Cement and Concrete Research 41 (2011) 1024–1036

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Comparison of methods for arresting hydration of cement

Jie Zhang, George W. Scherer *

Dept of Civil and Environmental Engineering, Princeton University, Princeton, NJ 08544, USA

A R T I C L E   I N F O

Article history:
Received 18 September 2010
Accepted 7 June 2011

Keywords:
Drying methods
Solvent exchange
Thermal Analysis
Microstructure
Characterization

A B S T R A C T

Arresting of cement hydration, followed by drying, is necessary to prepare samples for many techniques of microstructural analysis. This paper reviews the effects on microstructure and composition of cement paste caused by the most common drying techniques, including direct drying (oven, microwave, D-drying, P-drying, and freeze drying) and solvent exchange methods. Supercritical drying is proposed as a method that could effectively preserve the cement microstructure, but which has not been applied to cementitious materials. Experiments are reported that systematically quantify the effects of drying from several solvents, freeze drying, and direct drying of young paste. Freeze drying is an effective drying method to prepare samples for chemical analysis, but it might change the microstructure. Isopropanol exchange followed by ambient drying is the best known method for preserving the microstructure with minimal effect on the composition of cement.

1. Introduction

A wide variety of techniques has been used to characterize the composition and structure of calcium silicate hydrate (C–S–H), the early nucleation and growth of hydration products, and the pore structure of cement-based materials, due to our need to understand the hydration process of cement [1], and to develop models that describe and predict the properties of cementitious materials [2]. Most materials characterization techniques, such as X-ray diffraction (XRD), thermogravimetric analysis (TGA), nitrogen adsorption/desorption (NAD), mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), can only test dry samples. To obtain cement specimens at a defined degree of hydration (DOH), they must be subjected to a treatment that arrests the hydration reaction; then the sample can be crushed or cut, dried, and put under vacuum for examination. Preserving the microstructure is especially challenging for very fresh cement pastes that contain a lot of free water, but are mechanically weak and highly reactive. The purpose of this paper is to review the methods that have been used for sample preparation, and to identify those that are most satisfactory for preserving the chemical and/or physical state of the sample, particularly for young pastes.

Water in hydrated cement is present in many forms, often classified as structural water, gel water, and capillary water. Structural water includes water of crystallization and chemically bound, non-evaporable water that can only be extracted through hydrate decomposition. Gel water is held by capillary tension and strong hydrogen bonding on to the surface of the main cement hydration product, C–S–H gel. This water, which is in nanometer-scale pores, can be removed by evaporation at ambient or reduced pressure, at ambient or elevated temperature. Capillary water is the unbound water inside the pores that is available for reaction during hydration. When arresting hydration and drying cement paste, capillary water must be removed, while removal of the first two types of water may be undesirable, because the composition and microstructure of many of the cement hydrates could be altered, so that the dried sample would provide incorrect information about the microstructure and phases present in the cement paste. This is certainly true when structural water is removed. Water in the smallest gel pores is difficult to remove or replace, because those pores have the highest relative surface area, so the stresses related to surface tension of the receding water menisci generate temporary capillary pressure that may cause shrinkage of the sample and alter the fine pore structure of the cement paste [3–5]. The capillary pressure, P_{cap}, is related to the liquid/vapor surface tension, γ_{LV}, the contact angle between liquid and solid, θ, the specific surface area, S, the bulk density, ρ_B, and the porosity, ϕ, by [6]:

$$P_{cap} = \frac{\gamma_{LV}\ \cos(\theta) S \rho_B}{\phi}. \tag{1}$$

For water, $\gamma_{LV} = 0.072\ \mathrm{J/m^2}$, and for cement paste we can estimate $S \approx 50\ \mathrm{m^2/g}$, $\rho_B \approx 2000\ \mathrm{kg/m^3}$, and $\phi \approx 0.3$, so if $\theta \approx 0$, the capillary pressure during drying of cement paste is about $P_{cap} \approx 24$ MPa. Clearly, such a large pressure could alter the microstructure, particularly in small pores and/or young pastes.

The drying of hardened Portland cement paste has been the subject of considerable study since the 1960's, not only due to its

---

* Corresponding author. Tel.: +1 609 258 5680; fax: +1 609 258 1563.
E-mail address: scherer@princeton.edu (G.W. Scherer).

0008-8846/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2011.06.003

importance for durability, but also because of its impact on materials characterization. Desaturation, reaction between hydration products and solvents, desorption, and dehydration phenomena associated with drying may generate microcracking, capillary porosity alteration, collapse of gel pores, and mineralogical transformations [7]. Removing water without changing the specimen's microstructure and chemical composition is extremely difficult or impossible to accomplish; therefore, some specimen alteration is accepted to obtain any measurement at all [8].

The purpose of this paper is to examine the effects of several drying techniques on the mineralogy and microstructure of fresh cement paste, and to recommend the best pretreatments for different purposes of analysis. The first part of the paper is a detailed review of the literature, which extends the scope of earlier reviews [5,9,10] to the early stage of hydration.

There are two major methods for arresting hydration and removing water: direct drying (which is removal of water by evaporation or sublimation) and solvent exchange. The literature on these methods is reviewed in Sections 2 and 3, respectively; the results are summarized in Section 4. Our motivation for exploring this question is to find the best way to evaluate the degree of hydration of young pastes, but the literature on this topic is sparse, and some problems revealed by the review (kinetics of exchange, effect of duration of exposure to solvents) have not been fully explored. Therefore, an experimental study was undertaken, as described in Section 5.

2. Direct drying

2.1. Phase diagram of water

In all the direct drying methods, water is removed by transforming it into vapor. The phase diagram of water in Fig. 1 can be used to distinguish the various drying methods. If the cement paste specimen is at room temperature and atmospheric pressure before the drying technique is applied, then the water inside the cement paste is liquid. The interfacial tension from the boundary between the liquid and gas phase creates capillary suction, according to Eq. (1), that can cause microcracking and collapse of the delicate microstructure of the cement paste. Therefore, if the transition from the liquid to the gas state cannot be avoided, then the surface tension of the liquid should be minimized.

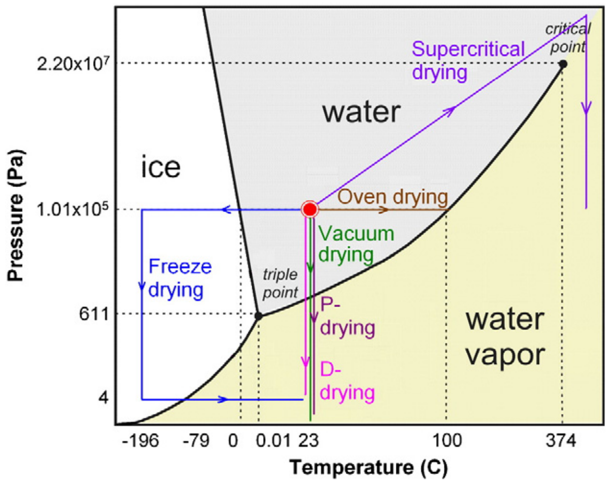

Fig. 1. The phase diagram of water. The transitions between the phases are shown using the diagram for the processes of freeze drying, oven drying, D-drying, P-drying, vacuum drying, and supercritical drying. The red point is the initial state of water in the sample at atmospheric pressure and room temperature. The arrows indicate the paths followed during the drying process.

During oven or microwave drying, the temperature is raised while atmospheric pressure is maintained. The vapor pressure of water, P_{vap}, increases until it reaches atmospheric pressure at the boundary of liquid–gas equilibrium (*i.e.*, the boiling point). The rate of evaporation increases as P_{vap} rises, so menisci form and capillary pressure develop in the liquid. As temperature increases, the surface tension of water drops, from about 0.073 J/m^2 at room temperature to 0.059 J/m^2 at 100 °C [11].

In vacuum drying, the pressure decreases without temperature increase, resulting in transfer of liquid water to the gas phase. D-drying and P-drying are similar processes, in which the vapor pressure of water is controlled by a trap containing dry ice/alcohol or magnesium perchlorate, respectively.

During freeze drying, the temperature of the sample is reduced immediately to −196°C by using liquid nitrogen, so the water is in the solid state. The specimen is placed into a freeze dryer under vacuum, resulting in sublimation of ice as the sample is slowly heated to room temperature. No capillary pressure is generated during sublimation, but the freezing process causes potentially damaging stresses from volume expansion, hydraulic pressure, and crystallization pressure [12,13]. Upon removal of the vacuum, the dry specimen returns to its initial conditions of room temperature and atmospheric pressure.

Critical point drying is done by increasing the temperature and pressure until the critical point of the pore liquid is exceeded, so that the fluid enters the supercritical state without crossing the liquid/gas boundary. While keeping the temperature high, the pressure can be lowered to atmospheric pressure as vapor is released from the vessel; then, by reducing the temperature, the specimen is left dry at room temperature and atmospheric pressure [8]. This cycle prevents the formation of a liquid/vapor meniscus in the pores, so no capillary pressure is exerted. To avoid the high critical point of water (374°C, 22 MPa [14]), it is common practice to exchange the pore fluid for a liquid with a low critical point, such as CO_2 (31.1°C, 7.4 MPa [11]) or Freon® R23 (25.6°C, 4.8 MPa [15]). Although widely practiced on inorganic gels [16], this method has apparently not been applied to cement paste.

2.2. Oven drying

Oven drying is probably the most widely used drying technique, with temperature typically between 60 and 105 °C at atmospheric pressure (101 kPa); in convective drying, a flow of dry air is circulated through the oven. When the specimen reaches a constant mass (typically, less than 0.1% of mass change per day), the drying is considered to be complete [8]. To prevent carbonation, it is necessary to remove CO_2 from the atmosphere (for example, by putting solid NaOH with high surface area into the oven), but this is rarely done.

Although oven drying effectively removes evaporable water, it has many drawbacks. Oven drying at 105 °C for 24 h removes the "unbound" water, but it also damages the microstructure [5,7]. It removes structural water from the cement pastes [8,17] and alters the pore structure [18,19]. Gallé [7] found that 105 °C drying caused ettringite and C–S–H to lose a significant amount of non-evaporable water, making this technique "unsuitable for preserving the fragile microstructure" of cement. Collier [9] found that oven-dried samples showed a noticeably higher weight loss in the TGA from 580 to 710 °C, associated with the release of CO_2 from calcite. Korpa and Trettin [5] compared freeze drying, D-drying and oven drying, and found the minimum surface area in oven-dried samples; similar results were found by Juenger and Jennings [19].

Beaudoin claims that less microstructural damage is done by drying at 105 °C for 3 h than for 24 h [20]. It is not clear whether this reflects the kinetics of evaporation from small pores (so that more evaporable water is retained), or the rate of decomposition of hydrated phases, or whether structural changes occur over a longer time as a result of diffusive processes or creep.

