

Effect of Colour Bearing Impurities of Alumina on Fused Cast Refractories

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Abstract

Universally, glass manufacturer prefers impurity-free glass tank furnaces in order to produce transparent glasses for pharmaceutical and high-end applications. The lining of the glass tank furnaces is normally made with superior quality of refractories. Therefore, alumina should be free from any colour-bearing impurity, in order to make a high purity fused cast refractory. During the molten glass making, in glass tank furnaces, corrosion of refractory lining happens because of chemical attack of slags at elevated temperatures. Subsequently, heavy element impurities in the oxide (i.e., alumina, used as a prime raw material for fusion cast refractory) are leached out from the lining of the furnaces and diffused into the structures of molten glass at elevated temperatures. Impurities such as Co, Ni, Ti, Cr, etc. present in alumina are mainly responsible for different types of visual colour of pharmaceutical and high-end glass, made in glass tank furnaces.

In the present study, this coloration issue of glass tank furnace refractories is addressed by identifying the route cause analysis of the coloration in the alumina. ICP-MS was used to analyze the trace level impurities of the alumina and required process changes were done to produce / generate the desired quality of alumina for such type of fused cast refractory application, in order to produce highly transparent glass, suited to the required application.

Keywords: Fusion, Colourless, Heavy metal, leaching, Refractory

1. Introduction

Glass has been produced for thousands of years dating from as early as 7000 B.C. [1] for its unique chemical, optical, electrical, and thermal properties. Hence, to meet the requirement of modern applications, glass must be transparent and have no adverse effect of any colour. It is also used in variety of applications like packaging required for jar food, bottles for drink, vials for cosmetics and pharmaceuticals, reinforcement structure for five stars building and construction, interior design and furniture, medical technology, biotechnology, life science engineering etc. In order to achieve these advanced properties, glass industry needs high value super refractory product for the lining of glass melting furnaces or glass tank furnaces. Fused cast Alumina – Zirconia – Silica (AZS) refractory [2] is most widely used for glass melting furnaces. Figure 1 shows a typical lining of AZS in glass tank furnaces and Figure 2 shows the flow of glass during the operation of furnaces. Generally, a melting furnace is used to manufacture the fusion cast AZS refractory, where pure zirconia, silica and fusion grade alumina are used as raw materials.

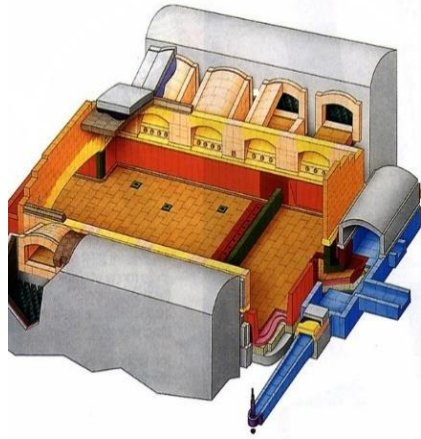


Figure 1. Glass tank furnaces [3], Figure 2. Inside of glass tank furnaces [4].

Alumina [5], Zirconia and Silica melt inside the furnace in developing homogenous compositional chemistry over the entire fused cast refractory material after solidification of molten liquid. The demand for melt cast AZS refractory is increasing day by day in the glass industry due to its property of highly corrosive resistance at high temperature. AZS refractory generally contains 25-30% glass phase (by volume). This glassy phase presents a disadvantage to AZS at service temperature for corrosion and simultaneously with the impurity oxides present in the alumina (which is used as the raw material of the fusion cast AZS refractory) leached out into the molten glass and creates non required colours. The impurity oxides present in alumina, such as Fe, Co, Cr, Ti, etc. [6], are responsible for different types of visual appearance upon the surface of pharmaceutical or any other high-end glasses. Hence there is a need to eliminate or reduce the oxides of impurities present in alumina to improve the quality of the high-end glasses in order to adapt them to modern applications.

Normally, the aluminum tri-hydrate (ATH) is used as the feed material for producing fusion grade alumina. A major volume of ATH is produced through Bayer process (Figure 3) with the use of bauxite as the raw material, which is a natural material deposited over the earth surface over a very long period of times.

