

BEHAVIOR OF RADIOACTIVE ELEMENTS (URANIUM AND THORIUM)
IN BAYER PROCESS

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Abstract

It is essential that alumina used for manufacturing electronic devices should contain an extremely low level of alpha-radiation.

The principal source of alpha-radiation in alumina is uranium, a minor source being thorium. Uranium in bauxite dissolves into the liquor in the digestion process and is fixed to the red mud as the desilication reaction progresses. A part of uranium remaining in the liquor precipitates together with aluminum hydroxide in the precipitation process. The uranium content of aluminum hydroxide becomes lower as the precipitation velocity per unit surface area of the seed becomes slower.

Organic matters in the Bayer liquor has an extremely significant impact on the uranium content of aluminum hydroxide. Aluminum hydroxide free of uranium is obtainable from the liquor that does not contain organic matters.

Introduction

Alumina produced by the Bayer process finds many applications other than aluminum production. Of various grades of alumina marketed for such non-metallurgical applications, those enjoying marked increase in demand in recent years is alumina for production of electro-ceramics or, more specifically, ceramic package for the computer memory devices.

Since technical innovation of the electronics industry has advanced the level of the memory integration year after year, however, radioactive elements of alumina have now become a serious nuisance.

The reason is that alpha-rays emitted by the radioactive elements hit and upset the stored data in memories, causing soft errors, as announced by Timothy C. May and Murray H. Woods of Intel Corporation.

In this background, we studied behaviors of radioactive elements in the Bayer process, with a view to determining how these radioactive elements find their way into alumina and establishing a method to eliminate them.

Analytical Method

Alumina and other materials required for the Bayer process contain radioactive elements in the order of parts per million or parts per billion. Establishment of analytical method for such microelements was, therefore, the most critical part of the present study.

In the early stage, we studied various methods including the absorptiometric analysis and radioactive analysis. Having found that the principal source of alpha-ray was uranium, we decided to use the fluorometric analysis to quantify the microelements^{2,3,4}.

With the fluorometric analysis, a specimen is melted with a flux and the product thereof is solidified after cooling. It is then exposed to ultra-violet ray and the intensity of the yellow-green fluorescence thereby generated is measured.

For direct measurement of alpha-ray, Low Background Alpha Counting System Model 850 supplied by Spectrum Science Co. was used.

Material Balance of Uranium and Thorium

In the paper published by Intel Corporation, uranium and thorium are listed as the source of alpha-ray in alumina. Attempts were therefore made to quantify uranium and thorium in bauxite, caustic soda, lime, red mud and aluminum hydroxide, with a view to establishing an approximate material balance of the two elements. The results are shown in Table I.

Table I
Uranium and Thorium Contents of Various Material and Products of Bayer Process

		Uranium (ppm)	Thorium (ppm)
Bauxite	Weipa, Australia	5.2	9.5
	Gove, Australia	2.5	10
	Bintan, Indonesia	3.5	7
Caustic soda		N.D.	N.D.
Lime		0.03	2.4
Aluminum hydroxide		0.5	0.02
Red mud		8.3	18

As the table clearly shows, it is bauxite that brings radioactive elements into the Bayer process. Thorium is found in bauxite in much larger quantity than uranium. An extremely low level of thorium, however, finds its way into product aluminum hydroxide, the remainder being discharged together with red mud.

On the other hand, about 90% of uranium contained in bauxite finds its way into red mud and about 10% into aluminum hydroxide. For this reason, the ratio of thorium and uranium in aluminum hydroxide becomes 1 : 25. The ratio of alpha-ray emitted by thorium and uranium was found to be 1 : 100, causing us to believe that the principal source of alpha-ray in aluminum hydroxide is uranium.

On the basis of the above finding, it was decided that the further study would be made focusing our attention on uranium.

Behavior of Uranium in Digestion Process

The rate of uranium dissolution into the liquor was sought by experimentally digesting bauxite using the spent liquor of the Bayer plant and synthetic sodium aluminate solution. The rate of dissolution was calculated under the following formula by measuring the contents of uranium and Fe_2O_3 in bauxite and red mud:

$$\text{Rate of dissolution (\%)} = \left(1 - \frac{\text{Ur}}{\text{Fr}}\right) \times 100 \frac{\text{Ub}}{\text{Fb}}$$

Where: Ub = Uranium concentration of bauxite
 Ur = Uranium concentration of red mud
 Fb = Fe_2O_3 concentration of bauxite
 Fr = Fe_2O_3 concentration of red mud

Tables II and III show composition of bauxite and spent liquor used in the present study.

