

FLUORIDE CHEMISTRY IN THE BAYER PROCESS

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Abstract

Sodium fluoride is a common contaminant in many alumina refineries. At the Worsley refinery, fluoride originates from the bauxite, and enters the process during milling and digestion. While the concentration of fluoride in process liquors is generally quite low, it undergoes a range of reactions with other species in the liquor stream that can cause serious problems with refinery operations and product quality. For example, fluoride is able to form a range of sparingly soluble double salts with other common impurities in Bayer liquors, which manifest as scales in evaporators, and under extreme conditions may also co-precipitate with gibbsite in the precipitation circuit. It is therefore surprising that the open literature of the alumina industry contains few references to the impact of fluoride on the Bayer process. In this paper, the results of laboratory investigations that describe the solubility behaviour of kogarkoite (a sodium fluoride sulphate double salt) in Bayer liquors, and the interactions of fluoride with a number of calcium species are presented. We also discuss the extent of fluoride substitution in the aluminate ion in solution, and describe the impact of kogarkoite co-precipitation with gibbsite on the operation of the Worsley refinery. In addition, details of a cost-effective fluoride control process stemming from these studies, applied at Worsley, are given.

1. Introduction

Fluorine forms 0.06% of the Earth's crust by weight [1], ranking it 13th in terms of relative abundance. In bauxites it appears to be equally ubiquitous, with reported concentrations typically between 0.01 and 0.30% [2,3,4,5]. In the Bayer Process, fluoride is extracted into solution during bauxite milling and digestion, where it forms a comparatively minor proportion of the anionic liquor impurity system. While its low concentration ensures it has relatively little effect on the physico-chemical properties of the liquor (such as boiling point elevation and gibbsite solubility), fluoride is capable of a number of more direct interactions with other species in a Bayer system that are detrimental to refinery operations and product quality.

For example, fluoride contaminates product gibbsite, and it has been suggested that it contributes to particle degradation in the transition from gibbsite to alumina [6]. Fluoride also exhibits a strong tendency to form salts that are sparingly soluble in concentrated Bayer liquor, and therefore tend to precipitate as scales on evaporator surfaces. Sodium fluoride is one example [6,7], although the sodium double salts with vanadate, phosphate and arsenate are probably more well-known ($\text{NaF} \cdot 2\text{Na}_3\text{XO}_4 \cdot 19\text{H}_2\text{O}$ where X = V, P, As) [2,6,8,9,10,11]. These latter double salts may be controlled by precipitation from evaporated and/or cooled refinery liquor, although disposal is an issue. Kogarkoite ($\text{NaF} \cdot \text{Na}_2\text{SO}_4$) is perhaps a less familiar double salt in the alumina industry, with few discussions of relevance appearing in the open literature [12,13]. This is surprising given the readiness with which it can precipitate from concentrated Bayer liquors when both fluoride and sulphate are present. At the Worsley refinery, it has been found in evaporator scales and in the solids from a salting-out process. In some circumstances, it can also co-precipitate with gibbsite.

In addition to salting out via evaporation, fluoride can be removed from Bayer liquor through its reaction with lime compounds (CaO or $\text{Ca}(\text{OH})_2$). At Worsley, the fluoride balance is maintained through reactions occurring in the causticiser and lime ageing (filter aid formation) circuits. While it is widely recognised that fluoride is removed in these systems, there is little discussion in the open literature

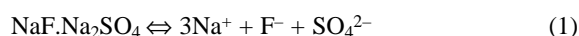
of the mechanism by which this occurs. The removal of fluoride with lime has been attributed to the formation of CaF_2 [7], which is sparingly soluble in dilute neutral solutions.

The input of fluoride and sulphate with bauxite at Worsley is substantial, rendering it especially susceptible to kogarkoite formation. Prompted by this, we investigated several options for fluoride control. Removal via salting out of the double salts mentioned earlier was impractical due to the large volume of liquor requiring treatment via deep evaporation, and issues associated with the separation and disposal of the precipitate. Consequently, we focussed our attention on the interactions of fluoride with lime in Bayer liquors, leading to an efficient fluoride removal process that has been implemented at the Worsley refinery [14]. In this paper we discuss this process, and how the fluoride species likely to be found in Bayer liquors influence both fluoride removal with lime and the composition of the solid phase formed. In addition, we discuss some aspects of kogarkoite chemistry, such as its solubility in Bayer liquor and the impact its co-precipitation with gibbsite can have on refinery operations.

