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Communication

Volume stability of calcium hydroxide in aggressive solutions

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Abstract

The role of calcium hydroxide in processes affecting the durability of concrete exposed to aggressive media was examined. Compacted calcium hydroxide specimens were immersed in various solutions including $MgCl_2$ and $MgSO_4$ and length changes were continuously monitored. The view that the formation of crystalline phases in cement systems is in itself not an a priori condition for expansion is discussed. Evidence for a dissolution/precipitation-based expansive mechanism is presented. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Mechanisms associated with deleterious reactions and the inherent volume stability of cement-based materials exposed to aggressive media have been the subject of much recent argument [1]. A recent comprehensive review by Brown and Taylor [2] summarizes eclectic views concerning the performance of concrete in sulfate solutions. It is apparent that no theory for expansion of cement systems in sulfate solutions is universally accepted.

Calcium hydroxide is present in cement systems in amounts up to about 26% by volume. Processes involving leaching and dissolution of calcium hydroxide in cement-based materials have been considered in durability investigations [3]. The possibility that the dissolution of a crystalline phase, e.g., $Ca(OH)_2$ is a significant factor contributing to expansion is examined in this study.

2. Compacts of calcium hydroxide as structural models

The use of compacted powders of unhydrated or hydrated cement minerals including calcium hydroxide to form solid bodies for use in studies of engineering behavior is now well established [4–6]. For example, both the modulus of elasticity and hardness of calcium hydroxide and cement paste are dependent on porosity. The log mechanical property — porosity relation for cement paste (in situ hydrated), ground and compacted cement paste and compacts of bottle hydrated cement and calcium hydroxide are colinear at porosities in the range of 20–50%. It is apparent that the bonds formed during the hydration reaction are similar to those formed by compaction. It is suggested that conclusions drawn from the performance of compacted cement minerals including calcium hydroxide can be considered representative of those obtained on normally hydrated materials.

3. Experimental

3.1. Materials

Calcium hydroxide: Reagent grade calcium hydroxide powder was used to fabricate all compacted specimens.

Reagents: Reagent grade ammonium nitrate, magnesium chloride, magnesium sulfate and sodium chloride were used to prepare the aqueous test solutions.

3.2. Compacts

Porous bodies in the form of circular discs (32-mm diameter × 1 mm thick) were prepared by powder compac-

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tion of calcium hydroxide at 170 MPa. The porosity of these samples (determined by helium pycnometric methods) was about 27%.

3.3. Length change measurements

Prisms (5 × 25 × 1 mm) were cut from the compacted disc samples and mounted on modified Tuckerman extensometers (accurate to one microstrain). These were placed in the test solutions (so that the specimens were completely immersed) and length change measurements were monitored continuously. The aqueous salt solutions were prepared at concentrations of 60 and 180 g/l.

4. Results and discussion

Length change versus time curves for the calcium hydroxide compacts immersed in the test solutions are presented in Fig. 1(a) and (b). The compacts immersed in saturated NH_4NO_3 solution expanded more than 0.8% in the first 5 min. At 1 h, expansions of the compacts immersed in the other test solutions ranged from 0.8% for the $MgCl_2$ (180 g/l) solution to approximately 0.08% for the $MgSO_4$ (180 g/l) solution. Expansions were in the following order: $MgCl_2$ (180 g/l) > $MgCl_2$ (60 g/l) > distilled H_2O > NaCl (180 g/l) > lime-saturated water > NaCl (60 g/l) > $MgSO_4$ (60 g/l) > $MgSO_4$ (180 g/l).

