

REFRACTORIES FOR MOLTEN ALUMINUM CONTACT PART II: INFLUENCE OF PORE SIZE ON ALUMINUM PENETRATION.

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(Presented at ALAFAR'01)

ABSTRACT

Refractory lining materials for cast house furnaces may be attacked and infiltrated by molten aluminum metal during furnace operation. The wetting of the refractories and physical properties like porosity and pore size distribution of the refractories determine the extent of the aluminum contact and infiltration. As the previous paper in this series indicated, physical parameters like density, porosity and overall chemical composition could not solely explain the observed behavior of refractory materials exposed to molten aluminum in laboratory cup-tests. The present paper demonstrates that refractory material pore size distribution are of key importance with respect to aluminum resistance, and the pore size distribution of the refractories are shown to be affected by firing temperature and chemical composition. The presented results indicate that materials that are not thermodynamically stable towards molten aluminum metal can be improved by optimized pore size distribution.

INTRODUCTION

The previous paper [1] showed that overall refractory parameters like apparent porosity and density cannot unambiguously predict aluminum resistance of refractory cast house furnace linings. Neither is the overall chemical composition the sole factor determining the reaction extents. Hence, it seems natural to investigate the microstructure of the material for some guiding principles regarding aluminum penetration and reaction in refractory linings.

Brick microstructure and parameters affecting it

The refractory material, which indeed has a definite, solid structure, can be defined by a set of macroscopic parameters, such as density, apparent porosity, mechanical

strength and overall chemical composition. Refractories are made up of refractory aggregates and binder materials. During production, binder materials together with the fine fractions of the refractory aggregate will make up the so-called matrix of the refractory. The matrix phase will also include pores formed during the processing, and generally the matrix phase is often referred to as the microstructure of the refractories. Hence, the materials can also be characterized by a set of microstructure parameters, such as pore size distribution, grain size distribution, and local chemical composition of matrix and aggregate(s). Often used as a rough simplification, the microstructure of the refractories is often considered to be the part of the material that can be measured in micrometers (μm), a simplistic view reflecting a certain degree of truth.

Refractory manufacture

The manufacturing process influences the resulting micro- and macrostructure of the materials. Raw material treatments like crushing, milling, classification and mixing influence on packing density, thus allow the producer to optimize properties like density, open porosity and pore size distribution [2]. During brick production, the forming process influences the physical properties and consequently the aluminum penetration into the refractory lining. An extruded brick will consist of more uncalcined clay used as a "lubricant" during production, and the final brick will generally have much smaller pores than a (dry-)pressed brick, although the open porosity may be the same for both bricks. With respect to castables and rammables, the installation procedure and the precision of the workers during installation, is crucial to obtain the desired material properties. Installation conditions may also strongly affect the micro- and macrostructure properties

[3,4,5], and as such strongly affect the aluminum resistance of the lining.

Firing temperatures will also affect aluminum resistance, as low temperatures tend to maintain smaller pores from the forming process, whereas a high firing temperature will promote coarsening and grain growth. High firing temperatures thus tend to leave refractory materials with relatively few, but large pores although the total porosity of the material may not change severely during firing. High firing temperatures also increase the glass content of aluminosilicate bricks, and generally glass will react faster than crystalline phases, thus enhancing the reaction with penetrating aluminum metal in the lining [6].

Raw materials and chemical composition

The influence of chemical composition on the resulting aluminum metal resistance is obvious. A simplification is to divide the refractory materials into an aggregate phase and a matrix phase. The aggregate phase is usually a "pure" and refractory mineral that, if selected skillfully, will be able to resist aluminum penetration and attack. The matrix phase however, is generally made out of binders (like cements, clays, phosphates, etc.) and fine grained material from the aggregate. Additionally, pores in the refractory are also usually accepted as a part of the material microstructure. Contaminants in the aggregate tend to accumulate in the fine fractions and the "dust", and hence the chemical composition of the matrix may vary substantially from the overall chemical composition of the refractory. This fact is important to remember when considering both chemical resistance toward aluminum metal and wetting of the refractory structure by the molten metal.

WETTING OF REFRACTORIES BY MOLTEN ALUMINUM METAL

In this paper we will address reactions between aluminosilicate refractories and molten aluminum metal. One cardinal condition for reaction between the two is hence that wetting of the refractories by the molten metal take place. If wetting does not occur, the reaction will not take place.

Numerous articles have addressed the principles on the wetting of different refractory materials by aluminum. One major problem concerning the measurement of the wetting angle of aluminum, is that the metals have high affinity toward oxygen. It is hence difficult to obtain an oxide-free surface layer on aluminum, and the presence of this oxide film will (strongly) influence the measurements [7]. This is shown in Fig. 1, where the influence of the oxide film thickness on the wetting angle is presented. It is seen from the figure that the extrapolated wetting angle of pure aluminum with no oxide film on sapphire at 800°C is estimated to be 80°, indicating that even at these low temperatures pure aluminum will wet its own oxide. The sudden decrease in wetting angle at around 900 – 1000°C shown in the figure have been proposed to be due to reaction between aluminum and alumina to form the gaseous species $Al_2O_{(g)}$. At low pressures (vacuum) the formation rate of this species is high. Furthermore, by increasing the temperature of the molten metal the wetting of alumina by aluminum metal becomes more pronounced. This is again shown in Fig. 1, and the figure also points to the wide range of wetting angles of molten aluminum on alumina reported in the literature [7]. Likewise, an increase in the exposure time results in a decrease in the wetting angle of aluminum on alumina, again shown in Fig. 1, where the measurements are performed at 700°C in vacuum [7]. The same behavior is generally observed for the wetting angle of aluminum on all ceramic substrates, most often due to a chemical reaction between the metal and the aluminum oxide film or a reaction between aluminum metal and the refractory itself. This phenomena is most commonly referred to as reactive wetting.

