when ferrous ammonium sulfate (or ferrous sulfate) is used.

The thermal decomposition of $RSO_4 \cdot Ti(SO_4)_2$ has been studied and found to be almost complete at 850°. The colored residues left at this temperature are intimate mixtures of titania and bivalent metallic oxides with or without a small amount of undecomposed substance and may be useful as paint materials.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE ROYAL INSTITUTE OF SCIENCE]

Recovery of Titania from the Bauxite Sludge

BY S. M. MEHTA AND S. R. PATEL

This paper deals with the amount of titania which may be recovered from its sulfuric acid solution in the form of $RSO_4 \cdot Ti(SO_4)_2$ by taking advantage of the formation of such compounds.[1] The following table contains data obtained with 0.1 g. titanium dioxide and the different bivalent metallic sulfate.

TABLE I

RECOVERY OF TiO_2 FROM H_2SO_4 SOLUTIONS OF $RSO_4 \cdot Ti(SO_4)_2$

R	RSO_4, g.	H_2SO_4, cc.	Recov., %
Zn	0.3	60	59.71
	.4	100	93.69
	.8	125	99.00
Cu	.4	100	90.33
	.6	100	97.40
	.8	125	99.04
Mn	.2	60	85.09
	.4	100	99.28
	.6	100	99.65
Co	.3	50	62.66
	.4	75	98.58
	.6	80	99.47
Mg	.3	50	67.98
	.4	60	99.19
	.6	80	99.74

The percentage recovery of titanium dioxide given in Table I was calculated from the weight of the precipitate of $RSO_4 \cdot Ti(SO_4)_2$ which was analyzed for its titanium contents. This was further checked from the estimation of titanium in the filtrate.

It will be observed from Table I that the recovery of titania increases as the amount of the bivalent metallic sulfate is increased and it reaches about 100% with the highest amount of the bivalent metallic sulfate used.

As titanium occurs together with a large proportion of aluminum in the bauxite sludge, the effect of aluminum sulfate on solutions of titania in sulfuric acid was studied, by following the general procedure outlined before.[1] With amounts of $Al_2(SO_4)_3 \cdot 18H_2O$ less than that of titania, the precipitates obtained are of titanyl sulfate containing only about 1% of aluminum, but when the amount of aluminum sulfate is increased to six or ten times, the precipitate obtained consists of anhydrous aluminum sulfate with about 2 to 3% of titanium. However with amounts of aluminum sulfate equal to or double that of titania, the precipitates appear to be mixtures of titanyl sulfate and anhydrous aluminum sulfate.

The bauxite sludge also contains silica and iron together with a certain proportion of the sulfate ions. In order to determine the conditions for the quantitative extraction of titania from such a material, experiments were carried out with artificial mixtures ultimately approaching the proportions present in the bauxite sludge. In the first instance, a mixture containing TiO_2 (0.1 g.) and $Al_2(SO_4)_3 \cdot 18H_2O$ (1.2 g.) was prepared and was treated with concd. sulfuric acid (sp. gr. 1.79, 180 cc.). This was heated to 230° for about an hour. The precipitate was separated from the liquid and was found to be aluminum sulfate containing 2.17% of titanium. When this experiment was repeated adding $Fe_2(SO_4)_3 \cdot 9H_2O$ (0.2 g.), the precipitate contained ferric iron as might be expected. The filtrate contained nearly 50% of titania which was precipitated quantitatively in the form of $ZnSO_4 \cdot Ti(SO_4)_2$ by heating the filtrate to boiling with the addition of $ZnSO_4 \cdot 7H_2O$ (0.4 g.).

It may be observed from what is stated above that a sample of bauxite sludge may be treated by this process for the recovery of titania. In the following paragraphs the analysis and the treatment of a sample of bauxite sludge have been given and in conclusion an outline of a modification of the process has been suggested.

TABLE II

ANALYTICAL DATA OF BAUXITE SLUDGE

Total loss on strong heating, %	51.65
Moisture, %	9.22
Sulfate, %	27.61
Titania, %	13.60
Ferric oxide, %	9.62
Alumina, %	18.82
Silica, %	5.65

Finely powdered (180-mesh) bauxite sludge (25 g.) was digested with concd. sulfuric acid (400 cc.) and heated until fumes of sulfuric acid were evolved. At the end of one hour the liquid was allowed to cool and separated from the solid by decantation.

Solid Residue.—This was treated with such quantity of water (about 100 cc.) that titanium, aluminum and iron were brought into solution leaving behind an insoluble residue of siliceous material. The clear liquid was separated from the insoluble residue and was reduced with zinc dust. At this stage the solution was partially neutralized with soda ash until it contained 1% free sulfuric acid. This liquid was diluted to about five times and heated so as to get the precipitate of metatitanic acid. This pre-

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(1) Mehta and Patel, THIS JOURNAL, **73**, 224 (1951).

cipitate was separated from the liquid and was added to the sulfuric acid solution obtained with the original bauxite sludge.

Sulfuric Acid Solution.—This solution to which metatitanic acid obtained from the solid residue was added was treated with the calculated quantity of zinc dust (about 6.4 g.). On heating, a clear solution was obtained first which with a rise of temperature gave a precipitate of $ZnSO_4 \cdot Ti(SO_4)_2$. It was separated and boiled with water to get metatitanic acid. This product was ignited and titania obtained from it was 99.12% pure with only traces of iron. The yield of titania obtained was 73.52%.

