THE EFFECT OF FOUR COMMON BAYER LIQUOR IMPURITIES

ON ALUMINA SOLUBILITY

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The effect of Bayer liquor impurities was tested on alumina solubility in precipitation and digestion. Impurities tested were the sodium salts of carbonate, sulfate, chloride and the composite effect of organic compounds.

All impurities tested were found to raise the solubility of alumina in precipitation thereby causing a negative effect on alumina production. The composite effect of the sodium organic compounds was found to raise the finishing precipitator ratios the most, followed in order by chloride, carbonate and sulfate.

Sodium carbonate was found to raise the solubility of alumina at digestion the most, followed by chloride, then sulfate. The composite effect of organic compounds did not increase the solubility of alumina in digestion. The effect of salts to raise the solubility of alumina in digestion can offset some of the production losses they cause in precipitation. Factors have been developed for the effect of each salt on precipitation and digestion so their composite effect may be calculated.

Introduction

Impurities in Bayer process liquors create many problems in alumina plants. The levels of impurities exist in a balance between incoming levels and those leaving the plant. Frequently a change in the process or raw materials will change the balance. In many cases the decision to remove impurities must be made only when weighed against the economic advantages to be gained by removing them. In order to accomplish this, the overall effect of the impurities on the process must be known. While there are a large number of impurities which affect the Bayer plant, four of the more common impurities found in the Bayer process liquor stream are sodium carbonate, sodium chloride, sodium sulfate and sodium organic compounds.

Reviews of the literature turn up numerous reports describing the effects of these impurities on the decomposition of Bayer liquor (1) but very little information may be found describing the effects of impurities on maximum attainable A/C ratios at the digesters. In order to determine the effect of impurities on overall production levels it was felt the effects at digestion as well as at precipitation should be measured. Laboratory studies were performed to measure the effect of these impurities on the solubility of alumina in digestion and also on the final precipitator A/C ratio in precipitation.

Experimental

In order to measure the effect of impurities it was decided to first determine the maximum solubility of alumina when digesting and precipitating alumina from reagent grade caustic with almost zero impurities present. These tests were then followed by determining the maximum solubility of alumina in digestion and precipitation when a single impurity was added to the reagent grade caustic. Each impurity was tested at three different concentrations so the effect would be measured over a wide range.

The measurement of the effect of the organic compounds present in our Bayer process liquor presented a special problem. There are so many compounds present it would be impossible to test them all. (Some 55 have been identified already.) Since sodium carbonate, sodium sulfate and sodium chloride represent most of the impurities present in our liquor, except for the sodium organic compounds, it was decided to measure the effect of organics as a group. Pure reagent grade caustic containing the identical amounts of sodium carbonate, sodium chloride and sodium sulfate as our plant liquor was tested for digestion maximum A/C and precipitation final A/C ratio. Then a plant liquor was tested and any difference in the solubility in digestion or precipitation could be attributed to all other impurities present in the liquor. In the case of our plant liquor the majority of the other impurities present are the organic compounds.

The caustic concentrations selected for the tests were 185 g/l for all digestion solubility studies and 200 g/l initial caustic concentration for all precipitation tests. A large sample of Jamaican bauxite was dried and pulverized. This bauxite was used for all digestion tests. Aluminum trihydrate was used to adjust the A/C ratio of all liquors. The liquors prepared for digestion tests were adjusted to .200 A/C while the precipitation liquors were adjusted to .670 A/C.

Digestion Studies

In order to determine the maximum solubility of alumina in digestion, a

procedure which we call the "extraction breakpoint" was used. The breakpoint is defined as the A/C ratio at which increasing the bauxite charge will result in a significant loss of extractable alumina from the bauxite. This will result in an increase in alumina in the mud, which is the preferred method of detecting the breakpoint A/C.

In order to determine the breakpoint a constant amount of the liquor to be used is measured into a lab digestion pressure vessel known as a "bomb." Bauxite is added to charge for an A/C ratio well below the breakpoint. The amount of bauxite to be charged may be calculated from the soluble alumina as determined by a bomb digestion at a very low A/C ratio. This maximum extractable alumina value is abbreviated as M.E.A. All other parameters, such as digestion time, temperature and other materials added to plant digesters, i.e., lime, were all selected to approximate the plant digestion conditions. After digestion, the clarified liquor is analyzed for A/C ratio and the mud is washed and dried followed by chemical analysis for Al_2O_3 and Fe_2O_3.

The digestion procedure was repeated at increased charge for A/C ratios until the liquor analysis showed a drop below the A/C ratio charged for, and the aluminum increased in the washed, dry red mud.

