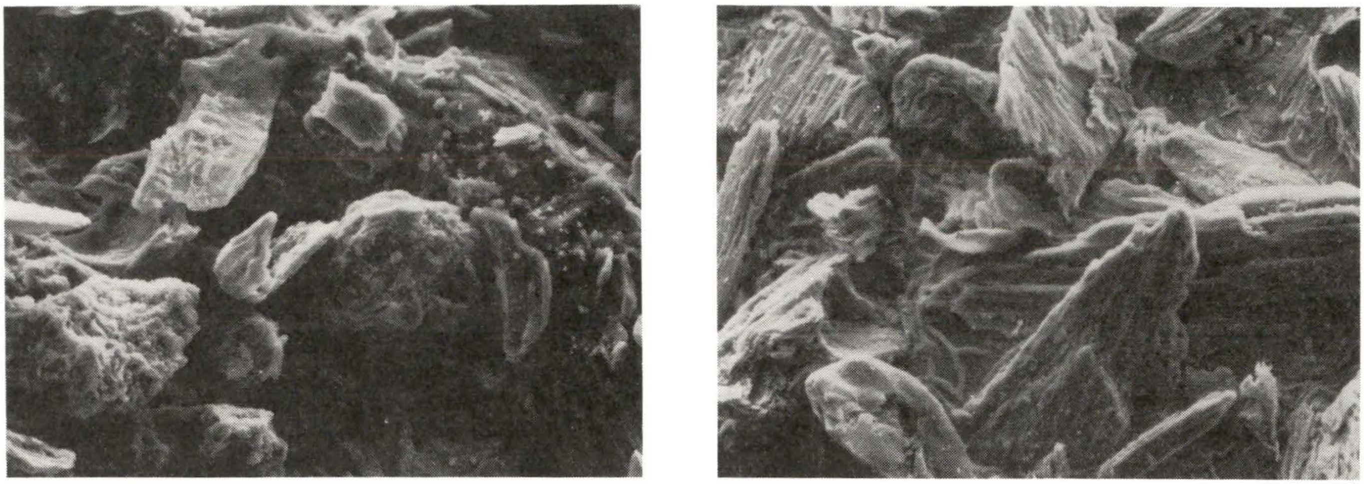
NA Not analyzed.

A sample of the combined tailings and screen oversize products recovered from sample A (spray quencher waste), sample B (cold cyclone waste), and sample C (hydrocylone waste) was submitted for examination of the coke particle surfaces by the SEM. Photomicrographs are shown in figure 6. The surfaces of the coke particles (easily flotable) of sample C were very clean, but the surfaces of the coke particles of samples A and B (did not float) were covered with particles of <10 μm diam. The photomicrograph for sample A was similar to that of sample B and is not shown. Semiquantitative analyses indicate that titanium was the major element (69 to 95 pct) present in the <10-μm-diam particles.

The combined tailings and screen oversize products from the gravity concentration of sample C (hydrocyclone waste) was processed in a 10-kg (22-lb) rotor-stator, batch flotation cell at a pulp consistency of 25 pct solids. The sample was conditioned for 5 min following additions of 0.10-kg/t (0.20-lb/ton) frother and 0.17-kg/t (0.39-lb/ton) collector. The results of the test are shown in table 9. The float product, from a single pass, contained 95.7 wt-pct C and represented 98 pct of the carbon present in the combined product. The coke product represents an additional 32.9-wt-pct reduction of the amount of sample C (hydrocyclone waste).

TABLE 9. - Analysis and distribution of carbon flotation products, 10-kg (22-lb) cell

Sample	Wt-pct	Analysis, wt-pct			Distribution, wt-pct		
		C	Si	Ti	C	Si	Ti
Tailings, sample C..	100	69.20	3.79	8.20	100	100	100
Float fraction......	71	95.7	.10	.91	98	2	8
Nonfloat fraction...	29	3.66	2.9	26.2	2	98	92



Sample B, x 300 **Sample C, x 200**

FIGURE 6. - Scanning electron microscope photomicrographs of coke particles.

Recovery of Elements From Leach Liquors

Preliminary tests were conducted on recovering Cb, Cr, and V from the leach liquors obtained by the leaching of samples A and B with 0.5*N* HCl.

