DISTRIBUTION SHEET

To Distribution	From Albert A. Kruger	Page 1 of 1			
		Date 17 July 1995			
Project Title/Work Order Glass Science Tutorial: Lecture #8, Introduction to Cementitious Systems for Low-Level Waste Immobilization, Professor J. Francis Young & Colleagues		EDT No. N/A			
		ECN No. N/A			
Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
Central Files	A3-88	X			
Course Attendees		X			
A. A. Kruger	H5-27	X			
OSTI (2)	A3-36	X			

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Glass Science Tutorial: Lecture #8, Introduction Cementitious Systems for Low-Level Waste Immobilization

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Westinghouse
Hanford Company Richland, Washington

Management and Operations Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for Public Release

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

LEGAL DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced from the best available copy. Available in paper copy and microfiche.

Available to the U.S. Department of Energy
and its contractors from
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
(615) 576-8401

Available to the public from the U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
(703) 487-4650

Printed in the United States of America

DISCLM-1.CHP (1-91)

RELEASE AUTHORIZATION

Document Number: WHC-MR-0507

Document Title: Glass Science Tutorial: Lecture #8, Introduction
Cementitious Systems for Low-Level Waste
Immobilization

Release Date: 7/20/95

This document was reviewed following the
procedures described in WHC-CM-3-4 and is:

APPROVED FOR PUBLIC RELEASE

WHC Information Release Administration Specialist:

Kara M. Broz

July 20, 1995

Glass Science Tutorial: Lecture #8, Introduction Cementitious Systems for Low-Level Waste Immobilization

Lecturers Prof. J. F. Young,
Prof. R. J. Kirkpatrick, Prof. T. O. Mason
and Dr. A. Brough

Date Published
July 1995

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Westinghouse
Hanford Company

P.O. Box 1970
Richland, Washington

Management and Operations Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for Public Release

WORKSHOP SCHEDULE

Tuesday, July 18

I.	Fundamentals - Composition and Hydration
(Chapters 1 and 2) Francis Young	8:00 - 10:15 a.m.
	Break	10:15 - 10:45 a.m.
I.	Fundamentals - Hydration Products
(Chapter 3) Jim Kirkpatrick	10:45 - 12:15 p.m.
	Lunch	12:15 - 1:30 p.m.
I.	Fundamentals - Microstructure
(Chapter 4) Francis Young	1:30 - 2:45 p.m.
	Break	2:45 - 3:15 p.m.
II.	Blended Cements - Pozzolans
(Chapter 5) Francis Young	3:15 - 5:15 p.m.

Wednesday, July 19

III.	Durability - Transport Properties
(Chapters 4 and 8) Tom Mason	8:00 - 10:00 a.m.
	Break	10:00 - 10:30 a.m.
III.	Durability - Long Term Performance
(Chapter 9) Jim Kirkpatrick	10:30 - 12:30 p.m.
	Lunch	12:30 - 1:45 p.m.
II.	Blended Cements - Blast Furnace Slags
(Chapter 6) Adrian Brough	1:45 - 2:45 p.m.
II.	Formation of Zeolites
(Chapter 7) Adrian Brough	2:45 - 3:45 p.m.
	Break	3:45 - 4:15 p.m.
	Question & Answers Session	4:15 - 5:15 p.m.

TABLE OF CONTENTS

Chapter 1	Composition and Properties of Portland Cement
Chapter 2	Hydration of Portland Cement
Chapter 3	Structure of Hydration Products
Chapter 4	Microstructure of Concrete
Chapter 5	Pozzolans
Chapter 6	Slags
Chapter 7	Zeolites
Chapter 8	Transport Properties
Chapter 9	Introduction to Geological Aspects and Long-Term Durability of Concrete

Chapter 1

COMPOSITION AND PROPERTIES OF PORTLAND CEMENTS

The product of portland cement manufacture-clinker-is a complex material both compositionally and structurally. In order to be able to predict cement performance, or to determine the cause of abnormal behavior, it is necessary to understand the physical and chemical make up of the clinker as possible. However before we consider this it is desirable to briefly review the general manufacture of cement.

A. MANUFACTURE

The mixture is heated in kilns that are long rotating steel cylinders on an incline. The kilns may be up to 6 meters in diameter and 180 meters in length. The raw materials mixture enters at the high end of the cylinder and slowly moves the length of the kiln due to the constant rotation and inclination. At the low end of the kiln, a fuel is injected and burned, thus providing the heat necessary to make the materials react. It may take up to 2 hours for the mixture to pass through the kiln, depending upon the length of the cylinder.

Figure 1. Chemical reactions in the rotary kiln.

As the mixture moves down the cylinder, it progresses through four stages of transformation. Initially, any free water in the powder is lost by evaporation. Next, decomposition occurs from the loss of bound water and carbon dioxide. This is called calcination. The third stage is called clinkering. it is during this stage the calcium silicates are formed. The final stage, is the cooling stage.

The marble-sized pieces produced by the kiln are referred to as clinker. Clinker is actually a mixture of four compounds which will be discussed later. The clinker is cooled, ground, and mixed with a small amount of gypsum (which regulates setting) to produce the general-purpose portland cement.

Water is the key ingredient which mixes with the cement to form a paste which binds the aggregate together. The water causes the hardening of the concrete through a process called hydration. Hydration is a chemical reaction in which the major compounds in cement form chemical bonds with water molecules. During hydration, the major compounds in cement incorporate the water molecules into their structures to become known as hydrates or hydration products. Details of this hydration process are explored in the next chapter.

B. COMPOUND COMPOSITION

During firing in the rotary kiln portland cement clinker forms four distinct chemical compounds: C_3S , C_2S , C_3A and C_4AF . The calcium silicates form relatively large crystals in the clinkering zone, while the alumina-based compounds crystallize during cooling from the liquid state. If we assume that equilibrium is maintained in the kiln and the compounds have their ideal stoichiometric formulae than we can calculate the relative proportions of each phase using the Bogue equations. These equations are derived from considering the combination of the constituent oxides on a molar basis. If any changes in compound stoichiometry are to be allowed for or other phases considered the Bogue equations are no longer valid.

The Bogue Equations:

Case A:	$A/F \geq$	0.64
	$C_3S =$	$4.071C - 7.600S - 6.718A - 1.430F - 2.852\bar{S}$
	$C_2S =$	$2.867S - 0.7544C_3S$
	$C_3A =$	$2.650A - 1.692F$
	$C_4AF =$	$3.043F$

$$\begin{aligned}
 \text{Case B:}^* \quad A/F &< 0.64 \\
 C_3S &= 4.071C - 7.600S - 4.479A - 2.859F - 2.852\bar{S} \\
 C_2S &= 2.867S - 0.7544C_3S \\
 C_3A &= 0 \\
 C_4AF^* &= 2.100A + 1.702F
 \end{aligned}$$

C. SPECIFICATIONS FOR PORTLAND CEMENT

ASTM C150 Specification for Portland cement. These are:

Type I	General Purpose	(~90%)
Type II	Moderate Heat Moderate Sulfate Resistance	(~4%)
Type III	High Early Strength	(~4%)
Type IV	Low Heat of Hydration	(0%)
Type V	Sulfate Resistant	(~2%)
White	(Type I or III)	(<1%)

The five types vary according to the proportions of the four clinker compounds each contain. Average compositions are given in Table 1. Of these Type I is by far the most common accounting for over 90% of annual production. The others are more specialized, although Type II is common in certain areas of the country.

The heart of ASTM C150 specifications are the chemical and physical characteristics; Tables 2 and 3 respectively. The specifications rely primarily on the cements conforming to certain physical requirements, such as fineness, expansion, setting, strength development, heat of hydration, etc. Thus the compositions given in Table 1 represent average values used by manufacturers to meet the physical requirements. Specific limitations on clinker compounds are placed only on C_3A , except for Type IV.

The differences in performance between the five types are designed to meet certain construction requirements. The two issues most germane to waste solidification are heat of hydration and sulfate attack. A typical mill certificate is shown, as well as the summary data for another cement supplied by the manufacturer. Mineral admixtures are commonly used now to modify the performance of Type I. When these admixtures in waste solidification - both to control chemistry and cost - the differences in cement types are

usually not particularly critical. Thus in most cases locally produced cement can be used. Occasionally a different cement may be necessary. Comparisons of the performance of the five types are given in Figures 2 and 3.

One aspect of cement chemistry that may be important is alkali content. Most modern cements have high alkali contents with sodium equivalent ($\text{Na}_2\text{O} + 0.66 \text{K}_2\text{O}$) $> 0.8\%$. In these cements alkali sulfates are present, either as arcanite (K_2SO_4), aphthitalite (Na_2SO_4) or calcium langbeinite (K_2SO_4). These cements may promote the early rapid formation of products such as ettringite (from C_3A) or syngenite (K_2SO_4) which can compromise the fluid properties of cement pastes or slurries. These compounds also tend to decrease setting time.

Table 1. Typical Chemical Composition and Properties of Portland Cements, ASTM Types I to V

	<i>I</i> ^a	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>
C_3S	50	45	60	25	40
C_2S	25	30	15	50	40
C_3A	12	7	10	5	4
C_4AF	8	12	8	12	10
C_2SH_2	5	5	5	4	4
Fineness (Blaine, m^2/kg)	350	350	450	300	350
Compressive strength ^b [1 day, MPa (lbf in. ²)]	7 (1000)	6 (900)	14 (2000)	3 (450)	6 (900)
Heat of hydration (7 days, J/g)	330	250	500	210	250

^aCSA designations are 10, 20, 30, 40, and 50, respectively.

^bASTM C109 2 in. mortar cubes.

Table 2. Chemical Requirements of ASTM C150 Standard Specification for Portland Cement^f

<i>Cement Type</i>	<i>I and IA</i>	<i>II and IIA</i>	<i>III and IIIA</i>	<i>IV</i>	<i>V</i>	<i>Remarks</i>
Standard requirements						
Silicon dioxide (SiO ₂), min., %	—	21.0	—	—	—	
Aluminum oxide (Al ₂ O ₃), max., %	—	6.0	—	—	—	
Ferric oxide (Fe ₂ O ₃), max., %	—	6.0	—	6.5	—	
Magnesium oxide (MgO), max., %	6.0	6.0	6.0	6.0	6.0	
Sulfur trioxide (SO ₃), max., %						
When (3CaO·Al ₂ O ₃) is 8% or less	3.0	3.0	3.5	2.3	2.3	
When (3CaO·Al ₂ O ₃) more than 8%	3.5	N.A. ^a	4.5	N.A.	N.A.	
Loss on ignition, max., %	3.0	3.0	3.0	2.5	3.0	
Insoluble residue, max., %	0.75	0.75	0.75	0.75	0.75	
Tricalcium silicate (C ₃ S), max., % ^b	—	—	—	35	—	
Dicalcium silicate (C ₂ S), min., % ^b	—	—	—	40	—	
Tricalcium aluminate (C ₃ A), max., % ^b	—	8	15	7	5	
Tetracalcium aluminoferrite + 2(tricalcium aluminate) (C ₄ AF + 2C ₃ A) or solid solution (C ₄ AF + C ₃ F) as applicable, max., %	—	—	—	—	20	
Optional requirements^c						
Tricalcium aluminate (C ₃ A), max., %	—	—	8	—	—	For moderate sulfate resistance
Tricalcium aluminate (C ₃ A), max., %	—	—	5	—	—	For high sulfate resistance
Sum of tricalcium silicate and tricalcium aluminate, max., %	—	58 ^d	—	—	—	For moderate heat of hydration
Alkalies (Na ₂ O + 0.685K ₂ O), max., %	0.60 ^e	0.60 ^e	0.60 ^e	0.60 ^e	0.60 ^e	Low-alkali cement

^aN.A., not applicable.

^bThe expressing of chemical limitations by means of calculated compounds does not necessarily mean that the oxides are entirely present as such compounds, or that the compounds have the exact stoichiometry implied.

^cThese apply only when specifically requested.

^dThis limit applies when tests for heat of hydration are not requested.

^eThis limit may be specified when the cement is to be used in concrete with aggregates that may be deleteriously reactive.

^fReprinted, with permission, from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103. Copyright.

**Table 3. Physical Requirements of ASTM C150 Standard Specification for
Portland Cement^f**

<i>Cement Type</i>	<i>I</i>	<i>IA</i>	<i>II</i>	<i>IIA</i>	<i>III</i>	<i>IIIA</i>	<i>IV</i>	<i>V</i>
Standard requirements								
Air content of mortar, ^a vol. %								
Max.	12	22	12	22	12	22	12	12
Min.	—	16	—	16	—	16	—	—
Fineness, specific surface, m ² /kg (alternative methods)								
Turbidimeter test, min.	160	160	160	160	—	—	160	160
Air permeability test, min.	280	280	280	280	—	—	280	280
Autoclave expansion, max., %	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Strength, not less than the values shown for the ages indicated below								
Compressive strength, lb/in. ² (MPa)								
1 day	—	—	—	—	1800 (12.4)	1450 (10.0)	—	—
3 days	1800 (12.4)	1450 (10.0)	1500 (10.3) 1000 ^b (6.9)	1200 (8.3) 800 ^b (5.5)	3500 (24.1)	2800 (19.3)	—	1200 (8.3)
7 days	2800 (19.3)	2250 (15.5)	2500 (17.2) 1700 ^b (11.7)	2000 (13.8) 1350 ^b (9.3)	—	—	1000 (6.9)	2200 (15.2)
28 days	—	—	—	—	—	—	2500 (17.2)	3000 (20.7)

Table 3 (cont.).

Time of setting (alternative methods)								
Gillmore test								
Initial set, min., not less than	60	60	60	60	60	60	60	60
Final set, h, not more than	10	10	10	10	10	10	10	10
Vicat test								
Initial set, min., not less than	45	45	45	45	45	45	45	45
Final set, h, not more than	8	8	8	8	8	8	8	8
Optional requirements ^c								
False set, final penetration, min., %	50	50	50	50	50	50	50	50
Heat of hydration ^d								
7 days, max., cal/g (J/g)	—	—	70 (290)	70 (290)	—	—	60 (250)	—
28 days, max., cal/g (J/g)	—	—	80 (330)	80 (330)	—	—	70 (290)	—
Strength, not less than values shown								
Compressive strength, lb/in. ² (MPa)								
28 days	4000 (27.6)	3200 (22.1)	4000 (27.6) 3200 ^b (22.1)	3200 (22.1) 2560 ^b (17.7)	—	—	—	—
Sulfate expansion ^e , 14 days, max., %	—	—	—	—	—	—	—	0.045

^aCompliance with the requirements of this specification does not necessarily ensure that the desired air content will be obtained in concrete.

^bWhen the optional heat of hydration or the chemical limit on (C₃S + C₃A) is specified.

^cThese apply only when specifically requested.

^dWhen the heat of hydration is specified, the (C₃S + C₃A) is not limited.

^eWhen sulfate expansion is specified, the C₃A and (C₄AF + 2C₃A) are not limited.

^fReprinted, with permission, from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103. Copyright.

marquette cement manufacturing company

TEST REPORT

Date Shipped April 20, 1978
 Cement Type II
 Silo/Bin No. 11
 CWT. 24,50 tons
 Car/Truck No. _____

For: Criss Concrete
West Va, Rt. #2
St. Marys, West Va. 26170

This Portland cement
 complies with current
 ASTM C 150 and Federal
 SS-C-1960/3 Specifications.

The data presented below is the average of the silo or bin from which this cement was shipped.

CHEMICAL DATA

	Test Value, %	Specification
SiO ₂ —	<u>23.1</u>	<u>21.0</u> Min.
Al ₂ O ₃ —	<u>4.1</u>	<u>6.0</u> Max.
Fe ₂ O ₃ —	<u>3.1</u>	<u>6.0</u> Max.
CaO —	<u>64.4</u>	<u>*</u>
MgO —	<u>3.3</u>	<u>6.0</u> Max.
SO ₃ —	<u>1.9</u>	<u>3.0</u> Max.
Loss on Ignition —	<u>0.7</u>	<u>3.0</u> Max.
Insoluble Residue —	<u>0.3</u>	<u>0.75</u> Max.
C ₂ S —	<u>46.0</u>	<u>*</u> Max.
C ₃ A —	<u>5.7</u>	<u>8.0</u> Max.
Na ₂ O Equiv. —	<u>0.44</u>	<u>*</u> Max.

* Not required by above specifications

REMARKS: _____

PHYSICAL DATA

	Test Value	Specification
Fineness, Blaine — cm. ² /gm.	<u>3610</u>	<u>2800</u> Min
Soundness, Autoclave — %	<u>0.04</u>	<u>0.80</u> Max
Time of Set, Vicat — Minutes — Initial	<u>110</u>	<u>45</u> Min
Final	<u>250</u>	<u>480</u> Max
Air Content — %	<u>9.1</u>	<u>12</u> Max
Compressive Strength:		
1 day — psi	<u>*</u>	<u>*</u> Min
3 day — psi	<u>2630</u>	<u>1500</u> Min
7 day — psi	<u>4880</u>	<u>2500</u> Min
	<u>*</u>	<u>*</u>

By: Jan Skwarecki
 Title _____

Jan Skwarecki, Manager, Quality & Pollution

LONE STAR INDUSTRIES, INC.
MARYNEAL PLANT

CEMENT TYPE III S-R. PLANT Maryneal, Texas

Chemical Analysis

SiO ₂	20.94
Al ₂ O ₃	2.84
Fe ₂ O ₃	4.78
CaO	65.60
MgO	2.34
SO ₃	3.11
Loss	0.63
Total	100.24
F	2.72
R	2.75
A/F	0.59

Compound Composition

C ₃ S	72.37
C ₂ S	5.50
C ₂ F	0.58
C ₄ AF	13.49
CaSO ₄	5.29
Free CaO	0.65

Physical Tests

N. C.	24.0
% Exp.	-.024
H ₂ O Cubes	-----
Flow	-----
% Air	7.5
% 325	96.6
Wagner	2600
Blaine	4670
Initial Set	2:00
Final Set	4:50
Vicat	60
% False Set	33

Compressive Strength

1 Day	2783
3 Day	4800
7 Day	5500
28 Day	6600

Figure 2. Influence of cement type on strength development.

Figure 3. Influence of cement type on heat of hydration.

CHAPTER 2

HYDRATION OF PORTLAND CEMENT

The setting and hardening of concrete are the result of chemical and physical processes that take place between portland cement and water, i.e., hydration. In order to understand the properties and behavior of cement and concrete some knowledge of the chemistry of hydration is necessary.

Hydration of Pure Cement Compounds

The chemical reactions describing the hydration of the individual cement compounds are complex and one approach to understanding them has been the study of the hydration of the individual compounds separately. This assumes that the hydration of each compound takes place independently of the others that are present in portland cement. This assumption is not completely valid, since interactions between hydrating compounds can have important consequences, but, at least for the silicates, it is a reasonable first approximation. The features described here refer specifically to hydration of cement or clinker compounds mixed with a limited amount of water (cement pastes) to simulate the conditions in concrete.

Calcium Silicates

The hydration reactions of the two calcium silicates (Eqs. 1 and 2) are stoichiometrically very similar, differing only in the amount of calcium hydroxide formed. The measured heats of hydration are also considerably different.

The principal hydration product is a calcium silicate hydrate. The formula $\text{C}_3\text{S}_2\text{H}_4$ is only approximately because the composition of this hydrate is actually variable over quite a wide range. It is a poorly crystalline material which forms extremely small particles in the size range of colloidal matter (less than $1 \mu\text{m}$) in any dimension. Its name, C-S-H, reflects these properties. In contrast, calcium hydroxide is a crystalline material with a fixed composition.

The reaction sequence of C_3S is most conveniently described by reference to the calorimetric curve (see Figure 1) which measures the rate of heat evolution with time. The heat flow from the sample is proportional

FIG. 1.

Rate of Heat Evolution During the Hydration of Tricalcium Silicate.

to the rate of reaction and is easily measured in the case of C_3S , which is the compound of major interest, since it comprises 40-70% by weight of cement. When first mixed with water a period of rapid evolution of heat (stage 1) occurs, which ceases within about 15 min. There follows a period of relative inactivity, the induction (or dormant) period (stage 2), which explains why portland cement concrete remains in the plastic state for some time. Initial set occurs in 1 to 3 hours, about the time C_3S has begun to react again with renewed vigor at the end of the dormant period. The silicate continues to hydrate rapidly, reaching a maximum rate at the end of the acceleration period (stage 3), which corresponds with the maximum rate of heat evolution. By this time (2 to 8 hours) final set has been passed and early hardening has begun. Thereafter the rate of reaction again slows down (stage 4) until it reaches a steady state (stage 5) within 12 to 24 hours.

The following processes occur at each stage (Table 3). On first contact with water, calcium ions and hydroxide ions are rapidly released from the surface of each C_3S grain; the pH rises to over 12 within a few minutes, which indicates a very alkaline solution. This hydrolysis slows down quickly but continues throughout the induction period. When the calcium and hydroxide concentrations reach a critical value, CH starts to crystallize from solution with the concomitant formation of C-S-H and the reaction of C_3S again proceeds rapidly. The induction period is apparently caused by the need to achieve a certain concentration of ions in solution before crystal nuclei form from which the hydration product grows. This is a requirement for many chemical reactions and is known as nucleation control. CH crystallizes from solution, while C-S-H apparently develops at the surface of the C_3S and forms a coating covering the grain. As hydration continues, the thickness of the hydrate layer increases and forms a barrier through which water must flow to reach the unhydrated C_3S and through which ions must diffuse to reach the growing crystals. Eventually, movement through the C-S-H layer determines the rate of reaction and hydration becomes diffusion-controlled. Reactions that are diffusion-controlled are quite slow and become slower as the thickness of the diffusion barrier increases. Thus, hydration tends to approach 100% completion asymptotically.

