

FACTORS AFFECTING RESIDUAL  $\text{Na}_2\text{O}$  IN PRECIPITATION PRODUCTS

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ABSTRACT

The aim of the present paper is to show how the residual  $\text{Na}_2\text{O}$  in precipitation products is related to the precipitation parameters and to the liquor composition. It is demonstrated that the soda pick-up is not due to micro- or macro-occlusions of mother liquor. It is also established that the soda pick-up during precipitation of  $\text{Al}(\text{OH})_3$  can be mainly explained in terms of the liquor supersaturation and is not directly affected by the size of the seed and/or product nor by soluble inorganic impurities such as  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$ . However, it is also demonstrated that some other sodium bearing impurities, such as soluble organics or fine particulate sodium oxalate can be incorporated within the growing crystals and can therefore contribute to soda pick-up.

INTRODUCTION

Soda (expressed as  $\text{Na}_2\text{O}$ ) is the major impurity in usual Bayer hydrate. There are considerable incentives for decreasing this soda in alumina; aluminum smelters request low levels of soda because aluminum fluoride consumption increases with the soda content of the alumina. It has been estimated that above 0.35%  $\text{Na}_2\text{O}$  in alumina, each 0.1% increase represents a cost of US\$ 2/tonne of alumina.\* For some applications of non-metallurgical aluminas and hydrates low soda might even be a prerequisite.

Soda in alumina trihydrate exists in two forms. The leachable portion, generally a small fraction of the total soda, can be controlled by the hydrate washing system. On the other hand, the non-leachable portion of the soda - the residual soda - is more difficult to control and the causes behind it are not well known. Consequently, it has been the object of many studies<sup>(1-7)</sup>. While these studies agree on the dominant factors affecting the residual soda, i.e. precipitation temperature and alumina concentration, there are still considerable uncertainties concerning the effect of some other factors, e.g. caustic concentration, inorganic and organic impurities, seed charge and size of product during hydrate precipitation. There is also much uncertainty as to the mechanism by which the residual soda in the product occurs. Mother liquor occlusions during precipitation have been

traditionally thought<sup>(1)</sup> to be the main cause for the soda pick-up in the product.

More recent studies<sup>(4, 7)</sup> tend to establish that the soda impurity is incorporated within the crystal structure; liquor occlusions are then thought to occur in micropockets\* due to the growth process itself engulfing any impurities in its path especially at high supersaturation which results in a highly polycrystalline type of growth.

Another theory<sup>(3, 5, 6)</sup> on the intracrystalline nature of the soda impurity claims that the mechanism of  $\text{Na}_2\text{O}$  incorporation is due to the  $\text{Na}^+$  substituting for  $\text{H}^+$  in the trihydrate crystalline lattice. Eremin<sup>(5)</sup> for example claims that the increase in soda with increasing particle size of plant products supports this theory.

Because of this lack of unified theory to explain the soda pick-up during precipitation, there is not yet any mathematical model applicable over a wide range of operating conditions<sup>(7)</sup> e.g. temperature, caustic concentration, seed charge. The object of the present paper therefore, is to re-examine the effect of the main precipitation parameters on the residual soda in product.

EXPERIMENTAL

The composition of the plant liquor used was adjusted to the required caustic concentration by evaporation. Synthetic liquors were prepared by dissolution of gibbsite in pure solutions. The solutions were analysed thermometrically for alumina and caustic\*\*.

Batch precipitation tests were carried out in 45 ml Parr bombs rotating in a temperature controlled water bath. Liquor volumes charged to the bombs were 25 ml. After the required precipitation time the slurries were filtered on

\* This corresponds to the cost of aluminum fluoride in the excess bath which has to be removed from the pots, plus the cost of soda added in the Bayer plant.

\*\* In accordance with North American Bayer Plant practice, alumina concentrations are expressed throughout as g/l and caustic soda concentrations as g/l equivalent  $\text{Na}_2\text{CO}_3$ .

preweighed sintered glass filters and washed thoroughly with hot distilled water. The liquor compositions after precipitation were calculated by mass balances from the weight of alumina hydrate precipitated (i.e. the yield) by taking into account the volume decrease of liquor as the alumina is precipitated from solution<sup>(8)</sup>:

$$v = \frac{\text{initial volume of liquor}}{\text{final volume of liquor}} = \frac{1}{1 - \text{yield} \times 0.0009} \quad (1)$$

so that the caustic concentration after precipitation is

$$(\text{Caustic})_{\text{final}} = (\text{Caustic})_{\text{initial}} \times v \quad (2)$$

and the alumina concentration after precipitation is

$$(\text{Al}_2\text{O}_3)_{\text{final}} = [(\text{Al}_2\text{O}_3)_{\text{initial}} - \text{yield}] \times v \quad (3)$$

Mass balances carried out to ascertain the precision of the thermometric method used for the analysis of the alumina concentration showed a very good agreement between the concentrations of the liquor determined by the thermometric method and by the mass balances.

The precipitation products were analysed for Na<sub>2</sub>O by flame emission photometry. The obtained value corresponds to the Na<sub>2</sub>O in the total product which consists of the seed and the new precipitate. The soda content in the new precipitate was calculated using the following equation<sup>(9)</sup> which assumes that the seed hydrate remains undissolved during precipitation:

$$\% \text{Na}_2\text{O in new precipitate}^* = \frac{(\% \text{Na}_2\text{O})_{\text{Prod.}} \times \text{Tot. prod.} - (\% \text{Na}_2\text{O})_{\text{seed}} \times \text{seed charge}}{\text{Total product} - \text{seed charge}} \quad (4)$$

As done by Kanehara<sup>(8)</sup>, the alumina equilibrium concentrations, C<sub>e</sub>, were established experimentally by following the evolution of the alumina concentration as a function of time and extrapolating the data to infinite time by using the well known rate equation:

$$\frac{dC}{dt} = -k(C - C_e)^2$$

where C is the alumina concentration at time t, k is a kinetic constant and C<sub>e</sub> is the alumina concentration extrapolated to infinite time.

