

## SOLUBILITY CONCENTRATIONS OF ARSENIC, FLUORINE, PHOSPHORUS AND VANADIUM IN EVAPORATED BAYER LIQUOR

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### Abstract

Arsenic, phosphorus and vanadium are extracted into Bayer liquor from bauxite and are accumulated in a refinery's liquor. Fluorine can enter the process with caustic, natural waters or bauxite-associated minerals. The accumulating inventories of these elements sometimes reach critical concentrations at which they may precipitate as scale in certain areas of a Bayer refinery. This precipitation may take the form of sodium fluoride and sodium-fluoro double salts of vanadium, phosphorus and arsenic, amongst other species.

This paper summarises the results of experiments to establish the solubility and the precipitation kinetics of *As*, *F*, *P* and *V* compounds precipitated from Gove process liquor at different temperatures. Results show that the solubility of these impurities generally increases with temperature and is inversely proportional to the caustic (soda) concentration. The collective behaviour of soluble *As*, *F*, *P*, and *V* species will be presented at different temperatures and caustic concentrations. The solubility of these species in weak Bayer liquor when lime is added is also measured and discussed.

### 1. Introduction

In the Bayer process, impurities can adversely affect liquor properties such as viscosity and density, and limit liquor productivity [1,2]. Impurities in process liquor reach steady-state concentrations as the result of a balance between inputs and outputs, and an increase in inputs and/or restriction in outputs naturally results in accumulation. At critical concentrations, some impurities can spontaneously precipitate as scale. Scale can increase the pressure drop in fluid transport systems, impinge on residence time in vessels, reduce heat transfer in heat exchangers and lower equipment availability. These consequences of scaling add to the cost of operating a refinery and are therefore undesirable.

Vanadium (*V*), phosphorus (*P*) and arsenic (*As*) are extracted from bauxite into Bayer liquor. Gove bauxite typically analyses as 0.07% vanadium (as  $V_2O_5$ ) and 0.06% phosphorus (as  $P_2O_5$ ) on a dry basis [3]. Arsenic is not normally analysed in Gove bauxite, but its liquor concentration is typically half that of vanadium. These elements are likely to be present in Bayer liquor as the general forms, vanadate ( $VO_4^{3-}$ ), phosphate ( $PO_4^{3-}$ ) and arsenate ( $AsO_4^{3-}$ ) ions. These elements may exist in several different forms of the oxide anion, depending on pH and other species present.

A number of complexes are also possible, although this would not generally be consistent with the low solubilities observed. These ions form weak electrolytes and at typical Bayer liquor sodium ion concentrations of 5 molar and higher, are probably strongly associated with the sodium ion.

There is some work in the open literature on the solubility of vanadium in Bayer liquors, generally inspired by the potential for commercial extraction, on which several patents have been granted. The "Societe Anonyme Pour L'Industrie De L'Aluminium" explain in a patent in 1958 [4], that the extraction of vanadium from bauxite can be solubility limited, and was about 30% of the total *V* in the case studied. This was confirmed by stripping of liquor vanadium and observing higher vanadium extraction in a subsequent bauxite digest with the stripped liquor. This is an important observation if the vanadium is being extracted for commercial value.

In their patent [5], Shalavina *et al* discuss the determination of solubility isotherms at a range of temperatures

and concentrations in the  $Na_2O-Al_2O_3-V_2O_5-H_2O$  system. They found "the solubility of vanadium pentoxide in sodium aluminate liquors largely depended on the lye (soda) concentration and on the temperature, whereas the aluminium oxide concentration in the starting liquors had practically no effect". They go on to observe that in the absence of fluoride and other impurities, a number of sodium vanadate hydrates precipitate. These phases were identified and the ranges of their existence determined. The precipitation of these phases results in a solid with higher commercial value, due to the high vanadium values and low impurities.

The patent also observes that the solubility of vanadate is not significantly influenced by the introduction of *As* or *P* in this system, nor by variations in the aluminate concentration. It is noted however, that the introduction of fluoride, markedly reduces the solubility of the vanadate, phosphate and arsenate ions. The patent does not go into further detail, although implying a thorough investigation of the system was undertaken.