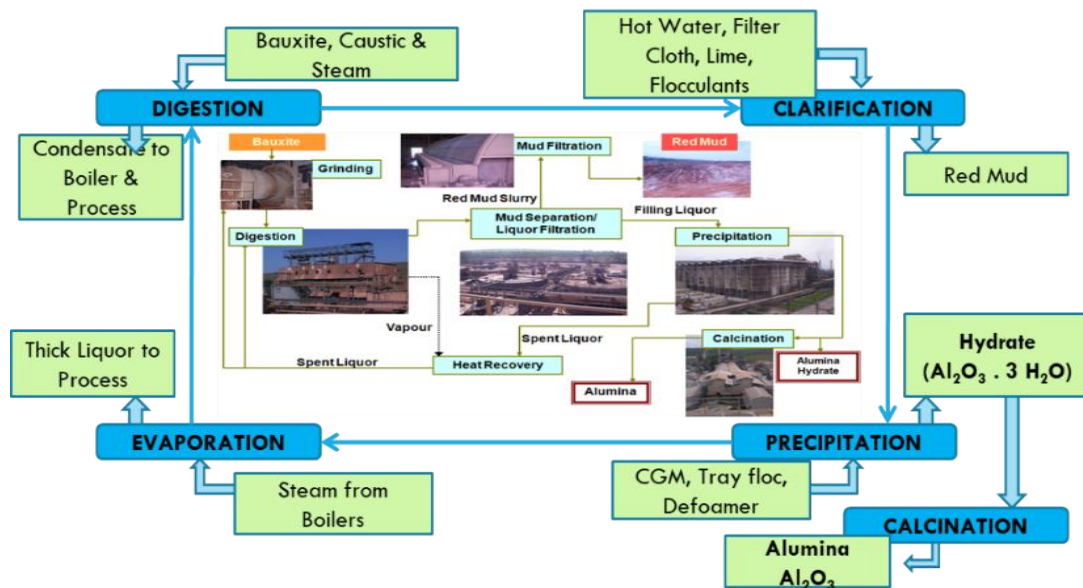


Figure 3. General process flow diagram.

It is worth to mention that this natural material contains different types of impurities (other than alumina) and while processing through the Bayer process, some of the impurities (partially) go into the ATH and subsequently into the fusion grade alumina, leading to the coloration of glasses produced through the glass tank furnace, lined with fused cast AZS refractories. Therefore, challenges lie in the removal of such kind of impurities from the fusion grade alumina to improve the quality of refractory required for manufacturing high-quality glasses [7].

2. Conceptual Approach

A detailed root cause analysis was done to identify the probable cause for the inclusion of impurities in the fusion grade alumina, produced through Bayer process. Accordingly, all the focused areas were identified, and actions were identified to reduce or eliminate the impurities, responsible for the generation of colour in the fused product. A typical cause – effect diagram is depicted in Figure 4.

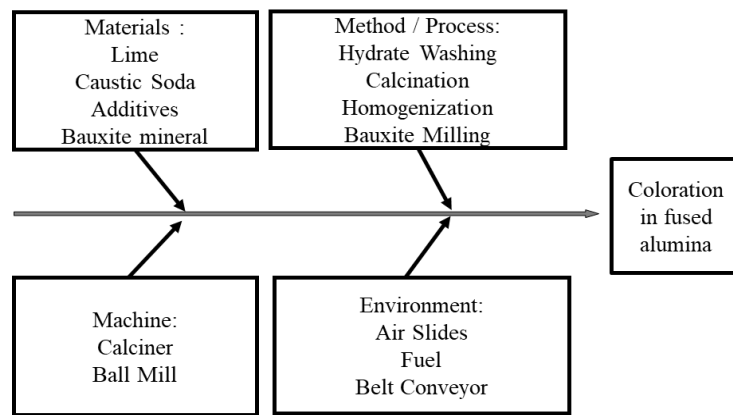


Figure 4. Cause – Effect Diagram for Root Cause Analysis.

