Iron Impurity in Liquor – Impact on Product Quality and Control Methods

Sagar S. Pandit[1], Vardhaman Patil[2] and Amit Gupta[3]
1. General Manager – Bayer Process Development
2. Deputy Engineer – Bayer Process Development
Hindalco Innovation Centre – Alumina, Hindalco Industries, Belagavi, India
3. Senior Lead Scientist
Aditya Birla Science and Technology Company, Navi Mumbai, India
Corresponding author: sagar.pandit@adityabirla.com
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Abstract

Alumina is generally produced from bauxites through the Bayer process and is the main raw material for the production of aluminium metal. In addition to this, chemical grade alumina is used for the production of adsorbents, abrasives, polishing agents, refractory materials, etc. In the Bayer process, bauxite is digested with caustic at temperatures ranging from 140 °C to more than 240 °C, depending on the bauxite characteristics, mainly tri hydrate alumina (THA) and mono hydrate alumina (MHA) which determine the digestion technology viz. low or high temperature, or a combination of both (i.e. double digestion). During bauxite digestion, some other impurity bearing minerals also react with caustic. One of the undesirable ones is iron which enters the liquor during high temperature digestion. This iron is present in the liquor in colloidal, suspended, and dissolved forms, and tends to co-precipitate with gibbsite (or THA) during agglomeration and growth stages. Beyond a certain concentration, this iron in THA is an undesirable impurity when the alumina is converted to aluminium metal, impacting its physical properties. Therefore, it is important to control the iron in liquor which involves studying its dissolution in liquor and its incorporation into THA. Several methods, such as the use of lime, some inorganic compounds to precipitate the iron in liquor and also operating at a higher charging A/C have been suggested to control the iron concentration in liquor to acceptable levels. Sand filtration and addition of bauxite residue also represent cost effective methods for controlling iron in liquor. This paper presents the study of iron dissolution and its incorporation into THA and also reviews the various methods available for reducing the iron in liquor to achieve acceptable product quality.

Keywords: Alumina, Bauxite, Digestion, Impurity, Iron.

1. Introduction

In the Bayer Process, bauxite is digested in caustic to form sodium aluminate liquor. It is well known that this liquor contains various impurities such as chlorides, sulphates, organics, and also iron. These impurities interfere with the precipitation of alumina from sodium aluminate liquor and get incorporated in the product alumina as an impurity.

One of these impurities is iron, which is present in three major forms namely suspended, dissolved and colloidal. Iron concentrations as low as 0.015 % in smelter grade alumina are sufficient to impact the cast house product specifications and also affecting the physical properties of the aluminium metal such as malleability and ductility.

Several methods have been developed and studied for the reduction of iron in Bayer liquor such as use of water-soluble ferrous salts for precipitating iron in liquor, sand filtration, addition of bauxite residue, hydrate fluidized bed technique and two stage precipitation.

This paper presents the study of iron dissolution and its incorporation into THA and also reviews the various methods available for reducing the iron in liquor to achieve acceptable product quality.

2. Origin and Nature of Iron in Bayer Liquor

2.1 Origin from Bauxite

Iron is the major impurity present in bauxite. Iron bearing minerals are mainly consisting of hematite, magnetite, limonite, goethite, and siderite. Dissolution of iron into Bayer liquor occurs during digestion. The iron input into the liquor depends on iron oxide concentration in bauxite, iron oxide particle's surface area, free caustic concentration, temperature of digestion, holding time and minerology of bauxite.

2.2 Nature of Iron in Bayer Liquor

Iron in liquor is present in three major forms namely : suspended, colloidal and dissolved iron. Generally, suspended iron accounts for ~ 20 %, and colloidal and dissolved iron account for 40 % each. Suspended iron can be measured through filtration of pregnant liquor and using turbidity meter, whereas colloidal iron can be measured by filtration and centrifugation. However, dissolved iron cannot be controlled and measured easily. Generally, 6–12 mg/L of iron is present in pregnant liquor and concentrations above 20 mg/L are not acceptable.

3. Effect of Iron in Liquor

The iron in liquor co-precipitates during THA precipitation and thus gets incorporated as an impurity into the product. The whiteness of the product is directly impacted by the iron concentration in the THA. It also reduces the current efficiency during the aluminium smelting process. Incorporation of trace amounts of iron into aluminium metal also influences its physical properties such as malleability and ductility.

4. Methods for Controlling Iron in Liquor

4.1 Optimising the Bauxite Quality

This method is the starting point for any refinery with an objective of controlling the iron in liquor and thereby improve the product quality. The major source of iron incorporation in liquor is from the bauxite processed in the refinery. Hence it is important to map the bauxite sources to understand the iron content as well as the mineralogical phases present in the bauxite and thereby assess the impact of these characteristics on the iron incorporation in liquor through detailed processability studies in the laboratory. Based on such studies, the bauxites with the lowest iron incorporation can be selected and the mine plan would be accordingly adjusted to ensure consistent supply of this bauxite to the refinery.

