

# INTERFERENCE EFFECTS OF IMPURITIES ON THE CRITICAL OXALATE CONCENTRATION

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## ABSTRACT

Impurities in the sodium aluminate liquor are mainly dependant on factors like bauxite quality and the technology adopted for making alumina. Effects of impurities on the quality of product, although known in general vary from plant to plant depending on the process parameters maintained and bauxite quality charged. Out of different impurities, oxalic carbon is the most dangerous one which is detrimental to product quality and yield. In the present investigation efforts have been made to study the interference effects of mineral carbonate, organic and oxalic carbon on the critical oxalate concentration of sodium aluminate liquor with respect to temperature, concentration and alumina to caustic ratio. Effect of lime on these impurities is also highlighted in the paper as a step for maintaining higher liquor causticity.

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## **1.0 INTRODUCTION**

Major amount of impurities enter through bauxite in an alumina plant. Out of all impurities, organics especially oxalic carbon and mineral carbonates play the major role in affecting process efficiency as well as product quality. The effects of these impurities also depend on the technology adopted and bauxite quality.

In recent years much work has been centred on the effect of various impurities on process efficiency with reference to organics (Teas et al., 1980). A considerable amount of work on impurities effect and control has been reported during 1990 International Quality Workshop at Perth, Australia. Oxalate has been found to effect the crystal growth during precipitation (Power et al., 1990). Various disposal methods for oxalates removal like lime treatment, UV-radiation, oxidation, microbial digestion etc. have been worked out at the Arvida Research and Development centre, Canada (Kwat, 1990). It has been reported (Chinloy, 1990), that due to poor solubility of oxalate it can be industrially removed due to its supersaturation at a higher concentration of caustic. However the effects of oxalate and its removal are very much dependent on the plant liquor and the level of impurities in the liquor.

Oxalic carbon solubility depends on various factors like temperature, concentration, alumina supersaturation and also to some extent on the level of organic carbon and mineral carbonate present in the system. Therefore in the present investigation it was intended to study the following aspects with respect to Nalco plant liquor.

- (a) Evaluate the impurities levels and to find their effect on the yield across precipitation (Patra et al., 1993)
- (b) To find the effect of concentration, temperature, alumina supersaturation on the critical oxalate concentration (COC) and also to study the interference effects of organics and mineral carbonate on the COC of oxalate, and ultimately on the quality of product and
- (c) Optimisation of oxalate removal parameters using lime with respect to Nalco plant liquor.

## **2.0 EXPERIMENTAL AND RESULTS**

All the experiments have been carried out at laboratory scale using plant liquor.

### **2.1 Critical Oxalate Concentration (COC)**

This is a test which determines the oxalate concentration at which sodium oxalate would precipitate out in a given condition. In the present study, the initial liquor has been analysed for parameters like concentration, alumina to

caustic ratio, mineral carbonate, organic carbon and oxalate level. The liquor taken for determination of COC contained 170.7 g/l  $\text{Na}_2\text{O}(t)$  and reaction time after all addition was kept for 5hrs. Sodium oxalate was added at 60°C under constant stirring till the oxalate crystal precipitated out. The point of precipitation is the COC of the liquor. Oxalate precipitates out to the level of apparent solubility. The result for one set of experiments is reported in Figure 1. From Figure 1 the COC of oxalate was found to be 0.440% of the  $\text{Na}_2\text{O}(t)$  of 170.7 g/l and on precipitation, the apparent solubility came down to 0.21% of  $\text{Na}_2\text{O}(t)$  which was even lower than the initial oxalate level in the liquor (0.274% of  $\text{Na}_2\text{O}(t)$ ).

