

The Shrinkage Behavior of Decalcified Cement Pastes

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Abstract: The shrinkage behavior of China GB175 P.O. 42.5 ordinary Portland cement hydrated pastes during and after accelerated decalcification-based leaching process was investigated and analyzed. The experimental results indicate that generally the decalcification, in which the pastes were decalcified by leaching in concentrated ammonium nitrate solutions, resulting in calcium-to-silicon molar ratios (Ca/Si) ranging from 3.23 down to 0.93, increased the subsequent drying shrinkage in reference to the not decalcified paste. Furthermore, the irreversible shrinkage increases quickly, in detail, almost linearly with the degree of decalcification during leaching, while the reversible shrinkage increases little. These results could give further insights on the interpretations of cement paste structures and on the shrinkage mechanisms of C-S-H.

Keywords: drying shrinkage, cement pastes, decalcification, weight loss, Ca/Si ratio

1. Introduction

Decalcification of cement paste is closely associated with various types of concrete deterioration. Calcium leaching occurs when cementitious materials are exposed to water or solution with calcium concentrations below the equilibrium concentration. Important examples include leaching by exposure to flowing fresh water or weak acids, which removes calcium from the paste altogether, and external sulfate attack, which reorganizes the cement paste in such a way that the calcium in portlandite [$\text{Ca}(\text{OH})_2$] and in C-S-H gel is transferred to gypsum and ettringite. The addition of mineral admixtures, such as silica fume and blast furnace slag, to cement paste causes a similar reorganization, with a lower Ca form of C-S-H gel forming at the expense of $\text{Ca}(\text{OH})_2$ and the typical high-Ca form of C-S-H gel.

Following the equilibrium conditions in the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ [1], first, the portlandite is dissolved, and then the C-S-H are decalcified,

reducing their Ca/Si ratio. The polymerization of C–S–H is known to increase with decreasing Ca/Si ratios [2], and an increase in the relative chain length during calcium leaching was reported from nuclear magnetic resonance studies by Porteneuve [3]. Adenot [4] showed that the leaching process is governed by the diffusion of calcium in the attacking water phase, and developed a 1D-model which accounts for the experimentally observed instantaneous dissolution of the distinct mineral phases. This work was extended by Mainguy et al. [5–7] for two-dimensional problems and cracked materials.

The critical importance of diffusion process for the kinetics of leaching process was the basis for the development of accelerated leaching techniques: replacing water with an ammonium nitrate solution was first introduced by Carde, while an electro-chemically induced leaching process was pioneered by Saito et al. [8] and Gerard [9]. While the ammonium nitrate solution achieves an acceleration of the leaching process due to the increased calcium concentration gradient in the attacking fluid phase, the electro-chemical acceleration results from a strong electrical potential difference.

The effects of decalcification on the mechanical properties of cement paste [10–14] have been studied and modeled. What is missing at present is a full understanding of the effects of decalcification, or changes in the calcium-to-silicon ratio (Ca/Si), on the shrinkage behavior of the cement pastes.

2. Experimental Procedures

2.1 Preparation of the Cement Pastes

The cement pastes used in this study were prepared by China GB175 P.O. 42.5 ordinary Portland cement (CN PO425) and deionized water. The details of the cement analysis are given in Table 1.

Table 1. Composition of CN PO425

Composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O
Content (%)	63.8	21.1	6.6	2.8	2.1	0.2	0.4

The water to cement ratio of the pastes is 0.50 by weight. They were mixed by hand, cast in the sealed 25 mm diameter plastic vials and shaped into cylinders. Afterward, the pastes were cured under room temperature (20±1 °C) until demoulded 24 hours after mixing. Afterward, the cylindrical hardened pastes were immersed in the saturated lime water which was filled in the plastic cups under room condition and cured for

other days until drying or leaching prior to drying. In this study, the pastes were cured for 180 days until drying or leaching prior to drying.

2.2 Preparation of Sample Discs

Thin discs, which were 0.8 mm thick and 25 mm in diameter, were cut for drying or leaching prior to drying from the pastes by precision saw when the pastes were ready for measurement. In order to precisely get the radial length change of the discs, three lines were drawn slightly and crisscrossed on each disc surface separated by approximately 120 degree angles. So the final radial length change of the disc is the average of the three.

