

CHAPTER 2

CHEMISTRY AND STRUCTURE OF HYDRATION

PRODUCTS

Paul Stutzman
National Institute of Standards and Technology
Gaithersburg, MD

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1 INTRODUCTION

This chapter covers papers published and abstracted in 1996 relating to cement hydration and the chemistry and structure of hydration products.

2 HYDRATION OF CEMENT PHASES

2.1 C₃A

Kuzel [1] studied the hydration reactions between C₃A, gypsum, and water using Rietveld refinements of XRD patterns. The accuracy of the method was estimated to be within 0.5% relative to the true values of control mixtures, and he was able to quantify the concentrations of these phases and ettringite as hydration progressed.

Rossetti and Medici [2] examined the influence of glassy and crystalline C₃A on sulfate resistance of synthetic white cements. They also examined resistance to sulfate attack with steam curing at 20°C and 90°C and autoclave steam curing at 190°C. Cements containing glassy C₃A were less expansive and also steam curing reduced sulfate expansion.

2.2 C₂S

El-Didamony *et al.* [3] used XRD and DTA to examine the hydration characteristics of β -C₂S in the presence of accelerators. They used CaCl₂, Ca(NO₃)₂, Ca(CH₃COO)₂, and K₂CO₃ on hydration of a B₂O₃-stabilized β -C₂S. They found portlandite and a tobermorite-like phase as hydration products, plus CaCO₃. The accelerators affected the hydration rate of β -C₂S.

2.3 CaO

Huisheng and Zhiyuan [4] found a relationship between the microstructure and hydration activity of CaO. Using XRD and microcalorimetry, they found that a larger crystallite size was associated with denser crystal structure, smaller free energy in crystal boundaries and surfaces, and lower hydration reactivity. The substitution of Fe³⁺ for Ca²⁺ appeared to slow its reactivity.

3 PORTLAND CEMENT

Marchand *et al.* [5] used optical and electron microscopy and mercury porosimetry to compare the microstructures of dry concretes, such as precast or roller-compacted concretes, to ordinary concretes. They found more heterogeneous paste microstructures, especially with the roller-compacted concretes. They also found many similarities between laboratory-prepared and precast concretes. The addition of supplementary mineral admixtures such as silica fume and fly ash improved paste homogeneity and densified the paste microstructure.

Jiang *et al.* [6] examined the physico-chemical parameters affecting coagulation of cement grains and found that a minimum critical concentration of calcium ions was necessary

for coagulation of the grains to occur, while a dispersive effect was found for very high concentrations. Svinning and Bremseth [7] used a partial least squares regression technique to examine the influences of clinker and cement microstructure on setting time and strength development.

Ichikawa *et al.* [8] examined XRD data on alite polymorphs and interstitial composition to estimate 28-day strengths.

McCarter and Tran [9] monitored changes in conductivity of portlandite–pozzolan mixtures and determined a pozzolanic activity index that reflects both the reaction rate and time to set.

Odler and Zhang [10–11] investigated high- SO_3 portland cement clinkers and cements and reported on the preparation of clinker and cement and on the properties of cements. Properties were similar to those of ordinary portland cements but setting times were shorter. Strength development and expansion properties were variable and appeared to be controllable by adjusting clinker compositions. They concluded that the savings in energy consumption in preparation may warrant additional work with these cements as alternatives to ordinary portland cement.

Bensted [12] examined the early hydration behavior of a portland cement containing montmorillonogypsum (a chemical byproduct gypsum from the acid-activated montmorillonite process). This cement also conformed to setting and compressive strength requirements, although water demand was higher, initial set lower, final set higher, and compressive strength lower (compared to a cement prepared using natural gypsum). More ettringite was formed initially, and C–S–H was formed at a lower rate than a comparable cement using natural gypsum.

Chartschenko *et al.* [13] examined factors affecting the hydration process and properties for expansive cements. A controlled increase in volume was achieved when external constraints such as temperature, moisture, and mechanical restraint were accounted for.

Dhir *et al.* [14] studied the influence of microstructure on the physical properties of self-curing concretes. High doses of a self-curing admixture resulted in reduced compressive strengths. This was attributed to an alteration of CH at the paste–aggregate interface and an alteration of the C–S–H gel morphology that reduced permeability. They suggested that the latter effect may be beneficial in production of lower permeability concretes.

Cabrera and Lynsdale [15] studied the effects of superplasticizers on portland cement hydration rates. They found a slight increase in rates at early ages.

Hearn [16] compared permeability values of mortar specimens using water and propan-2-ol. The latter fluid was selected because it exhibits no chemical or physical interaction with the hydration products. Permeability values for identical specimens were equivalent for the two fluids, but water had chemical and physical interactions with the

hydration products and residual cement that may change the permeability values. Shrinkage cracking due to drying resulted in a significant increase in permeability due to the collapse of the C–S–H gel layers. This increased permeability was reversed to an extent upon resaturation with water, whereas resaturation with propan–2–ol did not swell the C–S–H and thereby affect permeability.

4 HYDRATION UNDER SPECIAL CONDITIONS

4.1 Curing Temperature

Moranville–Regourd [17] examined the changes in microstructure of cement pastes as a result of elevated–temperature curing. Elevated–temperature curing was thought to affect stability of hydration products and result in changes in porosity, bound water, and ionic pore solutions. She found a delayed formation of ettringite in pre–existing microcracks and in the paste–aggregate interface where voids were presumed to result from thermally–induced drying shrinkage or mechanical stresses.

Zhang *et al.* [18] studied the influence of gypsum and anhydrite on hydration and strength of steam–cured concretes. Using curing conditions of 65°C for four hours, they found that optimum SO₃ contents were 4–5% and that higher strengths were obtained using anhydrite. Concrete prepared using anhydrite exhibited a higher nonevaporable water content, higher portlandite content, and lower pore volume and average diameter. They suggested that the higher [SO₄^{–2}] and lower [OH[–]] values were responsible for these differences.

Patel *et al.* [19] studied the microstructure and sulfate levels of steam–cured concretes. Concretes cured at 80°C showed a higher degree of hydration, larger C–S–H rims around cement grains, and more rimmed Hadley grains than concretes cured at lower temperatures. With longer curing, the effects of temperature became even more prominent. The differences in sulfur/calcium ratios of inner product C–S–H rims after water storage and laboratory storage were greater for the high–temperature–cured concretes, and microcracking after 120 days was greater in the high–temperature–cured concretes. The decrease in sulfur/calcium ratios of the C–S–H and an increase of the same in sulfoaluminate within Hadley grains indicated a movement of sulfate ions after prolonged water exposure. Elevated temperature curing appeared to result in higher sulfate levels and greater microcracking which, with the addition of water, may facilitate delayed ettringite formation.

Zhou *et al.* [20] studied the effects of saline waters on the hydration of oil well cements using DTA, XRD, TG, and SEM. They found strengths of cement slurries cured at 90°C and 160°C lowered with increasing salt content, and that the salt content affected CH formation and the interface between CH and C–S–H.

Bell *et al.* [21] studied the morphological development and forms of tobermorite from hydrothermally treated calcium silicate hydrate gels synthesized at pH 12.6 at 150°C. They

identified two distinct morphologies: fibers and platelets. Computer modeling indicated the (110) as the preferential plane for crystal growth for both morphologies.