3. Experimental

As explained earlier, ATH is the feed stock for producing fusion grade alumina and subsequently for producing purified fusion grade alumina and then for producing fused cast refractories for glass tank furnace. However, the impurities present in the alumina are mainly responsible for exhibiting different types of colours in the fused products, depending upon the nature of impurities and its content.

In the conventional Bayer process, it is very difficult to remove all types of impurities from the product. Therefore, stringent requirement of the final application, the Bayer ATH was modified through a newly developed process as depicted in Figure 5.

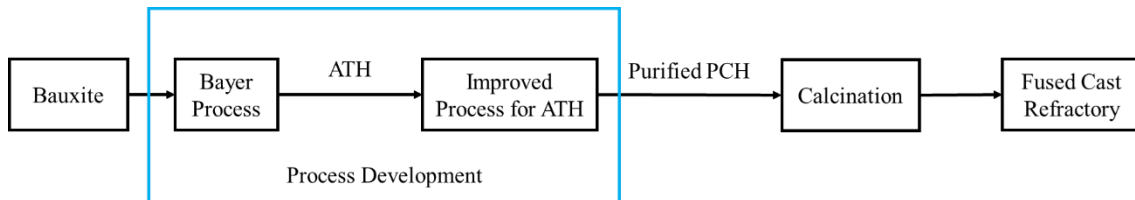


Figure 5. Process development for the purified PCH.

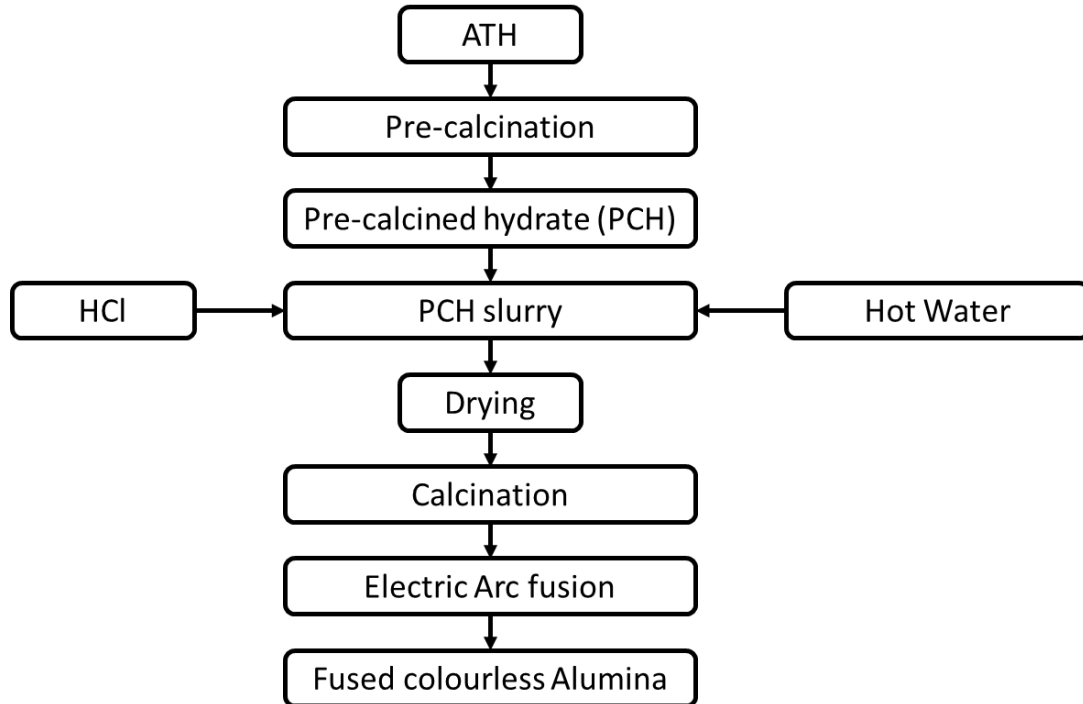


Figure 6. Process flow diagram for producing high purity fusion grade alumina.

In this process, the ATH was partially calcined and treated with acid solution for removing the impurities, present in the material. The details of the experiments are described in Figure 6. The final calcined product (fusion grade alumina) was also fused in an arc furnace Figure 7a) and characterized for the required properties. It could be seen from (Figure 7b) that the fused mass was purely white in colour, making it suitable for the application.

