The Thermal Insulation of Aluminium Electrolytic Cells

P. Bonadia, J.B. Gallo and V.C. Pandolfelli

The working life of aluminium electrolytic cells are markedly affected by their refractory lining. For that reason, smelters all around the world have teams of specialists who are in charge of designing and selecting the proper materials for pot lining, aiming at longer campaigns. This, however, is not a straightforward task, since the operational practices in the pot room are becoming increasingly more aggressive in order to attain higher productivity. The thermal insulation, which is part of the cathode-bottom lining, plays a major role in the cell´s heat balance, thus affecting its performance. There are a number of insulating materials available in the market, however, selecting the right one for a given pot design is not as simple as it may seem. The most suitable insulation is the one that places the critical isothermal lines (800 – 850 °C) in the right level of the lining and is able to withstand the load of the cathode blocks and barrier bricks without creeping. Some laboratory tests, such as the refractoriness under load and the thermal conductivity, have proved to be of great help to assess the quality and the performance of materials from different sources before moving to high cost industrial trials.

1 Introduction

Thermal insulation lining materials play an important role in aluminium electrolysis cells, as they may affect the operational life of all cathode components [1]. The literature in this topic [1–8] suggests that different properties can be attained from the insulating materials available in the market, especially regarding chemical resistance and thermo-mechanical behaviour. Additionally, a broad range of properties has been reported for the same type of material supplied from different manufacturers [4, 9]. This variation stresses the need for laboratorial tests as a basis for a more accurate cost-benefit analysis before moving to the industrial application.

The Hall-Heroult process, developed over a century ago, is still the most important industrial method used worldwide to produce primary aluminium. The greatest improvement achieved since its inception relates to the cell amperage, which increased from 5 kA to 300 kA [10], and will likely reach 500 kA (with a production of more than 3800 kg/pot/d) in the near future [11]. Increasing the amperage to attain higher aluminium production requires, among other things, the careful selection of materials and a suitable heat balance to keep the cells operating efficiently and to avoid shortening their working lives [12].

Sørlie and *Øye* [13], *Øye* and *Welch* [14] and *Siljan* [15] quoted that significant advances have been observed in terms of materials knowledge and pot design since the end of the 70’s. This progress comprises the use of graphitic and graphitized blocks, point feeder system, more acid electrolytes and compensation of magnetic fields. In spite of these improvements, the cathode life is still influenced by the chemical attack in its lining, including the refractories and the insulation.

A typical aluminium cell presenting the average percental heat losses values is illustrated in Fig. 1 [16]. The chemical attack and erosion, to which the sidelining materials are subjected, when in contact with liquid aluminium and bath, is extremely severe. Therefore, the best way to protect them is through the in-situ formation of a protective frozen ledge, which is achieved by controlling the heat loss through the side and end walls of the cell. In contrast, the lining at the bottom of the cell is considerably thicker, consisting

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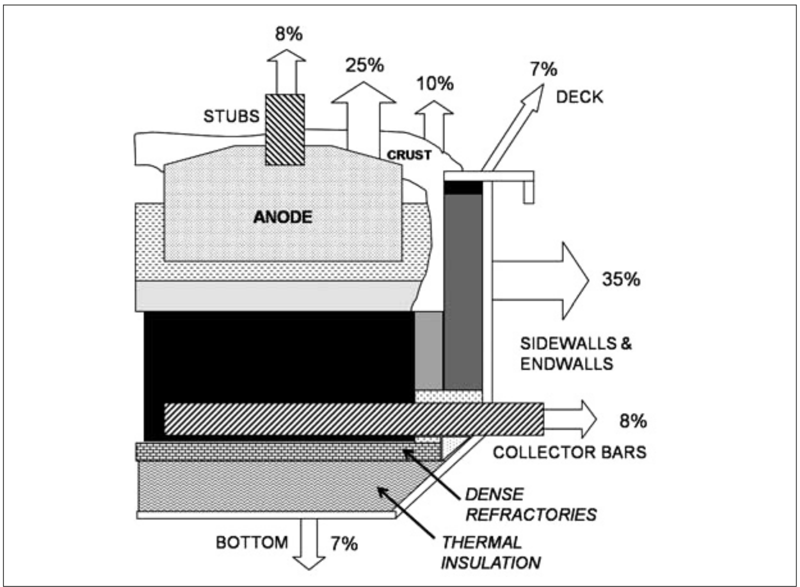

Fig. 1 **Average heat losses from an aluminium cell [16]**

of cathode blocks and additional layers of dense refractory and thermal insulating materials, which accounts for less than 10 % of the total heat losses.

