

REFRACTORIES FOR MOLTEN ALUMINUM CONTACT PART I: THERMODYNAMICS AND KINETICS

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ABSTRACT

The cast house has increasingly become an important metal production unit in the integrated aluminum smelters. The increased output of metal from the cast house furnaces has led to increased strain on the refractory lining materials. The attack and infiltration by molten aluminum metal during operation, resulting in chemical conversion of and mechanical stresses in the lining promoting increased energy consumption and reduced lining lifetime of the furnaces. The attack of molten aluminum metal is governed by molten metal properties, refractory properties and by the mineralogy of the formed solid and liquid phases in the deteriorated lining.

In this paper, some basic studies of the interaction between molten aluminum and refractory materials are presented, by means of thermodynamics and laboratory investigations. The laboratory studies are performed on different types of refractory raw material, and have been used to assess the influence of reaction kinetics in addition to thermodynamics. The observed extent of the aluminum attack is linked to chemical and mineralogical composition, as well as the physical properties of the refractory constituents. Thermodynamics and laboratory investigations have demonstrated that aluminum metal is capable of reducing more thermodynamically stable oxides through the formation of intermetallic species.

INTRODUCTION

The world aluminum industry is an important consumer of refractory materials worldwide. Refractory materials are used in all aspects of the industry, from the alumina calciners, via the primary production electrolytic cells, and to the cast house furnaces and other metal handling equipment. The aluminum industry is steadily growing,

and also becoming more cost efficient. This puts great demands on the refractory materials, in order to contribute to reduced operational costs. This can only be achieved by reducing the cost of the refractories per ton of metal output, i.e. a higher priced material can be accepted if the overall production cost is reduced (or overall metal output is increased).

Aluminum confinement refractory materials used in aluminum cast house furnaces serve three purposes:

**To preserve energy during operation, i.e., minimizing heat losses.*

**To protect the underlying insulation materials from percolating molten metal.*

**To protect the steel casing from high temperatures and liquid metal.*

In addition, it is of importance with respect to the quality of the cast metal that:

**The integrity of the lining materials are maintained during their service life, i.e., the materials should not react with the metal and either change the metal chemical composition nor disintegrate to form refractory inclusions.*

It is well known from the literature and practice that refractories used in holding and melting furnaces are subjected to severe attack by molten aluminum metal. The refractory deterioration is most severe in the area around the metal line, often referred to as the "belly-band" [1].

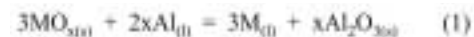
ALUMINUM - REFRACTORY INTERACTIONS

The chemical corrosion and deterioration of aluminum cast house furnaces is related to reactions between refractories and penetrating molten metal. To a certain extent, the diffusion of gases and volatile species into the lining will also result in deteriora-

tion, but in this paper we will be concerned with molten metal penetration only.

Thermodynamic Considerations

The deterioration of the refractory lining in cast house furnaces is governed by molten metal properties, refractory material properties and by the mineralogy of the reaction products, i.e. formed solid and liquid phases in the corroded lining. The most informative way to describe these factors is by the use of thermodynamics, and the chemical resistivity of an oxide based refractory material toward molten aluminum metal can be expressed by the general equation:



where M is a Metal. From this equation and existing thermodynamic data [2-4], it is possible to postulate the stability of refractories toward molten aluminum metal. This can be expressed through the so-called electrochemical/electromotive series of the metals as shown in Table I. All metals will reduce oxides below itself in the table, i.e., meaning that, for instance, calcium will react with any other oxide present in the table. The reaction with aluminum oxide in furnace lining refractories may take place according to the equation:



From Table I it can be deduced that all of the most commonly used refractory oxides will be thermodynamically unstable in contact with molten aluminum. Hence, it is obvious that materials based, on for instance, silica or silica containing minerals will be attacked and deteriorated as a result of long time exposure to aluminum. From the table it is also obvious that the presence of alloying elements like Mg and Ca will contribute to an aggravated chemical attack

on the refractory materials due to the reducing nature of these metals.

The thermodynamic impetus of reactions between molten aluminum and some of the more common refractory oxides are presented in Table II. The impetus is often referred to as the Gibbs-Free-Energy of the reaction, and when this free energy is below zero, the reaction is said to be spontaneous, thermodynamically speaking. However, a reaction with a negative Gibbs-Free-energy does not necessarily occur spontaneously in reality, due to reaction kinetics as will be described later.

A thermodynamic calculation program provided by MTDData [5] has been used to predict the thermodynamic stability of some of the more common refractory oxides towards molten aluminum metal. The predictions are in agreement with the data presented in Tables I and II, showing that oxides like ZrO₂, MgO and Al₂O₃ are considered to be stable in contact with molten aluminum. All silica-containing minerals are thermodynamically unstable towards aluminum, regardless whether they are present as free silica or silica containing compounds. However, with respect to calcium oxide, the computer program suggested that calcium oxide could indeed react with aluminum metal, not to form a simple oxide, but with the formation of an oxide and an inter-metallic phase, as seen from the phase diagram in Figure 1. The data presented in the phase diagram indicate that aluminum metal can react with both calcium and aluminum oxides as well as pure calcium oxide (lime) as shown in equations (3) and (4) below:



Numerous articles and papers have been presented on the reactions between aluminum and refractory materials. Most of the papers point to the detrimental effect of aluminum and some of its alloys on the commonly used oxide-based refractories in cast house furnaces. The “cheapest” refractory materials used are based on clay minerals, i.e. they contain varying amounts of silica. The silica will readily be reduced by aluminum according to the reaction [6-10]:



In the literature, this reaction is often cited as causing spalling of the refractory lining due to volume expansion. As can be

Table I: Electrochemical series (electromotive series) of selected metals at 1300K (1027 °C) with decreasing stability downwards. Thermodynamic data from Robie et al. [2], with estimated free energy values for solid sodium oxide and solid phosphorous oxide.

