Accelerated Aging of Concrete:
A Literature Review

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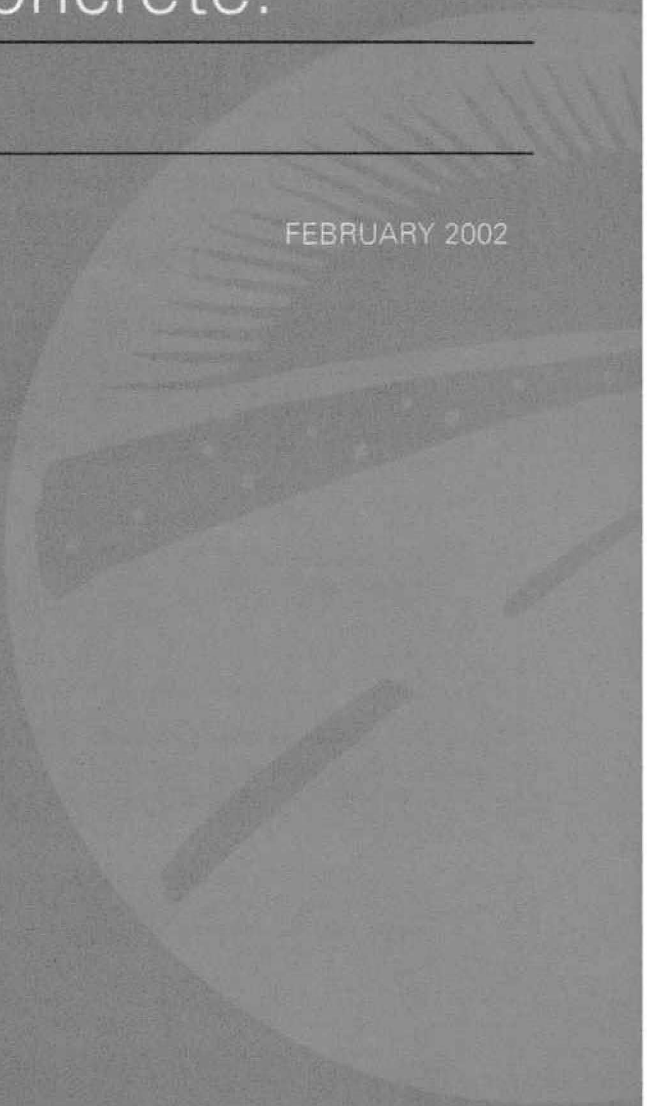

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Federal Highway Administration

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FOREWORD

This report provides a review of the literature on accelerated aging of concrete. It was undertaken as part of research on predicting the long-term environmental performance of Portland cement concrete (PCC) pavements containing coal fly ash. An accelerated aging regime involving temperature aging, cyclic loading, and freeze-thaw cycles was employed in this project to simulate natural long-term aging processes.

This literature review describes the general concept of aging, defines accelerated aging, and discusses thermal aging, the most common accelerated aging technique. Accelerated aging techniques used for several types of materials are reviewed, followed by a more thorough review of aging of concrete.

This report will be of interest to engineers and researchers who are interested in predicting long-term properties of concrete (or other materials) using an accelerated aging approach.

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Research and Development

NOTICE

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16. Abstract

This report provides a review of the literature on accelerated aging of concrete. It was undertaken as part of a research project on predicting the long-term environmental performance of Portland cement concrete (PCC) pavements containing coal fly ash. An accelerated aging regime involving temperature, cyclic loading, and freeze-thaw cycles was employed in this project to simulate natural long-term aging processes.

This literature review describes the general concept of aging of materials and defines accelerated aging. It describes accelerated aging procedures and applications of accelerated aging, and discusses thermal aging, the most common accelerated aging technique. Accelerated aging techniques and applications for several types of materials are described, followed by a review of accelerated aging procedures and applications for PCC.

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yards	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
NOTE: Volumes greater than 1000 l shall be shown in m^3.				
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5(F-32)/9 or (F-32)/1.8	Celcius temperature	°C
		ILLUMINATION		
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.71	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact)		
°C	Celcius temperature	1.8C + 32	Fahrenheit temperature	°F
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

* SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

(Revised September 1993)

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1. Introduction

1.1 Motivation

The intent of this work is to review the literature on the accelerated aging of concrete. Accelerated aging techniques applied to other construction materials were also included to provide a context in which to study artificial aging of concrete. This extended review addresses why and how these materials are artificially aged and how the results of their aging processes compare with those in concrete.

1.2 The Concept of Aging

Aging is a natural process that all materials experience over time. As defined in the German Standard DIN 50 035 (from 1), "aging is the totality of irreversible chemical and physical alterations that may occur within a material in the course of time." In this respect, the concept of aging has two main components: the development or "maturation" process in which the material forms an internal microstructure, and the degradation process in which it loses integrity. While both processes involve chemical (or more correctly, physicochemical) reactions, degradation often involves mechanical processes as well.

For example, for many materials the time-dependent development of useful mechanical properties such as hardness, toughness, compressive, tensile, or shear strength, or modulus of elasticity follows one of the patterns schematically illustrated in figure 1. Similarly, for the same material, microstructural characteristics such as porosity, or transport properties such as permeability, diffusivity, or absorptivity might change with time in a manner indicated in figure 2.

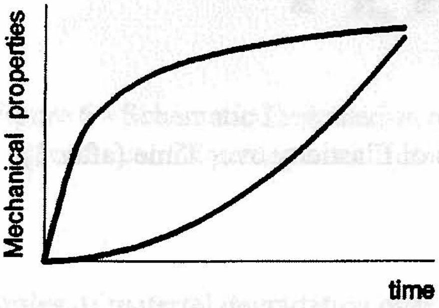


Figure 1 - Schematic Development of Mechanical Properties over Time

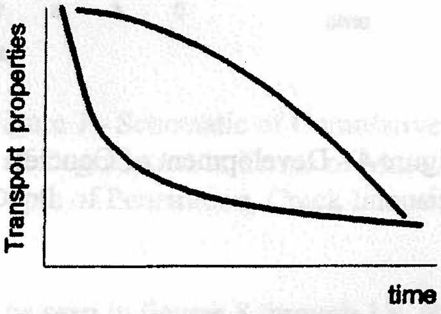
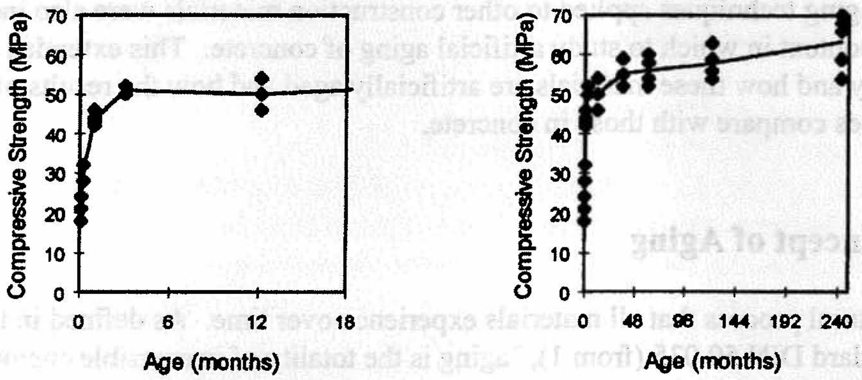


Figure 2 - Schematic Development of Transport Properties over Time

In the case of portland cement concrete, for example, the time-dependent development of the microstructure of the hardened cement paste (HCP) manifests itself in the development of compressive strength, modulus of elasticity, permeability, and other physical properties, as illustrated in figures 3 to 5. Strength gain is plotted in figure 3. Figure 4 similarly shows development of elastic modulus. Figures 3 and 4 are generically similar to figure 1, while the continuously decreasing permeability shown in figure 5 is schematically similar to figure 2.



(a) (b)

Figure 3 - Development of Concrete Compressive Strength over Time (after 2)

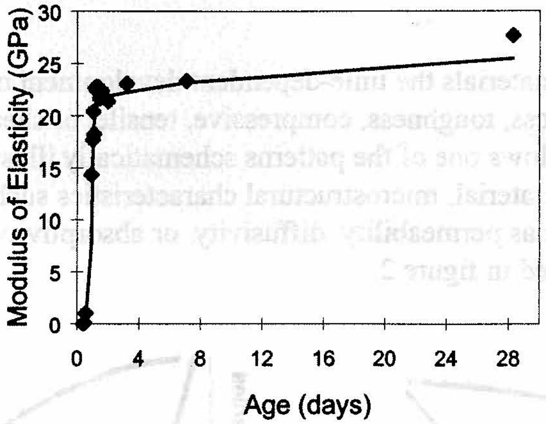


Figure 4 - Development of Concrete Modulus of Elasticity over Time (after 3)

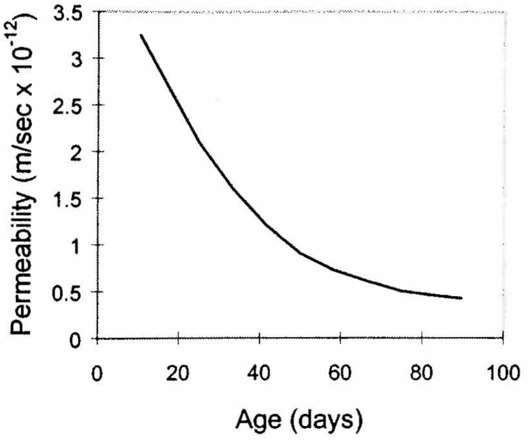


Figure 5 - Development of Concrete Permeability over Time (after 4)

The time-dependent *degradation* of materials likewise can be graphically represented as in figure 6 or 7. The first of these patterns indicates the reduction in mechanical properties such as strength or stiffness (elastic or dynamic modulus) as a function of time, while figure 7 shows a more direct measure of the extent of degradation via cumulative mass loss, depth of penetration, increased volume of cracking, etc. Note that in both figures the degradation may ultimately stabilize or it may become increasingly severe.

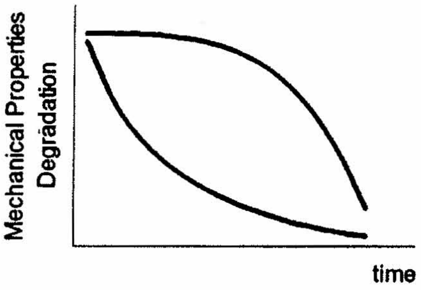


Figure 6 - Schematic Degradation of Mechanical Properties over Time

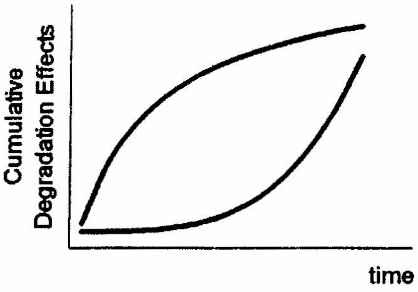


Figure 7 - Schematic of Cumulative Effect of Degradation in Terms of Mass Loss, Depth of Penetration, Crack Intensity, etc.