Jaubertie *et al.* [22] studied the hydrothermal transformation of tobermorite gel to a 1.0-nm tobermorite. The tobermorite gel was prepared by hydrothermal treatment of a mixture of silica and lime at 210°C for 25 to 1600 hours. When the proportion of lime was 37% or less, a Z-phase formed, in which the sheet spacing was constant but the a and b values were uncertain. Lime percentages between 37% and 42% resulted in formation of a 1.0-nm tobermorite without changes in the a and b values. In the presence of gryolite, this 1.0-nm tobermorite was stable but the Z-phase was metastable.

Kjellsen [23] studied the effects of heat curing and post-heat curing conditions on the microstructure and composition of C-S-H in high-performance concretes. The heat-cured concretes had a higher hollow shell porosity at later ages compared to normally-cured concrete. He concluded that, while the distribution of C-S-H within the cement paste matrix was not significantly influenced by heat curing, the composition was influenced by heat curing. He found an increase in the (Al+Fe)/Ca ratio of the inner product C-S-H with decreasing cure temperature. He suggested that this reflected a temperature-related influence on the diffusion of Al and Fe and the formation and distribution of AFt and AFm phases.

Takahashi *et al.* [24] investigated the effects of cement composition and silica on the microstructure and compressive strengths of autoclaved mortars. Using a w/s of 0.25, they found the compressive strength related to the mass of silica powder with maximum strengths obtained when the silica content was sufficient for complete consumption of CH. They found a correlation between pore volume and compressive strength. A relationship between compressive strength and formation of tobermorite was not seen. Excessive silica powder resulted in a decrease in compressive strength that was attributed to formation of gaps between the silica powder and matrix.

Wu *et al.* [25] studied the effects of autoclaving schedule, w/s, and calcium/silicon on the properties of autoclaved lime-sand concrete. The w/s had a pronounced effect on the total pore volume and pore size distribution. The most suitable w/s depended upon the fineness of the constituent materials. A minimum autoclaving time was necessary and depended on the pressure and calcium/silica with time, increasing with either an increase in calcium/silicon or lowering of pressure. The mass fraction of calcium hydroxide depended on autoclave schedule and calcium/silicon. A ratio of 0.5 resulted in a finished product with negligible calcium hydroxide content.

Klimesch *et al.* [26] examined the effects of chemical and physical properties on autoclaved cement-quartz pastes, with emphasis on the particle-size distribution of quartz. Portlandite and C-S-H volumes and compressive strengths increased using ground quartz. Autoclaving produced C-S-H of the tobermorite group with a relationship between crystallinity and surface area of the quartz. Drying shrinkage increased with quartz

fineness and was correlated to the crystallinity of the C–S–H. Optimum values were found when the surface area of the quartz equaled that of the cement.

4.2 Presence of Heavy Metals

Omotoso *et al.* [27] examined hydration products of tricalcium silicate pastes prepared with different amounts of Cr^{III} in solution. This simulation of waste product stabilization was used to examine hydration reaction products and leaching, using a standard acetic acid leaching test. Trivalent chromium accelerated the reaction of C_3S , Cr^{III} was found as calcium chromium hydroxide complexes, and Cr^{III} was immobilized in the hydration products.

Aldridge *et al.* [28] examined the use of zeolites imbedded in a portland cement matrix for disposal of radioactive wastes. Two of the zeolites reacted with calcium hydroxide in the paste to form calcium silicate hydrate; one cemented zeolite still contained calcium hydroxide after 1.5 years. The type of zeolite, particle size, and Cs-loading were factors in successful immobilization.

Fryda *et al.* studied the immobilization of cesium in a CAC–silica fume mixture. The formation of a zeolite in the chabazite family served to immobilize cesium during hydration and after setting. Destruction of the zeolite was found to occur at temperatures in excess of 750°C .

Ma *et al.* [30] demonstrated the potential for use of fly ash in waste disposal. They synthesized tobermorites by reacting both Class C and F fly ashes, portlandite, and mild hydrothermal treatment for use in immobilizing cesium and strontium. Tobermorites prepared using Class F fly ash appeared superior in immobilization of Cs and Sr. This superiority was thought to reflect the higher Al content of these fly ashes.

5 MINERAL ADMIXTURES

Bijen [31] discussed the use of slag and fly ash in concrete, including chemical and mineralogical aspects of activation and dissolution, effects on microstructure and durability, and potential difficulties such as sensitivity to curing, increased carbonation rates, and freeze–thaw durability.

Uchikawa *et al.* [32–33] studied hydration reactions, hydration products, and pore structures of concretes prepared using large volumes of mineral admixtures such as fly ash, slag, limestone, and a siliceous stone in the place of fine aggregate. They found an increase in viscosity and decrease in fluidity thought to be related to the increase in fine particles. Greater strengths were observed, attributed to densification by infilling by the mineral additions and pozzolanic reactions to produce additional C–S–H. They also saw an increase in creep for the fly ash concretes and reduction in the dynamic Young's modulus. These changes were considered to reflect the increase in paste content.

Bakharev *et al.* [34] examined cementitious materials with high proportions of fly ash and slag for their suitability in the immobilization of alkaline and carbonated waste solu-

tions. The materials were resistant to sulfate and carbonate exposure and to leaching. Microstructural studies indicated the development of a finer pore structure and reduction in permeability over time.

Sakai *et al.* [35] examined a low–heat, high–strength concrete prepared using highly pulverized blast furnace slag, silica fume, superplasticizer, and a low–heat cement. They found the mixture had low heat and high early strength and discussed their findings with respect to hydration products, pore structure, and combined water.

Li *et al.* [36] examined the effects of silica fume on the strength and microstructure of high–strength cement pastes. Using compressive strength, porosimetry, XRD, and evaporable and nonevaporable water measurements, they found that at w/c 0.24 strength decreased with increasing silica fume content. Addition of silica fume reduced maximum pore radius but not total porosity, and a 10% addition of silica fume resulted in consumption of all calcium hydroxide. Finally, they found the amount of nonevaporable water in the silica fume paste was less than expected, possibly reflecting decomposition of C–S–H and accompanying release of water.

Jensen and Hansen [37] found a significant increase in both autogeneous shrinkage and relative humidity changes as a result of adding silica fume to cement paste.

Wang and Adler [38] concluded that a significantly finer pore structure accounted for improved resistance to chemical attack of high–performance concretes incorporating silica fume and superplasticizers.

Wilfredo *et al.* [39] examined the morphological changes of aluminate phases when silica flour and alumina (gibbsite) were added to cement slurries. They used heat treatment to simulate oil well conditions and steam injection. The addition of alumina or silica flour promoted formation of a film on silicate crystals. The film morphology was related to the type of addition; it was granulated with alumina and needle–like with silica flour. They found that an addition of 15% alumina eliminated strength retrogression and was suitable for oil well applications utilizing steam injection.

Wu [40] studied hydration mechanisms of GGBFS used in high–strength alkali–activated cements. He examined factors affecting strength, including hydraulic activity of the slag, fineness, activator type and dosage, curing temperatures, compatibility, and water content.

Schiebel and Hardtl [41] reported on a pulverized fuel ash replacement in concrete for large–scale foundation panels. Requirements for the job included pumpability, low heat of hydration, low permeability, and strength development suitable for construction.

