INFLUENCE OF MINERAL PURITY ON MULLITE AND ANDALUSITE BASED REFRACTORIES

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Abstract

Andalusite and mullite are well known to provide high thermo-mechanical stability, therefore enhancing key properties such as thermal shock resistance and refractoriness under load. However, the performance of the refractory products based on mullite and andalusite can be strongly affected by the amount and the type of impurities associated with the main mineral.

This paper provides a review of the works carried out in the last few years in order to correlate the performance of refractory aggregates with the amount and type of impurity present in their structure.

A broad range of commercial products was deeply characterized regarding chemical and mineralogical composition, as well as dilatometry and heating microscopy. Refractory bricks and castables were produced from each type of andalusite and mullite in a laboratory scale, in order to establish a correlation between the raw material purity and the refractory performance.

For instance, low ferric oxide and alkali/alkali-earth oxide content in certain materials yield outstanding hot properties and CO resistance for the refractories in which they are used. The processing that goes into their production, participates in the superior performance, playing an important role in the densification of the material, thus impacting key properties, such as water demand and flowability.

Thermo-mechanical properties such as refractoriness under load and creep resistance were investigated, with a particular focus on the impact of impurity level. A significant improvement of these properties was achieved by reducing the amount of certain type of impurities, in particular alkali, alkali-earth and iron-oxides.

Introduction

Most of the acid refractory materials can be described on the system Al_2O_3 – SiO_2. This system is characterized by three mineralogical phases: silica (under his three mineralogical forms), mullite and corundum, that are thermodynamically stable at high temperature with a congruent melting point at respectively 1726°C, 1853°C and 2054°C [i].

Due to the high liquidus temperature and the high temperature of the eutectic (1595°C), aluminosilicates are generally considered as having good refractory properties, although their performance can be significantly affected by impurities.

In particular alkali, alkali-earth oxides or even iron oxides can be responsible of a significant drop of the refractory behavior, to the point that the impurity content is often considered as more critical than alumina in the determination of the refractory behavior.

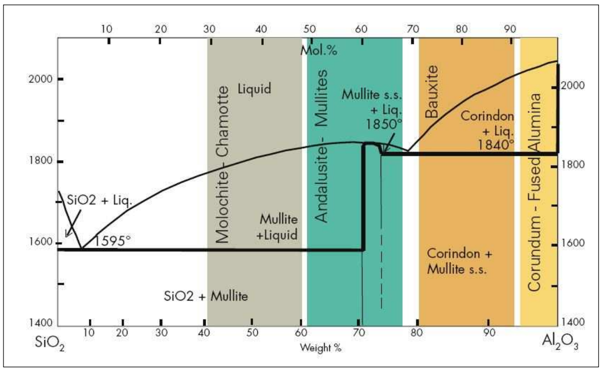

Figure 1 – phase diagram of SiO_2/Al_2O_3 system

This paper provides a review of the works carried out in the last few years with regards to the influence of aggregate and matrix purity on the performance of andalusite and mullite based refractories.

Andalusite

Among the aluminosilicate raw materials, andalusite is one of the best natural source of mullite, as it is available in sizes up to 8 mm and can be beneficiated in order to achieve a very high degree of purity.

Andalusite transforms into mullite at relative low temperature, with a minor volume expansion (+4.5%). For this reason, andalusite in refractory products can be used as fired (fired bricks) or unfired (unfired, bricks, castable, plastic mixes) therefore taking advantage of the expansion resulting from the mullitization stage.

Unlike most of the other aluminosilicates, the mullitization of andalusite does not involve any dehydration stage and therefore does not generate intrinsic porosity (See figure 2a,2b). For this reason, refractory materials based on andalusite, either raw or calcined, exhibit porosity significantly lower than bauxite or chamotte. When applied in castable, this specific behavior of andalusite results in an improved corrosion resistance as well as a lower water demand.

