EXAMINING THE EFFECTS OF THE PARTIAL REPLACEMENT OF CALCINED ALUMINA WITH KYANITE IN A 60% LOW CEMENT CASTABLE

Steven Ashlock, Kyanite Mining Corporation, Dillwyn, VA, USA

Dilip Jain, Kyanite Mining Corporation, Dillwyn, VA, USA

ABSTRACT

The partial replacement of calcined alumina with Virginia Kyanite™ in a 60% LCC in an attempt to enrich the matrix with mullite was examined. Previous work has shown that calcined alumina does not react as readily as believed to form secondary mullite. Bars of three different castable mixes were prepared and tested for MOR, CCS, density, and other properties. Chemistry and phase composition were evaluated using XRF and XRD respectively. Despite the lowering of the overall alumina content the majority of the castable properties were improved. The addition of -325m kyanite created mullite in the matrix after sintering to 1480°C and higher. In all three mixes some calcined alumina remained unreacted even after firing to 1600°C. The density is also increased as the -325m kyanite expands into and reduces the porosity of the refractory.

INTRODUCTION

The demands on refractories in the modern market are constantly changing and becoming more challenging.[1] Requests for longevity increases are commonplace from the buyer to the refractory supplier. In order to achieve this goal companies are increasingly enhancing the overall alumina content. This requires using more expensive higher end raw materials. One such material that is a staple of many high end alumina refractories is calcined alumina. Calcined alumina is added to improve refractoriness to the matrix.[2,3] It is also said to react with silica fume to form interstitial mullite.[4,5] It has long been known that mullite in the matrix greatly enhances the thermal shock capabilities of the refractory. However, research shows that the reaction between silica fume and/or silica and calcined alumina takes place at fairly high temperatures.[6,7] Most refractories would need to be heated to well above usage temperature in order to see this beneficial reaction.

Virginia Kyanite™ is a member of the sillimanite group of minerals.[8] The minerals that make up this group are kyanite, sillimanite, and andalusite. These minerals are used in a wide variety of refractory applications. One unique property of the sillimanite group minerals is conversion to mullite after calcination via the following reaction:

$$3(Al_2SiO_5) \xrightarrow{heat} 3Al_2O_3 \cdot 2SiO_2 + SiO_2 \qquad (1)$$

Kyanite has the lowest temperature of conversion of the group (1430°C) as well as the largest amount of expansion upon conversion at 17 volume percent. This expansion is used throughout the industry as a means of offsetting shrinkage of the other minerals in the refractory recipe. To achieve this goal the larger commercially available sizes of kyanite, such as -35, -48, and -100 mesh (425, 300, and 150 µm), are used. The finer mesh sizes such as -200m (75 µm) and -325m (45 µm) are used to increase the density of the refractory. Most of the expansion of this finer mesh kyanite is absorbed by the porosity thus increasing the bulk density. Fine mesh kyanite has another attribute than can be exploited: mullite formation in the matrix of the refractory.

TEST PROCEDURE

Three 60% alumina low cement castables (LCCs) were created to observe the change in castable properties as calcined alumina (A35-325) is replaced with Virginia Kyanite. The formulations, based off of mullite aggregates, are listed in **Table 1**. As the amount of 325m kyanite is increased the amount of 48m kyanite needs to be decreased. Too much kyanite in the refractory mix will cause an overexpansion that is detrimental. After mixing and water additions the mixes were vibration cast in 25x25x152 mm molds. The bars were allowed to cure overnight before demolding. The bars were then dried at 110°C before firing in an electric furnace. Firing conditions were a ramp of 5°C per minute with five hour hold times at either 1370°C, 1480°C, or 1600°C with a natural cool down.