Leachability Study

Tests were conducted to determine the effect of acid concentration on the leachability of the soluble metal chlorides present in the solid wastes from sample A (spray quencher waste) and sample B (cold cyclone waste). The samples were weighed and then loaded into sealed vials in an inert atmosphere glove box, owing to their hygroscopic nature. Since sample B consisted of a low-density material, the sample weight was reduced to accommodate the sample vials. The samples were leached with either distilled water or HCl solutions of 0.5*N*, 1.0*N*, 2.0*N*, and 4.0*N* concentration [100 ml (3.38 oz) for sample A and 80 ml (2.71 oz) for sample B]. The results (table 10) show an increase in weight loss from 17.2 wt-pct with a water leach up to 23.8 wt-pct using a 0.5*N* HCl solution (sample A). The weight loss of sample B increased from 4.00 wt-pct up to 12.2 wt-pct, respectively. Acid solutions stronger than 0.5*N* did not make any significant difference in the removal of soluble chlorides. An important factor observed during the study was the increased filterability of the slurries when using the HCl leach solutions. Chemical analyses of the solutions from the 0.5*N* HCl leach are shown in table 11.

TABLE 10. - Weight loss data from leaching sample A spray quencher and sample B cold cyclone

	Leach agent									
	Distilled water		0.5*N* HCl		1.0*N* HCl		2.0*N* HCl		4.0*N* HCl	
	A	B	A	B	A	B	A	B	A	B
Weight, g:										
Starting................	50.0	40.0	50.0	40.0	50.0	40.0	50.0	40.0	50.0	40.0
Ending..................	41.4	38.4	38.1	35.1	38.1	36.1	38.6	36.6	37.1	35.1
Loss....................	8.6	1.6	11.9	4.9	11.9	3.9	11.4	3.4	12.9	4.9
Weight loss.........pct..	17.2	4.00	23.8	12.2	23.8	9.75	22.8	8.50	25.8	12.2

TABLE 11. - Chemical analyses of 0.5*N* HCl leachates

Element	Sample A (spray quencher)		Sample B (cold cyclone)	
	g/L	oz/gal	g/L	oz/gal
Aluminum....	6.78	0.91	3.00	0.40
Calcium.....	2.54	.34	.18	.02
Chromium....	.88	.12	3.28	.44
Cobalt......	.18	.02	2.82	.38
Iron........	26.8	3.58	9.06	1.21
Magnesium...	1.96	.26	.68	.09
Manganese...	5.64	.75	.14	.02
Silicon.....	.01	<.01	.05	.01
Titanium....	.13	.02	4.52	.60
Vanadium....	.55	.07	4.36	.58
Zirconium...	.54	.07	6.04	.81

Hydrolysis

The initial treatment of the leachates of sample B (table 11) consisted of hydrolysis at elevated temperature and pressure (150° C, 60 to 70 psig) to precipitate Cb, Ti, and Zr as hydrated oxides, pH <1. Hydrolysis was done in a glass beaker enclosed in a stainless steel autoclave. Stirring was accomplished with a magnetic stirring bar. The results in table 12 show that 93.3 to 99.3 wt-pct of these elements were removed. Separation of the precipitated group into individual metal compounds was not investigated in this work; instead, recovery of the toxic V^{4+} from the ensuing filtrate was investigated.

Hydroxide Precipitation--Solvent Extraction

A precipitate containing the Al, Cr, and V was formed by adding NaOH to the filtrate from the hydrolysis step. Adjusting the pH from <1 up to 3.9 yielded a precipitate (table 12) that contained 93.4 to 99.6 wt-pct of the Al, Cr, V, and about 8 wt-pct of the Fe and 2 wt-pct of the Zr. The precipitated product, after redissolving in H_2SO_4, was contacted at pH 2 with a 6-pct solution of di-(2-ethyl-hexyl) phosphoric acid (D2EHPA) containing 3-pct isodecanol (IDA) in a kerosene carrier to preferentially extract vanadium from aluminum with only minimum extraction of chromium. The data in table 13 show that 41.2-wt-pct-V extraction was attained at 45° C with an aqueous-organic (A-O) ratio of 1:1. Only 0.51 wt-pct Cr and 1.56 wt-pct Al were extracted. At an A-O ratio of 1:2, the extraction of vanadium increased to 84.5 wt-pct, but the extraction of aluminum also increased to 15.3 wt-pct. The extraction of chromium remained about the same. A stripping shakeout test was made using organic phase material from the second extraction test containing 0.87 g/L (0.12 oz/gal) V. It was stripped in a single stage with 15-pct H_2SO_4 at an A-O ratio of 1:3.4 and gave a strip solution containing 1.86 g/L (0.25 oz/gal) V (63-pct recovery). This represents a reasonable recovery for the A-O ratio that was used.

