JOURNAL OF MATERIALS SCIENCE **38** (2003) 4957–4964

The use of compacts for durability investigation of cement-based materials

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Compacted specimens of ground hydrated Portland cement paste, brucite, gypsum, sodium chloride and table sugar were immersed in various solvents. The volume stability of the compacts was compared to that of non-compacted materials in the form of insitu hydrated Portland cement paste, single crystals of brucite and gypsum, and polycrystalline sodium chloride. Immersion in the various solvents resulted in the dissolution of the test samples. In all cases, dissolution was accompanied by an expansion of the material. The expansive behaviour of all systems and the suitability of using compacts as models for durability studies are discussed.

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1. Introduction

The volume stability of hydrated Portland cement and concrete is central to durability issues concerning exposure to aggressive media [1]. Disruptive expansions often occur in concert with deleterious reactions between hydrated cement phases (or cement minerals themselves) and ions in the pore solution present as a result of various transport processes [2]. Mechanisms of expansion due to reactions with specific ions, e.g., sulfate and chloride, have been extensively discussed in the literature [1, 3]. Actual degradation theories have focused on mechanisms occurring at the micrometer scale. In most cases, the deleterious expansions are attributed to pressures originating from the formation of crystalline phases such as ettringite and gypsum.

Numerous investigations have clearly emphasized the fact that the formation of new expansive phases may not be the sole cause of the volume instability of hydrated cement systems in contact with chemically aggressive solutions. For instance, a theory of expansion developed by Litvan [4, 5] attributes expansion to the solid dissolution process itself. That author has reported that porous solids, e.g., Vycor® glass, expand significantly when exposed to sodium hydroxide (0.1 M to 6.4 M) solutions [5]. Similar results were obtained for hydrated cement paste samples immersed in (1 N) hydrochloric acid and ethylene glycol [4]. Expansion was associated with dissolution of the glass and cement paste. The volume stability data for the porous silica glass reported by Litvan is relevant to this work. The length changes of 3-mm thick porous glass specimens exposed to sodium hydroxide solutions of various concentrations are reported [5]. Generally there is an initial expansion sometimes followed by a contraction and subsequent large expansion. Expansion values can exceed 0.3% depending on solution concentration and exposure time.

Possibilities for the cause of dimensional changes occurring on dissolution were:

- changes in surface free energy of the glass;
- a non-homogenous distribution throughout the pore-held solution leading to the generation of osmotic-like pressures;
- disjoining pressure due to double-layer effects;
- stress effects due to leaching;
- precipitation of products in spaces vacated by dissolved solids.

Arguments were presented in favour of surface energy changes as a major contributor to expansion. Adsorption of reaction products during the dissolution experiments can account for the observed contractions.

Litvan's work was extended to the study of volume stability of calcium hydroxide in various salt solutions [6]. The calcium hydroxide powder was compacted to form rigid, porous bodies. Significant expansions were observed in all of the solutions. Expansion was attributed, in part, to dissolution processes. This conclusion was supported by Feldman and Ramachandran [7] and Catinaud *et al.* [8] for hydrated C_3S and cement paste samples immersed in water and various salt solutions.

It was felt that dissolution phenomena might be a significant source of expansion for many minerals of interest to cement researchers. It was also apparent that a further evaluation and validation of the use of compacts for durability studies with these materials was warranted. A series of experiments was designed to evaluate the volume stability of both compacts and polycrystalline or single crystals of sodium chloride, gypsum and brucite in various solvents. Length changes of compacts of ground cement paste and normally hydrated cement paste specimens were also monitored in hydrochloric acid. In addition, an attempt at establishing the universality of the expansion association with dissolution phenomena was made using specimens of compacted table sugar. The object, then, of this study was to establish the efficacy of using compact specimens in durability investigations. Further improved understanding of expansion phenomena related to dissolution was sought.

2. The use of compacts for study of the durability of cement-based materials

Rigid porous bodies produced from compacted powders of Portland cement, hydrated Portland cement and several other inorganic minerals of interest to the construction industry have been used as structural models for scientific study [9]. The validity and value of the use of these compacts has been discussed in several publications concerned with engineering performance, surface chemical phenomena and durability assessment [10, 11]. A brief review of supporting evidence follows.

