

A THERMODYNAMICALLY BASED MODEL FOR OXALATE SOLUBILITY IN BAYER LIQUOR

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Abstract

Progress in developing a better understanding of sodium oxalate stability and crystallization behaviour is currently limited by inadequate oxalate solubility models. These models are inadequate because:

- they are specific to one refinery and to a narrow set of conditions
- they are empirically based and hence valid extrapolation is limited
- the oxalate solubility measurements used to develop the models were inadequate.

We have developed a model for sodium oxalate solubility which is based upon fundamental thermodynamic relationships and for which state-of-the-art techniques to measure oxalate solubility were used. The model can be used to predict sodium oxalate solubility over a wide range of conditions and for a wide range of Bayer liquors.

1 INTRODUCTION

Sodium oxalate is an impurity which limits alumina production from most Bayer refineries. Oxalate removal represents a significant fraction of the operating costs of many alumina refineries.

Typically, Bayer liquors are always supersaturated across the range of temperatures and total alkalinities (TA) of most concern, that is, the precipitation regime for hydrate. There is always a critical oxalate concentration (or a critical induction time) at which oxalate crystallization will commence in the hydrate precipitation circuit, often with disastrous consequences.

The oxalate supersaturation increases in either of two ways:

- with an increase in the dissolved oxalate concentration, or
- with a decrease of the equilibrium solubility.

In turn, the equilibrium solubility can be decreased by

- decreasing the temperature, or
- increasing the total sodium ion concentration.

The "safe" oxalate level is usually known only by bitter experience. However, it could easily be predicted if the kinetics of crystallization of sodium oxalate from Bayer liquors were known. The kinetics of crystallization of oxalate require measurements of rates of growth and nucleation, each of which is a function of oxalate supersaturation. Thus prior knowledge of oxalate supersaturation is a necessary requirement to measuring the oxalate crystallisation kinetics. However, it is difficult to quantify the degree of supersaturation as the equilibrium solubility is generally unknown.

If oxalate is crystallized from a Bayer liquor, the oxalate solubility converges towards the equilibrium solubility. The initial crystalli-

zation is rapid but it tails off after about one hour. After, say, three hours an apparent oxalate solubility concentration is reached. However, careful monitoring demonstrates that the oxalate concentration continues to decrease, even after a further week.

It is not sufficient to assume that the apparent oxalate solubility is equal to, or even related to the equilibrium solubility. The apparent solubility is only a measure of the level of stability caused by the presence of other organics. While it can be used to monitor methods for oxalate control,[1] it is totally unsuitable for any kinetic study. The equilibrium oxalate solubility must be used.

However, the equilibrium solubility is very difficult to measure. Approaching equilibrium from a supersaturated solution is very slow and the kinetics are complicated by the presence of other organics. Yet in most cases, this is the only method available to study a real Bayer liquor. The results of a previous study [2] suffer from this shortcoming.

Studying synthetic liquors has the appeal of being more "controllable". The solubility relationship establishes a more rigorous basis for determining the relationship between the concentration of oxalate and sodium ions and temperature. However, it is not this straightforward since solubility relationship is a function of the activities (not concentrations) of the sodium and oxalate ions.

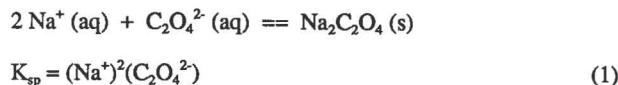
But it is not just these variables which are of interest. Hydroxide, aluminate and carbonate ions are also present in Bayer liquors and play a part in determining sodium activity. In addition there are a number of other inorganic anions and a vast array of organic anions, each of which also plays a part in influencing the sodium ion activity, and thus the oxalate ion activity.

The recent study by Bouzat and Phillipponneau [3] comes close to accounting for the influence of the major inorganic anions. However, they do not account for any of the organic anions present in the liquor. These organic species have their own sodium ion contribution and also will impact upon the sodium ion activity. Their study also suffers from the shortcoming of measuring equilibrium solubility in an already supersaturated solution. As has already been mentioned, supersaturated solutions of sodium oxalate take a long time to reach equilibrium, even for synthetic liquors. The absence of any measurable change in oxalate concentration with time does not mean that equilibrium has been reached.

