

REACTIONS IN THE BOTTOM LINING OF ALUMINIUM REDUCTION CELLS

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Abstract

The bottom lining in aluminium cells deteriorates due to chemical reactions with sodium vapour as well as with molten bath that penetrates the cathode carbon. The supposedly most important reactions in the system were studied, both theoretically and by experiments. The phase diagram for the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ was supplied with numbers for the equilibrium pressure of sodium as well as vectors showing the change in oxide composition during attack. It could be predicted that chamotte ends up as mainly nepheline. By exposing samples of firebricks to a fluoride melt at $950\text{ }^\circ\text{C}$ ("cup test") as well as to sodium vapour at $800\text{ }^\circ\text{C}$, it was found that materials high in silica were less deteriorated than materials rich in alumina. The reason is probably that the silica-rich materials formed larger amounts of a viscous glass phase. Some observations concerning the "lens" formed in industrial cells are also reported.

Introduction

Construction of the Bottom Lining

Commonly, the bottom lining in aluminium cells is constructed as shown schematically in Figure 1. The cathode carbon is resting on a levelling course of alumina or powdered chamotte. The refractories, as well as the insulation, may be made of bricks or bulk materials. The lining is sometimes supplied with steel plates as well as special barrier mixes designed to slow down the substances penetrating the cathode carbon.

A calculated temperature gradient in the bottom lining is also shown in Figure 1. As can be observed, the temperature drop through the cathode carbon is very small, due to its high thermal conductivity. The refractory layer has a temperature of around $800\text{ }^\circ\text{C}$, and most of the temperature drop between the metal and the surroundings takes place through the insulation.

Limitations

The present work is limited to refractory materials based on aluminosilicates although other materials such as olivine, which contains mainly silica and magnesia, are also used. The system $\text{Al}_2\text{O}_3\text{-SiO}_2$ contains the important compound mullite, $\text{Al}_6\text{Si}_2\text{O}_{13}$. Mixtures of mullite and alumina are termed high alumina bricks, while mixtures of silica and mullite are called chamotte.

There has been some discussion whether the conditions in the lining are reducing or oxidizing. There must be oxidizing conditions shortly after the start of a new cell, but oxygen and CO_2 present will very soon be consumed by reaction with sodium

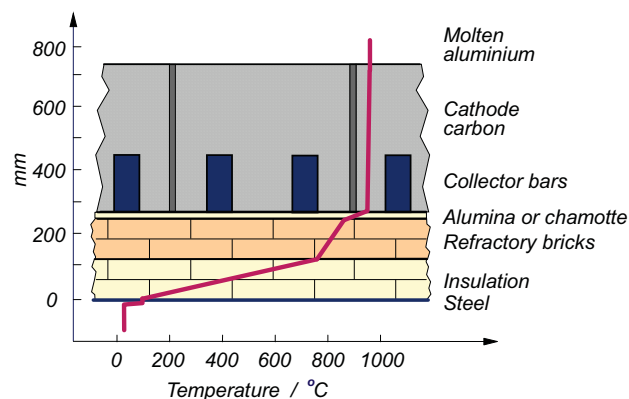


Figure 1. Schematic cross-section through a common bottom lining. The figure also shows the temperature gradient in the lining, calculated with data and dimensions as for new materials.

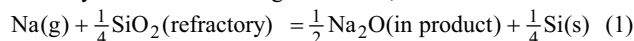
vapour. There is probably also oxidizing conditions close to the ends of the collector bars, since the openings in the pot shell are not gas tight. However, the reaction products appear to be gas tight (glass), which prevents the supply of more air. Finely dispersed metallic silicon has also been found. Therefore, it seems right to assume that the conditions are normally reducing, and the present account is limited to reducing conditions.

Deterioration of the Lining

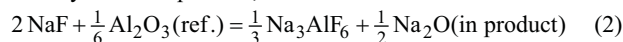
The purpose of the refractory bricks is to provide protection of the insulation underneath it, by reacting with and slowing down sodium and bath that penetrates the carbon blocks. The reactions result in the formation of a glassy "lens" underneath carbon. Several attempts have been made to understand the deterioration mechanisms of refractories used in aluminium cells; see the review articles by Siljan *et al.* [1a-d, 2]. It appears that a number of mechanisms must be involved. It is also clear that the role of sodium cannot be exaggerated. Moreover, reactions involving SiF_4 have been suggested [3, 4]. The present work is a continuation of a recent approach by Solheim and Schøning [5], where the vapour pressure of sodium at 1200 K was estimated.

