Preparation of Layer Nano-Silicate/Alumina Castable Composites

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Abstract: The effect of adding nano scale particles on rheological and mechanical properties of ultra low cement alumina castables was investigated. After clay purification by mechanical methods and obtaining nano-silicate layers materials, the characterization was conducted by using XRD. Then, the produced nano-silicate particles were added to the ultra low cement Alumina castable containing microsilica and reactive Alumina. Mechanical and rheological properties of castable were studied before and after firing at 1500 ºC. The results showed that d-spacing between nano-silicate layers was about 1.2 nm. Flow ability of the castables showed an increase of 5%, indicating decreasing the presence of some filler materials such as microsilica and reactive Alumina. Finally XRD results of fired samples indicated the existence of mulite as a desired phase in the samples.

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1. Introduction

The advantages of monolithic refractories are the main driving force for increasing researchers in this area which have shown great progress. The development of low and ultra low-cement castables (LCC & ULCC) started in the late 1970s. Low and ultra low-cement castables are relatively new class of refractories. They offer various advantages over conventional refractory bricks in terms of application rate as well as cost and flexibility, making them attractive to all other industrial users [1-5]. Also, they have the great advantage of setting and hardening quickly at room temperature so they can be used for building structures as well as for patching and coating bricks. Also, they offer various advantages over conventional refractory bricks in terms of application rate as well as cost and flexibility, making them attractive to all other industrial users [6-9].

Although, Evaluation of optimum amount and proportion of micro silica to reactive alumina for using in castables yields appropriate properties such as flowability and formation of desired mulite phase, but determination of the optimum ratio is one of the main scientists encountering difficulties.

From other hand the application of nano materials in refractories researchers have recently started which might end in unexpected results. It has been indicated that by replacing a part of these cements with nano scale particles, physical and mechanical properties of these materials have improved.

Successful performance of these castables during the installation and their high-temperature properties have been attributed to the ability of fine and ultra fine particles to fill in the voids between aggregates, resulting in the higher packing density [2,3]. Due to reduced cement content and higher packing density, the water demand in high-alumina castables is decreased remarkably. Therefore, both LCC and ULCC reinforced with nano clay exhibit better physical properties than the conventional medium-cement castables [1–4, 10]. Using nano particles in castables have also investigated in a limited extend. Most of the studies have been focused on self-flowing and electrical conductivity properties, for example [11,12]. In the present work, some modified nano clay was added in one kind of ULCC castable. The influence of adding nano particles to low cement alumina castables on the flowability, cold compression strength and formation of the desired mulite phase was then evaluated and compaired with ULCC conventional castables.

2. Experimental procedure

The local sodium bentonite with the mean particle size of 75 µm was used which its chemical component is shown in Table (1).

To modify the clay, a suitable modifier of (γ) - 3-aminopropyltrimethoxysilane of Sigma Aldrich was used. XRF method (Oxford-ED2000) was used for chemical analysis. After that, the clay was purified using a 2-inch Hydrosyclon apparatus. To do so, the suspension with 3 percent solid in distilled water was prepared and passed through cyclone in 1.5 Kg/cm^2 pressure. Montmorillonite particles with less than 6 microns were dried for using in modification process. In order to have modification after clay dispersion in distilled water, suspension with 3 percent solids was prepared and different percents of modifier materials ranging from 10 to 40 percent were used. The mixtures were heated at 80°C for 6 hours. Then, the products were washed with distilled water and dried. The method of intercalation of samples was studied using X-ray diffraction (XRD system, model Brocker).

The ULCC alumina castable was composed with Chinese bauxite (Al_2O_3>%88), high alumina cement (Secar 70), reactive alumina, micro silica, poly propylene fibers (<75μm) which their chemical composition are shown in Tables 2, 3 and 4 respectively.

Table 1. Chemical compounds of benttonite consumption (results of XRF tests)

Formula	**Con %**
L.O.I	13.2
Na_2O	2.04
MgO	2.22
Al_2O_3	14.59
SiO_2	61.03
SO_2	0.37
Cl	0.46
K_2O	0.76
CaO	0.77
TiO_2	0.22
Fe_2O_3	2.09
BaO	0.11

Table 2. Chemical compounds of Chinese bauxite

properties		Value (%)
Chemical composition	Al_2O_3	>%88
	SiO_2	%6 , max
	Fe_2O_3	%1.8 , max
	TiO_2	%4 , max
density (gr/cm^3)		3.4

Table 3. Chemical compounds of high alumina cement (secar 70)

properties		Value (%)	
		Min	Max
Chemical composition	CaO	26	29
	Al_2O_3	70	-
	SiO_2	-	0.5
	TiO_2	-	-
	Fe_2O_3	-	0.5
	Na_2O	-	-
	MgO	-	0.6
Fineness	Blaine(Cm^2/gr)	4000	-