Table II Composition of Bauxite Used

Supplied from:	Al_2O_3 (%)	Fe_2O_3 (%)	SiO_2 (%)	Reactive SiO_2 (%)	Uranium (ppm)
Weipa, Australia	54.9	12.7	5.1	3.7	5.8
Gove, Australia	50.8	16.9	2.6	2.1	2.5
Bintan, Indonesia	52.9	11.7	5.7	4.1	3.5

Table III Composition of Spent Liquor Used

	CS* (gr/l)	TS** (gr/l)	Al_2O_3 (gr/l)	A/C***	SiO_2 (gr/l)	U (mg/l)
Plant liquor	192	212	62	0.323	0.48	1.4
Synthetic liquor I	192	212	62	0.323	0.98	1.4
Synthetic liquor II	192	212	62	0.323	0.02	1.4
Synthetic liquor III	192	212	62	0.323	0.48	0.0

* Concentration of free caustic soda expressed in Na_2CO_3 equivalent.

** Concentration of free caustic soda (CS) plus sodium carbonate, expressed in Na_2CO_3 equivalent.

*** Weight ratio of Al_2O_3 and free caustic soda (CS).

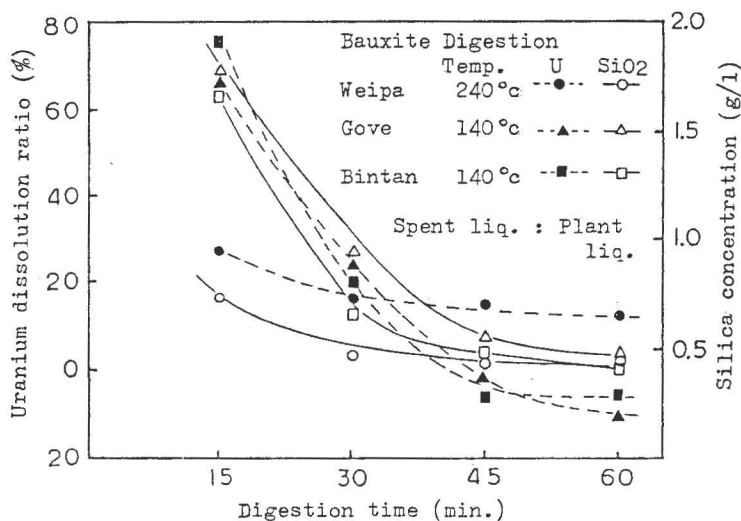


Fig. 1 Impact of digestion time on uranium dissolution ratio

Bauxite was added to the plant liquor until the Al_2O_3 charging ratio became 0.620 and digested at 140°C or 240°C, to study the change by time of the SiO_2 concentration of the liquor and the uranium dissolution ratio. The results are shown in Fig. 1.

As Fig. 1 clearly shows, the longer the digestion time, the lower the uranium dissolution ratio. This trend is quite similar to the trend of SiO_2 concentration of the liquor, indicating that the possibility of uranium dissolved in the liquor being caught by the desilication product.

In the case of the Gove and Bintan bauxite, the uranium dissolution ratios are expressed in negative numbers. This means that, in these cases, red mud contains uranium in a larger quantity than that brought into the liquor by bauxite.

To study this phenomenon more in detail, some additional experiments were undertaken.

First of all, spent liquors of different SiO_2 concentration were prepared by mixing synthetic liquors I and II and bauxite was digested in them for one hour to study changes in the uranium dissolution ratio under such circumstances. As shown in Fig. 2, the higher the initial concentration of SiO_2 in the spent liquor, the lower the uranium dissolution ratio, verifying the accuracy of the above-mentioned assumption that the uranium dissolved into the liquor is being caught by the desilication product.

Secondly, spent liquors of different uranium concentration were prepared by mixing the plant liquor and Synthetic liquor III and bauxite was digested in them for one hour to study changes in the uranium dissolution rate under such conditions. As shown in Fig. 3, the higher the initial uranium concentration of the spent liquor, the lower the uranium dissolution ratio. When the uranium content of bauxite is low and the initial uranium concentration of the spent liquor is high, in particular, the uranium dissolution ratio of the bauxite becomes minus, indicating that uranium

finds its way into red mud in much larger quantity than that brought into the liquor by bauxite.

