Essential Readings in Light Metals: Alumina and Bauxite.
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AUTOPRECIPITATION OF GIBBSITE AND BOEHMITE

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When thick bauxite slurry was heated up to 160°C, boehmite precipitation was observed and caused scale formation on the surface of heat exchangers in digestion step.

Under conditions of red mud separation, gibbsite precipitated on the red mud which did not contain boehmite. Boehmite precipitated only when it was already present in red mud. Goethite showed the largest seed effect on gibbsite precipitation among the minerals contained in red mud.

Calcium compounds suppressed the precipitation of gibbsite but did not of boehmite.

Introduction

Recently a system of bauxite slurry heating has been investigated and applied in alumina plants to conserve energy. The two-streams system in which spent liquor and bauxite slurry are separately heated has an advantage of low investment cost compared with a one-stream system. However, boehmite scale can be formed on the surface of heat exchangers when bauxite containing both gibbsite and boehmite is treated by the two-streams system.

In the red mud separation step, the autoprecipitation of alumina hydrate causes alumina loss. This paper presents test results on boehmite precipitation under digestion conditions and also on the autoprecipitation of gibbsite and boehmite in the red mud separation step.

Boehmite Precipitation in Digestion Step

Figure 1 shows a typical two-stream system. Thick bauxite slurry is heated in the slurry heaters by flashed steam.

When bauxite contains gibbsite and boehmite, liquor in the slurry heaters can become supersaturated with respect to boehmite, which corresponds to the region A shown in Figure 2.

Table 1 shows the test results on conversion from gibbsite to boehmite under isothermal conditions.

Boehmite formation occurs at temperatures above 170°C without boehmite addition, but it is observed at 150°C with boehmite addition. Boehmite scale was observed on the wall of the digestion bomb. This result suggests that the dissolution-precipitation mechanism [1)] contributes to the boehmite formation.

