Effects of Water Cooling of Green Anodes on Anode Furnace Operation

Trond Brandvik[1], Arne Petter Ratvik[2], and Tor Grande[3]
1. PhD Candidate
3. Professor
Department of Materials Science and Engineering, NTNU Norwegian University of Science and Technology, Trondheim, Norway
2. Senior Research Scientist
SINTEF Industry, Trondheim, Norway
Corresponding author: trond.brandvik@ntnu.no

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.

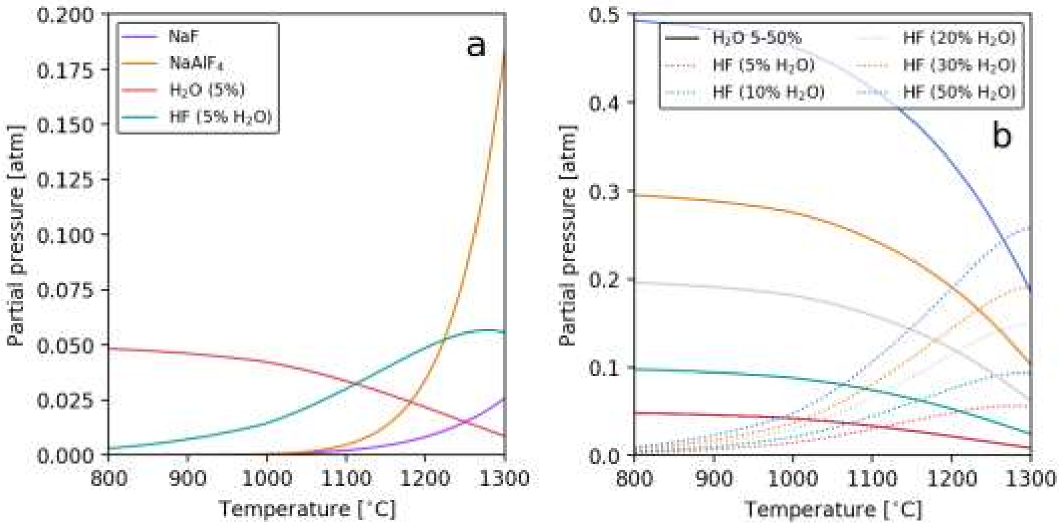

Figure 1. Partial pressures of fluorides for varying temperature (a) and both varying H_2O content and temperature (b).

3.2. Refractory stability in HF-rich environments

With HF present in the anode pit, the thermodynamic stability of the aluminosilicate refractories are potentially no longer only dependent on the presence of sodium fluorides in the furnace. Aluminosilicate refractory materials used in anode baking furnaces normally contains 40-60 wt% alumina with the remaining mostly being silica and some minor minerals [1,3,6]. For this compositional range, the dominating phase in the material is mullite ($Al_6Si_2O_{13}$). The stability of mullite in HF rich atmospheres is hence of great interest. As the temperature rises, mullite and HF react to form $SiAl_2F_2O_4$, alumina and water, in accordance with Reaction (3). This reaction describes the formation of a condensed oxyfluoride phase. The reaction is spontaneous at moderate temperatures.

$$Al_6Si_2O_{13}\ (s) + 4HF\ (g) = 2SiAl_2F_2O_4\ (s) + Al_2O_3\ (s) + 2H_2O\ (g) \qquad (3)$$

$SiAl_2F_2O_4$ is not thermally stable, and the stability of $SiAl_2F_2O_4$ is described by Reaction (4).

$$4SiAl_2F_2O_4\ (s) = 2SiF_4\ (g) + Al_2O_3\ (s) + Al_6Si_2O_{13}\ (s) \qquad (4)$$

Upon temperature increase above ~1100 °C, the reaction shifts to the right and SiF_4 becomes the dominating fluoride phase. As the temperature cycles during the baking cycle, Reaction (3) is favored at low temperature, while Reaction (4) is favored at high temperatures. Fluorine originating from the spent anode butts could thus be found both as a solid ($SiAl_2F_2O_4$) and in the vapor phase (SiF_4) indicating a potential dynamic fluorine reaction pattern.

