RI 9065

Bureau of Mines Report of Investigations/1987

Preparation of Titanium Feedstock From Minnesota Ilmenite by Smelting and Sulfation-Leaching

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UNITED STATES DEPARTMENT OF THE INTERIOR

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Donald Paul Hodel, Secretary

BUREAU OF MINES
Robert C. Horton, Director

This report is based upon work performed under a Memorandum of Agreement between NICOR Mineral Ventures and the Bureau of Mines.

Library of Congress Cataloging in Publication Data:

Nafziger, R. H. (Ralph H.)
Preparation of titanium feedstock from Minnesota ilmenite by smelting and sulfation-leaching.

(Report of investigations ; 9065)

Bibliography: p. 13.

Supt. of Docs. no.: I 28.23: 9065.

1. Titanium—Metallurgy. 2. Ilmenite. 3. Smelting. 4. Leaching. I. Elger, G. W. II. Title. III. Series: Report of investigations (United States. Bureau of Mines) ; 9065.

TN23.U43 [TN799.T5] 622 s [669'.7322] 86-600358

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere	L/min	liter per minute
°C	degree Celsius	lb	pound
cm	centimeter	lb/h	pound per hour
cm^3/min	cubic centimeter per minute	lb/min	pound per minute
g	gram	lb/mt	pound per metric ton
g/L	gram per liter	m	meter
h	hour	min	minute
kg	kilogram	mt	metric ton
kg/h	kilogram per hour	pct	percent
kW	kilowatt	st	short ton
kW•h/mt	kilowatt hour per metric ton	V	volt
L	liter	wt pct	weight percent

PREPARATION OF TITANIUM FEEDSTOCK FROM MINNESOTA ILMENITE BY SMELTING AND SULFATION-LEACHING

By R. H. Nafziger[1] and G. W. Elger[2]

ABSTRACT

As part of its program to help decrease the dependency of the United States on foreign imports of nonfuel minerals and to devise technology for the efficient and economic use of domestic resources, the Bureau of Mines smelted and sulfation-leached an ilmenite from northern Minnesota. The objective was to assess the feasibility of preparing chlorination-grade titanium feedstock. The concentrate was smelted with woodchips, coke, and soda ash in 91-kg- and 1-metric ton (mt)-capacity electric arc furnaces to form Ti-rich slag and commercial-grade pig iron. The slag contained from 67 to 77 wt pct titanium oxides and from 1.8 to 7.2 wt pct iron. Sulfation occurred in a 4.5-kg/h moving-bed reactor using SO_2-air mixtures at temperatures of 800° to 850° C to form soluble salts of the Ca, Mg, Mn,and Na impurities, which cause plugging of fluidized-bed chlorinators. Subsequently, the sulfated slag was leached in acid to remove the soluble sulfates. The final product from small-scale testing contained up to 95.5 wt pct TiO_2, a minimum of 0.6 wt pct Fe, and a minimum total of 0.3 wt pct of the four impurities of interest. The final product meets charge specifications for chlorination. However, more large-scale testing is necessary.

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INTRODUCTION

The United States depends upon imported rutile and high-grade ilmenite as raw materials for producing titanium and pigment-grade TiO_2. These raw materials are preferred over more abundant, lower grade domestic ilmenites because they contain significantly higher TiO_2 content. Although the United States possesses some rutile, the sources are limited and are far removed from market locations. In addition, the domestic production of synthetic rutile uses lower cost imported ilmenite. The country imports approximately two-thirds of its titanium raw material requirements, primarily from Australia and Canada (1).[3]

Domestic ilmenite and perovskite resources were estimated in 1983 to contain 31 million short tons (st) of titanium, in addition to rock deposits scattered throughout the country (1). The demand in the United States in 1983 was 523,000 st of titanium (1). Most of these materials contain too much Ca, Mg, and Mn to be used directly for making $TiCl_4$, an intermediate compound in the production of titanium metal and much of the pigment-grade TiO_2. During chlorination, these impurities form liquid chlorides, which have high boiling and low melting temperatures. Therefore, the liquid phase accumulates in the fluidized-bed chlorinator until it solidifies, plugging the reactor. In addition, iron oxides from the ilmenites react with chlorine to yield large amounts of iron chloride wastes, which require expensive disposal methods.

One domestic ilmenite resource is found in northern Minnesota, and NICOR Mineral Ventures has had an interest in this deposit for several years. The company approached the Bureau of Mines to apply the Bureau's recently devised purification technology to this deposit. A Memorandum of Agreement was signed between the Bureau of Mines and NICOR Mineral Ventures to conduct this research. This technology involves pyrometallurgically separating the titanium from the iron and subsequently sulfating and leaching the high-titania slag to provide a suitable feedstock for chlorination (2-5). The objective of this work was to assess the feasibility of smelting and sulfation-leaching the northern Minnesota ilmenite to produce a chlorination-grade feedstock using technology devised by the Bureau.

For many years, the Bureau performed research on the smelting of a wide variety of titaniferous materials. Pig iron suitable for steelmaking and high-titania slags were produced (6-8). More recent research devised technology showing that most domestic materials responded well to lower grade or byproduct reductants during smelting. The research also demonstrated that fluid slags could be obtained without contaminating fluidizers if from 8 to 12 wt pct Fe were present (9). Smelting experiments were conducted in a 25-kg, single-phase ac electric arc furnace and a 1-mt, three-phase ac furnace, both with carbon-lined shells to minimize contamination. Each material required a different smelting condition to optimize results (9).