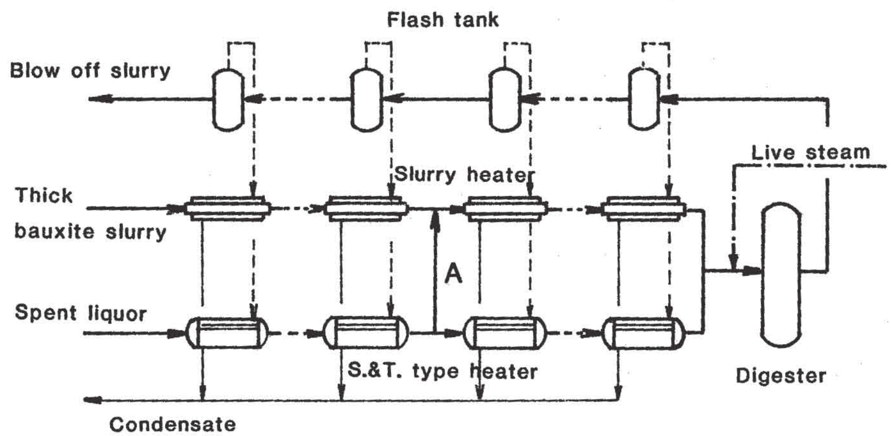

Fig.1 Typical two-streams digestion system

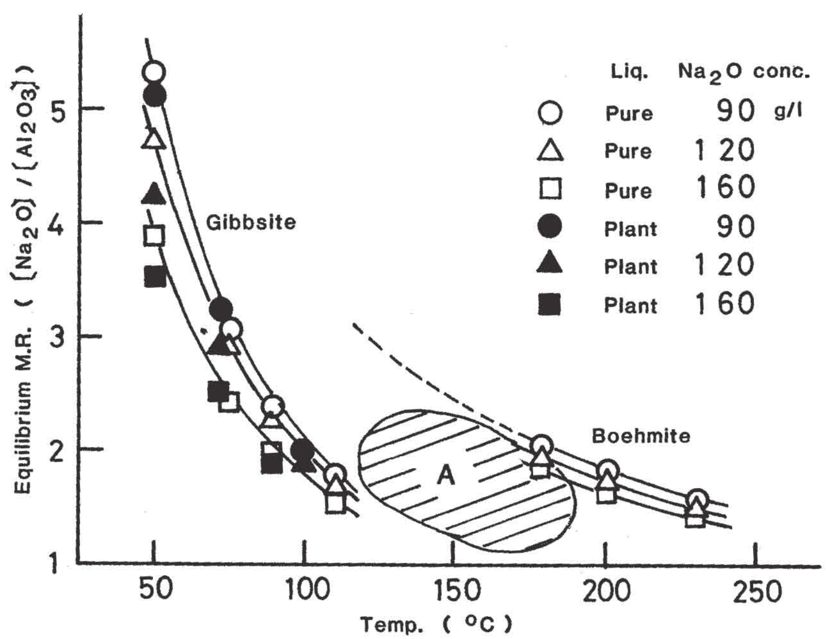

Fig.2 Solubility of gibbsite and boehmite in sodium aluminate solution

The higher solid concentration of bauxite slurry is preferable from the viewpoint of investment cost of heaters. However, thick bauxite slurry can cause boehmite scale on the heater surface.

In plant operation, conditions under which boehmite formation in the slurry heaters does not occur should be selected.

Table 1 - Conversion from Gibbsite to Boehmite during Digestion

Run No.	Charge 1)		Digestion Conditions		Liquor analysis after digestion			Boehmite formed 2)
	Gibbsite	Boehmite	Temp.	Time	C-Na_2O	Al_2O_3	M.R.	
	g/l	g/l	°C.	min.	g/l	g/l	-	%
1	221	0	150	30	126	164	1.26	0
2	221	0	150	60	126	162	1.28	0
3	221	0	170	15	125	177	1.16	0.2
4	221	0	170	40	123	174	1.17	2.0
5	221	17	150	30	127	164	1.27	2.0
6	221	17	150	60	125	163	1.26	2.0
7	201	0	180	5	115	167	1.13	2.0
8	201	0	180	45	115	167	1.13	7.1

1) Liquor Composition

Run No.	C-Na_2O	Al_2O_3
	g/l	g/l
1~6	138	72
7~8	128	63

2) Amount of formed boehmite based on charged gibbsite (%)

Table 2 shows the plant test results.

When charging gibbsite at lower than 1.1 M.R. boehmite, scale formed on the heater surface at temperatures above 160°C. In order to prevent this scale formation, M.R. of bauxite slurry should be increased to 1.1 by adding spent liquor as shown in Figure 1.

Table 2 - Boehmite Scale Formation on Plant Slurry Heaters

Operating Conditions		Scale (X-Ray Analysis)	
Temp.	M.R.	Sodalite	Boehmite
°C	-		
125	1.5	◎	✕
130~140	1.4	◎	△
160~165	1.0	○	○
160~165	1.1	◎	△

Intensity of main diffraction peak

○ : very strong

○ : strong

△ : weak

✕ : not detected

Autoprecipitation of Alumina Hydrate in Red Mud Separation Step

When red mud is separated in a settler, it contacts a supersaturated liquor (Na_2O = 100~150 g/l, M.R. = 1.4~1.7) for 10~50 hours. The autoprecipitation behaviours of gibbsite and boehmite under these conditions were investigated.

Effects of liquor composition and temperature

Figure 3 shows the holding test results of Bintan (Indonesian) red mud with different liquor compositions at a temperature of 90~95°C. In these experiments alumina was precipitated as gibbsite and boehmite was not detected.

The relationships between supersaturation degree (S.D = (Ao - Ae)/Ae) and the quantity of gibbsite precipitated from Figures 2 and 3, are shown in Figure 4.

The amount of gibbsite precipitated increases with increase S.D and is only a function of S.D in the range of caustic soda concentration of 120~160 g/l at 95°C. At a same S.D, the amount of gibbsite precipitated at 90°C is lower than that at 95°C. The autoprecipitation can be prevented when holding at 95°C for 48 h, when the S.D in the plant liquor is adjusted to be lower than 0.23.

It is seen from Figure 4 that autoprecipitation occurs more easily in a pure synthetic liquor than in the plant liquor. In the plant liquor, the absorption of organics on red mud prevents autoprecipitation.