The patent further discusses studies of the  $Na_2O-Al_2O_3-V_2O_5-(NaF, P_2O_5, As_2O_5, Cr_2O_3)-H_2O$  system, which showed that fluoride had a strong inhibitory effect on vanadate solubility, causing the precipitation of  $2Na_3VO_4 \cdot NaF \cdot 19H_2O$  along with sodium ortho-vanadate. The presence of arsenate and phosphate did not have an effect on vanadate solubility, but coprecipitation of arsenates and phosphates degraded the purity of the vanadate precipitated, which the process aimed to concentrate.

A related publication dealing more thoroughly with the system was not uncovered in our literature search.

Fluorine enters the process with caustic, natural waters, or in minerals associated with bauxite such as fluorospar. The fluoride ( $F^-$ ) ion is known to form very stable complexes at high pH, aluminium ( $AlF_6^{3-}$ ) and silicon ( $SiF_6^{2-}$ ) complexes are thought to be present in Bayer liquor and are likely to account for a high proportion of the fluoride present. Fluoride is also likely to be associated to some extent with the sodium ion.

The precipitation of sodium fluoride, sodium fluoro-vanadate, sodium fluoro-phosphate and sodium fluoro-arsenate are observed in strong liquor at low temperatures

in some Bayer refineries. Process patents [5,6,7] describing the precipitation of these salts under these conditions, have been granted dating back many decades. Other patents refer to this process as a precursor to an electrolytic process for the recovery of Gallium. The precipitation of these salts from evaporated liquor by cooling for impurity removal and for the commercial extraction of vanadium, is known to be practised at least in one refinery.

This case study examines the behaviour of As, F, P, and V compounds at different temperatures, seed charges and caustic concentrations in Gove process liquor at close to ambient temperatures. The solubility concentrations of these impurities were determined at different temperatures and caustic concentrations. Precipitation kinetics were examined to design a removal process for these phases.

A study of the effect of lime addition to a solution of these salts in weak Bayer liquor is also reported. This treatment could allow disposal of the cake with red mud, with a reduced chance of leaching potentially undesirable species into residue lake-water or the surrounding environment.

## 2. Experimental

### 2.1 Kinetic measurements

Portions of process liquor were evaporated to target a range of caustic concentrations. These starting liquors were sampled and analysed. Inorganic salt cake was prepared as seed for the solubility measurements by cooling strong spent liquor to 40°C and allowing a precipitate to form. Masses of this seed estimated to be well in excess of any single constituent's solubility were measured into 1000mL HDPE bottles. Portions of liquor were transferred into bottles and agitated in a rotating water bath at the required temperature. The bottles were sampled every 30 minutes for up to 3 hours. Liquor samples were filtered through 0.45 µm filter membranes, then cooled to room temperature for analysis.

### 2.2 Solubility of As, F, P, and V compounds

Solubility concentrations of As, F, P, and V were measured by allowing the liquors to equilibrate for 2 days at room temperature. This was to allow these salts to drop below their 35°C solubility concentrations, and solubilities at higher temperatures were achieved by dissolving seed as the temperature was progressively raised every 48 hours. It was expected that all the studied precipitates would increase their solubilities with temperature.

### 2.3 Analysis

Phase identification of the precipitate by X-Ray diffraction (XRD) used a pressed-powder technique. The V and P concentrations of liquor and solids were determined by XRF with fused disks. Arsenic was analysed by ICP. After appropriate dilution and acidification of the samples, fluoride was determined by micro distillation, before an ion specific electrode finish. As, F, P and V concentrations are reported as g/L equivalent As<sub>2</sub>O<sub>3</sub>, NaF, P<sub>2</sub>O<sub>5</sub>, and V<sub>2</sub>O<sub>5</sub> respectively.

Liquor caustic concentrations were determined by thermotitrator.

### 2.4 Liquor caustic concentrations

A range of caustic concentrations was achieved by dilution and evaporation of spent process liquor. Liquor caustic concentrations varied between 172-235 g/L (Na<sub>2</sub>O). The caustic/soda ratio of the liquors was constant.

### 2.5 Seed

Seed was prepared by cooling evaporated spent liquor to 40°C and agitating in a rotating water bath overnight before filtering through a 0.45 µm membrane. The filtered solids were displacement washed with a cold 200 g/L NaOH solution, then washed with saturated NaCl solution to minimise dissolution of the highly water soluble cake. The cake was dried and homogenised for use as seed in the experiments.