4.2 Use of Ferrous Salts and Flocculation for Iron Control

In this method [1], Bayer liquor is first treated with water soluble ferrous salts. These ferrous salts can be ferrous ammonium sulphate, ferrous acetate, ferrous citrate, ferrous fluoride, ferrous nitrate, ferrous sulphate, and ferrous sulfite. Required amount of a given ferrous salt is added to Bayer liquor maintained at a constant temperature and agitated four (4) times with a plunger. The precipitate is allowed to stand for some time to initiate the aging process, followed by addition of specified dose of polyacrylate flocculant. This method results in a reduction of iron in liquor by ~ 50–70 % [2].

4.3 Sand Filtration of Pregnant Liquor for Iron Control

The adsorption capacity of sand helps in the removal of iron from the liquor. Generally, this method is effective for removing suspended iron. Effective removal of 60 % of the iron is obtained by using washed and dried sand stacked in column. Alternatively, removal of iron can be obtained by filtering the liquor through a layer of sand [3].

4.4 Addition of Bauxite Overcharge or Bauxite Residue Addition

In this method, bauxite is overcharged to process, or bauxite residue is added to bauxite feed for digestion. The iron in liquor is removed by increasing the surface area available for the iron to reprecipitate. However, iron removal is not so efficient, and this method has some disadvantages like higher solids to be flocculated.

4.5 Addition of “as is” or Calcined Bauxite Residue to Filtrate Liquor

“As is” bauxite residue or calcined bauxite residue can be used to treat the filtrate liquor. Bauxite residue used is calcined at 375 °C for 16 hours. Quantities of 10 g/L of “as is” and calcined bauxite residue are added separately to filtrate liquor and treated for at 75 °C for 30 minutes. This method removes iron in liquor by up to 75 %. However, the cost of bauxite residue calcination is high.

4.6 Hydrate Fluidized Bed Technique

Uniform contact between solid hydrate and liquor for iron reduction is done in a column. Aluminium trihydrate is treated with liquor in fluidized condition in a column. Liquor flow rate, bed height and size of solids determine the iron removal rate. This method removes iron from liquor efficiently, but the cost of treating liquor is high and capex required is also high.

4.7 Iron Control by Using Hydrotalcite

Hydrotalcite activation is done through calcination at an optimum temperature. Activated hydrotalcite is used to treat the liquor at temperatures around 75–80 °C for 1 hour to achieve iron removal from Bayer liquor. In the experiment conducted, the hydrotalcite is calcined at 450 °C for around 1–2 hours and 1–10 g/L of calcined hydrotalcite is treated with Bayer liquor at 77 °C for 30 to 60 minutes. The anionic sites of the hydrotalcite act as sites for iron and other organic molecules removal. It is observed in these experiments that more than 50 % iron is removed from the liquor. This method also helps to improve the whiteness of the product hydrate after precipitation from such Bayer liquors.

5. Experimental Study for Controlling Iron Content in Liquor

Based on the review of the methods for controlling the iron content in liquor and the conditions prevalent in the refinery, studies were conducted to reduce the iron content in the liquor to < 50 ppm from the present level of 110 ppm [4]. The process development involved studying the various factors affecting the iron incorporation, options tested for reducing the iron in liquor viz. suspended bauxite residue (BR) optimization, TCA optimization and addition of iron removal aid to decanter overflow.

5.1 Optimisation of Suspended BR in Pregnant Liquor

Experiments were conducted to optimize the suspended bauxite residue solids in the liquor. Solid BR was added to the synthetic liquor on actual Fe_2O_3 in BR basis to study the effect of suspended BR on the Fe_2O_3 content in the product (by giving purity correction). The seed charge, tank slurry temperature and circulation time were adjusted according to the Belagavi refinery precipitation condition. After the required circulation time of 30 h, the slurry was filtered, and the product was washed thoroughly with hot water to remove the leachable soda. The liquor, after precipitation test, was analysed for caustic and alumina. The precipitated product hydrate was analysed for Fe_2O_3. The seed used remained the same throughout the experiment, with a 40 ppm Fe_2O_3 content. The test results are given in Table 1.

Table 1. Precipitation Test for Suspended BR Optimisation.

Doped BR solids, mg/L	5		10		15	
Precipitation start temp, °C	78		78		78	
Precipitation end temp, °C	63	58	63	58	63	58
Seed charge, g/L	300		300		300	
Productivity, g/L	67.6	69.1	63.9	67.0	63.5	66.9
Product Analysis						
Fe_2O_3 in Product, ppm	34.0	22.9	51.4	42.8	60.0	62.8
Fe_2O_3 in Seed, ppm	40	40	40	40	40	40
Fe_2O_3 in New Product, ppm (calc)	-6.0	-17.1	11.4	2.8	20.0	22.8

From the above table, the following observations can be made:

- The Fe_2O_3 in new product reduced with the reduction in the doped BR in synthetic liquor.
- The Fe_2O_3 in new product reduced with the increase in liquor productivity.
- At lower doped solids concentration of ~ 5 mg/L , the Fe_2O_3 in new product show negative values mainly due to lower Fe_2O_3 seed available for precipitation. However, this shows an increase with the increase in doped solids concentration.

