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Accessory Metals Content of Commercial Titanium Mineral Concentrates

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ACCESSORY METALS CONTENT OF COMMERCIAL TITANIUM MINERAL CONCENTRATES

By Jack C. White[1] and John B. Wright[2]

***ABSTRACT

This Bureau of Mines report assesses the resource potential of trace metals present in commercial Ti mineral concentrates. Metals of greatest interest are those defined as "strategic and critical" by the congressional handbook, U.S. Materials Import Dependency/Vulnerability. Metals of interest in Ti mineral concentrates are Cb, Cr, Ta, Th, U, V, and Zr.

Commercially available Ti mineral concentrates were studied. Characterization and analysis of major and minor constituents were performed by x-ray diffraction, neutron activation, inductively coupled plasma emission, atomic absorption, and classical wet chemical techniques.

Of the metals investigated, the Cb, Ta, and V content of some concentrates may be a significant potential resource, depending on their amenability to recovery.

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***INTRODUCTION

A goal of the Bureau of Mines is the maintenance of an adequate supply of minerals and metals to meet the national economic and strategic needs. In support of this goal, the Albany Research Center is conducting research on extraction of the metals Cb, Cr, Ta, Th, U, V, and Zr from Ti chlorination waste.

Chlorination of Ti mineral concentrates in fluidized-bed reactors is the method of production of the chemical intermediate $TiCl_4$, used in manufacture of all Ti metal and a major fraction of Ti dioxide pigments. Most chlorination plants are arranged such that the waste materials generated during chlorination are composited into a single process stream that contains the critical metals listed above.

This report describes the critical metals content of the Ti mineral concentrates used in chlorination plants. By characterizing the source materials it should be possible to calculate the critical metal content of any chlorination waste for any blend of Ti mineral concentrates used as chlorinator feed. Most of the Ti feedstocks described here are commercial materials available in large tonnage.

Titanium mineral concentrates used in chlorination plants are produced mostly from beach sand deposits by physical separation (beneficiation) processes. The Ti minerals of interest are rutile (TiO_2) or ilmenite ($FeO \cdot TiO_2$) and alteration products of ilmenite, often consisting mostly of pseudorutile ($Fe_2O_3 \cdot 3TiO_2$). Altered beach sand ilmenites are also used as the feedstock for the manufacture of synthetic rutile or rutile

substitutes used in chlorination plants. High Ti slag, made by carbothermic reduction of ilmenite, is also used in some chlorination plants.

The purpose of this study is to assess the resource potential of critical metals contained in the Ti mineral concentrates entering the chlorination process. The resource potential was determined by comparing the quantity of each critical metal with U.S. demand for the metal.

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The authors wish to thank the staff of the Oregon State Radiation Center for their continued support and interest in the many aspects of this project. We especially wish to thank Dr. Roman Schmitt, whose extensive knowledge and experience in radiochemistry contributed so much to the success of this project.

MINERALOGICAL CHARACTERIZATION AND CHEMICAL ANALYSIS

Characterization and analysis of the Ti mineral concentrates was done to determine both mineralogical and chemical compositions. Methods of analysis by the Bureau of Mines were x-ray diffraction, inductively coupled plasma emission (ICP), atomic absorption (AA), and classical wet chemical methods. Neutron activation and radiometric methods of analysis were done by the Oregon State Radiation Center Laboratory in Corvallis, Oregon.

Mineralogical Compositions

The bulk mineralogical compositions of the concentrates were determined by x-ray diffraction. Rutile concentrates listed in table 1 consist principally of the mineral rutile, the high pressure-high temperature polymorph of TiO_2. Rock ilmenites and some beach ilmenites (table 2) have the ilmenite crystal structure and composition ($FeO \cdot TiO_2$), whereas beach ilmenites altered by long exposure to weathering conditions consist in part or entirely of the mineral pseudorutile ($Fe_2O_3.3TiO_2$). Alteration from ilmenite to pseudorutile changes the Fe/Ti molecular ratio from 1/1 to 2/3 and thereby increases the TiO_2 content appreciably. Pseudorutile is the preferred starting material for two commercial synthetic rutile manufacturing processes.

Synthetic rutile is produced from pseudorutile by Kerr McGee Corp.[2] at Mobile, Alabama, by means of a modified Benelite Process. The synthetic product consists of microcrystalline aggregates of rutile of essentially the same shape and size as the original pseudorutile sand grains. A rutile substitute is produced by Associated Minerals at Capel, Australia, by the Western Titanium Process from pseudorutile concentrates mined at Eneabba, Western Australia. The rutile substitute consists of a complex mixture of rutile and Ti suboxide species, again of the size and shape of the original sand grains.