It was found that the values of C<sub>e</sub> obtained by precipitation tests were significantly higher than the reported solubility concentrations even after correction for the effect of liquor impurities<sup>(11)</sup>. However the equilibrium concentrations were preferred as they correspond to the actual amount of alumina which can be recovered from solution.

\* The percent Na<sub>2</sub>O is expressed, throughout the paper on alumina basis.

## RESULTS

### Residual Na<sub>2</sub>O as a Function of Liquor Occlusions

The evaluation of the amount of liquor occluded in Bayer hydrate was carried out by doping the liquor with a phosphorus tracer and determining the incorporation of this tracer in the product\*\*.

Phosphorus was charged as Na<sub>3</sub>PO<sub>4</sub> · 12H<sub>2</sub>O in Plant Bayer liquor at concentrations corresponding to 0, 0.38, 0.74, 1.5 and 3.0 g/L charges of P<sub>2</sub>O<sub>5</sub>. Results of the tests carried out under agglomerating conditions reported in TABLE 1, and results of the tests carried out under coarsening conditions reported in TABLE 2 show that the phosphorous is incorporated at a much lower rate than that expected if the soda pick-up was due to liquor occlusions.

### Effect of the Alumina Concentration

The relationship between the alumina concentration and the soda pick-up in the product was investigated with data obtained from batch tests where the alumina concentration decreases during the precipitation cycle and from continuous tests where the supersaturation is maintained constant.

#### 1) Batch Precipitation Tests

The variation of the soda in new product during a batch precipitation cycle as a function of the alumina concentration presented in TABLE 3, shows that the residual Na<sub>2</sub>O in product precipitated during the first two hours of the precipitation cycle where the alumina supersaturation is high - i.e. decreasing from 60 g/L to 40 g/L is also very high at 1.02%. The soda content in total new precipitate levels off to 0.546 at the end of the precipitation cycle where the supersaturation is low. As shown in the Appendix, these variations of Na<sub>2</sub>O in product were expressed as a function of the supersaturation by the following simple relationship which states that the soda pick-up is proportional to the square of the supersaturation<sup>(9)</sup>:

$$\frac{d\text{Na}_2\text{O}}{dC} = a(C - C_e)^2 \quad (6)$$

where C and C<sub>e</sub> are the alumina concentration at time t and at equilibrium respectively and "a" depends on the composition of the particular Bayer solution used.

It is shown in TABLE 3 that the integrated form of equation (6) derived in Appendix for the case of isothermal batch precipitation tests i.e.

\*\* The determination of phosphorus in alumina hydrate by an extraction/photometric procedure allowed the detection of P<sub>2</sub>O<sub>5</sub> concentrations from 0.3 to 20 ppm with a precision of ±0.15 ppm. To avoid any interaction of calcium and phosphorus during precipitation, calcium free liquor was used.



$$\%Na_2O = a' \frac{[(C_o - C_e)^3 - (C_t - C_e)^3]}{C_o - C_t} \quad (7)$$

with  $a' = 1.58 \times 10^{-4}$  for the Plant Bayer solution used, describes satisfactorily the variation of  $Na_2O$  in product as a function of the supersaturation.

TABLE 1

DETERMINATION OF LIQUOR OCCLUSIONS DURING AGGLOMERATION WITH A PHOSPHORUS TRACER

- Plant liquor 200 g/L caustic, 126 g/L  $Al_2O_3$
- Seed Charge 20 g/L (plant fine seed 0.36%  $Na_2O$ , 0.0005%  $P_2O_5$ )
- Temperature 74°C, Time 24 h.

$P_2O_5$ Added (g/L)	Yield (g/L $Al_2O_3$ )	Spent Liquor $Al_2O_3$ (g/L)	$Na_2O$ in Product Net (%)	$P_2O_5$ in Product (ppm)	
				Exptl.	Expected if Liquor Occlusions*
0	36.3	92.7	0.44	0.1	0
0.38	36.3	92.7	0.43	2	10
0.74	36.5	92.5	0.41	2	19
1.5	36.3	92.7	0.41	2	39
3.0	36.4	92.6	0.41	4	78

TABLE 2

DETERMINATION OF LIQUOR OCCLUSIONS DURING COARSENING WITH A PHOSPHORUS TRACER

- Plant liquor 200 g/L caustic, 124 g/L  $Al_2O_3$
- Seed Charge 150 g/L (Plant coarse seed, 0.376%  $Na_2O$ , 0.0003%  $P_2O_5$ )
- Temperature 68°C, Time 24 h.

$P_2O_5$ Added (g/L)	Yield (g/L $Al_2O_3$ )	Spent Liquor $Al_2O_3$ (g/L)	$Na_2O$ in Product Net (%)	$P_2O_5$ in Product (ppm)	
				Exptl.	Expected if liquor occlusions*
0	51.4	76.8	0.49	3	0
0.38	51.8	76.3	0.50	3	12
0.74	51.4	76.8	0.49	3	23
1.5	51.5	76.7	0.49	6	46
3.0	51.4	76.8	0.41	6	91

\* Assumes  $\%P_2O_5$  in the product in the same proportion as  $Na_2O$

$$\frac{\%P_2O_5 \text{ in } Al_2O_3}{\text{g/L } P_2O_5 \text{ in Liquor}} = \frac{\%Na_2O \text{ in } Al_2O_3}{\text{g/L } Na_2O \text{ in Liquor}}$$