2.3 Measurements of Weight and Diameters of Sample Discs

Fine digital balance with a resolution of 0.1 mg was used to measure the weight of discs. A satisfactory level of accuracy was achieved by this balance as indicated by the relatively small scatter in the data.

Digital caliper with a resolution of 0.01 mm was used to measure the changes in diameters of the discs. During the measurements of diameters, the caliper was mounted on a fixed surface. For each measurement, the length readings for three marked diameters were recorded.

Exposure of cement paste discs to carbon dioxide was minimized by flushing the dessicator with nitrogen after each open of the dessicator.

2.4 Leaching

Earlier studies [15,16] have shown that decalcification by leaching in the concentrated ammonium nitrate solution prior to drying may be the preferred way to study the effect of variation in Ca/Si ratio, Ca-OH content of C-S-H on the drying performance of cement pastes, so it was adopted. The silicate polymerization in C-S-H induced by leaching caused macroscopic shrinkage strains which may affect the drying shrinkage after leaching as a result of pre-shrinkage.

In this study, three kinds of leaching status for CN PO425 cement pastes were predetermined: the first was leached to Ca/Si ratio of 2.61, the second was 1.65, and the last was 0.93. All the Ca/Si ratios were estimated from correlations with weight loss which will be given later.

The concentration of ammonium nitrate solution was determined to be 6M (6 mol/l, 473g ammonium nitrate per 1kg deionized water).

During each experiment of leaching, at intervals of generally 3~5 min, each sample disc was removed from the leaching solution, the weight and three given diameters were quickly measured in the saturated surface dry state, and then the disc was promptly placed back in the stirred leaching solution. Care was taken to measure the samples in the saturated surface dry state in order to isolate the shrinkage strains contributed by decalcification only; drying shrinkage was not included.

The weight loss and shrinkage during leaching were determined in reference to the weight and diameters of the saturated, not leached status before leaching.

2.5 Rinsing

After the predetermined leaching was finished, the disc was immediately submerged in about 120 mL of deionized water and the solution was gently stirred from time to time for about 10-15 minutes to exchange the ammonium nitrate solution in the pores of the paste with water until the disc was water saturated.

2.6 Drying and Rewetting

The pastes were dried in the desiccator over saturated $\text{Ca}(\text{NO}_3)_2$ solution when drying is needed. The relative humidity (RH) and temperature in the desiccator were recorded by digital thermo-hygrometer. According to the record, the relative humidity kept constantly at $43\% \pm 2\%$, and the temperature at 20 ± 1 .

In order to distinguish the reversible and irreversible components of drying shrinkage, after drying, rewetting followed. The dried discs were quickly immersed in the saturated limewater, which was filled in a plastic cup, after the last measurement of drying.

The weight loss and shrinkage during drying and rewetting were determined in reference to the weight and diameters of the saturated, leached (if leached), rinsed (if rinsed) status before drying.

3 Results Analysis

3.1 Leaching Results

3.1.1 Change of Ca/Si Ratio during Leaching

Fig. 1 indicates the relationship between weight loss and the Ca/Si ratio of the CN PO425 cement pastes leached in 6M ammonium nitrate solution.

The weight of the disc was measured directly in the saturated surface dry state after leaching, no rinsing in deionized water. The weight loss was determined in reference to the weight of the saturated, unleached status before leaching. The Ca/Si ratio was deduced from the concentration of Ca and Si in the ammonium nitrate solution used for leaching, which were determined by EDTA complexometric and molybdenum blue colorimetric test methods respectively. These relationships were used to estimate the Ca/Si ratio of the paste during leaching in this experiment. The original Ca/Si ratio of the unleached pastes in this study is 3.23 obtained by chemical analysis.