Metal	Oxide	Free Energy per mole Oxygen
Y	Y ₂ O ₃	- 510 kJ/mole
Ca	CaO	- 499 kJ/mole
Mg	MgO	- 458 kJ/mole
Zr	ZrO ₂	- 428 kJ/mole
Ba	BaO	- 424 kJ/mole
Al	Al ₂ O ₃	- 420 kJ/mole
Ti	TiO ₂	- 354 kJ/mole
Si	SiO ₂	- 335 kJ/mole
Mn	MnO	- 298 kJ/mole
Cr	Cr ₂ O ₃	- 264 kJ/mole
Na	Na ₂ O	- 236 kJ/mole (Estimated)
Zn	ZnO	- 205 kJ/mole
P	P ₂ O ₅	- 178 kJ/mole (Estimated)
Fe	Fe ₂ O ₃	- 162 kJ/mole

Table II: Calculated Gibbs energy for reactions between refractory oxides and molten aluminum metal at selected temperatures. Thermodynamic data from Robie et al. [2], Janaf [3] and Barin [4].

Reactions studied Reaction temperature	Gibbs energy (kJ/mole)		
	800K	1200K	1600K
4Al + 3SiO ₂ = 2Al ₂ O ₃ + 3Si	-553.4	-503.1	-444.6
4Al + 3ZrO ₂ = 2Al ₂ O ₃ + 3Zr	-15.6	+23.9	+69.4
2Al + 3MgO = Al ₂ O ₃ + 3Mg	+119.8	+114.0	+40.5
2Al + 3CaO = Al ₂ O ₃ + 3Ca	+229.9	+234.3	+174.6
2Al + 3BaO = Al ₂ O ₃ + 3Ba	+8.2	+17.1	+22.6
4Al + 3TiO ₂ = 2 Al ₂ O ₃ + 3Ti	-455.7	-408.4	-358.2
2Al + Cr ₂ O ₃ = Al ₂ O ₃ + 2Cr	-498.0	-469.0	-437.7
2Al + 3ZnO = Al ₂ O ₃ + 3Zn	-615.7	-621.2	-732.4
2Al + Y ₂ O ₃ = Al ₂ O ₃ + 2Y	+246.1	+263.4	+284.0
8Al + 3Al ₆ Si ₂ O ₁₃ = 13Al ₂ O ₃ + 6Si	-1101.8	-965.3	-816.0
20Al + 3Al ₄ Mg ₂ Si ₅ O ₁₈ = 10Al ₂ O ₃ + 6MgAl ₂ O ₄ + 15Si	-2635.9	-2330.8	-1983.7
4Al + 3ZrSiO ₄ = 2Al ₂ O ₃ + 3ZrO ₂ + 3Si	-527.6	-490.6	-448.1

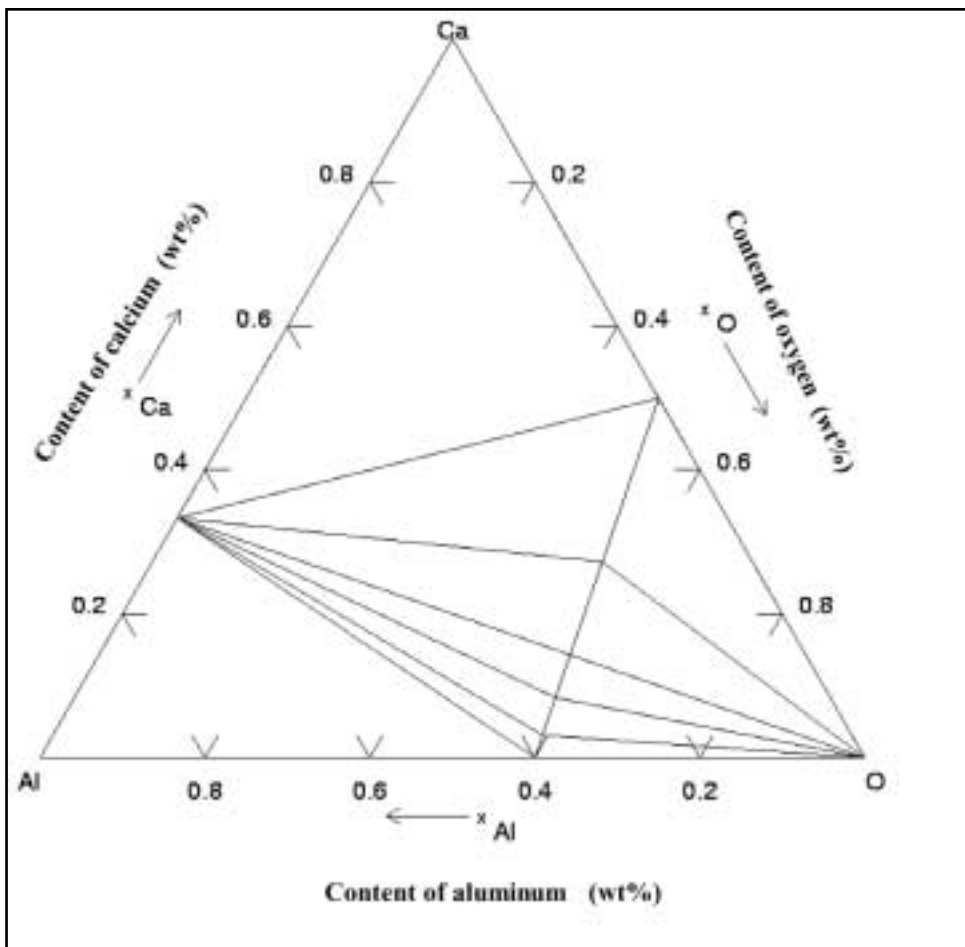


Figure 1. Calculated phase diagram of the system Ca – Al – O at 800°C according to MTDATA [5].