Bouzat and Phillipponneau do raise the valid concerns of using ad-hoc statistical modelling to derive a solubility calculation model. However, if the solubility models are sufficiently well-founded, they will indirectly account for interactions between the various species in solution.

2 APPROACH

We have chosen to model the sodium oxalate system as based on a simple K_{sp} relationship:



where the brackets () denote activities, not concentrations.

Using synthetic liquors, we have been able to control the concentrations of all ions of immediate interest. As mentioned above, it is not the ion concentrations which are important, but their activities. This is especially so in a water-deficient system such as Bayer liquor. The impact of other ions on the sodium ion activity is taken into account by including them in the model. The effect of temperature is modelled by an integrated form of the Gibbs-Helmholtz equation.

Although more elaborate theoretical models for complex systems have been developed [4,5], they require many interaction terms (some of which cannot be measured as the organics in Bayer liquor have not been fully identified). Other approaches [3] require ion association constants (which may or may not be known) and which are valid over the temperature range of interest.

3 EXPERIMENTAL

3.1 Measuring Solubilities

Synthetic Liquors The test liquors were prepared using analytical grade reagents, except for $\text{Al}(\text{OH})_3$, where a low soda, low organics aluminium hydrate (Alcoa C31) was used. Equilibrium was achieved by dissolution. Solid A.R. sodium oxalate was added to a test liquor which was then equilibrated in a water bath controlled to within $\pm 0.3^\circ\text{C}$. Although dissolution is generally rapid compared to crystallization, each sample was equilibrated for at least 24 hours. Tests showed that equilibrium was actually attained within 4 hours.

The test liquors were analysed for total caustic (TC), total alkali (TA) and alumina (Al_2O_3) by titration,[6] and oxalate was analysed in duplicate by gas chromatography. The oxalate analysis procedure is accurate within 2.2×10^{-4} mol/l (0.03 g/l) and has a precision (3 standard deviations) of 4.5×10^{-4} mol/l (0.06 g/l).

Plant Liquors Equilibrium solubilities were also measured in liquors from each Alcoa of Australia refinery. The liquors were depleted of oxalate by crystallization with high seed charges of sodium oxalate at low temperature. Although some other organics were also removed, the quantity was less than 0.1 g/l. This is considered to negligible given their predominant impact upon the equilibrium solubility is as a source of sodium ions.

The depleted liquors were diluted and evaporated to a range of TA concentrations (that is, maintaining a constant ratio of all ions). Solid sodium oxalate was dissolved into each depleted liquor as before. The equilibrated liquors were analysed for chloride and sulfate in addition to TC, TA and Al_2O_3 , oxalate and malonate.

3.2 Modelling Oxalate Solubility

Synthetic Liquors The domain of interest was as follows:

Temperature	40 - 70 °C	
NaOH	140 - 250 g/l	(TC, expressed as g/l Na_2CO_3)
Na_2CO_3	30 - 70 g/l	(TA - TC, g/l Na_2CO_3)
$\text{Al}(\text{OH})_3$	45 - 150 g/l	(expressed as g/l Al_2O_3)

NaCl	0 - 30 g/l
Na_2SO_4	0 - 25 g/l
CHOONa	0 - 15 g/l
CH_3COONa	0 - 20 g/l

The logarithmic form of the K_{sp} equation was used as a trial (equation 2), where α_i and β_i are the regression coefficients.

$$\ln([\text{ox}]) = \beta_1 / T + \beta_2 \ln(T) + \beta_3 T + \beta_4 T^2$$

$$+ \beta_5 \ln [\alpha_1 \text{TC} + \alpha_2 \text{CO}_3 + \alpha_3 \text{Al}_2\text{O}_3 + \alpha_4 \text{Cl} + \alpha_5 \text{SO}_4 + \alpha_6 \text{HCOO} + \alpha_7 \text{CH}_3\text{COO}] \quad (2)$$

The oxalate concentration is in mol/l, the temperature is degree Kelvin (K), and the anion concentrations are in g/l of the sodium salt (except TC and Al_2O_3 which are as previously defined). It may be seen that the first part of each equation reflects the temperature contribution. The regression coefficient for each anion is a measure of the sodium ion concentration required for a charge balance, less an ion-pair contribution. We would expect that β_5 should have a value close to 2 (i.e. natural logarithm of the squared term in Equation 1).

