INFLUENCE OF MINERAL AND ORGANIC IMPURITIES ON THE

ALUMINA TRIHYDRATE PRECIPITATION YIELD IN THE BAYER PROCESS

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Precipitation yields of alumina trihydrate from different sodium aluminate solutions, synthetic or industrial, with variable content in mineral and organic impurities, have been determined at different soda concentrations. The conditions of precipitation were the same for all the solutions. A mathematical model of experimental results, taking into account possible interactions between impurities, has been established, allowing to predict specific effect of each mineral impurity and overall effet of organic content. With the kinetic equation of precipitations, the use of the mathematical model permits the calculation of equilibrium composition of the aluminate solution as a function of the content of impurities. Calculated and experimental values are in agreement. So, with equilibrium values and the kinetic equation, it is possible to predict the precipitation yield of any liquor knowing its chemical composition and condition of precipitation (temperature, seed charge, retention time).

INTRODUCTION

It is well known that certain very soluble impurities accumulate in Bayer cycle liquors where they can reach high concentrations (1). These impurities affect the physical properties of liquors, increase through flows, and alter alumina precipitation yield, even though they have no effect on chemical properties.

It is imperative for alumina producers to control the level of these impurities. Numerous purification processes, specific to one or several impurities, have been developed in this direction, and still others are being studied (1).

From an economic point of view, selecting the most appropriate purification process for a given liquor requires knowing the productivity gain which can be attributed to the reduction of the impurity concentration. In light of this, several studies were carried out, which seek to approach the alumina solubility equilibria for liquors of variable chemical composition. These studies also lead to proposing empirical values for the effect of different impurities (1), this effect being hardy transposable from one liquor to the other.

In order to avoid the multiple tests which would be required for the study of each liquor and each purification process, we decided to construct a mathematical model relating the mass ratio

$$\frac{Al_2O_3}{Na_2O \ ctc}$$

at the end of precipitation, to the chemical composition of the liquor, taking into account :

- the entire ctc Na_2O concentration range found in the different plants,
- the possible interactions between mineral and organic impurities,
- the nature of the organic matters present in the liquor, which depends on the type of bauxite processed and on the conditions of digestion.

Study Procedure

This study concerned, first of all, the influence of mineral impurities on synthetic and industrial liquors, when the liquors are enriched by sodium salts of these impurities.

This method made it possible to construct a model of the effect of mineral impurities for each liquor.

This model was then used to compare the effect of organic matters for the various liquors with identical contents of mineral impurities.

It was then possible to model the influence of the ctc Na_2O concentration and of mineral and organic impurities on the mass ratio at the end of precipitation.

In the last step, the model was extended to include diverse precipitation conditions.

Experiment Procedures

1 - Conditions of Precipitation Tests

These tests were all conducted under identical conditions.

The mass ratio $\frac{AL_2O_3}{ctc\ Na_2O}$ (RP) of the liquor tested was adjusted to a value of 1.13 by hot trihydrate dissolution.

Washed hydrate, with a specific surface of $0.040\ m^2/g$, was utilized as seed. The seed load was 380 g of Al_2O_3 per liter of suspension.

100 ml of liquor and the corresponding seed were placed in a cup. The cups (a maximum of 12) were placed in a thermostat controlled bath at $55°C \pm 0.2°$, and were stirred by full rotation.

The RP was measured to the nearest 5×10^{-3}.

2 - Liquors Tested

The tests were conducted on synthetic liquors of aluminate loaded with mineral impurities and also on industrial liquors. Table I shows the impurity contents in the industrial liquors (% ctc Na_2O) as well as their origin.

Table I. Impurity Contents in Industrial Liquors							
Liquor no.	Carbonated Na_2O	Cl	SO_3	SiO_2	Org. C	Treated Bauxite	Digestion
1	11.8	4.8	0.9	0.5	0	Europe	High temp
2	10.7	2.1	0	0.5	2.5	Europe	High temp.
3	12.2	1.2	0.4	0.6	5.2	Africa	High temp.
4	13.4	3	1.4	0.5	7.7	Africa	High temp.
5	7.7	4.1	0.5	0.5	6.0	Australia	High temp.
6	17.5	9	1	0.5	20	Australia	High temp.

3 - Measurements

The evolution of RP at the end of precipitation in synthetic and industrial liquors was measured as a function of :

- the ctc Na_2O concentration within the 90 - 170 g/l range;
- the mineral impurity concentration up to the following contents :

  cbted Na_2O : 25 % ctc Na_2O

  Cl   : 12.5 % ctc Na_2O

  SO_3 : 10 % ctc Na_2O

  SiO_2 : 1 % ctc Na_2O

- the organic matter concentration.