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[2]Reference to specific products does not imply endorsement by the Bureau of Mines.

Table 1. - Analyses of rutiles and synthetic rutiles

Sample No.	Principal minerals	Source	Ti pct	Fe pct	Mg pct	Ca pct	Co[1] ppm	Cr[1] ppm	Mn[1] pct	V[1] ppm	Cb pct	Ta[1] ppm	Zr[1] ppm	Hf[1] ppm	Si ppm	Ce[1] ppm	Sc[1] ppm
1	Rutile	Richards Bay South Africa	57.3	0.86	0.05	0.06	1.5	740	0.011	2210	0.064	170	1180 ±400	310	0.95	90	61
2	Rutile	Sierra Leone West Africa	59.3	.85	.04	<.05	1.4	1,600	.0060	3100	.02	56	8600 ±200	210	.31	80	17
3	Rutile	Eneabba Western Australia	59.7	.62	.02	<.05	0.6	990	.0075	2890	.04	210	8200 ±300	200	.07	38	25
4	Rutile	New Castle NSW Australia	59.8	.34	.11	<.05	.8	1,130	.0039	3100	.028	220	6900 ±300	180	.02	26	37
5	Rutile	Brisbane QSL Australia	57.7	.69	.11	<.05	1.4	1,490	.0055	2880	.036	190	7400 ±400	190	.39	48	58
6	Rutile	Sao Paulo Brazil	57.0	.46	.02	<.05	.6	640	.0028	2130	.042	220	14400 ±300	390	.46	220	33
7	Rutile	Green Cove Springs Florida, U.S.A	59.5	1.26	.02	<.05	ND	630	.025	1390	.069	360	ND	47	<.01	<32	45
8	Rutile[2] anatase	Chavara India	57.4	.88	.07	<.05	1.3	1,420	.0028	2390	.053	550	8600 ±300	260	.36	ND	26
9	Rutile	Sri Lanka	59.8	.59	.03	<.05	.8	1,130	.0052	2780	.038	180	8000 ±200	210	.02	80	21
10	Synthetic rutile[3]	Capel Western Australia	58.4	2.03	.04	<.05	1.7	670	.031	820	.027	140	1060 ±200	20	.45	ND	63
11	Complex rutile substitute[4]	Eneabba Western Australia	57.0	3.68	.24	<.05	18	1,840	1.24	1200	.038	180	ND	27	.23	330	290

[1]Analysis by Neutron Activation Method at Oregon State University Radiation Center.
[2]Also known as "Q" grade.
[3]Synthetic rutile produced at Mobile, Ala., by Kerr McGee Corp. from altered ilmenite mined at Capel, Western Australia.
[4]Synthetic rutile produced at Capel, Western Australia from altered ilmenite mined at Eneabba, Western Australia.

Table 2. - Analyses of ilmenites and altered ilmenites

Sample No.	Principal minerals	Source	Ti pct	Fe pct	Mg pct	Ca pct	Co[1] ppm	Cr[1] ppm	Mn[1] pct	V[1] ppm	Cb pct	Ta[1] ppm	Zr[1] ppm	Hf[1] ppm	Si pct	Ce[1] ppm	Sc[1] ppm
12	Ilmenite	Brisbane QSL Australia	31.1	32.0	.70	<.05	89	7,900	1.03	950	.008	32	4800 ±200	110	.77	280	65
13	Ilmenite pseudorutile	Capel Western Australia	35.5	28.6	.15	<.05	45	230	1.07	750	.006	69	690 ±180	14	.22	90	79
14	Ilmenite pseudorutile	Newcastle NSW Australia	26.1	20.5	3.57	<.05	141	49,000	3.80	ND	.012	92	1900 ±200	44	.19	<40	88
15	Ilmenite rutile	Newcastle NSW Australia	23.0	25.6	1.64	<.05	90	23,000	1.01	1270	.009	78	ND	24	.01	150	124
16	Ilmenite pseudorutile	Manayalakurrchi India	33.7	28.2	.57	.08	71	630	.28	1120	.002	93	1100 ±200	29	.41	ND	66
17	Ilmenite	Orissa India	31.3	35.2	.44	.06	88	440	.43	1160	.013	61	ND	16	.21	ND	61
18	Ilmenite pseudorutile	Chavara India	37.6	23.6	.57	.08	59	930	.12	490	.019	87	5300 ±300	112	.22	ND	84
19	Ilmenite pseudorutile	Sri Lanka	33.8	27.5	.55	.26	72	840	.64	1300	.012	37	3300 ±300	66	.53	350	104
20	Ilmenite	Tahawus New York, U.S.A	29.0	35.3	1.44	.23	220	140	.33	610	<.01	2.4	ND	6	.50	ND	40
21	Pseudorutile Rutile	Eneabba Western Australia	37.0	23.5	.18	.08	55	1680	.77	910	.017	144	2800 ±300	61	.58	900	88
22	Pseudorutile Ilmenite	Sao Paulo Brazil	35.1	26.6	.30	<.05	52	370	.69	990	.014	71	950 ±250	22	.25	240	118
23	Pseudorutile rutile	Green Cove Springs Florida, U.S.A.	39.6	21.6	.16	.16	38	820	1.04	550	.012	78	ND	8	.01	90	53
24	Pseudorutile rutile	Green Cove Springs Florida, U.S.A.	41.1	17.6	.16	.34	31	720	.77	640	.010	141	860 ±250	13	.31	400	63
25	Pseudorutile rutile	Starke Florida, U.S.A.	36.9	20.2	.18	.13	36	490	.81	630	.012	139	1700 ±200	34	.40	100	56