TABLE 3

VARIATION IN RESIDUAL  $Na_2O$  AS A FUNCTION OF PRECIPITATION TIME IN A BATCH PRECIPITATION CYCLE

- Plant Bayer solution 201 g/L caustic
- Plant coarse seed 150 g/L (0.376%  $Na_2O$ )
- Precipitation temperature 68°C

Time (h)	Yield (g/L $Al_2O_3$ )	$Al_2O_3$ (g/L)	Percent $Na_2O$ in Product			
			Experimental		Calculated	
			Total	Net	Total	Net*
0	-	130.0	-	(0.376)	-	(0.376)
2	23.1	109.2	0.50	1.02	0.52	1.14
4	34.0	99.0	0.51	0.90	0.52	0.94
8	43.7	89.8	0.49	0.75	0.50	0.78
16	51.2	82.6	0.48	0.68	0.48	0.68
24	54.8	79.1	0.47	0.64	0.47	0.64
48	59.1	74.9	0.44	0.55	0.46	0.59
72	60.5	73.5	0.44	0.54	0.45	0.57
96	60.7	73.3	0.44	0.54	0.45	0.58

\* Calculated using equation (7) with  $C_e = 70.9$  g/L ( $k = 0.0046$  g/L/h)

ii) Continuous Precipitation Tests

Continuous precipitation tests were carried out in the bench scale precipitators described previously<sup>(10)</sup>. The purpose was to grow a narrow size fraction (i.e. 44 to 74  $\mu m$ ) of a seed at two sets of constant supersaturation levels. In the first series of tests, filtrate liquor at 0.750 ratio and 200 g/L caustic, was fed continuously to maintain a ratio of 0.600 in the precipitator. In the second series of tests filtrate liquor at 0.500 ratio and 200 g/L caustic was fed to maintain a ratio of 0.400. In both cases the precipitation temperature was maintained at 65°C with the corresponding equilibrium concentration for the alumina of 68.3 g/L. Consequently the alumina supersaturation levels maintained in these 2 series of tests were 51.7 g/L and 11.7 g/L respectively.

In both cases precipitation was continued until a target size of 90-95  $\mu m$  was obtained. Results in TABLES 4 and 5 show that the soda in new precipitate is fairly constant over the complete period of growth - i.e. 1.3% for the product obtained at 0.600 ratio and 0.13% for the product obtained at 0.400 ratio. These values agree relatively well with the prediction of the model equation (A8) relating the soda in product to the precipitation conditions for continuous operation developed in the Appendix, i.e:

$$\%Na_2O = 4.74 \times 10^{-4} (C_1 - C_e)^2 \quad (8)$$

For the test at ratio 0.600 the model gives  $\%Na_2O = 4.74 \times 10^{-4} \times 51.7^2$  or 1.3% and for the test at ratio 0.400 the model gives  $\%Na_2O = 4.74 \times 10^{-4} \times 11.7^2$  or 0.07%.

TABLE 4

SODA IN PRODUCTS PRECIPITATED IN A CONTINUOUS TEST AT 0.600 RATIO

- Plant Bayer Solution, 200 g/L caustic
- Precipitation Temperature 65°C

Particle Size (μm)	Percent Na <sub>2</sub> O in Product	
	Total	Net*
61 (seed)	(0.44)	-
71	0.77	1.35
83	0.96	1.30
85	0.99	1.32
86	1.00	1.31
92	1.05	1.30

\* Calculated by (4) assuming spherical particles

TABLE 5

SODA IN PRODUCTS PRECIPITATED IN A CONTINUOUS TEST AT 0.400 RATIO

- Plant Bayer Solution, 200 g/L caustic
- Precipitation Temperature 65°C

Particle Size (μm)	Percent Na <sub>2</sub> O in Product	
	Total	Net*
60 (seed)	(0.44)	-
63.5	0.39	0.14
65.0	0.38	0.15
70.5	0.32	0.12
75.5	0.28	0.11
78.5	0.26	0.12
83.0	0.25	0.14
86.0	0.25	0.14
96.0	0.22	0.13

\* Calculated by (4) assuming spherical particles

The SEM photomicrographs of corresponding products obtained at high and low supersaturation and presented in FIGURE 1 are quite interesting. It can be seen that the product obtained at high supersaturation and containing 1.3% Na<sub>2</sub>O tends to be covered by small monocrystals which indicate a growth via a surface nucleation mechanism while the product obtained at low supersaturation and containing 0.13% Na<sub>2</sub>O consists of large blocky monocrystals which indicate a growth via a surface defects mechanism.

Effect of the Precipitation Temperature

To ascertain the effect of the initial precipitation temperature on residual soda a first series of tests was carried out under isothermal conditions. The effect of cooling during precipitation was investigated in a second series of tests by cooling at a constant rate the precipitation slurries.

(i) Isothermal Precipitation

Precipitation tests were carried out at constant precipitation temperature, i.e. at 62 and 74°C respectively while precipitation time was varied from 2 to 96 hours.

Results reported in TABLE 6 show that, as expected, the soda in new precipitate decreases as the precipitation temperature is increased. For example, the Na<sub>2</sub>O content in products obtained after 24 hours at temperatures of 62 and 74°C is 0.82 and 0.42% respectively.\*

It is shown also in TABLE 6 that such variations of Na<sub>2</sub>O in product as a function of the precipitation temperature can be accounted for by the simple relationship (equation (7)), which states that the soda pick-up is proportional to the square of the supersaturation.

(ii) Uniform Cooling During Precipitation

To ascertain the effect of cooling during precipitation, the temperature was decreased uniformly from 74°C to 68°C over 24 hours (cooling rate of 0.25°C/h), from 74°C to 62°C over 24 hours (cooling rate of 0.5°C/h) and from 68°C to 62°C over 24 hours (cooling rate of 0.25°C/h). Results of the tests are reported in TABLE 7. As shown also in TABLE 7 the calculated values obtained by numerical integration of equation (A-7) of the Appendix are in good agreement with the experimental Na<sub>2</sub>O values.

