A METHOD FOR COMPARING THE HF FORMATION POTENTIAL OF ALUMINAS WITH DIFFERENT WATER CONTENTS

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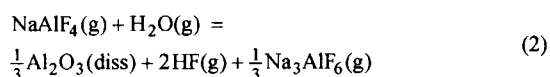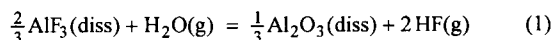
Abstract

In the aluminium industry today, smelters often have to rely on more than one alumina supplier. This creates diversity in the properties of smelter grade alumina (SGA). A method has been developed to compare the HF formation from aluminas containing different amounts of water. The water content of the different aluminas was determined by loss on ignition tests (LOI) and thermal gravimetric analysis (TGA). Further, the aluminas were added to a cryolitic melt kept in a gas tight furnace with a constant nitrogen flow rate. The HF concentration in the off gas during the alumina additions was measured in-situ using a tunable diode laser. A correlation between the quantity of water found from LOI characterisation and the amount of HF formed has been found. It was also found that in this laboratory setup, all types of water contribute to HF formation; structural hydroxyl, physisorbed and chemisorbed water.

Introduction

In the aluminium industry today, smelters often have to rely on more than one alumina supplier and this creates diversity in the properties of smelter grade alumina (SGA). One important property is the water content, and this affects the ability the alumina has to form HF.

The HF formation potential of an industrial alumina can be examined by measuring the HF concentration in the off gas during addition of alumina samples containing different amounts of water to a cryolitic melt.

Reactions 1 and 2 show how HF is formed when fluorides in an industrial bath or in the vapour phase above the bath reacts with moisture[1].

$$\tfrac{2}{3}AlF_3(diss) + H_2O(g) = \tfrac{1}{3}Al_2O_3(diss) + 2HF(g) \qquad (1)$$

$$NaAlF_4(g) + H_2O(g) =$$
$$\tfrac{1}{3}Al_2O_3(diss) + 2HF(g) + \tfrac{1}{3}Na_3AlF_6(g) \qquad (2)$$

Alumina contains different types of water: Structural hydroxyls (gibbsite and boehmite), physisorbed and chemisorbed water [2]. The physisorbed or surface adsorbed water is loosely bound to the surface of the alumina structure. Upon heating, this water is released at relatively low temperatures [3]. The structural hydroxyl is more strongly bound to the alumina structure in forms of hydroxyl groups in the crystal lattice of the alumina, such as $Al(OH)_3$ (gibbsite) and $AlOOH$ (boehmite)[3]. Higher temperatures are required for release of this water. It has been argued that the structural hydroxyls contribute more to HF formation than the physisorbed water with the reason being that during alumina feeding, the physisorbed water is rapidly flashed off before reaction with the fluorides can take place. [3]

Hyland et al. [3] have argued that structural hydroxyl contributes to HF formation in two ways. The first being instant HF formation when parts of the structural hydroxyls react with fluorides when the alumina enters the bath. The second is a more steady state HF formation from the structural hydroxyl. Hyland et al. argues that this takes place because the hydroxyl reacts with the electrolyte to form HF via an electrolytic process. [3]

Perander et al. [4] have suggested redefining the specification sheet of industrial alumina due to problems with predicting the behaviour of the alumina when being added to the bath. One problem with the existing specification sheet is the temperature ranges when reporting mass loss upon heating, i.e. LOI(RT-300°C) and LOI(300-1000°C). Gibbsite will leave mass losses in both LOI temperature ranges. Hence, the specification sheet fails to give any indication of the gibbsite content [4]. Alumina qualities that look similar on the specification sheets may show very different behaviour in the aluminium electrolysis cells. [5]

The purpose of this work has been to develop a laboratory set up that allows comparisons of the "HF formation potential" of different aluminas, by measuring the HF concentration in the off gas as a function of time during addition of alumina samples with different water contents to a cryolitic melt. The intention was also to investigate if the different types of water would have different impact on the HF formation; more specific, could it be verified that the structural hydroxyl contributes more to HF formation than surface adsorbed water. With this in mind, an industrial alumina quality was examined with respect to TGA and LOI characterization before it underwent the above mentioned measurements.