Slags and Other

Sample No.	Principal minerals	Source	Ti pct	Fe pct	Mg pct	Ca pct	Co[1] ppm	Cr[1] ppm	Mn[1] pct	V[1] ppm	Cb pct	Ta[1] ppm	Zr[1] ppm	Hf[1] ppm	Si pct	Ce[1] ppm	Sc[1] ppm
26	Pseudobrookite (slag)	Richards Bay South Africa	53.5	7.98	.64	.08	1.7	3030	1.32	2010	.018	56	2200 ±200	46	.72	240	109
27	Pseudobrookite (slag)	Sorrell Canada	49.1	9.02	3.12	.27	9.0	1320	.18	2880	.008	5	720 ±170	15	.96	< 6	85
28	Perovskite	Colorado U.S.A.	32.6	3.76	1.49	21.5	20	400	.085	160	.051	270	4000 ±300	11	1.44	ND	14

[1]Analysis by Neutron Activation method at Oregon State University, Radiation Center Laboratory.

High Ti slags produced by carbothermic reduction of ilmenite consist mostly of pseudobrookite, a crystalline structure that has a tolerance for large amounts of impurities in solid solution. Ti slag produced from beach ilmenite at Richards Bay, South Africa, is reportedly suitable for chlorination in some plants. Slag produced from rock ilmenite at Sorrell, Canada, is higher in impurities and reportedly is used as a blending feedstock in some chlorination plants, but its principal use is in sulfate route pigment production.

Chemical Analysis

Bureau of Mines analyses were performed on portions of the 1 Kg samples supplied by the producers. The samples were taken into solution with sodium peroxide fusion and analyzed as follows:

1. Cb - separation and concentration by wet methods, determination by ICP.
2. Fe, Ti - titrametric wet methods.
3. Ca, Mg - separation by wet methods, determination by AA.
4. Si - gravimetric wet method.

Tantalum, in the low concentrations contained in these samples, is near the detectability limits of ICP analysis. Because Ta was of special interest in this study, neutron activation analysis was employed for more accurate results. Other metals determined by the neutron activation method were Co, Cr, Mn, V, Zr, Hf, Ce, and Sc. Uranium and thorium were analyzed by a radiometeric method. Primary radiometric standards were supplied by the New Brunswick Laboratory, U.S. Department

of Energy. Neutron activation and radiometric analyses were performed by the Oregon State Radiation Center Laboratory. Analytical data are presented in tables 1, 2, and 3.

DISCUSSION

An overview of the resource potential of critical metals contained in Ti mineral concentrates was provided by calculations based on the analytical data in tables 1 and 2, and on U.S. metal consumption data published in the Bureau of Mines Yearbook (1984). The calculated values express metals content of Ti mineral concentrates as a percentage of U.S. demand for Cr, Cb, Ta, V, and Zr. For the purposes of these calculations, each Ti concentrate was assumed to supply the entire U.S. demand for Ti (table 4). A sample calculation is also presented. Columbium, Ta, and V are contained in substantial quantities amounting to one-fourth to one-third or more of U.S. demand in some concentrates. Zirconium is present in less significant amounts and Cr (except for samples 14 and 15, table 2) is present in insignificant quantities. Whereas, a significant fraction of U.S. demand for Cb, Ta, and V could potentially be satisfied by recovery from Ti concentrates, the concentrates are a dilute source.