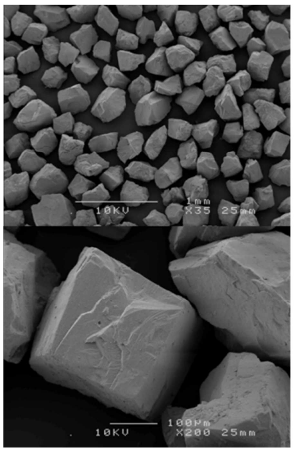

Figure 2a – Andalusite grains show no open porosity

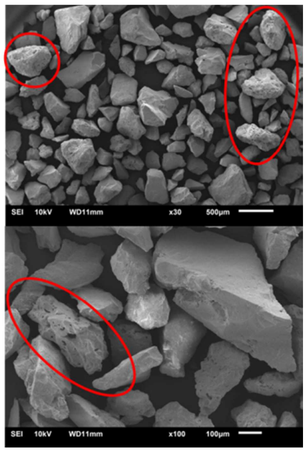

Figure 2b: Calcined minerals showing high surface porosity

Furthermore, the absence of a calcination stage in the production process, significantly reduces the carbon footprint associated to the mining and beneficiation of process of andalusite. Recent calculation established the quantity of CO_2 produced at 145kgCO_2/ton of andalusite, which is significantly lower than any other standard aggregate used in the refractory industry.

The process and the kinetic of mullitisation has been studied by several authors and it is fully described in the literature. Several works[ii], investigated the impact of impurities on the process and demonstrated a direct correlation between the mullitization rate and the purity of the starting andalusite mineral. After firing, the lower the amount of impurity the higher the amount of mullite will be achieved in the final refractory.

Premium Andalusite

Purity of andalusite product depends of the geological nature of the deposit as well as on the beneficiation process that is applied to concentrate the mineral. Indeed, the mineral ore contains less than 25% of andalusite and has to go through a large number of beneficiation stages before achieving the purity that is required for refractory application. The purification stages are applied on wet and dry environment and includes magnetical, densimetric, electrostatic sorting as well as floatation.

The amount of andalusite contained in final products can fluctuate considerable depending on the source and the grade. The result of a recent survey on commercial available andalusite in the refractory market are provided in table 1.

	Andalusite content (w/w)
Andalusite Standard grade 1	93%
Andalusite Standard grade 2	90%
Andalusite Standard grade 3	88%
Andalusite Standard grade 4	87%

Table 1 – Andalusite content of several andalusite grades available in the market

A study has been published in 2016[iii] comparing several grades of standard and premium andalusite. Each grade has been characterized according to the amount of and the nature of contained impurities. The following table reports the mineralogical composition of these grades (Table 2)

MINERALOGICAL COMPOSITION			
Component (wt.%)	Andalusite Premium	Standard Andalusite 1	Standard Andalusite 3
Andalusite	97	93	87
Illite/Muscovite	1	2	6
Kaolinite	0	trace	2
Feldspar	0	trace	1

Table 2 Mineralogical composition

Significant amount of layered silicates like illite and muscovite has been identified in the standard grade and actually constitute the main difference between premium and standard andalusite. This type of impurities are recognized to have an negative effect on the refractoriness of the material, adversely affecting all the thermo-mechanical properties due to the higher amount and lower viscosity of the amorphous phase.

It becomes obvious that the deformation of the hot material under load will be strongly decreased by a reduction of the amount of impurities, particularly when the impurities are concentrated in the matrix. An new recent study has been carried out in this respect, aiming to optimize the composition of a refractory brick in order to achieve the highest possible performance at high temperature.

A brick composition was developed containing two types of andalusite (premium and standard grade). The brick recipe was designed to reduce the amount of impurity in the matrix at the lowest possible level, and develop the highest possible amount of secondary mullite.