2. Kogarkoite in Bayer Liquor

Refineries that process bauxite containing reasonable levels of extractable fluoride and/or sulphate can be susceptible to kogarkoite formation. Generally, this will occur in the cooler and more concentrated liquor streams of the refinery, making the spent liquor evaporators the most vulnerable site for its formation. Testwork on Worsley refinery liquor has demonstrated that kogarkoite is less soluble than other common salts such as burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$), sodium carbonate, and anhydrous sodium sulphate and will tend to precipitate first. A similar effect has been found by Eremin et. al. [12,13] in synthetic aluminate systems containing Na_2CO_3 , Na_2SO_4 , and NaF. Using a deep evaporator, this property can be used to selectively remove fluoride and sulphate from the liquor stream. However, in spent liquor evaporators, where the kogarkoite supersaturation is comparatively low, it tends to grow as a scale on the heat transfer surfaces, affecting heat transfer efficiency and necessitating more frequent cleaning.

The dissolution equation for kogarkoite is shown in equation (1), and the activities of the component ions are related to kogarkoite solubility according to equation (2). Ideally, kogarkoite precipitation is prevented by controlling the activities of these ions in solution to ensure that their product according to equation (2) does not exceed the K_{sp} for a given temperature.



$$K_{sp} = a_{\text{Na}^+}^3 \cdot a_{\text{F}^-} \cdot a_{\text{SO}_4^{2-}} \quad (2)$$

Where $a_X = \gamma_X \cdot [X]$

and γ_X is the activity coefficient for species X.

The activity coefficient for a particular ion in solution is a function of the solution's ionic strength, which for strong Bayer liquors is sufficiently large that it may be considered invariant. It is sufficient for the purpose of this discussion to relate the solubility of kogarkoite to the concentrations of the component anions, rather than their activities, according to equation (3).

$$K_{sp} \propto [\text{Na}^+]^3 \cdot [\text{F}^-] \cdot [\text{SO}_4^{2-}] \quad (3)$$

Equation (3) indicates that the effect of sulphate and fluoride on solubility is considerably smaller than the effect of sodium, which is not only disproportionately higher in concentration due to the other sodium-bearing species in solution, but is related to the solubility by the cube of its concentration. Consequently, a relatively small decrease in the total soda content of the liquor (through dilution, or even the removal of an unrelated impurity such as sodium carbonate) can substantially decrease the likelihood of kogarkoite precipitation. In practice, however, most refineries will be operated so that the total soda is maintained at the highest practicable value, to maximise production. Where kogarkoite precipitation is a possibility, this value will be dependent upon the fluoride and sulphate concentration, and the aim therefore is to minimise either or both of these. When discussing the effect of these anions on kogarkoite solubility, it is useful to consider the product of their concentrations (the fluoride/sulphate concentration product) rather than each in isolation, as this combines their effect into a single term in equation (3).

Knowledge of the solubility of kogarkoite as a function of the component species and temperature is required to avoid scale formation in the evaporators. If the solubility is exceeded, immediate corrective action will usually require a reduction in the [S] concentration, and possibly an

increase in final precipitator temperatures (although the effect of temperature on kogarkoite solubility is not very pronounced). Either of these situations is undesirable and serves to illustrate the need to operate with a suitable safety margin between the baseline level of the fluoride/sulphate concentration product and the kogarkoite solubility limit in spent liquor evaporator discharge.

A particularly useful tool for determining this safe operating margin is a kogarkoite precipitation breakpoint analysis. In this experiment, a sample of spent liquor from the refinery is evaporated iteratively to produce a set of liquors with a range of concentrations exceeding present kogarkoite solubility limits. Some liquors are then seeded with synthetic kogarkoite crystals, while the remainder are left unseeded, and the entire batch allowed to come to equilibrium with respect to kogarkoite at the temperature of interest. Plotting the product of $[\text{F}^-]$ and $[\text{SO}_4^{2-}]$ against liquor [S] before equilibrium is reached, and overlaying the equivalent data after equilibrium is reached conveniently illustrates zones of varying stability, separated by two "breakpoints", as shown in Figure 1.

Breakpoint one in Figure 1 represents the point at which the solubility of kogarkoite for this liquor and temperature is just exceeded, and separates the stable and metastable zones. Spent liquor evaporators can operate at an [S] below breakpoint one without risk of scaling, while in the metastable zone the absence of kogarkoite seed should preclude kogarkoite formation. Experience has shown however that operating evaporators in the metastable zone is courting danger, as process fluctuations in temperature and liquor flow can easily result in an excursion in liquor [S] past breakpoint two. In this labile or unstable zone, kogarkoite formation is spontaneous, especially at rough flash vessel and pipe walls, and at other Bayer process scales that can provide a substrate for kogarkoite scale growth. With the system then effectively seeded, only a reduction in [S] to the stable zone will prevent further kogarkoite growth.