The percent of MEA extracted may be calculated by the following method:

$$\text{Percent of MEA Extracted} = \left[\frac{\left(\begin{array}{c} \text{Total} \\ \% \ Al_2O_3 \ \text{in Bx} \end{array} \right) - \left(\% \ Al_2O_3 \ \text{in Mud} \times \frac{\% \ Fe_2O_3 \ \text{in Bx}}{\% \ Fe_2O_3 \ \text{in Mud}} \right)}{\% \ \text{MEA in Bauxite}} \right] \times 100 \qquad (1)$$

The extraction breakpoint may be found by preparing a graph of the charged for A/C ratio versus the percent of MEA alumina extracted. Table I and figure 1 are examples of the extraction breakpoint data obtained when the Jamaican bauxite used in this study was digested in reagent grade caustic. The reagent grade caustic, after preparation at .200 A/C, contained a small amount of sodium carbonate. The breakpoint found in this test was .677 A/C. Later on when the effect of sodium carbonate on digestion breakpoint was determined, it was found that the breakpoint corrected for the small amount of sodium carbonate present would be .675 A/C at a caustic concentration of 185 g/l as Na_2CO_3.

Eleven additional breakpoint tests were conducted to determine the effect each impurity and concentration would cause on the digestion breakpoint. Table II is a listing of the liquors used for the breakpoint studies.

The salt to caustic ratios are used to compare the results of tests. This is necessary since the breakpoint data was conducted at 185 g/l while the precipitation studies were conducted at 200 g/l.

Table III is a summation of the breakpoint A/C increases found when each liquor of Table II was tested.

Figure 2 is a graphical representation of the data from Table III.

Table I. Extraction Breakpoint Data in Reagent NaOH

Bomb No.	Desired A/C	Charge Data			Bomb Discharge Liquor			
		grams Bx	ml Lime Slry	ml Water	A g/l	C g/l	S g/l	A/C
1	.540	73.90	10.5	86	98.7	184.5	190.5	.535
2	.570	81.18	11.6	80	105.7	184.9	190.6	.572
3	.600	87.51	12.5	76	110.6	184.4	190.3	.600
4	.630	93.80	13.4	71	116.5	184.8	191.2	.630
5	.660	100.05	14.3	66	121.7	185.0	191.0	.658
6	.670	102.13	14.6	65	122.8	185.0	190.8	.664
7	.680	104.12	14.9	63	124.4	185.3	190.8	.672
8	.690	106.27	15.2	62	125.5	184.6	191.1	.680
9	.700	108.34	15.5	60	124.3	185.0	191.5	.672
10	.720	112.46	16.0	57	123.6	186.3	192.0	.663

Charge Liquor Analysis (All Bombs Charged with 400 mls)   49.9   249.5   252.1   .200   1.203

Bauxite and Mud Analysis

Bomb No.	Desired A/C	% Al_2O_3	% Fe_2O_3	% of MEA Extracted	% Alumina Recovered
1	.540	13.19	52.13	98.1	99.9
2	.570	12.37	51.84	98.8	100.1
3	.600	12.82	50.92	98.2	99.9
4	.630	12.49	51.08	98.5	100.0
5	.660	13.05	50.65	97.9	100.0
6	.670	13.00	50.97	98.0	99.6
7	.680	13.55	50.59	97.5	99.7
8	.690	14.87	49.74	96.1	100.1
9	.700	18.44	47.57	92.1	100.3
10	.720	20.54	44.07	88.6	99.5