Tab. 1: LCC mix recipes

Mix	M60 3x4	M60 4x8	M60 8x 20	M60 20m	VM 325	Ky 48m	SF	A35 -325	Secar 71	Ky 325	SHMP/ SLS	H_2O
1	18	18	13	18	8	5.5	5.5	8	6	0	0.1/.02	5.7
2	18	18	13	18	8	4.5	5.5	4.5	6	4.5	0.1/.02	5.7
3	18	18	13	18	8	3	5.5	2.5	6	8	0.1/.02	5.7

Various castable properties were measured for each series of bars. Permanent linear change (PLC) was measured using calipers before and after firing. Bulk density, apparent porosity, and water absorption were measured using ASTM C20-00 (2015). ASTM C133-97 (2015) was used to test modulus of rupture (MOR) via three point bend and cold crushing strength (CCS) on 25x25x25 mm cubes. Chemical analysis was performed via X-Ray fluorescence (XRF) on a Panalytical PW2400 as well as phase analysis by X-ray diffraction (XRD) on a Panalytical Cubix[3] utilizing the Rietveld method.

RESULTS AND DISCUSSION

Chemistry

The chemistry results obtained via XRF are shown in **Table 2**. The most noticeable chemistry change is the decrease in alumina with increasing amount of -325m kyanite. This increase in kyanite, as a replacement for the pure calcined alumina, also slightly increases the iron and titania.

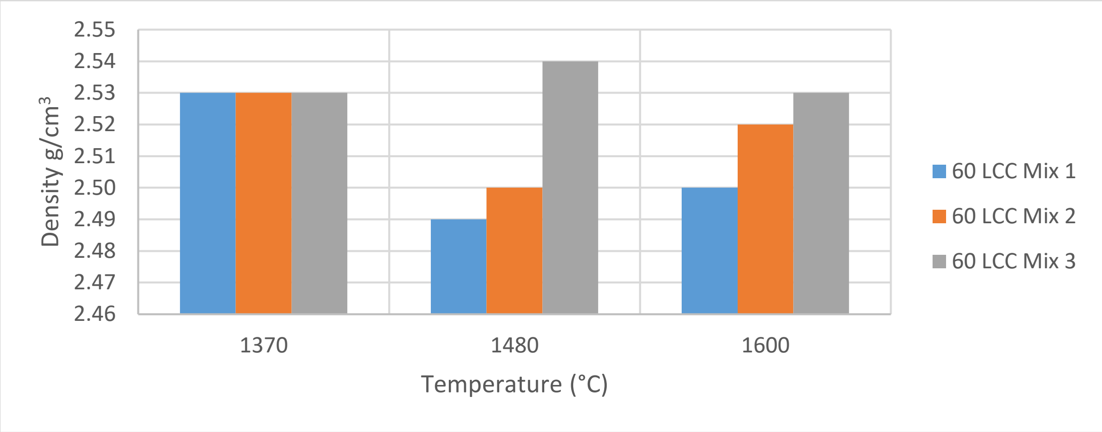
Tab. 2: Chemistry data of the castables in oxide percentages

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	Other
Mix 1	60.5	35.4	0.81	1.99	1.11	0.23
Mix 2	59.4	36.5	0.82	2.01	1.06	0.26
Mix 3	58.1	37.7	0.85	2.06	1.06	0.27

