# Anti – Scaling in the Alumina Industry: Characterisation of Scale Build Up

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#### Abstract

Scale growth in Bayer processes occurs when supersaturated aluminium hydroxide solutions come in contact with solid surfaces. Scale deposition on process equipment leads to reduced performance and increased downtime due to cleaning. A new anti – scaling technology, developed by Savcor Finn, utilises an electrochemical polarisation technique to reduce the scale growth at the vessel walls. The objective of this project is to research further into this technology to understand the mechanism in which it acts. This is achieved by creating synthetic Bayer liquor, and immersing mild steel plates into the liquor as a site for scale growth. Scale samples are then collected, with and without the application of the anti – scaling technology. Analysis of the scale samples will have the composition and properties of the scales to be determined, thus allowing for the benefits of the anti – scaling technology to be quantified.

### 1. Introduction

The Bayer process was first developed by Karl Joseph Bayer in 1887 to extract alumina from bauxite ore. To this day, the basis of the process has remained largely unchanged, however new technology to improve the efficiency of the process have been developed. One of the most pressing issues in the Bayer process is the formation of scale along the walls of process equipment, specifically precipitator tanks and thickeners. The scale build up, consisting largely of gibbsite with other impurities (Pearson, 2009), can reduce the volume of these vessels by up to one third, which can severely limit the production capabilities of the process. In addition, the scale formation is generally very hard and adhesive, requiring both caustic washing and mechanical removal. This leads to a long down time when a vessel needs to be cleaned, resulting in an overall lowering of the production capability, as well as exposure to a major safety risk for the crew that are responsible for the cleaning of these vessels. (Savcor Finn, 2009a)

One of the most prominent methods of reducing scale growth in the Bayer process is the use of an epoxy resin coating, which lowers the scales' adhesive ability to the walls of the tank (Pearson, 2009). Whilst these coatings are an effective means of reducing scale growth, they are not an economical solution to the problem, as the coatings need frequent replacement, resulting in long down times when they need to be replaced. An alternative study on the effect of fluid velocity at the vessel walls was also conducted, to see the effect on scale growth rates. Like the use of the epoxy resin coatings, whilst the method is effective at reducing scale growth rates, the application of the technique is uneconomical, due to the energy requirements for maintaining the fluid velocity at the tank walls. (Nawrath et. al, 2006)

A new anti – scaling technology, developed by Savcor Finn, limits scale growth along the walls of process equipment by utilising an electrochemical polarising technique, which acts at the wall of the vessel. Pilot tests of this new technology have proven that it is successful at limiting scale growth; however, the mechanism in which it operates has yet to be fully explored.

There are numerous benefits to the successful application of this technology to the Bayer process. The most significant is that there will be a direct increase in the alumina yield of the process, as the vessels will have increased volume and less down time with reduced scale build up (Savcor Finn, 2009b). Also, as the scale is largely composed of gibbsite, the precipitation yield will also increase with a reduced scale growth rate, as a larger proportion of the gibbsite will remain in the solution. The anti – scaling technology also reduces the hardness and adhesive ability of the scale formations, resulting in a much safer environment when the vessels are required to be cleaned (Savcor Finn, 2009a). The benefits of this technology are not only limited to the Bayer process, as any process that involves precipitation is likely to have issues with scale control. Thus, the understanding of the mechanism in which this technology operates will allow it to be tweaked, such that it can be applied to other processes.

This paper seeks to present the current findings of the investigation into the electrochemical scale growth inhibition mechanism. The results of the experiments to date will be presented, along with the expectations of the current experiments, the work that is to be completed by the completion of the project and the complications that are affecting the scale growth in the synthetic Bayer liquor.