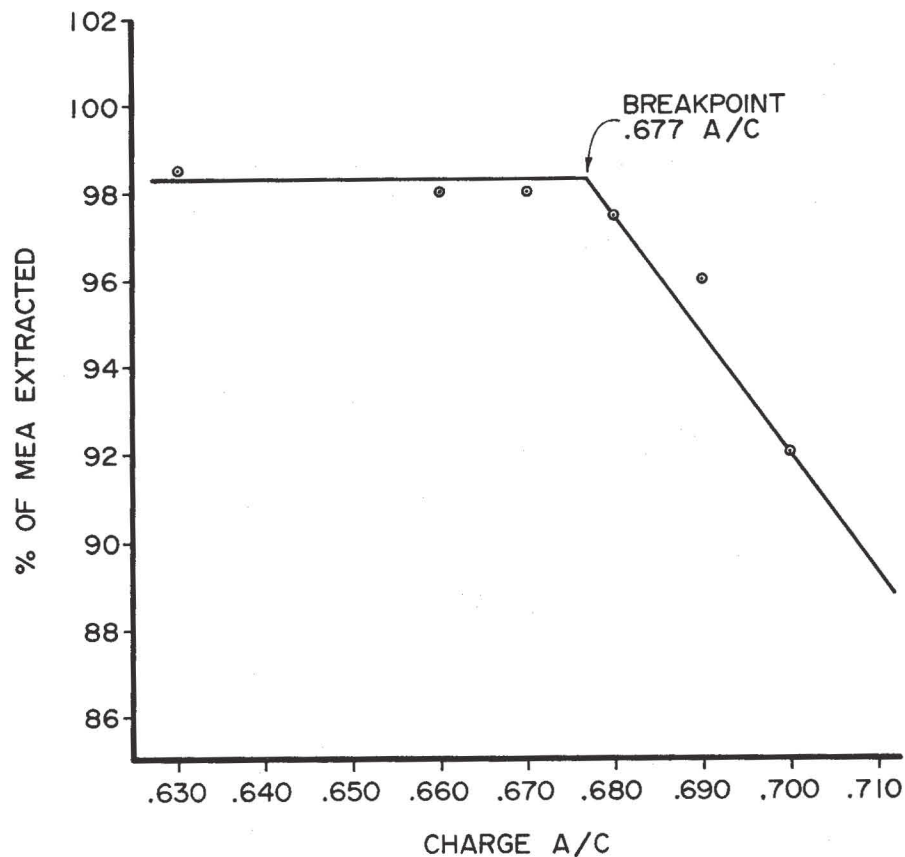Bauxite Analysis   47.79   19.59   Bauxite MEA = 43.65%

Figure 1 - Extraction breakpoint determination when Jamaican bauxite was digested in reagent grade caustic.

Digest conditions were:

Jamaica bauxite
2% Lime added to digest
Digest time: 70 minutes
Digest temperature: 238°C
Bomb held at 107°C for 2 hours
Discharge caustic = 185 g/l
Liquor impurities present = .010 Na_2CO_3/C only

Table II. Breakpoint Tests Conducted (185 g/l caustic)

Test	Impurity Added or Liquor Tested	Concentration of Impurity
1	Reagent Grade Caustic only	.010 Na_2CO_3/C
2	Sodium Carbonate	.100 Na_2CO_3/C
3	Sodium Carbonate	.200 Na_2CO_3/C
4	Sodium Carbonate	.400 Na_2CO_3/C
5	Sodium Chloride	.100 NaCl/C
6	Sodium Chloride	.200 NaCl/C
7	Sodium Chloride	.400 NaCl/C
8	Sodium Sulfate	.100 Na_2SO_4/C
9	Sodium Sulfate	.200 Na_2SO_4/C
10	Sodium Sulfate	.400 Na_2SO_4/C
11	Reagent caustic with chlorides, sulfates and carbonates at plant liquor concentration but no organics present.	
12	Plant liquor containing plant levels of organics.	

Table III. Breakpoint A/C Increase Caused by Various Impurities

Salt Tested	Salt Addition (Salt/Caustic)		
	+.100	+.200	+.400
Na_2CO_3	+.018	+.024	+.036
NaCl	+.016	+.022	+.029
Na_2SO_4	+.010	+.015	+.025
Organics	None found at .132 Na_2CO_3/C organic by Ignition		

Figure 2 - Effect of salts added to digest liquor on breakpoint A/C ratio.

Precipitation Studies

Precipitation studies to determine the effects of impurities on A/C ratios during precipitation were conducted. Large volumes of liquor containing the same salt/caustic ratio tested for the breakpoint study as listed in table II were prepared. The starting caustic concentration for each test was 200 g/l C and .670 A/C. A seed charge of 45 grams per liter of washed and dried fine aluminum trihydrate seed was added. Mechanical stirring was used and temperature was held constant at 65°C. Each test was allowed to precipitate for 72 hours with samples collected and analyzed at 0, 8, 24, 48 and 72 hours for alumina, caustic, total soda and density at 25°C. One liter of the liquor was placed in a two liter stainless steel beaker. The beaker was covered and reflux condenser affixed to prevent evaporation. Liquors were filtered through No. 40 filter paper before analysis.

Table IV is the data obtained from all precipitation tests.

Table IV. Effect of Salt Addition on Precipitation A/C (200 g/l)

Liquor Tested	A/C Found at Precipitation Times (hours after seeding)				
	(Precipitation Time)				
	8 hrs	24 hrs	48 hrs	72 hrs	
Reagent Caustic	.425	.342	.309	.286	(A/C Ratios)
Sodium Sulfate Added					
+.100 $\frac{Na_2SO_4}{C}$		+.010	+.010	+.011	Increase
+.200 $\frac{Na_2SO_4}{C}$		+.020	+.019	+.021	in A/C Ratio
+.400 $\frac{Na_2SO_4}{C}$		+.041	+.039	+.042	
Sodium Chloride Added					
+.100 $\frac{NaCl}{C}$		+.016	+.016	+.018	
+.200 $\frac{NaCl}{C}$		+.034	+.033	+.034	
+.400 $\frac{NaCl}{C}$		+.068	+.067	+.068	
Sodium Carbonate Added					
+.100 Na_2CO_3/C		+.012	+.013	+.016	
+.200 Na_2CO_3/C		+.026	+.027	+.030	
+.400 Na_2CO_3/C		+.053	+.055	+.058	
Organic by Difference* Effect Caused by .132 Na_2CO_3/C Organic Soda		+.022	+.030	+.034	