Physical Properties

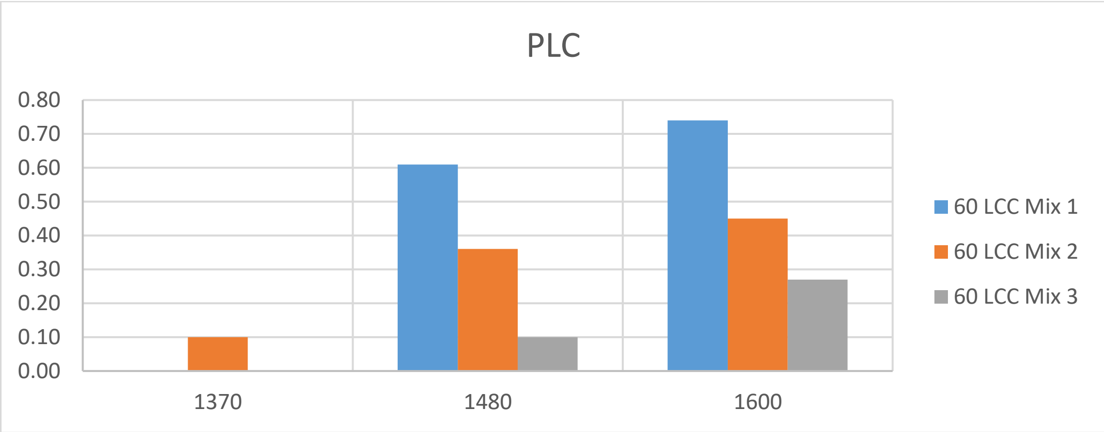
Bars of all three recipes were then fired and had their physical properties tested. The bulk density data is shown in **Figure 2**. The bulk density of all three castables was the same after firing to 1370°C. As the firing temperature increases the differences become apparent. Mix 3, the mix with the most -325 mesh kyanite, has the highest bulk density of the three mixes at both 1480°C and 1600°C. This is due to the high amount of expansion into the porosity of the refractory. This mix is also the only mix to maintain or even increase it's density with a higher firing temperature. Mix 1 and Mix 2 both had a lower density after firing to 1480°C but regained some of this value when firing to 1600°C. This decrease at 1480°C is likely due to the expansion of the 48m kyanite. Mix 1 contained more 48m kyanite thus the larger decrease in density. Evidence of this expansion into the pores was verified by looking at the apparent porosity. As the -325 kyanite increased the apparent porosity was lowered.

Fig. 2: Bulk Density



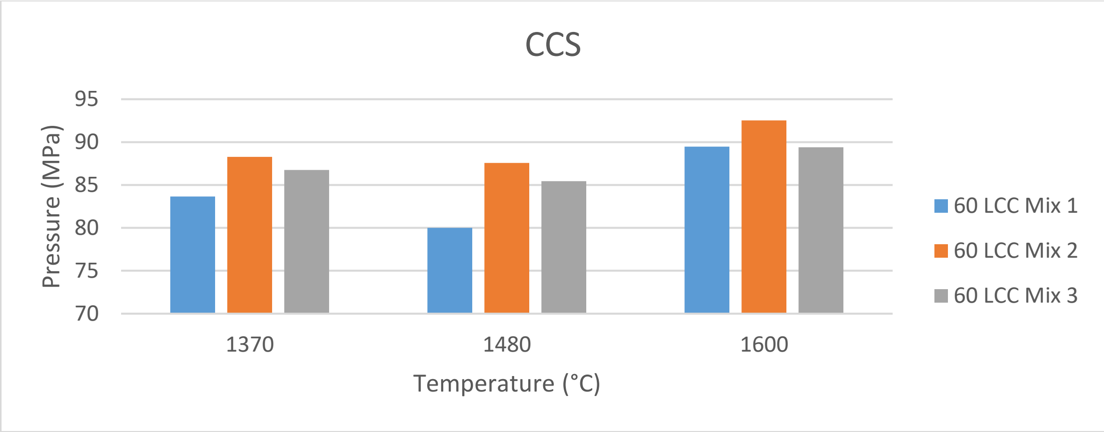
The permanent linear change (PLC) of the bars was examined. A graphical display of this data is shown in **Figure 3**. At 1370°C little to no expansion is seen. This is to be expected as this is below the temperature of expansion for kyanite. At 1480°C the expansion becomes more apparent due to the phase transformation and expansion of kyanite. All three mixes experienced further expansion when fired to 1600°C as amorphous is formed and bloating occurs. As seen in the XRD data examined later in this paper, a small additional amount of mullite is also formed after the 1600° firing. The secondary mullite formation contributes to the expansion at 1600°C. The mixes with higher amounts of 48m kyanite (Mix 1 and 2) showed the largest expansion at both of the higher temperatures.