6 COMPOUNDS

6.1 Calcium Silicate Hydrate

Larosa–Thompson and Grutzeck [42] reviewed current works on the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, and in particular examined aluminum substitution into C–S–H and tobermorite and the formation of hydrogarnet.

Cong and Kirkpatrick [43] studied structures of calcium silicate hydrates, 1.1-nm tobermorite, 1.4-nm tobermorite, jennite, calciochondrodite, xonotlite, and hillebrandite. They identified oxygen sites in tobermorite and jennite including both Si–OH and Ca–OH linkages. Structures of 1.4- and 1.1-nm tobermorite were similar, with 26% of the Ca^{+2} in the interlayer. Jennite had long, single silicate chains similar to 1.4-nm tobermorite, with Si–OH sites on bridging tetrahedra but with no interlayer Ca^{2+} . The Si sites in xonotlite and calciochondrodite were cross-polarized but did not contain Si–OH linkages.

In another paper, Cong and Kirkpatrick [44] examined single-phase calcium silicate hydrates with known compositions, whose calcium/silicon ratios ranged from 0.4 to 1.84, using ^{29}Si MAS NMR, XRD, and chemical analysis. They concluded that C–S–H formed a continuous structural series as opposed to different phases, that phase-pure C–S–H had calcium/silicon 0.6–1.54, and that both Si–OH and Ca–OH bonds occurred in C–S–H and were proportionate to the calcium/silicon ratio. They proposed a defect tobermorite model for the structure of C–S–H in which the individual layers had the basic structure of a 1.4-nm tobermorite. The layers had significant defects and were more disordered, and stacking disorder both between and within layers was considered responsible for local and long-range disorder and the variability of C–S–H. Cong and Kirkpatrick [45] used ^{17}O MAS NMR to investigate the structure of synthesized calcium silicate hydrate gel and found results consistent with XRD and ^{29}Si NMR data. This work served to corroborate the defect-tobermorite structural model for C–S–H developed earlier.

Viehland *et al.* [46] studied the short-range ordering, nanocrystallinity, and local compositional order of calcium–silicate hydrate gels in portland cement pastes. The TEM studies indicated homogeneous nanocrystalline regions in an amorphous matrix. The calcium/silicon appeared homogeneous, yet the local composition order appeared variable from region to region. Optical diffraction of these nanocrystalline regions indicated the coexistence of jennite and 1.4-nm tobermorite. These findings were considered consistent with Taylor's nanophasic model for C–S–H.

Lequeux and Richard [47] used X-ray absorption spectroscopy to study natural parawollastonite and synthetic calcium silicate hydrates (xonotlite, 1.4-nm tobermorite, hillebrandite and C–S–H). With the exception of tobermorite, the X-ray analysis fine-structure spectroscopy (EXAFS) data agreed with XRD results. The EXAFS data for tobermorite were similar to that for C–S–H, in which six O^- atoms are octahedrally coor-

minated around Ca with a mean distance of 0.241 nm. No sign of a regular Ca–Ca shell indicated that the Ca polyhedra may be disorderly arranged.

Kwan *et al.* [48] used ^{29}Si and ^{27}Al MAS NMR, solution pH, EM, and XRD to examine structures of aluminum–substituted calcium silicate hydrates. While XRD data indicated similar intermediate–range order of two aluminum–containing C–S–H phases, MAS NMR data indicated two structurally distinct C–S–H phases. The Q_1Q_2 C–S–H phase contained silicate chains, dimers and end groups and the Q_2 C–S–H phase contained predominantly silica chains. Each structure could accommodate 10 wt% aluminum in solid solution in octahedral and tetrahedral coordination.

Moss *et al.* [49] used impedance spectroscopy to study capillary and gel porosity of young (28 days) cement pastes during exchange of pore solution with methanol and isopropanol. The differences in the residual dielectric constant suggested two kinds of C–S–H gels in paste of 0.35 w/c and only one type in a paste of 0.70 w/c.

Rarick *et al.* [50] used nitrogen BET to examine the influence of drying time and storage time on the deterioration of cement paste surface area during D–drying. They found that storage time accounted for most of the variation in data and that there was a decrease in surface area with storage time. After two weeks storage, the surface areas were independent of D–drying time. They considered the possibility that carbonation plays a role in size reduction in the gel pores.

Sasaki *et al.* [51] studied the structural degradation of tobermorite during vibratory milling. Using ^{29}Si NMR, XRD, and TGA–DTA, they examined both Al–free and Al–substituted 1.1–nm tobermorites milled from 10 to 240 minutes in a tungsten carbide mill where the temperature was not allowed to exceed 40°C. Both tobermorites were found to decompose to amorphous C–S–H–like phases but the decomposition rate was greater for the Al–substituted tobermorite. The decomposition was found to begin in the bridge portion of the silicate double chain. In the Al–substituted tobermorite, breakage appeared to occur preferentially where Al had replaced Si. Heating of the amorphous C–S–H resulted in the formation of wollastonite, although no change in formation temperature was observed.

Zanni *et al.* [52] studied the hydration and pozzolanic reaction in reactive powder concrete by ^{29}Si NMR. Silica fume and crushed quartz consumption depended on the heat treatment temperature and time. They identified the formation of xonotlite at 250°C and found the average C–S–H chain length increased with an increase in temperature.

Vanis and Odler [53] prepared a mixture of hydroxyapatite and $\beta\text{-C}_2\text{S}$ using a sol–gel process and firing to about 700–1200°C. Firing to 1300°C resulted in the formation of tricalcium phosphate. The latter preparation exhibited hydraulic properties but was slow to cure at ambient temperature. Sodium phosphate, potassium phosphate, and ammonium phosphate served as catalysts for a significant improvement in hardening. The hydration products included hydroxyapatite with C–S–H and/or a C–S–P–H gel.

El Shafei *et al.* [54] examined sorption–desorption isotherms to study the pore structure of well hydrated C_2S and C_3S pastes at room temperature.

6.2 Calcium Aluminate Hydrates

Richard *et al.* [55–56] used NMR and X–ray absorption spectroscopy to study refractory cement phases CAH_{10} , C_2AH_8 , and C_3AH_6 , and to examine structural changes in CAH_{10} during heat treatment. They found a decrease in Ca–O distance and reduction of the number of oxygen neighbors in the first coordination shell upon heating. Aluminum sites became distorted as the CAH_{10} decomposed. The cross polarization MAS spectra indicated a progressive decrease in the Al^{VI} –H dipolar coupling and an associated loss of water.

Richard *et al.* [57] examined the local environment of Ca and Al in CAH_{10} and C_2AH_8 using X–ray absorption spectroscopy. They noted resemblance between structures of gibbsite (AH_3) and CAH_{10} and proposed a structural model for CAH_{10} based upon two rings of six edge–sharing $[Al(OH)_6]^{3-}$ octahedra linked by Ca ions. The C_2AH_8 was considered to be an AFm phase with interlayer aluminum atoms tetrahedrally coordinated.

Fu *et al.* [58] examined the effects of calcium aluminate hydrates on the formation of ettringite and expansion in CAC expansive cements. They found that portland cement expansion developed rapidly when using expansive additives based upon CAH_{10} and C_2AH_8 , while expansion was delayed and reduced when using an expansive additive based upon a C_3AH_6 mixture. Expansion and ettringite formation of portland cements containing hydrated CAC/CH additives were higher than those containing C_3AH_6 that was prepared at 38°C.