Probably the main advantage of working with compacts is that porosity control can be achieved by varying the pressure applied on the sample. Compaction pressure-porosity relationships for a variety of materials (e.g., hydrated Portland cement, calcium carbonate, pottery plaster and 0.4 nm molecular sieves) are generally linear with porosity decreasing with increasing pressure [9]. Porosity values have been shown often to be independent of the compact thickness up to 3 mm. Enhanced reproducibility of both porosity and mechanical property measurements is often observed when compacts are used. Strength and modulus of elasticity values, design parameters of importance to engineers, for both normally hydrated cement paste and ground and compacted cement paste are coincident when plotted versus porosity [12]. The relationship is semilogarithmic. It is apparent from this that bonds can be broken and remade on compaction.

There is also considerable evidence that compacts are valid and useful specimens for surface chemical investigation. Sorption isotherms (mass and length change) of normally hydrated cement paste and compacted powders of bottle hydrated cement are qualitatively and quantitatively similar [13]. Large primary and secondary hystereses are observed with both types of sample. Scanning loops are shown to exist over the entire humidity range. Surface area calculations (BET) using data from reconstructed reversible isotherms are similar to values obtained by N_2 sorption methods on both paste and compact specimens. Linear plots of length change versus weight change have been observed for these specimens and compacts of finely divided silica, precipitated calcium carbonate, calcium sulfate hemihydrate (details of how the authors separated sorption and hydration effects are provided in reference [14]), and calcium hydroxide. The curves all pass through zero.

It is known that at equal porosity a cement system having a larger percentage of fine pores generally has enhanced strength [15]. Therefore it can be inferred from the coincidence of the strength-porosity function and from the sorption isotherms that the pore size distribution of the compacted specimens and *in situ* hydrated specimen are similar. This inference can also be invoked from the equivalence between isotherms for compacts and *in situ* hydrated pastes.

The sorption isotherm data for porous materials can be used to calculate modulus of elasticity (E) values through application of the following Equation [13]:

$$E = \rho\sigma/\kappa \qquad (1)$$

where ρ is the solid density, σ is the solid surface area and κ is the constant in the Bangham equation relating length change and the change in solid surface tension.

The length change versus change in solid surface tension curves for cement paste and compacts were similar and linear [13]. Using this approach, Feldman calculated a value of $E = 29$ GPa [13]. Helmuth's estimate of E for the 'gel phase' was $E = 31$ GPa obtained by extrapolation of E versus porosity curves [16].

These values of E are for the non-porous solid phase (primarily C-S-H) of the paste. The length change isotherms obtained by Feldman were separated into reversible and irreversible components. The Bangham length change calculations employ data from the 'reversible' isotherm. The solid density term in Equation 1 is dependent on the amount of interlayer water. The estimates of E cited here would apply to a saturated specimen.

Feldman's calculations of E were similar for both paste hydrated cement and compacts of bottle hydrated cement. The length change versus change in solid surface tension curves for compacts of calcium carbonate and mixtures of calcium carbonate and finely divided silica were also linear and passed through the origin. Values of modulus of elasticity from sorption data on compacts is similar to those determined directly on neat cement samples [16].

Further reported test results indicate that compact specimens can be successfully used for durability studies. Bottle hydrated cement compacts preconditioned at various relative humidities have been employed in carbonation studies [17]. The humidity dependence for shrinkage is similar to that for hydrated paste prepared at approximately similar porosity. It was observed that carbonation shrinkage increased as the amount of free lime decreased. It was concluded that carbonation of combined lime resulted in greater shrinkage than free lime. Similar results for cement paste were obtained by Verbeck [18]. Studies of calcium hydroxide compacts immersed in isopropanol and methanol have shown similar length change behaviour to that observed for cement pastes indicating that calcium hydroxide contributes to volume stability in a manner similar to that of other hydrates [19].

