

MANAGEMENT AND CONTROL OF SILICA IN THE BAYER PROCESS

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Abstract

Management of reactive silica is a major focus of effort for most alumina producers. However, like many aspects within the Bayer process, the treatment of silica has both detrimental and advantageous aspects. Controlled formation and precipitation of sodium aluminosilicates – often referred to as desilication product or DSP – can substantially reduce the amount of silica in solution and so prevent or reduce the potential for silica contamination in alumina product. Additionally, removal of DSP from the circuit (for example in a desilication step) can also be used as a sink for other problem contaminants such as sulfate or chloride. On the other hand, DSP formation as scale in heat exchangers can substantially limit energy transfer and restrict flow capacity. A range of new technologies have recently been developed to address the differing aspects of silica control with the aim of enhancing the advantageous properties of DSP precipitation, while minimizing the detrimental aspects. A review of recent developments in improving control of silica in Bayer process liquor is presented, outlining new options for process operators to improve management of silica and gain better control in this process area.

1. Introduction

Alumina refinery operators have to deal with a range of problems caused by a wide variety of contaminants that are extracted from the bauxite into the liquor and impact on the Bayer process. Arguably, the issues of greatest concern to plant operators stem from the presence of silica in liquor. The presence of silica, and the mitigation of its effects occupy a substantial amount of time, energy and cost for all refineries.

By far the greatest issue silica in liquor poses to refineries is the loss of soda associated with precipitation of aluminosilicate compounds or what is commonly referred to as desilicated products (DSP). There is currently no widely accepted alternative method for removing silica from Bayer liquor which does not lead to soda loss. A side implication of this is that bauxites containing high amounts of reactive silica (>8 wt%) are effectively consigned to reserves. The caustic losses associated with processing such ores make their use uneconomic in conventional plant operations. Additional pre-treatment steps to reduce the reactive silica content of such ores are possible but the capital expenditure required to implement such steps again inhibits economic use of such bauxites.

The second major issue liquor phase silica poses is scale. Uncontrolled silica in liquor tends to precipitate in downstream tanks, heaters and vessels when process conditions change. The silica scale in heat exchanger surfaces often leads to poor heat transfer. Generally refineries will increase steam input to evaporator heaters in an attempt to generate the required condensate. However, this makes condensate generation an increasingly expensive exercise as scale deposition increases.

In addition to these significant issues, silica in liquor tends to co-precipitate with hydrate in precipitators and can therefore substantially compromise product quality.

Most refineries counter the effects of silica in liquor by pre-desilicating the bauxite slurry in the early stages of the process, prior to digestion. Whilst most of the reactive silica tends to dissolve and precipitate in desilication, there is almost invariably some residual reactive silica in the bauxite feeding digestion which tends to dissolve, raising silica levels in the digested slurry. In addition to this the higher temperatures and caustic concentration in digestion increases reactive silica solubility and the digester blow off liquor tends to contain elevated levels of silica

As well as these issues, there are also some useful aspects related to silica in liquor. The dissolution of reactive silica and precipitation of DSP is one of the key methods by which some of the notorious liquor contaminants such as sulphate, chloride and carbonate are removed from the process. The formation of DSP results in incorporation of these anions in the cage-like crystalline structures. Left in the liquor, these anions generally reduce liquor productivity and their removal through incorporation in the solid DSP is therefore a desirable outcome. Whilst refineries often operate specific, additional facilities for impurity control, removal of these species within the DSP complements their operation.

To take advantage of the positive aspects and control the undesirable effects of silica, a wide range of approaches have been considered and tried across the industry. Recent work within Nalco has now identified a number of additional, alternative strategies that may be employed to assist in the control of silica and these are outlined within this paper.

