Andalusite based raw materials for Refractory Castable: properties and application

Danilo Frulli, Dirk van der Heever, Florian Ahouanto, Christopher Parr, Imerys Refractory Minerals

1. Introduction

Andalusite is a natural raw material belonging to the sillimanite group, together with kyanite and sillimanite, available in sizes from 5µm up to 8mm. It is a pure aluminosilicate ($Al_2O_3.SiO_2$), with theoretical composition of **62.9% Al_2O_3 and 37.1% SiO_2**. A very complex beneficiation process is required to concentrate crystalline andalusite and separate it from gangue and unsuitable minerals. This process consists of several stages- crushing, milling/classification, magnetic/heavy media separation, as well as floatation, in order to achieve the highest possible purity.

Unlike most of the raw materials used in the refractory industry, andalusite does not require firing prior to use in refractory applications, thus leading to a lower carbon footprint (**145 kg CO_2/t** - from French ADEME Emissions factors), when compared to calcined aggregates (chamotte, sintered mullite or bauxite – ranging around **400 kg** to **750 kg CO_2/t**). Furthermore, this lack of calcination necessity results in specific/positive refractory properties, such as low porosity and small pore size.

Andalusite products are widely used in several refractory solutions, due to its intrinsic/advantageous characteristics. Although its main use/market is in refractories for the iron and steel industry, its use is now well developed in brick and castables for glass, aluminum, cement, and even the foundry industry. This is not only due to the fact that andalusite is a high quality mullite source (once fired), but also due to several other inherent properties which, will be described, in detail, in this paper.

2 Intrinsic Properties of Andalusite Mineral

2.a Reactive Mineral

Being that andalusite is not sintered during the purification process, it **is still quite reactive**. When fired, during brick manufacturing, or during castable end use, andalusite transforms into up to 80 weight percent of mullite (and 20 weight percent of silica rich phase), according to the thermal conditions detailed in fig. 1.

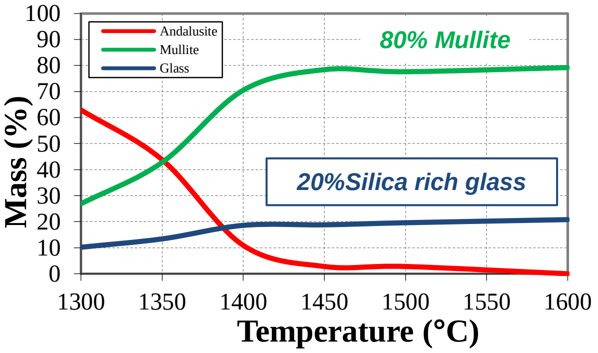


Fig 1. Phase weight content, according to sintering temperature

This silica-rich phase can be further transformed into secondary mullite by addition of alumina to the system in question.

Andalusite can be offered as an economic choice of mullite-forming precursor (when compared to “ex situ,” pre-formed mullite aggregates). The mullitization of andalusite is rapid and without the need for mineralizers. The initial mullitization process results in a **volume expansion (+4-5%),** which partially compensates for the natural shrinkage of certain refractory products/systems.

Sillimanite also provides volume expansion **(+6-7%)** during the mullitization process, but its mullitization occurs at a higher temperature than that of andalusite. As was shown in a recent paper [1], mullite aggregate can be processed/produced using sillimanite sand (which is readily available in India). But- its processing is complex and potentially expensive. High intensity milling (down to D50 of ~5µm) is necessary, along with the addition of mineralizers, via a briquetting/compacting route, prior to calcination. These steps are needed to achieve satisfactory mullitization and low porosity, which are necessary for monolithic applications.

Figure 2 details a thermal expansion comparison of andalusite and sillimanite products that have been milled down to the same particle size distribution.

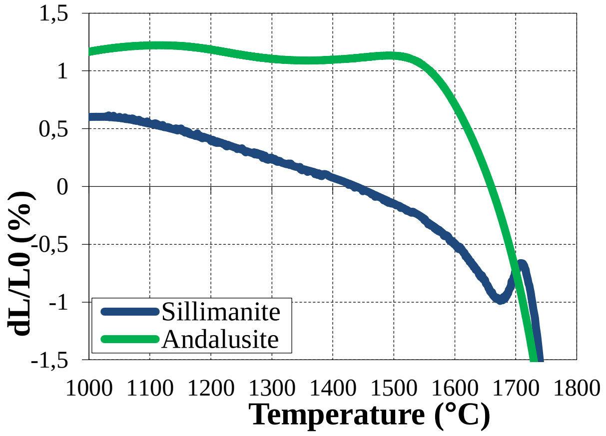


Fig 2. Thermal expansion of Andalusite & Sillimanite fines.