With regard to other refractory surfaces, the data presented in Table I shows a synopsis of reported literature values of the wetting angle of molten aluminum and alu-

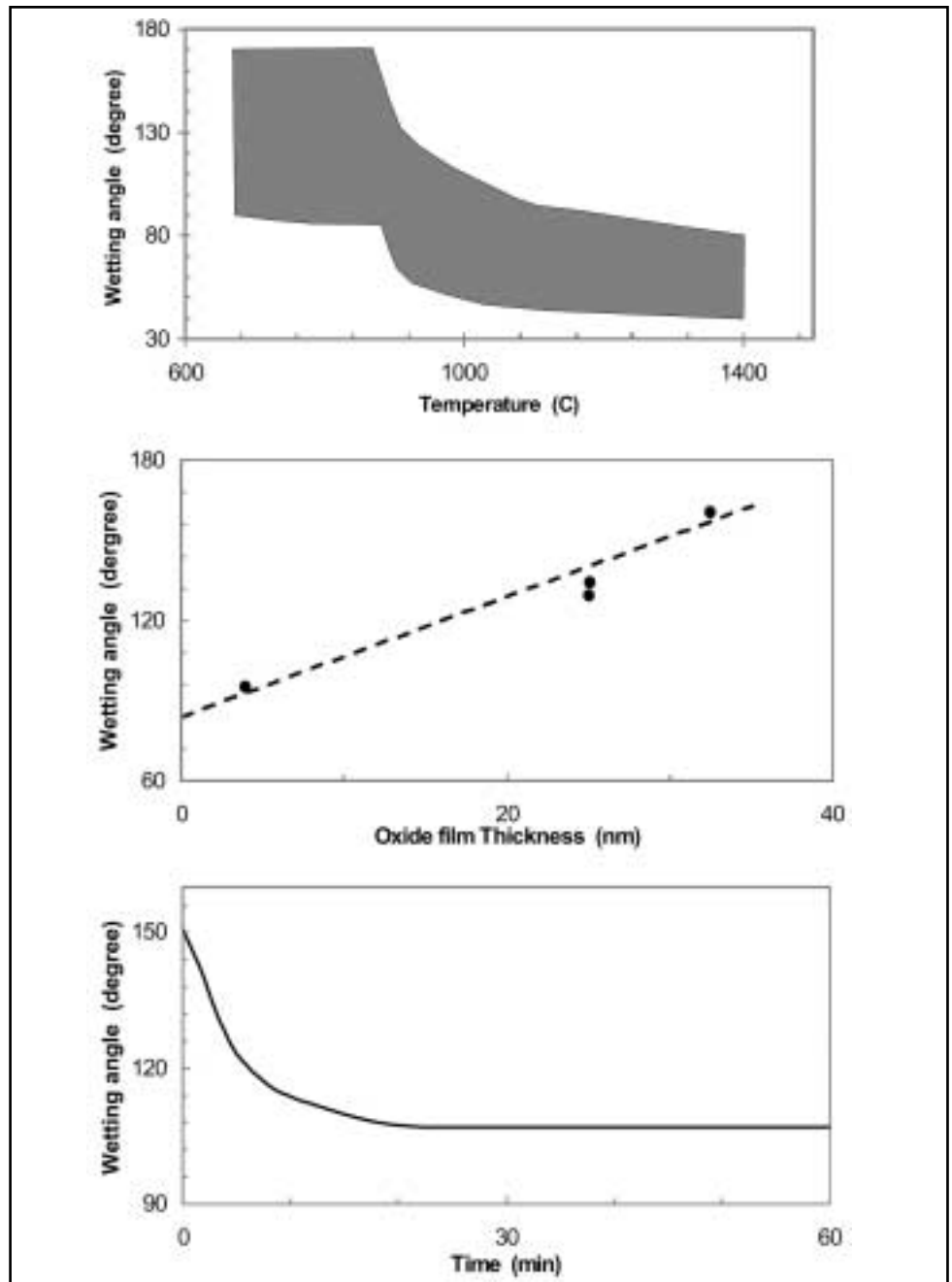


Figure 1. Wetting angle of aluminum on aluminum oxide(s), from Li [7].
Top: Literature range of the wetting angle of molten aluminum metal on alumina as a function of temperature in vacuum.
Middle: Influence of oxide film thickness on the wetting angle of aluminum on sapphire at 800°C in vacuum.
Bottom: Variation of the wetting angle of molten aluminum metal on sapphire at 700°C in vacuum as a function of time.

minum alloys [8-16]. From the data in Table I and Fig. 1 it can be concluded that:

- Aluminum can be considered to wet almost all known refractory oxides.
- Aluminum will also wet most refractory nitrides, borides and carbides.
- Generally a decrease in the wetting angle is observed with increasing temperature and increasing exposure

time, i.e., indicating reactive wetting through reaction of aluminum surface oxide film and the refractory material with molten aluminum.

The principles of wetting

The condition for wetting of a refractory material by molten aluminum metal is that the interfacial energy of the grain boundary

Table I.
Some reported literature values of aluminum wetting angle for different refractory material surfaces. Effect of temperature atmosphere and alloying components is also included, together with data references.

Metal	Substrate	Time (min)	Atm.	Wetting angle, ϕ				Ref.
				700°C	800°C	1000°C	1200°C	
Al	Al ₂ O ₃	15	Vac.	120	90	85	70	[8]
Al	Al ₂ O ₃	720	Vac.		75			[8]
Al	Al ₂ O ₃	2	Vac.			102		[9]
Al	Al ₂ O ₃	15	Vac.			81		[9]
Al	Al ₂ O ₃	300	Vac.			59		[9]
Al	Al ₂ O ₃	2	Vac.				90	[10]
Al	Al ₂ O ₃	60	Vac.				89	[11]
Al	Al ₂ O ₃	300	Vac.				82	[10]
Al	Al ₂ O ₃	720	Vac.				58	[12]
Al	AlN	15	Vac.	160			49	[13]
Al	AlN	30	Vac.			112		[13]
Al	BN	15	Vac.	160			31	[14]
Al	TiB ₂	0	Vac.			80		[14]
Al	TiB ₂	30	Vac.			86		[13]
Al	TiB ₂	60	Vac.			33		[14]
Al	TiC	30	Vac.			98		[13]
Al	TiN	30	Vac.			76		[13]
Al	SiO ₂	10	Ar		110			[15]
Al	SiO ₂	60	Vac.			140	76	[14]
Al	SiO ₂	120	Vac.	150	98	68*		[11]
Al	SiO ₂	180	Ar		78			[15]
Al	C	120	Vac.			160		[14]
Al	MgO	0	He/H ₂				79	[14]
Al	CaO	120	Vac.			100*		[11]
Al	SiC	60	Vac.			-78	-58	[14]
Al+6Mg	SiO ₂	10	Ar		-105			[16]
Al+6Mg	SiO ₂	180	Ar		-78			[16]
Al+3Mg	MgAl ₂ O ₄	10	Ar		>120			[16]
Al+3Mg	MgAl ₂ O ₄	180	Ar		80			[16]
Estimated "Best values"				Wetting angle, ϕ				
Metal	Substrate	Time	Atm.	800°C	1000°C	1200°C		
Al	Al-silicate	≥60	Reducing	85	75	65		
Al+1Mg	Al-silicate	≥60	Reducing	80	-	-		
Al+5Mg	Al-silicate	≥60	Reducing	75	-	-		
Al+5Zn	Al-silicate	≥60	Reducing	80	-	-		
Al+5Si	Al-silicate	≥60	Reducing	80	-	-		