Examples of material degradation over time can be seen in figures 8 through 13. For concrete materials, for example, the increase in scaling of a concrete surface from freeze-thaw action is shown in figure 8, while the long-term deterioration of a concrete slab from alkali-carbonate reaction is shown in figure 9.

Taking an example from the field of metallic corrosion, figure 10 shows the increase in corrosion of iron, zinc, and aluminum at atmospheric conditions over time, presented as cumulative mass loss per unit area. Figure 11 illustrates the degradation of a polypropylene sample subjected to UV radiation over time, as represented by the average number of chain scissions in one macromolecule. The degradation of an asphalt pavement due to oxidation over time can be seen indirectly by the increase of its viscosity, as shown in figure 12. Thermal degradation of wood over time can be indirectly assessed by the decrease in the modulus of elasticity, as illustrated in figure 13.

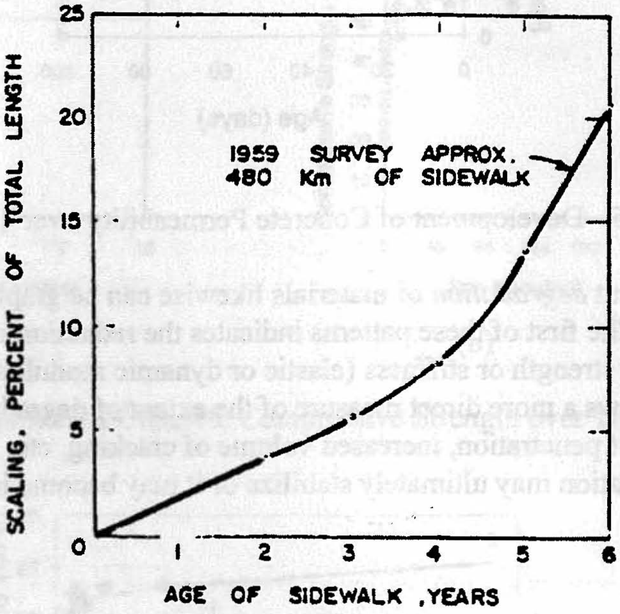


Figure 8 - Scaling of Concrete Pavement over Time (5)

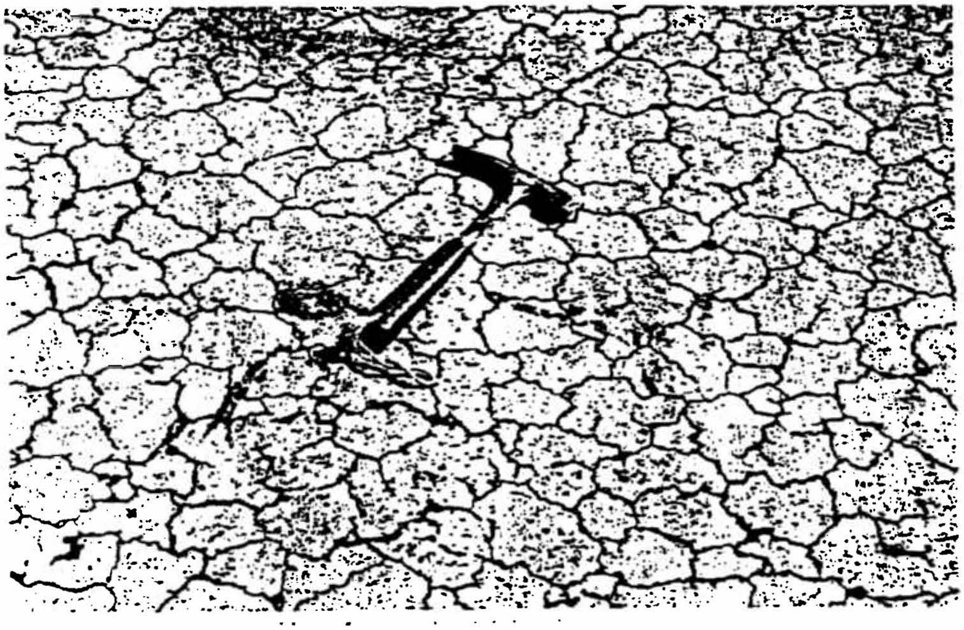


Figure 9 - Long-Term Alkali-Carbonate Reaction of a Concrete Slab (after 6)

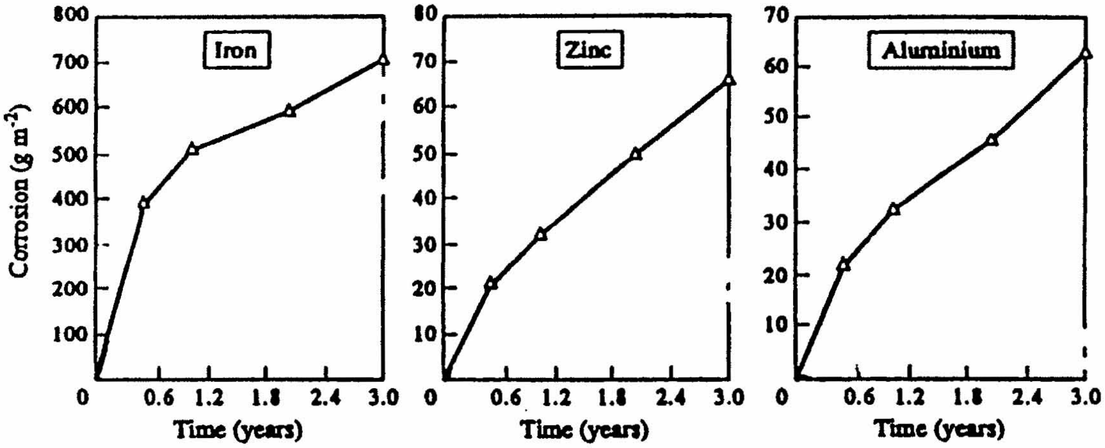


Figure 10 - Atmospheric Corrosion over Time for Various Metals (after 7)

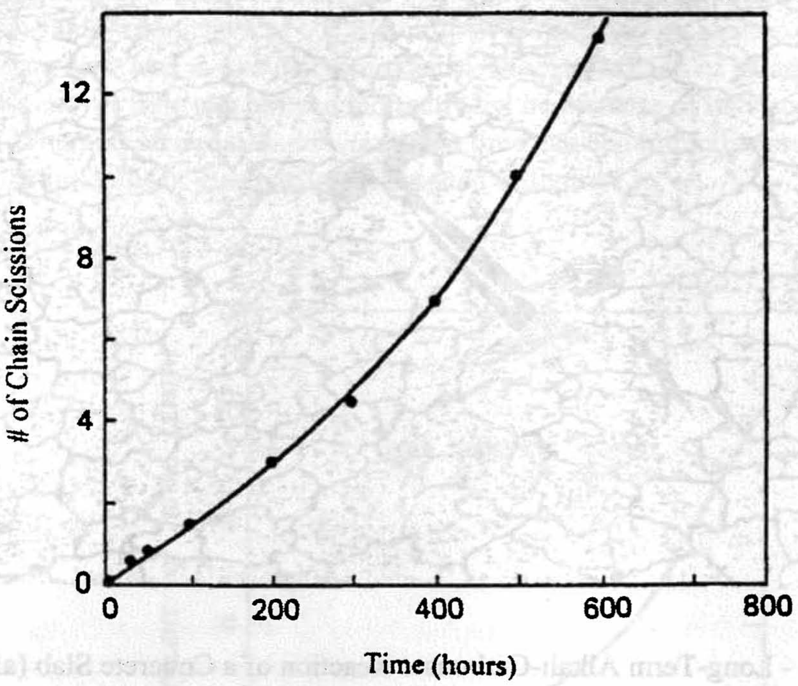


Figure 11 - Polymer Degradation over Time due to UV Radiation, as Reflected in the Average Number of Chain Scissions per Macromolecule (8)

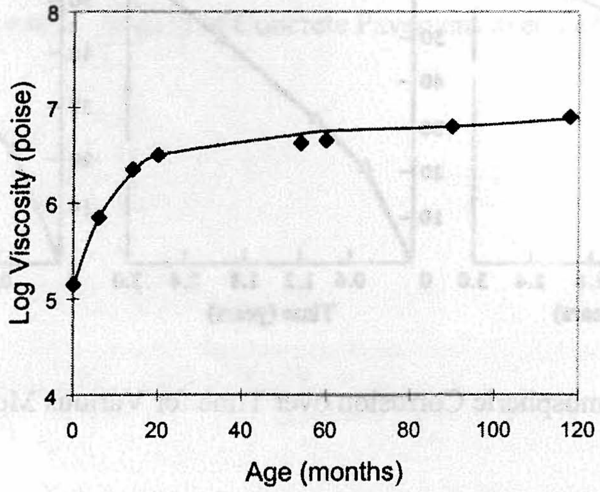


Figure 12 - Increase in Asphalt Viscosity over Time due to Oxidation (after 9)

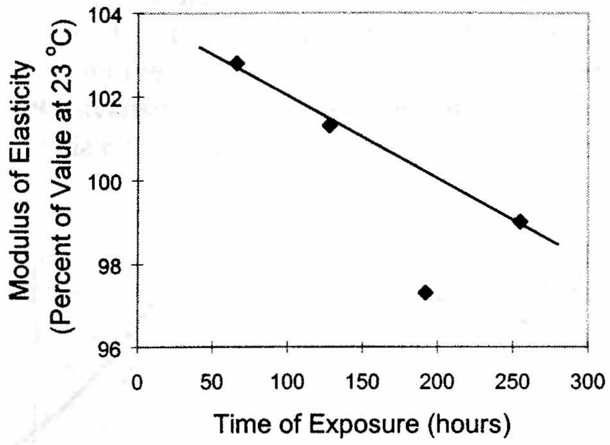


Figure 13 - Decrease of Wood Modulus of Elasticity over Time due to Thermal Degradation (after 10)

Finally, it is noted that in a given material, and under a particular set of exposure conditions, both development and degradation mechanisms can proceed simultaneously. This can be the case with portland cement/fly ash concrete, where hydration of the cement and pozzolanic reaction of the fly ash continue with time and temperature. A variety of mechanisms of degradation may be at work at the same time so that the behavior of the material at any given time is the net result of constructive and destructive processes.

1.3 Accelerated Aging

1.3.1 Definition

Accelerated aging is the process in which one or more of the development and/or degradation mechanisms of a material are intentionally accelerated. For the purposes of this review, a distinction between accelerated *development* and accelerated *degradation* will be emphasized, and the two concepts will be discussed individually throughout. The term "accelerated aging" will be used as the umbrella term to incorporate both accelerated development and accelerated degradation. Since many accelerated techniques are found in the literature under the heading of "accelerated test methods," (ASTM test methods, for example) that terminology will be used in this report as well. Further, the term "accelerated test method" will be used regardless of whether the method in question accelerates development or degradation processes, or both.