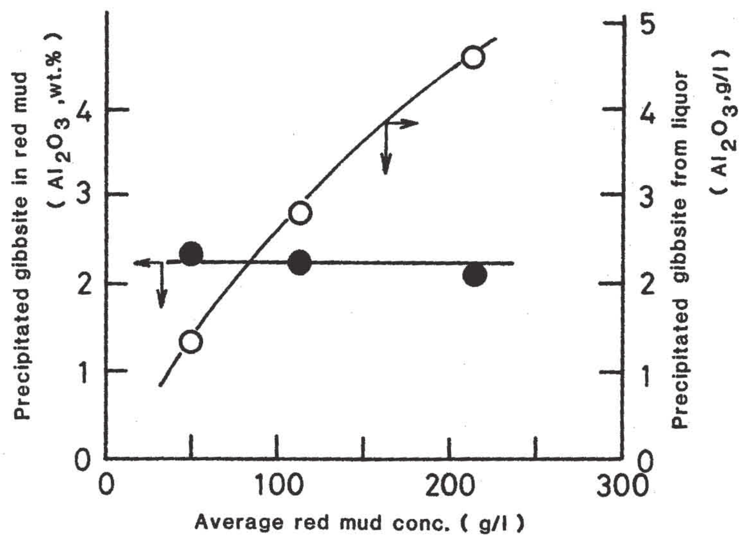

Fig.3 Effect of red mud concentration on precipitation of gibbsite

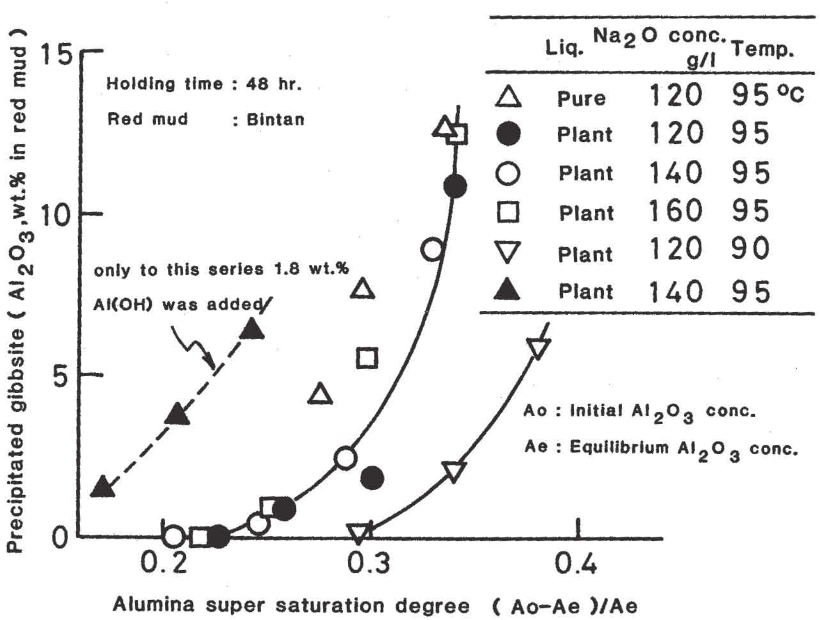

Fig.4 Effect of holding conditions on autoprecipitation

Induction Period

Figure 5 shows the change of precipitated gibbsite with the holding time.

The induction period increases with increasing M.R. in liquor. The precipitation rate increases steeply with the holding time according to the auto-catalyst effect of gibbsite.

The relationship between the induction period and S.D obtained from Figures 4 and 5 is plotted in Figure 6. The auto-precipitation does not occur, when operating conditions are selected to be in a region to the left side of the curve of Figure 6.

Seed effect of minerals in red mud

The red mud used in these tests was prepared from Bintan bauxite and contains neither gibbsite nor boehmite. Here, seed effects of gibbsite, boehmite, sodalite, hematite, goethite, anatase and rutile on autoprecipitation of alumina hydrate were observed.

(1) Seed effect of gibbsite:

Figure 4 shows the test results on the seed effect of the red mud to which 1.8% gibbsite was added. It is clear from Figure 4 that the seed effect is large and the complete extraction of gibbsite in digestion is necessary to prevent autoprecipitation.