In addition to the damage done by capillary pressure, microcracking may be induced in mortar and concrete as a result of differential thermal expansion of the aggregates and hardened cement paste during drying.

To avoid microcracking and decomposition of hydration products, vacuum oven drying at lower temperature can be used. Detwiler et al. [21] suggested that oven drying should be avoided above a temperature of 35 °C. Unfortunately, at such low temperatures, the hydration process is accelerated by heating [5], and specimens need a longer time to attain constant mass, so the degree of hydration and the microstructure will be altered.

2.3. Microwave drying

Microwave drying has been used for determining total water content [22] and for accelerated curing, but has not been reported for sample preparation. Microwave heating results from absorption of electromagnetic radiation by loosely coupled water molecules [23], leading to rapid heating and moisture transport, with significant potential time savings. Studies of microwave drying of stone indicate that the temperature gradient is reversed, with the interior being warmer during microwave drying [24], whereas the surface is warmer during convective heating [24].

Microwave oven drying has been used as a quality control tool and a rapid method to measure water content of as-delivered fresh concrete [22,25,26]. Kilogram-scale samples can be dried in about 15 min in a 900-watt microwave oven [22,25] . However, the heating from the microwaves can accelerate the cement hydration [27,28]. Furthermore, rapid thermal expansion of the pore liquid could cause damage [29], as could development of water vapor pressure inside the sample.

2.4. D-drying

D-drying, or dry ice drying, was first mentioned by Powers [30], and was proposed as a drying technique by Copeland and Hayes [31]. The D-drying apparatus consists of a vacuum desiccator attached to a vacuum pump through a side arm of a cold trap, which is cooled by a mixture of solid CO_2 and alcohol at a temperature of −79 °C. The partial pressure of water vapor over dry ice is 0.07 Pa [5]. The vacuum applied to facilitate the drying process should keep the pressure in the system below 4 Pa. Under these conditions, removal of pore solution is very slow. The time needed to reach a constant sample weight depends on many factors, such as the vacuum level, the sample weight being evacuated, and the sample size; for millimeter-sized samples, it takes approximately 14 days [5], and possibly longer [20]. Obviously, D-drying cannot promptly arrest the early hydration at the desired time.

D-drying is commonly identified as the best standard drying technique, because it is generally assumed to remove all of the physically adsorbed (unbound) water in the cement paste pores and to be the best microstructure-preserving drying method [5], [32]. It has been calculated that at a water vapor pressure of 0.07 Pa, the gel contains just a little more than two molecules of water per mole of C–S–H (called "tobermorite gel" by Brunauer [33]). Heating to constant mass at 105 °C in an atmosphere of uncontrolled humidity, but free from CO_2, can reduce the water content to approximately the same value.

Water retained in pastes subjected to D-drying or equivalent procedures is known as "non-evaporable" water. This is not a measure of chemically bound water, as some water from interlayer spaces (which is considered to be part of the chemically bound water) is lost under these conditions [34]. D-drying can nevertheless be used as a rough measure of the degree of reaction [35].

2.5. P-drying

P-drying, or perchlorate drying, is carried out at ambient temperature by placing the specimen to be dried over magnesium perchlorate hydrates (dihydrate and tetrahydrate) ($Mg(ClO_4)_2 \cdot 2H_2O$–$Mg(ClO_4)_2 \cdot 4H_2O$) of analytical grade purity to obtain a partial pressure of water of 1.1 Pa at 25°C [31]. Based on this vapor pressure, P-dried C–S–H gel is expected to contain ~2.8 molecules of water per mole of C–S–H [33].

2.6. Vacuum drying

Vacuum drying is typically done in a chamber with pressure ≤0.1 Pa, resulting in a vapor pressure of water similar to that achieved in D-drying [32]. Vacuum drying was found by Zhang and Glasser [32] to degrade ettringite and monosulphate, causing serious damage to the pore structure and increasing the pore volume. Diamond [36] found that this technique removed significantly less water than oven drying at 105 °C. However, Gallé observed [7] that vacuum-dried samples of hardened cement paste suffered stresses and microcracks similar to those found in samples dried in an oven at 60 and 105 °C. Moreover, this drying technique is slow, so it cannot effectively arrest early hydration at the desired time.

2.7. Freeze drying

It has been argued that freeze drying causes less damage to the microstructure than oven drying [37]. A specimen is immersed directly into liquid nitrogen (−196 °C) or placed in a container that is submerged into liquid nitrogen. After freezing, the specimens are evacuated in a freeze dryer at a low temperature (−78°C) and pressure (4 Pa). After 24 h of vacuum freeze drying, water is removed effectively from millimeter-sized particles of water-saturated hardened cement paste [18].

For small samples, freezing of pore water is almost instantaneous, so the cement hydration can be arrested immediately. Gallé [7] claimed that quick freezing at very low temperature prevents the growth of big ice crystals. However, extremely rapid cooling ($>10^6$ K sec^{-1}) is required to form an amorphous solid by preventing crystallization of water [38]. The rate of cooling in liquid nitrogen is less than required to vitrify the water in cement paste, owing to the formation of an insulating envelope of gas surrounding the specimen, [39]. Even if amorphous water formed in the specimen, it would recrystallize at about −130 °C, which is slightly above the glass transition temperature of water ($T_g \approx 136$ K) [40]; therefore, crystallization would occur during sublimation. To avoid this pitfall, Gillott [39] recommended that, prior to cooling in liquid nitrogen, the specimen be immersed in propane, isopentane, or Freon® 22. These compounds have a low freezing point, but a relatively high boiling point, so they are not vaporized as readily by heat from the specimen as is nitrogen; therefore, cooling is more efficient. Chilling with Freon® before freeze drying has been used in cement pastes by Moukwa and Aitcin [41]. Nevertheless, crystallization of the pore water is inevitable during these procedures, and the growth of the crystals is expected to damage the microstructure [42].

After freezing, the specimens are transferred into a freeze dryer. Under vacuum, the water molecules sublime directly from solid ice crystals to gas without passing through the liquid state, so the danger of capillary stresses is eliminated. However, in a study by Zhang and Glasser [32] of calcium sulphoaluminate cement, the high vacuum was found to degrade ettringite and monosulphate and to critically damage the pore structure. Konecny and Naqvi [18] found that the pores of hardened cement pastes were damaged by freeze drying. A study by Gallé [7] also found that this method produced cracks and alterations to the microstructure similar to oven drying, yet removed less of the water. A recent study by Collier et al. [9] observed by SEM that more microcracks (approximately 0.1 μm in width) were present in freeze dried samples than in samples exchanged into acetone and dried under ambient conditions.

2.8. Supercritical drying

Supercritical drying has been used for a variety of materials, in particular biological tissues and materials with a delicate layered structure, which need to be prepared for SEM observations by removing the water without collapsing the structure of the material. The first report on the use of supercritical drying to produce aerogels was published by Kistler [43]; a good review of the method was published by Gesser and Goswami [44]. Owing to the high porosity and fragility of the pore structure of a gel, when dehydrated under normal conditions, the gel collapses into a powder. However, when the gel is dehydrated under supercritical temperature and pressure conditions, the liquid vapor boundary within the pores of the gel no longer exists, so there is no capillary pressure, and the gel does not collapse on drying. It has not been applied in cement-based materials, but it has been mentioned as an alternative drying technique [8,39].

To avoid the high critical temperature of water, it is common to exchange the pore liquid for a fluid that has a lower critical point. Carbon dioxide (CO_2) is widely used, because of its low critical point (31.1°C, 7.38 MPa), but it would cause carbonation of cement pastes. Indeed, supercritical CO_2 has been used to densify cement paste for waste disposal [45,46]. Freon® could be used for supercritical drying of cement paste, because it is inert; however, because it is immiscible with water, an exchange solvent must be used. Supercritical drying is expected to preserve the structure, if an exchange solvent can be found that introduces minimal artifacts.

3. Solvent exchange

3.1. Solvent exchange mechanism

Table 1 lists the physical properties of solvents that have been used to exchange for water in cement-based materials. The corresponding properties of water are also included for comparison. An ideal solvent would have small molecular size, so that it can penetrate into the smallest pores to replace water. Lower boiling point (higher vapor pressure) facilitates removal of the solvent without heating to temperatures at which the structure and composition of cement might be affected. The solvent should be miscible with water to replace the water in the pores and stop the hydration. Fast diffusion of the solvent in water can arrest the hydration effectively. Lower surface tension can minimize pore structure damage upon drying.

3.2. Solvent exchange procedure

During solvent replacement, the specimen is first weighed and then immersed in an organic liquid. Upon immersion, the solvent diffuses into the paste and replaces the pore solution. Penetration of the solvent is monitored by the change in mass of the specimen. When the weight stabilizes, the solvent is removed by evaporation at ambient or elevated temperature, under atmospheric pressure or vacuum.

3.2.1. Sample size

Taylor and Turner [17], Hughes [47], Feldman and Beaudoin [10] and Beaudoin et al. [48,49] used small with 25–30 mm in diameter and 1–2 mm in thickness. The soaking time varied from 2 days [49] to 10 days [10]. Gran and Hansen [50] made cylindrical samples 5.5 mm in diameter and 10 mm in length, and found that the time needed to reach 95% exchange of the ethanol was nearly 3 weeks. Hughes [47] sawed samples into disks (33 mm in diameter and 3 mm in length), then tracked weight change during the exchange and found that after

Table 1
Physical properties of solvents used to exchange water in cement-based materials [11].

Substance	Formula	A (Å^2)[a]	ρ_L (g/cm^3)[b]	T_B (°C)[c]	Solubility in water at 25 °C	$D\times10^5$ (cm^2/s)[d]	γ_{LV} (mN/m)[e]	p_V (kPa)[f]	Reference
Water	H_2O	11.4	0.9982	100	–	–	71.99	3.17	
Acetone	$(CH_3)_2CO$		0.7899	56.6	Miscible	1.28	23.46	30.8	[9,17,55,74]
Ethanol	CH_3CH_2OH		0.7893	78.4	Miscible	1.24	21.97	7.87	[47,50,59–61,64,71]
Isopropanol	$(CH_3)_2CHOH$	27.2	0.7855	82	Miscible	2.02	20.93	6.02	[10,18,37,47–49,51,55,57,61,62,64,74]
Methanol	CH_3OH	18.1	0.7914	64.5	Miscible	1.28	22.07	16.9	[10,37,48,49,52,56–58,60,61,71,73,74]
Tetrahydrofuran	$(CH_2)_4O$		0.8892	66	Miscible		26.4	19	
Dimethyl sulfoxide (DMSO)	(CH3)2SO		1.1004	189 (melting 18.5)	Miscible		43.54 (20 °C)	0.0056 (20 °C)	[48]
Benzene	C_6H_6		0.8765	80	0.8 g/L	1.02	28.22	12.7	[74]
Cyclohexane	C_6H_{12}		0.7785	80.74	Immiscible		24.65	13	
Diethyl ether	$(C_2H_5)_2O$		0.7134	34.6	69 g/L (20°C)		72.8	53.3 (18°C)	
Hexane	C_6H_{14}		0.6594	69	Immiscible		17.89	20.2	
Pentane	C_5H_{12}		0.6262	36.1	0.1 g/L (20 °C)		15.49	68.3	[58]
Toluene	$C_6H_5CH_3$		0.8669	110.6	0.47 g/L		27.93	3.79	
An ideal solvent		small	–	low	miscible	fast	low	low	

[a] Molecular area cross-sectional area.
[b] Density at 20°C.
[c] Boiling point at 760 mm Hg.
[d] Diffusion coefficient in water.
[e] Surface tension at 25 °C.
[f] Vapor pressure at 25 °C.