Experimental Setup and Procedure

Characterisation of the aluminas
The water content in the aluminas was determined both by using thermal gravimetric analysis (TGA) and LOI measurements. The TGA was performed on a Netzsch QMS403C instrument. 20-30 mg of alumina was weighed out and kept in a small sample holder (∅=6 mm and h=4 mm). The samples were heated from room temperature to 1000°C with a heating rate of 10°C/min.

The LOI testing was performed with modified temperature ranges to be able to separate the physisorbed water more clearly from

chemisorbed water and structural hydroxyl. The modified temperature ranges was RT-160°C, 160-350°C and 350-1000°C. A hold time of two hours was performed at 160, 350 and 1000°C.

HF formation potential testing
Set up
A laboratory setup, shown in Figure 1, has been built to measure the HF formation potential of the various alumina samples. Figure 2 shows the setup inside the laboratory furnace. The radiation shields were made of nickel. A container holding the Pt-crucible with the cryolitic melt and the corresponding lid was made of nickel. The inside of the Pythagoras tube (h=72 cm, Ø=9.6 cm) was also covered by a nickel foil. Nickel was preferred as the material inside the furnace both to avoid surface adsorbed water to enter the furnace from sintered alumina material, and to avoid HF adsorbing on the materials inside the furnace. Both these two factors could lead to an unwanted higher baseline during the HF measurements.

Figure 1 show a schematic experimental setup used in the laboratory. 1/8'' PFA tubes were used to transport the nitrogen gas. The outer circuits of the laser were flushed with dry N_2 gas to remove any moisture from the transmitter and receiver compartments. Nitrogen gas was constantly purged through the furnace, and flow meters (A and B) were used to determine the nitrogen flow. The nitrogen gas also acted as a carrier gas for the HF formed. The main nitrogen gas flow into the furnace was from the bottom of the furnace. A small gas flow entered the furnace through the feeder tube to avoid blockage of the tube by condensation from the bath.

Chemicals
The cryolitic melt was made from a mixture of NaF and AlF_3 (cryolite ratio of 2.2). The AlF_3 had been sublimated to remove impurities and water. The temperature of the bath was 1000°C. A temperature of 1000°C created a superheat of 19.5°C [6]. NaF was stored at 160°C. No alumina was added to the bath initially, however, Leco analysis from a bath sample from one of the experiments showed that the initial alumina concentration was approximately 0.6 wt%.

Procedure
Alumina was added to the cryolitic melt and the HF and H_2O concentrations in the off gas from the furnace was measured in-situ using a tunable diode laser (NEO Lasergas II). A Y-shaped feeder system was used as shown in Figure 3. The left compartment consisted of a glass container to hold the alumina to be added to the melt. A silicon tube connected the glass container and the Y shaped tube. A clamp squeezed the silicon tube, and this clamp was unscrewed to release the alumina into the bath.