Fig. 3: Permanent Linear Change



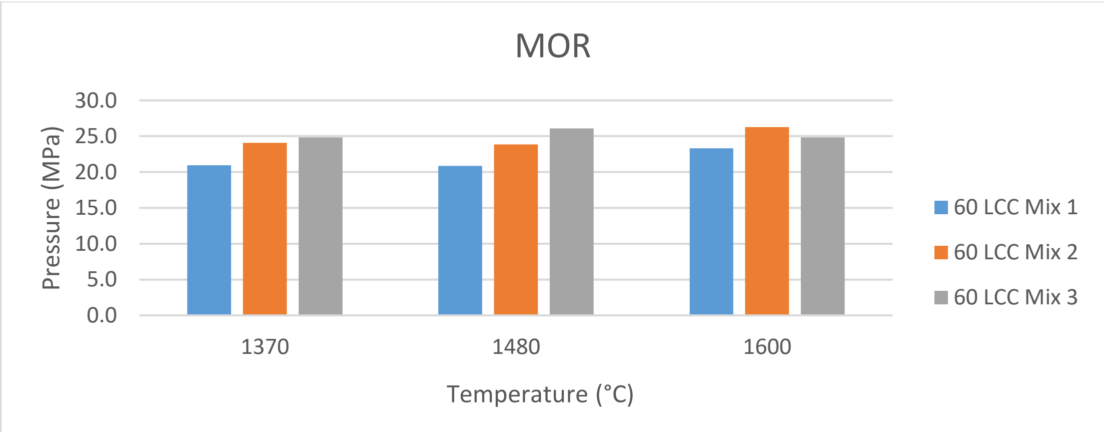
The cold crushing strength (CCS) of the mixes was then tested (**Figure 4**). The mixes containing -325m kyanite showed greater strength than the mix without at both of the lower temperatures. At 1600°C Mix 1 (89.5 MPa) actually had an almost equal CCS value to Mix 3 (89.4). Mix 3 had a lower CCS value than Mix 2 at every temperature. Mix 3 has the lowest alumina percentage and likely created the most amorphous phase when fired thus weakening of the mix. Mix 2 had the highest CCS values at all three temperatures. Previous studies on this system of mixes showed increasing strength with increasing 325m kyanite meaning Mix 3 was expected to exhibit the highest CCS values.[7] Results in this test were contradictory to our previous work and another study needs to be done to clarify the discrepancy.

Fig. 4: Cold Crushing Strength



The modulus of rupture (MOR) was the last of the physical properties tested. Results (**Figure 5**) showed higher results with an increase in the -325m kyanite. This trend is seen at all three firing temperatures with the exception of Mix 3 at 1600°C in comparison to mix 2. Gains in strength, while minimal, were seen as the mixes were fired to higher temperatures. The lower MOR values of Mix 3 at 1600°C are likely a result of the mix having the lowest overall alumina content and thus the highest amount of amorphous material present.

Fig. 5: Modulus of Rupture (3-point bend)



Phase Analysis

Each of the three mixes was examined using XRD for the presence of kyanite and corundum at all three temperatures. The goal was to determine that a) the kyanite had converted to mullite and b) to determine if there was any residual corundum or if it had been converted to mullite as well. To examine our first goal we look at **Figure 6**. This shows Mix 2 after firing to the three different temperatures. Here we can see the kyanite being converted at 1480°C. The kyanite peak at 28.0 has been highlighted for ease of viewing. Similar trends are shown in all three mixes.

We also can see from the XRD values that there is still some residual corundum in all three of the mixes even after firing to 1600°C. This can also be seen when looking at **Figure 7**. The corundum peak at 43.34 has been enlarged to show it is still present in the sample. The scan showing the highest percentage of corundum is Mix 1 with the least amount being shown in Mix 3.

Fig. 6: The kyanite peak is present at 1370°C but is gone upon conversion after 1480°C.

