Effect of bauxite characteristics and process conditions on control of silica and phosphate in Bayer liquor

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Abstract

Control of silica and phosphate levels in digested Bayer liquor is critical for the operation of any alumina refinery. High levels of silica lead to product contamination and unwanted scaling issues on the heater surfaces, whereas high levels of phosphate in liquor lead to alumina losses from the circuit due to its effects on liquor stability. Many alumina refineries face bauxite quality issues. They also face bauxite availability issues from a single source. Due to this, it has become imperative that bauxites from multiple sources need to be processed. Since these bauxites have different levels of silica and phosphate, adjustment in process conditions is a necessity to control silica and phosphate impacts. This paper presents the details of studies done on a number of bauxites of Indian origin, the experimental results obtained thereof. Importantly, it highlights the importance of suitable blending of the various bauxites feeding a refinery on a routine basis in, for the purposes of controlling silica and phosphate at desired levels.

Keywords: Bauxite quality; silica in Bayer liquor; phosphate in Bayer liquor.

1. Introduction

Bauxite ore consists of different mineral phases contributing to alumina, silica, iron oxide and titania as the major elemental oxides and other minor and trace impurities like phosphorous, vanadium, calcium, gallium etc. The proportion of these minerals differ from one bauxite source to another and often, even from the same source. When bauxite is digested in caustic liquor to extract alumina using the Bayer process, silica and various other impurities also go into solution. Six common impurities namely, vanadium, phosphorous, chlorine, sulphur, silica and fluorine, are present in liquor.

Silica is present in bauxite mainly as the kaolinite mineral ($Al_2O_3.2SiO_2.2H_2O$) and partly as quartz (SiO_2). Under the low temperature digestion conditions predominantly employed for gibbsitic bauxites, the kaolinite reacts with caustic but also simultaneously precipitates out as Bayer sodalite, also called desilication product (DSP - $3[Na_2O.Al_2O_3.2SiO_2.2H_2O]Na_2X$).

Liquor silica is automatically limited by the solubility of DSP. Sodalite is roughly twice as soluble in pregnant liquor as in spent liquor. Hence, the digester blow-off (DBO) liquor can never be desilicated to the solubility of sodalite in spent liquor passing through the heaters.

1.1 Effect of high silica and phosphate in DBO and why control is needed

Silica present in the liquor affects the Bayer process and the alumina trihydrate (ATH) product mainly in two ways:

i) When the liquor is passed through heaters for heat recovery and for achieving the desired temperature for digestion, the silica in the liquor precipitates out as hard sodalite scales on the heater surface. This is at an especially increased level at the high temperature end of the heater circuit due to kinetics. The scales inhibit heat transfer, adversely affecting heat recovery efficiency. They also call for maintenance of the heater tubes at an increased frequency.

ii) Higher levels of silica in DBO can also result in product contamination in the precipitation stage, through co-precipitation of silica with ATH, and post-precipitation phenomenon.

All bauxites contain some caustic soluble phosphates. The level can range from 0.03 % to up to 3 % as P_2O_5. Phosphate minerals have been identified as being calcium phosphate ($Ca_3[PO4]_2$), crandallite ($CaAl_3[PO_4]_2[OH]_5.H_2O$) and apatite ($3Ca_3[PO_4]_2.Ca[F,Cl,OH]_2$).

High phosphate levels in Bayer liquor can affect the process in the following ways:

i) It may decrease stability of pregnant liquor and/ or DBO by suppressing calcium solubility.

ii) It can affect liquor filtration through reaction with lime to form carbonate-apatite on the filter medium.

iii) It can cause difficulties by precipitation in equipment as a mixed-salt with vanadium ($NaF.2Na_3[PO_4,VO_4,AsO_4].19H_2O$).

1.2 How silica and phosphate are controlled

Silica in DBO liquor is controlled by improving the desilication efficiency up to digestion stage. This is generally achieved through adjustments in process conditions during pre-desilication, digestion and/ or post-desilication, wherever applicable. Increase in caustic concentration, pre-desilication/ digestion temperature, and pre-desilication/ digestion time are the key ways of achieving this.

