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Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash

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ABSTRACT

The effect of minor additions of limestone powder on the properties of fly ash blended cements was investigated in this study using isothermal calorimetry, thermogravimetry (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) techniques, and pore solution analysis. The presence of limestone powder led to the formation of hemi- and monocarbonate and to a stabilisation of ettringite compared to the limestone-free cements, where a part of the ettringite converted to monosulphate. Thus, the presence of 5% of limestone led to an increase of the volume of the hydrates, as visible in the increase in chemical shrinkage, and an increase in compressive strength. This effect was amplified for the fly ash/limestone blended cements due to the additional alumina provided by the fly ash reaction.

1. Introduction

Adding 5% limestone powder to Portland cement has been a point of discussions in the past. Proponents put forward energy savings during production, without impairing the quality of the cement and concrete properties. Whereas the opponents claim that limestone powder is merely an adulterant, leading to a reduction in quality [1,2]. One of the first incentives to allow carbonate additions to Portland cement was given by the oil shortage in the 1970's–1980's. This led to an adaption of the Canadian standard CAN3-A5-M83 permitting 5% limestone powder in Portland cement since 1983, followed by the Brazilian norm NBR-5732 adapted in 1988. The rising focus on greenhouse-gasses in the 1990's added to the motivation and in 2000 the proposal for the European standard EN 197-1 (CEN 2000) was accepted, followed by the ASTM C150 in 2004 and the AASHTO M85 in 2007.

A thorough review on the use of limestone powder in Portland cement is given by Hawkins et al. [3]. The effect of 5% limestone powder addition on short and long term macroscopical properties is generally small. Regarding the compressive strength, both enhanced strength and reduced strength have been reported upon limestone addition. A benefit of the addition of small amounts of carbonate is a reduction of the expansion observed upon sulphate attack, which is most prominent for cements with high C_3A-content [3,4]. It also leads to a reduction of the optimal gypsum content, which may result in a reduction of raw material costs. Some of the beneficial effects of limestone powder are attributed to its filler effect. Some researchers report an acceleration of the C_3S and an incorporation of the calcium carbonate into the C–S–H [5,6]. Additionally, limestone is known to interact with AFm and AFt phases. In an ordinary Portland cement without limestone powder, the C_3A and at a slower rate also the C_4AF will react with the calcium sulphate to form ettringite ($C_3(A,F)\cdot 3CaSO_4\cdot 32H_2O$). Upon depletion of the sulphates, the remaining C_3A and C_4AF will react with the ettringite to form monosulphate ($C_3(A,F)\cdot CaSO_4\cdot 12H_2O$) or hydroxy-AFm solid solution. In the presence of limestone, the AFm-carbonate equivalents such as monocarbonate ($C_3(A,F)\cdot CaCO_3\cdot 11H_2O$) are formed rather than the sulphate containing AFm phases. The AFt-carbonate equivalent has been observed by some researchers [7], but it is unlikely to form in a significant amount at ambient temperatures in a hydrating cements as it is less stable than the AFm phases [8,9]. The decomposition of ettringite to monosulphate when reacting with the remaining C_3A and C_4AF upon sulphate depletion is prevented as monosulphate is less stable than monocarbonate in the presence of limestone. The stabilisation of the voluminous, water rich ettringite instead of the less voluminous monosulphate, gives rise to an increase of the total volume of hydration products [10–13]. If some of the beneficial macroscopic effects observed for limestone additions up to 5%, are due to this chemical interaction, it is obvious that the impact will be greater for cements with a high C_3A and C_4AF content as observed by previous investigations [2].

The previous statements and observations brought the idea to investigate the effect of limestone powder additions on blended fly ash cements. Fly ash has generally higher alumina content than OPC. The reaction of fly ash brings additional alumina, which reduce the

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