The autoclave expansion of Portland cement compacts was shown to be as sensitive to different amounts of MgO as prism specimens containing varying quantities of MgO [20]. Similar expansion behaviour as a function of MgO content was observed. The use of compact specimens was also found to be a viable technique in an evaluation of the unsoundness of limes [21]. The results demonstrated that the compacts were much more sensitive to autoclave treatment than standard 25 × 25 × 282 mm prisms. The autoclave expansion in compacts is more than can be obtained in cement-lime bars with similar composition. An additional example of the effective use of compacts relates to the failure of plaster finish coat [22]. Expansion occurs as a result of post-hydration of magnesium oxide in the form of periclase.

3. Experimental

3.1. Materials

Cement Paste: Portland cement paste (cast in cylindrical moulds 31.7 mm diameter × 250 mm long) with a $w/c = 0.50$ was hydrated for 30 years. The saturated cement pastes were jacketed with rubber membranes containing a few drops of water. This allowed the specimens to be maintained at 100% RH without leaching of calcium hydroxide. The cement used was a normal type 10 Portland cement. Paste specimens were made by slicing 31.7 mm diameter × 1 mm thick discs from the cylindrical paste stock. The paste had a porosity of about 14% as determined by helium displacement measurements. The helium pycnometric technique involves conditioning the specimens at 11% RH prior to each determination [23]. The cement paste was ground to have an average particle size of about 25 μm, suitable for fabrication of compacts. The specimens were conditioned to 32% RH prior to immersion in the solvent.

Brucite: Large single crystals of brucite were obtained from Minerals Unlimited, Ridgecrest, California. X-ray diffraction spectra revealed no lines corresponding to the presence of other minerals.

Gypsum: Large single crystals of gypsum were obtained form Minerals Unlimited, Ridgecrest, California. X-ray diffraction revealed only the gypsum spectrum.

Halite: The non-porous polycrystalline halite was also obtained from Minerals Unlimited, Ridgecrest, California.

Sugar: Ordinary table sugar was used.

3.2. Compacts

Porous bodies in the form of circular discs (31.7 mm × 1 mm thick) were prepared by powder compaction of reagent grade $Mg(OH)_2$, $CaSO_4{\cdot}2H_2O$, NaCl and table sugar. Compacts were also produced from the ground hydrated Portland cement powder. Details are given in Table I. Porosity values were either calculated from density and gravimetric determinations or measured directly using helium pycrometric methods.

Measurement of porosity using other methods e.g., mercury porosimetry is less reliable due to microstructural limitations [24, 25].

3.3. Length change measurements

Prisms (5 × 25 × 1 mm) were cut from the solid crystalline specimens and the compacted disc samples for length change measurements. An accurate means of length change measurement was achieved with a modified Tuckerman gage extensometer (Fig. 1). This optical instrument measured length change with an accuracy of 1 microstrain. A brief description follows. The sample (1) was held against the knife edges (2 and 3) by a light spring (4), the sample resting on a holder (5). The optical system consisted of a fixed mirror (6) and a tilting mirror (7) which was one face of a rocking lozenge. The whole assembly was supported by a stand (8) and constructed of invar to minimize any thermal effects. Readings are taken manually with an optical collimator. This is convenient as they can be taken remotely through an optically flat lid placed on the vacuum desiccators.

TABLE I Compaction pressure and porosity values of various compact specimens

Compact	Pressure (Mpa)	Porosity (%)
NaCl	170.0	7.7
Sugar	170.0	13.5
$CaSO_4{\cdot}2H_2O$	680.0	11.5
Cement paste	340.0	17.5
$Mg(OH)_2$	340.0	35.4

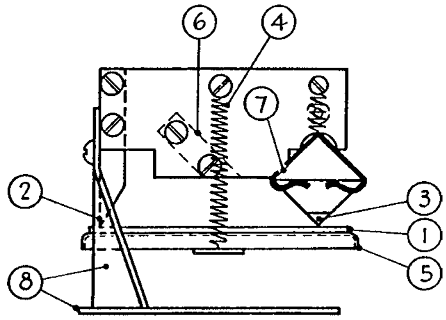


Figure 1 Schematic of Tuckerman extensometer.

It is noted that the sample is free to move and unrestrained. Force exerted on the sample is not significant. Similar length change results for cement paste immersed in HCl have been obtained by Litvan using linear variable differential transformer (LVDT) measuring devices where the applied force is nil [5]. In addition the knife edge of the Tuckerman extensometer contacts the specimen in a direction perpendicular to the direction of the length change measurement. Creep effects would be negligible in this direction. Calibrations of the Tuckerman extensometers with reference samples (e.g., metals) reproduce standard values of coefficients of thermal expansion.