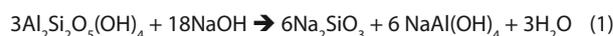
2. Silica Extraction and Removal

Silica enters the process with the bauxite as clays and other silica containing minerals. The range of materials will vary depending on the bauxite source but generally at least some component (the reactive silica) dissolves under digestion conditions resulting in silica of some form in solution. Under process conditions this typically then precipitates from solution as sodalite which is also known as desilication product or DSP. This material can be represented by the following formula:



where: X = OH⁻, Cl⁻, 0.5CO₃²⁻, 0.5SO₄²⁻

The two-step process of: (1) dissolution of silica from the bauxite, then (2) precipitation as DSP, is presented in the two equations below:



Both equation (1) and (2) occur in concert, with the amount of DSP precipitated depending on both the concentration of silica dissolved into solution and the prevailing conditions of temperature and caustic concentration. DSP has an inverse solubility such that increasing temperature results in more precipitation of solid material while cooling the temperature

results in more silica remaining in solution. This property of inverse solubility results in a number of issues and challenges in controlling the impact of silica on the process.

Generally, in low temperature digestion used for gibbsitic bauxite processing (<180 deg C) any quartz present in the bauxite will pass through digestion without reacting. In high temperature digestion used for boehmitic bauxite processing (220 to 270 deg C) and in the sinter process, so called "quartz attack" by caustic can occur leading to partial dissolution of quartz (equation 3).



Soluble silica generated from quartz attack precipitates to form DSP via the same reaction as shown in equation 2. However, the differences between soluble silica from clay minerals (equation 1) and soluble silica from quartz (equation 2) have significant consequences. Clay desilication as shown by equation 1 and 2 above leads to only caustic losses. Quartz attack, on the other hand, leads to both caustic and alumina losses.

3. Existing Methods of Silica Control

At a very basic level, the issues related to silica can be considered as a problem of impurity control. There is a constant input of silica into the process with the bauxite. To balance this, an equivalent outlet stream of silica from the circuit must be achieved. If the balance is appropriately controlled then the silica content of the liquor can be limited to a concentration that eliminates or at least limits any unwanted effects such as scale formation or product contamination. If the balance is not controlled, then such undesirable impacts are more likely to occur due to excessive silica in liquor.

Clearly then the control of silica issues in Bayer plants is reliant on control of both silica input and silica removal to ensure an appropriate balance is maintained. Such control then limits the concentration of silica in solution to a level below a critical operational limit.

In this sense, control of silica can be considered to be very similar to the issues related to other contaminants such as oxalate. The issues emanating from a build-up of oxalate in Bayer liquor are well established and documented [Lever, 1983; Brown and Cole, 1980]. These issues can be mitigated or controlled by a range of strategies which in general terms fall into three main categories:

- (1) Onput control – for example, removal or control of organics [Armstrong and Soucy, 2007; Deabriges, et al, 1977; Sato, et al, 1982; Shaw, 2005; Soucy, et al, 2004; Tardio et al, 2008]
- (2) Output control – enhancement or increased oxalate removal capacity [Grocott and Harrison, 1996]
- (3) Stability control – increasing the tolerable limit of oxalate within the process [Farquharson, et al, 1995]

While the issues of silica in the Bayer process may well be considered to be more complex than those related to oxalate, the basic principles of control across these three areas remain consistent for both of these contaminants. As a result, a number of technology options related to the different control strategies have been considered and developed across the industry.

3.1 Silica Input Control

Most refineries try and control (or at least monitor) the amount of reactive silica that is added to the process with the bauxite. Mining practices, selective blending and/or appropriate stockpile management is a key factor that refineries use and adjust in response to process conditions. However, this is clearly a less than ideal tool with limited options available. Additionally, blending of stockpiles is becoming increasingly problematic as reserves of high quality bauxite containing the most "desirable" quantities of silica are steadily reduced over time.

A reduction in the quantity of unwanted silica-containing minerals in the bauxite can be achieved through beneficiation (e.g. flotation, dry milling) prior to addition to the Bayer circuit [Massola, et al, 2009]. While examples of such processes are in operation and are reported to be very effective, installation of such beneficiation steps are generally capital intensive and as a result, the practice of bauxite beneficiation is not currently widespread within the industry.

3.2 Silica Output Control

One of the more common strategies is the practice of a desilication step within the circuit as part of the process. The main aim of desilication is to deliberately precipitate DSP in the form of a friable solid which can be removed from the process with the red mud and disposed. Typically desilication takes place immediately after milling but before digestion and involves holding the slurry under appropriate time and temperature conditions to allow the precipitation of DSP from solution. In this way, reactive silica that has been extracted from the bauxite into solution is precipitated from solution as DSP and is removed with the mud.