TABLE 12. - Recoveries obtained by subjecting leach liquor to hydrolysis at 150° C and sequential precipitation at pH 3.9

Material	Al	Cb	Cr	Fe	Ti	V	Zr
Hydrolysis precipitate, pct:							
Analysis...........................	0.08	8.10	0.42	0.37	15.4	0.03	21.4
Recovery...........................	0.63	99.3	5.39	0.91	93.3	0.18	97.2
pH 3.9 precipitate, pct:							
Analysis...........................	9.93	0.01	5.49	2.47	0.76	13.7	0.40
Recovery...........................	99.0	0.31	93.4	8.04	6.15	99.6	2.39
Residuals in filtrate:							
Analysis.....................g/L..	0.1	<0.01	<0.02	8.18	<0.02	<0.01	0.02
Nonrecovery..................pct..	0.32	<0.35	<1.18	91.0	<0.50	<0.23	0.388

TABLE 13. - Results of initial solvent extraction tests to separate vanadium from chromium and aluminum in redissolved pH 3.9 precipitate

	V	Cr	Al
EXTRACTION			
A-O ratio, 1:1:			
Aqueous..................g/L..	1.13	1.17	1.58
Aqueous...............oz/gal..	.15	.16	.21
Organic..................g/L..	0.79	0.0006	0.025
Organic...............oz/gal..	.11	.001	.003
Extraction...............pct..	41.2	0.51	1.56
A-O ratio, 1:2:			
Aqueous..................g/L..	0.32	1.29	1.44
Aqueous...............oz/gal..	.04	.17	.19
Organic..................g/L..	0.87	0.004	0.13
Organic...............oz/gal..	.12	.001	.02
Extraction...............pct..	84.5	0.61	15.3
STRIPPING			
A-O ratio, 1:3.4:			
Aqueous[1]..................g/L..	1.86	0.006	0.008
Aqueous[1]...............oz/gal..	.25	.001	.001
Organic..................g/L..	0.32	0.003	0.014
Organic...............oz/gal..	.04	<.001	.002
Back extraction..........pct..	63.1	37.0	19.4

[1] 15 pct H_2SO_4.

Direct Solvent Extraction

Owing to the added expense of using large quantities of reagents such as NaOH for precipitation and H_2SO_4 for redissolution, direct extraction of vanadium from the filtrate following hydrolysis and removal of Cb, Ti, and Zr was investigated. Tests were conducted to determine the effect of equilibrium pH on extraction, in the range pH 1.5 to 3.0, using an organic phase containing 6-pct D2EHPA and 5-pct IDA in a kerosene carrier. The A-O ratio was 1:1, the temperature was 45° C, equilibrium pH was adjusted with NH_4OH, and the contact consisted of 10 min of mild mixing on a wrist-action shaker. The results are shown in figure 7, where it can be seen that Fe^{3+} is more readily extracted than V^{4+}. Contamination (Al^{3+}) will occur at pH values higher than 2.

Shake out tests were conducted at 45° C with an equilibrium pH of 2.0. The aqueous feed was leach liquor after hydrolysis containing 4.11 g/L (0.55 oz/gal) V. The organic phase was 6 pct D2EHPA, 5 pct IDA , and kerosene. A McCabe-Thiele construction (1) of the data using A-O ratios of 5:1, 2:1, 1:1, 1:2, and 1:5 is shown in figure 8. The diagram shows the number of theoretical or ideal stages required to extract the vanadium. The data shows that 97-pct extraction of the vanadium could be obtained in two stages at an A-O ratio of 1:1 (fig. 8). However, third-phase material severely affected phase separation at the higher A-O ratios. Spectrographic analysis of these third-phase materials showed high phosphorus (10 to 100 pct P) with 0.3 to 3 pct Mg, Fe, Al, and V and lesser amounts of Ba, Ca, Mn, Pb, Ti, Sn, and Zr. Because of these insoluble complexes, four or more stages probably would be required for extraction of the vanadium.

