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A preliminary study of the influence of ions in the pore solution of hardened cement pastes on the porosity determination by low temperature calorimetry

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ABSTRACT

Thermodynamic modeling was used to predict the ionic concentrations in the pore solution of cement pastes at different temperatures during a freezing and melting measurement in low temperature calorimetry (LTC) studies. By using the predicted ionic concentrations, the temperature depressions caused by the ions presented in the pore solution were determined. The influence of the freezing/melting point depression caused by the ions on the determined pore size distribution by LTC was demonstrated. Thermodynamic modeling using the program PHREEQC was performed on the cylinder and powder samples of cement pastes prepared by two types of cements, i.e., CEM I 32.5 R and CEM III/B 42.5 N. Using the modeled ionic concentrations, the calculated differential pore size distributions for the studied samples with and without considering the temperature depression caused by the ions in the pore solution were compared. The results indicate that for the studied cement paste samples, the influence of the temperature depression caused by the presence of the ions in the pore solution on the determination of the pore size distribution by LTC is limited.

1. Introduction

Water confined in small pores freeze at lower temperatures compared with that of bulk water. The depressed freezing/melting point of water/ice due to pore confinement is related to the size of the pores [1]. Taking a porous material saturated with water as an example, the water confined in the material will gradually freeze accordingly to the pore sizes (assuming the material has several different pore sizes) as the temperature decreases. Similarly, the ice confined in the pores of the material will gradually melt as the temperature increases. As the freezing of water is an exothermic process and the melting of ice is an endothermic process, the heat flow evolution during the freezing and melting process can be recorded by calorimetric devices. Hence, the ice content can be estimated from the recorded heat flow in such a measurement. With the calculated ice content and the thermodynamic relation between pore size and the depressed freezing/melting point combined with other important assumptions, it is possible to determine the pore size distribution for the studied material. This is the principal concept of a method for porosity characterization, i.e., low temperature (micro-)calorimetry or LTC (also known as thermoporometry) [2]. This method was pioneered by researchers in a study of organic gels as early as in the 1950s [3] and later the method was generalized and proposed to be used for different materials, e.g., soil [4] and inorganic materials [5]. In recent years, LTC has experienced further development and it has been used to study many different types of porous materials [6].

The pore system in cement based materials is rather complicated, with the pore sizes ranging from nanometers to millimeters [7,8]. Porosity is an important parameter for cement based materials, because it influences, e.g., the strength, the shrinkage, the transport properties or permeability and the durability [9] of the materials. Moreover, the characteristics and properties of the pores are important in the modeling and understanding of some important processes for cement based materials, e.g., drying shrinkage [10], carbonation [11,12] and moisture transport [13,14]. For these reasons, an accurate characterization of the porosity for cement based materials is of great importance. LTC has been used to study cement based materials, e.g., in [15,2,16]. A major advantage of using LTC to characterize cement based materials, compared with the traditional methods developed for porosity characterization, e.g., mercury intrusion porosimetry (MIP), nitrogen

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adsorption/desorption (NAD) and scanning electron microscopy (SEM), is that the measurements can be conducted on virgin samples without any drying treatment [16–18]. The drying treatment often results in an alteration of the pore structure for cement based materials [19,20]. It should be mentioned that due to the fact that the liquid present in very small pores does not freeze and that the freezing/melting point depression of liquid in big pores is too small, the pores that can be studied by LTC are limited mainly to those with radii from about 2 nm to about 40 or 50 nm [21,16]. Water in larger pores is monitored, but the resolution is too limited to allow for determination of the actual pore size. Meanwhile, as an indirect method to study porosity, the analysis of the measured LTC data is not that straightforward. More related discussions can be found, e.g., in [22,23].

Extensive studies have been conducted with respect to the analysis of LTC data using pure water as the probe liquid, e.g., see [1,24–26,21]. However, the analysis of LTC data measured on cement based materials is complicated due to the fact that the pore liquid is not pure water but contains different types of ionic species [9,27]. Compared with the freezing/melting of pure water/ice, the presence of ionic species in a pore liquid may mainly cause two effects which would have important impact on the analysis of LTC data. Firstly, the freezing/melting point will be further depressed, depending on the ionic concentration of the pore solution. The temperature depression caused by ions can be predicted if the ionic concentration of the pore solution is known, e.g., see [28,29]. Secondly, the heat of fusion of the pore solution might be different from that of pure water. It has been demonstrated that the heat of fusion of a pore solution depends on the ionic concentration and the types of ionic species but the exact relation is not clear, e.g., see [30]. That is, even if the ionic concentration and the ionic species of a pore solution are known, the heat of fusion of the pore solution still might not be predictable. The main purpose of this work is to try to study the impact of ions present in cement pore solution on the porosity determination by the LTC method.