*Plant liquor compared to synthetic liquor with no organics but the same concentrations of NaCl, Na2SO4, Na2CO3.
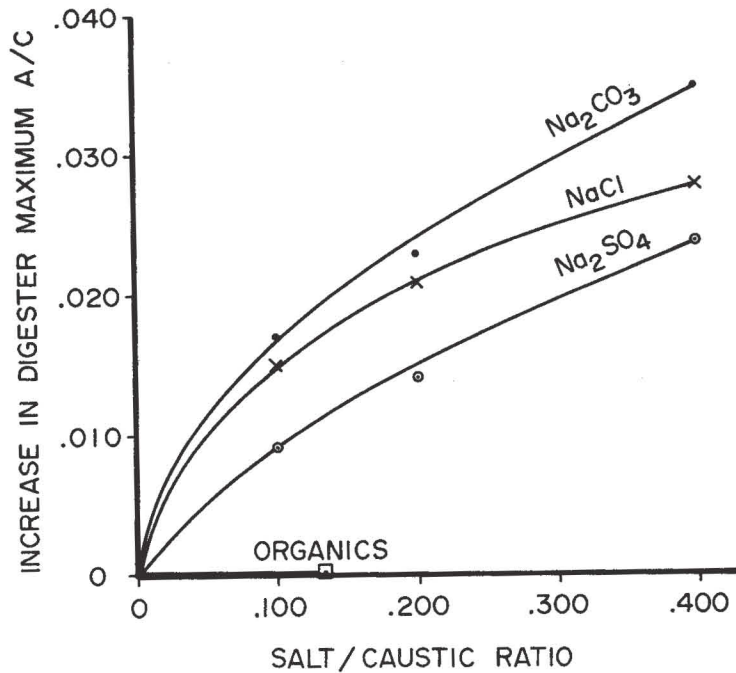
Figure 3 is a graphical representation of the 48-hour precipitation data. The 24-hour and 72-hour data would produce similar results since the increase in A/C ratio when compared to the synthetic liquor appears to be a constant difference. From this data it is concluded the organics resulted in the largest A/C increase in precipitation followed in turn by sodium chloride, sodium carbonate and sodium sulfate.
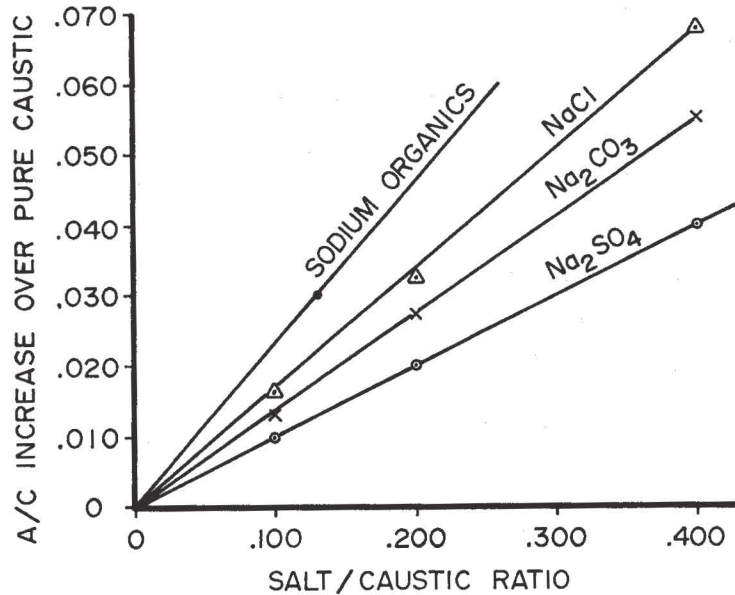
Figure 3 - Effect of salt additions on A/C ratio during precipitation (48-hour data).

Figure 4 - Comparison of breakpoint A/C increase versus precipitation A/C increase when Na2CO3 added.

Overall Effect of Impurities

Once the effects caused by the salts on digestion maximum A/C ratio and precipitator A/C ratio were identified, comparisons of the net effect they cause may be made.