Influences of Mineral and Organic Impurities

1 - Mathematical Modelling Using Experiment Data

Table II shows the experimental data (ctc Na_2O, impurity contents, RP at the end of precipitation) used for the mathematical modelling of the various synthetic and industrial liquors.

An empirical equation (1) was found, for each liquor, which establishes a relationship between the RP logarithm and the ctc Na_2O concentration at the beginning of precipitation and the mineral impurity concentrations.

$$Lny = k_0 + k1X_1 + k_2X_2 + k_{1,2}X_1X_2 + k_{1,3}X_1X_3 + k_{1,4}X_1X_4 + k_{1,5}X_1X_5 \tag{1}$$

with : Y : RP at end of precipitation

  X_1 : ctc Na_2O in g/l

  X_2 : content in cbted Na_2O as % ctc Na_2O

  X_3 : content in Cl as % ctc Na_2O

  X_4 : content in SO_3 as % ctc Na_2O

  X_5 : content in SiO_2 as % ctc Na

The k coefficients to be attributed to the various liquors studied were calculated by multiple regression and are given in table III.

The influence of silica was determined only for synthetic liquors. Its content remained constant for the other liquors, and its influence is included in coefficient k_1.

The data available for liquors 1 and 2 was insufficient for a specific modelling. It was confirmed that the model constructed for the synthetic liquors could well be applied for liquor 1 exempt of organic matters.

The low organic carbon content in liquor 2 made it possible, in a first approximation, to compare the RP fluctuation to those of the synthetic liquor.

Table II. Experiment Data for Mathematical Modelling of Synthetic and Industrial Liquors

Liquors 1 - (synthetic)   Organic C = 0

Impurities % ctc Na_2O

ctc Na_2O	cbted Na_2O	Cl	SO_3	SiO_2	RP at end of precip. measured	Calculated RP	Calculated RP	Calculated RP
170.2	0	0	0	0	0.530	0.538	0.540	0.543
160.0	0	0	0	0	0.51	0.514	0.516	0.518
158.2	0	0	0	0	0.51	0.510	0.511	0.514
148.2	0	0	0	0	0.48	0.487	0.489	0.490
118	0	0	0	0	0.425	0.425	0.426	0.426
108.3	0	0	0	0	0.410	0.407	0.407	0.408
105.4	0	0	0	0	0.398	0.401	0.402	0.402
98.4	0	0	0	0	0.392	0.389	0.390	0.390
156	0	0	0	0	0.500	0.505	0.506	0.508
156	5.1	0	0	0	0.540	0.528	0.529	0.535
156	9.8	0	0	0	0.565	0.551	0.551	0.561
156	15.0	0	0	0	0.590	0.577	0.577	0.592
106	0	0	0	0	0.402	0.402	0.403	0.404
106	3.5	0	0	0	0.405	0.407	0.407	0.408
106	8.7	0	0	0	0.412	0.415	0.413	0.415
106	13.7	0	0	0	0.419	0.422	0.418	0.422
106	19.4	0	0	0	0.426	0.430	0.425	0.429
160	0	2.1	0	0	0.527	0.521	0.522	0.524
160	0	5.6	0	0	0.532	0.532	0.532	0.535
160	0	12.5	0	0	0.565	0.555	0.553	0.566
105	0	3	0	0	0.401	0.406	0.406	0.406
105	0	7	0	0	0.408	0.412	0.412	0.412
105	0	10	0	0	0.414	0.417	0.416	0.417
105	0	15	0	0	0.424	0.425	0.424	0.425
160	0	0	2	0	0.516	0.521	0.522	0.522
160	0	0	4	0	0.525	0.528	0.528	0.526
167.2	0	0	0	0.6	0.542	0.543	0.541	0.538
157.8	0	0	0	0.6	0.521	0.519	0.518	0.516
147.3	0	0	0	0.6	0.510	0.495	0.494	0.491
170	12	3	1	0.5	0.629	0.628	0.625	0.644
149	12	3	1	0.5	0.548	0.557	0.553	0.563
147.2	12	3	1	0.5	0.545	0.555	0.551	0.556