Effect of the Caustic Concentration

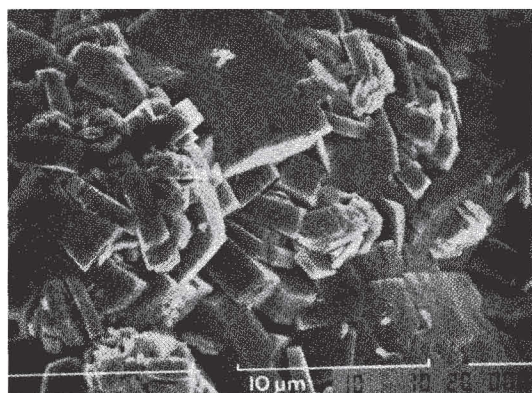
To ascertain the effect of the caustic concentration on the residual soda in products a series of 3 tests was carried out at 190, 225 and 250 g/L caustic respectively. To ensure a constant initial ratio the solutions at high caustic concentrations were obtained by evaporation of a filtrate liquor adjusted at 0.650 ratio.

Results of the tests, reported in TABLE 8, indicate that in general an increase in caustic concentration at constant initial ratio has no large effect on the residual soda. As illustrated in FIGURE 2, the effect appears also to be non-linear: while, at constant yield, the soda in product increased when increasing the caustic concentration from 190 g/L to 225 g/L it generally decreases with a further increase in caustic concentration to 250 g/L.

Analysis of these experimental results indicate also that the caustic concentration has no direct effect on the residual soda but only an indirect effect through the alumina supersaturation level since as shown in TABLE 8 the relationship (7), based on the assumption that the soda in product is proportional to the alumina supersaturation level only, predicts satisfactorily the variations in residual soda as a function of the variations in caustic concentration.

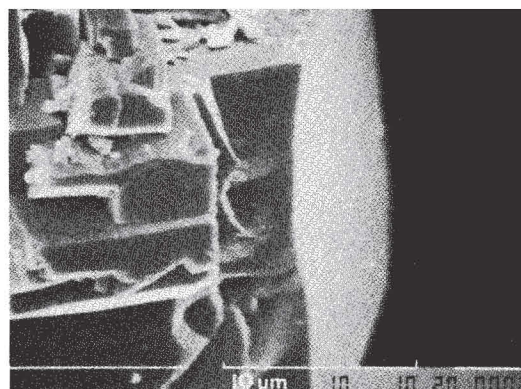
\* Results at intermediate temperature are reported in Table 3.





3500X

(a) 0.600 ratio: %Na<sub>2</sub>O : 1.3%



3500X

(b) 0.400 ratio: %Na<sub>2</sub>O : 0.1%

FIGURE 1

SEM PHOTOMICROGRAPHS OF PRODUCTS GROWN AT CONSTANT ALUMINA CONCENTRATIONS

TABLE 6

RESIDUAL Na<sub>2</sub>O AS A FUNCTION OF TIME AND TEMPERATURE (ISOTHERMAL PRECIPITATION)

- Plant Solution, 201 g/L caustic, 130.7 g/L Al<sub>2</sub>O<sub>3</sub>
- Plant coarse seed 150 g/L (0.376% Na<sub>2</sub>O)

Temp. (°C)	Time (h)	Yield (g/L Al <sub>2</sub> O <sub>3</sub> )	Spent Liquor Al <sub>2</sub> O <sub>3</sub> (g/L)	Na <sub>2</sub> O in Product (Net%)	
				Exptl.	Calc.*
62	2	20.5	112.1	1.32	1.47
	4	31.8	101.6	1.13	1.23
	8	42.6	91.4	0.98	1.02
	16	52.4	82.0	0.90	0.87
	24	56.6	77.9	0.82	0.81
	48	62.5	72.1	0.77	0.73
	72	64.7	69.9	0.74	0.71
96	66.2	68.4	0.71	0.69	
74	2	23.6	109.6	0.71	0.72
	4	32.7	101.2	0.59	0.59
	8	40.2	94.1	0.49	0.50
	16	46.0	87.6	0.45	0.44
	24	48.5	85.2	0.42	0.42
	48	50.8	83.0	0.42	0.40
	72	51.0	82.8	0.42	0.40
96	50.7	82.6	0.42	0.40	

\* Calculated by Equation (7) using Ce value of 65.8 g/L and 81.9 g/L at 62°C and 74°C respectively. (k values at 0.0030 and 0.0079 g/L/h respectively).

TABLE 7

EFFECT OF COOLING DURING PRECIPITATION ON Na<sub>2</sub>O IN PRODUCT

- Plant Bayer solution 201 g/L caustic, 130 g/L Al<sub>2</sub>O<sub>3</sub>
- Plant coarse seed: 150 g/L (0.376 %Na<sub>2</sub>O)
- Precipitation time 24 hours

Initial Temp. (°C)	Cooling Rate (°C/h)	Final Temp. (°C)	Yield (g/L Al <sub>2</sub> O <sub>3</sub> )	Spent Liquor Al <sub>2</sub> O <sub>3</sub> (g/L)	Na <sub>2</sub> O in Product (Net %)	
					Exptl.	Cal.*
62	0	62	56.6	77.9	0.82	0.81
68	0	68	54.8	83.1	0.64	0.65
74	0	74	48.5	85.2	0.42	0.42
68	0.25	62	55.0	79.9	0.59	0.55
			55.2	79.7	0.60	0.55
74	0.25	68	51.9	82.9	0.45	0.41
-	-	-	52.0	82.8	0.45	0.41
74	0.5	62	53.7	81.1	0.45	0.38
-	-	-	53.9	80.9	0.44	0.38

\* Calculation by numerical integration of equation A-7 of the Appendix. The variation of Ce and k with varying temperature and time are linear interpolation of the values reported in Tables 3 and 6.

