Reducing Reactive Silica Content in Washed Bauxite

David C. Davis[1], Michael LaRosa[2], Christopher Greulich[3], Ayana Santos[4]
[1]Senior Industry Technical Consultant
[2]Senior Account Manager
[3]Senior Chemist
[4]District Manager
Nalco Water, an Ecolab Company, Naperville, Illinois, USA
Corresponding author: ddavis@ecolab.com

Abstract

Lateritic bauxites containing high levels of reactive silica are economically disadvantageous to convert into alumina due to their relatively high consumption of caustic in the Bayer Process. Efforts to remove reactive silica from bauxite ore prior to shipment have largely focused on gravitational methods such as washing, screening and the use of hydrocyclones. The purpose of this work was to identify additives which might enhance this separation process economically. Initial testing consisted of laboratory centrifuge tests designed to simulate the gravitational forces in hydrocyclones. Additives that had the largest impact on separation efficiency were identified and these were also found to substantially reduce the viscosity of the slurry. One additive reduced reactive silica by greater than 40 % while increasing alumina recovery by approximately 20 % on a relative basis. Subsequent pilot scale testing confirmed both the laboratory method and the performance of this additive. This approach lends itself to use in a CCD circuit, which was validated in lab testing. Further trials are being planned at wash plants utilizing hydrocyclones and screens.

Keywords: Bauxite, reactive silica, washing, additives.

1. Background

As with most mineral resources, bauxite quality is generally deteriorating over time. The relative value of these deposits depends largely upon the concentration of alumina and silica, as well as the mineralogy of these constituents. Contracts for this raw material often specify a range of acceptable quality which may include penalties for failure to reach targeted assays and bonuses for exceeding them. These values are based not just on market forces but on the relative cost of processing the ore. Additionally, the desirability of the ore will depend upon the cost of mining and transporting it. Whether purchased on the open market or evaluated as an owned and internally utilized resource, the reactive silica content and available alumina are the primary considerations of bauxite users.

The rationale for increasing alumina content includes reduced transportation, processing, and disposal costs, assuming the alumina is of the proper form (gibbsite vs boehmite). Lower concentrations of reactive silica (generally kaolinite), will also reduce processing costs, mainly in the reduction of caustic soda required to remove the silica via precipitation of desilication product (DSP), the equations for which are shown below:

Kaolinite dissolution

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 6NaOH \rightarrow 2Na_2SiO_3 + 2NaAlO_2 + 5H_2O \qquad (1)$$

$$Kaolinite + Caustic \rightarrow Sodium\ Silicate + Sodium\ Aluminate + Water$$

Sodalite precipitation

$$6Na_2SiO_3 + 6NaAlO_2 + Na_2X + 12H_2O \leftrightarrow 3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)Na_2X + 12NaOH \qquad (2)$$

$$Sodium\ Silicate + Sodium\ Aluminate + Sodium\ Salt \ \rightarrow Sodalite + Caustic$$
$$Where\ X\ can\ be\ one\ of\ several\ inorganic\ anions\ such\ as\ Sulphate,$$
$$Carbonate, Nitrate, Aluminate, Chloride, or\ Hydroxide$$

So, despite releasing some of the free caustic consumed in the kaolinite dissolution in the precipitation step, each ton of reactive silica typically consumes 1 tonne or more of NaOH. It has been reported that 75 % of caustic losses are due to DSP formation [1], although this value may have increased since being reported. Caustic and bauxite can often comprise nearly half of alumina production costs, with caustic being the single highest cost additive to the process. At \$350 / t, a 1 Million Tonne per Year (MTPY) refinery processing a bauxite with 5 % reactive silica will incur a caustic loss via the above reactions of approximately \$40 / t of alumina, depending on the available alumina of the bauxite being processed. The price of caustic has historically been volatile, and its cost is driven by forces within the chlor-alkali market, which itself is dependent on the market for plastics. This further increases the financial risk associated with high silica bauxites.