Table II. Liquors 1 (synthetic) continued

Impurities % ctc Na_2O

ctc Na_2O	cbted Na_2O	Cl	SO_3	SiO_2	RP at end of precip. measured	Calculated RP	Calculated RP	Calculated RP
129.9	12	3	1	0.5	0.483	0.499	0.494	0.498
112.6	12	3	1	0.5	0.428	0.449	0.444	0.445
95.2	12	3	1	0.5	0.406	0.404	0.399	0.398
77.9	12	3	1	0.5	0.386	0.363	0.358	0.356
105	0	0	3	0	0.403	0.406	0.406	0.405
105	0	0	5	0	0.418	0.409	0.409	0.407
105	0	0	10	0	0.420	0.418	0.417	0.412
171.2	11.8	4.8	0.9	0.5	0.651		0.644	0.655
148	11.8	4.8	0.9	0.5	0.564		0.557	0.563
128	11.8	4.8	0.9	0.5	0.486		0.492	9.495
108.5	11.8	4.8	0.9	0.5	0.424		0.435	0.436
88.8	11.8	4.8	0.9	0.5	0.386		0.385	0.384

Table II. (cont.) Liquor 2 SiO_2 = 0.5 %   Org. C = 2.5 %

Impurities % ctc Na_2O

ctc Na_2O	cbted Na_2O	Cl	SO_3	RP end of precip.	Calculated RP (3)
174	10.7	2.1	0	0.665	0.658
163.7	10.7	2.1	0	0.615	0.616
153.5	10.7	2.1	0	0.587	0.577
129.8	10.7	2.1	0	0.480	0.496
109.8	10.7	2.1	0	0.417	0.437
94.7	10.7	2.1	0	0.379	0.397

Table II. (cont.) Liquor 3 SiO_2 = 0.6 %   Org. C = 5.2 %

Impurities % ctc Na_2O

ctc Na_2O	cbted Na_2O	Cl	SO_3	RP end of precip.	Calculated RP (1)	Calculated RP (2)
169.8	12.2	1.2	0.4	0.660	0.663	0.661
159.8	12.2	"	"	0.618	0.615	0.614
149.8	12.2	"	"	0.569	0.570	0.570
121.1	11.6	"	"	0.446	0.458	0.460
110.6	11.6	"	"	0.421	0.423	0.426
101.1	11.6	"	"	0.408	0.394	0.397
160	2	"	"	0.579	0.585	0.577
160	8.4	"	"	0.600	0.604	0.600
160	12.2	"	"	0.614	0.616	0.615
160	17.4	"	"	0.631	0.632	0.635
110	11.6	"	"	0.420	0.421	0.424
110.5	16.5	"	"	0.429	0.430	0.433
110.5	21.5	"	"	0.441	0.438	0.440
113.3	30.5	"	"	0.458	0.463	0.465
159	12.2	4.2	"	0.625	0.625	0.620
159	12.2	7.15	"	0.640	0.638	0.631
110.5	12.2	4.2	"	0.439	0.430	0.431
110.5	12.2	8.2	"	0.448	0.439	0.438
113.3	12.2	16.2	"	0.462	0.468	0.462
157	12.2	1.2	1.4	0.612	0.605	0.604
157	12.2	"	3.4	0.618	0.611	0.611
157	12.2	"	2.4	0.612	0.608	0.608
157	12.2	"	4.4	0.620	0.615	0.615
157	12.2	"	6.4	0.628	0.621	0.622
110.5	12.2	"	1.4	0.423	0.425	0.428
110.5	12.2	"	10.5	0.435	0.440	0.444
110.5	12.2	"	6	0.427	0.433	0.436

Table II. (cont.) Liquor 4 SiO_2 = 0.5 %   Org. C = 7.7 %

Impurities % ctc Na_2O

ctc Na_2O	cbted Na_2O	Cl	SO_3	SiO_2	RP and precip.	Calculated RP	Calculated RP
168.3	13.4	3	1.4	0.5	0.687	0.690	0.683
162.8	"	"	"	"	0.658	0.660	0.653
158.9	"	"	"	"	0.641	0.639	0.633
154.2	"	"	"	"	0.621	0.616	0.609
123.3	"	"	"	"	0.467	0.480	0.474
113.0	"	"	"	"	0.441	0.442	0.436
102.7	"	"	"	"	0.411	0.406	0.401
160	"	2.7	"	"	0.644	0.644	0.637
160	"	3.2	"	"	0.646	0.646	0.639
160	"	6.81	"	"	0.650	0.655	0.652
160	"	9.6	"	"	0.661	0.662	0.663
160	"	13.7	"	"	0.676	0.763	0.678
150	"	3	2.4	"	0.607	0.598	0.592
150	"	"	4.4	"	0.613	0.604	0.599
160.4	12.3	"	1.4	"	0.64	0.644	0.637
160.4	15.8	"	"	"	0.655	0.655	0.648
160.4	22	"	"	"	0.673	0.674	0.667
109	13	"	"	"	0.427	0.427	0.422
109	18.2	"	"	"	0.435	0.435	0.430
109	22.5	"	"	"	0.443	0.441	0.437
109	26.3	"	"	"	0.445	0.447	0.443
110	13	"	"	"	0.430	0.430	0.425
110	"	12.7	"	"	0.435	0.442	0.441
110	"	12.7	"	"	0.436	0.442	0.441
109	"	3	6.4	"	0.432	0.435	0.430
109	"	"	6.4	"	0.442	0.435	0.430
109	"	"	11.4	"	0.445	0.442	0.439
109	"	"	11.4	"	0.448	0.442	0.439
160.4	13.4	8	1.4	"	0.663	0.660	0.659
160.4	"	13	1.4	"	0.686	0.674	0.678
160.4	"	"	6.4	"	0.660	0.665	0.660
160.4	"	3	11.4	"	0.670	0.682	0.679