Unsuitable bottom insulation can lead to increasing operating voltage due to bottom ledge formation and heaving of the carbon blocks [3, 4, 16]. Conversely, excessive insulation can hasten the rate of bath incursion through the cathode, causing rapid deterioration of the underlying insulating materials [12, 17]. In both cases, higher bottom steel shell temperatures are detected after a certain operational time and the energy consumption increases, ultimately shortening the cell's life.

For optimal thermal balance, the cathode insulation is usually designed with the 800 – 850 °C isotherms placed inside the dense upper brick barrier layer. The idea is to certify that any infiltrating bath freezes before reaching the porous insulating materials, which normally have little resistance to fluoride melts and gases. In order to attain this objective, dense refractories must also be carefully selected in terms of chemical resistance and thermal conductivity.

However, not only chemical attack but also thermal creep can cause the insulation to collapse. *Tabereaux* [5] and *Siljan* [2] suggested that, wherever possible, insulating materials should not be subjected to temperatures exceeding 700 °C in order to minimize their tendency to creep under load.

It should be noted that, as the insulation densifies by either chemical reaction or creep, its thermal conductivity increases [18], impairing the cathode's original heat balance and leading to reduced energy effi-

Tab. 1 **Main properties of thermal insulating materials for pot lining [2]**

Parameter	Diatomite	Vermiculite	Perlite	Calcium silicate
Chemical composition [mass-%]				
Al_2O_3	8 – 9	10	10 – 15	< 1
SiO_2	73 – 77	47 – 59	65 – 75	48
MgO	< 1	11 – 18	1 – 3	< 1
CaO	< 1	1 – 3	1 – 5	45
Mechanical properties				
Cold crushing strength [MPa]	1 – 15	1 – 9	1 – 3	1 – 2
Termal conductivity at 600°C [W/m · K]	0,2 – 0.4	0,2 – 0,4	0,2 – 0,3	approx. 0,1
Thermal expansion 20 – 900 °C [%]	-0,2 – 0,2	-0,2 – 0,9	0,4 – 0,5	-0,2 – 0,0
Creep at 900 °C / 48 h and 0,05 MPa	up to 6 %	up to 10 %	not determined	< 1 %
Chemical resistance				
Fluoride gas	poor / moderate*	poor / moderate*	poor	poor
Aluminium	good	good / moderate*	good	good

*) The resistance towards fluoride gases increases with the density, the opposite trend is observed for aluminium attack

ciency. *Siljan* [2] states that the ideal insulating material should withstand high temperatures (> 800 °C), high loads (0,03 – 0,05 MPa) and attack from fluoride-containing vapours without densifying.

2 Types of insulation

Minerals such as vermiculite, calcium silicate, diatomite and perlite are the typical raw materials used for producing bottom insulating bricks or slabs [2], which are characterized by their high porosity (> 70 vol.-%) and low thermal conductivity (0,1 – 0,4 W/m·K). Siljan [2] and Tabereaux [5] summarized the main properties of these materials, as shown in Tab. 1. The wide range of variation observed for the thermo-mechanical properties (cold crushing strength and creep deformation) within the same insulating class is likely because pieces of different densities were included in the analysis.

The unusual good resistance to aluminium attack is attributed to the oxidation of the metal as it penetrates into the insulating material and reacts with the air entrapped in its porosity, thus forming an alumina layer that hinders further penetration.

From Tab. 1 it can be observed that materials with quite distinct properties are available for pot insulation. The choice of one or other depends on a number of factors, including the proper thermal conductivity to correctly place the isotherms in a given cathode design, the need for less creep, higher chemical resistance, local availability, cost, etc.

2.1 Moler

Moler bricks are produced from diatomaceous clays and are commonly used for pot insulation due to their low thermal conductivity, suitable strength at cathode operating temperatures and non-wetting behavior when in contact with aluminium [5]. The bricks are formed by extrusion and then fired to temperatures close to 1000 °C [3]. *Weibel et al.* [3] reported that this type of material provides a more constant insulation over time, presenting a relatively low degree of compression even after approximately 2000 d of operation in actual cells.

2.2 Diatomite

Diatomite is a silica rich mineral comprising numerous microscopic fossilized skeletons of aquatic plants, which are generated of hollow thin walled cells containing entrapped air [5]. By processing and forming this raw material into bricks or slabs, insulating materials of very low thermal conductivity are obtained. The low resistance to cryolitic bath, however, has limited the use of this insulation type in the primary aluminium industry [4, 5].