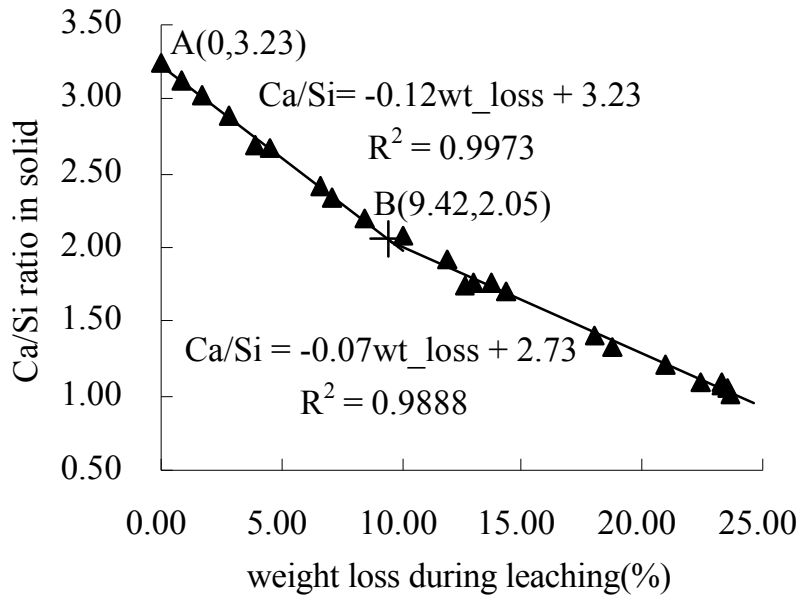


Fig.1. Relationship Between Weight Loss, wt_loss, and Ca/Si Ratio for CN PO425 Cement Pastes Leached in the 6M Ammonium Nitrate Solutions

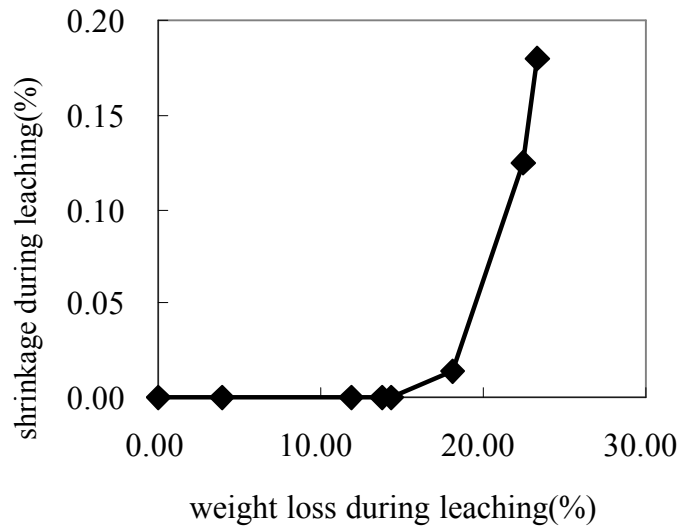
The data in Fig. 1 appears to show two linear curves, which intersect at a Ca/Si ratio of ~2.05, the point where Ca(OH)_2 is completely extracted which can be deduced by further calculations. The slope of the first linear region is close to the theoretical value expected if the changes in weight and Ca/Si ratio were only due to the replacement of Ca(OH)_2 with an equal volume of ammonium nitrate solution. The second slope of linear region can be attributed to the decalcification of C-S-H in cement pastes. [15]

What leads to the decrease of Ca/Si ratio during leaching is ammonium nitrate reacts with the cement paste by exchange reactions leading to the appearance of a salt of calcium, $\text{Ca(NO}_3)_2$, and release of gaseous ammonia, NH_3 , meanwhile, an expansive calcium nitro-aluminate, empirical formula $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca(NO}_3)_2\cdot 10\text{H}_2\text{O}$, is possibly formed by the