The specimens were placed in the test solvents (one liter of either HCl (1 or 3 N) or distilled water) contained in vacuum desiccators to avoid any contamination from an outside source and to eliminate trapping air pockets. The specimens were completely immersed (under vacuum) and length change measurements were monitored continuously. Measurements were made on up to 10 replicate specimens for each test condition. The technique has been successfully used in other studies, e.g., Feldman and Ramachandran [7] and Catinaud *et al.* [8].

TABLE II Typical expansion values of materials studied

Material	Expansion (%)	Immersion solution
Vycor® glass	0.2 ± 0.10 (15 h)	0.4 M NaOH
$CaSO_4 \cdot 2H_2O$ (single crystals)	0.63 ± 0.30 (0.5 h)	Distilled water
$CaSO_4 \cdot 2H_2O$ (compacted powder)	0.60 ± 0.30 (12 h)	Distilled water
$Mg(OH)_2$ (single crystals)	1.60 ± 0.40 (0.5 h)	1 N HCl
NaCl (polycrystalline solid)	0.45 ± 0.20 (30 s)	Distilled water
NaCl (compacted powder)	0.38 ± 0.18 (30 s)	Distilled water

4. Results and discussion

Large expansions were observed in all the experiments reported in this study (utilizing single crystal, polycrystalline or compacted powder specimens). Typical expansion results of the materials studied at specified times of immersion in aggressive solutions are summarised in Table II. All systems experienced expansion of 0.2% or larger under the conditions indicated.

It is apparent from the work of Litvan [5] with Vycor® glass and this work that there is appreciable scatter in the data. This is the reason up to 10 replicates were used. The variation in test results is due to the stochastic nature of the failure process. Materials experiencing large strains reported here undergo significant microcracking which is itself a stochastic process. This behavior is typical of many brittle materials. Variability will be further discussed in the discussion of the data. It is noteworthy, as previously stated, that Litvan used both a linear variable differential transformer (LVDT) measuring device and the optical measuring system used in this work verifying that the observed scatter was a consequence of material behavior. All replicates without exception experienced large values of expansion.

The volume stability of the various systems is briefly discussed in the following paragraphs. No contractions were observed. In fact some specimens, e.g. compacted sugar and cement paste in concentrated hydrochloric acid were digested. Litvan [5] attributed contractions observed during interactions between Vycor® glass and aggressive media to readsorption of reaction products subsequent to dissolution [5]. The evolution of the composition of the solid during the immersion experiments was not determined.

Length change versus time curves for cement paste ($w/c = 0.50$) and ground and compacted cement paste immersed in 1NHCl are presented in Fig. 2. Large expansions (1–2%) were observed within 1 h. The length change-time response is quantitatively similar for both paste specimens and compacts in 1 N solution. The response is faster for the compacted specimens in the 3 N solution (not shown) possibly due to the slightly higher porosity of the compacted specimens as well as the increased concentration of the solution.

It may be important to comment on the possible effect of heat release on the extent of the expansion due to dissolution of the cement paste in HCl. This effect would appear to be negligible. This can be readily estimated. The heat of dissolution values for C_3S paste, C_2S paste and Portland cement paste are similar and approximately 550 cal/g [26]. The heat capacity values for the aqueous acid solutions (i.e., 1 N and 3NHCl) are approximately 0.70 and 0.60 cal/g/°C.

Complete dissolution of a 2 g sample immersed in 1 L of acid would produce a temperature rise of approximately $(2 \times 550)/(0.70 \times 1000)$ or 1.5°C. This temperature rise would account for a thermal strain of about $10 \times 10^{-6} \times 1.5$ or 0.0015%. This is three orders of magnitude lower than the measured strains that exceed 2.0%.

