CATHODE REFRACTORY MATERIALS FOR ALUMINIUM REDUCTION CELLS

Christian Schøning*, Tor Grande** and Ole-Jacob Siljan***

* SINTEF Materials Technology, N-7034 Trondheim, Norway
** Department of Inorganic Chemistry, Norwegian University of Science and Technology, N-7034 Trondheim, Norway
*** Norsk Hydro ASA, Research Centre Porsgrunn, Norway

Abstract

The need for energy efficient long-life cathode designs have encouraged the development of new cathode lining refractories for aluminium reduction cells. The present paper gives an overview over refractory materials used in the aluminium industry. The performance of both traditional refractory linings and recently introduced dry barrier powder materials are summarised. Special attention is given to the considerable progress in the understanding of the deterioration of the cathode lining materials during operation, which have been obtained during the last decade in the authors laboratory in collaboration with the Norwegian aluminium industry.

Introduction

During the last few decades the aluminium industry has spent considerable efforts to increase the life span of the aluminium reduction cells. Major progress has been achieved through increased quality of the carbon cathode lining and better cell design [1]. Although the carbon lining has improved considerably, the life expectancy of a cell is still greatly influenced by the chemical attack on the refractory lining supporting the cathode lining. Penetration of electrolytic bath components through the carbon cathode causes significant mineralogical transformation in the refractory lining, which results in increased heat loss from the cathodes and thereby higher energy consumption. In the extreme cases the chemical reactions in the refractory lining may develop to cause a complete cathode block failure. The invasion of cryolitic bath into the cathode lining starts immediately after cell start-up. It is particularly intense during the first months of operation. Later on, the rate of penetration slows down due to

longer diffusion path of the bath constituents, but bath continues to diffuse through the carbon cathode throughout the operation life of the cell.

Fireclay materials are the most commonly used materials for refractory lining of industrial reduction cells [2]. The cell design is usually constructed such that the 800-850°C isotherms are within the main body of the upper, protective refractory barrier layer to minimise the deterioration of the insulation layer below. Due to lack of understanding the deterioration of alumino silicate refractories, new materials have been introduced in order to prevent or delay the deterioration, which is observed to occur for traditional firebrick linings. These powdered or granular penetration barrier materials based on calcium alumino silicates, aluminium silicates or magnesium silicates have been installed and tested in aluminium electrolysis cells [3]. The claimed advantage of some of these powdered materials, besides reduced installation costs, is that refractory phases are formed when the bath comes into contact with the lining and further penetration is inhibited. However, the experience from test cells indicates that the penetration of bath constituents and chemical reactions extend further down in the lining than previously assumed. Therefore, although suppliers have introduced improved versions of the barrier materials, fireclay refractories are still the dominant lining material used in the aluminium industry. Today apparently all materials which are not based on firebricks are by the producers called penetration barriers. As argued in this paper, firebricks with an optimum silica content is probably still the best penetration barrier so far available.

The present paper reviews the performance of both traditional refractory linings and recently introduced lining. First, we review

the refractory materials used in cathode linings in aluminium electrolysis cells. Secondly, the results obtained in laboratory tests and autopsies will be summarised. Special attention will be given to the considerable progress in the understanding of the deterioration mechanism of these materials, which have been obtained during the last decade in the authors laboratory in collaboration with the Norwegian aluminium industry.

Refractory materials

Generally refractories in the system Al_2O_3-SiO_2 is called "chamotte" if the alumina content is in the range 15-45 wt %. At higher alumina content (> 45 wt%) the materials are called high alumina. The dominating phases in chamotte are cristoballite (SiO_2), mullite ($3Al_2O_3 \cdot 2SiO_2$) and a silica rich glass. The refractoriness of chamotte materials increases with increasing alumina content. The refractoriness of the materials is less important in relation to the resistance towards fluoride melt attack.

Anorthite is a calcium aluminium silicate, which have been introduced as a chemical barrier (Chemobar) [4]. The chemical composition is near the mineral anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$). Both synthetic made, and natural mineral products have been used in cathode linings. So far anorthite has only been delivered as a powder (Chemobar), but a new dense shaped product will soon be on the marked.

