EVALUATION OF CHEMICAL ADDITIVES ON OXALATE REMOVAL RATE

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Abstract

Oxalate removal at the Worsley refinery is based on co-precipitation of oxalate with gibbsite, re-dissolution of the sodium oxalate crystals to obtain a sodium oxalate rich solution and re-crystallisation of sodium oxalate by addition of caustic soda solution and oxalate seed. The sodium oxalate crystals are filtered and disposed. Crystallisation of sodium oxalate is sensitive to the presence of other organic species as these impact the removal rate and morphology. These organic species originate from the bauxite and organic based additives dosed to enhance certain processes. Eight different additives used in precipitation, hydrate classification and washing at the Worsley refinery were investigated in laboratory batch tests for their potential impact on sodium oxalate crystallisation rate and stability. It was found that none of the additives had an impact on sodium oxalate stability, but three additives had a significant impact on the crystallisation rate.

1. Introduction

Chemical additives in the Bayer Process are often used to enhance the performance of certain process steps. For example crystal growth modifiers are used to enhance gibbsite agglomeration, defoamer to enhance pumping and cyclone performance and nucleation inhibitor to avoid gibbsite nucleation. Chemical additives can carry over to other parts of the Bayer Process and can have a negative impact. For example, oxalate crystallisation is a process which is sensitive to organic compounds [1,2,3,4]. Before a chemical additive is used in the Worsley refinery, it is tested for its impact on gibbsite precipitation rate, gibbsite particle size distribution and oxalate removal rate. Recent investigation has shown that the applied procedure did not adequately assess the effect of additives on oxalate removal behaviour. A procedure based on simulating the oxalate removal process in a batch reactor in the laboratory was developed.

A chemical additive can affect oxalate removal by forming a complex with the oxalate in solution, which can increase the solubility of oxalate to a higher apparent equilibrium value. Alternatively, an additive can affect the surface activity and crystallisation rate through adsorption on the oxalate surface resulting in surface poisoning and deactivation. These effects will be covered in a procedure determining the oxalate crystallisation rate and equilibrium solubility value.

Chemical additives used in the precipitation and hydrate washing area are evaluated by determining the crystallisation rate and equilibrium value in a laboratory batch reactor. The possible effects of additives on oxalate morphology and filtration rate are outside the scope of these tests.

1.1 Oxalate crystallisation model

The measured changes in oxalate concentrations over time are used to calculate the crystallisation rate and sodium oxalate equilibrium using equation (1).

$$\frac{d(Naox)}{d(t)} = -k \times e^{-Ea/RT} \times SA \times Naox_{apparent} \times \left(\frac{Naox_{t=t} - Naox_{apparent}}{Naox_{apparent}} \right)^{n} \quad (1)$$

Where k is the crystallisation rate ($secLm^{-2}$), SA is the seed surface area (m^2L^{-1}), $Naox_{apparent}$ is the calculated sodium oxalate equilibrium solubility (g L^{-1}) and n is the order of reaction. $Naox_{apparent}$ is $Naox_{equilibrium}$ plus the possible increase in oxalate solubility due to the additive (equation 2):

$$Naox_{apparent} = Naox_{additive} + Naox_{equilibrium} \quad (2)$$

Surface area is assumed to be constant during crystallisation, with plant oxalate cake being used for all test work. The order of reaction is 2.5, as shown in previous test work [5,6].

Crystallisation rate and $Naox_{apparent}$ are determined by fitting the data calculated using equation 1 to the measured data. Data fitting is done for the period 0 to 120 minutes to cover residence times in the tanks. The root mean square (RMS) value is a measure of how good the calculated value fits the measured value. As the crystallisation occurs very rapidly it is difficult to accurately measure the Naox concentration at zero minutes and so this value is calculated from volume and oxalate concentration of the starting liquors.