Since DSP has an inverse solubility, the precipitation of silica from solution is enhanced by higher temperatures. As a result, the desilication step requires maintenance of the digested slurry at elevated temperature for an extended period – typically hours.

A variety of process enhancements to improve the efficiency of the desilication process have been suggested and in some cases applied. These include the addition of silica in a soluble form [Robson, 1988] or the use of sodalite solids [The, 1992] or quartz [Forté, 1999] as seed to precipitate DSP. The use of reusable sodalite pellets for post-desilicating Bayer liquor has also been suggested [The, 1992].

Alternative methods using the same overall aim of improving the removal of silica from solution include a process in which hydroxysodalite seed was introduced into the digestion stage to reduce the silica concentration [Rodda and Shaw, 1997]. Ultrasonic irradiation treatment has also been used to remove silica from spent liquor [McCausland and Fennell, 2006].

While many of these methods have been tried and shown to be effective, a variety of operational problems in their implementation has meant that none of these enhancements have developed sufficiently to bring them to widespread practice within the industry.

3.3 Silica Balance Control – Prevention/Delay of DSP precipitation

While control of the input and output of silica to the process maintains a balance of material within the liquor, a third option for controlling the effects of silica is also available. This additional strategy aims to alter the liquor and/or process conditions to increase the tolerable limit of silica in solution. That is, prevent or delay the precipitation of silica from solution. Effectively, this prevents precipitation of DSP in those parts of the circuit where it is unwanted. A range of DSP scale inhibitors have been developed and promoted within the industry for this purpose [Spitzer, et al, 2008] and are in widespread application.

Effectively these products prevent DSP precipitation in those areas of the plant where the formation of solid DSP is undesirable; specifically heat exchangers and evaporation. However, it is essential that the silica that remains in solution and is not deposited on the heat exchangers in the presence of such reagents, eventually precipitates from the process at some point. Delay of precipitation, rather than prevention, is an essential property of such reagents so as to ensure no detrimental downstream issues resulting from unwanted silica build-up in liquor.

Without an appropriate “exit point” for the silica, the strategic objective of preventing precipitation of DSP where it is not wanted, while at the same time maintaining the silica balance within the liquor, cannot be achieved.

4. New Alternative Methods of Silica Control

Previous work in the area of silica control has tended to focus on individual issues or particular aspects related to silica in the process. Recent development work by Nalco has recognized that the overall control of silica in the Bayer process may require more than one strategy so a range of alternative solutions have been considered and developed in parallel. This approach aims to provide process operators with a greater range of operational levers which can be utilized (or not) as appropriate to the circumstances and particular nuances of individual plant requirements. As a result, the strategy aims at a more comprehensive means of controlling the impact of silica under a broader range of process conditions and bauxite qualities.

4.1 DSP Promoter

The development of a so-called “DSP Promoter” has been aimed at more effectively removing silica from the circuit by improving the efficiency of the desilication process. Typically the limitation of the desilication process in plant operations is not the solubility of DSP. That is, the holding time of the desilication step is typically shorter than that required to reach equilibrium in terms of silica. As a result, any improvement in the rate of DSP precipitation under desilication conditions will likely enhance the net mass of DSP precipitated (and therefore removed) from the circuit.

4.1.1 Test Methods

A series of laboratory based tests were conducted to assess a range of products as potential DSP promoters. Two types of test method were employed:

Test Method 1:

Bayer plant spent liquor was collected and the soluble silica concentration was increased by up to 3g/L by addition of a concentrated sodium silicate solution. This “spiking” of the liquor was designed to induce the precipitation of DSP under the test conditions. The spiked liquor was then sub-sampled (200mL) into a series of 250mL Nalgene® bottles. Promoter reagents were then added to individual bottles as appropriate (duplicate samples for each product/dose, triplicate undosed control samples). The bottles were then placed in a rotating water bath and held at 95oC for a period of 4 hours. After the test period, bottles were removed and the precipitated solids were filtered, washed then dried overnight. The mass of DSP precipitated from each treatment indicates the propensity to form DSP.