2.3 Vermiculite

According to *Santos* [19], the range of the chemical composition of vermiculites is not entirely known. However, an analysis of vermiculites from a South African, an American and 15 Brazilian mines indicated that the most important components are SiO_2 (23 – 44 %), Al_2O_3 (11 – 29 %), Fe_2O_3 (0,05 – 21 %), MgO (7 – 28 %), K_2O (0,07 – 7 %) and H_2O (3 – 30 %). When it is heated rapidly to temperatures in the 800 – 1100 °C range (in vertical or rotary kilns), vermiculite expands from 6 to 20 times its original volume due to the release of the water vapour [4, 5, 12, 19]. With the aid of a refractory silicate binder [1], the expanded lightweight granules are then pressed into bricks or slabs of varying densities for thermal insulation purposes. Sodium or potassium silicates are commonly used as binders, the former having a lower cost, though being less refractory than the latter one. Depending on the type of binder used, increased concentrations of CaO, Na_2O or K_2O can be detected in the material's chemical analysis [4].

In order to attain superior thermo-mechanical behaviour and cryolite resistance, some vermiculite producers have a special class of slabs with clay additions. Nevertheless, this procedure increases the material's density and thermal conductivity, usually limiting its application to cathodes that have enough room for two additional layers of less conductive materials in order to avoid excessive heat losses through the bottom of the shell.

Expanded vermiculite has a strong tendency to absorb water from the environment, a characteristic that makes it an interesting material for many uses [19, 20] (e.g. in agriculture). However, this same feature may alter its thermo-mechanical properties [8], and aluminium manufacturers should be aware of this aspect when using this sort of insulation.

2.4 Perlite

As described by *Tabereaux* [4], perlite is a naturally occurring siliceous volcanic rock containing 2 – 5 % water. Similar to vermiculite, it expands 4 to 20 times its original volume when rapidly heated to a specific condition within its softening range, above 870 °C. This generates countless tiny bubbles in the heat softened glassy particles, which accounts for its low thermal conductivity.

2.5 Calcium silicate

Calcium silicate slabs are produced from a filter-pressed mixture of silica and lime by an autoclaving process, whereby a microstructure containing mainly xonotlite needles is attained [1, 21]. Mechanical strength is developed at low temperatures through the formation of CS (C = CaO and S = SiO_2) hy-

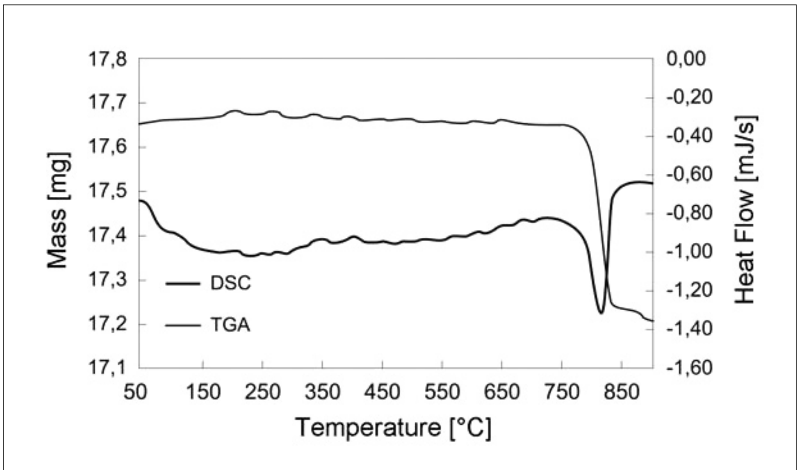

Fig. 2 **DSC/TGA for xonotlite; the mass loss and the endothermic peak around 815 °C are related to the hydroxyls decomposition and the simultaneous recrystallization to the low temperature wollastonite polymorph [22]**

drates, as described by *Krasselt* et al. [21]:

- dissociation of $Ca(OH)_2$ and SiO_2 to Ca^{2+}, OH^{1-} and formation of $(H_3SiO_4)^{1-}$ or $(H_2SiO_4)^{2-}$
- chemical reaction of all components and generation of $C_xS_yH_z$ complexes near the SiO_2 environment
- crystal growth of the complexes and transition from high CaO content to complexes with lower CaO content
- depending on the temperature, pressure and CaO/SiO_2 (C/S) ratio of the starting mixture, tobermorite ($5\ CaO \cdot 6\ SiO_2 \cdot 5{,}5\ H_2O$ with approximately 12 % H_2O) and/or xonotlite ($6\ CaO \cdot 6\ SiO_2 \cdot H_2O$, ~3 % H_2O) can be obtained.

