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Production of Titanium Dioxide Pigment From Perovskite Concentrates, Acid Sulfation Method

By A. E. Petersen, M. B. Shirts, and J. P. Allen

UNITED STATES DEPARTMENT OF THE INTERIOR



BUREAU OF MINES

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With an Appendix on Economic and Technical Evaluation by J. H. Schwier

**UNITED STATES DEPARTMENT OF THE INTERIOR
Manuel Lujan, Jr., Secretary**

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T S Ary, Director**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	lb	pound
d/yr	day per year	lb/(ft ² ·h)	pound per square foot per hour
ft	foot	Mgal	thousand gallon
ft ²	square foot	min	minute
g	gram	mL	milliliter
gal	gallon	mL/h	milliliter per hour
g/h	gram per hour	mL/min	milliliter per minute
g/L	gram per liter	MMBtu	million British thermal unit
g/min	gram per minute	pct	percent
g/mL	gram per milliliter	ppm	part per million
g/mol	gram per mole	rpm	revolution per minute
h	hour	st	short ton
h/d	hour per day	st/d	short ton per day
in	inch	st/(ft ² ·h)	short ton per square foot per hour
kW·h	kilowatt hour	μm	micrometer
L	liter	wt pct	weight percent

PRODUCTION OF TITANIUM DIOXIDE PIGMENT FROM PEROVSKITE CONCENTRATES, ACID SULFATION METHOD

By A. E. Petersen,¹ M. B. Shirts,² and J. P. Allen³

With an Appendix on Economic and Technical Evaluation by J. H. Schwier

ABSTRACT

To reduce U.S. dependence on imports of titanium, the U.S. Bureau of Mines has investigated the recovery of titanium from perovskite (CaTiO_3). Domestic perovskite deposits represent a significant, but untapped, titanium resource. An acid sulfation method was developed that will extract about 97 pct of the titanium and the columbium and 70 to 90 pct of the rare-earth byproducts from perovskite concentrates. A flow-sheet for recovering titanium as pigment-grade titanium dioxide (TiO_2) is discussed. Test work performed in developing each unit operation is described. The first three unit operations have been demonstrated using laboratory-scale continuous methods of operation: acid sulfation of perovskite concentrates, leaching sulfation residue to dissolve metal values, and precipitation of titanium oxysulfate monohydrate ($\text{TiOSO}_4 \cdot \text{H}_2\text{O}$) from the resulting leach filtrate. Batch testing of other unit operations was performed: $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ redissolution and iron reduction, precipitation of TiO_2 by hydrolysis, and regenerating recoverable acid with rare-earth byproduct recovery. Cost evaluation results are provided, indicating that processing perovskite concentrates by acid sulfation may be an economically viable means of producing TiO_2 .

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INTRODUCTION

Titanium is abundant in the Earth's crust in several mineral forms; the most utilized minerals are rutile (TiO_2) and ilmenite (FeTiO_3). About 95 pct of all titanium mined and processed is used as TiO_2 pigment and welding-rod coatings. The remainder is used for production of titanium metal and its alloys. The metal, mainly used in industrial and military applications, has low density, high strength, and excellent corrosion resistance.

Between 1975 and 1985 the United States increased its dependence on foreign titanium resources from about 48 pct to approximately 73 pct (1).⁴ In 1985, most of the imported material originated in Australia, Canada, Sierra Leone, and South Africa (2).

Rutile is the mineral of choice for producing both titanium metal and pigment. Concentrates may contain 95-pct or more TiO_2 . Reacting rutile or synthetic rutile with carbon and chlorine at temperatures near 1,000° C produces titanium tetrachloride (TiCl_4), from which either metal or purified TiO_2 pigment can be prepared. In comparison with using ilmenite, rutile processing encounters fewer environmental pollution problems and only about a 10th as much solid waste is generated. Rutile is more expensive than ilmenite. World and domestic sources of natural rutile are quite limited.

Ilmenite is more abundant than rutile, but contains large amounts of iron. In nature, the mineral contains from 40 to 65 pct TiO_2 depending on its geologic history. Ilmenite can be processed by several methods: (1) directly chlorinating high-grade or rutile-enriched ilmenite to produce TiCl_4 for pigment or metal production, (2) digesting finely ground ilmenite by sulfation and hydrolyzing to precipitate TiO_2 pigment, and (3) pretreating ilmenite to reduce its iron content, upgrading it to titaniferous slag or synthetic rutile. Producing titaniferous slag or synthetic rutile usually involves some form of reduction, followed by slagging, partial chlorination, or aqueous chemistry (3). Ilmenite is more expensive to process mainly because reagent consumption is higher and more waste is generated. There is a limited market for iron chloride (FeCl_3), copersas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) wastes produced from ilmenite, but some disposal is required.

An alternative titanium resource is perovskite. Perovskite has a formula weight of 135.98 g/mol, a Mohs hardness of 5.5, a specific gravity of 4, and usually a cubic crystal structure. Unaltered, perovskite has the color and luster of broken cast iron; partially altered, it is a pale gray-blue. At the surface, perovskite weathers to anatase, which is yellow in appearance. The mineral frequently contains small amounts of columbium and rare-earth

elements (4). Cerium, lanthanum, and small amounts of other rare earths are known to substitute for calcium in the perovskite lattice.

The 1985 edition of "Mineral Facts and Problems" (5) lists the domestic titanium mineral reserves at 0.2×10^6 st of titanium as rutile and 7.9×10^6 st of titanium as ilmenite. It shows a potential reserve quantity of 6.5×10^6 st of titanium as perovskite. This perovskite is contained in a large untapped deposit in the Powderhorn District, Gunnison County, CO. Evaluation has shown that the perovskite is contained in a pyroxenite mass along with other titaniferous minerals. Physical beneficiation studies have produced concentrates averaging about 50 pct TiO_2 , 2 pct rare earths, and 0.3 pct columbium (6-9).

Another deposit of perovskite occurs near Magnet Cove, Hot Spring County, AR. Its extent is unknown and samples from the area contained 5 pct or less TiO_2 . In both the Magnet Cove and the Powderhorn deposits, part of the titanium is found in nonreactive silicate mineral forms.

There has been substantial prior research on the production of pigment and metal from rutile or ilmenite ores, but only limited information has been published on work conducted with perovskite ores. Perovskite is rather refractory to acid digestion and is not suited to direct production of TiCl_4 by carbochlorination because of its high calcium content.

The U.S. Bureau of Mines reacted perovskite with carbon and lime in an electric arc furnace at high temperature to produce titanium carbide (TiC). The TiC was then chlorinated at relatively low temperature to produce TiCl_4 (9-10). Canadian researchers roasted perovskite at 1,200° C in hydrogen sulfide (H_2S) gas and then leached the resulting material to remove calcium and iron sulfides, leaving TiO_2 (11). Four methods of perovskite treatment were reported from the Soviet Union. In the first method, a sulfuric acid-ammonium sulfate [$\text{H}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$] fusion was employed followed by leaching and precipitation (12). The second method involved a H_2SO_4 leach containing $(\text{NH}_4)_2\text{SO}_4$, and titanium was eventually precipitated as a double salt of ammonia (13). In a third method, perovskite was acid baked with H_2SO_4 and leached with dilute acid to extract titanium (14). In the fourth method, nitric acid was used in an autoclave to extract titanium (15). In general, these methods are energy or reagent intensive or recoveries are lower than desired (<90 pct).

Several processes for recovering rare earths from ores are based on H_2SO_4 leaching (16-18). The most common method is to leach finely ground material with hot H_2SO_4 , which dissolves the rare earths and any thorium, leaving an insoluble residue. After thorium is precipitated by pH adjustment, the rare earths are precipitated using sodium

⁴Italic numbers in parentheses refer to items in the list of references preceding the appendixes at the end of this report.

hydroxide. The precipitation forms an insoluble double salt, $\text{Na(RE)SO}_4 \cdot x\text{H}_2\text{O}$, known as pink salt, where RE represents a rare-earth element.

Double salts containing rare earths are very common, the most important being sulfates and nitrates (19). Sulfate double salt solubilities fall into two general types: light rare earths, or lanthanum through europium; and heavy rare earths, or gadolinium through lutetium and yttrium. Double salts of the light rare earths are only slightly soluble, whereas heavy rare earths have significant solubilities. Addition of sodium sulfate (Na_2SO_4) has been used to precipitate light rare earths as double salts from sulfate leach solutions (20). This method recovered 98 pct of the total rare-earth content. Those rare earths remaining in solution were principally the heavy ones.

To reduce domestic dependence on foreign sources of titanium, the Bureau set about finding more economic and environmentally acceptable methods for processing perovskite. An acid sulfation method for producing TiO_2 from perovskite was developed that offers several advantages over present technology. Investigation results already published describe some methods for recovering byproduct values as well as methods and costs for recovering titanium as TiO_2 pigment (21-24). Two patents regarding the research have been granted (25-26). This report provides a description of the overall process, a description of test work performed in developing each unit operation, and results of the process cost evaluation study. Evaluations based on laboratory-scale studies indicate that perovskite concentrates can be economically processed in an environmentally acceptable manner.

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information. In addition, considerable help was provided that allowed for successful completion of the work by the following Bureau employees: D. A. Martin, chemist (retired), for development of sulfation, leaching, and rare-earth recovery methods; D. K. Steele, chemical engineer, and L. J. Froisland, group supervisor, for development of the sulfation and leaching operations; J. K. Winters, chemist (retired), and C. F. Davidson, group supervisor, for demonstration and development of rare-earth recovery operations, all currently or formerly on staff at the Salt Lake City Research Center, and T. A. Phillips, element manager, Division of Minerals and Materials Science, Washington, DC, formerly with the Office of Process Evaluation.

DESCRIPTION OF PROCESS

Chemical processing of perovskite initially involves reacting the concentrate with strong H_2SO_4 at boiling conditions and filtering off excess acid. The resulting residue, containing sulfates that are insoluble in strong acid, is treated with recycled dilute acid solution to dissolve the titanium, columbium, and rare earths. Filtrate recovered after dilute acid leaching is then treated by evaporation to precipitate titanium as $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ and filtered to recover excess acid. The rare earths and about half the columbium may be recovered as sulfate or oxide residue during regeneration of the acid (27-29). The $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitate is redissolved in water to provide pregnant liquor suitable for preparing TiO_2 . Final conversion of the titanium to TiO_2 involves reducing contaminating iron to the ferrous state, followed by hydrolysis, bleaching, and washing the resulting pigment. Treatment

of perovskite by acid sulfation methods also yields potential calcium sulfate (CaSO_4) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ byproducts.

Each process step described above has been laboratory-scale tested with satisfactory results. The sulfation, dilute acid leaching, and $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation steps were successfully tested under continuous operating conditions. An alternative method of rare-earth recovery, involving double-salt precipitation, was also successfully tested in a continuous unit.

The proposed process flowsheet (fig. 1), and the material balance (table 1), are based upon laboratory test results obtained using Colorado perovskite. Descriptions of the process equipment, conditions, and methods of operation are provided in appendix B.

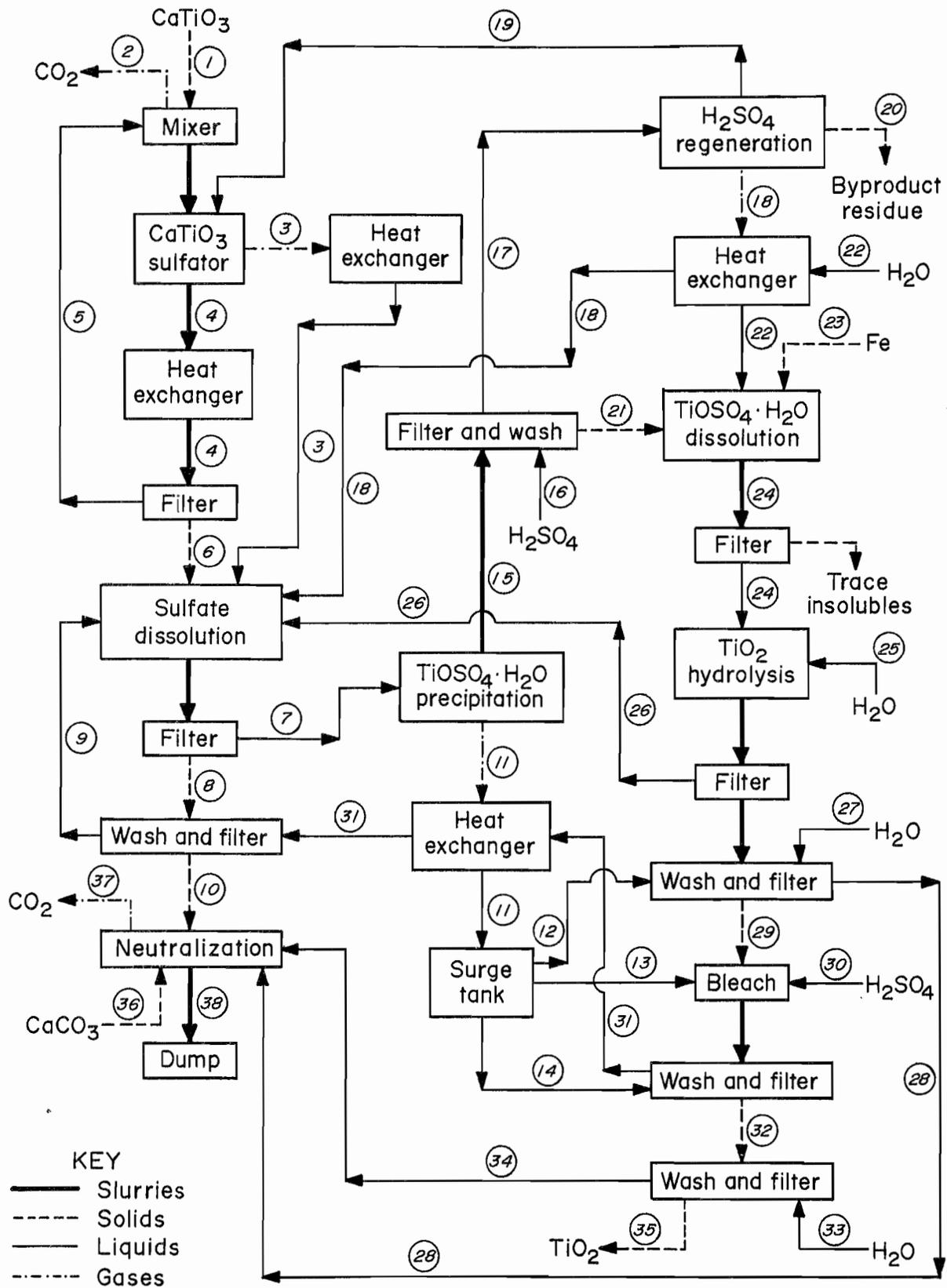


Figure 1.—Flowsheet for TiO_2 production from perovskite. (Circled italic numbers refer to stream description in table 1.)

Table 1.—Material balance for flowsheet shown in figure 1, weight units

Stream and description ¹	Ti	Ca	Fe	CO ₂	H ₂ O	H ₂ SO ₄	SO ₄	Other	Total	Den, g/mL
1—Perovskite concentrate	300	240	21	15				424	1,000	ND
2—Offgas				15					17	ND
3—Vapors or condensate					550	57			607	1.06
4—Sulfation overflow	301	247	23		241	2,262	1,827	124	5,025	ND
5—Recycle acid	1	7	2		168	1,578	26		1,782	1.82
6—Sulfated perovskite	300	240	21		73	684	1,801	124	3,243	ND
7—Leach filtrate	298	4	34		5,152	1,960	713	117	8,278	1.19
8—Damp residue	43	240	5		610	128	656	116	1,798	ND
9—Wash filtrate	37	2	4		2,825	305	89	12	3,274	1.07
10—Damp tailings	7	239	2		626	55	574	104	1,607	ND
11—Vapors or condensate					4,235	86			4,321	1.02
12—Part of stream 11					1,439	29			1,468	1.02
13—Part of stream 11					1,368	28			1,396	1.02
14—Part of stream 11					1,428	29			1,457	1.02
15—TiOSO ₄ ·H ₂ O slurry	298	4	34		917	1,874	713	117	3,957	ND
16—Makeup H ₂ SO ₄					118	1,060			1,178	1.82
17—Precipitation filtrate	2		17		890	2,629	64	17	3,619	1.65
18—Vapors or condensate					601	50			651	1.06
19—Regenerated acid					288	2,579			2,867	1.82
20—Byproduct residue	2		17		1		64	17	101	ND
21—TiOSO ₄ ·H ₂ O precipitate	296	4	17		145	305	649	100	1,516	ND
22—Water					1,728				1,728	1.00
23—Scrap iron			11						11	ND
24—Pregnant liquor	296	4	28		1,874	301	653	99	3,255	1.45
25—Water					1,837				1,837	1.00
26—Hydrolysis filtrate	4	2	14		1,818	419	41		2,298	1.10
27—Water	1				12,916			2	12,919	1.00
28—Hydrolysis wash filtrate	6	1	12		15,601	441	39	2	16,102	1.02
29—Washed TiO ₂ hydrolysate	287	1	2		530	1	53	185	1,059	ND
30—Makeup H ₂ SO ₄					21	185			206	1.82
31—Bleach, 1st wash filtrate	1	1	1		2,841	232	7		3,083	1.05
32—Bleached TiO ₂	286		1		506	11	46	185	1,035	ND
33—Water					14,070				14,070	1.00
34—Bleach, 2d wash filtrate	1		1		14,063	11	3		14,079	1.00
35—TiO ₂	285				513		43	185	1,026	ND
36—Limestone		224		246				89	559	ND
37—Offgas				246					246	ND
38—Neutralized slurry	14	464	5		30,396		1,113	112	32,104	ND

ND Not determined.

¹Streams are represented by circled italic numbers on figure 1.

SAMPLE PREPARATION

Development of process methods involved investigation of four perovskite samples, obtained from the Colorado and Arkansas deposits (two from each deposit). Partial chemical analysis for these as-received samples is shown in table 2.

The Colorado concentrate had previously been prepared by the property owners by crushing and grinding ore containing approximately 7 pct Ti through minus 35 mesh, magnetically removing magnetite, tabling the nonmagnetic fraction to recover perovskite, and cleaning the perovskite by dry high-tension electrostatic separation. This concentrate was used for all the test work presented in this report except where otherwise specified. It primarily consisted of CaTiO₃; however, minor amounts of other

calcium titanates: CaTi₂O₄, CaTi₂O₅, and CaTi₄O₈ were detected. Part of the minus 35-mesh Colorado concentrate was stage ground through minus 65 mesh and minus 100 mesh for use in grind-size studies. Particle size distribution of the three samples is shown in table 3.

The high-grade Colorado surface-rock sample (table 2) was further concentrated by crushing and grinding through minus 35 mesh and magnetically removing magnetite. Chemical analysis of the resulting product (table 4) is similar to the analysis of concentrate prepared by the property owners. The Bureau-prepared concentrate, however, does contain slightly higher quantities of Mg, carbonate (CO₃), and silica (SiO₂). A sample of this concentrate was ground to minus 65 mesh before use in sulfation.

The Arkansas surface and drill-core samples were ground through minus 65 mesh, tumbled, and magnetically treated to produce concentrates. Analyses for these concentrates are also shown in table 4. Mineralogical analyses show that the Arkansas samples contained titanium as perovskite, ilmenite, and an undetermined disseminated form associated with augite ($\text{CaMgSi}_2\text{O}_6$). Limited beneficiation of the Arkansas ore produced concentrates with significantly improved quantities of titanium and columbium.

Table 2.—Partial chemical analysis of perovskite samples received, percent

Component	Concentrate ¹	Surface rock ¹	Surface rock ²	Drill core ²
Ti	30.0	26.7	4.1	3.7
Ca	24.0	21.1	14.8	15.8
Fe	2.1	5.7	12.5	10.5
CO ₃	2.0	3.2	ND	ND
SiO ₂	1.6	9.9	ND	ND
Ce96	.73	ND	ND
Mg95	1.2	4.7	4.4
La49	.40	ND	ND
Al4	.41	4.4	3.7
Cb28	.28	.02	.02
Y027	ND	ND	ND
Th017	ND	ND	ND
U008	ND	ND	ND

ND Not determined.

¹Colorado.

²Arkansas.

Table 3.—Size distribution of Colorado concentrate, percent

Size, mesh	Sample 1 ¹	Sample 2 ²	Sample 3 ³
Minus 35 plus 48	17.6	0	0
Minus 48 plus 65	47.0	0	0
Minus 65 plus 100 . . .	20.4	69.1	0
Minus 100 plus 150 . . .	9.4	7.9	33.4
Minus 150 plus 200 . . .	3.1	6.5	27.6
Minus 200 plus 270 . . .	2.0	5.5	13.1
Minus 270 plus 4004	8.9	18.5
Minus 4001	2.1	7.4

¹As-received minus 35-mesh concentrate.

²Minus 65-mesh reground concentrate.

³Minus 100-mesh reground concentrate.

Table 4.—Analysis of Bureau-prepared concentrates, percent

Component	Surface rock ¹	Surface rock ²	Drill core ²
Ti	29.8	15.7	16.5
Ca	23.4	23.9	19.9
SiO ₂	3.7	19.3	14.4
CO ₃	2.9	.1	.1
Fe	2.0	5.3	12.1
Mg	1.3	2.7	1.5
Ce92	.64	.43
La50	.24	.20
Al33	1.42	.96
Cb32	.18	.20

¹Colorado.

²Arkansas.

EXPERIMENTAL DESIGN

Investigations focused on high-temperature (150° to 300° C), atmospheric-pressure H₂SO₄ digestion of perovskite concentrates to convert titanium, calcium, columbium, rare earths, and other elements to strong acid insoluble sulfates. Methods were then developed for dissolving and recovering metal values contained in the sulfation residue.

ACID SULFATION PROCEDURE

Two types of acid sulfation tests were conducted. Batch tests were performed to help pick operating conditions for continuous sulfation. Continuous tests were performed to more fully explore the complex relationship between variables, to determine what problems would be encountered in a continuous sulfation unit, and to provide sulfated product for subsequent leaching studies.

Batch Sulfation

In batch sulfation test work, 75-g samples of perovskite concentrate were treated in 1.5 L of hot H₂SO₄ solution. A 2-L glass reactor vessel was used, which had the wall fluted in four equal-spaced areas to form mixing baffles. The reactor was stirred, unless otherwise noted, at 1,000 rpm with a six-bladed Teflon⁵ fluorocarbon polymer impeller.

Small samples of the digestion slurry were periodically withdrawn by vacuum through a sampling tube and analyzed. To confirm the accuracy of these multiple sampling studies, tests were also conducted with sampling occurring only at the end of the test. The relative initial amounts of

⁵Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

concentrate and acid solution used in testing is referred to as the pulp-solids ratio.

Continuous Sulfation

Two different continuous sulfation units were operated. A nonstirred settler-type unit was used with minus 35-, 65-, and 100-mesh feed. A mechanically agitated two-stage sulfation unit was used with the coarser minus 35-mesh feed. The two systems were similar, except that in the first system, agitation was provided during sulfation by the boiling action of escaping steam; in the second system, additional agitation was provided by mechanical means.

Settler System

Perovskite concentrate was fed at 5.0 g/min by a 0.5-in-diameter screw feeder into a nonheated premixer. Fresh H_2SO_4 solution at room temperature, equivalent to that consumed by the sulfation reaction (7.0 mL/min), was added by pumping. The premixer was constructed from a 400-mL beaker, modified with three equal-spaced fluted areas to form mixing baffles. The premixer overflowed at the 150-mL level and was equipped with a baffle to prevent steam, in the subsequent sulfation unit, from discharging at the premixer. A 1-in-diameter, three-bladed polypropylene impeller provided the mixing action. At room temperature, perovskite reacted very slowly with acid; however, the small quantity of calcium carbonate (CaCO_3) contained in the concentrate was rapidly reacted, giving off carbon dioxide (CO_2).

The resulting slurry overflowed into a 2-L smooth-sided glass reaction vessel where the perovskite was rapidly sulfated. This vessel employed no stirring mechanism. Water produced through reaction formed steam that provided good agitation in the top half of the vessel. Solid reaction products settled to the bottom of the reactor and were continuously drained through a control stopcock. The reaction vessel was equipped with a heating mantle and a glass top with ports for feeding, temperature sensing, and steam exhaust. Water-cooled condensers were used to recover the exhaust steam.

A nominal 15-min sulfation time was used. This was done by feeding perovskite concentrate and acid into the sulfation unit for 15 min before opening the discharge drain. This volume of slurry in the reactor was then maintained by visual observation and manual control of the discharge stopcock.

To promote rapid reaction and to provide slurry fluidity, the pulp-solids ratio in the vessel was maintained at a low level (about 2 g of concentrate for each 20 mL of acid solution). This was accomplished by starting with and maintaining an excess acid-solution volume of about 650 mL in the sulfation unit. Settled material continuously

discharged from the bottom of the reactor and was recovered by filtration. Two 6-in-diameter Teflon fluorocarbon polymer vacuum filters were alternated to collect the sulfated perovskite and recover unused acid for recycle. This acid (about 7.0 mL/min) was continually pumped through a preheater back into the sulfation unit. After about 2-h of operation, steady-state conditions were reached.