6.3 Calcium Sulfoaluminates

Li. *et al.* [59] examined the mineralogy of simulated cemented low–level waste containing high amounts of Na_2SO_4 . They observed the formation of a mineral named the U–phase, an AFm–like layered structure associated with expansion upon transformation into ettringite. Their findings indicated U–phase formation was possible only at very high alkaline concentrations and in the presence of sulfate and alumina. Immersed specimens exhibited expansion and cracking that appeared to be associated with the U–phase transformation into ettringite. In an additional paper, Li and Le Bescop [60] examined the degradation mechanisms of cement–stabilized wastes by internal sulfate associated with the formation of the U–phase (a sodium–substituted AFm, a phase found in cement–stabilized wastes). The U–phase was considered to be responsible for deterioration of the specimens through two processes; 1) secondary formation of the U–phase, and 2) a transformation of U–phase to ettringite as alkali concentration decreased.

Bonen *et al.* [61] investigated the immobilization of simulated nonvitrifiable low–level radioactive wastes by carbonate–bearing AFm and AFt phases. They used a system composed of cement, metakaolin, gypsum, and (for some mixtures) slag designed to minimize

bleeding and transport properties. They found that the addition of gypsum resulted in an increase in calcium solubility and precipitation of hemiacarbonate, monocarbonate, portlandite, and possibly minor amounts of tobermorite. The first two of these phases were converted to ettringite. The transport properties of this system were comparable to those of a cement paste with a w/c of 0.50.

Takahashi *et al.* [62] studied the influence of hydration on autogenous shrinkage of cement pastes prepared using low heat and ordinary portland cements. Two points were noted in the autogenous shrinkage curve. The first point was related to the setting time of the cement and the second was when gypsum was consumed. Expansion between the first and second point was attributed to formation of ettringite, and shrinkage after this point was thought to be related to a morphological change in ettringite.

Talero [63] used XRD to examine ettringite formed from portland cement and cements containing pozzolans. He found that the formation of ettringite was greater in cements containing a pozzolan and appeared related to the reactive alumina in the pozzolan.

6.4 Calcium Hydroxide

MacTavish *et al.* [64] used NMR to study hydration of synthetic white cements through continuous quantitative monitoring of free water and CH during hydration. The development of CH and consumption of free water were quantitatively monitored. The pore size distribution was derived from such experiments.

Goni *et al.* [65] studied calcium hydroxide saturation factors in the pore solutions of hydrated portland cement fly ash pastes. At early ages, a 15% fly ash addition showed an increase in the degree of supersaturation with respect to portlandite, while at 35% fly ash addition the degree of supersaturation decreased. At later ages, the pore solution was undersaturated with respect to portlandite, especially with the 35% addition of a particular fly ash sample. The undersaturation at later ages was considered to reflect pozzolanic activity of the fly ash. Supersaturation at early ages was suggested to be related to an acceleration of the reactivity of the cements due to alkalis from the fly ash.

Carde *et al.* [66] examined the microstructural changes and mechanical effects due to leaching of calcium hydroxide from both neat cement paste and silica fume–cement paste. By monitoring the paste microstructure using XRD and microprobe, they observed a degraded zone characterized by loss of calcium hydroxide and decalcification of the C–S–H. The loss of strength was primarily due to loss of calcium hydroxide. Kinetics of leaching for both pastes were governed by diffusion.

Berra [67] found the expansion of mortars prepared with either a low– or high–alkali cement and reactive fused quartz to be related to the portlandite content and not to the amount of chloroaluminate or the pore solution OH concentration.

7 DETERIORATION REACTIONS AND THEIR MECHANISMS

Roy and Jiang [68] presented a historical account of durability and stressed the importance of using such knowledge in the specification and production of durable cements. Ex-

amples including the Pyramids of Egypt, the Acropolis in Athens, and the Taj Mahal in India demonstrated the effects of weathering. The deterioration of concrete was compared to geologic processes, physical and chemical, acting on rocks in these structures.

7.1 Chloride

Sirivivatanon *et al.* [69] investigated the field performance of 30-year-old portland cement and fly ash concretes exposed to flowing seawater. Both concretes exhibited similar chloride profiles even though the fly ash concrete had a lower binder content. The fly ash concrete had a greater carbonation depth, although no corrosion problems were found in either concrete.

Kurdowski *et al.* [70] exposed a synthesized tobermorite to chloride solutions and followed the changes by SEM and XRD. Upon immersion they found rapid expansion, followed by a leveling of the rate and later increase in the rate prior to disintegration. The XRD data indicated a complete disintegration of the tobermorite and remnant basic magnesium chlorides.

7.2 Carbonation

Houst [71] examined the role of carbonation in changes of cement paste microstructure and found a reduction in total porosity and specific area. The effects on pore size distribution depended on the w/c of the original material but indicated a greater reduction for pastes of lower w/c.

Roy *et al.* [72] studied carbonation of a 19-year-old building located in a tropical environment and found reduced carbonation depths for structural sections plastered with a sand-cement mortar. No carbonation was found where the plaster thickness exceeded 30 mm. Sections of higher concrete strength also exhibited less carbonation. A carbonation rate of about 5 mm per year was similar to other study measurements but greater than those estimated for temperate climates (1–3 mm/yr).

Maslehuddin *et al.* [73] studied carbonation-induced changes in phase composition in ordinary portland cement and blended cement mortars exposed to both salt contamination (0.8% Cl⁻ and 1.5% SO₃) and elevated temperatures. Calcite was found in the ordinary portland cement mortars while the blended cements contained calcite and aragonite. Salt-contaminated specimens contained greater quantities of carbonation product, possibly due to increases in pore solution alkalinity or changes in hydration rates and hydration product morphology as a result of the salt exposure.

Nakamura *et al.* [74] examined carbonation and strength changes in concretes exposed to different temperature and relative humidities for a period of five years. The concretes used ordinary, moderate heat, and high early strength portland cements, Class B blast furnace slag cement, Class B fly ash cement, and silica fume. They found that longer initial curing periods resulted in significant strength gains. Carbonation resulted in reduction of

portlandite in the outer regions and a reduction of the pH. Sulfur from decomposition of ettringite through carbonation was thought to migrate to the center of the concretes.

Thomas *et al.* [75] used nitrogen BET to examine the effects of carbonation on the surface area of hardened portland cement paste. Carbonation of C–S–H in pastes stored in plastic vials resulted in a decrease in surface area over time. They found a strong correlation between carbonation, as measured by thermogravimetry, and the decrease in surface area. Efforts to minimize carbonation should result in higher precision of nitrogen BET data.

Al–Kadhimi *et al.* [76] developed an accelerated carbonation procedure for studies of carbonation and corrosion. This method used specimens dried to a 60% relative humidity and a carbon dioxide gas atmosphere at 1.5 MPa pressure, and accommodated specimens up to 150 mm in diameter. On examination of thin sections using a petrographic microscope and of polished sections using an SEM, they found microstructural similarities between the accelerated specimens and those carbonated naturally.