In the breakpoint test, the equilibrium values of $[\text{F}^-] \times [\text{SO}_4^{2-}]$ reached in the seeded and unseeded systems describe the solubility curve for kogarkoite in this liquor, as Figure 1 illustrates. For initial liquors that are stable with respect to kogarkoite, that is, at [S] values below breakpoint one, kogarkoite seed should dissolve until $[\text{F}^-] \times [\text{SO}_4^{2-}]$ meets the solubility curve. Often however, dissolution is only partial or does not take place at all, even after several days. A similar difficulty in dissolving kogarkoite

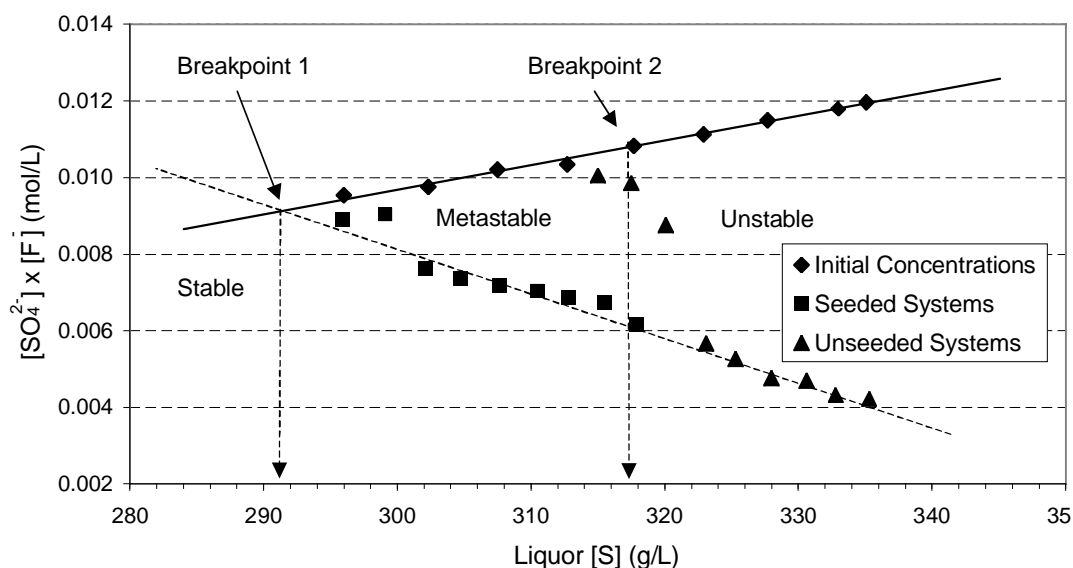


Figure 1 — Breakpoint analysis for a Worsley spent liquor.

scale in the refinery's evaporators has been observed when attempting to do so simply by reducing the evaporation [S] target. Even in pure synthetic Bayer liquors, kogarkoite dissolves very slowly, especially when the solution is close to saturation.

In rare instances, fluctuations in liquor fluoride and sulphate are severe enough to cause instability with respect to kogarkoite in the cooler regions of the precipitation circuit, notably the seed thickeners and seed storage tanks. Again, this is particularly so for a refinery operating with a high baseline fluoride/sulphate concentration product. Drifting into the metastable zone alone may not be sufficient to initiate precipitation, however the addition of a liquor stream containing kogarkoite crystals, such as evaporator discharge, can have damaging consequences. With seed material present, kogarkoite readily precipitates, and is capable of intergrowing with gibbsite and oxalate to form a diffuse three-dimensional network, an example of which is shown in the SEM image in Figure 2. Note that in the image no individual particles of gibbsite are discernable, as they are almost entirely coated in plate-like kogarkoite growth. The shape of a sodium oxalate needle is clearly visible in the upper right section of the image, although this too is almost completely overgrown with kogarkoite.

The overgrowth of gibbsite and sodium oxalate crystals with kogarkoite suggests that both of these compounds can act as seed for kogarkoite growth, although our laboratory tests indicate that the rate is slower than for pure kogarkoite seed. The ability of kogarkoite to grow on the surfaces of both gibbsite and oxalate provides a medium for these particles to attach and intergrow to form massive three-dimensional structures in solution.

In a classification environment, these three-dimensional clusters behave like poorly settling "rafts", reminiscent of the more well known oxalate/gibbsite rafts occasionally formed in the back end of precipitation circuits. If kogarkoite precipitation is substantial, then the settling of solids in a seed thickener can suffer markedly, with a high gibbsite solids loading reporting to the overflow liquor, and low underflow slurry densities. Experience has shown that solids

filtered from such underflow slurries are difficult to wash completely free of kogarkoite, and the potential therefore exists for kogarkoite to be directed to other areas of the precipitation circuit with the gibbsite seed. If the receiving precipitators are metastable with respect to kogarkoite, kogarkoite/gibbsite intergrowth can be initiated throughout the entire precipitation circuit, with serious consequences to product alumina quality.

These consequences include:

1. Generation of excessive gibbsite fines, due essentially to kogarkoite contamination of gibbsite growth surfaces. This induces excessive nucleation, as well as producing weak, poorly structured gibbsite particles prone to fracture in both precipitation and calcination.
2. Excessive impurity contamination of product alumina, stemming from the difficulty experienced in washing product gibbsite completely free of kogarkoite prior to calcination.