Agitated System

The equipment used for agitated-sulfation testing is shown in figure 2. The scale and type of equipment shown is representative of the scale and equipment used throughout the investigation.

Numbers in parentheses in this section refer to items of equipment found in figure 2. Perovskite concentrate was fed at a constant rate by a 0.5-in-diameter screw feeder (1) into a nonheated premixer (2) constructed from a 400-mL beaker. The construction of the premixer was described in the previous section. Fresh room-temperature acid, equivalent to that consumed by the sulfation reaction, was also pumped into the premixer. A 1-in-diameter, three-bladed polypropylene impeller provided the mixing action. Recycled acid was pumped at constant rate into a 2-L glass acid preheater vessel (3), modified to overflow at 1.6-L capacity. Overflows from the premixer and the acid preheater were fed separately into the upper reactor vessel (4) where, at elevated temperature perovskite was rapidly sulfated. The reactor vessels (4 and 5) were respectively 2-L and 1-L glass reactors, each equipped with a glass top with ports for feeding, temperature sensing, mechanical agitation, and steam exhaust. The reactors were stirred at 1,200 rpm using 2.25-in-diameter Teflon fluorocarbon polymer impellers. The reactor bottoms had fluted sidewalls to provide baffles for mixing. The bottoms were also equipped with a stopcock outlet to facilitate cleanout and a baffled overflow port at the 500-mL level. Overflow of slurry from the first reactor fed the second reactor, and overflow from the second reactor was filtered. The reactors were sealed and the overflow ports were baffled to ensure that water released by the sulfation reaction escaped only through ports in the reactor top, connected to water-cooled condensers. Two 6-in-diameter Teflon fluorocarbon polymer vacuum filters (6) were alternated to collect the sulfated perovskite and unused acid for recycle.

The retention time was controlled by adjusting the perovskite concentrate and acid solution feed rate. Mean retention times were determined by using a barium sulfate (BaSO_4) tracer and by analyzing effluent products. Calculations were based on assumption that the physical behavior of BaSO_4 was similar to that of sulfation reaction products.

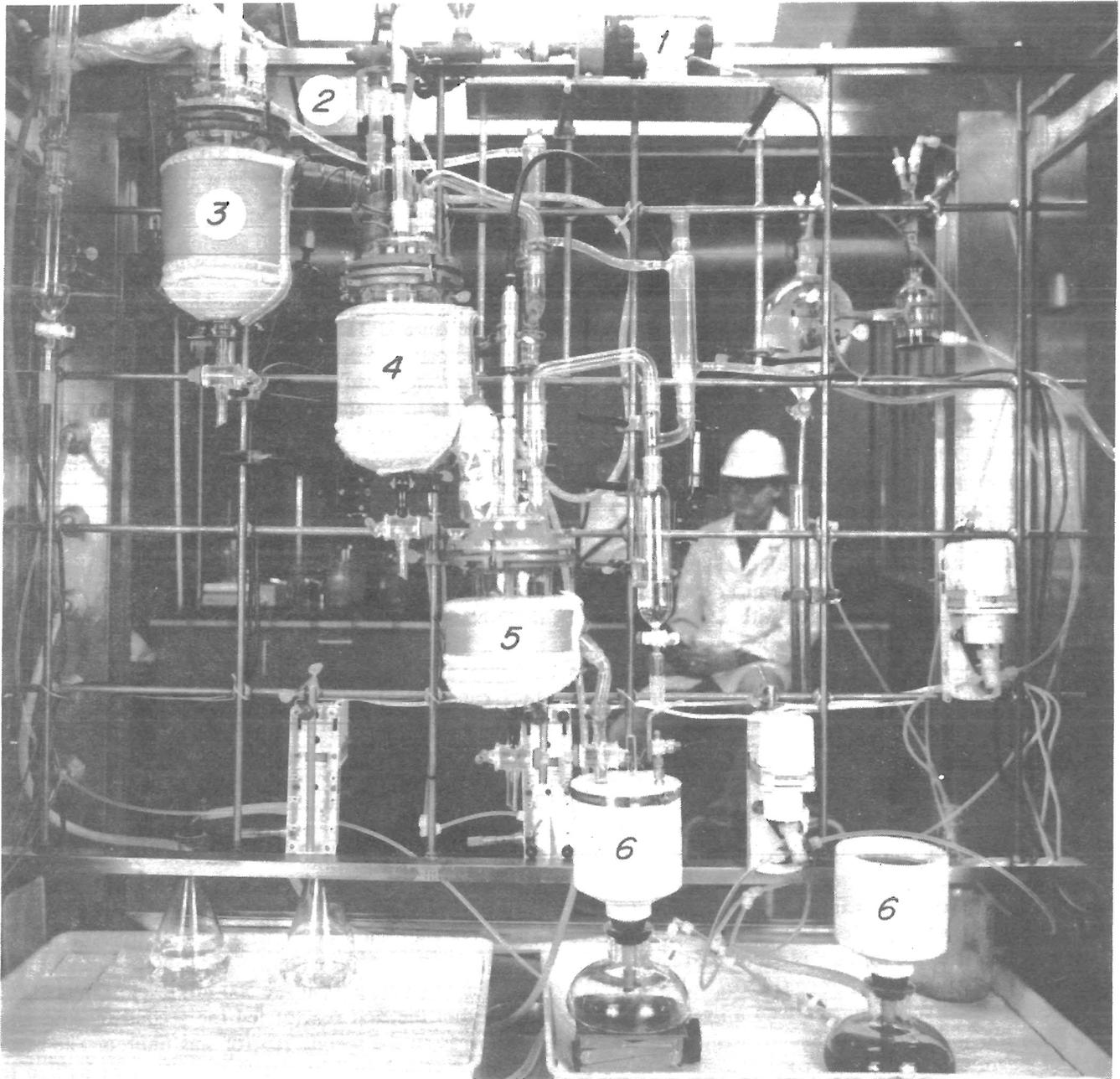


Figure 2.—Agitated continuous sulfation system. (Numbered equipment items are described in the text.)

WATER-LEACHING PROCEDURE

A standard batch water-leaching procedure was used to help determine the extent of sulfation achieved in each batch or continuous sulfation test. Batch leaching studies were performed to help determine conditions required for extracting titanium and byproducts from sulfated perovskite. Continuous leaching tests were then conducted to verify batch leaching results and to evaluate methods of continuous leaching.

Standard Leaching

Filtered residues from all sulfation tests were weighed, and then approximately 100-g of each sample was leached in 80° C water for 1 h with a solid-to-water weight ratio of 1:3. Leaching was accomplished in stoppered flasks heated on hotplates; stirring was done with a magnetic bar. The leached residues were filtered and washed with 300 mL of cold water. The filtrate and filter cake analyses were used to calculate extraction results and the degree of sulfation.

In batch sulfation tests, the overall degree of sulfation was determined by totaling constituents of the acid sulfation filtrate with those extracted during the standard leaching operation. After reaching steady-state conditions in continuous sulfation tests, the overall degree of sulfation was represented simply by the extraction results obtained through standard leaching of the sulfation residue.

Batch Leaching

Batch leaching studies were conducted in a 1-L glass vessel with sidewalls fluted to provide baffles for mixing. The four-neck glass top of the vessel was fitted to accommodate an impeller shaft, a temperature sensor, a condenser column (to prevent evaporation loss), and a water-cooled glass cooling coil (operated in only a few tests). A 1.75-in-diameter, three-bladed plastic impeller provided the agitation.

Before each test, the vessel was warmed to about 80° C in a heating mantle. The sample of sulfated perovskite was then leached with solution preheated to a temperature 20° C below the target operating temperature. Heat released by dissolution then raised the slurry temperature up to the desired range within 2 to 5 min. Slurry samples ranging from 80 to 100 mL were removed through a vacuum tube at time intervals of 15, 30, 45, 60, 75, and 90 min. Each sample was filtered and washed with 100 mL of cold water. The filtrates and dried residues were then analyzed to determine leaching results. The conditions used for all tests, unless otherwise stated, included leaching at 30-pct solids for 90 min at 60° C with a 1,100-rpm impeller.

Continuous Leaching

Continuous leaching of sulfated perovskite was studied to validate batch leaching data and to identify possible problems that might be encountered in large-scale leaching operations. Initial tests were conducted in a cocurrent system. Later, a countercurrent system was used in an attempt to improve the extraction of less-soluble rare-earth metal values.

Cocurrent Leaching System

In the cocurrent continuous leaching system, sulfated perovskite was fed at a constant rate by a 1-in-diameter screw feeder to the first of two leaching vessels. These vessels were 1- and 2-L glass reactors with fluted sidewalls to provide baffles for mixing. Both vessels were equipped with four-neck glass tops and modified at the side discharge point by the attachment of an overflow port and a steam baffle. In the first or upper vessel, the overflow port was positioned to allow for a 1,000-mL retention

volume. In the second or lower vessel, the spout was positioned to allow for a 400-mL retention volume. The total nominal retention time was about 90 min. Each vessel was agitated at 1,100 rpm by a 2.25-in-diameter, three-bladed Teflon fluorocarbon polymer turbine impeller.

The leaching pulp overflowed from the first vessel into the top of the second vessel, and from the second vessel onto a 6-in-diameter Teflon fluorocarbon polymer vacuum filter. The leach filtrate was recovered by pumping to a collection receiver. At 30-min intervals, the overflow slurry was advanced to a clean filter. The residue was then washed with either water or 20-pct H₂SO₄. The filtrate from washing was pumped to a reservoir system, from which it was metered and pumped to the first vessel for mixing with sulfated perovskite. Temperature control was achieved in both vessels with external heating mantles. The system was designed with internal cooling coils, but these were not needed.

Countercurrent Leaching System

In the first stage of countercurrent leaching, sulfated perovskite was fed by a 1-in-diameter screw feeder into a 2-L vessel, where it was mixed with solution recovered by filtering effluent from the second stage of leaching. This vessel had fluted sidewalls for mixing and was modified at the side discharge point by the attachment of an overflow port and a steam baffle. The vessel was also fitted with a four-neck glass top, with ports for feeding, temperature sensing, and mechanical agitation. The feed well was a 0.5-in-diameter glass tube with a flared funnel-type opening inserted through one of the necks in the reactor top. Required heat was supplied with an external heating mantle. A 1.5-in-diameter flat-bladed Teflon fluorocarbon polymer impeller provided agitation at about 1,000 rpm. The unit was operated so that the vessel retention volume was about 950 mL.

Slurry from this vessel overflowed to a 1-L settler with smooth side-walls. The settler was equipped with an external heating mantle, a bottom drain, and a four-neck glass top, with ports for slurry inlet, temperature sensing, mechanical agitation, and withdrawal of leach filtrate by pumping. The feed well was similar to that described above, except the glass tube extended down into the settling zone. The settler was slowly raked at about 3 rpm by a 2-in-high Teflon fluorocarbon polymer paddle, shaped to conform to the inside of the vessel. Pregnant liquor was drawn off the top by a pump and collected in a graduated cylinder. The heavier sludge reporting to the bottom of the settler was removed at a constant rate through the bottom outlet by a pump and fed to the second stage of leaching. A retention volume of about 1,000 mL was maintained in the settler.

Equipment for the second stage of leaching was similar to that used in the first stage, except the vessel was made from a 1-L glass reactor and was operated with a retention volume of about 260 mL. Stirring was provided at 250 rpm with a 2.25-in-diameter, three-bladed Teflon fluorocarbon polymer turbine impeller. This vessel was continuously fed by underflow from the settler and by filtrate obtained from washing the final leach tailings. Solids obtained by filtering the pregnant leach liquor at 30-min intervals were manually added back into the second stage of leaching through an available port in the top of the leaching vessel. Overflow from this stage of leaching was collected and filtered using a 6-in-diameter Teflon fluorocarbon polymer vacuum filtration unit. The resulting filtrate was continuously forwarded to the first stage of leaching by a pump. Solid tailing material recovered on the filter was advanced at 30-min intervals to a washing operation where it was washed with sufficient dilute acid solution (7.55-pct H_2SO_4) to provide adequate makeup solution for leaching. Filtrate produced by washing the tailing was continuously returned to the second stage of leaching by another pump.

RARE-EARTH PRECIPITATION PROCEDURES

Double-salt precipitation methods were investigated for recovering rare earths from perovskite leach filtrates. Na_2SO_4 was the precipitant used. Both batch and continuous precipitation methods were evaluated.

Batch Precipitation of Rare Earths

Batch tests were conducted by adding a measured amount of solid Na_2SO_4 to a fixed volume of leach filtrate and agitating in a constant temperature shaking bath for a specified time. The double-salt precipitate was filtered, and the resulting filtrate was analyzed for rare-earth content to determine the degree of precipitation.

To provide a larger quantity of solution for subsequent preparation of TiO_2 pigment, batch precipitation of rare earths from 9.6 L of leach filtrate was performed in a 4-gal plastic bucket heated with an immersion heater. Agitation was provided with a 1.75-in-diameter, three-bladed marine-type impeller operated at about 700 rpm. The top of the bucket was covered with plastic to minimize moisture loss by evaporation. Precipitation was accomplished by dissolving 30-g/L Na_2SO_4 in the stirred leach filtrate, followed by heating the solution to 60° C, and holding the solution at this temperature for 3 h. The precipitate was then recovered by filtration.

Continuous Precipitation of Rare Earths

Continuous precipitation was tested in a two-stage cocurrent system. Reactor temperatures were maintained

by circulating water from a constant temperature bath through jacketed sleeves on the reactors. Leach filtrate and Na_2SO_4 solution were heated to the same temperature as the precipitation reactors by using a constant temperature bath. The Na_2SO_4 was added in the upper precipitation reactor as a saturated solution. Solutions were mixed and the precipitated rare earths were maintained in suspension by stirring with a turbine-type impeller. Reaction time was determined by the flow rate at which the leach and Na_2SO_4 solutions were added to the reactors. Gravity feed was used to transfer the overflow from the first reactor to the second reactor, and from this reactor to the filter. A time-weighted average of the amount of rare earth removed from the solution was used to determine the degree of precipitation.

$\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ PRECIPITATION PROCEDURES

Both batch and continuous methods for precipitation of $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ from pregnant sulfate solutions were tested.

Batch Precipitation of $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$

Batch precipitation of $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ first required heating the leach filtrate in an Erlenmeyer flask to drive off water to concentrate the solution. Heat and agitation was provided using a magnetically stirred hotplate. The flask was insulated to minimize refluxing of moisture. When the boiling temperature reached 150° C, the solution was cooled to 140° C. The top of the flask was then covered with a loosely fitting rubber stopper containing the thermometer to help prevent further moisture loss. Temperature was maintained at 140° C, and mild magnetic agitation was employed until precipitation was complete. Sampling was performed by periodically aspirating and filtering small quantities of slurry to obtain solid precipitate and acid filtrate products. The degree of precipitation was determined by assaying for titanium.

Continuous Precipitation of $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$

Continuous precipitation of $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ was conducted in a 1-L glass reactor. This vessel had fluted sidewalls which served as mixing baffles, and was fitted with a steam-baffled overflow and a bottom outlet. The bottom outlet was not used. The volume inside the vessel occupied by slurry was about 430 mL. The reactor had a four-neck glass top fitted with ports for pumping in fresh feed solution, temperature sensing, continuous mechanical agitation, and steam exhaust. Agitation was supplied using a 1.5-in-diameter, flat four-blade Teflon fluorocarbon polymer impeller, rotated at about 440 rpm. Heat for evaporation was provided by a heating mantle. The top of the vessel was heated with electric resistance tape and was covered by insulation. Leach filtrate was continuously

pumped into the evaporation precipitation unit. Overflow slurry was discharged into a filter to separate the $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitate and acid filtrate. Distillate from the evaporator was recovered in a condenser unit.

H_2SO_4 REGENERATION PROCEDURE

Acid regeneration was tested with batch equipment. The 1-L glass evaporation unit used was similar to that used for $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation. The bottom of the evaporator, however, had no side or bottom outlets, and no method of agitation was employed. The four-neck glass top of the vessel was connected to an acid condenser and a collection unit. A glass thermometer was used in the upper part of the reactor to monitor vapor temperature. The other ports in the vessel top were closed with glass stoppers. An electric mantle supplied heat to the bottom of the unit while the top was heated with electric resistance tape. The unit was covered with insulation to minimize refluxing.

Filtrate from the $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation operation was heated until all the moisture and acid had been removed by evaporation. The H_2SO_4 and some moisture were recovered in the acid condenser. Residual salts were recovered from the bottom of the evaporator. The evaporation unit was designed primarily to produce a quantity of residual salts for evaluation. Rigorous concentration of the acid was not attempted.

$\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ DISSOLUTION AND IRON REDUCTION PROCEDURE

Dissolution of $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ and iron reduction was performed in a 5-L glass reaction vessel with fluted side-walls, as baffles for mixing. A four-neck glass reaction top was used. This provided ports for temperature sensing, mechanical agitation, and steam recovery. Agitation employed a 2.5-in-diameter, flat-blade Teflon fluorocarbon polymer impeller, rotated at about 670 rpm. The steam condenser minimized loss of moisture by returning it to the dissolution vessel. Heat was supplied by a heating mantle. Dissolution involved slurring the solids in aqueous solution and raising the temperature to 80° C for about 90 min. Sufficient iron metal was used to reduce all the Fe^{3+} to Fe^{2+} and reduce enough of the titanium to produce a solution containing about 1.5-g/L Ti^{3+} . Reduction with iron metal chips at 80° C required about 60 min. The solution was then filtered to remove a trace amount of insoluble material. The resulting pregnant liquor was stored in a closed plastic container with a protective CO_2 atmosphere, to limit oxidation of Ti^{3+} and Fe^{2+} .

TiO_2 HYDROLYSIS PROCEDURE

Precipitation of TiO_2 is facilitated by the addition of seed nuclei. The method of seed preparation used was similar to that outlined by Blumenfeld (29).

In some tests, seed was prepared from an iron-free acidic solution of titanium sulfate obtained by sulfation and aqueous dissolution of commercially obtained TiO_2 pigment. The method for digesting the TiO_2 was much the same as that previously described for sulfation and dissolution of titanium from perovskite. In other tests, the seed was prepared using pregnant liquor resulting from the $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ dissolution and iron reduction operation.

To prepare nuclei for seeding TiO_2 hydrolysis, the starting solution was gradually added over a 4- to 6-min period to an equivalent weight of water, heated to 85° to 99° C in an Erlenmeyer flask. Heat was supplied and agitation was provided with a combination magnetic-stir and hotplate unit. About 2 min after final addition of the starting titanium sulfate solution, before appreciable white precipitate had formed, the solution was removed from the hotplate and cooled to limit further precipitation.

Hydrolysis for production of TiO_2 pigment was performed in the same 5-L glass reaction unit previously used for $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ dissolution and iron reduction. Pregnant liquor produced in the $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ dissolution and iron reduction operation was first heated to about 99° C with the heating mantle. A measured quantity of the solution containing seed nuclei was then added. The seed material was mixed with the liquor using agitation provided by a 2.5-in-diameter Teflon fluorocarbon polymer impeller. Temperature was maintained and agitation was continued for several hours. The condenser minimized water loss due to evaporation. During the operation, a measured amount of water was added to facilitate precipitation. The method of water addition was obtained from a domestic pigment producer and is considered proprietary. The literature contains descriptions for methods of TiO_2 precipitation involving little or no water addition (30-32). After hydrolysis, the slurry was forwarded to the washing and bleaching operation.

PIGMENT WASHING AND BLEACHING PROCEDURE

Slurry from the hydrolysis operation was filtered to recover the acid filtrate and TiO_2 . The cake was washed with a dilute, pH 1.7, H_2SO_4 solution to wash away iron and soluble salts. The wash solution also contained a small amount of Ti^{3+} (0.05 g/L), to maintain reducing conditions. About 33 parts wash solution was used per part TiO_2 contained in the cake.

The Ti^{3+} used for preparing wash solution was obtained by metallic aluminum reduction of iron-free titanium solution previously described for preparing seed material in TiO_2 hydrolysis. The pigment industry also prepares Ti^{3+} wash solution by dissolving titanium metal in hydrochloric acid.

To bleach the pigment after washing, the damp cake was transferred back into the 5-L vessel used for hydrolysis, and slurried at 20-pct solids with solution containing 10-pct H_2SO_4 and 0.1-g/L Ti^{3+} . The slurry was heated to 60° C and temperature was maintained for a 6-h period, to remove iron and soluble impurities. Continuous agitation was supplied by the impeller at 240 rpm.

TEST RESULTS AND DISCUSSION

Test evaluations were conducted in the following areas of interest: (1) acid sulfation of perovskite, (2) leaching of metal values from sulfation residues, (3) recovery of dissolved rare earths by double-salt precipitation, (4) formation of $TiOSO_4 \cdot H_2O$ precipitates, (5) H_2SO_4 regeneration, (6) $TiOSO_4 \cdot H_2O$ dissolution and iron reduction, (7) TiO_2 hydrolysis, (8) pigment washing and bleaching, (9) pigment evaluation, and (10) toxicity of solid wastes.

ACID SULFATION TESTING

Batch acid-sulfation tests were conducted to determine effects of several operating variables on the rate of perovskite sulfation. Continuous sulfation tests were conducted for a comparison with batch test data and to determine if continuous operation afforded any advantage. Sulfated perovskite residues were subsequently leached by batch and continuous methods to help evaluate sulfation procedures and to determine optimum conditions for extraction of titanium and byproduct values.

Variables found to affect sulfation reaction rates included the degree of agitation, the pulp-solids ratio, the particle size, and the combination of the temperature and acid concentration. Temperature and acid concentration were considered as a single variable because all tests were conducted at the solution boiling point. By operating in this manner, a constant acid concentration was maintained. Operating at a temperature below the boiling point in continuous systems results in dilution of the acid with by-product water until the solution boiling point drops to the operating temperature.

During sulfation perovskite is digested and precipitates as $CaSO_4$ and one or more forms of titanium sulfate. Columbium and rare earths are also precipitated. At lower temperatures, the precipitation reaction is slower than at higher temperatures, and substantial quantities of titanium can be found in the acid filtrate. Titanium, precipitated as

The slurry was then filtered to separate TiO_2 pigment from the bleaching solution. The resulting pigment cake was finally washed to remove residual soluble ions. Washing used about 30 parts water per part contained TiO_2 .

SOLID WASTE TOXICITY TESTING

Solid wastes produced during leaching and solution neutralization were tested for hazardous waste identification using toxicity test procedures established by the U.S. Environmental Protection Agency (EPA) (33).

a salt during sulfation, is redissolved by water leaching of the sulfation residue. The degree of sulfation is determined after analyzing the acid filtrate produced during sulfation along with the filtrate and tailing produced by subsequent water leaching. The quantity of material reporting in the acid filtrate and the leach filtrate indicates the overall degree of sulfation. An example showing how the distribution of titanium changes with time when sulfation is performed at relatively low temperature (150° C) is shown in figure 3.

When the temperature is increased above 200° C, precipitation of titanium sulfate is very rapid and, except at short retention times, only low titanium concentrations

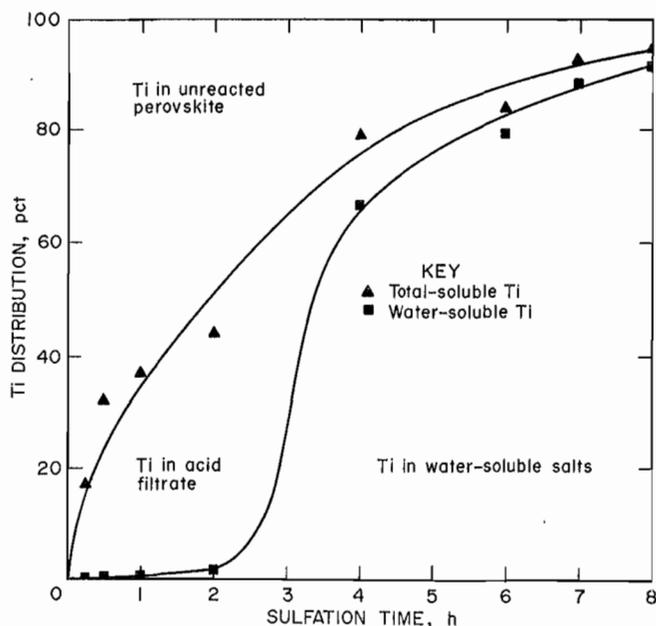


Figure 3.—Titanium distribution during sulfation. Sulfation with 64-pct- H_2SO_4 solution at 150° C using minus 100-mesh concentrate, 1:20 pulp-solids ratio, and 1,000-rpm impeller.

appear in the acid filtrate. Chemical analysis of acid sulfation filtrates and standard water leaching products are shown in table 5. Sulfation tests were conducted using minus 100-mesh concentrate at 250° C with 90-pct H₂SO₄ solution at a pulp-solids ratio of 1:20 and a 1,000 rpm impeller.