On a commercial scale, Quebec Iron and Titanium Corp. has been processing ilmenite in an electric arc furnace since 1950 (10-11). In Japan, Osaka Titanium Co., Ltd., has been producing a high-titania slag from ilmenites by electric furnace smelting (12).

Several years ago, the Bureau began investigating the use of lower grade domestic titaniferous materials to produce titanium-rich slags for use as substitutes for imported rutile in $TiCl_4$ production. An ilmenite concentrate from New York containing 45 wt pct TiO_2 was reduced carbothermically in an electric arc furnace to prepare a slag containing approximately 80 wt pct TiO_2 (3). The slag, containing 5.0 wt pct (CaO + MgO + MnO), was ground and pelletized, reacted with SO_2 and O_2 at 700° to 900° C on a bench scale, and leached with dilute HCl to remove the Ca, Mg, and Mn impurities as soluble sulfates. Approximately 0.4 wt pct (CaO + MgO + MnO) remained

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

after treatment at 900° C for 2 h (3). The process was tested on a larger scale in a pilot-scale unit capable of handling 4.5 to 9.1 kg/h of feed material. Mixtures of SO_2 and air were used for sulfation, followed by a water leach to remove impurities (4-5). Pertinent impurity levels were about 1 wt pct higher than those obtained from the bench-scale work. Nevertheless, the results showed this technique to be a promising method for decreasing impurities and thereby helping to lessen the U.S. dependence on foreign sources.

Although there is no universally acceptable maximum content for impurities in feed materials for chlorination to avoid the aforementioned problems, a maximum of approximately 1.0 wt pct was suggested by the National Materials Advisory Board (13), and that level was the target used in this investigation.

SMELTING TESTS

CHARGE MATERIALS

The materials used in all of the tests in the present investigation were derived from the Water Hen Intrusion. This is one of the larger intrusions in the southern portion of the Duluth Complex in northeastern Minnesota. This body is estimated to contain 60 million st of TiO_2, with the ore averaging approximately 13 wt pct TiO_2. The Water Hen Intrusion is noted for its high ilmenite content, little magnetite, and localized graphite concentrations.

For the initial test, drill core samples were beneficiated by grinding and subjecting 90 pct of the material to low-intensity magnetic separation, drying, and high-tension separation. The remainder was subjected to tabling, sulfide flotation, low-intensity magnetic separation, drying, and high-tension separation. Beneficiation was accomplished by the Mineral Resources Research Center (MRRC) at the University of Minnesota for NICOR Mineral Ventures. Analyses of the composite concentrate are given in table 1. The data show that the ore beneficiated at MRRC was unusually clean.

The remaining tests used a concentrate beneficiated at the Pickands Mather and Co. (PM) Research Laboratory in Hibbing, MN. The ilmenite was ground, concentrated on spirals, and underwent high-tension electrostatic separation. Analyses of this material also are presented in table 1. For comparison purposes, analyses of the New York ilmenite used in prior Bureau studies are shown in table 1.

Woodchips and metallurgical-grade coke were used as reductants in the smelting tests. The woodchips contained 16.3

TABLE 1. - Analyses of ilmenite concentrates from northern Minnesota[1] and from New York, weight percent

	Northern Minnesota		New York[2]
	MRRC[3]	PM[4]	
Total Ti as TiO_2..	51.6	47.4	46.6
Total Fe..	35.6	36.3	36.4
FeO.......	31.4	41.6	35.7
CaO.......	<.05	.36	.29
MgO.......	2.35	2.90	2.08
MnO.......	.47	.61	.35
Al_2O_3.....	.04	.30	.96
SiO_2......	.78	2.61	1.56
P.........	.004	ND	.04
S.........	.40	.28	.70
C.........	.008	.23	.16
Phases....	(5)	(6)	(7)

ND Not detected.

[1] Both Minnesota samples contained 0.01-0.1 Co, 0.001-0.01 Cu, <0.01 Ti^{3+}, and 0.03-0.3 V.

[2] Also contains 0.01-0.1 Cr, 0.0001-0.001 Cu, 0.003-0.03 Ni, and 0.02 V.

[3] Also contains 0.01-0.1 Cr and Ni.

[4] Also contains 0.003-0.03 Cr and 0.03-0.3 Ni.

[5] Ilmenite only.

[6] 77 ilmenite, 17 ilmenite-geothite, 3 ferromagnesian silicates, 1 magnetite, 0.5 graphite, 0.5 chalcopyrite and Cu.

[7] 96 ilmenite, 1 magnetite, 0.5 garnet, 0.5 pyroxene and feldspar, 1 pyrite and calcite.

wt pct fixed C and approximately 0.5 wt pct impurities. Analyses of the coke showed 95.4 wt pct fixed C, 0.98 wt pct S, 0.13 wt pct Fe, and approximately 0.7 wt pct added condensed impurities. For the smelting tests in the smaller furnace ("small-scale tests") the woodchips provided 55 to 56 pct of the carbon, with the remainder supplied by the coke. In the test using the large furnace ("large-scale test"), 75 pct of the C was present as woodchips. The small-scale tests indicated that a greater percentage of the carbon could be added as woodchips to more effectively smelt the material.

In all of the smelting tests, from 5.7 to 6.6 wt pct soda ash was added to maintain slag fluidity at the relatively low targeted iron contents (5 wt pct FeO) in the slag (3).

EQUIPMENT AND PROCEDURES

The small-scale tests were conducted in a 100-kg-capacity single-phase ac electric arc furnace with a carbon-lined shell. Details of this furnace were described previously (14). The larger 1-mt-capacity furnace was lined with carbon brick and had a hot-rammed carbon hearth. This furnace also was described in more detail elsewhere (9).