It is convenient to distinguish between liquid fluoride attack and attack by sodium vapour in describing the deterioration process. Laboratory data and tests mimic either sodium vapour exposure or exposure to liquid fluorides. In real life, the lining may deteriorate by a combination of "both types" of attack. The different types of attack on aluminosilicate materials at reducing conditions can simply be illustrated by the general equations below,

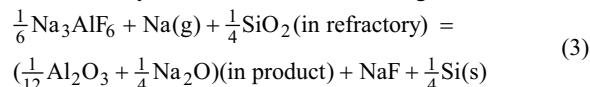
Attack by sodium at reducing conditions,



Attack by bath components,



Combined attack by sodium and bath at reducing conditions,



As will be shown in the following, the oxide phases formed in the deteriorated lining will be the same, regardless of the type of attack. The effect of the attack will also be the same, *i.e.*, the formation of a viscous melt bordering on unaffected firebrick. It has been known for a while that the lining deteriorates due to reactions with sodium vapour as well as with molten bath that penetrates the cathode carbon. Still, most laboratory tests and phase diagram studies have only taken the fluorides into consideration [6]. Only Schønning and Grande [7] have conducted an experimental study concerning the stability of refractory oxides in the presence of sodium vapour.

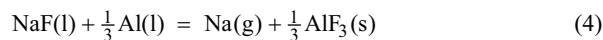
Phase Diagram

When the refractory is attacked by sodium or bath, the oxide phases in the reaction product will be in the ternary system SiO₂-Al₂O₃-Na₂O, which is shown in Figure 2. The diagram is subdivided into Alkemade triangles with one compound in each corner. When the total composition is within one Alkemade triangle, the oxide phases present are the ones in the corners. This means that for example mullite cannot co-exist with nepheline, since they are not in the same Alkemade triangle.

Thermodynamic Framework

The attack of the bottom lining is normally initiated by sodium. Sodium vapour, as well as intercalation compounds C_xNa, diffuse through the cathode carbon and enhances the wetting between carbon and bath. Thus, besides reacting with the refractories, an important role of sodium is “opening up the path” for infiltration of bath into the cathode and lining. As a to-the-point formulation; if it were not for sodium, the lining would last “forever”.

Sodium originates at aluminium-electrolyte interfaces, both at the top of the metal and at sludge resting on the bottom of the cell,



The vapour pressure of Na above the metal can be calculated by

$$p_{\text{Na}} = a_{\text{NaF}} \cdot a_{\text{AlF}_3}^{-1/3} \cdot \exp\left(\frac{-\Delta G_1^0}{RT}\right) \quad (5)$$

where p is the pressure [atm], a is the activity [-], ΔG⁰ is the change in standard Gibbs energy [Jmol⁻¹], R is the gas constant [Jmol⁻¹K⁻¹], and T is the absolute temperature [K].

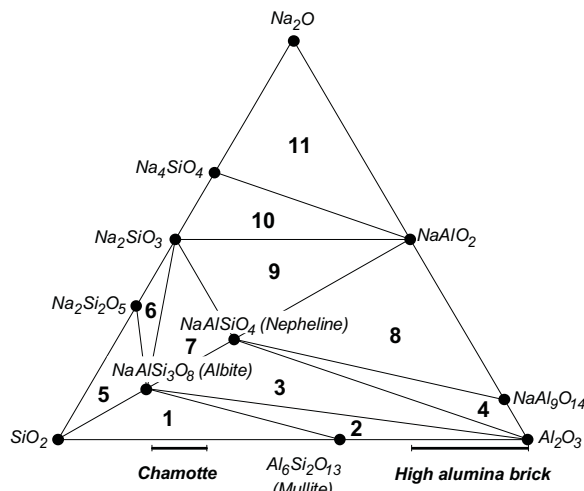


Figure 2. Stable compounds in the ternary system SiO₂-Al₂O₃-Na₂O at 1100 K. The Alkemade triangles are numbered for convenience.