During additions of alumina the only moisture source for was moisture from the alumina fed to the cell. The gas leaving the furnace was led into the laser for analysis and was then led into an HF trap containing 6M NaOH to neutralize the hydrogen fluoride. A flow meter was placed after the HF trap to measure gas flow out of the system. The remaining gas left the system through the ventilation system in the lab. The u-tube was added to the laboratory equipment for pressure monitoring and safety. If the tube leading the gas out of the furnace would have become blocked, the gas would be forced through the u-tube.
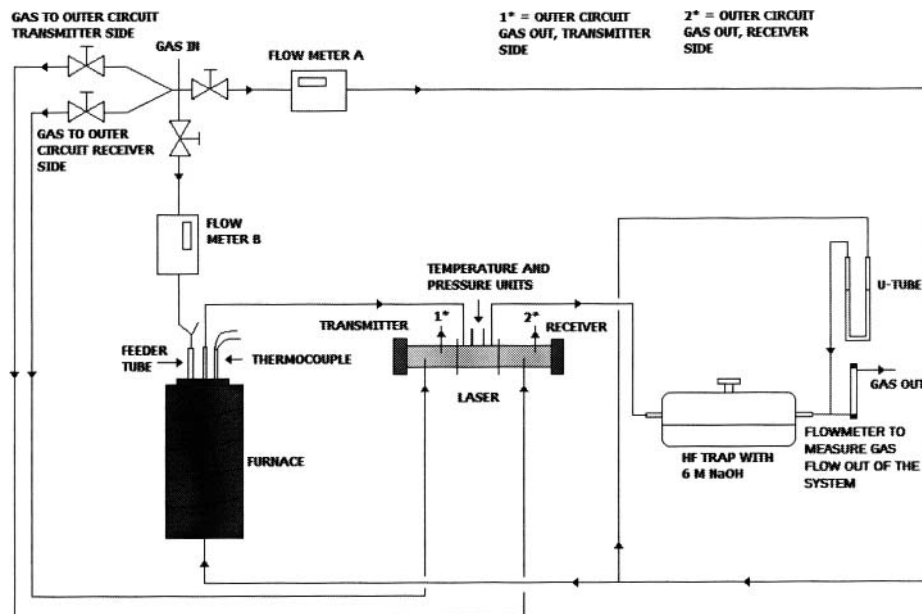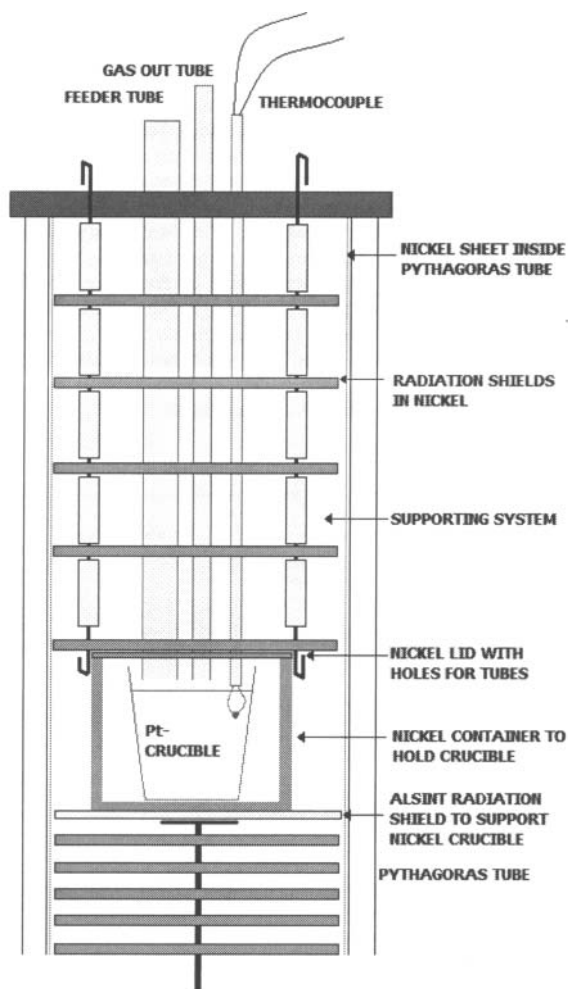

Figure 1: Schematic experimental setup.

Figure 2: Experimental setup inside the furnace. The yellow colour indicates material made of sintered alumina (alsint, Haldenwanger). The grey colour indicates material made of nickel (except for the Pt-crucible inside the nickel container).
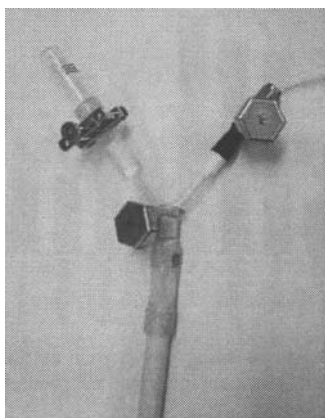

Figure 3: Feeder system.