If kogarkoite contaminates the precipitation circuit to this extent, corrective action will include raising precipitator temperatures, lowering liquor total sodium concentrations and maximising fluoride and sulphate impurity removal processes. Measures such as these will significantly reduce alumina production, until the material has been re-dissolved and normal white-side operation restored.

3. Fluoride Interactions in Solution

In solution chemistry, the affinity of fluoride and hydroxide anions for the aluminium cation $\text{Al}^{3+}_{(\text{aq})}$ is well known. Both of these anions are characterised as hard Lewis bases, or donor ligands, and form stable complexes with hard Lewis acids like the aluminium cation. In solutions with all three ions present, fluoride and hydroxide compete for ligand bonding sites on the aluminium ion, and factors such as ion concentration and temperature determine which species exist in solution. Sanjuan and Michard [15] (and references there-in) have examined systems of this nature and demonstrate the co-existence of $\text{Al}(\text{OH})_4^-$ and $\text{Al}(\text{OH})_3\text{F}^-$ at low fluoride concentrations and high pH.

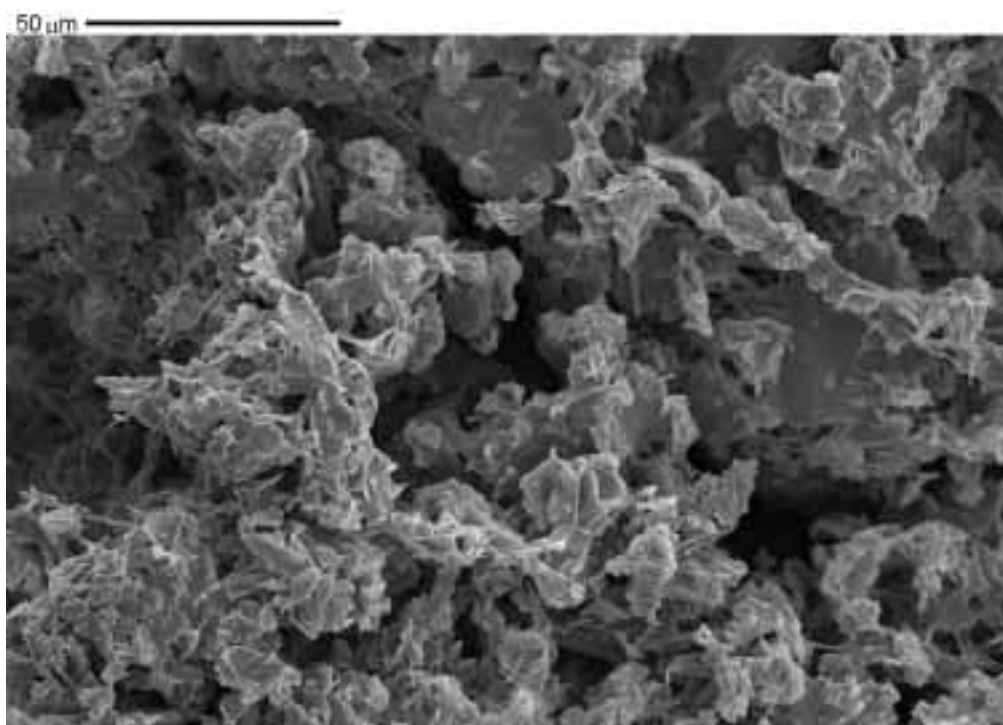
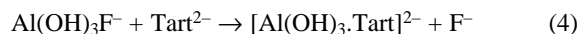


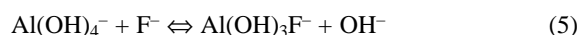
Figure 2 — SEM image of sodium oxalate/gibbsite solids overgrown by kogarkoite.

In dilute Bayer liquors, we have also found some evidence of fluoride substitution for hydroxide in the aluminate anion. This has been achieved by using capillary electrophoresis (or ionophoresis) to analyse solutions both with and without the addition of an aluminate complexing agent. Capillary electrophoresis separates ions in solution according to their size, charge and shape, allowing $F^-_{(aq)}$ to be separated from other fluoro-species. We have found that the presence of a complexing agent, such as tartrate for example, increases the concentration of $F^-_{(aq)}$ measured in a diluted sample of Bayer liquor, due to the release of bound fluoride according to the following equation.



In the analysis of fluoride by fluoride selective electrode, the use of tartrate to eliminate interferences of this nature is well established. Total fluoride measurements at Worsley using both capillary electrophoresis and fluoride selective electrode were in reasonable agreement.