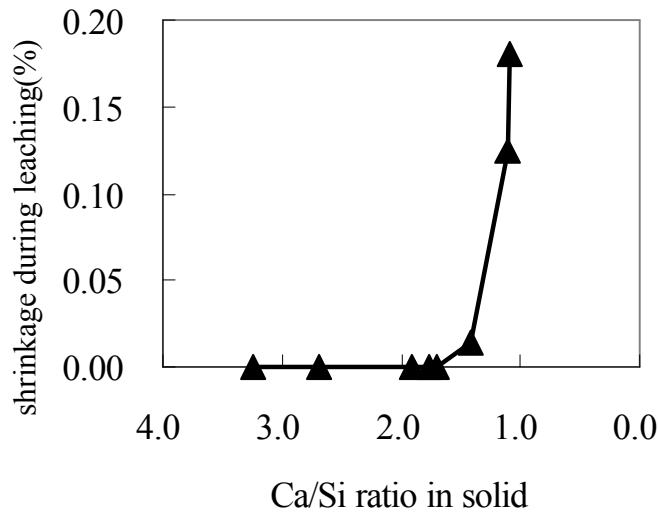
reaction of calcium nitrate with the hydrated aluminates which is like the “climbing salts” that are transported by water from a humid surface to a dry surface.[14]

3.1.2 Shrinkage during Leaching

The shrinkage only caused by decalcification during leaching experiment can be experimentally measured and plotted in Fig. 2. Ca/Si ratios were determined from the correlations with weight loss (see Fig. 1).



(a) Relationship between Shrinkage and Weight Loss in Decalcification



(b) Relationship between Shrinkage and Ca/Si Ratio in Solid during Decalcification

Fig.2. Radial Shrinkage caused by Decalcification and its Relationship with the Weight Loss and the Ca/Si Ratio in Solid during Leaching

From Fig. 2, it is obviously shown that when leached deeply enough, hydrated cement paste continues to shrink. The important observation is that shrinkage only becomes appreciable below Ca/Si ratio of ~ 2.0 , the point where $\text{Ca}(\text{OH})_2$ is completely extracted as mentioned above. Further decalcification below this point leads to significant strains that are almost comparable to those produced from drying at 43% relative humidity (see Fig. 3). That is, the contractions in the paste become particularly appreciable only when interlayer Ca^{2+} are removed from C-S-H below Ca/Si ~ 2.0 . The remove of Ca^{2+} from $\text{Ca}(\text{OH})_2$ caused less appreciable shrinkage. As known somewhat [14,17], when interlayer Ca^{2+} are removed from C-S-H, C-S-H will polymerize into other structures with longer chain which will lead to obvious shrinkage.

3.2 Drying and Subsequent Rewetting Results

As mentioned above, after the predetermined leaching was finished, the disc was immediately rinsed in deionized water to exchange the ammonium nitrate solution in the pores of the paste with water until the disc was water saturated. Afterwards, the subsequent drying and rewetting was done to investigate the effect of pre-shrinkage and the change of Ca/Si ratio on the drying behavior of cement pastes.

3.2.1 Length Change during Drying and Subsequent Rewetting

The length change of three kinds of rinsed cement pastes and the control (unleached paste) with drying and subsequent re-saturation time was measured and shown in Fig. 3. In Fig. 3, point O to point A and O to B is the drying process and after point A and B is the rewetting process.

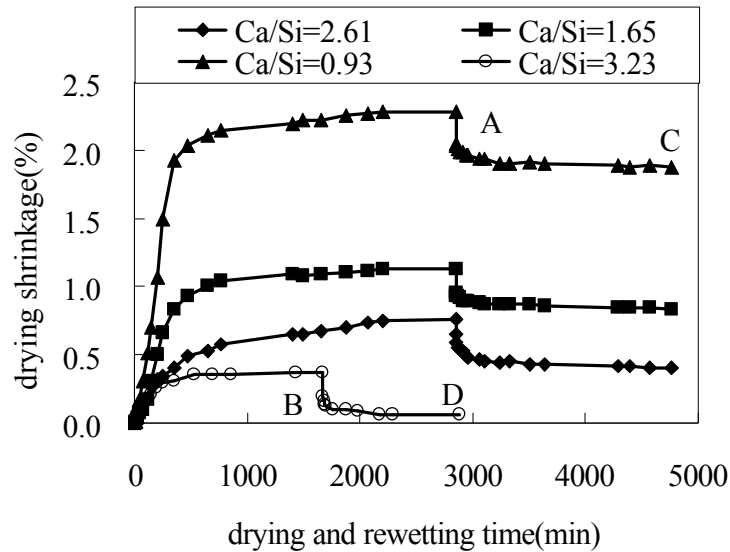


Fig.3. Radial Shrinkage Strains of 180 Days Old Cement Pastes as a Function of Drying and Subsequent Re-saturation Time