1000 min of soaking the weight reached equilibrium. In any diffusion process, the equilibration time, t_E, is given roughly by $t_E = a^2/D$, where a is the characteristic dimension and D is the diffusivity. In an exchange experiment, the length a would be the thinnest dimension of the sample, so an increase in thickness from 1 to 2 mm would cause an increase in exchange time by a factor of about 4, which is consistent with the results cited above.

If the sample is crushed into particles before exchange, then the process can be modeled as diffusion from a sphere into a surrounding bath. If the volume of the bath is much greater than that of the sample, then the composition of the bath can be assumed to be constant (*e.g.*, pure isopropanol). As shown in the Appendix, solving the diffusion equation for a sphere with an initial concentration C_0 and a constant surface concentration C_1, the average concentration in the particle, $\langle c(r,t)\rangle$, is given by

$$\frac{\langle c(r,t)\rangle - C_1}{C_0 - C_1} = \sum_{n=1}^{\infty} \frac{6}{n^2\pi^2} \exp\left[-n^2\pi^2\left(\frac{Dt}{a^2}\right)\right] \approx \frac{6}{\pi^2} \exp\left[-\pi^2\left(\frac{Dt}{a^2}\right)\right] \tag{2}$$

where the approximation applies when $Dt/a^2 > 0.1$, by which point the normalized concentration in the pores (*i.e.*, the left side of Eq. (2)) has dropped to about half its original value. The exact and approximate equations are shown in Fig. 7. The normalized concentration is reduced to 0.1% of its original value by the time that $Dt/a^2 \approx 0.65$. Using a typical value of diffusivity for alcohol in cement paste of $D \approx 1.0 \times 10^{-11}$ m^2/s [51], the time to replace the water with 99.9% isopropanol in a granule of cement paste with a radius of 1 mm would be roughly $(0.65)(0.001)^2/10^{-11} \approx 6.5 \times 10^4$ s ≈ 18 h.

3.2.2. Solution-to-sample ratio

Aligizaki [8] suggested that the solution:sample volume ratio be taken as 100:1, Day and Marsh [37] used solvent:pore water = 500:1 and Beaudoin *et al.* [48] used solvent : solid = 100:0.003, so there was no need to renew solvent. If the solvent is not renewed regularly, the solution-to-sample ratio must be high; however, a lower solution: sample ratio can be used if the solvent is renewed frequently.

This situation can be quantified by modeling the exchange as the diffusion from a spherical particle into a surrounding bath of finite volume (but well stirred, so that the concentration at the surface of the particle is equal to the average composition of the bath). The solution in this case is complicated (see Appendix), but the results obtained numerically show that equilibrium is obtained in about the same time as for the infinite bath; that is, $Dt_E/a^2 \le 0.65$. However, in this case, the equilibrium concentration depends on the porosity of the particles, ϕ, and the volume ratio of the bath, V_B, to that of the particles, V_P. The final composition of the pore liquid is

$$\frac{\langle c(r,\infty)\rangle - C_1}{C_0 - C_1} \approx \frac{\phi}{V_B / V_P + \phi} \tag{3}$$

where C_0 and C_1 are the initial concentrations in the pores and in the surrounding bath, respectively. Thus, if $\phi \approx 0.3$, the volume of the bath must be about 300 times greater than the total volume of particles, if the water content in the pores is to be reduced to 0.1%.

3.2.3. Frequency of solution renewed

To facilitate the diffusion process, the solvent should be renewed regularly, if the solution:water ratio is low. Parrott [52] and Day and Marsh [37] renewed solvent every hour during the first 24 h of the experiment and less frequently afterwards. Less frequency is needed if a higher solution:sample ratio is used and the solution is stirred. From Eq. (3), we see that when $\phi = 0.3$, if the liquid volume is 10 times greater than the sample volume, then the equilibrium concentration in the pores is 3% of its initial value; if the liquid is changed 2 more times, the concentration drops to $(0.03)^3$. To achieve the same dilution in a single exchange would take 1/3 as long, but requires 300 times more solvent.

3.2.4. Soaking time

The time needed for exchange of pore water with the solvent depends on the porosity, diffusivity, and the dimensions of the specimens tested. For example, it has been reported by Gran and Hansen [50] that for 3-year-old cylindrical white cement paste specimens 5.5 mm in diameter and 10 mm in length, the time needed can vary from 1 to 2 days for pastes with w/c = 1.0 up to 14–21 days for pastes with w/c = 0.3. This reflects the lower diffusivity in the denser paste: using the longer exchange time in each case, we estimate $D \approx 3 \times 10^{-11}$ m^2/s for w/c = 1.0 and 3×10^{-12} m^2/s for w/c = 0.3. Collier [9] immersed samples in acetone for 7 days. Struble and Stutzman [53] immersed their specimens in ethanol at a slightly elevated temperature (*e.g.*, 60°C) to reduce the exchange time. According to the Stokes–Einstein equation [54], the diffusivity is inversely related to the viscosity, so those properties have the same temperature dependence. The viscosity of water or ethanol only drops by about a factor of 2 on heating from room temperature to 60 °C, so the advantages of heating are modest. Of course, the temperature must not be raised so high that the structure of the paste is altered.

3.2.5. Solvent removal method

After arresting the hydration reaction, removal of the solvent has been performed using convective heating [55], vacuum drying at ambient temperature [56], evacuation followed by heating [10], or heating under vacuum [49]. Feldman and Beaudoin [10] concluded that after arresting the hydration, subsequent evacuation times and temperature of heating are relatively unimportant to the resulting pore size distribution. They claimed that water replacement using isopropanol followed by immediate evacuation and heating at 100 °C for 20 h caused less damage to the cement paste than replacement by methanol followed by heating for various periods. Beaudoin et al. [48] later recommended the use of isopropanol followed by vacuum drying for 24 h for exchange of saturated specimens. Mikhail and Selim [57] pointed out that drying temperatures exceeding 100 °C were needed to remove the adsorbed solvent molecules from hydrated cement paste. Unfortunately, such a severe drying treatment tends to remove structural water and results in an irreversible decomposition of the hydration products. Taylor and Turner [17] also concluded that organic liquids adsorbed so strongly onto the surface of hydrating C_3S that they could not be completely removed by vacuum drying or oven drying at temperatures that do not profoundly alter the cement paste.

3.2.6. Second replacement by other solvent

Studies by Litvan [58] indicated that exchanging first with methanol and then with pentane is the most effective method of preserving the microstructure of C–S–H in its saturated state. Pentane has a relatively low boiling point and small surface tension (as shown in Table 1). Beaudoin et al. [48] used dimethyl sulfoxide (DMSO), which has very low vapor pressure (Table 1), as the second solvent to replace methanol and isopropanol, to verify whether the first solvent replacement had a reversible effect on the length change. They concluded that the initial exchange with methanol has an irreversible effect on length change, while isopropanol has a reversible effect.

3.3. Physical interaction

It is generally agreed that drying following solvent exchange is less damaging for the original microstructure of hydrated cement-based materials than directly drying the water-saturated paste [33,34,47,49], owing to the relatively low surface tension of organic solvents. However, some solvents may react with cement hydration products during the exchange process and thus may alter their microstructure [17,48,59,60]. Discussions and investigations are still under way in this field [7,9,53,56,61].

3.3.1. Penetration into the pores

Mikhail and Selim [57] showed that different solvents have different accessibility to the pores in cement paste by conducting sorption tests on pre-dried samples. Isopropanol is a larger molecule than methanol: the molecular diameter of isopropanol is ~0.52 nm and that of methanol is ~0.42 nm. Length-change measurements reported by Feldman [62] indicate that immersion of thin cement paste samples in methanol results in large expansions, while samples immersed in isopropanol shrink. The increase of volume was associated with the penetration of the layered silicate structure by the relatively small methanol molecules. Parrott [63] found methanol provided the fastest exchange with pore water compared to other solvents. The length of exchange time did not have an effect upon the total porosity detected in paste made from C_3S, although methanol adsorption experiments indicated an irrecoverable drying shrinkage. Hughes [47] and Hughes and Crossley [64] found that while the penetration of methanol in saturated pastes containing silica fume appeared to be a standard counter-diffusion process, the immersion of similar specimens in isopropanol yields unexpected non-monotonic weight changes. This could be due to difficulty in penetration into the cement matrix by the larger isopropanol molecules, followed by chemical interactions of isopropanol with the cement paste.

3.3.2. Preserving or damaging the microstructure

Reports regarding microstructural changes following drying are highly contradictory. It is generally assumed that methods that yield dry samples with the highest surface area or smallest pores are the least damaging. This is not certain, because chemical reaction with solvents might yield a product with a fine texture. Moreover, the measurement methods apply stress to the sample that could alter the structure. Mercury intrusion is most likely to cause damage [65], but thermoporometry [66,67] exerts a stress almost one-tenth as large [68]. Even nitrogen desorption can cause significant deformation of delicate gel structures, because it involves evaporation of liquid nitrogen, which has a surface energy of ~9 mJ/m^2 [68]. There seem to be only two studies in which the pore size distribution was measured before and after drying. Villadsen [69] performed thermoporometry on a mature cement paste, then dried and resaturated it, and repeated the measurement. Similarly, Sun and Scherer [67] used thermoporometry to measure a mortar, then exchanged it into isopropanol, dried it, resaturated it with water, and repeated the measurement. In both cases, the pore size and pore volume increased after drying. The magnitude of the change should depend on the initial pore size and strength of the sample, and the surface tension of the liquid present during drying, as well as the pressure exerted by the measurement technique. These factors probably account for most of the discrepancies between the studies described in the remainder of this section.

By using MIP, Thomas [61] found that the pore size distributions of vacuum-dried cement samples were unaffected by methanol soaking. He concluded that solvent exchange techniques were suitable for the preparation of samples for pore structure determinations. Konecny and Naqvi [18] concluded that, compared to oven drying and freeze drying, solvent replacement with isopropanol produced the least damage, because MIP revealed more small pores after drying from isopropanol. Feldman and Beaudoin [10] concluded that methanol and isopropanol applied the least stress to the microstructure of cement. Collier [9], using acetone as his solvent, found that 16 solvent exchanged samples had higher total pore area than non-solvent-exchanged samples, as determined by the MIP. He explained this by the higher surface tension of water causing higher capillary forces in the non-exchanged samples, leading to partial collapse of the pores.