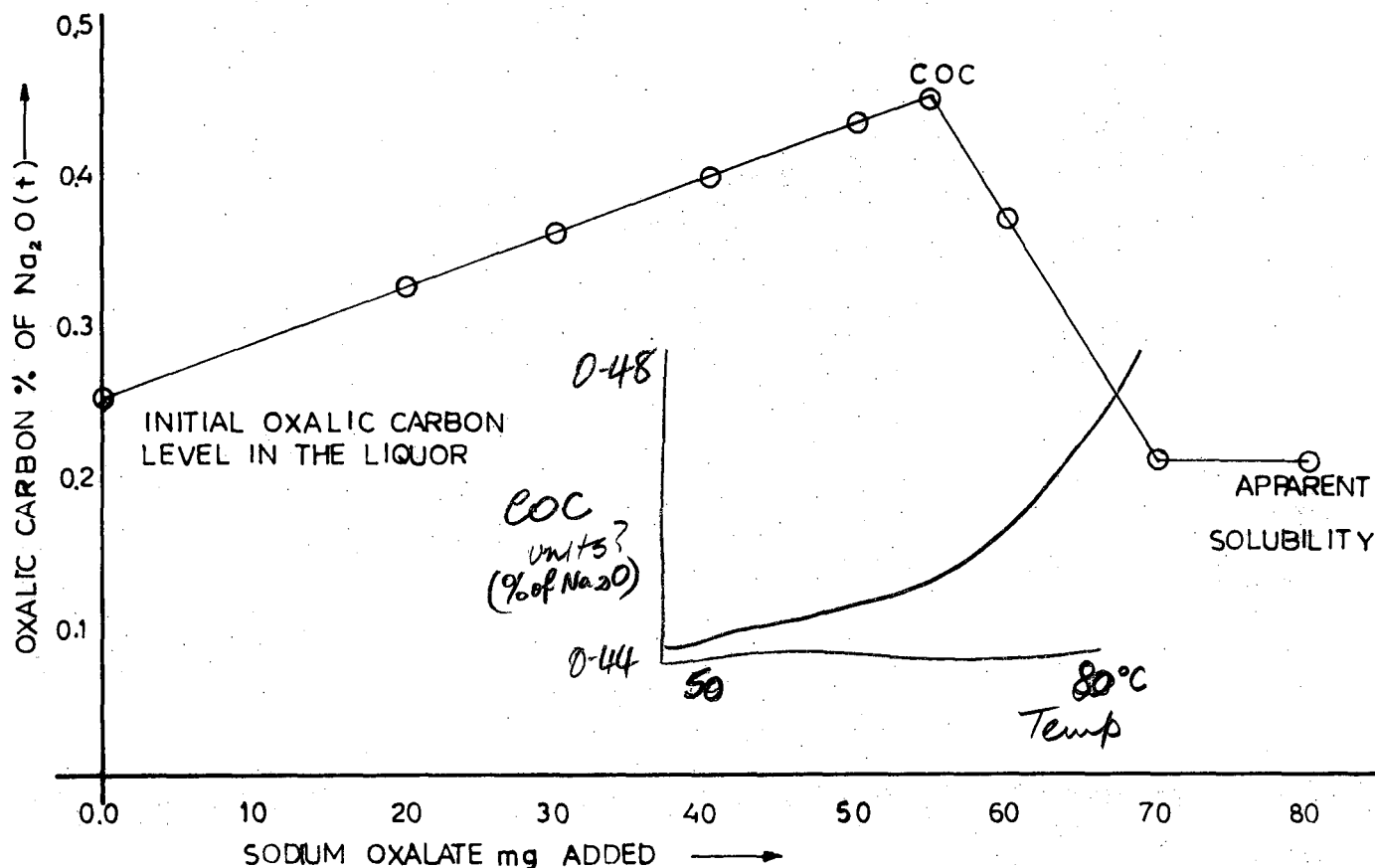


Fig 1. Determination of Critical Oxalate Concentration.

$\text{Na}_2\text{O}(t)=170.7\text{gpl}$ , Mineral Carbonate=11.8% of  $\text{Na}_2\text{O}(t)$ , Initial Oxalic Carbon=0.274% of  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}(c)=0.589$ , Reaction Time=5 hrs, Organic Carbon=2.2% of  $\text{Na}_2\text{O}(t)$ , Temperature=60°C

## 2.2 Effect of Temperature, Concentration and $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}(c)$ on COC

Experiments have been carried out to find the change of COC level with respect to the above mentioned parameters. Temperature has been varied from 50°C to 70°C, keeping all other parameters constant. Similarly soda concentration has been varied from 170 g/l to 290 g/l to establish the effect of soda on COC level, at a given mineral carbonate, organic carbon, temperature and alumina supersaturation. Finally the ratio of  $\text{Al}_2\text{O}_3$  to  $\text{Na}_2\text{O}(c)$  was varied from 0.589 to 1.103 with all other parameters remaining constant to observe the change in the COC of the liquor. These results are reported in Table 1, Table 2 and Table 3 respectively.