3.3. Implications of HF

Previous investigations of spent refractory lining have shown regions with SiO_2 depletion [1,6,7,9,10]. These observations are most pronounced close to the surface facing the pit atmosphere, demonstrating that the pit atmosphere is crucial for the depletion process. Formation of volatile SiO(g) under reducing atmosphere and high temperatures have been suggested as a possible mechanism for SiO_2 depletion [1,6,7]. The presence of HF in the pit opens up for an alternative mechanism for SiO_2 depletion. In the first part of the baking cycle, where the HF pressure is potentially highest and the temperature moderate, the condensed fluoride phase ($SiAl_2F_2O_4$) is formed. Once formed, the solid fluoride is not stable during the whole baking cycle. Above ~1100 °C, $SiAl_2F_2O_4$ decomposes to SiF_4(g), alumina and mullite. The dominating fluoride compound is thus shifting from $SiAl_2F_2O_4$ to SiF_4 during the baking process, enabling both Si and F to leave the furnace as SiF_4.

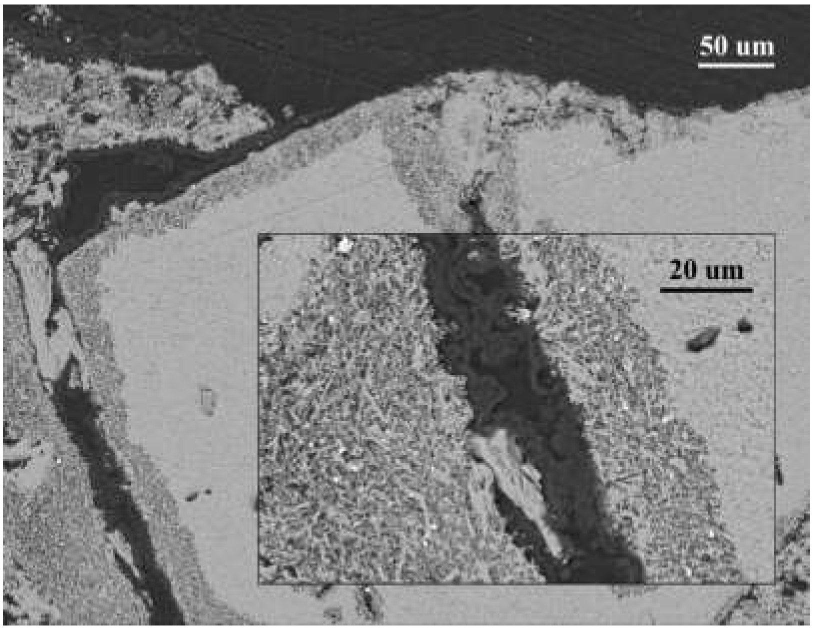

Figure 2. Spent lining from an open anode baking furnaces after 160 baking cycles. Regions facing the refractory surface and open porosity are clearly affected. The reaction layer is depleted of SiO_2, with only mullite and Al_2O_3 left in the structure [7].

SiO_2 depletion is often found as a reaction layer facing the outer parts of the refractory (Figure 2), or close to open porosity further into the lining [7]. The observed thickness of the reaction layer is up to ~200 µm, depending on the distance from the anode pit. The sample presented in Figure 2 is from an open top anode baking furnace collected after 160 baking cycles. Due to the thermal cycling during the carbon anode production, contributions from each baking cycle are most likely minor. By distributing the accumulated reaction layer observed in Figure 2 over 160 cycles, the increase in thickness per baking cycle is approximately 200-300 nm. The thickness of the reaction layer is observed to decrease from the refractory surface on the anode pit side and into the lining [7]. The chemical activity of the reactive gas species is largest in the anode pit, and decrease into the porosity of the lining. Based on the observation of the spent refractory lining the composition of the gas atmosphere, in combination with the baking temperature cycle, are of importance when considering possible mechanisms for SiO_2 depletion in the lining. SiO_2 depletion through the formation of HF and $SiAl_2F_2O_4$ corresponds well with the lack of observed fluorine in the spent lining. The mechanism enables both Si and F to exit the furnace as SiF_4, leaving mullite and alumina in the reaction layer. The overall degradation is however difficult to associate to the depletion of SiO_2 alone. A ~200 µm thick layer of SiO_2 depletion should not be the dominating factor for the macroscopic degradation of the lining observed after many cycles.