1.3.2 Significance

Accelerated aging methods are used either to simulate long-term development or degradation in a shorter time. Figures 14 and 15 schematically describe the purpose of accelerated aging techniques; figure 14 shows an accelerated development process and figure 15 shows an accelerated degradation process. These figures present a generic and an accelerated development and/or degradation curve over time, by plotting any specific property reflective of material behavior. The long-term behavior P_L occurs at time t_L. The goal of accelerated aging techniques is to produce P_L at a shorter time t_S.

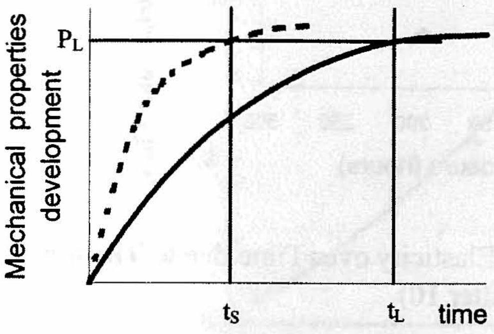


Figure 14 - Schematic Accelerated Development of Mechanical Properties over Time

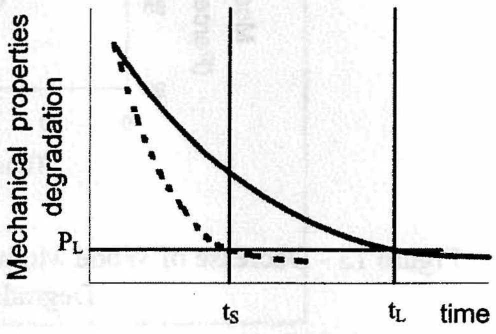


Figure 15 - Schematic Accelerated Degradation of Mechanical Properties over Time

1.3.3 Accelerated Aging Procedures

Experimental methods used to simulate the aging process normally consist of two parts. The first part is a specified *exposure* designed to provoke a development or degradation reaction that proceeds more rapidly than would normally be experienced in the expected service environment. The second part is a method to assess the extent of the material response or reaction, by *measurement* of affected material properties or behaviors.

To design a quantitatively meaningful test exposure, accelerated aging methods must be based on an understanding of the development/degradation mechanisms and the factors influencing them. Thus, these methods must isolate the influencing factors and suitably intensify their impact so as to accelerate the desired development or degradation without triggering material responses or reactions that would never have developed under actual service conditions, regardless of duration of exposure. In this report such unintentionally accelerated reactions will be referred to as "anomalous."

1.3.3.1 Factors Influencing Aging

As evidenced in figures 8 to 13, a number of factors influence aging. For many of these the magnitude of their impact depends on the specific material and mechanism of interest. In general, the factors contributing to development and to degradation are physicochemical or mechanical, and examples are shown in table 1. Expanded discussions are found in the next subsection and in chapters 3 and 4.

Accelerated aging procedures intensify the effect of one or more of these influences on development or degradation to force the chemical or physical mechanisms to proceed more rapidly than in the anticipated service environment. Several complications are common:

1. When intensification of a factor leads to both an increased rate of development and an increased rate of degradation, it is not certain that both mechanisms are accelerated to the same degree.
2. Efforts to accelerate a given mechanism can alter the fundamental nature of that mechanism, such that the net result is not representative of a longer-term exposure under more moderate conditions.
3. More than one factor may be simultaneously intensified, either intentionally or unintentionally. Complex interaction of multiple factors is likely to influence the net result.

1.3.3.2 Examples of Accelerated Aging

In the general case of metallic corrosion, for example, the rate of corrosive attack (a degradation process) can be accelerated by:

1. Increasing the temperature of the reactants.
2. Increasing the pressure (oxygen partial pressure, for example) of the reactants.
3. Increasing the concentration of the reactants (lowering the pH in the case of acid attack).
4. Increasing the exposed area of the reacting surfaces.
5. Removing corrosion products as they are formed to increase contact between aggressive solutions and bare metal.
6. Applying stress to the corroding metal to add the impact of microcracking to chemical degradation.
7. Applying cyclic stress to the corroding metal to add fatigue cracking and the mechanical working of cracks to the chemical degradation.

Table 1 - Common Factors Influencing the
Rates of Development or Degradation of Materials
(with examples from cement and concrete technology)

Chemical or Physicochemical Processes	Example of Influence in Material Development	Example of Influence in Material Degradation
Temperature	Increased temperature accelerates formation of calcium-silicate hydrates in portland cement paste.	Increased temperature accelerates formation of calcium-aluminum-sulfate compounds leading to sulfate attack.
Pressure	Increased water vapor pressure accelerates hydration of cement.	Increased water vapor pressure accelerates saturation of hardened cement paste, accelerates sulfate attack and alkali-aggregate reaction.
Carbonation	Increased CO_2 pressure accelerates carbonation, i.e., the formation of $CaCO_3$ in the pores of hardened cement paste.	Carbonation lowers pH and can accelerate corrosion of embedded metals in concrete.
Reactant Concentration	$CaCl_2$ admixture accelerates setting and early age strength gain of concrete.	$CaCl_2$ admixture accelerates corrosion of reinforcing steel.
Radiation Intensity	Incident solar radiation accelerates setting and strength gain of the top surface of concrete.	Incident solar radiation increases the vapor pressure of water near the surface and accelerates evaporation, drying, cracking, and decreases degree of hydration.
Externally Applied Load/Stress		Load-induced cracking reduces strength and modulus of elasticity, and accelerates penetration of liquids, gases, and dissolved solids.
Abrasion / Erosion	Abrasion/erosion can wear away soft exterior revealing a denser, stronger under-layer. Abraded specimens can show an improved performance in scaling tests.	Long-term wear can be estimated from short term exposure to a more intense wearing mechanism.
Fatigue Loading	Low stress fatigue cycles can increase the static strength of concrete.	High frequency or high intensity stress levels decrease the static strength of concrete.

As another example, the degradation of portland cement concrete due to either alkali-aggregate reaction (AAR), or delayed-ettringite formation (DEF - the expansive growth of hydrated calcium-aluminum-silicate macro crystals in hardened concrete) can be accelerated by:

1. Increasing the temperature of reactants.
2. Aging the specimens in an autoclave with elevated pressure and temperature.
3. Increasing the alkalinity and/or pH of the environment or the alkali-reactivity of the aggregate in the case of AAR, or increase sulfate, aluminum, or calcium concentration in the case of DEF.
4. Increasing the availability of water to drive swelling of alkali-silica gel, or to promote ettringite formation and expansion.
5. Crushing the samples to increase surface area for a given mass, or using a finer reactive aggregate or a finer cement.
6. Initiating the degradation process as soon as possible after casting the samples (to minimize the degree of microstructural development at the time the degradation begins).
7. Performing the accelerated test on concrete with a high porosity and permeability (usually obtained by a high water/cement ratio) to accelerate transport of the aggressive chemicals through the hardened cement paste microstructure to the reaction sites.
8. Applying stress to the concrete to cause microcracks that facilitate transport of aggressive media to reaction sites.
9. Conducting tests in association with other degradation mechanisms to hasten breakdown of microstructure. This facilitates transport of aggressive media and increases exposed surface area, and can be done by combining AAR, DEF, and freeze-thaw damage.

Specific experimental examples of factors that accelerate wood and metal degradation are graphed in figures 16 and 17.

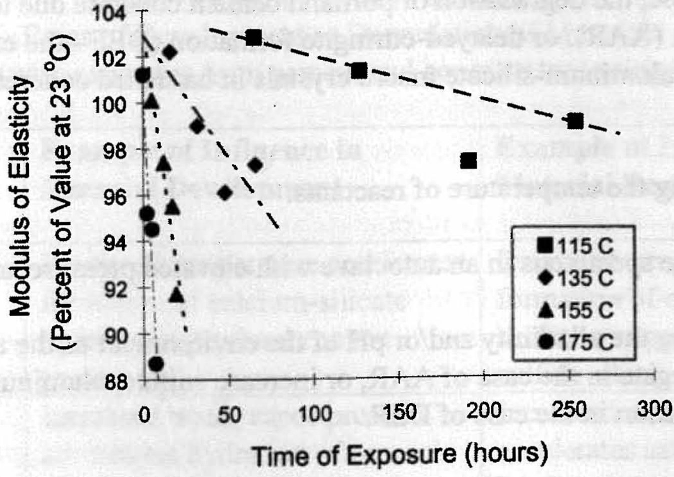


Figure 16 - Wood Modulus of Elasticity over Time at Different Temperatures (after 10)

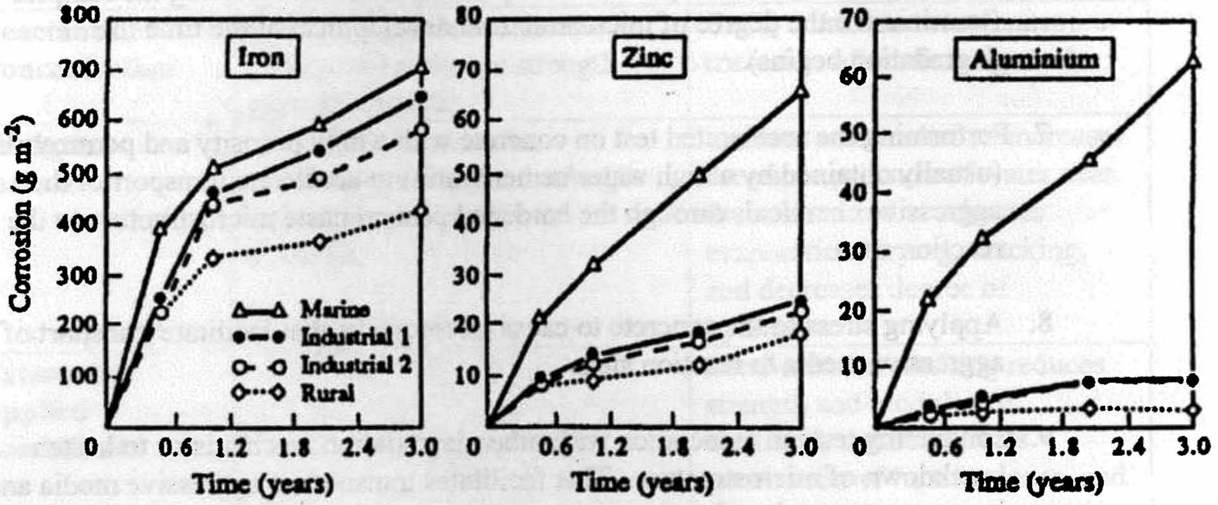


Figure 17 - Atmospheric Corrosion of Metals over Time in Different Locations (after 7)

An extension of figure 13, figure 16 illustrates the change in the modulus of elasticity of wood over time as a result of change in temperature. As mentioned above, the decrease in modulus is a result of thermal degradation of wood, dependent on the temperature to which the wood is exposed. Note that as the temperature is increased, the modulus is decreased, such that a given reduction in elastic modulus can be achieved in a shorter time by exposure to a higher temperature.