**Table 1**  
**Effect of Temperature on COC**

$\text{Na}_2\text{O}(t) = 173.0 \text{ g/l}$ ,  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}(c) = 0.589$ ,  
Mineral carbonate = 11.8% of  $\text{Na}_2\text{O}(t)$ , Organic carbon = 2.1% of  $\text{Na}_2\text{O}(t)$   
Initial oxalic carbon = 0.275% of  $\text{Na}_2\text{O}(t)$ , Organic carbon = 2.1% of  $\text{Na}_2\text{O}(t)$

Temperature °C	$\text{Na}_2\text{O}(t) \text{ g/l}$	COC(% of $\text{Na}_2\text{O}(t)$ ) :
50	173.0	0.438
60	173.0	0.440
65	173.0	0.448
70	173.0	0.462

**Table 2**  
**Effect of soda concentration on COC**

$\text{Al}_2\text{O}_3/\text{Na}_2\text{O}(c) = 0.589$ , Mineral carbonate = 12.0% of  $\text{Na}_2\text{O}(t)$ ,  
Temperature = 60°C, Organic carbon = 2.2% of  $\text{Na}_2\text{O}(t)$ ,  
Oxalic carbon = 0.275% of  $\text{Na}_2\text{O}(t)$

$\text{Na}_2\text{O}(t) \text{ g/l}$	$\text{Na}_2\text{O}(c) \text{ g/l}$	COC(% of $\text{Na}_2\text{O}(t)$ )
170	149.60	0.440
185	162.80	0.435
235	206.80	0.334
290	255.20	0.200

**Table 3**  
**Effect of  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}(c)$  on COC**

Temperature = 60°C, Mineral carbonate = 12.0% of  $\text{Na}_2\text{O}(t)$   
Oxalic carbon = 0.279% of  $\text{Na}_2\text{O}(t)$ , Organic carbon = 2.0% of  $\text{Na}_2\text{O}(t)$

$\text{Al}_2\text{O}_3/\text{Na}_2\text{O}(c)$	$\text{Na}_2\text{O}(c) \text{ g/l}$	COC (% of $\text{Na}_2\text{O}(t)$ )
0.581	147.90	0.442
1.011	148.00	0.443
1.052	146.80	0.441
1.103	147.30	0.443

### 2.3 Interference effect of Mineral carbonate and Organic carbon on the COC

Plant liquor of about 11.6% mineral carbonate was used to find the COC under constant  $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}(c)$  ratio, temperature and organics. Mineral carbonate was then increased from 11.6 to 18% of  $\text{Na}_2\text{O}(t)$  by addition of inorganic carbonate keeping other parameters constant, and the COC values were determined. Results are tabulated in Table 4.

In the second part of the experiment organic carbon was varied along with mineral carbonate, to find the interference effect on the COC of liquor. Other parameters were kept constant. The results are reported in Table 5.

**Table 4**  
**Effect of mineral carbonate on COC**

$\text{Al}_2\text{O}_3/\text{Na}_2\text{O(c)} = 0.586$ , Initial oxalic carbon = 0.257% of  $\text{Na}_2\text{O(t)}$   
Organic carbon = 2.22% of  $\text{Na}_2\text{O(t)}$ , Temperature = 60°C

Mineral carbonate % of $\text{Na}_2\text{O(t)}$	$\text{Na}_2\text{O(c)}$ g/l	COC (% of $\text{Na}_2\text{O(t)}$ )
10.60	153.8	0.442
13.60	153.0	0.420
15.61	152.90	0.398
18.60	152.70	0.390

**Table 5**  
**Interference effect of Mineral carbonate and Organic carbon on COC**

$\text{Al}_2\text{O}_3/\text{Na}_2\text{O(c)} = 0.589$ , Temperature = 60°C,  
Initial oxalic carbon = 0.275% of  $\text{Na}_2\text{O(t)}$ ,  $\text{Na}_2\text{O(c)} = 149.5$  g/l

Organic carbon % of $\text{Na}_2\text{O(t)}$	Mineral carbonate % of $\text{Na}_2\text{O(t)}$	$\text{Na}_2\text{O(t)}$ g/l	COC (% of $\text{Na}_2\text{O(t)}$ )
2.2	12.0	169.89	0.440
2.5	13.0	171.84	0.438
3.5	14.0	173.84	0.425
4.5	15.0	175.86	0.408
6.5	16.0	177.98	0.394
10.5	18.0	182.32	0.391

#### 2.4 Removal of Oxalate using Lime

In order to optimise oxalate precipitation as calcium oxalate, treatment with lime was carried out with different concentrations of plant liquor. Parameters such as concentration, lime dose and temperature were studied. The following experiments have been carried out;

- Lime addition was varied from 5g/l to 25g/l at 45°C, 55°C and 75°C. Results are reported in Table 6.
- Optimum lime addition was made under best temperature (for oxalate reaction) for different concentrations of plant liquor. Results are reported in Table 7.

Oxalate analysis was carried out in the filtrate liquor from all experiments.