Refractory materials based on the mineral olivine are also used in refractory linings. Olivine is a solid solution of the major mineral forsterite ($2MgO \cdot SiO_2$) and the minor phase fayalite ($2FeO \cdot SiO_2$). Both forsterite bricks and powders (Drycast and Olibar 1901) are commercially available. The Drycast and Olibar 1901 powders are not pure forsterite products, but contains significant amounts of aluminio silicates in order to improve the cryolite resistance.

Table 1 gives an overview of the oxide composition and some physical properties of refractory materials.

Table 1. Chemical composition, bulk density and thermal conductivity at 600°C of the most common refractory materials.

Refractory material	Al_2O_3 wt%	SiO_2 wt%	MgO wt%	CaO wt%	Fe_2O_3 wt%	Na_2O wt%	Bulk density (g/cm³)	Thermal cond. 600°C (W/mK)
Alumino (silicates). Alumina (powder)	≈100						1.0	0.2 - 0.3
High-alumina (bricks)	46-90	10-49					2.3 -3.3	1.5 - 3.0
Firebricks	18-45	50-75	<0.5	<0.5	1-2	1-3	2.0-2.2	1-1.5
Anorthite Chemobar (powder)	3	48		15	1	3	2.1	0.4
Olivine Forsterite bricks		41	51		7		2.7	1.5
Drycast (powder)	12	44	37		5		2.3	1.2
Olibar 1901(powder)	4	44	42		7		2.3	0.8

Laboratory tests for cryolite resistance of refractories

The most common method to evaluate the resistance of refractory bricks to fluoride attack is the so-called cup test. The cup is prepared by drilling a cylindrical well in the refractory brick. The cup is then filled with eutectic mixture of Na_3AlF_6 and NaF and the test cup is heated for 24 hours at 950°C in air. The recovered brick is then cut diagonally and the cross section is examined to find the reacted/dissolved volume of the brick. Powdered materials are tested by a modified version of the cup test. In this case the powder is compacted in a graphite crucible and the remaining space in the crucible is filled with the cryolitic melt.

Hardly any bricks of fireclay are completely penetrated by the fluoride melt. Early in the process it is formed a reaction layer of viscous silicate melt near the surface of the brick. In most cases its observed that the well is only slightly attacked in the bottom, while the sidewall attack is severe. Gradually the silica rich melt which is formed, flows down and creates a protective layer in the bottom of the cup. The molten phase is often observed to phase separate, and a viscous, relatively non-reactive silicate melt is formed at the bottom and most of the corrosive fluoride melt remains in the phase at the top. Further dissolution in the bottom has to take place via ion transport through the silicate melt. The extent of the reaction and thickness of the silicate melt in the bottom of the cup has been observed to clearly depend on the silica content in the brick. Fig. 1 illustrates the attack of fluoride melt on three different firebricks with different silica content. The relation between cryolite resistance and the silica content of different firebricks is shown in Fig. 2.
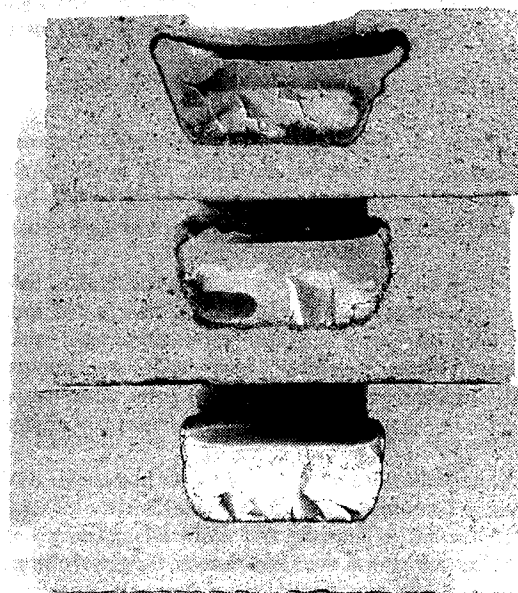

Figure 1. Firebricks with various silica content after the cup test. The brick on the top has a SiO_2-content of 55-wt%, the brick in the middle 60-wt%, and the brick at the bottom 70-wt%.