*Measured at 900°C.

(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 [17]:

$$\gamma_{sl} = 2 \gamma_{gb} \cos(\phi/2) \quad (1)$$

Wetting then occurs when the wetting angle between the molten aluminum and the refractory material is lower than 90° ($\phi < 90^\circ$). Under thermodynamic equilibrium and steady state conditions, the relation between the wetting angle and the surface tensions is given by the equation:

$$\cos\phi = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv} \quad (2)$$

where γ_{sv} is the surface tension of the solid substrate (refractory), γ_{lv} is the surface tension of the liquid (metal) and γ_{sl}

again is the interfacial tension between the solid substrate and the liquid. Equation (2) is the so-called Young's equation.

Considering the information in Table I and Fig. 1, it can be assumed that aluminum metal will wet any refractory material based on common oxide minerals such as alumina, silica and mixtures thereof. As molten aluminum is brought into contact with alumino-silicate refractories, the molten metal may penetrate into the structure through pores and cracks. Regarding this penetration, there are three different conditions that will determine the degree of penetration.

- Closed porosity in the refractory materials will not be exposed to molten metal until a chemical reaction between the metal and the

refractory has "eaten" its way through the pore wall. In refractory materials, only about 10% of the total porosity is closed porosity, and hence we can for all practical purposes conclude that closed porosity will have no effect on molten aluminum penetration and penetration rates.

- Open porosity characterized by blinded pores extending from the surface of the refractory, will be filled with aluminum metal. The metal intrusion is governed by a balance in the hydrostatic pressure of aluminum and the back pressure constituted by the compressed atmosphere in the pore. This penetration depth is then determined by the equation [17]:

$$\Delta P = (2 \gamma \cos\phi) / r \quad (3)$$

where ΔP is the hydrostatic pressure, $\gamma (= \gamma_{sv})$ is the metal surface tension and r is the pore radius.

- Open porosity characterized by continuous pores extending from the surface to the "back side" of the refractory. Such pores will be completely filled with molten aluminum metal, and the penetration rate will amongst others be dependent on the physical properties of the metal and the pore structure. This will be discussed in more detail below.

By accepting these presumptions, we see that for open pores and cracks in the refractory structure there is no minimum pore size to prevent metal intrusion, as long as the molten metal (alloy) wets the refractory material. Hence, we can only reduce the penetration rate of molten aluminum (alloys) into the refractory structure. Possible methods for reducing metal penetration will be discussed below, involving the altering of refractory parameters affecting the microstructure as well as the physical characteristics of the penetrating metal.

Influence of pore size on aluminum penetration

Once wetting has occurred, the refractories are susceptible to attack and degradation by molten metal. The metal can attack the refractory aggregates and the matrix phase, on the surface of the material, but also attack the interior of the refractory structure by infiltration of the pore system of the lining. The penetration rate is

expressed in equation (4) below, named Poiseuilles law [17]:

$$dl/dt = d^2 \Delta P / (32\eta l) \quad (4)$$

In this equation, l is the penetration depth, η is the viscosity of the molten metal, d is the pore diameter, ΔP is the hydrostatic pressure (due to gravity or capillary forces) and t is time. From equation (4) it is seen that to reduce the penetration depth, it is favorable to have a melt with high viscosity and a refractory with a low pore size. Given the high fluidity of most molten aluminum alloys, it can be deduced that the only practical way to reduce metal penetration is through the reduction in refractory material pore size. Clavaud and Jost [18], Chatterjee [19] and Miyawaki and Hongo [20] have amongst others mentioned the importance of refractory material pore size. However, none of these authors have discussed in depth the influence of pore size on aluminum and aluminum alloy penetration.

By integrating equation (4) with respect to l and t , we obtain the equation:

$$l = \sqrt{[(2 d^2 \Delta P) / (32\eta) \cdot t]} \quad (5)$$

According to Lee and Zhang [17] the term ΔP can be expressed by:

$$\Delta P = (4 \gamma \cos\phi) / d \quad (6)$$

Where γ ($= \gamma_{sv}$) is the molten metal surface tension and ϕ (as before) is the wetting angle. By inserting ΔP from equation (6) into equation (5) and simplifying, we get the following expression for the penetration rate.

$$l = \sqrt{[(d \gamma \cos\phi) / (4\eta) \cdot t]} \quad (7)$$

From the literature [21,22,23], we can obtain data for the surface tension and viscosity of aluminum metal and different aluminum alloys. Such data are presented in Table II, and from the table it can be concluded that:

- The viscosity and surface energy of molten aluminum decreases with increasing temperature.
- Generally, addition of small amounts (≤ 5 wt%) alloying elements does not have a severe effect on the surface energy nor the viscosity of the metal. Aluminum can be considered to wet almost all known refractory oxides.