7.3 Sulfate

Yang *et al.* [77] studied the effects of the paste–aggregate interfacial zone on sulfate attack. Using a quartz sand modified by calcination with calcium carbonate produced a surface layer of belite. They found that the resistance of the mortar to sulfate attack improved substantially when using the treated quartz sand compared to mortars with untreated sand.

Li *et al.* [78] studied sulfate damage in solidified waste containing high sulfate levels by examination of the influence of the formation of the U–phase, a sodium–substituted AFm, on expansion of the system $C_3A + C_3S + Na_2SO_4$. They found that the U–phase formation was facilitated by an external water supply and resulted in a large expansion.

Taylor and Gollop [79] examined chemical and microstructural processes that affect concrete durability. From a variety of studies, they found that C–S–H was attacked by both $MgSO_4$ and Na_2SO_4 solutions, with the latter being less aggressive. Aluminum in C–S–H or hydrotalcite was not available for reaction with sulfate solutions. Sulfur from slag blends entered hydration products both as sulfides and sulfates. Expansion and cracking were an indirect or direct result of the formation of ettringite, while softening and disintegration were due to disintegration of C–S–H; and C–S–H disintegration was more important in slag blends than in portland cements.

In an SEM–EDS study of sulfate attack, Gollop and Taylor [80] examined paste cubes prepared with a slag–cement blend that were stored in solutions of sodium sulfate or magnesium sulfate for a period of six months. Gypsum and, for the magnesium sulfate–immersed specimens, gypsum and brucite were found in veins near the surfaces of the cubes but appeared different than in those observed earlier in neat cement pastes with less gypsum. Decalcification of the C–S–H was observed in both sets of specimens but appeared

to be more substantial in the magnesium sulfate-immersed specimens. Deterioration was thought to result from the weakening of the C–S–H through decalcification and expansion and cracking due to formation of ettringite. The decalcification affected slag–cement blends more than portland cements and may account for the reported softening and deterioration characteristics of slag–cement blend concretes.

Gollop and Taylor [81] also compared different slag blends exposed to magnesium and sodium sulfate solutions. They observed decalcification of the C–S–H and formation of ettringite. Little gypsum was formed in the sodium sulfate-soaked pastes while brucite, serpentine, and gypsum formed in the magnesium sulfate-soaked pastes. There was a relationship between Al_2O_3 available for ettringite formation and susceptibility to degradation in sodium sulfate solutions. In magnesium sulfate exposure, slag blends performed poorly relative to ordinary portland cement or sulfate-resisting portland cements. For sodium sulfate exposure, the more durable specimens contained a higher proportion of slag, slags low in Al_2O_3 , or sulfate-resisting portland cements (through addition of calcium sulfate to portland cements).

Ferraris *et al.* [82] studied sulfate attack on laboratory mortars cast to provide different geometries and exposed to sodium-sulfate solutions with controlled pH (7, 9, and 11). They examined the formation of reaction products as a function of depth and degree of expansion and discussed the mechanics of expansion and cracking.

Crammond and Halliwell [83] examined sulfate attack in which the primary deterioration mechanism was the disintegration of C–S–H and formation of thaumasite. They discussed conditions necessary for attack with an emphasis on temperature, sulfate concentrations, limestone aggregate source, and cement type.

Allan and Kukacka [84] examined the permeability and leach resistance of cementitious grouts to sulfates. The study involved a Type V and a Type I cement with different levels of slag replacement, and one mix with 5% silica fume replacement. They found the degradation resulted in a significant increase in permeability and leachability of hexavalent chromium unless slag was used. The Type V cement or Type I with 80% slag appeared to perform the best. The Type I with 30% slag and Type I with 5% silica fume were more effective during the first six months of testing, but later lagged behind the Type V and Type I–80% slag blends.

Ehrich and Bock [85] devised a test procedure for corrosion by biogenic sulfuric acid. The procedure employed a test chamber with a 1 m³ volume, a temperature of 30°C, humidity of 98%, H₂S atmosphere, and one of several species of sulfur oxidizing bacteria.

Haynes *et al.* [86] investigated damage of field concretes by soil containing sodium sulfate. They did not consider this to be sulfate attack but an interaction of sulfate with hydration products. Concretes exhibited surface scaling that eventually led to complete disintegration.

Macsik and Jacobsson [87] performed field and laboratory tests on concretes exposed to sulfate soils. They found that local redox conditions controlled the reactions where soils

can change from aerobic near the surface to anaerobic at depth, that availability of sulfur and iron was depth-dependent, and that the mechanisms allowing release of acidic ions were dependent on depth.

Irasser *et al.* [88] examined sulfate attack on concretes incorporating mineral admixtures such as fly ash, natural pozzolans, and slag. They found an increased resistance to sulfate attack but greater surface scaling due to sulfate salt crystallization.

Fu and Beaudoin [89] described mechanisms responsible for delayed ettringite formation in portland cement, including the influence of C_3A and nucleation of ettringite in cracks. Diffusion of reactant ions through the pore solution was key to the nucleation of ettringite in cracks.

Fu and Beaudoin [90] subjected concretes prepared using Type I, III, and V cements to wet-dry, freeze-thaw, and loading-unloading cycles to induce microcracking. They found that use of a Type III cement, high-temperature curing, and severe thermal drying led to microcracking in concretes and mortars by delayed ettringite formation.

Thaulow *et al.* [91] discussed delayed ettringite formation with respect to concrete composition, curing conditions, and exposure conditions. Based upon laboratory and field examinations, they concluded that delayed ettringite formation (DEF) is an internal sulfate attack. They also concluded that the term DEF should only be used for moist-exposure expansion and cracking of improperly heat-cured concretes. Concrete composition, curing conditions, and subsequent exposure conditions were significant factors. Gaps around aggregates were a typical manifestation of DEF, and these gaps may contain ettringite.

Lewis and Scrivener [92] examined microchemical effects of curing and delayed ettringite formation in mortars cured at 90°C using clinkers of differing SO_3 contents. Using SEM/X-ray microanalysis, they found a relatively uniform expansion of the cement paste in contrast to growth of ettringite at paste-aggregate interfaces.

Bonen and Diamond [93] examined the characteristics of delayed ettringite deposits in ASR-affected steam cured concretes. They found a relationship between ettringite morphology and location within the paste and its chemical composition. Ettringite found along aggregate boundaries, in cracks, and in air voids had an ideal chemical composition, while ettringite found within the cement paste exhibited much lower SO_3 levels.

Hime [94] studied the causes of failure of selected precast concrete products and identified delayed ettringite formation as the reason for expansion and cracking. He detailed the mechanism behind the failure and explored means to prevent future occurrences.

The eighteenth meeting of the International Cement Microscopy Society included a panel discussion on delayed ettringite formation with a number of noted speakers invited to present their views. Scrivener [95] examined the conditions necessary for delayed ettringite formation in relation to precast railroad ties. She stated that elevated temperatures are necessary, sulfate-resisting cements do not appear to be susceptible, additions of sulfate to a clinker shows a pessimum effect in the subsequent amount of expansion, cements

with a high surface area appear more susceptible, increased alkalis appear to increase susceptibility, and the content of MgO appears related to expansion. She then presented arguments against the theory that crystallization around aggregates causes expansion and evidence for an overall expansion of the paste. She concluded that a connection between ettringite formation and expansion has not been established. Hime *et al.* [96] suggested causes of DEF are excessive steam curing temperatures, excessive placement temperatures, excessive temperature after placement, excessive sulfate content, and the presence of excessive or slowly soluble sulfates in the clinker. They also suggested that petrographic identifications of ASR reaction gel may actually be ettringite. Diamond [97] argued that features of DEF in steam-cured and nonsteam-cured concretes are similar and that no special mechanism for the steam-cured concretes appears supportable. Cracking only partly enveloping aggregates appears incompatible with the proposed homogeneous paste expansion theory. Erlin [98] stressed the need for a standardized terminology through acceptance of a set of definitions for ettringite and its modes of occurrence. He then discussed different modes of occurrence of ettringite and possible damage to concrete by it and other phenomena.