1.2 Standardised conditions

As the starting conditions of the laboratory tests were not constant and subsequently may affect the crystallisation rate and apparent oxalate solubility, normalised starting conditions were used in equation 3. The standardised starting conditions were Naox at start, surface area at start and $Naox_{equilibrium}$.

$$\frac{d(Naox)}{d(t)} = -k \times e^{-Ea/RT} \times SA \times Naox_{apparent} \times \left(\frac{Naox_{t=t} - Naox_{apparent}}{Naox_{apparent}} \right)^{n} \quad (3)$$

1.3 Area three and four additives.

The additives used in the precipitation and hydrate classification and washing areas included:

- Additive 1 - Crystal Growth Modifier (CGM).
- Additive 2 – Flocculant for hydrate
- Additive 3 – Flocculant for hydrate
- Additive 4 – Nucleation inhibitor
- Additive 5 – Antifoam
- Additive 6 – Dewatering aid
- Additive 7 – Defoamer
- Additive 8 - Dewatering aid

1.4 Oxalate removal in the plant

The oxalate removal system modelled in this test consists of:

1. Co-precipitation of sodium oxalate with gibbsite,
2. Re-dissolution of the sodium oxalate crystal to give a sodium oxalate rich solution,
3. Mixing oxalate rich solution with sodium rich solution in a controlled manner to form sodium oxalate crystals of the right size and morphology. The crystallisation rate is controlled by the soda concentration (A/C/S analysis) and temperature. The system is seeded with sodium oxalate to enhance the crystallisation rate and filtration rate. The crystallisation time is approximately 20 minutes.

2. Procedure

To negate any affects on oxalate crystallisation due to poisons in the oxalate rich stream, a synthetic oxalate-rich solution was used in all tests.

2.1 Raw Materials

- The sodium rich solution is evaporated spent liquor, which is pressure filtered using a 0.2µm membrane as soon as possible after collection.
- Plant oxalate cake. Plant oxalate cake is analysed for its moisture, solid sodium oxalate and insoluble solids content.
- The oxalate rich solution is prepared by dissolving gibbsite (Malakoff Pty Ltd) and analytical grade sodium hydroxide, sodium carbonate, sodium sulphate, sodium oxalate and sodium chloride in water.
- Plant additives which are used in the precipitation and hydrate filtration area. The dosages for the additives were calculated from plant data averaged from 1st quarter of 2007. A worst case scenario was assumed, where all additives added to the process passed through to the oxalate crystallisers. The doses are summarised in Table 1.

Table 1: Plant additive dosages used for test work

Additive	Dosage additive to lab crystallisers [mL/L]
1	0.042
2	0.031
3[(a)]	0.051
4	8.5
5	0.08
6	0.06
7	0.026
8	0.048

(a) Additive 3 is diluted in the plant before being added to the lab crystalliser tank

2.2 Analytical procedures

Alumina (A), Caustic (C) and Soda(S) - (A/C/S)
The A/C/S was analysed with the method as described in AQW 1996[7].

Sulphate/Oxalate
Sulphate and oxalate were analysed with a method based on Ion Chromatography (IC). The relative standard deviation of the method is 4.3%.

2.3 Test conditions

Tests were carried out in a batch crystalliser using the following target conditions:

- Temperature - 65°C
- Stirring - 800 rpm
- S_{target} was 220 g/L after mixing
- Oxalate seed concentration was 150g/L of plant oxalate cake (wet).
- Test volume was approximately one litre.

2.4 Crystallisation Rate Test

- The oxalate and sodium rich solutions were pre-heated separately to 65°C.
- The required mass of plant additive was weighed onto the lid of the bottle with the oxalate rich solution.
- Just before the start of the test, plant oxalate cake was added to the preheated oxalate rich solution and vigorously shaken.
- The oxalate and sodium rich solutions were mixed in the batch reactor to achieve the target soda concentration. Frequent samples were taken and analysed for oxalate content over a two hour period. The sample taken as close as possible to t=0 minutes was also analysed for A/C/S.
- At the completion of a test approximately 200 mL of test slurry was used for oxalate solubility determination. Fifty grams of synthetic sodium oxalate was added to the slurry which was then cooled to room temperature for 24 hours. The slurry was reheated to 65°C and after 5 days analysed for oxalate content, giving $Naox_{equilibrum}$.

3. Results and Discussion

3.1 Control test

The test work was conducted over a period of several months. To ensure that the variation of the procedure was reproducible over the time period, a control test was run each time new raw materials were collected or prepared.

3.1.1 Crystallisation rates

The crystallisation rate and the apparent solubility were determined for each control using fitted data calculated from equation 1, section 1.1 (see Table 2 and Figure 1). These values and the root mean square (RMS) of the fit are summarised in Table 3. The relative standard deviation for Naox analysis in the laboratory is 4.25% resulting in a measurement error of about 0.08 g/L in a measurement of 2.0 g/L. As the RMS of the fitted data is in the same order as the measurement error for Naox analysis, it is considered that the model describes the crystallisation data properly.