To summarize, the observed SiO_2 depletion can be caused by formation of HF formation due to the presence of water in the green anodes. The presence of water may also have and important additional energy cost, which is further treated below.

3.4. Energy consumption due to water in green anodes

During the production of prebaked anodes, the anodes are mixed and formed at temperatures above the softening point of the pitch (typically around 150-190 °C) [11,12]. To regain structural integrity, the anodes need to be cooled down below the softening temperature of the pitch prior to storage and baking. This process is often carried out through water cooling, resulting in absorption of water into open porosity of the green anodes. If proper measures is not taken, water remains in the pores of the green anodes and follows the green anodes into the baking furnace, and is thus heated up together with the anodes. The energy consumption related to anode baking would thus include the cost of heating water. The extra energy consumption due to water is interesting form an economical perspective.

The fuel cost related to the baking of carbon anodes is typically around of 2 GJ/ton baked anode [13,14], in addition to the heat supplied through burning of volatiles form the pitch. The energy consumption related to heating of water can be estimated by assuming a carbon anode porosity of 20 % and that a fraction of this porosity is filled with water. The volume of the anodes are calculated from the average weight (1020 kg) and density (1.6 g/cm^3) and related to the operation of an open top anode baking furnace. When considering the heating and vaporization of water, the liquid is heated from 25 °C and the gas up to 150 °C. By varying the amount of water in the open porosity, and relating the additional heat to a fixed total energy consumption, the fraction of energy spent on evaporation of water can be calculated as presented in Figure 3.

