

Thermodynamic Assessment of the Chemical Durability of Refractory Lining in Anode Baking Furnaces

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Abstract

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The aluminosilicate refractory lining in anode baking furnaces undergoes thermal cycling and are exposed to harsh chemical environments. Consequently, the thermal stability and chemical durability of the refractory material is important for the lifetime of the lining. Here, we present a thermodynamic assessment of the stability of the aluminosilicate materials resembling the chemical environment of the anode baking furnace. Volatile species (NaF, NaAlF₄, SiO, CO, etc.) from anodes were identified based on typical chemical composition of green anodes. The most likely chemical reactions of the volatile species and the oxide components in the lining are evaluated. The variation in the volatility of substances due to the thermal cycling and reducing conditions during anode baking was examined in particular. Changes in the mineralogical composition in the lining were predicted based on the thermodynamic calculations and these are summarized in form of isothermal predominance phase diagrams. Formation of sodium aluminosilicate phases and volatile SiF₄ are proposed to be the main consequence of the chemical degradation of the lining due to traces of the cryolite in the green anodes.

Keywords: Anode baking furnace; refractory lining; degradation.

1. Introduction

Carbon anodes constitute an important part in the process of aluminum electrolysis [1,2]. Today, mostly pre-baked carbon anodes are used in modern electrolysis plants due to their higher current efficiency, lower cell voltage and lower energy consumption, compared to the Söderberg anodes [3,4]. The production of pre-baked anodes takes place in anode baking furnaces, separated from the electrolysis process. The principle of pre-baked anode production is quite similar from plant to plant, with some variations with respect to the furnace design [5], i.e. open or closed furnace. Green anodes, made out of coke, recycled anode butts and pitch, are stacked within the furnace and exposed to thermal treatment. As the green anodes are heated up, the structural integrity is reduced when reaching the softening point of the pitch [5]. To prevent any deformation, the green anodes are placed in a confined space (the pit) with no room for movement. To avoid carbon oxidation during baking, the anodes are covered with packing material, usually fine-grained carbon materials such as petroleum coke or metallurgical coke [5]. The recycled anodes used as a precursor in green anode production originates from the electrolysis cell, where the anodes are taken out of operation when they reach approximately 20-25 % of their original size. Besides the anode cover materials, the anodes are exposed to the cryolite bath during operation, and some of the bath and anode cover materials are transferred with the anodes. Impurities, like sodium and fluorine, originating from frozen bath and anode cover materials, are therefore found in increased amounts in the green anodes compared to the expected amounts based on the impurity level of the petroleum coke [1,6].

In the anode baking furnace, the anodes are separated from the hot flue gas by aluminosilicate refractory walls. The operational temperature in the furnace cycles from ambient conditions to 1200-1300 °C in cycles of 20-30 days. During the heat cycle, the cryolite contamination in the green anodes will evaporate as gas species such as NaF and NaAlF₄. The presence of such gaseous species will, together with the temperature cycling under reducing conditions, create harsh operational environments for the refractory walls. In time, the refractory wall will degrade causing its operational performance to decrease, and ultimately lead to the need of replacement of the lining [7,8].

Mineralogical changes in refractory materials due to exposure to sodium and fluorine containing compounds have been thoroughly investigated during the last couple of decades [1,2,7–18]. The focus has primarily been on cathode refractory lining in aluminum electrolysis cells. When aluminosilicate refractories are exposed to sodium fluoride, a series of reactions occur, depending on the silica/alumina ratio in the bricks and the amount of fluoride. The main reaction products are the sodium aluminosilicate phases nepheline (NaAlSiO₄) and albite (NaAlSi₃O₈), together with cryolite (Na₃AlF₆) and β-alumina (NaAl₉O₁₄ or NaAl₁₁O₁₇) [9,10]. In addition, both SiF₄ and NaAlF₄ have been detected during melt intrusion, constituting the dominating gas specie for high and low silica content respectively [11]. The phase stability of aluminosilicate refractories during NaF exposure has been summarized in a degradation map, primarily based on mass balances [9]. Later, Tschöpe et al. [17] investigated the phase stability in aluminosilicate refractories during exposure to Na(g). The result was summarized in a similar degradation map. Autopsy of a lining from anode baking furnaces have revealed the presence of mullite (Al₆Si₂O₁₃), corundum and cristobalite, in addition to an amorphous phase [1,2,7]. The amorphous phase was most abundant close to the anode side of the refractory, corresponding with elevated sodium content in the samples. No sign of fluorides was found in the spent lining [1,2,7].

In this work, a thermodynamic assessment of the chemical stability of the aluminosilicate refractories during anode baking is reported. First, possible reactions between the refractory material and volatile fluorides originating from the recycled anode butts are evaluated. These findings are summarized in form of degradation maps, and compared to similar findings for the degradation of refractory materials in aluminum electrolysis cells. Finally, the effect of other trace impurities in the green anodes and the effect of reducing conditions during the baking process are evaluated.

3. Method

In order to investigate phase stability in aluminosilicate refractories during exposure of volatile sodium fluorides, a thermodynamic assessment was carried out. The thermochemical software FactSage (version 7.0) was used to carry out equilibrium calculations through minimization of Gibb's energy. FactSage is a thermochemical software containing various modules and databases, enabling the user to do a variety of equilibrium calculations [19]. In this work, the *Equilibrium* module has been used in combination with the *FactPS* database to analyze the phase composition during various amounts of NaF and NaAlF₄. The objective of this assessment has been to predict chemical stability for aluminosilicate materials as a function of NaF or NaAlF₄ exposure. The compositional range from pure silica to pure alumina was thus investigated. From a refractory corrosion perspective, a “worst case” scenario has been investigated, with increasing amount of volatile sodium fluorides at a temperature in the upper region of the operational conditions (1300 °C).

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6. References

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