

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

S. Sankaranarayanan

Vice President and Head: Hindalco Innovation Centre - Alumina,
Hindalco Industries Limited, Belgaum, India
Corresponding author: s.sankaranarayanan@adityabirla.com

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 ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) 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 ($\text{DSP} - 3[\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}] \cdot \text{Na}_2\text{X}$).

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 P₂O₅. Phosphate minerals have been identified as being calcium phosphate (Ca₃[PO₄]₂), crandallite (CaAl₃[PO₄]₂[OH]₅.H₂O) and apatite (3Ca₃[PO₄]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.2Na₃[PO₄,VO₄,AsO₄].19H₂O).

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 Na₂CO₃
 A = Alumina concentration, g/L as Al₂O₃

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 than 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.

2.2 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.