The term “vapour pressure” may refer to the sodium vapour itself, but also to the activity of sodium in different forms (dissolved in bath, dissolved in metal, intercalation compounds, *etc.*). The key point is that elementary sodium, once formed, can take different forms and still be at equilibrium with its own vapour.

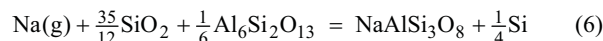
The sodium vapour pressure was estimated [5], see Figure 3. The NaF/AlF₃ molar ratio in the bulk of bath is often close to 2.2, but it may be a little less acid in the sludge at the cell bottom. It seems reasonable to conclude that the vapour pressure of sodium at the cathode is normally about 0.02-0.03 atm (log p_{Na} = -1.7 - -1.5). This represents the maximum possible vapour pressure in the lining. From the vapour pressure of Na above pure liquid Na, it was concluded that the vapour formed at the cathode will not condense until below approximately 600 °C, which is well below the refractory lining (Figure 1).

Thermodynamic data for the oxides (ΔG⁰) were taken from Barin [8], with the exception of β-alumina (represented as NaAl₉O₁₄). ΔG⁰ for that compound was roughly estimated from thermodynamic and activity data for Al₂O₃, NaF, and AlF₃. The data for substances other than oxides were taken from JANAF [9].

Attack by Sodium Vapour Only

Equilibrium Sodium Pressure

The general reaction between sodium and compounds in the refractory (or in intermediate deterioration products) at reducing conditions is given by Equation (1). For Alkemade triangle No. 1 in Figure 2 this reaction becomes,



Although similar reactions can be formulated with aluminium as product, Si(s) will be more stable [5].

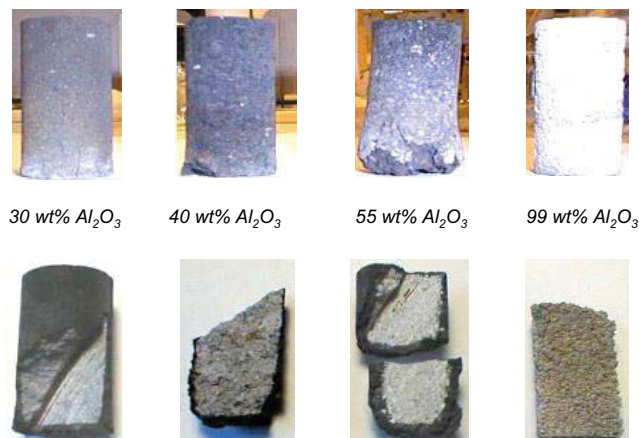
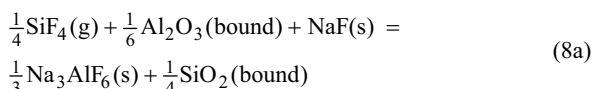
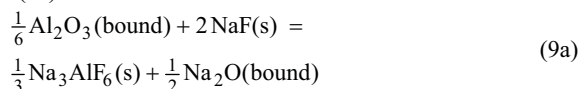


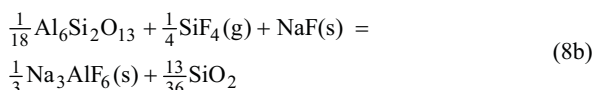
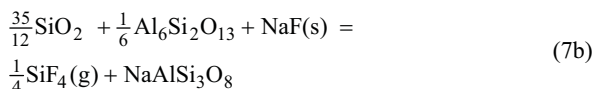
Figure 4. Samples of materials with different alumina content exposed to sodium vapour at 800 °C for 4 h. Upper row – pictures taken shortly after removal from the furnace, lower row – the same samples after cutting.