calculated from the thermodynamic data, however, the reaction actually causes a volume reduction of about 26 vol%. Hence, the spalling effect of aluminum infiltration and corundum formation in the lining must be due to other factor(s), most probably due to a pressure build-up from crystallization of corundum perpendicular to the thermal gradient (isotherms) or a contraction of the refractory caused by the volume reduction. Investigations performed on aluminosilicate refractories [6] have shown that silica is reducible in all forms by molten aluminum, and that mullite reacts more or less at the same rate as pure, free silica

Mg present in the liquid aluminum metal promotes the refractory conversion. Magnesium is, as seen from Table I, a strong reducing agent and will hence actively participate in the conversion reactions, for instance, by reacting with aluminum oxide with the formation of spinel phase:



This reaction is accompanied by a volume expansion of about 17 vol% and may account for refractory material spalling as well as through crack formation promoting increased metal penetration.

Reaction Kinetics Considerations

In order for aluminum metal to attack and deteriorate refractory linings, two conditions must be fulfilled:

- *The refractory materials must be reducible by molten aluminum metal, and*
- *The two reacting species must be in contact with each other.*

The first of these conditions was discussed in the previous section, and the second condition is linked to the reaction kinetics. When considering attack by molten metals on the refractory materials, wetting between the two phases must occur. The general condition for wetting is that the interfacial energy of the grain boundary (γ_{gb}) balances with the interfacial energy of the solid liquid interface (γ_{sl}). The relationship between these energies and the dihedral (wetting) angle (ϕ) is given by the equation:

$$\gamma_{sl} = 2 \gamma_{gb} \cos(\phi/2) \quad (7)$$

Wetting occurs when the wetting angle between the molten metal (aluminum) and the refractory is smaller than 90° ($\phi < 90^\circ$). With respect to wetting of refractories by molten aluminum metal and the influence of refractory material and metal phase properties, this will be discussed in a subsequent paper of the authors. However, as a temporary conclusion, it can be assumed that aluminum metal can be considered to wet almost any refractory material used in aluminum cast house furnaces [11-14], including its own oxide (Al_2O_3).

Additionally, the kinetics factor will also influence the rate of reaction. From other investigations [7,9] it is established that a glassy phase reacts more rapidly than a crystalline phase, and the same relationship is expected to be valid also for silica and silica-containing species. Also, presence of impurities, like alkalis, may affect the reaction kinetics through “parasitic” reactions causing volume expansion and cracking of the protective alumina deposit on the lining surface [10,15].

ALUMINUM RESISTANCE OF REFRACTORY MINERALS

To investigate the validity of the thermodynamic predictions in real life melting furnaces, a total of seven different refractory minerals and two commercial grade chamotte (fireclay) bricks were tested in this series. Mineralogical and chemical compositions of the tested refractory aggregates are given in Table III.

In order to eliminate or reduce the effect of physical parameters on the deterioration studies, the refractory minerals and the brick materials were crushed and passed through a sieve of 45 μm opening. This fine aggregate powder was then cold isostatic pressed at 2000 bar into a solid rod, and then sintered under optimized conditions* to provide nearly 100% dense samples. As can be seen from Table III, the milling, densification and sintering of the refractory mineral produced samples of very low porosity. With the exception of the calcium-aluminate mixture (cement phase), all of the samples had an open porosity of less than 0.6 vol% and more generally less than 0.2 vol%.

*Several sintering tests were performed on each type of material to optimize the sintering conditions prior to the “real” sample sintering.

The rods of the sintered refractory mineral samples were dipped into and exposed to pure molten aluminum (99.73% Al, 0.2% Fe and >0.1% Si) at 815 °C for 72 hours. The test set-up used is illustrated in Figure 2 below, and the furnace atmosphere was air (oxidizing). After the exposure, the samples were retracted from the molten metal and cooled in the furnace under natural cooling rates. All of the samples were inspected visually and then cut by a diamond-wheel saw for assessing the extent of attack. Powder X-ray diffraction and light microscopy, and, if necessary, Scanning Electron Microscopy (SEM), were used for further examinations.

Figure 3 presents photographs of the cut samples after aluminum exposure. The photographs are labeled according to the sample identification shown in Table III, where the term **RA** means **R**efractory **A**ggregate and the lower case letter refers to the sample identification (a through i). From the photographs it is evident that neither alumina (**RA-a**) nor magnesia (**RA-b**) nor zirconia (**RA-c**) are corroded by molten aluminum metal at 815 °C. The molten metal does not wet any of these materials, and the metal is only slightly attached to the samples. The cut sample of yttria stabilized zirconia (**RA-c**) showed an obvious discoloration in the part of the sample immersed in the molten metal. However, investigations by means of X-ray diffraction revealed no changes in the mineralogical composition of the material, and the origin of the discoloration is unknown. The addition of yttrium oxide to zirconia does not seem to have a negative effect, since both yttria and zirconia are thermodynamically stable against aluminum metal. All in all, the photographs of the samples **RA-a** through **RA-c** show that the refractory minerals exposed to molten aluminum metal behave as predicted from the thermodynamic calculations.

The two minerals, mullite and cordierite, reacted clearly with aluminum metal as can be seen from the photographs **RA-d** and **RA-e**, respectively. The mullite had a thin reaction layer on the sample surface, and X-ray analysis confirmed the presence of corundum and an aluminum silicon alloy in the reaction products. The reaction is then taking place according to equation (8) below. This reaction causes a volume contraction of about 18 vol%. With respect to the cordierite mineral, photograph **RA-e** shows that despite the extremely low open

Table III. Material specifications and physical parameters of refractory minerals and chamotte bricks tested against aluminium resistance at 815 °C.