TABLE 3

Sequence of Hydration of the Calcium Silicates

<u>Reaction Stage</u>	<u>Kinetics of Reaction</u>	<u>Chemical Processes</u>	<u>Relevance to Concrete Properties</u>
1. Initial hydrolysis	Chemical control; rapid	Initial hydrolysis; dissolution of ions	-
2. Induction period	Nucleation control; slow	Continued dissolution of ions	Determines initial set
3. Acceleration	Chemical control; rapid	Initial formation of hydration products	Determines final set & rate of initial hardening
4. Deceleration	Chemical and diffusion control; slow	Continued formation of hydration products	Determines rate of early strength gain
5. Steady State	Diffusion control; slow	Slow formation of hydration products	Determines rate of later strength gain

C_2S hydrates in a similar manner, but much more slowly because it is a less reactive compound than C_3S . In addition, the heat of hydration of C_2S is less than C_3S , so that the calorimetric curve is not easy to measure experimentally. However, the curve is similar in form to that of C_3S (see Figure 1) with a much less intense second peak.

Hydration, like other chemical reactions, is sensitive to temperature, the rate of reaction increasing with temperature, but the temperature dependence being related to the extent of reaction. Hydration is most sensitive to temperature through stage 3 when the reaction is chemically controlled. Once hydration is completely diffusion-controlled in stage 5, it is much less temperature-sensitive, although the diffusion coefficient of the hydrate barrier will vary with temperature. The overall effect of temperature is illustrated in Figure 2, which compares the amount of hydration of C_3S at different temperatures. The activation energy of C_3S hydration (calculated in the normal way from reaction rate constants at different temperatures) is about 40 KJ/mole during stage 3, and 25 KJ/mole by stage 5. The corresponding values for C_2S hydration are about 60 KJ/mole and 30 KJ/mole. Above 100°C the chemistry of hydration changes significantly.

Tricalcium Aluminate

The primary initial reaction of C_3A with water in the presence of a plentiful supply of gypsum is:

FIG. 2

Effect of Temperature on the Hydration of Tricalcium Sulfate.

Ettringite* is a stable hydration product only while there is an ample supply of sulfate available. If the concentration of SO_4^{2-} in solution drops, then ettringite becomes unstable and converts to monosulfate:

The overall reaction of C_3A can thus be represented by:

Both steps in the hydration of C_3A (Eqs. 3 and 4) are exothermic.

*Several alternative names and ways of writing their formulae are in use for ettringite and monosulfate. They have been traditionally called calcium sulfoaluminate hydrates, although the $\bar{\text{S}}$ is present as SO_4^{2-} ions in both compounds; $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$ is sometimes called "monosulfoaluminate". The formulae of ettringite can be written as $\text{C}_3\text{A} \cdot 3\text{C}\bar{\text{S}} \cdot \text{H}_{32}$ and that of monosulfate as $\text{C}_3\text{A} \cdot \text{C}\bar{\text{S}} \cdot \text{H}_{12}$. Ettringite is the name given to a naturally occurring mineral of the same composition and is a specific composition in the general group of AFt phases (Al_2O_3 - F_2O_3 - trisulfate), when Al can be partly or completely replaced by F_2 (see hydration of ferrite phases) and SO_4^{2-} - by other anions: however, it is often used as a synonym for AFt. Similarly $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$ is one particular composition in the general group of AFm phases (Al_2O_3 - Fe_2O_3 - monosulfate). The recommended systematic names for ettringite and monosulfate are, respectively, 6-calcium aluminate trisulfate-32-hydrate and tetra calcium aluminate-12-hydrate.

The hydration of C_3A is slowed down as ettringite creates a diffusion barrier around C_3A analogous to the behavior of C-S-H during the hydration of the calcium silicates. This barrier is broken down during the conversion to monosulfate and allows C_3A to react rapidly again. The calorimeter curve for hydrating C_3A (Figure 3) looks qualitatively much like the curve for C_3S , although the underlying reactions are quite different and the amount of heat evolved is much greater. The first heat peak is completed in 10 to 15 min. and is primarily due to the formation of

Fig. 2

Hydration of C_3A with Sulfate (a) Calorimeter Curve
(b) Sequence of Hydration

Fig. 3A

Hydration of C_3A without Sulfate (a) Calorimeter Curve
(b) Sequence of Hydration

ettringite. The onset of the second peak coincides with the beginning of the conversion of ettringite to monosulfate and depends on the amount of sulfate available. The more gypsum there is in the system, the longer the ettringite will remain stable. Conversion to monosulfate will occur in most cements within 12 to 36 hours, after all the gypsum has been used to form ettringite.

The formation of monosulfate occurs because of a deficiency of sulfate ions necessary to form ettringite from all the available hydroxyaluminate ions. When monosulfate is brought into contact with a new source of sulfate ions, then ettringite can be formed once again:

Gypsum is added to portland cement clinker to curb the vigorous initial reaction of C_3A with water, which can lead to flash set, due to the rapid formation of calcium aluminate hydrates:

These hydrates, which are members of the AFm group and closely related structurally to monosulfate, are not stable and convert readily to yet another hydrate, C_3AH_6 .

The high heat evolution accompanying Eq. 7 means that the temperature of hydrating C_3A pastes can easily rise several tens of degrees Celsius. (Fig 3A) Above 30°C conversion of C_4AH_{13} and C_2AH_8 to C_3AH_6 is very rapid, but once C_3AH_6 has nucleated crystal growth can readily occur even below 30°C . Direct formation of C_3AH_6 occurs only at high temperatures 80°C ;

Formation of hexagonal hydrates around the grain will retard further hydration of C_3A , but conversion to C_3AH_6 destroys this layer and allows rapid hydration. The rate of conversion depends on temperature. It occurs above 20°C and rapidly above 30°C . In pure pastes of C_3A , rapid hydration and high heat evolution causes rapid conversion to C_3AH_6 in the first few minutes. The heat evolution curves shows conversion to C_3AH_6 only when retardation of this reaction occurs. See Figure 5. The hexagonal hydrates can be written using the general formula

where Y is a series of different anions and x is a variable quantity depending on Y. Compounds containing many different Y have been obtained in the laboratory. Those compounds that are likely to occur in cements pastes are:

$Y = OH$	$x = 12$	C_4AH_{13}
$Y = Al(OH)_4^-$	$x = 12$	C_2AH_8
$Y = SO_4^{2-}$	$x = 12$	$C_4A\bar{S}H_{12}$ monosulfoaluminate
$Y = CO_3^{2-}$	$x = 11$	$C_4A\bar{C}H_{11}$ monosulfoaluminate
$Y = Cl^-$	$x = 10$	$C_4ACl_2H_{10}$ chlorealuminate

(Note a similar series $C_3A \cdot 3CaY_2(1) \cdot H_{32}$ also occurs, but only ettringite $C_3A \cdot 3CaSO_4 \cdot H_{32}$ ($C_6A\bar{S}_3H_{32}$) occurs in cement pastes).

When quite small amounts of gypsum are present, there may still be unreacted C_3A present when all of the ettringite has been converted to monosulfate. In such cases AFm phases having compositions intermediate between $C_4A\bar{S}H_{12}$ and C_4AH_{13} are formed. These can either be mixtures or solid solutions: the latter written as $C_4A(\bar{S},H)H_{12}$ [or $C_3A \cdot (C\bar{S},CH) \cdot H_{12}$].

The hydration of C_3A may thus be summarized in Table 4.

TABLE 4

Formation of Hydration Products From C_3A

$C\bar{S}H_2/C_3A$ Molar Ratio	Stable Hydration Products Formed
3.0	Ettringite
3.0-1.0	Ettringite + monosulfoaluminate
1.0	Monosulfoaluminate
<1.0	$C_4A\bar{S}H_{12}$ - C_4AH_{13} solid solution
0	C_3AH_6 (Hydrogarnet)

It should be remembered that C_3A is a reactive compound. If a sufficient concentration of sulfate ions is not attained very rapidly it is possible that AFm phases ($C_4A\bar{S}H_{12}$, C_4AH_{13} , C_2AH_8 , or intermediate compositions) may form as transient phases in the first few minutes of hydration. Some researchers believe an amorphous gel phase always precedes the formation of crystalline compounds. Small amounts of C_3AH_6 may even form during this early period, or may form much later from conversion from AFm phases. Impure C_3AH_6 , in which A is partially substituted by F and S giving compositions within the hydrogarnet series, is obtained observed in small quantities in hydrated cement pastes.

Ferrite Phase

C_4AF forms the same sequence of hydration products as does C_3A , in the presence of gypsum, but the reactions are slower and evolve less heat. C_4AF seldom hydrates rapidly enough to cause flash set, and gypsum retards C_4AF hydration even more drastically than it does C_3A . Changes in the composition of the ferrite phase affect only the rate of hydration. As the iron content is raised, hydration becomes slower. Iron oxide apparently plays the same role as alumina during hydration (i.e., F can substitute for A in the hydration products). As can be seen in Eqs. 11 and 12*, there is insufficient lime in C_4AF to form the AFm phases unless amorphous hydrous oxides of iron or aluminum form also. However, in cement the supply of Ca^{2+} and OH^- from other hydration reactions makes the formation of these hydrous oxides unlikely.

*In these equations the use of a formula such as $C_6(A,F)\bar{S}_3H_{32}$ indicates that Fe_2O_3 and Al_2O_3 occur interchangeably in the compound, but the A/F ratio need not be the same as that of the parent compound.

In the absence of sulfate ions, sulfate-free AFm phases will be formed analogous to Eq. 7. The thermodynamically stable phase is $C_4(A,F)H_6$,

which is analogous to C_3AH_6 in the iron-free system.

Structures of Hydration Products

The following summarizes the principal features of the structures of the hydration products formed in reactions already discussed.

<u>Compound</u>	<u>Particle Characteristics</u>			<u>Structural Features</u>
	<u>Crystal- line</u>	<u>Ave. Size</u>	<u>Morphology</u>	
C-S-H	No	$\sim 100\text{\AA}$	Acicular, Intermediate	Amorphous; Variable stoichiometry. Probable structure akin to an amorphous clay (allophane) - discussed later
CH	Yes	0.01-1mm	Hexagonal plates (prisms)	Layers of OH^- and Ca^{2+} . Cleavage planes.
Ettringite	Yes	1-10 μ m	Hexagonal needles	Columnar structure (Fig. 6) with SO_4^{2-} and water molecules between columns
Hexagonal Hydrates	Yes	$\sim 1\mu$ m (thickness $\sim 0.01\mu$ m)	Very thin hexagonal plates	"Negative clay" Calcium aluminate sheets with positive charges held together with negative anions (Fig. 7).
C_3AH_6	Yes	0.5-5 μ m	Cubic polyhedra	Close-packed array of $Al(OH)_6$ polyhedra with Ca^{2+} between

COLUMNS: $Ca_6 Al(OH)_6 \cdot 24 H_2O$
 Al OCTAHEDRAL COORDINATION
 Ca 8-COORDINATION 4 OH & 4 H_2O
 (SHARES EDGES OF ADJACENT OCTAHEDRA)

INTERCOLUMNAR REGION: 3 SO_4^{2-}
 2 H_2O

Crystal Structure of Ettringite

LAYERS: $[Ca_2 Al(OH)_6]^+$ Ca & Al IN OCTAHEDRAL COORDINATION

INTERLAYER REGION: X^-
 X H_2O (DEPENDS ON NATURE OF X)

Crystal Structure of Monosulfate

Hydration of Portland Cement

Kinetics

The rate of hydration during the first few days is in the approximate order $C_3A > C_3S > C_4AF > C_2S$ (figure 4a). It must be remembered, however, that no two preparations of any of these compounds will hydrate at exactly the same rate because their reactivities will be affected by differences in crystal size and crystal imperfections, which are determined by the rate of cooling of the preparation. Reactivity is also influenced by particle size and particle size distributions determined by the extent and nature of grinding, fineness, and the rate of cooling of the clinker.

There are additional factors in cement. The reactivities of the clinker compounds are affected by the presence of impurities, which probably explains the fact that alite and belite (impure C_3S and C_2S as they occur in clinker) hydrate faster than do pure C_3S and C_2S (Figure 4b). The hydration of C_3A and the ferrite phase will also be affected by the above factors. Impurities may affect reactivity by (i) random ionic substitution in the crystal lattice with the creation of lattice defects, (ii) more extensive changes in the crystal structure resulting from changes in atomic packings and hence crystal symmetries, (iii) formation of separate precipitates at grain boundaries, or (iv) combinations of the above three. The reactivity of each clinker compound is also affected by the fact that the other compounds are also undergoing hydration.

Compound Interactions

The assumption made earlier that the cement compounds hydrate independently is a reasonable one for many purposes, but is not entirely true. For example, C_2S hydrates faster in the presence of C_3S because of changes in the concentrations of Ca^{2+} and OH^- in solution. These changes will also affect the hydration of C_3A and C_4AF . It has been shown that these latter compounds consume sulfate ions during hydration and so they will be in competition for the available sulfate ions. The more reactive C_3A can be expected to consume more sulfate than will C_4AF , thereby increasing the reactivity of C_4AF , since it forms less ettringite than would be expected. Gypsum increases the rate of hydration of the calcium silicates, which also compete for sulfate during hydration, because C-S-H incorporates significant amounts of sulfate, alumina, and iron into its structure. It has been estimated that the quantity of hydrated aluminum and iron compounds (principally Aft and AFm phases) that form in a paste may be only about half the theoretical quantity calculated from the compound composition of the cement. Similarly the fraction of sulfate which is combined in such hydrates may be much less than half of the total sulfate present in the cement. On the other hand silica is also incorporated in ettringite and monosulfate when they are formed in cement pastes.

Another example is in the existence of an optimum gypsum content for the development of maximum strength in a cement paste. One explanation is that too high a gypsum content results in the formation of excessive amounts of ettringite after the paste has hardened, causing unrestrained expansion and disruption of the paste microstructure, whereas too low a gypsum content allows the AFm phases (eq. 10) to form before

FIG. 4

Rate of hydration of the cement compounds: (a) in pastes of the pure compounds; (b) in cement paste. (Alite and Belite are respectively C_3S and C_2S containing impurity atoms in solid solution and are the forms of C_3S and C_2S as they occur in cement).

the end of stage 2 of C_3S hydration, so that the resulting consumption of lime prevents the nucleation of the hydration products of C_3S , thereby extending the induction period. Another viewpoint explains the optimum gypsum content by the fact that gypsum accelerates C_3S hydration, but at the same time lowers the intrinsic strength of C-S-H due to the presence of sulfate ions in its structure. Since there is a different optimum gypsum content for maximum strengths at different ages, both explanations may contribute to the phenomenon. The interaction between C-S-H and sulfate ions may help explain the observation that there is also an optimum gypsum content for minimum drying shrinkage, which is not the same as for strength. The sulfate ions involved in the hydration process can come from sources other than gypsum. Some clinkers contain K_2SO_4 , on other soluble alkali sulfates, which can also influence the course of reactions as described above.

A typical calorimetric curve of a portland cement is shown in Figure 5. The second heat peaks of both C_3S and C_3A can generally be distinguished, although their order of occurrence can be reversed. When the C_3A peak occurs before the main C_3S peak, and if the C_3A content is low, it may not be easily distinguished.

FIG. 5

Rate of heat evolution during the hydration of portland cement.

Setting and Hardening

The setting time of a cement paste (initial set) corresponds closely to the end of the induction period when normal setting behavior is observed. This would suggest that setting is controlled primarily by the rate of hydration of C_3S , although many investigators believe setting is controlled by the recrystallization of ettringite. Abnormal setting behavior (premature stiffening, false set or flash set) can undoubtedly be traced to reactions involving C_3A and/or gypsum. Setting problems are often the result of changes in the rate of the early reactions which can be affected by the presence of alkali oxides, chemical admixtures, or temperature. Details of abnormal setting will not be discussed here.

The rate of early hardening is also primarily determined by the hydration of C_3S and strength gain over the first 24 hours is roughly proportional to the area under the heat peak. It can be seen from Figure 6 that strength is primarily derived from the hydration of the silicates. The contribution from C_3A and C_4AF are quite small even though they hydrate rapidly. This is probably due to the large expansion that accompanies ettringite formation and the disruption of microstructure during the conversion of ettringite to monosulfoaluminate. In the first two to three weeks strength primarily depends on C_3S hydration and the strength development of a cement is a function of C_3S content (as well as cement fineness). C_2S , however, contributes to long term strength, as illustrated in Figure 7.

Schematic View of Setting in Cement Pastes

The strength of a paste thus depends on the degree of hydration of the calcium silicates. In pure pastes the degree of hydration can be fairly readily determined by quantitative x-ray diffraction analysis, but the analysis is more difficult in portland cement because peaks of the two phases overlap each other. It is common to use the bound water (non-evaporable water) as a measure of degree of hydration of portland cement, but this is not a very satisfactory approach because each compound hydrates at different rates. Furthermore, the hydration products of C_3A and C_4AF (which contribute little to strength) make a major contribution to bound water values, particularly at early ages. Bound water contents should thus be used with considerable caution and only on a comparative basis.

Heat of Hydration

The quantity ΔH , which is given in the hydration equations, is the heat of hydration (or enthalpy) and represents the residual energy in the system after the redistribution of energy has occurred with the breaking and making of chemical bonds during hydration. ΔH is a thermodynamic quantity that can either be determined by calculation or measured experimentally.

It is possible in theory to calculate the heat of hydration of portland cement at any given time if the compound composition, the amount of hydration that has occurred for each compound, and ΔH for reaction, are known. However, it is not always easy to determine the amount of hydration and ΔH is not known for every reaction, as can be seen in Table 5. Effective values of ΔH in J/g for each compound as it hydrates

FIG. 6

Compressive Strength Development in Pastes of Pure Cement Compounds

FIG. 7

Strength of Concretes made with Different ASTM Types of Portland Cements (As the C_3S content increases the C_2S content decreases)

TABLE 5

Heats of Hydration of the Cement Compounds

Reaction	-ΔH (J/g) for Complete Hydration			
	Pure Compounds		Clinker*	Cement*
	Calculated	Measured	Measured	Measured
$C_3S \rightarrow C-S-H + CH$	~ 380	500	570	490
$C_2S \rightarrow C-S-H + CH$	~ 170	250	260	225
$C_3A \rightarrow C_4AH_{13} + C_2AH_8$	~1260	-	-	-
→ C_3AH_6	900	880	840	-
→ monosulfoaluminate	-	-	-	~1200
$C_4AF \rightarrow C_3(A,F)H_6$	520	420	335	-
→ monosulfoaluminate	-	-	-	400

*These numbers were determined from regression analyses (see Eq. 15) of heats of hydration of ground clinker (no added gypsum), or cement.

in cement have been determined by multiple regression analyses of heat of hydration data for portland cements of known compound composition (Eq. 14 and 15).

$$H_{(3 \text{ days})} = 240 (C_3S) + 50(C_2S) + 880 (C_3A) + 290 (C_4AF) \quad (14)$$

$$H_{(1 \text{ year})} = 490(C_3S) + 225(C_2S) + 1160(C_3A) + 375(C_4AF) \quad (15)$$

The quantities C_3S , C_2S , and so on, are expressed as weight fractions of the cement. There is good agreement between the various values of ΔH where comparisons can be made (see Table 5).

ΔH is given in J/g to allow ready calculation of heat evolution from the hydrating cement in concrete. If this heat is not allowed to escape (i.e., if adiabatic conditions exist), the temperature rise can be quite large as shown in Figure 8. In mass concrete, true adiabatic conditions can be approached when concrete volumes are large in comparison to the surface from which the heat can be dissipated to the surroundings. The generation of high internal temperatures occurs primarily over the first few days when the concrete is still relatively plastic, and will not cause immediate damage. However, trouble may occur during subsequent cooling when the concrete has gained rigidity, since the resulting thermal stresses may well lead to tensile cracking. One way temperature rises can be controlled is by lowering the total heat of hydration of a cement. This can be accomplished by the reduction of C_3S and C_3A , since these compounds have the highest heats of hydration, and the highest rate of heat evolution.

FIG. 8

Rate of heat evolution measured as a rise in temperature of mass concrete stored under adiabatic conditions.

Volume Changes During Hydration

An important aspect of microstructural development is the degree of porosity during hydration. All the hydration products of the cement compounds have lower specific gravities and larger specific volumes than the cement compounds themselves (see Table 6). Thus, every hydration reaction is accompanied by an increase in solid volume, which leads to a decrease in porosity.

A knowledge of porosity can be very useful since it has such a strong influence on paste properties, particularly strength and durability. In principle, the total porosity in a paste (but not pore-size distributions) can be calculated quite simply, by estimating the volume changes using the chemical equations describing hydration of each compound together with the specific gravities of the appropriate species. In practice, the problems of compositional variations, particularly with C-S-H, and ionic substitutions make this quite a difficult exercise. It also requires a knowledge of the compound composition of a cement and the rate of hydration of each compound.

It is not only the total volume change that is of interest, but also the way in which this change is manifested. Calcium hydroxide either grows around solid particles or stops growing in a particular direction when it meets such obstacles, and the same is true of C-S-H. Thus, the hydration of the calcium silicates is not accompanied by an increase in the total volume of the paste. The hydration products will only occupy space that is available to them within the paste, which is the volume originally occupied by the mix water. If this space is filled before

TABLE 6

Physical Data Determining Volume Changes That
Occur During Hydration

Cement Compounds			Hydrated Compounds		
Compound	Density (kg/m ³)	Molar Volume* (10 ⁻⁶ m ³)	Compound	Density (kg/m ³)	Molar Volume* (10 ⁻⁶ m ³)
C ₃ S	3150	72.4	C-S-H	2350#	153
C ₂ S	3310	52.4	CH	2240	33.2
C ₃ A	3030	89.1	C ₆ A ₃ H ₃₂	1780	727
CSH ₂	2320	74.2	C ₄ A ₃ H ₁₂	1950	313
Portland Cement	3150	-	C ₄ AH ₁₃	2060	265
			C ₂ AH ₈	1950	165
			C ₃ AH ₆	2520+	150

*Gram Molecular Weight divided by density

#Value depends on the water content of C-S-H, which is related to how much intrinsic porosity is included in the structure. The number used was determined for material of composition C₃S₂H₄ which has been dried to 11% rh.

