LIGHTWEIGHT ALUMINOSILICATE AGGREGATE FOR HIGHER TEMPERATURE REFRACTORY APPLICATIONS

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ABSTRACT

For years, refractory producers have struggled to find an insulative/lightweight (LW) aggregate to use in bricks and monolithics for applications above 1370C: petrochemical, power, cement dry calciners, steel ladle covers, preheaters, etc. Our research team is developing a range of lightweight aluminosilicate calcines that can be used in lightweight formulations capable of reaching 1538C and beyond. Obviously, the main feature of these products is the exceptional refractoriness, associated with a density significantly lower than regular aluminosilicates. But, these materials are also quite interesting in that their open porosity is generally quite low, allowing for casting/gunning/pumping at lower than normal water content than for products based on most other insulative materials. In comparison, this positively affects the dry-out and reheat shrinkage characteristics, at elevated T, of formulations based on this innovative LW material.

These new LW aggregates allow for the development of a range of finished products: Reduced Cement Insulating Castables, Traditional Insulating Castables and Gunning Castables where, in practice, Mulcoa 43LW acts very similar to normal Mulcoa aggregates.

This study examines the properties of conventional and low cement castable formulations based on our company's 43% alumina LW product.

INTRODUCTION

For years, our refractory customers have inquired about a lightweight material capable of reaching the temperatures/for the applications described in the abstract. Because such materials have not routinely been available in the US market, two part linings, consisting of a hard, dense hot-face lining, coupled with an insulating back-up lining, have routinely been used for all sorts of higher temperature insulative applications. The North American market has been dominated by the use of perlite, vermiculite, and other lower T insulating materials, in conjunction with some higher T aluminosilicate aggregates. Most of these mixes struggle above 1370C, mainly due to two reasons: the high amount of water needed for placement, and the low refractoriness of the aggregates used in the mixes. The high water content creates porosity and then shrinkage, after heating to elevated temperatures. Obviously, the low melting point of the raw materials comes in to play here, as well.

A few different higher temperature lightweight aggregates are available in the European market, but even these do not seem routinely capable of withstanding the elevated temperatures needed in the most exacting applications (that require an insulative material). In our development work, the main focus was to create a highly refractory aggregate that exhibited very little reheat shrinkage.

MATERIALS AND METHODS

Mulcoa 47 (46% alumina aluminosilicate calcine) is one of the staple raw materials used in the North American refractory market. We chose to base our LW aggregate on that material's chemistry. This material is produced using the highly-gibbsitic kaolins from Southwest, Georgia. In order to reduce the normal density of this calcine (which is normally approximately 2.62 g/cc), we added high purity porogenous material to the raw clays, prior to extrusion. Absolutely no organics (for burnout purposes) were introduced into the material. This resulted in an aluminosilicate calcine with a bulk density of approximately 1.70 g/cc, as well as an extremely high (in comparison) amount of closed porosity. Total porosity of this material is approximately 40%, with half of that being closed porosity; obviously, this is a real plus, in terms of potential for mixes with low thermal conductivity.

Mineralogically speaking, the material consists mostly of mullite, cristobalite, and glass.

Tab 1: Specifications

Chemical analysis (%)

Al^2O^3	43,3
SiO^2	52,7
Fe^2O^3	1,40
TiO^2	1,80
CaO	0,13
MgO	0,13
K^2O	0,42
Na^2O	0,00
P^2O^5	0,00
ZrO^2	0,00
LOI	0,04
SUM	**100,00**

XRD-Mineralogy (%)

Mullite-	57
Corundum	1
Tialite/Armalcolite	1
Rutile	trace
Quartz	1
Tridymite	1
Cristobalite	20
Amorphous	19
SUM	**100**

Closed Porosity (%)- 21.1 Total Porosity (%) -37.9

As you can see from the picture, the porosity is well distributed, and the material looks quite homogenous, with several different types of pores, ranging in size from very large to quite small (figure 1), with many other types of voids and cracks also present in this material (figure 2).