### 2.6 Temperature

Experiments were conducted at temperatures of 30, 35, 40, 45 and 50°C.

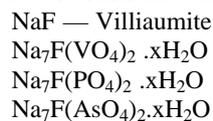
### 2.7 Lime treatment of the precipitate

A pre-measured amount of burnt lime was slaked in 100mL water at 60°C in a rotating water bath for an hour. The precipitate (10g) was added into the samples and conditioned for another hour in the water bath. Solutions were filtered and sampled for impurity analysis. Burnt lime charge varied between 70 and 150g/L.

## 3. Results and Discussions

### 3.1 Composition of the precipitate

The XRD analysis showed the presence of the following crystalline phases. Elemental analysis of the precipitate was consistent with the phase analysis.



### 3.2 Solubility concentrations

Liquor concentrations were measured after 2 days at each of four increasing temperature steps. The results at different temperatures over the range of caustic concentrations are summarised in Figure 1 for vanadium, in Figure 2 for phosphorus, in Figure 3 for arsenic and in Figures 4 for fluorine respectively.

The solubility concentrations of V, P and As indicate that the solubility of all sodium-fluoro double salts of As, P and V increased with increasing temperature and diminished by increasing ionic strength (caustic). Fluorine concentrations showed the same dependence on ionic strength, but unlike behaviour of the other elements investigated, showed an apparently small and contrary dependence on temperature. The increasing temperature steps appeared to result in further precipitation of F.

One explanation for this behaviour may be that the solubility of the NaF phase that is present in the precipitate determines the fluoride concentration. Fluoride concentration entirely reflects the solubility of the solid NaF, while As, P and V concentrations are determined by the solubility of the sodium-fluoro double salts.

Soluble fluoride is in equilibrium with both, NaF and the sodium fluoro double salts phases. Soluble As, P and V are in equilibrium with the sodium double salts only, however, their concentrations also depend on the fluoride concentration that is determined by the NaF solubility. As the solubility of the sodium double salt is increased with temperature the As, P and V concentrations increase due to the dissolution of the double salts. The NaF solubility does not change much with temperature the fluoride concentration remains almost constant via further precipitation of NaF. The solubility of both, NaF and the sodium fluoro double salts phases decreases with increasing ionic strength, all As, F, P and V concentrations decrease.

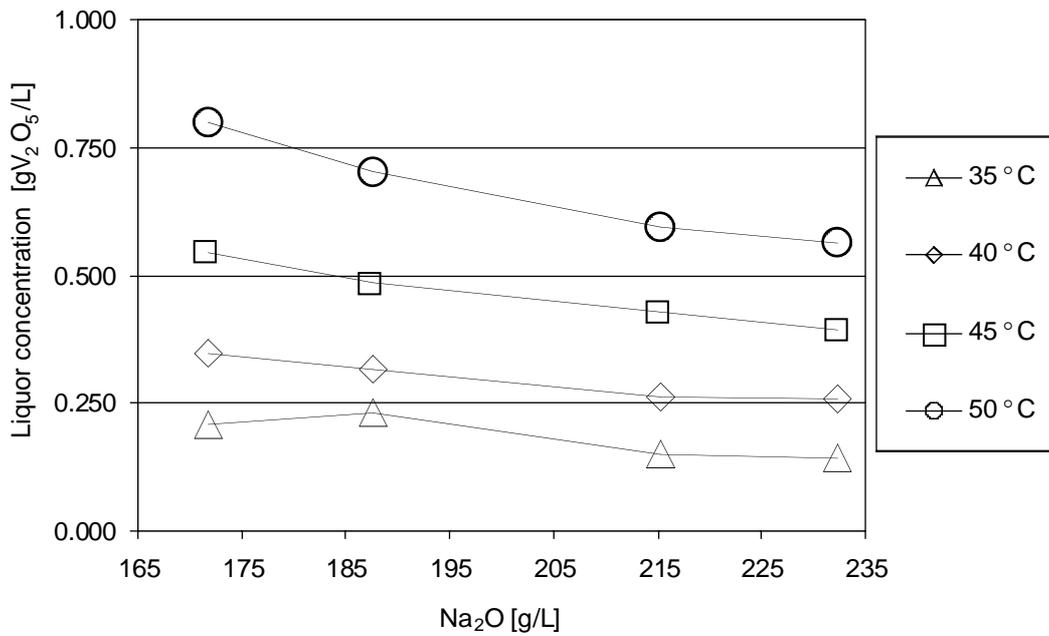


Figure 1 — Solubility concentration of V as the function of caustic and temperature