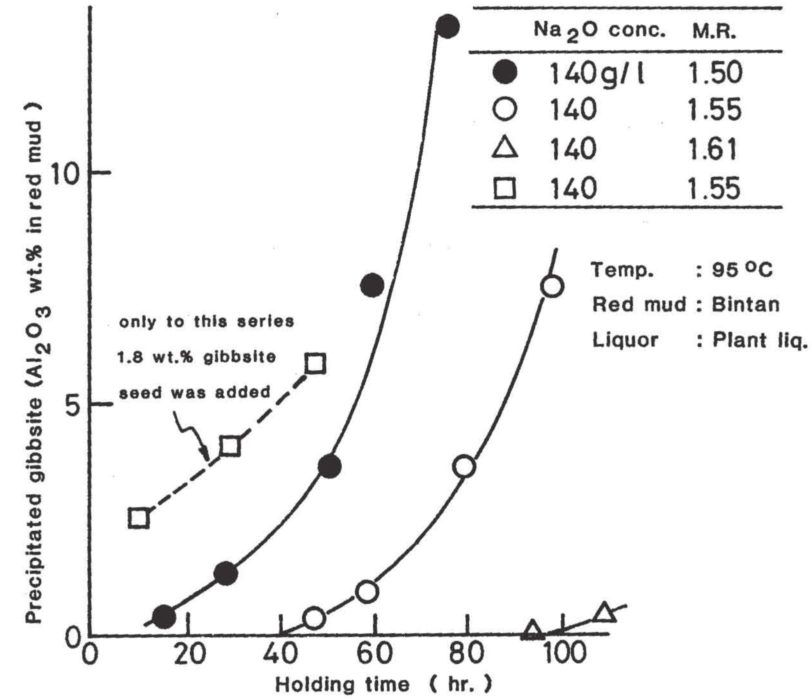

Fig.5 Fffect of holding time on autoprecipitation

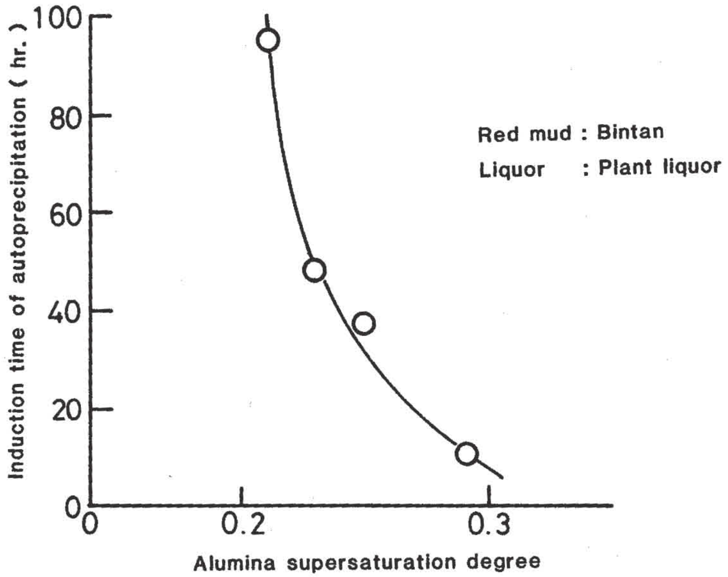

Fig.6 Effect of alumina supersaturation degree on induction time at 95 °C

(2) Seed effect of boehmite:

The holding experiments were performed using the Weipa red muds with different boehmite contents. The test results are shown in Table 3. Different from the previous results with Bintan red mud, the red mud containing boehmite causes boehmite precipitation. However, the seed effect of boehmite is much smaller than that of gibbsite on the precipitation of alumina hydrate.

Table 3 - Seed Effect of Boehmite in Red Mud

Liq. Composition			Initial boehmite in red mud	Autoprecipitated**	
Na_2O conc.	Al_2O_3 conc.	S.D*		Gibbsite	Boehmite
g/l	g/l		%	%	%
120	121	0.25	0	0	0
120	121	0.25	10	0	0
120	121	0.25	22	0	0.7
120	127	0.31	10	0	1.1
120	127	0.31	22	0	2.8
120	127	0.31	35	0	5.9

Holding conditions : plant liquor, 95°C, 48 h.

* Based on gibbsite solubility

** Weight percentage in red mud as Al_2O_3

(3) Seed effect of other minerals:

Table 4 shows the test results on the effect of minerals. Goethite shows the largest seed effect on gibbsite precipitation. This effect can be caused by its structural similarity to gibbsite. Because of higher content of goethite in Bintan red mud, its effect is higher than that of Weipa red mud. Boehmite precipitation was not observed in any of the tests.

