ACID CLEANING OF TITANIUM BASED SCALES FORMED ON PREHEATERS IN THE BAYER PROCESS

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Abstract

Today, Bayer process is the basic method for producing alumina from bauxite. Bauxite does not only contain alumina but also contains iron, silicon, titanium and other impurities. Impurities are also dissolving with alumina in hot caustic solution and results to scale formation on several sections of the process. Because of the changing working conditions on different parts of the Bayer process, scale formation occurs having different characteristics at different parts of the process. Scales must be cleaned periodically due to the decreasing heat transfer efficiency and increased energy costs due to scale build up on the heat exchanger surfaces. As the characteristics of the scales are changing form one section to another there is not only one effective solution to remove all kind of scales. The purpose of this study is to find effective chemical compositions for acid cleaning of TiO_2 containing scales on Bayer process.

1. Introduction

The purpose of the Bayer process is to extract aluminium hydroxide from bauxite ore. The high temperatures that is required for the digestion of bauxite, results in an increased dissolution of mineral impurities present in the ore. X-ray difractogram of seydisehir bauxite ore is shown in Fig 1.

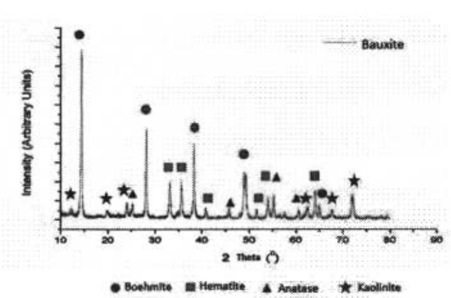

Fig 1. X-ray diffractogram of bauxite samples from Eti Aluminium Inc., Seydisehir

The main phases that are present in the bauxite used by Eti Aluminium Inc., Seydisehir are boehmite, hematite, anatase and kaolinite. A typical chemical composition of the bauxite used by ETİ Aluminium is shown in Table 1.

Table 1. The chemical composition of the Eti Aluminium Inc., Mortaş and Doğankuzu bauxite ores

Oxides	% Mortaş	% Doğankuzu
Loss Of Ignition	12-13	12-13
Al_2O_3	56-57	57-58
SiO_2	8-9	7-8
Fe_2O_3	17-18	17-18
TiO_2	2-3	2-3
CaO	0,5-1	0,5-1

One of the most important problems which are affecting the Bayer process plants is the scale formation on heat exchanger equipments and solution transfer pipes in the process. The most important problems that the scale formation causes in alumina refinery plants are reduction of heat transfer efficiency due to the scale formed on the heat transfer surfaces, decreased amount of solution transfer due to reduced diameter of the solution transfer pipes and loss of alumina and caustic with the resulting scale.

2. Titanium-Bearing Minerals:

The main titanium bearing phases that can be seen in the Bayer process are anatase, rutile, sodium titanate and calcium titanate. The dissolution behavior of the various titanium oxide phases in Bayer process was mentioned in the works of R. Chester at al [1]. It was also claimed that different effects of titanium including the negative impacts of scale formation, titanium in the alumina product and inhibition of boehmite extraction in the high temperature process.

The presence of anatase, sodium titanate and rutile is shown to impact on the dissolution of boehmite. Anatase was found to impact boehmite dissolution the most, with sodium titanate having an intermediate effect and rutile impacting the least **[2]**.

Anatase and rutile (TiO_2) are inert under LTD (low-temperature digestion) conditions. However, under HTD (high-temperature digestion) conditions, when the iron content in the bauxite is low (<5%), anatase is attacked. The reacted titania then reacts with boehmite to prevent its complete extraction **[3]**.

In the present study, investigations were carried out to find effective acid cleaning solution for Ti- containing scale at Eti Aluminium Inc. plant. Scale samples were collected from the different parts of Bayer plant of Eti Aluminium Inc,. The parts where the scale samples were collected is shown in dashed lines on a process flowchart of ETI Aluminium in Figure 2 and these scales were characterized and dissolution tests were performed on Ti- containing scales. Chemical composition of the scale samples are shown in Table 2.