+In cement the A in C₃AH₆ is partially substituted by F and S, which raises the density to close to 3000 kg/m³

complete hydration has occurred, further hydration will virtually cease.

Quite the contrary occurs when ettringite is formed from C₃A or the ferrite phase. Ettringite crystals will make space for themselves when their crystal growth is impeded by solid material. If the impediment is a rigid material, crystal growth pressures will develop at the point where growth has been stopped. It has been estimated that ettringite may develop crystal growth pressures as high as 240 MPa (35,000 lb/in.²). In a paste that has not yet hardened ettringite has plenty of room in which to form or can make additional room by pushing aside obstructing cement grains. Once the paste has gained rigidity, however, the extra space necessary for continued formation of ettringite is created by expanding the total volume of the paste. Ordinarily, only very small expansions occur during the hydration of portland cement pastes through the crystallization of ettringite, because only small amounts form after the paste has hardened. But if too much gypsum is added, then more ettringite will be formed long after setting which may disrupt the paste sufficiently to lower the compressive strength of the paste or even, in extreme cases, cause cracking.*

*This is known as unsoundness and for this reason cement standards, such as ASTM C150, often limit the amount of $\bar{S}$ that can be present in a cement. Unsoundness can also be caused by the expansive formation of Ca(OH)₂ or Mg(OH)₂ from uncombined CaO or MgO in the cement.

Sulfate Resistance

Whenever ettringite forms it will create large expansions because of its low density. When a hydrated paste comes in contact with an external supply of sulfate ions, ettringite (or other AFt phases) can form from the AFm phases present in the paste (see Eq. 6). Experience has shown that a sulfate-resistant cement is obtained by lowering its C_3A content (see Table 2). This limits the amount of AFm phases from which ettringite can form. These cements have higher C_4A contents so that apparently either ettringite forms less readily from AFm phases with high F contents, or else the ettringite that does form results in less overall bulk expansions. However, cements with very high C_4AF contents will have impaired sulfate-resistance indicating that the same underlying chemistry does occur.

Summary and Conclusions

This module has attempted to show how hydration of the constituent compounds affects the performance of portland cements. A summary is presented in Table 7. The influence of the hydration products on

TABLE 7

Characteristics of Hydration of the Cement Compounds

<u>Compounds</u>	<u>Reaction Rate</u>	<u>Amount of Heat Liberated</u>	<u>Contribution to Cement</u>	
			<u>Strength</u>	<u>Heat Liberation</u>
C_3S	Moderate	Moderate	High	High
C_2S	Slow	Low	Low initially, high later	Low
$C_3A + CSH_2$	Fast	Very high	Low	Very high
$C_4AF + CSH_2$	Moderate	Moderate	Low	Moderate

durability is not considered here (apart from a brief and incomplete discussion of sulfate resistance) because it is a topic deserving of separate treatment. Further, no consideration has been given as to how the hydration products interrelate physically to develop the matrix known as hardened cement paste (i.e., the microstructure of the paste). This will be the subject of a separate module.

CHAPTER 3

STRUCTURE OF HYDRATION PRODUCTS

1. Structure of Calcium Aluminate Hydrates

(a) Ettringite ($C_6A\bar{S}_3H_{32}$)

General formulae: $C_3A \cdot 3CaY \cdot H_{32}$

$Y = SO_4^{2-}$ ettringite: only common compound

$Y = (OH)_2$ } can perhaps form in unusual circumstances,
(e.g., low temperatures). Partial substitution
in ettringite formed in cement hydration

$= CO_3^{2-}$

Several other species have been synthesized (see Table 1).
Analogues exist (see Table 2); silicate analogues, thaumasite, is found in deteriorated concrete. The structure (see Figure 1) is made up of columns of $[Ca_3Al(OH)_6 \cdot 12H_2O]^{3+}$ running the length of the pencil-shaped crystals. The columns are held together by Ca^{2+} and the anions. Channels between the columns filled with water molecules, and sulfate ions.

TABLE 1. Substituted Ettringite Species

Minerals (Dunn et al. (7))

ETTRINGITE	Ca_6Al_2	$(SO_4)_3$	$(OH)_{12} \cdot 26H_2O$
THAUMASITE	Ca_6Si_2	$(SO_4)_2(CO_3)_2$	$(OH, O)_{12} \cdot 24H_2O$
JOURAVSKITE	$Ca_6Mn^{4+}_2$	$(SO_4)_2(CO_3)_2$	$(OH)_{12} \cdot 24H_2O$
CHARLESITE	$Ca_6(Al, Si)_2$	$(SO_4)_2(B(OH)_4)(OH, O)_{12}$	$\cdot 26H_2O$
STURMANITE	$Ca_6(Fe, Al)_2$	$(SO_4)_2(B(OH)_4)(OH)_{12}$	$\cdot 26H_2O$

Reported Ettringite Structure Phases*

Oxyanion Site	
$(SeO_4)_3$	Foret et al. (8)
$(CrO_4)_3$	Foret et al. (8); Bensted and Prakash Varma (9); Buhlert (18) Pöllmann (16)
$(CO_3)_3$	Carlson and Berman (13); Struble and Brown (14); Pöllmann (16)
$(ClO_3)_6$	Jones (15)
$(BrO_3)_6$	Jones (15)
$(IO_3)_6$	Jones (15); Buhlert (18)
$(NO_3)_6$	Pöllmann et al. (16)
$(SO_3)_3$	Pöllmann et al. (16)
$(OH)_6$	Flint and Wells (17); Pöllmann et al. (16)
$(B(OH)_4)_2(OH)_4$	Pöllmann et al. (16)
$(B(OH)_4)_4(OH)_2$	Pöllmann et al. (16)

*All compositions include the nominal $Ca_6[Al(OH)_6]_2 \cdot 24 H_2O$ in the columns and variable H_2O in the channels.

TABLE 2. Analogues of Calcium Sulfoaluminates $C_6Z\bar{S}_3Hy$

$Z = Fe_2O_3$ (F)	Prepared synthetically Formed from C_4AF solution with A. $d = 9.77\text{\AA}$
$Z = Cr_2O_3$	Found in the Hatrurite deposit in Israel
$Z = Ge_2O_3$	Prepared synthetically
$Z = Ga_2O_3$	Prepared synthetically
$Z = SiO_2$ (S)	Prepared synthetically. $d = 9.50\text{\AA}$

$C_6S(\bar{S}, \bar{C}, H)H_{26}$ = thaumasite
(Product of concrete deterioration)

 $C_4Z\bar{S}Hy$

$Z = Fe_2O_3$ (F) = Prepared synthetically
Formed from C_4AF as a solid solution with A
Basal spacing = $9.0\text{\AA}$

Note: Iron, germanium and gallium analogs of C_4ZHy have also been prepared.

Dehydration. There are conflicting results concerning behavior of ettringite on drying. There is general agreement that the X-ray diffraction pattern remains unchanged on drying to below 30% rh or heating to 60°C , but there is disagreement as to whether any water of crystallization is lost during this period. Estimates as high as 15 molecules of H_2O lost have been made. Stronger drying below 10% rh has been variously reported to collapse the lattice spacings (see Table 3), or to destroy the X-ray pattern entirely. Dehydrated, amorphous ettringite can be rehydrated above 85% rh (see Figure 2).

TABLE 3. Reported Change in Longest D-Spacing of Ettringite During Dehydration

Temperature ($^\circ\text{C}$)	20	60	110	145	200
Moles of H_2O	32	20	8	6	2
d-spacing ($\text{\AA}$)	9.8	9.8	7.7	7.4	—

Figure 1. Schematic representation of ettringite crystal structure: A) structure of columns; B) packing of columns.

Figure 2. Sorption isotherm and corresponding XRD patterns on ettringite at 20°C.

(b) Hexagonal hydrates (C_4AYH_x)General formulae: $C_3A.CaY.H_x$

$Y = (OH^-)_2$	$x = 12$	C_4AH_{13}	
$Y = [Al(OH)_4^-]_2$	$x = 4$	C_2AH_8	
$Y = SO_4^{2-}$	$x = 12$	C_4ASH_{12}	monosulfoaluminate
$Y = CO_3^{2-}$	$x = 11$	C_4ACH_{12}	monocarboaluminate
$Y = (I^-)_2$	$x = 10$	$C_4A(Cl)_2H_{10}$	monochlorocaluminate (Friedel's salt)
$Y = (NO_3^-)_2, CrO_4^{2-}, (Br^-)_2,$			formed in the presence of admixtures

The crystal structure (see Figure 3) is a layer structure that can be described as a "negative clay." $Ca_2Al(OH)_6^+$ sheets are formed from Ca-OH layers in which Al replaces every third Ca atom. The sheets are held together by the anions which occupy special sites on the surface. Water molecules are also held between the layers, but much more loosely. The basal spacing gives rise to a strong (001) reflection in the X-ray diffraction pattern.

Figure 3. Schematic representation of the crystal structure of the hexagonal hydrates.

Drying can remove some of the water forming new hydrates. The interlayer (basal) spacing changes depending on the nature of the anion and the number of water molecules (see Table 4). Thus, loss of water will cause a bulk contraction of the crystal.

TABLE 4. Variation in Basal Spacing for Different Hexagonal Hydrates and Water Contents

Nature of Anion (Y)	Number of water molecules in formula (x), relative humidity (rh) and basal spacing (Å)				
OH ⁻	r.h.	100%	85%	10%	0% (120°C)
	x	18	12	10	6
	Å	10.7	$\alpha=8.2, \beta=7.9$	7.4	5.6
Al(OH) ₄ ⁻	r.h.	100%	85%		0% (>105°C)
	x	9	4		1-2
	Å	?	10.6		8.6
SO ₄ ²⁻	r.h.	100%*	85%	10%	0%
	x	14	12	10	8
	Å	9.6	9.0	8.2	8
CO ₃ ²⁻	r.h.	100%			0% (>120°C)
	x	11			6
	Å	8.2			7.2

* Below 8°C a 10.3Å monosulfoaluminate containing 16H₂O is formed. It transforms spontaneously to the 9.6Å hydrate above on warming.

In addition the possibility exists for two different anions to be present in the same crystal, i.e., solid solutions can occur. Two most important examples are:

1. SO₄²⁻/(OH)₂; forms as end product in C₃A + C $\bar{S}$ H₂ system if A/S < 1.
2. CO₃²⁻/(OH)₂; C₄AH₁₃ will react with atmospheric CO₃²⁻ to form the hemicarboaluminate (C₃A. (C $\bar{C}$)_{0.5}(CH)_{0.5}.H₁₂). One crystal form of C₄AH₁₃ contains small quantities of "essential" CO₂.
3. SO₄²⁻/H₂SiO₄²⁻; may form in close to calcium silicates particles in cement hydration.

Like ettringite, alumina can be substituted by iron (see Table 2) and analogues of gallium and chromium have been reported. When formed from C_4AF , the hexagonal hydrates are partially substituted with iron, but the A/F ratio is much higher in the hydrates than in the parent compound.

(c) C_3AH_6 Hydrogarnet (C_3AH_6)

Close packed array of Ca^{2+} and $Al(OH)_6^{3-}$ octahedra, in cubic symmetry. Crystal morphology is based on various polyhedra derived from a cube with corners removed (e.g., dodecahedra, icosahedra, etc.). The compound loses 4-1/2 molecules of water above 300°C.

The compound is isostructural with grossularite (C_3AS_3) and a solid solution occurs between these two end members. One SiO_2 tetrahedron replaces two H_2O molecules in the structure. Hydrogarnet is only a minor phase in the hydration of Portland cement, it will contain some silica as well as iron substituting for aluminum.

2. Structure of Calcium Hydroxide

Calcium hydroxide is a crystalline material with a strong XRD pattern and sharp loss of hydroxyl water at 400-500°C to form CaO. This dehydration can be used for quantitative analysis. Crystals form as stubby hexagonal prisms in which sheets of $Ca(OH)_6$ octahedra (see Figure 4) are stacked parallel to the end faces (001 plane). The distance between sheets (the basal spacing) is 4.9Å which is a strong XRD peak. Sheets are much more closely packed than in hexagonal hydrates because no ions and water molecules between them, but crystal tend to cleave under shear along the basal planes. The 4.9Å peak intensity is very sensitive to preferred orientation.

Figure 4. Crystal structure of $Ca(OH)_2$: arrangements of linked $Ca(OH)_6$ octahedra within a single layer. Parts of three rows of octahedra are shown. The lightly dotted faces of the octahedra are lying flat, with their points away from the observer.

It should be remembered that:

1. Crystals are not pure in cement paste since they occlude partially hydrating grains during growth.
2. Growth habit modified due to "poisoning" by silicate anions (see Figure 5). Small quantities of silica can be detected in CH crystals growth in cement pastes or silica solutions.

Figure 5. Morphological variations of calcium hydroxides.

3. Structure of C-S-H

C-S-H is difficult to study for the following reasons:

- (i) Poor crystallinity – amorphous
- (ii) Very small particle size – colloidal ($\sim 100\text{\AA}$ dimension)
- (iii) Large surface area
- (iv) Variable morphology
- (v) Variable composition

The molecular structure can only be deduced indirectly, and various structural models have been proposed to describe and predict properties.

- (i) Crystal Structure. X-ray diffraction patterns show only 3 broad bumps at 2.8, 3.0 and 1.8 $\text{\AA}$. Structural resemblance to C-S-H (I) and tobermorite has been suggested (see Figure 6) on basis of diffraction patterns. It is believed that this analogy is overdrawn, bumps are due only to short range order between silica tetrahedra and CaO octahedra.
- (ii) Size. Require electron microscopy to resolve C-S-H and even the high resolving power (100-20 $\text{\AA}$ depending on technique) is not sufficient to always distinguish different forms (see below).

Figure 6. Typical X-ray powder patterns for tobermorites, represented as line diagrams.

- (iii) Surface Area. Surface area depends on the way in which it is measured. As seen in Table 4 no two methods the same result. Surface area measured by any technique is dependent on factors such as w/c, temperature and time of hydration fineness, etc. The surface area measured also depends on how the sample was treated prior to measurement and the history of the paste. This is summarized in Table 5 and indicates that we are dealing with an unstable material. Storage at different relative humidities also influence rate of decrease of surface area. Maximum change occurs when C-S-H is held at 50-60% rh for prolonged periods.

TABLE 5. Surface Area of C-S-H as Measured by Different Experimental Methods

Method	Temperature of Measurements	Moisture Condition	Surface Area m ² /g
Adsorption of water	20°C	D-dry	300-400 m ² /g
Adsorption of nitrogen	-198°C	D-dry	10-100 m ² /g
Low angle X-ray scattering	20°C	Wet Dry	700-800 m ² /g 200 m ² /g
NMR relaxation spectroscopy	20°C	Wet	200 m ² /g

TABLE 6. Variation of Surface Areas in C-S-H Under Different Experimental Conditions

A. Different Drying Regimes

<u>Treatment</u>	<u>Method Used</u>	<u>Surface Area</u> (m ² g)
Normal D-drying		
First desorption	H ₂ O	286
First adsorption	H ₂ O	182
Normal D-drying	N ₂	105
Solvent replacement (methanol/pentane)		
Distillation	N ₂	210
Critical point	N ₂	205
Vacuum		
methanol	N ₂	155
ethanol		110
isopropanol		175
Saturated	LA X RS	708
Normal D-drying	LA X RS	224 → 707*
Oven-drying at 105°C	LA X RS	180 → 651*

B. Different Pastes Treatments Before Drying

Saturated	LA X RS	708
Heated in saturated condition at 105°C	LA X RS	399
Saturated	N ₂	70
Held at RT, 200 days	N ₂	30
Held at 45°C, 200 days	N ₂	20
Held at 75°C, 200 days	N ₂	10

* Value on Resaturation.

- (iv) Variable Morphology. Two distinct morphologies have been observed by both SEM and TEM.

	<u>SEM</u>	<u>TEM</u>	<u>Morphological Analog</u>
A	Aciculae. Mostly flattened and pointed, but some rod-shaped	Fiber bundles and rolled sheets	C-S-H (II). Cigar-shaped fiber-bundles (tactoids)
B	Unresolved material (foils or spherical)?	Crumpled foils	C-S-H (I) Crumpled foils

Diamond has suggested for morphological types of C-S-H based on SEM observations.

Outer C-S-H	Type I	Aciculae (needles)
	Type II	Lace-like, honeycombed or reticulated forms in presence of CaCl_2
Underlying C-S-H	Type III	Layered material? Unresolved
	Type IV	Spherical particles? Unresolved

Different morphological descriptions are obtained by TEM. The use of special "wet cells" or, more recently the environmental SEM (ESEM), has shown that the formation of aciculae is an artifact of drying. Jennings and Pratt proposed an alternate morphological classification.

- (v) Variable Composition. Composition of C-S-H written in the form C_xSH_y ; thus characterized by C/S ratio = x and H/S ratio = y. Composition has to be determined indirectly as follows:

1. Determine unhydrated silicate and calcium hydroxide quantitatively.
2. Determine bound water in paste quantitatively.
3. Determine C/S and H/S ratio by differences.

$$\text{e.g., } C/S = \frac{C_o - C_u - C_{CH}}{S_o - S_u} \quad \text{and} \quad H/S = \frac{H_b - H_{CH}}{S_o - S_u}$$

where C_o, S_o = initial quantities of C, S

C_u, S_u = quantities of C, S attributed to the unhydrated silicate

C_{CH}, H_{CH} = quantities of C, H attributed to calcium hydroxide

H_b = quantity of water fixed by hydration (bound water).

Problems arise in determining these quantities. Unhydrated silicates can be determined by QXDA; calcium hydroxide can be determined either by QXDA, thermal analysis or chemical extraction methods, but these don't give the same results.

Thermal analysis	15.5 wt%
QXDA	12.0 wt%
Extraction Methods	12.7-19.9 wt%

It has been suggested that thermal analysis includes "amorphous CH" which is not detected by QXDA, chemical extraction can remove line from the C-S-H. Recently C/S ratios have been determined directly using X-ray analysis with SEM or TEM. A comparison of different methods is given in Table 7.

TABLE 7. Typical C/S Ratios According to Different Experimental Measurements

<u>Method of Determining CH</u>	<u>Scale</u>	<u>Typical C/S Ratio</u>	<u>Remarks</u>
Chemical Extraction	cm ³	1.4 – 1.6	Over range of hydration times
Thermogravimetry	cm ³	1.6 – 1.9	
Microanalysis (SEM)	μm ³	1.7 – 2.5 Mean 1.9	Mature paste
Microanalysis (TEM)	nm ³	1.3 – 1.8 Mean 1.6	Range of hydration times
Microprobe Analysis		~ 1.6	Low accelerating voltage; wavelength dispersion detectors.
Microprobe Analytical TEM		~ 1.6	Dispersed particles; range 1.0-3.0
SEM-EDS Analysis		~ 1.6	Polished surfaces; allowance for beam spread

C/S varies with time of hydration, temperature of hydration and to some extent on fineness and w/c. During course of hydration C/S changes until a stable value is reached (see Figure 7). The changes are different with C₃S and β-C₂S, but the composition is prone to high errors at early hydration and must be viewed with caution. Large discrepancies are observed in C₃S hydration. C/S will also vary when reactive silica pozzolans are added.

Figure 7. Variation of C/S with time of hydration.

H/S Ratio

Bound water determined by heating a dried paste. But water is lost continuously from C-S-H not in abrupt steps as in other hydrates (see Figure 8). This is because water is held in all states in C-S-H: water held

Figure 8. Comparison of water loss from C-S-H and other Hydrated Products.

in small pores, physically adsorbed water, structural water, and hydroxyl water. The H/S ratio will depend on the extent to which C-S-H is dried. Four reference drying points have been suggested (see Table 8).

TABLE 8. Various Drying Conditions of C-S-H

Drying Condition	Water Vapor Pressure	Water Held	Suggested Composition
> 90% rh		Adsorbed, S and H	$C_{1.65}SH_{4.0}$
11% rh	1.7 torr	Structural & hydroxyl	$C_{1.65}SH_4$
P-dry	8×10^{-3} torr	Hydroxyl	$C_{1.65}SH_{1.15}$
D-dry	5×10^{-4} torr	Hydroxyl	$C_{1.65}SH_{1.05}$
Oven Dry	105°C	Hydroxyl	$C_{1.65}SH_{1.05}$

4. Molecular Structure of C-S-H

(a) Tobermorite

Figure 6 shows the X-ray diffraction pattern for 11.4Å tobermorite which for many years has been considered to be the structural model for C-S-H. The crystal structure is shown in Figure 9. Infinite silicate chains are considered on either side of a distorted calcium hydroxide sheet, such that silica tetrahedra share edges with Ca-O octohedra, to form repeating layers. All oxygens in the sheet are shared, but only two out of three silica tetrahedra; the third silica share edges with the two condensed with the sheet. This arrangement of the silicate chain is very similar in calcium silicates and is called a dreierkelten unit. The dreierkelten chains form ribs along the sheet. When the sheets are stacked the ribs match up forming channels, much like corrugated cardboards. Calcium ions in the channels provide electro-neutrality and water molecules are also present.

Formula:

↑↓

↑

(b) Part of the Ca—O sheet from a single layer of 11.3 Å tobermorite, with a single, attached dreierkette (idealized); based on the results of Megaw and Kelsey [85]. Parts of three rows of CaO_6 polyhedra within the sheet are shown.

(a) The crystal structure of 11.3 Å tobermorite (idealized) based on the results of Megaw and Kelsey [85]. Left: projection on (010). Right: projection on (100). Small, full circles denote Ca^{2+} ions. Thick lines outline SiO_4 tetrahedra. Thin lines represent Ca—O bonds. The exact positions of the interlayer water molecules and Ca^{2+} ions are unknown. (From Taylor [70].)

Figure 9. Representation of crystal structure of tobermorite: (a) projecture along the b and a axes; (b) schematic of arrangements of polyhedra.