Similarly, figure 17 illustrates the corrosion of different metals over time as a result of exposure to salt solutions. In this case, the material degradation is a function of the reactant concentration, such as salts and acids. Note that as the location changes from marine to rural (i.e., highest concentration of reactants to lowest), the amount of material lost to corrosion decreases. Increasing the concentration of reactants can therefore accelerate corrosive degradation of metal.

1.3.3.3 Influence of Temperature

Temperature is commonly varied to accelerate aging methods since it is fairly easy to control and has a strong influence on the rates of chemical reactions. The main principle of thermal aging, as quantitatively explained in chapter 2, is that if a chemical reaction occurs at a certain rate at a given temperature, then it will occur faster at an elevated temperature, and that the relative rate increase can be predicted from the study of chemical kinetics. Thus, many chemically driven development or degradation mechanisms are accelerated in the laboratory by high-temperature exposure.

A specific example of thermal aging is shown in figure 18. In concrete materials, the term “degree of hydration” refers to the fractional extent of the reaction between cement and water, where degree of hydration of 100 percent ($\alpha = 1$) indicates that all of the cement has hydrated (a limit state rarely reached in concrete in actual service). Since hydration is a chemical reaction, it is influenced by temperature, as seen in figure 18. The extent of hydration is also an indication of level concrete development, since the hydration products interconnect to create the material microstructure. The results in figure 18 clearly show that increasing the temperature increases degree of hydration, which in turn accelerates microstructural formation.

Reflective of the many different materials and variables influencing aging, there are a large number of accelerated aging methods for both specific and general applications. In 1978, ASTM published a standard for developing accelerated test methods to aid prediction of service life of building components and materials - ASTM E 632 (12). The methodology presented in this standard has greatly influenced the development of several other methodologies for accelerated tests (13). Some of these methodologies and most of the ASTM accelerated test methods are reviewed in chapters 3 and 4.

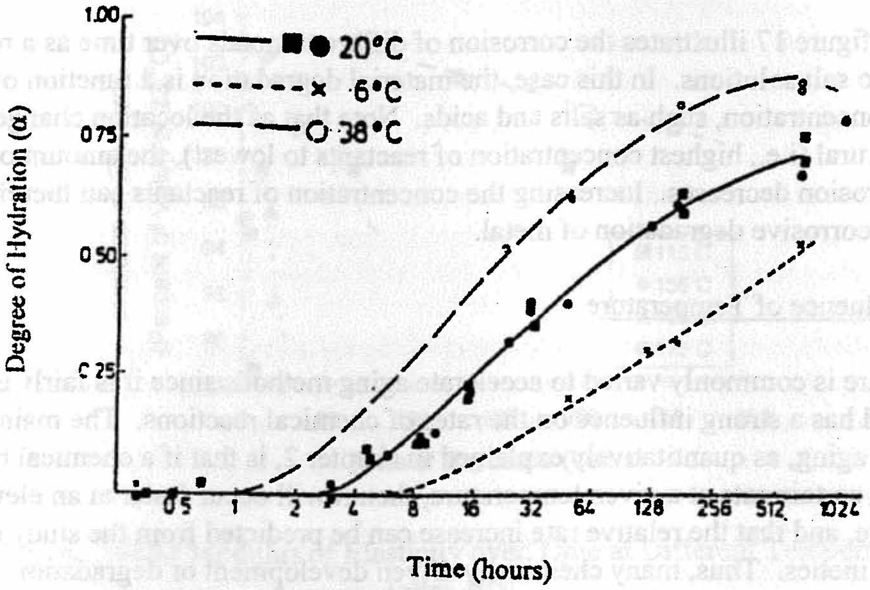


Figure 18 - Concrete Degree of Hydration over Time at Different Curing Temperatures (11)

1.3.4 Applications of Accelerated Aging

There exist two main uses of accelerated aging techniques. The first is for quality control and estimation of service life. In this case accelerated aging techniques are applied to *test samples* that have been selected to represent materials to be used in service. The long-term behavior of the material in service is then predicted on the basis of the short-term but accelerated behavior of the artificially aged samples. In portland cement concrete development, for example, test samples (of the same material used in a structure) are artificially aged to estimate long-term compressive strength. In a similar manner the long-term degradation (or resistance to degradation) of a material in service can be approximately predicted by artificially aging samples in an accelerated manner.

The second use of the accelerated aging is to intentionally modify a material prior to its use and exposure in service. In this case artificial aging is used to more rapidly produce a certain desirable property in the *material*. Aluminum is anodized to accelerate development of a tight oxide layer on the surface of the bare metal. Concrete masonry units and other precast concrete products are often steam cured under high temperature and, in some cases, high pressure to accelerate cement hydration and thus artificially age the materials prior to use. In cast-in-place concrete, heating the concrete can reduce the delay often associated with wintertime construction operations. Heating counters the slow rate of strength gain induced by low concrete temperature. Intentional creation of a degraded material is less common, but does apply to some materials such as plastics, in which accelerated biodegradability is desirable.

1.4 Principles

For both accelerated development and accelerated degradation procedures several considerations have been identified (12, 14). Fundamentally, accelerated aging methods should be designed to produce normal development and/or degradation mechanisms in a reduced amount of time. Effective accelerated aging methods must adhere to the following four principles:

1. Understand the development/degradation mechanisms.
2. Identify the factors influencing development/degradation.
3. Simulate natural aging processes so as not to create new mechanisms nor to interfere with those that would occur ordinarily under normal service conditions.
4. Recognize the possible interaction between simultaneous development and degradation processes.

Since complying with these four principles is challenging, all results from accelerated aging methods must be carefully interpreted and correlated with actual long term data.

The difficulties inherent in developing effective accelerated aging methods have their origin in the intricacies of the natural aging process. For example, in the case of a primarily mechanical process of degradation, such as fatigue cracking (externally applied load) or freezing and thawing damage (internally applied pressure due to ice formation), the results may vary depending on testing techniques. Increasing the intensity and/or frequency of the cycles of applied load can approximate accelerated degradation in these cases. When the intensity of a fatigue cycle is increased, however, cracks can be initiated that would not have been initiated at a lower stress level regardless of the number of load cycles. Similarly, increasing the frequency of load cycles can produce anomalous results whenever the increased frequency does not allow key restorative or degrading mechanisms to take place between load cycles. In the case of simple fatigue cracking of concrete, slowly applied load cycles permit time for autogenous healing of cracks.

In the more complicated case of cyclic freeze-thaw damage, slowly applied freeze-thaw cycles permit time for build up of ice accretion during the freeze-cycle, and time for permeation of water and deicing salts and the development of osmotic pressure during the thaw cycle. Faster cycle times therefore do not necessarily provide reliable accelerated aging in all cases. Correlation with field material performance is necessary for service life prediction.

In concrete materials, for example, workmanship and field conditions can significantly affect the potential degradation and performance of concrete in service. The workmanship and conditions may not be reflected in smaller scale laboratory specimens and testing (15). Concrete test samples employed in accelerated degradation processes do not always correspond to concrete in normal conditions because of inherent differences in curing, placing, or finishing techniques (16). In addition, special consideration should be taken when applying an accelerated degradation technique, since the degradation and development processes are intertwined. The accelerated degradation procedure, therefore, should be initiated only after a certain level of microstructural development has been achieved, such that the effects of artificially accelerated degradation mechanisms in the undeveloped material will be minimized.

1.5 Application to This Project

This research project seeks to understand and to predict the long-term environmental performance of PCC pavements containing coal fly ashes. The project will be evaluating long-term mechanical properties such as compressive strength, characteristics of the cement and concrete microstructure, durability-related properties such as frost resistance, and environmental stability issues such as the tendency for undesirable constituents of the fly ash to be leached from the hardened concrete. While it would be most useful to conduct such a study on pavement concrete exposed to a natural environment for a period of years, neither budget nor time is available to do so. It is desired, therefore, to artificially accelerate the aging of recently cast concrete specimens in such a manner that subsequent testing will reflect longer-term behavior of the material.

Elevated storage temperature is the principal means of accelerating the developmental aging of the concrete. This will increase the rate of the cement-water hydration reaction, and the rate of the pozzolanic reaction (a fly ash reaction in which amorphous silica, calcium-hydroxide, and water are the reactants). As a result of this acceleration, thermally treated test specimens will have a more advanced degree of hydration and a more advanced extent of pozzolanic reaction at the end of the thermal treatment period than will their counterparts stored at normal temperature. Following this artificially accelerated development of the material, the ASTM C 666 freeze-thaw test will be used to accelerate the degradation of the material in response to rapid cycles of freezing and thawing, while cycled loading will be applied to accelerate the formation of microcracks.

Following the principles outlined in the previous section, the first task is to identify and understand the mechanisms being accelerated. At a minimum these would include the following:

1. Hydration of portland cement.
2. Pozzolanic reaction of the fly ash.
3. The mechanism by which accelerated hydration and pozzolanic action changes microstructure so as to affect porosity, permeability, absorptivity, diffusivity, and rate of carbonation.

4. The mechanism by which accelerated hydration and pozzolanic action changes microstructure so as to affect compressive strength and other mechanical properties.

5. Both stabilization and de-stabilization of deleterious ash constituents in a developing hardened cement microstructure with changing transport properties.

6. Both stabilization and de-stabilization of deleterious ash constituents in response to changes in the chemistry of the internal environment of the cement paste, as calcium hydroxide is liberated by hydration of cement, and then subsequently reacts with silica in the pozzolanic reaction, and as the mobility changes for alkalis such as sodium and potassium.

7. The fundamental mechanism of freeze-thaw damage due to rapid cycling via ASTM C 666.

8. The fundamental mechanism of microcrack formation due to rapid cyclical stress.

9. The fundamental mechanism by which deleterious constituents of the fly ash are leached from the hardened cement concrete matrix.

Of the above mechanisms, sufficient information is currently available to permit a more or less reliable, quantitative estimate of the effects of artificial aging only for number 4 (development of compressive strength). Inferences can be made concerning mechanisms 1 through 3 (effects of hydration and pozzolanic activity). The industry has generally concluded that service life cannot be predicted from rapid freeze-thaw testing, except that successful performance in ASTM C 666 to 300 cycles generally suggests acceptable long-term performance in service. Failure at less than 300 cycles is generally not interpretable in terms of a tolerable number of natural freeze-thaw cycles or a prediction of number of years of satisfactory service life.