In Fig. 3, the effect of pre-leaching process on drying shrinkage can be easily investigated. From Fig. 3, it is indicated that the unleached paste has the lowest drying shrinkage and the total shrinkage is increased with the decrease of Ca/Si ratio which is caused by the leaching in 6M ammonium nitrate solution. When the Ca/Si ratio is down to 0.93, the leached pastes has much higher total drying shrinkage which is about 6 times higher than the control, and sometimes it makes the disc crack.

It is also shown in Fig. 3 that shorter period of time is needed to reach the equilibrium condition after drying for unleached cement paste than for leached pastes (see also in Fig. 4).

In order to explain the mechanism of drying shrinkage, the reversible and irreversible drying shrinkage of the rinsed pastes and the control were calculated from Fig. 3 and shown in Fig. 5 which will be discussed later.

3.2.2 Weight Change During Drying And Subsequent Rewetting

Based on the method described in this study, it is easy to obtain the weight loss during drying and subsequent rewetting as well as other process. The weight loss during drying and subsequent rewetting were measured, calculated, and illustrated in Fig. 4 to get further insights about the drying shrinkage behavior of the decalcified cement pastes.

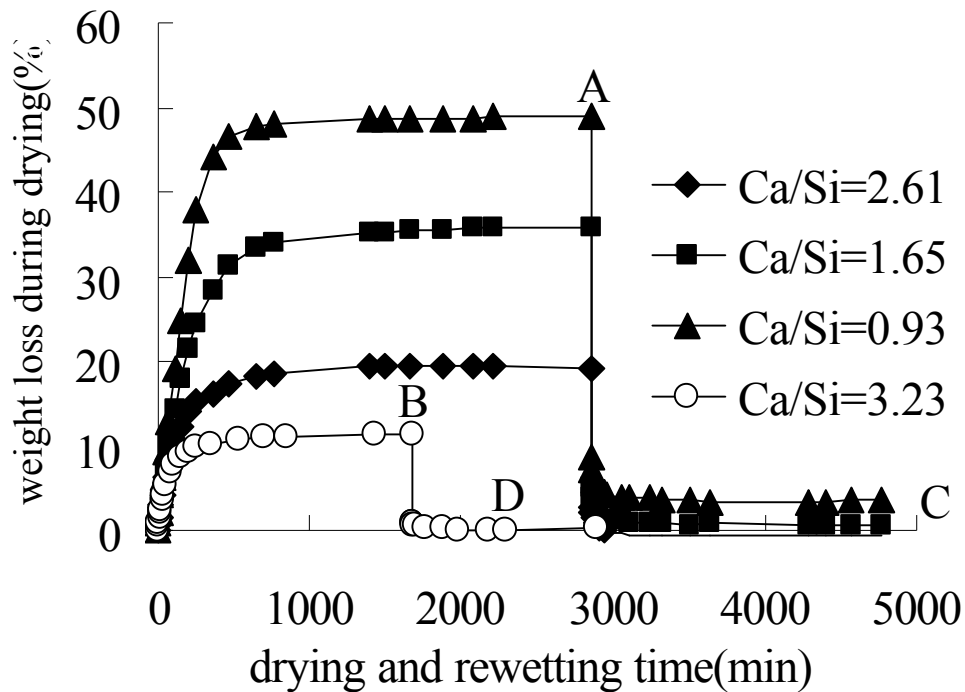


Fig.4. Weight change during drying and subsequent rewetting as a function of time

From Fig. 4, the effect of pre-leaching on the weight loss during drying can also be easily investigated. That is, the unleached paste has the smallest loss of weight and the total weight loss is increased with the decrease of Ca/Si ratio due to the leaching. When the Ca/Si ratio is down to 0.93, the leached pastes has much higher weight loss which is about 4.5 times more than the control.