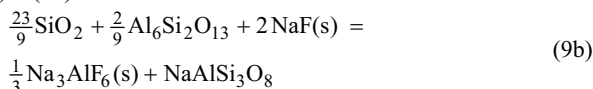
(7a) + (8a):



Alkemade triangle no. 1 in Figure 1 can be used as an example,



(7b) + (8b):



If Eq. (7) gives the higher pressure of SiF₄(g), Eq. (8) will be shifted towards the right hand side, and Eq. (9) (identical with Eq. (2)) represents the total turn-over. On the other hand, if Eq. (8) gives the higher pressure of SiF₄, Eqs. (8) and (9) must both be shifted towards the left hand side.

The pressures of SiF₄ in each Alkemade triangle were calculated from Reaction (7) as well as from Reaction (8), assuming unit activity for the solid phases. The real pressure will be equal to the lower pressure resulting from these reactions (or else, SiF₄ would be consumed by the other reaction, as explained above). It was assumed that all solid phases have unit activity. The pressures are given in Figure 5. The highest calculated pressures were 5.4 · 10⁻⁵ atm and 2.5 · 10⁻⁷ atm, found in Alkemade triangles no. 5 and no. 6, respectively. Those Alkemade triangles are not very interesting in practice, so it can be concluded that the vapour pressure of SiF₄ in the lining is negligible.

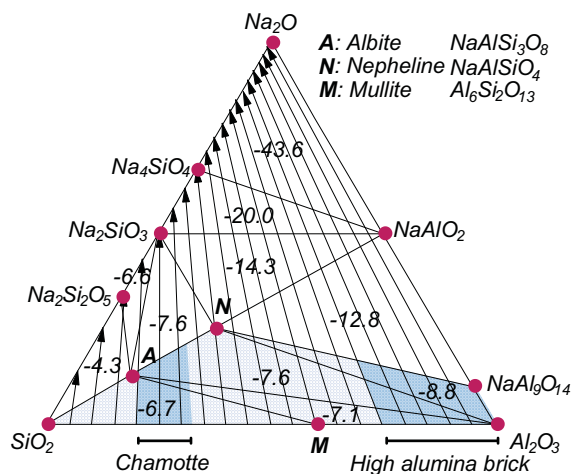


Figure 5. The ternary system SiO₂-Al₂O₃-Na₂O exposed to fluoride melts at 1100 K. The numbers indicate the logarithm of the SiF₄ pressure, the shaded area indicates the Alkemade triangles where Reaction (9) is possible ($\Delta G^0 < 0$), and the vectors indicate the direction of change in the oxide composition during attack.

The change in Gibbs free energy for Reaction (9) was also calculated. The Alkemade triangles where the reaction is possible ($\Delta G^0 < 0$) are marked in Figure 5. It should be mentioned, though, that the assumption of unit activity for the condensed phases is not very well justified in this case, especially if the reactants and/or products are partly liquid.

Experimental: The Cup Test

The most common method to evaluate the resistance of refractory bricks towards attack by molten fluoride is the so-called cup test. The test method is proposed as an ISO-standard. Test pieces measuring approximately 110 x 100 x 64 (75) mm are used in the test. A well (“cup”) with 55 mm diameter and 40 mm depth is drilled in the centre of the test piece. The bottom of the hole is surface ground, and the test piece is dried at 110 °C for 24 h before being filled with 150 g of a powdered mixture consisting of 60 weight percent cryolite and 40 weight percent sodium fluoride (NaF/AlF₃ molar ratio 6.33, close to Na₃AlF₆/NaF eutectic). The test cup is placed in a furnace and heated in air for 24 hours at 950 °C. The recovered brick is then cut diagonally, and the cross section is examined to find the reacted/dissolved volume of the brick. Since there is no metal or sodium vapour present, the test elucidates the effect of Reaction (9) above.

Hardly any fireclay bricks tested have been completely penetrated by the fluoride melt. Early in the process, a reaction layer of viscous silicate melt is formed near the surface of the brick. In most cases, it has been observed that the well is only slightly attacked at the bottom, while the sidewall attack may be severe. The reason for this seems to be that the silica rich melt formed gradually flows down and creates a protective layer at the bottom of the cup. Often, the melt separates into two liquid phases; a viscous relatively non-reactive silicate melt is formed at the bottom, and most of the fluorides remain on top. Further dissolution at the bottom then has to take place via ion transport through the silicate melt, which is a slow process.