(b) Jennite

Formule shows a C/S ratio of 0.83, which is nowhere close to 1.65 for C-S-M. Jennite is a related material where alternate dreierketten chains are omitted. The formula then becomes:

Even jennite has a C/S ratio of only 1.5.

(c) C-S-H

It is now generally accepted that C-S-H can be regarded as silicate polymer and thus formation of C-S-H involves the polymerization of silicate tetrahedra present in the original calcium silicates. Three methods of analysis of the degree of silicate polymerization have been developed:

1. Rate of complexing with molybdic acid (followed spectrophotometrically).
2. Derivatization with trimethylsilyl groups (separated chromatographically).
3. ^{29}Si NMR spectroscopy.

The sequence of polymerization seem to be:

Orthosilicate is attributed wholly to anhydrous silicates, while the initial formation of C-S-H seems to involve mostly disilicate. The arrangement of dimers are such that pentamers will form and ultimately longer chains (the polysilicates) (see Figure 10). At later ages, at higher temperatures the polysilicate will increase at the expense of the dimer, while penta- and octamers act as intermediates. The amounts of trisilicate and tetrasilicate are always very small and are probably due to side reactions due to derivatization.

Figure 10. Columns of linked CaO_6 octahedra sharing oxygen atoms with (A) Si_2O_7 groups, (B) Si_5O_{16} groups and (C) dreierketten. In the latter, the tetrahedra that occur in pairs related by mirror planes are described in the text as 'paired', and those not so related as 'bridging'; the repeat distance of the chain (3 tetrahedra) is 0.73 nm.

4. Models of C-S-H

(a)

(b)

Fig. 11. (a) Powers-Brunauer model of C-S-H
(b) Feldman-Sereda model of C-S-H

Fig. 12 Simplified pore model of C-S-H (after Kondo, et al. - Tokyo model).

Fig.13 Munich model of C-S-H proposed by Wittman.

Fig.14 Behavior of C-S-H on drying and rewetting

Figure 5. C/S ratio determined by chemical analysis for C-S-H samples formed from solutions with indicated Ca concentrations. C-S-H forms with a continuous range of compositions.

CHAPTER 4

MICROSTRUCTURE OF CONCRETE

1. Development of Paste Microstructure

1.1 Summary of Hydration

Figures 1 and 2 show schematically the heat evolution and microstructural evolution of Portland cement. These representations emphasize the dominance of C_3S in hydration and thus the progress of hydration can be represented by the five stages used to describe the hydration of C_3S . The hydration of C_3A is regarded as a superimposed set of reactions.

Stage I (0-15 min)	Initial rapid hydration of C_3A + gypsum to form ettringite. Rapid reaction of C_3S . Rapid release of soluble alkalis in high alkali cements.
Stage II (15 min - 2 hrs)	Dormant period, paste remains fluid. Ettringite continues to form slowly, but very little hydration of C_3S .
Stage III (2-8 hrs)	End of the dormant period corresponds approximately to initial set. Hydration of C_3S is rapid again. Crystallization and rapid growth of CH and C-S-H. Ettringite continues to form slowly and may start to transform to monosulfoaluminate, depending on the A/S ratio. Final set occurs 1-2 hrs after the start of Stage III.
Stage IV (8-24 hrs)	Build-up of C-S-H around C_3S again begins the transformation to diffusion-controlled kinetics, with changing diffusion coefficient. Conversion of ettringite to monosulfoaluminate is completed.
Stage V (> 24 hrs)	"Steady-state," diffusion controlled kinetics. Continued decrease in paste porosity and increase in strength.

The time at which ettringite (AFt) converts to monosulfate (AFm) (the "shoulder" peak in Figure 1) varies considerably from one cement to another and can often occur in Stage III when C_3A contents are low. Some investigators have suggested that an unresolved peak occurs late in Stage VI or early in Stage V corresponding to the ferrite phase converting from AFt to AFm.

Figure 1. Schematic representation of cement hydration.

Figure 2. Schematic picture of the setting and hardening process.

(a)

(b)

Figure 3(a). Partially hydrated C_3S particle showing close contact between the C-S-H coating (B) and the anhydrous core (A). (The crack is due to drying).
 (b) Partially hydrated cement particle with separated shell of hydration. Rods and plates of AFt and AFm are seen between the shell and the core.

1.2 Role of C_3A

While early work on microstructural development confirms that the structure is largely controlled by C_3S hydration, C_3A hydration is not a simple superposition. In C_3S pastes C-S-H forms a continuous coating (or shell) around the unreacted particle (Figure 3a). However, in cement pastes a gap is often observed between the shell and the core (Figure 3b). These are called "Hadley grains" (after the graduate student who first observed them) or hollow shell hydration. The formation of the Hadley grains is shown schematically in Figure 4. It is thought that deposition of ettringite crystals in the early stages of hydration forms a mesh or template on which C-S-H forms at a short distance from the reacting surface. During rapid hydration in Stage III and IV the C-S-H shell grows outward. Later the shell grows inward and the gap may eventually close up. If the cement particles are too small ($< 3 \mu m$) the gap does not close and small holes are left in the microstructure. With particles ($> 10 \mu m$) unreacted cement remains after the gap is closed, and later C-S-H now forms in situ.

1.3 Setting of Cement Paste

Setting is a transition from liquid-like behavior (fresh paste) to a rigid solid mass, which takes place gradually. It is traditionally measured by resistance to penetration (Figure 5) which is the basis of the ASTM tests. Initial set represents the beginning of setting and final set the end of the process, but these are arbitrary definitions not based on material properties.

The onset of Stage III in the calorimetry curve can be taken as an approximate measure of initial set (Figure 6). Recently the change in yield stress, which is one of the rheological parameters which describes the flow behavior of fresh cement paste, has been shown to correspond closely with the calorimetric data (Figure 6A).

Figure 4. Summary of microstructural development for a grain of cement.

(a) Unhydrated section of polymineralic grain (scale of interstitial phase is slightly exaggerated). (b) -10 min. Some C_3A (and/or Fss) reacts with calcium sulfate in solution. Amorphous, aluminate-rich gel forms on the surface and short AFt rods nucleate at edge of gell and in solution. (c) -10 h. Reaction of C_3S to produce "outer" product $C-S-H$ on AFt rod network leaving $\sim 1 \mu m$ between grain surface and hydrated shell. (d) -18 h. Secondary hydration of C_3A (and/or Fss) producing long rods of AFt . $C-S-H$ inner product starts to form on inside of shell from continuing hydration of C_3S . (e) 1-3 days. C_3A reacts with any AFt inside shell forming hexagonal plates of AFm . Continuing formation of "inner" product reduces separation of anhydrous grain and hydrated shell. (f) -14 days. Sufficient "inner" $C-S-H$ has formed to fill in the space between grain and shell. The "outer" $C-S-H$ has become more fibrous. (g) -years. The remaining anhydrous material reacts by a slow solid state mechanism, to form additional "inner" product $C-S-H$. The ferrite phase appears to remain unreacted.

Figure 5. Change of penetration resistance with time.

Figure 6. Heat development curves (left) and microstructural development (right) of normally setting cement (A) and abnormal setting (B).

Normal setting is controlled by C_3S hydration (Figure 6a), but problems of early stiffening can be associated with abnormal reactions involving C_3A and sulfates. False set is a phenomena of early stiffening that can be removed by prolonged mixing or remixing. It is analogous to the stiffening of plasters. Indeed the hydration of hemihydrate (which is formed by over-heating in the finish mills) is one cause of this:

Another involves the presence of potassium sulfate in high alkali cements:

Both gypsum and syngenite form needle-like crystals similar to ettringite, in morphology which create felt-like structures. Ettringite generally does not cause flash set, but occasionally recrystallization of ettringite (Figure 6b), or delayed formation of ettringite will do so.

Figure 6A. Variation of yield stress of fresh cement paste ($w/c = 0.45$) with hydration time. The sharp increase at about 135 min. indicates initial set.

2. Microstructure of Concrete

2.1 Microstructural Features of Concrete

As shown in Tables 1 and 2, concrete can be probed at several levels. Micrographs of concrete at various levels are shown in Figure 7. The microstructure of hardened cement paste and the cement aggregate interface is discussed in more detail.

Figure 7. Microstructure of concrete (180 days): (a) nominal magnification (NM) $\times$ 25. A large particle of granite aggregate and several small particles of sand can be seen in a matrix of cement paste. (b) NM $\times$ 100; the distribution of anhydrous cement in the paste can be seen more clearly. There is very little anhydrous material in the narrow ribbon of paste between two sand grains to the right of the micrograph. (c) NM $\times$ 400; distribution of the calcium hydroxide and large pores in the cement paste can now be seen. (d) NM $\times$ 1600 microstructure between two partially reacted cement grains. (e) NM $\times$ 6000 detailed microstructure of hydration products.

TABLE 1.

STRUCTURAL FEATURES OF CONCRETE

Macrostructure	Coarse aggregate + Mortar <ul style="list-style-type: none"> • Coarse aggregate packing • Segregation • Entrapped air voids
Mesostructure	Fine aggregate + Paste <ul style="list-style-type: none"> • Fine aggregate packing • Entrained air void system • Interfacial zones • Local inhomogeneities • Fracture planes
Microstructure	Hardened cement paste <ul style="list-style-type: none"> • Solid matrix • Pore structure
Nanostructure	Hydration products <ul style="list-style-type: none"> • Silicate structure of C-S-H • Morphology of CH

TABLE 2.

STRUCTURE LEVELS OF CONCRETE

Macrostructure	Visual observation <ul style="list-style-type: none"> • Features > 1 mm in size
Mesostructure	Optical microscopy <ul style="list-style-type: none"> • Features > 10 μm in size • Up to 500x magnification
Microstructure	Electron microscopy <ul style="list-style-type: none"> • Features > 10 nm in size • Up to 10,000x magnification
Nanostructure	High Resolution TEM <ul style="list-style-type: none"> • Features < 10nm in size • Up to 500,000x magnification

2.1 Hardened Cement Paste

Figures 8 and 9 show examples of hardened cement pastes at an early age. Figure 8 clearly shows the development of the capillary pore structure, calcium hydroxide crystals and the grains of C_3S with surrounding C-S-H coatings. Figure 9 is Portland cement paste after only one day hydration and shows ettringite needles growing in the pore space. The major constituents of a partially hydrated paste are:

1. C-S-H
2. Capillary pores
3. Calcium hydroxide
4. Calcium sulfoaluminate hydrates
5. Unhydrated cement residues

The relative proportions of the solid hydration products are given in Table 3.

TABLE 3. Major Components of Hardened Cement Paste (hcp) (w.c. = 0.50)

Component	Approx. Vol. Fraction (%)	Relevance to Paste Performance
C-S-H	55	Colloidal microporous material. Forms the continuous matrix in hcp.
Calcium Hydroxide (CH)	15	Forms relatively large crystals. Solubility ~ 1g/liter.
Capillary Porosity	15	Remnants of water filled space. A spectrum of irregular pores ranging in diameter from > 100 nm to < 5 nm.
Calcium Sulfoaluminate Hydrates	10	A relatively unimportant component unless sulfate ions are present.
Unhydrated Residues	5	Remnants of original cement that have not reacted. Ordinarily a small fraction that can be neglected.

Figure 8. Scanning electron micrograph of a tricalcium silicate paste hydrated for 10 days showing calcium hydroxide crystals (C) growing in the pore space. Anhydrous cores (A) are at the center of the hydrating grains.

Figure 9. Scanning electron micrograph of Portland cement paste hydrated for 1 day.

These relative proportions in Table 3 have been estimated from hydration chemistry but can be determined quantitatively by SEM-EDS. The mature paste can be examined by scanning electron microscopy (see Figure 10), either as a fracture surface (Figure 10b), or as a polished surface by secondary electron imaging (Figure 10a), or by backscattered electron imaging (Figure 10c).

2.2 Cement-Paste-Aggregate Interface

The structure of cement paste adjacent to an embedded material (aggregate, rebar or fiber) is modified by the embedment. Wall effects create poor packing of cement grains, resulting in a high porosity adjacent to the embedded feature. Figures 11 and 12 show such features. The modified volume extends 20-50 μm from the surface of the embedment and is called the transition zone. It consists of three regions that can be seen microscopically:

1. The duplex layer, 1-2 μm thick.
2. A calcium hydroxide layer.
3. A porous layer.

Sometimes one region is not clearly seen. Quantitative microscopic analysis (Figure 13) shows the high local porosity. This is accompanied by an absence of residual unhydrated in the same region. It is thus expected that the transition zone will be a point of weakness, although with time the porosity will be reduced, as hydration proceeds.

2.3 Pore Structure

The pore structure is a very important characteristic of cement paste. Pores are a continuum of sizes with very irregular geometry (see Figure 8). The problem is measuring total porosity and pore size distributions various distinctions have been proposed for dividing porosity into different classifications. The traditional means of measuring pore size distribution are:

Mercury intrusion porosimetry (MIP)	Pores $> 10 \mu\text{m} - 0.005 \mu\text{m}$ (50Å)
Water vapor adsorption (H_2O)	Pores $< 0.03 \mu\text{m}$ (300Å)
Nitrogen adsorption (N_2O)	Pores $< 0.03 \mu\text{m}$ (300Å)

These methods suffer from approximations which are principally due to the following assumptions:

- (i) a regular pore geometry;
- (ii) all pores are interconnected; and
- (iii) pore size distributions do not change on drying.

Examples of MIP curves are shown in Figures 14 and 15.

Figure 10. (a) Cut and polished section of a mature tricalcium silicate paste showing residual anhydrous cores (A) embedded in hydrated matrix. Dark grey regions (G) are C-S-H, light grey areas (H) are calcium hydroxide. (Calcium sulfoaluminates are not present). (b) Fractured surface of a mature tricalcium silicate paste showing anhydrous cores (A) and calcium hydroxide (H) embedded in a matrix of C-S-H. Note fracture passes indiscriminately through all these components. (c) Back-scattered electron image of cut and polished section of mature Portland cement paste.

Figure 11a. Cement paste – aggregate interface in Portland cement concrete: porous interface and crack along aggregate, G = aggregates, C = cement.

Figure 11b. Cement paste – aggregate interface in Portland cement concrete, P = oriented crystals of portlandite Ca(OH)_2 , G = aggregate.

Figure 12. Fiber-paste transition zone; (a) schematic representation
 (b) SEM micrograph showing cross-section of zone
 (c) detail of CH layer.

(a)

(b)

Figure 13. Analysis of interfacial zone: (a) residual unhydrated cement; (b) capillary porosity.

Figure 14. Intrusion curves for a series of hydrating portland cement pastes.

Figure 15. Effect of curing temperature on intrusion curves of C₃S pastes.

Several different ways have been used to differentiate between pores. The classical and simplest distinction is that proposed by Powers and co-workers in the 1950's:

- Capillary pores – remnants of water-filled space above 100Å diameter, which depend on w/c.
- Gel pores – pores associated with C-S-H; i.e., they are an intrinsic part of the material. These pores have diameters less than 100Å and are independent of w/c.

Capillary pores are associated with formation of menisci and the associated capillarity effects: i.e., r.h. dependence on water loss and development of capillary stresses. Gel pores, actually including some small isolated capillary pores, are predominantly pores in which capillarity effects cannot occur since water menisci cannot form. These are often called micropores, and have restricted openings. To these should be added interfacial pores which are generally greater than 0.1 μm (1000Å) (see Figure 16).

The IUPAC classification for porous materials can also be applied to hardened cement paste.

Macropores:	Large capillaries	> 500Å diameter
Mesopores:	Small capillaries	25-500Å diameter
Micropores:		< 25Å diameter

Comparisons of the two classifications are shown in Figure 17. Interfacial pores represent the larger macropores, while intrinsic C-S-H porosity is in the form of micropores. These two systems are fundamentally similar, when it is remembered that experimental measurements really measure pore openings. Thus isolated capillary pores can only be accessed through micropores.

Figure 16. Effect of interfacial zone on pore structure of paste.

POWERS

GEL		CAPILLARY		AIR VOIDS	
2.5		50		10,000	
10					
PORE DIA (nm)					
IUPAC					
MICRO		MESO		MACRO	
				AIR VOIDS	

Figure 17. Comparison of pore size distributions.

3. Volume Relationships in Hydrated Cement Pastes

When predicting properties of cement pastes it is often desirable to be able to estimate the relative proportions of the individual components. Theoretically this can be done using the stoichiometric chemical equations describing the hydration process, e.g.:

If one knows the densities of each component then it is possible to calculate the volume changes during hydration and the proportions by volume. Densities for the major components are given in Table 4.

TABLE 4. Physical Data Determining Volume Changes That Occur During Hydration

Initial Cement Compounds			Hydration Products		
Compound	Specific Gravity	Molar Volume	Compound	Specific Gravity	Molar Volume
		(GMW*/ ρ) 10^{-6}m^3			(GMW#/ ρ) 10^{-6}m^3
C ₃ S	~ 3.5	~ 72.4	C-S-H	*	*
C ₂ S	3.28	52.4	CH	2.24	33.2
C ₃ A	3.03	89.1	C ₆ AS ₃ H ₃₂	~ 1.75	715
C ₄ AF	~ 3.73	~ 128.0	C ₄ ASH ₁₂	1.95	313
M	3.58	11.0	MH	2.37	24.3
CSH ₂	2.32	74.2	C ₄ AH ₁₃	~ 2.02	~ 260
CSH _{1/2}	2.74	52.9	C ₂ AH ₈	1.95	165
Portland Cement	3.15	-	C ₃ AH ₆	2.52	150

* Value depends on the water content of C-S-H which is related to how much "gel porosity" is included in the structure.

GMW = gram molecular weight, ρ = density in g/m³.

There are several problems with this approach, the major ones being:

1. The composition and density of C-S-H depends on the degree of drying, e.g.;

D-dry	$C_{1.65}SH_{1.15}$	$\rho = 2.6 \text{ g/cm}^3$
11% rh-dry	$C_{1.65}SH_2$	$\rho = 2.3 \text{ g/cm}^3$
Saturated	$C_{1.65}SH_4$	$\rho = \sim 1.9 \text{ g/cm}^3$

It is not always known how much additional water is associated with C-S-H, or the most appropriate density.

2. Cement paste is a multicomponent system like the parent material. It is difficult, if not impossible, to accurately determine how much each cement compound has hydrated at any particular time.

Power's Equations

Therefore, the best approach to the problem is an empirical one in which average values for hydration and paste properties are obtained by experiment. This was done 30-40 years ago by T. C. Powers and his co-workers at P.C.A. Using data obtained from water vapor adsorption experiments, they were able to deduce a series of equations that can be used to estimate the volume proportions in hardened cement pastes.

During hydration of cement definite quantities of gel are formed as definite amounts of water are consumed. We can calculate these quantities in terms of degree of hydration (m) and w/c using relationships derived from Powers in his adsorption studies. Table 5 defines the various terms used, and Figure 16 shows the results of calculations using the following equation.

TABLE 5. Glossary of Terms used in Power's Equations

W_0 = initial amount of water used.
W_0/C = initial water to cement ratio.
W_n = non-evaporable water content (1000°C).
W_g = evaporable water (105°C).
v_c = specific volume of cement.
v_w = specific volume of water.
P_c = capillary pore volume.
P_g = gel pore volume.
P_u = empty pore volume.
m = degree of hydration (maturity).
V_0 = critical volume of paste.
V_g = volume of cement gel.
V_β = volume of solids.

Assume no water is lost or gained during hydration. $w/c = 0.50$

$w/c = 0.42$

Figure 18. Volumes computed by Power's equations.