7.4 Freeze–Thaw

Stark and Ludwig [99] suggested that freeze–thaw deterioration of concretes exposed to deicing salts is not just a physical problem. The instability of certain hydration products influenced freeze–thaw durability, though it was less significant than air-entraining agents or w/c.

Wang *et al.* [100] presented a technique to study ice formation and propagation in concrete. Controlled cooling allowed them to monitor the solid–liquid interface. Ice did not completely fill the pores, and supercooled, alkali-rich pore solution existed. They also monitored the formation of ice in entrained air voids.

Gudmundsson [101] examined deteriorated bridge piers in Iceland. They found the most severe damage in the lower portion of the tidal zone, less damage upward, and no deterioration in the splash zone. Deterioration manifested itself as scaling of cement paste exposing the aggregates. The surface paste was depleted in Ca and enriched in Mg, and air voids and cracks were filled with ettringite. They concluded that the filling of the air voids lowered the concrete resistance to freeze–thaw cycling and this phenomenon was the predominant cause of deterioration.

Pigeon *et al.* [102] studied surface microstructure and scaling resistance of concretes with either troweled or cut surfaces exposed to deicing salts and freezing conditions. They used an SEM to examine the outer paste microstructure in concretes with 0%, 20% and 40% replacement of cement with fly ash. All concretes with a troweled surface exhibited a very porous outer skin. The higher porosity of the troweled surfaces reduced their resistance to scaling. Fly ash affected the surface layer by increasing its thickness and porosity.

7.5 Magnesium Salts

Reichenberg and Sylla [103] examined the effects of magnesium on concrete by storing prisms in a magnesium chloride solution for a period of ten years. They measured an initial mass increase and considered it to reflect a reaction between the MgCl_2 in solution and the hydration products, causing as dissolution of calcium and precipitation of brucite. Precipitation of brucite, calcite, and aragonite appeared to reduce permeability of the surface layer and slow the exchange reactions. They suggested that a $\text{Mg}(\text{OH})_2$ concentration of 2500 mg/l was the boundary between nonaggressive and aggressive conditions.

Horiguchi *et al.* [104] examined the durability of concrete breakwaters in a cold marine environment in northern Japan. They found substantial wear, up to 1 m in tidal zones, for some of the concretes and a correlation between wear depth and compressive strength. Maximum chloride content was generally found deep inside the structures and not at the surface. The presence of aragonite, gypsum, ettringite, and calcite indicated seawater-related decomposition of the concretes. Statistical analysis indicated that strength, chloride penetration depth, and position between high and low tide levels were significant in prediction of remaining service life.

Gofñi *et al.* [105] studied the effects of temperature on leaching of Ca^{+2} and OH^- at 20 °C and 40 °C. They concluded that the controlling mechanism for calcium leaching at both temperatures was diffusion and that the diffusion coefficients increased slightly with temperature. Estimates of the degraded layer at 90 days and 300 years were 1 mm and 37 mm, similar to values from previous studies.

8 REACTIONS AT THE PASTE/AGGREGATE INTERFACE

Kobayashi [106] examined the characteristics of the paste/aggregate interfacial zone with aggregates coated with limestone powder or ground blast furnace slag. Using Vickers hardness and fluorescence microscopy they observed a decrease in the width of the interfacial transition zone.

Hanehara *et al.* [107] studied the influences of aggregate surface texture on the microstructure of the paste/aggregate interfacial zone. They found the surface structure of the aggregate influenced the orientation and morphology of calcium hydroxide crystals. They concluded that the limestone and sandstone aggregates had few sites for precipitation, so the lack of calcium hydroxide concentrations resulted in a greater adhesive strength.

Scrivener and Nemati [108] studied the interfacial transition zone by impregnating the cement paste pore structure with Woods metal. This compound appears very bright in backscattered electron SEM images and serves to highlight voids. They demonstrated interconnectivity of the voids and showed increased connectivity of paste in the interfacial zone.

Yang *et al.* [109] examined the process of sulfate attack on cement mortars with emphasis on the role of the interfacial zone. They found that the resistance was influenced by the

interfacial zone as mortars with larger zone widths expanded faster. Pretreatment of the aggregate resulted in a marked improvement in interfacial zone thickness and a significant increase in resistance to sulfate attack.

Tamimi [110] used a two-stage mixing procedure to improve the cement paste–aggregate interface. This method involved an initial mixing of aggregate and cement at 25% of the final water content, followed by addition of the remaining water and final mixing. This procedure resulted in an improvement in compressive strength, which was related to a more dense interfacial zone microstructure.

9 MICROSCOPY AND IMAGE ANALYSIS

Grattan–Bellew [111] described investigation methodology and microstructural features of concretes exposed to different aggressive environments.

Rivera–Villarreal and Krayner [112] examined ancient structural concretes of pre-Hispanic builders in Central America. Excavation of the El Tajín archeological site revealed a collapsed lightweight flat concrete roof 43 x 8 m in size. Cores extracted from the roof were petrographically examined to determine mechanical properties, materials, aggregate sources, mineralogy, and pozzolanic reactions.

Jensen [113] examined the microstructure of sculptures dating to the early 1900's from Denmark using a petrographic microscope. Winnefeld and Knöfel [114] used optical and electron microscopy to examine historic mortars from the 19th century. These mortars were nonhydraulic and hydraulic lime mortars, mortars with pozzolanic additives such as brick dust, trass, and slag, and mortars with charcoal, shells, pigments, animal hair, and proteins. They apply an analytical process developed in their laboratory to characterize the materials for both evaluation of deterioration causes and effects, and for duplication of materials.

Diamond and Wang [115] applied quantitative image analysis of SEM backscattered electron images to examine the effects of superplasticiser on cement paste microstructure. They found the area fraction of unhydrated cement was greater and the area fractions and size distribution of capillary pores were reduced. Calcium hydroxide content was increased in area and grain size with a decrease in average distance between grains.

Damidot and Sorrentino [116] explored the difficulties in using an environmental SEM to study cementitious materials. They demonstrated how water removal from concentrated solutions may result in a rapid precipitation of solids and lead to incorrect interpretations. This process was thought to be more problematic at the early stages of hydration when the pore solution is supersaturated with respect to some hydrates.

Kjellsen and Jennings [117] observed microcracking in high-performance cement pastes exposed to drying and wetting conditions in an environmental SEM. They saw microcracks in specimens that had not been dried (about 90% relative humidity) and consid-

ered them to be an intrinsic feature of low w/c pastes. These cracks widened upon drying and closed with the introduction of moisture.