The difference between total and unbound fluoride determinations by capillary electrophoresis indicated that between 20% and 30% of the total fluoride in a diluted Bayer liquor sample is not present as $F^-_{(aq)}$. This suggests an equilibrium exists between the different species of fluoride in solution, described by equation (5).



We believe that this equilibrium is significant even in concentrated Bayer liquors, although we cannot establish this with the simple solution analyses we have used here. We do, however, have other strong supporting evidence from our investigations into the reactions that occur between slaked lime slurry and fluoride in Bayer liquors, detailed in the following section.

4. Fluoride Removal with Lime

In laboratory tests in which tricalcium aluminate ($Ca_3[Al(OH)_6]_2$ — TCA) was formed, fluoride removal from solution was *strongly* influenced by the A/C of the liquor. The relationship is illustrated in Figure 3. In these experiments, liquors of varying A/C were prepared by digesting gibbsite into refinery spent liquor. This ensured that $[Al(OH)_4^-]$ and $[free\ OH^-]$ were the only parameters to vary, while maintaining a constant liquor [C]. The liquor

was preheated to 100°C prior to the addition of hot lime slurry, and total fluoride removal was measured by solution phase analysis on completion of the reaction.

From equation (5), an increase in A/C will shift the equilibrium to the right, increasing $[Al(OH)_3F^-]$ and decreasing $[F^-]$. The positive correlation between liquor A/C and fluoride removal therefore suggests that $Al(OH)_3F^-_{(aq)}$ plays a critical role in the formation of the solid fluoride phase. This is difficult to reconcile with a mechanism involving the formation of CaF_2 , which is expected to be favoured by higher $[F^-]$, and therefore by lower liquor A/C.

X-ray diffraction (XRD) scans of solids recovered from these experiments failed to show any CaF_2 reflections, even at fluoride concentrations of 3.3% w/w in the solid phase, or 6.8% as CaF_2 . To indicate whether XRD peaks should be discernable at this CaF_2 concentration, a scan was performed on some TCA to which synthetic CaF_2 was added to give a total fluoride level of 6.2%. Two strong and well-resolved CaF_2 reflections were found at d-spacings of 3.15 and 1.93 Å in the spiked TCA, each at an I_{rel} in excess of 10% of the strongest TCA reflection. This is a strong indication that crystalline CaF_2 is absent from the solids formed in the systems examined.

In an attempt to discover the nature of the bonding to fluoride in the TCA, X-ray Photoelectron Spectroscopy (XPS) analysis was used [16]. Although it can be used for qualitative and quantitative elemental analysis, this technique is particularly useful in analysing the bonding environment of an element within a compound. The Auger parameter for fluorine in a high-fluorine TCA sample was compared with that for LR Grade BDH CaF_2 to determine if the fluorine bonding environments were equivalent. The conclusion of this work was that the fluorine in the sample is not present as CaF_2 . Unfortunately, comparison of the bond energies with a range of analogous compounds was unsuccessful in identifying the nature of fluoride bonding within the solid's structure.

The role of $Al(OH)_3F^-$ in fluoride removal becomes clear when considering the potential reactions this anion can undergo with lime. In the TCA formation system, $Ca(OH)_2$ rapidly reacts with $Al(OH)_4^-$ in solution to form the hemiacarbonate type hydrocalumite [17], according to equation (6).

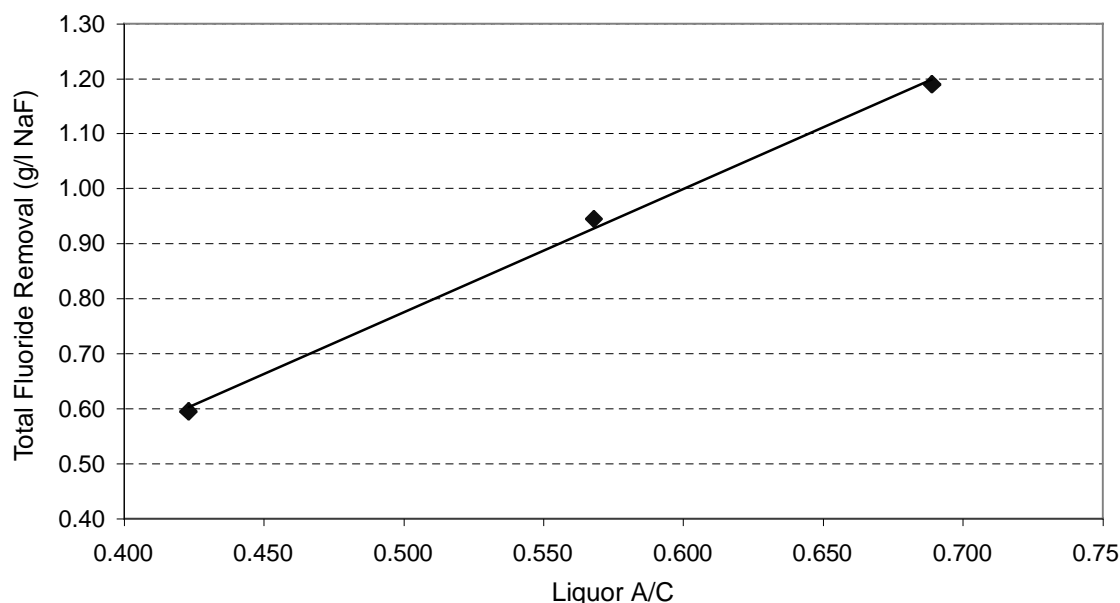
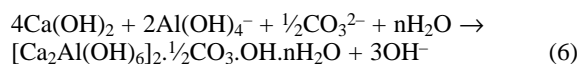
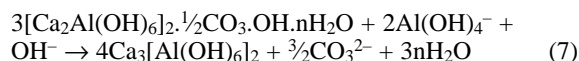