Mineral and supplier	Sample	Density (g/cm ³)	Porosity (%)
		True	Open
Al ₂ O ₃ , CS400/MS Martinswerk	RA-a	3.85	0.17
MgO, Fluka 63089	RA-b	4.35	=0
YZS*, 3% Y ₂ O ₃ , MEL Chemicals	RA-c	6.03	0.01
3Al ₂ O ₃ ·2SiO ₂ , Synthetic, SINTEF	RA-d	2.93	0.08
2MgO·2Al ₂ O ₃ ·5SiO ₂ , Borgestad	RA-e	2.18	0.06
SiO ₂ , Quartz rod used as received	RA-f	n.d.	<0.05
CaO-Al ₂ O ₃ , CA-14, Alcoa (0.2%Na ₂ O)	RA-g	3.50	4.91
Chamotte A, 26 wt% Al ₂ O ₃	RA-h	2.50	0.56
Chamotte B, 36 wt% Al ₂ O ₃	RA-i	2.35	0.44

* Yttria stabilized zirconia.

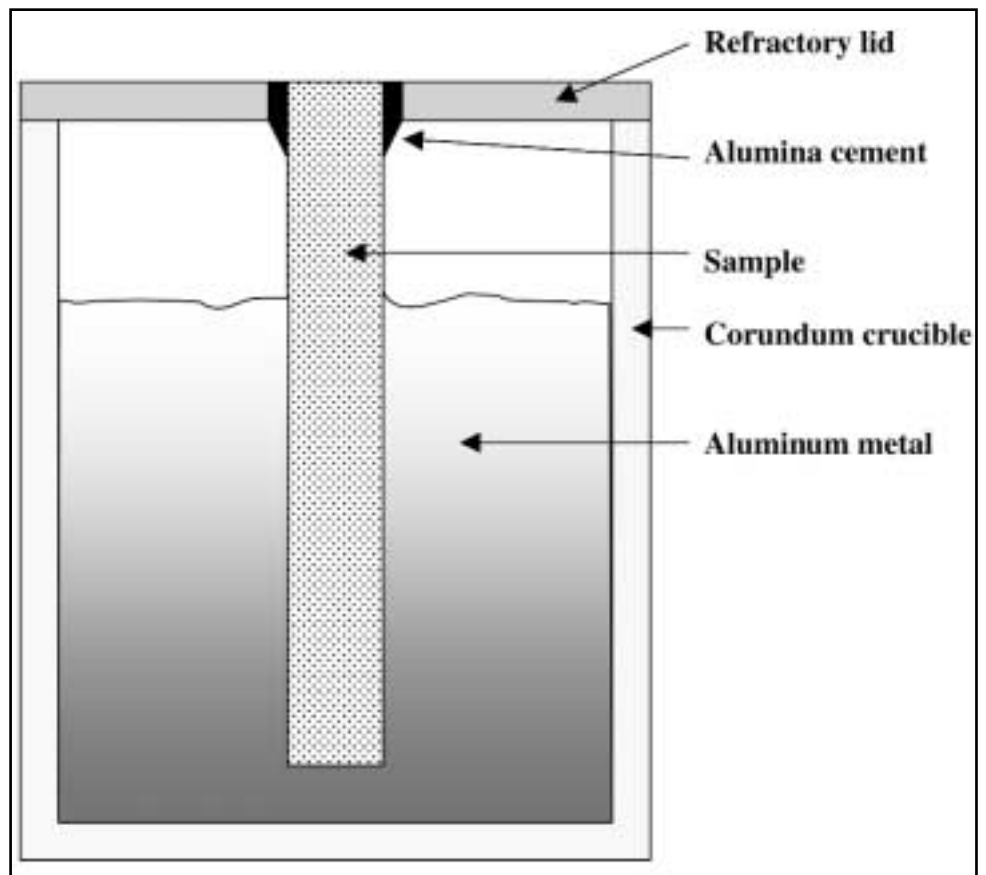


Figure 2. The experimental set-up used in the investigations on aluminum resistance of refractory minerals.

porosity of the sample, severe attack takes place. The cordierite phase wets aluminum well, and assists in “pulling” the metal upward and far above the metal line in the crucible. The reaction products formed, according to equation (9) below, cause a con-



siderable volume contraction of about 30 vol% and results in formation of veins of aluminum metal penetrating the sample. This is also evident from the photograph.

As predicted from the thermodynamic data, the reaction between aluminum metal and silica glass is vigorous. The sample, after exposure, is presented in photograph **RA-f** in Figure 3, and the X-ray analysis confirmed corundum formation according to reaction (5). Aluminum had completely penetrated the almost 100% dense sample, and several veins of aluminum can be seen in the lower part of the (immersed) sample. This is a clear evidence of metal penetration into the “shrinking” sample due to corundum formation accompanied by a volume decrease in the reaction product.

On the basis of the phase diagram for the system Al-Ca-O shown in Figure 1, it is predicted that an inter-metallic phase can be formed in a reaction between aluminum and calcium-aluminate phases. The kinetics and thermodynamic impetus will be affected by the stoichiometry of the calcium-aluminate phase(s) in the samples. Sample **RA-g** consisted of a rod formed from a calcium aluminate cement CIP'ed (cold isostatic pressed) and sintered. After exposure to pure aluminum, a thin reaction layer on the sample surface was identified. Analysis of the reacted material revealed the presence of the inter-metallic phase Al_2Ca , in accordance with the thermodynamic predictions.