Metal base	Viscosity of liquid (Ns/m ²)					Ref.
	700°C	800°C	900°C	1000°C	1200°C	
Al	0.0118	0.0098	0.0086	0.0077	0.0064	[21]
	0.0112					[22]
Al + 1%Mg	0.0117					[21]
	0.0113					[22]
Al + 5%Mg	0.0111					[21]
Al + 5%Zn	0.0119					[21]
	0.0108					[22]
Al + 5%Si	0.0112					[21]
	0.0083					[22]

Metal base	Surface energy of liquid (mN/m)					Ref.
	700°C	800°C	900°C	1000°C	1200°C	
Al	861	844	830	816	786	[21]
	858		817		757	[23]
Al + 1%Mg	658					[21]
	887	852				[22]
Al + 5%Mg	601					[21]
	837	801				[22]
Al + 5%Zn	846					[21]
	892	858				[22]
Al + 5%Si	808					[21]

By applying the expression given in equation (7), we can calculate the intrusion depth of aluminum metal in refractory materials, as shown in Fig. 2. With respect to surface energy and viscosity, the average reported value in Table II for each temperature and metal composition is used as input data for the calculations. Regarding the wetting angles of aluminum metal (alloys) on alumino-silicate refractories, the so-called **best values** given in Table I are used in the calculations. From the plots in Fig. 2 it is clear that the major important factors with respect to metal intrusion are the refractory material pore size and the wetting angle. This is in agreement with the predictions presented earlier and observations reported in the literature [8-20]. The pore size, of course, has the greater effect of the two, although the influence of the wetting angle cannot be neglected. The effect of temperature is limited, of course assuming that the predicted reduction in wetting angle is valid (Table. I). In line with the previous discussions, increasing exposure times will lead to increased intrusion depths, as increased exposure times will decrease the wetting angle. Alloying elements on the calculated intrusion depths is limited, again due to the confined effect

on viscosity, surface tension and wetting angle.

The performed calculations of course suffer from three major elements of uncertainty, namely:

- The effect of changes in the composition of the penetrating metal due to reaction with refractory materials and dissolution of reduced refractory metal species into the molten aluminum,
- The influence of a thermal gradient in the lining is neglected, and
- The precipitation of solids (i.e., alumina) in the molten metal will increase the viscosity and as such influence on metal intrusion depths.

INVESTIGATIONS AND RESULTS

To investigate the effect of pore diameter and pore distribution on refractory material deterioration in molten aluminum contact, the following series of experiments were performed. Five different alumino-silicate based refractories were mixed, cast (or rammed/pressed) and cured according to supplier specifications. Thereafter the samples were pre-fired at 800°C, 1000°C, 1200°C and 1400°C before exposing them

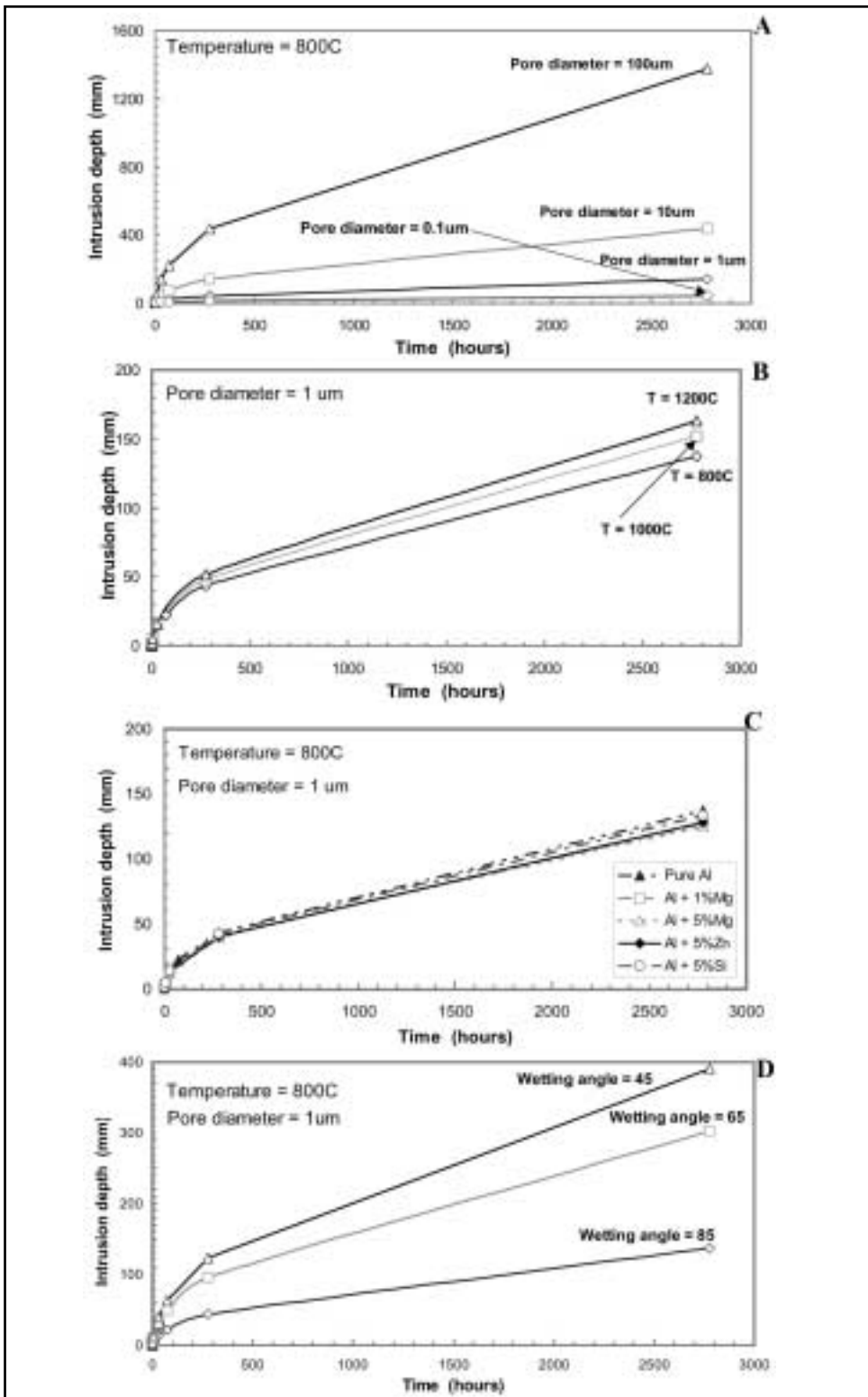


Figure 2. Calculated effect of metal intrusion depths as a function of time for aluminum silicate refractory materials. Data for the calculations are taken from Table I.