According to *Shaw et al.* [22], tobermorite and xonotlite dehydrate to form wollastonite ($CaO \cdot SiO_2$), the anhydrous form of calcium silicate, in the temperature range of 835 – 855 °C and 780 – 835 °C (Fig. 2), respectively. Such phase transformations can cause a more pronounced shrinkage around the dehydration temperatures, as observed by *Tabereaux* [7], *Kaplan* [23], *Bonadia* [8] and colleagues. This aspect will be discussed in a latter section in this paper.

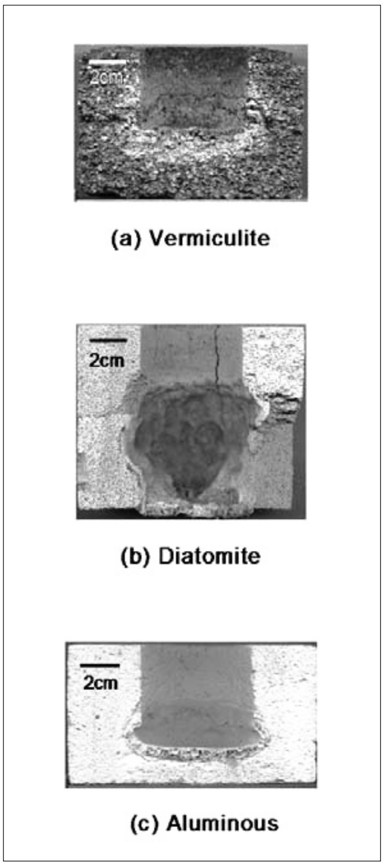

Fig. 3 **Bath attack on vermiculite, diatomite and aluminous insulating materials [26]**

Tab. 2 **Typical porosity and permeability values for a barrier brick and insulating materials [8, 24, 26]**

Parameter	Barrier brick	Vermiculite	Calcium silicate	Aluminous	Diatomite
Density [kg/m³]	2670	430	230	840	450
Porosity [%]	16,3[1]	73[2]	92[2]	75[2]	80[2]
k_1 [10^{-12} m²]	0,14	15	0,03	3,6	---
k_2 [10^{-9} m]	4,9	7000	20	17 000	---

[1]Apparent porosity, [2]Total porosity, [3]Permeability measured according to the methodology described by Innocentini and Pandolfelli [25]

2.6 Aluminous insulating bricks

Although less usual, fired aluminous insulating bricks can also be used for pot lining. They are produced based on high Al_2O_3 clays and may, in some instances, be added of pure calcined alumina to improve its chemical purity and high temperature properties. The production process involves the steps of blending the raw materials, forming and sintering with the aid of additives that burn out during firing (e.g. saw dust) to generate a high degree of porosity.

The sintering process physically binds the particles together, considerably enhancing the material's thermal stability and thermomechanical properties. However, higher density and thermal conductivity values are attained [23], which reduces the insulating power of the material.

3 Chemical properties

Thermal insulating materials inherently present low resistance to cryolite attack, mainly because of their high porosity and permeability, which cannot efficiently avoid bath penetration. Once reacted they densify by a twofold effect:

- their pores are filled with bath and
- they lose cohesion, thereby compressing under the load of the upper lining materials.

This is the reason why insulating slabs always have to be protected by barrier bricks, no matter whether they are placed at the bottom or at the lower side walls of the cathode. Tab. 2 compares the density, porosity and permeability levels of a typical alumino-silicate dense brick with those of insulating pieces [8, 24].

Although the calcium silicate presented in Tab. 2 possesses a relatively low permeability when compared to the other materials, its resistance to cryolite is considered to be very poor [2, 4] (Tab. 1). This feature might be attributed to its higher porosity (92 %) and, more likely, to its chemical composition, leading to the formation of a low melting point silicate glass [4].

The electrolytic bath that may attack the insulating materials is most likely a mixture of cryolite (Na_3AlF_6) and sodium fluoride (NaF), i.e. a high ratio bath ($NaF / AlF_3 > 1{,}5$ by weight), as shown by *Lossius* and *Øye* [27] after the autopsy of 16 industrial cells.

The traditional cup test can be used to rank the insulating materials according to their cryolite resistance, although a quantitative result is not always possible to be attained. In fact, in this test the material undergoes to a more aggressive condition than the actual one, namely because the testing temperature has to be at least above that of the $NaF\text{-}Na_3AlF_6$ eutectic point (~ 890 °C), otherwise the bath would not melt and attack the specimen. Nevertheless, in actual cathodes, the insulating layer rarely faces temperatures above 850 °C in its hottest interface. Additionally, the direct contact of a NaF-rich bath with the insulating slabs is quite an unusual situation, since, in practice, it is expected that the corrosive agent comprises a combination of fluoride gases and only minor amounts of bath, which are likely to reach the lower layers of the lining only after the barrier bricks have been severely attacked.