Typical total charges for all of the tests consisted of from 63 to 68 wt pct ilmenite concentrate, 23 to 29 wt pct woodchips (dry basis), 1 to 3 wt pct metallurgical-grade coke, and 5.7 to 6.6 wt pct soda ash. The charge components were mixed and blended before feeding. Smelting procedures for each smelting test were similar. Approximately 6.5 to 13 pct of the entire charge excluding woodchips initially was fed into the furnace and a molten pool established. Subsequently, the furnace was filled with the charge mixture including woodchips and kept full throughout the tests until the feed was depleted. Bath temperatures and slag samples were taken throughout the tests to maintain sufficient bath fluidity and to monitor Fe and Na levels. After all of the feed was charged into the furnace and smelted, and a satisfactory bath temperature established, slag and metal were tapped from the furnace and suitable samples were taken for analyses.

RESULTS

Small-Scale Tests

Operational variables for the small-scale tests are summarized in table 2. These tests were conducted at approximately 400 A and 45 V. The tests operated smoothly with no specific problems. A gradual decrease in iron content was noted in the slag as the tests progressed. It was important to tap the furnace promptly as soon as the charge was entirely melted to avoid increasing slag viscosity.

Compositions of the tapped metal and slag are tabulated in table 3. Since the MRRC concentrate contained fewer impurities than those in the PM material (table 1), a larger amount of gangue oxides were contained in the slags derived from the latter concentrate. Noteworthy also are the different phase assemblages in the two slags. Slags made from the cleaner MRRC concentrate had less Ti present in the pseudobrookite structure.[4] This means that more Ti was present in other phases, such as rutile. This situation is more amenable to the formation of soluble compounds of impurities in the sulfation step. Greater Na levels in this slag contributed to a separate sodium-containing phase.

In the test using the MRRC concentrate, materials balances showed that iron and titanium recoveries were 78 and 85 pct, respectively. Final slag basicity (defined as $(CaO + MgO)/SiO_2$ on a weight basis) was 2.0, and 132 pct of the stoichiometric requirement of carbon necessary to reduce all iron oxides to metallic iron was used. In the other small-scale smelting test, iron and titanium recoveries were 89 and 82 pct, respectively, with a final slag basicity of 0.74. In this test, 164 pct of the stoichiometric carbon requirement was

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[4] $M_2O_3 \cdot TiO_2$, where M can be Fe or Ti, or $MO \cdot 2TiO_2$, where M can be Fe, Mg, or Ti.

TABLE 2. - Operational variables for smelting tests on northern Minnesota ilmenites

	Small-scale tests		Large-scale test:
	MRRC conc	PM conc	PM conc
Total charge............lb..	153.8	238.5	2,652
Av feed rate.........lb/min..	5.35	2.43	22.6
Melt rate...........lb/min..	0.23	1.58	2.18
Av bath temp............°C..	1,626	1,564-1,595	[1]1,492
Tap temp................°C..	1,540	1,610	[1]1,525
Energy consumption, kW•h/mt:			
Charge....................	987	1,098	1,310
Slag......................	2,919	2,874	2,445
Metal.....................	6,221	5,870	6,140
Electrode consumption, lb/mt:			
Charge....................	41.6	29.4	35.8
Slag......................	123	76.8	66.9
Metal.....................	262	157	168
Metal weight............lb..	24.4	44.6	566
Slag weight.............lb..	51.9	91.1	1,421
Slag tapped............pct..	28.3	29.3	63.3
Productivity..........lb/h..	14.0	17.4	141.5
Coke used.......lb/mt metal..	159	215	308

[1] Low readings may be due to thermocouple malfunction.

TABLE 3. - Analyses of tapped products from smelting northern Minnesota ilmenites, weight percent

	Small-scale tests				Large-scale test:	
	MRRC concentrate		PM concentrate		PM concentrate	
	Slag	Metal[1]	Slag	Metal[1]	Slag	Metal[1]
TiO_2....	57.4	0.3 -3	38.7	0.01-0.1	54.3	0.003 -0.03
Ti_2O_3...	19.1	NAp	34.8	NAp	15.3	NAp
FeO.....	5.29	NAp	2.28	NAp	9.10	NAp
Total Fe	4.11	Balance	1.77	Balance	7.08	Balance
CaO.....	.36	NAp	1.18	NAp	.97	NAp
MgO.....	4.19	.1 -1	5.84	NAp	4.94	.0001- .001
MnO.....	0.04 - .4	.10	.88	.17	.89	.002
Al_2O_3...	.85	.01- .1	2.04	NAp	1.40	.001 - .01
SiO_2....	2.10	.16	7.72	.020	7.17	.05
Na_2O....	10.4	.03- .3	5.94	NAp	12.3	NAp
S.......	.47	.11	.46	.099	.24	.48
P.......	<.001	.007	.076	.020	.011	.022
C.......	.20	3.50	.06	3.77	.08	1.71
Ni......	.003 - .03	.01- .1	0.001 - .01	.03- .3	0.003 - .03	.03 - .3
Cu......	.0001- .001	.01- .1	.0001- .001	.03- .3	.0001- .001	.03 - .3
Cr......	.01 - .1	NAp	.003 - .03	.01- .1	.01 - .1	.003 - .03
V.......	.003 - .03	.3 -3	.03 - .3	.03- .3	[2].27	.001 - .01
Others..	NAp	(3)	NAp	(4)	NAp	(5)
Phases..	(6)	(7)	(8)	(7)	(9)	(7)

NAp Not applicable. [1] Constituents appear in element form only.