Also with respect to the two commercial grade chamotte materials, these samples are completely penetrated and corroded by the metal. The two chamotte materials had an alumina content of 26 wt% and 36 wt% for the samples denoted **RA-h** and **RA-i**, respectively. From the photographs of samples **RA-h** and **RA-i**, it seems that within the investigated range, the alumina content does not play an important role in the deterioration process. Both materials are more or less completely infiltrated and attacked by the metal, and the metal has also wetted both materials equally well and been “sucked” upward far above the metal line in the crucible. Again, the volume reduction accompanied by corundum formation has led to the penetration of aluminum metal in veins in the corroded samples.

The investigations performed show that refractory aggregates react with molten aluminum as predicted from thermodynamic considerations. Even for samples with almost no open porosity (less than 0.6%), silica or silica-containing minerals will react with aluminum

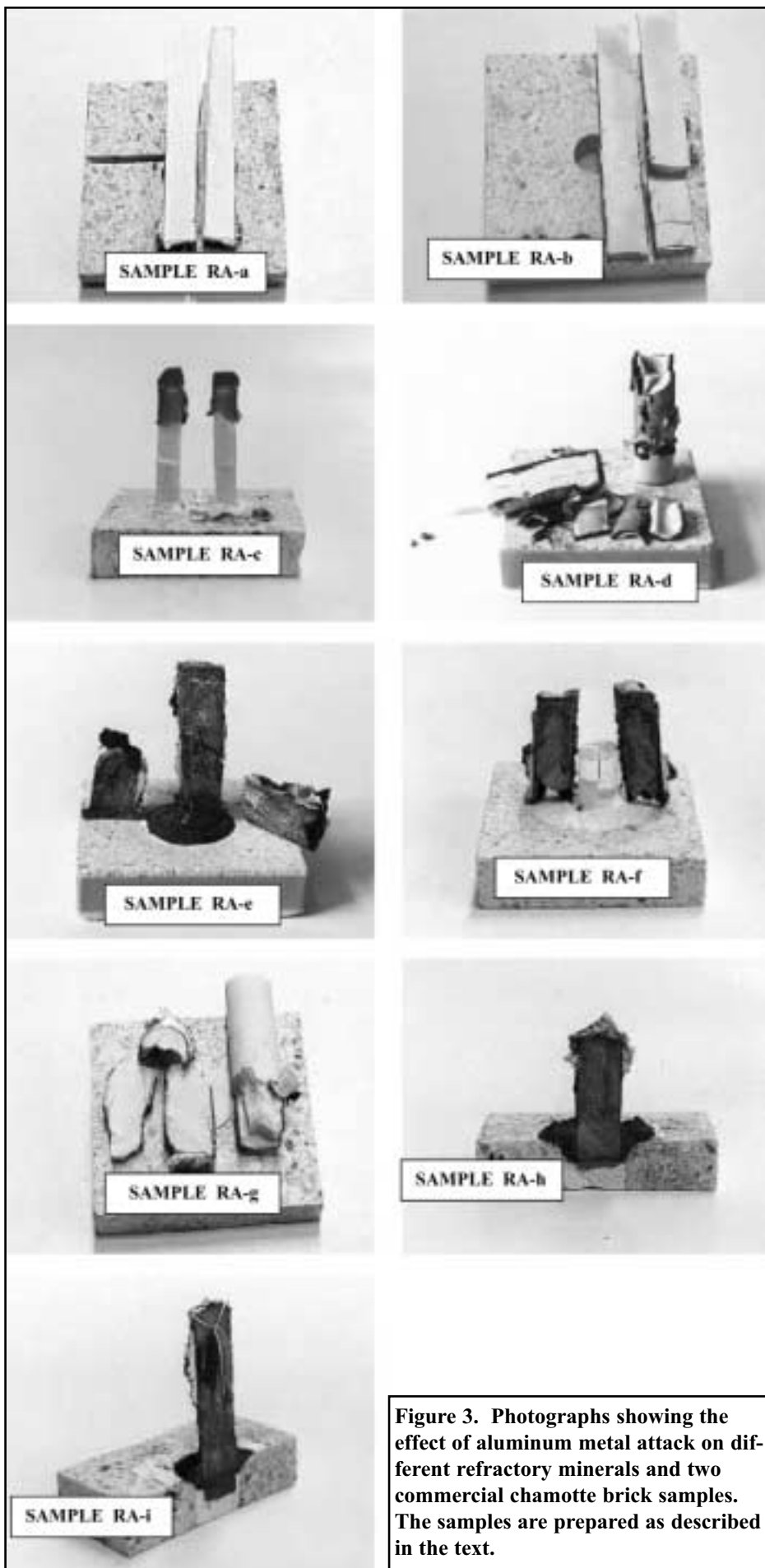


Figure 3. Photographs showing the effect of aluminum metal attack on different refractory minerals and two commercial chamotte brick samples. The samples are prepared as described in the text.

metal. Reactions accompanied by volume reductions are subjected to penetration of more metal, seen as metal veins in the samples. On the other hand, reactions causing volume expansion due to the formed reaction products tend to cause cracking of the sample and, as such, enhance metal penetration and reaction rates. The reaction kinetics are fast relative to the time scale of the performed tests. Hence, the investigations seem to indicate that reaction kinetics is more or less unimportant to the reaction rates. This can, of course, not be true, and in addition to the long exposure times (72 hours), the lack of temperature gradients will promote rapid reactions. Also, it is believed that a fine grained material reacts more rapidly than a coarse aggregate, due to the larger surface area (higher energy) of the fine-grained material.