A series of comparative tests was conducted to determine whether better phase separation and extraction are obtained using (1) 6-pct D2EHPA with no additive, (2) 6-pct D2EHPA with a 3- to 5-pct tributyl phosphate additive (TBP), or

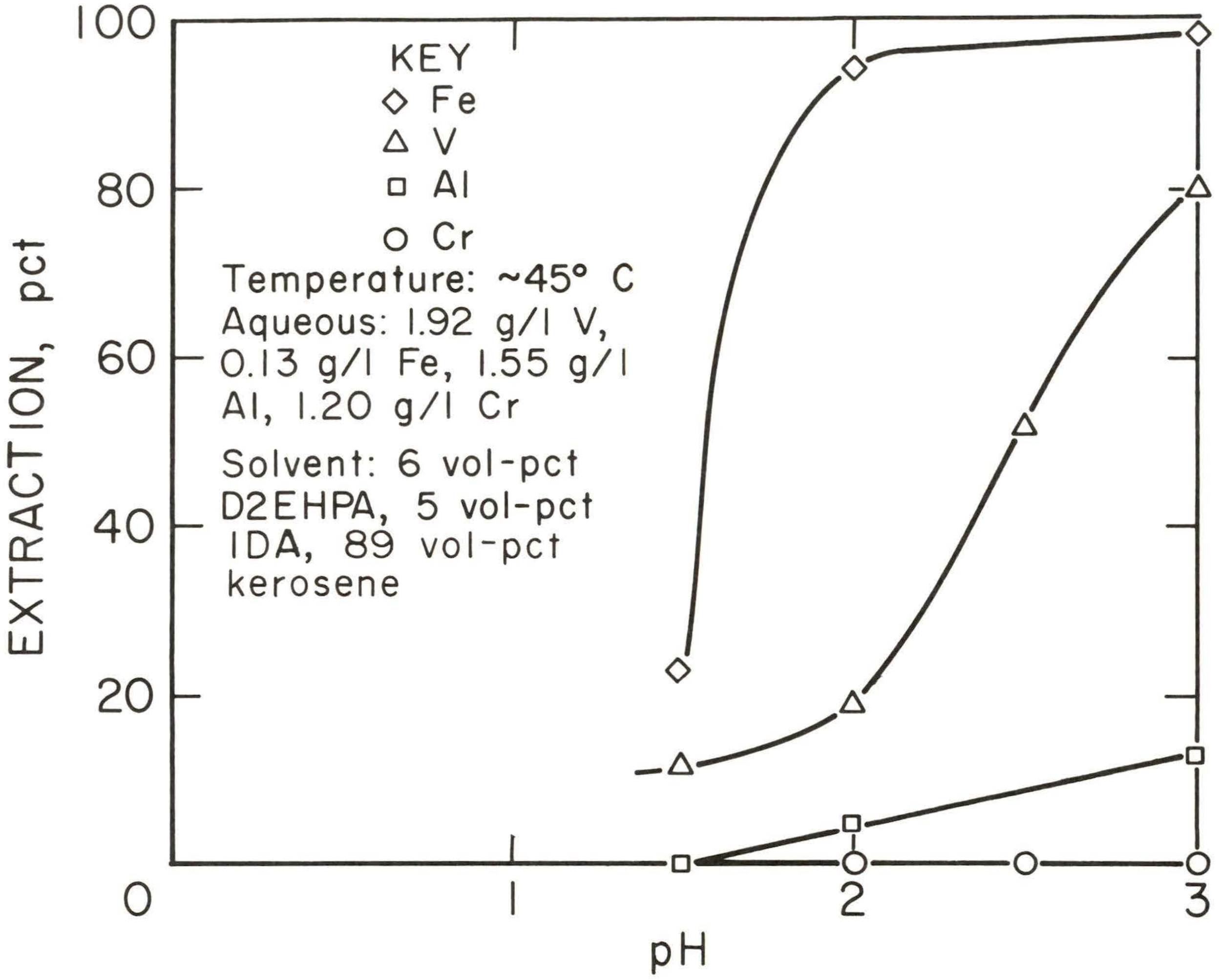


FIGURE 7. - Effect of pH on extraction.

(3) 6-pct D2EHPA with a 3- to 5-pct IDA additive. The amount of vanadium extracted from leach liquor containing 4.06 g/L (0.54 oz/gal) V (A-O ratio 2:1) was 6.14 g/L (0.82 oz/gal) V with no additive, 6.87 g/L (0.92 oz/gal) V with TBP additive, and 6.56 g/L (0.88 oz/gal) V with IDA additive. In addition, improved phase separation occurred with the TBP. Therefore, both better extraction and phase separation were obtained by adding 3 to 5 pct TBP to the 6 pct D2EHPA.