Figures 4, 5, 6 and 7 are comparisons of the breakpoint A/C increase versus the precipitation A/C increase resulting from the addition of each salt. The difference in the two curves may be considered the actual losses which will occur in an alumina plant as the impurity builds up in the liquor stream.
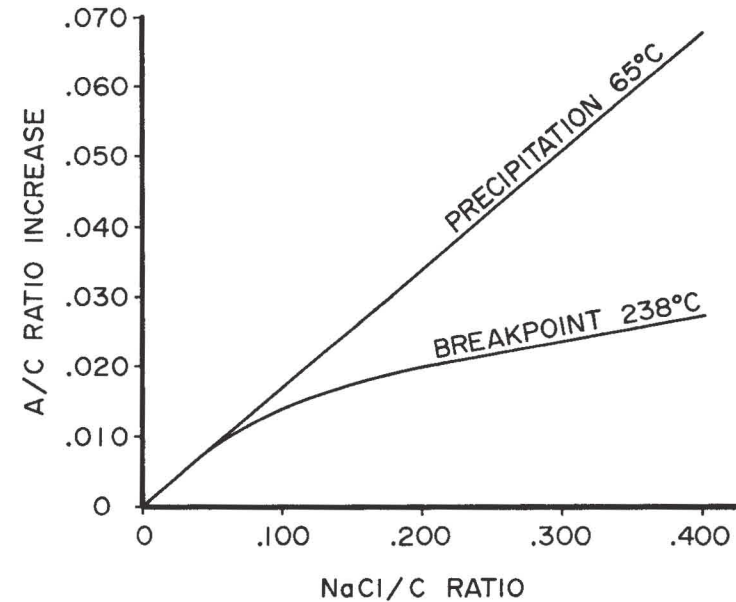

Figure 5 - Comparison of breakpoint A/C increase versus precipitation A/C increase for sodium chloride.
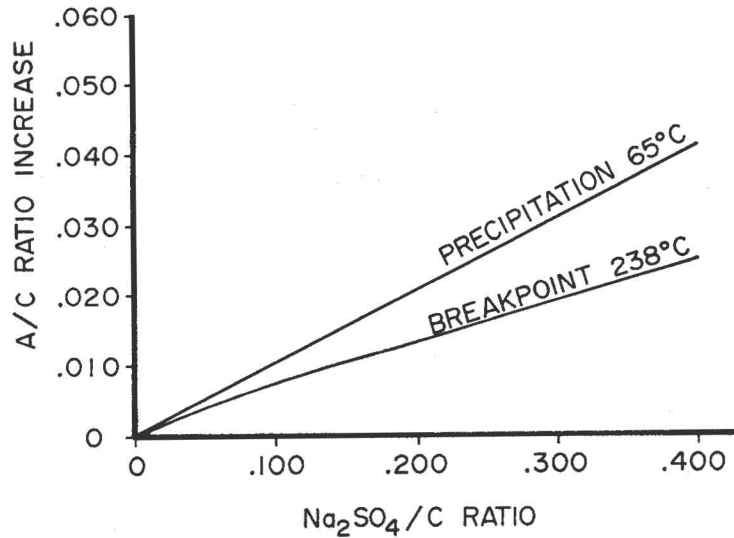
Figure 6 - Comparison of breakpoint A/C increase versus precipitation A/C increase resulting from sodium sulfate addition.
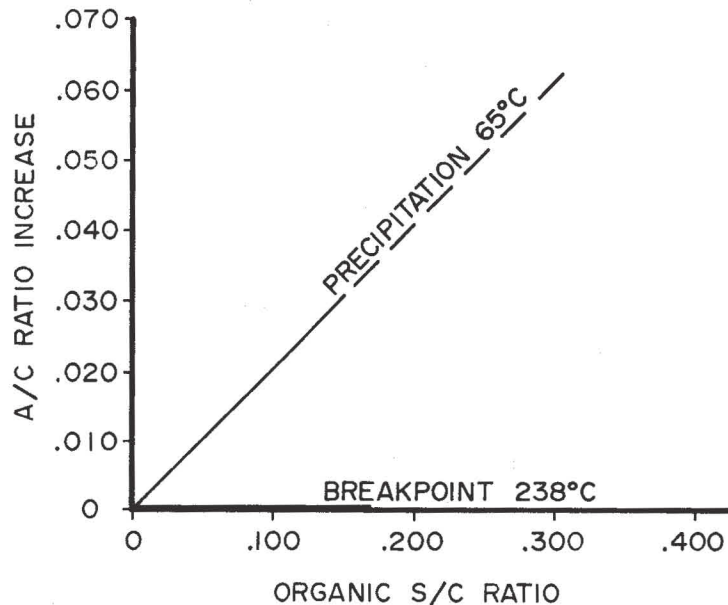

Figure 7 - Comparison of breakpoint A/C increase versus organic A/C increase resulting from organics present in plant liquor.