This graph clearly exhibits a downward shift (at increasing temperature) for the sillimanite material. Thus, the use of sillimanite to stabilize shrinkage/volume stability of refractory castable systems requires very high working temperature, and long residence/firing time…which are rarely achievable during the normal application end use. Recent x-ray diffraction testing has suggested that (approximately) only **half** of the sillimanite (milled to a D50 of 30µm) tested actually transforms to mullite and glassy phase, when fired at 1650°C (for three hours). Obviously, this is quite different from andalusite mullitization.

2.b Composite at microscale

Andalusite exhibits a unique microstructure, once mullitized, composed of a mullite single crystal with a capillary network filled by silica-rich glass. Capillaries form highly interconnected tubes with diameters in the micrometer range, which are elongated along the c-axis common to the neoformed mullite and the parent andalusite crystal. **Mullite has an orthorombic structure, like the andalusite crystal**.

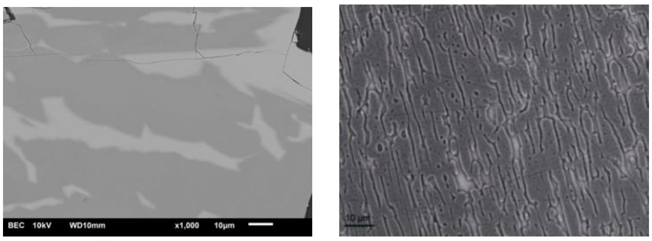


Fig 3. Left side, mullitized sillimanite microstructure [3]. Right side, mullitized andalusite microstructure

Mullite formation is topotactically-oriented, due to the similar structure and lattice parameters of the andalusite and mullite crystals. This microstructure is partially responsible for the outstanding physical properties of andalusite-based refractories (in spite of the approximately 20% glass content of mullitized andalusite). Conversely, the structure of sillimanite, once transformed to mullite (plus amorphous phase), shows more a random arrangement of the mullite crystal and silica-rich phase. Particular orientation or intricate microstructure is not observed.

2.c Thermo-Mechanical properties

Andalusite is well known to provide **high resistance to thermal gradient and thermal shocks** for refractory solutions. This is directly linked to several properties of the andalusite:

- The anisotropy of its thermal expansion along the 3 axes, which leads to micro-cracks formation in the refractory, and thus inhibits the propagation of critical cracks. It is worth noticing that this anisotropy is preserved on mullitized andalusite crystal [2].

	Along a Axis	Along b Axis	Along c Axis
TEC ($10^{-6}.K^{-1}$)	12.20	9.00	3.00

Fig 4. Thermal expansion anisotropy of the andalusite cristal

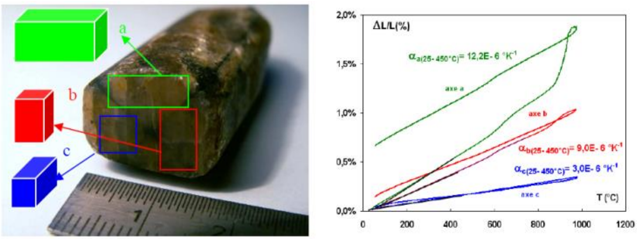


Fig 4. Thermal expansion coefficient of andalusite mono-crystal

- Silica-rich phase entrapped in the mullite network acts as a shock absorber, as well as a “healing agent,” as it softens, with increasing termperature. Microcracks are deflected and stopped in glass zones. Further heat treatment leads to the additional curing of existing cracks:

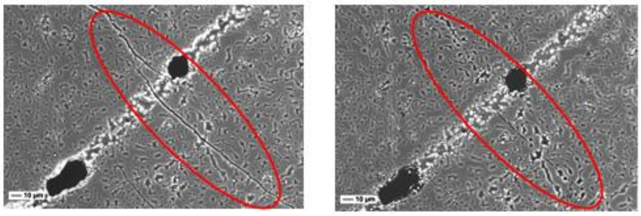


Fig 5. Recovery of the crack of andalusite grain after 10mn at 1200°C

Andalusite-based refractories exhibit very **high refractoriness under load**. This can be explained by the high viscosity of the amorphous phase (linked to the low amount of impurities present), and also due to its unique microstructure, especially the high rigidity of its mullite network. Thus, **the silica-rich phase is not detrimental to the thermo-mechanical properties** of andalusite-based castable; on the contrary, this phase is part of the reason why andalusite has outstanding thermal properties. This helps make andalusite a cost-effective alternative to high alumina aggregates (bauxite, BFA) currently available in the market.

Andalusite’s intrinsic properties yield several characteristics that are desired for monolithic castable development: positive expansion (PLC), good refractoriness under load (RUL), and good carbon monoxide (CO) resistance. All of these will be investigated and discussed in the next section.

3 Properties of Andalusite-based castable

3.a Comparison of andalusite, chamotte, mullite & bauxite based LC castables.

A typical LCC (low cement castable) recipe (Tab 3) was used for a comparative study on refractory aggregates. The particle size distributions of the castables were calculated to fit a Dinger–Funk model, with n-value equal to 0.21. Maximum grain size was fixed at 5mm and minimum at 0.1µm. Andalusite was compared versus chamotte (45% alumina), sintered mullite (60% alumina), and Chinese bauxite (86% alumina), for all fractions. Particle size distribution (PSD) in weight was kept constant. The matrix

Fig 7. Microstructure of castable sintered at 1500°C)

composition was designed in order to obtain secondary mullite in the andalusite-based castable.

	%	LCC$_{Cham}$	LCC$_{Anda}$	LCC$_{Baux}$	LCC $_{C/B}$	LCC $_{Mullite}$
Fraction 3-5 mm	**16**	45N	D59	B86	65% C45 + 35% B86	Mu 60
Fraction 1-3 mm	**20**	45N	D59	B86	65% C45 + 35% B86	Mu 60
Fraction 0-1 mm	**24**	45N	D59	B86	65% C45 + 35% B86	Mu 60
Fraction 160µm	**20**	45N	KF	B86	65% C45 + 35% B86	Mu 60
Calcined alumina	**10**	AC44B6				
Fume silica	**5**	Microsilica				
70% Al_2O_3 cement	**5**	Secar 71				
Additive	**+0.15**	Dispersant				
H_2O %		7.2	5.2	5.4	6	5.4
Flowability (%)		109	104	103	103	98
Setting Time (min)		275	370	330	285	350

Weight %	Al_2O_3	Fe_2O_3	$Na_2O + K_2O$	SiO_2	CaO+ MgO	TiO_2
LCC$_{Cham}$	47.6	1.1	0.55	47.5	1.9	1.35
LCC$_{Anda}$	62	0.4	0.25	35.65	1.6	0.1
LCC$_{Mullite}$	60	0.9	0.2	35.2	1.6	2.1
LCC$_{Baux}$	86	0.8	0.2	8.4	1.7	2.9
LCC $_{C/B}$	61.8	1	0.45	32.4	1.8	1.8

Tab 1.Castables recipe, setting parameters & chemical compositions

Please note that the level of impurity for the andalusite-based castable is very low compared to other materials used, especially in terms of the iron and titania content.

The castables were dry-mixed for two minutes in a planetary mixer. After adding water, the castables were wet mixed for four minutes. Setting time was measured with the temperature method.

After setting, the test bars (40x40x160mm) were left at room temperature for 24 hours and then dried for 24h at 110°C. Permanent linear change has been measured according to sintering temperature and can be observed in Fig.6. Strong shrinkage is related to sintering and glass formation. Expansion is due to mineralogical transformation or formation of new solid phases that grow inside the matrix. Only the andalusite-based castable exhibited a positive linear change after firing. During normal service, at high temperature, castables containing andalusite exhibit a slight increase in volume due to mullitization. This same phenomenon can be also observed in bricks. Because of this, andalusite helps compensate for potential crack formation in castables (due to matrix sintering) and the natural presence of joints between bricks. **This expansion cannot be obtained with calcined aggregates.**

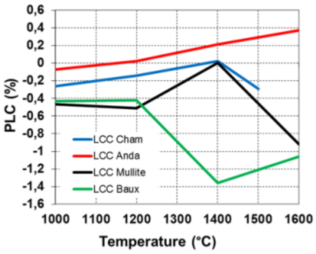


Fig 6. Permanent Linear Change according to temperature

Additional characterization of the castables included hot property testing. This was investigated through hot modulus of rupture (HMOR) and refractoriness under load (RuL) testing. RuL was performed on all of the castables using 50x50mm cylinders dried at 110°C, in accordance with ISO1893 (Fig 7).