The silica solubility in Bayer pregnant liquor is given by the Oku-Yamada equation;

$$\text{Equilibrium silica in Liquor, g/L as } SiO_2 = 1.58 \times 10^{-5} \times C \times A$$

where C = Caustic concentration, g/L as Na_2CO_3
A = Alumina concentration, g/L as Al_2O_3

As is well-known, it is not practically possible to get any reaction to proceed to its end. Hence, the actual silica level in DBO liquor would be higher that indicated by the equilibrium solubility, as calculated above.

Based on experience with different bauxites and plant conditions, it is generally accepted that if the following conditions are satisfied, desilication efficiency can be considered to be acceptable.

$$\text{(a) Silica ratio} = \frac{\text{Actual silica level in DBO, g/L}}{\text{Equilibrium silica, g/L}} < 1.27$$

$$\text{(b) Silica super-saturation} = \text{Actual silica level in DBO} - \text{Equilibrium silica} < 0.15 \text{ g/L}$$

Phosphate in Bayer liquor is controlled mainly through reaction with lime compounds to form insoluble carbonate-apatite and removed with bauxite residue. Lime compounds are added prior to digestion stage or immediately after it, to the DBO. Some refineries practice the process of concentrating and cooling spent liquor to precipitate out the mixed-salt as enumerated earlier to reduce phosphate and other impurities in a controlled manner.

2 Experimental details and results

2.1.1 Silica control

Different sets of experiments were conducted to study the effect of silica content in bauxites. These are presented below:

2.1.2 Optimisation of process for desilication of high silica bauxites under Belgaum plant conditions

Bauxites with k.silica content of 4, 7 and 10 % were used for these studies. Initially pre-desilication (PDS) tests were conducted under different conditions of temperature and time followed by digestion under a single set of conditions (Temp: 140 °C, Time: 35 min, Target A/C: 0.695).

The results related to silica behavior are presented in Table 1.

Table 1. Effect of PDS conditions on silica behavior.

(k.silica in bauxite: 7 %)

PDS temperature, °C	85			90			95		
PDS time, h	8	12	16	8	12	16	8	12	16
Silica ratio	1.32	1.29	1.21	1.31	1.30	1.28	1.37	1.35	1.33
Silica super-saturation, g/L	0.18	0.16	0.12	0.17	0.17	0.16	0.21	0.19	0.18

With 8 hours of PDS time, it is not possible to achieve acceptable desilication. As PDS temperature is increased from 85 °C to 90 °C to 95 °C, silica ratio and silica super-saturation both show an increasing trend, even at 12 & 16 hours of PDS time. Confirmatory tests were done at 85 °C. Results are presented in Table 2 below.

Table 2. Confirmatory tests.

(PDS temperature: 85 °C)

PDS time, h	12	16		
k.silica in Bauxite, %	7	4	7	10
Silica ratio	1.34	1.37	1.35	1.37
Silica super-saturation, g/L	0.19	0.21	0.20	0.21

It is not possible to achieve desired desilication by adjusting only the PDS conditions with 35 minutes of digestion time.

Further tests were conducted by varying the digestion time. Results are presented in Table 3.

Table 3. Tests with different digestion time.

(PDS temperature: 85 °C)
(PDS time: 16 h)
(Digestion temperature: 140 °C)

k.silica in Bauxite, %	4			7			10		
Digestion time, min	35	45	60	35	45	60	35	45	60
Silica ratio	1.19	1.15	1.28	1.24	1.21	1.27	1.27	1.26	1.23
Silica super-saturation, g/L	0.11	0.09	0.16	0.13	0.12	0.16	0.15	0.15	0.13

At 35 min and 45 min digestion times, there is an increase in silica ratio and silica super-saturation with an increase in k.silica in bauxite. There is improvement in desilication with increase in k.silica in bauxite at 60 min of digestion time.

From the above set of experiments, it is seen that the plant has to maintain PDS conditions of 85 °C and 16 h consistently. However, digestion time needs to be optimized based on k.silica in bauxite and has to be increased to 60 min for k.silica of 7 % and above.

2.1.3 Desilication of low silica Utkal bauxites

Bauxite containing about 1 % k.silica was used. Three different bauxite grinds were evaluated. Some tests were also done by changing the caustic concentration of both ex-PDS and DBO liquor. Results have been presented in Table 4, Table 5 and Table 6 below.