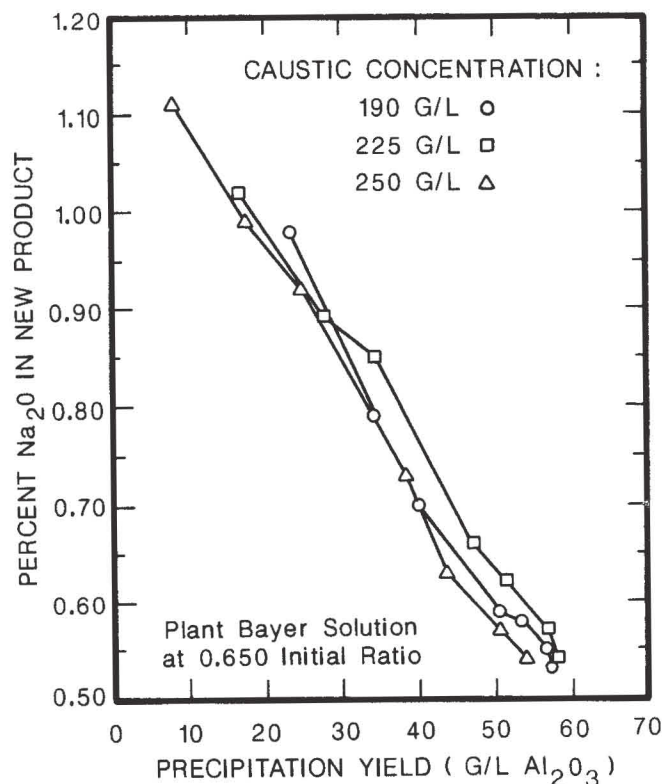


FIGURE 2

Na<sub>2</sub>O IN PRODUCT AS A FUNCTION OF THE CAUSTIC CONCENTRATION AND PRECIPITATION YIELD

Effect of the Seed Charge

Experiments were carried out with seed charges varying between 50 g/L and 300 g/L corresponding to seed surface areas varying between 2 m<sup>2</sup>/L to 12 m<sup>2</sup>/L. Results of the tests, reported in TABLE 9, show that the residual soda in product decreases when the seed charge is increased. The effect is significant since an increase in the seed charge from 50 to 200 g/L (or an increase of the seed surface area from 2 to 8 m<sup>2</sup>/L) decreases the net residual soda by 0.20%. The effect is due to lower alumina concentrations attained, at finite time, when the seed charge is increased and, as expected, it can be predicted by the relationship (7), relating the percent Na<sub>2</sub>O to the supersaturation level.

Residual Na<sub>2</sub>O as a Function of Particle Size

It is well known<sup>(5)</sup> that the coarsest fractions of a plant product tend to contain more residual soda. Such an increase in residual soda as a function of particle size is illustrated in TABLE 10, for a product from a Bayer Plant of the Alcan group.

However, laboratory data indicate that the soda pick-up is independent of the size of hydrate: the data from TABLES 4 and 5, clearly show that the soda pick-up is constant when a hydrate seed is grown from 60 to 90-95 μm at constant supersaturation.

TABLE 8

EFFECT OF THE CAUSTIC CONCENTRATION ON Na<sub>2</sub>O IN PRODUCT

- Plant Bayer solution evaporated to different caustic concentrations.
- Plant coarse seed: 150 g/L (0.376 %Na<sub>2</sub>O)

Caustic Conc. (g/L)	Time (h)	Yield (g/L Al <sub>2</sub> O <sub>3</sub> )	Al <sub>2</sub> O <sub>3</sub> (g/L)	Na <sub>2</sub> O in Product (Net %)	
				Exptl	Calc.*
190	0	-	123.3	-	-
	2	23.20	102.2	0.98	1.01
	4	34.25	91.9	0.79	0.82
	6	39.95	86.5	0.70	0.74
	16	50.39	76.4	0.59	0.60
	24	53.38	73.4	0.58	0.57
	48	56.65	70.21	0.55	0.53
	72	57.15	69.7	0.53	0.53
225	0	-	146.6	-	-
	2	16.48	131.9	1.02	1.19
	4	27.49	121.9	0.89	0.99
	6	34.28	115.7	0.85	0.87
	16	47.07	103.7	0.66	0.68
	24	51.24	99.8	0.62	0.63
	48	56.62	94.6	0.57	0.57
	72	57.86	93.4	0.54	0.56
250	0	-	163.9	-	-
	2	8.06	157.0	1.11	1.27
	4	17.42	148.8	0.99	1.09
	6	24.61	142.4	0.92	0.95
	16	38.45	129.9	0.73	0.74
	24	43.55	125.3	0.63	0.67
	48	50.51	118.8	0.57	0.59
	72	53.91	115.6	0.54	0.55

\* Calculated by equation ( 7) with Ce values of 66.9, 89.1 and 108.7 g/L respectively.

Furthermore, the experimental data presented in TABLE 11, shows that a fine seed, of a median size of 35 μm, does not tend to give a product which is lower in soda impurity than the product obtained with a coarse seed of a median size of 80 μm.

Consequently the observed increase in residual soda with the size of plant product seems to be due to process conditions only and not to any fundamental mechanism<sup>(5)</sup>; based on the concept that the alumina supersaturation controls the residual soda, one would suspect in fact that the finest fraction of a given crop of hydrate to be lowest in residual soda since the fines are usually produced, or grown, towards the end of the precipitation circuit, i.e. where the alumina supersaturation is low. Conversely, we would expect that the coarsest fractions to be highest in residual soda since these particles are produced, or grown, at higher supersaturation.