Returning to the aforementioned four principles of accelerated aging, identification of mechanisms is followed by identification of the factors most likely to affect those mechanisms. At a minimum, these would include:

Factors Influencing Development

1. Temperature

2. Availability of moisture

3. Reactivity of fly ash

4. Relative proportions of reactants

5. Extent of natural development prior to accelerated aging

Factors Influencing Degradation

1. Temperature

2. Extent of accelerated development prior to accelerated degradation

3. Availability of moisture, humidity, moisture content, degree of saturation

4. Minimum and maximum temperatures during freeze-thaw cycles

5. Duration of both freeze and thaw periods and cycle frequency

6. Duration and frequency of cyclic stress application

Of these factors, current knowledge permits reliable estimation of the accelerating effect of temperature only. Inferences can be drawn for the effects of moisture and freeze-thaw behavior.

The third principle is to avoid anomalous reactions in the accelerated aging process. For this reason the elevated storage temperature is being held to a maximum of 60 °C, so as to not initiate reactions that would not have occurred at lower temperatures, regardless of exposure time. While this temperature appears to be a safe limit for normal portland cement hydration reactions, questions remain, such as:

1. Will temperatures as high as 60 °C cause anomalous reactions in the fly ash or, more importantly, anomalous reactions with its deleterious constituents?

2. Will accelerating hydration in the presence of moisture drive the degree of hydration to values higher than experienced in service?

3. Will accelerating the typically slower pozzolanic reaction in the presence of moisture drive the degree of pozzolanic reaction to values higher than experienced in service?

The fourth principle of accelerating aging warns of possible interaction effects. Of the multiple possibilities in this project, the most significant is likely to be the interaction between accelerated hydration and pozzolanic reactions and the degree to which deleterious ash constituents are stabilized.

The main objective of this project is to assess the long-term environmental and structural effect of using fly ash in concrete pavements. Two benefits resulting from accelerated aging methods applied in this project are to gain insight into the mechanisms and factors involved in concrete/fly ash development and degradation and to determine the feasibility of using accelerated aging methods for long-term material performance. Ideally, the cumulative project results will not only be applicable to the specific model concrete pavements, but also will further scientific understanding of material behavior in general.

1.6 Organization

This report reviews the literature associated with accelerated aging of concrete and other construction materials. Chapter 2 addresses thermal aging, a widely used accelerated aging technique, especially significant for accelerating concrete microstructural development. Chapter 3 identifies development and deterioration mechanisms and their associated accelerating techniques for several construction materials. Chapter 4 focuses on accelerated aging of concrete, highlighting the effect of thermal aging on the microstructural development and explaining development/degradation mechanisms and accelerated test methods.

2. Thermal Aging

2.1 Introduction and Chemical Basis

Thermal aging is the most common accelerated aging technique for any material with chemically driven development/degradation processes. Thermal aging is based on the fact that most chemical reactions occur faster at higher temperatures.

The rate of a generic chemical reaction of the form:

$$aA + bB \longrightarrow cC \quad [1]$$

in which a, b, and c are the number of moles of reactants and products for a balanced equation, is often described by an equation of the form below (17, 18) called the rate law:

$$v = k_t\ [A]^n [B]^m \quad [2]$$

where:

v = rate of a chemical reaction (mol/s),
$[A],[B]$ = activity of reactants (mol/l),[1]
n,m = constants, often called reaction orders, and
k_t = factor assumed to be independent of concentration and time, called the rate constant.

The rate of the chemical reaction (v) in the equation above can be expressed in terms of either the disappearance of the reactants or the appearance of the product. Although in the simplest and ideal case the exponents n and m are equivalent to a and b, the rate equation cannot in general be inferred from the stoichiometric equation (19). The exponents n and m must be determined experimentally. The order of the reaction in terms of reactant A is given by n, while the reaction order in terms of reactant B is given by m. The sum of n and m is the "overall" reaction order, which defines the units of the rate constant.

Determination of the absolute rate of a reaction therefore requires experimental development of the "order" constants n and m, experimental determination of the activities, and experimental determination of the rate constant, k_t. It is often sufficient, however, to determine only the relative rate of the reaction under one particular set of conditions, for comparison with the rate at some other set of conditions. In such case, and assuming that as the conditions of interest vary the activities or orders of the reaction

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[1] "Activities" are the molar concentrations corrected for "interactions between the solute species in solution, and between the solute and the solvent" (19). The lower the molar concentration of the reactants, the closer are the values of activities and concentrations.

do not change, it is only necessary to compute the changes in rate constant k_t to make a statement about relative reaction rates. Thus, for most quantitatively accelerated aging processes, the actual rates of chemical reactions remain unknown, reporting only that aging conditions were maintained to increase the rate of development or degradation by a factor of "X times" relative to the rate under some other, or standardized, conditions.

2.2 Thermal Aging

2.2.1 Background

The influence of temperature on the rate of chemical reactions has been studied by many researchers since 1850 (20). In 1889, the Swedish chemist Svante Arrhenius found that in general, when there is a continuous supply of reactants, the rate constant obeys the following equation, known as the Arrhenius equation. According to many current texts, most chemical reactions approximately follow the Arrhenius equation (18-22).

$$k_t = A\ e^{-E/RT} \qquad [3]$$

where:

k_t = rate constant,
E = activation energy (J/mol),
R = universal gas constant (8.314 J/K-mol),
T = absolute temperature (K), and
A = constant or "frequency factor."

The idea of an activation energy for chemical reactions comes from the notion that molecules must possess a certain minimum amount of kinetic energy to react, following the Boltzmann distribution law (22). This energy is necessary to transform reactants into products. In exothermic reactions, like cement hydration, the reactants are in a higher energy state than the products. Activation energy is the difference between the energy required to trigger the reaction and the energy level of the reactants. The total heat evolved is equivalent to the difference in the energy levels of the reactants and the final products. Figure 19 illustrates this concept.

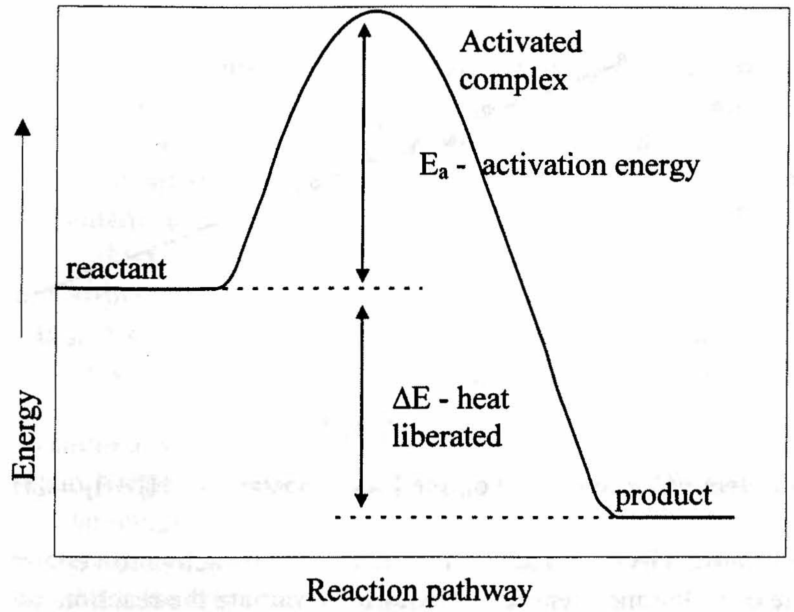

Figure 19 - Energy Profile during Reactions (after 17)

The energy is transferred through collisions of molecules. The frequency factor A is a reaction-dependent constant related to the frequency of collisions and to the probability that the collisions are favorably oriented for the reaction to occur, with atoms suitably positioned to form new bonds (17). Recall first that the measured temperature of a substance is actually the average temperature of the molecules present, and that the distribution of molecular energies about this mean is given by the Boltzmann distribution law (22). The higher the average temperature of a substance, therefore, the larger the number of molecules possessing the minimum kinetic energy necessary to react. Stochastically speaking, the higher the temperature, the greater the probability of a molecular collision that leads to a reaction.

Calculation of the activation energy is performed by experimentally obtaining reaction rates at different temperatures. According to Equation 3, when ln (k_t) is plotted against 1/T, a linear plot is obtained in which the activation energy is the slope divided by the universal gas constant. This plot is often referred to as an Arrhenius plot. Figure 20 shows the Arrhenius plot for the thermal dependence for a sample chemical reaction between $H_2(g)$ and $I_2(g)$. The activation energy thus calculated is 163 kJ/mol.

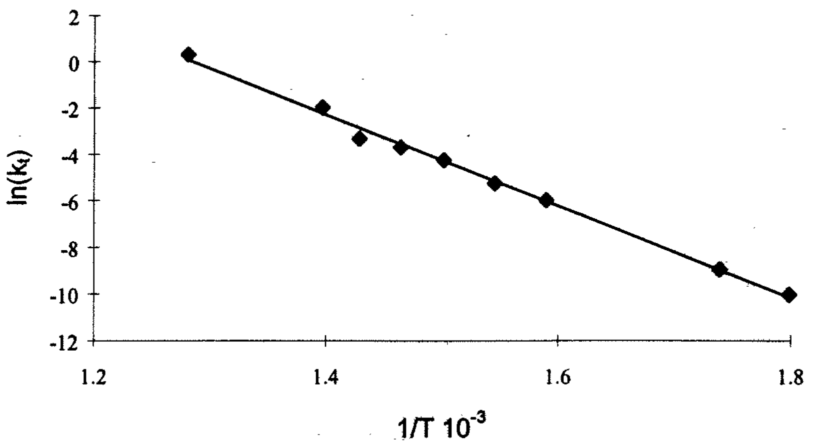

Figure 20 - Effect of Temperature on the Rate Constant for $H_2 + I_2 = 2HI$ (after 23)

The temperature sensitivity of a reaction is indicated by its activation energy (E). The higher the value of E, the more energy is required to initiate the reaction, meaning that the rate of the reaction will be highly sensitive to temperature. Figure 21 shows the influence of E on the rate constant. For example, the rate of a chemical reaction with an activation energy of 60 kJ/mol is nearly 20 times faster at 60°C than at 20°C. On the other hand, if the activation energy is 20 kJ/mol, the reaction rate is only about three times faster at 60°C than at 20°C.