On the basis of the above findings, it was concluded that uranium in bauxite dissolves into the red liquor in the digestion process but a significant part of it is taken away in red mud being caught by the desilication product.

Behavior of Uranium in Precipitation Process

How is then the amount of uranium that finds its way into aluminum hydroxide affected by the precipitation conditions? To find an answer to the question, we measured the uranium concentration of aluminum hydroxide precipitated under different conditions from mixtures of the pregnant liquor and the spent liquor of the Bayer plant. The varying factors selected for the study are shown in Table IV.

Experiments were made under the two different standards, Standards I and II, and the obtained data were subjected to analysis of variance. As a result, it was found that the surface area of the seed has the most significant impact on the uranium concentration of the precipitated aluminum hydroxide, followed by precipitation temperature. The principal effects of surface area of seed and precipitation temperature on the uranium concentration are shown in Fig. 4.

To reduce the uranium concentration of the precipitated aluminum hydroxide, the surface area of the seed should be increased and the precipitation temperature should be raised. This finding indicates that the uranium concentration of aluminum hydroxide can be lowered by simply reducing the precipitation rate per unit surface area of seed.

The relationship of average precipitation rate per unit surface area of the seed on one hand and uranium concentration on the other was, therefore, studied with respect to aluminum hydroxide produced commercial plant and at laboratory. The results are shown in Fig. 5.

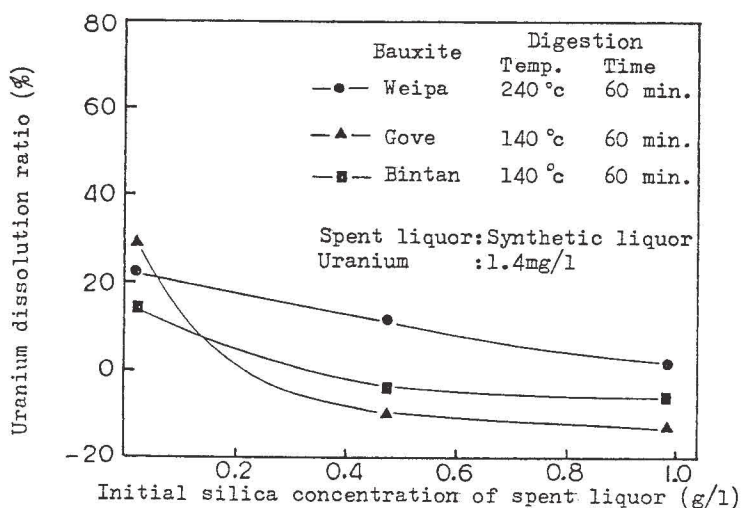


Fig. 2 Impact of initial silica concentration of spent liquor on uranium dissolution ratio

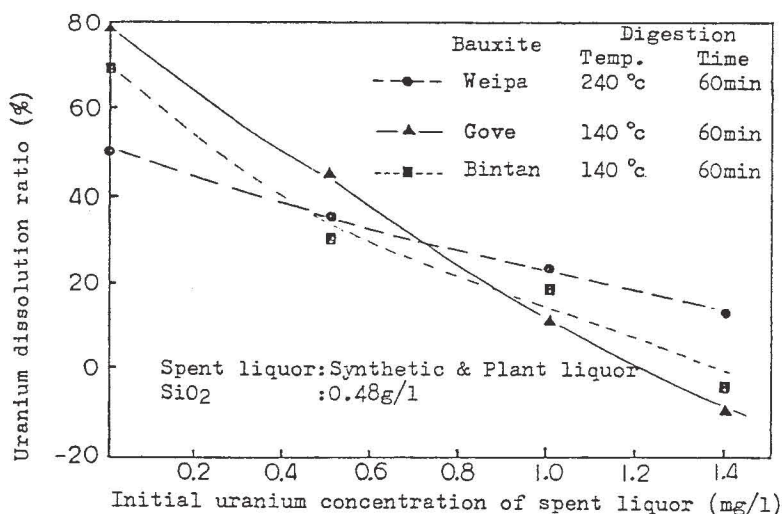


Fig. 3 Impact of uranium concentration of spent liquor on uranium dissolution ratio