The authors contend that the dissolution of solids is an expansive process that applies in many cases to volume change observed for cement-based materials

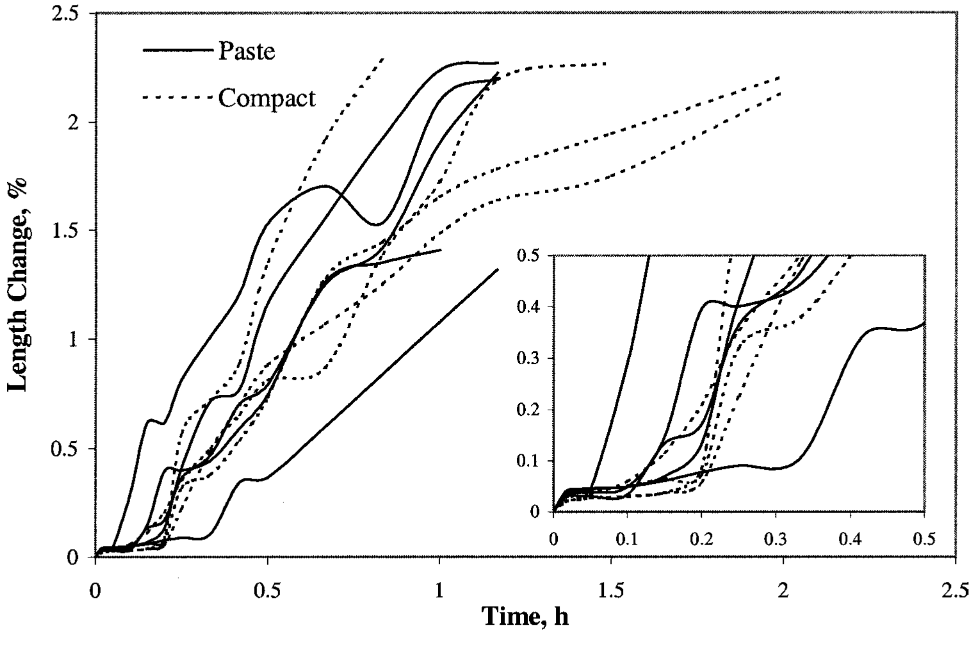


Figure 2 Length changes of hydrated Portland cement paste ($w/c = 0.50$) and compacts of ground hydrated Portland cement paste immersed in 1NHCl acid.