3.2.3 Reversible and Irreversible Drying Shrinkage

According to Fig. 2, Fig. 3 and further experimental results, the length change during leaching, rinsing, drying and rewetting of paste is obtained as shown in Fig. 5, the former two of which is labeled as “in leach” and “in rinse” respectively. Furthermore, the reversible (i.e., the difference between the ultimate strains obtained after drying and re-saturation) and irreversible (i.e., the final change in length after the specimen has been dried and re-saturated) shrinkage during drying can be calculated according to Fig. 3 as illustrated in Fig. 5 labeled as “reversible dry” and “irreversible dry” respectively.

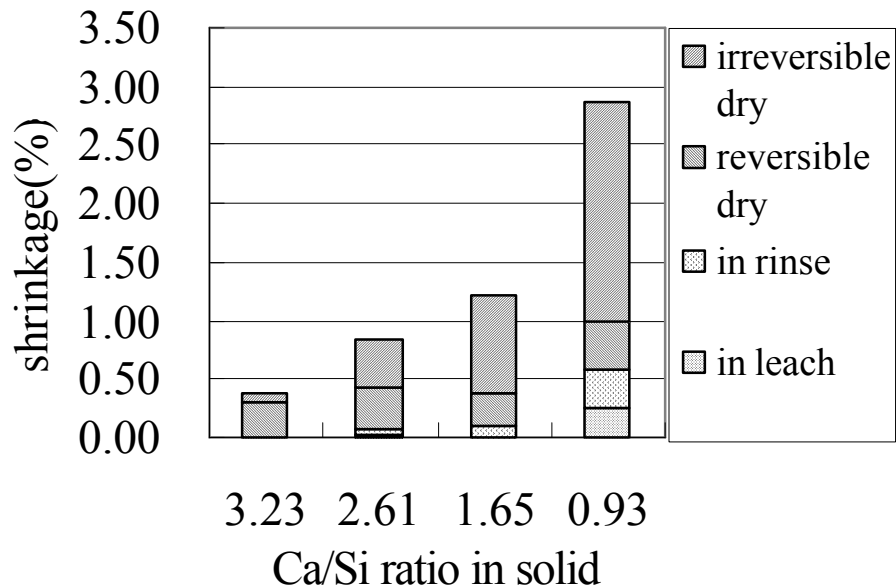


Fig.5. Radial shrinkage respectively caused by decalcification, rinsing, and drying which was divided into reversible and irreversible strains

Based on the results in Fig. 5, it is known that with the decrease of Ca/Si ratio due to decalcification, the total shrinkage is fast increased including gradually increasing leaching shrinkage, subsequent rinsing shrinkage, almost constant reversible drying shrinkage and sharp increase of irreversible drying shrinkage. It is noted that the irreversible shrinkage increases almost linearly with the degree of decalcification.

As known, drying removes water first from the larger pores and then progressively from smaller and smaller pores which shows the very important effects of pore structure and pore size distribution on the shrinkage behavior of cement pastes. It is also known that the primary driving force for shrinkage at relative humidity (RH) levels from 100% down to 43% is capillary tension in the pores, and disjoining pressure between the particles of cement. Both of these processes are intrinsically reversible, so irreversible shrinkage strains must result from physical or chemical changes to the paste. These changes are generally considered to be a rearrangement of the C-S-H gel particles on drying, and must be associated with permanent changes in the packing density. It is very necessary to get further insights about the micro mechanism of drying shrinkage based on the future research works and achievements.

4. Conclusions

(1) During leaching process, decalcification happens and leads to continuing loss of weight along with a relatively stable volume at the beginning when the remove of Ca^{2+} is from $\text{Ca}(\text{OH})_2$ followed by a obviously shrink due to the polymerization of C-S-H, that is, the interlayer Ca^{2+} are removed from C-S-H.

(2) During drying of the leached pastes and the control, the remove of water from the paste causes continuous loss of weight along with the rebuild of the structures which leads to the shrinkage of the cement pastes. The total shrinkage is increased with the decrease of Ca/Si ratio which is caused by the leaching.

(3) As for the decalcified cement pastes, with the decrease of Ca/Si ratio due to decalcification, almost constant reversible drying shrinkage and sharp increase of irreversible drying shrinkage were investigated. And the irreversible shrinkage increases almost linearly with the degree of decalcification.

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