A glassy layer will act as an effective penetration barrier and, thereby, prevent further attack. It is interesting that the amount of glass formed, as well as the viscosity of the protecting melt, both increase with increasing silica content in the firebrick. It has been found that the thickness of the silicate melt in the bottom of the cup increases with increasing silica content, whereas the extent of the attack decreases. Figure 6 illustrates the attack of fluoride melt on three firebricks with different silica content. The relationship between the silica content and the cryolite resistance, defined as the dissolved or reacted area measured at the cross-section of the test pieces, is shown in Figure 7. Below 30 weight percent silica in the material, there is a tendency of melt penetration through the bricks, due to insufficient glass formation.

This is exactly the same trend as observed in the sodium vapour test. The visual appearance of the attack also looked similar; it is hardly possible to distinguish by eye whether a sample has been exposed to a fluoride melt or to sodium vapour.

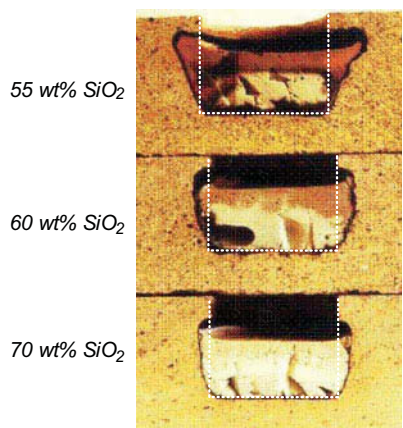


Figure 6. Chamotte firebricks with different silica contents after the cup test. The dotted lines show the approximate dimensions of the original well.

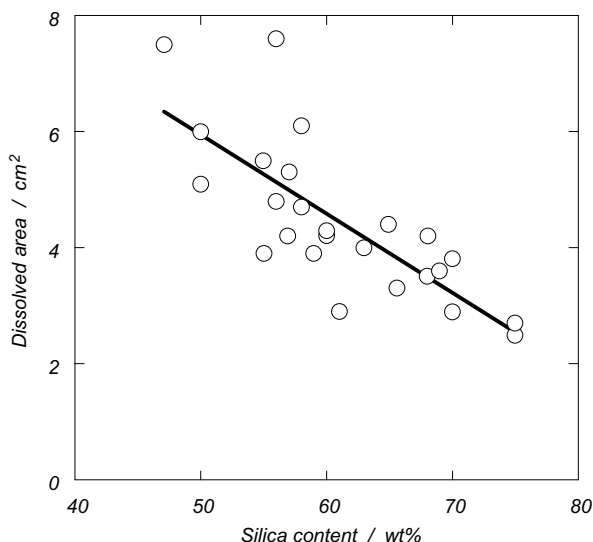
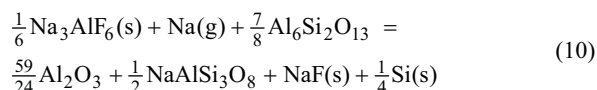


Figure 7. The relationship between cryolite resistance and the silica-content of different firebricks [11].

Combined Attack by Sodium Gas and Fluorides

Calculations

Although most of the pores in the cathode carbon will be blocked by liquid and solid bath components, carbides, nitrides, etc., sodium can still penetrate the cathode in the form of intercalation compounds. This opens up the possibility of combined action of sodium and fluorides; see the general reaction (3) above. Using Alkemade triangle no. 2 as example,



The equilibrium sodium pressure was calculated, see Figure 8. The equilibrium pressure of sodium is clearly lower than the maximum possible pressure ($\log p_{\text{Na}} = -1.7 - -1.5$) in all Alkemade triangles except no. 10 and no. 11. Still, it can be doubted that the alkemade triangles no. 8 and 9 will be affected, since the vapour pressure of sodium will be lower than the maximum pressure due to diffusion. As indicated, chamotte will end up as mainly nepheline, and high alumina materials end up as mainly β -alumina. This is the same result as with attack by sodium vapour.