Other studies indicated that solvent exchange could affect the pore structure of cement. Parrott et al. [70] found that methanol replacement changed the pore size distribution of C_3S paste, based on surface area measurement by nitrogen adsorption. Pore structure alterations caused by removing water from the pores could be minimized by relatively short exchange periods, so that about half of the pore water was exchanged. This would imply that the chemical interaction of methanol with paste is more destructive than the higher capillary pressure during evaporation of water. Beaudoin [60] found that the NAD surface area was changed significantly by straight-chain aliphatic alcohols (methanol, ethanol, butanol, amyl alcohol, hexanol, octanol, and decanol). Particularly large changes in porosity and pore size distribution were reported to result from decanol treatment, which is not expected, based on the surface tension or reactivity of that molecule. However, the samples in ref. [60] were pre-dried in a vacuum vessel at 110 °C for 3 h before any vacuum saturation with solvents; during this oven drying, the microstructure could be damaged. Moreover, the higher alcohols would be difficult to remove, owing to their low vapor pressure; therefore, the low measured surface area might reflect blocking of the smaller pores by retained alcohol. Beaudoin [71] reported that the surface area of calcium hydroxide samples nearly tripled after immersion in methanol for 24 h. Based on MIP and length measurements, Feldman and Beaudoin [10] found that methanol increased the threshold pore diameter, while isopropanol did not. Beaudoin and Tamtsia [49] used shrinkage measurement and real time a.c. impedance spectra, and observed the lowest shrinkage for the isopropanol-exchanged specimens; however, the isopropanol exchange did not appear to preserve the structure, because the relative size of the high-frequency arc was consistent with a pore coarsening effect from drying.

Vichit-Vadakan and Scherer [72] found that the exchange with isopropanol seemed to be done after about 2 weeks of soaking for a mature rod of Type III cement paste about 6 mm in diameter; however, the weight change then accelerated and more isopropanol was taken up over 6 weeks. By that time, the amount of isopropanol absorbed corresponded to the porosity found by weight loss at 105 °C, and the permeability had risen by 100 times, while the modulus only decreased by ~5%. As discussed before, the weight loss at 105 °C overestimates the porosity, so the isopropanol was probably reacting with the paste or invading the interlayer space. This could account for the difference in swelling behavior seen in methanol and isopropanol: the smaller methanol molecule immediately exchanges for water in the interlayer space, so the body expands; the larger isopropanol does not immediately enter the C–S–H, but it osmotically extracts water from the interlayer space, so the body contracts. Eventually, the alcohol penetrates the C–S–H, causing microstructural change that is reflected in the increased permeability of the paste. This is consistent with the nonmonotonic weight changes observed by Hughes and Crossley [47,64], mentioned earlier.

3.4. Chemical interaction

On the basis of differential thermal analysis (DTA), Parrott [56] found no signs of chemical interaction of cement pastes with organic liquids, including methanol, upon heating samples to 750 °C in a nitrogen atmosphere. Similarly, based on XRD and infrared spectroscopy (FTIR), Thomas [61] found no evidence of a reaction product due to the interaction of either methanol and CH or methanol and cement paste at room temperature.

In contrast, many studies have reported the reaction of solvents in cement. The presence of organics is especially undesirable if any form of thermal analysis is to be carried out, since on heating they react with C–S–H to give CO_2. Methanol, for instance, has been found to react with portlandite to form "carbonate-like materials" by Day, who heated the sample to 1000 °C in a TGA [73]. Methanol is reported to bind with hydrating and mature cement paste, and resists desorption by vacuum drying or vacuum followed by heating to 200 °C [60]. Calcium methoxide or a methylated complex was identified by XRD,

Table 2
Comparison of drying techniques.

Technique	Process	Pros	Cons	Stop hydration effectively?	Suitable for analysis
Oven drying	Atmospheric pressure, $35 \le T$ (°C) ≤ 105	fast	Microcracking, degrade C–S–H, ettringite	no	
Microwave drying	Lower power, several minutes	fastest	Destroy microstructure	yes	
D-drying	Vacuum <4.2 Pa, solid $CO_2 +$ alcohol at -79°C, 14 days	Definition of “non-evaporable” water	Remove some bound water	no	
P-drying	1.1 Pa, room temperature		Contains residual pore water	no	
Vacuum drying	Vacuum chamber 0.1 Pa		Degrade ettringite and monosulphate, increase pore volume, damage pore structure, Remove less water	no	
Freeze drying	Submerge in liquid $N_2 > 15$ min, then place in a freeze dryer for >1 day	Less damage to structure No hydration products change	Degrade ettringite and monosulphate	yes	MIP, TGA
Supercritical drying	Replace pore water by solvent, then freon, supercritical drying of freon	Preserve pore structure	Expensive complex process	yes	Microscopy
Solvent exchange	Solvent renewed regularly, then dried in a desiccator	Small damage to pore structure; gives finest pore size distribution applies least stress Isopropanol is the best solvent	May partially dehydrate the C–S–H and ettringite; interaction with cement, could be sorbed into cement phases and not be removed without affecting microstructure	yes	MIP, NAD microscopy

DTA, and FTIR, as reaction products between methanol and $Ca(OH)_2$ at 22 °C [71]. Length-change experiments reported by Beaudoin et al. [74] indicate that other solvents, such as isopropanol, also react chemically with calcium hydroxide.

Most solvents are strongly adsorbed on cement paste and cannot be entirely removed by conventional drying techniques [61,74]. Feldman et al. [63,70] argue that methanol and other organic liquids penetrate the layered silicate structure. Isopropanol and methanol vapor isotherms reported by Mikhail and Selim [57] were characterized by a marked hysteresis at low relative pressures after several adsorption–desorption cycles, even after prolonged vacuum drying at room temperature. Taylor and Turner [17] pointed out that reaction of acetone with CH could lead to aldol condensation, affecting TGA results. Beaudoin et al. [48,74] observed significant color and length changes for the samples immersed in acetone, which were interpreted as signs of strong chemical interaction between acetone and calcium hydroxide; however, the chemical reaction products were not identified. Mitchell and Margeson [55] also found that arresting cement hydration in acetone affected the DTG peaks for calcium carbonate at approximately 630 °C. Beaudoin et al. [48,74] found that other solvents, such as benzene and isopropanol, could react chemically with calcium hydroxide; the length of CH crystals increased when immersed in methanol, isopropanol, and acetone. In an investigation of the length change of saturated Portland cement pastes immersed in various organic solvents, Feldman et al. [29,30,32] found that methanol interacts with the hydrated cement and is unsuitable for measuring diffusivities; however, isopropanol was concluded to be an acceptable fluid for diffusion coefficient measurements in hydrated Portland cement, because it is relatively inert.

4. Comparison of drying methods

Table 2 summarizes the findings of many studies of drying methods for cement paste. Most researchers used MIP, NAD or SEM to evaluate the effect on microstructure, and TGA or XRD to detect the compositional changes after drying. Moukwa and Aitcin [41] used MIP to compare the effects of three drying procedures for arresting hydration and drying of cement pastes following 14 days of hydration. Oven drying for 24 h at 105 °C opened pores in the range of 0.02–0.1 μm. They concluded that freeze drying followed by oven drying could be a suitable procedure in MIP measurement. Konecny and Naqvi [18] compared direct oven drying, isopropanol replacement drying, and two freeze-drying procedures, and concluded that solvent replacement with isopropanol was preferable for MIP samples, although it is more time consuming than freeze drying. Similarly, Feldman and Beaudoin [10] concluded that isopropanol exchange was less destructive than vacuum drying with or without oven drying, and drying at 11% relative humidity. Gallé [7] compared oven drying at 60 °C and 105 °C, vacuum drying and freeze drying. He found that oven drying generated significant damage of the microstructure in the range of capillary porosity, and concluded that freeze drying was best for MIP samples. Unfortunately, to reduce the duration of the experiments, he did not use any solvent replacement technique. Juenger and Jennings [19] studied causes of variation in determining the surface area and porosity of cement paste by NAD measurement. They compared oven drying at 105 °C, D-drying, and exchange with methanol followed by D-drying, and concluded that D-drying gave more consistent and reliable results in NAD. Korpa and Trettin [5] compared freeze drying, D-drying, P-drying and oven drying of 28-day-old paste. Based on NAD, TGA and NMR, they concluded that no method could remove only the unbound water and preserve the microstructure; however, compared to other methods, freeze drying is slightly better. Unfortunately, the authors did not include solvent replacement methods in their study. Collier et al. [9] compared acetone exchange, freeze drying, oven drying at 60 °C, and vacuum drying of 7-day-old paste. Using XRD, TGA, SEM and MIP, they concluded that none of the methods of arresting hydration appeared to cause any major difference to the composition and microstructure of hardened cement pastes containing high levels of slag and ash. Freeze drying appeared to cause more microstructural cracking than acetone exchange, but the quantitative determination of the CH content of the paste could be erroneous; unfortunately, they did not test “safer” solvents (*e.g.*, isopropanol).

We can summarize the results as follows (where “>” means “better”):

1) To preserve microstructure: solvent replacement > freeze drying > oven drying.
2) To preserve composition: freeze drying > oven drying > solvent replacement
3) To save time: oven drying > freeze drying > solvent replacement
4) All the techniques more or less dehydrate C–S–H and ettringite.
5) Solvent replacement creates chemical artifacts in the specimens by reaction with hydration products or by strong adsorption.
6) D-drying, P-drying, and vacuum drying are similar processes. They cannot arrest the hydration effectively, owing to slow water removal. They are better for microstructural preservation than oven drying, but not as good as solvent replacement.

5. Experimental procedure

Most of the earlier studies focus on mature paste, so the results are not necessarily applicable to measurement of the degree of hydration (DOH) of young pastes. Here we describe an experimental study emphasizing the impact of solvent exchange and freeze drying on the apparent DOH of young pastes. Particular care is taken to insure complete exchange without exposure to CO_2.