Table II. (cont.) Liquor 5 SiO_2 = 0.5 %   Org. C = 6 %

Impurities % ctc Na_2O

ctc Na_2O	cbted Na_2O	Cl	SO_3	RP end of precip.	Calculated RP (1)	Calculated RP (3)
168.8	7.7	4.1	0.5	0.644	0.652	0.644
160	"	"	"	0.608	0.615	0.609
158.6	"	"	"	0.605	0.610	0.603
148.8	"	"	"	0.568	0.571	0.567
127.4	"	"	"	0.495	0.496	0.495
110	"	"	"	0.440	0.442	0.443
108	"	"	"	0.434	0.436	0.438
100	"	"	"	0.419	0.414	0.416
108	"	"	"	0.437	0.436	0.438
150.2	13.2	5.6	1.3	0.606	0.609	0.605
160.3	"	"	"	0.652	0.656	0.650
170.3	"	"	"	0.698	0.706	0.697
158	6.8	"	"	0.608	0.611	0.603
158	13.1	"	"	0.641	0.644	0.639
158	16.9	"	"	0.659	0.665	0.661
158	20.6	"	"	0.679	0.687	0.684
158.2	7.7	7.3	0.5	0.619	0.621	0.613
158.2	"	10.4	"	0.633	0.634	0.623
157	"	4.1	1.5	0.605	0.606	0.600
157	"	"	3.5	0.612	0.611	0.604
157	"	"	5.5	0.621	0.617	0.609
108.4	12	"	0.5	0.439	0.442	0.445
108.4	16.6	"	"	0.445	0.447	0.452
108.4	7.9	9.1	"	0.446	0.447	0.448
108.4	7.8	14.1	"	0.454	0.457	0.456
108.4	7.7	4.1	5.5	0.439	0.444	0.444
108.4	"	"	10.5	0.447	0.451	0.451
108.4	"	"	7.5	0.444	0.447	0.447

Table II. (cont.) Liquor 6 SiO_2 = 0.6 %   Org. C = 20 %

Impurities % ctc Na_2O

ctc Na_2O	cbted Na_2O	Cl	SO_3	RP end of precip.	Calculated RP (1)	Calculated RP (2)
89.7	9.6	9	1	0.411	0.412	0.413
89.7	9.6	19	11	0.434	0.432	0.436
179.3	9.7	9	11	0.855	0.856	0.864
179.3	9.9	19	1	0.866	0.863	0.882
89.3	21	9	11	0.427	0.429	0.429
89.3	21	19	1	0.428	0.430	0.434
130.5	20	9	1	0.591	0.597	0.592
130.5	20	19	11	0.646	0.639	0.641
127.7	15	14	6	0.587	0.587	0.589
130.1	15.1	14	6	0.590	0.599	0.601
119.5	18.5	4	0	0.531	0.529	0.524
103.7	"	"	"	0.467	0.464	0.462
94.3	"	"	"	0.433	0.429	0.428

Table II. (cont.) Liquor 4 Diluted in Org. C

Impurities % caustic Na_2O

ctc Na_2O	cbted Na_2O	Cl	SO_3	SiO_2	Org. C	Measured RP	Calculated RP
150.6	6.7	1.5	0.7	0.25	3.85	0.550	0.547
131	6.7	1.5	0.7	0.25	3.85	0.471	0.480
110	6.7	1.5	0.7	0.25	3.85	0.411	0.417

Table III. k Coefficients Calculated by Multiple Regression

Liquor	k_0	$10^4 x k_1$	$10^4 k_2$	$10^4 k_{1,2}$	$10^4 k_{1,3}$	$10^4 k_{1,4}$	$10^4 k_{1,5}$
Synthetic and 1	- 1.391	45.3	- 81.0	1.10	0.38	0.41	2.1
3	- 1.693	70.9	0	0.32	0.45	0.33	-
4	- 1.739	76.0	7.0	0.24	0.25	0.33	-
5	- 1.463	55.1	- 10.5	1.2	0.41	0.28	-
6	- 1.512	65.1	- 62	0.9	0.28	0.25	-

The correlation coefficient between the values calculated and those observed is 93 % for the synthetic liquor and exceeds 99 % for the other liquors.