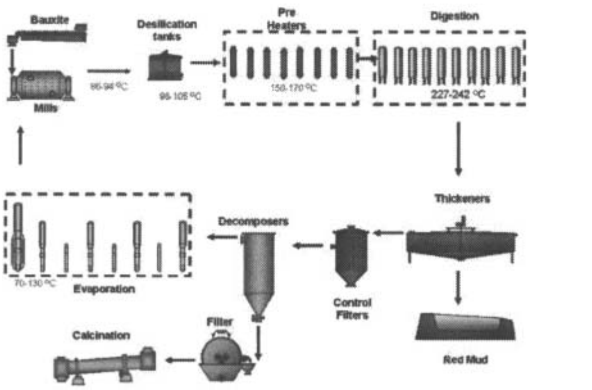

Figure 2. Scale sampling regions of the bayer process

Table 2. The chemical composition of the scale samples

Groups	LOI	Al_2O_3	SiO_2	Na_2O	Fe_2O_3	TiO_2	CaO	MgO	K_2O	SO_3
Pre heater	13,3	13,3	4,1	5,1	7,1	37,8	16,3	3,0	-	-
Digestion	8,8	22,5	10,5	10,8	15,8	19,8	3,3	4,0	-	-
evaporation unit	6,99	29,40	31,40	22,10	3,50	-	-	-	0,80	5,69

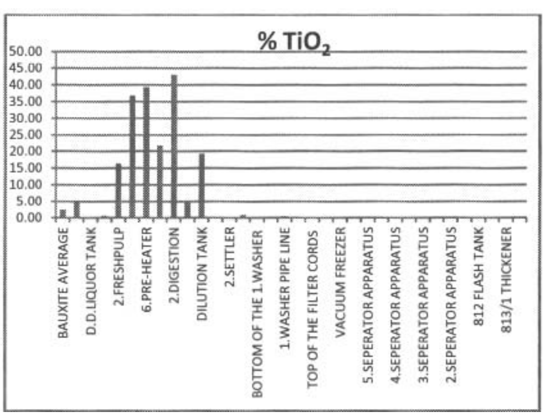

Chart 1. TiO_2 ratio on scales at different part of Eti Aluminium Inc.

As can be seen in the Chart 1, TiO_2 ratio is much more on the digestion and pre-heater unit scales of Eti Aluminium Inc. and cleaning of these units are serious concern of the plant.

XRD results show detailed analysis of autoclave and pre-heater scales in Figure 3 and Figure 4.

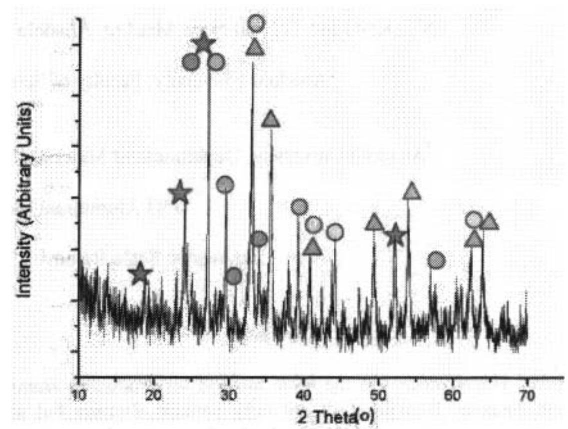

Figure 3. XRD analysis of digestion autoclave scales ( ) calcium titanate, (★) cancrinite, ( ) rutile, (▲) hematite, (●) calcium magnesium

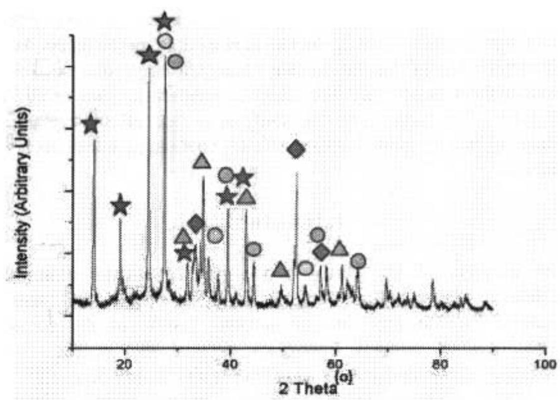

Figure 4. XRD analysis of pre-heater scales (★) Cancrinite, (▲) Hematite, (●) Calcium Titanate, (●) calcium magnesium

3. Scale Removing

There are two ways of scale removal.