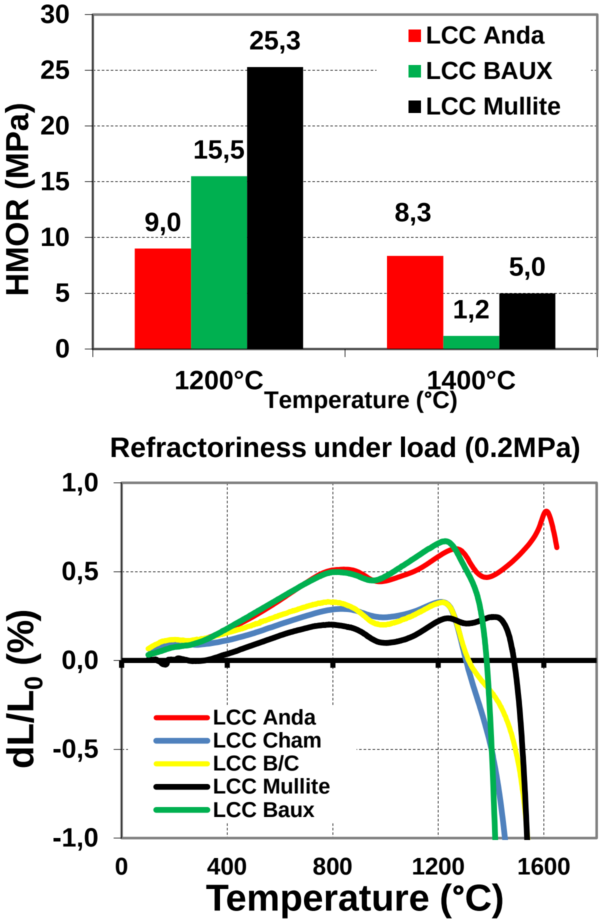


Fig 7. Hot modulus of Rupture (top) and Refractoriness Under load (bottom)

The thermo-mechanical stability of andalusite-based LCC is quite good between 1200°C and 1400°C. On the other hand, viscoplastic behavior of bauxite-based castable is confirmed. HMOR results at 1400°C are quite low for the bauxite-based castable, and the corresponding RuL measurement shows tremendous sagging in that same temperature range.

In Fig 7, please note the extremely high RuL value for the andalusite-based LCC (T0.5% >1650°C), when compared to the other materials tested. In comparison, the sintered mullite-based castable exhibits lower RuL, even though overall alumina content of the two mixes is quite similar. In an andalusite-based LCC, the mullitization process is mostly complete after firing for 5 hours, at 1500°C. If you look at the contact between the castable matrix and andalusite grains, at higher magnification (Fig 8.), you can clearly see the typical microstructure of the mullitized andalusite: glass (G1) trapped in a mullite needle network (M1). The matrix is also totally recrystallized into a mullite (M2) - glass (G2) network. The secondary mullite of the matrix and the primary mullite of the grains are highly

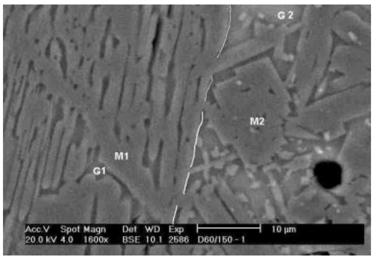
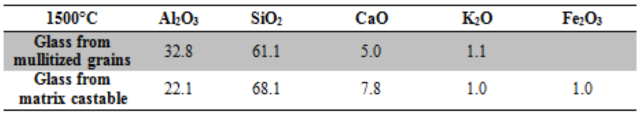


Fig 8. Microstructure of andalusite-based castable sintered at 1500°C

interconnected. Bonding between the matrix and mullitised andalusite helps to explain the good mechanical properties of the LCC at 1400°C despite the development of glass in the grains and the matrix.