Figure 3 — Effect of reactant liquor A/C on fluoride removal during a typical TCA formation reaction.



The somewhat slower transition of hydrocalumite to TCA then follows, described by equation (7).



We initially suspected that $\text{Al}(\text{OH})_3\text{F}^-$ was capable of being substituted for $\text{Al}(\text{OH})_4^-$, during the formation of hydrocalumite and that fluoride was retained in the solid phase in the transition to TCA. In addition to the effect of A/C, supporting evidence for the incorporation of fluoride into TCA comes from observations on fluoride removal in causticising systems. It is well known that when causticising Bayer liquor, lime is ultimately consumed by two competing reactions, the formation of 1) CaCO_3 , and 2) TCA. It became apparent that the degree of fluoride removal from solution during causticisation was related directly to the proportion of lime reacting to form TCA. For example, when causticising liquors from the refinery's mud washing circuit using Worsley's causticisation technology [17,18], lime efficiencies of greater than 95% are achieved, but no fluoride is removed from solution. Conversely, performing the same causticisation experiment at a range of lower lime efficiencies, thereby creating a range in levels of TCA formed, produced a proportional response in fluoride removal.

The incorporation of fluoride into the solid phase in this way is also consistent with the inability of XRD to detect a discrete fluoride bearing solid phase, even at relatively high fluoride concentrations. If indeed fluoride is incorporated into TCA, at the highest fluoride concentration achieved in the solid phase during this study (3.3% w/w), the stoichiometry of the solid phase can be written as $\text{Ca}_3\text{Al}_2(\text{OH})_{11.34}\text{F}_{0.66}$. If the location of fluorine atoms in the crystal matrix is random, then at this small degree of fluoride substitution, the separation of crystal planes are unlikely to be altered sufficiently to produce a measurable change in the d-spacings of an x-ray powder diffraction scan.

To better understand the fluoride removal mechanism, fluoride concentration was examined during the transition of $\text{Ca}(\text{OH})_2$ to TCA. Surprisingly, it was found that the formation of hydrocalumite plays very little role in removing fluoride from solution, and it is during the transition from

hydrocalumite to TCA that 90% of the total fluoride removal takes place. This is illustrated by the chart in Figure 4, which shows fluoride removal during the complete transition from lime to TCA. Overlaid on this chart is the change in aluminate concentration in solution during this transition. The large initial reduction in aluminate results from the rapid conversion of lime to hydrocalumite, while the more gradual decrease after five minutes corresponds to the slower conversion of hydrocalumite to TCA, as described by equation (7). Clearly from this chart, fluoride removal parallels TCA formation.

Since the total fluoride concentration in Bayer liquors is typically low, the proportion of aluminate that can be fluoro-substituted will also be low. For example, in Worsley liquor to precipitation, only 1% of the total aluminate can be fluoro-substituted, even if the equilibrium described in equation (2) lies completely to the right (that is, 100% of the fluoride in solution is present as $\text{Al}(\text{OH})_3\text{F}^-$). Indeed, in hydrocalumite, fluoride inclusion is approximately in proportion to the ratio of $[\text{Al}(\text{OH})_3\text{F}^-]$ to $[\text{Al}(\text{OH})_4^-]$ in solution. This is the expected behaviour, and indicates that $\text{Al}(\text{OH})_3\text{F}^-$ is simply statistically distributed within the structure in the same proportions as in solution.

By contrast, fluoride incorporation into TCA is surprisingly high, being found in proportions that are an order of magnitude higher than the ratio in solution, clearly indicating that $\text{Al}(\text{OH})_3\text{F}^-$ is preferred over $\text{Al}(\text{OH})_4^-$ in crystallising TCA. The reasons for this preferential inclusion are not clear at this stage, but it can be inferred that the Gibbs energy of the fluoro-substituted TCA is lower than "normal" TCA.