Other material properties than the silica content are of less importance for the results of the cup test. Apparently, a correlation between apparent porosity and cryolite resistance is expected, but this is not a general rule. This particular correlation is only significant when comparing firebricks with constant silica content and different open porosity as illustrated in Fig. 3.
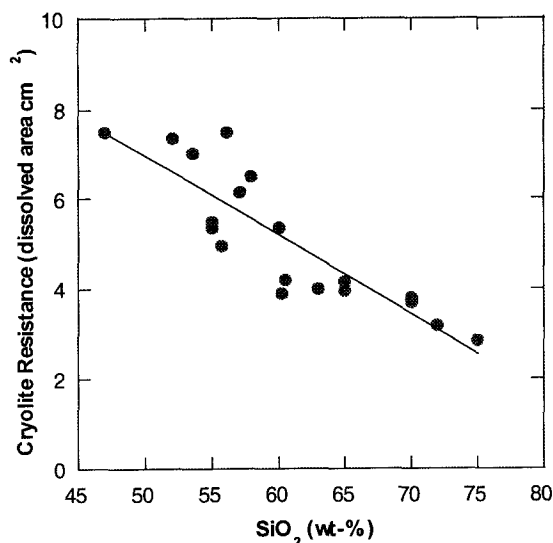

Figure 2. The relation between cryolite resistance and the silica-content of different firebricks [5].
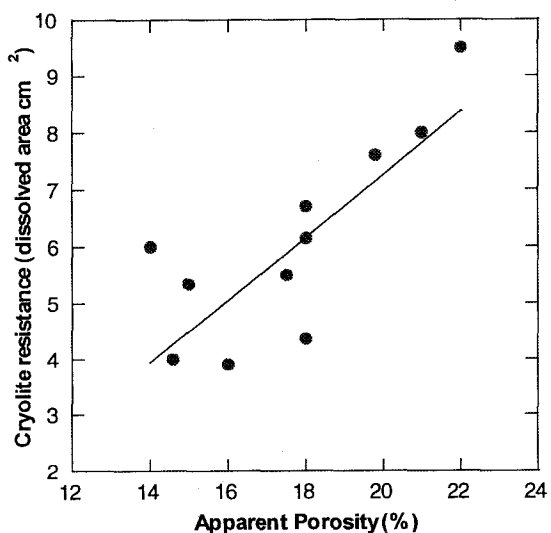

Figure 3. Correlation between cryolite resistance and open porosity of firebricks with constant silica content [5].

The finger test is another well-known method to test the cryolite resistance of refractories. In this method rectangular shapes of the test material are exposed to molten cryolitic melt at a given time and temperature. The recovered shape is examined and the reacted volume relative to the original dimensions is estimated.

The third important cryolite test is the so-called polarised test [6]. A cylindrical test specimen is placed inside a carbon crucible, which works as a cathode during electrolysis. The anode is a carbon crucible containing the cryolitic electrolyte. After the electrolysis the cathode containing the refractory material is cut in two and the cross section is examined. Siljan has investigated the correlation between the results obtained by the polarised test and the cup test [7]. The results obtained are shown in Fig. 4. The results of the two methods seem to be relatively good correlated. The ranking of the 8 tested materials was identical for both tests.
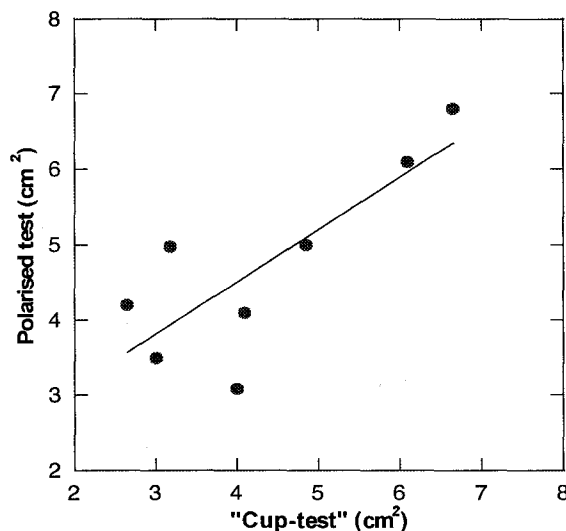

Figure 4. The correlation of the results of the polarised test and cup test of 8 different chamotte refractories reported by Siljan (1994) [7].