ALUMINUM RESISTANCE OF ALUMINO-SILICATE CASTABLES

As shown in the previous section, silicates will react rapidly with aluminum metal even if they are “disguised” as silica-bearing phases like mullite, glass, etc. Hence, one would expect a drive toward aluminum furnace lining materials that do not contain silica. However, internationally, alumino-silicate refractories are still the most widely used lining material in aluminum handling furnaces due to their relatively low cost, availability and good thermal and mechanical properties in the prevailing temperature regime of these furnaces. The second series of tests performed in this work, consisted of exposing a number of different alumino-silicate based castables to aluminum metal.

One of the most commonly described problems in aluminum furnace operation is the corundum growth phenomenon. The photograph in Figure 4 shows the formation of a “corundum mushroom” in the metal line of an electrically (top) heated filter box. The mushroom contains a matrix of aluminum oxide completely soaked with aluminum metal, so that the metal is also present as a continuous phase. It is now more or less commonly accepted that there exist two possible mechanisms for corundum growth:

- External corundum growth, and
- Internal corundum growth.

External corundum growth occurs from the surface of the aluminum metal in the

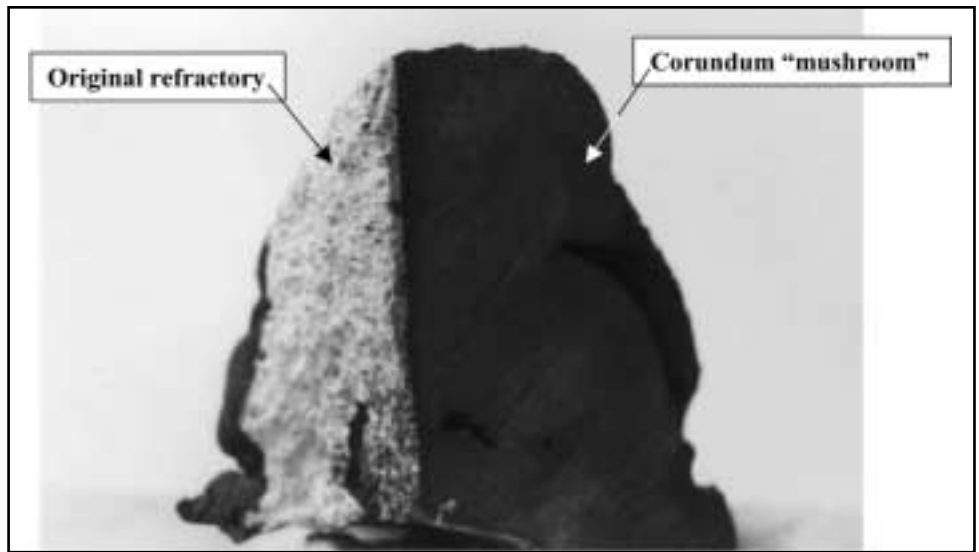


Figure 4. Photograph showing a corundum mushroom formed on the refractory wall lining in the metal line of an electrically (top) heated filter box.

triple point junction between aluminum, refractories and atmosphere. Through a wick/sponge action of the capillary pores in the formed corundum layer, aluminum is sucked upward in the lining and oxidizes at levels above the metal surface, i.e., forming a corundum mushroom or nodule on the furnace wall [16]. If magnesium is present at sufficient levels in the molten metal, it is believed that the so-called DIMOX process [17] is the cause of corundum growth. The DIMOX process includes formation of alumina, magnesium aluminum spinel and magnesium oxide layers on the metal surface, promoting the growth of corundum slag. Allaire and Guermazi [1] have showed that external corundum growth is enhanced by:

- Increasing partial pressure of oxygen, where oxygen may originate from the furnace atmosphere or penetrate through the permeable lining materials.
- Presence of alloying elements like silicon (Si) and magnesium (Mg).
- Presence of salts like cryolite (Na_3AlF_6).

Internal corundum growth is due to the reduction of refractory oxides by aluminum metal penetrating through the pore system of the refractories and direct oxidation by air in the pores. As described earlier, some of the less noble oxides will be reduced to an aluminum alloy and aluminum oxide (corundum), and internal corundum growth is enhanced by[1]:

- Decreasing partial pressure of oxygen [1,15].

- Increasing metal temperatures, i.e. increasing furnace temperatures [1,6,18,19].
- Increasing pre-firing temperature of the refractories.
- Presence of salts like cryolite (Na_3AlF_6).

In order to retard or prevent the direct reaction between silica and aluminum, so-called anti-wetting agents are often used [10, 20] in the refractories. The purpose of these agents, usually $BaSO_4$, AlF_3 and/or CaF_2 , is to prevent the reaction between silica and aluminum metal. It is questionable whether the effect of the anti-wetting aggregates can be contributed to the added components. At temperatures above 900 – 1100°C, the anti-wetting additives seems to lose their effect, probably due to reaction(s) with the matrix components and thus forming new minerals that are attacked by aluminum. In the case of barium sulphate, it is most likely the conversion to barium anorthite ($BaAl_2Si_2O_8$) that accounts for the loss of “anti-wetting” effect [21]. The transformation of the $BaAl_2Si_2O_8$ from an orthorhombic to a monoclinic symmetry, accompanied by a volume decrease of 3 vol% that may cause increased metal penetration into the refractory.

Laboratory testing of aluminum resistance

The performed test program hence took its basis in the testing of several alumino-silicate-based castables exposed aluminum metal. A total of six different commercial castables were tested in this series, with the

main minerals and the chemical compositions given in Table IV.

The materials were prepared as described by the producers and cast with the correct amounts of water in the shape of standard refractory bricks (230x114x64 mm³). The cast samples were left to set and cure for 16 hours in the mold and then another 24 hours at room temperature without the mold before drying at 110 °C for 20 hours. The samples were then finally fired at a predetermined temperature for approximately 24 hours, before being cooled and then a hole is drilled in the middle of the half-brick sample to contain the molten metal during the test. The aluminum metal used in the test had a composition as given in Table V. Three different test modes were used:

- Program I: Pre-firing at 800°C, cooling and exposure at 800°C for 72 hours.
- Program II: Pre-firing at 800 °C, cooling and exposure at 1200 °C for 72 hours.
- Program III: Pre-firing at 1250°C, cooling and exposure at 800°C for 72 hours.