Table 4. Effect of digestion temperature and bauxite grind.
(PDS temperature: 92 °C)
(PDS time: 20 h)
(Digestion target A/C: 0.728)
(DBO caustic: 240 g/L)
(Digestion time: 45 min)

Bauxite grind, %passing 35 mesh	80		90
Digestion temperature, °C	140	145	145
Silica ratio	1.56	1.41	1.42
Silica super-saturation, g/L	0.37	0.27	0.27

Table 5. Effect of PDS time and ex-PDS caustic.
(Bauxite grind: 80% passing 35 mesh)
(PDS temperature: 95 °C)
(Digestion target A/C: 0.728)
(DBO caustic: 240 g/L)
(Digestion temperature: 145 °C)
(Digestion time: 45 min)

Ex-PDS caustic, g/L	225		240	
PDS time, h	20	24	20	24
Silica ratio	1.33	1.35	1.37	1.32
Silica super-saturation, g/L	0.21	0.23	0.24	0.22

Table 6. Effect of DBO caustic and bauxite grind.
(PDS temperature: 95 °C)
(PDS time: 20 h)
(Ex-PDS caustic: 240 g/L)
(Digestion target A/C: 0.728)
(Digestion temperature: 145 °C)
(Digestion time: 45 min)

DBO caustic, g/L	240			270		
Bauxite grind, %passing 35 mesh	80	90	100	80	90	100
Silica ratio	1.37	1.35	1.38	1.35	1.39	1.39
Silica super-saturation, g/L	0.24	0.23	0.25	0.29	0.33	0.32

Under any of the conditions studied, desired desilication was not achieved.

2.2 Phosphate control

Tests were conducted with bauxites containing different levels of P_2O_5 in the range of 0.08 % to 0.24 %. Lime addition to PDS was done in the range of 0 to 12 moles CaO per mole of P_2O_5 in bauxite. Results are presented in Table 7 below.

Table 7. Effect of P_2O_5 in bauxite and lime addition.

P_2O_5 in bauxite,%	0.24					0.17					0.08				
P_2O_5 in digestion feed liquor, g/L	0.44					0.40					0.40				
Lime addition, moles CaO/ mole P_2O_5	0	3	6	9	12	0	3	6	9	12	0	3	6	9	12
P_2O_5 in pregnant liquor, g/L	0.62	0.47	0.43	0.39	0.37	0.51	0.48	0.38	0.40	0.40	0.44	0.43	0.41	0.38	0.33
THA extraction, %	93.0	94.5	93.3	93.8	93.4	93.9	95.4	95.8	95.3	95.4	96.8	96.5	96.6	96.2	95.5

Six moles of CaO per mole of P_2O_5 in bauxite results in acceptable P_2O_5 control in DBO (equivalent to P_2O_5 in digestion feed liquor). As P_2O_5 in bauxite increases, there is a trend to decreasing THA extraction.

3 Summary and conclusion

It is important to control silica and phosphate in DBO liquor to desired levels to avoid or minimize the ill-effects post-digestion. It is seen that when silica in bauxite varies (either too low or too high), it is extremely difficult to achieve desired desilication. Similarly, when P_2O_5 content in bauxite feed to digestion changes, it is essential to add lime equivalent to six moles of CaO per mole of P_2O_5 in bauxite so that phosphate content in DBO can be controlled to that in digestion feed liquor.

Many alumina refineries, especially in India, suffer from lack of availability of uniform quality of bauxite. Bauxite from different deposits is being used by these refineries, as per availability at a particular point in time. Due to inadequate stock, the refineries are compelled to process these bauxites as and when they are received. There have been times when the silica content in bauxite had been very low (1 - 2 %) whereas at other times, it can be up to 7 – 8 %. Similarly, P_2O_5 content in bauxite changes with the source of bauxite. Refineries can be designed to process bauxites with silica and phosphate at either end of the spectrum for ensuring proper control, it is practically impossible to "adjust" process conditions within a narrow range in an operating refinery to cater to such wide variation in bauxite quality to control silica and phosphate in DBO liquor at desired levels.

Hence, it is essential that the quality of bauxite feed to the process is fairly uniform on a daily basis. A good system of inventory of different sources of bauxite and a system for blending of these bauxites are basic requirements to ensure uniform quality bauxite feed to the process.