Table 2: Experimental data for Control 1 fitted to equation (1)

Control 1		
Seed concentration, gL^{-1}	150	
Order of reaction	2.5	
Rate, min^{-1}	0.826	
RMS	0.07	
$Naox_{apparent}$ gL^{-1}	2.27	
$Naox_{additive}$, gL^{-1}	0.31	
Time, min	Fitted	Measured
0	7.46	7.46
0.25	3.78	3.89
0.5	3.61	3.45
1	3.36	3.37
1.5	3.21	3.20
2	3.11	3.13
3	2.96	2.96
5	2.77	2.80
7	2.69	2.72
10	2.61	2.62
15	2.53	2.52
20	2.49	2.47
30	2.44	2.40
45	2.40	2.34
60	2.38	2.32
90	2.35	2.31
120	2.34	2.26
$Naox_{equilibrium}$		1.96

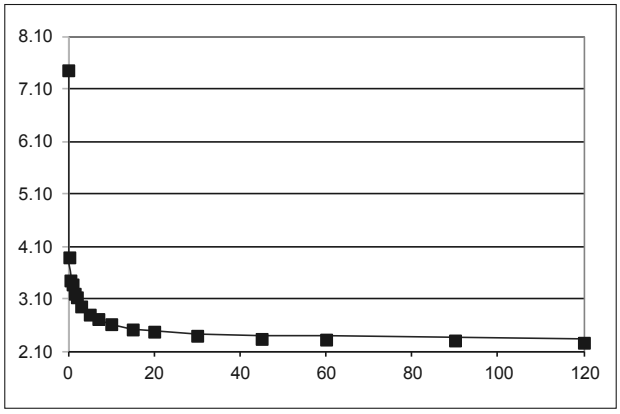

Figure 1: Experimental data for Control 1 fitted to equation (1).

Table 3: Crystallisation rates, $Naox_{equilibrium}$, $Naox_{additive}$, $Naox_{apparent}$ and RMS for control tests, determined from fitting calculated data from equation 1 to measured data for each test.

Control	Cryst. rate k $secLm^{-2}$	$Naox_{equilibrium}$ gL^{-1}	$Naox_{additive}$, gL^{-1}	$Naox_{apparent}$, gL^{-1}	RMS of fit
1	0.826	1.96	0.31	2.27	0.07
2	0.656	1.90	0.22	2.12	0.14
3	0.910	2.02	0.30	2.32	0.03
4	0.689	2.00	0.27	2.27	0.07
5	0.738	2.04	0.26	2.30	0.11

The crystallisation curves using the normalised starting conditions are presented in Figure 2 and Table 4. All crystallisation curves fall within the 95% confidence intervals, indicating that the procedure is reproducible. The average Naox concentration at 20 minutes is 2.62 g/L, with a variation of 0.07 g/L (see Table 4).

Table 4: The Naox concentrations at 20 minutes for each control curve under standardised conditions The $Naox_{equilibrium}$ and Naox concentration at start values are 2.1 g/L and 8.00 g/l respectively.

Control	$Naox_{t=20\ min}$ gL^{-1}
1	2.66
2	2.59
3	2.63
4	2.64
5	2.62

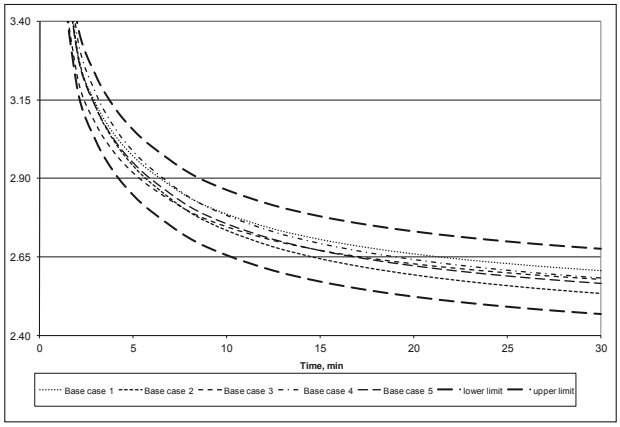

Figure 2: Crystallisation curves constructed from data calculated using equation (3) with normalised starting conditions. The upper and lower limits are the 95% confidence levels for the average of the control values

3.1.2 Oxalate equilibrium

$Naox_{equilibrium}$ is independent of the main sodium source (see Figure3), indicating again that the procedure is reproducible. The average value is 1.98 g/L and has a variance 0.06 g/L smaller than the confidence interval (0.08 g/L, 95% two sided).

