COMPLEX BINDERS SYSTEMS BASED ON MINERALOGICAL HIGH REFRACTORY COMPOUNDS

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Abstract This paper aims to present the achieving a complex binder systems with high mineralogical refractory compounds. For achieving this purpose there were sintered two types of alumina cements based on CA_2 and CA_6, compounds with the highest refractoriness from the Al_2O_3-CaO system.

Keywords: calcium di-aluminate, calcium hexa-aluminate, alumina cement, complex binder systems.

1. INTRODUCTION

Binder systems are complex heterogeneous mixtures in which each of the materials used in their accomplishment has well defined properties.

Thus, for a making complex binder system, besides the main component, in this case super aluminous cement base on super high refractory compounds, must be utilize and other materials to improve properties such as e.g. workability, setting time, hydraulic properties and potential the presence of other types of bonding in addition to the hydraulic one and improve mechanical properties at ambient and high temperature, too.

But, before the achieving of the complex binder system should be studied carefully and chosen the binder matrix - the main component.

The purpose of this paper is to show how to achieve this thing, and some of the issues that must be taken into account in the achieving the cements based on high refractory mineralogical compounds as the starting point in achieving complex binder systems.

Worldwide demand for refractory materials that can be used at temperature ever higher has increased continuously. Using a material which in addition possesses a high pyroscopic and chemical resistance to different types of attack made by the gases or chemicals present at place of their use.

Regarding the super aluminous cement, it is used successfully to achieve refractory concrete with good refractory properties, but their improvement is always desirable [1].

This is the purpose of the present authors, who attempted by studying the binary system CaO-Al_2O_3, specific to the super aluminous cements, to find an alternative to cement base on CA + CA_2.

It is known the fact that in the calcium aluminates series, the increase alumina/ calcium ration of the mineralogical compounds lead on the increase of refractory properties, but in the same time a decrease in the hydraulic properties [2 - 4].

The major mineralogical compounds with refractory properties from the CaO-Al_2O_3 binary system use for industrial purpose are CA (calcium mono-aluminates) and CA_2 (calcium di-aluminates) [5]. But, in this binary system is a mineralogical compound with higher refractory properties, calcium hexa-aluminates (CA_6). However, due to high temperature at it is formed and poor binder properties, its use was restricted only as a secondary mineralogical compound in the super aluminous cement or has been used as aggregate in some super refractory concretes [6 - 8].

It is nevertheless interesting to achieve and to use on industrial scale complex binder systems with mineralogical compound that have high refractory properties. Even if their manufacturing technology would ultimately lead to a higher cost of these materials, their use over a longer period of time is convenient from an economic perspective.

2. MATERIALS CHARACTERIZATION

To carry out the first phases for achieving the complex binder systems, refractory binder matrix should be used.

To achieve this goal was chosen to carry out two super refractory cements, the first cement based on CA_2 and CA_6 and the second one based on CA_2, the latter representing cement for comparison.

The choice of super refractory cement composition was made on the consideration to obtain a refractory cement to have the high refractory property and still have hydraulic properties at room temperature [1].

To achieve this compromise, the cement composition should include in addition to mineralogical compound with the highest refractoriness from the system, CA_6 and a compound how can interact with water to form hydraulic bound, this having to be supplied by CA_2, known the fact that although the interaction with water of this compound is slower, as it leads to good mechanical strength [7].

The raw materials used to achieve the both types of cements were reactive alumina and calcium carbonate as a source of calcium oxide, both with advanced purity.

2.1 Reactive alumina

Because the presence of impurities decreases the refractory properties of the cements obtained and finally those of refractory concrete, the raw material should not have in their compositions oxides like TiO_2, Fe_2O_3, SiO_2, alkalis and elements like sulphur, even the presence of CaO is strictly limited, though this is one of raw materials [6 - 7]. All these things require the use of very pure raw materials, leading ultimately to a higher cost of product sinter.

To see if the alumina used corresponds to the intended use, it has been chemically characterized and the data obtained are presented in Table 1.

Table 1. The oxide composition of the reactive alumina

Al_2O_3	SiO_2	Fe_2O_3	Alkalis
99.50	0.15	0.20	0.15

As is it can be seen, the chosen reactive alumina is in terms of composition suitable for use in achieving super alumina refractory cements.

The presence of SiO_2, Fe_2O_3 or alkali will not affect in any way the sintering temperature or the refractory properties of the cements, it is because their presence in low enough quantities so that their influence is minimal.

Regarding the content of aluminium oxide from reactive alumina used, it is high, exceeding 99%, making it usable in making valuable alumina cements.

2.2 Calcium carbonate

As a source of CaO, calcium carbonate produced by Merker was used, purity 99.70% according to the bulletin of analysis that accompanied the product purchased, and the presentation was the chemical composition is in Table 2.

The high purity is desirable to achieve a final product in which the influence of various impurities to be undetectable, as in the case of alumina, too.