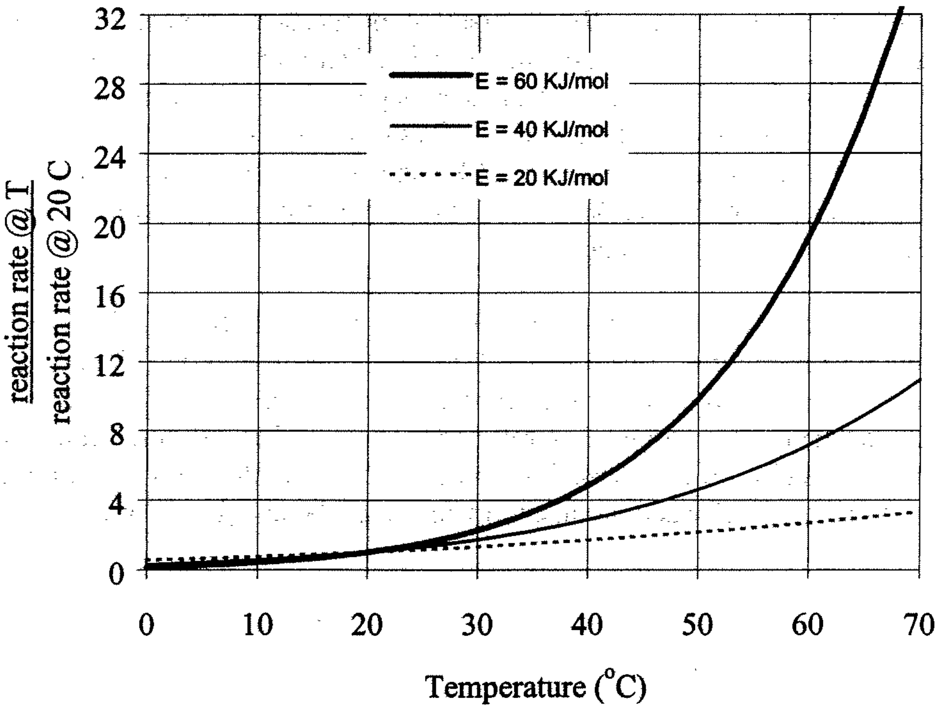

Figure 21 - Influence of Temperature on the Rate of Chemical Reactions

2.2.2 Application

The basis for thermal aging is that, for a particular chemical reaction of interest, if Arrhenius behavior is assumed and activation energy assumed or determined experimentally, the Arrhenius equation can be used to obtain rate constants as a function of temperature. Having determined a rate constant, and assuming that activities and orders of reaction remain constant over the range of temperatures selected, relative reaction rates can be obtained. Thus, elevated temperature is used to accelerate the aging processes, and the Arrhenius approach allows one to estimate how much further the aging processes have progressed than for specimens stored at some other temperature for the same duration of exposure.

There are several caveats when conducting Arrhenius-type aging. First, not all chemical reactions conform to Arrhenius behavior, i.e., the Arrhenius plot of figure 20 is not always linear over the temperature range of interest. Second, the assumptions that all factors in the fundamental rate equation (equation 2) remain constant with temperature is not always valid. Third, the rate equation assumes that there is always a constant source of reactants, at a concentration that does not vary with time. Similarly, Arrhenius assumes that temperature is the only factor that limits the rate of reaction. In many cases, however, transport issues ~~such~~ as diffusion of reactants or diminishing concentrations of reactants can modify reaction rate over time. Fourth, and finally, one must recognize the likelihood that as temperature is elevated, the resulting reaction process or products may differ from those at lower, more normal temperatures. As such, thermal aging procedures must recognize a maximum feasible temperature so as not to initiate anomalous reactions. Provided that proper limits are maintained, thermal rate equations have immense potential for accelerating aging of all types of materials.

3. Aging of Materials

3.1 Introduction

Accelerated aging techniques (for both development and deterioration) are applicable for numerous materials and products in all types of industries. This section highlights several materials, which, along with concrete, are the primary colors in today's engineering materials palette. In describing key accelerated aging techniques for each of these selected materials, this section is intended to provide an overview of current practices, rather than a comprehensive study. The information is organized so as to first identify the significant development and/or deterioration mechanisms, describe the associated accelerated tests and techniques, and discuss experimental results and evaluations. Considerations and problems associated with accelerated aging methods are presented following the material information.

In general, accelerated aging techniques were developed to predict and control material behavior and properties. Some of these techniques are intended to accelerate the developmental stage of a material, such as concrete or vulcanized rubber, either for quality control assessment or early use. The majority of these techniques are used to predict service life or durability, by simulating long-term exposure conditions in an abbreviated amount of time. Once informed of the expected material durability, the designer can adjust the design or material application as necessary to extend the lifetime of the product or structure. The remaining small fraction of these techniques is used to accelerate deterioration so as to intentionally shorten material service life, as in the case of biodegradable plastics.

3.2 Selected Materials

3.2.1 Metals

3.2.1.1 Introduction

Comprised of regular assemblies of metal atoms, metals are a versatile material used in numerous engineering applications. Metal atoms are characterized by their valence electrons, which are an integral part of the metallic bonds holding the different atoms together (17). The fact that the valence electrons are loosely bound to their atoms, however, means that they can be removed easily in chemical reactions (24). In particular, metallic materials are susceptible to oxidation-reduction reactions that cause the metals to deteriorate. This deterioration process, called corrosion, is a significant problem in many metals exposed to moisture and air. Since corrosion can be a very slow process, determining metal deterioration and service life over a long period of time is difficult. As such, many durability prediction studies for metals utilize accelerated aging techniques.

3.2.1.2 Mechanisms (24-27)

One type of metal corrosion, called wet corrosion, occurs when metals are exposed to a wet or moist environment. The defining electrochemical reaction of wet corrosion can be characterized by an anode, a cathode, and an electrolyte that connects them. Activated by a difference in potential, the metal anode corrodes, transferring electrons to the cathode, and then dissolves as metal ions into the electrolyte solution. The reaction at the cathode, which depends on the corrosive solution, consumes the electrons in a reduction reaction. In neutral or basic solutions, the cathode reaction is the reduction of oxygen; in acid solutions it is the reduction of hydrogen ions. Given sufficient electrons (i.e., the metal has not fully corroded), the speed of the cathode reaction depends on the diffusion of reducible atoms or ions from the corrosive solution. The rates of both the anodic and cathodic reactions and the diffusion reaction are accelerated with increasing temperature.

Two common examples of wet corrosion are an exterior metal surface in contact with acid rain or salt spray. Wet corrosion can also occur when metal elements are embedded in other materials, such as nails in damp wood or reinforcing bars in concrete, provided there is sufficient electrolyte to facilitate the reaction. All three cases lead to metal deterioration, often evident by visible corrosion products. When the metal ions react with the cathode, they form reaction products such as rust. Other times, the ions react with the electrolyte, leaving deposits in the medium.

Another metal corrosion mechanism that requires an electrolyte solution is called galvanic corrosion. This deterioration mechanism occurs when two metals of different potentials are connected by an electrolyte. The metal that is more reactive becomes the anode and the other is the cathode; the anodic metal corrodes first. The closer the two metals are physically and/or the larger the difference in their potentials, the faster the corrosion will proceed. The principle of galvanic corrosion is often used for metallic coatings (such as nickel on steel), in which a more anodic, sacrificial metal is used to protect the primary metal.

Corrosion of metals can also occur from exposure to gases. The most common example of this for metals is exposure to oxygen, which results in oxidation. In this mechanism, the surface metal atoms react with the adjacent oxygen molecules to create oxides as corrosion products. In some cases, the reaction produces sufficient oxides to form a thin layer that covers the entire metal surface and acts as a protective barrier against further corrosion. Such metals, including stainless steel, titanium, and aluminum, are called passive.

The chemical corrosions described above often occur in concert with mechanical deteriorations. Erosion corrosion, for example, results when a corrosive solution quickly traverses a metal surface, such as hard pounding acid rain. Stress corrosion cracking is the metal deterioration caused by tensile stresses and corrosion simultaneously. Metal deterioration from such combined factors is particularly critical, since the chemical and mechanical processes are mutually accelerating; corroded regions are more susceptible to stress and erosion, and erosion and stress cracking are more likely in already corroded regions.

3.2.1.3 Accelerated Deterioration for Durability Prediction

In general, procedures to accelerate degradation from exposure follow one of two methods (28) The first method is to increase exposure time to normally intermittent weathering conditions, such as maintaining continuous exposure to sunshine or rain. The other method is to increase the intensity of the exposure beyond that normally occurring, such as exposing a material to a highly concentrated acid, rather than the usual dilute level. In addition, exposure tests often utilize both options, in an attempt to maximize test effectiveness.

Since there are a vast number of metals and exposure conditions, there are a large number of associated accelerated corrosion tests. Most of the tests combine the two methods mentioned above, maintaining continuous exposure (or continuous cyclic exposure) to more severe conditions than normal. Regardless of method, the main goal of all these tests is to accelerate the corrosion process so as to simulate long-term corrosion effects in a reduced amount of time. Once the test samples are artificially aged, their material properties are evaluated and then compared with those of field samples or other aged samples.

One of the most common tests is the ASTM B 117 salt spray test method (29), which subjects specimens to a salt solution through a controlled fog mist at 35 °C temperatures. Designed to assess the performance of metallic coatings on metal (30), it can be used for ferrous and nonferrous metals, and best simulates the corrosive effects of outdoor exposure on automobile hardware (31). Two variations on ASTM B 117 are the ASTM B 287 acetic acid salt test method and the ASTM B 368 copper accelerated salt spray (CASS) test methods (32, 33). Designed for coatings that offer considerable corrosion protection, these procedures use a reduced pH environment to be about twice as corrosive as the standard ASTM B 117 method.

The ASTM D 2247 one-hundred percent relative humidity test method (34) subjects test samples to high humidity environments and elevated temperature. It is especially applicable to metallic surfaces exposed where water or condensation can accumulate. The variations on this test method [such as ASTM G 60, ASTM D 3459, and ASTM D 2246 (35-37)] allow for varied relative humidity levels, cycling humidity with corrosive liquid exposure, drying cycles, or drastic temperature variations. In conjunction with increased relative humidity and temperature, the ASTM B 605 sulfur dioxide test method (38) relies on the corrosive capabilities of concentrated sulfuric acid in the testing of otherwise corrosive resistant tin-nickel or other inert coatings.

In addition to isolated corrosion test methods, several ASTM standards combine both tensile stress and corrosion simultaneously to cause stress-corrosion deterioration. The

ASTM G 37 standard (39), for example, creates tensile stresses in copper-zinc alloys and then subjects them to an ammonia/copper sulfate solution simulating a moisture and ammonia vapor environment. The ASTM G 44 method (40), intended primarily for aluminum and ferrous alloys that are exposed to air, subjects samples to alternating cycles of immersion in an aqueous sodium chloride solution and then air drying. For similar alloys that contain little or no copper, the ASTM G 103 test method (41), which creates tensile stresses in Al-Zn-Mg alloys and then immerses the alloys in a boiling sodium chloride solution, was developed.