Table IV Varying Factors of Precipitation Process

	Standard I	Standard II
Surface area of seed	5 m ² /l pregnant	10 m ² /l pregnant
Precipitation temperature	50°C	60°C
Initial A/C ratio of pregnant liquor	0.62	0.57
Precipitation time	24 hr	48 hr

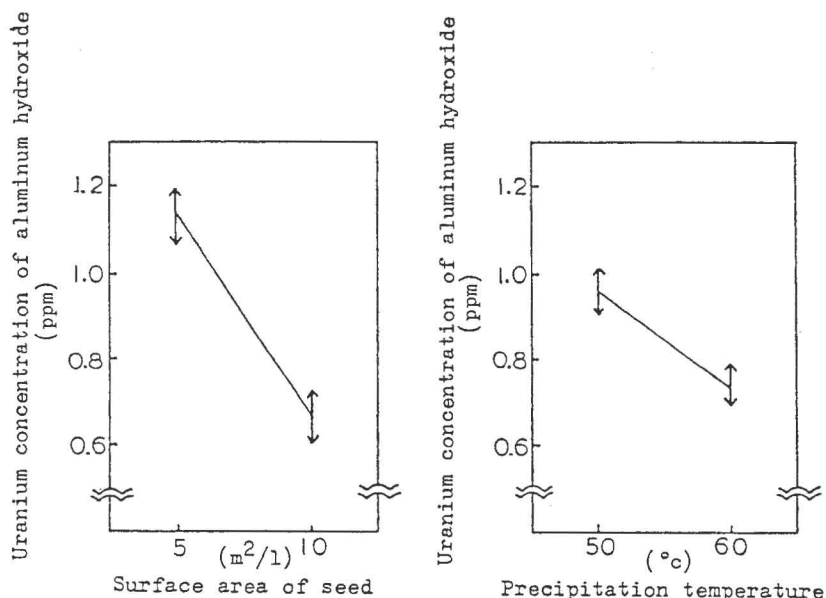


Fig.4 Principal factors affecting uranium concentration of aluminum hydroxide

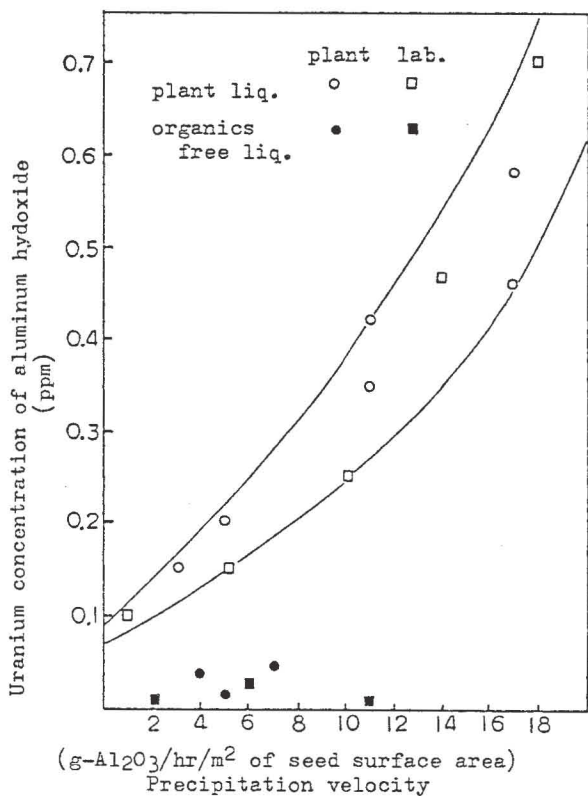


Fig. 5 Impact of Precipitation Rate on Uranium Concentration of Aluminum Hydroxide

As it is clear from Fig. 5, practically no difference was found in the relationship between aluminum hydroxide produced at the commercial plant and that manufactured at the laboratory.

When aluminum hydroxide was precipitated from an organics-free sodium aluminate solution obtained from our liquor burning process, however, the results were quite different from those of aluminum hydroxide precipitated from the plant liquor.

As shown by marks ● and ■ in Fig. 5, it contained but an extremely low level of uranium and, furthermore, the uranium concentration was not affected by the precipitation rate.

In the liquor burning process, organic compounds in the plant liquor is completely removed but uranium remains as it is, without undergoing decomposition or sublimation.