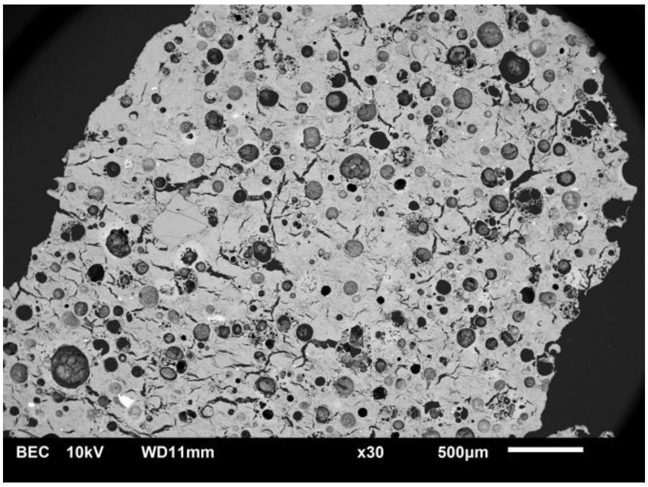

Fig. 1: Porosity- SEM of grain x30 magnification

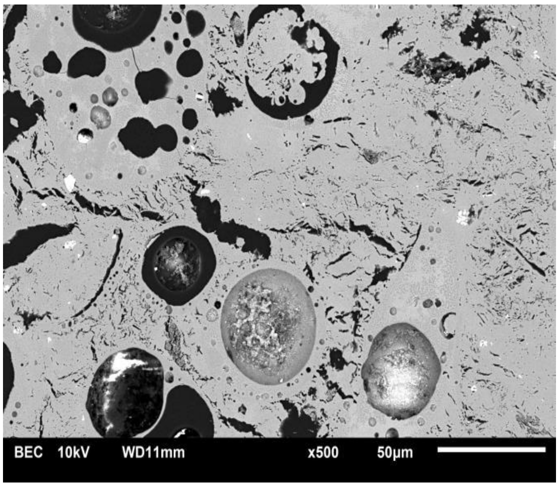

Fig. 2: Porosity-SEM of grain x500 magnification

One of the ways we characterized this material, in terms of its high temperature behavior, was through the use of dilatometry. The curve in figure 3 shows how this material compares to competitive European materials. Obviously, this new product is much more stable at high temperature than the competitive materials, exhibiting much less shrinkage.

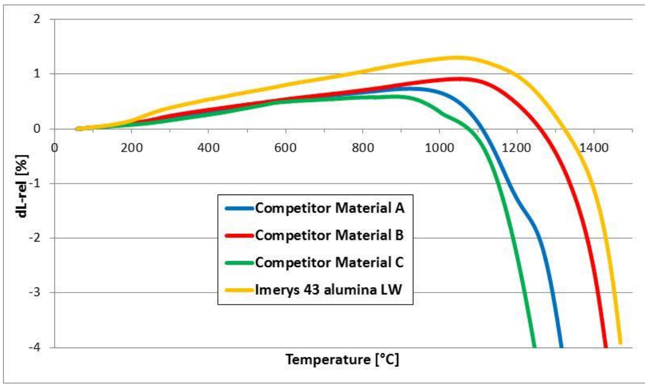

Fig. 3: Dilatometric test results of European competitive materials and the Imerys LW product

Our research team decided to test our high temperature lightweight material in two different types of monolithic formulations: a conventional castable formulation and a low moisture/low cement castable formulation. The conventional castable is based on standard castable sizing (Furnas packing principle), whereas the LCC is much finer than normally expected for LCC formulations. This was done for two reasons: 1) to try to further reduce the density of the “as cast” material, and 2) in order to try to encourage our customers to use finer LW aggregate in their formulations. During crushing of normal LW aggregates, those materials are susceptible to generating more fines than normally expected, when crushing a higher T refractory aggregate. But, because this new product is a true ceramic, from start to finish, fines generation during crushing is less than would normally be expected, especially if some sort of organics were used for burnout/density reduction. Part of the test was proving that a great deal of finer material could be used in the formulation. The formulae can be seen in Table 3.

Tab. 3: Low Cement vs. Conventional Castable Formula

Low Cement Castable Formulation (%)		
43% alumina LW	3/4	5.00
	4/8	15.00
	8/14	10.00
	-14	30.00
Kyanite -325M		10.00
Calcined Alumina -325M		12.50
Silica Fume		7.50
70% alumina Calcium Aluminate cement		10.00
STPP		0.10
SHMP		0.05
Polyethylene fibers		0.08
Total		100.23

Conventional Castable Formulation (%)		
43% alumina LW	3/4	15.00
	4/8	18.50
	8/14	10.00
	-14	20.00
47% alumina calcine 200M		17.50
Ball Clay		1.50
51% alumina Calcium Aluminate cement		17.50
Total		100.00

We compared these formulations to each other, as cast, in terms of their cold crushing strength (2), hot modulus of rupture(4), reheat shrinkage/expansion(1), bulk density, thermal conductivity (5), and CO resistance (3).

