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The influence of barium sulphate and barium carbonate on the Portland cement

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Abstract

Shielding of different types of radiation should be studied these days when there is a great development in the field of nuclear science. Barium ions can shield different type of radiation, therefore, by incorporation of barium ions into the system of Portland clinker, a binder with shielding properties can be made. The work is focused on influence of barium ions on the formation of Portland clinker and its properties. As a source of barium, barium sulphate and barium carbonate were added to raw meal. Clinkers and cements with a different amount of barium were prepared and the effect of barium on the clinker and cement properties respectively was studied. By Rietveld analysis (using X-Ray diffraction) and microscopic point counting method, the ratio of clinker phases was studied. With increasing amount of barium, the alite : belite ratio was decreasing and the amount of free lime was increasing. Sulphate decelerates the decreasing ratio and causes grow of alite crystals to great dimensions. The presence of barium in different phases was observed by SEM with EDS. The highest amount of barium was found in belite and clinker melt. In clinker melt, conglomerations of barium were formed. Furthermore, a difference in formation temperature of clinker phases was observed and some elementary tests were done on prepared cements according to the European standards.

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Keywords: Portland clinker; alite; belite; barium oxide; Portland cement; raw meal; barium carbonate; barium sulphate

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1. Introduction

Portland cement is a very widely used hydraulic binder all over the world mostly in construction. Appropriate batching and mixing with water and aggregate causes high strength and long-term volume stability after hardening. Properties of this mortar or concrete depend mostly on clinker phase composition which is influenced by foreign ions in raw meal, among other things. This work is focused on the influence of barium compounds on the formation of Portland clinker and Portland cement respectively.

Cement with a content of barium could be used as a binder resistant to different types of radiation. Nowadays, other shielding materials are common such as leaded glass or a plate of lead. However, for some applications lead is not the best choice. To protect a whole building or to build a shelter resistant to radiation would be easier and less destroyable to use concrete with barium.

A small research on clinker with a content of barium has shown the effect of barium ions on clinker composition. If barium ions are a part of raw meal, barium incorporates into crystal lattice of alite, belite and interstitial phase. Some authors found no barium in ferrite, only in tricalcium aluminate [1]. Due to a different crystal lattice of clinker minerals, different amount of barium ions can substitute calcium ions or only incorporate into the lattice. Belite lattice can incorporate more foreign ions than alite lattice. The ratio of barium in alite and barium in belite remains the same at different percentage of barium in clinker [2].

Juel et al. [2] studied presence of BaO in clinker minerals and they found that the highest content is present in belite and melt, in alite there is only a small amount. The amount of BaO increases in every mineral linearly with increasing content of BaO in the whole clinker. Ba^{2+} ions substitute Ca^{2+} ions and an appropriate amount of free lime is formed. However, after exceeding a certain concentration of BaO, barium ions inhibit crystallization of alite or decompose alite in favour of belite and free lime.

Some authors were looking for a miscibility limit of barium in alite, Kurdowski and Wollast [3] determined it as 2.96 wt. % at 1600 °C. Appendino and Montorsi [4] tried another way by finding composition of compound formed at 1450 °C ($Ca_{1,86}Ba_{0,14}SiO_4$), and they established that tricalcium silicate is not capable of dissolving quantities of BaO far in excess of 1 mol % (1.99 wt. %). Katyal et al. [1] prepared samples of pure alite and its solid solutions with different amount of BaO. Free lime increases slowly with increasing amount of barium in these samples up to a certain amount of BaO, after 1.85 wt. % free lime starts to increase rapidly. By recalculation of wt. % to mol %, it is clear that Ba^{2+} ions substitute Ca^{2+} ions up to around 1.85 wt. % of BaO in the sample. At higher values of BaO, alite formation is inhibited or it causes alite decomposition with formation of free lime and belite.

Addition of barium induces changes in crystal structure. Barium ions are much bigger than calcium ones (1.43 Å and 1.06 Å respectively.), thus dimensions of crystal lattice are changed. 0.1 – 4 wt. % of BaO in alite stabilizes other polymorphic modifications, consecutively T_1, T_2 a M_1 [1]. In belite structure, high temperature modifications are more stable, firstly α' (α_L' and α_H') then α [2].

A small amount of BaO raises strength of concrete after 28 days due to higher reactivity of C_2S. With 0.3 wt. % BaO, the strength increases by 20 %, 0.5 wt. % causes higher strength by 10 % and with 0.7 wt. % BaO, there is no change in reactivity [5].

BaO exists only as a part of a compound, in this work, $BaCO_3$ and $BaSO_4$ is used. Therefore, the clinker is influenced by the whole compound. Pure barium carbonate decomposes around 1098 °C [6], BaO is probably present in mineral formation separately without CO_2. Pure $BaSO_4$ melts first around 1580 °C, $BaSO_4$ influences probably mineral formation as a whole compound or with an effect of SO_3 [7].

SO_3 in raw meal regulates modification and percentage of alite in clinker. Usually, alite is present in industrial clinker in M_1 or M_3 modification or its mixture. The presence of SO_3 stabilizes M_1 modification and with a low alkali content, alite : belite ratio decreases and crystal size of alite grows [2,8,9]. Substitution of silica ions for sulphate ions is four or five times easier in belite than alite and it is accompanied by two aluminium ions. AlO_4^{5-} and SO_4^{2-} substitute SiO_4^{4-}. With higher amount of sulphate ions, content of belite increases so as incorporation of aluminium ions [10]. Simultaneously, amount of C_3A is reduced [10,11]. The effect of SO_3 can be compensated by MgO or alkalis (Na_2O and K_2O) [8,9,10].

The difference in mineral ratio has an effect also on cement quality. Cement with low alite, tricalcium aluminate and alkali content gains its strength slower, however, it has better sulphate resistance [10,11].