1500°C	Al_2O_3	SiO_2	CaO	K_2O	Fe_2O_3
Glass from mullitized grains	32.8	61.1	5.0	1.1	
Glass from matrix castable	22.1	68.1	7.8	1.0	1.0

Tab 2. Glass composition by EDS

The glass from the mullitized grains is enriched in alumina and poorer in calcium than the glass of the matrix (Tab 4?.). A glass with the following composition (Al_2O_3= 30%, CaO =10%, SiO_2=60%) should be liquid above 1700°C [3]). With regards to the existence of K and Fe in the matrix glass, the melting temperature of the glass of the matrix should be lower but in the same range. In any case, the viscosity of such a silica glass should be very high (>20 poises).

High viscosity of the glass, combined with a mullite bonding, explains the hot mechanical properties of the castable. As a result of this study, it appears that just the alumina content of an aggregate and/or a castable is not enough to describe its hot mechanical behavior. Type/ quantity of impurities and grain microstructure are key parameters used to predict the behavior of an aggregate in a low cement castable.

The introduction of finely ground/pure andalusite in bauxite and BFA-based castablea has been studied, with the target of increasing the mullite network inside the matrix and the viscosity of the glassy phase (for bauxite). This study is described in the next section.

3.b Improvement of Bauxite & BFA based LC castable with the addition of Andalusite in the Matrix.

Introduction of 10 - 18.5% of fine Kerphalite (andalusite) into bauxite and BFA-based castables has been investigated, in terms of physical properties and thermo-mechanical properties. Listed below the castable recipe used for that testing:

Grade	Size grade	Ref BFA	BFA 10 KF	BFA 18 KF	Ref BAUX	BFA 10 KF	BAUX 18,4 KF
BFA	6,3-0,2	55,2	55,2	55,2			
Bauxite	6,3-0,2				55,2	5,2	55,2
BFA	**0,2-0,063**	**12,1**	**8,4**				
Bauxite	**0,2-0,063**				**12,1**	**8,4**	
KF160	**0,2-0,063**			**8,4**			**8,4**
KF55	**0-0,055**		**10**	**10**		**10**	**10**
Tabular Alumina	**0-0,045**	**12,7**	**6,4**	**6,4**	**12,7**	**6,4**	**6,4**
Calcined Alumina	< 0,045	7					
CTC20	< 0,045	3					
Micro-silice	< 0,001	5					
Secar 71	< 0,063	5					
Défloculants		0,15					
Citric Acid		0,015					

Tab 3. Castable recipes

Chemical composition of these formulae has been measured, through X-Ray fluorescence (Tab 4.). One can see the logical decrease of overall alumina content, with the introduction of andalusite…but also the variation in impurity content. **There is an overall decrease of impurities (such as titania, iron and alkali/alkali earths) for the bauxite-based castable**. The impurity level for the BFA-based castable showed a slight increase, with the introduction of andalusite.

Ref	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SiO_2	CaO	MgO	TiO_2	Total
Ref BFA	90,16	0,10	0,14	0,08	5,66	1,57	0,21	1,66	99,57
BFA + 10 KF	86,49	0,12	0,11	0,10	9,40	1,57	0,20	1,58	99,57
BFA + 18,4 KF	83,73	0,14	0,10	0,10	12,41	1,56	0,17	1,38	99,60
Ref BAUX	84,47	1,27	0,19	0,26	8,87	1,61	0,21	2,36	99,24
BAUX + 10 KF	81,05	1,23	0,16	0,26	12,50	1,61	0,20	2,25	99,25
BAUX + 18,4 KF	78,86	1,08	0,15	0,23	15,25	1,59	0,18	1,99	99,32

Tab 4. Castable Chemical Composition

In figure 9, the Permanent Linear Change of fired castable (at 1500°C) is shown, according to the amount of KF introduced into the recipes. The trend of an **increase in the PLC value, with the introduction of KF, is clearly shown**. A positive PLC for fully andalusite-based LCC castable has been established (>0.2%) in Part 3.b. 20% of fine andalusite was needed to fully compensate for the initial shrinkage of the castable, but 10% was enough to already see an impact on PLC. This phenomenon can be observed no matter what aggregate was used in this study.