Currently a number of bauxite producers, in Brazil, Indonesia and Australia for example, wash lateritic ores to remove kaolinite via processes utilizing screens and or hydrocyclones. These facilities comprise approximately 25 % of the global bauxite tonnage, or more than 60 MTPY [2].

The separation of the kaolinite and other clays from the desired alumina is by size, as the density of these components is similar [3]. Large volumes of water, often more than one ton per ton of bauxite feed, are required to facilitate this separation. The waste material is typically collected in dams created at source's mine site. This practice increases storage costs as well as corporate liability.

Reducing waste and economically processing lower grade bauxites are of such concern that they are addressed in the Alumina Technology Roadmap, a producer-led initiative to coordinate efforts aimed at improving the industry's long-term viability [4]. Given this, it is easy to understand the industry's interest in addressing the rising kaolinite content in bauxite ores.

2. Initial Developmental Work

Over the past several years, alumina producers have asked suppliers such as Nalco for additives which might enhance the washing of bauxites, specifically to remove more of the kaolinite. Nalco evaluated numerous compounds, focusing initially on dispersants and surfactants which might further isolate the kaolinite from the rest of the slurry, with limited success.

Beginning in 2016, a new team of Nalco researchers was assigned this project and the first task they handled was the development of a laboratory method that mimicked hydrocyclones in typical bauxite wash plants. The procedure uses a centrifuge, operating at an rpm and duration designed to match the g-forces in the wash plant, to spin sample vials which are then separated by volume prior to analysis. The overflow and underflow of these vials were found to be very similar in size and consistency to that of known wash plants. It thus was possible to evaluate many chemistries in a relatively short time.

Table 1 shows data generated using this method, showing that consistent and reproducible results could be obtained.

Table 1. Variability of untreated (Control) sample analyses.

		Total Al_2O_3	**Total SiO_2**	**A/S Ratio**
Control	Underflow	46.65	14.31	3.26
Control	Underflow	46.58	14.65	3.18
Control	Underflow	46.46	15.92	2.92
Control	Underflow	46.20	15.39	3.00
Control	Underflow	46.13	14.86	3.10
Control	Underflow	45.79	15.36	2.98
Control	Underflow	45.72	14.73	3.10
Control	Underflow	45.02	15.28	2.95
	Average	46.07	15.06	3.06
	St. Dev.	0.51	0.48	0.11
Control	Overflow	42.11	21.27	1.98
Control	Overflow	42.09	21.34	1.97
Control	Overflow	40.72	23.71	1.72
Control	Overflow	41.76	22.07	1.89
Control	Overflow	41.79	21.88	1.91
Control	Overflow	41.86	21.96	1.91
Control	Overflow	42.15	21.25	1.98
	Average	41.78	21.93	1.91
	St. Dev.	0.46	0.80	0.08

Initial screening showed that the samples which had the largest decreases in underflow (product) kaolinite concentrations were those which also produced a noticeable reduction in slurry viscosity. Past work on viscosity modifiers in other mining applications required dosages 2 - 5 times the amount required here and were usually dispersants or surfactants. In this case, the addition of charge neutralizing polymers, which might be collapsing the Stern Layer around both the kaolinite and the gibbsite, produced slurry viscosity reductions of up to 90 % at dosages less than 500 ppm.

3. Viscosity and Separation Efficiency

It is well established that the viscosity of a liquid or slurry affects settling rates and hydrocyclone split efficiencies. For the velocity of free settling particles in a fluid, Stoke's Law applies:

$$V = \frac{g\, d^2(\rho_1 - \rho_2)}{18\, \mu} \quad (3)$$

Where:

V	Settling Rate, m/hr
g	Gravitational Constant, m/s^2
d	Particle Diameter, m
$\rho 1$	Particle Density, g/cm^3

ρ2	Fluid Density, g/cm^3
μ	Fluid Viscosity, g/m·s^{-1}

For hydrocyclones, d_{50} cut size has been shown to be approximately proportional to the square root of the fluid viscosity, although the power value has been reported to vary [5].
Treated slurries in this work experienced a marked decrease, a typical result shown in Figure 1.