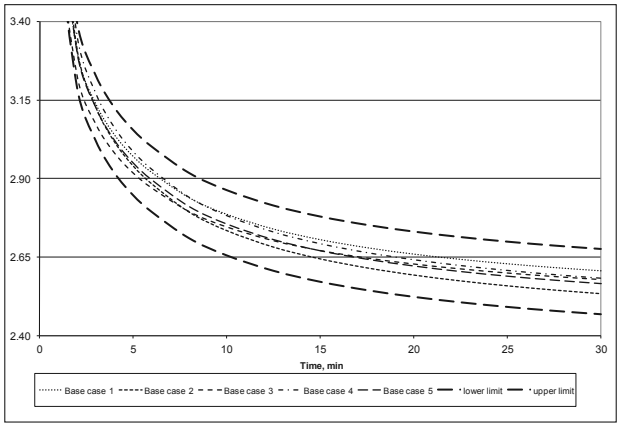

Figure 3: $Naox_{equilibrium}$ values for each control plotted against S concentrations at the time the Naox equilibrium value was measured

Comparison of crystallisation rates and $Naox_{equilibrium}$ for the control tests shows that the reproducibility is set by the analysis of sodium oxalate. It also shows that tests are independent of the raw materials collected and prepared at different times.

3.2 Effect of additives on oxalate removal

3.2.1 Crystallisation Rates

To determine the effect of the plant additives on the oxalate crystallisation rate, crystallisation curves were constructed as outlined in section 3.1.1.

The crystallisation rate and the apparent solubility were determined for each additive test using fitted data calculated from equation 1. These values and the RMS of the fit are summarised in Table 5. The RMS of the fit for all tests is in the same order as the measurement error for Naox analysis in the laboratory, indicating that the fit is good for all tests.

Table 5: Crystallisation rates, $Naox_{equilibrium}$, $Naox_{additive,}$ $Naox_{apparent}$ and RMS for control tests and additives, determined from fitting calculated data from equation 1 to measured data for each test.

Additive	Cryst. Rate k $secL m^{-2}$	$Naox_{equilibrium}$ gL^{-1}	$Naox_{additive}$ gL^{-1}	$Naox_{apparent}$ gL^{-1}	RMS of fit
Control average	0.764	1.98	0.27	2.25	0.08
1	1.030	2.03	0.43	2.46	0.04
2	0.872	2.01	0.31	2.32	0.05
3	0.899	2.03	0.31	2.34	0.04
4	0.740	2.04	0.34	2.38	0.05
5	0.867	2.05	0.30	2.35	0.07
6	1.018	1.95	0.38	2.33	0.05
7	1.030	2.05	0.48	2.53	0.06
8	0.969	2.03	0.42	2.45	0.04

Crystallisation rate k and $Naox_{apparent}$ values from Table 5 are used to construct crystallisation curves for comparison of the additive tests with the control average, under standard conditions. The Naox concentration at 20 minutes for each test under standardised conditions is listed in Table 6.

Table 6: Calculated Naox concentrations at 20 minutes for each test under standardised conditions. The $Naox_{equilibrium}$ and Naox concentration at start are set the same in each case so the results can be compared. Their values are 2.1 g/L and 8.00 g/l respectively.

Additive	$Naox_{t=20\ min}$ gL^{-1}	$\Delta Naox_{t=20\ min}$ control minus additive gL^{-1}
Control average	2.63	
1	2.75	0.12
2	2.65	0.02
3	2.71	0.08
4	2.64	0.01
5	2.63	0.00
6	2.71	0.08
7	2.81	0.18
8	2.76	0.13

A plant additive is considered to have a significant effect if the crystallisation curve fall outside the 95% confidence levels for the control average. Using this criterion it can be seen from Figure 4 that three additives (1, 7 and 8) significantly reduce the crystallisation rate of oxalate and hence the oxalate removal rate. Two of the three additives were suspected to have an effect on oxalate removal rate, showing that this procedure of evaluating the crystallisation rate and apparent solubility is a useful tool.