TABLE 9

EFFECT OF SEED CHARGE ON Na<sub>2</sub>O IN PRODUCT

- Plant Bayer liquor 200 g/L caustic, 126 g/L Al<sub>2</sub>O<sub>3</sub>
- Seed Charge: 150 g/L (Plant coarse seed 0.376% Na<sub>2</sub>O)
- Initial temp. 68°C, cooling 0.3°C/h
- Precipitation Time 24 hours

Seed Charge (g/L)	Yield (g/L Al <sub>2</sub> O <sub>3</sub> )	Spent Liquor Al <sub>2</sub> O <sub>3</sub> (g/L)	Na <sub>2</sub> O in Product (Net %)	
			Exptl.	Calc.*
50	42.8	86.5	0.68	0.65
100	50.3	79.3	0.55	0.56
150	53.5	76.1	0.52	0.53
200	55.9	73.8	0.48	0.51
250	57.7	72.0	0.48	0.49
300	58.6	71.1	0.48	0.48

\* Calculated by equation (7) with C<sub>e</sub> = 70.9 g/L (no allowance for cooling was made).

TABLE 10

RESIDUAL Na<sub>2</sub>O AS A FUNCTION OF PARTICLE SIZE IN A PLANT PRODUCT

Size Fraction (μm)	Weight Percent	Na <sub>2</sub> O (%)
0-210	100	0.368
45-63	10.7	0.307
63-88	31.6	0.324
88-125	40.8	0.361
125-177	10.5	0.394

Effect of Inorganic Impurities

The effect of the main Bayer inorganic impurities, i.e. Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and NaCl, on the residual soda in precipitation products was tested by adding the same equivalent Na<sub>2</sub>O concentration, i.e. 33 g/L Na<sub>2</sub>O, of each impurity in Plant Bayer solution.

Results of the tests are reported in TABLE 12. It can be seen that the effect of these

TABLE 11

RESIDUAL Na<sub>2</sub>O IN PRODUCTS OBTAINED WITH FINE AND COARSE SEEDS

- Temperature 62°C, Time 4 h
- Plant Bayer liquor: 202 g/L caustic, 127.2 g/L Al<sub>2</sub>O<sub>3</sub>

Type	Seed			Spent Liquor Al <sub>2</sub> O <sub>3</sub> (g/L)	Yield (g/L Al <sub>2</sub> O <sub>3</sub> )	Na <sub>2</sub> O in Product (Net %)	
	Charge (g/L)	Surface Area (m <sup>2</sup> /L)	Na <sub>2</sub> O (%)			Exptl.	Calc.*
Fine Seed	65	5.4	0.360	99.8	30.2	1.09	1.11
Coarse Seed	150	5.4	0.376	98.4	31.6	1.05	1.07

\* Calculated by equation (7), with C<sub>e</sub> = 65.8 g/L

TABLE 12

EFFECT OF INORGANIC IMPURITIES ON Na<sub>2</sub>O IN PRODUCTS

- Plant Bayer solution 200 g/L caustic, 130 g/L Al<sub>2</sub>O<sub>3</sub>
- Seed : 150 g/L coarse seed (0.376% Na<sub>2</sub>O)
- Temperature 68°C, Time 24 hr.

Impurity added (g/L)	Al <sub>2</sub> O <sub>3</sub> Equil. Conc. C <sub>e</sub> (g/L)	Yield (g/L Al <sub>2</sub> O <sub>3</sub> )	Spent Liquor Al <sub>2</sub> O <sub>3</sub> (g/L)	Na <sub>2</sub> O in Product (Net %)	
				Exptl.	Calc.*
None	70.9	54.8	79.1	0.59	0.64
Na <sub>2</sub> CO <sub>3</sub> (56 g/L)	76.6	47.8	87.3	0.60	0.58
Na <sub>2</sub> SO <sub>4</sub> (75 g/L)	77.7	47.5	89.0	0.61	0.60
NaCl (62 g/L)	80.2	44.6	91.7	0.54	0.55

\* Calculated with equation (7) with C<sub>e</sub> values reported in this Table.

inorganic impurities on the residual soda in product is not very large and statistically not really significant.

Effect of Organic Impurities

Since inorganic impurities, e.g. Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and NaCl, are unable to explain the differences in soda pick-up between plant and synthetic liquors shown in TABLE 13, it would be useful to ascertain if organic impurities could contribute to the Na<sub>2</sub>O contamination of the product. Two organic impurities were tested: humic matter and particulate sodium oxalate.

(i) Effect of Humic Matter

Humic acids from Pfaltz and Bauer Inc. were dissolved in a synthetic Bayer solution at 150°C for 2 hours. After digestion the liquor was filtered through a precoated Whatman 40 filter paper to remove any colloidal particles. Results of precipitation tests with the original synthetic solution and the solution in which up to 2.5 g/L humic matter was added are reported in TABLE 14. These results show that humic matter present in Bayer solutions can increase the residual Na<sub>2</sub>O in the products. For example the residual soda in the new product after 24 hour precipitation time is increased from 0.49 to 0.67% with 2.5 g/L humic matter added to the solution. Note, however, that with this amount of organic matter added, the Na<sub>2</sub>O content of the product is still lower than that obtained with Plant liquor (i.e. value predicted by equation (7)). It is shown also in TABLE 14, that the effect of humic acids on the residual Na<sub>2</sub>O is nonlinear and that a maximum value is obtained by the addition of a very small quantity, i.e. 0.25 g/L.