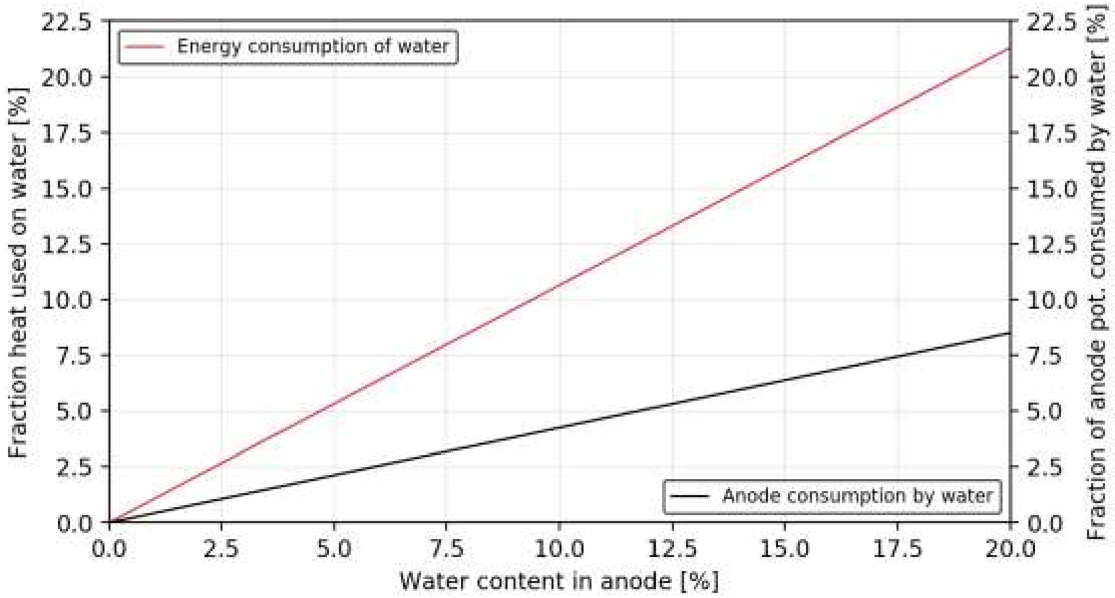

Figure 3. Fraction of total energy consumption spent on heating and vaporization of water (red). Fraction of anode that can potentially react with water, if all water reacts in accordance to Reaction 5.

The energy consumption related to heating and vaporization of water constitutes a significant part of the total energy consumption. If 10 % of the open porosity is filled with water, approximately 10 % of the overall energy cost of baking anodes is related to evaporation of water. The baking step is the most expensive in the production of carbon anodes for aluminum electrolysis. Taking into account the volume of carbon anodes produced, and the total cost of baking such anodes, it is a great potential for cost reduction by controlling the water content in the green anodes.

Due to the way green anodes are produced, they need to be cooled below the softening point of the pitch in order to maintain structural integrity. If water cooling is the most effective way of cooling, then it would be beneficial to address the effect of soaking time on the final water content. If the anodes could be removed from the cooling bath at an earlier stage in the process, then the residual heat would help dry the anodes. This would probably prolong the cooling process, and thus require larger storage facilities for the anodes while being cooled (and dried) in air, but could have a significant positive effect on the overall cost of the anode baking.

3.5. Gasification of carbon by water

Another aspect with water being present in the anodes are the reactions occurring between carbon and water as presented in Figure 4. At elevated temperatures, carbon and water reacts to form CO and H_2 in accordance to Reaction 5. This reaction is dominating above 700 °C, converting all available water vapor into H_2 and CO gas. Below 700 °C, the thermodynamic equilibrium concentrations are controlled by a variety of chemical reactions. Upon temperature decrease, the kinetic barrier for achieving thermodynamic equilibrium is increasing, hence the reactions are kinetically controlled in disfavor of e.g. CH_4.

$$C\ (s) + H_2O = CO\ (g) + H_2\ (g) \qquad (5)$$

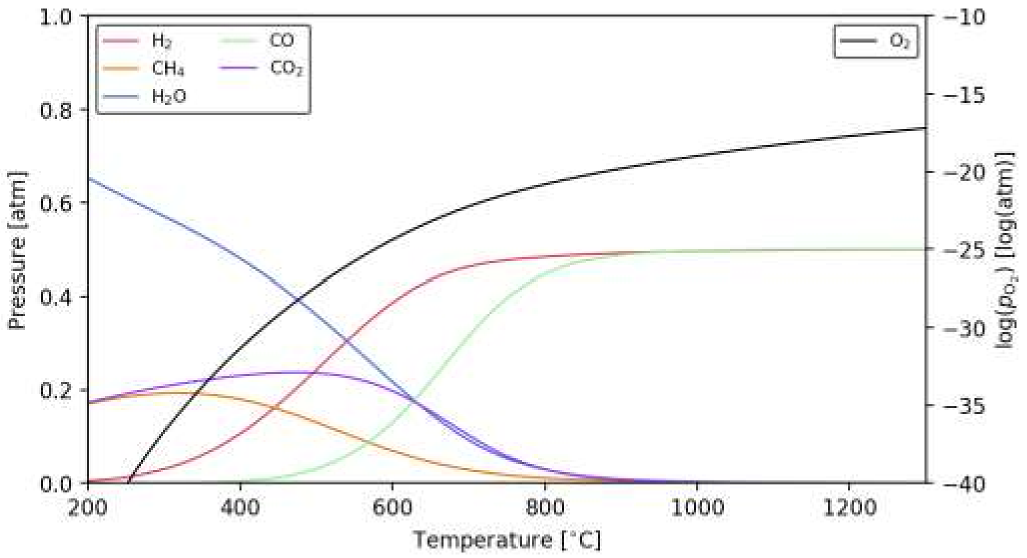

Figure 4. Thermodynamic equilibrium concentrations for carbon and water at increasing temperatures. The dominating reaction converts all available carbon and water vapor into CO(g) and H_2(g) above 700 °C.