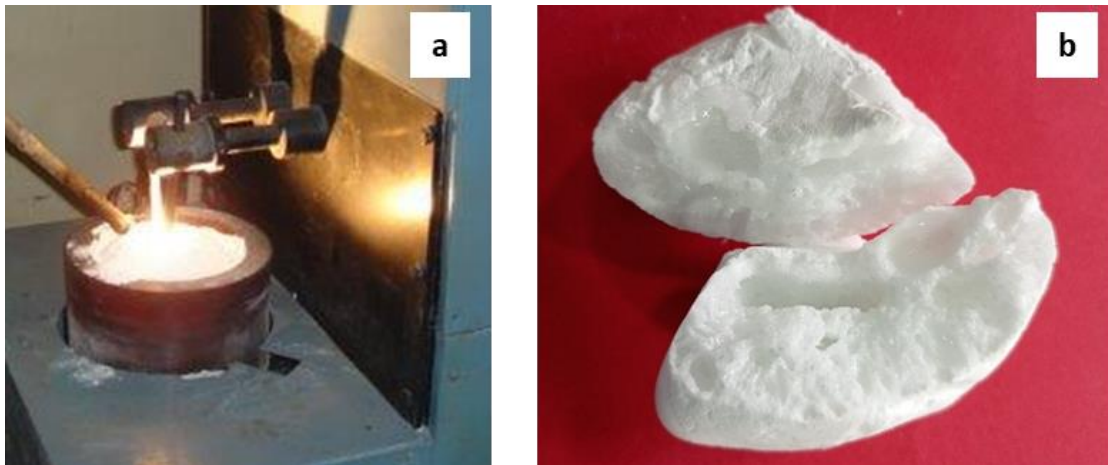


Figure 7. (a) Arc melting furnace and (b) white fused alumina.

4. Results & Discussion

Based on the studies (Table 1) conducted earlier [4], it was observed that the impurities like Ni, Co, Ti, Fe etc. are mainly responsible for exhibiting different types of colours in the fused alumina.

Table 1. Heavy elements and the concentration level for exhibiting colours [8].

Constituents	Concentration (ppm)	Colour
Ni	10	Pale blue
Ni	100	Intense greenish blue
Co	100	Intense blue
Ti	100	Pink or brown
V	100	Light greenish blue
Cr	100	Intense pink
Cu	100	Light grey
Fe	200	Light grey
Fe	400	Intense grey

Table 2. ICP – MS analysis of ATH.

Element	Fe	K	Mn	Ni	Na	Mo	Sb	Ti	Cr	Co
ATH (ppm)	113.05	19.77	0.35	1.92	2082.5	4.2	0.875	229.25	0.087	0.087

Hence, this aspect was investigated in detail in the present study. During partial calcination of hydrate, the crystalline structure disintegrates resulting into a high surface area, which is generally amorphous in nature and thus facilitating the leaching the contaminants from the structure. It could also be seen that some of the impurities were already in the initial ATH and that is why the normal calcined alumina (low as well as high calcined) was showing off white / medium white colour. However, when the ATH was treated to reduce some of these colour bearing impurities (Table 3), especially Fe, Co, Cr, Ti, the product exhibited white colour in the fused mass (Figure 8).

Table 3. Whiteness of fusion grade alumina.

No	Samples	Acid Washings	Appearance	Whiteness Index of fused mass(%)
1	ATH (low calcined)	No	Off white	50
2	ATH (high calcined)	Yes	Medium white	52
3	PCH (washed & calcined)	Yes	Pure white	65
4	Calcined alumina (general)	Yes	Medium white	51