The situation with gibbsite is different again: The partition co-efficient for fluoride in gibbsite is very low [6]. At Worsley, fluoride incorporation into gibbsite appears to be approximately 0.01% w/w as fluoride. This is more than an order of magnitude lower than that expected from the solution equilibria, and suggests that in the decomposition reaction of $\text{Al}(\text{OH})_3\text{F}^-$, gibbsite crystallisation is favoured by the structural incorporation of hydroxyl ions, and preferentially returns fluoride ions to solution.

Other practical aspects of fluoride removal in TCA formation systems that we have investigated are the effects of the initial total fluoride concentration (reported here as $[\text{NaF}]_0$), and the ratio of reactant liquor volume to lime slurry volume. Each aspect was examined specifically

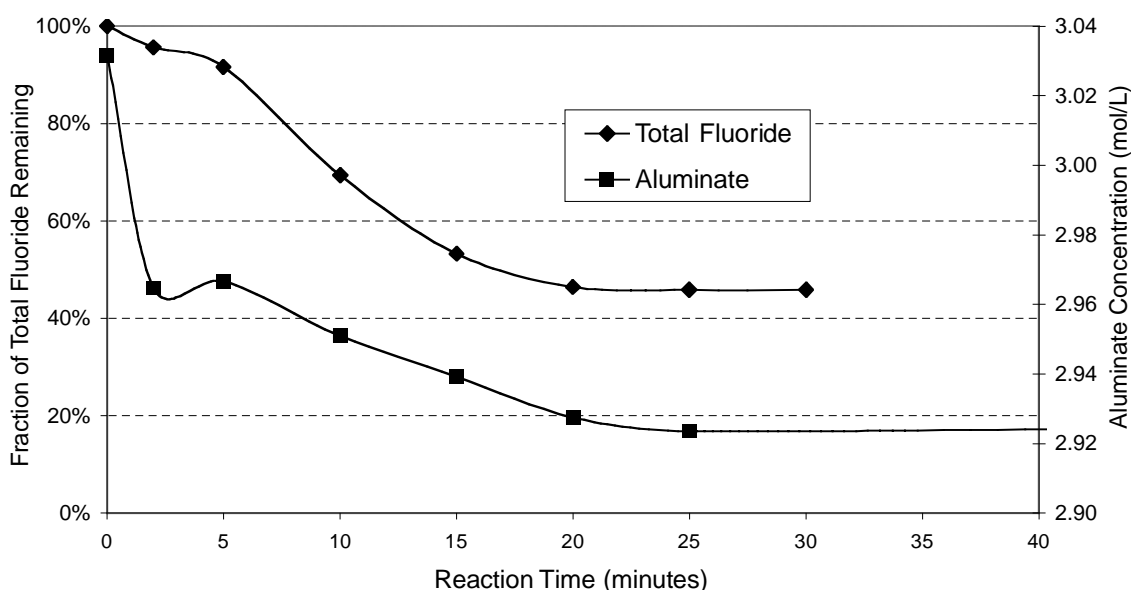


Figure 4 — Changes in total fluoride and aluminate concentrations during the transition from lime to TCA.

through its effect on the lime efficiency of fluoride removal, that is, the moles of fluoride removed per mole of lime consumed. Lime efficiency is an important consideration, particularly for a refinery that relies on the reaction with lime to balance fluoride input with bauxite. In addition to fluoride accumulation in process liquor, inefficient lime use can result in both excessive lime consumption and high alumina losses through surplus TCA formation.

In a series of TCA formation tests in which the initial sodium fluoride concentration, $[\text{NaF}]_0$, was the only parameter varied, we found that the lime efficiency of fluoride removal is directly proportional to $[\text{NaF}]_0$ over the range examined, as illustrated in Figure 5. The test was configured to ensure that fluoride in solution was always in excess. The positive effect of $[\text{NaF}]_0$ is not unexpected and while it does not reveal anything significant about the reaction mechanism, it is consistent with our theory describing the influence of total fluoride concentration on $[\text{Al}(\text{OH})_3\text{F}^-]$ according to equation (5), and the preferred incorporation of $\text{Al}(\text{OH})_3\text{F}^-$ into TCA.

In another series of TCA formation tests, the volume of reactant liquor and $[\text{NaF}]_0$ were held constant while the

volume of lime slurry, and therefore the quantity of $\text{Ca}(\text{OH})_2$ added, was varied. This relationship is illustrated in Figure 6.

Up to ratios of about 20:1, the efficiency of fluoride removal is strongly affected by the ratio of reactant liquor to lime slurry, but returns diminish at higher ratios until there is little improvement beyond 25:1. This relationship is a reflection of differing rates of change in total fluoride concentration during the fluoride removal reaction. As the ratio is increased, the quantity of $\text{Ca}(\text{OH})_2$ added to a fixed volume of liquor decreases, consuming less fluoride in total from solution. However, as the total fluoride concentration remains higher during the course of the fluoride removal reaction, more fluoride per unit of lime is incorporated into the solid phase. This is an extension of the effect of varying $[\text{NaF}]_0$ illustrated previously. The effect diminishes at higher ratios because each successive reduction in $\text{Ca}(\text{OH})_2$ addition has less of an influence on total fluoride concentration.