The mean deviation between the values calculated and those observed is less than 0.01 RP unit (cf. RP calculated in Table II).

2 - Quantification of the Influence of Mineral Impurities

This quantification may be approached by taking the derivative of the equation with respect to the variable representative of the impurity.

The RP increment (Δ Y) per % of impurity is given by (2)

$$\Delta Y = (k_{1,2} X_1 + k_2) Y \text{ for carbonate}$$
$$\Delta Y = k_{1,i} X_1 Y \text{ for impurity i} \qquad (2)$$

These equations show that the influence of the impurity depends on the ctc Na_2O concentration, on the origin of the liquor, and its global impurity content, through Y, which is the RP at the end of precipitation.

For example, the increments were calculted for ctc Na_2O concentrations of 110 g/l (Table IV) and 160 g/l (Table V).

The influence of mineral impurities appears 2 to 3 times less at 110 g/l than at 160 g/l.

Table IV. RP Increments per % of Impurities/ctcNa_2O Relative to Mineral Impurities in Various Liquors with ctcNa_2O Concentrations of 110 g/l

Δ RP x 10^4 per % of impurities/ctcNa_2O

Liquor	cbted Na_2O	Cl	SO_3
of pure aluminate	1.7	1.7	1.8[5]
1 (and 2)	1.75	1.85	2.0
3	1.5	2.15	1.55
4	1.4	1.2	1.55
5	1.2	2.0	1.4
6	1.8	1.5	1.3

Table V. RP Increments per % of Impurities/ctc Na_2O Relative to Mineral Impurities in Various Liquors with ctc Na_2O Concentrations of 160 g/l

Δ RP x 10^4 per % of impurities/ctcNa_2O

Liquor	cbted Na_2O	Cl	SO_3
of pure aluminate	4.9	3.1	3.4
1 (and 2)	5.75	3.7	4.0
3	3.15	4.5	3.25
4	2.9	2.6	3.4
5	5.4	4.0	2.8
6	6.0	3.3	2.9

For carbonate, two groups of liquors were found in the 160 g/l concentration :

- one consisting of liquors 3 and 4 (from plants processing African bauxite), wherein the increment is 3 x 10^{-3} ;

- the other consisting of liquors 1,5 and 6 wherein the increment is almost two times greater.

This was perhaps the result of the interaction between mineral impurities and organic impurities in the liquor.
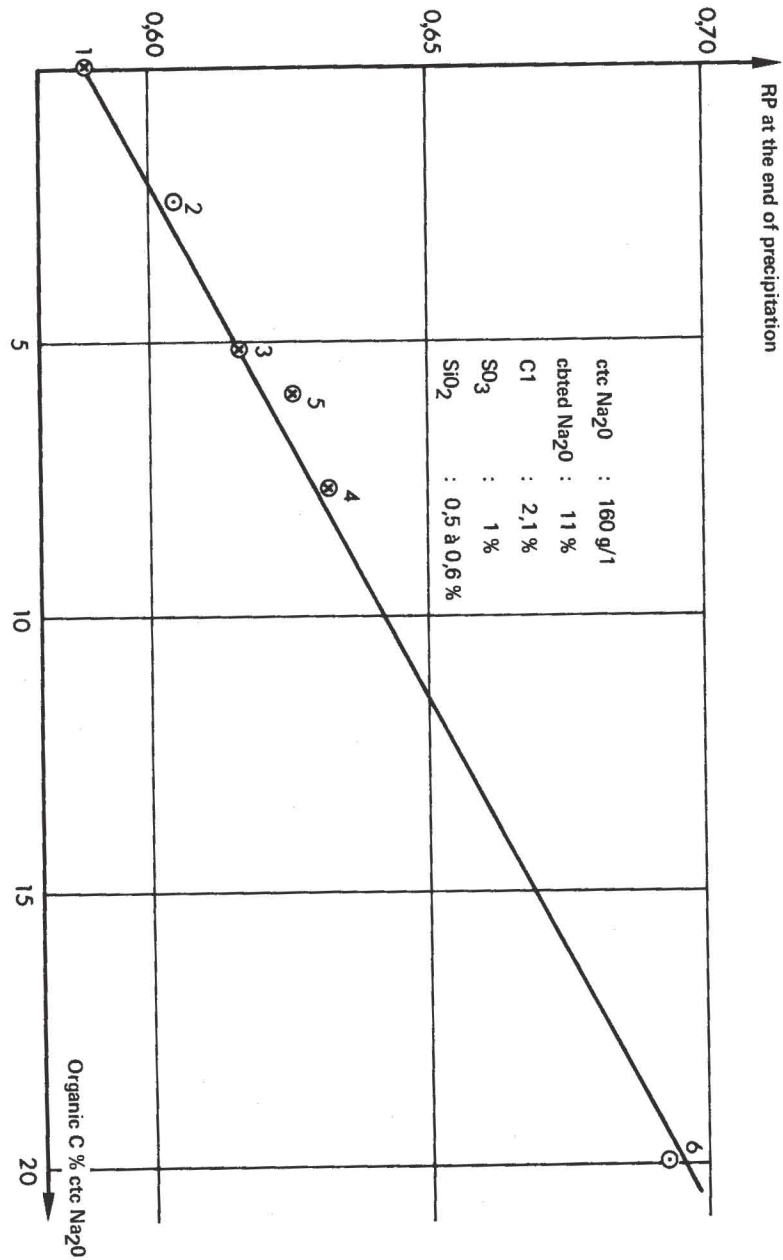
3 - Influence of Organic Matters