[2] V_2O_5. [3] 0.01-0.1 Co, 0.01-0.1 Zr, and 0.001-0.01 Mo.

[4] 0.01-0.1 Co, 0.001-0.01 Mo. [5] 0.01-0.1 Co, 0.003-0.03 Mo.

[6] 40-100 pct $Na_{0.23}TiO_2$; 1-10 pct ilmenite, pseudobrookite structure + ?.

[7] Not determined. [8] 40-100 pct pseudobrookite structure; 5-30 pct Ti_3O_5.

[9] 40-100 pct $Na_{0.23}TiO_2$; 20-60 pct pseudobrookite structure.

TABLE 4. - Iron and sodium contents of slag from 1-mt smelting test, weight percent

Time, min	Total Fe	Na	Time, min	Total Fe	Na	Time, min	Total Fe	Na
50.0	11.9	4.43	164.9	14.3	4.43	242.3	8.11	4.13
80.0	13.6	4.36	188.0	14.1	4.25	260.0	8.17	4.69
110.2	14.3	4.21	213.2	12.5	4.46	([1])	7.42	3.61
139.4	13.7	4.24	230.8	9.00	4.42	([2])	4.51	4.69

[1] Final tap slag. [2] Slag remaining in furnace.

employed. A metal suitable for further refining was produced.

Large-Scale Test

Pertinent variables for the test using the 1-mt furnace also are listed in table 2. Approximate average amperages, phase-to-ground voltages, and phase-to-phase voltages for this test were 3,075, 46, and 89, respectively. Again, the smelting operation proceeded smoothly. The Fe and Na contents of the slag as a function of time are given in table 4.

For the large-scale test, tapped metal and slag compositions are listed in table 3. As noted in the small-scale tests, higher levels of Na in the slag resulted in a separate sodium-containing phase. Iron and titanium recoveries were 100 and 88 pct, respectively. Final slag basicity was 0.95, and 160 pct of the stoichiometric carbon requirement was used.

SULFATION-LEACHING TESTS

SLAG PREPARATION

The slag products from the small-scale smelting tests were ground separately to pass through a 35-mesh screen, and the ground materials were subjected to magnetic separation to remove approximately 1 wt pct of the material as metallic iron. Charges of each ground slag, prepared for small-scale sulfation testing, were blended with 4 wt pct bentonite binder and, in some instances, with 2 wt pct S to determine if effective diffusivity was limiting impurity sulfation. During heating of the slag pellets in the kiln, oxidation of the sulfur to SO_2 created additional pores within the pellets. The blended charges were moistened with water before pelletizing. The pellets were approximately 0.6 cm in diameter. In addition, some of the slag charges were preleached[5] with a 5-wt-pct-HCl solution to decrease the FeO, Na_2O, and SiO_2 contents before pelletizing. The pelletized charges were dried in a small oven at 150° C.

Tapped slag from the smelting of PM concentrate in the 1-mt furnace was crushed to minus 0.69 cm in diameter, and the crushed material was subjected to dry magnetic separation before undergoing stage grinding in a ball mill to a minus 35-mesh (500-µm) product. To prepare feedstock for large-scale sulfation, the ground slag was blended with 2 wt pct each of bentonite and elemental sulfur and sufficient moisture to form 0.95-cm-diam by 1.59-cm-long cylindrical pellets. The pellets were oven-dried at 150° C and screened to remove the minus 35-mesh fines that could cause sticking and agglomeration of the bed within the sulfation reactor.

EQUIPMENT

Two types of reactors were employed in the slag sulfation tests. In the small-scale experiments, a fixed-bed reactor was used, and the gaseous reactants were fed into its top. The large-scale tests utilized a moving-bed reactor with the

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[5] In this report, "preleaching" refers to acid treatment of the slag before sulfation. On the other hand, "leaching" is performed after the slag has been sulfated.

slag fed in the top and the reactant gases in the bottom, using a countercurrent mode of operation.

For the small-scale tests, a 5.1-cm-diam, vertical-shaft reactor was used to sulfate 50-g charges. The reactor, made from clear quartz, was divided at the midpoint by a slotted support for the charge. The reactor was similar to that employed previously to sulfate slag charges derived from New York rock ilmenitem (5). The reactor was provided with a gas inlet in its top and a gas exit line in its bottom. Flow rates of incoming SO_2 and O_2 were measured with rotameters, and the exit gases were scrubbed with a sodium hydroxide solution before release to the atmosphere. The reactor was heated by enclosing it within a tube furnace equipped with electrically heated resistance elements.

The main components of the large-scale equipment employed to continuously sulfate slag pellets in a moving bed consisted of a horizontal rotary kiln and a vertical-shaft furnace equipped with a 10.2-cm-ID silicon carbide tube that served as the reaction chamber. These units were described previously (4). The 10.2-cm-diam kiln was used to indurate and oxidize the slag pellets before they underwent sulfation in the adjacent reactor. Slag pellets were fed from a charge bin through a rotary airlock ("star") valve to the kiln, and the discharged, oxidized product was fed into the top of the shaft furnace. The 1.2-m-long, 1-kW heated section of the reactor was surrounded by auxiliary, electrically heated elements. Thermocouples were spaced every 30.5 cm along the outside wall of the reactor to measure approximate bed temperatures, along with a thermocouple to control temperatures automatically. A mixture of SO_2 and air entered the moving bed below the heated section of the reactor, which was enclosed within an insulated containment shell. The gas mixture flowed upward through the bed. The pellets flowed downward in the bed by gravity and were withdrawn through a screw conveyor from the bottom of the reactor. A scrubbing column containing an Na_2CO_3 solution was employed to neutralize the SO_2 and SO_3 constituents in the offgas.