Siljan [2] reported results of fluoride gas attack on insulating materials (Tab. 1), showing that vermiculite and diatomite based materials attained better qualitative results

Tab. 3 **Pore structure and thermal conductivity of calcium silicate, vermiculite and alumina based insulating materials [8]**

Parameter	Calcium silicate	Vermiculite	Aluminous
Apparent density [kg/m³]	230	430	840
Total porosity [%]	92	73	75
Mean pore diameter [µm]	0,3	1,1	---
80 % pores in range [µm]	0,1 – 0,4	0,2 – 13	---
Intruded Hg Vol. [cm³/g]	3,3	1,1	---
Thermal conductivity at 600 °C [W/m · K]	0,14	0,26	0,31

when compared to perlite and calcium silicate.

Tabereaux [4] carried out cup tests in a series of thermal insulating materials under different experimental conditions. In general, it was observed that vermiculite and perlite presented reasonably good results, whereas calcium silicate and diatomite were completely corroded by cryolite. It is important to stress, however, that dissimilar performances were observed for vermiculite and diatomite depending on the material's producer. For the latter, it can be inferred that one of the samples, which performed well under cryolite attack contained moler (an admixture of diatomite and clay), a material with known good bath resistance. The author also pointed out that the use of a NaF-rich bath enhanced the extension of the chemical attack. *Bonadia* et al. [26] obtained similar results in cup tests performed on the vermiculite- and diatomite-based materials presented in Tab. 2 (Fig. 3). The latter was completely dissolved by the high ratio bath (eutectic mixture of NaF and Na_3AlF_6) at 910 °C, whereas the former still kept its original shape, though being soaked by the corrosive agent. An aluminous material (73 % Al_2O_3 - Table 2) was also included in the analysis and, according to Fig. 3, attained the best results, being only slightly attacked by the bath.

From the physical characteristics presented in Tab. 2, it can be noted that the aluminous material possesses the highest density among the tested specimens, a fact that may partially explain its high cryolite resistance.

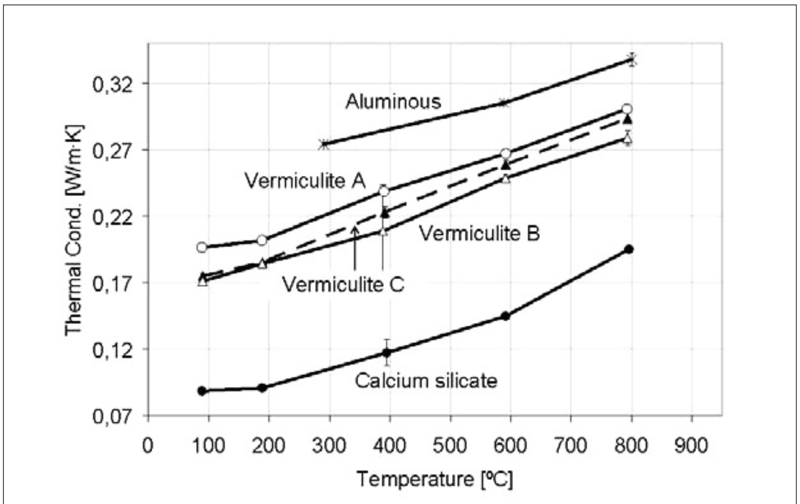

Fig. 4 **Thermal conductivity of thermal insulating materials [31]**

In a modified version of the cup test, *Johansson* [6] attempted to quantitatively demonstrate that the cryolite resistance increases with the insulating density, regardless of its chemical nature. The present authors, however, believe that a balance between density and chemical composition should be considered if a cryolite resistant insulation is aimed.

Whenever materials of low chemical resistance have to be used in the cathode in order to take advantage of one of its good properties (like the low thermal conductivity of the calcium silicate), they are generally placed in the lowermost insulation layers. It is usual to place them underneath one or two layers of vermiculite or perlite, which would react less extensively with the bath components.

Some cathode designs use the so-called vapour steel barriers on top of the insulating slabs in order to protect them from gaseous species and molten electrolyte. *Allaire* [28] questioned the effectiveness of such steel plates, claiming that they would rapidly oxidize under use, thus offering no resistance to sodium vapour diffusion. In this analysis it was assumed that a low sodium vapour pressure in the cathode, as a result of a low ratio bath (NaF / AlF_3 = 1,2 by weight), would lead to a relatively high oxygen partial pressure and speed up the oxidation of the steel sheets. Nevertheless, this theory is in disagreement with the work of *Lossius* and *Øye* [27], who demonstrated that the bath which penetrates through the lining materials is, in fact, a high ratio one (NaF / AlF_3 > 1,5 by weight). Therefore, it is reasonable to believe that the steel barrier would keep its integrity during a significant time of cell operation and cope with its function, unless there is a molten aluminium infiltration through cracks and openings in the lining materials, readily dissolving it [29].