Table 4. Chemical compounds of reactive alumina

properties		Value (%)
Chemical composition	Al2O3	100-99
	SiO2	0.08، max
	Fe2O3	0.03،max
	Na2O	0.25،max
	MgO	0.04،max
	L.O.I 20-100	0.3،max
D50 (μm)		2-1
Green density (gr/cm^3)		2.7-2.5
Sinter density (gr/cm^3) $\frac{1720^\circ C}{2h}$		3.9-3.85

2.1. Sample preparation

In this research, castables were prepared from a kind of bauxite as a basic mixture (according to table. 5).

Table 5. Chemical compounds of provided Castables

Sample Cod	Castable Mixture					T.P.P
	baux ite	reactive Alumina	micro Silica	High Alumina Cement	Nano Clay	
Castable with micro silica & reactive alumina A1	86	7	4	3	-	0.12
Castable with nano clay A2	86	-	-	3	11	0.12

Castables with different particle size distributions were prepared using the Andreassen equation with n-values equal to 0.28 and maximum aggregate size of 4.75 mm. A part of castable mixture with 5wt.% water prepared and its flowability was measured by flow table (ASTM C 230). The other part poured into the moulds with vibration. After demoulding, the samples were cured for 24 h at room temperature and cured samples were dried at 110 °C for 24h. Then, they were fired at various temperatures of 1000, 1250 and 1500°C, for 2 h. Then samples were tested for cold crushing strength (C.C.S) and bulk density. Also samples were characterized for phase investigation by XRD method.

3. Results and Discussion

The results of previous research [13-15] show that conventional clay by applying a suitable purification and modification process can be used in the formulation of nanocomposites. As it is shown in XRD studies (Fig.1), most of the detrimental impurities such as Quartz, Cristobalite, Calcite, Gibbsite and Feldspar were mainly separated from clay and the final product is clay with sodium Montmorillonite as a major phase.

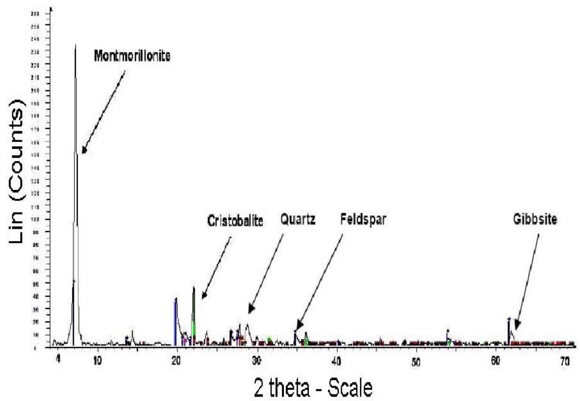

Figure 1. XRD spectrum, local pure sample

Based on Fig.2, it is obvious that interlayer spacing of 12.43Å in unmodified samples was increased to 20.43Å after modification. As it has been mentioned in the literature, the replacement of Mg with Al in Montmorillonite induces negative load in crystal which can be neutralized with sodium ions or similar ions in nature [13].

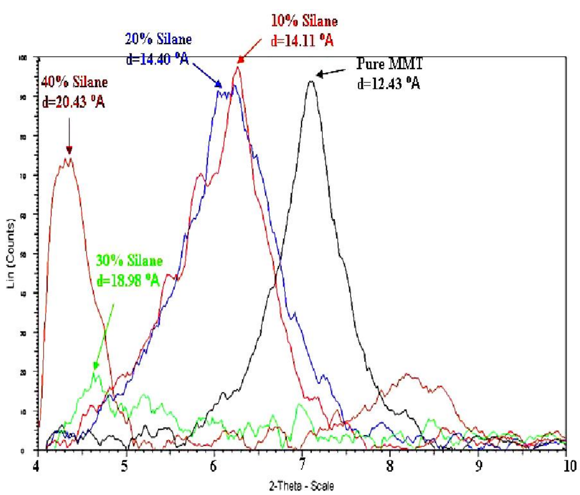

Figure 2. XRD peaks vs. Weight% of silane (For 10 to 40 wt.%)

As it is shown in the modification process, the organic compounds are placed between clay layers and the interlayer spacing was increased as a result of this process. 40 wt.% silane was selected as the optimal percent for modifier material in modification process. Using fine materials in ULCC and LCC castables causes improvement in flowability. Also, formation of suitable phases enhances compression strength and high temperature properties. Fig. 3 shows the comparison of the flowability of alumina microsilica castable (AMC) and nano clay castable (NCC).