A three-stage batch extraction test was conducted on leach liquor (A-O ratio 1:1) to provide loaded organic phase material for conducting a stripping test. The organic phase was 10 pct D2EHPA and 3 pct TBP in a kerosene carrier. The duration of the test was 9-1/2 cycles, and the pH of the aqueous feed was adjusted to 1.8 at 45° C before the start of the test and between each stage. The aqueous feed contained the following in grams per liter (ounces per gallon): 3.68 (0.49) V, 8.95 (1.20) Fe, 3.10 (0.41) Al, and 1.17 (0.16) Ti. The loaded organic from the ninth cycle contained the following in grams per liter (ounces per gallon): 3.50 (0.47) V, 0.82 (0.1) Fe, 0.10 (0.01) Al, and 0.48 (0.06) Ti. The aqueous raffinate contained only 0.01 g/L (10^{-3} oz/gal) V showing that the test attained near complete extraction of the vanadium. A stripping test was conducted on the loaded organic.

The stripping isotherm shown in figure 9 was prepared using 15-pct H_2SO_4 as

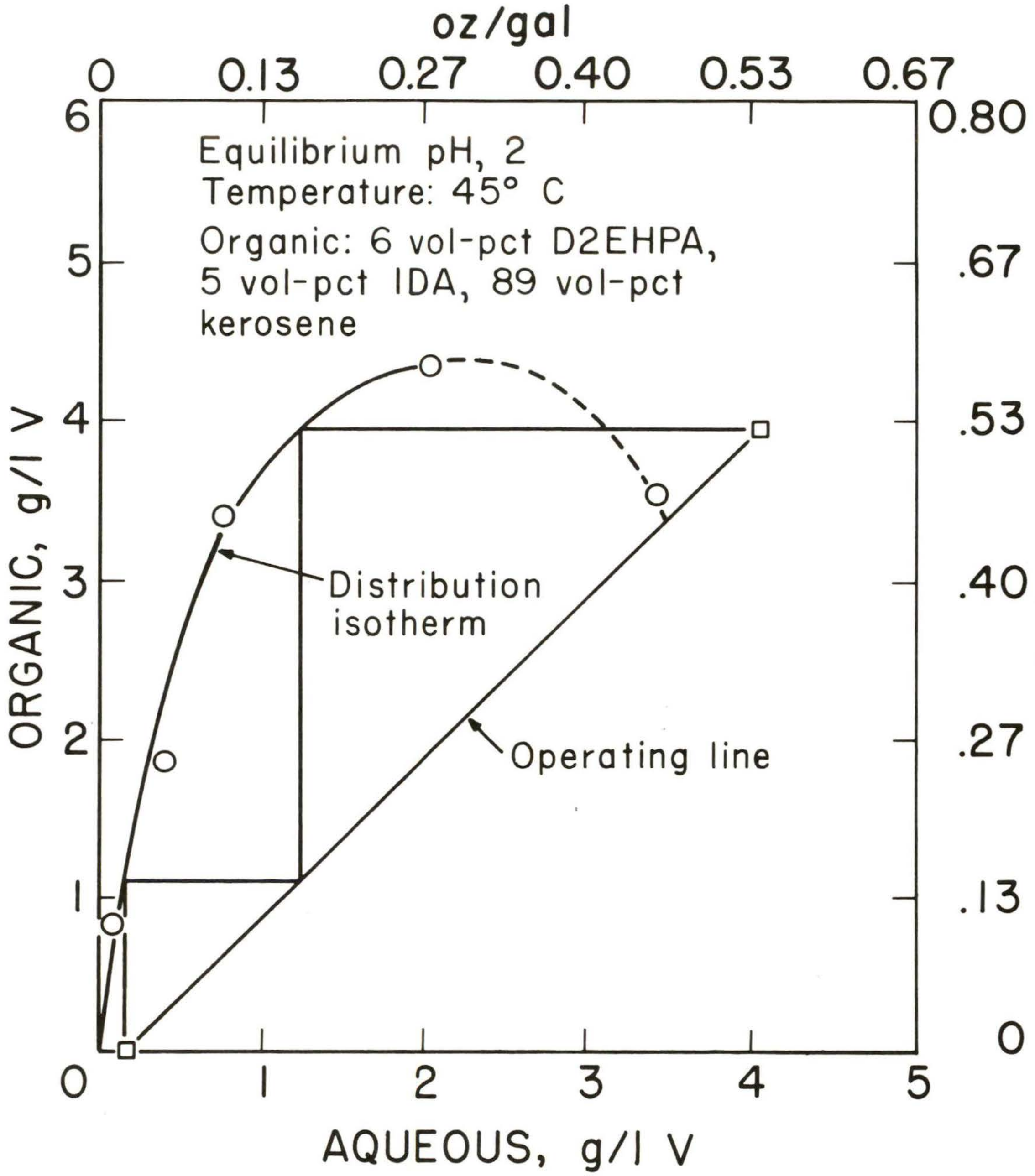


FIGURE 8. - McCabe-Thiele construction for the extraction of V^{4+}.