The equations of interest were solved by a non-linear least squares procedure (SAS procedure NLIN, Marquardt-Levenberg).

Plant Liquors As mentioned above, a liquor from each refinery was depleted of oxalate and either diluted or evaporated. The TA of the liquors ranged from 40 to 300 g/l, the test temperature ranged from 35 to 71°C. An analysis of one liquor is given below:

TC	207.8 g/l
TA	250.1 g/l
Al_2O_3	84.8 g/l
NaCl	15.6 g/l
Na_2SO_4	22.1 g/l
NaF	1.9 g/l
TOC	26.1 g/l

The plant liquor results were not used in fitting the model. Instead, these results were used as a "confirmatory" data set for the solubility model derived from the synthetic liquor tests. A correlation model for each refinery was developed but these models are only loosely based on thermodynamic considerations.

4 RESULTS

4.1 Synthetic Liquor

Convergence criteria could not be met using Equation 2. Instead, the higher order temperature terms were discarded and three empirical parameters were introduced to account for lack of fit.

The final fitted equation for synthetic liquor is:

$$[\text{ox}] = 134 \times \exp \{ -1166.4 / T_k + 0.5110 \times \ln(T_k) + 7 \cdot 10^{-5} \times T^2 - 1.7252 \times \ln [0.0482 \times \text{TC} + 0.0248 \times \text{CO}_3 - 0.0171 \times \text{Al}_2\text{O}_3 + 0.0540 \times \text{Cl}] \}$$

$$\begin{aligned}
 &+ 0.0214 \times \text{SO}_4 \\
 &+ 0.0464 \times \text{HCOO} \\
 &+ 0.0173 \times \text{CH}_3\text{COO}] \\
 - &8 \cdot 10^{-6} \times (\text{TC} - 100)^2 \\
 + &0.0173 \times (\text{TC} / \text{Al}_2\text{O}_3)^2 \quad (3)
 \end{aligned}$$

where the oxalate concentration is now in g/l of the sodium salt, T_k is the absolute temperature (K), and T is the Celsius temperature ($^{\circ}\text{C}$). It should be noted that the parameters are very highly correlated as might be expected from this type of model.

4.2 Plant Liquors

The plant data have been fitted for the TA regimes of greatest interest (TA 220 - 300 g/l). It should be noted that the plant liquors contain appreciable concentrations of anions not considered in the synthetic liquor model. To accommodate these ions, "reasonable" values for the anion parameters were used. Formate and acetate were dropped as separate terms and were replaced by a ubiquitous total organic carbon (TOC) term. The estimates of the fitting parameters for fluoride and TOC were 0.07 and 0.08 respectively.

After fitting, some of the remaining lack-of-fit was taken up by a constant term for each refinery, that is, the synthetic model over-estimated the equilibrium solubility in plant liquors. However, the corrections were not unreasonable and ranged from 0.0009 to 0.0015 mol/l (0.12 - 0.19 g/l). Although some lack of fit remains, it is estimated to be about 0.0005 mol/l (0.07 g/l), which is comparable to the measurement error.

The success of this model can be judged from Figure 1.

5 APPLICATIONS

5.1 Impact of Temperature and Sodium Ion Concentration

As is readily apparent in Figure 1, increasing the total sodium ion concentration or decreasing the temperature results in a decrease in the equilibrium solubility. Over the temperature range studied, the changes are monotonic. There is no increase in solubility as noted by Bouzat and Phillipponneau suggesting that their observation of increasing oxalate solubility at higher sodium ion concentration is almost certainly an artifact of their oxalate solubility measurement procedure (i.e. approaching equilibrium from a supersaturated as opposed to an undersaturated solution).