It is important to notice, however, that the vapour barrier approach may not be necessary if a proper heat balance is coupled with efficient barrier bricks. These bricks are able to form a protective glassy phase on their interface with the penetrating bath, thus hindering cryolite and gas diffusion further down in the cathode.

4 Physical properties

The most important physical properties for insulating materials are the thermal conductivity, creep resistance and refractoriness under load. The first one is largely responsible for setting the position of the isotherms in the cathode and defining the heat flux through the shell bottom, whereas the two latter ones show how easily the material deforms under the action of load and temperature as a function of time, thus highlighting the long term behaviour of the material in the pot.

4.1 Thermal conductivity

The thermal conductivity fundamentals are well described in the literature [30], so only the most relevant topics are briefly presented in this section.

In dielectric solids, the heat is conducted mainly through phonons and photons, and the predominance of one of these mechanisms is largely dependent on the temperature. Phonon conductivity may be considered "the propagation of anharmonic elastic waves through a continuum or the interaction between quanta of thermal energy called phonons" [30]. In a crystalline solid, the atoms vibrate around their equilibrium positions and the amplitude of such vibrations increases with temperature. Due to chemical bonds, the vibration of adjacent atoms are not independent, leading to the generation of elastic waves that propagate throughout the solid and are responsible for the heat transfer.

As the temperature rises, the number of thermally activated phonons increases, as does the frequency of phonon-phonon interactions. Accordingly, the mean free path for the phonons is shortened and the thermal conductivity of the solid is decreased. Like temperature, microstructural defects such as pores and grain boundaries also promote phonon scattering.

Heat conduction by photons (quanta of electromagnetic energy) becomes important at high temperatures, since it is proportional to T^{3+x} (where T is the temperature, and experimental results have shown that $0,5 < x < 2$). Nevertheless, the amount and size of pores through which the radiation is conducted also strongly influence the efficiency of heat transfer.

Large pores are effective scattering centers at low and moderate temperatures (due to phonon scattering), but at high temperatures they turn into "highways" through which the photons can conduct heat. In contrast, if the porosity is kept constant but the size of the pores is reduced, the number of radiation shields (pores) increases and the thermal conductivity at high temperature decreases. Therefore, from a microstructural point of view, an effective thermal insulating material is composed of as many small closed pores as possible.

Tab. 4 Lining approaches assessed by *Weibel* et al. [3]

Layer (from the bottom)	Product A	Product B	Product C
Layer 1	Moler (550 kg/m³)	Moler (750 kg/m³)	CaSi (245 kg/m³)
Layer 2	Moler (550 kg/m³)	Moler (750 kg/m³)	Moler (750 kg/m³)
Layer 3	Barrier brick (2200 kg/cm³)	Barrier brick (2200 kg/cm³)	Barrier brick (2200 kg/cm³)

Calcium silicate is a material known by its low thermal conductivity (Fig. 4). Such characteristic can be explained by its unique pore structure, presenting high porosity and pore volume combined with a very low pore diameter (in the submicron range), extremely narrow pore size distribution and a small quantity of connected pores (low permeability) [8, 23]. Tab. 3 compares the pore structure of a calcium-silicate- and a vermiculite-based insulating material, along with their thermal conductivities. An aluminous insulating was also included in Tab. 3 to show that high density fired materials generally present higher thermal conductivity values (Fig. 4) due to the formation of a structure with good interparticle contacts [23].

Andersen and *Mikkelsen* [1] measured the thermal conductivity of moler, perlite, calcium silicate and vermiculite based insulating slabs by the so called hot disk method. It was shown that the thermal conductivity increases with density, independently of the insulation type, and, in some instances, it also varies with the specimen orientation, i.e., parallel or perpendicular to the moulding direction.

For the calcium silicate [1], the organic fibers were aligned perpendicularly to the forming direction, leading to a thermal conductivity 10 % higher in this same orientation at 800 °C. Higher forming pressures favour the alignment of grains and pores perpendicular to the compaction direction, thus generating anisotropic microstructures, as observed for the vermiculite samples. From the vermiculites tested, the densest one (1200 kg/m³) presented a 10 % lower thermal conductivity in the direction parallel to that of compaction in the temperature range of 20 – 800 °C. The anisotropic features of vermiculite have also been reported by *Kaplan et al.* [23], stressing that special attention should be taken during sample preparation and thermal conductivity measurement while testing and selecting materials for cathode insulation.