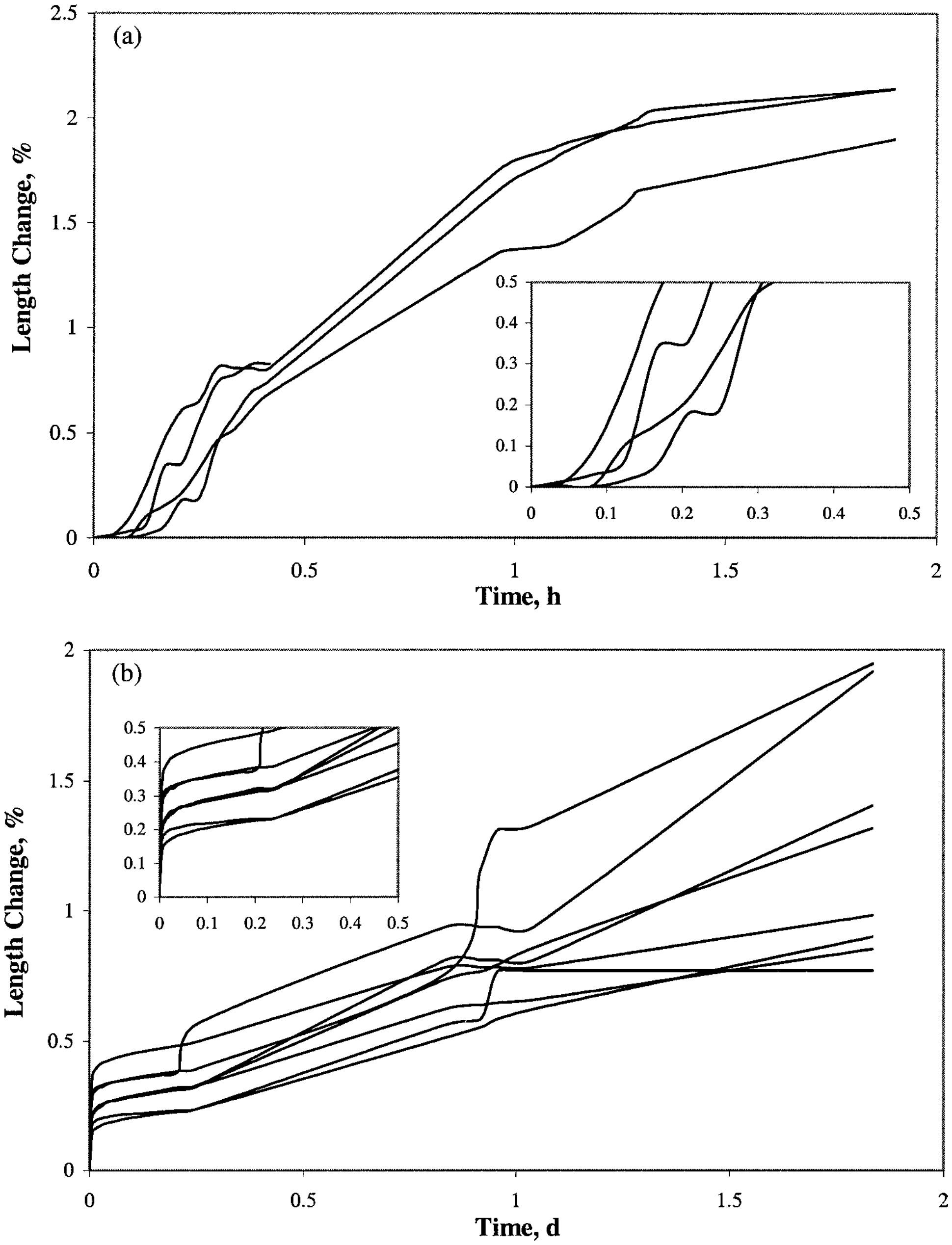


Figure 3 Length changes of (a) gypsum single crystals and (b) compacted gypsum powders immersed in distilled water.

exposed to aggressive media. Volume change measurements of both non-porous and porous materials are useful to test this hypothesis as other mechanisms e.g., disjoining pressure are less likely to occur on dense non-porous specimens. Further the use of single crystals eliminates any influence of boundary effects. Significant expansion was also observed for the $CaSO_4 \cdot 2H_2O$ compacts and single crystals immersed in distilled water, Fig. 3. It was not expected that the magnitude of expansion be similar but rather that it be significant in engineering terms in both cases. Expansions were quantitatively and qualitatively similar for both the compact and the single crystal specimens although the time to attain the level of expansion was much larger for the compacted specimens. Expansion values up to 2% were observed at one day.

Single crystals of brucite ($Mg(OH)_2$) expanded rapidly (0.5 to 2%) within the first 30 minutes upon immersion in 1NHCl, Fig. 4. The brucite compacts were difficult to prepare at most compaction pressures. The most satisfactory compacts were prepared at 35% porosity. These brucite compacts expanded rapidly in the first few seconds of immersion in 1NHCl. The large porosity was obviously a factor affecting the very rapid rate of dissolution and volume change. Nevertheless, it was clear that both compacted specimens and solid single crystals experienced large expansions associated with dissolution phenomena.

Non-porous sodium chloride polycrystals and specimens composed of compacted powders were immersed in distilled water, Fig. 5. The solid crystals expanded rapidly (0.13–1.5%) in the first minute. The compacted specimens (7.7% porosity) expanded at a similar rate (0.6–0.8%) in the first minute. Sodium chloride crystals can be found in concrete surface pores due to winter salt applications. The dissolution-expansion behaviour of the salt crystals may be a contributing