**Table 6**  
**Removal of oxalate by treatment with lime at different temperature**  
 $\text{Na}_2\text{O}(t) = 234.8 \text{ g/l}$ , Reaction time = 45 minutes

Lime g/l	Temperature- 45°C		Temperature-55°C		Temperature-75°C	
	Min. $\text{CO}_3$ of % $\text{Na}_2\text{O}(t)$	Oxalic.C % of $\text{Na}_2\text{O}(t)$	Min. $\text{CO}_3$ of % $\text{Na}_2\text{O}(t)$	Oxalic.C % of $\text{Na}_2\text{O}(t)$	Min. $\text{CO}_3$ of % $\text{Na}_2\text{O}(t)$	Oxalic.C % of $\text{Na}_2\text{O}(t)$
0	11.96	0.281	11.96	0.281	11.96	0.281
5	11.94	0.278	11.81	0.278	11.40	0.279
10	11.84	0.275	11.68	0.255	10.93	0.268
15	11.50	0.271	11.40	0.205	9.68	0.256
25	11.20	0.241	10.80	0.190	9.35	0.252

**Table 7**  
**Effect of liquor caustic concentration on removal of oxalate by treatment with lime**  
Temperature = 55°C, Reaction time = 45 min., Lime addition = 25g/l  
Initial mineral carbonate = 11.8% of  $\text{Na}_2\text{O}(t)$ ,  
Initial oxalic carbon = 0.28% of  $\text{Na}_2\text{O}(t)$

Liquor concentration $\text{Na}_2\text{O}(c)$ g/l	After Lime addition		% of Removal (of Oxalate)
	Min.carbonate% of $\text{Na}_2\text{O}(t)$	Oxalic carbon % of $\text{Na}_2\text{O}(t)$	
214	10.80	0.182	35.00
150	10.60	0.190	32.14
85	9.94	0.228	18.57
27	9.60	0.239	14.64

### 3.0 DISCUSSION

Among the various Bayer impurities, the presence of oxalic carbon in the system is quite detrimental to the yield and quality of the product. Oxalic carbon is a part of the total organics which enter the process during bauxite dissolution. The sodium oxalate remains in the circuit and continues to build up till it attains an equilibrium level, which can be determined from the oxalate input and output balance. As oxalate rises to the critical level (COC), it tends to precipitate fine oxalate crystals and thus the concentration of oxalate in liquor falls to the apparent solubility level. This has been found to be 0.21% of  $\text{Na}_2\text{O}(t)$  for Nalco plant liquor. The COC although constant in pure caustic changes with respect to liquor quality under different conditions. From Table 1 it can be seen that the COC of oxalate is enhanced at higher temperature, which can be attributed to the higher solubility of oxalate at higher temperature. The solubility of oxalates inversely related to soda concentration. The normal COC value of 0.440% for 150 g/l came down to 0.2% for 255g/l soda as  $\text{Na}_2\text{O}(c)$  (Table 2). On changing the alumina supersaturation there was not much effect on the COC of liquor (Table 3). Due to causticisation of plant liquor, the mineral carbonate changes in an operating plant. To establish the interaction of mineral carbonate and organic carbon, COC was determined under varied quantities of these two impurities. It can be seen from Table 4 that, on increasing the mineral carbonate alone, there was a fall in the COC of liquor and it looks as though one has to be careful beyond 18% of carbonate

in the liquor. However this again depends on the plant liquor oxalate level as well as precipitation conditions. When organic carbon was increased in the liquor (Table 5), a part of it was converted in to carbonate during the experiments, changing the later. A similar trend of fall in COC level was obtained due to the change in carbonate level. Thus it should be made clear that the increase of organics does not affect the COC, and thus the product quality, unless they contribute to the oxalate pick up in the circuit.

Treatment of lime for removal of calcium oxalate precipitate is not new. This work has tried to optimise the parameters for a particular plant liquor. From Table 6 and Table 7 it can be seen that maximum oxalate separation was achieved using a highly concentrated liquor at a medium temperature of 50-55°C. The reaction kinetics of oxalate and carbonate seem to be reverse with respect to temperature. Higher temperature accelerates the causticisation of carbonate with lime, whereas it increases oxalate solubility in the liquor thereby reducing precipitation of calcium oxalate.

#### 4.0 CONCLUSION

Studies of the influence of various plant parameters on COC levels and of interference effects help to understand the performance of plant liquors. As the plant grows older these studies are essential to control impurities in order to maintain quality of alumina. Effects of oxalates, carbonate and organics under different conditions were established in this investigation for Nalco plant liquor.

Oxalate is the most important impurity in the Bayer liquor for maintaining product quality. As oxalate degrades the quality of product hydrate by precipitating fines, it is essential to identify and optimise a method for separation of oxalate once it is close to the COC level. Treatment of lime was optimised in this investigation for precipitation of calcium oxalate, which can be separated and processed further.

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