Table 5.—Products of acid sulfation and water leaching

(Test conducted using minus 100-mesh concentrate at 250° C with 90-pct H₂SO₄ at pulp-solids ratio of 1:20 and 1,000-rpm impeller)

Sulfation time and sample	Ti	Ce	La	Cb
2.5 min:				
Acid solution g/L . .	15.1	0.62	0.25	0.21
Water-leach solution . . . g/L . .	1.6	0.14	0.06	0.02
Water wash g/L . .	0.2	<0.01	<0.01	<0.01
Residue pct . .	14.0	0.38	0.18	<0.01
5 min:				
Acid solution g/L . .	2.8	0.03	0.02	0.08
Water-leach solution . . . g/L . .	20.7	0.65	0.32	0.18
Water wash g/L . .	1.7	0.08	0.04	0.01
Residue pct . .	3.9	0.26	0.08	<0.01
10 min:				
Acid solution g/L . .	1.8	0.03	0.01	0.10
Water-leach solution . . . g/L . .	22.1	0.68	0.33	0.22
Water wash g/L . .	1.8	0.07	0.03	0.01
Residue pct . .	1.5	0.19	0.06	<0.01
120 min:				
Acid solution g/L . .	1.3	0.01	0.01	0.18
Water-leach solution . . . g/L . .	31.4	0.79	0.41	0.39
Water wash g/L . .	3.8	0.13	0.06	0.04
Residue pct . .	1.6	0.30	0.09	<0.01

These data clearly show that the titanium, and to a large extent the columbium and rare earths, are initially solubilized by the acid and then precipitated.

Batch Sulfation

The operating variables investigated included agitation, pulp-solids ratio, grind size, the combination of temperature and acid concentration, and extended sulfation time.

Effect of Agitation on Sulfation

Batch sulfation tests were conducted using impeller speeds of 0, 300, 600, 1,000, and 1,200 rpm, which ranged from no mechanical agitation to vigorous agitation. Sulfation conditions included operating at 200° C, in 1-h tests conducted with minus 35-mesh material and 80-pct H₂SO₄, at a pulp-solids ratio of 3:20 (3.0 g of concentrate to 20 mL of acid solution). Use of the various impeller speeds sulfated 36, 58, 64, 87, and 87 pct, respectively, of the titanium (fig. 4). Under these conditions, increased agitation always increased the percent titanium sulfation.

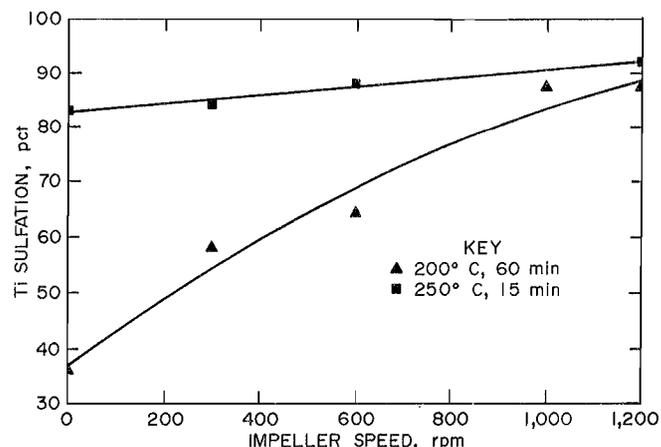


Figure 4.—Effect of agitation on sulfation. Sulfation using minus 35-mesh concentrate and 3:20 pulp-solids ratio.

Results from a similar series of tests conducted at 250° C for 15 min are also plotted in figure 4 and show that at this high temperature, the effect of impeller speed is nearly eliminated. A 15-min test conducted without mechanical agitation at 300° C with 96-pct H₂SO₄ achieved 95-pct sulfation of the titanium using minus 35-mesh concentrate. Similar 15-min tests conducted at 250° C with 90-pct H₂SO₄ using minus 100-, 65-, and 35-mesh concentrates respectively achieved 96-, 93-, and 87-pct sulfation of the titanium. Sulfation results obtained in tests conducted at 200° C with 80-pct H₂SO₄ were significantly lower than those obtained with higher temperature and acid concentration even though the retention time was extended to 1 h.

To minimize agitation effects and to provide consistency in testing, all further batch-sulfation work was conducted at 1,000 rpm. The complete listing of sulfation and water leaching results for columbium, cerium, lanthanum, and titanium can be found as tests 1-18 of table A-1, found in appendix A.

Even in tests conducted without mechanical stirring, the slurry was agitated by the boiling action of water vapor released through chemical reaction. When tests were run with finer mesh concentrate or when the temperature and acid concentration were increased, the boiling action increased visibly.

Effect of Pulp-Solids Ratio on Sulfation

Increasing the ratio of concentrate weight (gram) to acid solution volume (milliliter) decreased titanium sulfation. With 80-pct H₂SO₄, at 200° C, using minus 35-mesh concentrate and a 1,000-rpm impeller, 92-pct sulfation was achieved in 2 h when the pulp-solids ratio was 1:20. As shown in figure 5, when the ratio increased to 8:20, the percent sulfation decreased to 71 pct.

Maximum sulfation was not appreciably affected by the pulp-solids ratio, but the time required to achieve maximum sulfation generally increased as the ratio increased. Over 90-pct sulfation occurred in 2 h at ratios of 1:20 and 3:20 and in 4 h at a ratio of 5:20. At a 8:20 ratio, only 83-pct sulfation occurred in 6 h; however, titanium sulfation was still increasing when the test was terminated. These data are presented in table A-1, tests 19-22.

Effect of Grind Size on Sulfation

The initial grind size of concentrate was varied to determine the effect on titanium sulfation. Part of the minus 35-mesh concentrate was used directly and part was stage ground to minus 65 mesh and minus 100 mesh. The samples were sulfated in time studies conducted with a pulp-solids ratio of 1:20 using 80-, 90-, and 96-pct H_2SO_4 solutions at temperatures of 200°, 250°, and 300° C while using a 1,000 rpm impeller. Sulfation residues were then treated by standardized water leaching.

Sulfation tests conducted using minus 35-, 65-, and 100-mesh concentrate at 200° C for 2 h in 80-pct H_2SO_4 sulfated 92, 95, and 96 pct, respectively, of the titanium. As indicated in table A-1, tests 19, 28, and 29, the sulfation time required to achieve maximum sulfation decreased as particle size decreased. Maximum sulfation was achieved in 2 h, 1 h, and 30 min for the minus 35-, 65-, and 100-mesh concentrates, respectively. Thus, decreasing the particle size had little effect on the maximum amount of titanium sulfated, but did increase the sulfation rate.

Similar sulfation time studies were conducted at 250° C with 90-pct H_2SO_4 , and at 300° C with 96-pct H_2SO_4 . (See table A-1, tests 27 and 30 through 34.) As previously seen, the finer mesh perovskite reacted more rapidly. Operating at higher temperatures and acid concentrations shortened the time required for sulfation and slightly improved overall titanium sulfation.

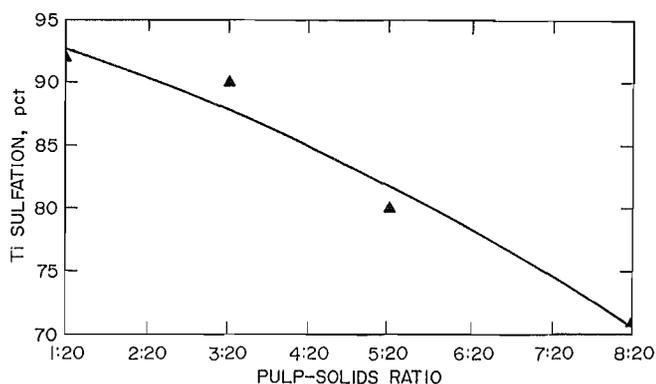


Figure 5.—Effect of pulp-solids ratio on sulfation (grams of concentrate to milliliters of acid solution). Sulfation for 2 h at 200° C with 80-pct H_2SO_4 using minus 35-mesh concentrate and 1,000-rpm impeller.

Effect of Temperature and Acid Concentration on Sulfation

Sulfation of perovskite concentrate was investigated over a temperature span of 150° to 300° C. The tests were run at acid solution boiling points, with the H_2SO_4 concentration ranging from 64 to 96 pct. All sulfation tests were run at the 1:20 pulp-solids ratio with a 1,000-rpm impeller.

Sulfation of minus 35-mesh concentrate at temperatures of 200°, 250°, and 300° C with 80-, 90-, and 96-pct H_2SO_4 for 2 h, respectively sulfated 92, 94, and 95 pct of the titanium. Little benefit was gained by raising the temperature above 250° C. (See figure 6 and table A-1, tests 19, 30, and 32.)

Sulfation tests were conducted with minus 100-mesh concentrate at 150°, 165°, 185°, 200°, 225°, 250°, and 300° C, with the following respective acid concentrations, in percent: 64, 70, 76, 80, 86, 90, and 96. (See table A-1, tests 26-27, 29, and 34 through 37.) The degree of titanium sulfation achieved within 2 h in each test was 44, 90, 98, 96, 97, 96, and 96 pct, respectively. Underlined values

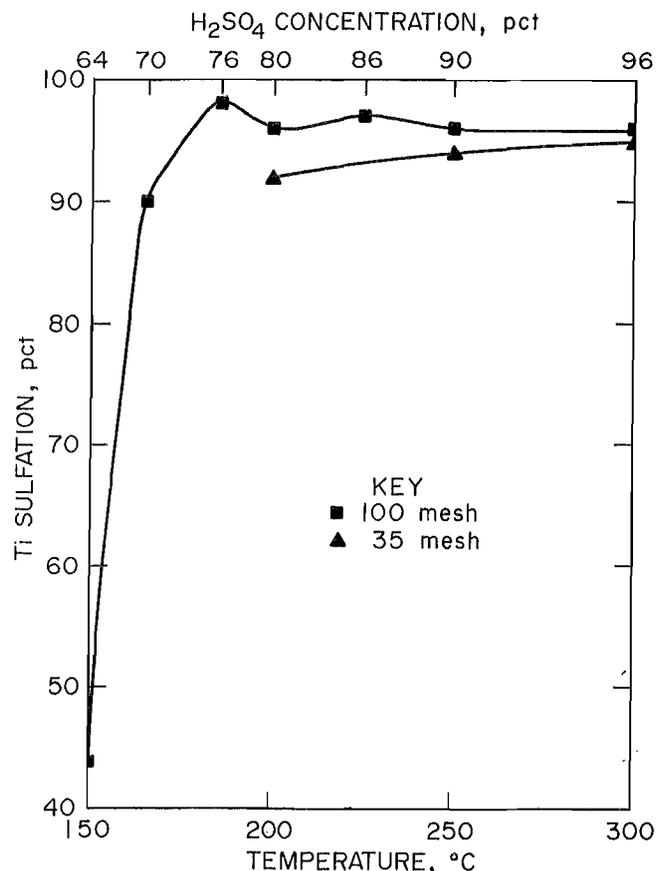


Figure 6.—Effects of temperature and acid concentration on sulfation of coarse- and fine-mesh concentrates. Sulfation retention time 2 h, 1:20 pulp-solids ratio, and 1,000-rpm impeller.

were determined by extrapolation of test data. These data indicate that when minus 100-mesh concentrate was used, raising the temperature above 185° C had little benefit (fig. 6). Filtration of the slurry was rapid when the sulfation temperature was >200° C, and slower when sulfation occurred at lower temperatures.

Using minus 100-mesh concentrate, 90 pct or better titanium sulfation was calculated to be achieved in 2.5 min at 300° C, in 3 min at 250° C, in 24 min at 200° C, and in 6 h at 150° C. These temperatures correspond to boiling acid concentrations of 96, 90, 80, and 64 pct, respectively. When operating at the lower temperatures, much of the titanium remained in the acid filtrate after sulfation. Extending sulfation time precipitated most of the titanium contained in the acid, as strong acid insoluble salts. Converting 90 pct of the titanium to salts that were soluble in water or dilute acid required 9 min at 300° C, 12 min at 250° C, 1.1 h at 200° C, and 6.7 h at 150° C when minus 100-mesh concentrate was used. These data show that the rate of perovskite sulfation increased as the operating temperature and acid concentration increased (fig. 7). Using minus 65-mesh and minus 35-mesh concentrate shifted these curves to the right, i.e., using coarser concentrates lengthened the time needed for sulfation. (See table A-1 for a complete listing of data.)

Effect of Extended Time on Sulfation

Evaluation of the batch test data indicated that the optimum conditions for maximum titanium sulfation would involve reacting finely ground concentrate with strong

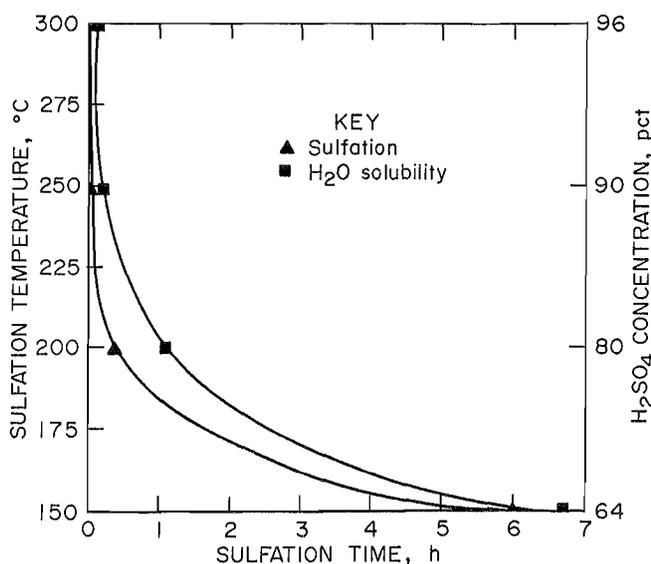


Figure 7.—Time requirements for 90-pct Ti sulfation and for 90-pct Ti conversion to water-soluble salts. Sulfation using minus 100-mesh concentrate, 1:20 pulp-solids ratio, and 1,000-rpm impeller.

H₂SO₄ solution at high temperature, using a low pulp-solids ratio and strong agitation. Based on this information, a test was conducted to determine whether extending the sulfation time would have a deleterious effect.

Test conditions involved treating minus 100-mesh concentrate at 250° C with 90-pct H₂SO₄ solution at a pulp-solids ratio of 1:20 and a 1,000-rpm impeller. The results show that maximum sulfation and water-solubility were achieved after 20-min reaction time and remained at this high level for an additional 2 to 3 h before an apparent decline in recoverability was observed (fig. 8). (See table A-1, test 27.)

Sulfation Comparison of Concentrates

Comparison sulfation tests were conducted using two samples of Arkansas concentrates and two Colorado concentrates. The tests were conducted at 300° C with 96-pct H₂SO₄ using minus 65-mesh concentrate at a pulp-solids ratio of 1:20 and a 1,000-rpm impeller. Because part of the titanium in Arkansas perovskite concentrates was locked up in silicate minerals, overall sulfation was lower than that achieved using more pure Colorado perovskite concentrates.

The maximum sulfation of the concentrated Arkansas drill-core sample was about 63 pct compared with 86 pct for the concentrated Arkansas surface ore sample. Treatment of the Colorado concentrates, one prepared by the property owner and the other prepared by the Bureau resulted in 96- and 94-pct Ti sulfation, respectively. Samples prepared from surface rock seemed to take slightly longer to reach maximum sulfation. This may have been related to partial weathering of the perovskite. The time required to achieve maximum sulfation was similar on three of four samples (about 5 to 10 min). (See figure 9 and appendix A, table A-2.)

X-ray diffraction analysis of both Arkansas leach residues after 5 min of reaction showed no unreacted

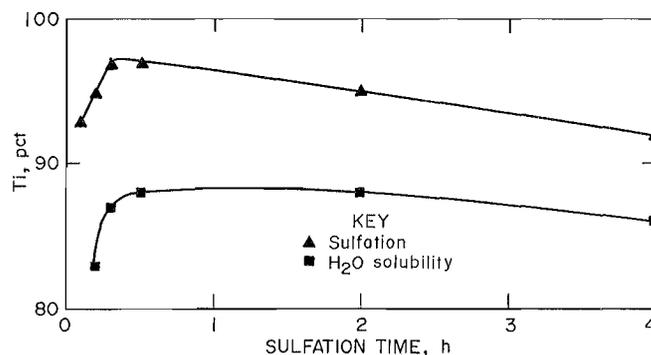


Figure 8.—Effect of sulfation time on titanium sulfation and water solubility. Sulfation at 250° C using 90-pct H₂SO₄ with minus 100-mesh concentrate, 1:20 pulp-solids ratio, and 1,000-rpm impeller.

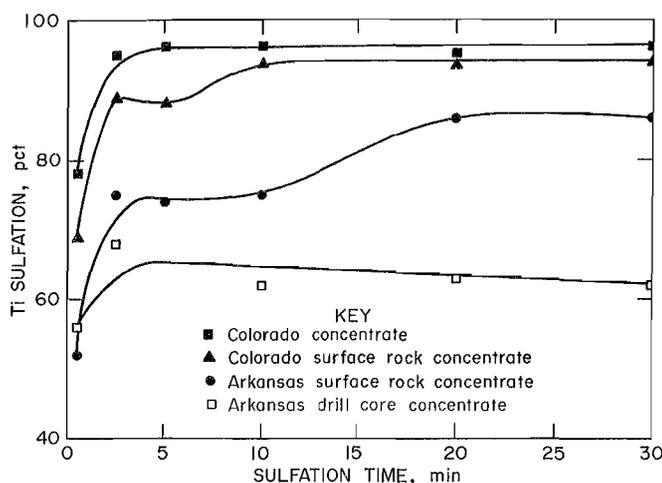


Figure 9.—Sulfation comparison of various perovskite concentrates. Sulfation at 300° C using 96-pct H₂SO₄ with minus 65-mesh concentrate, 1:20 pulp-solids ratio, and 1,000-rpm impeller.

perovskite. The titanium that remained in the samples was disseminated and seemed to be associated with silicate minerals. It appears, therefore, that the perovskite contained in both domestic deposits responds similarly to acid sulfation.

Byproduct Sulfation

Although titanium is the predominant valuable element in perovskite, the ores and concentrates also contain appreciable quantities of columbium and rare earths that could be recovered. Data on columbium and rare-earth sulfation and water leaching are listed in table A-1.

Usually, operation variables that affected titanium sulfation also affected columbium sulfation. In most tests, the percent sulfation for titanium and columbium was very similar. At low pulp-solids ratios, more of the columbium tended to remain in the acid sulfation filtrate. As the pulp-solids ratio increased, a greater percentage of the columbium precipitated and was recovered by water leaching. Apparently, during sulfation the solubility limit was more easily reached at higher pulp-solids ratios.

Rare-earth sulfation and water-leaching results were not always consistent, but some trends and conclusions can be drawn. The degree of rare-earth sulfation was increased by increased agitation, lower pulp-solid ratios, decreased concentrate particle size, and increased reaction time. The effects of temperature and acid concentration were more difficult to assess. For tests conducted with little or no mechanical agitation, increased temperature and acid concentration generally improved rare-earth recovery. Rare-earth sulfation, as measured by the combined extraction into the acid filtrate and the water-leaching solution, was generally best at sulfation temperatures between 185°

and 250° C (76- to 90-pct acid concentrations). At temperatures and acid concentrations below 225° C and 90-pct H₂SO₄, the precipitation of rare earths was relatively slow, especially at low pulp-solids ratios.

Some of the data suggests that at least part of the rare-earth material precipitated during acid sulfation is not recovered during water leaching. Under optimum conditions, rare-earth extractions ranged from 70 to 90 pct. Lanthanum extraction often exceeded cerium extraction by 5 to 15 pct.

Continuous Sulfation

Two methods of continuous sulfation were tested: a settler system and an agitated system. In the settler system, relationships between the concentrate particle size and the combination of temperature and acid concentration were investigated. In the agitated system, the variables studied included the pulp-solids ratio, reaction time, and the combination of temperature and acid concentration.

Settler Sulfation

Studies were performed to determine how fine the perovskite would need to be ground to permit complete reaction in a settler-type sulfation unit. Tests were conducted at 300° C with 96-pct H₂SO₄ and perovskite concentrate ground to minus 35, 65, and 100 mesh. The pulp-solids ratio was about 2:20. A 15-min nominal retention time was used.

The standard water-leaching results show that excellent extractions were achieved in all three tests. In continuous sulfation studies, the extractions obtained by water leaching represent the overall degree of sulfation achieved. Extractions for titanium and columbium ranged from 94 to 98 pct, and extractions for lanthanum and cerium ranged from 72 to 86 pct (table 6).

Table 6.—Extraction by water leaching following continuous-settler sulfation, percent

Sulfation conditions	Ti	Cb	La	Ce
300° C, 15 min:				
Minus 100 mesh . . .	97	96	86	72
Minus 65 mesh	94	98	82	ND
Minus 35 mesh	96	95	85	75
250° C, 15 min:				
Minus 100 mesh . . .	97	98	85	77
ND	Not determined.			

Water leaching of residues produced by sulfating minus 100-mesh concentrate at 250° C with 90-pct H₂SO₄ under similar conditions also achieved high-extraction results. Attempts to sulfate at 250° C with minus 35-mesh material,

however, were mechanically unsuccessful. The coarse concentrate fed into the top of the reactor tended to short circuit to the bottom drain before it was completely sulfated. Precipitation reactions occurring in the discharge throat caused bridging or plugging of the discharge.

Filtration of precipitates was very fast. In filter leaf tests, where minus 100-mesh material that had been sulfated at 300° C, a 2-in-thick cake was formed in about 0.067 min with a 14-in Hg vacuum. The production rate of sulfate residue would be about 770 lb/(ft²-h).

Results obtained in the settler sulfation system were quite consistent with those previously obtained in batch testing. Coarse concentrates required more time for completion of digestion and precipitation reactions. If minus 35-mesh concentrates were to be sulfated at 250° C, equipment design changes would be needed to prevent short circuiting.

Agitated Sulfation

A two-stage mechanically agitated sulfation unit with overflow discharge was designed to lengthen the sulfation time and to prevent short circuiting of coarser (minus 35-mesh) perovskite concentrates. The effects of the following variables were investigated: pulp-solids ratio, reaction time, and the combination of temperature and acid concentration. Standard water-leaching results, representing overall sulfation, appear in table 7.

Table 7.—Extraction by water leaching following continuous-agitated sulfation, percent

Sulfation conditions	Ti	Cb	La	Ce
250° C, 20 min:				
Test 1 ¹	98	98	85	72
Test 2 ²	93	94	78	64
250° C, 13 min: Test 3 ² . .	93	94	76	62
250° C, 26 min: Test 4 ² . .	97	98	82	66
300° C, 26 min: Test 5 ² . .	97	98	88	73

¹3:20 pulp-solids ratio, grams to milliliters.

²8:20 pulp-solids ratio, grams to milliliters.

Excellent sulfation results were obtained with minus 35-mesh concentrates in the two-stage stirred continuous unit. This indicated that problems of short circuiting were eliminated. Operating with a 1,200-rpm impeller at 250° C with 90-pct-H₂SO₄ solution at a pulp-solids ratio of 3:20 and a median retention time of 20 min (test 1) resulted in sulfation residues, which were then water leached with the following extraction results, in percent: 98 Ti, 98 Cb, 85 La, and 72 Ce.

Previous batch sulfation studies were limited to using low pulp-solid ratios, except at temperatures of 200° C and below. At temperatures above 200° C, reactions became too violent to be contained in the reaction vessel when

pulp-solids ratios above 3:20 were used. Under continuous operating conditions, the use of higher pulp-solids ratios became possible. Increasing the pulp-solids ratio from 3:20 up to 8:20 in a continuous-sulfation test reduced the degree of metals sulfation only 4 to 8 pct (compare table 7, tests 1 and 2). By increasing the sulfation time, the degree of sulfation was further improved (tests 2-4). Even though a high pulp-solids ratio (8:20) was used, allowing 26 min for sulfation at 250° C produced excellent subsequent water-leaching results, in percent: 97 Ti, 98 Cb, 82 La, and 66 Ce. Extending the sulfation time would likely further enhance subsequent rare-earth dissolution. Raising the sulfation temperature and acid concentration to 300° C and 96-pct H₂SO₄ improved subsequent rare-earth extraction, in percent: 97 Ti, 98 Cb, 88 La, and 73 Ce (test 5).

To obtain material balance information for steady-state continuous sulfation, the unit was operated for an uninterrupted 27-h period. This afforded 3 h to reach steady state, followed by 24 h for acquiring material balance information and assessing the general performance of the system.

The operating conditions selected were identical to those used in test 4 of table 7. Minus 35-mesh Colorado perovskite was reacted with 90-pct H₂SO₄ at 250° C and a pulp-solids ratio of 8:20 (400-g/h concentrate to 1,000-mL/h acid solution). The median residence time was 26 min, and a 1,200-rpm impeller was used. Samples were taken every 2 h. Products exiting the lower sulfation unit averaged about 65-pct solids. A scanning electron photomicrograph of a sulfation product granule is provided in figure 10.