Mathematical Approach

Breakpoint Calculation

An attempt to express the data for breakpoint A/C increases and precipitation A/C increases resulting from salt additions mathematically was made. It was noticed that if the impurities added to the pure caustic were converted to their respective Na_2O equivalents and the summation of these concentrations plotted against the breakpoint A/C increases obtained, a reasonable agreement was obtained between the effect caused by each salt and its effect on breakpoint. This data is displayed in figure 8. This data would suggest the influence of impurities on breakpoints is a cumulative function of their Na_2O content.

From the slope of the line in figure 8 an equation was derived which can predict the breakpoint at various levels of the three impurities (Na_2CO_3, $NaCl$, Na_2SO_4). Organics did not produce a change in breakpoint and were not considered.

$$\text{Breakpoint A/C Ratio} =$$

$$.11363 \left[\frac{(g/l\ Na_2CO_3 \times .585)+(g/l\ Na_2SO_4 \times .436)+(g/l\ NaCl \times .530)}{g/l\ Caustic} \right] + .6825 \quad (2)$$

Since the above equation is good for only 185 g/l caustic it is necessary to correct any data obtained for changes increased or decreased caustic concentration would cause. Lab digests at different caustic concentrations gave a change of .00075 A/C ratio points for each gram per liter caustic change. Utilizing this data, one may adjust the data obtained from equation (2) for various caustic concentrations with the following equation:

$$\text{Breakpoint Change} = (g/l\ \text{caustic in digestion} - 185) \times .00075 \quad (3)$$

Precipitation Calculations

In order to calculate the expected A/C ratios with various concentrations of impurities, an equation was developed. The curve for precipitation from pure caustic was found to "best fit" a logarithmic curve (Figure 9). The 24-, 48-, and 72-hour A/C values obtained during precipitation were corrected for the small amount of sodium carbonate present and, using the best fit method, the following equation was determined:

$$\text{Finish A/C Ratio} = \left[.49295 - .048019\ ln(\text{cycle time in hours}) \right] \quad (4)$$

It was noticed that each time an impurity was added and a precipitation test was performed, the A/C ratio increase was the same at any point between 24 and 72 hours. (See Table IV.)