- Chemical cleaning
- Mechanical cleaning

Chemical cleaning method includes circulation, fill and soak, cascade, foam, vapor phase organic and steam-injected cleaning techniques. Chemical cleaning is widely used to clean many types of equipment but it has some disadvantages like corrosion and hazardous, toxic effects of cleaning solution.

Mechanical cleaning includes hydrolic (water cleaning, high-pressure water blasting and ultrasonic cleaning), abrasive (rodding, drilling, sandblasting, pipping and scraping, turbining, explosive removal of pipe deposits) thermal cleaning (steam cleaning) **[4].**

In Eti Aluminium, Seydisehir plant, TiO_2 shows itself as the main scale on preheater and digestion units of the Bayer process. In Bayer process, scales generally consist of sodium aluminosilicate phases and HF, HCl and H_2SO_4 acids are used for chemical cleaning effectively but if TiO_2 occurs in the scale then it gets more difficult to clean.

TiO_2 is a basic oxide and will react with concentrated sulfuric acid to produce a soluble species. In the research of A.G. Suss at al, which is about protecting the heater surfaces and scale removal, it was mentioned that the Ti-containing scales are actively reacting with oxalic acid, slowly or selectively react with sulfuric and hydrofluoric acids. In this article, they recommended **10% HCl + 10% $H_2C_2O_4$ + 4% HF** mixture for cleaning Al-, Fe- ,Ti-containing scales **[5]**.

Another acid treatment of TiO_2 is performed by Zhang et al **[6].** They found that Fe_2O_3, Al_2O_3, and Sc_2O_3 in bauxite residue is soluble in dilute hydrochloric acid solution, but the TiO_2 component is soluble in sulphuric acid solution. Because of this reason they proposed a two-step acid leaching process. They reported that the first leaching process was completed using 6 mol/L HCl solution with the leaching rate of Sc_2O_3 being over 80% and the leaching rate of TiO_2 at approximately 1%. Then the insoluble residue from the HCl leaching process was treated by the H_2SO_4 leaching process. In this process the leaching rate of TiO_2 was found to be 96.57% **[7].**

4. Description of the Experiments

Scales having 1,5 and 3,0 mm thickness are collected from digestion and pre-heater units of the plant and they were used as the samples for finding the effective solution to clean Ti-containing scales. **H_2SO_4, HCl, CH_3COOH, HNO_3, $H_2C_2O_4$, HF** acids and their different compositions were used for the experiments at room temperature and their scale solving and corrosion effects on the results were compared. Correlation of scale dissolution rate with scale thickness and dynamic solvent were also investigated.

Pre weighed scale samples were placed in acid solution and after a certain period of exposure to the acid solution the remaining scale samples were washed, dried up and weighed again. After that, scale dissolution ratio was calculated by the following formula **[(First weight- Second weight) / First weight] x 100.**

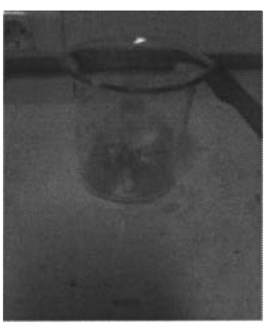

Figure 5. Experimental setup for dynamic solvent

To simulate the dynamic acid solution cleaning for scale removing in the actual plant, an experimental setup is designed to make the acid solution dynamic. Designed setup is shown in Figure 5. In this setup, a platform is placed to the bottom of beaker and solution is stirred with magnetic stirrer. Scale sample is placed on top of the platform thus the scale sample gets into touch with a dynamic acid solution. With this experimental set up, the scale dissolution rate was seen to be increased by 30 %.