Chemical detoriation of refractory linings

An ideal dense lining with no open porosity and which is inert to cryolitic melts will stop the penetrating bath just below the cathode block. In a real cathode lining the refractory materials are nothing like inert to the molten fluoride electrolyte, and the penetrating melt dissolves/reacts with the lining. The chemical reaction results in formation of new mineral phases that will partly crystallize in the reaction zone. The reaction will not terminate before the melt is saturated with all the components in the refractory lining, or the melt has completely crystallised due to changes in the composition of the melt or due to temperature changes as the melt penetrate deeper down in the refractory lining. Penetration of fluoride melt in the open pore structure of the lining material will result in densification of the refractory material and an increase in the thermal conductivity of the lining. The thermal balance of the cell will therefore not stabilise before
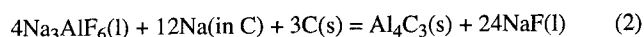
the penetration of the fluoride melt has been suppressed or completely terminated.

So far there has not been a general agreement on the criteria to ensure good cryolite resistance. Several have notified the importance of a high solidus temperature in the system defined by the refractory material and the attacking fluoride melt [4,6]. A high solidus temperature will clearly reduce the solubility of refractory materials in the fluoride melt and thereby reduce the penetration depth of the electrolyte. However, it is important to note that the theoretical limit is the $NaF-Na_3AlF_6$ eutectic, which is 888°C [8]. A high solidus temperature is therefore only one of several important factors.

Penetration of bath through the carbon cathode continues throughout the entire cell lifetime. The top layer of the lining, which already has reacted with molten fluorides, will therefore be exposed to "fresh" bath components. Hence, it is not only the solubility of the refractory material in molten electrolyte that determines the extent of reaction, but also the solubility of the reaction products in the molten fluorides. Due to the continuous supply of "fresh" bath components it is impossible to avoid a molten layer between the carbon cathode and the refractory lining. However, the molten layer will be less harmful if the viscosity is sufficiently high, as this will strongly retard the diffusion of bath components as illustrated in Fig. 1.

A thorough understanding of the phase relation in the system constituted by penetrating melt and the refractory materials has been considered as the most productive approach to the present industrial problem. The following discussion of the chemical deterioration of refractory linings is therefore mainly based on phase diagrams. However, as argued above the viscosity of melts containing significant amounts of silicates are also important to consider. As the viscous properties of mixtures of fluorides and oxides are not well understood, we have applied a semi empirical method developed by Moynihan [9] to be able to evaluate the viscosity of molten mixtures of silicates and fluorides [10].

The chemical composition of the fluoride melt penetrating through the cathode carbon blocks is enriched in NaF relative to the acidic electrolyte melt according to Siljan (1990) [11], Sørlie and Øye (1992) [1], and Oprea (1996) [12]. The increased content of NaF above a cryolite ratio (CR) of 3 has been explained by the reactions [1]

$$Al(l) + 3 NaF(l) = 3 Na(in C) + AlF_3(l) \qquad (1)$$

$$4Na_3AlF_6(l) + 12Na(in C) + 3C(s) = Al_4C_3(s) + 24NaF(l) \qquad (2)$$

The fluoride melt, to which the refractory materials are exposed, is most likely mainly a mixture of NaF and Na_3AlF_6. In the following the chemical stability of the most important refractory materials in molten $NaF-Na_3AlF_6$ environments is discussed.

High alumina and chamotte refractories

We will first focus on the chemical reactions between *pure* alumina and cryolitic melts. The viscosity of $NaF-Na_3AlF_6-Al_2O_3$ melts is less than 1 P in the actual temperature range [13]. The kinetics of the reaction between alumina and the molten fluorides is therefore expected to be fast relative to the lifetime of the cell. The deterioration mechanism of pure alumina linings is therefore governed by phase equilibrium, and the thermal balance of the cathode determines the penetration depth. The fluoride melt will relatively fast penetrate the open pore structure of the lining until it hits the isotherm corresponding to the solidus temperature. The actual phase equilibria are described by the phase diagram of the system $NaF-AlF_3-Na_2O-Al_2O_3$ reported by Foster et al. [14]. The only chemical reaction to consider is the formation of β-alumina ($Na_2O·11Al_2O_3$)