Between every feeding of the bath the silicon tube and the glass container had to be changed. A new addition of alumina was made when a stable baseline had been obtained.

To get the most out of each experiment, the general idea was to add as many samples as possible during one experiment (typically 10-11). This would lead to an increase in the alumina concentration of approximately 0.9 wt% and a corresponding reduction in the AlF_3 concentration. Under the assumptions that the partial pressure of water is constant, the alumina activity coefficient in the relevant range is constant, and disregarding the change in AlF_3 concentration, the theoretical change in HF formation can be expressed as:

$$\frac{p_{HF}}{p_{HF}^0} = \left(\frac{c_{Al_2O_3}^0}{c_{Al_2O_3}} \right)^{1/6} \qquad (3)$$

Figure 4, showing the theoretical change in the equilibrium partial pressure for HF (g) as a function of alumina content, demonstrates that this change can be neglected for the relatively small changes in alumina concentration caused by the additions. Still, to check for any effects of order and/or time the addition sequence was varied.
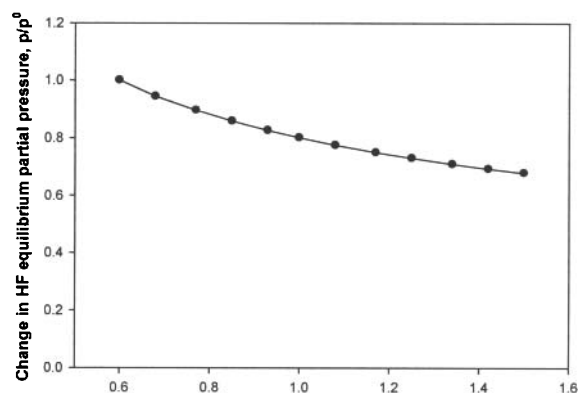

Figure 4: Theoretical change in equilibrium partial pressure for HF as a function of alumina content calculated from Equation 3. It was assumed constant H_2O partial pressure and alumina activity coefficient in the relevant range. The change in AlF_3 concentration was disregarded.

Four separate experiments were performed with the laboratory setup. The HF formation potential was examined for:

- Smelter grade alumina heat treated for two hours at various temperatures before addition (RT, 160°C and 350°C)
- Mixtures of Bayer gibbsite and alumina that had been calcined in the laboratory (high in α-alumina). Various ratios of Bayer gibbsite samples to calcined alumina were tested.
- Humidified SGA (high in physisorbed water).

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- Pure calcined alumina. This alumina quality was added in all the experiments as a reference to check the reproducibility of the experiments.

SGA was humidified by placing the alumina in a tight container on a tray with a water bath below. The alumina powder was left in this humid environment for three days at room temperature. Then the humidified SGA was mixed with SGA dried at 160°C for two hours. Samples of the mixture were tested for HF formation upon addition to the bath. All samples of alumina tested in this work were primary alumina.

Results

Characterisation of the aluminas

The aluminas were characterised by TGA and LOI. Figure 5 shows the thermograms for the calcined alumina, SGA and Bayer gibbsite.
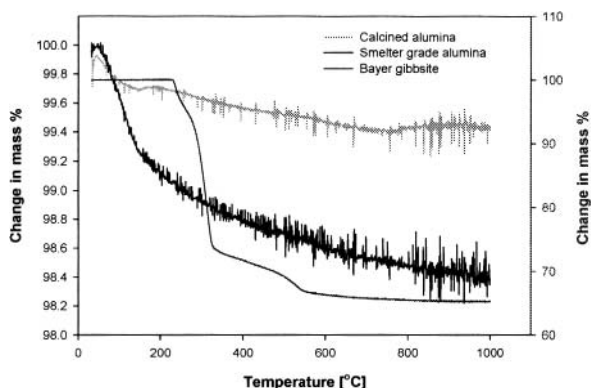
Figure 5: Thermograms for alumina calcined in the laboratory, Bayer gibbsite and smelter grade alumina. The calcined sample is relatively high in α-alumina. Upon heating, the Bayer gibbsite will transform into boehmite by release of two out of three water molecules. The last water molecule in boehmite is further released during the temperature interval of approximately 350-540°C. Both the grey and black curves refer to the left y-axis.