Test Method 2:

Bayer plant bauxite desilication feed slurry (>40% solids) was collected and 200mL sub-samples added to a series of 250mL Nalgene® bottles. Promoter reagents were then added to individual bottles as appropriate (duplicate samples for each product/dose, triplicate undosed control samples) and the bottles were then placed in a rotating waterbath at 95oC for 4 hours. At intervals during the test period sub-samples from each bottle were taken and centrifuged to separate the solids. The supernatant liquor was then sampled, filtered and analysed by ICP. SiO₂ in solution was reported. The reduction of SiO₂ in solution over time was indicative of the formation of solid DSP under typical plant desilication conditions.

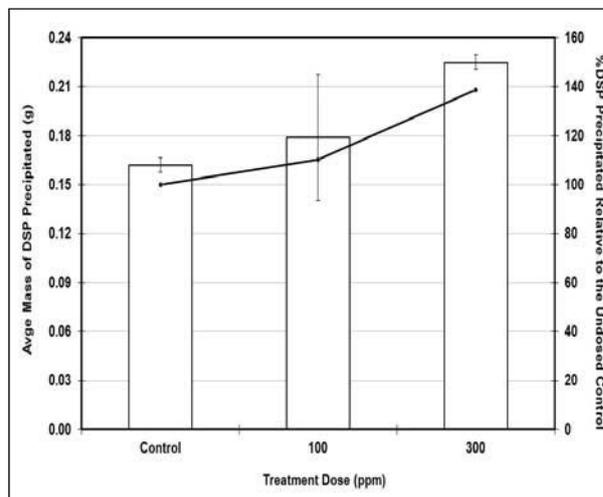


Figure 1. Impact of DSP Promoter product addition on the mass of DSP precipitated in treated versus untreated spent liquor samples. Average mass (g) is plotted as columns (left hand axis) while percentage of solid precipitated relative to the control sample is also shown (line, right hand axis).

Effectively, the addition of the promoter product results in a substantial increase in the amount of DSP precipitated over the course of the test. Figure 2 shows the impact of dosing a promoter product to plant slurry and the effect this has on the rate of DSP precipitation. In this test, addition of the promoter product enhances the rate of precipitation of DSP despite the presence of the mud solids. This indicates that the promoter material is not simply acting as a seed source for DSP precipitation but is indeed enhancing the precipitation of DSP from solution.

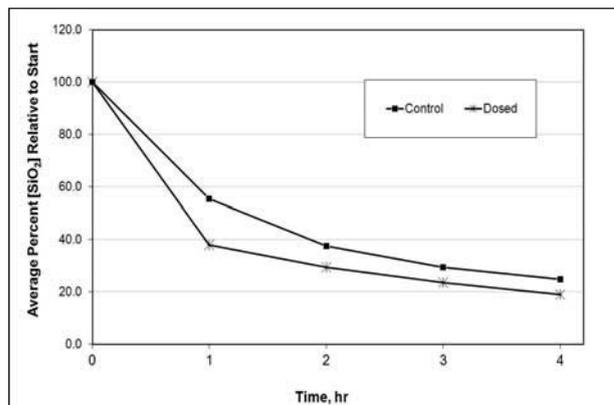


Figure 2. Reduction in SiO₂ content of the liquor for dosed and undosed samples of desilication feed slurry. Percentage of SiO₂ concentration relative to the starting concentration is plotted.

It also demonstrates that the results observed using test method 1 (liquor only) are consistent with the results obtained using actual plant slurries indicating that data obtained for a range of products using method 1 (liquor only) may well be applicable to desilication slurry conditions.

4.2 DSP Inhibitors

Inhibition of DSP scale focuses on delaying the precipitation of DSP to a point in the process beyond a critical area of concern – typically heat exchangers and evaporators. While a number of reagents are currently commercially available [Spitzer, et al, 2008] Nalco has been developing a range of alternative reagents again aimed at preventing DSP precipitation where it is not wanted, but not completely inhibiting the formation of DSP where it is required in critical downstream processes such as desilication.

Laboratory testing using methods similar to method 1 used for the assessment of DSP Promoters and described above were used. In the testing of the promoter products an increase in the amount of DSP precipitated was observed. Using the same method but applying an inhibitor product, a decrease in the amount of DSP is observed. Using this method Nalco has now identified a broad range of chemistries which actively inhibit the formation of DSP solid.

