26/3/76

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DEPARTMENT OF MINES.

South Australia.

RB25

GEOLOGICAL SURVEY LABORATORIES.

CHEMICAL RESEARCH SECTION.

CR/TR 5

The effect of ferric iron on the hydrolysis of titania from Radium Hill ore leach liquors.

by

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May 1st, 1953.

INTRODUCTION.

Adventitious build-up of titania in anion exchange resin columns, during the early period of pilot plant operation, has resulted in reduced column loadings for Uranium. Presumably the resin bead pores become choked with titania hydrolysed from the feed liquors and while saturation loadings are not significantly affected, a consequent reduction in diffusion rate prevents satisfactory loadings from being obtained except by using very slow liquor flow rates or three or more columns in series during adsorption.

For this reason it was desirable to explore methods for removing titanium from the sulphate leach liquors.

The investigations described are part of work carried out in an attempt to remove titanium from sulphuric acid leach liquors obtained from leaching Radium Hill ore. Initial efforts were aimed at varying the conditions of dilution and neutralisation of digester pulp. Results showed that while the titanium content of liquors could be reduced considerably, there still remained sufficient to cause interference at a later stage of the process. It was concluded that failure to hydrolyse titanium completely was due to the ferric iron present which presumably formed a stable complex with the titanium. Attempts to remove ferric iron and titanium by adjusting the pH of the diluted digester pulp to 3.0 - 3.5 were not successful, owing to simultaneous loss of much of the uranium.

It was decided to reduce the ferric iron in filtrates from the diluted pulp before adjusting the pH with calcium carbonate. Reduction of the ferric iron content to less than 1 g/litre was successfully accomplished by the use of both metallic iron and electrolysis but the latter process was preferred on account of the greater degree of control it afforded. The removal of titanium from reduced liquors was effected by adjusting the pH to values from 1.4 to 2.5 depending on the temperature. At 70°C a pH value of 2.2 - 2.5 was necessary for complete hydrolysis but at 100°C the titanium could all be removed at a pH of 1.4. The hydrolysis at

the lower pH ranges was carried out by boiling with steam and a series of tests was carried out to show the influence of both ferric iron and pH on the stability of the titanium.

EXPERIMENTAL.

1. Effect of temperature on dilution.

Samples of digester pulp from the Pilot Plant were used for the tests which were carried out as near as possible to the normal Plant practice. Samples of pulp weighing 367 g. were taken representing 200 g. ore. The pulp was heated to about 90°C, poured into the dilution water and stirred mechanically during the whole period of subsequent treatment. The amount of water used for diluting 367 g. pulp was 730 ml. in accordance with Pilot Plant procedure and the calcium carbonate for neutralisation was added in the form of a slurry with water.

Figures showing the effect of temperature of dilution and variation in time of heating are given in Table I. The diluted pulps were brought to pH 1.6 with calcium carbonate following the stated time of reheating. The final volumes of liquor obtained after filtration and washing were approximately 1 litre.

TABLE I

Temp. of dilution water	Time reheated after dilution	Total heating time.	Final pH	Total $CaCO_3$ added	TiO_2 in liquor g/200 g. conc.
Room temp.	Nil	Nil	1.6	10 g.	7.5 g.
90°C	Nil	Nil	1.6	14 g.	5.55
90°C	15 mins.	60 mins	1.6	22 g.	5.5
90°C	30 mins.	90 mins.	1.6	22 g.	4.57
90°C	60 mins.	80 mins.	1.7	22 g.	4.17

It seems evident from these figures that little significant reduction in titanium content of liquors can be obtained by this means unless the time of heating after neutralisation is increased considerably. An increase in the pH of the pulp may lead to loss of

uranium by adsorption or co-precipitation (Table III).

2. Increased Dilution time. Attempts were made to increase the time of dilution of the hot pulp by adding it at a controlled rate to the dilution water. A "Quickfit" one litre wash bottle was used as container and the pulp was forced out of the delivery tip by means of slight pressure. It was considered that the slower rate of addition of pulp to the dilution water might result in more complete hydrolysis of titanium by reason of the lower acidity during the greater part of the operation. In actual fact no great improvement was noted. Figures in Table II show the effect of slow dilution with other conditions as indicated. In all tests 367 g. hot pulp were used equivalent to 200 g. ore. Calcium carbonate was added as a slurry in water following the period of reheating.