The thermal conductivity of the insulating material largely influences the position of the isotherms in the pot. Hence, selecting the less conductive insulation is not always the best solution. *Øye* [17] presented the case study of an over-insulated pot that had lasted for only 300 d (good pots last for 2000 to 3000 d) due to the rapid ingression of bath components, caused by positioning the freezing isotherms too low in the cathode. Moreover, *Bonadia et al.* [8] made thermal simulations in a generic cathode design showing the displacement of the high temperature isotherms by replacing one layer of the original thermal insulation with a material of lower thermal conductivity, thus leading to an unsuitable heat balance.

Certainly, the as measured thermal conductivity of insulating materials is an important property, however, one must bear in mind that during use they are simultaneously exposed to corrosive agents and compressive loads that may lead them to densification, hence modifying the thermal balance originally designed for the pot [3]. *Allaire* [18] demonstrated that the thermal conductivity of vermiculite and calcium silicate pieces may increase from 7 to 42 % after being compressed to 60 % of their original height. Additionally, the graphitization of the cathode blocks [13] and the densification of the barrier bricks [2] along the cathode working

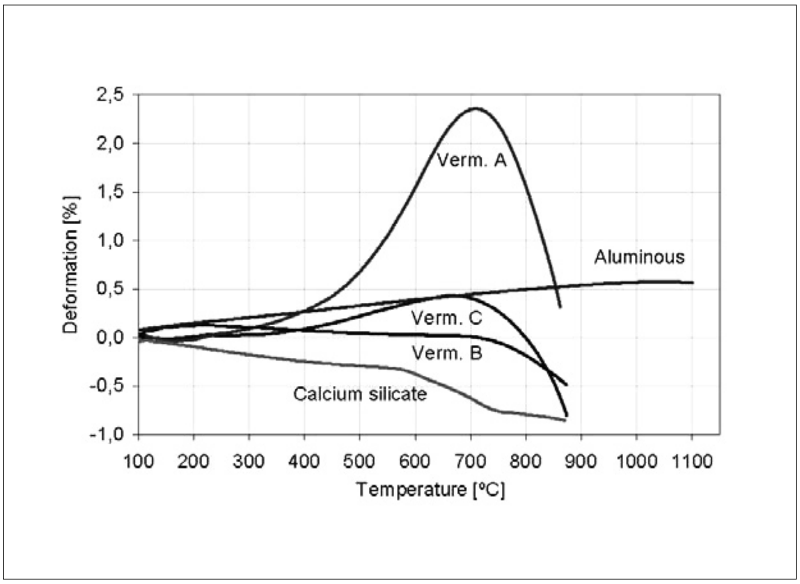

Fig. 5 **Refractoriness under load curves (0,02 MPa) for vermiculite (producers A, B and C), calcium silicate and aluminous insulating materials [31]**

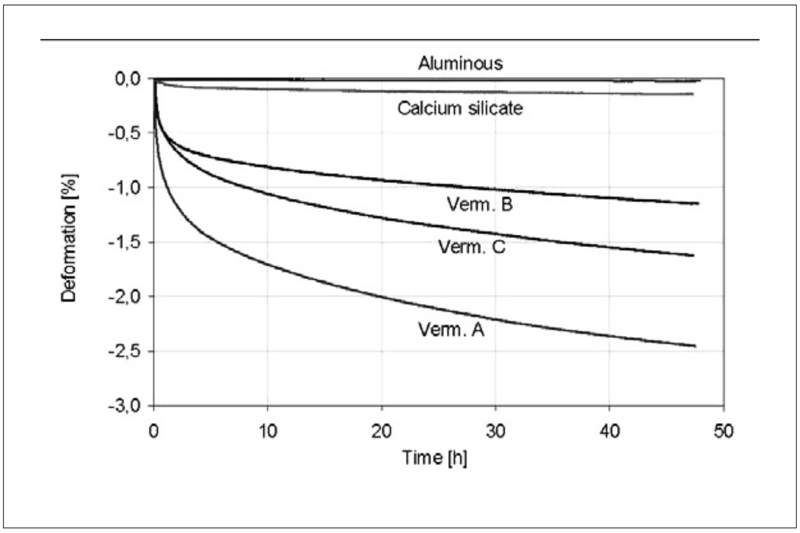

Fig. 6 **Creep curves for vermiculite (producers A, B and C), calcium silicate and aluminous insulating materials [31]**

life make the conditions even more severe for the insulation, since the temperature tends to increase throughout the whole cathode lining.