Table 3. - Analyses of titanium concentrates for uranium and thorium by the Radiometric Counting Method[1]

Sample	[2]U-609	[3]Error, pct	Th-583	Error, pct
1	50.45	0.5	55.55	1.6
4	44.95	.5	5.57	10.9
5	44.92	.5	15.78	4.2
6	44.59	.6	75.66	1.3
7	19.46	.8	17.92	3.0
8	84.25	.4	28.56	2.9
10	6.60	2.5	60.44	1.5
12	8.30	1.6	63.32	1.1
13	6.11	2.2	91.74	1.0
14	12.03	1.0	25.43	2.1
15	8.82	1.4	30.87	1.8
16	23.99	1.1	403.09	.7
17	3.83	3.3	80.11	1.1
18	40.15	.8	497.47	.7
19	16.30	1.1	110.45	1.0
20	.04	41.5	.17	57.5
22	13.36	1.5	208.10	.8
23	13.48	1.1	42.65	1.6
24	27.61	.8	120.81	1.0
25	9.21	1.4	39.23	1.6
26	6.06	2.2	55.58	1.4
27	.38	11.5	1.16	17.4
28	54.12	.6	180.91	.9

[1]Missing Analyses (2,3,9,11 etc.) were due to insufficient sample (approx. 750 g) required for application of this analytical method.

[2]Uranium weights calculated using Ra-226 photopeaks. Thorium weight calculated using the Th-232 photopeaks.

[3]Error represents statistical counting error only.

Three factors, however, cause the Cb, Ta, and V contents to be of interest. First, averaging the analyses of the nine rutile samples listed in table 1, (samples 1 through 9), it is apparent that Cb, Ta, and V are present in much higher concentrations in rutile than in average crustal rocks (table 5). In rutile, the tantalum concentration ratio is much higher than the Cb or V ratios. In Green Cove Springs, altered ilmenite (sample 24) and in Sorrell Slag (sample 27) the concentration ratios differ markedly from those of rutile; higher for Cb and lower for Ta, especially for Ta in slag. The ratio for V is higher in the slag.

Table 5. - Concentrations of critical metals in average rutile, altered beach ilmenite, and slag, compared with average crustal rock

Critical metals	Average crustal rock, ppm[1]	Average rutiles concentrations		Beach ilmenite concentrations		Sorrell slag concentrations	
		ppm	ratio	ppm	ratio	ppm	ratio
Cb	20	430	21.5	1,000	50	800	40.
Ta	2.0	240	120.	141	70	5	2.5
V	135.	2,541	19.	640	4.8	2,800	21.

[1]Brian Mason and Carlton B. Moore, Principals of Geochemistry, John Wiley & Sons, 4th ed., 1982, pp. 46-47.

Secondly, the removal of TiO_2 by chlorination causes additional concentration of the remaining metals. Because of its high TiO_2 content, the concentration during chlorination of rutile is higher than it is for ilmenites or slag. For example, the average TiO_2 content of the nine rutile samples of table 1 is 97.75 pct; then the average chlorination concentration factor for these rutiles is $\frac{1}{1-.9775} = 44$. It should be noted that chlorination concentration factors are extremely sensitive to small amounts of impurities in rutile. Concentration of

Table 4. - The content of critical metals in Ti mineral concentrates expressed as a percentage of U.S. demand[1]

	Critical metal, pct[2] of U.S. demand				
Sample No.	Cb	Cr	Ta	V	Zr
1	48	0.23	25	45	18
2	14	.47	8.0	61	12
3	28	.29	30	56	12
4	20	.33	31	60	9.8
5	27	.45	28	60	11
6	31	.20	33	43	22
7	49	.19	51	27	1.4
8	39	.43	81	48	13
9	27	.33	26	54	11
10	20	.20	20	16	1.5
11	28	.57	27	24	0.5
12	11	4.4	8.7	35	13
13	7.0	.11	16	25	1.7
14	20	33	30	67	6.2
15	17	18	29	64	1.1
16	28	.33	23	39	2.8
17	18	.25	17	43	0.5
18	21	.43	20	15	12
19	15	.43	9.3	45	8.3
20	<15	.08	.70	24	.3
21	20	.80	33	29	6.5
22	17	.18	17	33	23
23	13	.36	17	16	.64
24	10	.31	29	18	1.8
25	14	.23	32	20	3.9
26	14	1.0	8.9	43	3.5
27	6.9	.48	.86	68	1.2
28	66	.21	70	5.7	10.