5.2 Impact of Hydrate Precipitation

A liquor is slightly de-stabilized with respect to oxalate precipitation by the precipitation of hydrate. At constant temperature and concentrations of all anions except aluminate, the equilibrium solubility is as shown in Figure 2.

However, in a refinery situation, the actual position is much worse because hydrate precipitation is controlled by lowering the temperature down a bank of precipitators. Typically, the temperatures range from about 80°C to 60°C . As noted above, the drop in temperature will further decrease the equilibrium solubility. This correction is shown in Figure 2.

Hydrate precipitation also occurs with a loss in volume as water is removed from solution. This has the added effect of increasing the concentrations of all ions remaining in solution, further decreasing the equilibrium solubility. This additional impact is also shown in Figure 2. The actual oxalate concentration also increases due to the

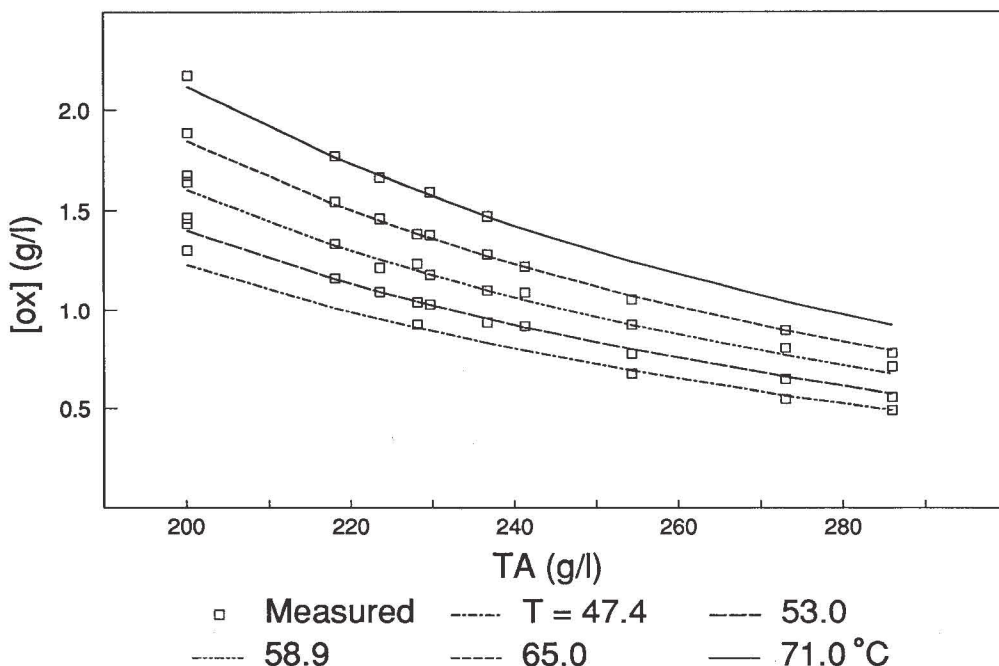


Figure 1: Comparison of measured (plant liquor) and predicted oxalate solubilities as a function of TA at various temperatures.