An organics-free sodium aluminate solution obtained from this process contains, therefore, the same level of uranium as the plant liquor. The fact that aluminum hydroxide precipitated from such sodium aluminate solution contains much less uranium indicates a possibility that organic compounds in the Bayer process plays an important role in contamination of aluminum hydroxide with uranium.

To confirm such a possibility, pregnant liquors of different organics concentration were prepared by mixing the plant liquor and the organics-free sodium aluminate solution. Composition of the plant liquor and the organics-free liquor used for preparation of the pregnant liquors is shown in Table V.

Table V Composition of Plant Liquor and Organics-Free Liquor Used for Preparation of Pregnant Liquors

	CS (g/l)	TS (g/l)	Al ₂ O ₃ (g/l)	A/C	Organic C (g/l)	U (mg/l)
Plant liquor	192	212	118	0.615	17	1.4
Organics-free liquor	192	196	118	0.615	0	1.2

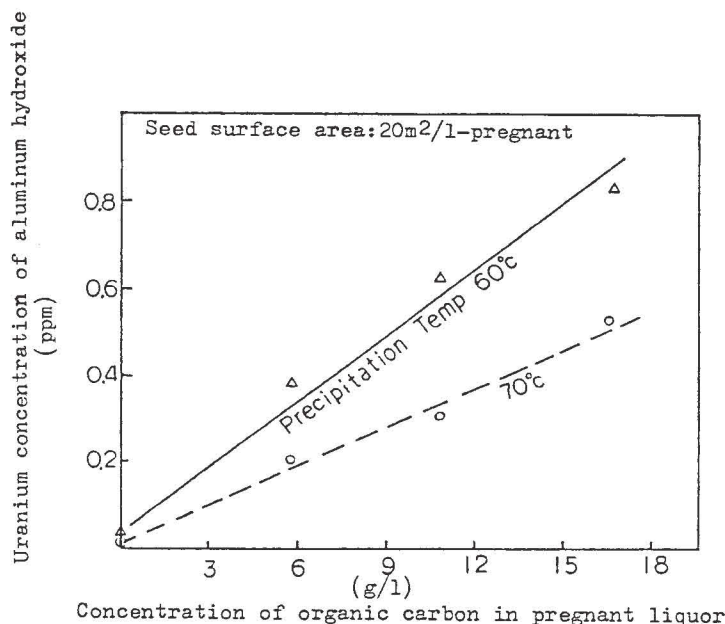


Fig.6 Impact of organics on uranium concentration of aluminum hydroxide

Aluminum hydroxide was precipitated from each batch of these pregnant liquors to study the relationship between the uranium concentration of aluminum hydroxide and the organics concentration of the pregnant liquor. The results are shown in Fig. 6.

Fig. 6 clearly shows an extremely good relationship was found between the two. The uranium concentration of aluminum hydroxide was found to increase straight up with the increase in the organics concentration of the pregnant liquor.

Today, materials for ceramic package of the computer memory devices are required to have alpha-ray emission volume of less than 0.01 counts/cm²·hour, which is equivalent to uranium concentration of less than 0.1 ppm.

To achieve such a low level of uranium concentration, it is necessary to reduce organics in the pregnant liquor to less than 2 grams/liter in terms of carbon.

In the case of Showa Aluminum Industries, aluminum hydroxide precipitated from the above-mentioned organics free sodium aluminate is used for production of alumina having an extremely low level of alpha-ray emission rate to supply the product to electro-ceramics manufacturers.

Conclusion

The present study has revealed the course by which radioactive elements (principally uranium) find their way into alumina. Also, it has become clear that the uranium concentration of aluminum hydroxide can be reduced by controlling the precipitation conditions. It indeed is good news for production of electro-ceramics grade alumina that the uranium concentration of aluminum hydroxide can be reduced dramatically by reducing organics in the pregnant liquor.

References

1. T.C. May and M. H. Woods, "A New Physical Mechanism for Soft Errors in Dynamic Memories", paper presented at International Reliability Physics Symposium, 1978.
2. N. Homma et al, "U and Th Analysis of LSI Constituent Materials", Electrical Communication Laboratory Technical Journal 29 (9) (1980) pp 81-91.
3. M. Sakanoue and M. Ichikawa, "The Fluometric Determination of Small Amounts of Uranium", Japan Analyst 10 (1961) pp 645-651.
4. J. Akaishi and A. Yabe, "Some Cautionary Problems of Fluometric Determination of Uranium", JAERI-memo 3622.
5. Patent applied for.