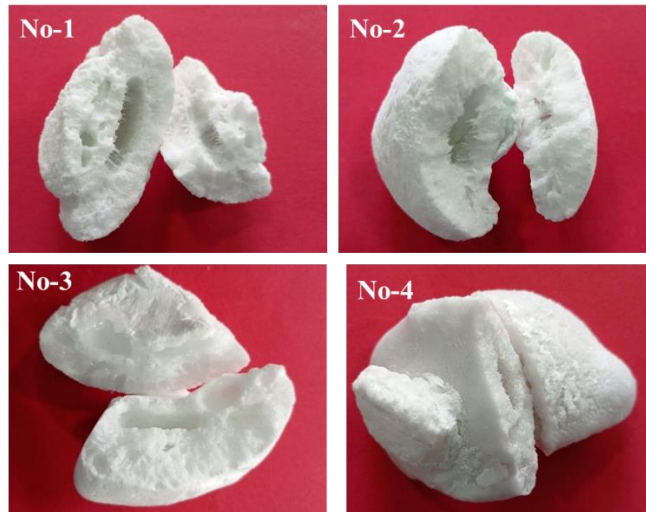


Figure 8. Photos of fused products, prepared with different types of fusion grade alumina.

Table 4. ICP -MS analysis of the fusion tested sample (ppm).

S. No	Fe	K	Mn	Ni	Na	Mo	Sb	Ti	Cr	Co
1	92	8.9	0.1	0.3	667	1.4	0.5	175.2	0.05	0.05
2	64.6	11.3	0.2	1.1	1190	2.4	0.5	130.7	0.05	0.05
3	89	0.01	0.01	0.1	443	0.00	0.4	30.8	0.01	0.01
4	37.5	12.8	0.3	1	1320	1	0.5	97.2	0.05	0.05

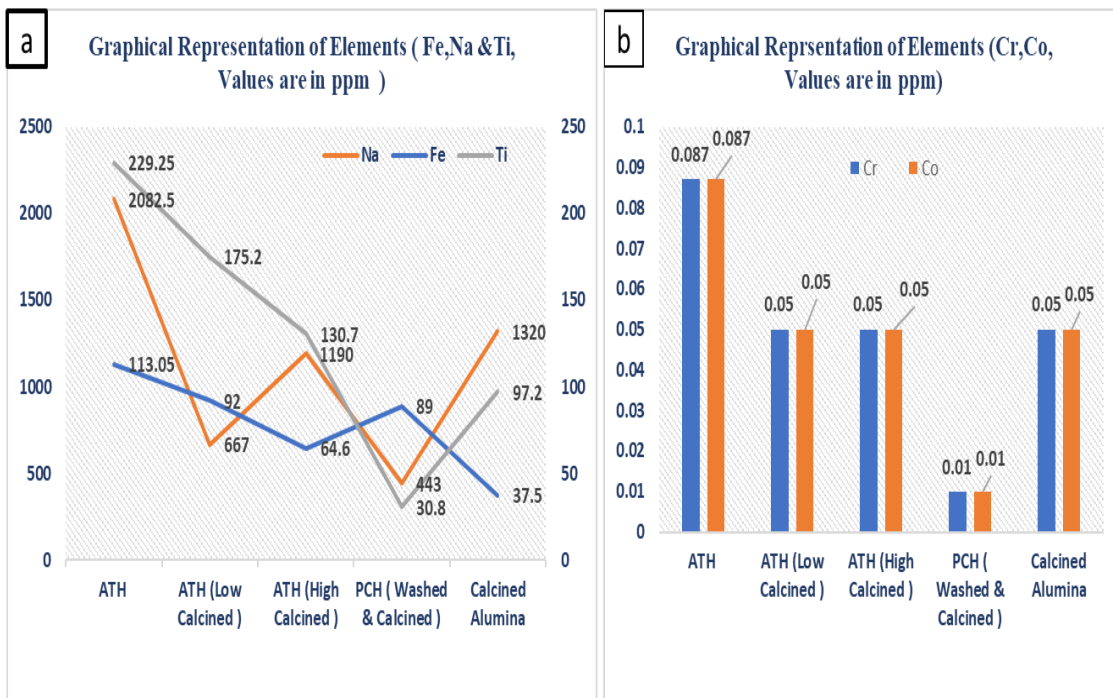


Fig 8. Graphical representation of elements (a) Fe, Na & Ti and (b) Cr, Co.

5. Conclusion

The process developed for producing low impurity alumina, having low level of Fe, Co, Cr, Ti, etc. compared to as calcined alumina of Bayer process is very much suitable for producing a good quality fused cast refractory.

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