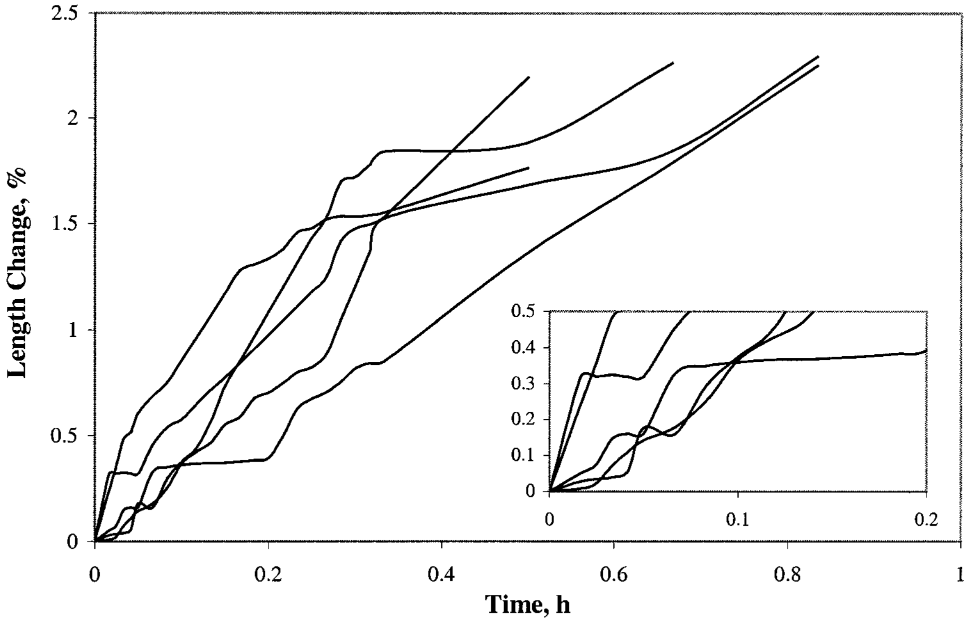
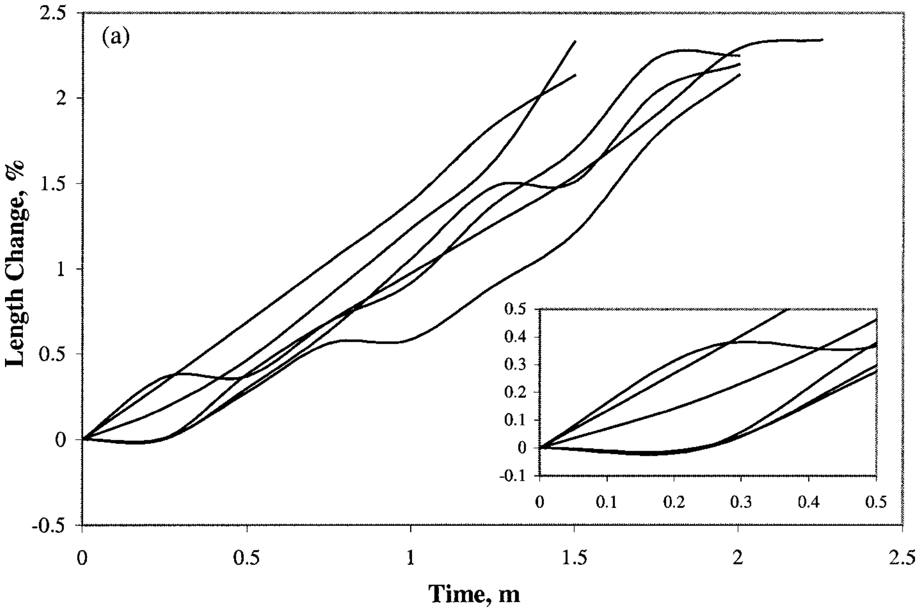


Figure 4 Length changes of brucite single crystals immersed in 1NHCl acid.