$$12 NaF(l) + 34 Al_2O_3(s) =$$
$$3(Na_2O·11Al_2O_3) (s) + 2Na_3AlF_6(s) \qquad (3)$$
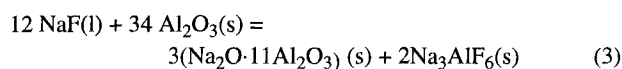
Formation of β-alumina will take place in alumina linings when they are exposed to NaF. It is important to notice the significant lower density of β-alumina relative to the density of α-alumina (Al_2O_3). This may induce significant volume changes in reacted lining. The solidus temperature at excess of NaF is the ternary eutectic at 881°C where β-alumina coexists with NaF(s) and $Na_3AlF_6(s)$ [14]. The solubility of alumina in the fluoride melt is low at high NaF-content and is increasing with increasing Na_3AlF_6-content. At CR<3 the solidus temperature drops with more than 200° [14]. High alumina linings are therefore vulnerable when exposed to acidic fluoride melts.

The authors have considered mullite ($3Al_2O_3·2SiO_2$) as a reasonable model compound for high alumina and chamotte refractory linings. The following discussion is based on the findings when mullite is exposed to NaF and Na_3AlF_6. In materials with high alumina content, formation of nepheline ($NaAlSiO_4$) in addition to β-alumina will occur due to the presence of silica

$$6 NaF(l) + 3 SiO_2(s) + 2 Al_2O_3(s) =$$
$$3 NaAlSiO_4(s) + Na_3AlF_6(s) \qquad (4)$$
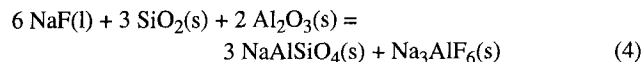
Rutlin and Grande [15], have confirmed the combination of reaction (3) and (4) in experiments where mullite have been exposed to pure NaF. The formation of nepheline and β-alumina demonstrate that NaF is not coexisting with aluminium silicate refractories.

Siljan [11], observed that $SiF_4(g)$ is formed when mullite is exposed to molten Na_3AlF_6

$$Na_3AlF_6(s) + 3Al_2O_3·2SiO_2(s) =$$
$$2NaF(l) + NaAlSiO_4(s) + 3Al_2O_3(s) + SiF_4(g) \qquad (5)$$
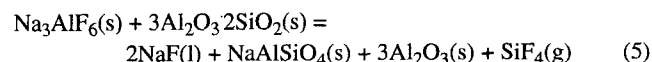
However, this reaction does not reflect the phase equilibria at low temperatures where $Na_3AlF_6(s)$ is coexistent with silica and alumina (mullite is not stable relative to alumina and silica below ~1000°C). If the diffusion of volatile fluorides into the lining is neglected, Na_3AlF_6 will not react with the lining material but acts as a solvent for NaF and the oxide minerals in the reaction zone. Near the carbon blocks there will be an excess of molten fluorides, and the phases which will be present are α- or β-alumina, nepheline and the fluoride melt. The solidus temperature in this region is 856±7°C [15], more than 100° below the operation temperature of the cell. The quaternary eutectic melt is mainly molten $NaF-Na_3AlF_6$ with minor concentrations of alumina and nepheline [15]. The eutectic melt is therefore not expected to be very viscous.

At the lower edge of the reaction zone there will be an excess of the refractory material and NaF deficiency. Here β-alumina converts to α-alumina and nepheline reacts with silica in the lining to form albite $(NaAlSi_3O_8)$ [15].