The presence of water does however not affect the chemical activity of oxygen, which is mostly controlled by temperature (as shown in Figure 4). The reducibility of the pit atmosphere should therefore not vary significantly with the water content in the anodes. Previous works have linked the depletion of SiO_2 to the formation of volatile SiO(g) in reducing atmosphere and 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

Financial support from the Norwegian Research Council and the partners Hydro, Alcoa, Elkem Carbon and Skamol through the project ”Reactivity of Carbon and Refractory Materials used in metal production technology” (CaRMa) is acknowledged.

8. References

[1] F. Brunk, Corrosion and Behavior of Firecal Bricks used in the Flues of Open Anode Baking Furnaces, Light Met., (1995) 641–646.
[2] P. Prigent, M.L. Bouchetou, Gaseous Corrosion of Alumino-Silicate Refractories in Anode Baking Furnaces used for Aluminium Produciton Part 2, Interceram, 58 (2009) 202–209.
[3] P. Prigent, M.L. Bouchetou, Gaseous Corrosion of Alumino-Silicate Refractories in Anode Baking Furnaces used for Aluminium Produciton Part 1, Interceram, 58 (2009) 121–126.
[4] P.R.T. Tiba, B.H. Teider, F. Figueirdo, J.B. Gallo, V.C. Pandolfelli, Systematic analysis of flue wall bricks used on anode baking furnaces, Light Met., (2010) 1015–1019.
[5] T. Brandvik, A.P. Ratvik, T. Grande, Thermodynamic Assessment of the Chemical Durability of Refractory Lining in Anode Baking Furnaces, ICSOBA 2016, (2016).
[6] T. Brandvik, A.P. Ratvik, Z. Wang, T. Grande, Investigations of Spent Refractory Lining in an Anode Baking Furnace, Light Met., 4 (2017) 1281–1288.
[7] T. Brandvik, Z. Wang, A.P. Ratvik, T. Grande, Autopsy of Refractory Lining in Anode Kilns with Open and Closed Design, Int. J. Appl. Ceram. Tech., DOI: 10.1111/ijac.13108, (2018).
[8] T.A. Aarhaug, T. Brandvik, O.S. Kjos, H. Gaertner, A.P. Ratvik, A study of anode baking gas composition, in: Light Met., 2018: pp. 1379–1385.
[9] Z. Wang, S. Rørvik, A.P. Ratvik, T. Grande, Formation of Carbon Build-Up on the Flue Wall of Anode Baking Furnace, Light Met., (2017) 1265–1274.
[10] N. Oumarou, D. Kocaefe, Y. Kocaefe, Investigation of the refractory bricks used for the

flue wall of the horizontal anode baking ring furnace, Ceram. Int., 42 (2016) 18436–18442.

[11] C. Sommerseth, R. Thorne, A. Ratvik, E. Sandnes, H. Linga, L. Lossius, A. Svensson, The effect of varying mixing temperatures and baking level on the quality of pilot scale anodes—a factorial design analysis, Metals (Basel)., 7 (2017) 74.

[12] K. Azari, H. Alamdari, G. Aryanpour, D. Picard, M. Fafard, A. Adams, Mixing variables for prebaked anodes used in aluminum production, Powder Technol., (2013).

[13] F. Keller, P.O. Sulger, M.W. Meier, D.S. Severo, V. Gusberti, Specific Energy Consumption in Anode Bake Furnaces, Essent. Readings Light Met. Electrode Technol. Alum. Prod., 4 (2013) 408–413.

[14] International Aluminium Institute, Prebaked Anodes for Aluminium Electrolysis, (n.d.) 1–20.