SMALL-SCALE SULFATION-LEACHING TESTS

Procedures

In the sulfation step, the CaO, MgO, MnO, and Na_2O constituents in slag react selectively with SO_2 and O_2 or air at temperatures used to form water-soluble compounds that are subsequently leached from the sulfate product. A promoter, such as soda ash, added with the ilmenite charge in the previous smelting step, is required to promote sulfation of these constituents (2).

The procedure used to sulfate the slag, which was derived from both ilmenite concentrates, was similar to that used in upgrading slag from New York rock ilmenite (3). Each pellet charge was placed in the reactor, and the system was usually flushed with argon during heatup to the desired operating temperature. In tests involving oxidation of slag before sulfation, the charge was heated in an oxygen atmosphere. After the operating temperature was reached, equal volumes of SO_2 and O_2—each flowing at 110 cm^3/min—were passed through the charge for 2 h. The sulfated charge was cooled in an SO_2 atmosphere and removed from the reactor. The material was ground to minus 35 mesh, and a 5-g portion of the ground material was leached in 0.1 L of stirred 1-wt-pct-HCl solution for 1 h at ambient temperature. The resultant slurry was filtered, and the separated solids were washed with fresh water before they were dried and sampled for chemical analyses.

Results

Table 5 shows the effects on the composition of the leached products of preleaching and oxidizing the slag charges before sulfation at temperatures of 750 to 900. The best upgrading of slag derived from both concentrates was obtained in test 5 using a charge that was preleached and oxidized before sulfation at 850° C. The upgraded product contained 95.6 wt pct TiO_2 with 0.08 wt pct CaO,

TABLE 5. - Partial chemical analyses of sulfation-leached slags prepared from Minnesota ilmenite concentrates

Test	Operating conditions			Chemical analyses of leached slag, wt pct								
	Leached before sulfation[1]	Oxidized before sulfation	Sulfation temp, °C	TiO_2	CaO	MgO	MnO	Na_2O	Al_2O_3	Fe_2O_3	SiO_2	S
SLAG FROM MRRC CONCENTRATES (SMALL SCALE)												
1......	No	No	800	NA	0.08	2.42	0.48	0.43	NA	NA	NA	0.27
2......	No	No	900	NA	<.07	2.44	.48	.46	NA	NA	NA	.24
3......	No	Yes	800	88.9	.08	1.71	.35	.32	0.93	4.45	2.96	.26
4......	No	Yes	750	89.6	.12	1.77	.45	.39	.87	4.27	2.04	.21
5......	Yes	Yes	850	95.6	.08	.22	<.01	.13	.23	1.15	2.17	.29
6......	Yes	No	850	88.7	<.07	2.10	.41	.44	1.08	4.65	3.17	.26
SLAG FROM PM CONCENTRATE (SMALL SCALE)												
7[2].....	No	No	800	85.4	0.12	0.36	<0.06	0.37	1.41	2.26	9.72	0.21
8......	No	Yes	800	86.4	<.07	.22	<.06	.34	1.51	1.47	9.33	.15
9......	No	Yes	900	85.9	<.07	.46	<.06	.61	1.78	2.80	9.33	.18
10[2]....	No	No	900	86.1	<.07	.53	<.06	.57	1.83	1.66	9.31	.17
11.....	Yes	No	850	94.9	<.07	.25	<.06	.16	.81	1.26	3.17	.10
12.....	Yes	No	900	93.9	<.07	.48	<.06	.18	.87	1.04	2.98	.11
SLAG FROM PM CONCENTRATE (LARGE SCALE)												
13[2]....	Yes	Yes	800	77.6	0.17	1.67	0.24	0.24	1.32	9.25	8.24	0.31
14[2]....	Yes	No	800	84.2	.29	1.54	.21	.36	.85	6.62	6.05	.26
15[2,3]..	Yes	No	800	83.2	.08	1.14	.15	.23	NA	7.62	NA	.26

NA Not analyzed.

[1] Leached in acid solution containing 5 wt pct HCl at ambient temperatures, filtered, and dried.

[2] 2 wt pct elemental S added to slag mixture before pelletization.

[3] 5 wt pct Na_2CO_3 added to slag mixture before pelletization.

0.22 wt pct MgO, and <0.01 wt pct MnO as pertinent impurities. With respect to the PM materials, slag made in the small-scale smelting test responded better to sulfation-leaching than did that from the large-scale furnace. In test 11, a product upgraded to 94.9 wt pct TiO_2 with low levels of pertinent impurities was obtained from a charge sulfated at 850° C. Preleaching the slag with 5-wt-pct-HCl solution before sulfation reduced its SiO_2 content by about two-thirds, from 7.72 to 2.78 wt pct. The resultant preleach liquor contained constituents with the following concentrations, in grams per liter: 0.06 Ca, 0.92 Na, 0.18 Mg, 0.16 Mn, 0.86 Si, 0.25 Al, and 0.41 Fe. A charge of slag prepared in the 1-mt furnace with an FeO content of 9.10 wt pct (table 3) was upgraded to only 84.2 wt pct TiO_2. This demonstrates that high-iron slags are more difficult to upgrade.