1. Non-evaporable water content (W_n)

$$\begin{aligned} W_n &\propto m \\ &= 0.24 \text{ mC grams} \end{aligned}$$

2. Water associated with the gel (W_g)

$$\begin{aligned} W_g &\propto \text{the amount of gel} \\ &\propto m \\ &= 0.18 \text{ mC grams} \end{aligned}$$

3. Volume of solids (V_β)

$$\begin{aligned} V_\beta &= \text{volume of (cement + gel water + non-evaporable water)} \\ &= CV_c + W_n V_n + W_g V_w \\ &= CV_c + 0.18 \text{ mC} + 0.18 \text{ mC}^* \\ &= CV_c (1 + 1.13 \text{ m}) \end{aligned}$$

[* Note: Equal volumes of W_g and W_n]

4. Original volume of cement and hydrate water (V_o)

$$\begin{aligned} V_o &= \text{volume of cement + initial volume of free water combined as} \\ &\quad \text{gel water and non-evaporable water} \\ &= Cv_c + (W_n + W_g) v_w \\ &= Cv_c + 0.24 \text{ mC} + 0.18 \text{ mC} \\ &= Cv_c (1 + 1.31 \text{ m}) \\ V_o - V_\beta &= 0.06 \text{ mC} \end{aligned}$$

5. Volume of gel (V_g)

$$\begin{aligned} V_g &= \text{volume of (cement reacted + non-evaporable water + gel water)} \\ &= mCv_c + 0.24 \text{ mC}v_w + 0.18 \text{ mC}v_w \\ &= mCv_c + 0.18 \text{ mC} + 0.18 \text{ mC} \\ &= 2.13 \text{ mC}v_c \\ &= 0.68 \text{ mC} \end{aligned}$$

When $m = 1.0$, $V_g = V_\beta$. At all other times $V_g < V_\beta$

6. Gel pore volume (P_g)

$$\begin{aligned} P_g &= \frac{\text{volume of gel water}}{\text{volume of gel}} \\ &= \frac{0.18 \text{ mC}}{0.68 \text{ mC}} \\ &= 26.5\% \end{aligned}$$

7. Capillary pore volume (P_c)

$$\begin{aligned}
 P_c &= [\text{original volume of cement + mix water}] - [\text{volume of} \\
 &\quad \text{unhydrated cement + gel}] \\
 &= [cV_c + W_oV_w] - [(1-m) cV_c + 2.13 mCV_c] \\
 &= c \left(\frac{W_o}{c} - 0.36 m \right)
 \end{aligned}$$

8. Limiting water; cement ratios

a) space limitations

$$P_c = c \left(\frac{W_o}{c} - 0.36 m \right)$$

$$\text{When } P_c \geq 0 \text{ at } m = 1$$

$$\frac{W_o}{c} \geq 0.36$$

b) water limitations

$$\begin{aligned}
 W_{\min} &= W_n + W_g \\
 &= 0.24 mC + 0.18 mC \\
 &= 0.42 mC
 \end{aligned}$$

$$\text{Therefore } \frac{W_{\min}}{c} \geq 0.42 \text{ for complete hydration}$$

9. Empty pore volume (P_u)

$$\begin{aligned}
 P_u &= P_c - \text{volume of water in capillaries} \\
 &= (W_o - 0.36 mC) - (W_o - 0.42 mC) \\
 &= 0.06 mC
 \end{aligned}$$

4. Microstructure – Property Relationships

4.1 Strength-Porosity Relationships

A relationship between the w/c ratio and strength was first recognized by Feret in the late 19th Century (Eq. 1). Later Abrams in work at the University of Illinois developed a more efficient relationship (Eq. 2)

Feret's Law:

$$\sigma_c = A \left[\frac{V_c}{V_c + V_w + V_a} \right]^2 \quad (1)$$

Abram's Law:

$$\sigma_c = \frac{A}{B^{1.5} (w/c)} \quad (2)$$

where

$$A \approx 100 \text{ MPa}, B \approx 4$$

It was not until the 1940's that Powers and Brownyard specifically showed that w/c was actually controlling the capillary porosity. Powers' expression (Eq. 3) includes the degree of hydration in the gel-space ratio (X), thereby incorporating the effect of curing. Powers' equation is a special case of the more general Balshin equation (Eq. 4), which has been used in the ceramics field, since $X = 1-P$, where P is capillary constant

Powers' Eq.:

$$\sigma_c = \sigma_o X^3 \quad (3)$$

Balshin:

$$\sigma = \sigma_o (1-P)^n \quad (4)$$

The intrinsic strength at zero porosity (σ_o) is equal to 100 MPa, which is similar to that of Abram's Law given by the constant A. Indeed Abrams and Powers' expressions give similar predictions of strength versus capillary porosity. This is a very low value for intrinsic strength and reflects the inherent weakness of the microporous C-S-H, as well as the weakness of the interfacial bond. If total porosity (experimentally determined by loss of evaporable water) is used instead of capillary porosity than σ_o is still relatively low and still reflects the lower binding energy of the surface forces within C-S-H.

Cement pastes also obey the Ryshkevitch equation (Eq. 5) very well. This expression is in common use by ceramists. Another strength-porosity expression is the Schiller equation (Eq. 6)

Ryshkevitch:

$$\sigma = \sigma_0 \exp(-BP) \quad (5a)$$

or

$$P = B \ln \frac{\sigma_0}{\sigma} \quad (5b)$$

Schiller:

$$\sigma = \sigma_0 \left[1 - \left(\frac{P}{P_{\text{crit}}} \right)^c \right] \quad (6a)$$

$$\rightarrow \sigma = D \ln \frac{P_{\text{crit}}}{P} \quad \text{when } P \approx P_{\text{crit}} \quad (6b)$$

$$P = P_0 \exp(-D\sigma) \quad (6c)$$

(In Eqs. 5 and 6 B and D are empirical constants). The distinction of the Schiller equation is that it recognizes a critical value of porosity (P_{crit}) above which there is no measurable strength. However, Figure 19 shows that in the region of most typical paste properties all equations give very similar predictions.

When very high strength pastes ($w/c < 0.25$) are made by various techniques, it is found (Figure 20) that such samples have a different Schiller curve than that of conventional pastes (although P_{crit} is about the same). An intrinsic strength of 700 MPa (100,000 psi) or greater is found. In these materials the higher strength is attributed to the high proportion of crystalline material in the matrix as the result of limited hydration. Unhydrated cement residues now form a major part of the matrix and contribute to strength. When the C-S-H is made more crystalline by high temperature curing the strengths further increase.

This has been shown in other studies using the Ryshkevitch equation for analysis. When cement pastes are autoclaved to produce a crystalline tobermorite matrix much higher intrinsic strengths are obtained (Figure 21). However, the curves crossover and at high porosities a crystalline matrix is weaker than one based on amorphous C-S-H. Such pastes have much coarser porosity, indicating the importance of pore size as well as total porosity. C-S-H is a superior space filler, but inherently weak, whereas tobermorite is denser, but inherently strong. Thus a mixture of crystalline and amorphous component should provide superior properties. This is illustrated in Figure 22 in a schematic representation of optimal matrix composition.

Figure 19. Strength vs. porosity for hardened cement pastes.

Figure 20. Schiller plots for hardened cement pastes.

Figure 21. Ryshkevitch plots for hardened cement pastes.
 AB, pastes hydrated at ordinary temperatures;
 CD, autoclaved pastes; EF cement-fly ash pastes
 autoclaved.

Figure 22. Strength isobars for paste matrix of varying crystallinity.

The relationship between pore size and matrix strength is shown in Figure 23. A variety of crystalline matrices were prepared with different crystalline sizes and hence mean pore sizes. System I is based on Tobermorite; II on a semi-crystalline form of C-S-H, III a mixture of C-S-H and gehlenite hydrate (C_2ASH_8), IV a mixture of C_2ASH_8 and hydrogarnet (C_3AH_6), and V based on C_3AH_6 alone. The pore size distribution in Figure 23b is determined by mercury intrusion porosimetry. A clear relationship between mean pore size and strength is shown in Figure 23c.

It was mentioned earlier that the interfacial bond will affect strength, due to the weak bond caused by localized porosity. Figure 24 shows a theoretical analysis based on simple composite models. It shows that strength is increased by only about 30% if a perfect bond is achieved. This comparatively small effect is due to the way aggregate filler controls crack formation and propagation, which is beyond the scope of this course.

2.2 Transport Properties

The capillary pores provide a continuous network through which water and dissolved species may percolate over time. Flow of ratio is governed by D'Arcy's Law:

$$\frac{dv}{dt} = K_p \frac{\Delta h \cdot A}{l} \quad (7)$$

where $\frac{dv}{dt}$ is the flow of water, Δh is the pressure load, l is the thickness, A is the area, and K_p is the permeability coefficient (m/s). It has been shown that K_p can be related to mean pore size (Figure 25), as defined by the maximum slope in the MIP curve (Figure 26). This quantity can be considered as the mean, minimum radius (r_∞) of the connected pore system.

The relationship between r_∞ and K_p is given by Eq. 8:

$$K_p = 1.7 r_\infty^{3.3} \times 10^{-24} \text{ m/s} \quad (8)$$

where r_∞ is given in nm. The equation suggests that for micropores ($r_\infty < 1.25$ nm) the value of $K_p \approx 10^{-20}$ m/s. This would represent the intrinsic permeability of C-S-H.

More recently impedance spectroscopy has been used to determine the electrical conductivity (σ) of cement paste. The conductivity is controlled by both the physical resistance of the tortuous pore system and the conductivity of the pore fluid. The latter (σ_0) is experimentally measured on expressed pore solution (or simulated pore solution). The relative conductivity (σ/σ_0) is a measure of the tortuosity of the capillary pore system, and can be related to relative curve diffusivity by the Einstein-Stokes equation (see also Figure 27a).

$$\frac{\sigma}{\sigma_0} = \frac{D}{D_0} \quad (9)$$

(a)

(b)

(c)

Figure 23. Effect of different pore size on strength.

Figure 24. Effect of bond on strength of concrete or mortar.

Figure 25. Permeability coefficient vs. pore radius.

The relationship to water permeability is given by the Katz-Thompson equation (see also Figure 27b):

$$K_p = k r_{\infty}^2 \left(\frac{\sigma}{\sigma_0} \right) \quad (10)$$

It has also been shown recently both experimentally and by computer simulation that the interfacial transition zones are percolating above a certain volume fraction of added sand. This is observed experimentally by mercury intrusion at relatively low pressures (corresponding to effective pore radii > 0.1 - $0.2 \mu\text{m}$). Thus the volume of intrusion can be related to the intruded volume of macropores

$$K_p = A \epsilon_{\text{macro}}^b \quad (11)$$

K_p can also be related to total porosity in a similar relationship to Eq. 1 even if the pore structure is not known since the value of r_{∞} decrease as total porosity decreases.

2.3 Drying Shrinkage

Hardened cement pastes undergo 1-2%, volumetric shrinkage on drying due to moisture loss from the microstructure. Water loss occurs from both capillary pores and the micropores of C-S-H, and introduces internal stresses which cause the observed strain. It should be noted that drying is very slow since the rate-controlling step is molecular diffusion of water in the micropores.

Plots of shrinkage versus relative humidity (r.h.) and weight loss are shown in Figures 28 and 29 respectively. As the r.h. is lowered capillary stress is induced by loss of water from pores (the Young-LaPlace equation)

$$\sigma_{\text{cap}} = \frac{2\gamma}{r} \quad (12)$$

The development of capillary stress with r.h. is shown in Table 6. This stress squeezes water from the micropores. In addition the thickness of adsorbed layers spontaneously decrease to maintain equilibrium with the changing r.h. Thus the micropores empty as well, allowing the C-S-H gel structure to collapse. This is referred to as the "disjoining effect". The two effects are synergistic. The net effect is that the C-S-H behaves as a solid with a high compressibility under the hydrostatic compressive stress leading to bulk contraction. Once the C-S-H gel structure is altered, changes in local bonding prevent complete regeneration of the original structure. Hence only partial swelling is observed. The irreversible shrinkage is observed primarily on the first drying cycle.

Figure 26. Determination of continuous pore radius from MIP curves.

(a)

(b)

Figure 27. Use of impedance spectroscopy to determine transport properties. (a) σ/σ_0 vs. w/c compared with D/D_0 vs. w/c ; (b) permeability calculated by Eq. 10 compared with experiment.

Figure 28. Shrinkage vs. relative humidity of exposure.

Figure 29. Shrinkage vs. weight loss at equilibrium.

Below 50% r.h. capillary stress disappears, once the pores have been emptied, and water now exists only as 1-2 monolayers on surfaces, and between the layers of the tobermorite structure. The latter are very strongly adsorbed and only start to be removed below 10% r.h. Collapse of the layers now occur leading to increased shrinkage, which is again only partially reversible. Removal of interlayer water is most likely encountered in practice in exposure to high temperatures ($> 100^{\circ}\text{C}$).

These phenomena explain the shrinkage-weight loss curves measured during the drying process (Figure 30). The initial, flatter portion of the curve is dominated by loss from capillary pores. When pores are large a lot of water is lost without much capillary stress developing and shrinkage is small. More shrinkage occurs when the pores are finer and the stress is higher. Near the end of the curve water is primarily being lost from the micropores resulting in high shrinkage with relatively small loss of water.

By this type of analysis it has been shown that capillary pores $> 30\text{ nm}$ contribute little to shrinkage and that micropores dominate shrinkage behavior. Thus the microstructure can be qualitatively linked to drying shrinkage. For example pastes that are cured at higher temperatures show less shrinkage. There are two reasons for this. First, the pore structure is coarse, thus the capillary stress is lower. Second, the C-S-H gel structure is denser and more stable thus the disjoining effects of losing micropore water is lower. The same effect is observed when pastes are kept long periods in a moist condition. The process is caused aging and is observed in all amorphous hydrous phases.

(a)

(b)

Figure 30. Use of shrinkage-weight loss curves during drying (a) to compute contributions of shrinkage from capillary pores (stage A) and micropores (stage B). (b) Contributions of each shrinkage component to pastes cured under different conditions.

Chapter 5

POZZOLANS

There are a number of natural and by-product aluminosilicate materials that react with Portland cement and are commonly used as supplementary cementing materials. These fall into two major categories: metallurgical slags and pozzolans. Slags from the steel industry are discussed in the next chapter.

Pozzolan materials are amorphous alumino-silicates that react with the calcium hydroxide formed from hydration of the calcium silicates. They are not cementitious in the absence of lime. Pozzolans were used by the Romans to form hydraulic concretes and the name is a corruption of Puozzoli - a village in the Bay of Naples where a high quality pozzolan was mined.

A wide range of materials show pozzolanic characteristics. These can be divided into materials formed at or near ambient temperatures and those formed at high temperatures.

A. Amorphous silicas formed under ambient conditions

- diatomaceous earth
- weathered clays and zeolites
- weathered volcanic glasses (tuffs)
- geothermal silica

B. Silica glasses formed at high temperatures

- volcanic ash
- volcanic lava (pumice, scoria)
- fly ash
- silica fume*
- rice husk ash*
- calcined clays (metakaoline)*

(*These materials are amorphous, but not glassy)

Chemical Composition

These materials may be quite variable in chemical composition and physical characteristics because they are either natural materials or the by-products of large industrial processes. Thus it is important that they be well-characterized. Typical analyses are shown in Table 1. In addition synthetic pozzolans originating from combustion processes may contain some unburned carbon. usually the amount is less than 2 wt.%, but rice husk ash may contain over 10 wt.%. Only small amounts of carbon will give a

pronounced black color, since carbon black is a good pigment, but otherwise will not affect properties. However, amounts above 5 wt.% could cause other problems. The amount of carbon present is usually estimated from loss on ignition.

Table 1

Typical Bulk Analyses of Pozzolans

<u>Material</u>	S	A	F	C	N	K
Volcanic Glass	50-70	15-10	1-6	2-10	2-4	2-10
Volcanic Tuffs	45-75	10-20	1-10	1-10	0-2	2-7
Diatomaceous Earth	~85	~2	~2	---	<1	---
Fly Ash Class F	>50	20-30	0-20	<5	(Variable)	
Class C	>30	15-25	0-10	20-30	(Variable)	
Silica Fume	85-98	<2	<10	---	(Variable, low)	
Rice Husk Ash	85	---	---	---	---	1-2
Metakaolin	97	(S + A + F)		---	---	---

Phase Composition

However, bulk composition does not give an idea of phase composition, thus an x-ray diffraction analysis is essential. Ideally there should be no crystalline compounds present since they are not pozzolanic. This is the case with silica fume, but seldom so with fly ashes, which contain a mixture of the two (see Figure 1). Glasses are generally identified by broad humps in the pattern, which cannot be measured quantitatively. Generally the amount and reactivity of a glass is estimated through a pozzolanic test where it is reacted directly with lime and the consumption of lime (Table 2) or the rate of strength development is monitored.

Table 2

Pozzolanic Reactivity

<u>Material</u>	<u>Pozzolanic Reactivity</u> mg Ca(OH) ₂ per g
Bauxite, calcined	534
Microsilica, silica fume	427
Blast furnace slag	40
Pulverised fly ash	875
Polestar 501, metakaolin	950-1150 (range)

Fly Ash

Fly ashes are one of the most common pozzolans used in concrete construction. Typical analyses and phase compositions are given in Table 3 for three fly ash sources. Two classes of the fly ash can be identified from their chemical composition: Type F and Type C. Type F fly ashes have low CaO contents (generally < 5 wt.%) and inert crystalline compounds. They mostly originate from bituminous and sub-bituminous coals from East of the Mississippi River. Type C fly ashes have high CaO contents and originate from the lignite coals found in Western States. As seen in Table 2 the crystalline phases may be cementitious in their own right. These ashes can cause problems in use and should be avoided if possible.

Sometimes fly ashes have high alkali contents. If present in the glass they will not cause problems, but often alkalis come from salts sprayed into the electrostatic precipitators to improve their operation. These will then be water soluble and their effects will be the same as adding them separately as an admixture.

Table 3

Composition of Three Commercial Fly Ashes

Chemical Analyses	<u>Class C</u>		<u>Class F</u>
	A	C	E
CaO	37	30	4
SiO ₂	30	31	60
Al ₂ O ₃	17	8	21
Fe ₂ O ₃	7	9	9
SO ₃	4	?	--
K ₂ O	0.3	0.9	4.6
Na ₂ O	0.6	4	--
Crystalline phases	Quartz	Quartz	Quartz
	C ₃ A	Haematite	Mullite
	C $\bar{S}$	C $\bar{S}$	Haematite
	C ₄ A ₃ $\bar{S}$	C	
	C $\bar{C}$	C $\bar{C}$	
	C ₃ S	K $\bar{S}$	
	KN $\bar{S}$ ₂	N $\bar{S}$	

Reactive Pozzolans

Silica fume, rice husk ash, and metakaolin are all classes as highly active pozzolans ("superpozzolans"). Rice husk ash and metakaolin contribute to strength as early as one day, while silica fume takes 2-3 days. In contrast, Class C fly ash requires 5-7 days and Class F fly ash 14-21 days. Silica fume has been available commercially since 1980 and is now widely used in bridge decks as impermeable overlays for corrosion protection. It is also a necessary ingredient for very high strength concrete. metakaolinite has only recently become commercially available, but promises to be a strong competitor for silica fume. Rice husk ash has very high carbon contents, which has held back commercial exploitation; but affordable technology has been developed to remove the carbon and low burning temperatures without reducing pozzolanic activity.

Physical Characteristics

Of importance here are: particle size distribution (p.s.d.), particle shape and density. Fly ashes generally have a similar p.s.d. to cement, (Figure 2) although occasionally they will be finer. Silica fume is much finer, being submicron in size. Surface area is usually a good estimate of particle size, as shown in Table 4. However it can be seen that rice husk ash has a very high surface area because of its cellular structure.

Table 4

Physical Characteristics of Synthetic Pozzolans

Pozzolan	Main Particle Size (μm)	Surface Area M^2/g	Particle	Density (cm^3/g)
Fly Ash (F&C)	10-15	~1	Spherical or Angular	~2.4
Silica Fume	~0.2	~20	Spherical	2.2
Rice Husk Ash	~15	15	Irregular (cellular)	
Metakaolinite	~1	15	Platelet	
PORTLAND CEMENT	10-15	<1	Angular	3.2

Pozzolanic Reactions

The pozzolanic reaction, as observed with fly ash is given by:

Equation 2 contributes most effectively to strength, but both reactions convert calcium hydroxide to more insoluble hydrates. The higher amounts of calcium aluminate hydrates formed by the pozzolanic reaction can cause problems if sulfates are present in the environment. In such cases pozzolans low in alumina should be selected. The pozzolanic reactions have a low enthalpy and thus Eq. 1 has the effect of raising the belite content of the cement. Like belite the reaction is low in the case of fly ash (Figure 3).

However silica fume is not only much more reactive than fly ash and further reduces the CaO/SiO_2 molar ratio of the C-S-H

In both cases the C-S-H has a similar silicate structure to that formed in normal hydration, but the degree of silicate polymerization is higher. Silica fume can thus be regarded as a pozzolan for both CH and C-S-H.

The initial hydration of C_3S is actually accelerated by silica fume. This is because the silica is so reactive it lowers the $[\text{Ca}^{2+}]$ and $[\text{OH}^-]$ in solution (Figure 4) by the formation of C-S-H at the surface of silica particles. As a result the C_3S formed a less complete coating of C-S-H at its surface and dissolves faster, thereby reaching the maximum supersaturation for CH earlier.

Using the above equations it is possible to estimate the amount of a pozzolan required to completely consume all CH. For a typical fly ash this is about 30 wt.% of a Type I cement. However over 40 wt.% of silica fume is required.

Pozzolans will react more rapidly when the pH is higher. For example, metakaolin is thought not to react when the pH is below 13.2; a value readily reached in most portland cement pastes. The effect of pH on the dissolution of Class F fly is given in Figure 6, which would represent the range of values for high alkali and low alkali cements. The activation energy is < 10 KJ/mole. Thus, pozzolans will react at high pH in the absence of calcium hydroxide. Then the hydration products will depend on both temperature and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. At room temperature alkali silica gels will form; at high

temperatures zeolites will form if sufficient alumina is present. Metakaolin is an important component of the alkali-activated "geopolymer" cement in which zeolites are an important component of the binder.

Effects on Microstructure

Because fly ash reacts quite slowly, remnants of fly ash spheres can be seen even in pastes that are several months old. Frequently the formerly smooth surface becomes textured as glass reacts leaving a network of unreactive crystals (Figure 7).

Thus it is usually easy to tell if a concrete had fly ash added to it by an SEM examination. On the other hand silica fume cannot be readily seen by SEM because of its small size. Indeed pastes with high contents of silica fume have very featureless microstructures, and an absence of large calcium hydroxide crystals (Figure 8a). Metakaoline will show similar microstructures

In addition, because of their small particle size both silica fume and metakaolin reduce the size of or even eliminate, the interfacial transition zone. The contrast between Figures 8a and 8b clearly show the differences in microstructure.

Pore Structure

At a given water/binder ratio (w/b) pastes containing fly ash have a coarser pore structure, because less total reaction has occurred. After prolonged curing fly ash actually creates a slightly finer pore structure (Figure 9). Adequate moist curing is essential and a higher curing temperature greatly accelerates hydration.

Being very much finer silica fume can pack between cement grains thereby, creating a finer pore structure. The higher rate of pozzolanicity reduces porosity still further. The fine particle size also eliminates the highly porous interfacial zone and the accumulation of CH at the interface. As a result of these changes the microstructure of cement pastes containing silica fume are much more uniform. However, because of its high fineness silica fume has a high water demand and additions above 5 wt.% require more water to maintain a given workability, unless a plasticizer is used.

Paste Properties

The finer pore structure obtained with silica fume greatly reduces permeability (Table 5), particularly at high w/b. Strength is also improved with the addition of silica fume (Figure 7). Silica fume has an "efficiency factor" of 3.0 (i.e. adding 11b of silica fume is equivalent to adding 31b of cement).