Concentrations of metal ions in the acid filtrate increased during the first 3 h of operation and remained relatively constant thereafter. Steady-state concentrations in the acid filtrate for the following elements averaged, in

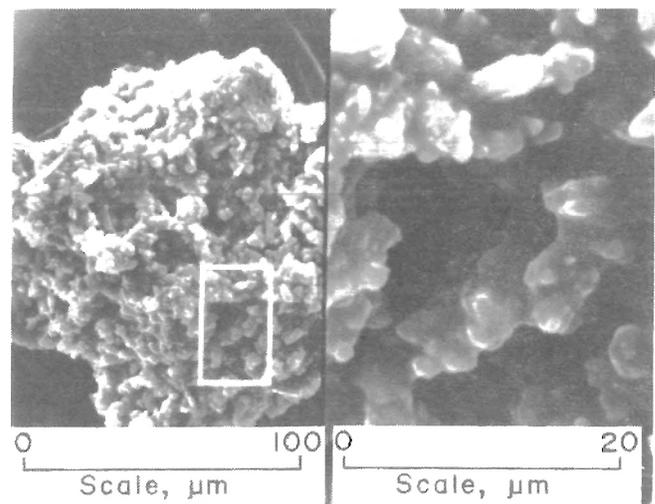


Figure 10.—Granule of sulfation product.

grams per liter: 4.0 Ca, 0.67 Fe, 0.49 Ti, 0.25 Cb, 0.25 Mg, 0.09 Pb, 0.06 Ce, and 0.06 La.

The residues produced were leached by the standard method to find the overall degree of sulfation. The following average water-leaching results were obtained, in percent: 97.5 Ti, 97.5 Cb, 83.2 La, and 71.1 Ce.

Material balance showed that treating 1.0 lb of the concentrate required about 2.7 lb of fresh H_2SO_4 . This produced 3.3 lb of sulfated material containing 9.4-pct Ti. The condensed sulfation vapors contained 9.4-pct H_2SO_4 .

The system operated quite smoothly for most of the test, requiring a small amount of downtime (<10 min) on two occasions to remove solids plugging the 0.5-in.-diameter conduit between sulfation vessels.

When the equipment was disassembled after completing the test, accretions of hardened sulfates were found on the sides of both sulfation vessels, slightly above the fluid level (fig. 11). This accumulation could be attributed to drying of splattered solids on glass surfaces heated by the exterior heating mantle. Such an explanation, however, did not account for accumulation of deposits on cooler piping, which drained the upper sulfation vessel, while pipes draining the lower sulfation vessel were free of deposits. Deposition in piping between the sulfation vessels indicates that a nominal 13-min retention time in the initial sulfation vessel was inadequate for precipitation of sulfates and at least part of the accumulation must be attributed to formation of insoluble sulfates. By the time solutions exited the lower vessel, sufficient precipitation had occurred so that accretions no longer formed. Sulfation and precipitation of acid-insoluble salts were completed in about 30 min at 250° C.

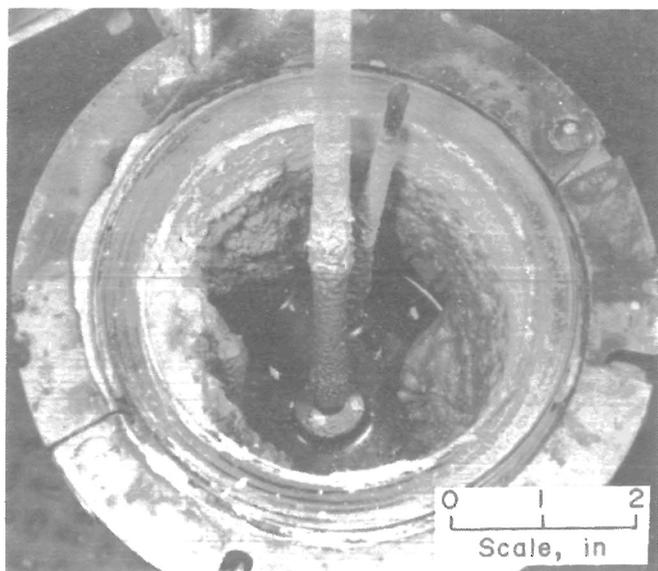


Figure 11.—Bottom Interior of lower sulfation vessel after 27 h of continuous operation.

These results indicate that sufficient retention time must be provided in the first sulfation stage to digest completely the perovskite and precipitate the insoluble salts. If the retention time is sufficient to eliminate short circuiting of unreacted perovskite, it is unlikely that a second-stage vessel for sulfation would be required. Previously described batch tests show that a 2-h retention time may be used without significant titanium loss. Using one-stage continuous sulfation with a 2-h retention time is recommended.

Unavailability of important thermodynamic data prevents calculation of a rigorous heat balance; however, observations made during operation of the laboratory-scale continuous sulfation unit indicate that heat provided by the reaction, together with that used in preheating the acid, will be sufficient to sustain reaction and maintain constant acidity through evaporation of water as steam.

No satisfactory commercial sulfation unit is available. Therefore, the following type of unit was used for the cost evaluation. The unit, shown in figure 12, is designated for continuous operation. Sulfuric acid and slurried perovskite

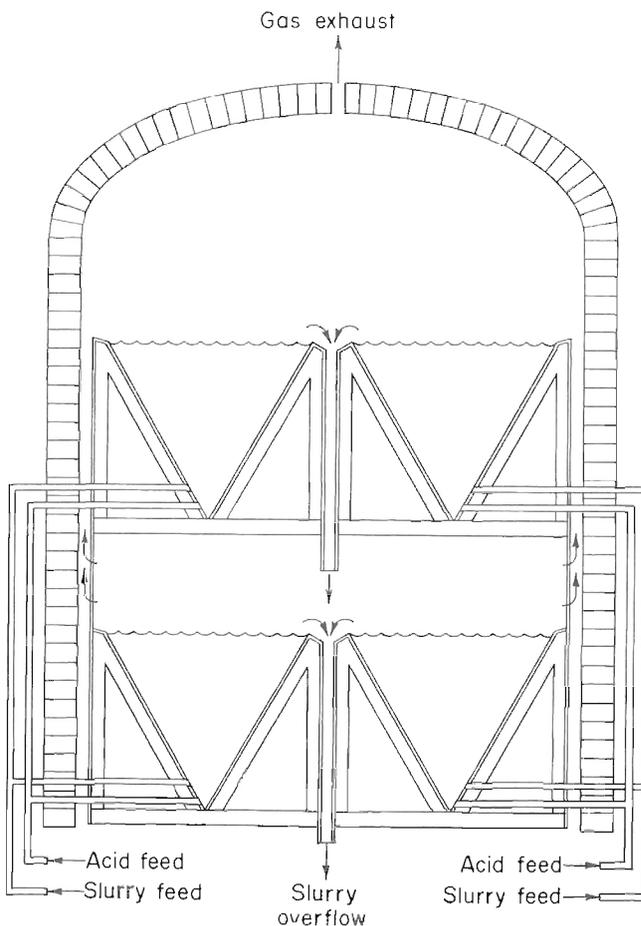


Figure 12.—Cross section of sulfation unit.

concentrate are introduced at multiple sites along the bottom of wedge-shaped reaction troughs. Water produced during the sulfation reaction is vaporized, causing a boiling action that keeps the slurry suspended until it overflows a weir. Steam and acid mist escape through the exhaust at the top of the reactor. To prevent the boiling action from becoming too violent, a feed rate of about 0.25 st of perovskite concentrate per day per square foot of surface area is maintained. Minus 35-mesh perovskite can be sulfated at 250° C within 30 min.

For cost evaluation purposes, the sulfation unit was sized with an average retention time of about 2 h. This permitted maximizing the surface area (required for gas-liquid phase disengagement) while minimizing the number of reaction troughs required. A 2-h retention time also ensures that precipitation is complete, thus preventing a buildup of sulfates on the walls of drainage pipes. The reaction troughs, drainage pipes, and support structure are constructed of enameled steel. The enclosing structure is made of acid-resistant brick encased in a lead-lined mild steel shell. Cleanout drains and entry ports are provided to facilitate maintenance operations. Temperature and pressure sensors are provided to aid in control. The unit is insulated to conserve heat.

LEACH TESTING

Leach testing was conducted using primarily two samples of sulfated perovskite. The first sample was an accumulation of residues produced during continuous testing of the settler sulfation reactor. This material was used for batch leaching investigations. The second sample was collected during the last 24 h of the previously described 27-h agitated sulfation test. This material seemed to be slightly better sulfated and was used for cocurrent continuous leaching studies and in a washing study used to prepare feed for countercurrent continuous leaching. Chemical analyses of both sulfated materials are provided in table 8.

Table 8.—Analysis of sulfation residues used in leaching studies, percent

Sample and use	SO ₄	Ti	Ce	La	Cb
1—Batch Leaching	76	10.5	0.30	0.15	0.10
2—Continuous leaching . .	77	9.4	.27	.12	.09

Batch Leaching

Batch studies were conducted to determine the effect of certain variables in leaching sulfated perovskite and to provide data for developing a continuous leaching unit. An analysis of the sulfate material used in these studies is provided in table 8. Leaching variables investigated included temperature, initial solution acidity, and percent solids.

Effect of Temperature on Leaching

The effect of temperature in batch leaching was determined by tests conducted at 40°, 60°, 80°, and 100° C. Other conditions included leaching with water at 30-pct solids for up to 90 min with a 1,100-rpm mixer impeller. The resulting extraction curves for titanium, columbium, cerium, and lanthanum are shown in figure 13.

The titanium extraction rate increased sharply with increasing temperature. At 100° C, titanium dissolution reached 94 pct within 15 min. At this temperature, however, hydrolysis caused reprecipitation of titanium over a period of time.

The columbium extraction rate also increased sharply with increasing temperature. Leaching at 100° C dissolved 94 pct of the columbium within 15 min, and no reprecipitation of columbium was observed over a 90-min period.

Increasing the temperature increased the initial rate of dissolution for cerium and lanthanum; however, rare-earth recovery was limited at the higher operating temperatures. Raising the temperature from 60° to 100° C, for example, reduced the maximum cerium recovery from 80 to 23 pct, while the maximum lanthanum recovery dropped from 90 to 35 pct.

Water leaching at temperatures above 60° C typically caused the anhydrous CaSO₄ produced during sulfation, to hydrate and form CaSO₄·2H₂O. Studies suggest that

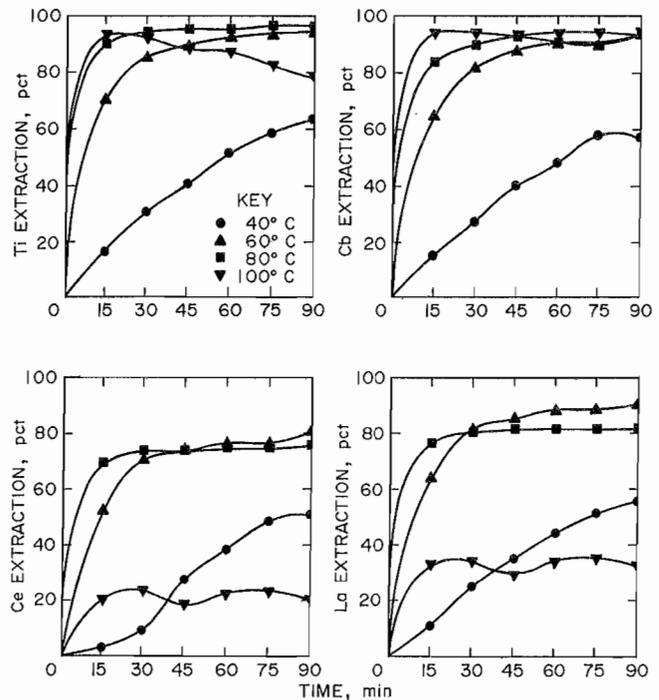


Figure 13.—Effect of temperature on extraction. Leaching with water at 30 pct solids and 1,100-rpm impeller.

lower rare-earth recoveries at higher leaching temperatures may have been related to the formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or a calcium-rare-earth double salt. It was shown, for example, that nearly all the residual cerium could be recovered from tailings material by re-leaching in HCl solution if the percent solids was kept low enough to dissolve all the residual $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Similar tests conducted at higher percent solids dissolved little of the residual cerium.

The overall optimum temperature for batch water leaching of sulfated perovskite was about 60°C . At this temperature, the problems of titanium reprecipitation posed no threat, and the recovery of rare-earth elements was highest. Leaching for 90 min at 60°C dissolved, in percent: 94 Ti, 93 Cb, 90 La, and 80 Ce.

Effect of Initial Solution Acidity on Leaching

Tests were conducted with initial aqueous leaching solutions containing 0-, 10-, 20-, and 30-pct H_2SO_4 . Batch leaching sulfated perovskite at 30-pct solids for 90 min at 60°C with a 1,100-rpm impeller produced the extraction results shown in figure 14. Increasing the acidity seemed to have little or no effect on titanium dissolution; however, the recovery of other metal values was decreased. Leaching with 30-pct H_2SO_4 , for example, recovered 10 to 27 pct

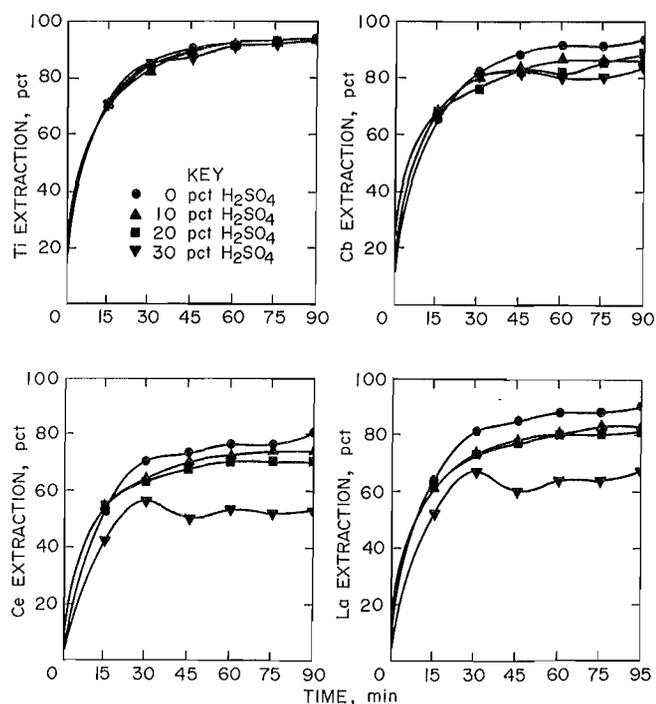


Figure 14.—Effect of solution acidity on extraction. Leaching at 60°C with 30 pct solids and 1,100-rpm impeller.

less columbium, cerium, and lanthanum than leaching with plain water.

Effect of Percent Solids on Leaching

The effect of leaching sulfated perovskite at various solid-to-liquid ratios was studied in tests conducted at 20-, 30-, 40-, and 50-pct solids. The results obtained by batch leaching with water for 90 min at 60°C and a 1,100-rpm impeller are shown in figure 15. Leaching at a higher percent solids tended to lower the recovery of metal values. At 50-pct solids, for example, the following extractions were obtained, in percent: 91 Ti, 85 Cb, 76 La, and 64 Ce. These results were 3 to 16 pct lower than those obtained by leaching at 30-pct solids.

Re-leaching the tailings material was effective in dissolving additional quantities of titanium, columbium, cerium, and lanthanum. This suggested that countercurrent leaching could offer an advantage, especially with respect to rare-earth recovery.

Continuous Leaching

Continuous leaching studies were conducted to help establish the validity of batch leaching results and to determine what problems would be encountered in continuous leaching systems. Both cocurrent and countercurrent leaching methods were tested.

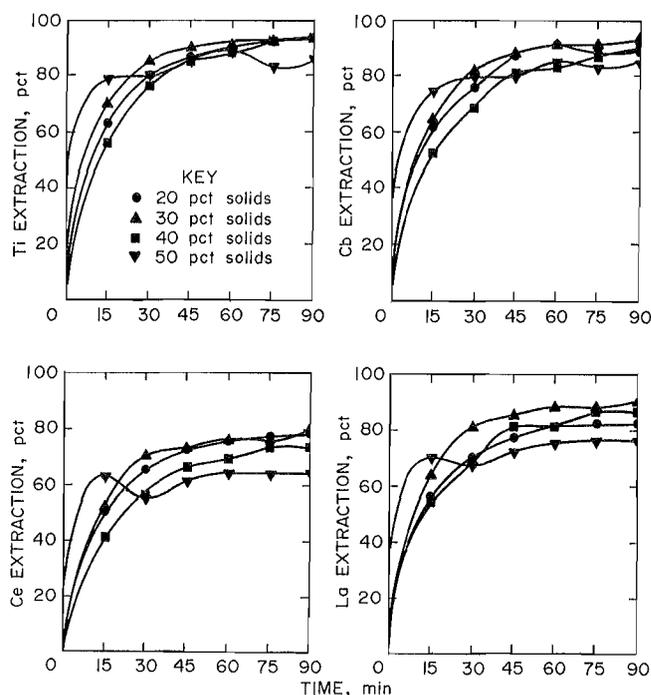


Figure 15.—Effect of percent solids on extraction. Leaching with water at 60°C and 1,100-rpm impeller.

Cocurrent Leaching

An agitated two-stage cocurrent leaching system was used to study the following variables: temperature, percent solids, and initial solution acidity. An analysis of the sulfate material used in these tests is provided in table 8. The results of cocurrent leaching are provided in table 9.

Table 9.—Continuous leaching results, cocurrent system

Test	Temp, ° C	Solids, pct	Acidity, ¹ pct	Extraction, pct			
				Ti	Cb	La	Ce
1	70	42	0	97	96	76	58
2	60	40	0	91	92	75	65
3	60	50	0	92	92	60	40
4	60	40	20	93	87	55	34

¹Initial.

The best extraction results were obtained in test 1 by cocurrent leaching the sulfation residues for about 90 min at 70° C with water at 42-pct solids and a 1,100-rpm impeller. The following extractions were obtained, in percent: 97 Ti, 96 Cb, 76 La, and 58 Ce. The titanium and columbium extractions compared well with batch results, but the rare-earth extractions were 10 to 15 pct lower than expected.

The results of tests 1 and 2 show that raising the leaching temperature from 60° to 70° C improved the extraction of most species even though the percent solids was slightly higher.

Results of tests 2 and 3 indicate that using a lower percent solids improved rare-earth extraction. Leaching with 20-pct-H₂SO₄ solution, as shown in test 4, had little or no adverse effect on titanium and columbium extraction, but significantly decreased the extraction of rare earths.

No operating problems were encountered with cocurrent continuous leaching. The resulting tailings consisted of anhydrous CaSO₄, gangue material, and a small amount of coarse perovskite. Filtration of solids was rapid.

Countercurrent Leaching

Studies were conducted to determine whether metal extraction could be further improved by using a two-stage countercurrent leaching system. Washing the sulfated material before countercurrent leaching was evaluated as a preliminary step. Increasing rare-earth metal extraction and obtaining detailed material-balance information was of primary interest.

Preliminary to countercurrent leaching, sulfated perovskite was washed with dilute acid solution. Washing was done to remove entrained acid, to help lower the ionic strength of solution in the subsequent leaching operation. Two methods of washing were investigated. Sulfated

perovskite, produced in the 27-h continuous sulfation test (table 8, sample 2), was used in the washing study.

A one-stage washing method was attempted with very negative results. When 367 mL of 9.4-pct-H₂SO₄ solution was used directly to wash 1,000 g of sulfated material, in a Buchner funnel, the mass heated and solidified. Contacting dilute solution directly with 90-pct H₂SO₄, contained in freshly sulfated perovskite, released sufficient heat to initiate dissolution of various sulfate species. As the temperature continued to rise, moisture was driven off and the mass solidified.

A two-stage method of washing, coupled with using a smaller quantity of wash solution, eliminated the solidification problem. For the first stage of washing, sulfated material was loaded into the Buchner funnel and rinsed with filtrate from the second wash stage. An analysis of the resulting high-acid filtrate is provided in table 10. The second stage of washing involved contacting the partially washed solids with 9.4-pct-H₂SO₄ solution, similar to that available from various recycle streams. Filtrate from this operation was advanced to the first stage of washing. An analysis of the final washed sulfate residue is also provided in table 10.

Table 10.—Analysis of products obtained by washing sulfated perovskite

Component	Filtrate g/L	Residue pct
SO ₄	1,274	67.9
Ti	5.0	10.1
Ca79	8.4
Fe57	.69
Cb20	.09
Ce	<.03	.32
La013	.16
U	<.0001	.0023

Using 100 mL of 9.4-pct H₂SO₄ to wash 1,000 g of sulfated perovskite removed about 60 pct of the available free acid. Washing extracted the following elements, in percent: 2.7 Cb, 0.9 Fe, 0.46 Ti, 0.1 Ca, 0.1 La, <0.09 Ce, and <0.04 U. Washing the sulfated perovskite in a two-stage operation, first using a strong acid solution followed by using a more dilute acid solution, minimized dissolution of titanium and other species.

To determine what effect two-stage washing of sulfated perovskite might have on the solubility of important metal species, a quantity of the wash residue (table 10) was batch leached by the standard method. The resulting extractions, in percent: 95.8 Ti, 98 Cb, 49 La, and 37 Ce, can be compared with extractions obtained from unwashed sulfates, in percent: 97.5 Ti, 97.5 Cb, 83 La, and 71 Ce. These results show that the washing operation had little or

no effect on titanium and columbium solubility. Extraction of both cerium and lanthanum, however, was 34-pct lower when the washed sulfates were leached compared with treatment of unwashed sulfates. Preliminary washing seemed to lower subsequent rare-earth solubility, probably through association of the rare earths with calcium.

Continuous countercurrent leaching was then performed using the wash residue shown in table 10. Leaching was performed in an agitated two-stage countercurrent unit at 52-pct solids using 7.55-pct H_2SO_4 solution at 60° C with an overall nominal retention time of 196 min. The leaching unit was tested six days for up to 6 h a day. Samples from 9 h of operation, considered to be most representative of the steady state, were combined and assayed to provide material balance information.

Countercurrent leaching was operated with few interruptions, except the usual heat up and cool down of the system at the beginning and end of each day. Occasionally, trouble was encountered with the solids feeder. Operation of the settler was rather inefficient. Only 37-pct of the solid material reported to the underflow. Rotary filtration equipment would have been much more suitable in this application. There was little or no buildup of solids on reactor surfaces.

Filtration of solids was rapid. Based upon earlier filter leaf tests, rotary vacuum filtration after leaching would have a dry residue production rate of about 47 lb/(ft²·h). A 3/16-in-thick filter cake is formed in about 2.6 min with a vacuum of 14-in Hg.

Extractions obtained by countercurrent leaching, along with those results previously obtained by washing the sulfated perovskite, are provided in table 11. A high degree of extraction was achieved for titanium, columbium, iron, and uranium. Rare-earth extractions were even lower than those obtained by batch leaching using the standard leaching method. The results suggest that countercurrent leaching did little to improve recovery of rare earths. Countercurrent leaching would have higher capital and operating cost and lower rare-earth recovery, when compared with cocurrent leaching.

Table 11.—Extractions by initial washing and countercurrent leaching, percent¹

Component	Initial washing	Countercurrent leaching
Cb	2.7	91
Fe9	90
Ti5	97.2
Ca1	.4
La1	43
Ce	<.09	31
U	<.04	90

¹Extractions relative to the content of sulfated perovskite before washing.

Tailings emanating from the countercurrent leaching operation were composed primarily of $CaSO_4$. Table 12 provides the tailing assay results. The table also provides assays of a heavy and a light fraction obtained from dried tailings material by repulping and decantation methods. About 2 pct of the tailing was recovered as heavy material. This material consisted mostly of coarse $CaSO_4$, calcium-magnesium-iron silicates, and unreacted or partially reacted perovskite. A scanning electron photomicrograph of partially reacted perovskite, rimmed with $CaSO_4$, is provided in figure 16. About 90 pct of the tailing was recovered as lightweight material. This lightweight $CaSO_4$ fraction contained most of the undissolved cerium and lanthanum, but little titanium or silica. The balance of the tailing (about 8 pct) was middling material composed primarily of $CaSO_4$ and silicates.

Table 12.—Analysis of tailing materials, percent

Component	Leach tailings	Heavy fraction	Light fraction
SO_4	67	22	68
Ca	25	22	26
Si	1.2	22	.35
Ce95	.48	.97
Ti83	9.3	.34
La31	.27	.28
Fe20	2.3	.26
Cb016	.11	.009
Y012	.011	.014
Th	<.003	.006	<.003
U001	.001	.002

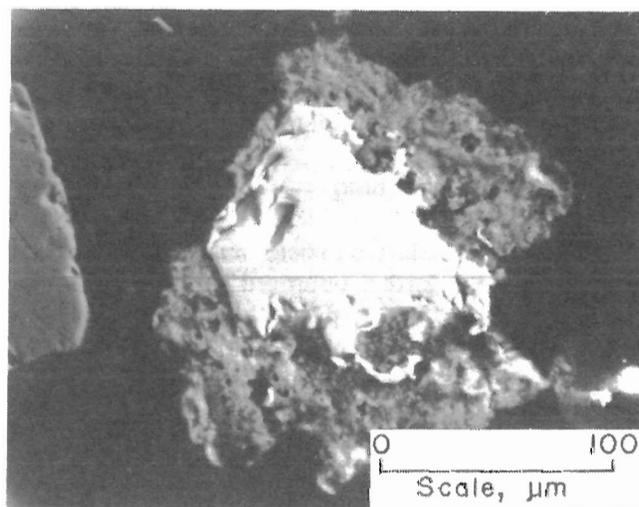


Figure 16.—Perovskite rimmed with $CaSO_4$ in leach residue.