One may argue that the impact of ions on the freezing and melting behaviors of the pore solution of cement based materials can be studied by using a model material with a simple pore structure. An artificial cement pore solution can be prepared and used to saturate the model material. By comparing the freezing and melting behaviors of pure water and an artificial pore solution in the same type of model material, the impact of the ions can be studied. However, it should be mentioned that an important characteristic of the pore solution of cement based materials is that the pore walls (cement hydrates) have a great buffering capacity as demonstrated in thermodynamic modeling studies, e.g., see [27,31,32], i.e., ions will precipitate when the concentrations in the pore solution are higher than saturation for the considered reactions and ions will diffuse from the cement hydrates into the pore solution if the concentrations are lower than the saturation of the reactions considered. The implication is that the freezing of a pore solution of cement based materials may not be able to be represented or related to the freezing of an artificial cement pore solution in a model material. There is no buffering effect, as described above between pore walls of a model material, e.g., the mostly used silica gels or porous glass, and the artificial pore solution. The artificial cement pore solution in a model material will become more and more concentrated as water freezes out, since the salts are not likely to be included into ice crystals [33,34], while the ionic concentration of pore solution of cement based materials might not change that much during freezing depending on the chemical interaction with the cement hydrates. Consequently, the ionic concentration of the artificial pore solution in a model material may differ significantly from the pore solution as more water freezes out in the case of cement based materials, even though the initial concentrations are about the same. Thus, studying the freezing behavior of an artificial cement pore solution in model materials may not necessarily give useful information in the process of understanding the impact of ions on the freezing behavior of the pore solution in cement based materials.

It is noted that in order to minimize the influence of the ions in the analysis of LTC studies, the preconditioning of cement based samples by curing them in a big amount of (lime)water for a relatively long time has been suggested, e.g., see [15,16]. In this approach it is assumed that the alkalies leach out of the sample and then allowing the pore liquid to be approximated to be dilute. Consequently the freezing of the diluted pore solution could be assumed as that of pure water [16]. However, a LTC experimental study compared the freezing and melting behaviors of the pore solution of cement paste samples preconditioned in a big amount of saturated limewater for a relatively long time and in a small amount of limewater [35]. The results showed limited difference. That is, it is questionable whether the preconditioning is effective enough. It should also be remarked that the leaching process may result in some changes of the porosity of the studied cement based materials, e.g., see [36,37].

The difficulty to directly determine the impact of ions in cement pore solution on the freezing and melting behaviors by experiments is realized. Thermodynamic modeling is a very useful tool and it has been applied to cement science very successfully, e.g., see [38,27,39,31,40,41]. In this work, a preliminary study is conducted to explore the ionic concentrations in the pore solution of cement pastes at different temperatures during freezing and melting measurements in LTC studies. By assuming chemical equilibrium and using experimental LTC data, thermodynamic modeling is used to predict the ionic concentrations in the pore solution of cement pastes. With the predicted ionic concentrations, the temperature depressions caused by the ions can then be determined. The main focus of this work is to demonstrate the influence of the freezing/melting point depression caused by the ions in the pore solution of hardened cement pastes and how this affects the determined pore size distribution.

2. LTC study and results

2.1. Materials and calorimetric measurements

Two types of cement, i.e., CEM I 32.5 R and CEM III/B 42.5 N, were used to prepare the cement paste samples used in this study. The chemical composition of the cements are shown in Table 1. The water-to-cement ratio was 0.4 for all the pastes prepared. The fresh paste samples were mixed by a paddle mixer. After mixing, the fresh pastes were cast into cylindrical plastic vials ensuing proper compaction. The dimension of the plastic vials was about ϕ15 mm × 50 mm. The hardened cement paste samples were demolded after one day of sealed curing at room temperature (about 20 °C) and then placed into slightly bigger plastic flasks (∼ϕ25 mm × 60 mm) filled with saturated limewater for curing at room temperature. CEM I and CEM III are designated to describe the hardened cement pastes in the following description.

Both cylinder and powder samples of the cement pastes were studied. To obtain the powder samples, the cylinder samples as prepared were used. The cylinders of cement pastes were firstly vacuum saturated with saturated limewater and then the crushing and grinding of the samples was conducted in a carbon dioxide free chamber to avoid carbonation. After that, the ground paste powders (passed through a 315 μm sieve) were placed into the plastic vials (with dimension of ϕ15 mm × 50 mm as mentioned earlier, which are used as sample holders) till about half the volume and then saturated limewater was added to immerse the powders. This procedure was also conducted in the carbon dioxide free chamber. In