Table 5
Permeability of Concrete with Silica Fume

Cement Content (16/yd ³)	Silica Fume (wt.%)	w/b	K _p (m/s)
170	0	2.4	120 × 10 ⁻¹⁰
	10	2.3	10 × 10 ⁻¹⁰
	20	2.0	0.6 × 10 ⁻¹⁰
320	0	0.9	0.5 × 10 ⁻¹⁰
			50,000 × 10 ⁻¹⁵
	10	1.0	95 × 10 ⁻¹⁵
675	20	0.8*	18 × 10 ⁻¹⁵
	0	0.5	7 × 10 ⁻¹⁵
	10	0.6*	136 × 10 ⁻¹⁵
	10	0.45*	8 × 10 ⁻¹⁵

*Plasticizing agent added.

By contrast fly ash has an efficiency factor of only 1.5-2.0 for long term strength. At shorter ages the strength of a cement paste containing fly ash is lower at a given w/b because of the low reactivity of fly ash.

A comparison of strength development with different pozzolans is given in Table 6.

Table 6
Comparison of Strength Development

Pozzolan	3 days	Relative Strength		
		7 days	28 days	90 days
None	100	100	100	100
Fly Ash	75	80	85	90
Silica Fume	155	130	140	125
Metakaolin	170	160	155	125
Rice Husk Ash	85	85	90	100

Figure 1. X-ray diffraction patterns of pozzolans.

CF $\sim 20 \text{ m}^2/\text{g}$

Class F $\sim 1 \text{ m}^2/\text{g}$

Class C

Cement $< 1 \text{ m}^2/\text{g}$

Rice Husk Ash $\geq 50 \text{ m}^2/\text{g}$

cellular

Metakaolin $\sim 15 \text{ m}^2/\text{g}$

Figure 2. Physical characteristics of pozzolans.

Figure 3. Rate of pozzolanic reactions.

Figure 4. Effect of silica fume on early C_3S reaction.

Figure 6. Mercury porosimetry curves of paste with and without fly ash.

(a)

(b)

Figure 7. SEM of fly ash particles: (a) unreacted; (b) partially reacted.

(a)

(b)

Figure 8. SEM of mortars [1 = aggregate; 2 = paste]. (a) with silica fume added; note smooth paste and absence of CH at interface. (b) without silica fume; note massive CH and rougher paste.

Figure 9. Pore size distribution of pastes with fly ash.

Figure 10. Pore size distribution of pastes with silica fume.

Chapter 6

Blast Furnace Slags

Slag Formation

Metallurgical slags are widely produced, the most common being those from the iron and steel industry. A flux is added to the iron ore, and combines with the gangue in the ore to form a slag as shown in Figure 1; typically the flux used is limestone or dolomite, and the gangue consists mainly of aluminosilicates. The slag contains predominantly a mixture of oxides of calcium, magnesium, silicon and aluminum. The purified and reduced iron and the slag both run to the bottom of the blast furnace, Figure 2, where they are separated by the difference in density, and tapped off. A typical flow chart for the inputs and products of the blast furnace is given in Figure 3.

Figure 1: The reactions occurring in an iron producing blast furnace.

Figure 2: Schematic diagram of an iron producing blast furnace

Figure 3: Flow chart showing the approximate material flows through a typical blast furnace (approximate mass %).

Table 1: Chemical composition of some metallurgical slags (in wt %)

	Ferrous Slags			Non-Ferrous Slags			
	Iron Blast Furnace		LD Slag	Pb-Zn	Ni	Cu	P furnace
	France	Japan	Germany	UK	Canada	S. Africa	USA
SiO ₂	35	31	13	18	29	34	41
CaO	43	37	47	20	4	9	44
MgO	8	8	1	1	2	4	1
Al ₂ O ₃	12	16	1	6	1	6	9
FeO+MnO	0.4	0.7	31	38	53	44	1
CaO/SiO ₂	1.2	1.2	3.6	1.1	0.1	0.3	1.1

Figure 4: Oxide compositions of a range of materials used in cements. Normalized to C+S+A = 100%.

Figure 5: Compositional diagram for calcium aluminosilicates containing 10% mass of MgO, showing thermodynamically stable phases.

Glass Content

Slags typically have compositions, as shown in Figure 4, intermediate between Portland cement and Class F fly ashes. Some typical values are given in Table 1; the blast furnace slags are the main materials finding commercial application in cements, and the other slags lie beyond the scope of this chapter. When blast furnace slags are cooled in air they crystallize as non-hydraulic calcium magnesium silicates, as shown in Figure 5, with only

small amounts of slow reacting hydraulic components such as dicalcium silicate. To enhance reactivity, the slag must be rapidly quenched from the melt to form a reactive glass; this is done by means of a water spray, and there are a number of different processes used. The effect of glass content upon the reactivity of the slag is seen in Figure 6, where the compressive strength of a 3 day old sample is seen to increase considerably with increased glass content of the slag. There is some evidence, however, that small quantities of included crystalline material can enhance reactivity by generating strain in the glassy phase / providing nucleation sites. It can be seen in Figure 7 that reduction of the quantity of crystalline material below 5% (i.e. a glass content of above 95%) is detrimental to strength development.

Figure 6: 3 day compressive strength development of mixes containing slag and having variable glass content

Figure 7: Relationship between merwinite crystal content and strength development of standard ISO mortars (76% slag, 19% clinker, 5% gypsum)

Table 2: Quenching processes for blast furnace slag

Process	Water consumption	Residual moisture
Granulation	100m ³ /ton	30%
	3m ³ /ton(pressure)	30%
Pelletization	1m ³ /ton	10%

Quenching

Two techniques are in general use for quenching, granulation and pelletization. In granulation, Figure 8, water is sprayed into the slag, which breaks up into small granules. In pelletization, Figure 9 the slag is dropped onto a rapidly rotating cooled metal drum, and pellets are thrown off, and separated on the basis of size; the smaller granulated material has a high glass content, and is ideal for use in cements. The coarser pellets find use as lightweight fillers. Following quenching the slag must be dried and ground to cement fineness in a mill; pelletization results in formation of granules with a lower water content (Table 2), reducing drying costs. In the production of blends with cements, the slag can either be interground, or the ground powders mixed; intergrinding is difficult, since the slag granules are significantly harder than cement clinker.

The primary use of slag is as a supplement to Portland cement. In Europe ground slag has been blended with Portland cement for about 50 years. In the USA Portland slag cement blends fell out of favor in the 1950's, presumably with the decline of the iron production industry. Recently several new granulation plants have been built. Generally the slag is sold separately as a mineral admixture rather than as part of a blended cement.

Composition and Reactivity

In the following section, the schematic 2D representations of 3D structures utilize the notation shown in Figure 10(a). The glass is a calcium magnesium aluminosilicate, and thus differs significantly in structure from a highly polymerized silica glass. In a crystalline silica, shown schematically in Figure 10(b), all the silicate tetrahedra are ordered with bond angles which are not strained. In a silica glass, Figure 10(c), the silicate tetrahedra are organized randomly, with a wide range of bond lengths and angles, and thus there is considerable strain in the structure at the atomic level, and the structure is of higher energy and more reactive than the crystalline compound. The glasses in slags differ from those in silica glasses in that they contain significant quantities of elements other than silica.

Figure 8: Diagram of a typical modern slag granulator.

Figure 9: Diagram of a typical slag pelletizer.

Figure 10: (a) Notation used to represent silicate tetrahedra in 2D, (b) a layer out of a crystalline silica, (c) a 2D representation of a silica glass, (d) and (e) 2D representations of a calcium silicate glass ((e) has a higher level of calcium substitution), and (f) a 2D representation of a calcium aluminosilicate glass; alumina tetrahedra are distinguished by shading.

Calcium breaks up the polymerized network in the glass, forming ionic bonds, $\text{Ca}^+ \text{OSi}$, rather than covalent Si-O-Si linkages, as shown in Fig 10(d). Introduction of further calcium, Figure 10(e), (or magnesium, which behaves in the same manner) leads to increased breakdown of the polymerized network in the glass. The effect of aluminum substitution into the glass is more complex, since it is incorporated into the network.(Fig 10(f)).

Breaking up the network increases the reactivity of the glass; attack by water occurs first at points of low connectivity. Thus glasses with a high content of network breaking oxides such as calcia and magnesia are more reactive, all else being equal. In practice quenching rate, the incorporation of minor elements, and other factors are also important. Figure 11 shows typical distributions of silicate anions found in a range of materials; it can be seen that the anions in slag are highly depolymerized, with mainly monomers and dimers. Similar conclusions can be drawn from ^{29}Si MAS NMR(Figure 12), where the peak position of approximately -72ppm is characteristic of a highly depolymerized system. The broad x-ray diffraction peak at approximately $30^\circ 2\theta$ (Figure 13 - $\text{Cu}_{K\alpha}$ radiation) is also characteristic of a highly depolymerized glass.

Figure 11: TMS determinations of the quantities of various silicate anions in assorted slags and other materials

Figure 12(a): ^{29}Si MAS NMR spectrum of a typical slag glass. For comparison, a spectrum of a partly hydrated silica fume is shown in (b). Note that the peak for the slag glass corresponds more closely with the depolymerized hydrate than with the polymerized silica glass peak

Figure 13: x-ray diffraction spectrum ($\text{CuK}\alpha$ radiation) of a typical blast furnace slag; note the broad peak at approximately $30^\circ 2\theta$, corresponding to the depolymerized calcium magnesium silicate glass.

Table 3: Some hydraulic moduli of granulated slags from chemical analyses (%)

Slag	1	2	3	4	5	6	7
C/S	1.31	1.26	1.22	0.95	0.93	1.30	1.34
$\frac{C+M+A}{S}$	1.88	1.88	1.79	1.63	1.39	1.98	1.92
$\frac{C+M+2/3A}{S+1/3A}$	1.52	1.57	1.51	1.32	1.15	1.55	1.41
A/S	0.43	0.36	0.34	0.41	0.34	0.51	0.45

Since the degree to which the network is broken up is determined by the composition, it is possible to use moduli based upon the composition to screen slags for reactivity. Some typical moduli are $\%CaO/\%SiO_2$ and $(\%CaO+\%MgO+\%Al_2O_3)/\%SiO_2$. Values for some commercial granulated slags are given in Table 3. Some countries place limits upon the values of these moduli in their standards for slags. The role of aluminum is difficult to treat by moduli, as demonstrated in Figure 14, where it can be seen that increasing aluminum content in one slag increases reactivity, but only up to a certain level; this might be expected - alumina itself is highly inert. Note also that the strength gains differ at different ages, so different slags may perform better for different applications.

Figure 14: Influence of alumina content on reactivity of quenched slag from a single plant

Hydration

Quenched slag is hydraulic in its own right, but upon initial contact with water, a calcium depleted layer is formed, as shown in Figure 15 which makes further reaction proceed very slowly (years). Thus to be commercially useful, slag must be activated chemically as shown in Table 4. Although the activators modify the initial products, the overall matrix composition is not necessarily significantly changed. In the rest of this chapter we concentrate upon the activation of slag by OPC, since this activation method is the most widely used, and has been studied in greatest detail.

Figure 15: Reaction of slag with pure water

Table 4: Activation of quenched blast furnace slag

Activator	Hydration Products	Commercial Use
---	C-S-H + AFm	---
Ca(OH)_2	C-S-H + AFm	Portland-Slag cements
Alkaline salts	Alkali subst. C-S-H C_2ASH_8 (stratlingite)	Rapid hardening slag cements ("Pyrament")
CaSO_4	AFt	Supersulphated cements

In the hydration with OPC, inner product CSH is produced around both the clinker and slag grains, and outer product CSH surrounds these. AFm is also produced, along with phases containing magnesium and aluminum, which are partly located within the slag inner product. The major reactions occurring in the hydration of Portland slag cements are shown in Figure 16. The Ca:Si ratio of the C-S-H formed is lower than for OPC hydration, and in addition, the quantity of aluminum bearing phases is increased. With small slag additions, Ca(OH)_2 will remain, but with high additions of slag, all the Ca(OH)_2 will react to form C-S-H etc. This effects the speciation of the aluminates, since stratlingite is only stable in the absence of Ca(OH)_2 . Figure 17 shows the effect upon Ca:Si ratio of outer product C-S-H of increasing substitution of ground granulated blast furnace slag(GGBFS). It can be seen that the Ca:Si is around 1.7 for pure OPC, but falls to 1.2 for complete substitution of GGBFS. At the same time, the Al:Ca ratio rises, from about 0.1 for C-S-H from pure OPC, to 0.2 for C-S-H from pure slag. This corresponds

to about 20% substitution of Al atoms into the tobermorite-like silicate backbone of the C-S-H. Additional Al and Mg are found in regions of C-S-H intimately surrounding reacting slag particles; it would appear that these are due to mixing with a very finely divided magnesium aluminum hydroxide phase.

Figure 16: The major reactions occurring during the hydration of blends of slag and portland cement. Inner product is material intimately surrounding the reacting particles; outer product is material that cannot be associated with a particular particle of slag or Portland cement clinker.

Figure 17: Graph showing the variation of Ca:Si and Al:Si ratios with degree of substitution of ordinary Portland cement by slag.

Standards

Standards for slag manufacture and use, as either an admixture, or in blended cements, vary from country to country. The following information is not intended to be comprehensive, but to give some indication of the factors considered.

In Germany and Japan, for example, compositional limits are placed upon potential slags. The moduli of slags that may be used must satisfy $(\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3) / \text{SiO}_2 > 1.0$ (or 1.4 in Japan)

In contrast, the United States standards are largely performance based; the tests are performed upon standard mortars. The following ASTM standards concern the use of slags in hydraulic cements:

ASTM C595

This is standard specification for blended cements, with designations for cements comprising different blending admixtures. There are three grades utilizing slag

Slag cement (>70% Slag with OPC or Lime)

Portland-blast furnace slag cement (25-70% Slag)

Slag-modified Portland cement (<25% Slag)

Some restrictions are placed upon the activity and composition of the slag used and general performance specifications (28day compressive strengths of mortars etc.) are also applied, with a number

ASTM C1157

This specification is for a generic blended cement, and only general performance specifications apply

ASTM C989

This specification applies for the use of GGBFS which will be added at the mixer for use to make blended cements in cements and mortars; performance standards are applied based upon performance of specified blends with cements in mortars, and there are a number of subgrades, based upon the strength of mortars relative to a standard mortar made from OPC alone.

ASTM C1073

This is essentially a test to determine the hydraulic activity of ground slag by reaction with alkali; a strength test is performed upon alkali activated slag mortars at 24 hours. The results do not necessarily correlate well with the 28 day strengths of blended cement samples containing the same slag, and so the test is largely restricted to QC in the production of slags.

Heat generation

Adiabatic temperature profiles for hydration in water of a range of blends from 100% OPC through to 100% slag are shown in Figure 18; such adiabatic curing occurs in emplacement of large masses of a cement, where the heat of hydration is unable to escape. It can be seen that increasing substitution of slag leads to reductions in heat output. This is not necessarily the case though, since slag can be activated strongly by the application of heat, or of an aggressive alkaline solutions. For example, in Figure 19, hydration of blend containing 50% slag at 27°C leads to reduced isothermal heat output relative to OPC. In contrast, hydration of the same blend at 60°C leads to increased heat output. Thus a slag blend that starts to give off heat will accelerate its own reaction, and give off further heat,

to a much greater extent than would OPC. Figure 20 shows the effect of replacing fly ash with slag for immobilization of a simulated offgas solution buffered to high pH by the addition of 1M Na as the hydroxide. The slag is strongly activated in this system, and can give rise to significant heat releases, particularly at the high slag replacement levels.

Figure 18: Adiabatic heats of hydration for slag substituted for type I OPC in a 1:2.75 mortar. Temperature rises are from room temperature.

Figure 19: Isothermal heats of hydration for slag substituted for type II OPC at 27C and 60C

Figure 20: Hydration of cement/slag/fly ash/clay blends with an alkaline solution; total adiabatic heat evolution as a function of composition.

Strength Development

At early ages, strength development in slag cement pastes is somewhat slower than that for equivalent OPC pastes, but ultimate strengths can be similar. Some representative data is shown in Figure 21 for air entrained concrete containing granulated slag.

Figure 21: Age versus compressive strength for air entrained concrete with various levels of OPC replacement by USA granulated slag.

Porosity

The porosity of slag cement systems is generally more finely divided than that of comparable systems containing cement only. For example, mercury intrusion data for pastes hydrated at 45°C for 14 days are shown in Figure 22; while the overall porosity is similar for the two systems at about 0.2cc/cc of paste, the size distribution is considerably different. For the OPC paste, the porosity mainly occurs at about 125Å, while for the blended paste, the bulk of the porosity is finer, at about 30-60Å. This increased fineness of the porosity is important in improving the durability of cements containing slag. Further improvements in the pore size distribution of slag cements pastes are seen with longer times, as calcium hydroxide reacts the remaining slag and the porosity is partially filled by deposition of products.

Figure 22: Pore size distributions, calculated from mercury intrusion data for portland cement and Portland cement / slag (60:40) pastes. W/C 0.4, hydrated 14 days at 45°C.

Chloride Diffusion

Chloride diffusion is important in the durability of reinforced concrete structure, since chloride ions cause pitting corrosion to occur at reinforcing bars, and thus lead to rapid degradation of a structure. Slag cement concrete have much lower diffusion rates for chloride ions than OPC pastes, and has been utilized frequently to improve durability for structures in aggressive environments, such as concrete exposed to sea water or deicing salts. For example, the Rance tidal barrier in France utilizes slag cements, as do many other marine structures. Some typical depths of penetration of chloride ions are given in Table 5, and some measured diffusion rates are shown in Figure 23. In addition to the finer porosity of slag cement pastes, slag cement may also reduce the diffusion rates of chloride ions by means of binding in chloroaluminates.

Table 5: Penetration depths for chloride ions in OPC and slag cement pastes

Curing Temperature	23	38
Curing Time	28	7
Diffusion Temperature	38	38
Depth of Penetration mm in 4 weeks		
Portland Cement	12	18
Cement/Slag (35/65)	5*	4

* 8 weeks diffusion

Figure 23: Effective chloride diffusion constants for Cl⁻ in cement and slag cement hardened pastes at a range of temperatures.

Alkali Silica Reaction

Addition of slags to cement pastes can also help control the alkali silica reaction, by lowering the level of alkali in the pore solution, and lowering the cement content of the mix. Since this degradation mechanism concerns the attack by pore solution of poor quality aggregates, it is not considered here. Cements for immobilization of waste are highly unlikely to contain aggregate.

Sulfate Resistance

This is an important degradation mechanism of cement pastes. Sulfate ions react with the aluminates in the cement paste to form ettringite, which has a high water content and low density, and thus can be expansive. Slag cements are found to have good resistance to sulfate attack as shown in Figure 24. Low expansions were observed in a very severe accelerated test.

Figure 24: Sulfate resistance of mortar bars for various levels of addition of granulated slag; the alkali sulfate reaction causes expansion. This test is accelerated by use of extremely high levels of sulfate.

Carbonation

Carbonation involves the reaction of basic components of cement paste with atmospheric or dissolved carbon dioxide. Initially free calcium hydroxide in the paste reacts; with further carbonation, calcium oxide is removed from the C-S-H which become progressively more siliceous, and eventually transforms to a silica gel. Since pozzolanic cements such as slag cements contain less OPC, and thus less calcium oxide, they have a lower capacity to neutralize carbon dioxide, and thus carbonate more rapidly. Carbonation lowers the pH sufficiently that embedded reinforcing iron is no longer passivated and starts to corrode. The improved pore structure of slag cement pastes may, however, partially offset this effect.

Immobilization

Slag cements typically contain 2-3% of sulfur, largely as sulfide and polysulfide species. These result in immobilization by two potential mechanisms. Firstly, sulfides may form insoluble precipitates with various metallic species, though this may be extremely slow under the high pH conditions in a cement paste. This mechanism may provide an immobilization for a range of polarizable metal ions, such as mercury and lead. Additionally, the sulfides are reducing, and can reduce species within the cement pore solution. For example, the very soluble and difficult to immobilize Cr(VI) ion, chromate, is stable in OPC, but in a slag cement is reduced to Cr(III), which forms a largely insoluble hydroxide at the pH of a cement pore fluid. A Pourbaix diagram is shown in Figure 25. Note, however, that reduction may be extremely slow, as shown in Figure 26. Similar chemistry can be expected for a range of transition metal ions and actinides.

Figure 25: Pourbaix diagram for chromium, showing approximate regions for pH and Eh in typical cement systems.

Chromate Cr(IV) Immobilization (Schematic)

Figure 26: Time dependence of immobilization of chromate in OPC and slag cements.

Summary

- Slag needs to be predominantly glassy for high reactivity
 - High quenching rates required
 - Reactivity partly controlled by composition
- Slag not hydraulic on its own; activation required
 - OPC
 - Alkali
 - CaSO_4
- Heat output reduced relative to OPC
 - but strongly dependent upon activation by
 - Elevated temperatures (e.g. adiabatic curing)
 - High levels of alkali
- Dense microstructure
 - Low diffusivity
 - High durability
- High sulfide content
 - Strongly reducing
 - Can help immobilize
 - transition metals (e.g. Chromium),
 - metalloids(e.g. Lead)
 - actinides
- Durability Good

Chapter 7

Zeolites and Cements

Introduction

Zeolites were first discovered as natural minerals with unusual properties, for which they were named. These minerals boiled and lost water upon heating vigorously, but this water loss was reversible - the crystalline morphology and the atomic structure was not irreversibly altered unless the minerals were heated considerably above the point at which water loss occurred. Thus the materials were given the name zeolite, or boiling stone, from the Greek, *zeo* - to boil, *lithos* - stone.

Zeolites consist of a microporous aluminosilicate framework, which contains weakly held water that can be removed (in the same way that water can be dried out of sponge without affecting the structure of the sponge). Figure 1 shows a formal representation of the sieve like structure of zeolite A, a synthetic commercial material. The porosity of zeolites can be quite high; Figure 2 shows the range of typical values, with as much as 0.5cc water accommodated in 1cc of hydrated zeolite. It can be seen that as the water content increases, the density of the silicate framework decreases, as might be expected.

Figure 1: A formal representation of the sieve like structure of zeolite A. There is an Al or Si centered at each corner, and an oxygen in the middle of each edge. In addition the structure accommodates water molecules and cations, but these are not shown for clarity.