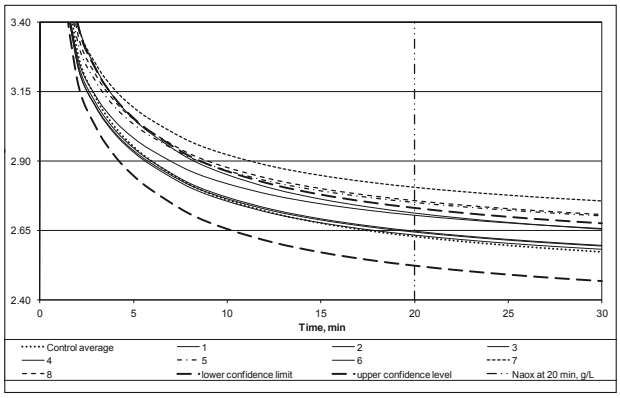

Figure 4: Fitted data using equation (3) with normalised starting conditions. The upper and lower limits are the 95% confidence levels for the average of the control values

Plotting the calculated Naox concentration at 20 minutes for each test and the control average shows that additives 1, 7 and 8 are significantly higher (see Figure 5).

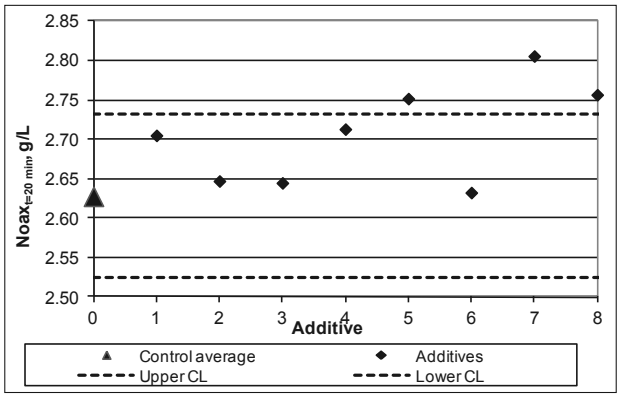

Figure 5: Naox concentration (calculated) at 20 minutes for each additive and the control average. Red solids lines are the confidence interval (CIL) of 95% 2-sided

3.2.2 Oxalate equilibrium.

The effect of plant additives on oxalate solubility can be determined by comparing the $Naox_{equilibrium}$ values for each additive test with the control average (see Figure 5). The control average $Naox_{equilibrium}$ is 1.98, the measurement error of analysis for this value is +/- 0.08 g/L. The $Naox_{equilibrium}$ for the additive tests range between 1.90 – 2.05 g/L, all within the confidence limits indicating that none of additives had a significant effect on oxalate solubility.

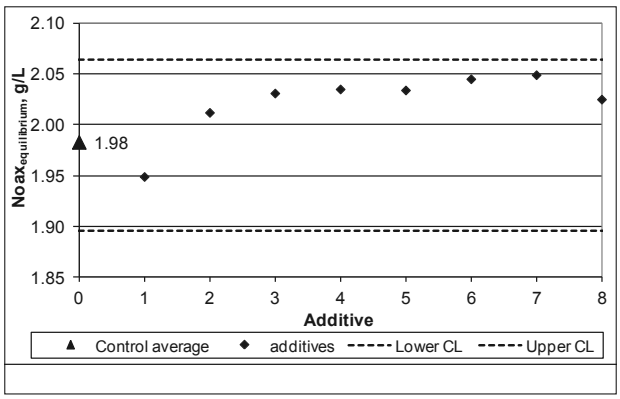

Figure 6: $Naox_{equilibrium}$ values for each additive and the average of the controls.

4. Conclusions

Comparing the oxalate crystallisation rate and stability of the control with that of the plant additives, the following conclusion can be made.

- The procedure described in this paper for evaluating the effect of additives on oxalate behaviour proved to be a useful tool and can assist in preventing the use of chemical additives that effect oxalate removal rate.
- Based on a 95% confidence level for the average of all the control results, three of the eight plant additives had a significant effect on oxalate crystallisation rates at the doses tested.
- The plant additives tested do not have any significant effect on oxalate stability at the doses tested.
- Oxalate solubility and crystallisation rates are not dependent on the liquor composition in the concentration ranges used in this investigation.
- The crystallisation rate test procedure used is reproducible, using different plant liquors, within a 95% confidence level. The standard deviation between control tests is 0.08 g/L which is of the same order as the accepted standard deviation for the Naox analysis procedure used.

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