## 2. Experimental Process

### 2.1. Synthetic Bayer Liquor Preparation

The precipitation of gibbsite from synthetic Bayer liquor is a result of the presence of the aluminate ion,  $Al[(OH)_4]^-$ . The synthetic Bayer liquor is created using aluminium metal ot alumina powder, according to the reactions shown in Equations 1 or 2 below. Table 1 outlines the components and concentrations of each solution.

$$2Al + 2NaOH + 6H_2O \rightarrow 2Na^+ + 2Al[(OH)_4]^- + 3H_2$$
 Equ. [1]

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na^+ + 2Al[(OH)_4]^-$$
 Equ. [2]

Component	Al Metal	Al <sub>2</sub> O <sub>3</sub>	NaOH	$C_2H_2O_4$	NaCl	Na <sub>2</sub> CO <sub>3</sub>
Solution A	134.9 g/L	-	250 g/L	3.37 g/L	-	-
Solution B	134.9 g/L	-	250 g/L	3.37 g/L	6 g/L	10 g/L
Solution C	-	150 g/L	160 g/L	3.37 g/L	-	-

 Table 1: Synthetic Bayer liquor components and concentrations for first batch of experiments (Counter at al. 1997, Lee 1998)

The synthetic Bayer liquor was created directly in the stainless steel vessel, due to the extremely caustic nature of the solution. The components were placed into the bottom of the stainless steel vessel. Half of the required sodium hydroxide (AJAX Pellets, 98.9% NaOH, 1% Na<sub>2</sub>CO<sub>3</sub>) was placed into the stainless steel vessel, and all the components were dissolved in water. Half of the required aluminium (99% purity) is then slowly added to the solution to minimise the heat produced from the reaction. No external heating was required, due to the heat generation from the reaction in the stainless steel vessel. When the aluminium has been added, the remaining sodium hydroxide is added and dissolved into the solution. Finally, the remaining aluminium is dissolved slowly into the solution, before covering the stainless steel vessel with plastic wrap. This is to prevent excess carbon dioxide absorption from the air, leading to an increase in sodium carbonate concentration, as well as to prevent excessive water loss through evaporation, resulting in a change in the solution concentration.

### 2.2. Experimental Rig

The experimental process that has been used to quantify the effects of the anti – scaling technology is a small scale model of an industrial precipitator tank. Figure 1 shows the current experimental setup. The setup consists of two stainless steel pots that are suspended in a heating bath, to keep them at a constant temperature. The pots are fixed to a stainless steel support framework, to counteract the buoyant forces of the heating fluid, which will keep them immersed in the heating fluid. The stainless steel framework is clamped to the heating bath to ensure the pots are kept level in the heating fluid. In each stainless steel pot is a created solution of synthetic Bayer liquor, consisting of components that a commonly found in industrial Bayer liquor. In each solution, two mild steel plates are suspended in the solution to act as a precipitation surface for the scale formation. The mild steel plates are hung from a PVC rod, with a set of grooves cut into it to ensure the plates are fixed in position.

Before the mild steel plates are inserted into the synthetic Bayer liquor, the surface is polished by grades 160, 320, 600 and 1200 silicon carbide sandpaper. After each grade of sandpaper was used, the steel plate was washed in ethanol, before the next grade was used. The surface is prepared as such to improve the likelihood of scale growth on the surface of the steel plates, due to the abrasion formed by the grinding, as well as producing a surface which will allow for direct comparisons to be made between the grown scale samples. Immersed in each stainless steel vessel will be a 55 x 55 mm mild steel plate, and two 10 mm x 10 mm mild steel plates, for XRD and SEM analysis. These plates were prepared in the same fashion as the large hanging plates.

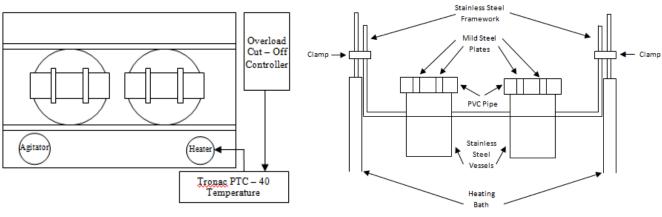


Figure 1: Schematic diagram of experimental setup from a top (left) and side (right) perspective

The required operating temperature for the Bayer process is in the range of 74 -  $85^{\circ}$ C. To achieve this temperature, a heating bath has been used, with a mixture of ethylene glycol and water as the heating fluid. The heating setup consists of an overload cut-off controller, a Tronac PTC – 40 temperature controller and heating element with a temperature sensor. The overload cut-off will shut – off the heater at a pre – determined temperature, in this case 90°C, to prevent the heating fluid from going above the specified temperature. This is kept to prevent a safety hazard, should the heating fluid overheat, as well as to provide better control of the temperature. To minimise water loss through evaporation, due to the high temperature of the heating fluid, a polystyrene cover has been cut out to be placed onto the heating fluid.