$$NaAlSiO_4(s) + 2\ SiO_2(s) = NaAlSi_3O_8\ (l) \qquad (6)$$

Albite, which is an excellent glass former, will not crystallize but remains molten together with cryolite. The phase composition along the composition line sodium fluoride-mullite reported by Rutlin and Grande [16] are shown in Fig, 5. The important phases formed in the reaction between NaF and mullite are β/α-alumina, nepheline and albite.
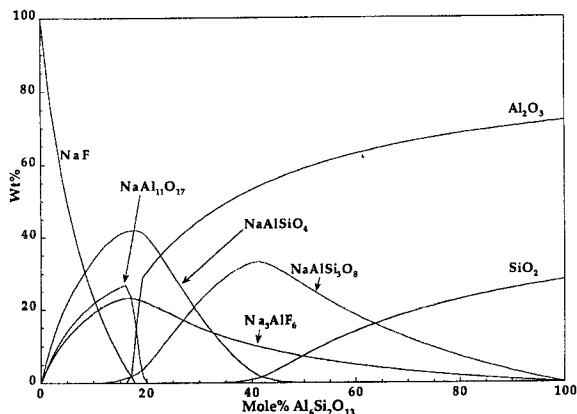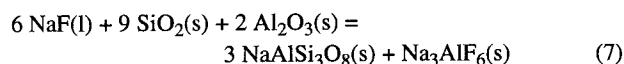

Figure 5. Phase composition along the composition line sodium fluoride- mullite [16].

At intermediate silica content (> 47 wt% silica) in the refractory lining, β -alumina will no longer be present in the reaction zone. In such refractory linings nepheline and albite are formed by a combination of reactions (4) and (6)

$$6\ NaF(l) + 9\ SiO_2(s) + 2\ Al_2O_3(s) =$$
$$3\ NaAlSi_3O_8(s) + Na_3AlF_6(s) \qquad (7)$$

At very high silica content in the lining (> 72 wt% silica) there will be alumina deficiency and nepheline will no longer be formed. Based on the reactions presented above the phase composition as a function of the silica content in the lining can be found. This is illustrated in Fig. 6. The content of Na_3AlF_6 in the penetrating bath can be neglected for simplicity since Na_3AlF_6 is always a reaction product. Six quaternary systems are defined in Fig. 6. The phase equilibria in some of these systems have been investigated in the authors laboratory. The presence of albite in addition to NaF and Na_3AlF_6 results in the lowest solidus temperature. It is therefore tempting to claim that formation of albite should be avoided by keeping the alumina content high. However, we are then neglecting the important effect of the viscosity of the active melt.
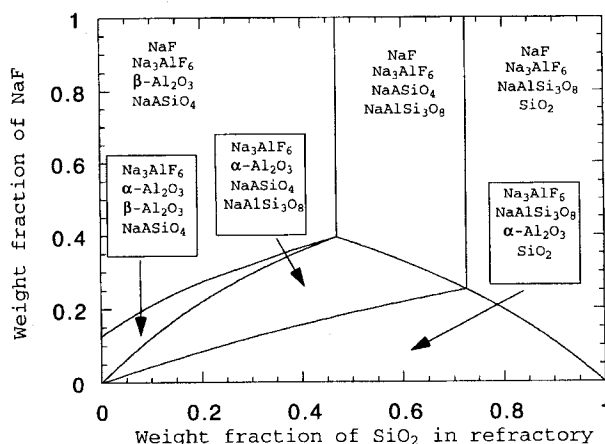

Figure 6. Phase composition during NaF-attack on alumino silicate refractories. The phase composition is given as a function of the silica content in the refractory material and the weight fraction NaF relative to the amount of aluminium silicate refractory.

The important result in Fig. 6 is the identification of nepheline and albite as the secondary silicate phases formed during the deterioration of aluminio silicate refractories. In order to qualitatively explain the observation of viscous melts and liquid-liquid phase separation as observed in cup test, Rutlin and Grande have performed investigations on the phase equilibria between nepheline or albite and fluorides [16,17]. Liquid-liquid phase separation in the binary system NaF-nepheline has previously been reported [18]. However, the solubility of nepheline in NaF is very low, and the two liquid phase region does not extend below 1000°C [18]. In contrast, Na_3AlF_6 and nepheline was observed to be miscible [16], but the two liquid phase region extend into the ternary system. The liquid-liquid phase separation is however terminated above 1000°C due to the low solubility of nepheline in NaF. The presence of only nepheline can not explain the phase separation observed in cup tests. Liquid-liquid phase was also observed in melts containing albite [18]. The formation of albite is therefore most likely the explanation of the phase separation
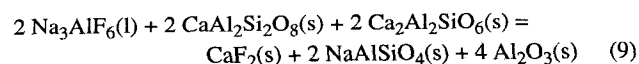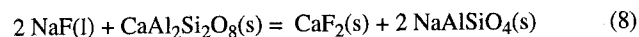
observed in cup tests. Based on these findings the cryolite resistance is expected to be higher at intermediate silica content as shown in Fig. 6 where albite is the most important reaction product.