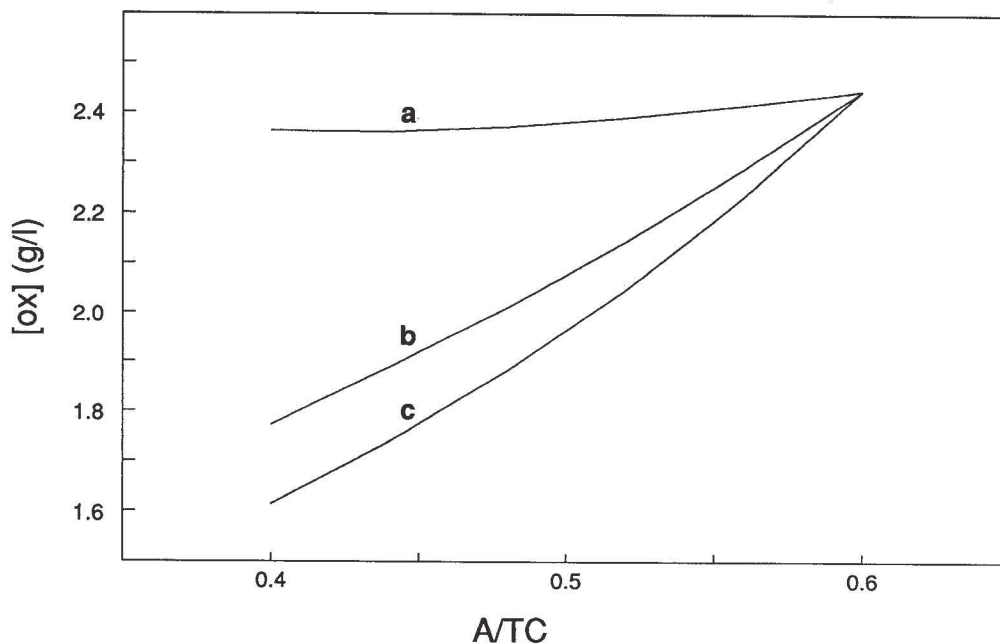


Figure 2: Calculated oxalate solubility as a function of A/TC under conditions: a) constant volume and temperature; b) constant volume, decreasing temperature; c) decreasing temperature and volume.

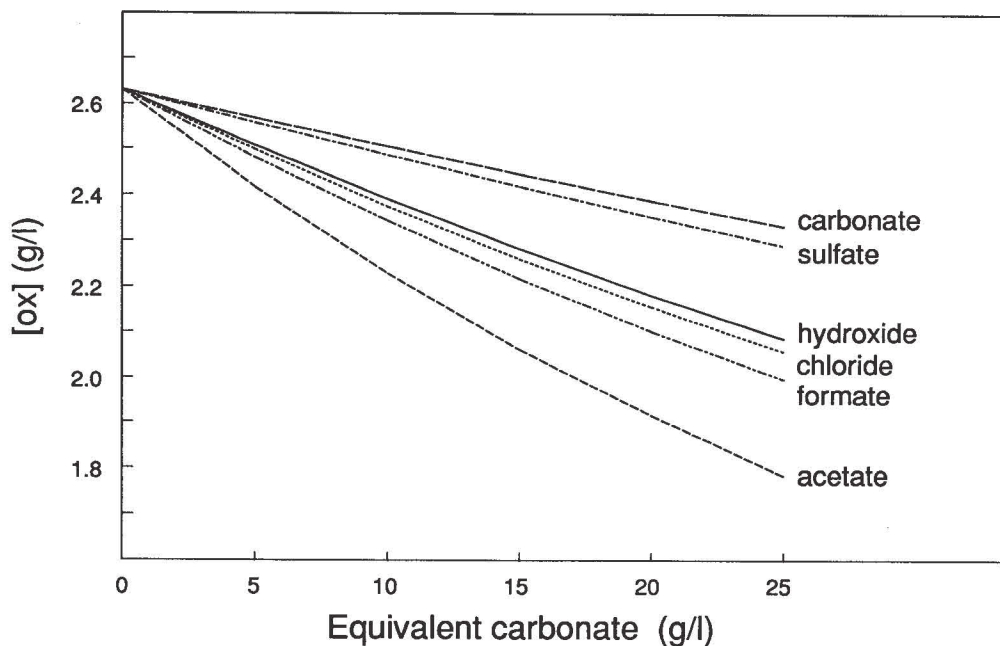


Figure 3: Calculated oxalate solubility as a function of added salt concentrations, adjusted to an equivalent sodium carbonate basis.

volume decrease. Consequently, the oxalate supersaturation rises significantly during the course of hydrate precipitation. As an example, given an initial oxalate concentration of 3.2 g/l in green liquor, the supersaturation ratio will increase from 1.33 to 2.07 in the course of hydrate precipitation.

5.3 Impact of Various Anions

The effect of the various anions present in Bayer liquor upon oxalate solubility is most easily appreciated visually. After adjusting the salt concentrations to an equivalent carbonate basis, the resultant dependencies are shown in Figure 3.

The curves can be explained by ion-pairing. As may be expected carbonate and sulfate have much higher ion-pairing constants than for the monovalent ions.[7] The anions with greater ion-pairing constants will "retain" more sodium. Thus, the free sodium ion concentration will not increase as much as for an anion with a smaller ion-pair constant.