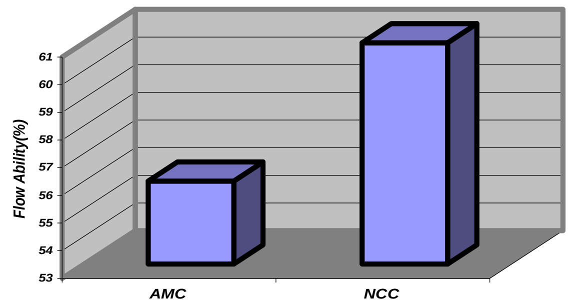

Figure 3. The comparison of AMC and NCC castable flowability

The test results revealed that the best flow was obtained for NCC castables because nano clay particles are finer than micro silica and reactive alumina as the matrix of castables.

The comparison of the effect of nano clays with microsilica and reactive alumina on castables fired in 1000, 1250 and 1500 °C is shown in fig. 4. Results indicate that NCC samples have higher strength in comparison with samples containing microsilica and reactive alumina. Based on this result, by using nano clay particles, desirable mulite phase is obtained at lower temperatures.

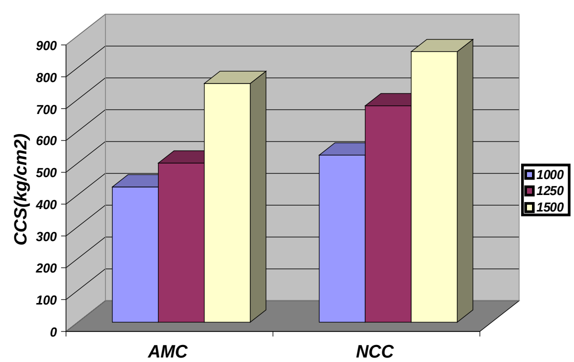

Figure 4. The comparison of the effect of nano clays with microsilica and reactive alumina on castables fired in 1000°c, 1250°c and 1500 °c

3.1. Phase investigation

Fig.5 shows X-Ray diffraction pattern of NCC and AMC castables in 1000 °C. As can be seen in fig. 5 the desirable mulite phase has higher intensity for NCC in comparison with AMC castables. As mentioned before, this phase has an important role in improving the mechanical strength and thermal shock resistance of the refractory. In NCC castables mulite forms from one material (nano clay) uniformly but in AMC castables this phase forms from two materials (reactive alumina and microsilica). So, if these fine materials don't distribute uniformly in aggregates, formation of the desire mulite phase does not occur. Mullite ($3Al_2O_3$–$2SiO_2$) rarely occurs as a mineral in nature. It is a characteristic, strong and thermo-dynamically stable product in the high-temperature solid-state reaction between silica (SiO_2) and alumina (Al_2O_3) [11,12]. Mullite has recently become a candidate as a high-temperature structural material because of its good chemical stability and excellent physical properties [12]. In low and ultra low cement concretes (LCC and ULCC), fine silica and alumina powders, contained in their matrices, lead on firing to form in situ mullite in the bond phase as a network of needles at 1300°C. The elongated needle-like mullite crystals grow and lock the structure to create a strong refractory bond system so improving the mechanical properties of the castable and strengths the microstructure of the binding matrix [4,5].

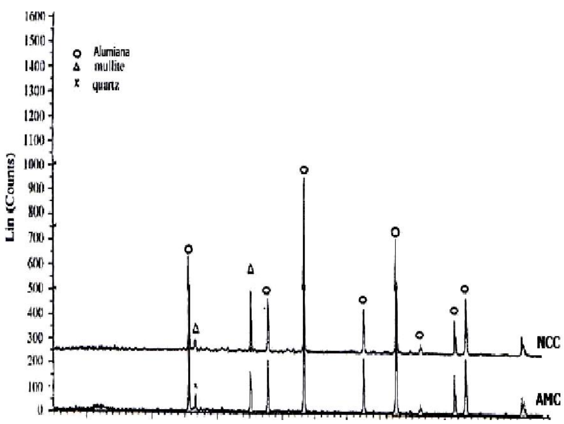

Figure 5. X-Ray diffraction pattern of NCC and AMC castables in 1000°C

4. Conclusion

The rheological and mechanical properties of nano clay castables were investigated and compared with conventional ultra low cement castables. Results indicated that as the modifier percent was increased from 10 to 40 percent, interlayer spacing was increased from 12.43 Å in unmodified sample to 20.43 Å after modification. Also, 40 Wt. % silane was selected as the optimum percentage of modifier material in modification process. Flowability of NCC castables improved about 5 % in comparison with AMC castables. Mechanical properties of NCC castables in high temperature are better than AMC castables. Finally, Using nano clays in castables lead to increasing of the desired mulite phase in fired samples.

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