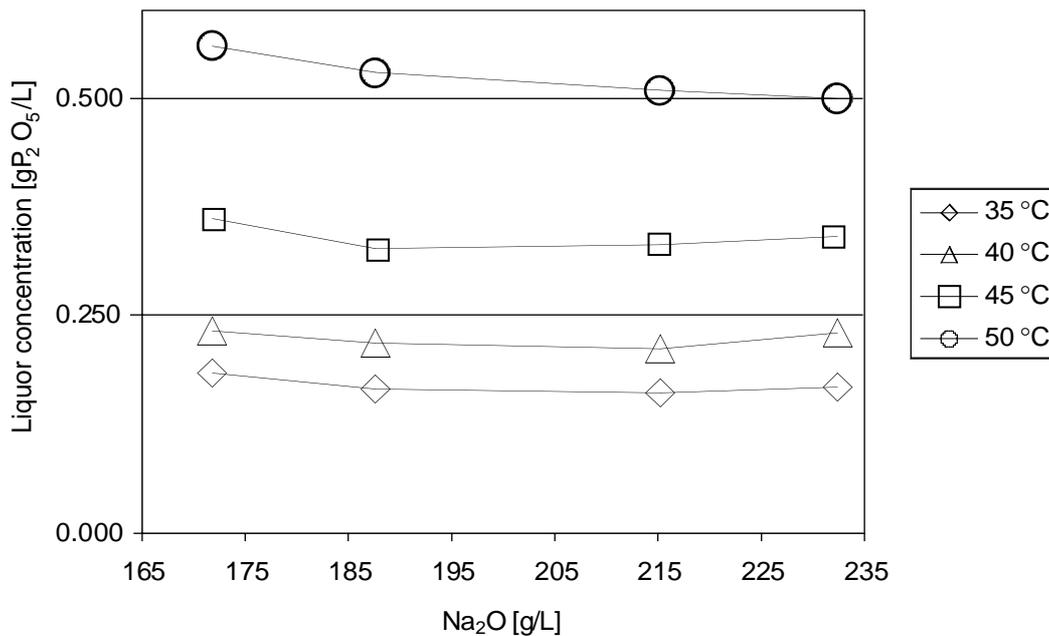


Figure 2 — Solubility concentration of P as the function of caustic and temperature

**3.3 Precipitation from seeded and un-seeded liquors**

The effect of the seed on precipitation kinetics was examined. Results are shown in Table 1.

Table 1 — Precipitation from seeded and un-seeded liquor at 30°C

time [min]	Un-seeded				5g/L seed charge			
	V <sub>2</sub> O <sub>5</sub> [g/L]		P <sub>2</sub> O <sub>5</sub> [g/L]		V <sub>2</sub> O <sub>5</sub> [g/L]		P <sub>2</sub> O <sub>5</sub> [g/L]	
	A	B	A	B				
0	1.02	1.02	0.52	0.52	1.02	1.02	0.52	0.52
180	0.92	0.75	0.48	0.40	0.13	0.12	0.10	0.10

Results show that precipitation of V and P phases occurred in both seeded and un-seeded liquors, but seed had a major effect on kinetics. After 3 hours, more than 80% of the vanadate and phosphate content had precipitated from seeded liquor, while the un-seeded liquors were slow to precipitate.

**3.4 Effect of Seed**

The effect of seed charge was examined using 1, 2 and 5 g/L solid concentration at 30°C. Figure 5 plots the concentration of V vs. time at different seed charges. Figure 6 plots the concentration of P vs. time at different seed charges.