A plastic clay with high alumina content (RR40 from Imerys Ceramics) was selected to achieve this result. The recipe was completed with the appropriate amount of calcined alumina (Almatis CT9FG) in order to maximize the formation of secondary mullite (Table 3)

RAW MATERIAL	%
Andalusite 1 – 3 mm	40
Andalusite 0 – 1 mm	30
Andalusite 0 – 0.09 mm	12
Calcined Alumina CT9FG	13
Clay RR 40	5

Table 3 – brick recipe

The brick was sintered at 1500°C for 5h, and then tested for creep in compression at 1400°C followed the deformation for 50h. The curves for the creep at the constant temperature of 1400°C are shown in figure 3.

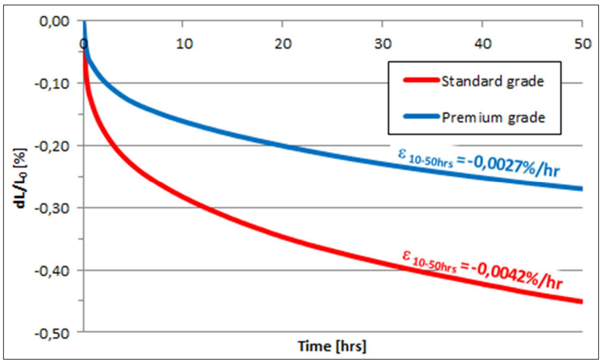

Figure 3 – Curves for the creep at constant temperature

The Creep in Compression obtained with the Premium Andalusite brick is 0.12% (5-50h) significantly lower than the same brick manufactured with standard grade (0.19%).

Mullite

Mullite, which is a mineral existing under the form of $3Al_2O_3$ $2SiO_2$ (typical of sintered mullite) or $2Al_2O_3$ SiO_2 (typical form of fused mullite), provides attractive properties for refractory systems which include low thermal expansion, low thermal conductivity, good chemical stability, and excellent thermo-mechanical stability. Unfortunately, mullite rarely occurs as natural raw material. Consequently, the development of mullite in commercial refractory has to be achieved by firing various aluminosilicate, with suitable chemical composition, involving clays, calcined kaolin and various fine silica and alumina.

The purity of the material used in the aggregate, and even more in the matrix, is recognized to have a major impact on the refractory performance.

Several types of refractory raw materials based on mullite have been developed over the years, with different composition and properties, depending on the feed-stock as well as the processing process. The grades containing 60% Al_2O_3 has become a real standard for brick and castable applications across the world.

Imerys manufactures and supply mullite based material from the site located in Andersonville, Georgia (USA). In terms of processing, clays are cage-dried/roller-milled prior to extrusion (under heavy vacuum). The main reason for this is to achieve maximum density/minimum porosity during sintering. The final product is a real testament to the clays and processing that go into its production, and there is no doubt that the choice of the feed-stock as well as the specific process are both key to achieve the properties that make this type of mullite a reference in the global refractory market.

Sintered mullite is not the only possible option available, in the market, for production of 60% alumina refractories. Some refractory companies blend lower alumina aluminosilicates with bauxite to produce a sometimes/occasionally-usable substitute for products normally based on mullite.

There are also other producers of 60% alumina aluminosilicates currently being used in the refractory industry across the world. The main point of this section is to describe how different types of mullite, containing various amount of impurities, compare with the reference mullite manufactured in Georgia (mullite 1).

Chemical Analyses (XRF):

Oxide	Mullite 1	Mullite 2
Al_2O_3	60.3	61.0
Fe_2O_3	1.25	1.67
Cr_2O_3	0.03	0.05
SiO_2	35.1	33.3
TiO_2	2.71	2.58
ZrO_2	0.2	0.19
CaO	0.02	0.43
Na_2O	0.015	0.01
K_2O	0.05	0.30
P_2O_5	0.09	0.16

Table 4 – chemical analyses of Mullites used for the experimental work (XRF)

Mullite 1 is an alumina silicate with roughly 60% of Al_2O_2, a fairly low amount of Fe_2O_3 (1.25%) and an extremely low amount of alkalis. On the other hand, the the product “Mullite 2” contains a great deal of alkali- and alkali-earth oxides, when compared to “Mullite 1”. This product appears to be based on a mix of high ferric oxide, diasporic-bauxite and lower alumina clays. Obviously, the relatively high lime, potassia and ferric oxide content of this material could have quite deleterious effects in certain refractory applications, especially when compared to “Mullite 1”.