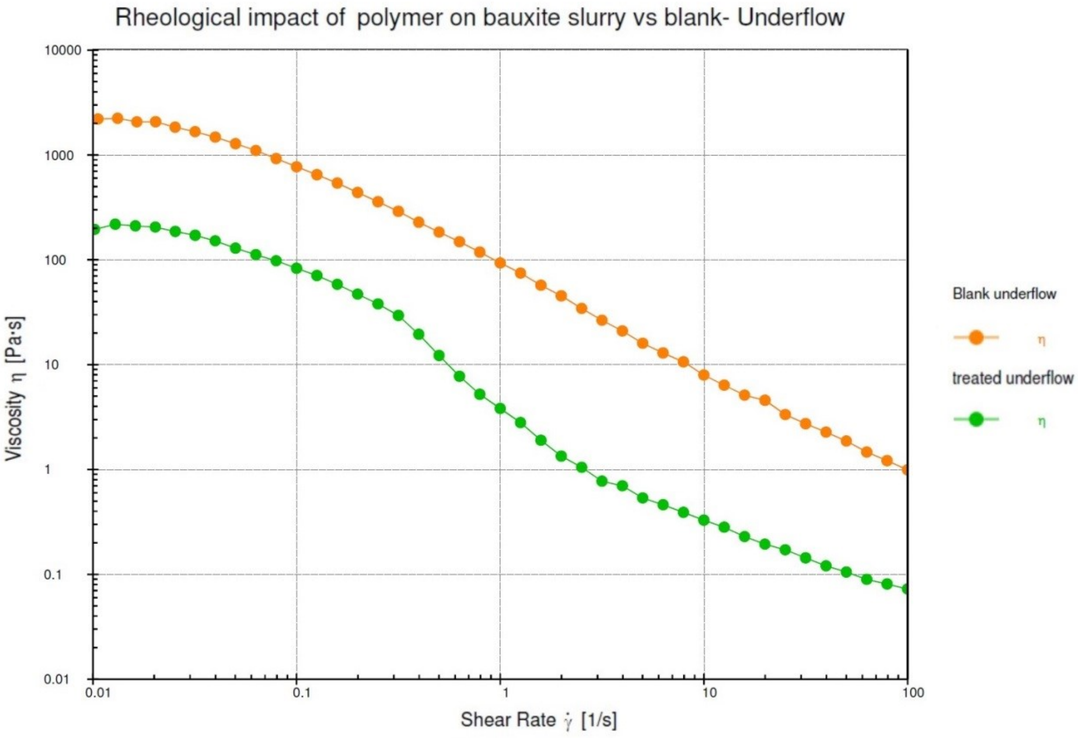

Figure 1. Anton Paar shear sweep of treated bauxite slurry.

Using the power relationship between viscosity and d_{50} size, a change of this magnitude would lower d_{50} cut size 68%, sending significantly more of the finer kaolinite to the overflow while retaining more of the coarser gibbsite.

4. Treatment Program Development

Initial results (Table 2) showed that certain charge-neutralizing polymers were effective in lowering total silica reporting to the overflow.

Table 2. Early screening test results.

		Treated Analyses			Change vs Control		
Program	**Sample**	**Total Al_2O_3**	**Total SiO_2**	**A/S Ratio**	**Total Al_2O_3**	**Total SiO_2**	**A/S Ratio**
1	Underflow	48.6	11.1	4.38	2.53	-3.96	1.32
2	Underflow	48.9	11.0	4.45	2.83	-4.06	1.38
1	Overflow	40.3	24.5	1.64	-1.48	2.57	-0.26
2	Overflow	39.7	25.5	1.56	-2.08	3.57	-0.35

Programs 1 and 2 were isolated and further investigated to minimize the dosage required to achieve the maximum rejection of kaolinite while also increasing gibbsite retention. Several other additives were evaluated, including the use of a second product, but the focus for now remains on optimizing and proving the efficacy of the charge-neutralizing polymers. The best of these additives yielded results in dosages as low as 140 ppm.