Samples of sulfated and leached products were examined by X-ray diffraction to identify the phases present. Generally, the sulfated charges contained 40 to 100 wt pct rutile, and 1 to 10 wt pct each of a pseudobrookite-type phase, cristobalite, and $TiO_2(SO_4)_3$. In some instances, these charges also contained 1 to 10 wt pct of $CaSO_4 \cdot MgSO_4$. After leaching, the slags contained 40 to 100 wt pct of rutile, and <1 wt pct each of anatase, cristobalite, and a pseudobrookite-type phase.

The liquors from the leaching of sulfated slags contained constituents usually with the following concentrations, in grams per liter: 0.14 to 0.15 Ca, 0.6 to 0.63 Mg, 0.11 to 0.12 Mn, and 0.77 to 0.79 Na. Spectrographic analyses of solids recovered from leach liquors evaporated to dryness indicated the following, in weight percent: 1 to 10 each of Ca, Mg, and Na; 0.1 to 1 each of Fe and Mn; 0.01 to 0.1 each of Si and Ti; 0.001 to 0.01 of Ni; and 0.0001 to 0.001 of Cu.

LARGE-SCALE SULFATION-LEACHING TESTS

Procedures

The procedure used to sulfate slag prepared in the 1-mt furnace was similar to that previously described (4-5). The operating conditions used are shown in table 6.

Briefly, the reactor was preheated to the operating temperature and maintained there for 30 min while a moving bed was established. Metered flows of SO_2 and air were introduced into the bottom of the reactor while slag pellets were fed into the rotary kiln. The quantity of SO_2 used was equivalent to 150 pct of stoichiometric required to sulfate the CaO, MgO, MnO, and Na_2O constituents in slag. An oxygen flow to the kiln oxidized the C, FeO, and Ti_2O_3 constituents in the slag. The residence time of the pellets in the heated region of the reactor was approximately 4 h.

The stream of sulfated pellets was sampled after the first 8 h of operation, and sampling continued at 1-h intervals until the end of the test. Selected stream samples were ground to minus 35 mesh, and the ground material was leached according to the procedure described previously for the small-scale tests. Large-scale leaching of sulfated pellets was not performed since the results of the leached stream samples, which are reported later, were not as good as expected.

Results

Composition of the preleached slag feed is shown in table 7. According to data in tables 3 and 7, preleaching the feedstock before sulfation reduced its FeO content from 9.1 to 6.2 wt pct, its SiO_2 content from 7.17 to 4.96 wt pct, and its Na_2O content from 12.3 to 4.38 wt pct.

Partial compositions of leached stream samples sulfated in the shaft furnace reactor are shown in table 8.

TABLE 6. - Operating conditions for continuous sulfation of titania slag derived from PM ilmenite in large-scale testing

Reactor preheat temp...........°C..	800
Duration of test................h..	48
Slag feed rate..............kg/h..	4.5
SO_2 flow..................L/min..	5.5
Air flow...................L/min..	15.7
O_2 to kiln................L/min..	7.2

TABLE 7. - Composition of preleached slag[1] used in continuous sulfation tests, weight percent

TiO_2............................	76.2
FeO............................	6.2
CaO............................	.67
MgO............................	4.77
MnO............................	.74
Al_2O_3............................	.82
SiO_2............................	4.96
Na_2O............................	4.38
Others............................	1.26

[1] Derived from large-scale smelting test with PM concentrate; analyzed before addition of 2 wt pct each of S and bentonite binder.

TABLE 8. - Partial compositions of selected leached slag samples sulfated in large-scale test

Sample	Constituent analyses, wt pct				
	TiO_2	CaO	MgO	MnO	Na_2O
2.........	83.4	<0.05	2.62	0.35	0.36
19........	80.6	.22	3.15	.43	1.36
38........	81.7	.25	3.05	.41	.66
47........	80.2	.39	3.73	.52	1.36

These results indicate the slag prepared from the PM material did not respond to continuous sulfation in the moving-bed reactor as well as it did in the smaller static-bed reactor (table 5).

X-ray diffraction data indicated that stream samples 2 and 47 in table 8 before leaching contained 40 to 100 wt pct of rutile and 1 to 10 wt pct each of a pseudobrookite-type phase, ilmenite, $TiO_2(SO_4)_2$, and $Na_2O{\cdot}Fe_2O_3{\cdot}6TiO_2$. Apparently, the Na_2O formed the compound $Na_2O{\cdot}Fe_2O_3{\cdot}6TiO_2$ rather than promoting impurity sulfation. X-ray diffraction data indicated that the leached stream samples contained 40 to 100 wt pct rutile and 1 to 10 wt pct each of a pseudobrookite-type phase and other unidentified compounds.

During sulfation, no problems were encountered with sticky reaction products coating the surfaces of the pellets and causing the pellets to agglomerate. Because the oxidation of Ti_2O_3 to TiO_2 in the slag is a highly exothermic reaction (4), conducting it in the adjacent kiln minimized the buildup of heat within the bed. Bed temperatures reached a maximum of 850° C using oxidized pellets as feed. Feeding the pellets directly to the sulfation reactor without prior oxidation would have caused bed temperature to exceed 850° C.

A material balance for oxidation and sulfation of slag pellets in the shaft furnace is shown in figure 1. The data shown are averages taken over the entire 48-h test. The slag gained 6.7 wt pct on sulfation. The stream samples lost 18.9 wt pct in small-scale leaching.