To supplement existing standards and better simulate actual environmental conditions, scientists have developed additional accelerated corrosion test methods. Altmayer (31) describes a lactic acid test procedure in which lacquered brass and copper alloys are tested for resistance to tarnishing by common handling (perspiration). The samples are immersed in a lactic acid solution, dried in air, and then suspended in an airtight chamber above an acetic acid solution. To better simulate dynamic changes in the environment, Sato et al. (42) developed an accelerated corrosion apparatus for stainless steel, which combines exposure to a sodium chloride solution, elevated temperature, and tensile load, all to adjustable degrees.

Not all accelerated corrosion test methods correspond to the entire service life of a material. To simulate just the early phases of atmospheric corrosion of aluminum-zinc alloy coatings, for example, Simpson (43) created an electrochemically monitored etching method. The method requires immersing the samples in an aqueous sulfuric acid solution and then selectively removing the chemically active phases that would corrode during the initial atmospheric exposure. Since this etching is comparable only to initial atmospheric exposure, its results can be used to predict field performance for a given time, but not service life or failure.

3.2.1.4 Results/Correlations

Correlation of accelerated laboratory data with actual long-term results is crucial to the applicability of accelerated testing results. Multiple research teams, two of which are noted here, have investigated these correlations. Drazic and Vascic (44) investigated two accelerated corrosion techniques in parallel with five-year field tests at an atmospheric corrosion station. Using two low alloyed Cr-Mo steels and two non-alloyed steels in the lab, they performed both an immersion test in an aerated sodium chloride solution and a salt chamber test. Simultaneously, they exposed similar samples at the high temperature, high relative humidity, salty, and windy atmosphere at an outside corrosion station. They determined that the accelerated laboratory results and field data were related linearly for up to two years and logarithmically between two and five years, thus allowing them to make more confident predictions.

Using available corrosion data at industrial and marine sites, Lyon et al. (45) completed a correlation experiment for the aluminum, galvanized steel, and steel components found in some overhead electrical power transmission conductors. To simulate the internal corrosion from chloride and the external corrosion associated with sulfate, they performed a cyclic wet/dry exposure test with the proper ratios of sulfate and chloride ions in salt spray solutions in a heated test cabinet. Comparing their results with field corrosion data, they determined that the wet/dry cyclic test method accelerates atmospheric corrosion rates of zinc (as part of the galvanized steel), steel, and aluminum by a factor of 25-50.

Based on literature review of the relationships between accelerated and atmospheric corrosion, however, Boelen et al. (46) found that, in general, such correlations were either poor or nonexistent. They concluded that, despite the amount of relevant data recorded, no accelerated test has yet simulated the results in natural environment conditions with either sufficient accuracy or reproducibility. To develop an accelerated corrosion test method or confirm the results of an existing one, therefore, they emphasized that one must acquire data of the actual corrosion parameters and an understanding of the particular corrosion mechanisms.

3.2.2 Polymers

3.2.2.1 Introduction

Although many materials can be classified as polymers, this section focuses specifically on plastics, rubbers, and polymeric organic coatings. Polymers consist of smaller molecular units called monomers, which are linked together in long separate chains. Although this linking, or polymerization, process is common to all polymers, individual polymer characteristics vary widely. In some types of polymers, the polymer chains remain entirely separate or only weakly connected such that the material is flexible or malleable. In other types, the polymer chains become cross-linked with the application of heat or pressure, creating a more rigid material (25). In all cases, the properties of the material are defined by the length, strength, and interaction of these polymer chains. To properly assess and accelerate polymer behavior, therefore, one must understand how development and deterioration mechanisms affect the polymer chains.

A critical issue in the study of polymers is the relationship between polymer deterioration over time and material service life. As such, a majority of accelerated aging tests for polymers are designed to predict material durability. In most cases, the deterioration of polymers (like the corrosion of metals) is a process to be prevented, or at least delayed, so as to extend the service life of the material; accelerated aging techniques are therefore performed on trial specimens to estimate durability so that the necessary precautions can be taken. In other cases, however, shortened service life may actually be desirable, such as for plastics that serve a single use and then are discarded; accelerated aging techniques are used in these instances to shorten the life (and landfill term) of the material. In addition, accelerated aging techniques are used to hasten the vulcanization process of rubbers (in which the polymer chains are cross-linked for additional material rigidity) so as to increase the material service life on the front end. The following discussion will focus first on deterioration mechanisms and associated accelerated aging practices, since deterioration is the main application of accelerated polymer aging. Information about the accelerated vulcanization process of rubber will be presented separately afterwards.

3.2.2.2 Deterioration Mechanisms (8, 25, 28, 47, 48)

The main factors that influence polymer deterioration over time are light (especially UV radiation), moisture, oxygen, heat, mechanical stresses, and microbiological organisms (though to a lesser degree). It is important to note that, while each of these factors can of its own accord cause polymer deterioration, the factors rarely, if ever, act individually in practice and often combine in a nonadditive manner. Typical polymer deterioration is therefore defined by multiple degradation mechanisms resulting from a combination of factors.

The deterioration of a polymer by exposure to light or radiation is called photodegradation. In simplified terms, this process causes bonds along the polymer chain to break and cross-links between polymer chains to form. The material undergoes shrinkage and becomes more brittle, and is thus more susceptible to moisture and temperature effects. In addition, photodegradation often causes material discoloration. Photodegradation reactions can be accelerated by increases in temperature.

When polymers are exposed to or immersed in water, the resulting chemical reaction is hydrolysis if the material is sufficiently hydrophilic. The bonds along the polymer chain break and the material swells, causing decreases in both modulus of elasticity and strength. In addition, moisture can enable the leaching of soluble products formed during other reactions.

Exposure of polymers to oxygen causes oxidative degradation. In this process, the oxygen reacts with and is absorbed by the polymer. The polymer chains grow in length (chain propagation) but branch and break in the middle, degrading their integrity. This process can be accelerated by the combination of both oxygen and heat (thermal oxidation) or oxygen and UV light (photooxidation).

The breaking of bonds along the polymer chain by thermal degradation requires temperatures significantly higher than ambient. (The threshold value varies for different polymers; for PVC it can be as low as 150°C.) In general, not even the maximum temperatures likely outdoors (60-80°C) are high enough to break polymer bonds. Instead, these serve to accelerate other reactions, such as caused by UV light or oxygen. As such, increased temperature is a major component in many accelerated aging techniques. The main difficulty with combining high temperatures with other deteriorating factors is that, if the temperatures are increased enough to activate thermal degradation and thus alter the deterioration mechanism, the end result may no longer simulate actual long-term conditions.

Resulting from such actions as cyclic loading or abrasion, mechanical stresses cause polymer chains to rupture. Materials with cross-linked polymer chains are more susceptible to mechanical stress deterioration since brittle materials are more prone to fracture than are flexible ones. Mechanical stresses are usually inversely related to temperature, since decreasing temperature leads to increased material rigidity.

Finally, biodegradation is a chemical deterioration process catalyzed by enzymes produced by microorganisms. This process is most efficient in environments with high relative humidity, warm to hot temperatures, and no light. For aerobic bacteria, supplemental oxygen is also necessary. Natural polymers are susceptible to biodegradation, but synthetic ones are often resistant.

3.2.2.3 Accelerated Deterioration Methods for Durability Prediction

As noted above, the majority of accelerated aging techniques for polymers are used to predict material durability or service life. Applied to test samples, these methods produce artificially aged specimens whose material properties are evaluated and compared with field materials following completion of the aging procedure. Like their counterparts for metals, many of these accelerated aging methods simulate long-term conditions by increasing the intensity of deterioration factors, either singly or in combination.

Two ASTM standards accelerate photodegradation of plastics by exposure to concentrated radiation, without additional assistance from temperature. Specifically for indoor materials, the ASTM D 4674 test method (49) was developed to test the color stability of plastics exposed to indoor fluorescent lighting and window-filtered daylight. In this test, the material color change is monitored as samples are simultaneously exposed to very-high output white fluorescent lights and intermittent energy from glass-filtered fluorescent UV sunlamps. The ASTM D 4364 procedure (50) accelerates outdoor weathering using concentrated natural sunlight. This test specifies the use of two Fresnel-reflector outdoor weathering machines, both of which incorporate a system of mirrors arranged to focus concentrated sunlight on a tray of air-cooled, mounted specimens. One of these machines performs the test without water to simulate desert, arid, and semi-arid exposure conditions. The other machine features a programmable water-spraying cycle simulating exposure in subtropical, semi-humid, and temperate regions.

Many of the remainder of ASTM accelerated aging tests for polymers combine different deterioration factors with temperature. The acceleratory effects of heat in polymer degradation are especially useful when increasing the intensity of a deterioration factor is difficult, such as exposure to oxygen or air. The ASTM D 865 test (51), for example, simulates thermal oxidation, by subjecting rubber samples to a specified elevated temperature (ranging from 70 to 250°C) in a closed test tube filled with air. As variations on this test, both the ASTM D 573 and D 1870 tests (52, 53) specify circulating (rather than stagnant) air with similar elevated temperatures. Two other ASTM tests, D 454 and D 572 (54, 55), utilize pressurized environments, or air and oxygen, respectively, in combination with elevated temperatures.

Several other ASTM methods utilize the effects of temperature to accelerate mechanical degradation and moisture deterioration (such as hydrolysis). The ASTM D 395 test method (56), for example, subjects rubber samples to compressive stresses at specified temperatures (from 70 to 250° C). The ASTM D 3137 test (57) combines high humidity (close to 100 percent) with 85° C temperatures to test the hydrolytic stability of rubbers. Finally, the ASTM D 756 method (58) documents seven different test procedures for plastics, six of which involve varying levels of elevated temperature (38 to 80° C) in combination with extremes of humidity (oven dry to 100 percent relative humidity), and one that exposes samples to alternating high and low temperatures (-57 to 80° C).

While these ASTM tests and others collectively include all the degradation mechanisms for plastic, no one standard test simulates true environmental exposure or weathering. The plastics industry, therefore, has developed several artificial weathering devices that attempt to incorporate more of the factors found in outdoor exposure. The Weather-Ometer, for example, uses a xenon arc source to simulate the effects of ultraviolet energy from sunlight, which can be applied in combination with varying temperatures and relative humidity (59).

Researchers at the Université Blaise Pascal in France (60) also developed two machines to test solid polymeric materials in accelerated conditions. The SEPAP 12.24 apparatus exposes samples to both intense light, from mercury sources filtered by borosilicate envelopes, and elevated temperature. A variation on the former model, SEPAP 12.26H exposes samples to similar conditions, but while rotating in aerated and thermoregulated water. Depending on the tested sample, the water can have several functions: as a mechanical abrasive on the outer layers, as a matrix swelling material, and as a chemical reactant.

Specifically for structural plastics in construction or building, Sasse and Schrage (1) designed a combined accelerated weathering and mechanical stress testing apparatus and method. In this test, samples are subjected to four-point bending stress, in which the tensioned areas are exposed to weathering. The loading can be either constant or stepwise changing so as to create the actual tensile stresses, and the weathering conditions are created by xenon lamp radiation, elevated temperature, and humidity.