Using the slope of the lines derived when plots of the impurity/C ratio versus A/C ratio of each impurity were made, linear factors were derived which could account for the A/C increase due to each impurity. This data was then added to the original equation for pure caustic and the following equation resulted:
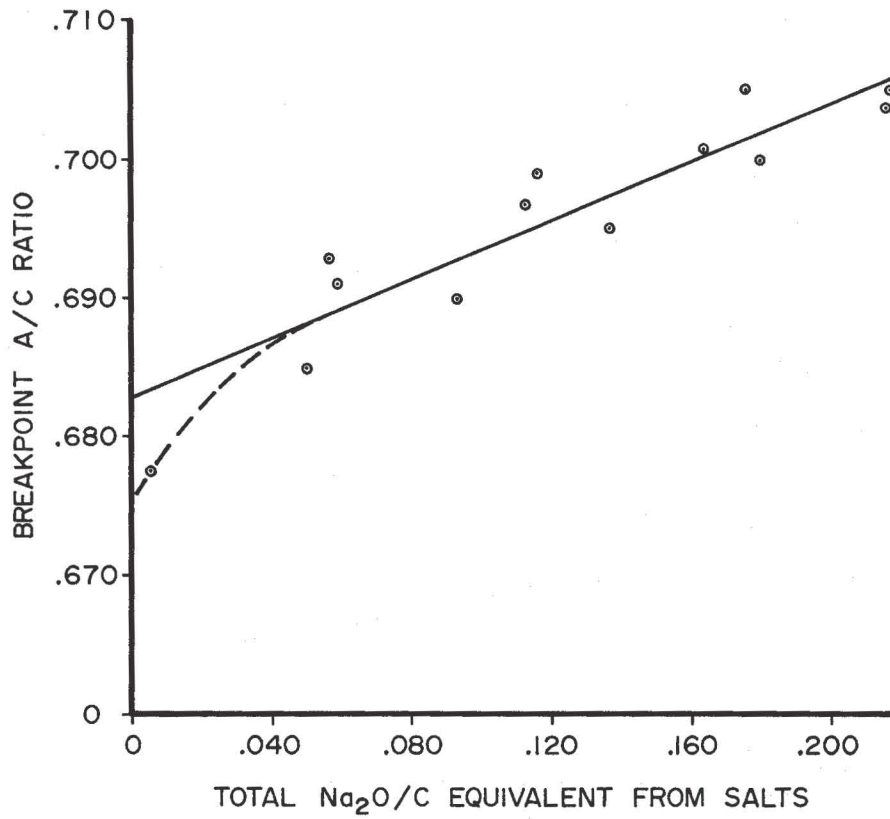
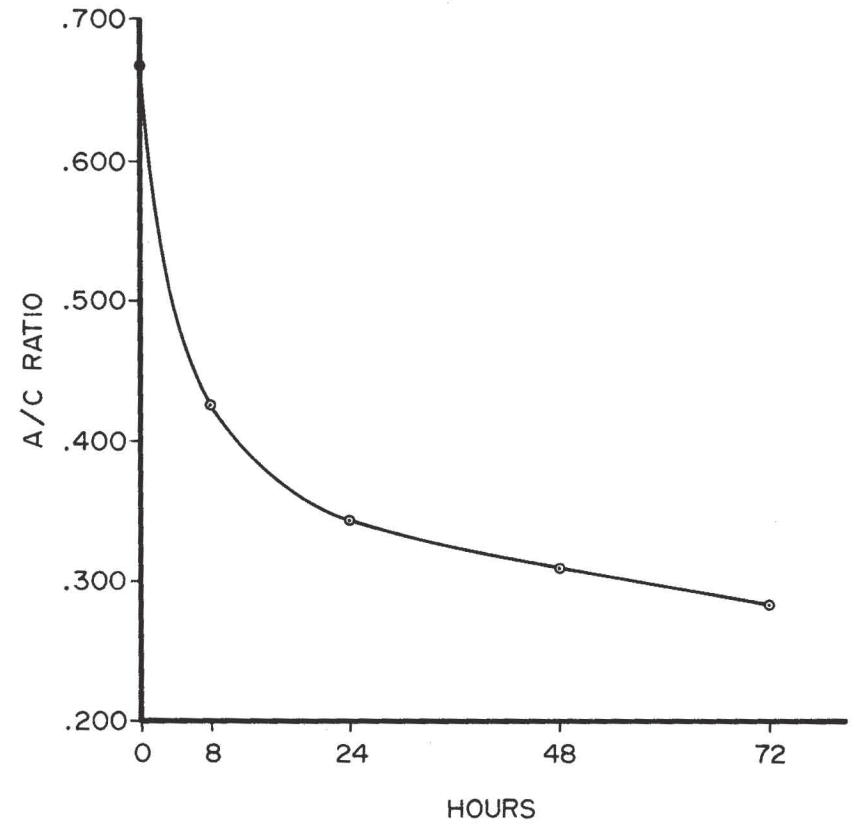Figure 8 - Combined impurity breakpoint curve.

Figure 9 - Precipitation curve for Al_2O_3 from pure caustic (.013 Na_2CO_3/C)

Final A/C =

$$\left[.4987 - .049799 \ln (\text{cycle hrs})\right] + \left(\frac{Na_2CO_3}{C} \times .140\right) +$$

$$\left(\frac{NaCl}{C} \times .170\right) + \left(\frac{Na_2SO_4}{C} \times .100\right) + \left(\frac{\text{Organic "S"}}{C} \times .195\right) \tag{5}$$

This equation was tested against the precipitation tests performed and gave good results.

Other Data from Tests

During the digestion tests with various levels of the different salts added to pure caustic, it was noticed the percent of MEA extracted increased sharply as sodium carbonate was added to the pure caustic. Lime was present in the digests and is commonly used with Jamaican bauxite for conversion of goethite iron mineral to hematite with subsequent extraction of any alumina in the goethite. The muds from the various digests were examined by x-ray diffraction and it was found the sodium carbonate present in the digest liquor significantly improved conversion of goethite to hematite over pure caustic. Figure 10 shows the increase in goethite conversion from the various digests. It has been previously reported that sulfate and chloride improve goethite to hematite conversion (2), but our data suggests sodium carbonate is even more effective. Figure 11 shows the extraction improvement in alumina obtained as the salts present improved goethite conversion.
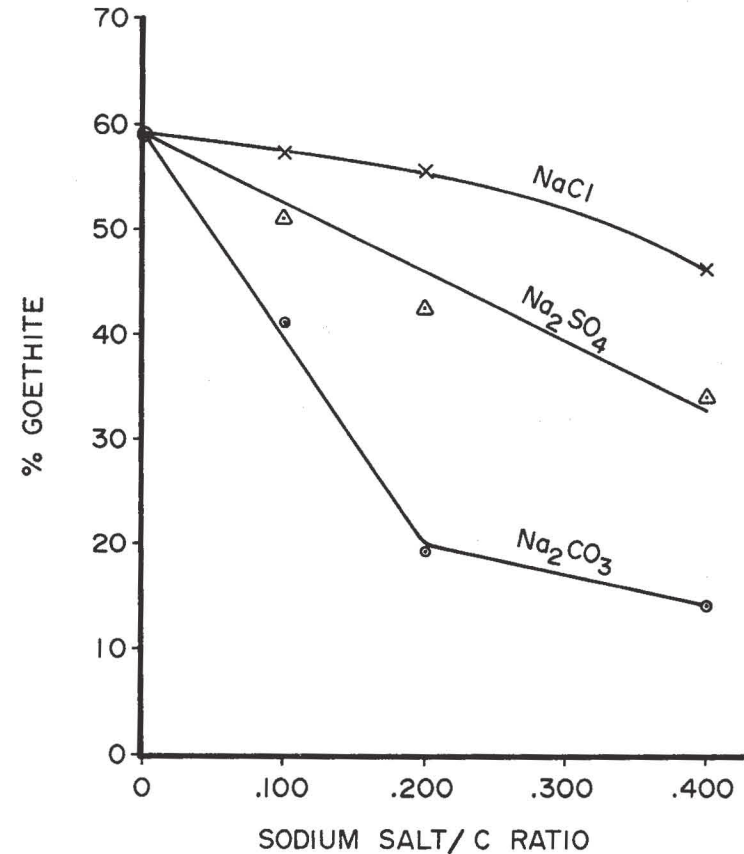