A study of both batch and continuous leaching results suggests that high rare-earth extractions can only be achieved in continuous leaching systems if performed at lower percent solids. Cocurrent leaching of freshly sulfated perovskite at about 33-pct solids should result in satisfactory extraction of all important metal values.

RARE-EARTH PRECIPITATION TESTING

Precipitation of rare earths from leach filtrates by formation of sodium double salts was studied. Both batch and continuous-precipitation systems were tested. A large quantity of filtrate, from countercurrent continuous leaching, was treated by batch methods to remove rare earths and prepare solution for further processing to produce TiO_2 pigment.

Batch Rare-Earth Precipitation

Batch precipitation studies were conducted to investigate the following variables: Na_2SO_4 addition, precipitation time, temperature, and various dissolved ions. Tests involved using leach filtrates with the composition shown in table 13.

Table 13.—Composition of leach filtrates used in testing, grams per liter

Component	Filtrate 1	Filtrate 2
SO_4	561	532
Ti	85.0	97.0
H^+	8.1	7.0
Ce	1.4	1.0
La	1.1	.61
Ca86	.26

Filtrate 1 was treated to show the main effects of temperature, retention time, and Na_2SO_4 addition on lanthanum precipitation. Lanthanum recovery increased with an increase in each of the test variables. Lanthanum recovery was much more dependent on increases in time and Na_2SO_4 addition at the lower temperatures than at higher ones (fig. 17). At a solution temperature of 85° C, differences in recovery were much less pronounced. There was only a 10-pct difference in recovery for reaction times between 15 and 180 min for Na_2SO_4 additions of 50 g/L, compared with a 30-pct difference at 25° C. Best recoveries occurred at 85° C with Na_2SO_4 additions >20 to 30 g/L. At 25° C, increasing the reaction time from 15 to 180 min raised the recovery 40 to 50 pct.

Figure 18 shows the effect that temperature had on the recovery of lanthanum when using 30 g/L Na_2SO_4 to treat filtrate 1 with a 1-h retention time. A sharp increase in recovery occurred for temperatures up to 60° C. Above

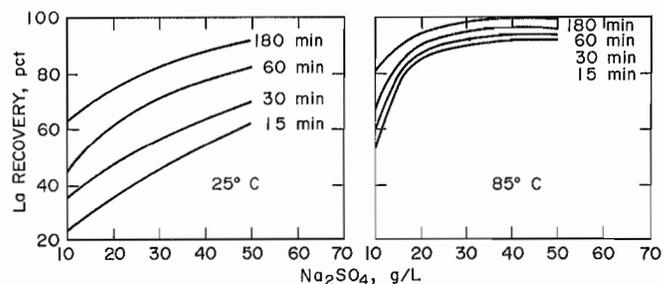


Figure 17.—Effects of time and temperature on lanthanum recovery.

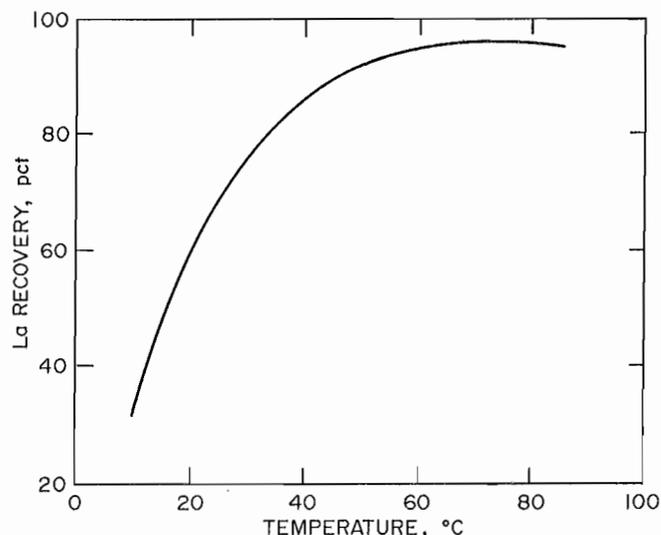


Figure 18.—Effect of temperature on lanthanum recovery. Precipitation for 1 h with 30 g/L Na_2SO_4 .

this temperature, only small increases in recovery were observed. Highest recovery depended on the solution temperature and sulfate addition. The higher the temperature, the lower the amount of Na_2SO_4 needed to obtain the same recovery. For example, using 30-g/L- Na_2SO_4 addition and a 1-h retention time at 40° C gave >80-pct-La recovery; a 50-g/L- Na_2SO_4 addition was required to obtain this same recovery at 25° C.

Trends in precipitation of the different rare earths can be summarized by comparing cerium and lanthanum recoveries. Figure 19 shows the relationship between cerium and lanthanum recoveries as a function of time when using 30 g/L Na_2SO_4 to treat filtrate 1 at 25° C. The recovery of both elements increased with time, but cerium recovery was always greater than that of lanthanum. At the more efficient conditions of higher temperature or Na_2SO_4 addition, differences in recovery were much less pronounced and nearly complete recovery of both elements became possible. Therefore, precipitation of the various light rare earths can be expected to follow these trends, but at slightly different levels.

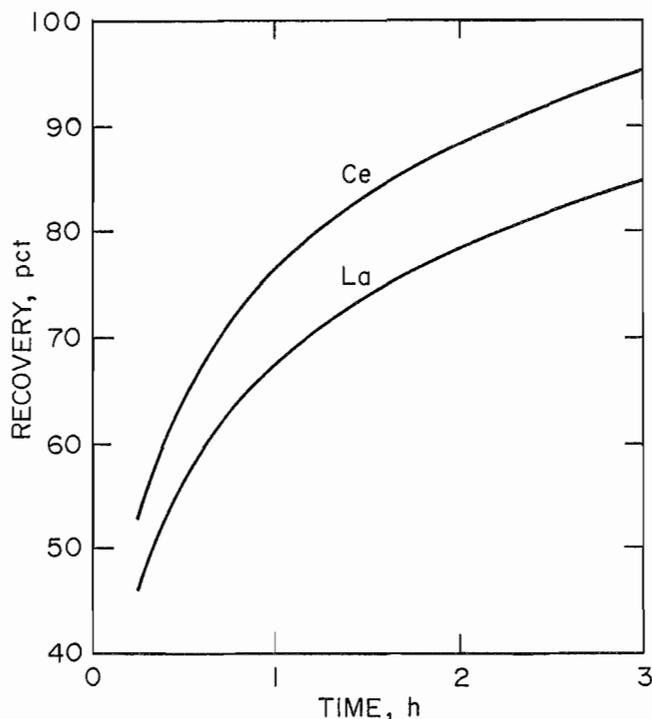


Figure 19.—Comparison of cerium and lanthanum recoveries. Precipitation at 25° C with 30 g/L Na₂SO₄.

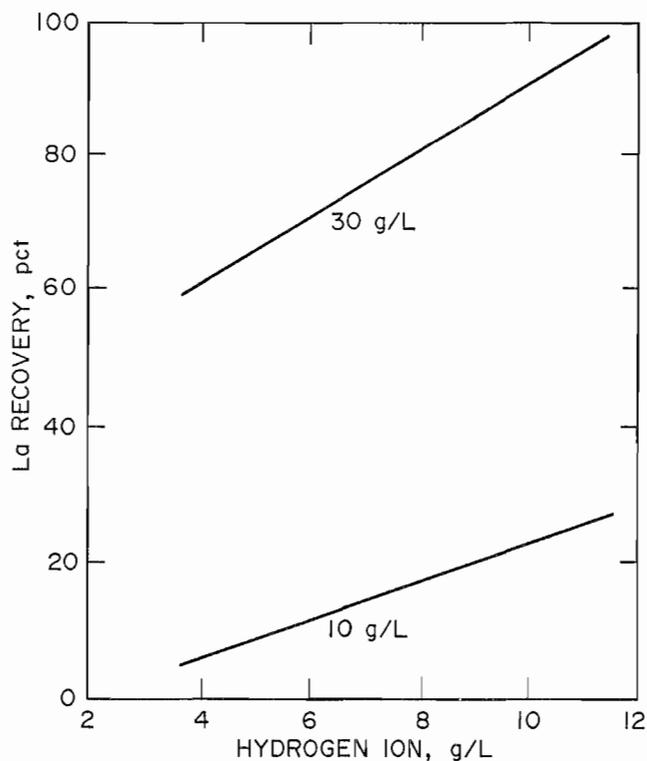


Figure 20.—Effect of hydrogen ion concentration on lanthanum recovery. Precipitation at 60° C for 3 h with 10 and 30 g/L Na₂SO₄.

Titanium and hydrogen ion (H⁺) concentration affected precipitation of the lanthanum. Tests were conducted using leach filtrates containing much lower amounts of titanium and H⁺ than those shown in table 13. The concentrations of titanium and H⁺ were varied by adding either concentrated leach filtrate or H₂SO₄. Results of these tests are shown in figures 20 and 21. Increasing titanium or H⁺ gave better rare-earth recovery. Lanthanum had a linear increase in recovery with hydrogen ion concentration at both 10- and 30-g/L-Na₂SO₄ additions. However, the amount of acid that can be added to the leach filtrate is limited because of the cost associated with acid recovery. The same linear effect was seen for titanium concentrations up to 70 to 80 g/L when using 30 g/L Na₂SO₄.

Batch precipitation of rare earths was performed to prepare solution for subsequent continuous TiOSO₄·H₂O precipitation studies and eventual TiO₂ pigment production. In this case, batch rare-earth precipitation involved using filtrate 2 (table 13) produced during the continuous countercurrent leaching study. Precipitation was accomplished using 30 g/L Na₂SO₄ at 60° C for 3 h, followed by filtration. The filter cake was washed with 50-pct H₂SO₄, to remove entrained solution. This left a damp cake that was dried by heating in a beaker on a hotplate. Analysis of the resulting dried material is provided in table 14. A scanning electron photomicrograph of rare earth double-salt precipitate is provided in figure 22.

Table 14.—Analysis of dried rare-earth precipitate

Component	pct	Component	pct
SO ₄	61.6	Th	0.18
Ce	13	Fe14
La	7.1	Y08
Nd	4.8	Dy043
Na	4.1	Eu021
Ca	3.2	Cb013
Ti92	U	<.001
Sm66		

Precipitation in the preceding manner recovered about 99 pct of the cerium and lanthanum. About 26 pct of the thorium initially contained in the perovskite was also recovered in the precipitate. Little or none of the uranium was precipitated.

Continuous Rare-Earth Precipitation

Rare-earth recovery in a continuous precipitation unit was studied with conditions similar to those used for batch recovery tests. Tests were run at 25° and 60° C with 30 g/L Na₂SO₄. Comparison of the batch and continuous results shows that the overall rare-earth recoveries are

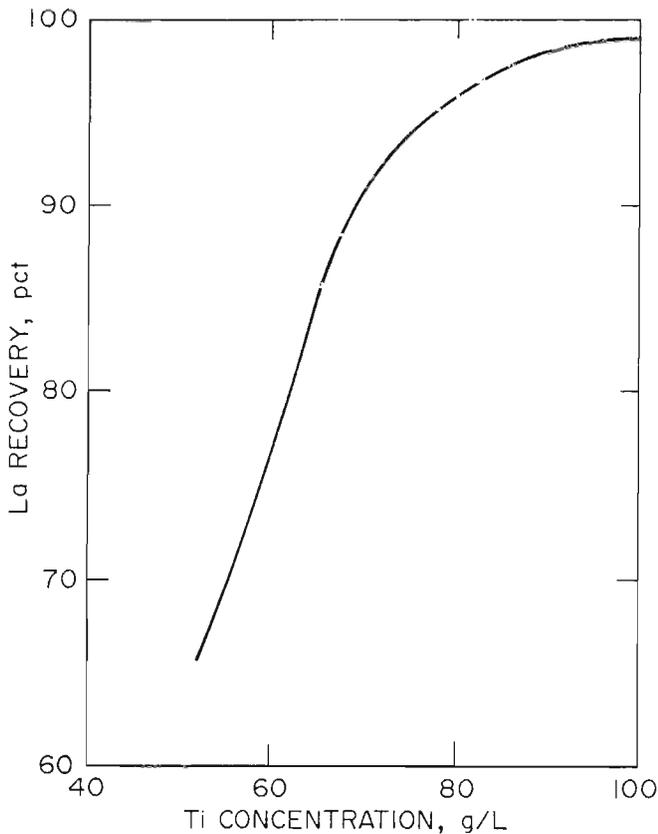


Figure 21.—Effect of titanium concentration on lanthanum recovery. Precipitation at 60° C for 3 h with 30 g/L Na_2SO_4 .

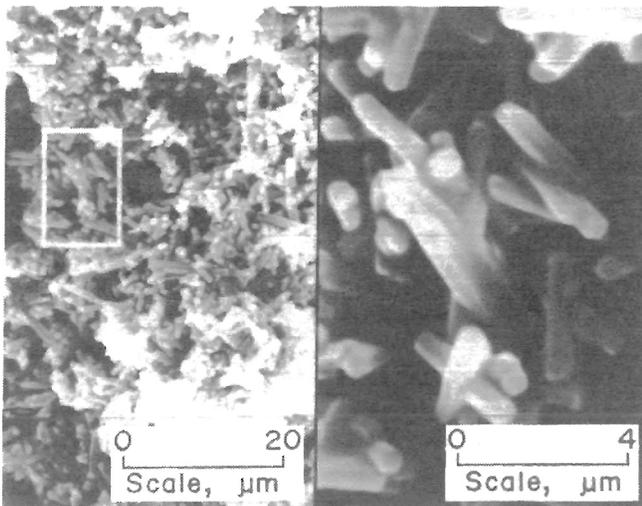


Figure 22.—Rare-earth double-salt precipitate.

similar (table 15). The same trends observed in batch tests were observed in the continuous tests. Rare-earth recovery increased with increased precipitation time and

higher temperature. Lanthanum recovery was also less than cerium recovery.

Table 15.—Comparison of rare-earth recoveries obtained by continuous and batch precipitation, percent

Temp, °C	Time, h	Ce		La	
		Continuous	Batch	Continuous	Batch
25 ..	3.0	96	97	95	84
60 ..	.5	96	96	90	91
60 ..	1.0	99	98	91	92

$\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ PRECIPITATION TESTING

Solutions resulting from leaching of sulfated perovskite contain more H_2SO_4 than is desirable for direct hydrolysis of TiO_2 . Methods were developed for treating leach filtrates by precipitating water-soluble, low-acid $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ and recovering an enriched solution of H_2SO_4 . Studies were conducted using both batch and continuous methods of operation. Few investigations were performed. Attention focused on preparing a $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitate that would completely redissolve in water.

Batch $\text{TiSO}_4 \cdot \text{H}_2\text{O}$ Precipitation

Batch precipitation studies were conducted to determine effects of temperature, SO_4 -Ti mole ratio in the initial feed solution, and seeding. Leach filtrate used for investigations had the following initial composition, grams per liter: 436 SO_4 , 109 Ti, 1.9 Ce, 1.4 La, and 1.1 Cb

Effect of Temperature on Precipitation

A series of tests were conducted to determine the effect of temperature on precipitation. In each test a 150-mL sample of the above leach filtrate was combined with 100 g of concentrated H_2SO_4 and heated in an agitated Erlenmeyer flask to a temperature of 150° C by boiling off excess water. The flask was then loosely fitted with a rubber stopper containing a thermometer, to monitor temperature while minimizing further moisture loss. The temperature was allowed to drop to the target precipitation temperature used in the test: 120°, 130°, or 140° C. Precipitation was accomplished by maintaining the target temperature for 3 h. At the end of each test the resulting slurry was filtered to recover the precipitate.

The results (table 16) show the amount of precipitation attained at each temperature. Columbium precipitation tends to lag that of titanium. The amount of cerium and

lanthanum found in the precipitate is roughly equivalent to that contained in acid solution wetting the unwashed precipitate.

Table 16.—Effect of temperature on $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation, percent

Temp, °C	Ti	Cb	Ce	La
120	12	10	3	1
130	84	54	22	14
140	99	68	23	16

Effect of Initial SO_4 -Ti Mole Ratio on Precipitation

Tests were conducted to determine the effect of the initial SO_4 -Ti mole ratio on precipitation. In this series, 150 mL aliquots of leach filtrate were combined with 40, 60, 80, or 100 g of concentrated H_2SO_4 and then heated as in the previous section, to a boiling temperature of 150° C. The flasks were then covered with a loosely fitting rubber stopper containing a thermometer. The temperature was lowered to 140° C and held at that level until precipitation was complete. Periodic samples were withdrawn from the agitated slurry by aspiration to provide information on the extent of precipitation.

It was important that the resulting precipitate contain only low levels of entrained H_2SO_4 . If the amount of entrained acid is too high, subsequent precipitation of TiO_2 pigment becomes difficult. To help determine suitability of $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ products, final precipitate SO_4 -Ti mole ratios were determined. Results of the study are provided in table 17.

Table 17.—Effect of initial SO_4 -Ti mole ratio on $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation

Initial SO_4 -Ti mole ratio in solution	Time, h	Precipitation, pct				Final SO_4 -Ti mole ratio in precipitate
		Ti	Cb	La	Ce	
3.16	3	1	1	0.3	0.2	2.6
	5	9	7	5	5	2.3
	7	75	54	36	37	2.0
	26	98	91	83	85	1.2
3.74	3	11	11	0	3	.8
	4	38	24	5	7	1.5
	5	100	77	46	53	1.2
	23	100	83	65	79	2.0
4.3	3	35	22	4	6	1.4
	4	99	68	16	26	1.5
	5	100	70	18	28	1.6
	23	100	77	54	57	2.0
4.69	3	99	68	16	23	1.4

¹Lanthanum-cerium data shown in figure 25.

The results indicate that a rather complex precipitation mechanism was involved. Precipitate formed from solutions lower in free acid tended to be very fine grained (fig. 23). Fine-grained precipitates retained more acid in the filtration cake. Initial precipitates formed from solutions containing higher SO_4 -Ti mole ratios were coarse grained and relatively dry upon filtration (fig. 24). When all the precipitate was coarse grained, air could be drawn through the cake during filtration. This removed most of the residual acid filtrate within 2 min. With extended precipitation time, even the precipitate produced from solutions containing higher SO_4 -Ti mole ratios became more difficult to filter and difficult to redissolve in water.

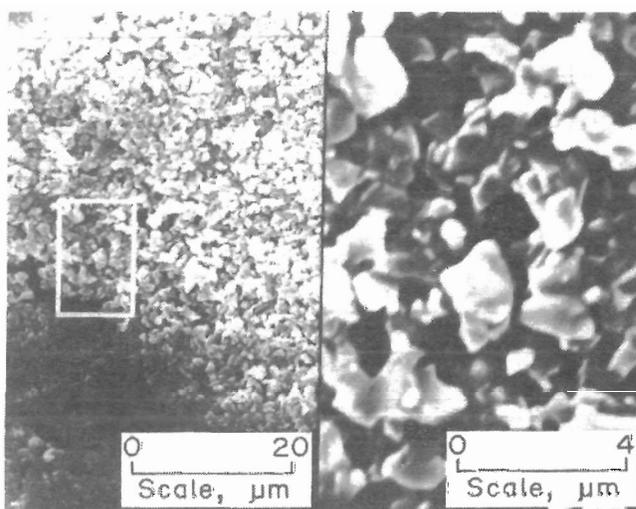


Figure 23.—Fine-grained $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitate.

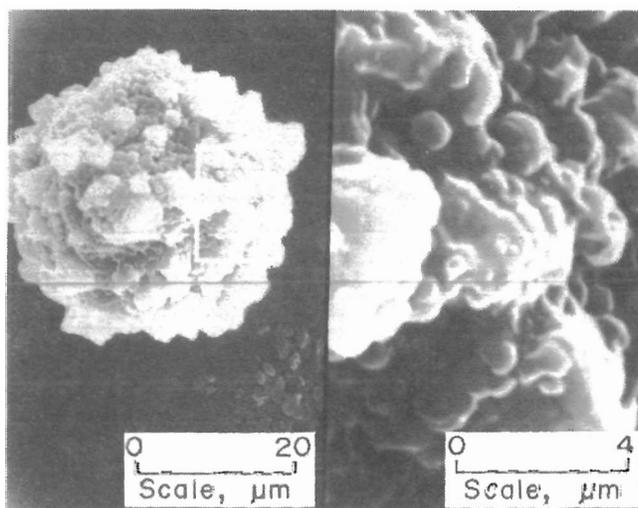


Figure 24.—Coarse-grained $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitate.

Precipitation of $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ with SO_4 -Ti mole ratios suitable for rapid aqueous dissolution and subsequent precipitation of TiO_2 pigment seemed to require the SO_4 -Ti mole ratio of the initial solution to be at least 4.33. As the SO_4 -Ti mole ratio of the initial solution was raised, precipitation rates also increased. Precipitates formed from solutions with initial high SO_4 -Ti mole ratios were found to redissolve in water in as little as 15 min at 60°C .

Precipitates formed from solutions with initial low SO_4 -Ti mole ratios were more difficult to redissolve, requiring up to 90 min at 80°C . Precipitates formed from solutions with initial low SO_4 -Ti mole ratios tended to have X-ray diffraction patterns that deviated further from the standard $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ pattern. Additional diffraction lines observed in samples prepared from the lower sulfate solutions could not be directly linked to any patterns on file for titanium-sulfate compounds. It is felt, however, that the lines were probably related to formation of precipitates with an increased degree of hydration. Such precipitates are known to be more difficult to redissolve in water.

The initial SO_4 -Ti mole ratio or acidity of solution also influenced rare-earth precipitation. As this ratio or the initial acidity of solution increased, rare-earth precipitation decreased. Figure 25 shows how the cerium and lanthanum content of unwashed precipitate decreased with increasing initial solution SO_4 -Ti mole ratio.

Comparison of the amount of rare earth contained in precipitates with the amount of acid entrained in each

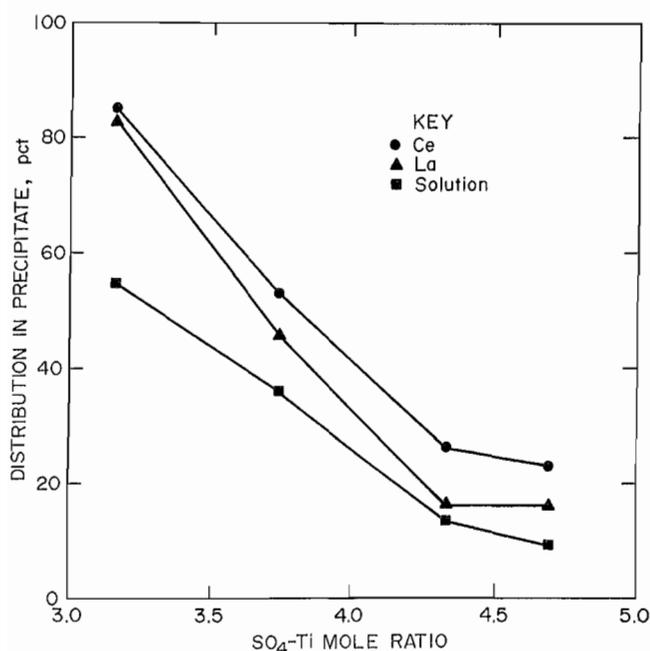


Figure 25.—Distribution of cerium, lanthanum, and acid solution in unwashed $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitates. Precipitation at 140°C with variation of initial solution SO_4 -Ti mole ratios.

unwashed precipitate indicates that 99 to 87 pct of the lanthanum and cerium can be retained in the acid filtrate if the initial SO_4 -Ti mole ratio in the starting solution is 4.33 or more. The precipitate would be washed with strong acid solution to recover entrained filtrate. Rare earths not precipitated would be recovered as sulfates or oxides in the acid regeneration operation. This approach to rare-earth recovery would probably be cheaper than using Na_2SO_4 precipitation methods. If the rare earths were allowed to cohydrolyze with the titanium, the color of resulting pigments would likely be impaired.

Effect of Seeding on Precipitation

The type of $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitate formed seemed to depend somewhat on the proper formation of seed nuclei. Precipitation studies were, therefore, conducted to determine what effect seeding would have.