A = Influence of pore size on aluminum metal penetration at 800°C.

B = Influence of temperature on aluminum metal penetration. The assumed refractory pore diameter is 1 µm.

C = Influence of alloying compounds on aluminum metal penetration at 800°C and the assumed refractory pore diameter is 1 µm.

D = Influence of wetting angle on aluminum penetration at 800°C and the assumed refractory pore diameter is 1 µm.

towards molten aluminum at 800°C in the so-called cup-test [1]. After exposure, the samples were cut in two diagonally by means of a diamond wheel saw and the extent of metal adherence, penetration and reaction was measured.

The tested materials were:

- Two high alumina castables, denoted as material **E** and **F**, also used for investigations in the previous paper.
- A silica-enriched test sample, denoted **F+S**, obtained by substituting the anti-wetting additive CaF_2 in the silica-free material (**F**) by for an equal amount on weight basis by micro-silica.
- Two phosphate-bonded materials marked **G** and **H**. The first being a pressed, low-fired brick material and the latter a rammed material.

Table III shows some essential physical and chemical characteristics of the tested samples. The degree of aluminum attack in the cup-test is based on the same rating as described in the previous paper. The composition of the aluminum metal used in the cup-tests is given in Table IV. The results presented in Table III indicate that the temperature has a strong influence on the aluminum attack. An increase in pre-firing temperature clearly leads to an increase in the aluminum metal attack of the refractories. The effect of the temperature is especially predominant when the pre-firing temperature exceeds 1200 - 1300°C.

One explanation for this observed behavior may of course be that increasing pre-firing temperatures induce changes in the material microstructure. Hence, this property of the exposed samples was subjected to close examination by means of mercury intrusion measurements. The basis for the analytical method is the fact that the mercury does not wet the refractory oxides, and the intrusion into the pores can hence only be obtained by exerting an external pressure to the liquid mercury. The relationship between the applied pressure and the materials pore size can then be obtained from equation (3) given earlier in this paper. One serious drawback of this method arises from the fact that pores may be shaped as a bulb or flask with the thin neck facing the outer surface of the sample. The hydrostatic pressure determining the mercury intrusion into such pores is of course the diameter of the pore neck. Once the hydrostatic pressure is sufficient to cause liquid mercury

ry to penetrate this pore neck, the larger pore volume behind the neck will also be filled with mercury. Hence, the relatively large pore diameter in the bulk of the bulb/flask will be assumed to have the same pore diameter as the pore neck, giving an incorrect pore size measurement. However, it is believed that this error is small and does not have a significant effect on the results presented here.

Figure 3 shows one example of curves for pore size distribution in a refractory material tested in the present work. The curves are obtained from measurement on material **E**, and show the change in pore size distribution as a function of pre-firing temperature. As can be seen from the figure, increasing firing temperature results in a growth of pore dimensions. This is of course due to the coarsening process taking place in the material. During this process, small pores are eliminated through grain growth, leaving behind larger pores in the material structure. The data presented in Figure 3 is representative for most aluminosilicate materials, documented through analysis of pore size distribution in other materials not shown here. Materials with other chemical compositions and/or binding systems may (will) of course have different shapes and evolutions of the curves, but generally the same trends will be observed in most refractory materials. This is also in line with the data presented in Table III in this work. Two distinct effects can be seen to appear simultaneous in the material shown in Figure 3:

- *The pores grow larger in the material, leading to an increased average pore diameter (elimination of small pores).*
- *The volume fraction of pores with a small diameter is hence strongly diminished in the material, i.e., a larger fraction of the open pores is receptive to metal penetration.*

In Figure 4, the measured pore radius of the tested materials is shown as a function of the pre-firing temperature. The graph is based on measurements of the mean pore radius, and as can be seen from the figures, a relatively sharp increase mean pore radius is observed at temperatures between 1200°C and 1400°C. This is however only true for the aluminosilicate materials, and does not apply to the pure alumina and lime material **F**. Aluminosilicate materials will start to sinter at temperatures around 1300°C for high purity materials.

Table III. Chemical composition and physical properties of refractory materials tested against aluminum penetration on the so-called "cup-test". Temperatures in the table indicate pre-firing temperature of the refractory materials.					
Material	E	F	F+S	G	H
Al ₂ O ₃ (%)	93.0	94.0	94.0	77.0	89.0
SiO ₂ (%)	5.0	0.2	3.2	10.0	8.0
CaO (%)	1.1	5.8	5.8	0.4	0
Fe ₂ O ₃ (%)	0.1	0.1	0.1	1.5	1.0
(Na,K) ₂ O(%)	0.5	0.5	0.5	0.4	0.2
P ₂ O ₅ (%)	0	0	0	2.0	1.6
BaO (%)	0	0	0	4.5	0
CaF ₂ (%)	0	3.0	0	0	0
Density (g/cm ³)*	2.95	2.58	2.58	3.01	3.07
Open porosity (%)*	18.5	30.5	ca. 30	16.1	11.2
Gas permeab. (nP)*	-0	-0	-0	-0	-0
Mean pore radius					
800°C (µm)	0.142	0.153	0.095	3.350	0.068
1000°C (µm)	1.189	1.189	-	-	0.141
1200°C (µm)	1.679	1.679	0.430	-	0.474
1400°C (µm)	4.732	1.679	19.500	18.836	18.836
Median pore radius					
800°C (µm)	0.096	0.159	-	0.957	0.070
1000°C (µm)	0.592	1.037	-	-	0.144
1200°C (µm)	1.084	1.643	-	-	0.486
1400°C (µm)	4.398	1.700	-	25.040	18.500
Test duration (h)**	72	72	72	72	72
Aluminum resist.**					
800°C (#)	0	0	0	0	0
1000°C (#)	0	0	-	-	0
1200°C (#)	3	1	1	-	1
1400°C (#)	5	1	4	1	6

* After firing at 800°C.