the stripping solution to allow high vanadium concentrations suitable for processing into anhydrous oxide. Organic to aqueous (O-A) ratios of 15:1, 10:1, 5:1, 2:1, and 1:1 were used. Because of the high ratios, the mixtures were shaken on a wrist action shaker for periods of up to 1 hr with intermittent warming to 45° C in a water bath to insure equilibrium. Solutions were then left overnight in the water bath to promote phase separation. Figure 9 shows that stripping may be done in a single stage at an O-A ratio of 10:1. The aqueous concentration would then be 29 g/L (3.87 oz/gal) of V at 85-pct recovery. The drop in concentration shown at an O-A of 15:1 in figure 9 was probably caused by depletion of the acid.

Ion Exchange Resins

A preliminary test was conducted to determine if ion exchange resins could be

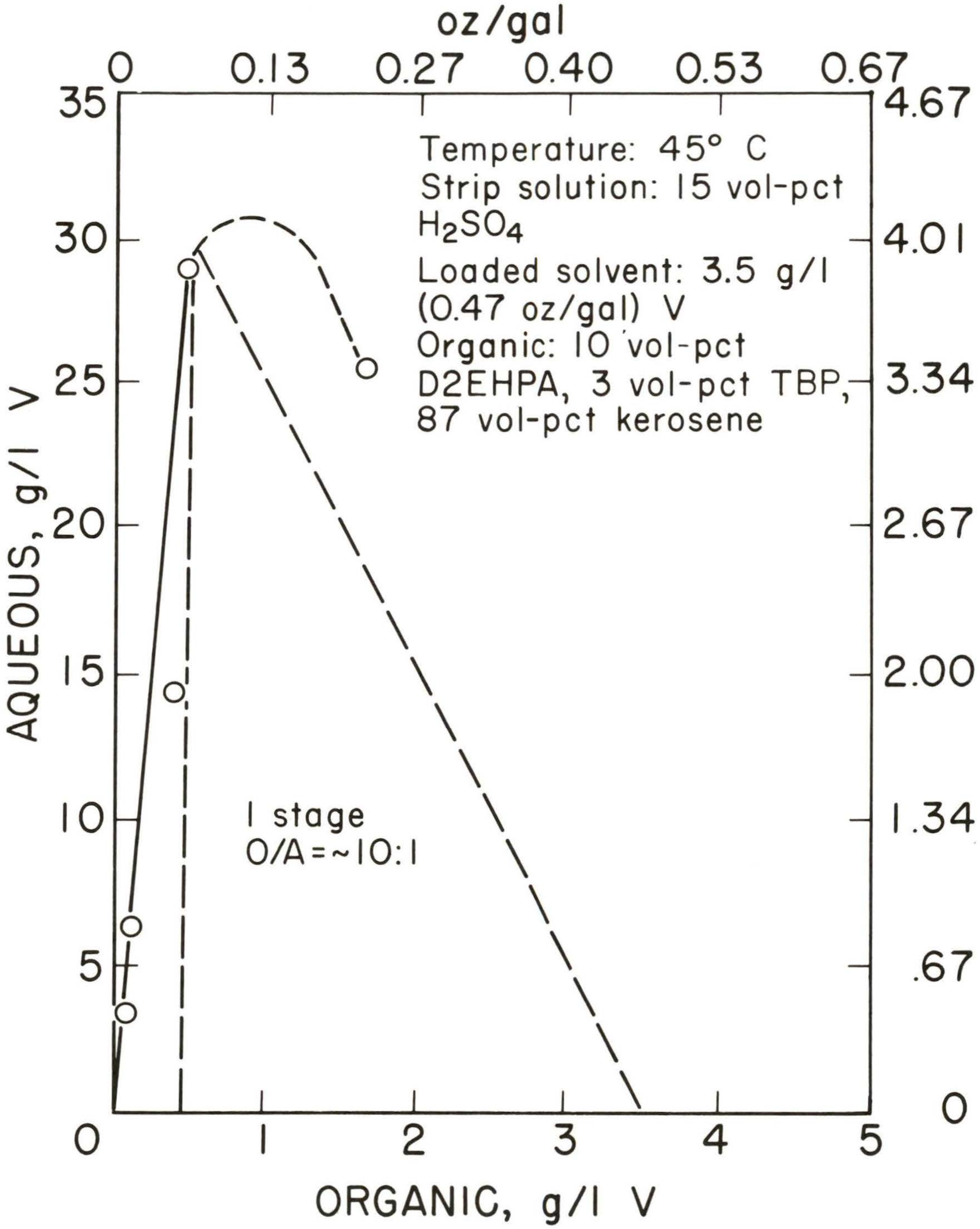


FIGURE 9. - Stripping isotherm for recovering vanadium.