A quantity of starting liquor (113.5 mL) with a density of 1.4 g/mL, containing 623 g/L SO_4 and 76.3 g/L Ti (SO_4 -Ti mole ratio = 4.07), was prepared by adding 35-pct- H_2SO_4 solution to the leach filtrate. This liquor was heated to a boiling temperature of 150°C in the usual manner. The flask was then loosely stoppered and held at 140°C for 300 min to ensure complete precipitation. Samples of slurry were periodically withdrawn from the agitated slurry by aspiration and filtered. Filtration products were assayed to determine the degree of titanium precipitation and the SO_4 -Ti mole ratio of precipitates. The test was then duplicated with an equal quantity of fresh starting liquor, except 10 g of previously prepared $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitate (SO_4 -Ti mole ratio = 1.35) was added as seed material while the solution was being cooled to the 140°C precipitation temperature. Comparison of precipitation results for these two tests is provided in figures 26 and 27.

Results show that titanium was completely precipitated within 90 min when seeding was used. Without seeding, precipitation required 60 min longer. When precipitation was seeded, SO_4 -Ti mole ratios in the resulting $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ product remained low throughout the 5-h period. By the time all the titanium was precipitated in the non-seeded test, filterability had deteriorated. Filtrate recovered at 90 min in the seeded test contained 0.8-g/L Ti and 1,112-g/L SO_4 (mostly as free H_2SO_4). The filtrate density (1.6 g/mL) indicates that the H_2SO_4 concentration was about 70 pct.

Continuous $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ Precipitation

A test was conducted to see if $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ could effectively be precipitated in a continuous system. This test was also performed to determine whether a more dilute feed solution (such as that described as stream 7 of table 1) could be treated. Low rare-earth filtrate, produced

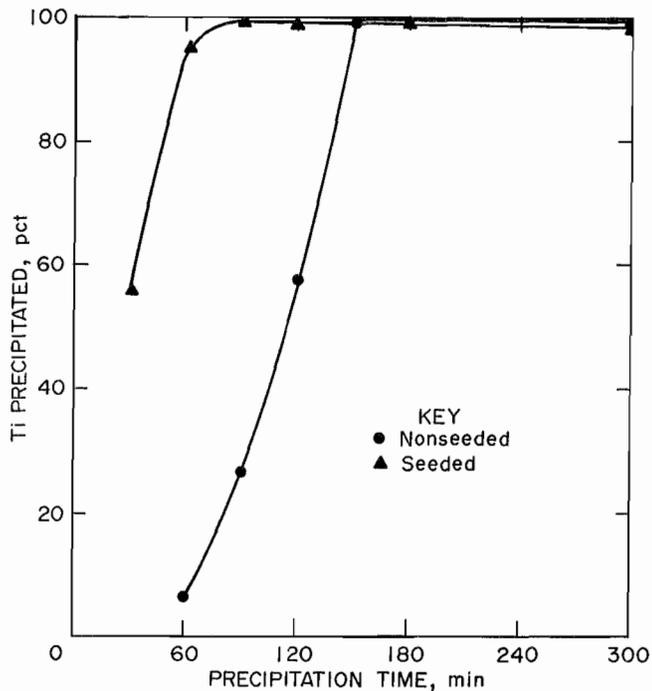


Figure 26.—Effect of seeding on precipitation of $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$. Precipitation at 140°C with initial solution $\text{SO}_4\text{-Ti}$ mole ratio = 4.07.

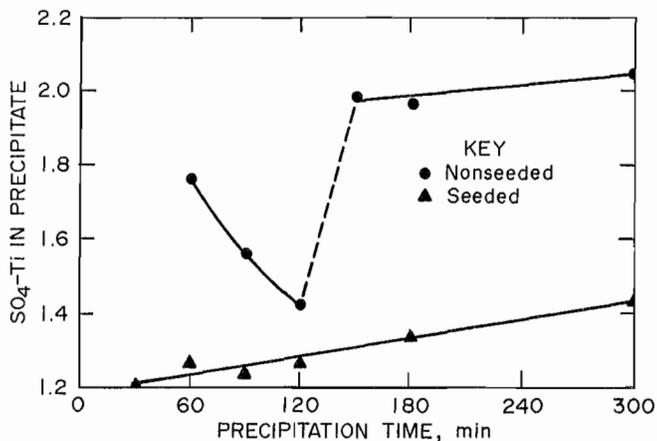


Figure 27.—Effect of seeding on $\text{SO}_4\text{-Ti}$ mole ratio of precipitates. Precipitation at 140°C with initial solution $\text{SO}_4\text{-Ti}$ mole ratio = 4.07.

from filtrate 2 (table 13) by previously described batch Na_2SO_4 precipitation methods, was used. This filtrate was diluted with water and the acidity was adjusted by adding a small amount of H_2SO_4 . The solution analysis was as follows, in grams per liter: 405 SO_4 , 47.7 Ti, 2.7 Fe, and 0.36 Cb. The $\text{SO}_4\text{-Ti}$ mole ratio was 4.24, and the density at room temperature was 1.3 g/mL.

This solution was fed to the $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation unit at about 5.43 mL/min. Higher addition rate was prevented because evaporation was limited by the rate

of heat transfer from the heating mantle through the glass reactor wall. Precipitation was accomplished by maintaining an average constant boiling temperature of about 140°C . A nominal retention time was calculated to be about 3.4 h, based on the volume of overflowing acid slurry. Overflow from the single-stage reaction vessel was filtered to recover the precipitate.

The precipitation unit operated very smoothly. Reaching conditions that were considered to be representative of the steady state took several days of intermittent operation. At the end of each day, the pump feeding the system, the heating mantle, and the stirring impeller were simply turned off. At the beginning of each day, the acid-precipitate mixture was repulped and raised to the precipitation temperature before beginning to feed fresh solution. The continuous precipitation system appeared to be self-seeding. Very little buildup of precipitate on the reactor sidewall was observed.

Filtration using a Buchner funnel formed a cake 0.20 in thick within 0.33 min at a vacuum of 14-in Hg. Precipitates with $\text{SO}_4\text{-Ti}$ mole ratios of 1.5 and 1.75 were recovered at the corresponding production rates of 96 and 257 lb/(ft²-h) in 1.17 and 0.50 min, respectively.

Allowing air to be drawn through the cake for an extended period during filtration removed most of the free acid from the surface of precipitate granules. The following recoveries were obtained in unwashed precipitate filtered for 22 min, in percent: 95 Ti, 62 Cb, 57 Fe, 28 SO_4 , and 10 Na. The $\text{SO}_4\text{-Ti}$ mole ratio of this precipitate was only 1.22. For each liter of solution treated, 0.316 L of acid filtrate (density of 1.5 g/mL), 0.610 L of condensate, and 203 g of precipitate were produced. Assays for resulting filtrate, condensate, and precipitate are provided in table 18. Scanning electron photomicrographs of two precipitate granules are provided in figure 28, showing product variability observed.

Table 18.—Continuous $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation products

Component	Filtrate, g/L	Condensate, g/L	Precipitate, pct
SO_4	925	0.15	55.4
Na	13	ND	.23
Ti	7.5	ND	22.7
Fe	3.8	ND	.79
Cb4	ND	.10
ND	Not determined.		

Precipitation for 3 to 4 h in batch systems recovered about 99.5 pct of the titanium. The difference between batch and continuous results was primarily attributed to short circuiting in the continuous system. Starting with a more dilute feed solution in the continuous system may also have slowed precipitation. Adding a second-stage

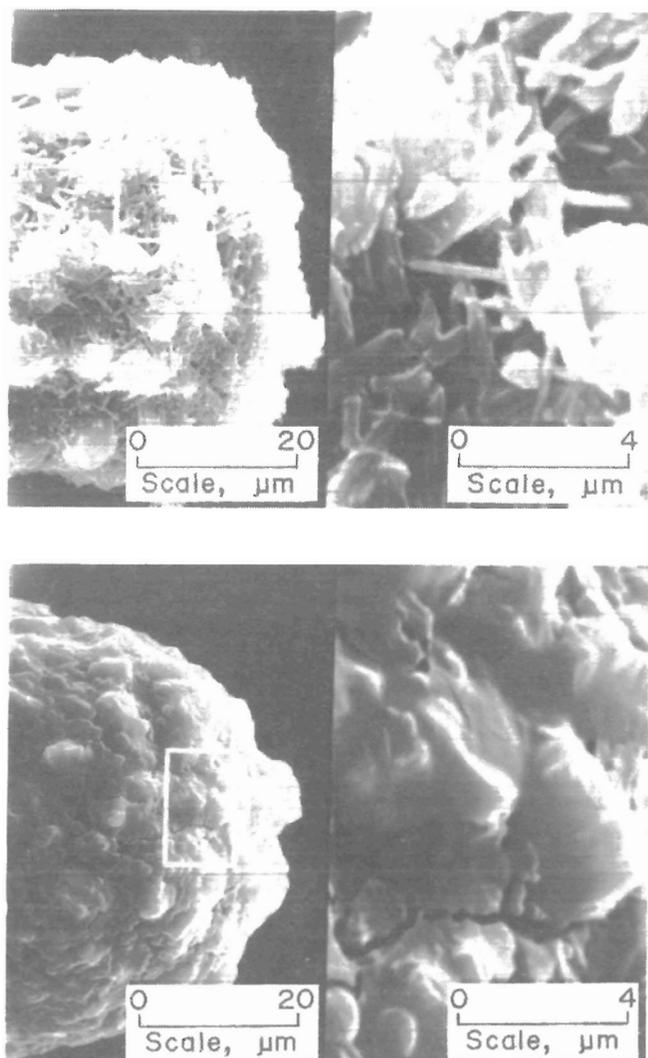


Figure 28.— $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitates formed by continuous methods. Top, dendritic surface; bottom, granular surface.

precipitation chamber to the continuous precipitation unit would likely reduce solution short circuiting and increase precipitation up to those levels obtained in batch systems. If short circuiting was substantially eliminated, the overall retention time would be reduced to about 2 h. Operating at a slightly higher temperature would tend to increase precipitation rates.

H_2SO_4 REGENERATION

One test involving acid regeneration was conducted to recover salts contained in the high-acid filtrate produced during $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation. Heating 1,000 mL of filtrate from the previously described continuous $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation test to boil off all the water and free H_2SO_4 resulted in a dry sulfate residue weighing

121 g. The residue was composed primarily of sodium, titanium, and iron sulfate salts. The following residue assays were obtained, in percent: 78 SO_4 , 11 Na, 6.5 Ti, 1.7 Fe, 0.33 Cb, 0.05 Th, and 0.036 Y. This residue contained about 77 pct of the thorium. This amount combined with that previously recovered by Na_2SO_4 precipitation of rare earths accounted for all of the thorium initially contained in the perovskite.

Filtrate from the $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation operation (stream 17 of the figure 1), which is fed to the acid regeneration operation, would normally contain <1-g/L Ti, because short circuiting of titanium rich solution would be prevented. The filtrate would contain 5- to 10-g/L Fe because filtrate recovered in the TiO_2 hydrolysis and pigment bleaching operation would be recycled to provide makeup solution for leaching. If the Na_2SO_4 precipitation method for recovering rare earths is not used, the filtrate from $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitation would contain little or no sodium, but would contain up to 5-g/L total rare earths. Regenerating H_2SO_4 from such a solution by evaporation would produce a residue consisting primarily of iron and rare-earth sulfates. The residue could be processed to remove iron and recover the rare earths.

$\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ DISSOLUTION AND IRON REDUCTION

To prepare a quantity of pregnant liquor suitable for hydrolysis of TiO_2 pigment, $\text{TiO}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ precipitate, produced in the previously described continuous precipitation section, was used. The precipitate was dissolved in acidified $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution in a stirred reaction vessel heated to 80°C for 90 min. The $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ was added to simulate buildup of iron through recycle of iron-containing acid solutions. A stoichiometric excess of iron metal chips was then added to reduce all the iron to Fe^{2+} and produce a solution containing about 1.5-g/L TP^+ . The iron chips dissolved through contact with the solution at 80°C by stirring for about 60 min. The resulting solution (similar to stream 24 in table 1) was filtered to remove traces of insoluble residue. The filtrate production rate was about 434 lb/(ft²-h) with a vacuum of 14-in Hg. This production rate was obtained using a Buchner funnel.

The resulting pregnant liquor contained 220-g/L TiO_2 , with about 0.5 mole of free H_2SO_4 per mole of contained titanium. The density was 1.5 g/mL at room temperature. Analyses for the filtrate and insoluble residue are provided in table 19. The filtrate was stored in a closed plastic container flushed with CO_2 to limit reoxidation. Less than 0.06 g of waste residue was obtained for each 1,000 g of liquor filtered. About 0.75 lb of residue would be generated for each short ton of TiO_2 product. The production amount of this residue was too small to permit testing for hazardous waste toxicity.

Table 19.—Filtrate and waste residue assays

Component	Filtrate, g/L	Residue, pct
SO ₄	456	16
Ti	132	8
Fe	34	1
Na	1.5	ND
Cb64	.1
Mg6	1
Al5	1
Ca1	5
U02	ND
Ba	<.003	9
ND	Not determined.	

TiO₂ HYDROLYSIS

Samples of TiO₂ pigment were precipitated from the titanium-rich filtrate, prepared in the TiOSO₄·H₂O dissolution and iron reduction section. Pigment precipitation involved adding a specified quantity of TiO₂ seed material to the heated pregnant liquor and maintaining the solution temperature near the boiling point (about 100° C) until precipitation was complete.

The time required for batch precipitation of the titanium depended on the amount of seed material used. When seed material was prepared from solution equivalent to 0.24 wt pct of the hydrolysis feed liquor, precipitating 97 pct of the titanium required about 18 h. When seed material was prepared from solution equivalent to 1.7 wt-pct of the hydrolysis feed liquor, precipitation required about 3.5 h.

Excessive agitation during hydrolysis tended to form deposits on the hot-glass sidewalls above the solution line. Material thus precipitated had a darkened color, apparently because iron in the thin film of solution became oxidized as it deposited. Operating with less agitation significantly decreased the amount of deposit formed on glass surfaces. The discoloration, apparently, could also have been prevented by limiting access of oxygen to the system.

TiO₂ pigment formed during hydrolysis was separated from the barren solution by filtration. About 70 pct of the uranium contained in solution fed to the TiO₂ hydrolysis operation was accounted for in the hydrolysis filtrate. Additional uranium would be removed during the subsequent washing and bleaching operations designed to remove iron contamination and other salts. Analysis showed that final pigment samples contained <5 ppm U.

PIGMENT WASHING AND BLEACHING

The TiO₂ slurry produced in the preceding hydrolysis section was filtered and washed to recover the pigment.

To prevent iron from discoloring the pigment, it was important to limit oxidation of iron contained in solution during the filtering and washing. Wash solution containing 0.05-g/L Ti³⁺ at pH 1.7 was used to maintain reducing conditions. Care was also taken to keep the surface of the filter cake damp to avoid sucking air through the cake.

Filtration and initial washing recovered about 90 pct of the sulfate contained in the liquor fed to the hydrolysis operation. The recovered filtrate had a density of 1.186 g/mL at room temperature, and the analysis was as follows, in grams per liter: 265 SO₄, 20 Fe, 2.6 Ti, 0.75 Na, and 0.052 Cb. The free-acid content of this solution was about 227 g/L. In a commercial operation, it is anticipated that recovered acid filtrate would be returned to dissolve sulfated perovskite, or would at least be added to the leach filtrate (stream 7 of figure 1) prior to precipitation of TiOSO₄·H₂O.

As additional wash solution passed through the pigment cake, a very dilute acid filtrate was produced. In a commercial operation, it is likely this solution would be neutralized with lime to form CaSO₄·2H₂O waste.

About 33 parts of wash solution was used for each part of TiO₂ contained in the cake. No attempt was made to determine whether using less wash solution would have an adverse effect on product purity.

Studies to assess filtration rates during washing indicated that a filtrate production rate of 36 to 83 lb/(ft²·h) could be achieved with cake thicknesses of 1.25 to 0.44 in, respectively. This corresponds to an overall dry cake production rate of about 0.9 to 2.2 lb/(ft²·h). A pigment producer has indicated that dry cake production rates as high as 40 lb/(ft²·h) can be achieved with the use of certain flocculents.

After initial filtration and washing the pigment was bleached to remove residual iron. The precipitate was repulped at 20-pct solids in solution containing 10-pct H₂SO₄ and 0.1-g/L Ti³⁺. The slurry was heated to 60° C for 6 h. Undiluted filtrate recovered at the end of this time contained, in grams per liter: 0.3 to 0.7 Ti, 0.032 Na, and 0.0028 Fe. The iron content of this solution indicates that the pigment iron contamination had been reduced by about 20 ppm. All of the titanium in the filtrate was in the Ti⁴⁺ valence state. This indicates a possible need for higher concentrations of Ti³⁺ in the bleaching solution or limiting air access to the bleaching slurry.

After bleaching, the slurry was filtered and washed with about 30 parts of water per part contained TiO₂. The filtrate and dry-cake production rates were similar to those obtained during filtration and washing of freshly hydrolyzed pigment.

In a commercial operation, undiluted bleaching filtrate would be returned to provide makeup solution for leaching sulfated perovskite. Dilute wash solution would be advanced to wash freshly hydrolyzed TiO₂ or would be

neutralized to precipitate contained impurities. The damp filter cake would be advanced to a roasting operation to remove contained sulfate and to consolidate the pigment crystal structure. After roasting, the pigment would proceed to the grinding and pigment finishing operations.

PIGMENT EVALUATION

Samples of washed and bleached TiO_2 pigment were sent to commercial pigment producers for roasting studies and product evaluation. Chemical analyses (table 20) showed that the pigments contained low quantities of iron and other discoloring elements.

Pigment A was precipitated using insufficient solution for seed preparation. This resulted in an excessive amount of time for precipitation of 97 pct of the contained TiO_2 . Pigment B was produced in 3.5 h, at a somewhat lower level of recovery, using an increased amount of solution for seed preparation. Production of pigment C used an even higher amount of solution for seed production. Using seed solution equivalent to 1.7 wt-pct of the feed liquor precipitated 90 pct of the titanium in only 3 h. At this level of seed addition, about 3.5 h would be required to achieve 97-pct Ti precipitation.

In preparing feed liquor for precipitation of pigment C, iron reduction was performed during the $TiOSO_4 \cdot H_2O$ dissolution operation rather than subsequent to dissolution. The higher copper content of pigment C would suggest that iron reduction after dissolution of $TiOSO_4 \cdot H_2O$ is preferable to simultaneous dissolution and reduction.

About half of the columbium reports as pigment. Methods of roasting have been described that prevent columbium from discoloring TiO_2 products (34).

Iron concentrations as high as 50 ppm may be tolerated without adversely affecting the pigment. The very low level of iron found in the pigment samples suggests that less rigorous washing and bleaching methods may be used. This would help lower pigment filtration costs.

Uranium was not detected in the pigment products (<5 ppm U). The thorium content of pigments was not determined, but analyses indicate that all of the thorium initially contained in the perovskite can be accounted for in the combined residues from Na_2SO_4 precipitation of rare earths and H_2SO_4 regeneration.

Microtrac evaluation showed that mean particle size of the roasted pigments ranged from 2.08 to 2.24 μm . Scanning electron photomicrographs of unroasted and unground pigment sample C are provided in figure 29. The unground mean particle size required for high-quality roasted pigments is normally much smaller than those submitted for evaluation, about 0.5 to 0.8 μm . The coarseness of the pigment samples diminished tinting strength and adversely influenced other pigment characteristics. The large particle size also made it difficult to assess whether higher than normal concentrations of columbium had any adverse effect. Milling can improve the quality of pigments, but it cannot be expected to substitute for state-of-the-art precipitation procedures in a competitive market.

The large particle size of these pigment samples apparently resulted from using too low a concentration of free acid in the solution fed to TiO_2 hydrolysis or using inadequate seed material during TiO_2 hydrolysis. The evaluations indicated that higher grade pigments would be obtained with additional work in the following areas: (1) using a somewhat higher free acid content in the solution fed to TiO_2 hydrolysis, (2) preparing more effective

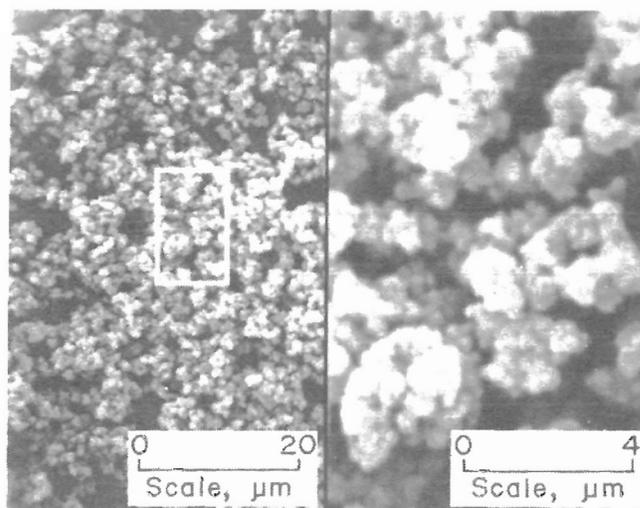


Figure 29.—Unground TiO_2 pigment.

Table 20.—Results of pigment sample evaluations

Pigment	Seed solution, wt pct	Precipitation time, h	Impurity analyses, ppm					Mean particle size, μm
			Cb	Fe	Cu	Cr	U	
A	0.24	18	3,600	7	0.8	0.3	<5	2.08-2.24
B76	3.5	1,900	14	.4	1	<5	2.15-2.22
C	1.7	3.0	2,800	13	3.8	.4	<5	2.12

TiO₂ seed material, and (3) evaluating the use of additives with calcination. Methods of hydrolysis, TiO₂ seed preparation, and calcination are well known by those skilled in the art.

SOLID WASTE TOXICITY TEST RESULTS

Solid waste from sulfation processing of perovskite can be classed as two basic types: (1) insoluble material, primarily CaSO₄, remaining after aqueous leaching of sulfated perovskite (stream 10 of figure 1), and (2) precipitate, composed primarily of CaSO₄·2H₂O, obtained by neutralization of streams 28 and 34 in figure 1. Samples of CaSO₄ and CaSO₄·2H₂O waste, obtained during processing of Colorado perovskite, were leached using the extraction procedure toxicity test established by the EPA (33).

Hazardous metal concentrations were much lower than allowable standards, indicating that neither material would be classified as hazardous waste (table 21).

Table 21.—Toxicity test results, milligrams per liter

Metal ion	Allowable maximum	Final solution concentration	
		CaSO ₄ waste	CaSO ₄ ·H ₂ O waste
Ba	100.0	18	18
Ag	5.0	<.1	<.1
As	5.0	.005	<.005
Cr	5.0	<.2	<.2
Pb	5.0	<.2	<.2
Cd	1.0	<.01	<.01
Se	1.0	<.002	<.002
Hg2	<.0005	<.0005

COST EVALUATION

A cost evaluation (appendix B) was based on the figure 1 flowsheet and the material balance provided in table 1. A recovery of 95-pct TiO₂ was estimated for treating concentrates containing 50-pct TiO₂. Perovskite concentrate and H₂SO₄ consumed in processing were estimated to cost \$60/st and \$70/st delivered, respectively.

The annual plant production capacity was 63,000 st of finished TiO₂. Continuous plant operation for 330 d/yr allowed 35 d/yr of downtime for inspection, maintenance, and unscheduled interruptions. Equipment costs, mainly from published sources, were adjusted for a Marshall and Swift index of 894.7 (second quarter, 1989). Depreciation is based on a straight-line, 20-year period.

A domestic TiO₂ producer supplied estimates on the cost of finishing roasted TiO₂ precipitates. Finishing includes grinding, chemically treating the pigment surface, and preparing the product for market.

A summary of fixed capital and production costs associated with sulfation processing and pigment finishing operations is provided in appendix B.

The total production cost (\$1,090/st of TiO₂ produced) compared favorably with the market price of anatase pigment, about \$2,040/st. The estimated interest rate of return on investment after taxes was about 24 pct.

Recovery of acid by regeneration keeps the overall acid requirement low: about 2.9 st of acid per short ton of TiO₂ produced. This compares with 2.5 to 4 st of acid per short ton of TiO₂ produced from ilmenite (35).

The combined quantity of solid waste (primarily CaSO₄ leach tailing and CaSO₄·2H₂O neutralization precipitate) totals about 4.0 st per short ton of TiO₂ produced. Processing ilmenite of corresponding TiO₂ grade by established acid sulfation methods would generate at least 60 pct more solid waste, composed of about two-thirds FeSO₄·7H₂O and one-third CaSO₄·2H₂O.

CONCLUSIONS

Perovskite is an important potential resource for titanium. The Bureau has developed technology for reacting perovskite concentrates with H₂SO₄, achieving a very high degree of sulfation. Tests have shown that the sulfation residues produced can be leached in aqueous solution, extracting up to 97 pct of the titanium and significant amounts of rare earths and columbium. Results obtained on a laboratory scale indicate that the sulfation and leaching operations can be performed in continuous systems. Resulting liquors can be further processed to separate and recover byproduct values and recover the titanium as TiO₂ pigment.