Weibel and colleagues [3] performed cathode autopsies and collected samples of the used insulating materials for thermal conductivity measurements. The recorded data were used as an input for a heat-balance software that allowed the comparison of a 2000 d old cathode with a new one based on as measured materials properties. The assessed lining approaches are described in Tab. 4. In general, approaches A and B showed a 10 to 15 % increase in heat losses, whereas the initially less conductive assembling C became 25 % less efficient in use due to the high degree of creep experienced by the lower calcium silicate layer (CaSi).

4.2 Thermo-mechanical behaviour

The thermo-mechanical properties of insulating materials were investigated by *Tabereaux* [7], *Siljan* [2], *Kaplan* [23], and *Bonadia* [8] et al. These authors showed that each type of insulation presents particular characteristics as a function of temperature, which depend not only on the mineral used for its production but also on the processing conditions and the quality control of the producer.

Kaplan and colleagues [23] reported the changes in linear dimensions for vermiculite, calcium silicate and fired insulating materials. It was clearly observed that quite distinct behaviours can be attained depending on the source of the vermiculite sample. Some specimens displayed a significant shrinkage around 200 °C, which could be attributed to the release of adsorbed water, and a high coefficient of thermal expansion up to 700 °C, which in turn might be associated with the undesirable presence of unexpanded vermiculite grains in the slab. Such grains expand when reheated, contributing to a poor thermal stability of the insulating piece and thus demonstrates the lack of quality control from the producer.

The refractoriness under load (RUL) curves with low loads (0,02 MPa) presented by Bonadia [31] agrees with the thermal expansion results reported by *Kaplan* et al. [23]. Fig. 5 shows the different profiles for three vermiculites from different producers, including the great expansion experienced by material A up to 700 °C.

Another interesting feature of the vermiculite insulating bricks is their tendency to sinter at relatively low temperatures, thus shrinking at a fast rate above 700 – 750 °C. In addition to that, the silicate binders normally used in these materials start softening around this temperature range, increasing the deformation, as shown in Fig. 5. The softening point of vermiculite containing materials at ~ 700 °C was named High Temperature Critical Point (HTCP) by *Tabereaux* and *Stewart* [7] and, whenever possible, should not be exceeded by the insulating slab during operation.

According to *Kaplan* [23], calcium silicate based materials tend to shrink as the temperature is raised. However, the shrinkage rate becomes much more pronounced from 750 – 800 °C onwards [7, 23], which can be correlated to physical transformations taking place in its microstructure, namely the dehydration of phases such as xonotlite (Fig. 2) and tobermorite to form wollastonite. This behaviour could also be observed on the RUL curves shown in Fig. 5, although the physical transformation range is shifted to lower temperatures (570 – 730 °C).

Fired materials are usually more dimensionally stable as the temperature is raised, especially if they are sintered at temperatures higher than that of testing. The fired high alumina material displayed in Fig. 5 highlights its high refractoriness when compared to other insulation types. Additionally, its creep resistance (Fig. 6) is very impressive, showing virtually no deformation under a load of 0,02 MPa at 850 ºC for 48 h. Nevertheless, it is interesting to note that non-fired materials are most of times preferred for pot lining, mainly because of their lower cost, possibility to be formed in larger and more complex shapes, simpler installation and reduced number of joints [23].

Fig. 6 draws the attention to the good performance of calcium silicate under creep when compared to vermiculites A, B and C. This means that such material may provide a time stable lining for cathodes that require higher insulation, however, it is imperative that the slabs be very well protected from molten bath and fluoride gases, as pointed out in section 3.

The creep curves (Fig. 6) also illustrate the different performances attained by vermiculites from different manufacturers, indicating that material A, for instance, would tend to collapse earlier in the pot life, thus leading to a poorer efficiency of the electrolytic cell.

5 Concluding remarks

The selection of thermal insulating materials for potlining is not a straightforward task, since a number of options with widely different performances can be found in the market. Although there are indications that certain types of materials tend to have a predictable performance under specific conditions, laboratorial tests are essential for an ultimate cost-benefit analysis, the main properties being cryolite resistance, thermal conductivity, refractoriness under load and creep resistance.

Additionally, in order to attain the best performance from the selected materials, the electrolytic cell should be designed with a suitable heat balance. The so-called critical isotherms (800 – 850 °C) should be placed at the level of the barrier bricks otherwise the ingress of bath into the cathode lining would rapidly deteriorate the as measured properties of the insulating bricks or slabs.

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