Figure 2: Reported saturation capacities of zeolites for water plotted against the number of atoms of Al+Si per 1000 cubic angstroms of zeolite framework.

The aluminosilicate framework has the formula TO_2 ; where T represents an atom, either an Al or a Si placed upon a tetrahedral site, and surrounded by four oxygens. Each oxygen is bridging to an adjacent tetrahedral site. For the case of $\text{T}=\text{Si}$, then the material has no overall charge, the +ve charge on the Si^{4+} ion is balanced by the -ve charges on two oxide O^{2-} anions. However, for the case $\text{T}=\text{Al}$, then the charges do not balance, and the overall formulae becomes AlO_2^- . This has to be balanced by the inclusion of cations into the structure. There are no free negative ions to chelate the cations directly, so they become located in the porosity of the zeolite, adjacent to sites in the framework where aluminate species are located. Silicon and aluminum T sites are represented in Figure 3; it can be seen that the oxygen atoms complicate the structure, and it is common in visualizing zeolite structures to use a highly simplified notation.

Figure 3: The tetrahedral building blocks of zeolites. On the left, a Si with four oxygens around it, each shared with an adjacent T site, and on the right, an Al also surrounded by four oxygens; in this case, the charge is not balanced, and the deficit must be made up by adjacent positive ion such as sodium.

In this simplified notation, illustrated in Figure 4, each T-O-T linkage is represented by a straight line, with the T atoms located at the end of the line; thus oxygen atoms are located in the middle of each line, and the vertices where lines meet represent the positions of the T sites. Al and Si sites are not distinguished; this does not matter, since often the positioning is not well understood. Note that the T-O-T linkages are actually bent though drawn as straight. The cation positions are also usually omitted. The major strength of the notation is to provide some simplification in order to visualize these complex structures.

Figure 4: Diagram showing the representation of T-O-T bonds as straight lines with the T sites at the vertices.

Figure 5 shows an example of a zeolite structure drawn in this simplified notation, with just the straight lines drawn on the right, and with the oxygens superimposed on the left hand part of the framework. It can be seen that much detail is lost by omission of the oxygens, but that it is only possible to view the internal details of the structure when the oxygens are removed. The structure, for the synthetic Linde type A (LTA) zeolite (as shown above) consists of large cavities opening into each other by means of 8 membered rings; it is into this network of porosity that the water is able to be reversibly absorbed.

Figure 5: The crystal structure of Linde type A zeolite. Oxygen atoms are shown in the left hand side of the structure as the large spheres, and sodium ions as the small spheres; the Al and Si atoms are located upon the vertices of the line network.

The formula then of a typical zeolite will be

$M(\text{AlO}_2)(\text{SiO}_2)_x \cdot n\text{H}_2\text{O}$, where $M = \text{M}^+$, or $(1/2)\text{M}^{2+}$, or a mixture of various cations.

where in general $x > 1$, since if $x < 1$, then there will have to be Al-O-Al linkages within the framework, and these are generally of higher energy, though they have sometimes been observed. n is variable, and will depend on the nature of the cations in the system; if the cations are bulky, then there will be less space left in the structure for water absorption.

Cation Exchange

As noted above, the cations in zeolites are only weakly held in the porous structure. The porosity enables exchange of these cations for other cations (including H^+), and thus these materials can act as ion exchangers. For example, a zeolite material can be used to replace the calcium cations in hard water with sodium cations, as shown in Figure 6. The sodium form of the zeolite can be regenerated by the application of a concentrated solution of sodium ions (e.g. salt), to drive the equilibrium back the other way.

Figure 6: Schematic diagram showing the application of zeolites for ion exchange. The cations are only held within the structure by weak coulombic forces, and can readily be displaced by other ions. The high microporosity of the systems facilitates the diffusion of ions in and out of the structures.

Molecular Sieving

If the water is removed from a zeolite structure, then the material possesses a very high surface area, and other materials can be absorbed into the cages. Indeed, zeolites are sometimes used as “getters” for vapors (e.g. in sealed unit double glazed window panels). For a material to be absorbed, however, it must be sufficiently small to pass through the windows and into the cages of the zeolite structure. Thus the absorption is size selective, and ions can be sieved. An important commercial application is illustrated in Figure 7, where n-octane and iso-octane can be separated by absorption into LTA zeolite. These materials, the ratio of which is important in determining the anti-knock characteristics of petroleum gas are otherwise closely similar in properties, and extremely difficult to separate. n-octane can pass through the windows and get into the structure, while the slightly fatter iso-octane is excluded.

Figure 7: Windows of the Ca-form of zeolite LTA; molecules of n-octane (right) can pass through the windows, while molecules of the branched species iso-octane (left) cannot.

Zeolite Mineral Formation

Zeolite minerals are formed geologically under hydrothermal conditions or in salt solutions. A reactive aluminosilicate glass, such as volcanic ash, is subjected to heat and/or pressure and/or long time periods in the presence of salt bearing water. A number of scenarios are possible.

- Volcanic ash may be buried to great depth, and thus subjected to considerable heat and pressure in the presence of water. As the severity of the conditions increases with increasing depth, the glass reacts to form first a hydrous zeolite; further heat and pressure result in the formation of a zeolite with a lower water content. Finally under the most extreme conditions feldspars are formed; these minerals are related structurally to the zeolites, but the structures are much more compact, and they contain no water. Thus zones containing different species are formed, as illustrated in Figure 8(a).
- Over smaller distances, Figure 8(b), water percolating through a deposit of reactive glass can pick up alkali and become extremely reactive; again, a series of zones may be formed, though generally the environment is too hydrous for feldspars to form.
- Intrusion of a magma body into a deposit of suitable glass can cause heating, and the formation of zones of alteration, from feldspars close to the intrusion, through regions of zeolites, out to the unaltered glass, Figure 8(c).
- An evaporating lake can also cause alteration - as it evaporates it becomes smaller, and increasingly salt rich. Thus significant alteration will occur near the middle, with less alteration around the outside regions, Figure 8(d).

Figure 8: Geologic formation of zeolites by alteration of glass, (a) by burial, (b) in an open hydrologic system, (c) around a magma intrusion, and (d) in saline, alkaline lake deposits. + represents unreacted glass, A- hydrous zeolites, B - less hydrous zeolites, and C - feldspars.

Zeolites in Cementitious Systems

Zeolite have three potential areas of use in cementitious systems. They can be used as pozzolans to provide a reactive source of aluminosilicates, they can be added to cements in order to remove species from the pore fluid by ion exchange, as in the immobilization of PWR and BWR resins in cements. Under appropriate conditions, zeolites can be formed *in situ* during the hydration of a blended cement.

Zeolites as Pozzolans

Zeolites have a high surface area, and contain aluminosilicate species; thus they find application as pozzolans. When reacted with free lime, they are attacked, and the aluminate and silicate species released to participate in the formation of the ordinary products of cement hydration. They have found little application in the US, but China has large deposits of zeolites, and historically has manufactured cement very inefficiently (in the 70's, 2/3 of cement production still came from vertical kilns). About 20% of the cement production is blended with zeolitic pozzolans.

Zeolites are found to increase the period during which a concrete is workable, probably by the removal of species from solution by absorption and/or ion exchange. Alkali ions are readily absorbed; the addition of zeolite can lower the level of alkali ions in the pore fluid, and control the expansion of poor quality reactive aggregates. Even with a very high alkali cement, ZC, Figure 9, the expansion of reactive aggregate is controlled, while the use of a lower alkali cement, DC, without addition of zeolite, results in expansion. Levels of zeolite addition can be limited by the very high water demand resulting from the large surface area.

Figure 9: Effect of zeolite addition upon the alkali aggregate reaction. Sample DC is cement with a moderate level of alkali. ZC are samples containing cements with much higher alkali contents blended with zeolite. It can be seen that the DC sample experiences significant expansion, while the ZC samples are dimensionally stable.

The mechanism of the reaction of cesium loaded clinoptilolite zeolite with a cement system has been studied in some detail. Cesium ions are readily displaced from the zeolite by ion exchange with calcium ions. In the hydration of blended slag cements containing the same zeolite, the zeolite was gradually consumed, as shown in Figure 10. The reaction was somewhat temperature dependent; nevertheless, a significant reaction rate would be expected, at the temperatures likely in any large scale depository environment. Over 40% of zeolite would be needed to ensure that excess zeolite remained after the cement clinker had all been hydrated.

Figure 10: Isothermal plots showing the fraction of clinoptilolite consumed in the reaction with cement for times up to 1000 hours (~40 days).

Zeolites as Additives

Zeolites have been proposed as additives in cement to control the behavior of ions not readily immobilized by the normal products of cement hydration. Cesium is one such ion, and zeolites have been used to reduce the leaching of cesium ions from cement stabilized wasteforms which contain cesium loaded BWR and PWR organic ion exchange resins. In a slag cement matrix, the addition of zeolite or acid clay was found to significantly reduce the rate at which cesium ions were leached from the resins, as shown in Figure 11. The efficiency of the admixtures in preventing leaching approximately correlated with the selectivity of the admixture for cesium ions, shown in Figure 12. However only relatively young samples appear to have been tested, so it is possible that at longer times the zeolite may be pozzolonomically consumed, and the rate of leaching may increase. The presence of

slag in the wasteform may, however, serve to react with the lime produced by cement hydration, and to protect the zeolite. Further work is required to determine the behavior of these complex systems.

Figure 11: Leaching of cesium ions from slag cement wasteforms containing spent resins and additives to control cesium leaching.

Figure 12: $\text{Cs}^+/\text{Ca}^{2+}$ ion exchange isotherms for the additives used in Figure 11, showing the strong affinity of the natural zeolite and acid clay for Cs^+ ions.

In Situ Zeolite Formation - Zeolite Cement Composites

Table 1 shows the composition of some materials that typically react to form zeolites under geological conditions. Also shown are the compositions of representative US fly ashes. The compositions are close, particularly for alumina and silica, which are the ingredients required for the silicate framework. The alkali levels in the fly ashes are lower, but extra alkali is readily added in the solution. The varying levels of iron are not of much importance; most of the iron in fly ashes is present as inert iron oxides. The class C fly ash contains much higher levels of calcium oxide than do the other materials.

Reaction of the rhyolitic glass with sodium hydroxide solution is found to give Na-P1 and sodalite zeolites, depending upon the exact conditions, as shown in Figure 13. Na-A and faujasite zeolites can also be formed, though the Na-A does not persist over long time periods. Basaltic glasses undergo similar reactions.

The pH of the reaction medium is important in determining the Al/Si ratio of the zeolite formed; higher pH is found to give zeolites with a higher Al/Si ratio. This effect can be seen in the products formed in Figure 13, where at low pH (low NaOH content), Na-P1 is formed (Al/Si ratio approximately 0.3), while at higher pH, sodalite is formed (Al/Si = 1). In an open system, the addition or removal of silicate also effects the products formed. This may be important in cement systems, where the dissolution of clinker phases adds silicate ions, and the formation of CSH removes them.

Table 1: Comparison of approximate oxide composition of two glasses which can be converted to zeolites geologically, and of class F and C fly ashes.

Oxide	Tuff		Fly Ash	
	Rhyolitic	Basaltic	Class F	Class C
SiO ₂	70	46	50	33
Al ₂ O ₃	13	19	24	20
Fe ₂ O ₃	1	8	12	8
CaO	1	7	2	26
Na ₂ O	5	8	2	2
K ₂ O	4	4	2	1

Figure 13: Schematic graph showing the compositional regions for formation of zeolites in the NaOH/rhyolitic glass system. The top part of the graph is very dilute compared to realistic values in a cement system - the aim of the work was to synthesize and separate commercially useful zeolites from a cheap starting material.

Similar reactions are indeed observed with high fly ash cement systems, although temperature is important. For example, mixtures of Class F fly ash and slag hydrated with an alkaline solution give relatively normal cement hydration products for isothermal hydration at room temperature. Adiabatic curing, however, raises the temperature sufficiently to allow zeolite formation. Hydration of calcium aluminosilicate glasses with CsOH solution at 90C gives rise to a range of zeolites. The levels of Cs ions leached from the systems, Figure 14, are low, and for systems with above about 20% alumina, very low levels of Cs are found in the pore solutions.

Figure 14: Comparison of 90 day cesium ion concentration (mM) for cesium hydroxide doped samples of reactive glasses cured at 90C. Samples 1-5 were glasses of the given composition; hydration of such reactive glasses is likely to approach equilibrium faster than hydration of a blended cement of the same overall composition, where early hydration reactions may tie up materials in kinetically stable materials such as CSH, AFm and AFt.

Hydration of blends high in fly ash with sodium hydroxide or similar systems gives rise to a range of products, with zeolites forming at 45C and above; the following zeolites are most often observed.

- Na-P1
- Sodalite
- Cancrinite
- Faujasite (at the lower temperatures, and transiently at higher temperatures)

Generally these zeolites are the sodium form; calcium form zeolites can also be formed, but this is less readily achieved, due to the much lower solubility of calcium silicate relative to sodium silicate. Much more vigorous conditions are required in order to produce these calcium zeolites. They have been observed in some cement systems, however, particularly those cured for prolonged periods at high temperatures, or with vigorous agitation (in modeling studies systems are often agitated to speed the onset of thermodynamic equilibrium). Zeolites such as Ca-P are also predicted to form in slag blends at high temperature by thermodynamic modeling studies. Of course in cement systems, there is alkali in the pore fluid, and this may act as a catalyst in the formation of calcium zeolites.

Three of the species produced in cement systems are now considered in a little more detail.

Na-P1

This structure, based on the gismondine (GIS) framework, is shown in Figure 15; double aluminosilicate chains are cross linked to form a structure consisting of T_8O_8 channels running in all three dimensions. There is ready diffusion of the ions in and out of the structure by way of the channels, and the material is an effective ion exchanger, with a high affinity for Cs^+ , Rb^+ , Sr^{2+} and Ba^{2+} . Sometimes in cements, the calcium form can be found; this appears to have similar ion exchange properties.

Figure 15: Crystal structure of the aluminosilicate framework of Na-P1; the network of lines describes the framework; the shading is simply to help visualize the structure.

Sodalite

This structure is much more compact, with a lower water content. It consists of close packed sodalite cages, as shown in Figure 16. The largest openings into the cages are the T_6O_6 hexagonal rings, and there is not a network of open channels as in Na-P1. The cages can get filled up with salt molecules during synthesis, displacing the water. Thus the properties of this zeolite (strictly not a zeolite when the water has been displaced by salts) are rather different. For example, the small openings into the cages result in ion sieving, as shown for a range of zeolites in Table 2; exchange of cesium ions is not possible except at very high temperatures. Indeed these materials have been proposed as hosts for cesium and iodine ions, and even for noble gases, which can be forced through the windows at high pressure and temperature and remain trapped inside when the structure is cooled.

Figure 16: The framework structure of the sodalite zeolites

Table 2: Ion sieving properties of some common zeolites

Exchanger	Windows (dimensions in Å)	Exchangeable ions	Non-exchangeable ions
Analcime	6- and 8-rings (~2.2)	K^+ and smaller	Cs^+ and larger
Ultramarine	6-rings (~2.3)	K^+ and smaller	Cs^+ and larger
Sodalite hydrate	6-rings (~2.3)	K^+ and smaller	Cs^+ and larger
Chabazite	8-rings (3.7 × 4.2)	$n\text{-alkyl-NH}_4^+$	$iso\text{-alkyl-NH}_4^+$, NMe_4^+ , etc.
Zeolite A	8-rings (4.3)	$n\text{-alkyl-NH}_4^+$	$iso\text{-alkyl-NH}_4^+$, NMe_4^+ , etc.
Clinoptilolite	10-rings (3.5 × 7.9 Å) 8-rings (3.0 × 4.4 Å)	$n\text{-alkyl-NH}_4^+$	NMe_4^+ , $iso\text{-butyl-NH}_4^+$

Cancrinite

This zeolite, shown in Figure 17 consists of 1 dimensional $T_{12}O_{12}$ channels. As with sodalite, salts can be intercalated into the structure; in this case, into the channels. The material can undergo ion exchange, though the selectivity is apparently not reported. There is some evidence that the channels can become blocked under some conditions. The structure is related to sodalite, though this is not immediately apparent from the structure! The materials can be formed from the same layers, stacked in different ways; there are a number of other possibilities listed in Table 3.

Figure 17: The framework structure of the zeolite cancrinite.

Table 3: Layer sequences in sodalite cancrinite minerals

No. of layers in repeat unit	Layer sequence	Space group	a (Å)	c (Å)	Name
2	ab	P6	12.72	5.19	Cancrinite
3	abc	P $\bar{4}3m$	8.87	—	Sodalite
4	abac	P $6_3/mmc$	12.91	10.54	Losod
6	ababac	P $\bar{6}m2$	12.85	16.10	Liottite
8	ababacac	P 6_3mc	12.77	21.35	Afghanite
10	abcabcbacb	P $\bar{3}m1$	12.88	26.76	Franzinite

The similarity between cancrinite and sodalite means that relatively minor changes in the solution composition can effect which phase forms. This is illustrated in Figure 18, where it is shown how aluminosilicate squares can be joined in different ways to form different structures. Minor changes in solution can promote one or other of the processes. It is found that the salts that can be intercalated into sodalite can sometimes cause the formation of cancrinite instead. A wide range of sodalites and cancrinites have been formed. Table 4 shows the zeolites formed with a range of salts; once the salts are in

the sodalite the bulky anions are potentially immobilized since they are much larger than the six ring windows. This may provide a route for the immobilization of anionic species which otherwise can be difficult to immobilize. Immobilization of a range of anions in a zeolite cement composite made from fly ash and sodium hydroxide is shown in Figure 19. Immobilization of chromate, in a system in which a mixture of sodalite and cancrinite formed, was reasonably effective, but the results are disappointing for the other anions.

Figure 18: The condensation of 4-ring anions to give cubic anions or a double crankshaft chain. The composition of the solution will determine which process is favored.

Table 4: Products formed for synthesis of sodalites and cancrinites in the presence of added salts. These results are for synthesis from kaolinite under specific conditions.

Sodalite with:	Cancrinite with:
Alkali solution alone	Na_2SO_4
NaCl	Na_2SeO_4
NaBr	$\text{Na}_2\text{CrO}_4^d$
NaI	Na_2MoO_4
NaF^b	$2 \text{ g } \text{Na}_2\text{FeO}_4 + \text{Fe}^{\text{III}} + 12 \text{ M } \text{NaOH}^e$
NaClO_3	Na_3VO_4
NaClO_4	NaMnO_4 (large excess)
Na_2SO_3	NaNO_3
Na_2S^c	$\text{Cu}(\text{NH}_3)_4\text{SO}_4 + \text{excess } \text{NH}_3^f$
Na_2WO_4	
Na_3PO_4	
HCOONa	
CH_3COONa	
$(\text{COONa})_2$

Figure 19: Anion immobilization in a system consisting of class F fly ash reacted with 10M NaOH at 90C for 28 days. 80mM of the oxoanions of Cr, Se, Mo, Re or W was added to the system. Immobilization was effective for chromate only. Sodalite and cancrinite zeolites were found.

In the presence of cement, the early hydration can be influenced significantly by what ions are present in solution. Thus hydration of a high fly ash blended cement with an alkaline solution, with and without carbonate ions gives significantly different products, both in terms of zeolites, and in terms of calcium silicates, as shown in Figure 20.

Figure 20: X-ray diffraction (CuK_α radiation) of the products for cement zeolite materials resulting from reaction of an alkaline solution with a high fly ash cement blend at 90C for 28 days, in the presence and absence of carbonate anions. The products in the two systems are significantly different. With carbonate, sodalite (S) is the predominant zeolite; without it, Na-P1 (P) is dominant. The crystallinity of the CSH (CSH) also differs in the two systems, and the carbonated system contains significant quantities of crystalline CSH (tobermorite - T). Other phases include a rheology aid (Att - attapulgite clay), Q - quartz, A - alite from the cement clinker, and C calcium carbonate.

The reaction routes in these cement zeolite materials are influenced significantly by the ordinary cement phases. Thus in the material shown in Figure 20, with a carbonate containing solution, the sodalite zeolite is not formed directly, see Figure 21. Initially, the aluminum is deposited in an AFm phase, which later dissolves; the zeolite is formed at this stage.

In conclusion it should be noted that these cement zeolite composite materials appear to have relatively good durability. The development of microstructure is shown in Figure 22. It can be seen that a cement zeolite composite with water to solids ratio of 1 has a similar normalized conductivity to a OPC paste with a typical W/C ratio of 0.5. The normalized conductivity is related to the tortuosity of the pore structure of the material. Thus the favorable ion exchange properties of zeolites appear to combined with the normal properties of a cement matrix.

Figure 21: Adiabatic hydration of a high fly ash cement blend with an alkaline carbonated solution. Selected area diffraction patterns showing the phase evolution from AFm to sodalite hydrate. AFm = AFm, Sod = Sodalite.

Figure 22: Normalized conductivity as a function of time for some cement zeolite composites (high fly blended cement, water to solids ratio=1, highly alkaline solution) and an ordinary Portland cement paste.