## 3. Results

After 15 days of having the mild steel plates immersed in the synthetic Bayer liquors, a precipitate formed on the surface of the mild steel plates. Figures 2 shows the precipitates formed in each solution, after they have been removed from the mild steel plates.

The precipitate that formed on the surface of the plates shows clear signs of deposition rather than scale growth. Figure 3 shows the location of the precipitation on the surface of the plates. The figure clearly shows that the precipitate is in the highest concentration in two regions on the plate; the bottom of the plate, and the top of the plate. This is most likely to be resultant from a concentration gradient in the stainless steel vessel, as there is no agitation. Also, due to the elevated operating temperature, water loss in the synthetic Bayer liquor will result in a variation of the liquid level in the stainless steel vessel. The variation in liquid level is the most likely cause for the precipitation at the liquid level on the mild steel plate.



Figure 2: The collected precipitate from the surface of the mild steel plates in solution A (left) and solution B (right)

Whilst the precipitate that was collected from each solution appeared to be the same, there was a large difference in the quantity that was collected. One of the plates from solution A had 3.58 g of the precipitate scraped off, whilst one of the plates from solution B only had 1.94 g. The presence of the sodium carbonate and sodium chloride in solution B is the likely cause for the decrease in precipitation from the liquor, as the solutions are identical apart from these two compounds.

The precipitate was easily washed from the surface of the mild steel plates with water, which further enforced the belief that the precipitate was not scale, as scale would be far more adhesive to the surface of the mild steel. XRD analysis will be completed to confirm that the precipitate is not the scale growth that is expected.



Figure 3: Precipitate formation on mild steel plates in solution A (left) and solution B (right)

## 4. Future Work

### 4.1. Current Experimental Technique

Solution C, as listed from Table 1, is currently being tested. The synthetic Bayer liquor is also being subsequently heated to 90°C and cooled to 65°C periodically, to induce the solution to be supersaturated. When the synthetic Bayer liquor is heated, the solubility limit of the alumina will be higher, resulting in more alumina dissolving to form the aluminate ion. As the liquor cools back to the desired process temperature, the solubility limit of the alumina will decrease, resulting in the liquor becoming supersaturated. This will enhance the precipitation of aluminium hydroxide from the liquor. The same mild steel plates that were used in the first two solutions will also be immersed into the new liquor, however they will be prepared with only 600 grit silica carbide sandpaper.

The use of alumina powder to form the synthetic Bayer liquor may provide a more realistic approach to creating the liquor, as bauxite ore is composed largely of aluminium oxide. The solution is created in a similar fashion to that using aluminium metal, however all of the caustic and alumina can be added directly into solution, as no gas is evolved from this reaction. The dissolution of the alumina powder was observed to be very rapid, due to the high contact surface area.

### 4.2. Analysis Techniques

#### **4.2.1. X** – ray Diffraction

Powder X – ray diffraction analysis is to be carried out on the grown scale samples to determine the composition of the scale. The scale samples are first heated at 60°C for 24 hours, to dry the samples and improve the crystallinity. The scale is then ground to approximately 10  $\mu$ m particle size, before being mounted into the sample holder. X – ray diffraction plates are inserted into the synthetic Bayer liquor for direct analysis via X – ray diffraction after drying.

#### 4.2.2. Optical and Scanning Electron Microscopy

Optical and scanning electron microscopy analysis was conducted to determine the crystal structure of the scale, and to better understand the growth mechanism of the scale. Optical microscopy is used to give a rough visual image of the scale formation. Scanning electron microscopy gave a more detailed image of the scale samples, allowing for the determination of two distinct layers; a growth layer and an accumulated layer.

#### 4.2.3. Mechanical testing

The mechanical testing procedures that are to be used are Rockwell microhardness testing and adhesion testing. The hardness and adhesive ability of the scale are important features to test, as it directly relates to the ability of the scale to adhere to the tank walls, and the ease of removal of the scale once it has attached to the tank.

## 5. References

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