Table 3. Lower dosage of Program 1.

		Treated Analyses			Change vs Control		
Program	**Dosage, ppm**	**Total Al_2O_3**	**Total SiO_2**	**A/S Ratio**	**Total Al_2O_3**	**Total SiO_2**	**A/S Ratio**
Control	0	46.07	15.06	3.06	-	-	-
1	175	48.60	11.14	4.36	2.53	-3.92	1.30
1	140	48.47	10.93	4.43	2.4	-4.13	1.38
1	140	48.57	10.88	4.46	2.5	-4.18	1.41

Note that Tables 1-3 show total alumina and silica values.

The efficacy of the program on the intended species, available alumina (gibbsite) and kaolinite was confirmed in subsequent testing shown in Table 4.

Table 4. Program efficacy results.

		Treated Analyses			Change vs Control		
Program	**Dosage, ppm**	**Available Al_2O_3, %**	**Reactive SiO_2, %**	**A/S Ratio**	**Available Al_2O_3, %**	**Reactive SiO_2, %**	**A/S Ratio**
Control	0	32.99	11.31	2.92	-	-	-
2	175	39.07	7.54	5.18	6.08	-3.77	2.26
2	158	40.39	7.19	5.62	7.40	-4.12	2.70
2	158	40.97	7.49	5.47	7.98	-3.82	2.55

5. Using a CCD Circuit to Further Improve Results

It seemed possible that the chemistries employed were selective enough to allow the use of a CCD circuit to further increase alumina retention and the rejection of reactive silica. A laboratory simulation of a 4-stage CCD circuit in which each stage was treated with lower dosages of the most promising additive program showed that alumina could be increased by 12.2 % and silica reduced by 14.7 % (absolute values).

Table 5. Simulation of a 4-Stage CCD Wash Circuit.

	Program 1 Actual Dosage (g/ton)	**Total Alumina (%)**	**Total Silica (%)**	**Al/Si (%)**
Blank	0	42.66	20.23	2.11
1st Stage Washer Simulation	100	51.08	11.36	4.50
2nd Stage Washer Simulation	100	53.03	8.08	6.56
3rd Stage Washer Simulation	100	54.54	5.57	9.79
Final (4th) Stage Product	100	54.82	5.50	9.97

In fact, the benefits of the fourth stage are minimal, as most of the recovery was completed by stage 3. The economic efficacy of this approach is unclear, as it may also be possible to achieve similar results with a multi-stage hydrocyclone process.

6. Additional Benefits and Future Work

Justification for use of such additives, as covered earlier, are largely based on the reduction of soda losses. However, given the increase in recovered alumina, there may be lower production, transportation, and waste storage costs for the refineries. Ore sources once considered unprofitable might be utilized if efficiency improvements are large enough. Assuming the washed bauxite is lower in moisture, there could be additional transportation and process dilution savings. Some of these economic advantages are necessarily impacted by existing contract arrangements in which the value of the ore is based upon assays for reactive silica and alumina. This would affect the magnitude of the economic benefit from this approach, both for the refinery and the bauxite supplier.

Pilot plant and full-scale plant tests are planned which will include in their design the optimization of dosage, finalizing the overall program to be utilized, and the evaluation of alternative process streams for treatment.

7. References

1. Donaldson, D. J. Alumina Technology Course, p. 46.
2. Van Deursen, Caio. Dewatering Methods and Disposal of Waste from Bauxite. Master’s Thesis, University of Sao Paulo, 2016, p.8.
3. Van Deursen et al., Bauxite Fines Recovery Via Desliming and Concentration. Proceedings of 33rd International ICSOBA Conference, Dubai, UAE 29 November – 1 December 2015.
4. http://www.world-aluminium.org/media/filer_public/2013/01/15/fl0000422.pdf