A practical example is that increased chloride concentration should be of greater concern than increased sulfate concentration since the chloride will decrease oxalate solubility more and therefore should also decrease oxalate stability more than sulfate.

5.4 Existing Refinery Implications

Alcoa of Australia refineries practise oxalate removal via a separate side-stream process, the feed to which is evaporated spent liquor. The crystallization reaction approaches an apparent equilibrium concentration relatively quickly. This apparent equilibrium concentration is dependent upon the seed charge and is also dependent upon the TA, with a minimum oxalate concentration occurring at TA values of 230 - 250 g/l. As shown in Figure 4, it is well above the true equilibrium oxalate solubility as measured for a plant liquor.

The solubility model predicts a monotonically decreasing solubility, as is confirmed by approaching the equilibrium by dissolution in a plant liquor. Therefore, there is a loss of oxalate yield (i.e. a difference between the true and apparent oxalate solubilities). This can be ascribed to the effect of other organics within the liquor which inhibit the oxalate crystallization process.

5.5 Projected Refinery Implications

As with most refineries, Alcoa of Australia is attempting to increase alumina yield by decreasing the levels of some of the impurities and

by increasing TC. However, while removing some of the impurities will decrease the total sodium ion concentration, there may not be an attendant increase in oxalate solubility (and therefore oxalate stability). Instead, the gains from decreasing impurities may be offset by the increase in TC. The effect of increasing the liquor TC from 180 to 225 g/l is shown in Figure 5.

This conceptual figure shows that increasing the TC without any removal of impurities will result in a decrease in oxalate solubility. If the TC remains constant and the impurities are reduced, then a significant increase in oxalate solubility results. However, with increased TC and reduced impurities, the oxalate solubility will still be lower, Δ , than its current value. We can deduce that the oxalate stability will also decrease and therefore achieving the target production increase will require either an expanded oxalate removal system or the introduction of new oxalate control technology.

6 FUTURE DEVELOPMENTS

Since the data in synthetic liquor were collected, we have made significant improvements in our analytical capabilities for TC, TA and Al_2O_3 . [8] Thus the opportunity exists to improve the overall accuracy of the fit to the model. Also we are now able to extend the model to cover some of the anions not considered previously, and to improve the representativeness of the model to Bayer liquors.

7 CONCLUSIONS

The model is adequate for predicting the solubility of sodium oxalate in a range of synthetic liquors. Given the complexity of Bayer liquor chemistry, it is unlikely that more sophisticated models will provide better predictors of the solubility of oxalate current, given the present accuracy and precision of oxalate analysis.