TABLE II

Temp. of dilution water	Dilution time	Time reheated after dilution	Total $CaCO_3$ added	Final pH	TiO_2 in liquor g/200 g. conc.
90°C	15 mins.	30 mins.	Nil	1.1	3.9
90°C	15 mins.	30 mins.	20 g.	1.75	2.1
80°C	18 mins.	Nil	25 g.	1.9	4.4

3. Other Dilution Conditions. Other tests included (1) Further increased dilution time (60 minutes), (2) Addition of calcium carbonate to hot pulp before dilution, (3) Addition of hot pulp to dilution water containing calcium carbonate as a slurry. All of these were without significant effect on the titanium content of the liquors.

As a result of the foregoing attempts to hydrolyse the titanium, it was concluded that the presence of ferric iron might have a protective effect on the titanium in solution.

4. Effect of ferric iron on hydrolysis of Titanium. A series of samples was prepared from a bulk sample of liquor in which the ferric iron content and pH were varied for comparison of the hydro-

lysis effect. Hydrolysis was carried out by bringing the liquor to the boil over a gas burner and maintaining at the boil by passing steam with a little external heat to keep the volume constant. Steam was passed for 30 minutes after which the precipitated titania was separated and weighed. Any ferric iron which precipitated with the titania was extracted by digestion with dilute hydrochloric acid. There was no alteration in the ferrous iron content of the liquors so that the difference in the ferric iron figures before and after hydrolysis represents the amount removed from solution.

The results of the tests carried out on these liquors are given in Table III. 100 ml. of a liquor containing 8.0 g. titania/l. were used for each test. The pH of each sample was adjusted by addition of calcium carbonate and the calcium sulphate removed by filtration.

TABLE III.

COMPOSITION OF LIQUOR BEFORE HYDROLYSIS			COMPOSITION OF LIQUOR AFTER HYDROLYSIS			TiO_2 Recovered
Fe^{+++} g./100 ml.	U_3O_8 g./100 ml.	pH	Fe^{+++} g./100 ml.	U_3O_8 g./100 ml.	pH	%
.045	.19	1.3	.045	.19	1.1	96
.21	.19	1.3	.160	.19	1.1	82
.39	.19	1.3	.310	.19	1.1	56
.60	.19	1.3	.474	.19	1.1	32
.045	.19	1.5	.033	.19	1.2	98
.27	.19	1.5	.10	.19	1.2	87
.41	.19	1.5	.13	.19	1.15	71
.65	.19	1.5	.443	.19	1.15	22
.045	.19	1.6	.03	.19	1.3	100
.25	.19	1.6	.08	.19	1.3	85
.47	.19	1.6	.14	.19	1.2	79
.67	.19	1.6	.32	.19	1.2	28
.03	.19	1.8	.036	.19	1.5	100
.24	.19	1.8	.053	.19	1.3	100
.39	.19	1.8	.095	.19	1.25	86
.58	.19	1.8	.16	.19	1.2	81

The results of four series of tests are shown graphically in Fig. 1. Curve D indicates that titanium can be hydrolysed completely at pH 1.8 in the presence of as much as 2.5 g. Fe^{+++}/l. Hydrolysis of titanium is incomplete in more acid liquors except at low concentrations of ferric iron. Fluorimetric assays of the

liquors for uranium before and after hydrolysis did not show any appreciable loss due to adsorption or co-precipitation.

5. Removal of Ferric Iron and Titanium at high pH. It was thought that it might be possible to remove both titanium and ferric iron by adjusting the pulp to a fairly high pH, say 3.0 - 3.5, with subsequent filtration. This was found to be the case but results showed that a considerable amount of uranium was lost in the residues and could not be recovered by washing. In connection with these tests, it was also expected that aeration of the diluted pulp at pH 3.0 - 3.5 would result in oxidation of ferrous iron to ferric iron thus removing all the iron from solution. In actual fact, practically no ferrous iron was oxidised during periods of aeration up to 1½ hours at near boiling temperature and at pH 3.5.

Results of these tests are shown in Table IV. The quantities taken were the same as previously, namely 367 g. pulp diluted with 730 ml. water. The values for uranium oxide, titania and ferrous iron in an unneutralised liquor are shown for comparison.

TABLE IV.