5.1. Materials

Three types of cements were used: Type I ordinary Portland cement, white Portland cement, and Class H oil well cement. Early age cement paste samples were mainly prepared from Class H cement. The water-to-cement ratio (w/c) used was 0.35, except for an older sample (113 d) with w/c = 0.38. The mixing procedure, described in detail in ref. [75], began by adding ~550 g of cement over ~30 s to a blender running at ~3500 rpm. Mixing continued at 3500 rpm for another 30 s, then at ~9300 rpm for an additional 30 s. The mixer was stopped and the paste was scraped down from the walls of the jar. After 2.5 min of resting, the blender was turned on again at a speed of 9300 rpm for 30 s. To avoid carbonation, the mixing water was deionized and freshly boiled. After mixing, the pastes were placed in a polypropylene container (55 mm in diameter and 45 mm in height) and exposed to vacuum for 5 min to evacuate the air bubbles. The containers were then sealed and immersed in a water bath maintained at 25 °C until required for testing. After curing for the required time, cement paste was crushed and the hydration was arrested by the various methods described below. Pieces ~3 mm in diameter were chosen from the middle of the cement sample. For experiments involving Class H cement, samples were taken at the following time intervals: 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, 10 h, 12 h, 1 d, 1.5 d, 2 d, 3 d. Initial and final setting times were determined by the Vicat test (ASTM C191). Samples that were to be tested after more than 3 days of hydration were removed from the molds 1 day after casting, and stored in limewater to prevent carbonation. When it was time to dry the samples, they were taken out of the limewater and the surface water was wiped off before conducting the drying process.

Every precaution was taken in the present study to avoid any CO_2 attack from mixing (boiled distilled water and fresh cement), curing (sealed container with lime water), preparation (no additives), and TGA (high quality nitrogen as a purge). Therefore, if any carbonation occurred, it was from the drying method.

5.2. Freeze drying

When using freeze drying to stop cement hydration, a 10 g (~5 mL) sample of cement paste was placed in an 8 mL glass vial and securely sealed with Al foil. The vial was completely submerged in liquid nitrogen until transfer to the freeze dryer. The vials were removed from the liquid nitrogen with tongs and small holes were poked into the foil cover to allow water vapor to escape. The vials were immediately placed in a flask and connected to a Virtis Benchtop freeze dryer, in which temperature and vacuum were held at -77.7 °C and to 4.8 Pa, respectively for at least 2 days. Thereafter, the sample was kept in a vacuum chamber until further measurements.

5.3. Solvent replacement

To compare with freeze drying, companion samples were submerged in solvents to stop hydration. Two grams of each sample were placed into 20 mL glass vials that were filled with the appropriate solvent. Solvents used in this study were acetone, ethanol, isopropanol and tetrahydrofuran. To our knowledge, tetrahydrofuran has not been used previously for arresting hydration. The vials were capped and rotated for 5 min at a very low speed, then placed back into the chemical fume hood. Solvents were refreshed every 1 h for the first 5 h, and then once a day for a week. The samples were soaked in the solvents for 14 days prior to analysis, if not specified otherwise in the following. Based on Eq. (2), we estimate that 2 days of soaking would have been sufficient for complete exchange. Upon completion of the solvent exchange, samples were dried in a Secador mini desiccator cabinet with nitrogen flowing at a rate of 3.2 L/min until the weight stabilized. The samples were then stored in a vacuum chamber.

5.4. TGA

The degree of hydration was calculated from the weight loss measured by TGA (7HT, Perkin Elmer). Each 50 mg crushed sample was heated with the same temperature program: (i) held at 28 °C for 10 min; (ii) heated to 105 °C at 5°C/min; (iii) held for 30 min; (iv) heated to 1000 °C at 5 °C/min. High purity dry nitrogen flowing at 20 mL/min was used for the sample purge.

The degree of hydration, α, can be calculated from [35,76,77]:

$$\alpha = \frac{W_n}{n} - \mathrm{LOI} \tag{4}$$

where n is the mass proportion of non-evaporable water of the fully hydrated cement paste, LOI (Loss On Ignition) is the normalized weight loss of the unhydrated cement, and W_n is the normalized weight loss of the hydrated sample, given by

$$W_n = \frac{W_{105^\circ\mathrm{C}} - W_{1000^\circ\mathrm{C}}}{W_{1000^\circ\mathrm{C}}} \tag{5}$$

where W_T is the fractional weight loss at temperature T. The total weight fraction of non-evaporable water, n, calculated from the compositions using tabulated coefficients [78], is 0.23 for Class H cement, 0.23 for white Portland cement, and 0.25 for Type I cement, respectively.

From Eqs. (4) and (5), weight loss between 105 and 1000 °C is used to calculate degree of hydration. If carbonation has occurred because of exposure to the atmosphere, the weight loss used to calculate DOH must be corrected by taking account of the formula weights of calcium carbonate and hydroxide. Unfortunately, this correction is not trustworthy when solvent exchange is used, because the nature of the carbon compounds contributing to the weight loss is not known.

6. Results and discussion

6.1. Solvent type

Figs. 2 and 3 show the TGA weight loss and the corresponding derivative curves for Class H cement with w/c = 0.38 hydrated for 113 days, dried by freeze drying, or following solvents replacement with isopropanol, tetrahydrofuran, ethanol or acetone. One control sample without pre-drying was compared to the others (that is, the wet paste was put directly into the TGA). All the curves are similar below 600 °C. Above 600 °C, the curves from the sample without drying and the sample after freeze drying show a plateau, which means that there was no decarbonation of the sample. However, all the solvent-exchanged samples have an obvious weight loss after 600 °C and keep losing weight until after 1000 °C. Isopropanol causes the least weight loss, followed by tetrahydrofuran and ethanol; acetone causes the largest weight loss. The derivative curves in Fig. 3 show multiple peaks corresponding to this weight loss.

A color change was observed in the acetone-soaked sample: the liquid in the vessel changes from clear to a yellow to brownish color. This observation and the TG results are consistent with reports in the literature that acetone could form diacetone alcohol or 4-hydroxy-4-methyl-2-pentanone. This reaction is reversible and occurs in the presence of a base catalyst. A commonly reported catalyst is barium hydroxide, which has properties similar to those of calcium hydroxide. The reaction product, diacetone alcohol, (boiling point 166 °C) may adsorb on portlandite crystals [55]; when heated in the TGA, the film may react with the surface of the portlandite to form calcium carbonate, which is decarbonated at higher temperature. Other solvents, such as ethanol and isopropanol, are not known to undergo the same type of aldol reaction, although they do undergo elimination reactions in the presence of base catalysts [55]; again, adsorption on portlandite crystals is possible. Thus, if any form of thermal analysis is to be carried out, solvent exchange is undesirable, but isopropanol causes the least reaction in cement.

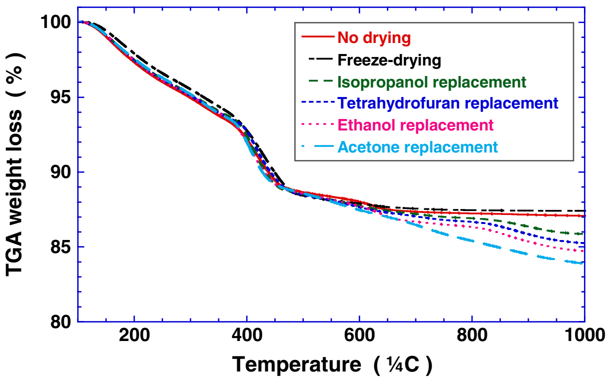

Fig. 2. TGA curves of Class H cement paste (w/c = 0.38, 113 days hydration age) dried by different techniques. "No drying" means the sample was tested in TGA without any pre-drying.

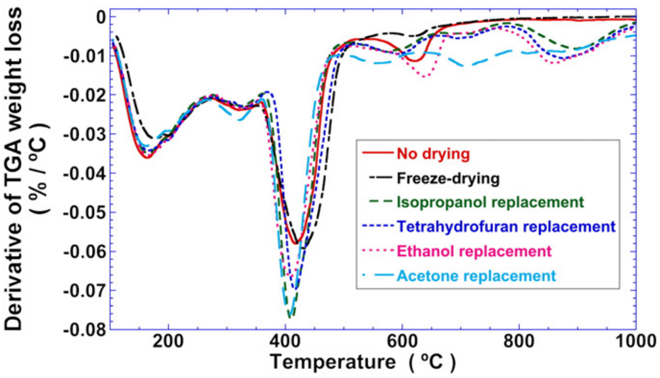

Fig. 3. Derivative of TGA curves of Class H cement paste (w/c = 0.38, 113 days hydration age) dried by different techniques.

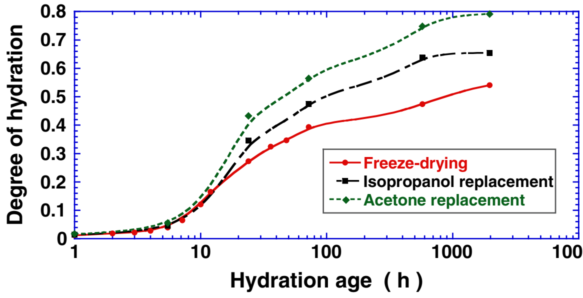

Fig. 4. Degree of hydration curves calculated from TGA results; Class H cement paste with w/c = 0.35 dried by different techniques.

6.2. Sample age

The standard method to determine the degree of hydration is to use the weight loss measured by TGA in Eqs. (4) and (5), However, if there is any accidental carbonation or other reactions, the degree of hydration is overestimated. Normally, carbonation in the TGA can be corrected by calculating the CO_2 loss in the decarbonation region (600–750 °C) and converting into a CH loss from the dehydroxylation region. However, from Fig. 2, the weight loss of solvent exchanged samples after 500 °C is continuously increased and correspondingly there are multiple peaks in the differential curves in Fig. 3. Therefore, the traditional carbonation correction method cannot be applied. Fig. 5 shows that directly heating the undried sample in the TGA in a flow of very pure N_2 can also prevent any carbonation and get a result close to that of the freeze-dried sample. However, samples will continue hydrating while awaiting measurement, so hydration must be arrested by exchange with a non-reactive solvent or freeze drying to determine the degree of hydration as a function of reaction time.

Fig. 4 shows the degrees of hydration versus time calculated from Eqs. (4) and (5). Hydration was arrested at time intervals up to

Table 3
TGA loss of weight (%) of Class H cement paste (w/c = 0.35).