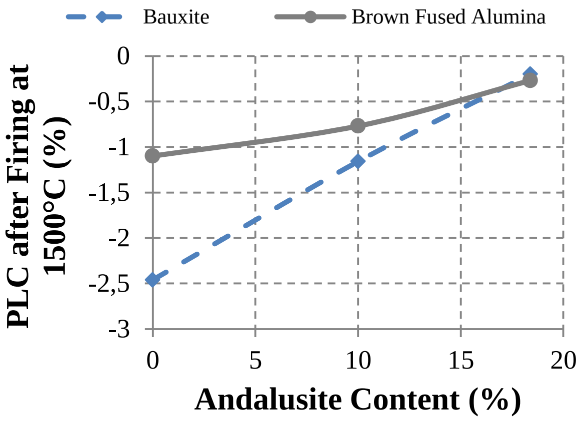


Fig 9. Permanent Linear Change according to andalusite weight content

The refractoriness under load test results (Fig 10.) confirm the remarkable thermal stability of the castables in which 10% to 18.4% of andalusite was added into the matrix (replacing a portion of bauxite, BFA & tabular alumina). If sagging starts at the same temperature for all castables, the sagging is reduced when 10% andalusite is added, and even removed with 18.4% andalusite, at up to more than 1550°C for brown fused alumina based LCC. The effect of andalusite on RuL occurs for both aggregates but is more efficient/pronounced for brown fused alumina.

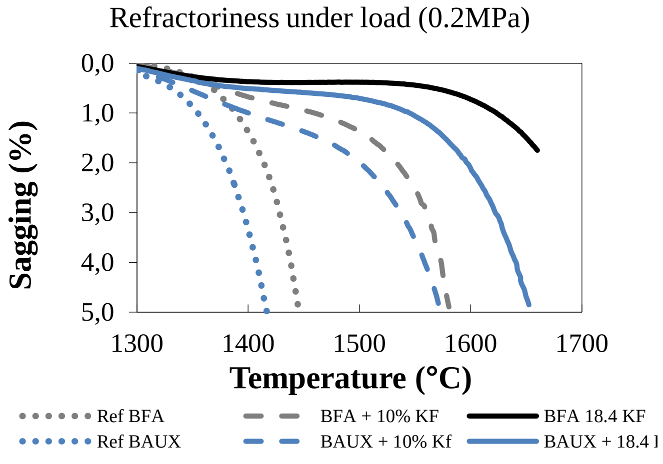


Fig 10. Refractoriness under Load with addition of andalusite

3.c CO resistance of Andalusite based castable

The resistance to corrosion by carbon monoxide is a critical property in many castable application, with applications in the aluminum and petrochemical industries being good examples. This is also the case for critical applications in the iron and steel industries, such as the refractory for HBS or DRI furnaces. The decomposition of the carbon monoxide is known as the Boudouard reaction and leads to the formation of $C_{(s)}$ in and on the surface of the refractory in a certain temperature range. That decomposition can be catalyzed by the presence of Fe_xO_y particles, and is influenced by the size and specific area of those particles [4]. This highlights the importance of raw material purity on the CO resistance of castables. Several grades and particle size distributions of andalusite have been tested using ASTMC288 conditions. The castables were pre-fired at 540°C for 5h and tested in a CO atmosphere at 500°C over 200 hours. The recipe used is in Tab.5, where White Fused Alumina was replaced by test materials of the same PSD.

Type	Size	%Wt
Calcium Aluminate Cement	-	20
WFA	0-0.5	20
WFA	0.5-1	20
WFA	1-3	20
WFA	3-5	20

Tab 5. Standards Recipe for CO resistance castable testing

The classification is shown in Tab.6 and shows the importance of purity of the initial andalusite used.