Temp. of dilution and heating	Total time of heating	Time Aerated	$CaCO_3$ added	Final pH	U_3O_8 in liquor g/200 g. Conc.	TiO_2 in liquor g/200 g. Conc.	Fe^{++} in liquor g/200 g. Conc.
90°C	45 mins.	Nil	Nil	1.1	1.85 g.	3.9 g.	8.8 g.
90°C	20 mins	20 mins.	35 g.	2.0	1.67	<0.25	8.4
90°C	30 mins.	Nil	40 g.	2.5	1.46	<0.25	8.4
90°C	90 mins.	90 mins.	47 g.	3.6	0.89	<0.25	8.5

6. Reduction of Ferric Iron in liquors. Reduction of liquors was carried out with metallic iron in the form of steel wool as supplied for household cleaning. This was found to be effective when used in a glass column with liquor flowing through or when attached to a glass rod and swirled in the liquor. Reduction of the acid liquor (pH approximately 1.0) was rapid and almost 100 per cent efficient. However, it was difficult to control the rate of reduction and

frequently the liquor became over-reduced with production of uranous ion which was lost during the neutralising procedure.

It was considered vital that a more controllable process for reduction of ferric iron should be available for large scale operation, and experiments were carried out using an electrolytic reductor. This work is the subject of a separate report. Results achieved so far indicate that there should be no difficulty in obtaining a reduced liquor of the required composition. The ideal liquor is one in which some ferric iron remains in order to ensure that no uranous ion is present, but the concentration should not exceed, say .5 g. Fe^{+++}/l.

7. Neutralisation of reduced liquor. Liquors were adjusted to the required pH by the addition of precipitated calcium carbonate as a slurry with water. Initial additions were made to liquor at room temperature but this was found to be unsatisfactory. Reaction between the calcium carbonate and sulphuric acid was delayed at room temperature presumably because of the formation of calcium bicarbonate in which calcium sulphate must be appreciably soluble.

When the temperature of the liquor was raised to 70°C before addition of the calcium carbonate, the reaction was much more vigorous and calcium sulphate appeared much more rapidly. Precipitation of titania generally commenced at about pH 1.7 and subsequent experience showed that practically all could be hydrolysed at pH 2.2 - 2.5. It was found, however, that loss of uranium tended to be serious if the pH rose above 2.5 and this figure is considered to be the upper limit for production of satisfactory liquor.

8. Composition and Properties of Neutralised, Reduced Liquor. Liquor which has been reduced and neutralised as described is noticeably different in appearance to unreduced liquor. The reduced liquor after neutralisation is a bright blue-green colour, whereas the unreduced liquor is much darker in appearance due to

the ferric iron present. The reduced liquor is more stable owing to the removal of titanium during the neutralisation and loadings on resin columns are improved due to a number of conditions. These include:-

(1) Higher pH of liquor. (Up to 2.5)

(2) Absence of ferric iron.

(3) Lower sulphate content. (The sulphate set free by hydrolysis of titanium is precipitated as calcium sulphate during neutralisation.)

(4) Absence of titanium, eliminating hydrolysis problems.

The composition of typical acid leach liquors before reduction and neutralisation is shown in Table V. The constituents are expressed in g/200 g. concentrate in order to enable comparison with final liquors which were at varying dilution.

TABLE V.

	Liquor 1.		Liquor 2.	
	g/l.	g/200 g. conc.	g/l.	g/200 g. conc.
U_3O_8	1.3	1.85	1.85	1.85
Fe^{+++}	8.5	12.0	12.0	12.0
TiO_2	5.7	8.0	6.6	6.6

In Table VI the figures show the composition of liquors produced by reduction of ferric iron and neutralisation at 70°C to the pH stated. Saturation loading figures for some liquors on I. R. A. 400 ion exchange Resin are also given. The loading figure for a solution of pure uranyl sulphate is included for comparison. The uranyl sulphate solution contained 50 g. SO_4''/l. (as magnesium sulphate) and the sulphate content of the liquors should be comparable although no actual figures were determined.

Cont.

TABLE VI.