Table 1 shows the results from the LOI testing with the modified temperature ranges for the alumina qualities used in the HF formation potential experiments.

Table 1: Loss on ignition (LOI) measurements with modified temperature ranges.

Quality	RT-160°C	160-350°C	350-1000°C
Calcined	0.50	0.15	0.08
Bayer gibbsite	0.19	28.89	5.72
SGA	1.14	0.44	0.64
Humidified SGA	13.69	0.62	0.80

HF formation potential

Figure 6 shows a graph of the HF concentration in outlet gas during addition of several alumina samples. It is seen that the HF concentration increases rapidly immediately after addition and then declines back to baseline. Figure 7 shows the corresponding bar graph with integrated HF formation for the results of the

experiment presented in Figure 6. The integrated HF formation was calculated by using Riemann sums for the 30 minutes following each addition of alumina. The number of moles of HF was divided by the amount of alumina added to account for any variations in the quantities of alumina added. From Figure 6 it can also be seen that the water concentration in the off gas peaked for each alumina addition. However, the water measurements are not emphasised to a large extent in this article due to some limitations with the laser measuring the off gas. With further improvements considering the water measurements of the laser this could be a great contribution to the understanding of the water release of alumina during addition to cryolitic melts. The addition order of the SGA with the various heat treatments was randomized. Calcined alumina was added first and last in all the four experiments to test the reproducibility of the method both within each experiment and between the experiments.
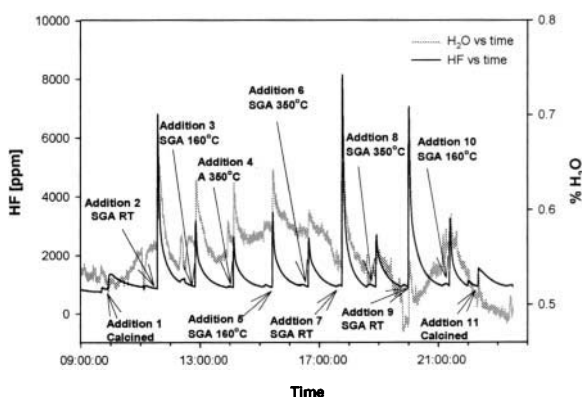
Figure 6: A graphical presentation of the raw data from the experiment where SGA with various heat treatments was added to the bath. Calcined alumina was added to the bath as the first and last addition to check the reproducibility of the method. The addition order of the SGA with various heat treatments was randomized.
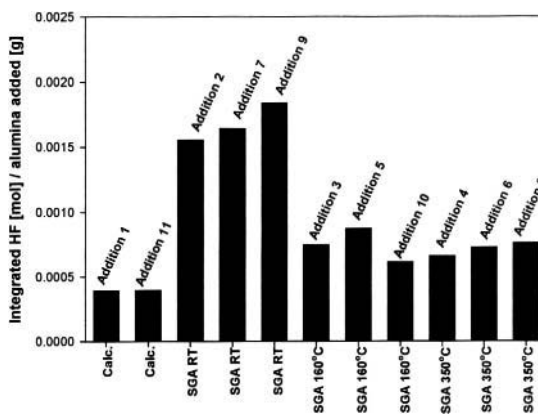
Figure 7: Bar chart showing the impact of the various heat treatments on the SGA on the integrated HF formation.
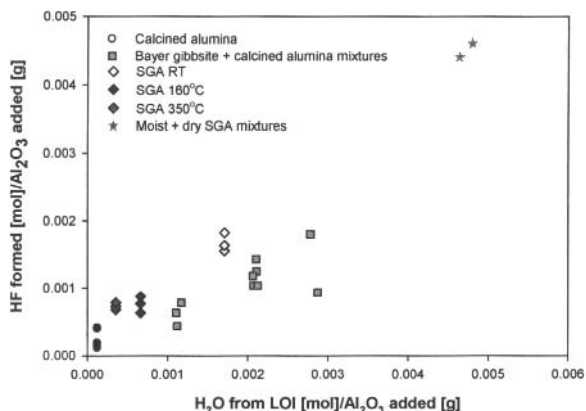
Figure 8: Moles of HF formed for the various alumina qualities vs. H_2O found in the alumina from the LOI measurements. Both HF values and H_2O values have been adjusted for the sample weight. The results presented here are a summary of the results from four separate experiments.