It should be noted that the test conditions are specifically chosen to enhance the amount of DSP precipitated (spiking of the liquor). In this way, sufficient DSP is precipitated in the undosed control samples to allow discernment of inhibitory effects that result in lower amounts of DSP precipitated. As a result, complete inhibition of solid formation is neither expected nor required within this test to demonstrate efficacy. Results of a dose response test using one of the family of inhibitor products identified is shown in figure 3.

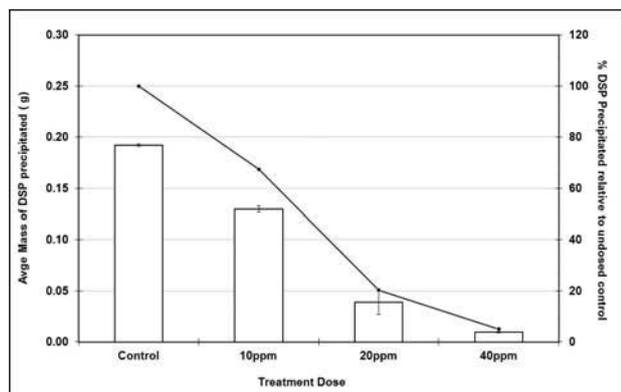


Figure 3. Dose response of Nalco DSP inhibitor product showing inhibition of DSP precipitation with increased dose. Average mass (g) is plotted as columns (left hand axis) while percentage of solid precipitated relative to the control sample is also shown (line, right hand axis).

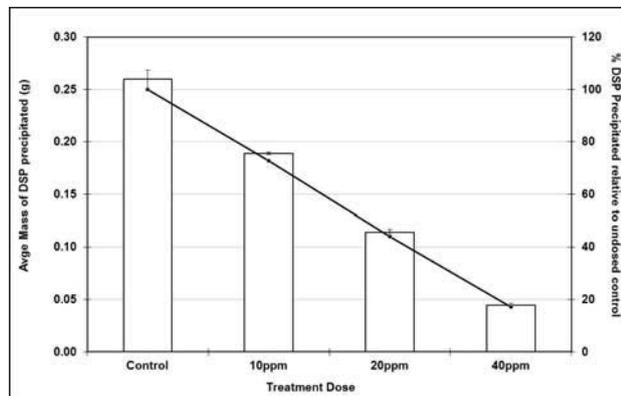


Figure 4. Average mass of DSP precipitated in the presence of ~2 g/L alumina trihydrate solids. Average mass (g) is plotted as columns (left hand axis) while percentage of solid precipitated relative to the control sample is also shown (line, right hand axis).

Under plant conditions spent liquor flowing to heat exchangers is rarely free of solids with the most common contaminant being trihydrate. Therefore the performance of the new inhibitor in the presence of hydrate solids was assessed in a series of tests. Figure 4 shows the dose response of the inhibitor product in the presence of ~2g/L trihydrate solids.

Additionally, however, it is important to ensure that the inhibitory effect of this product is not carried through to the downstream processes of the plant. In order to assess this, a standard bottle test was also conducted in the presence of mud solids. The same treatments on liquor without mud solids were run in parallel. Figure 5 shows the results, indicating that the inhibitor has little or no impact on DSP precipitation when mud is present.

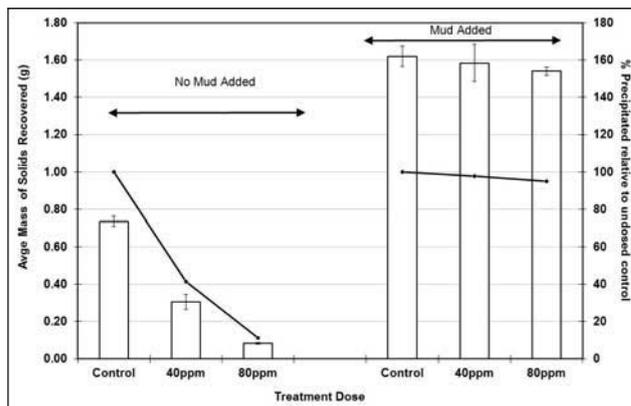


Figure 5. Impact of DSP inhibitor in the presence of red mud. Mud solids of 0.8g/L were included in "mud added" bottles.