Table 2. The chemical composition of calcium carbonate

$CaCO_3$, %	Residue in CH_3COOH, %	Residue in HCl, %	Cl^-, %	SO_4^{2-}, %	Alkalis, %
99.7	≤0.2	≤0.005	≤0.005	0.03	≤1.5

3. THE ACHIEVING OF SUPER ALUMINA CEMENTS BASED ON HIGH REFRACTORY MINERALOGY COMPOUNDS

3.1 Raw material mixing

To achieve super aluminous cement based on CA_6 and CA_2, for the choice of composition of the raw materials mixture and the optimal temperature heat treatment was examined the $CaO-Al_2O_3$ binary system shown in Fig. 1.

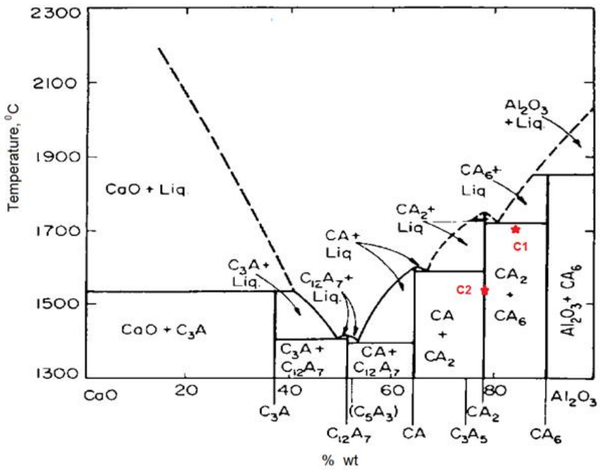

Fig. 1. The $CaO-Al_2O_3$ binary system
Note: C1 represent the composition for the clicker based on CA_6 and CA_2;
C2 represent the composition for the clicker based on CA_2.

The oxide composition specific to each type of clinchers is shown in Table 3.

Table 3. The chemical composition of super aluminous clinchers

Composition	Reactive alumina, %	Calcium oxide, %
C1	85.0	15.0
C2	74.0	26.0

The choice of optimum admixture of raw materials and heat treatment temperature are very important for achieving alumina clinkers, because each mineralogical compound is formed within a specific temperature and composition range and any deviation will lead at the movement from the optimum range.

Another very important thing for achieving quality clinker is the technological scheme followed to obtain the clinkers.

3.2 Heat treatment of the admixture of raw materials

To obtain briquettes for heat treatment, the mixture homogenate was wetted with a mixture of water and polyvinyl alcohol in 1/1.5 ratio and after that the mixture was press at a pressure of 10 MPa to bring the two precursors in a more intimate contact for the interaction to be easier. The technology scheme used for achieving the super alumina clinkers is shown in Figure 2.

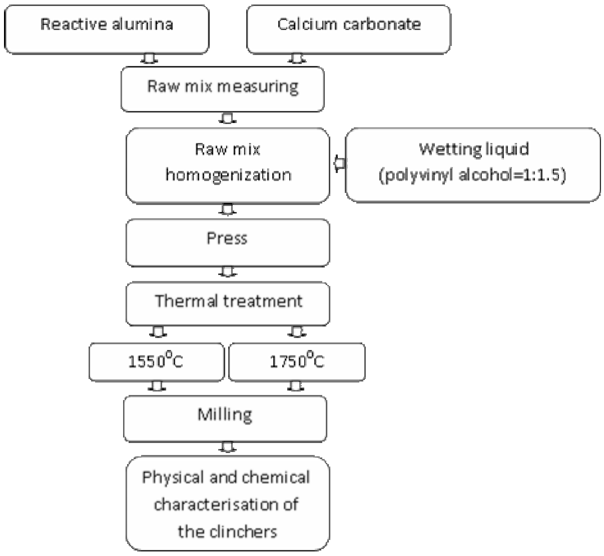

Fig. 2. The technological scheme used for achieving the super alumina clinchers

Heat treatment temperature for each type of cement was chosen after the analysis of the CaO-Al_2O_3 binary system. Thus, for the cement with main mineralogical constituents CA_6 and CA_2, the heat treatment temperature was 1750^0C, and for the second type of cement based on CA_2 was 1550^0C.

After the briquettes were subjected to heat treatment, they were ground to a specific surface of 3500 cm^2/g.

The choosing of the specific area that clinchers must be milled to obtain cements is very importance. The data from the literature of the literature indicates a specific area between 2200-2900 cm^2/g, but this area is given for the alumina cements with high reactivity, such as those based on the CA + CA_2.

In this case, because the reactivity of cements with water is not very high due to the mineralogical composition should be compensate by a high specific surface [7].

3.3 Physicochemical characterisation of the super alumina cement based on high refractory mineralogical compounds

To find out if made in clinker formed the mineralogical compounds would highly refractory properties, they were subject to investigations by X-ray diffraction and characteristic peaks for the samples obtained were compared with those from the existing databases.