CHAPTER 8

Transport Properties of Cement Pastes

Professor Tom Mason
Northwestern University
Evanston, Illinois

Transport Properties Outline

- General Transport Equations
- Engineering Ramifications
- Understanding the Coefficients
- Measurement Methods
- Conductivity "Shortcuts"
- Ordinary Cement Paste Results
- Cementitious Wasteform Results

Ionic Diffusion (Fick's Law):

$$J_i = -D_i \frac{\Delta c_i}{\Delta x}$$

- J_i = flux in #/m²-s
- D_i = diffusion coefficient in m²/s
- c_i = concentration in #/m³
- Δx = thickness

Permeability (d'Arcy's Law):

$$v = K_p \frac{\Delta h}{\Delta x}$$

- v = flow rate in m³/m²-s
- K_p = permeability in m/s
- Δh = hydraulic pressure in m of water
- Δx = thickness in m

Transport Properties: Engineering Ramifications

Concrete Durability

- Chloride Penetration
- Carbonation
- Sulfate Attack
- Drying/Wetting
- Freeze/Thaw Damage

Wastewater

Containment

- Bleeding
- Leaching

Phase Volumes (OPC) (Mindess & Young)

$w/c=0.50$

$\alpha=1.0$

Parallel Conduction/Diffusion

Interconnectivity: the β Factor

Typical Ionic Diffusivities

- 10^{-8} to 10^{-7} m²/s in water (pore fluid)
- 10^{-13} to 10^{-11} m²/s in mature cement pastes
- $\beta\phi$ must account for 10^{-5} to 10^{-4}

Capillary Porosity vs. Time

Hydration and Connectivity

Parallel Pipes ($\beta=1$, $\phi=\text{const}$)

$$A_p = \phi A_{tot}$$

$$A_p = \phi A_{tot}$$

$$D = D_o \beta \phi \neq f(r_p)$$

Parallel Pipes ($\beta=1$, $\phi=\text{const}$)

$$n_p = \phi A_{\text{tot}} / \pi r_p^2$$

$$n_p = \phi A_{\text{tot}} / \pi r_p^2$$

pipe flow rate/pressure head $\propto \pi r_p^4$

$$K_p \propto r_p^2 \beta \phi$$

The Katz-Thompson Equation

$$K_p = \frac{1}{226} r_c^2 \beta \phi = \frac{1}{226} r_c^2 \left(\frac{\sigma}{\sigma_o} \right)$$

- r_c = the mean, minimum radius of the connected pore network (defined by the maximum slope in mercury intrusion porosimetry-MIP)

Determination of r_c by MIP

J. F. Young

Permeability of OPC (w/c=0.51, Mindess & Young)

Age (days)	K_p (m^2/s)	$K_p/K_p(\text{fresh})$
fresh	10^{-5}	1
1	10^{-8}	10^{-3}
7	10^{-11}	10^{-6}
28	10^{-13}	10^{-8}
240	10^{-18}	10^{-13}

Permeability vs. Pore Radius

A "Simple" Permeameter

From Hearn and Mills (1991)

"Simple" Permeameters

From Ludirdja, Berger & Young

Diffusion: Serial Sectioning

$$c(x, t) / c_s = [1 - \text{erf}(\frac{x}{2\sqrt{Dt}})]$$

The Conductivity "Shortcut"

- Diffusivity (the Nernst-Einstein Eq.)

$$\frac{D}{D_o} = \frac{\sigma}{\sigma_o}$$

- Permeability (the Katz-Thompson Eq.)

$$K_p = \frac{1}{226} r_c^2 \left(\frac{\sigma}{\sigma_o} \right)$$

Impedance Spectroscopy (IS)

Typical Impedance Spectra

OPC, w/c=0.35

Bulk Conductivity vs. Time

Pore Solution Concentrations

OPC, $w/c=0.50$

$[OH^-]$ vs. Time (OPC)

Pore Solution Conductivity

Normalized Conductivity

OPC, OPC-SF

The Role of Kinetics

Shortcut vs. Measured K_p 's

Normalized Transport (D , σ)

Measured values from Nyame & Illston

Designing a Cement-Based Wasteform

$$\text{Both } D_i, K_p \propto \phi \beta$$

$$K_p \propto r_p^2$$

- We have to live with the capillary porosity.
(ϕ should be as large as is feasible.)
- We can only work to keep the pores from
“communicating” with each other.
(r_p and β should be as small as possible.)

Phases by Volume

From Reinhardt (1992): water-cured

Wasteform Strategies (high ϕ)

- Hydration
 - Pore "maze"
 - Pore subdivision
 - Pore sealing
- Precipitation
 - Pore clogging

Temperature Schedule

Normalized Conductivity vs. Time

Ionic Concentration of Pore Solution vs. Time

XRD patterns (Brough et al. MRS 1994)

[OH] Equivalent of Expressed Pore Solution

Nitrate Leachability Index vs. Temperature (from Lokken)

Permeability vs. Time

Normalized Conductivity vs. Time (Metakaolin systems)

Conclusion: How to Make a Better Mousetrap (Wasteform)

- Must be pourable without bleeding (cement-based rheology)
- Must soak up a lot of water (a “sponge”)
- Must solidify (cell walls must become rigid)
- Must lock up the water (cell walls must become impermeable; arteries clogged)

INTRODUCTION TO GEOLOGICAL ASPECTS AND LONG-TERM DURABILITY OF CONCRETE

Geology of the Hanford Region

The oldest rocks in the Hanford site are Miocene basaltic lava flows of the Columbia Volcanic Plateau (Figure 1).

*Columbia Plateau Volcanism 13-25 M.Y.B.P.

FIGURE 1. The geologic time scale. Shown to the right is a very simplified diagram showing the development of life. Not included on the diagram are many types of invertebrate fossils such as clams, brachiopods, corals, sponges, snails, and so forth, which first appeared in the Cambrian or Ordovician and have continued to the present.

The Hanford site is located in a geological structure called the Pasco Basin formed by folding of the basaltic rocks (Figure 2). Overlying the basalts are a series of sediments of Pliocene and Pleistocene age (ca. 7 million to 13,000 years before present) deposited in this topographic basin (Figure 3). On top of these sediments are recent surficial deposits (Figure 4).

Figure 2 Geologic Structures of the Pasco Basin and the Hanford Site

The Pliocene and Pleistocene sediments are central to understanding the Hanford site. During the Pliocene the Pasco Basin was apparently the site, at various times, of lakes and rivers, resulting in the deposition of sediments typical of these environment: mud, silt and sand (see Table 1 for grain sizes). These sediments are now known as the Ringold formation (Figure 3). A formation is a mappable geologic unit.

After most of the Ringold formation was deposited, there apparently was a period of weathering, soil formation and deposition of some gravels, resulting in the formation of discontinuous deposits at the top of the Ringold formation.

On top of this unit is the Hanford formation, which is composed primarily of silt, sand and gravel (Figure 3). The sediments of this unit were deposited by the so-called Missoula floods during glacial time, between 12,700 and 15,500 years before present. These floods are the result of rapid unblocking of glacially dammed lakes (Figures 5 and 6), and are one of the most extraordinary events in recent geological history. There were apparently several tens of these floods occurring over a period of ca. 3,000 years at intervals of a few tens of years.

S9211085.17

FIGURE 3. Generalized Stratigraphy of the Suprabasalt Sediments Beneath the Hanford Site.

S9211085.43

FIGURE 4. Landforms of the Pasco Basin and the Hanford Site

TABLE 1 Grain-size scale for sediments, showing Wentworth size classes, equivalent phi (ϕ) units, and sieve numbers of U.S. Standard Sieves corresponding to various millimeter and ϕ sizes

U.S. Standard sieve mesh		Millimeters	Phi (ϕ) units	Wentworth size class
GRAVEL		4096	-12	
		1024	-10	Boulder
		256	-8	
		64	-6	Cobble
		16	-4	Pebble
	5	4	-2	
	6	3.36	-1.75	
	7	2.83	-1.5	Granule
	8	2.38	-1.25	
SAND	10	2.00	-1.0	
	12	1.68	-0.75	
	14	1.41	-0.5	Very coarse sand
	16	1.19	-0.25	
	18	1.00	0.0	
	20	0.84	0.25	
	25	0.71	0.5	Coarse sand
	30	0.59	0.75	
	35	0.50	1.0	
	40	0.42	1.25	
	45	0.35	1.5	Medium sand
	50	0.30	1.75	
	60	0.25	2.0	
	70	0.210	2.25	
	80	0.177	2.5	Fine sand
	100	0.149	2.75	
	120	0.125	3.0	
	140	0.105	3.25	
	170	0.088	3.5	Very fine sand
	200	0.074	3.75	
MUD	230	0.0625	4.0	
	270	0.053	4.25	
	325	0.044	4.5	Coarse silt
		0.037	4.75	
		0.031	5.0	
		0.0156	6.0	Medium silt
		0.0078	7.0	Fine silt
		0.0039	8.0	Very fine silt
		0.0020	9.0	
		0.00098	10.0	Clay
		0.00049	11.0	
		0.00024	12.0	
CLAY		0.00012	13.0	
		0.00006	14.0

FIGURE 5

Map of Columbia River valley and tributaries. Irregular small-dot pattern shows maximum area of glacial Lake Missoula east of Purcell Trench ice lobe and maximum extent of glacial Lake Columbia east of Okanogan lobe. Dashed-line pattern shows area that, in addition to these lakes, was swept by the Missoula floods. Late Wisconsin Cordilleran icesheet margin (heavy-dot pattern) is from Waitt and Thorson (1983, Fig. 3-1). Large dots indicate sites of bedded flood sediment mentioned text or figures: B, Burlingame Canyon; L, Latah Creek; M, Mabton; N, Ninemile Creek; P, Priest valley; S, Sanpoil valley; Z, Zillah. From Waitt (1985, Fig. 1).

FIGURE 6

Map of Cordilleran ice margin (modified after Richmond, 1986), glacial Lake Missoula, and major flood outburst routes. BRL=Bull River Lobe; FL=Flathead Lobe; PTL=Purcell Trench Lobe; PRL=Priest River Lobe; TRL=Thompson River Lobe. Glacial Lake Missoula=cross hatched area. Arrows show major flood outburst routes.

The timing of these floods and the recurrence of glacial periods during the Pleistocene are usefully compared to the 1/2-lives of relevant radionuclides (Figure 7).

FIGURE 7 Oxygen isotope curves for oceanic cores covering long periods of Quaternary time and drawn to a common time scale (from Shackleton and Opdyke 1973, 1976 and Van Donk 1976). Originally published in part by Geological Society of America.

+Oldest known fully modern humans.

At the Hanford site the Ringold and Hanford formation sediments are of the order of 100m thick, and the water table is in Ringold or Hanford formation at various localities (Figure 8)

FIGURE 8

Most of the sediment sequence is in the unsaturated zone above the water table (Figure 9).

FIGURE 9

Designation of hydrologic soil-profile horizons. Note that this figure is idealized and that one or more of these horizons may be absent in a given situation. After Todd (1959).

The water table dips generally to the east, and the direction of transport in the saturated zone is towards the Columbia River (Figure 10).

FIGURE 10 Hanford Site Water Table Map, June 1989 (Smith and Gorst 1990)

The ground water is fresh (total alkalinity of ca. 125 ppm) with a low sulfate content (ca. 34 ppm; Table 2). Natural recharge rates within the site appear to be very low 0 - 1 cm/year.

Table 2 Provisional Background Values for Hanford Site Groundwater^(a)

Constituent (Conc.)	PNL Results ^(b)	WHC Provisional Threshold Values
Aluminum (ppb)	<2	<200
Ammonium (ppb)	<50	<120
Arsenic (ppb)	3.9±2.4	10
Barium (ppb)	42±20	68.5
Beryllium (ppb)	<0.3	<5
Bismuth (ppb)	<0.02	<5
Boron (ppb)	<50	<100
Cadmium (ppb)	<0.2	<10
Calcium (ppb)	40,400±10,300	63,600
Chloride-All (ppb)	10,300±6,500	NC
Chromium (ppb)	4±2	<30
Copper (ppb)	<1	<30
Fluoride (ppb)	370±100	1,340 775 ^(c)
Iron-Mid (ppb)	NA	291
Lead (ppb)	<0.5	<5
Magnesium (ppb)	11,800±3,400	16,480
Manganese-All (ppb)	7±5	NC
Mercury (ppb)	<0.1	<0.1
Nickel (ppb)	<4	<30
Nitrate (ppb)	NA	12,400
Phosphate (ppb)	<1,000	<1,000
Potassium (ppb)	4,950±1,240	7,975
Selenium (ppb)	<2	<5
Silver (ppb)	<10	<10
Silicon (ppb)	NA	26,500
Sodium (ppb)	18,260±10,150	33,500
Strontium (ppb)	236±102	264.1
Sulfate (ppb)	34,300±16,900	90,500
Uranium (pCi/L)	1.7±0.8	3.43
Vanadium (ppb)	17±9	15
Zinc-All (ppb)	6±2	NC
Field Alk. (ppb)	NA	215,000
Lab Alk. (ppb)	123,000±21,000	210,000
Field pH	NA	(6.90, 8.24)
Lab pH	7.64±0.16	(7.25, 8.25)
TOC (ppb)	586±347	2,610 1,610 ^(c)
Field Cond. (umho/cm)	NA	539
Lab Cond. (umho/cm)	380±82	530

Hydraulic conductivities determined from pumping tests are in the range 0.01 to 0.1 m/s, typical values for sands and gravels (Table 3). These values are much greater than lab measurements of small samples, as is usually the case.

Table 3 Range of Values of Hydraulic Conductivity and Permeability

Conversion Factors for Permeability and Hydraulic Conductivity Units

	Permeability, k^*			Hydraulic conductivity, K		
	cm ²	ft ²	darcy	m/s	ft/s	U.S. gal/day/ft ²
cm ²	1	1.08×10^{-3}	1.01×10^8	9.80×10^2	3.22×10^3	1.85×10^9
ft ²	9.29×10^2	1	9.42×10^{10}	9.11×10^5	2.99×10^6	1.71×10^{12}
darcy	9.87×10^{-9}	1.06×10^{-11}	1	9.66×10^{-6}	3.17×10^{-5}	1.82×10^1
m/s	1.02×10^{-3}	1.10×10^{-6}	1.04×10^5	1	3.28	2.12×10^6
ft/s	3.11×10^{-4}	3.35×10^{-7}	3.15×10^4	3.05×10^{-1}	1	6.46×10^5
U.S. gal/day/ft ²	5.42×10^{-10}	5.83×10^{-13}	5.49×10^{-2}	4.72×10^{-7}	1.55×10^{-6}	1

*To obtain k in ft², multiply k in cm² by 1.08×10^{-3} .

Long-Term Durability of Cement and Concrete

Ca- and Ca-Si-Al based cements are inherently durable. Most of their components (minerals) are thermodynamically stable, and there are many examples of existing cements many thousands of years old.

Lime mortar was used by the ancient Greeks and Romans and there are many remaining examples of structures made with these mortars (e.g., Figure 11). Lime was made by heating of limestone at ca. 1000°C via the reaction

Hardening was due to formation of portlandite from lime/water mixtures via the reaction

Further hardening occurred by carbonation via

Excellent durability was obtained by thorough mixing and ramming. These cements were non-hydraulic. That is, they would not set under water.

FIGURE 11 The Pont du Gard at Nîmes

The Greeks and Romans also knew how to make hydraulic cements by calcining limestones which contained clay (analogous to modern Portland cements). They mixed this cement with sand and finely ground volcanic tuff (pozzolans) or crushed burnt brick to produce extremely durable and water resistant cement and concrete. The Pantheon in Rome (second century A.D.) is made of such concrete and is one of the best preserved buildings from the ancient world (Figure 12).

FIGURE 12 The interior of the Pantheon. (Giovanni Paolo Panini; National Gallery of Art, Washington, D.C., Samuel H. Kress Collection)

The Greeks and Romans also knew how to make very durable plasters and pipe linings.

Most of this technology was lost until the development of modern technology in the 1700's. The Eddystone lighthouse in Cornwall, England, was built in the 1750's with pozzolanic cement and stood for 126 years before being removed (Figure 13). It was still in good condition.

Modern Portland-type cements were developed in the early to mid 1800's and by 1900 production and use in construction was reasonably well standardized.

FIGURE 13 Smeaton's Eddystone Lighthouse. (Photograph courtesy of H. A. Newlon, Jr.)

There are other examples of even longer-term durability of cement components from the geological record. One example is from Scawt Hill, Ireland, where C-S-H formed by hydration of C₂S occurs near the surface. This material is apparently stable, even in the wet climate of Ireland.

An even more impressive example occurs in a series of sedimentary rocks in Israel and Jordan (Figure 14). In this sequence, spontaneous combustion of bituminous chalks and clay-rich limestones (up to 26% organic matter) produced temperatures up to ca. 800°C (Figure 15). This combustion took place about 13.6 ± 2 million years before present and within 80 - 90 m of the surface (Figure 16). It was limited by oxygen supply. The mineralogical results of this heating were primarily Ca silicates and Ca aluminosilicates, and include all the important phases in cement clinker (Table 4). The hydration products include ettringite, tobermorite, portlandite, and an undescribed amorphous gel.

From a cement durability standpoint, this occurrence indicates that both unhydrated and hydrated cement phases are stable over many millions of years in near surface environments.

FIGURE 14
Location map and schematic stratigraphic location of the M.Z. complex. The large

Table 4 Some characteristic minerals in the M.Z.
their compositions and known occurrences.

Mineral	Composition	Cement chemical nomenclature
(a) High temperature-low pressure decarbonation assemblage:		
Diopside ^{b,c}	CaMg(SiO ₃) ₂	C MS ₂
Periclase ^{a,c}	MgO	M
Wollastonite ^{b,c}	CaSiO ₃	β CS
Monticellite ^{a,c}	CaMg(SiO ₄)	C MS
Gehlenite ^{a,c}	Ca ₂ Al ₂ [(Si,Al) ₂ O ₇]	C ₂ AS
Spurrite ^a	Ca ₅ [CO ₃ , (SiO ₄) ₁]	C ₅ S ₂ C
Rankinite ^{a,c}	Ca ₃ Si ₂ O	C ₃ S ₂
Merwinite ^{a,c}	Ca ₃ Mg(SiO ₄) ₂	C ₃ MS ₂
Larnite ^{b,c}	β-Ca ₂ SiO ₄	β-C ₂ S
Grossular ^b	Ca ₃ Al ₂ SiO ₄	C ₃ AS ₃
Brownmillerite ^{a,c}	Ca ₂ Al ₂ (Fe) ₂ O ₅	C ₄ AF
Mayenite ^{a,c}	Ca ₁₂ Al ₁₄ O ₃₃	C ₁₂ A ₇
Pseudowollastonite ^{a,c}	α-CaSiO ₃	α-C ₂ S
Hatrrurite ^c	Ca ₃ SiO ₅	C ₃ S
(b) The lower temperature assemblage of hydration and recarbonation:		
Ettringite ^{d,e}	Ca ₆ [Al(OH) ₆] ₂ (SO ₄) ₃ · 26H ₂ O	
Apophyllite ^{d,e}	KF Ca ₄ (Si ₈ O ₂₀) · 8H ₂ O	
Tobermorite ^{d,e}	Ca ₄ H ₄ [Si ₃ O ₉] ₂ · 4H ₂ O	
(9.3;10;11.3-11.7;12.6;14A varieties)		C ₅ S ₆ H ₉ , C ₅ S ₆ H ₅ , C ₅ S ₆ H ₁₁ ..
Portlandite ^{d,e}	Ca(OH) ₂	
Bayerite ^e	Al(OH) ₃	
Aragonite ^d	CaCO ₃	
Vaterite ^{d,e}	μ-CaCO ₃	

^aSanidine facies. ^bPyroxene-hornfels facies. ^cPortland cement clinker or slags
^dLate hydration and carbonation phases of low temperature. ^eHydrated Portland cement

FIGURE 15

Petrogenetic grid of univariant decarbonation reactions in the M.Z. See text, (15).

Abbreviations: Ca-calcite; Kaol-kaolinite; Qtz-quartz; Gr-grossular; Dol-dolomite; Di-diopside; Wo-wollastonite; An-anorthite; Ge-gehlenite; Co-corundum; Sp-spurrite; Br-brown-millerite, La-larnite.

FIGURE 16

Schematic section through the Hatrum-rim basin, stressing the relationship between the M.Z., the underlying unmetamorphosed rocks and the internal stratigraphy of the M.Z.

Mechanisms of Attack of Cement

The mechanisms by which cements and concretes are attacked are well understood (Table 5). For a cement waste form buried at the Hanford site the environment is very benign, and most of the important mechanisms for, e.g., attack of buildings and roads are not important. For the waste forms, the most important mechanisms are likely to be carbonation and leaching, which would take place over geological time if the waste forms are properly protected. Corrosion of reinforcement steel is possible if it is used.

Table 5
Durability of Concrete

Chemical attack
Leaching and efflorescence (P) ^a
Sulfate attack (P)
Alkali-aggregate reaction (A) (Chapter 6)
Acids and alkalis (P)
Corrosion of metals (R)
Physical attack
Freezing and thawing (P, A)
Wetting and drying (P) (Chapter 18)
Temperature changes (P, A) (Chapter 19)
Wear and abrasion (P, A) (Chapters 6, 19)

^aLetter(s) in parentheses indicates the concrete component most affected, in order of importance: A, aggregate; P, paste; R, reinforcement.

Similarly, most causes of cracking of cement and concrete are likely to be unimportant (Table 6). Depending on the temperatures, rates of heating and rates of moisture loss (if it occurs), thermal cracking and drying shrinkage cracking could occur.

Table 6
Causes of Cracking in Concrete

<i>Component</i>	<i>Type</i>	<i>Cause of Distress</i>	<i>Environmental Factor(s)</i>	<i>Variables to Control</i>
Cement	Unsoundness	Volume expansion	Moisture	Free lime and magnesia
	Temperature cracking	Thermal stress	Temperature	Heat of hydration, rate of cooling
Aggregate	Alkali-silica reaction	Volume expansion	Supply of moisture	Alkali in cement, composition of aggregate
	Frost attack	Hydraulic pressure	Freezing and thawing	Absorption of aggregate, air content of concrete, maximum size of aggregate
Cement paste	Plastic shrinkage	Moisture loss	Wind and temperature	Temperature of concrete, protection of surfaces
	Drying shrinkage	Moisture loss	Relative humidity	Mix design, rate of drying
	Sulfate attack	Volume expansion	Sulfate ions	Mix design, cement type, admixtures
	Thermal expansion	Volume expansion	Temperature change	Temperature rise, rate of change
Reinforcement	Electro-chemical corrosion	Volume expansion	Oxygen, moisture	Adequate concrete cover