DISCUSSION OF RESULTS

SMELTING TESTS

One of the objectives of the smelting experiments was to prepare a slag containing impurities in as low levels as possible with approximately 5 wt pct FeO and approximately 6 wt pct Na_2O for slag fluidization. The composition of the charge materials has a direct influence on the slag composition. No difficulty was experienced in preparing a high-purity titaniferous slag on a small scale from the very clean MRRC concentrate. (Compare table 1 with table 3.) Oxide impurities in the slag (excluding Fe, Na, and Ti) totaled 7.5 to 7.9 wt pct. The FeO content in the product slag was acceptable for sulfation-leaching experiments. In terms of FeO and total Ti levels, the same was true for the slag prepared from the PM concentrate in the small-scale furnace. However, the same oxide impurities totaled 17.7 wt pct in slags made from this material. The slag analyses (table 3) indicate that more reducing conditions prevailed in the small-scale test that used the PM concentrate. Nevertheless, the higher level of impurities reflects the greater amount of impurities present in the PM concentrate (table 1), particularly SiO_2 and Al_2O_3. The MRRC concentrate was beneficiated using low-intensity magnetic separation and drying steps; the PM material was subjected to gravity concentration involving spirals. Both beneficiation procedures included the use of a high-intensity sepseparation step. Differences in the beneficiation procedures used by MRRC and PM that could have affected the final concentrate composition are summarized in table 9.

A cleaner concentrate using the PM process is possible with a finer grind (to minus 65 mesh). The magnetite (Fe_3O_4) in the Water Hen material is closely bound with the serpentinized olivine [$2(Fe,Mg)O{\cdot}SiO_2$] and would carry

TABLE 9. - Differences between MRRC and PM beneficiation procedures for Water Hen ilmenite possibly affecting concentrate composition

	MRRC	PM
Scale.............	Bench..	Pilot plant.
Grind.............	Finer[1].	Coarser[1].
LIMS[2].............	Yes....	No.[3]
Charge to high-tension separator	Sized..	Not sized.

[1] Finer or coarser than -35 mesh.

[2] Low-intensity magnetic separation step.

[3] Not used because no significant magnetic product was present in preliminary test work.

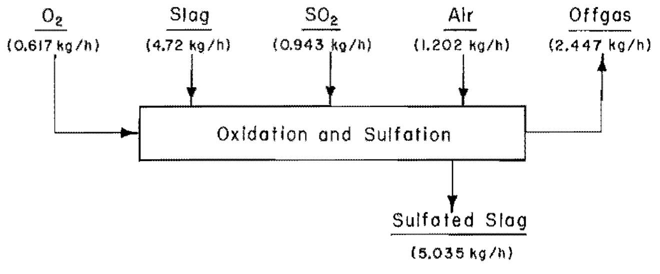

FIGURE 1.—Material balance for oxidation and sulfation of slag pellets in vertical-shaft furnace.

significant amounts of SiO_2 and MgO with it during beneficiation. Titanium recoveries were low (approximately 64 pct) at the spiral step and may account for a higher percentage of gangue material. Low-intensity magnetic separation could remove up to another 5 wt pct gangue material (especially SiO_2 and MgO).

Associated with the aforementioned problems was the difficulty in decreasing the iron content of the slag to acceptable levels in the large-scale smelting test (table 3). It is believed that this difficulty was associated with the higher SiO_2 contents in the PM concentrate used in this test compared with that in the MRRC concentrate (table 1). More acidic slags (i.e., those containing more SiO_2) tend to retain iron more readily than do basic slags. Two explanations for this observation are possible: (1) Either the magnetite was intimately locked with the SiO_2, and/or (2) iron silicates, which were difficult to reduce, were formed in the slag during smelting. Increased iron also stabilizes the pseudobrookite-type structure, thus preventing it from yielding more iron to the metal during smelting. Excessive SiO_2 in the charge materials can cause a more viscous slag, resulting in greater energy consumption (table 2).

On the other hand, analytical evidence shows that the large-scale test using the PM concentrate was conducted under more oxidizing conditions than was the small-scale test. Higher oxygen pressures decrease the pseudobrookite-type structure (table 3), which promotes the formation of rutile. This was probably the condition that prevailed during the small-scale test using the MRRC concentrate.

In general, the small-scale smelting test using the MRRC concentrate yielded the most acceptable results. This test used 132 pct of the stoichiometric fixed carbon requirements to reduce all of the iron. The woodchips accounted for 55.8 pct of the carbon used. More total carbon was used in the tests with the PM concentrate (160 to 164 pct of the stoichiometric carbon requirement) and woodchips accounted for 55.2 and 42.2 pct of the carbon used in the small- and large-scale smelting tests, respectively. On the basis of these results, it is recommended that approximately 120 to 130 pct of the stoichiometric carbon requirement be used. A 50-50 mixture of woodchips and coke appears acceptable.

SULFATION-LEACHING TESTS

Slags from the small-scale smelting of MRRC and PM concentrates required preleaching before sulfation in order to obtain upgraded products having TiO_2 contents approaching those of natural rutile. The slag prepared from the MRRC concentrate contained 40 to 100 wt pct $Na_{0.23}TiO_2$ (table 3), and it was preleached to reduce its Na_2O content of 10.4 wt pct to below 6 wt pct. The slag derived from PM concentrate with 5.94 wt pct Na_2O and 2.28 wt pct FeO, on the other hand, responded directly to sulfation, but a preleaching step was employed that reduced the SiO_2 content of the slag from 7.72 to 1.83 wt pct. Good sulfation of the Ca constituent was noted in both slags from small-scale smelting tests.