Figure 8 shows the integrated HF formation found for all additions for the various aluminas in the experiments vs. the water content in each sample found from the LOI measurements. Both the HF and H_2O values have been divided by the amount of alumina added in each addition to eliminate any variations in the alumina quantity added to the melt.

Discussion

Characterisation of the aluminas

From the characterisation part of the aluminas through TGA and LOI testing, it is evident that the SGA used in these experiments contain little gibbsite. SGA at room temperature contains a certain amount of physisorbed water. The moistened SGA samples contain a substantial amount of physisorbed water. This is shown from the LOI testing on the sample.

The Bayer gibbsite contains almost no physisorbed water due to its low surface area. However, the amount of gibbsite present in the sample is high. Upon heating some of this gibbsite is transformed into boehmite by release of two out of three water molecules from gibbsite. At higher temperatures (above 350°C) also water from boehmite is released.

The calcined alumina samples contain only a small amount of moisture, the most prominent being some physisorbed moisture.

The new temperature intervals when performing LOI testing show a more clear distinction between the different water sources in the aluminas.

HF formation potential testing

From Figure 8 a clear correlation between the total quantity of water found from LOI characterisation and the amount of HF formed is observed. The addition sequence does not seem to matter, and it seems that both structural hydroxyl, physisorbed and chemisorbed water contribute to the HF formation. It may appear as though the gibbsite has had a lower impact on the HF generation than SGA (grey squares contra diamond shaped points

in Figure 8). The reason for the somewhat lower slope might be that these samples were different from the SGA with respect to other properties than LOI such as particle size, surface area, and thus behaves differently.

In this setup, the physisorbed water (samples represented with "star shaped points" in Figure 8 are high on LOI(RT-160)) has had a high impact on the HF generation. This is contrary to what was expected from earlier reports [3]. One reason may be the relatively long residence time of the gas in the reaction chamber in the present setup. Any vapour that flashes off will have sufficient time to undergo hydrolysis (with bath or vapour). Another important difference in conditions from mentioned article is that in the current work the additions were conducted without any electrolysis taking place.

It should be noted that the absolute amounts of HF generated for the various aluminas is much higher than what is observed in industrial cells if the numbers are converted to kg/ton Al, something which again probably is linked to details in this setup and the fact that the industrial baths have somewhat higher alumina activities and lower AlF_3 activities. The draught is also higher in industrial cells, giving the flashed off physisorbed water a higher possibility to leave the reaction zone for HF formation. However, the amount of HF formed for each alumina is rather reproducible, giving a good basis for comparing various samples. The method has already proven useful for comparing the HF generation potential for different industrial alumina qualities where also other properties than water content was taken into account [5].

Conclusion

From this work it can be concluded that a method has been developed to measure the HF formation potential of aluminas containing different types and amounts of water. The obtained results have proved reproducible within the experiments, as well as in between experiments. Also, the addition order of the aluminas does not influence the amount of HF formed for each alumina addition.

In this particular setup, all types of water contribute to HF formation: structural hydroxyl, physisorbed and chemisorbed water.

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