Hydration age	Arresting method	105–250 °C	250–350 °C	350–600 °C	600–1000 °C	DOH (%)
5.5 h	Freeze drying	0.314	0.161	0.513	0.049	4.0
	Isopropanol	0.337	0.192	0.517	0.124	4.6
	Acetone	0.322	0.162	0.752	0.159	5.5
1 day	Freeze drying	1.548	0.945	3.305	0.432	27.3
	Isopropanol	1.738	0.976	3.603	1.430	34.6
	Acetone	1.579	0.967	3.994	2.940	43.3
3 days	Freeze drying	2.158	1.303	4.469	0.767	39.3
	Isopropanol	2.321	1.365	4.822	1.801	47.5
	Acetone	2.206	1.327	5.144	3.330	56.5
24 days	Freeze drying	2.734	1.869	5.291	0.392	47.4
	Isopropanol	3.031	1.910	6.109	2.308	63.9
	Acetone	2.976	2.091	6.442	3.783	74.8
82 days	Freeze drying	3.094	2.180	5.826	0.454	54.1
	Isopropanol	3.196	2.149	6.158	2.139	65.5
	Acetone	3.418	2.282	6.761	3.564	79.2

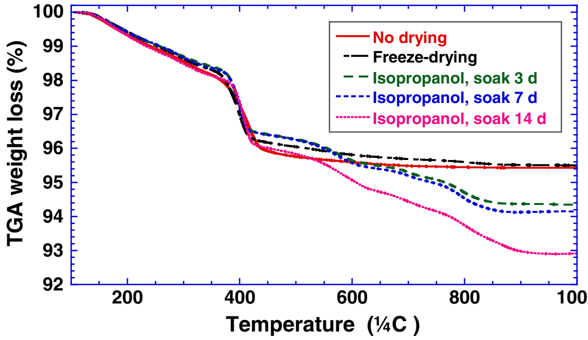

Fig. 5. TGA curves of Class H cement paste (w/c = 0.35, 1 day hydration age) dried by freeze drying and isopropanol replacement followed by N_2 flow dry. Various periods (3 days, 7 days and 14 days) was used for soaking samples in the solvent. “No drying” means the sample was tested in TGA without any pre-drying.

82 days by freeze drying, isopropanol replacement, and acetone replacement. Owing to the interaction between hydration products and solvents, leading to carbonation in the TGA, degrees of hydration from samples arrested in isopropanol and acetone are both larger than that obtained by the freeze drying method. For example, at the very early hydration age corresponding to initial setting (5.5 h), the degree of hydration from the freeze dried sample is 4%, but for the ones arrested in isopropanol and acetone it is 4.6% and 5.5%, respectively. The 15% and 37.5% over-estimation of the degree of hydration caused by the solvent interaction could be seriously misleading. For example, if one tries to interpret the degree of hydration at the setting point in terms of percolation theory, errors caused by inefficient hydration arrest or artifacts from carbonation lead to serious discrepancies [79]. For cement pastes after 82 days of hydration, the degrees of hydration from freeze dried, isopropanol- and acetone-arrested sample are 54%, 65% and 79%, respectively. Thus, there are also unacceptable errors in the cement hydration analysis for isopropanol, which is the “best” solvent.

Table 3 shows that there is an obvious weight loss from solvent-arrested samples, while the freeze dried samples show much less weight loss above 600 °C. Weight losses corresponding to the decomposition of gypsum and ettringite at 105–250 °C, C–S–H and carboaluminate decomposition at 250–350 °C, and the decomposition of CH at 350–600 °C are similar for all arresting methods [35]. The major weight loss difference occurs above 600 °C.

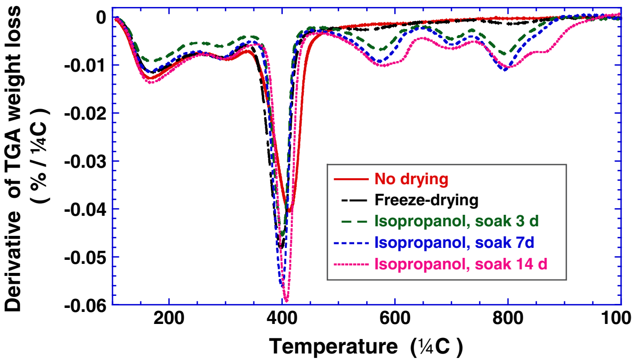

Fig. 6. Derivative of TGA curves of Class H cement paste (w/c = 0.35, 1 day hydration age) dried by freeze drying and isopropanol replacement followed by N_2 flow dry. Various periods (3 days, 7 days and 14 days) was used for soaking samples in the solvent. “No drying” means the sample was tested in TGA without any pre-drying.

6.3. Soaking time

If insufficient soaking time is permitted, the pore water, especially in the finer pores, will not be completely replaced by the solvent. However, Figs. 5 and 6 show that longer soaking time results in more carbonation. Isopropanol replacement introduced 26%, 31% and 57% more weight loss at 1000 °C for soaking times of 3, 7, and 14 days, respectively. Clearly, the sample should be removed from the solvent as soon as possible, taking account of the influence of particle size, pore size and porosity on the rate of exchange.

7. Conclusions

The water removal method used for pretreatment prior to chemical analysis or pore structure measurements can affect the results obtained. Many researchers have evaluated different drying techniques to test their effectiveness for water removal and/or to identify damage caused to the pore structure. Complete drying without any chemical and/or physical effects is not possible in practice. It is obvious that the selection of the appropriate technique for water removal depends on a number of factors, such as the time available, the property of interest of the material examined, and the equipment available. For some procedures, such as XRD, the presence of organic material may not matter, but even here the possibility of decomposing or altering hydrated aluminate phases must be considered. For electron microscopy and pore structure analysis, solvent exchange with isopropanol best preserves the microstructure. Isopropanol exchange could also be used as the first step to conduct supercritical drying, which is the method that is most protective of the microstructure, as it eliminates capillary pressure. Freeze drying has been found satisfactory for chemical analysis by TGA. Oven drying should be avoided for any purpose, other than measuring total moisture content. For arresting the hydration of young saturated cement, freeze drying and solvent exchange with isopropanol are the most effective techniques found to date.

Acknowledgments

The authors gratefully acknowledge the financial support provided by Halliburton. We are indebted to Prof. Robert Prud'homme (Chemical Engineering, Princeton University) for the use of his freeze dryer and to Prof. Andrew Bocarsly (Chemistry, Princeton University) for the suggestion to use tetrahydrofuran as an exchange solvent.

Appendix *Diffusion in a sphere*

This analysis applies to diffusion from a spherical region of radius a into a surrounding spherical region of radius b. In one case, the concentration is held constant between a and b (so the size of b is irrelevant), so the problem describes solvent exchange between a spherical particle and an infinite stirred bath. In the second case, the bath is stirred, but finite, so there is a no-flux boundary condition at $r = b$.

There is assumed to be only radial dependence, so the diffusion equation is

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial t^2} + \frac{2}{r}\frac{\partial c}{\partial t}\right). \tag{6}$$

Since we are describing diffusion within a porous body, we must be careful about the definition of concentration. If c refers to the composition of the liquid in the pores, then the composition of the porous particles is $\phi\, c$, where ϕ is the porosity (= volume fraction of pores). The diffusion coefficient in the porous body, D, is the diffusion coefficient of the pore liquid, D_L (assumed to be independent of composition), divided by the tortuosity, τ. The flux over the surface of the particle (into the bath) is

$$J = -\phi D \left.\frac{\partial c}{\partial r}\right|_{r=a}. \tag{7}$$

Case 1 — infinite stirred bath

Letting $u = r/a$ and $\theta = Dt/a^2$, Eq. (6) can be written as

$$\frac{\partial c}{\partial \theta} = \frac{\partial^2 c}{\partial u^2} + \frac{2}{u}\frac{\partial c}{\partial u}. \tag{8}$$

In this case, the initial concentration of the liquid inside the sphere is $c[r,0] = C_0$ and the boundary condition is $c[a,t] = C_1$, so

$$c[u,0] = C_0, 0 \le u \le 1 \tag{9}$$

$$c[1,\theta] = C_1, \theta > 0. \tag{10}$$

Using the Laplace transform to solve this differential equation, the result is

$$\frac{c[u,\theta]-C_1}{C_0-C_1} = -2\sum_{n=1}^{\infty}\frac{(-1)^n\ \sin(n\,\pi\,u)}{n\,\pi\,u}\ \exp\left(-n^2\pi^2\theta\right). \tag{11}$$

With Eq. (11), we can calculate the average concentration of the liquid in the sphere by averaging over its volume

$$\frac{\langle c[u,\theta]\rangle - C_1}{C_0-C_1} = \frac{3}{4\,\pi\,\phi}\int_0^1 4\,\pi\,\phi\,u^2\left(\frac{c[u,\theta]-C_1}{C_0-C_1}\right)du \tag{12}$$

and the result is

$$\frac{\langle c[u,\theta]\rangle - C_1}{C_0-C_1} = \sum_{n=1}^{\infty}\frac{6}{n^2\pi^2}\ \exp\left(-n^2\pi^2\theta\right). \tag{13}$$

The average concentration approaches C (so the exchange is complete) by the time that $Dt/a^2 \approx 0.5$. By the time that the normalized concentration has dropped to 0.01, and the first term of the sum is dominant (Fig. 7), so

$$\frac{\langle c[u,\theta]\rangle - C_1}{C_0-C_1} \approx \frac{6}{n^2}\ \exp\left(-\pi^2\theta\right). \tag{14}$$

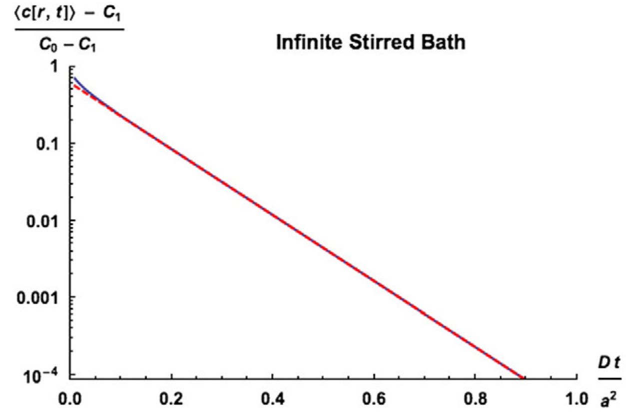

Fig. 7. Normalized concentration in the pores of a spherical particle with initial concentration C_0 surrounded by an infinite bath at concentration C_1. The solid curve is the exact solution and the dashed (red) curve is the approximation given in Eq. (2).