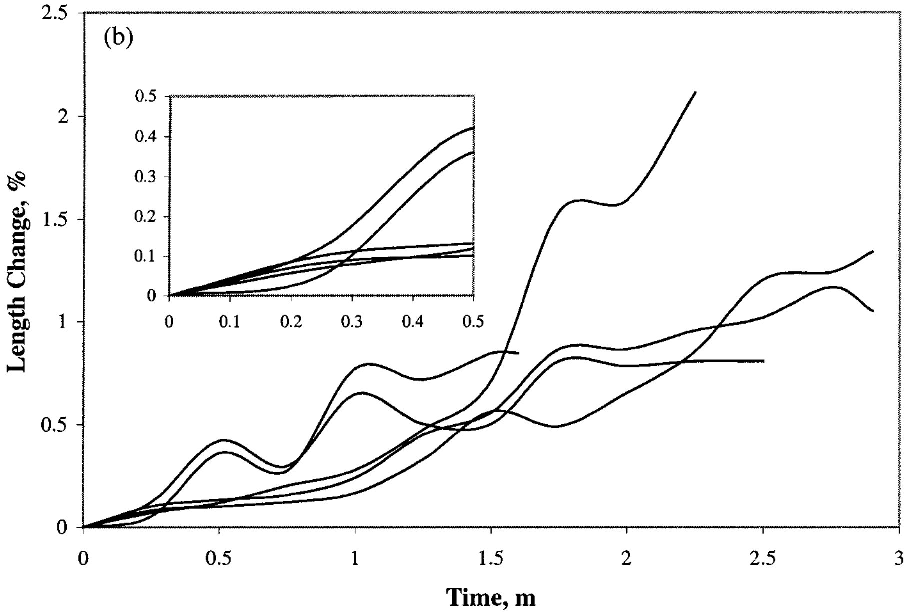


Figure 5 Length changes of (a) sodium chloride polycrystalline solid and (b) compacted sodium chloride particulates.

factor to internal stress generation and concrete damage.

A compacted specimen of common table sugar was immersed in distilled water to test the universality (as it applies to compounds commonly found in cement-based materials) of the dissolution-expansion process. The compact expanded to a value approaching 1% prior to complete dissolution within a few seconds.

It is apparent that there is considerable variability in all the test results although the general trend of the data for each specimen under each condition is similar. Some of the variability may be attributed to statistical variation in the strength of the material e.g., cement paste will exhibit variations in strength determining parameters such as porosity and pore size distribution. The average strength of the 30 year old pastes in this study was 85.1 ± 5.2 MPa (compression). Variations in material properties also occur for Vycor® glass where variability may be due to the leaching process used during production. Variation in the strength of single crystals would however not be expected to be a primary cause of variations in length change due to the absence of porosity and grain boundaries. The test results for the gypsum single crystals, notwithstanding, are particularly scattered. There is a possibility that some microcracking may have occurred during specimen preparation. This would of course affect the rate of dissolution. A large variability is however also observed for compacted gypsum powders. Variation with the compacted samples may be due to differences in strain energy (at particle boundaries uniformly distributed throughout) stored during the compaction process although it is unlikely the single crystals are in a stressed state.

The rate of dissolution of compacts may be sensitive to minor variations in pore size distribution. This sensitivity is not observed for mechanical behaviour of the compacted specimens.

All the materials relevant to cement-based systems (compacts, single crystals, or polycrystalline solids) expanded when immersed in various solvents. The materials ranged from hydrated Portland cement to table sugar. It was also apparent that compacts responded qualitatively in a manner similar to the naturally occurring solid specimens. Further, it appears that a similar quantitative response for compacts can be obtained with the appropriate choice of porosity value. This value varies for each system.

The results obtained on single crystals and polycrystalline solids tend to indicate that the dissolution induces expansion that is not caused by any osmotic effects or disjoining-pressure phenomena. The expansion of single crystals also tends to demonstrate that expansion is not necessarily linked to any stress-release mechanisms. Globally, the data tend to confirm that the initial expansion is linked to the dissolution process itself. Dissolution results in a decrease in surface energy which is the primary impetus for much of the expansion. Cracking at large strains would also contribute to expansion. Swelling of cement paste is unlikely to be significant as the specimens were conditioned to 32% RH prior to immersion in the solvent. Swelling due to intercalation effects is minor at this humidity.

5. Conclusions

1. Dissolution of solids (relevant to cement-based materials) immersed in solvents is associated with expansive processes.
2. The dissolution of hydrated Portland cement or salts present in the pore solution of cement-based materials is generally expansive. This may be a contributing factor affecting durability and service-life of concrete structures.
3. Rigid, porous bodies fabricated by powder compaction exhibit quantitatively similar expansive behaviour to non-porous, naturally occurring mineral solids when immersed in solvents.
4. Compacts can often be suitable models for durability studies of cement systems.

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Received 20 August 2002
and accepted 18 August 2003