Grande and Rutlin have shown that the viscosity of NaF and Na_3AlF_6 is increasing several orders of magnitude when albite is added to the molten fluoride [10]. The viscosity was estimated by using the semi empirical method presented by Moynihan [9]. These results demonstrate that the presence of albite in the reaction zone between aluminium silicate refractory linings and molten cryolitic bath results in a dramatic increase (several orders of magnitude) in the viscosity of the active melt. An increased viscosity of the penetrating melt will strongly retard further penetration. Based on these findings, Grande and Rutlin proposed that formation of albite is the major explanation of the viscous melts observed in cup tests and amorphous phases observed in spent pot linings [10].

The kinetics of the crystallisation of albite is very slow, and albite-containing melts will therefore form glasses when cooled to room temperature. The amorphous phases observed in autopsies of old cathode linings are probably due to the formation of albite (and to some degree nepheline) in the fluoride-infiltrated part of the lining. The solidus temperature observed for spent pot lining would strongly be influenced by the presence and the amount of amorphous phases. The amorphous phase will become molten on reheating, and will act as a solvent of some of the crystalline phases in the spent pot lining. The dissolution of the crystalline phases will start significantly below the true equilibrium solidus temperature. This is probably the explanation of the significant lower solidus temperatures reported for spent pot linings [19] compared to the equilibrium solidus temperatures observed in the present laboratory work [16,18].

Anorthite based refractories
Two studies have been conducted in our laboratory in order to investigate the deterioration of anorthite based linings [20,21]. The experience with dry powder anorthite based linings in Søderberg and Prebaked cells have been reported by Siljan et al. [2]. The performance of the cells indicates that these types of materials do not improve the resistance against penetration of molten fluorides relative to traditional linings. According to the patent by Seltveit [4], anorthite and gehlenite ($Ca_2Al_2SiO_6$) based linings will react with molten fluorides and form solid products

$$2\ NaF(l) + CaAl_2Si_2O_8(s) = CaF_2(s) + 2\ NaAlSiO_4(s) \qquad (8)$$

$$2\ Na_3AlF_6(l) + 2\ CaAl_2Si_2O_8(s) + 2\ Ca_2Al_2SiO_6(s) =$$
$$CaF_2(s) + 2\ NaAlSiO_4(s) + 4\ Al_2O_3(s) \qquad (9)$$

In this manner the solidus temperature should be increased above the electrolysis temperature and thereby retard the penetration of the fluoride melt.

The phase relations in the quaternary system $NaF\text{-}CaF_2\text{-}NaAlSiO_4\text{-}CaAl_2Si_2O_8$ have been studied by Færøyvik et al [17]. The phase diagram of the system is shown in Fig. 7. Reaction (8) was confirmed experimentally, and the solidus temperature at NaF deficiency was observed at 1095°C, which supports the basic idea of the advantage of anorthite based linings. However, at excess amounts of NaF the solidus temperature was observed at 805°C which is considerably lower than the electrolysis temperature. As pointed out, bath penetration continues throughout the entire cell lifetime and will lead to the exposure of already reacted material to "fresh" bath components.
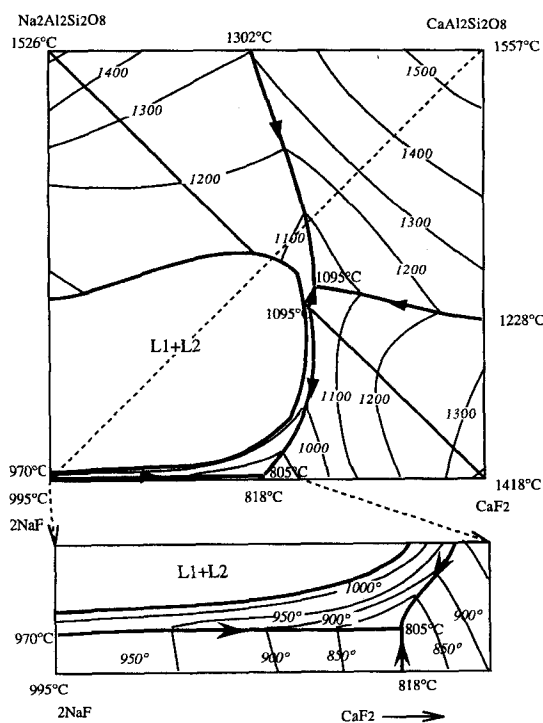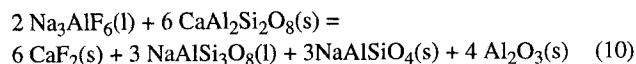