RESULTS AND DISCUSSION

Tab. 4: Overall Analysis

	LCC	Conventional
Reheat Linear Change (%)		
(C)		
316	-0.10	-0.02
816	-0.23	-0.09

(C)		
982	-0.35	-0.17
1316	0.22	-0.14
1482	0.34	-1.08
Bulk Density (pcf)		
316	122	108
816	122	108
982	123	108
1316	120	107
1482	121	111
CCS (psi)		
316	8241	3320
816	11441	3489
982	12809	3506
1316	11319	3652
1482	15302	12639
HMOR (psi)		
982	2349	618
1316	293	108
1482	95	12
Thermal Conductivity (W/m-C)		
20	1.54	1.01
250	1.32	0.82
500	1.25	0.81
750	1.28	0.91
1000	1.33	1.03
1250	1.33	1.05
1473	1.23	0.91

Even though the LCC was much finer than the conventional castable, the water required for casting was still dramatically lower for the LCC, at 10% (versus 16% for the conventional formulation). Bulk density at all temperatures was significantly higher for the LCC (again, even though it was, by far, the finer of the two mixes). Due to the density difference between the two mixes, there was a moderate difference between the two mixes when it came to thermal conductivity. The LCC exhibited a slightly higher thermal conductivity than the conventional mix, again presumably due to the lower inherent porosity of that mix (mainly because of the much lower water required for casting of the LCC). Generally speaking, the thermal conductivity was quite low for both formulations, at just on both sides of 1 W/m-C for each mix (which is quite outstanding for such “refractory” LW formulations).

Cold crushing strength for the LCC was quite outstanding; mix design/water requirement for casting certainly favored the LCC, which was confirmed. The cold crushing strength of the conventional castable was comparatively weaker, across the board, presumably due to the general, comparative “weakness” of the predominantly cement (and high water content) bonding used in the conventional formulation (except at elevated temperature). The HMOR values for the LCC were quite good at all three temperatures, versus the conventional castable, as expected, although we did expect to see a slightly higher value at 1482C for the LCC than was exhibited. Still, the LCC did have acceptable structural integrity at that temperature. In terms of reheat expansion, neither mix shrank appreciably, even at higher temperatures, which was exactly as we had hoped. The LCC actually showed a slight expansion at 1316C (presumably at least partially due to the generally high kyanite content of the mix), and also exhibited only mild shrinkage at 1482C. The conventional castable only shrank just over 1% at 1482C, which is quite good for any conventional LW formulation.

In terms of CO resistance (at 100 hours), there was a telling difference between the two mixes. The LCC generally exhibited A/B level results, with 7 of 10 bars completely unaffected, and 3 others with only minor surface pop-outs. Very little carbon inundation occurred in these samples, again presumably due to the very low overall comparative porosity of this formulation. Pictured below is an example of a cast LCC bar, pre-test (figure 4) and an unaffected LCC bar (figure 5), after the 100 hour CO disintegration test:

Fig. 4: LCC cast bar, pre-CO disintegration test

Fig. 5: LCC cast bar, after 100 hour CO disintegration test

Generally speaking, the conventional castable failed the CO testing, presumably due to the much higher cast porosity of that mix (due to the very high water content needed for casting). Most of the bars were completely cracked, with a high degree of surface pop-outs. All bars seemed quite inundated with carbon. Conventional bars (figure 6- pre-test; figure 7 post- test) are pictured below:

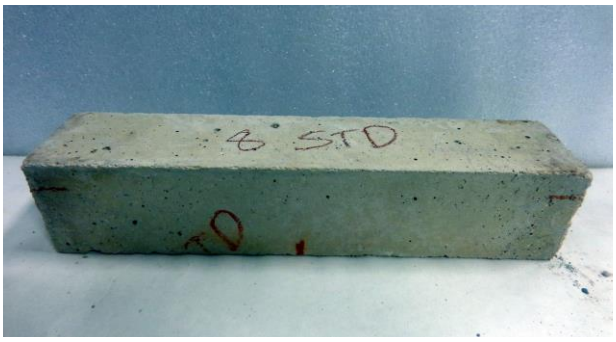

Fig. 6: Conventional cast bar, pre-CO disintegration test

Fig. 7: Conventional cast bar, after 100 hour CO disintegration test

CONCLUSIONS

Our team was definitely able to produce a high temperature lightweight aggregate capable of reaching 1482C, and possibly beyond. Even using an extremely fine-grained mix, we were able to produce a LCC based on this material that exhibited very good to decent hot strength, low density and thermal conductivity, and quite acceptable to outstanding resistance to carbon monoxide disintegration. The green strength of the LCC was quite outstanding- much better than exhibited during previous monolithic testing of competitive European lightweight aggregates. Reheat expansion for all mixes tested was quite good, even with the elevated water content needed for casting the conventional formulation. We expect that monolithics based on our new 43% alumina lightweight aggregate would be quite outstanding (especially in comparison to other LW monolithics available in the market today) for extremely high temperature insulating applications…especially for petrochemical and power applications. This material performed so acceptably during our testing, that it is even in the realm of possibility to think that monolithics based on this 43% alumina lightweight material could be used to design one part/single layer linings, capable of having an acceptable hot face and back-up lining, again all in one layer. The benefit of this possibility, from a time/efficiency standpoint, makes this material a potential game-changer for our industry.

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