Sulfation of perovskite concentrates can be accomplished in a single-stage reaction vessel. Excellent sulfation results can be achieved in continuous systems at pulp solids levels as high as 8 g of concentrate to 20 mL of acid solution. Agitation required in the reactor can be provided by the boiling action of escaping steam. In a continuous system, digesting minus 35-mesh perovskite concentrate at 250° C with 90-pct H₂SO₄ solution at a pulp-solids ratio of 8:20 requires a minimum retention time of 30 min. To ensure against precipitation of salts on drainage piping surfaces, a retention time of 2 h is recommended.

Residues recovered by filtration of the sulfation discharge can be leached in continuous systems to extract the metal values. The resulting residue consists of anhydrous CaSO_4 and gangue material. Optimum conditions involve leaching the sulfation residue for about 90 min at temperatures between 60° and 80° C with aqueous or dilute acid solutions while using low to moderate mechanical agitation. If agitation is too violent, the final filtration rate may be impaired. In continuous leach systems, no problems of plugging were encountered if agitation was sufficient to keep the solid materials suspended.

Leach filtrate can be treated to precipitate $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ and to recover excess acid by continuous laboratory-scale methods of operation. Over 99 pct of the titanium can be precipitated within 2 h after evaporation to concentrate the solution to a boiling point in the range 140° to 150° C. The rare earths and about half the columbium remain in the recyclable acid filtrate.

The $\text{TiOSO}_4 \cdot \text{H}_2\text{O}$ precipitate is redissolved in water. The dissolved iron and a small amount of titanium are reduced to Fe^{2+} and Ti^{3+} with metallic iron. Dissolution is completed within 90 min at 80° C. Subsequent reduction with iron chips requires about 60 min. Filtration of the reduced solution generates only about 0.75 lb of insoluble waste material per short ton of TiO_2 produced. The pregnant filtrate contains about 220 g/L TiO_2 .

TiO_2 pigment can be precipitated from the reduced filtrate in about 3.5 h by hydrolysis at temperatures near 100° C with the addition of seed material. Following precipitation, the TiO_2 is washed and bleached with dilute H_2SO_4 . After rewashing with water, the TiO_2 contains

about 8 pct SO_4 , which is eventually removed by roasting. Pigments with low levels of iron, copper, and chromium were produced. Evaluations showed that preparing high-quality pigments, required in a competitive market, will necessitate additional research on methods of pigment hydrolysis, seeding, and calcination.

About 70 to 90 pct of the rare-earth elements can be dissolved after sulfation of perovskite concentrates. Two methods of rare-earth recovery may be used. One method involves precipitation of a sodium-rare-earth double salt. The light rare earths are precipitated in 1 to 3 h after adding 20 to 30 g/L Na_2SO_4 , using mild agitation at about 60° C. The second method for recovering rare earths seems simpler and is preferred. This approach recovers the rare earths in the solid residue obtained from regeneration of H_2SO_4 .

About 97 pct of the columbium is solubilized during leaching of sulfated perovskite. About half this columbium reports with the rare earths in the solid residue obtained from acid regeneration. The remaining columbium reports with the pigment.

An evaluation was performed to determine the cost of preparing TiO_2 pigment from perovskite by the sulfation processing methods developed. The combined cost of sulfation processing and pigment finishing (\$1,090/st of TiO_2) compared favorably with the corresponding market price of anatase pigment, about \$2,040/st. The estimated interest rate of return on investment after taxes was about 24 pct. These results indicate that processing perovskite concentrates by acid sulfation may be an economically viable means of producing TiO_2 .

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APPENDIX A.—ADDITIONAL SULFATION DATA

Table A-1.—Batch-sulfation data

Test	Sulfation conditions					Results, pct										
	Time, min	Impeller, rpm	Pulp-solids ¹	Grind, mesh	Temp, °C	Sulfation				Water leaching						
						Cb	Ce	La	Ti	Cb	Ce	La	Ti			
1 ...	60	0	3:20	-35	200	61	52	49	36	49	10	8	32			
2 ...	60	300				87	68	70	58	74	16	13	53			
3 ...	60	600				84	64	71	64	76	12	16	62			
4 ...	60	1,000				91	74	83	87	80	25	33	86			
5 ...	60	1,200				90	75	86	87	88	36	54	86			
6 ...	15	0	3:20	-35	250	97	61	73	83	15	59	70	82			
7 ...	15	300				85	60	73	84	68	57	68	83			
8 ...	15	600				92	66	78	88	75	61	69	87			
9 ...	15	1,200				94	63	75	92	75	60	68	91			
10 ..	5	0				71	48	54	71	37	35	41	48			
11 ..	5	300	3:20	-35	200	74	55	61	74	29	36	44	41			
12 ..	5	600				81	50	58	73	36	37	42	45			
13 ..	5	1,200				77	64	71	74	26	54	62	31			
14 ..	15	0				3:20	-35	300	98	73	86	95	61	71	84	94
15 ..	60								75	64	76	75	58	12	16	74
16 ..	60		78	68	77				77	61	14	17	76			
17 ..	15		95	75	87				93	72	74	85	92			
18 ..	15		96	89	95				96	76	88	93	94			
19 ..	60	1,000	1:20	-35	200	86	87	88	87	24	15	9	67			
	120					93	90	92	92	47	15	9	87			
	180					92	90	92	92	52	18	9	87			
	240					92	93	94	91	46	16	9	86			
	300					94	92	84	91	51	18	9	86			
20 ..	30	1,000	3:20	-35	200	80	73	78	59	55	21	30	58			
	60					88	75	86	65	76	30	65	63			
	120					92	85	92	90	84	42	45	88			
	180					93	85	87	90	87	37	39	89			
	300					67	51	67	55	66	34	34	53			
21 ..	60	1,000	5:20	-35	200	81	70	82	79	77	38	45	78			
	120					79	73	83	80	74	48	47	79			
	180					93	80	89	87	90	78	52	86			
	240					94	91	92	90	88	80	58	89			
	300					95	88	92	89	92	72	66	88			
22 ..	30	1,000	8:20	-35	200	70	64	75	49	69	56	65	48			
	60					86	65	80	68	81	60	78	61			
	120					85	83	86	71	75	53	58	77			
	180					92	85	73	77	91	83	72	65			
	240					ND	67	86	80	ND	64	84	79			
	300	95	72	85	82	94	70	83	81							
	360	90	ND	87	83	88	ND	83	82							
23 ..	2	1,000	2:20	-35	250	74	63	76	64	3	21	15	12			
	5					87	67	78	88	83	62	72	81			
	10					87	68	83	94	32	64	67	91			
	30					ND	62	75	96	ND	58	70	91			
	60					91	64	78	96	35	76	73	35			
24 ..	.5	1,000	2:20	-35	300	ND	ND	ND	45	ND	ND	ND	37			
	2					ND	ND	ND	82	ND	ND	ND	78			
	5					ND	ND	ND	90	ND	ND	ND	87			
	10					ND	ND	ND	72	ND	ND	ND	69			
	30					ND	ND	ND	87	ND	ND	ND	84			
	60	ND	ND	ND	92	ND	ND	ND	90							
25 ..	.5	1,000	3:20	-35	300	67	48	54	39	50	45	51	36			
	2					99	77	88	87	43	75	86	85			
	5					99	79	89	93	33	75	87	91			
	30					97	86	89	90	31	71	86	88			
	60					98	76	79	77	55	64	76	74			

ND Not determined.

¹Ratio of solids (grams) to acid (milliliters).

Table A-1.—Batch-sulfation data—Continued

Test	Sulfation conditions					Results, pct												
	Time, min	Impeller, rpm	Pulp-solids ¹	Grind, mesh	Temp, °C	Sulfation				Water leaching								
						Cb	Ce	La	Ti	Cb	Ce	La	Ti					
26 ..	15	1,000	1:20	-100	150	18	25	25	17	<1	3	2	<1					
	30					33	32	38	32	1	4	4	<1					
	60					47	46	52	37	1	6	6	1					
	120					ND	ND	ND	44	ND	ND	ND	2					
	240					84	76	82	79	24	9	7	67					
	360					86	ND	ND	84	18	ND	ND	80					
	420					96	90	94	93	53	24	20	89					
27 ..	480	1,000	1:20	-100	250	97	92	97	95	36	22	21	92					
	2.5					99	97	94	96	4	13	14	6					
	5					99	84	91	93	58	79	84	76					
	10					99	90	94	97	59	81	80	88					
	20					99	91	95	98	52	83	86	88					
	30					99	85	89	98	81	69	73	89					
	60					99	84	90	96	23	74	80	86					
28 ..	120	1,000	1:20	-65	200	96	85	93	96	9	73	81	89					
	240					92	88	94	92	1	72	78	87					
	30					92	90	93	91	4	0	2	3					
	60					95	93	97	95	49	8	11	84					
	120					96	94	95	95	56	11	12	91					
	180					96	93	95	92	57	13	13	88					
	240					96	92	95	95	57	12	13	91					
29 ..	300	1,000	1:20	-100	200	97	93	97	96	60	10	12	92					
	30					98	94	98	97	5	1	3	10					
	60					97	94	96	93	46	4	2	84					
	120					97	92	98	96	59	6	11	92					
	240					99	97	97	98	62	1	3	94					
	30 ..					.5	1,000	1:20	-35	250	76	75	70	51	19	5	6	1
						2.5					91	93	92	78	43	30	82	53
10		98	87	91	97	51					75	78	83					
20		95	90	95	98	50					79	85	86					
30		91	51	84	95	27					38	78	85					
60		99	40	80	98	25					24	73	89					
120		95	79	79	94	25					66	76	87					
31 ..	180	1,000	1:20	-65	250	91	84	89	93	29	68	76	87					
	.5					79	19	19	68	11	1	2	1					
	2.5					98	96	97	93	29	33	40	39					
	7					99	85	93	99	51	80	85	89					
	10					93	87	94	99	76	86	93	86					
	20					99	85	93	99	76	84	92	88					
	30					99	91	94	99	59	81	82	89					
32 ..	60	1,000	1:20	-35	300	99	85	92	99	21	76	85	90					
	120					95	82	90	91	23	70	79	84					
	180					91	85	91	94	22	70	77	88					
	.5					37	44	45	68	9	23	23	7					
	2.5					93	72	79	78	58	66	73	70					
	10					98	80	89	91	58	75	84	84					
	20					99	82	89	93	61	77	84	86					
33 ..	30	1,000	1:20	-65	300	98	78	86	96	51	75	81	90					
	60					99	79	88	96	51	71	82	90					
	120					95	80	90	95	40	69	83	91					
	180					96	81	87	95	56	74	80	92					
	.5					87	74	79	78	47	67	73	69					
	2.5					96	80	88	95	38	77	86	90					
	5					98	80	89	96	39	76	84	91					
33 ..	10	1,000	1:20	-65	300	98	80	87	96	49	76	85	91					
	20					99	86	92	95	41	81	86	89					
	30					ND	80	87	96	ND	75	82	91					
	60					99	85	88	97	30	78	82	92					
	180					98	83	89	96	35	74	80	95					

ND Not determined.

¹Ratio of solids (grams) to acid (milliliters).

Table A-1.—Batch-sulfation data—Continued

Test	Sulfation conditions					Results, pct							
	Time, min	Impeller, rpm	Pulp-solids ¹	Grind, mesh	Temp, °C	Sulfation				Water leaching			
						Cb	Ce	La	Ti	Cb	Ce	La	Ti
34 ..	0.5	1,000	1:20	-100	300	92	39	85	89	46	25	80	81
	2.5					99	80	88	97	42	76	84	92
	10					99	81	90	96	40	77	85	91
	20					99	73	84	97	41	68	79	91
	30					99	84	90	96	45	80	84	91
	60					99	87	92	96	49	79	83	91
	120					99	81	87	96	36	72	79	91
	180					99	85	91	96	9	77	84	92
35 ..	15	1,000	1:20	-100	225	99	97	98	96	9	55	61	11
	30					99	98	99	97	34	83	87	58
	60					99	98	99	97	59	61	63	92
36 ..	90	1,000	1:20	-100	185	99	98	99	97	61	64	68	93
	60					95	88	93	95	5	4	3	5
	120					99	93	97	98	25	11	10	43
	180					99	92	97	96	59	17	15	94
37 ..	240	1,000	1:20	-100	165	99	83	99	97	62	10	16	94
	300					99	87	99	99	61	11	17	95
	180					92	82	88	94	11	9	9	26
	240					89	86	91	96	42	16	15	88
	300					89	87	93	98	43	17	16	94
38 ..	360	1,000	1:20	-100	165	92	90	94	98	42	15	14	94
	420					93	87	92	98	47	14	14	93
38 ..	120	1,000	1:20	-35	200	86	89	92	92	48	4	5	86
39 ..	7	1,000	1:20	-35	250	99	84	92	98	29	80	85	85
40 ..	60	1,000	1:20	-65	200	98	90	97	93	58	9	9	90
41 ..	7.5	1,000	1:20	-65	250	99	82	91	99	33	80	87	87
42 ..	60	1,000	1:20	-100	200	98	94	93	95	57	9	8	88

ND Not determined.

¹Ratio of solids (grams) to acid (milliliters).

Table A-2.—Batch-sulfation comparisons for various perovskite concentrates, percent

(Sulfation conditions: 1,000-rpm impeller, 1:20 pulp-solids ratio, minus 65-mesh material 300° C)

Time, min	Sulfation		Water leaching		Time, min	Sulfation		Water leaching	
	Cb	Ti	Cb	Ti		Cb	Ti	Cb	Ti
COLORADO CONCENTRATE					ARKANSAS SURFACE ROCK CONCENTRATE				
0.5 ..	87	78	47	69	0.5 ..	51	52	2	3
2.5 ..	96	95	38	90	2.5 ..	87	75	19	64
5 ...	98	96	39	91	5 ...	92	74	20	66
10 ..	98	96	49	91	10 ..	93	75	5	20
20 ..	99	95	41	89	20 ..	94	86	17	52
30 ..	ND	96	ND	91	30 ..	93	86	11	40
COLORADO SURFACE ROCK CONCENTRATE					ARKANSAS DRILL CORE CONCENTRATE				
0.5 ..	72	69	25	61	0.5 ..	63	56	<1	<1
2.5 ..	92	89	31	82	2.5 ..	86	68	19	45
5 ...	95	88	34	81	10 ..	88	62	18	34
10 ..	96	94	3	87	20 ..	92	63	17	35
20 ..	96	94	32	86	30 ..	88	62	27	55
30 ..	96	94	36	88					

ND Not determined.

APPENDIX B.—ECONOMIC AND TECHNICAL EVALUATION

By Joan H. Schwier¹

PLANT DESCRIPTION

For this evaluation, a plant has been designed to process 400 st/d of perovskite concentrate. Existing U.S. sulfation process pigment plants are approximately the same size. The analysis of the perovskite concentrate is listed in table B-1.

Table B-1.—Perovskite concentrate analysis

<i>Component</i>	<i>pct</i>
TiO ₂	50.0
Ca	24.0
Fe	2.1
CO ₂	1.5
Other ¹	22.4
<u>Total</u>	<u>100.0</u>

¹Includes about 2 pct rare earth and about 0.2 pct Cb.

Mixing perovskite concentrate with 90-pct H₂SO₄ forms titanium and calcium sulfates that are insoluble in concentrated acid. After the excess acid is separated, the resulting sulfates are leached with dilute acid to dissolve the titanium. Boiling the leach solution precipitates the titanium as TiOSO₄·H₂O. After the precipitate is dissolved in water, it is reprecipitated as TiO₂ by boiling the resulting solution. For descriptive purposes, the plant is arbitrarily divided into 10 sections: concentrate receiving, sulfation, sulfate dissolution, precipitation, dissolution, hydrolysis, calcination, pigment finishing, acid regeneration, and neutralization.

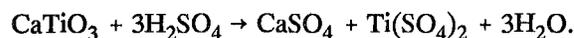
Concentrate Receiving Section

Perovskite concentrate is received by rail or truck and dumped into a receiving hopper. It is assumed that the plant is located close to the millsite. From the hopper the concentrate is conveyed to storage silos, which are designed to hold a 30-day supply. Concentrate is withdrawn from storage as required and conveyed to the sulfation section.

Sulfation Section

After leaving the concentrate receiving section, perovskite concentrate is fed to an agitated tank and mixed with

90 pct H₂SO₄, which is recycled from the subsequent filtration step. Any carbonates in the concentrate react immediately, generating CO₂, which is vented. The perovskite slurry is then pumped to one of three sulfation vessels and mixed with additional H₂SO₄, which has been preheated to 250° C. Concentrate and H₂SO₄ react to form Ti(SO₄)₂ and CaSO₄ by the following reaction:



Laboratory studies indicated that this reaction is exothermic enough to maintain the reaction temperature of 250° C; however, thermodynamic data are not available to check this information. The acid concentration in the sulfation units is maintained at 90 pct, since enough heat is available to boil most of the water.

Since laboratory investigations indicated that standard leaching tanks would be unsatisfactory because of their limited surface area, a special design was developed. In order to obtain a final design, pilot plant scale research is needed.

Three vessels, 42 ft long by 10 ft wide, are used in the plant design. Each vessel contains horizontal troughs, 2 ft wide by 2 ft deep running the length of the vessel. The external portions of the vessels are designed with a steel shell, lined with lead and acid-resistant bricks, while the internal portions are constructed of enamel-covered steel. The trough design provides sufficient surface area to accommodate the vigorous boiling action. About 4 ft² of surface area per short ton of concentrate per day is reported to be required. Concentrated acid and acid-concentrate slurry are fed through pipes at the bottom of each trough. Sulfated slurry overflows the sides of each trough and is collected at the bottom of the vessel. The intense boiling of the slurry provides sufficient agitation. Water and acid vapors produced are vented from the top of the vessel and condensed in a heat exchanger. A 30-min retention time is required for the minus 35-mesh concentrate.

After leaving the sulfation vessels, the slurry is cooled to 40° C in heat exchangers and fed to a rotary-vacuum drum filter. Excess acid is removed by the filter and pumped back to the mixing tank. The filter cake is conveyed to the sulfate dissolution section.

Sulfate Dissolution Section

The sulfated perovskite, a mixture of titanium, calcium, and iron sulfates is leached with a mixture of condensate,

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filtrate, and spent washings maintaining temperatures between 60° and 80° C. The titanium and iron sulfates dissolve, leaving the CaSO_4 in a residue. This slurry is filtered on rotary-vacuum drum filters with a dry residue production rate of 0.02 st/(ft²-h). The titanium-rich leachate is then pumped to the precipitation section, and the filter cake is washed with filtrate produced in the product bleaching step. Spent washings are used in leaching, and the filter cake is conveyed to the neutralization section.

Precipitation Section

The titanium-rich leachate is fed to a multiple effect evaporator. Concentration of the acid to approximately 70-pct free acid causes the titanium to precipitate as titanyl sulfate ($\text{TiOSO}_4 \cdot \text{H}_2\text{O}$).

Slurry from the evaporator is pumped to two precipitation tanks in series. The combined residence time in the evaporator and the precipitation tanks is approximately 2 h. The slurry from the second tank is pumped to a rotary-vacuum drum filter. The recovered acid is pumped to the acid regeneration section, and the filter cake is washed with H_2SO_4 and conveyed to the dissolution section. Vapor from the evaporator is condensed and collected in a storage tank. The condensate is used in the washing operation following hydrolysis.

Dissolution Section

Filter cake from precipitation is dissolved in water in a dissolution tank operating at 80° C. The resulting solution is mixed with fine scrap iron, such as turnings, in a reduction tank where the scrap iron reduces Fe^{3+} in solution to Fe^{2+} , preventing their coprecipitation in the subsequent hydrolysis step. Iron and any other solids in solution are removed by precoated pressure-leaf filters. The filtrate is then pumped to the hydrolysis section. The solids are collected in bins and periodically transported by a front-end loader to a disposal site.

Hydrolysis Section

Hydrolysis of the pregnant solution from the dissolution section is a batch operation. Solution is fed to one of five stirred hydrolysis tanks and boiled at ambient pressure with TiO_2 seed for about 3 h. A hydrated TiO_2 precipitates from solution, leaving a 23-pct H_2SO_4 solution, which is used in sulfate dissolution. A flocculant is added, and the slurry is filtered in pressure-leaf filters with a filtration rate of 40 lb/(ft²-h). The filter cake is washed to remove the remaining acid and dissolved iron. The wash solution consists of dilute H_2SO_4 with a small quantity of Ti^{+3} added to prevent any oxidation of the iron. Spent washings are pumped to the neutralization section.

The washed precipitate is then fed to bleach tanks and mixed with a 10-pct H_2SO_4 solution to dissolve the residual iron. This bleaching step has a retention time of 6 h at 60° C. Condensate from the precipitation section is used as both the wash solution in the previous step and as makeup solution for bleaching. A flocculant is added to the bleached slurry, then filtered in pressure-leaf filters, and washed first with dilute acid and then with water. The initial filtrate is pumped to the sulfate dissolution section, while the washings are pumped to the neutralization section. The resulting filter cake is conveyed to the calcination section.

Calcination Section

The TiO_2 filter cake contains about 8 pct SO_4 , which can only be removed by calcination. The filter cake from the hydrolysis section is fed to a rotary kiln. Maintaining the temperature between 800° and 1,000° C dehydrates the TiO_2 and drives off sulfates as sulfur trioxide (SO_3). After collecting dust from the stack gas, the gas stream is scrubbed with a lime slurry. The roasted TiO_2 is quenched in water.

Pigment Finishing Section

Finishing by conventional technology will be required, but was not included in the U.S. Bureau of Mines research. Capital and operating costs were obtained from a pigment producer and are included in the economic analysis. Because the equipment for this section was not designed, no description is included.

Acid Regeneration Section

Monsanto's acid regeneration process appears to be the most practical. In this process, the spent acid, including any dissolved salts, is spray roasted to convert the H_2SO_4 to sulfur dioxide (SO_2) and water vapor. The gas product is cleaned, then fed to a contact acid plant. Most of the dissolved salts are recovered as a dry SO_4 or oxide product from the calciner. This technology is available from Monsanto as a turnkey system, which can recover 98 pct acid from a 70-pct acid feed, including waste-heat recovery.

Neutralization Section

Solutions containing dilute acids that cannot be used must be neutralized. These solutions are filtrates from the initial washing of the TiO_2 precipitate and from the second washing of the bleached TiO_2 . The solutions are pumped to neutralization tanks and mixed with pulverized limestone, which forms gypsum. The resulting slurry is then pumped to a tailings pond. The water from the tailings

pond is pumped back to the plant and used as process water.

ECONOMICS

Capital and operating cost estimates for a plant based on the preceding description are presented. Although a plantsite has not been selected, it is assumed that the plant will be located near the perovskite concentrator (Gunnison County, CO). It is also assumed that the plant will be close to most utilities and facilities, including a rail line.

In the preparation of most economic evaluations, it is necessary to make many assumptions. One example of such an assumption is that most of the plant will operate three shifts per day, 7 days per week. Another example is that land cost has not been included in the capital and operating cost estimate. Whenever an important assumption is made, it is documented in this report.

Because of the numerous assumptions present in any of its economic evaluations, the Bureau strives to present its evaluations in a detailed format. This allows a user the flexibility to make any adjustments that would enable the evaluation to reflect a particular situation.

Capital Costs

The capital cost estimate is of the general type, called a study estimate by Weaver (36).² This type of cost estimate is usually expected to be within 30 pct of the cost to build the plant described. However, in this estimate, the major capital cost items are the sulfation vessels, for which there are insufficient design data available to prepare a reliable design and cost. Therefore, no accuracy limits for the cost estimates are projected at this time.

The estimated fixed capital cost on a second quarter 1989 basis [Marshall and Swift (M and S) index of 894.7] for a plant processing 400 st/d of perovskite concentrate is approximately \$137 million with finishing (table B-2) and approximately \$91 million without finishing.

Concentrate receiving equipment and reagent receiving equipment are designed to operate one shift per day, 5 days per week. The remainder of the plant is designed to operate three shifts per day, 7 days per week, 330 d/yr. The remaining 35 days are for scheduled and unscheduled downtime.

Equipment costs for the process are based on cost-capacity data and manufacturer's 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 dissolution tanks are steel, lined with lead- and acid-resistant bricks.

Table B-2.—Estimated capital cost¹

Fixed capital:	
Concentrate receiving section	\$1,917,700
Sulfation section	11,096,900
Sulfate dissolution section	4,374,600
Precipitation section	5,704,300
Dissolution section	755,400
Hydrolysis section	7,281,800
Calcination section	4,894,600
Finishing section	30,211,200
Acid regeneration section	24,100,800
Neutralization section	1,571,900
Steam plant	2,803,800
Subtotal	<u>94,713,000</u>
Plant facilities, 10 pct of above subtotal . . .	9,471,300
Plant utilities, 12 pct of above subtotal . . .	11,365,600
Total plant cost	<u>115,549,900</u>
Tailings pond	6,104,000
Land cost	0
Subtotal	<u>121,653,900</u>
Interest during construction period	14,955,500
Fixed capital costs	<u>136,609,400</u>
Working capital:	
Raw material and supplies	2,624,800
Product and in-process inventory	5,619,300
Accounts receivable	5,619,300
Available cash	<u>4,585,200</u>
Working capital cost	18,448,600
Capitalized startup costs	1,366,100
Subtotal	<u>19,814,700</u>
Total capital cost	<u>156,424,100</u>

¹Basis: M and S equipment cost index of 894.7.