** Exposure temperature is 800°C, and the temperatures refer to firing temperature prior to exposure.

Table IV. Chemical composition of aluminum metal used in the cup-tests.						
Element	Al	Fe	Si	Cu	Mn	Mg
Composition (%)	ca. 97	0.35	0.22	0.17	0.95	1.23

Increasing content of alkalis and other liquid phase promoters will lower the on-set temperature for the sintering process in addition to work as sintering accelerators (liquid phase sintering). The sintering process will severely change the microstructure, i.e. amongst others the pore size distribution of the material. This will lead to a change in the materials ability to withstand aluminum intrusion, as have been theoretically deduced earlier in this

paper and presented graphically in Figure 2. For pure alumina and lime materials this process does not take place until the temperature is at least 1400 – 1450°C. This phenomena explains why the sample **F** does not seem to alter its pore structure during pre-firing at the selected temperatures. However, by adding small amounts of silica to this material, sample **F+S**, we observe that a tremendous change in pore diameter is obtained when the pre-firing temperature

exceeds 1200°C. The same trends may be observed by plotting median pore radius [2] versus temperature (see Tab. III).

So far we have been able to show that due to sintering in the materials, the pore size distribution of the materials change, and increasing firing temperatures leads to higher amounts of large pores in the materials. However, the aim of this work was to elaborate a possible relationship between material pore size and aluminum resistance. Figure 5 shows the obtained correlation between aluminum resistance and pore size distribution of the tested materials. Again the graphs are given as functions of mean and median pore size.

Al₂O₃ – SiO₂ castables

The data in Figure 5 on the alumino-silicate based castables, samples E and F+S, show that when the mean* (and median) pore radius exceeds approx. 0.5 to 1.0 μm, the aluminum resistance drops considerably. This is noticed as a sharp increase in the Aluminum Resistance Index number, as higher numbers reflects increasingly severe penetration and reaction with metal. X-ray analysis of the reaction zones clearly points to the formation of corundum and an Al-Si alloy in the reacted material, in line with previous results [1]. No data with respect to median pore radius of material F+S is available.

In the “pure” alumina and lime castable, sample F, the mean (and median) pore radius never exceeds about 1.7 μm. Although some adherence of aluminum metal to the refractory sample was detected after pre-firing to 1400°C, no metal penetration into the refractory sample was detected. Reaction between the refractory and the molten aluminum was neither detected, and hence the formation of the inter-metallic species Al₂Ca was not observed. The formation of this inter-metallic compound was expected from thermodynamics and laboratory investigations, and it is believed that its lack of appearance is due to kinetic hindrance under the present test conditions.

* Mean pore radius is the calculated diameter from the total volume and the total pore surface area, obtained from the quantity of pressure-infiltrated mercury.

Median pore radius is the diameter representing 50% of the quantity of pressure-infiltrated mercury, by volume.

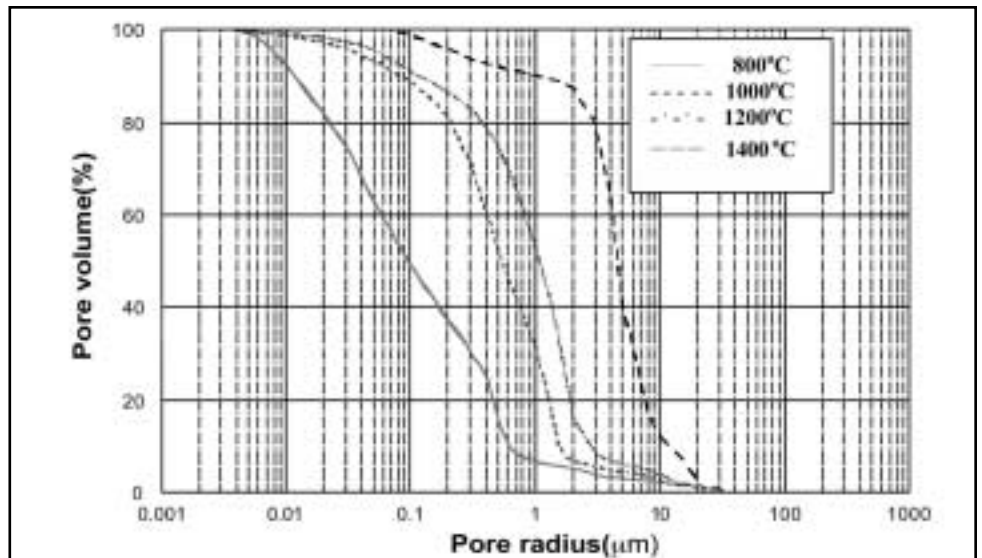


Figure 3. Measured pore size distribution of refractory material E after pre-firing prior to aluminum resistance testing in the so-called “cup-test”.

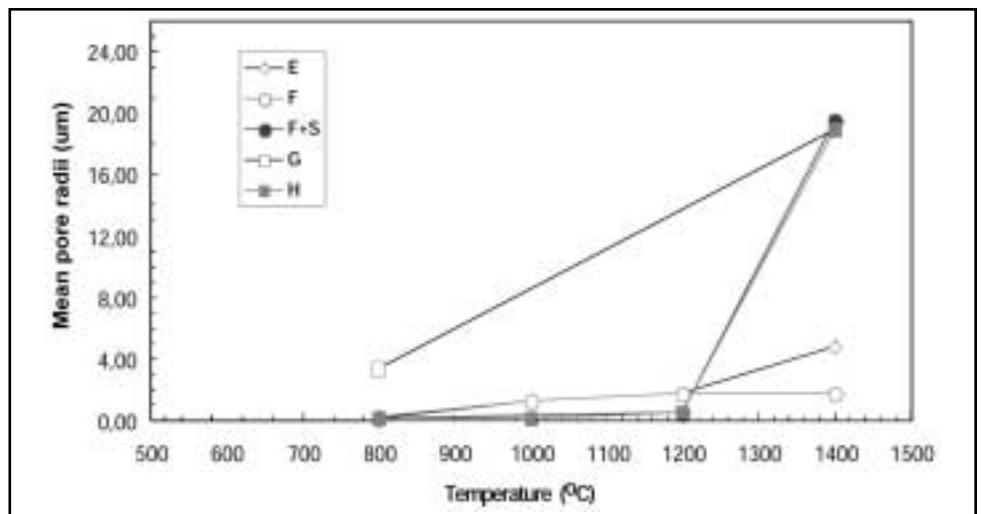


Figure 4. Measured change in mean pore diameter as a function of temperature in refractory materials investigated in this work. The definition of mean pore diameter is given elsewhere in the text.