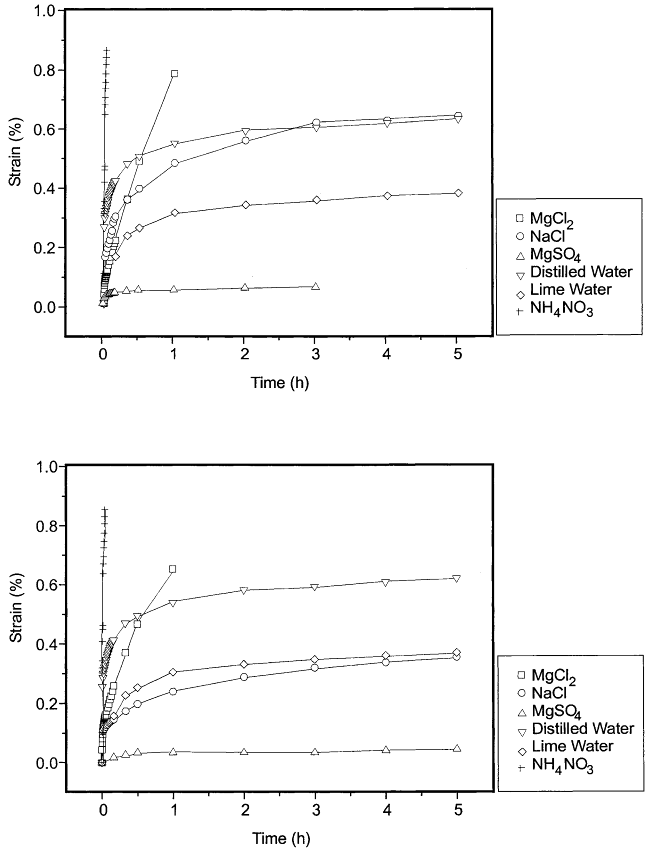

Fig. 1. (a) $Ca(OH)_2$ compacts in various solutions (180 g/l). (b) $Ca(OH)_2$ compacts in various solutions (60 g/l).

Expansions of porous glass specimens exposed to NaOH solutions of various concentrations (0.4 to 3.2 M) have been attributed to the change in surface free energy of the glass [7]. Similarly, expansions of cement paste immersed in 1.0 N aqueous HCl are ascribed to the strain energy release on dissolution [8]. Contractions were sometimes observed after initial expansions. This was, for example attributed to the adsorption of the reaction products on the undissolved glass [7]. The adsorption was considered concentration dependent. The reaction products apparently protected the glass from further alkali attack.

The calcium hydroxide compacts expanded in all of the test solutions. It is suggested that dissolution of this important component of hydrated cement systems is intrinsically expansive. Expansion of the compacts in saturated calcium hydroxide solution is apparently anomalous as dissolution should not occur. The possibility of a double-layer effect in this solution is being investigated (using NMR techniques) by the authors.

The solubility of calcium hydroxide (using the Reardon simulation [9]) in aqueous salt solutions over a wide range of concentration was in the following order: $MgSO_4$ > $MgCl_2$ > NaCl. Precipitates identified included: brucite and gypsum ($MgSO_4$ solution); brucite and calcium oxychloride at high solution concentrations ($MgCl_2$ solution).

The order of the expansion indicated earlier was not in the order of the respective solubilities. In fact, immersion in the $MgSO_4$ solution gave the lowest expansion in spite of having the highest solubility with respect to calcium hydroxide dissolution. This can be explained by the possibility of competing forces between the dissolution of the calcium hydroxide (expansive) and the coating of calcium hydroxide particle surfaces with reaction products, e.g., brucite and gypsum (contractive). This process is rate of dissolution and concentration dependent. It also likely depends on the nature of the precipitate. Hence the net length change effect varies with solution type and results in larger observed expansions for immersion in $MgCl_2$ solution.

The significance of these relatively large expansions becomes clearer when the sorption characteristics of calcium hydroxide compacts are considered [10]. The water sorption isotherm is a normal type II isotherm. The weight change isotherm exhibits both primary and secondary hysteresis. The length change isotherm clearly indicates that by 40% RH most of the length change (about 0.16%) has taken place. The length change versus weight change curve is linear up to about 35% RH where one to two molecular layers are adsorbed. This linear behavior has been observed for adsorption of water on porous glass, calcium carbonate, calcium sulphate hemihydrate and hydrated portland cement. This is taken to indicate that the length change up to 35% RH is due largely to physical adsorption. The calcium hydroxide compacts in this study were conditioned at a relative humidity of about 45% RH before exposure to the various test solutions. This means that the measured length changes upon immersion in the test solution are in addition to those already experienced at 45% RH.

5. Conclusions

(1) Crystalline hydration products (in hydrated cement systems) such as calcium hydroxide are sources of potential expansion when immersed in chloride and sulfate solutions.

(2) The mechanism of expansion of cement-based materials immersed in sulfate solutions may be based on a dissolution/precipitation process involving existing crystalline phases, e.g., calcium hydroxide.

(3) The magnitude of the expansion of calcium hydroxide solids in chloride and sulfate solutions does not appear to correspond to their relative solubility in these solutions. Rather the process of expansion appears to be influenced by both the solubility and the nature of the reaction products, which may impede further dissolution.

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