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A sorption balance study of water vapour sorption on anhydrous cement minerals and cement constituents

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ABSTRACT

The phenomenon of water vapour sorption by powdered cement constituents exposed to different relative humidities and temperatures was studied. The individual clinker phases C_3S, C_2S, C_3A, C_4AF, calcium sulfates and CaO were tested. Using a water sorption balance, the amount of chemically and physically sorbed water per unit of surface area of the powders and the relative humidity at which water sorption starts to occur on the phases were determined. Various cement clinker phases prehydrate very differently. CaO and C_3A were found to be most reactive towards water vapour whereas the silicates react less. CaO starts to sorb water at very low RHs and binds it chemically. Beginning at 55% RH, orthorhombic C_3A also sorbs significant amounts of water and binds it chemically and physically. Water sorption of C_3S and C_2S only begins at 74% RH, and the amount of water sorbed is minor. Calcium sulfates sorb water predominantly physically.

1. Introduction

The phenomenon of water vapour sorption by cement powders exposed to humidity is known as prehydration of cement. Industrial cements may undergo some prehydration already during the manufacturing process. There, a first contact with water can occur in the mill where clinker is ground together with gypsum at elevated temperature (90–120 °C). Under these conditions, gypsum dehydrates and releases water which can react with the clinker. Furthermore, cement producers sometimes lower the milling temperature by spraying e.g. 2% of water into the mill. Even during storage in the cement silo where temperature may get as high as 70–80 °C, prehydration may proceed due to the continuous release of water from the interground gypsum as long as the temperature exceeds 42 °C [1]. Therefore, cement may already be prehydrated before it is delivered to the customer. Thus, the properties of cement can fluctuate considerably, depending on its history of manufacture and storage.

After delivery and in industrial use, cement may be further stored for several months or even a year before usage. For dry-mix mortars, for example, the usual shelf life is 6 months to 1 year, as stated on the bags. Alteration of the cement properties during storage is highly undesirable, but has been repeatedly noticed by users [2–5]. Such phenomenon may lead to cement failure and is prevalent in climates characterized by relatively high temperature and humidity. The principal consequences of prehydration for the engineering properties of cement are increased setting time, decreased compressive strength and heat of hydration, altered rheological properties and poor response to superplasticizer addition [6–9].

In particular, the surface composition of the individual clinker phases may be affected due to prehydration. Thus, the quality of cement must be assessed based on a profound understanding of the processes occurring during its fabrication and storage. Despite its importance, due to its complex nature and the difficulties associated with the analysis of hydration layers which extend to only a few nanometers in thickness, prehydration of cement is not well understood from the aspect of the interdependency of numerous chemical reactions. Obviously, prehydration of cement is far more complex than the sum of each individual prehydration reaction. Thus, this study on prehydration of pure clinker phases was performed to provide an understanding of the key processes taking place during sorption of water in the complex system of cement.

Ordinary Portland cement (OPC) consists of several clinker phases. The main constituents are variants of: calcium silicates (Ca_3SiO_5 and Ca_2SiO_4), calcium aluminate ($Ca_3Al_2O_6$), and ferrite ($Ca_4Al_{4-x}Fe_xO_{10}$) which are commonly denominated as C_3S, C_2S, C_3A and C_4AF, respectively. Jensen et al. showed that the clinker minerals C_3S, C_2S and C_3A have fundamentally different sensitivities to moisture [10]. For example, C_3A was shown to hydrate at lower relative humidities than either C_3S or C_2S. However, while some factors that govern clinker reactivity towards water vapour such as e. g. the free energy of the mineral's surface are known [11], we still lack in a complete understanding of the mechanisms by which certain cement components are more sensitive to prehydration than others.

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