Case 2 — finite stirred bath

In this case, the initial concentration is C_0 in $0 \le r \le a$ and $C_1(t)$ in $a \le r \le b$, and there is no flux across $r = b$. The initial condition is

$$c[r,0] = C_0 + (C_1 - C_0)H[r-a] \tag{15}$$

or

$$c[u,0] = C_0 + (C_1 - C_0)H[u-1] \tag{16}$$

where $H[x]$ is the Heaviside step function, which is zero when $x<0$ and unity when $x>0$. At the outer boundary, there is no flux:

$$\left.\frac{\partial c}{\partial r}\right|_{r=b} = 0. \tag{17}$$

The ratio of the volume ratio of the bath to that of the particle is $R = \frac{b^3-a^3}{a^3}$, so $\frac{b}{a} = (1+R)^{1/3} \equiv B$, and

$$\left.\frac{\partial c}{\partial u}\right|_{u=B} = 0. \tag{18}$$

To preserve symmetry,

$$\left.\frac{\partial c}{\partial u}\right|_{u=0} = 0. \tag{19}$$

To solve this problem, it is better to proceed indirectly. First, we solve for diffusion from the spherical region $0 \le r \le a$ with a time-dependent boundary concentration, $c[a,\theta]$. Then we require that the boundary concentration account for conservation of mass. The number of moles diffusing out of the sphere is

$$n[t] = -4\,\pi\,a^2\phi\int_0^t D\left.\frac{\partial c}{\partial r}\right|_{r=a} dt \tag{20}$$

or

$$n[\theta] = -4\,\pi\,a^3\phi\int_0^\theta \left.\frac{\partial c}{\partial u}\right|_{u=1} d\theta. \tag{21}$$

Assuming that the outer region is stirred, the concentration at the boundary is

$$c[a,t] = C_1 + \frac{n[t]}{(4\pi/3)(b^3-a^3)} \tag{22}$$

or

$$c[1,\theta] = C_1 - \frac{3\ \phi}{B^3-1}\int_0^\theta \left.\frac{\partial c}{\partial u}\right|_{u=1} d\theta. \tag{23}$$

Taking the Laplace transform of the boundary concentration, and letting $k = 3\phi/(B^3-1)$, the transformed solution of Eq. (8) is

$$\mathrm{LT}[c[u,\theta]] = \frac{C_0}{s} - \frac{(C_0-C_1)}{\left(-k/s + 1 + k\ \coth\left[\sqrt{s}\right]/\sqrt{s}\right)}\ \frac{\sinh\left[u\sqrt{s}\right]}{s\,u\ \sinh\left[\sqrt{s}\right]} \tag{24}$$

or

$$\mathrm{LT}\left[\frac{c[u,\theta]-C_1}{C_0-C_1}\right]=\frac{1}{s}-\frac{1}{\left(-k/s+1+k\ \coth\left[\sqrt{s}\right]/\sqrt{s}\right)}\ \frac{\sinh\left[u\sqrt{s}\right]}{s\ u\ \sinh\left[\sqrt{s}\right]} \tag{25}$$

where s is the transform parameter and LT indicates a transformed function. The long-time limit is

$$\lim_{\theta\to\infty} c[u,\theta]=\lim_{s\to 0}\left(s\tilde{c}\ [u,s]\right)=\frac{3C_1+C_0k}{3+k} \tag{26}$$

so

$$\frac{c[u,\infty]-C_1}{C_0-C_1}=\frac{k}{k+3}=\frac{\phi}{B^3-1+\phi}. \tag{27}$$

The average concentration of the liquid in the sphere is found by averaging over its volume:

$$\frac{\langle c[u,\theta]\rangle-C_1}{C_0-C_1}=\frac{3}{4\,\pi\,\phi}\int_0^1 4\,\pi\,\phi\,u^2\left(\frac{c[u,\theta]-C_1}{C_0-C_1}\right)du \tag{28}$$

or,

$$\frac{\langle c[u,\theta]\rangle-C_1}{C_0-C_1}=\frac{k-3}{k\,s}+\frac{3}{k\left(-k+s+k\sqrt{s}\ \coth\left[\sqrt{s}\right]\right)} \tag{29}$$

At equilibrium, we expect the concentration to be the number of moles originally in the sphere,

$$n_0=\frac{4\pi}{3}a^3\phi C_0 \tag{30}$$

plus the moles originally in the bath,

$$n_1=\frac{4\pi}{3}\left(b^3-a^3\right)C_1 \tag{31}$$

distributed over the whole liquid volume,

$$V=\frac{4\pi}{3}a^3\phi+\frac{4\pi}{3}\left(b^3-a^3\right) \tag{32}$$

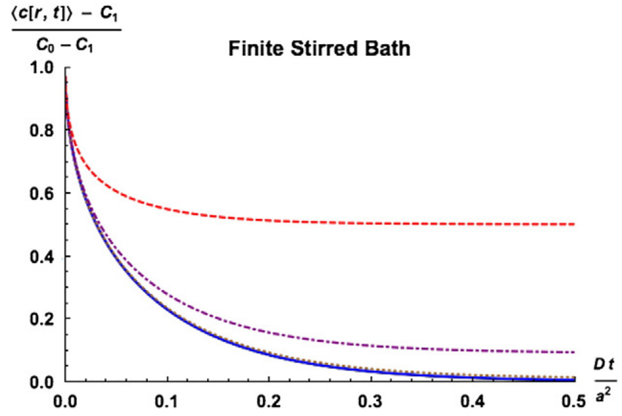

Fig. 8. Time dependence of the normalized average concentration for the case of finite stirred bath with various k. Solid blue line is $k=0.0003$; curve for $k=0.003$ is identical and overlapped by the solid blue curve. Dotted pink line is $k=0.03$. Dash-dotted purple line is $k=0.3$. Dashed red line is $k=3$.

so the final average concentration is

$$\langle c[u,\infty]\rangle=\frac{a^3\phi\,C_0+\left(b^3-a^3\right)C_1}{a^3\phi+\left(b^3-a^3\right)}=\frac{\phi\,C_0+\left(B^3-1\right)C_1}{\phi+B^3-1} \tag{33}$$

and the normalized concentration is

$$\frac{\langle c[u,\infty]\rangle-C_1}{C_0-C_1}=\frac{\phi}{B^3-1+\phi}=\frac{\phi}{(b/a)^3-1+\phi} \tag{34}$$

Taking the limit of the general solution as $\theta\to\infty$ leads to the expected result:

$$\lim_{\theta\to\infty} c[u,\theta]=\frac{3C_1+C_0k}{3+k}=\frac{\phi\,C_0+\left(B^3-1\right)\,C_1}{\phi+B^3-1}. \tag{35}$$

Eq. (29) cannot be inverted, so we numerically evaluate the time-dependence of the average concentration as a function of the parameter k:

$$\mathrm{LT}\left[\frac{\langle c[u,\theta]\rangle-C_1}{C_0-C_1}\right]=\frac{1-3/k}{s}+\frac{3/k}{s\left(-k/s+1+k\ \coth\left[\sqrt{s}\right]/\sqrt{s}\right)}. \tag{36}$$

This analysis uses the package Numerical Inversion (Copyright © 2000 by Arnaud Mallet). The algorithm for numerical inversion of the Laplace Transform is based on ref. [80]. The only parameter is k. The volume ratio of the bath to the particles is $B^3-1=3\Phi/k$. Given $\Phi\approx 0.1$–0.4, if $B=b/a$ ranges from 1.5 to 10, then $0.0003<k<0.4$. Fig. 8 shows the normalized concentration curves over the relevant range of k. Comparing the results for the finite and infinite bath, the difference only becomes visible for $k\geq 0.03$.

References

[1] J.W. Bullard, H.M. Jennings, R.A. Livingston, A. Nonat, G.W. Scherer, J.S. Schweitzer, K.L. Scrivener, J.J. Thomas, Mechanisms of cement hydration, Cement and Concrete Research In Press, Corrected Proof. doi:10.1016/j.cemconres.2010.09.011.

[2] J.J. Thomas, J.J. Biernacki, J.W. Bullard, S. Bishnoi, J.S. Dolado, G.W. Scherer, A. Luttge, Modeling and simulation of cement hydration kinetics and microstructure development, Cement and Concrete Research In Press, Corrected Proof. doi:10.1016/j.cemconres.2010.10.004.

[3] H.M. Jennings, J.W. Bullard, J.J. Thomas, J.E. Andrade, J.J. Chen, G.W. Scherer, Characterization and modeling of pores and surfaces in cement paste: correlations to processing and properties, Journal of Advanced Concrete Technology 6 (1) (2008) 5–29.

[4] R. Deshpande, D.W. Hua, D.M. Smith, J.C. Brinker, Pore structure evolution in silica gel during aging/drying. III. Effects of surface tension, Journal of Non-Crystalline Solids 144 (1992) 32–44.

[5] A. Korpa, R. Trettin, The influence of different drying methods on cement paste microstructures as reflected by gas adsorption: comparison between freeze-drying (F-drying), D-drying, P-drying and oven-drying methods, Cement and Concrete Research 36 (2006) 634–649.

[6] G.W. Scherer, Theory of drying, Journal of the American Ceramic Society 73 (1) (1990) 3–14.

[7] C. Gallé, Effect of drying on cement-based materials pore structure as identified by mercury intrusion porosimetry: a comparative study between oven-, vacuum-, and freeze-drying, Cement and Concrete Research 31 (2001) 1467–1477.

[8] K.K. Aligizaki, Pore Structure of Cement-Based Materials: Testing, Interpretation and Requirements, Taylor & Francis, London and New York, 2006.

[9] N.C. Collier, J.H. Sharp, N.B. Milestone, J. Hill, I.H. Godfrey, The influence of water removal techniques on the composition and microstructure of hardened cement pastes, Cement and Concrete Research 38 (6) (2008) 737–744.

[10] R.F. Feldman, J.J. Beaudoin, Pretreatment of hardened cement pastes for mercury intrusion measurements, Cement and Concrete Research 21 (2–3) (1991) 297–308.

[11] D.R. Lide, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 2003–2004.

[12] G.W. Scherer, J.J. Valenza II, Mechanisms of frost damage, Materials Science of Concrete, vol. VII, American Ceramic Society, Westerville, OH, 2005, pp. 209–246.

[13] J. Marchand, R. Pleau, R. Gagné, Deterioration of concrete due to freezing and thawing, Materials Science of Concrete, vol. IV, American Ceramic Society, Westerville, OH, 1995, pp. 283–354.

[14] L. Haar, J.S. Gallagher, G.S. Kell, NBS/NRC Steam Tables, Hemisphere Publishing Corp, Washington, D.C., 1984.

[15] BOC Edwards Safety Data Sheet, Suva 23, Freon 23 (Trifluoromethane, R23).

[16] C.J. Brinker, G.W. Scherer, Sol-Gel Science, New York, Academic Press, 1990.

[17] H.F.W. Taylor, A.B. Turner, Reactions of tricalcium silicate paste with organic liquids, Cement and Concrete Research 17 (4) (1987) 613–623.

[18] L. Konecny, S.J. Naqvi, The effect of different drying techniques on the pore size distribution of blended cement mortars, Cement and Concrete Research 23 (1993) 1223–1228.

[19] M.C.G. Juenger, H.M. Jennings, The use of nitrogen adsorption to assess the microstructure of cement paste, Cement and Concrete Research 31 (6) (2001) 883–892.

[20] J.J. Beaudoin, A discussion on "The use of nitrogen adsorption to assess the microstructure of cement paste" by M.C.G. Juenger and H.M. Jennings, Cement and Concrete Research 32 (5) (2002) 831–832.

[21] R.J. Detwiler, L.J. Powers, U.H. Jakobsen, W.U. Ahmed, K.L. Scrivener, K.O. Kjellsen, Preparing specimens for microscopy, Concrete International 23 (11) (2001) 51–58.

[22] M. Nagi, D. Whiting, Determination of water content of fresh concrete using a microwave oven, Cement, Concrete and Aggregates 16 (2) (1994) 125–131.