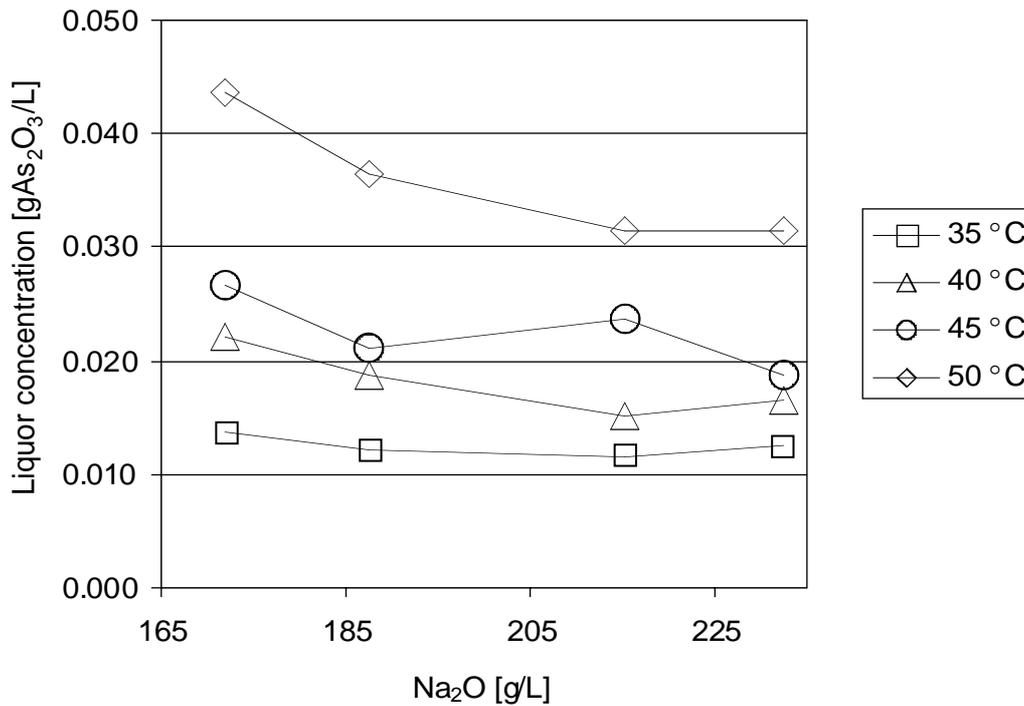


Figure 3 — Solubility concentration of As as the function of caustic and temperature

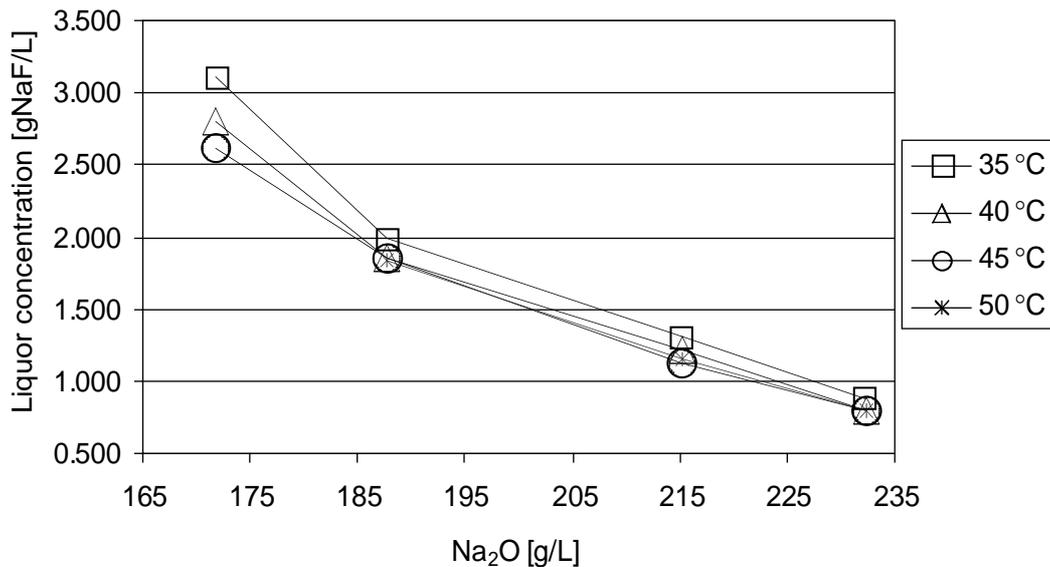


Figure 4 — Solubility concentration of F as the function of caustic concentration and temperature

Results show that the precipitation of V and P was very rapid. Significant yield, greater than 80%, was achieved in the first 30 minutes for all seed charges tested. Under the given conditions, the seed charge had no effect on vanadium precipitation whilst the phosphorus removal was slightly effected.