Thaulow *et al.* [118] examined alkali silica gels and ettringite formed in steam-cured, prestressed railroad ties. Chemical compositions of the gels were similar to those reported in the literature and varied in calcium depending upon the proximity to aggregate or cement paste. Ettringite compositions were close to stoichiometrical values, though slightly lower in sulfur. The XRD analyses demonstrated that the ettringite was crystalline.

Thaulow and Jakobsen [119] reviewed of the application of optical microscopy in the diagnosis of chemical deterioration of concrete. They presented case studies on alkali-silica reaction, sulfate attack, delayed ettringite formation, and acid attack. They discussed the use of crack patterns, paste texture, and secondary mineralization in the diagnosis. The potential difficulties due to multiple mechanisms were also discussed.

Moukwa [120] examined the physical and microstructural behavior of concretes (0.41 w/c) exposed to actual and laboratory-simulated arctic environments. Thermal strains were found to be a significant factor concerning durability. Freeze-thaw cycles were limited. Dissolution of portlandite was noted but appeared to be limited to the outer skin of the concrete.

Lin *et al.* [121] examined microscopical features of fire-damaged concrete using SEM and optical microscopy. Cracking around aggregate edges and within the paste was observed after temperatures of 300 °C were reached, while concretes exposed to temperatures in excess of 500°C showed decomposition of the hydration products and more extensive cracking around aggregates and within the paste. Rehydration products were observed in the cracks after fire-damaged concretes were sprayed with water. They also discussed repair materials for fire-exposed concretes.

Ghosh and Nasser [122] examined the effects of high temperature and pressure on strength and elasticity of lignite fly ash and silica fume concretes. They found a decrease in compressive strength and static modulus with a rise in temperature and observed a deterioration of the binding matrix. The C-S-H appeared to densify at temperatures up to 71°C but decomposed upon heating to 232°C.

Guise *et al.* [123] examined fire damaged concretes and developed a procedure using color and petrographic techniques to assess damage and cracking and to explore the thermal history of the concrete.

Saad *et al.* [124] studied the effects of silica fume on concrete phase composition and microstructure after fire exposure. They noted a decomposition of portlandite in the temperature range of 450 to 550°C, of the main hydrates at 400 to 600°C, and of calcium carbonate above 600°C. The addition of silica fume (10%) consumed portlandite and these concretes appeared stable up to 300°C. Addition of 20 to 30% silica fume resulted in cracking at temperatures slightly above 100°C.

Sarkar and Coleman [125] examined deteriorated concrete from an underground tank for waste water. They found the ceiling of the tank to have the greatest deterioration with the effluent level also damaged. The outer skin of the concrete contained gypsum layers indicative of sulfate attack.

Kjellsen and Monsøy [126] explored procedures to prepare flat, polished specimens of high-performance concrete for SEM imaging and microanalysis. These materials were difficult to prepare as their low permeability inhibited permeation by most epoxy resins. They presented methods for successful specimen preparation.

Lange *et al.* [127] used SEM and confocal microscopy to study fracture surfaces of fiber-reinforced mortars. They used a roughness number, defined as the ratio of estimated surface area to nominal surface areas. Surface roughness measurements were shown to correlate with fracture properties.

10 MODELING

Garboczi and Bentz [128] presented a set of digital microstructural models that, when used in conjunction with each other, provided properties for use as input for simulations at the next higher level. They employed a calcium silicate hydrate model for the nanometer level, hydrated cement paste at the micrometer level, and a mortar or concrete at the millimeter or meter level. This methodology was demonstrated for ionic diffusivity. Navi and Pignat [129] developed a particle kinetics model for three-dimensional simulations of microstructure development by hydration of tricalcium silicate. Their model addressed effects of interparticle contacts, and the accessibility of water on the rate of hydration and formation of hydration products.

Boumiz *et al.* [130] applied ultrasonic, calorimetric, and conductometric techniques to examine hydration reactions in cement pastes and mortars in order to develop a better understanding of their mechanical properties at early ages. Two mechanisms were seen in the development of mechanical properties: 1) connectivity of the cement particles, modelled using percolation, and 2) filling of capillary pores by hydration products.

Van Breugel and Koenders [131] developed a model to simulate the effects of elevated temperature curing on the porosity of cement-based systems. They examined the effects of w/c and curing temperature, demonstrated calculations for porosity and autogeneous shrinkage, and identified regions for potential cracking due to stress concentrations.

Neubauer *et al.* [132] presented a two-dimensional finite-element shrinkage algorithm to examine effects of the structure and properties of the interfacial zone on elastic modulus and shrinkage. They compared model results with experimental data for a 0.35 w/c mortar at 65% hydration. They predicted that the elastic modulus of the interfacial transition zone was $\frac{1}{3}$ to $\frac{1}{2}$ that for bulk cement paste and that the unrestrained shrinkage was similar to that of the bulk cement paste.

Van Breugele *et al.* [133] examined drying shrinkage in concretes using models for simulation of strength and stress in structures at the macro level.

Delagrave *et al.* [134] developed a model for leaching of calcium from concrete that considered thermodynamic equilibria between the pore solution and the hydration products. They devised a set of experiments on cement paste for validating their model and examined the pastes by electron microprobe and TGA/DTA. Their test data showed the kinetics of degradation were sensitive to microstructure. The reduction of water or the use of silica fume imparted substantial changes in microstructure, reducing diffusivity and increasing the resistance of the paste to calcium leaching. They also found that the portlandite content was a very significant factor in controlling calcium diffusion.

Bournazel and Capra [135] presented a model for degradation of concrete structures due to chemical attack that extended from the microlevel, chemical reactions between hydration products and pore solution ions, to the macro level. They provided examples of early age cracking and alkali–aggregate reaction.

Carde *et al.* [136] developed a model for the effects of leaching on mechanical properties of cement–based materials. This model incorporated leaching of portlandite and decalcification of C–S–H and demonstrated the importance of portlandite leaching on the deterioration of cement paste.

Gérard *et al.* [137] presented a modeling approach to evaluate long–term durability of concrete used for radioactive waste disposal. They incorporated chemical and mechanical loads and considered their eventual couplings. Validation experiments on leaching and permeability, mechanical behavior under tensile loading, microstructure and cracking were presented.

Adenot and Richet [138] presented a model for the chemical degradation of cement paste by water and compared it experimental data for validation. Their model indicated that the diffusion coefficients of the degraded region and of surface gel were very important factors in concrete durability.

Chau and Rogers [139] developed a computer model for prediction of long–term performance of reinforced concrete structures using a mechanistic approach to model concrete degradation, ground water infiltration, and leaching.

11 OTHER CEMENTS

Lin and Glasser [140] studied the hydration of calcium sulfoaluminate cements, the hydration characteristics, the effects of accelerating and retarding admixtures, and the composition and microscopy of hydration products. These cements are interesting because they are fired at lower temperatures. They found that clinker mineralogy influenced reactivity and expansion, and that cements with added lime, gypsum, and calcium aluminates were expansive, whereas cements consisting of calcium sulfoaluminate and belite hydrated rapidly yet produced dimensionally stable products.

George [141] examined the durability of CAC concretes compared to portland cement concretes exposed to sulfates and sea water. He contended that properly prepared CAC concretes were not prone to reinforcement corrosion due to carbonation. Acid resistance of CAC concretes at pH 3.5–4 may actually be better because the cubic hydrate exhibited greater resistance. Other factors in the longer service lives included the relative insolubility of reaction products and greater acid neutralization capacity.