5.2 Iron Removal Aid Addition to Decanter Overflow

Iron removal aid addition to decanter overflow was studied for removal of colloidal fraction of iron from Bayer liquor. The iron removal aid was diluted to a specific concentration, and it was added to decanter overflow liquor along with Tri Calcium Aluminate (TCA) for a given time. The liquor was then filtered to separate the residue and analysed for iron content. The results of the testwork with iron removal aid chemical is given in Table 2 and Figure 1 respectively.

Table 2. Results of Iron Aid Removal Addition.

Sl.No	Decanter Overflow volume, mL	Iron Removal Aid Dosage, ppm	TCA Addition, mL	Iron in Liquor, ppm	% Iron Reduction to Blank
1	200	*As Is	3	40.0	-
2	200	**Blank	3	9.0	0
3	200	75	3	3.5	61
4	200	100	3	3.5	61
5	200	200	3	1.8	80

* As is – Decanter O/F liquor without addition of TCA and iron removal aid.

** Blank – Decanter O/F liquor without addition of Iron removal aid

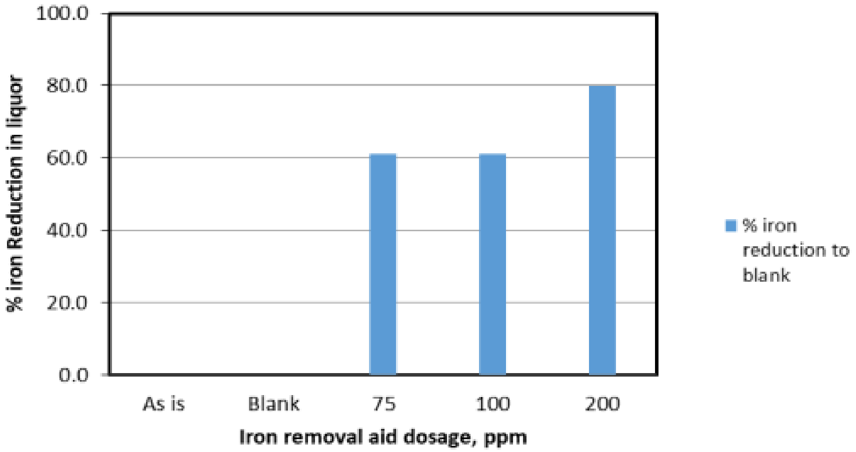

Figure 1. Percentage Iron Reduction in Liquor v/s Iron Removal Aid Dosage.

6. Conclusions

Iron in liquor precipitates along with product and gets incorporated as an impurity to the end product Higher concentration of iron in product, affects the physical properties of metal such as malleability and ductility. It is possible to remove colloidal and suspended iron form the Bayer liquor. However, dissolved iron is difficult to control and remove. Use of ferrous salts followed by flocculation method removes the iron to a greater extent. Encouraging results were obtained with sand filtration of pregnant liquor, filtrate treatment with calcined bauxite residue and hydrate fluidized bed technique. Considering the ease of application, use of iron removal aid was considered for studies on controlling the iron in liquor. The iron removal aid was added to the decanter overflow liquor along with TCA. The iron removal aid showed a percentage reduction of ~60–80% with a dosage of 100–200 ppm. Analysis of the Impact Benefit for some of the main processes is given below in Table 3.

Table 3. Impact Benefit Analysis for Iron Removal Processes.

Process	Impact	Benefit
Bauxite overcharging / BR addition	• Higher bauxite consumption • Higher specific energy consumption	✓ Higher surface area for iron reduction ~10 % ✓ No CAPEX required
Sand Filtration of Pregnant liquor	• Handling / disposal of sand after filtration • Higher soda loss • CAPEX required	✓ ~60 % iron reduction in liquor ✓ Can run for higher cycles
Addition of calcined BR to filtrate liquor	• Higher energy requirement • CAPEX / OPEX is high	✓ ~75 % iron reduction in liquor
Two stage hydrate precipitation	• Lower liquor productivity • Higher specific energy consumption	✓ ~30 % reduction in iron in liquor
Treatment of liquor with fluidised THA	• CAPEX/ OPEX is high	✓ ~80 % reduction in iron in liquor
Treatment with iron removal aids	• Increase in liquor organics over time • Higher treatment costs	✓ ~60 % iron reduction in liquor ✓ Easy application

Overall, it is important to control the iron in liquor by adopting the above methods based on the technical feasibility for ensuring the right quality of product.

7. References

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