Figure 7. The phase diagram of the ternary reciprocal system $NaF\text{-}CaF_2\text{-}NaAlSiO_4\text{-}CaAl_2Si_2O_8$ reported by Færøyvik et al [20]

Rutlin and Grande have investigated the phase equilibria when anorthite is exposed to pure cryolite [21]. The chemical reaction between anorthite and Na_3AlF_6 is

$$2\ Na_3AlF_6(l) + 6\ CaAl_2Si_2O_8(s) =$$
$$6\ CaF_2(s) + 3\ NaAlSi_3O_8(l) + 3NaAlSiO_4(s) + 4\ Al_2O_3(s) \qquad (10)$$

The solidus temperature along the composition line $Na_3AlF_6\text{-}CaAl_2Si_2O_8$ was observed as low as 716 ± 20°C. The formation of $CaF_2(s)$, $NaAlSiO_4(s)$ and $Al_2O_3(s)$ were confirmed by X-ray diffraction, while the formation of albite was induced from mass balances and the presence of glass in the samples. Rutlin and Grande suggested a deterioration mechanism of anorthite materials based on their own findings together with those reported by Færøyvik et al [20].

Forsterite based materials

The chemical properties of forsterite materials in molten fluoride environments have not been investigated thoroughly. However, the experience with dry powder forsterite based linings in Søderberg and Prebaked cells has been reported by Siljan et al. [2]. The performance of the cells indicates that neither of these types of materials are stable against molten fluorides. Some preliminary laboratory tests have also been conducted in the authors laboratory where synthetic forsterite $Mg_2SiO_4(s)$ has been used as a model compound [5]. The reaction pattern seen in laboratory cup tests of forsterite bricks differ from firebricks in the way that most of the fluoride melt relatively quickly penetrates the brick material before any reaction takes place. The reaction between cryolite and forsterite has been verified to be:

$$Na_3AlF_6(l) + Mg_2SiO_4(s) = 2\ NaMgF_3(s) + NaAlSiO_4(s) \quad (11)$$

However, the preliminary studies have not revealed the phase relations when forsterite is exposed to sodium fluoride. The solidus temperature when forsterite is exposed to NaF and Na_3AlF_6 has been observed at 765 and 885°C respectively.

The preliminary laboratory tests demonstrate no indications that forsterite materials are superior to traditional fire clay refractories. To increase the resistivity towards molten fluorides the commercial dry powders based on olivine contains significant amounts of aluminium silicates or clays in the finest fraction. We propose that the better performance of such materials are due to a reaction pattern which is related to the one observed in traditional fireclay linings.

Forsterite materials have a higher thermal conductivity than both firebricks and anorthite, which possibly will increase the thermal stability of these lining concepts during operation life.

Conclusion

Penetration of bath through the carbon cathode continues throughout the entire cell lifetime. The top layer of the lining, which already has reacted with molten fluorides, will therefore be continually exposed to "fresh" bath components. Hence, it is not only the solubility of the refractory material in molten electrolyte that determines the extent of reaction, but indeed also the solubility of the reaction products in the molten fluorides. Due to the continuous supply of "fresh" bath components it is impossible to avoid a molten layer between the carbon cathode and the refractory lining. However, the molten layer will be less harmful if the viscosity is sufficiently high because this will strongly retard the diffusion of bath components.

High viscosity is obtained when albite is formed due to fluoride attack on the lining. We therefore propose that the traditional firebrick with relatively high silica content is probably still the best penetration barrier so far available.

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