The models constructed made it possible to compare the RP at the end of precipitation of various liquors which had identical mineral impurity compositions, and therefore to approach the overall influence of organic matter.

Figures 1 and 2 show the influence of org. C respectively at 160 and 110 g/l concentrations for the following mineral impurity concentrations :

cbted Na_2O : 11 % SO_3 : 1 %

Cl : 2.1 % SiO_2 : 0.5 to 0.6 %

At 160 g/l the fluctuation of RP as a function of the organic carbon content is represented by a straight line with a slope expressed as (3) :

Figure 1 - Influence of Organic C at 160 g/1

ctc Na2O	:	160 g/1
cbted Na2O	:	11 %
C1	:	2,1 %
SO3	:	1 %
SiO2	:	0,5 à 0,6 %

ctc Na2O	:	110 g/1
cbted Na2O	:	11 %
C1	:	2,1 %
SO3	:	1 %
SiO2	:	0,5 à 0,6 %
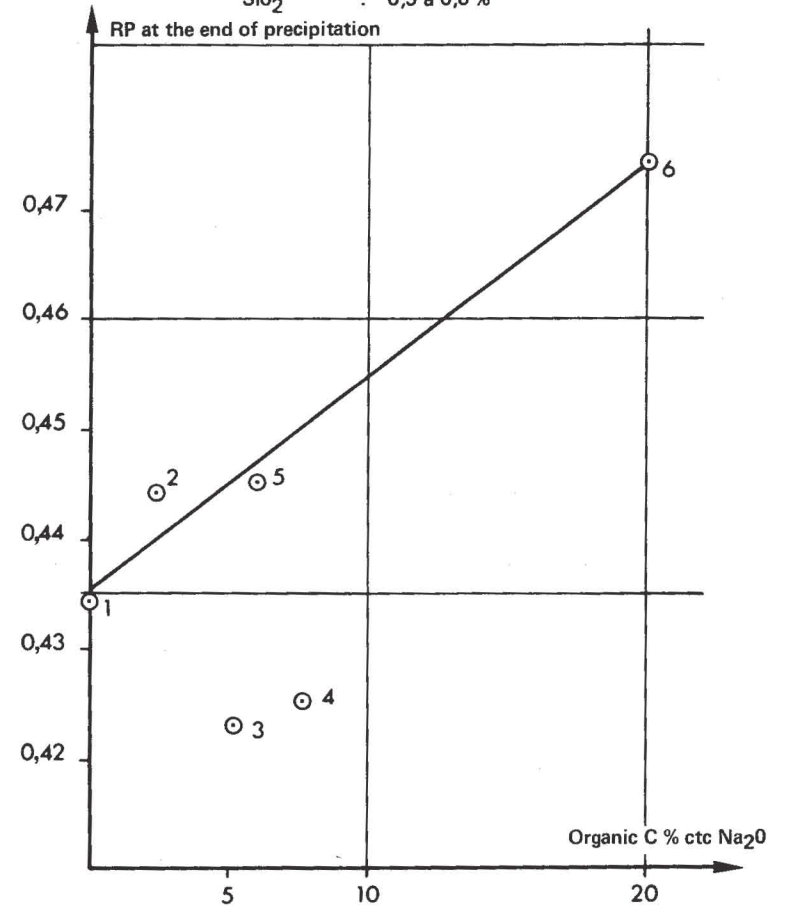
Figure 2 - Influence of Organic C at 110 g/1

$\triangle$RP = 0.0057 per % org. C, or 0.0035 per g/l of org. C (3)

At 110 g/l. fluctuation is smaller for liquors 1, 2, 5 and 6 (4).