Liquor No.	U_3O_8 g/l.	U_3O_8 g/200 c. conc.	TiO_2 g/l	TiO_2 g/200 c. conc.	Fe^{+++} g/l.	Final pH	U_3O_8 loading I.R.A. 400 Mg/g. dry Resin
1	1.1	1.75	.21	.35	<.5	2.4	-
2	1.0	1.75	.35	.63	<.5	2.1	185
3	1.0	1.77	.25	.45	<.5	2.4	190
4	1.0	1.77	.70	1.25	<.5	2.0	-
5	1.25	1.85	.18	.27	<.5	2.5	210
6	1.45	1.85	.14	.18	<.5	2.5	230
7	2.1	-	-	-	-	2.2	226

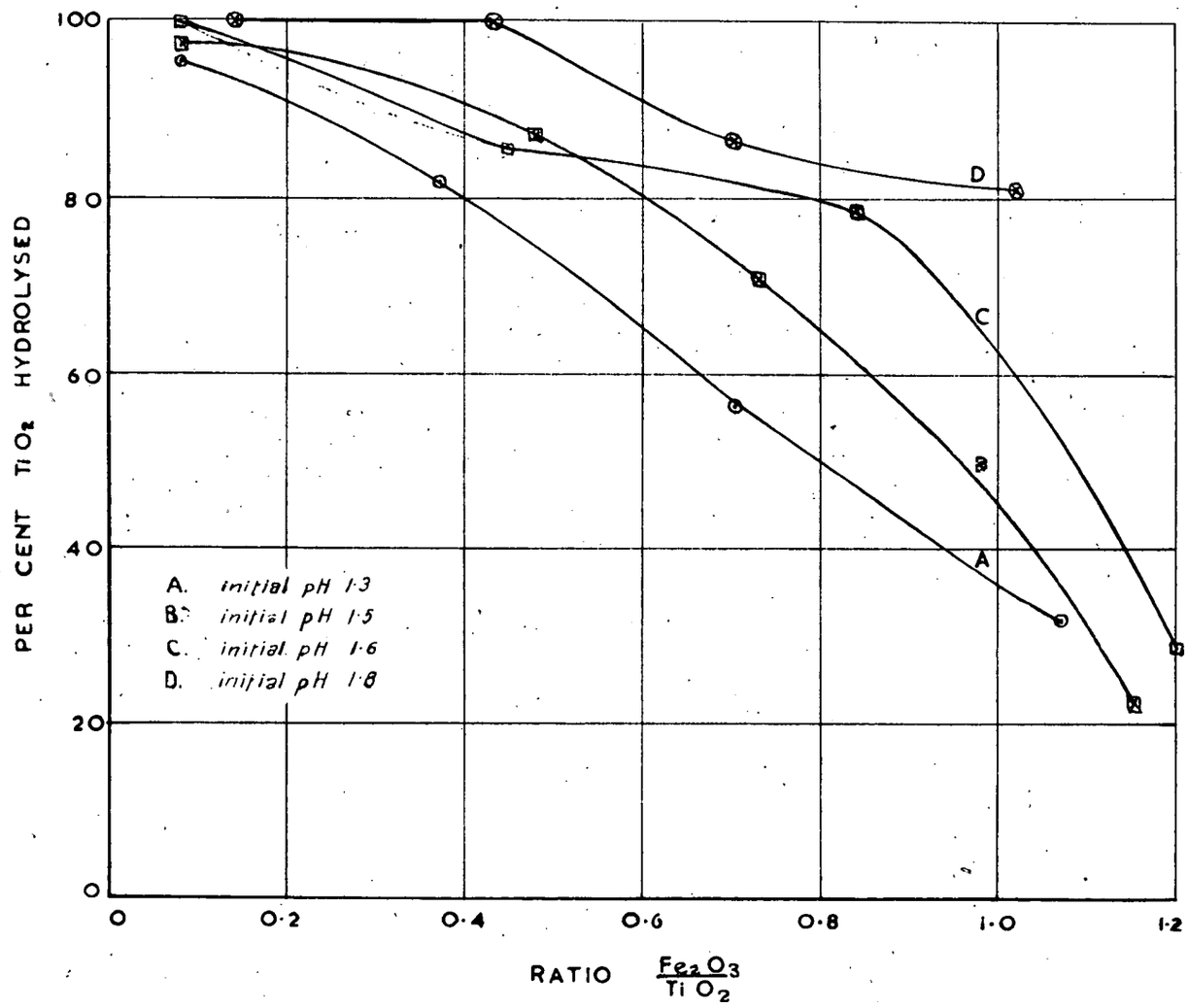

FIG. 1

S. A. DEPT. OF MINES					
Approved	Passed	Drn.	URANIUM INVESTIGATIONS	D.M.	Scale
		Tcd. A.G.W.	EFFECT OF FERRIC IRON ON HYDROLYSIS OF TITANIUM FROM RADIUM HILL SULPHATE LEACH-LIQUORS.	Req.	US-175
Director	G.D.	Ckd. J.W.T.			
		Exd.			Date 8-5-53