The following reactions occur in solution **[4]:**

Hydrochloric acid HCl:

$$CaCO_3 + 2HCl = CaCl_2 + CO_2\uparrow + H_2O \qquad (1)$$

$$Na_2O.Al_2O_3.nSiO_2.2H_2O + 8HCl = SiO_2.nH_2O + 2NaCl + 2AlCl_3 \qquad (2)$$

Oxalic acid $H_2C_2O_4$:

$$2Fe_2O_3 + 6H_2C_2O_4.2H_2O = 2\ Fe_2(C_2O_4)_3.5H_2O + 3H_2O \qquad (3)$$

$$Fe_2O_3.H_2O + 3H_2C_2O_4.2H_2O = Fe_2(C_2O_4)_3.5H_2O + H_2O \qquad (4)$$

On interaction with Ti-compounds, oxalic acid gives soluble complex compound $Ca_2[Ti\ (C_2O_4)_4]$.

Sulfuric acid H_2SO_4:

$$TiO_2 + H_2SO_4 \rightarrow H_2TiO_3 + SO_3 \qquad (5)$$

Hydrofluoric acid HF:

$$CaCO_3 + 2HF = CaF_2 + CO_2\uparrow + H_2O \qquad (6)$$

$$Na_2O.Al_2O_3.nSiO_2.2H_2O + 14HF = SiO_2.n\ H_2O + 2NaF + 2H_3AlF_6 \qquad (7)$$

5. Results

Dissolution results are shown in Chart 2

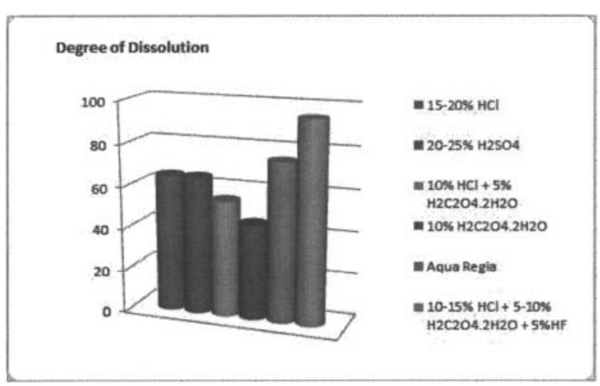

Chart 2. Scale dissolution degree with acid solutions

We achieved the best dissolution for the Ti- containing scales with **10-15 %HCl + 5-10 %$H_2C_2O_4.2H_2O$ + 5%HF** mixture.

Effective dissolution also can be seen if you use **HNO_3** instead of **HCl** in **10-15%HCl + 5-10 %$H_2C_2O_4.2H_2O$ + 5% HF** mixture.

HNO_3 is also effective as HCl. It shows the same effect on scale dissolution but HNO_3 is more corrosive than HCl.

Because of the hazardous effects of HF, it was tried to be kept as minimum as possible in the acid solution. But due to it's known effect on scale dissolution HF is also investigated here in this work. Although HF acid has hazardous effects in the plant it plays an important role on the scale dissolution. With addition of %5 HF, observed scale dissolution rate was increased by 30%.

For best results, cleaning procedure can be done by complex treatment with **10-15%HCl + 5-10% $H_2C_2O_4.2H_2O$ + 5%HF, H_2SO_4** and water cleaning.

6. Conclusions

- There is huge effect on increasing scale dissolution with decreased scale thickness, dynamic acid solution and addition of HF.
- Dissolution rate was decreased with increased thickness and layer of scale. Dissolution rate was decreased by 20 to 30 % with increased 1 mm of scale thickness.
- With the addition of a small amount of HF (5%) to the acid mixture, the scale dissolution rate was increased by 30 %.
- HNO_3 is also effective on the scale dissolution but it has also corrosive effects on metals.
- 10-15% HCl + 5-10% $H_2C_2O_4.2H_2O$ + 5% HF composition is recommended for Ti- containing scales.

7. Acknowledgements

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8. References

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