	Iron (%)	CO ASTM
D60 0-1 mm	0.42	A/B
D60 1-3 mm	0.45	A/B
D60 3-5 mm	0.44	B
D59 0-1 mm	0.58	A/B
D59 1-3 mm	0.56	B
D59 3-5 mm	0.58	A/B
Andalusite A	0.71	C
Andalusite B	0.96	C
Andalusite C	0.86	C
Andalusite D	1.12	D

Tab 6. Product Iron content & Classification according to ASTM

High purity/low iron grades (Durandal D59 & D60, as well as Randalusite Premium), in all the particle size distributions tested, overperformed all other andalusite products tested. D60 & D59 have a very low amount of available impurity for catalysis of the Boudouard reaction. There is a definite trend between the iron content and the CO resistance results; but it is difficult to perfectly correlate those two values. CO resistance depends on both the particle size and specific surface of the iron particles, meaning that a low amount of iron in the raw material will not necessary lead to a CO resistant product, in the end. Nevertheless, by reducing the iron content in raw materials, it is definitely possible to increase the overall/potential CO resistance of a refractory solution. The nature of the impurities and their location inside the ore, prior to processing, usually determines its ability to be removed. Even with extreme treatment/beneficiation, certain mineral inclusions, especially some that are potentially iron-bearing particles, cannot be easily removed, no matter what process is applied.

4 Conclusion

Andalusite has intrinsic properties, once sintered (mullite precursor, composite microstructure, and thermal shock resistance) that yields castable and brick that exhibit very high thermo-mechanical stability.

A comparison of andalusite, chamotte, bauxite and sintered mullite-based LC castable has been performed showing some advantage for the andalusite-based castable. In particular, the advantages include excellent volume stability (positive permanent linear change), as well as hot mechanical performance stability (hot modulus of rupture for andalusite castable, at 1200°C and 1400°C, of about 10 Mpa). In term of refractoriness under load, andalusite products outperform other solutions, thanks to the very unique microstructure of mullitized andalusite, as well as the high viscosity (at high temperature) of the glass formed during mullitization. Also, it has been shown that primary mullite formed within andalusite aggregate and the secondary mullite formed in the castable matrix become highly interconnected, which greatly enhances these good thermo-mechanical properties.

Some of the benefit associated to andalusite can be obtained in bauxite or brown fused alumina-based castables, by using andalusite as secondary component. Indeed, addition of 10-20% of fine andalusite helped to compensate for the shrinkage, at high temperature, of castables containing no andalusite, and considerably helped compensate for their sagging at high temperature.

Finally, it has been shown that, when CO resistance of castable is necessary, particular attention has to be paid to the purity of the andalusite used. High quality andalusite grades, such as Durandal D59 and D60, yield class A/B results, whereas all others andalusite grades tested exhibited much lower CO resistance.

References

[1] Synthetic mullite aggregate from sillimanite beach sand for improved castable linings, G. Bhattacharya[1], C. Wöhrmeyer[1], C. Parr[1], [1]Kerneos, Kolkata, India,H. S. Tripathi[2], A. Ghosh[2],[2]CSIR-Central Glass & Ceramic Research Institute, Kolkata, India,Irefcon 2016, Hyderabad, January 2016

[2]Mahdi Ghassemi kakroudi, Thesis Comportement thermomécanique en traction de bétons réfractaires : influence de la nature des agrégats et de l'histoire thermique : 2007

[3] P.Hubert, Relation between microstructure and refractory propertiesin andalusite based low cement castables, Polish Ceramic Society, 2003

[4] N. Bost∗, M.R. Ammar, M.L. Bouchetou, J. Poirier, The catalytic effect of iron oxides on the formation of nano-carbon by the Boudouard reaction in refractories: Journal of the European Ceramic Society 36 (2016) 2133–2142

[5] P.Hubert, Application of a high temperature calcined andalusite in fired bricks and low cement castables, UNITECR 2003

[6] P.Hubert, BEHAVIOUR OF ANDALUSITE IN LOW CEMENT CASTABLES: COMPARISON WITH OTHER AGGREGATES, Tehran International Conference on Refractories, 4-6 May 2004

[7] Ildefonse, J.P.; Gabis, V.; Rigaud, M.; Rebouillat. L.; Daniellou, P.; Dubreuil, P.: Mullitization of andalusitein bricks and castable, UNITEECR 1997,Proccedings, Vol 2, New Orleans, 899–907

[8] J.Poirier, M.L.Bouchetou, L.Colombel, P.Hubert"Andalusite : an attractive raw material for its excellent thermal shock resistance"Refractories Worldforum 1 93-102 2009