$\triangle$RP = 0.010 per % org. C or 0.0018 per g/l of org. C (4)

For liquors 3 and 4 the influence of org. C appears nil if not beneficial.

4 - Underline General Model of the Influence of Mineral and Organic Impurities

The examination of models for the 5 industrial liquors leads us to establish 2 groups in order to study the influence of organic substances.

The first group consists of liquors 3 and 4 from plants that process African bauxites. The second group consists of liquors 2, 3 and 6 from plants that process Australian or European bauxites.

By regrouping the experiment data relative to these 2 groups it is possible to perform multiple regressions to find 2 equations which relate the RP at the end of precipitation to the chemical composition of the liquor. The data concerning the synthetic liquors that contain no organic impurities, and also liquor 1, were taken into account in both models.

By introducing an interaction between the carbonate content and the org. C content (X6), the following equation (5) is obtained in both cases :

(5)

$$LnY = k_0 + k_1X_1 + k_2X_2 + k_6X_6 + \sum_{i=2}^{6} k_{1i}X_i + k_{2,6}X_6 + k_{1,2,6}X_1X_2X_6$$

The k constants relative to both liquor groups are shown in Table VI.

The statistical correlation of the models is greater than 99%, and the mean deviation between the values observed of the RP and the calculated values is less than 0.01 RP. The results obtained are strictly valid only under the kinetic precipitation conditions of laboratory testing.

The values observed and calculated are compared in Table II, (index 2 concerns the model for the 1st group and the real index 3 the model for the 2nd group).

Underline Transposition of Results to Other Precipitation Conditions

The purpose of this transposition is to determine the possibility of predicting the RP of a liquor at the end of precipitation, knowing its chemical composition (ctc Na_2O, impurities) and the precipitation parameters (temperature, seed load, retention time).

This transposition is possible given a kinetic model which takes into consideration not only the precipitation parameter, but also solubility at alumina equilibrium (equilibrium $RP = RP_e$).

The transposition involves the following procedures :

- Utilization of the kinetic model for calculating the liquor composition at the alumina solubility equilibrium (RP_e) on the basis of the measurements carried out.

- Modelling of equilibrium RP as a function of the chemical composition of the liquor and of the temperature.

- Combination of the RP_e model and the kinetic model to determine the RP at the end of precipitation as a function of the initial chemical composition of the liquor and the physico-chemical parameters of the precipitation reaction.

Table VI.   k Constants for Both Groups of Liquors

	1st group African bauxites	2nd group Australia
k_0	- 1.39	- 1.397
k_1	0.00455	0.00462
k_2	- 0.0101	- 0.0115
k_6	- 0.0479	- 0.00730
$k_{1,2}$	0.000121	0.000139
$k_{1,3}$	0.0000351	0.0000358
$k_{1,4}$	0.0000365	0.0000244
$k_{1,5}$	0.000161	0.0000608
$k_{1,6}$	0.000393	0.000108
$k_{2,6}$	0.00145	0.000394
$k_{1,2,6}$	- 0.0000126	- 0.00000389

1 - Underline Kinetic Model

We utilized a kinetic model (6) constructed by our laboratories for liquors 2, 4 and 5, and previously presented in (3) :

$$RP(t) = RP_e + \frac{RP_i - RP_e}{1 + k (RP_i - RP_e) t}$$

(6)

with k constant of velocity = (A +B.C) x m x s exp. (-E/RT)

where   :

- $RP(t)$: RP at instant t
- RP_i : RP at instant t = 0

- RP_e : RP at liquor equilibrium (t_e) which depends on the temperature

- A and B : constants characteristic of the liquor
- C   : concentration in ctc Na_2O at time t
- m   : seed mass at time t
- s   : seed specific surface area
- E   : activating energy of reaction
- R   : constant of perfect gases
- T   : temperature in °k

2 - Calculation of Equilibrium RP

The kinetic equation makes it possible to calculate RP_e from :

- the known value of RP_i.
- the RP value measured at the instant t.
- the values of c and m at instant t, easily calculated by using the values at the instant t = 0.

For this calculation, it is also necessary to know the constants A and B characteristic of each liquor.

In the case of liquors 2, 4 and 5, the kinetic study made it possible to determine the values of these constants by attributing an activating energy common to the three liquors (Table VII).