The results of the investigations are presented in Table IV, and along with the results are also given some important physical parameters of the materials. Figure 5 presents photographs of selected samples after aluminum exposure and cutting. With respect to the aluminum resistance listed in Table IV, the numbers refers to an internal scale used by the authors, where the numbers from zero to seven reflect different extents of reaction. The number zero (0) is the best grade, i.e. no reaction and no adhesion of metal to sample, and the number seven (7) the worst grade reflecting total degradation and fracture of the sample. The numbers one to six reflect different grades of reaction, from only adhesion of metal (1) to extensive and severe metal penetration and reaction (6).

From even a superficial glimpse at the results in Table IV, it can be noted that there are few, if any, clear trends in the observed reaction extents versus physical and chemical parameters. However, some general trends can be outlined from the results:

- Generally, the aluminum resistance seems to increase with increasing alumina content in the castables. This is in agreement with earlier results [6], and is also in agreement

Table IV. Chemical composition and physical properties of seven aluminosilicate castables tested against aluminum metal in a so-called cup-test. Materials are pre-fired and then exposed towards molten aluminum metal.

Material		A	B	C	D	E	F
Al ₂ O ₃	(%)	51.0	70.4	83.0	78.0	93.0	94.0
SiO ₂	(%)	42.0	25.1	11.0	10.3	5.0	0.2
CaO	(%)	3.9	1.2	1.5	1.4	1.1	5.8
Fe ₂ O ₃	(%)	0.9	1.2	1.5	1.4	0.1	0.1
(Na,K) ₂ O	(%)	0.4	0.1	0.5	0.5	0.5	0.5
BaSO ₄	(%)	0	0	0	6.0	0	0
CaF ₂	(%)	0	0	0	0	0	3.0
Density (g/cm ³)*		2.38	2.75	2.79	2.86	2.95	2.58
Open porosity (%)*		17.0	12.0	19.8	18.3	18.5	30.5
Gas permeab. (nP)*		~0	~0	~0	~0	~0	~0
Test duration (h)		72	72	72	72	72	72
Aluminum resist.**							
800/800°C	(#)	2	0	1	1	0	0
800/1200°C	(#)	2	3	3	2	1	1
1250/800°C	(#)	4	2	2	2	5	1

*After firing at 800°C.
**The temperatures refer to firing and exposure temperature, respectively.

Table V. Chemical composition of the aluminium metal used in the cup-test. Metal used is an alloy named 310401.

Element	Al	Fe	Si	Cu	Mn	Mg
Composition (%)	ca. 97	0.35	0.22	0.17	0.95	1.23

with the thermodynamics presented earlier in this work. However, the results show, that even at low silica contents, this mineral is readily reduced by aluminum metal if the proper conditions are met.

- There seems to be no apparent correlation between the castable density and its aluminum resistance. In the same way, no relation can be observed between the apparent porosity and the aluminum resistance. This is in agreement with the results presented by [6].
- The analysis of the castables after firing to 800 °C also showed that air permeability could not be used as a predictive parameter with respect to aluminum resistance in the performed tests.
- The effect of anti-wetting additives like CaF₂ and BaSO₄ are "obscure" and no clear conclusions could be

made. However, for one of the samples (C) an improvement could be detected when anti-wetting additive was used (D).

- The effect of temperature however, is unambiguous. An increase in both pre-firing temperature and exposure temperature results in a decrease in the aluminum resistance. From the experiments performed in this work, it seems clear that the effect of pre-firing temperature is the most important factor of the two.

The parameters presented in Table IV are overall chemical composition and average physical parameters of the investigated castables. As the test results are somewhat inconsistent, we will have to search for other explanations of the observations. With the exception of material F, all of the tested materials are thermodynamically unstable toward aluminum metal, due to the silica content. Even though a decrease in

the silica content generally seems to improve the aluminum resistance, the high alumina material named **E** exhibited the lowest aluminum resistance when pre-fired to 1250°C. Therefore, it seems logical to investigate the effect of mineralogy and micro-structure of the materials.

Earlier in this paper, aluminum resistance of pure mineral phases CIP'ed and sintered into dense rods with almost no open porosity was presented. These investigations indicated that silica as a mullite phase reacted less rapidly than free silica or silica in a glassy phase (chamotte bricks). It can be deduced from phase diagrams that all castables with a silica content below 28 wt% will consist (ideally) of mullite and corundum as the primary phases. Such materials should then react less rapidly (i.e. exhibit improved aluminum resistance) compared to materials of higher silica contents. One complicating factor, however, is the presence of other oxide phases and impurities. Since these impurities tend to gather in the matrix and form glasses at high temperatures, this may lead to a decrease in the aluminum resistance. This effect is distinctive even in high alumina materials, as the matrix phase may have a completely different chemical and mineralogical composition from the bulk phase. As pointed out by, among others, Allaire and Guermazi [1] the matrix phase is most disposed to aluminum attack.

The photographs in Figure 5 shows three of the tested castables after pre-firing at 1250°C and subsequent aluminum exposure at 800°C for 72 hours in an oxidizing atmosphere. The silica-free, high-alumina material (sample **F**) shows no sign of aluminum penetration into the pore system of the castable, and a neglectable adherence of aluminum to the material could be detected. As a counterpart, the second high-alumina castable (sample **E**) which contains the same amount of alumina, but with 5 wt% micro-silica, shows evidence of extensive penetration into the pore system and conversion of the silica mineral(s), and the aluminum metal also shows good wetting of the refractory. However, the corundum aggregate in the castable is virtually unaffected by the metal penetration, as predicted from the thermodynamics. Sample **C**, which is a more conventional high-alumina, low-cement castable shows only moderate metal penetration, but the adherence of the metal to the refractory was good. The beginning penetration of aluminum metal has led to some conversion of the matrix phase, evident as a black layer towards the metal in the refractory "cup".