(ii) Effect of Solid Sodium Oxalate

Finely ground laboratory grade Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was added to the plant fine seed charged for agglomeration tests in Plant Bayer liquor adjusted to 200 g/L caustic, 0.630 ratio and 4.4 g/L soluble Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. Results of precipitation tests reported in TABLE 15, show that solid sodium oxalate can contribute significantly to the Na<sub>2</sub>O contamination of the product. For example the addition of 0.1 g/L solid sodium oxalate with the fine seed increases the residual soda by nearly 0.1%. Results show also that the products obtained with a contaminated fine seed contain significant amounts of extreme fines (e.g. 10 µm).

CONCLUSIONS

This work has established that the residual soda pick-up during precipitation of Al(OH)<sub>3</sub> can be mainly explained in terms of the liquor supersaturation. In other words the supersaturation or driving force for precipitation is the prime factor which opens the way for Na<sub>2</sub>O to enter the hydrate crystal lattice. Decreased Na<sub>2</sub>O in product can be obtained by a more orderly growth process, that is by maintaining a low driving force for precipitation. This can generally be done by precipitating at a higher temperature.

While it has been shown that some soluble impurities present in plant Bayer solutions such as Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and NaCl do not contribute directly to any soda contamination, it has been demonstrated that some other sodium bearing impurities, such as soluble organics or fine particulate sodium oxalate, can be incorporated within the growing crystals and therefore can contribute to soda pick-up.

It has been demonstrated that the soda pick-up is not due to micro- or macro-occlusions of mother liquor. This is consistent with the findings that soluble impurities are not contributing directly to the soda contamination and is consistent also with the finding that the

TABLE 13

COMPARISON OF RESIDUAL Na<sub>2</sub>O PICK-UP FROM SYNTHETIC AND PLANT BAYER SOLUTION

- Seed : 150 g/L coarse seed (0.376% Na<sub>2</sub>O)
- Temperature 68°C, Time 24 hr.
- Initial Conditions : Caustic 201.1 g/L, Al<sub>2</sub>O<sub>3</sub> = 130 g/L
- Final Conditions : Caustic 213.5 g/L, Al<sub>2</sub>O<sub>3</sub> = 69 g/L

Bayer Solution	Na <sub>2</sub> O in Product (%)	
	Total	Net
Synthetic	0.42	0.49
Plant (calc.)*	0.54	0.78

\* Calculated with equation (7) which applies for Plant Liquor using the same initial and final conditions as for synthetic solution.

TABLE 14

EFFECT OF THE CONCENTRATION OF HUMIC ACIDS ON RESIDUAL Na<sub>2</sub>O IN PRODUCT

- Temperature 68°C, Time 24 hours
- Seed Charge 150 g/L plant coarse seed at 0.376% Na<sub>2</sub>O
- Synthetic Bayer solution 200 g/L caustic, 130 g/L Al<sub>2</sub>O<sub>3</sub>

Humic Acids Added (g/L)	Yield (g/L Al <sub>2</sub> O <sub>3</sub> )	Spent Liquor Al <sub>2</sub> O <sub>3</sub> (g/L)	Na <sub>2</sub> O in Product (%)	
			Total	Net
0	65.0	69.0	0.42	0.49
0.13	65.1	68.9	0.45	0.56
0.25	65.3	68.7	0.48	0.64
0.53	65.3	68.7	0.49	0.66
1.25	65.0	69.0	0.49	0.66
1.88	64.7	69.3	0.49	0.66
2.50	63.6	70.4	0.49	0.67

caustic concentration itself has no direct effect on the residual soda.

It appears that the correlation between the soda content of the product with its attrition strength outlined in a previous paper<sup>(11)</sup> is not fortuitous since it has been shown that both soda pick-up and attrition strength increase with increasing liquor supersaturation. It can be expected therefore that in most cases, the residual soda in the product will directly correlate with its calcination strength. There is a point of difference however: while the attrition strength is highly dependent on particle size<sup>(11)</sup> the soda pick-up is independent of the size of the product.



**TABLE 15**

EFFECT OF FINE SOLID SODIUM OXALATE ON SIZE AND  $\text{Na}_2\text{O}$  CONTAMINATION OF THE PRODUCT

- Plant Bayer solution adjusted to 200 g/L caustic, 126 g/L  $\text{Al}_2\text{O}_3$  and 4.4 g/L  $\text{Na}_2\text{C}_2\text{O}_4$
- Initial Temperature  $76^\circ\text{C}$  (uniform cooling  $0.2^\circ\text{C}/\text{h}$  after 5 hours)
- Precipitation Time 43 hours
- Seed Charge 45 g/L plant fine seed (0.369%  $\text{Na}_2\text{O}$ )

Solid Sodium Oxalate Added (g/L)	Yield (g/L $\text{Al}_2\text{O}_3$ )	Percent Less Than ( $\mu\text{m}$ )				Na <sub>2</sub> O in Product (%) Based on $\text{Al}_2\text{O}_3$	
		10	50	70	100	Total	Net
0	54.9	0.1	0.7	21.5	88.3	0.40	0.42
0.1	58.1	1.0	20.5	70.0	97.3	0.46	0.51
0.5	59.7	4.8	39.7	81.7	96.3	0.51	0.57

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REFERENCES

1. Griesing, G., *Erzmetall* XVII No. 9, 1964, pp. 478-486.
2. Wefers, K., The Question of the Alkali Content of Technical Aluminum Hydroxide, *Erzmetall* 1965, 18(9), pp. 453-463.