For this, from the cements were taken representative samples which were then passed entirely on 90 µm sieve, to the ensemble of crystalline grains and were then subjected to X-ray diffraction.

The information obtained from X-ray diffraction of the super aluminous cement based on CA_2 + CA_6 is shown in Figure 3.

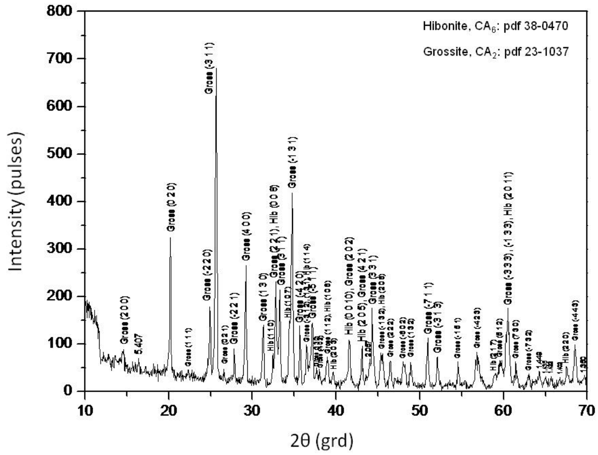

Fig. 3. The X-ray diffractogram of super alumina cement base on CA_2 + CA_6

It may be noted that in the sample were formed the high refractory mineralogical components want. In terms of intensity of the characteristic peaks of crystallized compounds can be observed that the characteristic peaks of CA_2 compound is well defined, which means that this compound is well crystallized.

This good crystallization of CA_2 is due to high temperature which has been sintered the mixture of raw materials to obtain the super aluminous cement and this because in the raw materials used to obtain the alumina clincher weren't found impurities which could affect the development of crystals or novel mineralogical compounds that could negative influent the refractoriness of the cement produced.

Regarding to the second compound present in the super aluminous cement, CA_6, the intensity of the peaks is not so great as for CA_2, which means that the crystallization of this compound isn't so great, but this is normal for this compound, the dates from the literature shows that under the temperature of 1806^0C, the temperature under which β-CA_6 form is found, this compound is well crystallized, but without the negative influences on the refractoriness [6].

In the Figure 4 is present the X-ray diffractogram which was obtained for the second cement base on CA_2.

In terms of mineralogical composition of this cement is apparent that in addition CA_2 and CA was formed, this is often meet in the sintering of this type of cement.

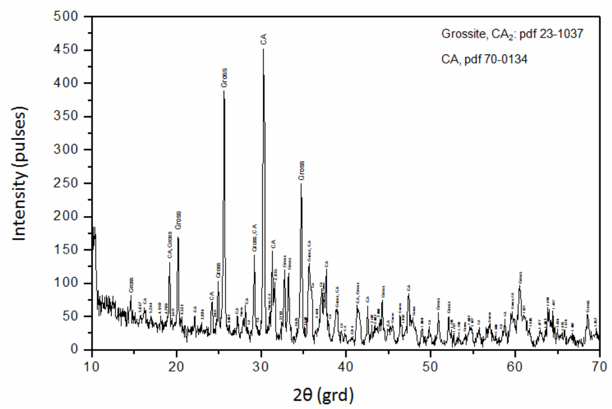

Fig. 4. The X-ray diffractogram of super alumina cement base on CA_2

This is because the kinetics of formation of the CA is faster and it is influent by the temperature. With all this, because the composition chosen for this cement is characteristic for formation of CA_2 and because X-ray analysis performed is qualitative and not quantitative, it can be concluded that the amount of CA found is small and can be negligible and will not in any way influence the behaviour of cement.

As to the CA_2 crystallization can be observed that the intensity of the peaks is large and the sharp peaks lead to the conclusion that in the cement has been a good crystallization of the mineralogical compound desired.

Thus, one can say the following characterization using X-ray diffraction that the impute purpose, that of the sintered aluminous cements base on high refractory mineralogical compounds was achieved.

Because in the cements have not been formed other mineralogical compounds than those wanted, this lead to the conclusion that refractoriness of the sintered cements will be good, but other investigations must be made for a better understating of the cements properties, like mechanical strength, porosity, etc. and of course perhaps the most important of all the behaviour of high temperature.

4. CONCLUSIONS

For carrying out the super alumina cement whit good fire resistance, high purity raw materials must be used, because is almost impossible to use natural raw materials because of their impurities.

Therefore to achieve the cements in this study were used synthetic materials, which leaded on the desire cements based on CA_2 and respectable CA_6.

However, the choice of optimum temperature and the chemical composition have also positively influenced the crystallization of these compounds.

Nevertheless, for an advanced understanding of the behaviour of the cements, further investigation may be conducted to see how it could be used for practical use of such cements.

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