[23] K. Suhajda, M. Novotny, J. Skramlik, Monitoring of effectivity of microwave desiccation by means of rod plug-in Antenna, NDT.net — The e-Journal of Nondestructive Testing, http://www.ndt.net/article/v13n06/skramlik.pdf 2008.

[24] C.K. Wei, H.T. Davis, E.A. Davis, J. Gordon, Heat and mass transfer in water-laden sandstone: microwave heating, AICHE Journal 31 (5) (1985) 842–848.

[25] T.R. Naik, B.W. Ramme, Determination of the water content of concrete by the microwave method, Cement and Concrete Research 17 (6) (1987) 927–938.

[26] T.E. Nantung, Determination of Water-to-Cement Ratio in Fresh Concrete Using Microwave Oven, in SHRP Product Evaluation, Indiana Department of Transportation, Research Division, 1998.

[27] X. Wu, J. Dong, M. Tang, Microwave curing technique in concrete manufacture, Cement and Concrete Research 17 (2) (1987) 205–210.

[28] P. Rattanadecho, N. Suwannapum, B. Chatveera, D. Atong, N. Makul, Development of compressive strength of cement paste under accelerated curing by using a continuous microwave thermal processor, Materials Science and Engineering: A 472 (1–2) (2008) 299–307.

[29] H. Ai, J.F. Young, G.W. Scherer, Thermal expansion kinetics: method to measure permeability of cementitious materials: II application to hardened cement pastes, Journal of the American Ceramic Society 84 (2) (2001) 385–391.

[30] T.C. Powers, T.L. Brownyard, Studies of the physical properties of hardened Portland cement paste, ACI Journal, Proceedings 43 (1947).

[31] L.E. Copeland, J.C. Hayes, The determination of non-evaporable water in hardened Portland cement pastes, PCA, Bulletin 47 (1953).

[32] L. Zhang, F.P. Glasser, Critical examination of drying damage to cement pastes, Advances in Cement Research 12 (2) (2000) 79–88.

[33] S. Brunauer, Tobermorite gel: the heart of concrete, American Scientist 50 (1962) 210–229.

[34] J.J. Thomas, H.M. Jennings, A.J. Allen, Determination of the neutron scattering contrast of hydrated Portland cement paste using H_2O/D_2O exchange, Advanced Cement Based Materials 7 (3–4) (1998) 119–122.

[35] H.F.W. Taylor, Cement Chemistry, , Thomas Telford, London, 1997.

[36] S. Diamond, A discussion of the paper "Effect of drying on cement based materials pore structure as identified by mercury intrusion porosimetry—a comparative study between oven, vacuum and freeze drying" by C. Gallé, Cement and Concrete Research 33 (2003) 169–170.

[37] R.L. Day, B.K. Marsh, Measurement of porosity in blended cement pastes, Cement and Concrete Research 18 (1) (1988) 63–73.

[38] P.G. Debenedetti, Metastable Liquids: Concepts and Principles Princeton University Press, Princeton, New Jersey, 1996.

[39] J.E. Gillott, Importance of specimen preparation in microscopy, Soil Specimen Preparation for Laboratory Testing, American Society for Testing and Materials, Montreal, Canada, 1976, pp. 289–307.

[40] P.G. Debenedetti, Supercooled and glassy water, Journal of Physics: Condensed Matter 15 (45) (2003) R1669–R1726.

[41] M. Moukwa, P.C. Aitcin, The effect of drying on cement pastes, Cement and Concrete Research 18 (5) (1988) 745–752.

[42] G.W. Scherer, Freezing gels, Journal of Non-Crystalline Solids 155 (1) (1993) 1–25.

[43] S.S. Kistler, Coherent expanded aerogels, The Journal of Physical Chemistry 36 (1932) 52–64.

[44] H.D. Gesser, P.C. Goswami, Aerogels and related porous materials, Chemical Reviews 89 (4) (1989) 765–788.

[45] J.B. Rubin, J.W. Carey, C.M.V. Taylor, Enhancement of Cemented Waste Forms by Supercritical Co_2 Carbonation of Standard Portland Cements, Los Alamos report no. LA-UR-97-1859, , 1997, p. 6.

[46] C.A. Garcıa-Gonzalez, N.e. Grouh, A. Hidalgo, J. Fraile, A.M. Lopez-Periago, C. Andrade, C. Domingo, , New insights on the use of supercritical carbon dioxide for the accelerated carbonation of cement pastes, The Journal of Supercritical Fluids 43 (2008) 500–509.

[47] D.C. Hughes, The use of solvent exchange to monitor diffusion characteristics of cement pastes containing silica fume, Cement and Concrete Research 18 (2) (1988) 321–324.

[48] J.J. Beaudoin, B. Tamtsia, J. Marchand, H.R. Myers, Solvent exchange in partially saturated and saturated microporous systems length change anomalies, Cement and Concrete Research 30 (3) (2000) 359–370.

[49] J.J. Beaudoin, B.T. Tamtsia, Effect of drying methods on microstructural changes in hardened cement paste: an A. C. impedance spectroscopy evaluation, Journal of Advanced Concrete Technology 2 (1) (2004) 113–120.

[50] H.C. Gran, E.W. Hansen, Exchange rates of ethanol with water in water-saturated cement pastes probed by NMR, Advanced Cement Based Materials 8 (1998) 108–117.

[51] R.F. Feldman, Effect of predrying on rate of water replacement from cement paste by propan-2-oL, Reprinted from II Cemento 85 (3) (1988) 193–202.

[52] L.J. Parrott, Effect of drying history upon the exchange of pore water with methanol and upon subsequent methanol sorption behaviour in hydrated alite paste, Cement and Concrete Research 11 (5–6) (1981) 651–658.

[53] L. Struble, P. Stutzman, Epoxy impregnation of hardened cement for microstructural characterization, Journal of Materials Science Letters 8 (6) (1989) 632–634.

[54] R.B. Bird, W.E. Stewart, E.N. Lightfoot, R.B. Bird, W.E. Stewart, E.N. Lightfoot, Transport Phenomena, , Wiley, New York, 1960.

[55] L.D. Mitchell, J.C. Margeson, The effects of solvents on C–S–H as determined by thermal analysis, Journal of Thermal Analysis and Calorimetry 86 (3) (2006) 591–594.

[56] L.J. Parrott, Thermogravimetric and sorption studies of methanol exchange in an alite paste, Cement and Concrete Research 13 (1) (1983) 18–22.

[57] R.S. Mikhail, S.A. Selim, Adsorption of organic vapors in relation to the pore structure of Portland cement pastes, Special Report 90: Symposium on Structure of Portland Cement Paste and Concrete, Highway Research Board, National Research Council, 1966, pp. 123–134, Washington, DC.

[58] G.G. Litvan, Variability of the nitrogen surface area of hydrated cement paste, Cement and Concrete Research 6 (1) (1976) 139–143.

[59] D.H. Bager, E.J. Sellevold, How to prepare polished cement product surfaces for optical microscopy without introducing visible cracks, Cement and Concrete Research 9 (5) (1979) 653–654.

[60] J.J. Beaudoin, Interaction of aliphatic alcohols with cement systems, Reprinted from II Cemento 83 (1986) 199–210.

[61] M.D.A. Thomas, The suitability of solvent exchange techniques for studying the pore structure of hardened cement paste, Advances in Cement Research 2 (5) (1989) 29–34.

[62] R.F. Feldman, Diffusion measurements in cement paste by water replacement using propan-2-ol, Cement and Concrete Research 17 (4) (1987) 602–612.

[63] L.J. Parrott, An examination of two methods for studying diffusion kinetics in hydrated cements, Materials and Structures 17 (2) (1984) 131–137.

[64] D.C. Hughes, N.J. Crossley, Pore structure characterization of GGBS/OPC grouts using solvent techniques, Cement and Concrete Research 24 (7) (1994) 1255–1266.

[65] R.A. Olson, C.M. Neubauer, H.M. Jennings, Damage to the pore structure of hardened Portland cement paste by mercury intrusion, Journal of the American Ceramic Society 80 (9) (1997) 2454–2458.

[66] M. Brun, A. Lallemand, J.F. Quinson, C. Eyraud, A new method for the simultaneous determination of the size and the shape of pores: the thermoporometry, Thermochimica Acta 21 (1) (1977) 59–88.

[67] Z. Sun, G.W. Scherer, Pore size and shape in mortar by thermoporometry, Cement and Concrete Research 40 (5) (2010) 740–751.

[68] G.W. Scherer, D.M. Smith, D. Stein, Deformation of aerogels during characterization, Journal of Non-Crystalline Solids 186 (2) (1995) 309–315.

[69] J. Villadsen, Pore structure in cement based materials, Tech. Rep. 277. Building Materials Lab, Technical Univ, Denmark, 1992, (ISSN 0908–3871).

[70] L.J. Parrott, W. Hansen, R.L. Berger, Effect of first drying upon the pore structure of hydrated alite paste, Cement and Concrete Research 10 (5) (1980) 647–655.

[71] J.J. Beaudoin, Validity of using methanol for studying the microstructure of cement paste, Materials and Structures 20 (115) (1987) 27–31.

[72] W. Vichit-Vadakan, G.W. Scherer, Measuring permeability of rigid materials by a beam-bending method: III cement paste, Journal of the American Ceramic Society 85 (6) (2002) 1537–1544.

[73] R.L. Day, Reactions between methanol and Portland cement paste, Cement and Concrete Research 11 (3) (1981) 341–349.

[74] J.J. Beaudoin, P. Gu, J. Marchand, R.E. Myers, Z. Liu, Solvent replacement studies of hydrated Portland cement systems — the role of calcium hydroxide, Advanced Cement Based Materials 8 (2) (1998) 56–65.

[75] J. Zhang, E.A. Weissinger, S. Peethamparan, G.W. Scherer, Early hydration and setting of oil well cement, Cement and Concrete Research 40 (7) (2010) 1023–1033.

[76] P. Mounanga, A. Khelidj, L. Ahmed, V. Baroghel-Bouny, Predicting Ca(OH)2 content and chemical shrinkage of hydrating cement pastes using analytical approach, Cement and Concrete Research 34 (2) (2004) 255–265.

[77] CVCCTL, Technical note VCCTL-01: estimation of the degree of hydration of Portland cement by determination of the non-evaporable water, VCCTL Tech Note, 2009.

[78] P. Bentz, P. Lura, J.W. Roberts, Mixture proportioning for internal curing, Concrete International (2005) 35–40 (February).

[79] G.W. Scherer, J. Quintanilla, S. Peethamparan, J. Zhang, E.A. Weissinger, S. Torquato, Hydration and percolation at the setting point, Cement and Concrete Research.

[80] H. Stehfest, Algorithm 368 — numerical inversion of Laplace transforms, Communications of the ACM (1970) 47–49 (and 624).