### 3.5 Disposal of the precipitate

The precipitate is considered potentially hazardous both to the process and the local environment, due to the arsenic, fluoride and vanadium compounds in the cake. These compounds readily dissolve in water, and this mobility makes the secure disposal of the cake more difficult and expensive.

Calcium compounds of some of these anions, such as CaF<sub>2</sub>(fluorite), CaO.As<sub>2</sub>O<sub>5</sub>.3H<sub>2</sub>O (haidingerite) and Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.5H<sub>2</sub>O( calcium pyrophosphate pentahydrate) are known to have low solubility. No reference to calcium vanadates could be found, there is substantial evidence of its intercalation in a series of compounds often referred to as hydrocalumites (calcium aluminium double layered hydroxides) formed when slaked lime (Ca(OH)<sub>2</sub>) is added to Bayer liquor under favourable conditions.

In these tests, the precipitate (including residual strong Bayer liquor), was added to a slaked lime slurry of different solids densities. Concentrations of elements of interest were measured in solutions to determine the effect of the lime on solubility. Results are tabulated in Table 2.

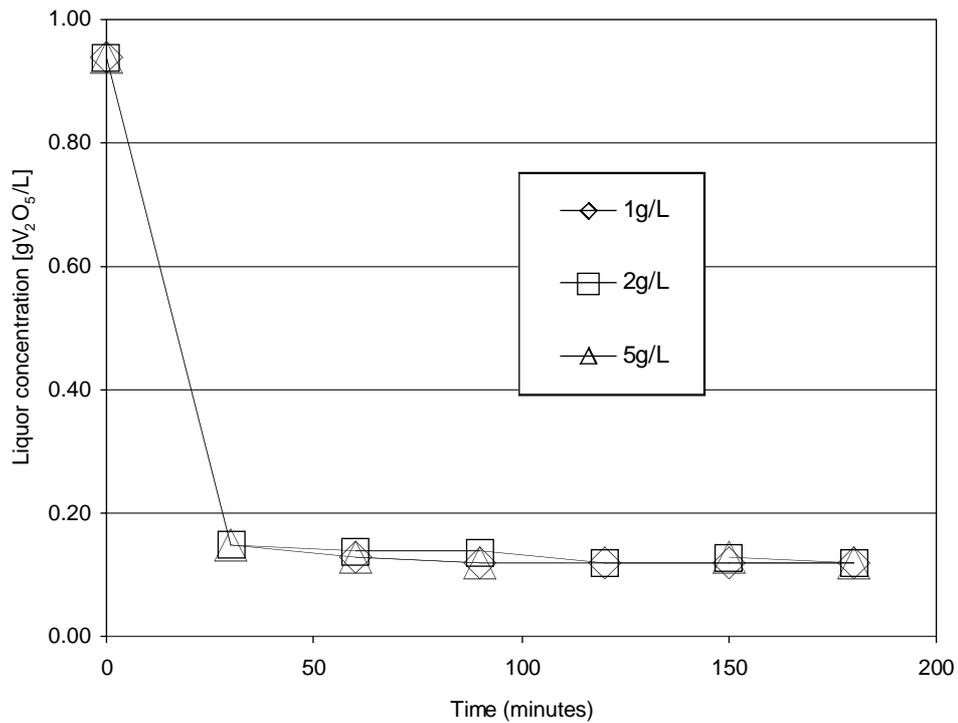


Figure 5 — Kinetics of V precipitation at different seed charges at 30°C

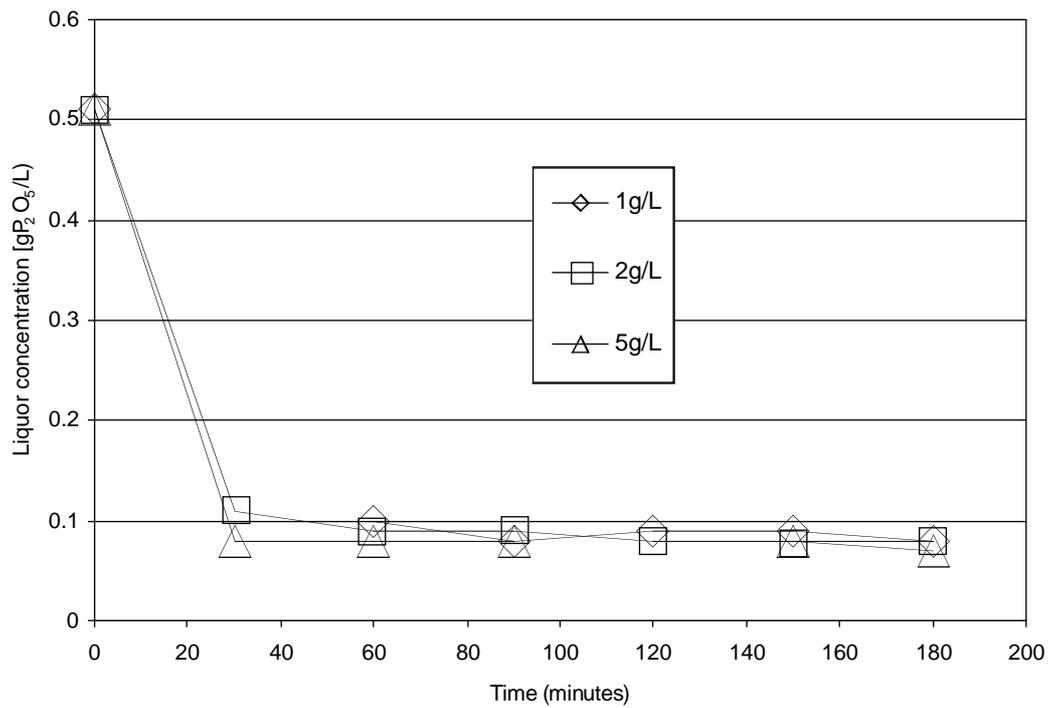


Figure 6 — Kinetics of P precipitation at different seed charges at 30°C

Table 2 — Lime treatment of the precipitate

burnt lime charge	P	V	F	As	Al
[g/L]	[g/L]	[g/L]	[g/L]	[g/L]	[g/L]
0	1.52	5.48	9.36	0.80	1.44
70	0.00	0.03	0.26	0.00	0.58
100	0.00	0.04	0.00	0.00	0.48
150	0.00	0.06	0.00	0.01	0.28

Although no solid phase analysis has yet been attempted, it is assumed that insoluble calcium compounds are formed and/or the previously mentioned intercalation is responsible for the apparently low solubilities measured.