Table 4 - Seed Effect of Various Minerals

Mineral	Autoprecipitated*	
	Gibbsite	Boehmite
	%	%
Sodalite	0.6	0
Goethite	18.6	0
Hematite	0	0
Anatase	0	0
Rutile	0	0
Bintan red mud	2.1	0
Weipa red mud	0.7	0

Holding conditions: plant liquor (Na_2O 120 g/l), Al_2O_3 127 g/l), 95°C, 48 h.

* Weight percentage precipitated on seed as Al_2O_3

Suppression of Autoprecipitation

Calcium compounds are know to inhibit the precipitation of gibbsite [2,3]. The holding tests of Bintan red mud with calcium carbonate were done in the temperature range from 75 to 95°C with different caustic soda concentrations (Na_2O, 80~130 g/l).

As shown in Figure 7, the suppression effect of calcium carbonate on gibbsite precipitation increases with decreases of temperature and caustic soda concentrations.

Table 5 shows the test results on the suppression effect for the red mud with boehmite. By the additional of calcium carbonate, gibbsite precipitation is suppressed; on the other hand, boehmite precipitation is accelerated.

Table 5 - Effect of Calcium Carbonate Addition to Red mud

Plant liquor Compositions		$CaCO_3$	Precipitated*	
Na_2O conc.	Al_2O_3 conc.	(wt. % of red mud)	Gibbsite	Boehmite
g/l	g/l	%	%	%
80	83	0	29.5	1.4
80	83	2	3.8	5.4
80	73	0	6.3	2.2
80	73	2	1.6	2.5

Holding conditions : 75°C, 30 h, Initial red mud contains 1.0% of gibbsite and 1.4% of boehmite.

* Weight percentage of red mud as Al_2O_3

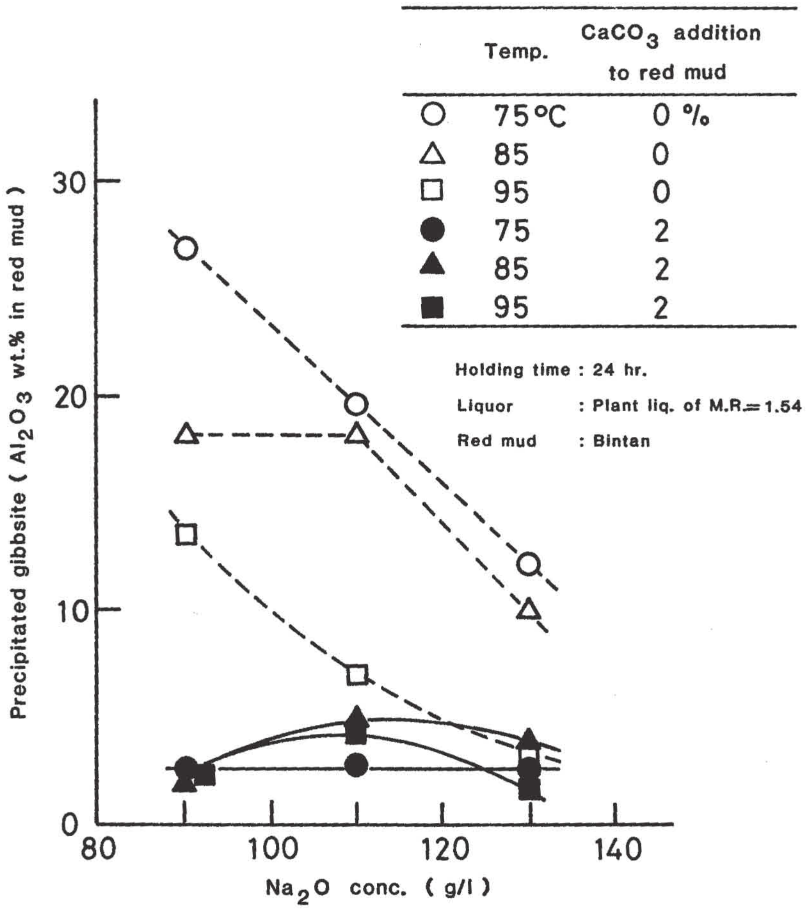

Fig.7 Effect of calcium carbonate addition to red mud on autoprecipitation

References

1) G. Yamaguchi, Kogyo Kagaku Kaishi, 66, 770 (1963).

2) S. Shiota, K. Muto, Aluminium (Japan), 3, 245 (1943).

3) B. Gnyra, N. Brown, Power Tech., 11, 101 (1975).