For Mg and Mn, the sulfation proved to be more difficult owing to the partitioning of these impurities in other phases. Previous tests in this laboratory with slags prepared from New York rock ilmenite showed that effective conversion of Mg and Mn in the slag to soluble compounds by SO_2-O_2 mixtures depends on the oxidation of the pseudobrookite-type phase to rutile (3, 5). As mentioned previously, increased FeO contents tend to stabilize the pseudobrookite structure (16).

Although the slag prepared in the 1-mt smelting furnace was preleached in efforts to reduce its FeO and Na_2O contents, the material did not respond well to continuous sulfation in the shaft furnace reactor. Preleaching the material did not lower its FeO content to the level achieved with PM material prepared on a small scale.

The slag with the lower FeO and Na_2O contents responded directly to small-scale sulfation at 800° C with a residence time of 2 h. However, sufficient time for experimentation was not available to optimize the operating variables

TABLE 10. - Comparison of compositions of sulfation-leached slags and commercial titanium raw materials, weight percent

Constituent	Sulfation-leached slags[1]			Commercial titanium raw materials (15)			
	Minnesota rock ilmenite		New York rock ilmenite	Richards Bay titania slag	Natural rutile conc	Synthetic rutile	Ilmenite sand conc
	MRRC	PM					
TiO_2	95.6	94.9	88.0	85.5	96.1	92.5	60.8
Fe_2O_3	1.15	1.26	6.15	8.5	0.5 - .7	3.1	29.5
CaO	.08	<.07	<.07	1.09	.02	.03	.29
MgO	.22	.25	.30				
MnO	<.01	<.06	.03	1.6	.01	1.0	1.07
Al_2O_3	.23	.81	NA	1.4	.35	1.2	.98
SiO_2	2.17	3.17	NA	1.8	.58	1.5	.77
Na_2O	.13	.16	.12	NAp	NAp	NAp	NAp
ZrO_2	NA	NA	NA	NAp	.92	.14	.23
V_2O_5	NA	NA	NA	.45	.65- .7	.2	.22
S	.29	.10	.17	NA	NA	NA	NA

NA Not analyzed. NAp Not applicable. [1] Results of small-scale testing.

such as reaction temperature, time, and slag composition on impurity sulfation.

Table 10 shows that the compositions of sulfated and leached slags derived from Minnesota and New York ilmenite concentrates in small-scale tests compared very favorably with those of commercially available titanium raw materials used as feedstocks in chloride process plants. The Bureau slags were derived from low-grade ilmenites, whereas Richards Bay slag and synthetic rutile are produced from high-grade ilmenite sand concentrates such as the one shown in table 10. A sulfation-leached slag derived from the New York ilmenite (included for comparative purposes) contained pertinent impurity levels comparable to those shown for upgraded Minnesota slags.

SUMMARY AND CONCLUSIONS

This research showed that an ilmenite concentrate from northern Minnesota can be smelted, sulfation-leached to provide a suitable high-TiO_2 feed material for subsequent chlorination. However, a relatively clean concentrate must be used for smelting to avoid excessive levels of iron in the slag, which are detrimental to efficient sulfation-leaching operations. A concentrate containing only ilmenite is preferred. The concentrate should contain less than 2 wt pct SiO_2, 2.5 wt pct MgO, and 1 wt pct Al_2O_3, and should possess at least 29 to 30 wt pct total Ti. Sufficiently high bath temperatures (~1,600° C) are necessary to promote the desired reactions and to avoid excessive slag viscosity. To maintain slag fluidity at the relatively low targeted iron levels, soda ash should be added uniformly throughout the smelting test to avoid excessive Na levels (6.0 wt pct) in the product slag that could result from sporadic additions and that might require preleaching and/or preoxidation prior to the sulfation step. Iron levels in the slag should be maintained below 5 wt pct FeO. In combination with the pseudobrookite structure alone, the $Na_{0.23}TiO_2$ phase is deleterious to sulfation-leaching. Additional phases in the slag make it more amenable to sulfation. At least 120 pct of the stoichiometric amount of fixed carbon required to reduce all of the iron should be used throughout the smelting test to decrease and maintain suitable iron levels in the slag.

Prereduction of the titaniferous material may result in a more easily controlled smelting operation and yield a suitable slag for sulfation-leaching.

Static-bed tests showed preleached slag charges that contained less than 5 wt pct

FeO and 6 wt pct Na_2O responded the best to impurity sulfation by SO_2-O_2 mixtures at temperatures of 850° C and lower. Upgraded slags with compositions essentially comparable to those of natural rutile were obtained from the sulfated charges. The Ca impurity was the easiest to sulfate; Mg and Mn proved to be more difficult to sulfate in slags with the higher FeO and Na_2O contents.

Continuous sulfation of pelletized preleached slag in a vertical-shaft furnace reactor was performed at temperatures of 800° to 850° C, but the relatively high FeO and Na_2O contents of the feed impeded good sulfation of the impurities. Also indications were that the Na_2O additive present as $Na_2O \cdot Fe_2O_3 \cdot 6TiO_2$ was not an effective sulfation promoter since the constituent did not sulfate along with the impurities.

Results of this research have demonstrated the strong possibility that an additional significant domestic titaniferous resource could be used when necessary to prepare chlorination-grade feedstock, thereby decreasing U.S. reliance on foreign imports. However, more large-scale testing is necessary.

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U.S. GOVERNMENT PRINTING OFFICE: 1987 - 605-017/40111

INT.-BU.OF MINES,PGH.,PA. 28388