Al₂O₃ – SiO₂ phosphate bonded materials

Figure 5 shows that material H behaves very much as expected for phosphate bonded materials [19]. At low pre-firing temperatures the mean pore radius is kept small. By increasing the pre-firing temperature from 1200 to 1400°C, the mean pore radius increases almost two orders of magnitude, and the increased pore radius is reflected in the sharp increase in aluminum resistance index number. The photographs presented in Figure 6 show the increased aluminum attack on materials H as the pre-firing temperature is increased.

The same trend is, however, not observed with respect to material G. Even though

the pore radius increases severely after pre-firing at 1400°C, this increase is not reflected in a similar increase in the aluminum resistance index number. This may be due to changes in mineralogical composition of the material during firing, or due to addition of some sort of anti-wetting additives. However, more investigations are necessary to clarify the behavior of this material.

Influence of pore size on aluminum resistance

From the results presented in Figure 5, it seems that there is a limiting mean pore radius, below which aluminum penetration and attack on alumino-silicate refractories does not take place. According to the figure, a best “guestimate” for the maximum

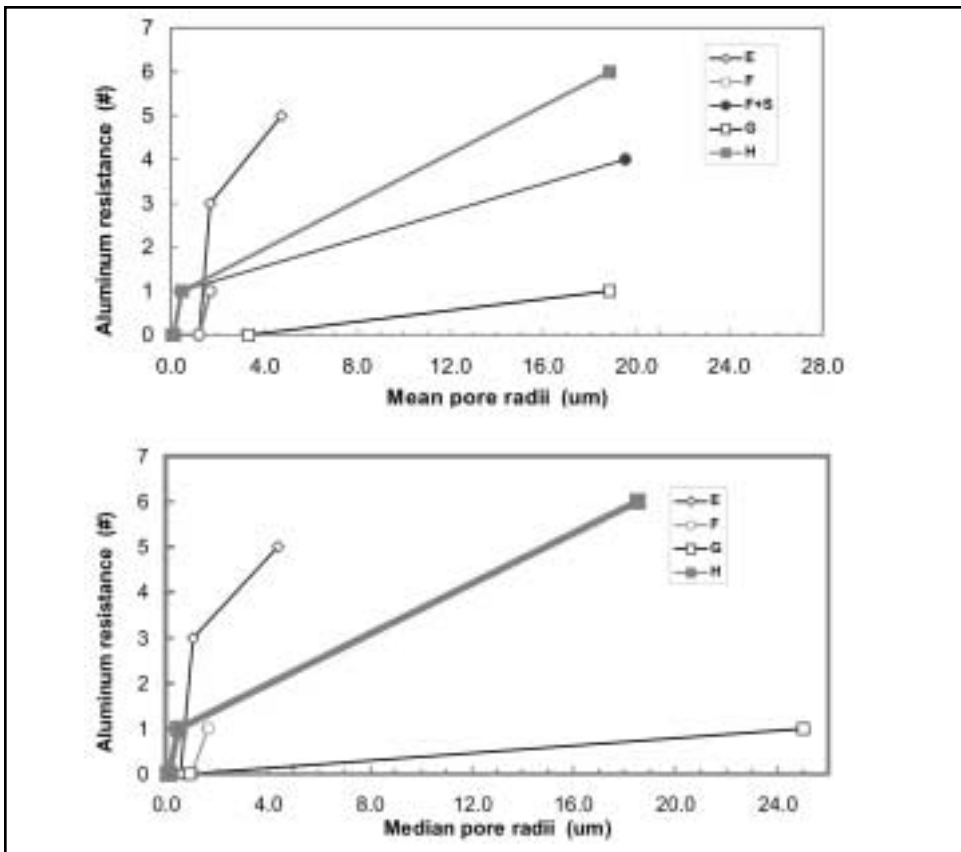


Figure 5. Observed relationship between aluminum resistance index number and mean (top) as well as median (bottom) pore radius of the investigated refractory materials. The description of mean and median pore diameter is given elsewhere in the text.

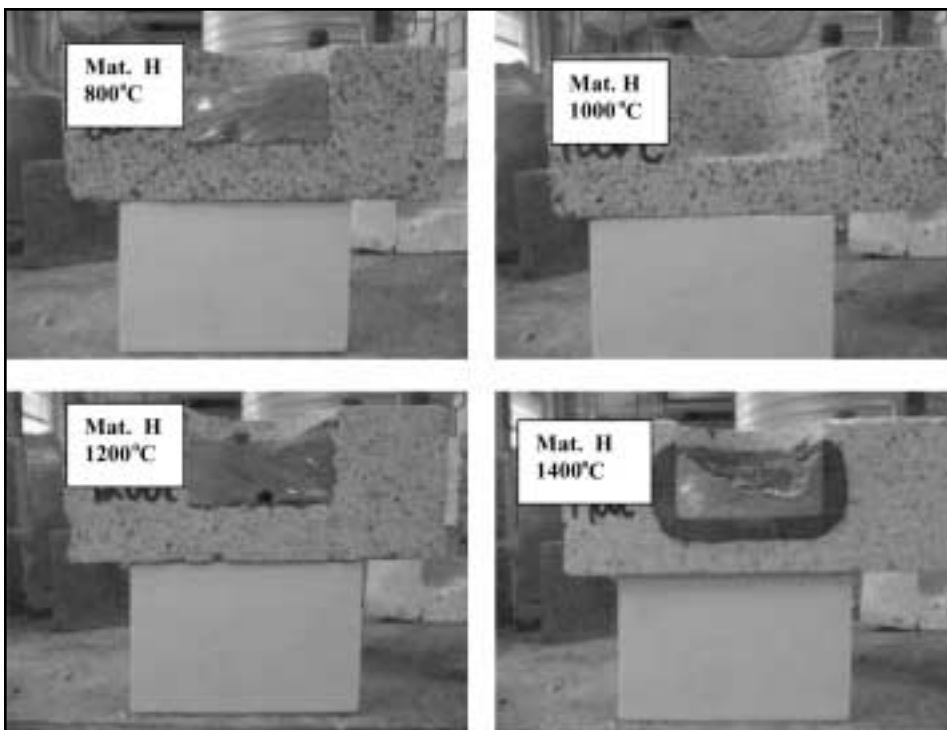


Figure 6. Photographs showing the test samples of material H after exposure to molten aluminum at 800°C. Pre-firing temperatures of samples are given in the pictures.

pore radius is between 0.5 and 1.0 µm, meaning that for pores with a diameter exceeding 1.0 – 2.0 µm aluminum penetration and subsequent attack on silica in the refractories will take place. This is in good agreement with earlier predictions [18]. With respect to the performed calculations presented in Figure 2, the predicted limiting pore radius from Figure 5 seems a little bit higher than the results from the theoretical calculations. This is believed to be due to uncertainties in the input data as well as than effect of the simplifications applied to the calculations.