Factors for piping, instrumentation, structures, insulation, etc., except for the foundation and electrical factors, are assigned to each section using as a basis the effects that fluids, solids, or a combination of fluids and solids may have on the process equipment. The foundation cost is individually estimated for each piece of equipment, and a factor for the entire section is calculated from the total. The electrical factor is based on 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 that are 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. Engineering cost and administration and overhead cost are estimated at 5 pct each 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 Bureau did not include pigment finishing in its research program because it uses known technology. However, an annual fixed capital cost of \$525 per short ton was obtained from a pigment producer and used in this economic study in order to provide a complete plant cost.

²Italic numbers in parentheses refer to items in the list of references preceding appendix A.

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 included in the section costs. Included under plant facilities are the costs of material and labor for auxiliary buildings, such as offices, shops, laboratories, and cafeterias, and the cost of nonprocess equipment, such as office furniture, together with safety, shop, and laboratory equipment. Also included are labor and material costs for site preparation, such as site 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. Land investment is not included in this estimate. Also, 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 (table B-2) is estimated from the following items: (1) raw material and supplies 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 cost for 30 days), and (4) available cash (direct expenses for 30 days). Capitalized startup costs are estimated as 1 pct of the fixed capital (table B-2).

Operating Costs

The estimated operating costs are based on 330 days of operation per year over the life of the plant. The operating costs are divided into direct, indirect, and fixed costs (table B-3).

Direct costs include raw materials, utilities, direct labor, plant maintenance, payroll overhead, and operating supplies. The transportation costs are included in the cost of the raw materials. Electricity, water, and natural gas are purchased utilities. Raw material and utility requirements per short ton of TiO_2 are shown in table B-4. The daily thermal requirements are shown in table B-5.

Direct labor costs are estimated on the basis of assigning 4.2 employees to each position that operates 24 h/d, 7 days per week. The cost of labor supervision is estimated as 15 pct of the labor 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, which includes vacation, sick leave, social security, and fringe benefits, is estimated as 35 pct

of direct labor and maintenance labor. The cost of operating supplies is estimated as 20 pct of the cost of plant maintenance.

Table B-3.—Estimated annual operating cost

	Annual cost	Cost per short ton TiO_2
Direct cost:		
Raw materials:		
Perovskite concentrate at \$60/st	\$7,920,000	\$126.32
Sulfuric acid at \$70/st	12,788,200	203.96
Scrap iron at \$68/st	98,700	1.57
Limestone at \$26/st	1,921,900	30.65
Flocculant at \$2.25/lb	37,900	.60
Chemicals for steam plant water treatment	23,500	.37
Total	22,790,200	363.47
Utilities:		
Electric power at \$0.036/kW-h	398,500	6.36
Process water at \$0.25/10 ² gal	54,200	.86
Natural gas at \$3.75/10 ⁶ Btu	13,041,500	208.00
Total	13,494,200	215.22
Direct labor:		
Labor at \$12/h	2,620,800	41.80
Supervision, 15 pct of labor	393,100	6.27
Total	3,013,900	48.07
Plant maintenance:		
Labor	2,400,400	38.28
Supervision, 20 pct of maintenance labor	480,100	7.66
Materials	2,400,500	38.29
Total	5,281,000	84.23
Payroll overhead, 35 pct of above payroll ¹	2,063,000	32.90
Operating supplies, 20 pct of plant maintenance	1,056,200	16.85
Pigment finishing	8,088,300	129.00
Total direct cost	55,786,800	889.74
Indirect cost, 40 pct of direct labor and maintenance	3,318,000	52.92
Fixed cost:		
Taxes, 1 pct of total plant cost	1,216,500	19.40
Insurance, 1 pct of total plant cost	1,216,500	19.40
Depreciation, 20-year life	6,830,500	108.94
Total operating cost	68,368,300	1,090.40

¹Direct labor and supervision, maintenance labor and supervision.

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

Table B-4.—Raw material and utility requirements

		Quantity per short ton of TiO ₂
Raw materials:		
Perovskite concentrate	st ..	2.105
H ₂ SO ₄	st ..	2.914
Scrap iron	st ..	0.023
Limestone	st ..	1.179
Flocculant	lb ..	0.268
Utilities:		
Electric power	kW-h ..	176.574
Process water	10 ² gal ..	3.456
Natural gas	10 ⁶ Btu ..	55.466

**Table B-5.—Daily thermal requirements,
million British thermal units**

Section and item	Steam	Natural gas
Sulfation:		
Heat exchangers	327.10	0.00
Heat exchanger	61.60	.00
Subtotal	<u>388.70</u>	<u>.00</u>
Sulfate dissolution:		
Heat exchanger	<u>386.30</u>	<u>.00</u>
Precipitation:		
Precipitation evaporator	<u>1,571.90</u>	<u>.00</u>
Hydrolysis:		
Hydrolysis tanks	5.70	.00
Seed preparation tanks	3.40	.00
Subtotal	<u>9.10</u>	<u>.00</u>
Calcination: Calciner	<u>.00</u>	<u>1,041.00</u>
Acid regeneration:		
Acid regeneration plant	<u>-570.90</u>	<u>6,241.80</u>
Total process requirements	<u>1,785.10</u>	<u>7,282.80</u>
Steam plant	<u>-1,785.10</u>	<u>3,255.76</u>
Total	<u>0.00</u>	<u>10,538.56</u>

A cost of pigment finishing was obtained from a pigment producer (table B-3). This cost includes both direct and indirect operating costs, but is not broken down by item. Taxes, insurance, and depreciation for this step, combined with costs for the balance of the plant, are shown under fixed costs.

Fixed costs include the costs of taxes (excluding income taxes), insurance, and depreciation. The annual costs of both taxes and insurance are each estimated as 1 pct of the plant construction costs. Depreciation is based on a straight-line, 20-year period.

The estimated annual operating cost for the proposed plant is approximately \$68 million with finishing (table B-3) and approximately \$56 million without finishing. Based on an annual production of about 63,000 st (190 st/d), the cost per short ton of calcined TiO₂ with and without finishing is approximately \$1,090 and \$890, respectively.

Products

The primary product is an anatase pigment. A plant using 400 st/d of perovskite concentrate produces approximately 190 st/d TiO₂. Overall recovery is 95 pct. Operating 330 d/yr, the plant's annual production of TiO₂ is about 63,000 st. This is approximately the scale of existing SO₄ processing plants.

In addition, about 775 st of combined anhydrite and waste gypsum is produced. It is assumed that these impure products are discarded. Less than 1 st/d of waste solids of unknown analysis is produced. These solids can also be discarded since they are not soluble in dilute H₂SO₄ and are assumed to be environmentally harmless.

PROFITABILITY

The current published price of anatase-type pigment is about \$1.02/lb (37) or \$2,040/st. Based on this product value and the estimated operating cost of \$1,090/st, the estimated interest rate of return on investment after taxes is about 24 pct.

The estimated operating cost is based on a concentrate cost of \$60/st. Costs for mining and concentrating perovskite are not within the scope of this evaluation. The \$60/st cost is based on a June 1987 quotation. Doubling the concentrate cost to \$120/st will increase the operating cost to approximately \$1,200/st TiO₂.

DISCUSSION OF COSTS

The costs presented do not include costs for recovering a rare-earth byproduct, which could be recovered during the production of recycle acid and in the tailings.

H₂SO₄ requirements are a major cost item because approximately 2.9 st of H₂SO₄ is consumed per short ton of TiO₂ product. At \$70/st of acid, H₂SO₄ costs \$204/st of TiO₂ product. H₂SO₄ cost is based on smelter acid at \$25/st plus \$45 for shipping. The effect of delivered cost of H₂SO₄ on the interest rate of return and operating cost are shown in figure B-1.

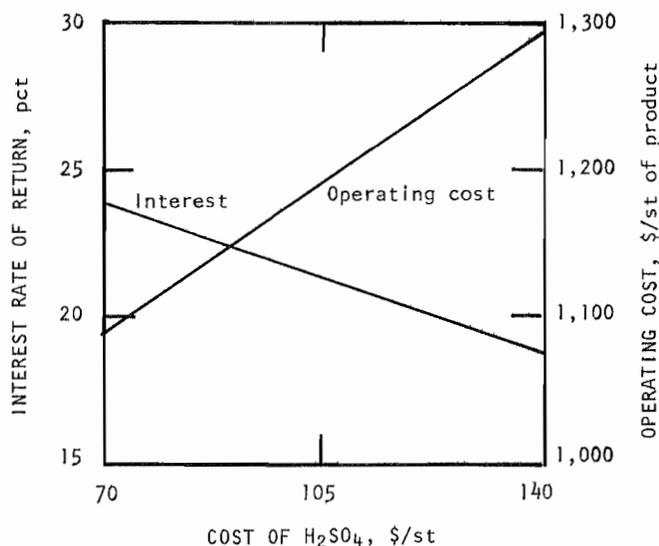


Figure B-1.—Effect of H₂SO₄ price on profitability and operating cost.

The formation of CaSO₄ during sulfation and neutralization of the dilute and contaminated acid streams is the major cause of the loss of acid. Recycling the acid that is neutralized would be one means of reducing acid consumption. However, due to the dilute solutions, recycling is expected to increase operating costs and does not appear to be practical.

Since 1.4 st of acid are consumed per short ton of concentrate, it could be cost effective to locate the plant close to the source of acid and to ship the concentrate.

Another option would be to build an H₂SO₄ plant on-site. However, the high capital cost for an acid plant makes the rate of return on investment unattractive. Thus, this option is not presented in this study.

Major capital cost items in this process are the sulfation units. These are novel units that are not produced on a commercial basis. At the present time, scaleup data are not available. It is recommended that further research be done. The equipment cost summary tables for each section is shown in tables B-6 through B-13 at the end of this report.

ENVIRONMENTAL CONCERNS

CO₂ is generated during sulfation and waste acid neutralization steps. Exhaust of these gases to the environment should not present a hazard. H₂SO₄ vapors, especially those from handling concentrated acid at or near its boiling point, could be both an environmental and occupational hazard. However, control techniques are well known and are incorporated in the plant design where appropriate,

The primary waste stream from the process is byproduct gypsum and anhydrite. It is not expected to be a problem to dispose of this waste, perhaps some of it could be used as wallboard. However, no credit has been included.

HEALTH AND SAFETY

The primary concern for this process is the safe handling of the hot, concentrated H₂SO₄ solutions and slurries. Since this process is similar to the commercial SO₄ process for producing TiO₂, it is assumed that safe handling practices are known. Catastrophic failure of process equipment releasing H₂SO₄ must be prevented or controlled and is considered to be a part of the plant design.

Because employees' health could be affected by H₂SO₄ fumes, collection and scrubbing equipment are included in this plant design.

Table B-6.—Equipment cost summary, concentrate receiving section

Item	Equipment ¹	Labor	Total
Belt feeder	\$8,000	\$1,300	\$9,300
Belt conveyor	75,700	12,700	88,400
Belt feeders	24,400	3,800	28,200
Belt conveyor	27,400	8,000	35,400
Cyclone dust collector	5,300	200	5,500
Total	140,800	26,000	166,800
Unloading hopper ²			21,300
Silos ²			754,700
Total equipment cost × factor indicated:			
Foundations, × 2.133			300,400
Buildings, × 0.181			25,500
Structures, × 0.070			9,900
Instrumentation, × 0.030			4,200
Electrical, × 0.148			20,900
Piping, × 0.100			14,100
Painting, × 0.020			2,800
Miscellaneous, × 0.100			14,100
Total			391,900
State sales tax			37,500
Total direct cost			1,372,200
Field indirect, 10 pct of total direct cost			137,200
Total construction cost			1,509,400
Engineering, 5 pct of total construction cost			75,500
Administration and overhead, 5 pct of total construction cost			75,500
Subtotal			1,660,400
Contingency, 10 pct of above subtotal			166,000
Subtotal			1,826,400
Contractor's fee, 5 pct of above subtotal			91,300
Section cost			1,917,700

¹Basis: M and S equipment cost index of 894.7.

²Installed cost.

Table B-7.—Equipment cost summary,
sulfation section

Item	Equipment ¹	Labor	Total
Feed hopper	\$13,300	\$100	\$13,400
Belt feeder	6,100	1,000	7,100
Mixing tank	10,400	2,800	13,200
Pumps	30,000	4,200	34,200
Pumps	35,500	5,000	40,500
Condensers	12,600	800	13,400
Condensers	63,300	2,500	65,800
Heat exchangers	29,700	2,100	31,800
Acid feed tank	49,300	10,900	60,200
Pump	2,300	800	3,100
Heat exchanger	4,600	400	5,000
Heat exchanger	132,400	2,100	134,500
Rotary-vacuum drum filters	429,200	22,400	451,600
Filtrate surge tank	9,400	3,800	13,200
Pump	5,800	900	6,700
Belt conveyor	18,700	5,200	23,900
Dilute acid surge tank Pump	54,200	8,800	63,000
Surge tank	5,000	1,200	6,200
Surge tank	8,500	4,100	12,600
Total	920,300	79,100	999,400
Acid sulfation vessels ²			5,159,100
Cooling tower			22,800
Total equipment cost × factor indicated:			
Foundations, × 0.182			167,900
Buildings, × 0.398			366,100
Structures, × 0.150			138,000
Insulation, × 0.105			96,300
Instrumentation, × 0.120			110,400
Electrical, × 0.065			60,300
Piping, × 0.500			460,200
Painting, × 0.040			36,800
Miscellaneous, × 0.100			92,000
Total			1,528,000
State sales tax			231,000
Total direct cost			7,940,300
Field indirect, 10 pct of total direct cost			794,000
Total construction cost			8,734,000
Engineering, 5 pct of total construction cost			436,700
Administration and overhead, 5 pct of total construction cost			436,700
Subtotal			9,607,700
Contingency, 10 pct of above subtotal			960,800
Subtotal			10,568,500
Contractor's fee, 5 pct of above subtotal			528,400
Section cost			11,096,900

¹Basis: M and S equipment cost index of 894.7.²Installed cost.Table B-8.—Equipment cost summary,
sulfate dissolution section

Item	Equipment ¹	Labor	Total
Feed bin	\$62,900	\$1,100	\$64,000
Screw feeder	18,800	1,000	19,800
Dissolution tanks	120,700	22,300	143,000
Pumps	31,400	5,300	36,700
Pumps	31,400	5,200	36,600
Rotary-vacuum drum filters	763,000	39,900	802,900
Sump	11,600	3,900	15,500
Pump	5,800	1,200	7,000
Pump	3,100	700	3,800
Feed tank	2,600	1,700	4,300
Pump	5,000	400	5,400
Feed tank	10,100	4,000	14,100
Pump	5,000	1,100	6,100
Belt conveyor	12,200	3,300	15,500
Pumps	13,800	3,200	17,000
Surge tank	63,100	11,500	74,600
Surge tank	20,200	6,100	26,300
Pump	5,800	1,200	7,000
Heat exchanger	15,600	800	16,400
Total	1,202,100	113,900	1,316,000
Total equipment cost × factor indicated:			
Foundations, × 0.161			193,700
Buildings, × 0.319			383,900
Structures, × 0.070			84,100
Insulation, × 0.173			207,500
Instrumentation, × 0.050			60,100
Electrical, × 0.060			72,500
Piping, × 0.450			540,900
Painting, × 0.020			24,000
Miscellaneous, × 0.100			120,200
Total			1,686,900
State sales tax			127,200
Total direct cost			3,130,100
Field indirect, 10 pct of total direct cost			313,000
Total construction cost			3,443,100
Engineering, 5 pct of total construction cost			172,200
Administration and overhead, 5 pct of total construction cost			172,200
Subtotal			3,787,500
Contingency, 10 pct of above subtotal			378,800
Subtotal			4,166,300
Contractor's fee, 5 pct of above subtotal			208,300
Section cost			4,374,600

¹Basis: M and S equipment cost index of 894.7.

**Table B-9.—Equipment cost summary,
precipitation section**

<i>Item</i>	<i>Equipment¹</i>	<i>Labor</i>	<i>Total</i>
Precipitation evaporator	\$1,135,700	\$87,600	\$1,223,300
Surge tank	5,600	1,500	7,100
Pump	6,500	1,400	7,900
Dilute acid storage tank	223,000	42,900	265,900
Precipitation tanks . . .	48,600	16,200	64,800
Pumps	56,500	5,800	62,300
Rotary-vacuum drum filter	191,500	10,000	201,500
Sump	1,500	1,200	2,700
Pump	5,800	1,100	6,900
Pump	2,300	800	3,100
Acid feed tank	6,700	6,400	13,100
Total	1,683,700	174,900	1,858,600
Total equipment cost × factor indicated:			
Foundations, × 0.144			242,100
Buildings, × 0.228			383,900
Structures, × 0.070			117,900
Insulation, × 0.131			221,400
Instrumentation, × 0.050			84,200
Electrical, × 0.026			44,200
Piping, × 0.450			757,700
Painting, × 0.020			33,700
Miscellaneous, × 0.100			168,400
Total			2,053,500
State sales tax			169,500
Total direct cost			4,081,600
Field indirect, 10 pct of total direct cost			408,200
Total construction cost			4,489,800
Engineering, 5 pct of total construction cost			224,500
Administration and overhead, 5 pct of total construction cost			224,500
Subtotal			4,938,800
Contingency, 10 pct of above subtotal			493,900
Subtotal			5,432,700
Contractor's fee, 5 pct of above subtotal			271,600
Section cost			5,704,300

¹Basis: M and S equipment cost index of 894.7.

**Table B-10.—Equipment cost summary,
dissolution section**

<i>Item</i>	<i>Equipment¹</i>	<i>Labor</i>	<i>Total</i>
Dissolution tank	\$16,400	\$3,500	\$19,900
Pump	5,800	1,100	6,900
Reduction tank	2,600	1,700	4,300
Scrap iron feed bin . . .	5,200	100	5,300
Belt feeder	6,100	1,000	7,100
Pressure-leaf filters . . .	33,500	2,100	35,600
Pump	3,600	200	3,800
Precoat mixing tank . . .	5,200	1,700	6,900
Pump	3,600	200	3,800
Sump	32,900	13,700	46,600
Pump	5,800	1,100	6,900
Total	120,700	26,400	147,100
Waste bin ²			1,700
Front-end loader			15,100
Total equipment cost × factor indicated:			
Foundations, × 0.723			87,200
Buildings, × 1.409			170,100
Structures, × 0.070			8,400
Instrumentation, × 0.050			6,000
Electrical, × 0.140			16,900
Piping, × 0.450			54,300
Painting, × 0.020			2,400
Miscellaneous, × 0.100			12,100
Total			357,400
State sales tax			19,200
Total direct cost			540,500
Field indirect, 10 pct of total direct cost			54,100
Total construction cost			594,600
Engineering, 5 pct of total construction cost			29,700
Administration and overhead, 5 pct of total construction cost			29,700
Subtotal			654,000
Contingency, 10 pct of above subtotal			65,400
Subtotal			719,400
Contractor's fee, 5 pct of above subtotal			36,000
Section cost			755,400

¹Basis: M and S equipment cost index of 894.7.

²Installed cost.

Table B-11.—Equipment cost summary,
hydrolysis section

Item	Equipment ¹	Labor	Total
Hydrolysis tanks	\$60,500	\$22,300	\$82,800
Pumps	5,200	600	5,800
Seed preparation tanks	4,300	700	5,000
Pumps	28,000	4,000	32,000
Pressure-leaf filters . . .	593,400	24,800	618,200
Sump	55,600	700	56,300
Belt conveyors	41,000	5,600	46,600
Hoppers	224,400	400	224,800
Screw feeders	40,900	2,100	43,000
Bleach tanks	140,600	21,600	162,200
Pump	4,300	1,000	5,300
Feed tank	6,400	2,700	9,100
Storage tank	21,400	3,700	25,100
Pump	2,200	400	2,600
Pumps	17,800	2,400	20,200
Mixing tank	3,800	1,200	5,000
Pump	5,000	1,200	6,200
Pumps	9,600	500	10,100
Flocculant feed tank . .	10,100	2,900	13,000
Pressure-leaf filters . . .	527,500	27,600	555,100
Belt conveyor	48,300	14,200	62,500
Sump	2,100	1,300	3,400
Pump	6,500	1,200	7,700
Sump	6,000	2,600	8,600
Pump	4,100	2,000	6,100
Total	<u>1,869,000</u>	<u>147,700</u>	<u>2,016,700</u>
Total equipment cost × factor indicated:			
Foundations, × 0.260			485,600
Buildings, × 0.467			872,700
Structures, × 0.070			130,800
Insulation, × 0.135			251,700
Instrumentation, × 0.050			93,500
Electrical, × 0.046			85,900
Piping, × 0.450			841,000
Painting, × 0.020			37,400
Miscellaneous, × 0.100			186,900
Total			<u>2,985,500</u>
State sales tax			208,100
Total direct cost			<u>5,210,300</u>
Field indirect, 10 pct of total direct cost			521,000
Total construction cost			<u>5,731,300</u>
Engineering, 5 pct of total construction cost			286,600
Administration and overhead, 5 pct of total construction cost			286,600
Subtotal			<u>6,304,500</u>
Contingency, 10 pct of above subtotal			630,500
Subtotal			<u>6,935,000</u>
Contractor's fee, 5 pct of above subtotal			346,800
Section cost			<u>7,281,800</u>

¹Basis: M and S equipment cost index of 894.7.Table B-12.—Equipment cost summary,
calcination section

Item	Equipment ¹	Labor	Total
Hopper	\$57,500	\$200	\$57,700
Screw feeder	2,700	400	3,100
Calciner	1,132,500	355,200	1,487,700
Cyclone dust collectors	94,700	1,100	95,800
Scrubber	49,200	5,100	54,300
Hopper	12,800	100	12,900
Belt feeder	6,100	1,000	7,100
Agitation tank	2,100	1,700	3,800
Pump	1,700	300	2,000
Rotary cooler	83,800	14,000	97,800
Hopper	56,800	100	56,900
Vibrating screen	9,300	1,200	10,500
Hammer mill	33,200	4,900	38,100
Belt conveyor	15,500	4,300	19,800
Total	<u>1,557,900</u>	<u>389,600</u>	<u>1,947,500</u>
Total equipment cost × factor indicated:			
Foundations, × 0.365			568,200
Buildings, × 0.120			187,100
Structures, × 0.070			109,100
Insulation, × 0.005			7,900
Instrumentation, × 0.100			155,800
Electrical, × 0.029			45,600
Piping, × 0.100			155,800
Painting, × 0.020			31,200
Miscellaneous, × 0.100			155,800
Total			<u>1,416,500</u>
State sales tax			138,300
Total direct cost			<u>3,502,300</u>
Field indirect, 10 pct of total direct cost			350,200
Total construction cost			<u>3,852,500</u>
Engineering, 5 pct of total construction cost			192,600
Administration and overhead, 5 pct of total construction cost			192,600
Subtotal			<u>4,237,700</u>
Contingency, 10 pct of above subtotal			423,800
Subtotal			<u>4,661,500</u>
Contractor's fee, 5 pct of above subtotal			233,100
Section cost			<u>4,894,600</u>

¹Basis: M and S equipment cost index of 894.7.

**Table B-13.—Equipment cost summary,
neutralization section**

<i>Item</i>	<i>Equipment¹</i>	<i>Labor</i>	<i>Total</i>
Neutralization tanks . .	\$115,600	\$41,000	\$156,600
Pumps	41,800	5,200	47,000
Belt conveyor	43,600	8,500	52,100
Belt feeder	7,400	1,200	8,600
Belt conveyor	25,200	7,700	32,900
Hoppers	51,700	300	52,000
Belt feeder	6,100	1,000	7,100
Pumps	33,800	5,200	39,000
Total	<u>325,200</u>	<u>70,100</u>	<u>395,300</u>
Unloading hopper ²			21,300
Total equipment cost × factor indicated:			
Foundations, × 0.471			153,100
Buildings, × 0.847			275,600
Structures, × 0.070			22,800
Instrumentation, × 0.050			16,500
Electrical, × 0.143			46,500
Piping, × 0.350			113,800
Painting, × 0.020			6,500
Miscellaneous, × 0.100			32,500
Total			<u>667,100</u>
State sales tax			40,900
Total direct cost			<u>1,124,600</u>
Field indirect, 10 pct of total direct cost			112,500
Total construction cost			<u>1,237,100</u>
Engineering, 5 pct of total construction cost			61,900
Administration and overhead, 5 pct of total construction cost			61,900
Subtotal			<u>1,360,900</u>
Contingency, 10 pct of above subtotal			136,100
Subtotal			<u>1,497,000</u>
Contractor's fee, 5 pct of above subtotal			74,900
Section cost			<u>1,571,900</u>

¹Basis: M and S equipment cost index of 894.7.

²Installed cost.