Additional work indicated that the mechanism of action of this inhibitor is likely to be surface related with the product being a surface active material. From this, and the results shown here it is surmised that the inhibitor readily adsorbs to mud particles (or the existing DSP material present in mud) however, it is inactive on trihydrate surfaces. Given the downstream processes and the requirements for their operation, such a mechanism is ideal to ensure little or no disruption to the operation of processes such as desilication or trihydrate precipitation.

The mechanism of the inhibitor appears to be a surface active process where the inhibitor molecule adsorbs onto the surface of pre-crystallite DSP material and thereby prevents the surface acting as a seed point for further solid deposition. While this mechanism appeared to be consistent with the evidence, it was initially unclear as to whether this resulted in merely a slowing of the overall precipitation of DSP or whether addition of the new inhibitor product resulted in an increase in the solubility of DSP – thus resulting in more material in solution and less scale deposited.

To assess this possibility, a kinetic study of DSP formation was conducted. The results of this test are plotted in Figure 6. Clearly the addition of inhibitor results in a slowing of DSP formation in the initial period. However, after 24 hours the amount of material deposited from all samples is almost equivalent. This indicates that the main mechanism of action for the inhibitor is indeed a kinetic process whereby the deposition is slowed and the overall solubility of DSP is virtually unaffected.

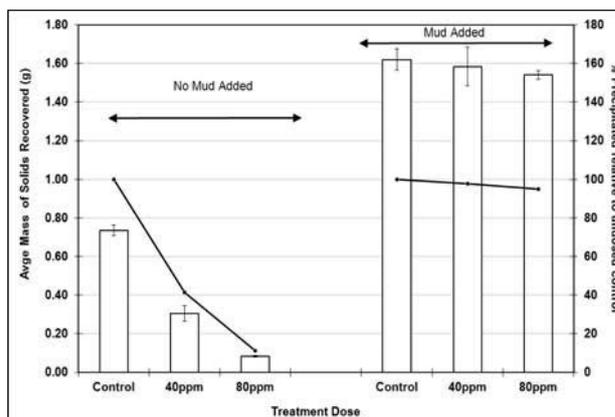


Figure 6. Average DSP mass taken from bottle test samples over a 24 hours period. Duplicate samples of each treatment were removed, filtered and solids washed and dried. Averages are shown.

4.3 DSP Recoverer

While control of precipitation of silica as DSP can be achieved, it is well recognized that one of the main issues related to silica is the loss of caustic (and alumina) as a major component of DSP. This caustic loss must be replaced leading to substantial costs to operators. While the precipitation and removal of DSP is advantageous in one sense due to the removal of silica (and other undesirable contaminants such as sulfate and chloride) the concomitant loss of caustic is an unwanted side effect.

Nalco is currently actively pursuing potential means that might allow operators to remove silica from the circuit in forms other than as DSP. This would allow operators to control silica while minimizing the costly losses of caustic related to DSP removal.

5. Summary and Conclusions

The treatment and control of silica is a major issue for all Bayer process operators. The presence of silica in the process liquor results in a number of potentially undesirable impacts including product contamination and scale formation. Changing process conditions to mitigate these undesirable outcomes can result in substantial costs to operators in terms of production, soda, energy and water.

A number of separate processes and control strategies have been proposed and/or used to assist in controlling the impacts of silica on process operations. Typically these can be categorized as focused on one of three areas:

- Control of silica input
- Control of silica output
- Control of silica in solution

Nalco is developing a holistic approach to silica control and are continuing to develop appropriate strategies and chemical programs to address the entire range of challenges that increasing silica content of bauxites presents across plant operations. Potential applications include:

- DSP Promoter: to enhance the removal of silica as DSP from the process
- DSP Inhibitor: to control the formation of DSP scale but not interfere in downstream processes
- DSP Recoverer: to remove silica in a form that reduces the loss of caustic

Together these applications have the potential to allow operators to more effectively control silica, and the issues related to silica, across the entire Bayer circuit.

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