Effects of Water Cooling of Green Anodes on Anode Furnace Operation

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Abstract

Water can be present in significant amounts in green anodes due to cooling with water after the forming process. The chemical environment in the pit can potentially be affected by the presence of water and may cause degradation mechanisms of the refractory lining so far not considered. A thermodynamic assessment of the role of water on formation of HF(g) due to traces of cryolite bath in the green anodes is presented. It is shown that water results in the formation of HF, and subsequently, it is predicted that HF will react with the refractory materials forming a solid oxyfluoride phase at moderate temperatures. The oxyfluoride is however not thermally stable during the whole baking cycle and SiF_4 will evaporate upon further heating. Finally, the effect of water on carbon gasification and CO and H_2 production during anode baking is also addressed. The findings are discussed in relation to previous studies of the degradation of refractory linings in anode baking furnace.

Keywords: Water cooling, volatile HF, anode baking furnace, refractory lining.

1. Introduction

The importance of sodium fluorides in relation to degradation processes of refractory material in anode baking furnaces has been investigated in several works [1–4]. Studies of spent lining from anode baking furnaces have revealed large amounts of sodium in spent linings. These observations demonstrate the occurrence of reactions between volatile sodium fluorides and aluminosilicate refractory lining. Thermodynamic calculations have illustrated how cryolite, when present in green anodes, can be a source of significant levels of sodium fluorides vapor in the pit during baking [5]. At elevated temperatures, the refractory lining will react with both volatile NaF and $NaAlF_4$ forming various sodium aluminosilicates and $SiF_4(g)$, in accordance to stability diagrams reported earlier [5]. In contrast to the abovementioned studies, recent investigations of both open and closed anode baking furnaces have shown little or no traces of sodium in the spent lining [6]. Consequently, the proposed reactions between volatile fluorides and the refractory lining are not as dominating as reported earlier, demonstrating that other mechanisms is the main cause for degradation of the refractory linings in the furnaces. The reducing atmosphere in the bottom of the pit has been given some attention in that respect, but it has been difficult to conclude on a single mechanism [6,7]. Recent *in situ* experiments of gas composition in the anode baking furnace during baking have given some valuable insight regarding the chemical conditions which the refractories are being exposed to [8]. Transient concentration of e.g. CO and CO_2 were recorded, in addition to large concentration CH_4 in the first part of the firing cycle. Moreover, the study did show significant levels of water vapor in the furnace during the first part of the baking cycle, expected to origin from the extensive use of water cooling of green anodes. The presence of water in the anodes prior to heat treatment introduces new chemical aspects not considered before. Here, the previous calculations of reactions in a dry gas atmosphere is expanded to comprise the effects of water vapor. The aim of this work was to address the effect of water on the refractory stability at elevated temperatures. The cost of heating and evaporating water was discussed and related to the total energy cost of the anode baking process. The effect of water on carbon gasification was finally also discussed.

2. Thermodynamic assessment

A thermodynamic assessment was carried out with the thermochemical software FactSage 7.2. In the first part of the assessment, phase stability was investigated in a system consisting of cryolite, carbon and water at various temperatures, through equilibrium calculations by minimization of Gibb's energy. Subsequently, the result from the first part was used to determine the stability of aluminosilicate refractories in similar environments. This work was based on the *Equilibrium* module in combination with the *FactPS* database as described earlier [5].

3. Results & Discussion

3.1. Volatile Fluorides

The major effect caused by the entry of water in the anode pit is the formation of gaseous HF. The volatility of $NaAlF_4$ and NaF is not affected and the vapor pressure remains as reported earlier as long as solid cryolite is present [5]. This is summarized in Figure 1a, where the vapor pressure of $NaAlF_4$, NaF, HF and water are shown as a function of temperature with 5 mol% water present in the pit atmosphere. A significant volatility of fluorides caused by the formation of HF is evident at lower temperatures. The partial pressure of HF is as high as 0.01 bar at 850 °C, meaning that the refractory lining in the pit is exposed to fluoride containing gas at considerably lower temperatures than previously anticipated. As the amount of water in the system increases, the partial pressure of HF increases accordingly as shown in Figure 1b. The presence of water together with cryolite during anode baking could thus be source of volatile HF at temperatures significantly below that of the volatile fluorides $NaAlF_4$ and NaF.

The two dominating chemical equilibria discussed are Reaction (1) and (2). Reaction (1) shows the formation of liquid NaF and gaseous $NaAlF_4$. There is also a considerable vapor pressure of NaF, even though it remains stable as a liquid.

$$Na_3AlF_6\,(s) = 2NaF\ (liq) + NaAlF_4\,(g) \tag{1}$$

The addition of water to the system enables the second equilibrium presented in Reaction (2).

$$9Na_3AlF_6\ (s) + 14H_2O\ (g) = 28HF\ (g) + 26NaF\ (liq) + NaAl_9O_{14}\,(s) \tag{2}$$

Here, cryolite reacts with water and forms gaseous HF, in addition to liquid NaF and β-alumina. Reaction (2) is the main cause of the enhanced volatility of the fluorides due to the presence of water in the pit.

elevated temperatures [1,6,7]. Since water does not affect the oxygen activity and hence not the degree of SiO formation, water vapor would not influence the process of SiO_2 depletion.

Reaction (5) demonstrates that carbon and water vapor reacts and forms CO and H_2 above 700 °C and thereby potentially reduce the carbon output from the anode baking furnace. The amount of carbon reacted with water according to Reaction (5) is shown in Figure 3. With 10 % water content in the anode, approximately 4 % of the anode could potentially react with the water.

6. Conclusions

Due to water cooling of green anodes, water may remain in the porosity in the green anodes. The presence of water in the green anodes could influence the anode baking furnace and the baking process. Here, it was shown by thermodynamic calculations that water and cryolite from spent anode butts will react to form HF(g). HF in the pit atmosphere will further react with the refractory lining, and the reaction with HF can potentially explain the previously observed depletion of SiO_2 at the surface of the refractory lining. Presence of water in the anodes would also increase the total energy consumption of the baking process. Anode baking is a costly step in the anode production process, and reductions in cost can be made by minimizing the water content in the green anodes. Finally, water vapor will react with the anodes and form CO and H_2, consequently reducing the carbon content in the baked anodes. Altogether, the present analysis point out the importance to reduce the water content in the anodes.

7. Acknowledgement

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8. References

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