CONCLUSIONS

The theoretical evaluations presented in this paper were focused on the influence of refractory material microstructure, expressed as pore size distribution, on aluminum resistance. With respect to aluminum penetration into the open pore structure of the bricks, the calculations performed in this work show that: the intrusion is mainly influenced by:

- The pore size of the refractory material is the most important parameter governing the meal intrusion into the refractory open pore structure.
- Another significant parameter, yet less influential, is the wetting angle, also strongly influenced by the furnace temperature.
- Other physical parameters like metal viscosity and metal surface energy does not significantly affect the intrusion depths. Small amounts (≤ 5 wt%) of alloying elements does not have a severe effect on the surface energy nor the viscosity of the metal*.

The performed laboratory investigations were aimed at disclosing possible relationships between the refractory microstructure and the aluminum resistance. By means of mercury intrusion method, the pore size distribution of the refractories was characterized, and the aluminum resistance of the investigated alumino-silicate materials was

*Hence, enrichment of components like Si formed in the reaction between aluminum and silica will not severely change physical parameters of the molten metal phase. This is contradictory to the effect of dissolution of refractory oxides in oxide based slag attack on refractories [17,24], where the viscosity and surface energy of the altered slag composition may vary substantially from the "original" slag phase.

determined by measuring the adherence and penetration/reaction of metal into the samples. The investigations disclosed that:

- Increasing the pre-firing temperature leads to development of larger pores on the expense of small pores, due to coarsening. A higher content of silica in the refractories will promote this change, due to the action of liquid phase sintering.
- For refractory castables containing alumino-silicates there is a clear tendency for reduced aluminum resistance with increasing pore diameter. The investigations indicate that when the pore diameter exceeds 1 – 2 μm , aluminum penetration and subsequent reactions between metal and refractories occur. This “limiting” pore size for aluminum penetration is in good agreement with earlier literature data [18,20].
- For refractory castables based on pure alumina and lime, small pore diameters (<2 μm) is maintained even at pre-firing temperatures as high as 1400°C. This is due to the lack of liquid phase in the material to assist the sintering at these temperatures. Accordingly, no metal penetration into the materials can be detected.
- For phosphate bonded refractories based on alumino-silicates, the investigations gave diverging results. One of the studied materials followed the same development in pore size distribution as alumino-silicate castables, whereas in the other material increasing pore size had seemingly no effect on aluminum resistance.

Further investigations to study the influence of other microstructure parameters are necessary to obtain a complete understanding of the reaction between molten aluminum metal and alumino-silicate refractories. However, as a temporary conclusion, it may be stated that alumino-silicate refractories can be made to resist aluminum attack if the pore radius of the material is kept below 0.5 – 1.0 μm .

ACKNOWLEDGEMENTS

Thanks are due to Hydro Aluminum AS for financial support and allowing the publication of these results. The help of Borgestad Fabrikker AS in the preparations and supply of some of the investigated materials, is also gratefully acknowledged. Valuable comments and discussions with

Prof. Tor Grande of The Norwegian Technical University (Trondheim, Norway) is greatly appreciated.

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hydrates that create bonds between anhydrous grains in the system. The hydration of calcium aluminate cement is complex, but can be considered an exothermic process and heat evolution is a result. By measuring this increase in temperature under adiabatic conditions, setting time can be measured.

Calcium aluminate cement shows two exothermic temperature rises. The first occurs when the cement and water come into contact with each other. The rapid dissolution of cement to form a solution saturated in lime and alumina causes the first heat rise. The cement continues to dissolve at a much-reduced rate; ultimately, a massive precipitation of hydrates occurs with simultaneous dissolution of remaining anhydrous cement.

Test procedure and Equipment

Rapid and easy methods for measuring an exothermic profile have been developed. A thermocouple probe consisting of a platinum rhodium thermocouple can be hooked directly to a multichannel data logger. By utilizing a large fresh sample consisting of approximately 100 pounds of castable, the thermocouple is embedded in the center of the castable. The container utilized is a 5 gallon plastic bucket. This bucket is, in turn, placed in a large 20 gallon cooler. Measurement of temperature is automatically recorded on the data logger and stored in the memory of a computer. The information received can be used to plot a time/temperature profile of the exothermic behavior of the castable.

Results

Many types of castable have been measured for exothermic profile (EP). A low cement castable based on 7.5% cement is included as well as a cement rich/alumino-silicate aggregate system.

The low cement castable with complex additive system exhibits two exothermic profiles one at 60 minutes and the other 120 minutes. The slight rise at 60 minutes should not be dismissed as this may well correlate to the end of working time. Depending on the formulation the rise may proceed or follow the stiffening of the castable. Also, this type of profile is present in certain types of 80% CAC. The first rise correlates to gross flocculation of the fine high surface area alumina contained in these cements. An interesting point is that the dwell between the two temperature rises can be seriously affected by the for-

mulation. The first rise is more likely a false set and may lead to a false impression that physical strength exists.

The cement/alumino-silicate castable profile exhibits a higher exothermic profile owing to the increase in cement content – 30% versus 7.5% in a low cement castable.

Summary

This paper attempts to look at alternative methods to establish criteria for the consistency, flow decay, and setting time of calcium aluminate based castables. By no means does this paper serve to impose such methods as standards, but to stimulate interest and ideas to generate future standards to help improve the subjectivity often associated with present procedures.

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