used to recover the vanadium, chromium, and columbium in leachates of titanium chlorination processing wastes. The solution used was a 0.5*N* HCl leachate of sample B (cold cyclone waste). Dowex 50, strong acid resin, was washed with 10-pct ammonium citrate, 3*M* HCl, and rinsed. The column bed volume was 32 ml (1.08 oz). A total of 25 ml (0.85 oz) of sample [4.36 g/L (0.58 oz/gal) V, 3.28 g/L (0.44 oz/gal) Cr, 2.82 g/L (0.38 oz/gal) Cb] was passed through the resin bed at a flow rate of 1.25 ml/min (0.04 oz/min). Water was flushed through the resin bed, and a first fraction of 73 ml (2.47 oz) was collected.

TABLE 14. - Preliminary ion exchange testing data

Source	V		Cr		Cb		Distribution, wt-pct		
	mg	Gr	mg	Gr	mg	Gr	V	Cr	Cb
Sample, 25 ml (0.85 oz)........	109	16.79	82	12.63	71	10.93	100.0	100.0	0.0
Flush: Fraction 1, 73 ml (2.47oz)[1]....................	4	.62	ND	ND	41	6.31	3.7	0	57.7
Elution:									
Fraction 2, 46 ml (1.56 oz)[2].	1	.15	ND	ND	ND	ND	.9	0	0
Fraction 3, 43 ml (1.45 oz)[2].	12	1.85	ND	ND	ND	ND	11.0	0	0
Fraction 4, 73 ml (2.47 oz)[2].	35	5.39	3	.46	ND	ND	32.1	3.7	0
Regeneration:									
Fraction 5, 73 ml (2.47 oz)[3].	5	.77	7	1.08	ND	ND	4.6	8.5	0
Fraction 6, 65 ml (2.20 oz)[4].	29	4.47	26	4.00	ND	ND	26.6	31.7	0

ND Not detected. [1] H_2O. [2] 1 pct H_2O_2, 0.1*M* HCl_4. [3] 3*M* HCl. [4] 9*M* HCl.

Materials balance calculations based on the analyses of the sample effluent (table 14), fraction 1 show that 96.3 wt-pct of the vanadium and 42.3 wt-pct of the columbium were absorbed onto the resin in the column. An elution solution was prepared of 1-pct H_2O_2 and 0.1*M* $HClO_4$. Three fractions of the elution solution [46 ml (1.56 oz), 43 ml (1.45 oz), 73 ml (2.47 oz)] were passed through the column and collected. The column was then regenerated with 73 ml (2.47 oz) of 3*M* HCl, followed by 65 ml (2.20 oz) of 9*M* HCl. The data in table 14 show that 44.0 wt-pct of the vanadium complexed with the H_2O_2 and was carried through in the elution fractions. Another 31.2 wt-pct was removed during regeneration of the resin bed with HCl. A possible solution to increase the recovery of vanadium might be larger elution volumes, but this might also increase chromium contamination. Although it was only a single test, it is useful to note that (1) 58 pct of the columbium was recovered in the initial water flush, (2) 43 pct of the vanadium was eluted and recovered with the hydrogen peroxide, and (3) 40 pct of the chromium was recovered during regeneration of the resin. It should also be noted that while the Cb recovery was only 58 pct, separation was 100 pct.

DISCUSSION OF RESULTS

Results of this investigation showed that chloride plant wastes from the $TiCl_4$ spray quencher and cold cyclone units responded well to physical beneficiation to recover the unreacted titanium minerals and coke as high-grade products. Prompt leaching of these wastes with 0.5*N* HCl is recommended to minimize contact of the associated metal chloride impurities with atmospheric moisture. The impurity chlorides, especially those of columbium react with atmospheric moisture to form HCl and finely divided oxychloride particles that cause problems during subsequent filtration by blinding the filter cloth. There also is a significant quantity, estimated to be 1 to 4 pct, of $TiCl_4$ present in these wastes that forms finely divided oxide particles. This is the most probable source of the <10-µm-diam particles that were deposited on the surfaces of the petroleum coke particles. This further emphasizes the necessity for prompt leaching of these wastes, as clean coke surfaces are essential for an efficient recovery during selective carbon flotation. Having clean coke surfaces would also eliminate the added expense of adding a surfactant to the flotation cell.