The critical parameters outlined thus far can be drawn together to describe a process in which the objective is maximum fluoride removal from Bayer liquor at an

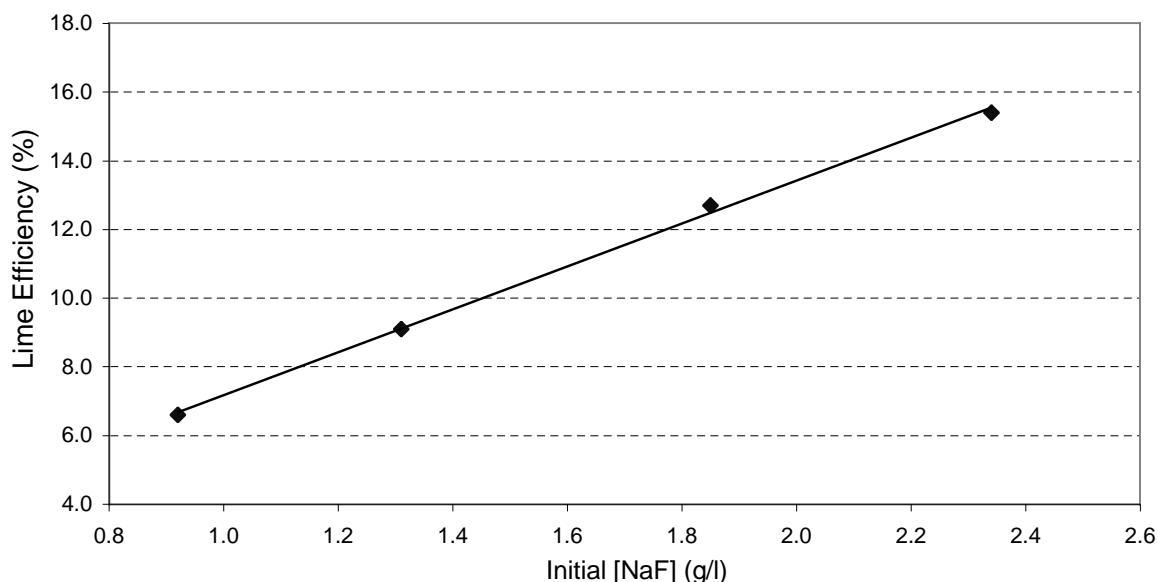


Figure 5 — Effect of $[\text{NaF}]_0$ on the lime efficiency of fluoride removal.



Figure 6 — Effect of varying the ratio of reactant liquor volume to lime added on fluoride removal

optimum lime efficiency. In short, such a process will require; 1) a feed liquor high in total fluoride, 2) a feed liquor high in A/C, and 3) a high ratio of reactant liquor volume to lime slurry volume. Of course the combined slurry must be high enough in temperature (ideally $>100^{\circ}\text{C}$) and allowed sufficient reaction time to ensure complete conversion of $\text{Ca}(\text{OH})_2$ to TCA. Such a process is outlined in more detail in Worsley's impurity removal patent application [14]. This process is capable of being used to remove other anionic impurities in a manner similar to that described here for fluoride, also discussed in the patent application.

The long term stability of TCA after disposal is an important advantage when comparing this process with deep evaporation. Ionic salts like kogarkoite are soluble in water, and it is not sufficient to simply dispose of them with the refinery mud residue, as they will tend to re-dissolve and return to the process through the refinery lake water. The special consideration they require for disposal can also add substantially to the overall cost of their removal from plant liquor. TCA however is very stable, and can be

disposed of through the mud washing circuit and out to the mud lakes without fear of fluoride dissolution.

5. Conclusions

We have examined fluoride's combination with sulphate to form the double salt kogarkoite, and the conditions required for it to precipitate from Bayer liquor. The detrimental consequences to refinery operation of kogarkoite co-precipitation with gibbsite have also been reviewed.

In addition, the removal of fluoride from solution through its reaction with lime was investigated in detail. From these investigations, we conclude that some fluoride in solution substitutes into the aluminate anion, thus forming $\text{Al}(\text{OH})_3\text{F}^-_{(\text{aq})}$ and facilitating the inclusion of fluoride into the crystal matrix of tri-calcium aluminate. All experimental evidence gathered in this study is consistent with the theory that fluoro-substituted TCA is the solid phase responsible for fluoride removal from Bayer liquor, and not CaF_2 . A number of factors that improve the efficiency of fluoride incorporation into TCA have been identified and drawn together to describe an effective fluoride removal process.

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