The graphic representations of A and B as a function of the org. C content (linear for A, quadratic for B) made it possible to approach the values of these constants for the other liquors. This calculation was not made, however, for liquor 6, since the org. C content is too far removed from the known domains of the constants A and B.

Table VII. Activating Energy Common to the 3 Liquors

Liquor	2	4	5
E kcal/mole	18.96	18.96	18.96
A x 10^{10}	18.23	13.7	11.34
B x 10^{10}	- 0.0854	- 0.061	- 0.0436
org. C % ctc Na_2O	2.5	6	7.7

Equilibrium RP were calculated using the experiment data given above and the values in table II.

3 - Modelling of Equilibrium RP's

The modelling leads to the formulation of an equilibrium RP logarithm analagous to that found for the time period of 46 hours.
Table VIII shows the k' coefficients to be attributed to the various liquors.

Table VIII. k' Coefficients for the Various Liquors

Liquor	k'_0	$10^4 k'_1$	$10^4 k'_2$	$10^4 k'_{12}$	$10^4 k'_{13}$	$10^4 k'_{14}$	$10^4 k'_{15}$
Synthetic and 1	- 1.936	39.7	- 10.2	0.13	0.41	0.43	2.3
3	- 1.721	64.3	0	0.37	0.52	0.40	-
4	- 1.832	75.0	0	0.34	0.28	0.36	-
5	- 1.4805	47.0	- 11.8	0.13	0.47	0.32	-

4 - Influence of Temperature on the Equilibrium RP

MISRA (4) proposed an equation (7) which gives, for pure liquor, the variation of equilibrium RP as a function of temperature :

$$Ln\ RP_e = 6.2106 - 2486.7/T + 1.0975\ C_{Na2O}/T \qquad (7)$$

The temperature correction to be applied to the equilibrium RP calculated at 55°C can be given by the following equation (8), if it is accepted that the influence of the impurities contained in the liquor does not significantly fluctuate when the temperature is near 55°C.

$$Ln\ RP_{e(T)} = Ln\ RP_e\ (55°C) - 2486.7\ (\frac{1}{T} - \frac{1}{338}) + 1.0975\ C_{Na2O}\ (\frac{1}{T} - \frac{1}{338}) \qquad (8)$$

The validity of this correction equation was confirmed for liquor 5. Table IX gives a comparison between the deviations of RP_e between 55°C and 65°C, measured by experiments and calculated.

It was confirmed, under various precipitation conditions, that the calculation of the RP, for synthetic liquors 1, 3, 4 and 5 carried out by using the model established for each liquor on the RP_e, the correction of temperature, and the kinetic model, lead to a value that comes to the nearest 0.01 unit of RP (max. deviation noted : 0.02) to that which was measured.

The good agreement observed for synthetic liquors, including for pure aluminate liquors, led to admit that mineral impurities have little influence on the coefficients A and B of the velocity constant.

Table IX. Deviations of RP_e between 55° and 65°C

ctc Na_2O	Observed RP_e 65° - RP_e 55°	Calculated RP_e 65° - RP_e 55°
120	0.100	0.098
140	0.108	0.108
160	0.115	0.115
180	0.123	0.130

A fluctuation of liquor productivity induced by a modification of its mineral impurity composition will therefore be almost the same for variable kinetic conditions of precipitation. The same does not hold true for organic impurities, as they modify the velocity constant of the reaction.

A precise knowledge of their influence would make it possible to calculate the equilibrium RP at 55°C of a liquor with a given chemical composition so as to be in agreement with one of two models established.

Back calculation of RP for other precipitation conditions however, requires a more concise knowledge of the temperature correction to be applied to the equilibrium RP, especially for those liquors rich in impurities.

CONCLUSION

On the basis of precipitation tests conducted under specific conditions, two empirical equations were established, one relative to African bauxites, the other relative to European and Australian bauxites, making possible the calculation, to the nearest 0.0 1 unit RP, of the RP at the end of precipitation as a function of the ctc Na_2O concentration and of the concentrations of mineral and organic impurities of the liquor.

These equations emphasize the importance of purification processes, and make it possible to easily determine, for each liquor, the soda concentration that leads to the maximum yield.

Studies carried out on some liquors confirmed that by using a kinetic model the results could be transposed to other conditions of precipitation.

The combination of established empirical equations and of the kinetic model will make it possible to calculate the productivity of a liquor, whatever its chemical composition and precipitation conditions, once the influence of organic impurities on the velocity constant have been modelled, and once the influence of organic impurities on the equilibrium RP variation with temperature have been more accurately defined.

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