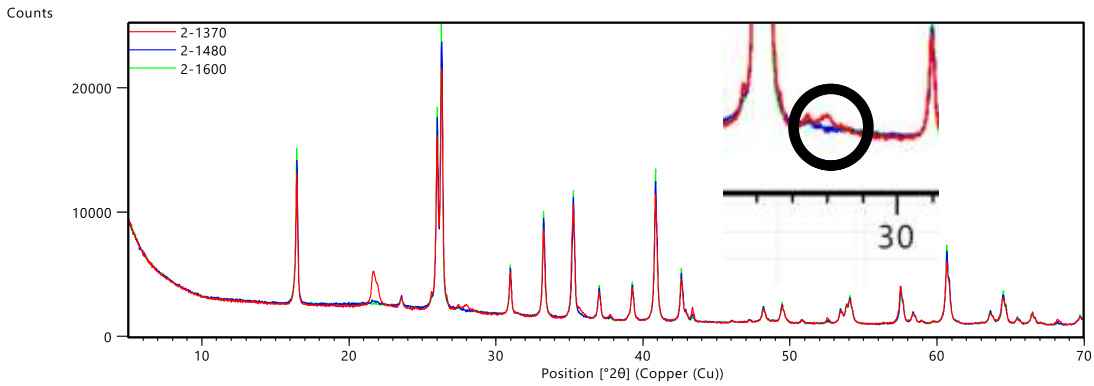
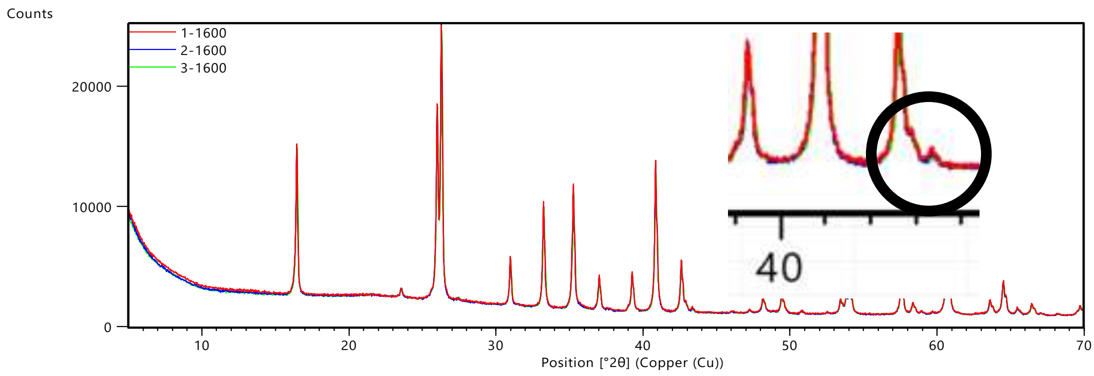


Fig. 7: XRD shows that corundum is still present even after firing to 1600°C.



All three of the mixes showed an increase in mullite as the temperature increased. This can be seen in the scans peak height and in Rietveld analysis. The largest gain in mullite percentage was seen between 1370 and 1480°C. This is to be expected as the kyanite is converting to mullite between these temperatures. A smaller gain is seen between 1480 and 1600°C. This is a clear indication that some secondary mullite is being formed in the firing process. However, as stated earlier, there is still corundum present even at 1600°C. Unfortunately, the secondary mullite formation did not completely consume all of the calcined alumina intended for that purpose. Mix 3 had the highest amount of mullite present after each of the higher firing temperatures. This is to be expected as Mix 3 contained the highest percentage of kyanite and thus the highest amount of mullite formation not associated with secondary mullite formation involving calcined alumina.

CONCLUSION

The partial replacement of calcined alumina with -325 mesh kyanite showed several advantages. Density increases were seen as -325m kyanite was introduced and allowed to expand to fill the porosity of the castable. The addition of -325 mesh kyanite also improved both MOR and CCS when the amount of calcined alumina and- 325 mesh kyanite were equal. At a higher percentage of kyanite these values lowered, likely due to the increasing amount of impurities in the castable.

Further testing would need to be done in order to determine the ratio of calcined alumina to kyanite at which the properties begin to decline. Although the overall alumina content is reduced with kyanite addition, the replacement of calcined alumina with -325 mesh kyanite appears to be beneficial. Lastly, despite popular belief, XRD analysis showed that even when firing to 1600°C calcined alumina did not completely react with silica to form secondary mullite. Replacing some of the calcined alumina with -325m kyanite guarantees the formation of mullite in the matrix.

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