Autopsies

The visual appearance and extension of the various reaction zones in the lining varies over a wide range, depending on the cell age and operational conditions. Still, the mineral phases identified in the different layers appear to be the same, even though the relative quantities vary. Typically, the used lining consists of intact, but sometimes compressed insulation, underneath more or less reacted refractories. The boundary between reacted and intact refractories is usually razor-sharp. The reacted refractories contain albite and nepheline, as well as sodium fluoride and silicon metal [11].

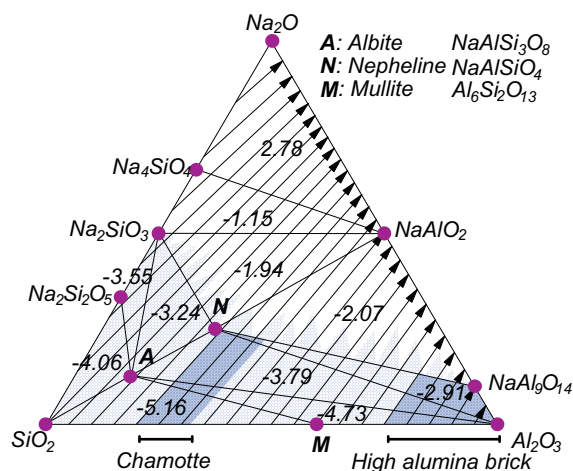
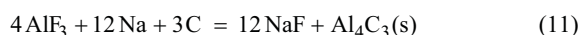


Figure 8. The ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ exposed to sodium vapour and cryolite 1100 K. The numbers are the logarithm of the sodium pressure [atm], the vectors indicate the direction of change in the oxide composition during attack, and the shaded areas indicate the Alkemade triangles where the reactions are possible, assuming a sodium vapour pressure of about 0.02 atm.

Above the reacted refractory material, there is a “build-up” consisting of cryolite, sodium fluoride, nepheline, alumina, silicon, aluminium, aluminium carbide, FeSi, and Fe-Al alloys. This glassy layer is often easily distinguishable. In the literature, the build-up and the reacted firebrick are commonly termed “lens-material”.

The weight of the lining may almost double in old cells. This is due to the material coming down through the cathode carbon, mainly fluorides. As mentioned, the fluorides are present in the reacted firebrick, at least in the upper part of this layer, but the main part of the fluoride phases are located within the build-up. The formation of build-up and deterioration of the firebricks appear to begin immediately after start-up of a new cell, and the amounts increase throughout the cell’s life, as shown in Figure 9.

There is always a large surplus of NaF in used linings (this is the reason for using a high NaF/AlF₃ ratio in the cup test). It is well known that there will be reactions in the pores in the cathode carbon that increase the NaF/AlF₃ ratio, e.g., the formation of aluminium carbide,



Although the bath coming through the carbon thus already may be rich in NaF, the excess NaF will react with the refractories and form cryolite (Reaction (2)). To maintain the very high NaF/AlF₃ ratio found in old cells, it seems necessary to assume that reactions with both fluoride and sodium takes place in the lining (Reaction (3) above).

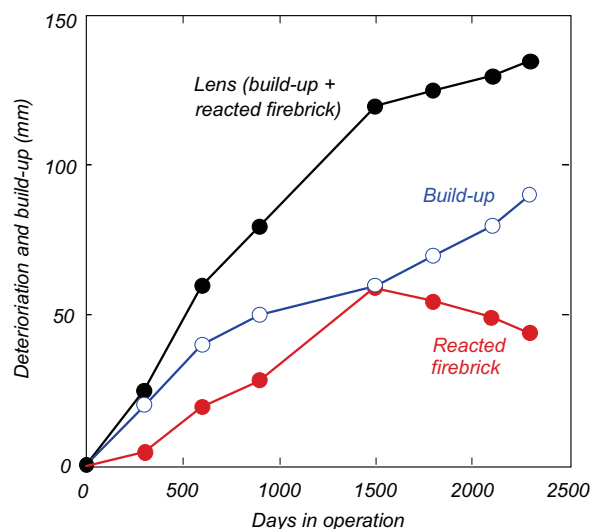


Figure 9. Amounts of reacted firebrick and build-up in linings from disconnected cells of different age.

Acknowledgement

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