As the mixture of titania with certain metallic oxides are used as paint materials, the sulfuric acid solution referred to above may be treated with sulfates of zinc, copper, manganese or cobalt and titanium precipitated as the compound $RSO_4 \cdot Ti(SO_4)_2$ and finally decomposed thermally to give colored products containing titania and the metallic oxides.[1]

Before concluding, a modification of the procedure outlined above for the treatment of bauxite sludge may be mentioned. The finely powdered bauxite sludge may be mixed with zinc dust and then digested with concd. sulfuric acid so as to obtain a solid material containing most of the titania. This solid may then be separated from the liquid and treated with water so as to bring titanium, aluminum and iron into solution leaving only insoluble siliceous material. This liquid can then be treated in the same manner as already given before to obtain metatitanic acid.

In an actual experiment carried out according to the above procedure the percentage recovery of titania was found to be 76.47.

Summary

The recovery of titania from its sulfuric acid solution in the form of $RSO_4 \cdot Ti(SO_4)_2$ has been found to be about 100%.

When solutions of titania in sulfuric acid are heated in the presence of aluminum sulfate, substances which appear to be either titanyl sulfate with small amount of aluminum or aluminum sulfate with small amount of titanium are obtained.

By experimenting with artificial mixtures containing TiO_2, $Al_2(SO_4)_3 \cdot 18H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ approaching the proportion present in the bauxite sludge, it is shown that titania can be recovered quantitatively from its sulfuric acid solution in the form of $ZnSO_4 \cdot Ti(SO_4)_2$.

It is shown that from a sample of bauxite sludge titania can be recovered by taking advantage of the formation of $RSO_4 \cdot Ti(SO_4)_2$ which either can be hydrolyzed and then ignited to give pure titania or can be decomposed thermally into colored residues which may be useful as paint materials.

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The Behavior of Solutions of Titanium Dioxide in Sulfuric Acid in the Presence of Certain Bivalent Metallic Sulfates

BY S. M. MEHTA AND R. P. PONCHA

Following the general procedure described in the previous paper[1] two more compounds, *viz.*, $NiSO_4 \cdot Ti(SO_4)_2$ and $CdSO_4 \cdot Ti(SO_4)_2$ were obtained when titanium dioxide (0.1 g.) and metallic bivalent sulfate (0.1 to 0.6 g.) were heated with sulfuric acid (sp. gr. 1.8, 50 cc.). Similarly when titanium dioxide (0.1 g.) and calcium sulfate (0.4 to 0.6 g.) were heated with sulfuric acid (sp. gr. 1.8, 50 cc.) a precipitate was obtained which agreed with the formula $CaSO_4 \cdot Ti(SO_4)_2$. Weinland and Kühl[2] have described the preparation of the latter compound by a slightly different method. These authors dissolved titanium dioxide (1.6 g.) and calcium sulfate (5 g.) each separately in concd. sulfuric acid, the former in 200 cc., the latter in 100 cc. On mixing these two solutions and concentrating the liquid the product containing calcium was isolated. It may be observed in this connection that if their method is followed the liquid requires prolonged boiling before the precipitate is obtained, while using the method described in this work the compound is more readily obtained. It is found that these compounds are deliquescent and readily soluble in dilute hydrochloric acid.

When attempts were made to prepare compounds containing strontium and barium, $TiOSO_4$ was invariably obtained instead. This appeared surprising since Weinland and Kühl[2] have described isolation of a compound $SrSO_4 \cdot Ti(SO_4)_2$ and $2BaSO_4 \cdot 3Ti(SO_4)_2$ by following a method similar to that used for the preparation of the compound containing calcium.

In order to ascertain if the compounds containing strontium and barium are ever possible, experiments were carried out using concd. sulfuric acid (40 cc.) and titanium dioxide (0.1 g.) with varying amounts of strontium sulfate and barium sulfate. The quantities of the former taken for this purpose were 0.2, 0.4, 0.8 and 1.0 g., while those of the latter were 0.1, 0.2 and 0.6 g. In all these experiments the product obtained was $TiOSO_4$. The $TiOSO_4$ which separated out from solutions containing strontium sulfate and barium sulfate dissolved readily on heating in dilute hydrochloric acid but was only partially soluble in concd. hydrochloric acid even on boiling. From the above facts the conclusion seems inevitable that the compounds containing strontium and barium described by Weinland and Kühl[2] do not appear to exist and they have probably handled $TiOSO_4$ contaminated with the mother liquor containing strontium sulfate and barium sulfate. Another interesting fact to be noted in this connection is that the theoretical values of titanium, barium and sulfate given by these authors do not correspond with the formula $2BaSO_4 \cdot 3Ti(SO_4)_2$. This is made clear in Table I.

TABLE I

	Titanium, %	Barium, %	Sulfate, %
Weinland and Kühl	9.89	23.69	66.19
Recalcd. values	12.1	23.1	64.8

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[1] Mehta and Patel, THIS JOURNAL, **73**, 224 (1951).

[2] Weinland and Kühl, *Z. anorg. Chem.*, **54**, 253 (1907).