Dunster *et al.* [142] examined two concrete structures in aggressive marine environments, constructed in the 1930's using CAC. The concretes were well made and had excellent durability. They found the outer region had a zone of low conversion which may have reduced the sulfate and chloride permeation. The outer 5–15 mm had a much lower permeability than the interior. One section exhibited cracking in the interior, but the cracking did not appear to have seriously impacted the long-term durability.

Goñi *et al.* [143] examined the behavior of CAC in highly alkaline environments. The structures that failed did not fit the traditional failure scenario of carbonation and alkaline hydrolysis. They proposed that humidity played a significant role and suggested a sequence of alkaline dissolution, alkaline hydrolysis, and carbonation.

Degenkolb and Knöfel [144] studied lime- and slag-based mortars utilizing expansive additives (CAC, metakaolin, and calcium aluminate sulfate). The addition of these expansive materials was intended to compensate for shrinkage and to produce expansive mortars. The expansion appeared related to the morphology of ettringite, which was influenced by pH. Lime mortars with high pH and calcium hydroxide concentration tended to produce thin needles of ettringite and gel-like aggregations that resulted in expansion. Slag-based mortars had lower pH values and concentrations of calcium hydroxide. Ettringite morphology tended toward thick, columnar crystals and exhibited low expansion.

Garg *et al.* [145] examined a phosphogypsum-lime-fly ash binder and found those cured at 50°C showed decreased porosity and better strength and mass retention after wet/dry and temperature cycling than those cured at 27°C.

Middendorf *et al.* [146] examined the microstructure and properties of fine cement suspensions for injection applications. Mechanical strengths were increased but the increased water demand and accompanying shrinkage behavior had a negative influence on mechanical strengths. Addition of fine-sized fly ash and chemical admixtures helped to reduce water demand and to enhance rheological and mechanical properties.

Igarashi *et al.* [147] developed a low-heat portland cement concrete for use in low-temperature environments. The cement was improved by using a highly pulverized blast furnace slag and increased calcium sulfate. These improvements were attributed to the formation of C-S-H and ettringite.

Su *et al.* [148] studied the microstructure of styrene acrylate polymer-modified cement pastes at early ages using an environmental SEM. The polymer was adsorbed on the cement grains after mixing and tended to slow the hydration reactions. The remaining

polymer was dispersed in the pore solution, forming a film after free water was removed via hydration and evaporation.

Fu *et al.* [149] used zeolites to prevent conversion of CAC hydration products to hydrogarnet. They found no strength reductions. Strätlingite was preferentially formed. Little to no hydrogarnet phase was found using XRD analysis.

Ding *et al.* [150] investigated the hydration characteristics of a CAC blended with zeolite and containing added inorganic salts or alkalis. Mortars incorporating sodium salts showed no strength reductions after curing at 38°C for 150 days. They concluded that the sodium salts promoted strätlingite formation and inhibited formation of hydrogarnet.

Sugama and Carciello [151] examined CAC modified with sodium metasilicate and containing lightweight mullite–shelled microspheres for geothermal well–cementing applications. Advantages included low densities (<1.25 g/cc), a retarding effect on the cements, formation of sodium calcium silicate hydrate and boehmite by hydrothermal reaction between the cement and sodium metasilicate, and a reaction between the microspheres forming boehmite and analcime. The hydrothermally–enhanced microstructures at temperatures of 300°C produced a dense microstructure with reduced porosity and permeability.

Nawa [152] detailed the current status of belite–rich cements for applications ranging from high–strength, highly flowable concretes, to low–heat, high–strength concretes. He examined properties for these concretes and compared them to ordinary portland cement concretes.

Okamura [153] examined the mineralogy and hydration of belite–rich cements and their influence on strength development in mortars. Belite–rich cements were found to produce more C–S–H and less portlandite. The C–S–H did not fill up all the available pore space. Small pores were filled with C–S–H at later ages and the generation of a uniform layer of C–S–H was suggested to be the reason that belite–rich cements show strength development at later ages.

Chatterjee [154] reviewed the history of belite cements, examining their development, synthesis, and utility and stressing their potential not only in energy conservation but in durability. Later, Chatterjee [155] examined the future technological options of belite cements through an examination of processing techniques, use in blended cements, and durability.

Malek and Roy [156] examined alkali–activated cements and reported on the nature of the hydration products, their durability, and their potential for suppressing alkali–aggregate reactions in concretes.

Tsuchida [157] examined the hydration characteristics of alinite–rich clinkers prepared from incinerated garbage burnt at different temperatures. Initial hydration was slower than that of ordinary portland cement with the formation of calcium hydroxide, ettringite, and Friedel’s salt, and a later conversion of ettringite to monosulfate. Mortar

strengths were lower than those of portland cement. Higher strengths were achieved with clinker burned at lower temperatures. He considered that control of burning and gypsum additions could be used to optimize the clinker.

Uchikawa and Obana [158] explored the possible manufacture and utilization of Ecocement, which is manufactured using waste materials. Control of cement hydration properties may be affected through modification of alumina and chlorine. Setting time was related to the amount of calcium chloroaluminate, the type of gypsum, and the sulfur/alumina ratio, and was extended through use of citric acid.

Moriya [159] examined the applications of Ecocement as a soil stabilizing agent. This cement contains several hundred times the chloride content of ordinary portland cement, and concern was focused on leaching and steel corrosion. Use of slag reduced the amount of chloride leached proportional to the replacement level and resulted in higher compressive strengths.

Scheetz and Hoffer [160] examined means of solidifying wastes using a sodium silicate-activated portland cement. Increased additions of sodium silicate accelerated hydration and reduced the amount of calcium hydroxide. Strengths increased with moderate sodium silicate additions but decreased with high additions.

Jonasson and Ronin [161] used strong vibration of a silica fume cement to create what they termed energetically modified cements. This binder was intended for use in pastes, mortars, and concretes. The vibration energy was used to reduce water content. Improved strength and frost resistance were attributed to reduced porosity.

Sugama and Baldwin [162] investigated a calcium phosphate cement and a Class G cement containing silica flour at the interface with various metal substrates. With the calcium phosphate cement, they found an $\text{AlO}(\text{OH})$ phase forming that served to weaken the interface. The Class G cement accelerated corrosion of the cold-rolled and stainless steel, but the corrosion product, Fe_2O_3 , appeared to serve as an anchor for the major hydration product, xonotlite, and strengthened the interface. Zinc-coated steel surfaces were attacked by the high pH solutions of the Class G cement and had lower interfacial bond strengths.

Teoreanu *et al.* [163] examined hydration of aluminate-slag systems using metallurgical slags and fly ashes that were using sodium sulfate and sodium carbonate.

Dehua and Chuanmei [164] studied the effects of aluminates on the phases and strengths of magnesium oxychloride cements. They found that the addition of a reactive aluminate resulted in a conversion of reaction products from $5\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ (called the 5 1 8 phase) to a $3\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ (3 1 8 phase), while the addition of an inert C_2AS phase did not create this phase conversion. This conversion through addition of small amounts of reactive aluminates did not appear to affect the compressive strengths of the product.

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