CONCLUSIONS

The tests and evaluations performed in this paper were concerned with studying aluminum attack of mainly alumino-silicate refractory materials. Thermodynamics and laboratory investigations clearly showed that silica is reduced to silicon metal and corundum in the presence of molten aluminum, irrespective of silica being present as free SiO₂, as a glassy phase or as a constituent in a silica-bearing mineral (Al₆Si₂O₁₃). The precondition for the reactions to take place is, of course, the wetting of the refractory oxides by molten aluminum.

The performed investigations show that, at 815°C, refractory aggregates will react with molten aluminum as predicted from thermodynamic considerations. Even for samples with almost no open porosity (less than 0.6%), silica or silica-containing minerals will react with aluminum metal. The tests also showed that reactions with silica bearing minerals resulted in a volume decrease due to corundum formation. The voids formed in the materials due to this volume decrease acted as "suction pipes" allowing aluminum to be drawn upward in the material to corrode areas above the metal line. On the other hand, reactions causing volume expansions may cause cracking of the sample and as such enhance further metal penetration and reaction. Due to the long exposure times used

in the experiments, influence of reaction kinetics were impossible to observe.

The experiments also demonstrated the formation of an inter-metallic compound, Al₂Ca, when exposing aluminum metal to a calcium oxide – alumina material. The tests showed that this reaction takes place at temperatures as low as 800 °C of the pre-fired material. This observation points to the fact that the cement binder itself in castables is vulnerable to attack by molten aluminum metal, in contrast to earlier predictions [22].

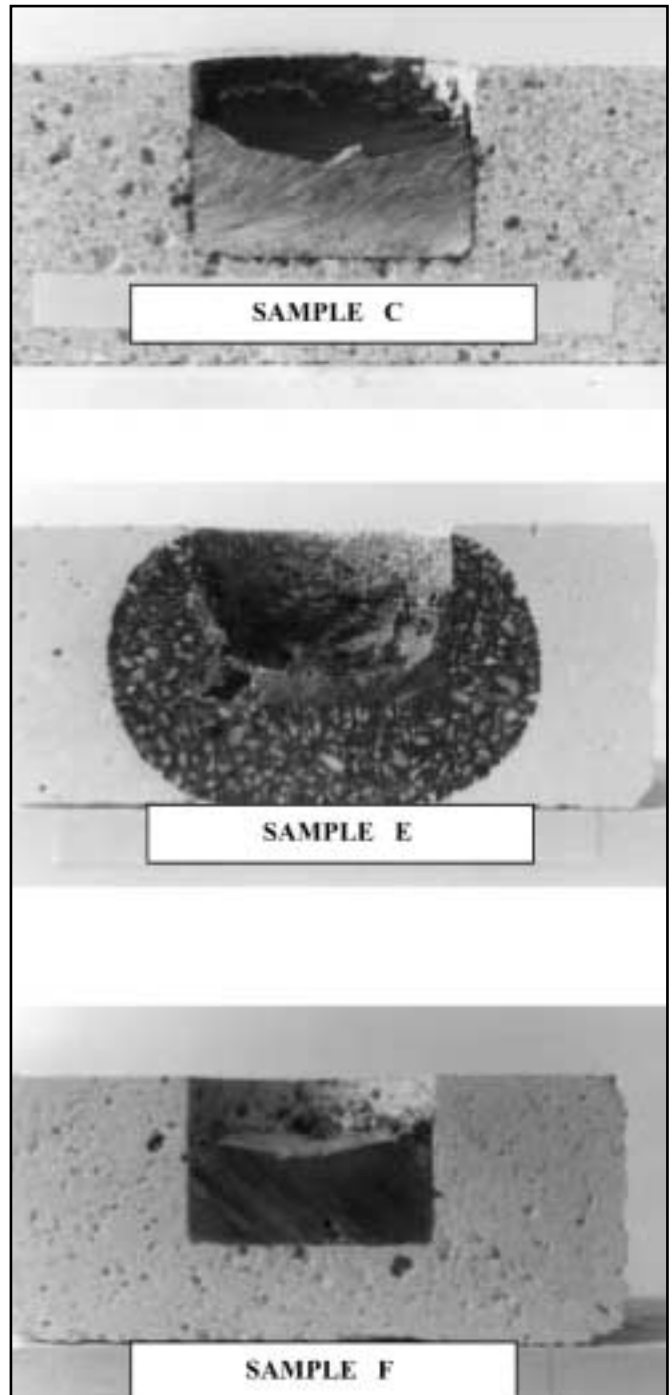


Figure 5. Photographs showing the effect of aluminum metal attack on selected alumino-silicate refractory castables materials. The samples are prepared as described in the text.

Aluminum resistance tests performed on real aluminosilicate castables have shown that:

- **Aluminum resistance generally increases with:**

- Increasing aluminum oxide content.
- Addition of anti-wetting additives.

- **Aluminum resistance generally decreases with:**


- Increasing silicon oxide content.
- Increasing pre-firing temperature.
- Increasing exposure temperature.

The performed tests, however, are not conclusive. It is therefore suggested that rather than overall chemical composition and physical parameters, a study of the micro-structure and mineralogy of the castables are necessary to fully understand the mechanisms involved in aluminum resistance of refractory oxides. This will be the topic of the succeeding paper in this series.

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