[1]Metal consumption figures from Minerals Yearbook 1984 in short ton units.

Ti - 552,400	Ta - 650
Cr - 314,820	V - 4,761
Cb - 1,300	Zr - 64,740

[2]Sample calculation for Ta in sample 1:

Given: Ti consumption, 1984 = 552,444 short tons
Ta analysis of sample 1 = 170 ppm
Ti analysis of sample 1 = 57.3 pct (from table 1)

$$\text{Then: } \frac{\frac{552,400}{.578} \times 170 \times 10^{-6}}{650 \text{ St.Ta}} \times 100 = 24.995 \text{ pct of annual demand}$$

metals during chlorination of ilmenite and slag is much lower due mostly to their higher Fe content. For rutile the product of natural concentration and chlorination concentration factors are remarkably large numbers especially for tantalum (table 6). In contrast, combined concentration factors for ilmenite and slag are much lower than for rutiles. Rutile, therefore, is of greatest interest as a potential source of critical metals.

Table 6. - Concentration factors for Cb, Ta, and V

Critical metals	Natural concentration factor			Chlor. concentration factor			Combined concentration factor		
	Rutile	Ilmenite	Slag	Rutile	Ilmenite	Slag	Rutile	Ilmenite	Slag
Cb	21.5	50	40	44	3.18	5.55	946	159	222
Ta	120.0	70	2.5	44	3.18	5.55	5,280	223	13.9
V	19.0	4.8	21.	44	3.18	5.55	836	15.3	117

A third favorable aspect of chlorination waste is that the Cb, Ta, and V may be in acid soluble form as chlorides that should provide a favorable starting point for separations and recovery.

Analysis of a rutile derived chlorination waste may be calculated assuming complete chlorination of the rutile and no dilution of the waste during the chlorination process. Recalculating the concentration factor for rutile sample #1 (which is lower than average in TiO_2) and multiplying by the analyses in table 1 provide the data of table 7:

Table 7. - Calculated analysis of waste from chlorination of rutile sample no. 1

Calculated waste analysis, pct			
Fe	19.5	Si	21.6
Cr	1.7	Zr	22.7
Mn	.45	Co	.0034
V	4.76	Hf	.70
Mg	1.13	Ce	.20
Ca	1.36	Sc	.14
Cb	1.45	Th	.13
Ta	.39	U	.11

Sample calculation:

$$57.3 \text{ pct Ti} \times \frac{79.9}{47.9} = 95.6 \text{ pct } TiO_2$$

$$\frac{1}{1-.956} = 22.7 \text{ concentration factor}$$

The calculated analysis is a complex mixture of metals that may prove difficult to separate into marketable products. An additional potential problem is the Th and U content, which may be high enough to be of concern in material processing and disposal. The thorium content of titanium mineral concentrates varies over a wide range; less than 1 ppm in rock ilmenite to almost 500 ppm in one beach sand ilmenite (table 3). Presumably a significant fraction of the thorium is contained as discrete grains of monazite, a rare earth phosphate mineral that may contain as much as 8 pct Th. Physical separation of the monazite from the concentrates prior to chlorination would appear to be the preferable means of reducing the thorium content of chlorination wastes.

An additional consideration is that particles of Ti minerals and coke, quartz, silicates, and refractory chlorinator lining material blow out of the fluidized bed chlorinator. These particles would dilute the

calculated chlorinator waste analysis presented in table 7. The situation is further complicated by the work of Paige, Mussler, and Elger[3] who have shown that unreacted rutile, coke, and silicates can be recovered from chlorination waste by simple physical separation equipment, presumably leaving the critical metals of interest in relatively dilute mixtures.

CONCLUSIONS

1. Data presented above will serve as a guide in considering Ti mineral concentrates as potential sources of some critical metals.
2. Cb, Ta, and V appear to be of the greatest economic significance.
3. The high natural concentrations of Cb, Ta, and V in rutile, multiplied by the chlorination concentration ratio, provides high concentrations of these metals in chlorination waste compared to the concentrations in average crustal rocks.
4. Separations to provide marketable products from the complex mixture of metals in the chlorination waste may be difficult.

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[3]Paige, J. I., R. E. Mussler, and G. W. Elger. Physical Beneficiation of Titanium Plant Solid Wastes: Recovery of Titanium Minerals and Coke. BuMines RI 8737, 1982, 23 pp.

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