Figure 10 - Effect of added salts on goethite to hematite conversion in digestion.
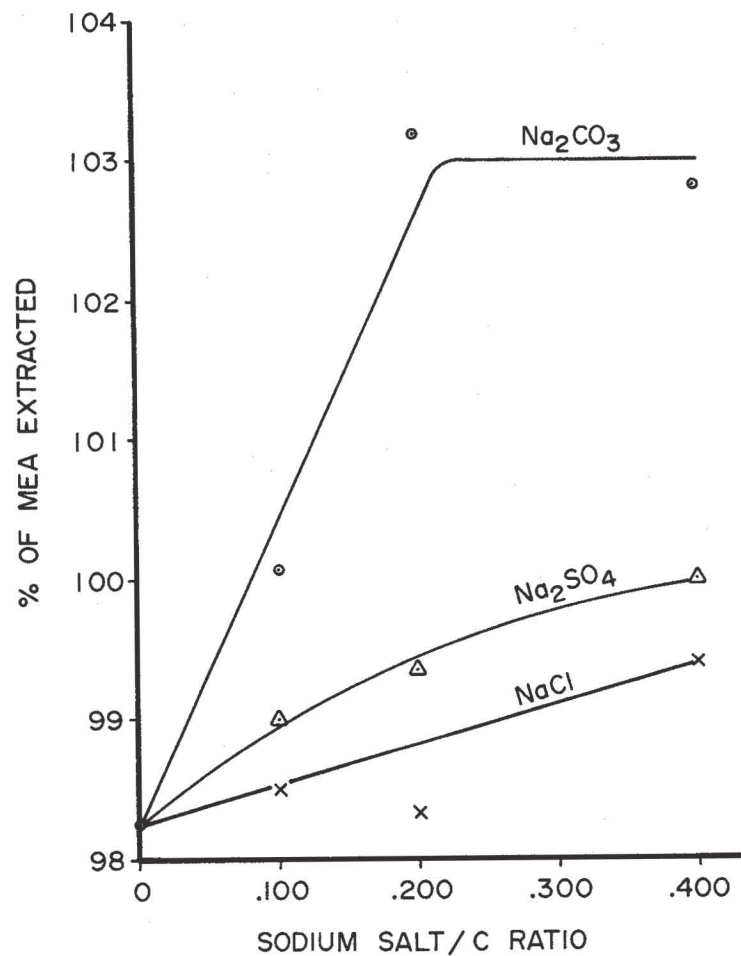
Figure 11 - Effect of added salts on alumina extraction due to goethite conversion.

Conclusions

Impurities present in Bayer liquor resulted not only in higher A/C ratios in precipitation but also in the ability to digest bauxite at higher A/C ratios offsetting to some degree the alumina losses they may cause in the precipitation of alumina. Of the four impurities tested, the organic salts present in the alumina plant liquor can result in the greatest losses of production since they increased precipitator final A/C ratio the most, but did not increase solubility of alumina in digestion.

The impurities also were shown to play an important role in the conversion of goethite to hematite and alumina extraction.

References

(1) T. G. Pearson, "The Chemical Background of the Aluminum Industry," pp. 9, 29, 30, Lectures Monographs and Reports, No. 3, 1955, The Royal Institute of Chemistry.

(2) K. Solymar, U.S. Patent 3,944,648; March 16, 1976.