The benefits that may be obtained by installing a hydrocyclone in the waste stream circuit to partially beneficiate the waste before gravity concentration (tabling) are shown by the results that were obtained with sample C (hydrocyclone underflow waste). Most of the slime fraction of this sample was removed at the plant in the overflow stream from the hydrocyclone. Among all of the samples studied, the best recovery of unreacted titanium minerals was obtained with the hydrocylone underflow waste. This sample, which was promptly leached, also gave the best recovery of petroleum coke from a single pass through the flotation cell. No surfactant was required with this material, which further points out the importance of prompt treatment of chlorination wastes.

The lime-neutralized waste did not respond well to gravity concentration or selective carbon flotation because the waste particles were coated with fine lime particles. The lime was not washed off by the water used during tabling or the agitation-mixing in the flotation cell. However, tabling produced a titanium mineral concentrate analyzing 69.0 wt-pct TiO_2, which is slightly better than Florida sand ilmenite concentrate (63 wt-pct TiO_2). The concentrate, however, would require further treatment before it would be suitable for recycle to a fluidized-bed chlorinator.

It is estimated that 5 to 10 pct of the titanium mineral fed to a fluidized-bed chlorination reactor is carried out mechanically, with the exit gas stream and collected as waste material in adjacent process units. The results of this investigation show that the incorporation of the following steps would result in more efficient use of the imported feedstocks:

1. Prompt leaching of the chloride wastes with 0.5*N* HCl to minimize hydrolysis of metal chloride impurities and the formation of finely divided oxychlorides.

2. Partial beneficiation of the waste (hydrocyclone or water elutriation) to reduce the amount of slimes.

3. Treating the wastes by gravity concentration (tabling) and selective carbon flotation to recover high-grade titanium ore and petroleum coke products.

Owing to the fine particle size range of both the recovered concentrate and coke flotation products, these materials would require agglomeration to the size range of virgin feedstocks before they could be recycled. Otherwise they would probably be entrained again as solid particles in the gas stream leaving the chlorination reactor.

Recovering the valuable elements from leach liquors derived from titanium mineral chlorination residues by solvent extraction is a complex problem due to the many elements (Al, Ca, Cb, Cr, Fe, Mg, Mn, Si, Ti, V, and Zr) present. Problem areas included formation of third-phase insoluble metal-ion-extractant complexes that inhibited phase separation. These appeared first in the aqueous phase and eventually in the organic phase. When the organic phase was repeatedly contacted with fresh aqueous feed, phase separation was severely inhibited after four contacts.

Comparative tests in phase separation showed better disengagement and phase separation when solutions were warmed to 45° C and 3 to 5 pct TBP was used as an additive to the organic phase.

However, some promising results were observed:

1. Heating liquors at elevated temperature and pressure (150° C, 60 to 70 psig) hydrolyzes and removes Cb, Ta, Ti, and Zr as hydrated oxides.

2. Extraction of 97-pct of the V^{4+} in the filtrate can be obtained in two stages at an A-O ratio of 1:1.

3. An ion-exchange technique successfully separated the columbium from the leachate.

However, further research is needed in these areas.

SUMMARY AND CONCLUSIONS

Four samples of solid waste materials from chloride processing of titanium minerals were treated by gravity concentration to produce a recyclable titanium mineral concentrate and by selective carbon flotation to produce a recyclable petroleum coke fraction. Pelletization of the recovered products to obtain the same size range as fresh feedstock would be required to prevent loss as entrained solid particles from the fluidized-bed reactors.

The proposed gravity concentration procedure produced titanium concentrates containing 69.0 to 90.7 wt-pct TiO_2, with titanium recoveries ranging from 69.2 to 89.0 wt-pct. All the concentrates, with the exception of the concentrate from sample D (lime-neutralized filter cake), should be recyclable. The concentrate from sample D has a grade (69.0 wt-pct TiO_2) slightly better than Florida sand ilmenite concentrate (63.0 wt-pct TiO_2), but it would require further treatment to lower the levels of the high-boiling-point impurities (Ca, Mg, Mn) that form liquid chlorides and are troublesome in fluidized-bed chlorination reactors.

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