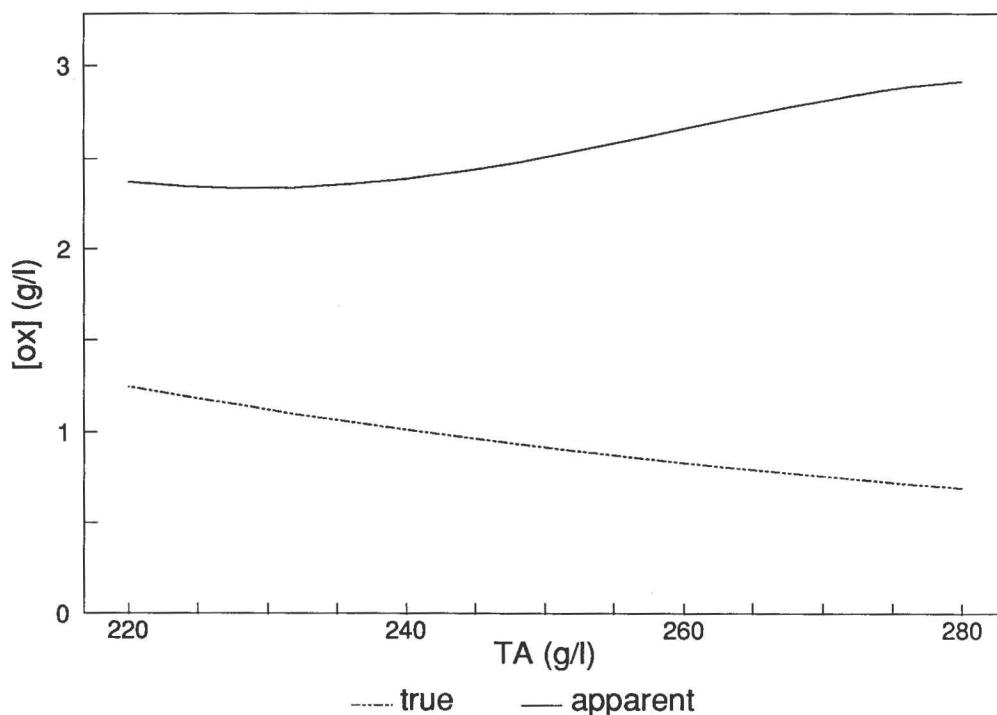


Figure 4: Calculated true and apparent equilibrium oxalate solubilities as a function of TA.

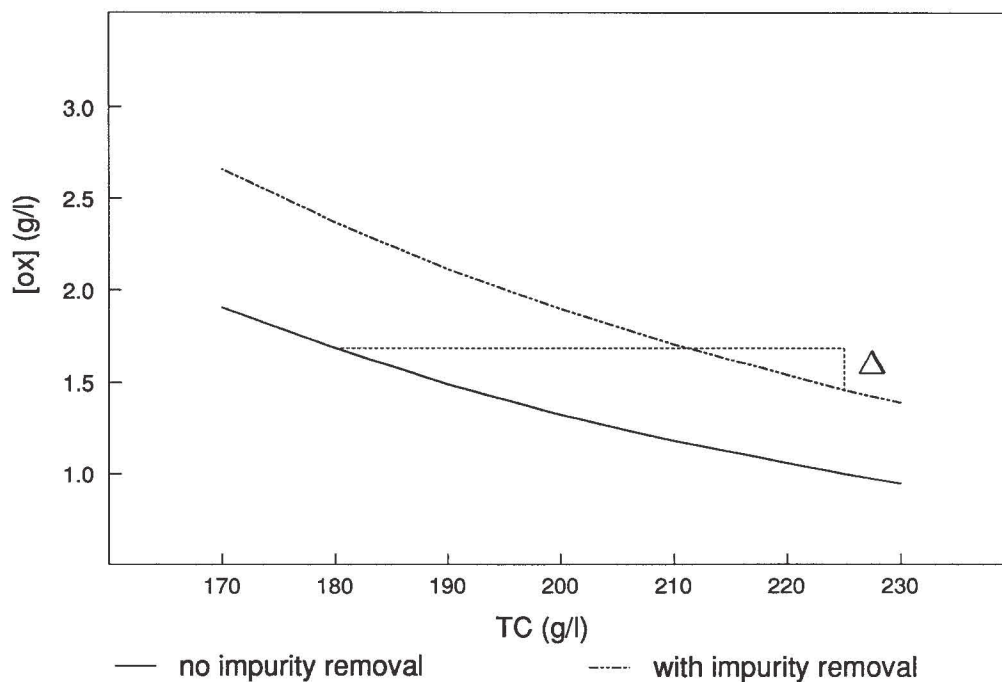


Figure 5: Calculated equilibrium solubility of oxalate as a function of increasing TC at 65°C.

Significantly, the model is deficient with respect to the multitude of organic compounds which are found in Bayer liquors. While it is impractical to include each of these in any model, it is feasible to consider the various sub-classes of organics, such as humates, and treat them as a family. It could be possible to measure their sodium ion contribution using a synthetic liquor and so expand the model.

Obvious care must be taken. We should expect that the suite of organics will differ from refinery to refinery, even for bauxites sourced as closely as are the bauxites of Alcoa of Australia.

With some modifications, the model can adequately predict the oxalate solubility in actual liquors. Thus, the model can be used to assess current plant performance, predict the impact of increases in impurity levels and to forecast changes in oxalate stability which may arise from refinery changes.

8 ACKNOWLEDGEMENTS

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