#### 4. Conclusions

The cooling of evaporated Bayer liquor resulted in a precipitate comprising of salts of As, F, P and V. The analysis of the precipitate revealed that the phases in the

salt cake were Villiamite (NaF) and sodium fluoro double salts of As, P and V.

The solubility of the precipitate was investigated at temperatures between 35-50°C and at caustic concentrations between 172-232gNa<sub>2</sub>O/L. Results revealed that the solubility of all sodium fluoro double salts of As, P and V increased with increasing temperature and diminished by increasing ionic strength (caustic).

According to the solubility of the sodium fluoro double salts with temperature and ionic strength, the solubility concentrations of As, P and V increased with increasing temperature and decreased with increasing ionic strength. Fluorine concentration was primarily determined by the NaF solubility. Fluorine concentration decreased with increasing ionic strength, however, inverse temperature dependence was observed.

Results show that the precipitation of the sodium fluoro double salts of V and P is rapid with seed present. Greater than 80% of the potential yield was achieved in the first 30 minutes at the low seed charges trialled. Under the narrow range of seed charges tested, the seed effect on precipitation kinetics was small.

The solubility of the precipitate can be reduced with lime treatment. This ensures a safe disposal of the As, F, P and V impurities.

Solubility and precipitation kinetics data presented allow the design of an impurity removal process. This process can remove As, F, P and V effectively from the liquor stream and can replace the traditional phosphorus removal of lime addition into the digestors. The lime addition during bauxite digestion causes alumina loss via tricalcium aluminate formation from the high temperature green liquor. In the alternative process, the lime is added to the inorganic cake that precipitates readily from cooled evaporated liquor.

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