The result of these additional contaminants will be exhibited in testing described later in this paper.

Minerals	Mullite 1	Mullite 2
Mullite	78	77
Tialite/Armalcolite-Fe	1	2
Rutile	trace	1
Quartz	trace	0
Corundum	2	1
Cristobalite	Trace	0
Amorphous	18	19

Table 5: Mineralogy of the two grade of mullite (XRD)

Obviously, the main component of the two materials is mullite. The higher iron and titania content in the second product is reflected in the higher, comparative tialite/armalcolite/rutile levels present. The higher amount of amorphous phase is reflective of the larger amount of glass forming alkali/alkali earth oxides contained in that material. Obviously, those ions, in greater percentage, can have a dramatic effect on hot properties of refractory materials.

Grain Density:
Results for the three materials are as follows (in g/cc):

	Bulk densities (g/cc)
Mullite 1	2.78
Mullite 2	2.70

There is a very clear difference between the two products, when it comes to bulk density.
We certainly believe that this large delta between the two products has a great deal to do with the plasticity of at least a portion of the clays used, as well as the high degree of processing of the raw feed, prior to calcining. The differences noted above were definitely reflected in finished product testing, as water content needed to achieve the same flowability, in castables produced using lower density calcines, differed by between 0.25-0.5% (more), when compared to castables produced using Mullite 1.

Finished Product Testing:
Imerys‘ refractory research center (CARRD, located in Villach, Austria) conducted blind hot load/creep testing for this paper. This testing was done using all three calcines, sized to the exact same fractions, used in the same standard formulation:

RAW MATERIAL	%
Mullite 3 – 5 mm	16
Mullite 1 – 3 mm	20
Mullite 0 – 1 mm	24
Mullite 0 – 0,09 mm	20
CT9 FG	5
RG 4000	5
Secar 71	5
Microsilica	5
Storage 24hrs at 20°C	
Drying 24hrs at 110°C	
Sintering at 1500°C/5hrs	

Table 6 – Castables recipe

This formulation was slightly finer than normally expected for a LCC, with a fair portion of the aluminosilicate calcine material making up the matrix of the castable. This was obviously done to help accentuate the effect of the calcine, itself, in these castable formulations.

Refractoriness Under Load (RuL) and Creep in Compression (CiC) testing were run for all products in question. For both tests, a hood-type furnace with counterweights was used. Since we tested according to the European Standard EN 993-8 (RuL) and EN 993-9 (CiC), the load applied was 0,2 MPa (which corresponds to about 40kg on a 50mm diameter cylindrical sample). There was a hole drilled in the middle of each cylinder, in which a thermocouple was placed to measure the exact temperature of each sample during testing. For both measurements, the load was placed on the sample from the beginning. Heating rate was 30°C/min up to 1000°C and 10°C/min. at higher temperatures.

Test results were as follows:

RuL

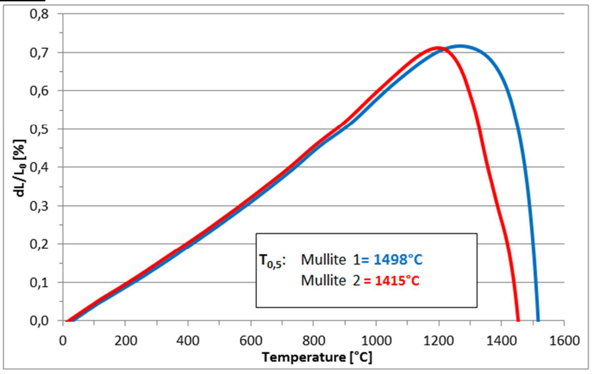

Figure 4 – RuL test result

CiC

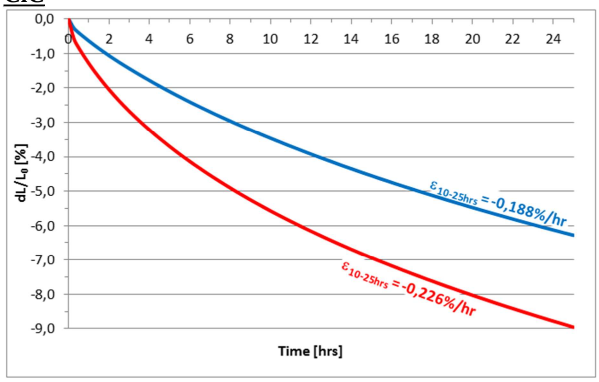

Figure 5 – CiC test result

Interpretation of the results:

In terms of the RuL and CiC testing, it is quite apparent that the sample named Mullite 1 performed at a much higher level. This result certainly makes sense, when you review the chemistry, density, and water demand of the materials tested. Despite the slightly lower amount of alumina, Mullite 1 shows a superior hot mechanical behavior, which can be definitely ascribed to the lower amount of impurities, in particular K_2O (0.05% vs 0.30%), Fe_2O_3 (1.25% vs 1.67%) and CaO (0.02% vs 0.42%).

Conclusion

New technical requirements as well as stronger focus on productivity have forced mineral producers to redesign their product portfolio. Purity and reliability are becoming the keys to reduce failure risk and enhance productivity in all refractory applications.

Aluminosilicate minerals are also evolving towards high purity. Premium grades of andalusite and mullite have been developed in order to maximize the amount of mullite achievable after firing, reinforcing the matrix of brick and castable and in return enhancing hot properties as well as corrosion resistance.

The amount of impurities (Na_2O + K_2O + CaO + MgO + Fe_2O_3 + TiO_2) have been reduced to an unparalleled level, allowing a significant change of the structure of the refractory material, with particularly regards to mineralogical composition, amount and viscosity of the amorphous phase. This improvement is even more significant when comparing aluminosilicate with alternative system based on bauxite, which always carries higher amount of impurities in the matrix of the refractory system and suffers of poor creep resistance under repeated thermal cycling[iv].

Premium andalusite and mullite are more and more regarded as bauxite replacement in many industrial application requiring outstanding performance and reliability. Iron & steel industry is likely to be the most concerned, although this type of evolution is also typical of many other refractory applications. Typical examples of it are the permanent and wear lining of steel ladles, torpedo ladles, iron ladles and any steel & iron vessel requiring extreme hot mechanical performance associated with thermal shock resistance and low thermal conductivity to reduce thermal losses.

Imerys Refractory Minerals, in collaboration with the CARRD - the Imerys R&D Center for Refractory and Abrasive - is running several projects aiming to design and develop an appropriate selection of grades for these applications. Beside creep resistance and RuL, the full characterization of thermal conductivity, volume stability and CO resistance of premium andalusite and mullite grades in comparison with Bauxite is in progress and will be presented in the coming year.

We believe the availability of higher purity grades as well as a more accurate understanding of their properties and performance, will open the door to the formulation of new type of bricks, castable, plastic mixes as well as composite solutions, optimized to generate technical synergies across the full range of minerals.

[i] “Revisited equilibrium diagram. » S. Aramki, R.Roy, journal of American Chemical Society, 45, (5), pp229-242, 1962

[ii] “Kinetics of Mullitization..”, M.L. Bouchetou, J. Poirier, J.P. Ildefonse, P. Hubert; UNITECR 2005 Proceedings, Orlando 2005, p 360-364

[iii] “Properties and Applications of Andalusite Based Refractories and the Influence of Mineral Impurities on the Behaviour of Refractories Made Thereof”, S. Moehmel, D. Frulli, F. Ahouanto, D. van den Heever, 7th International Symposium on Refractory Proceedings, Xi’an 2016

[iv] Dr A. Buhr ; Dr M. Koltermann : « Neue feuerfeste Roh… », 39th International Colloquium on Refractories, Aachen, 1996, pp 161-165