3. Wefers, K., On the Chemical Technology of Bauxite Digestion. The System  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ , *Metall*, 1967, 21 (5), pp. 422-431.
4. Ohkawa, J., Study of Precipitation Conditions for Low Soda Hydrate, *Monthly Journal of Shimizu Works #80*, NKK, August 1978, p. 18.
5. Eremin, N.I., Cherepanova, M.I., Maksakova, M.A., *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, "Statistical Studies of the Nature of an Alkali Inclusion in the Structure of Aluminum Hydroxide Particles", 1980, (3), p. 55-58.
6. Eremin, N.I., Cherepanova, M.I., Shmorgunenko, N.S., Maksakova, M.A., Study of the Nature of the Inclusion of an Alkali Impurity in the Structure of Aluminum Hydroxide, *Leningrad Mining Institute*, No. 2, 1980, pp. 49-52.
7. Ohkawa, J. Tsuneizumi, T. and Hirao, T., Technology of Controlling Soda Pick-up in Alumina Trihydrate Precipitation, *Light Metals*, 1985, p. 345.
8. Kanehara, M., Formulation of Alumina Hydrate Precipitation Rate in Bayer Process for Plant Design and Operation - *Light Metal*, 1971, p. 87.
9. Lindsay, J.G., Kinsman, W.P.C., to Aluminum Laboratories Limited, Method of Producing Low Soda Content Alumina, Montreal, Quebec, U.S. Patent 3,201,199, 17 August 1965.
10. Sang, Jean V., Continuous Precipitation Simulation - *Light Metals*, 1986, pp. 191-198.
11. Sang, Jean V., Factors Affecting the Attrition Strength of Alumina Products - *Light Metals*, 1987, pp. 121-128.

A1

A2

APPENDIX

DERIVATION OF THE RELATIONSHIP BETWEEN RESIDUAL  $\text{Na}_2\text{O}$  IN PRODUCT AND LIQUOR SUPERSATURATION

It has been shown that the variations of  $\text{Na}_2\text{O}$  in product as a function of the main precipitation parameters - i.e. precipitation time, precipitation temperature, initial ratio, caustic concentration, seed charge etc. - can be expressed as a function of the corresponding variations in liquor supersaturation by the following simple relationship:

$$\frac{d\text{Na}_2\text{O}}{dC} = a(C - C_e)^2 \quad (\text{A-1})$$

where  $C$  is the alumina concentration at time  $t$  and  $C_e$  is the alumina concentration at equilibrium.

Equation (A-1) states that the amount of soda precipitated per gram of alumina is proportional to the square of the supersaturation. This equation has to be integrated in the case of a batch operation while the differential form can be used for continuous operation.

A.1 Integral Forms of the Relationship for Batch Operation

The quantity of soda (as g/L  $\text{Na}_2\text{O}$ ) precipitated from time 0 to time  $t$  is assuming "a" constant:

$$\Delta\text{Na}_2\text{O} = \int_0^t a(C - C_e)^2 dC = a \int_0^t (C - C_e)^2 dC \quad (\text{A-2})$$

Since the quantity of alumina (as g/L) precipitated from time 0 to time  $t$

$$\Delta C = \int_0^t dC \quad (\text{A-3})$$

combining equations (A-2) and (A-3), the percent  $\text{Na}_2\text{O}$  in new product is

$$\% \text{Na}_2\text{O} = \frac{\Delta\text{Na}_2\text{O}}{\Delta C} \times 100 = \frac{a \int_0^t (C - C_e)^2 dC}{\int_0^t dC}$$

Equation (A-4) can be readily integrated in the case where it is assumed that the alumina equilibrium concentration,  $C_e$ , is constant throughout the precipitation cycle. This is approximately the case for isothermal precipitation\*. In the case of cooling during precipitation, the alumina equilibrium concentration,  $C_e$ , varies as a function of time and only a numerical integration can be carried out.

A.1.1 Relationship for Isothermal Precipitation

In this case we obtain:

$$\% \text{Na}_2\text{O} = a' \frac{[(C_o - C_e)^3 - (C_t - C_e)^3]}{C_o - C_t} \quad (\text{A-5})$$

where  $C_o$  and  $C_t$  are the alumina concentrations at time 0 and  $t$  respectively and  $C_e$  is the alumina equilibrium concentration.

The constant  $a'$  depends on liquor composition. It has been estimated for one particular plant liquor, from batch data obtained at different precipitation temperatures ranging from  $62^\circ\text{C}$  to  $74^\circ\text{C}$ . The average value obtained was  $1.58 \times 10^{-4}$ .

A.1.2 Relationship for Cooling During Precipitation

In the case of cooling during precipitation the alumina equilibrium concentration varies as a function of the precipitation time since it is a function of the temperature. In that case the integration of equation (A-4) can be carried out if we express the alumina concentration  $C$  as a function of the precipitation time,  $t$ , by the integral form of equation (5).

$$C - C_e = \frac{C_o - C_e}{1 + k(C_o - C_e)t} \quad (\text{A-6})$$

By substitution of equation (A-6) in equation (A-4) we obtain:

$$\% \text{Na}_2\text{O} = 1.58 \times 10^{-4} \times 3 \times \frac{\int_0^t \frac{(C_o - C_e)^4}{[1 + k(C_o - C_e)t]^4} dt}{\int_0^t \frac{(C_o - C_e)^2}{[1 + k(C_o - C_e)t]^2} dt} \quad (\text{A-7})$$

Equation (A-7) can be numerically integrated in the case where the variation of  $k$  and  $C_e$  as a function of the precipitation time,  $t$ , are known.

A.2 Differential Form of the Relationship for Continuous Operation

Note that in equation (A-5) a factor  $1/3$  was introduced in the integration of equation (A-4). Therefore the corresponding equation for continuous operation is:

$$\% \text{Na}_2\text{O} = 4.74 \times 10^{-4} (C_i - C_e)^2 \quad (\text{A-8})$$

where  $C_i$  is the alumina in the  $i$ -th precipitator.

\* In fact as the caustic concentration varies during precipitation this equilibrium solubility changes as a function of time. However such changes are small and this concentration will be considered to be constant throughout the precipitation cycle.