3.2.2.4 Results/Correlations

When experimental results fit a governing equation, they can be used to predict behavior outside the range of experimentation. Since many polymer deterioration mechanisms are temperature sensitive, results from polymer accelerated aging tests often fit the Arrhenius rate-temperature equation. Pett and Tabar (61), for example, performed a thermal aging test on natural rubber vulcanizate specimens by heating them to different temperatures in an air circulating oven. Since their results matched the rate-temperature Arrhenius equation, they were able to predict long-term behavior of the rubber at any temperature. Likewise, Nichols and Pett (62) recorded the thermoxidative aging response of chlorosulfonated polyethylene and chlorinated polyethylene samples in an atmosphere of hot flowing air. They too found that the rate constants correspond to predicted Arrhenius behavior.

Although the Arrhenius equation is suitable for accelerated thermal experiments, it does not account for superimposed stresses. For the case of coupled temperature and stress, therefore, Vicic et al. (63, 64) identified several other possible expressions, by Bouche, Eyring, and Zhurkov. Although they noted several material experiments whose results were correlated with the above expressions, Vicic et al. emphasized that, since these expressions imply a constant activation energy, they may not be accurate when extrapolated to extreme conditions. Accelerated tests should therefore be performed on reference materials along with the unknown samples.

The predictive capabilities of accelerated aging techniques (whether or not they fit a rate equation) should be applied carefully, however, for their results are of no use if laboratory conditions were not an adequate simulation of long-term exposure. Indeed, if an artificially aged specimen experiences different deterioration mechanisms than its counterpart in the field, then its behavior is likely an inaccurate predictor of the service life or durability of the field specimen. Several of the ASTM methods described above advise that test results may not exactly correlate with field performance since conditions vary widely during natural aging. In addition, they note that results are useful as a means for judging service quality; further application requires correlation with actual results on a case-by-case basis.

This great need for studies that correlate laboratory results with long-term field data (as noted in the section on metals) is central to all accelerated aging techniques and applications. One such correlated study was performed by the Cleveland Society for Coatings Technology Technical Committee (65, 66) in a multi-phase experiment on polymeric coatings systems. In this long-term study, the committee members tested nine different coatings systems in nine exterior exposure sites and with five accelerated test methods. The exterior sites, which were located throughout the country, represented heavy marine exposure, heavy industrial exposure, heavy smog, and high humidity and rainfall.

All of the accelerated test methods either were in use at the time or had been proposed as alternatives to existing methods. The first test was the standard ASTM B 117 salt spray test. Two other tests involved cyclic wet/dry fog exposure tests, one with a sodium chloride spray and the other with a solution of ammonium sulfate and sodium chloride. The fourth test alternated the aforementioned cyclic wet/dry fog test with a UV/condensation exposure test, in which samples were subjected to heat combined with cycles of UV light and condensation. The final method combined three cycles: immersion to specified electrolyte, drying, and UV radiation.

The results from the accelerated tests (run from 1000 to 2000 hours, depending on the test) were compared first with those from the exterior exposure sites at the end of 6 months. Only the fourth test showed significant correlation with natural weathering. To allow for greater differentiation after longer exposure, the accelerated test results were then compared with the one-year exposure results. At this time, the correlation between the fourth test results was even stronger, but the correlations between the other test results and the exterior ones were weaker than they had been at six months. Based on these results, the researchers concluded that correlations may be maximized at a certain level of weathering and then weaken as the weathering progresses. The research team is currently considering the effects of additional exposure time, stronger irradiance, as well as the use of undercured specimens as the test continues.

3.2.2.5 Accelerated Deterioration Methods for Reduced Material Life (8)

In addition to being used for durability prediction, accelerated aging techniques can be applied to field materials to intentionally shorten their service life. Most of these practices involve material additions to the polymer. Photodegradation, for example, can be accelerated by adding a photosensitizer that has a high absorption coefficient for UV light. When this compound decomposes it helps stimulate the photodegradation reaction. Biodegradation can be accelerated in a similar manner, by adding molecules to the polymer chain that are susceptible to microbe attack or by combining the polymer with biodegradable materials.

3.2.2.6 Accelerated Development of Vulcanized Rubber (67)

Comprised of randomly coiled, yet separate, polymer chains, rubber initially exhibits plastic behavior, in that it retains its deformed shape after loading. When mixed with hot sulfur, however, the rubber experiences irreversible chemical and physical changes. During this process, called vulcanization, polymer chains form cross-links and the material becomes predominantly elastic instead. Many rubbers used in practice are vulcanized so that they behave elastically.

The process of vulcanization (or curing) occurs slowly, since sulfur occurs in a stable ring and must be made active to react. There are naturally occurring materials in rubber that accelerate these reactions, but the resulting process is still quite slow. As such, natural rubbers are often supplemented by additional organic and inorganic accelerators. A number of these accelerators and their properties are described in ASTM D 4818 (68). Synthetic rubbers tend to cure even more slowly than their natural counterparts, so they are candidates for even more powerful accelerators.

Accelerators are useful to speed up the vulcanization process, but they can be detrimental to the final material if not applied carefully. In many cases, use of the fastest possible accelerator will not yield the optimum end material with a maximum tensile strength or modulus of elasticity. During the vulcanization process, heat is applied first to the exterior of the material and then conducted slowly to the interior. If vulcanization proceeds too quickly, there is a danger that the outer layers of material will be fully vulcanized before the inner layers even begin to react; slower accelerators should therefore be used with thicker materials. In addition, since rubbers are not always vulcanized directly after formation and vulcanization preparation, a fast accelerator may cause vulcanization while the material is in storage.

3.2.3 Asphalts

3.2.3.1 Introduction

A subset of bituminous materials, asphalts are comprised of aggregates bound together with bitumen or tar. The binder bitumen is produced naturally from petroleum or in crude oil distilling refineries. Bituminous materials are then formed by combining aggregates with bitumen in a hot mixing process (25). Although bituminous materials are commonly used as road pavements, they can also be used (with or without additional aggregate) as either roofing materials or waterproof coatings.

During both the initial hot mix process and the material's subsequent service life, asphalts experience hardening of the bitumen binder. Some of this hardening is beneficial, for it provides the material with sufficient rigidity for service. Over time (and with increasing exposure to air, heat, and light), however, the hardened material becomes brittle and thus susceptible to cracking and further mechanical degradation. Thus, the hardening of asphalt is both material development and degradation. Since the degradation process is significantly slower, the main application for accelerated asphalt aging tests is durability and service life prediction.

3.2.3.2 Deterioration Mechanisms (25, 69-72)

A number of different mechanisms cause the hardening of asphalt over time, the most influential of which are volatilization and oxidation. In the first mechanism, volatile components diffuse to the surface of the material and then evaporate. This decreases the low molecular weight fraction of the material and thus increases its viscosity. In the second mechanism, resins in the asphalt combine with oxygen in the air to create new molecules called asphaltenes. The incorporation of asphaltenes into the asphalt structure increases the high molecular weight fraction of the material, also increasing its viscosity.

Both of the aforementioned mechanisms can be accelerated with increasing temperatures (and oxidation is also catalyzed by UV and IR radiation). Since temperatures during the hot mix process are significantly higher than those during field service, both volatilization and oxidation occur faster and to a greater extent during mixing. Yet, it is worth noting that the nature of the reactions and oxidation products differ at the two temperatures (80° C outside maximum vs. 200° C mixing temperature).

3.2.3.3 Acceleration Deterioration Methods

The two most common accelerated asphalt aging tests, both of which are documented in ASTM, are the thin-film oven (TFO) and its variation, the rolling thin-film oven (RTFO) tests (73, 74). Outlined in ASTM D 1754, the TFO test heats asphalt films to 163 °C in an oven for 5 hours. Likewise, the RTFO test (ASTM D 2872), follows the same procedure with films moving in rolling containers, so as to increase the sample exposure to oxygen. Measurements of viscosity, permeability, and ductility for the artificially aged samples are taken upon completion of the test, for comparison with data from other aged and field samples.

A number of other asphalt aging tests, initially inspired by the TFO and RTFO tests and then modified over time, have been developed (9) A microfilm durability test (at 107 °C for 4 hours) was developed to approximate the actual thickness of the film in asphalt concrete mixes. This test was subsequently modified to reduce the temperature to 99 °C and increase the time to 24 hours. A further modification (the rolling microfilm oven - RMFO - test) specified that the film be deposited on the inner surface of an RTFO bottle and aged using an RTFO oven, so that the sample remain agitated during testing.

A separate test was developed to age samples oxidatively at 130 °C for 24 hours by passing hot air through a gas chromatographic column. The uncertainties in data from both this test and the RMFO test as a result of possible volatile loss inspired a further modification of the RMFO test to include a calibrated capillary tube that controls the volatile losses. The main problem with this last modification was its limited use resulting from a very small asphalt sample size of 0.5 g. As a response to this, an alternative thin-film alternative accelerated aging (TFAA) test specifying instead a 4-g sample was developed. In this test, samples are dissolved and heated at 133 °C for 3 days in rotating RTFO bottles fitted with capillary tube stoppers. The 113 °C temperature for the TFAA test was chosen to correlate results with those from another test, the California tilt oven test. Named for its simulation of California's desert climate, this test is a variant on the RTFO test, in which the asphalt sample is contained in an RTFO bottle in a slightly tilted oven, but at 113 °C for 7 days.

3.2.3.4 Results/Correlations

According to Petersen (9), the ASTM tests may not accurately simulate long-term asphalt aging, since they were designed to reflect the hardening during only the hot mix process. In these tests, samples often experience more volatile loss and less oxidative aging and hardening than they would in the field over time. These shortcomings were partially the motivation for Petersen to develop the TFAA test. Although the oxidation kinetics in the TFAA test do not necessarily reflect those in the field, the level of oxidative hardening and the amount of volatile loss were found to be consistent with field-aged asphalt samples.

In contrast to skepticism of TFO and RTFO long-term estimations, Huang et al. (75) identified more recent research concluding that even in high-temperature accelerated tests, asphalt aging mechanisms were very similar to those in the field. As such, Huang and his coworkers performed a multi-phase accelerated aging test with four methods: the TFO and RTFO tests, the California tilt oven test, and the Strategic Highway Research

Program (SHRP) pressure air vessel test. The SHRP pressure vessel test subjects samples simultaneously to increased air pressure of 300 psia at a temperature of 100°C. They tested samples representative of a specific field asphalt via all four methods, so as to compare the four accelerated methods against field aging. In general, they concluded that all artificially aged samples had rheological properties similar to the specimens aged in the field in Florida. Specifically, results from an RTFO test at 185°C for 75 minutes match those of 1-year field aging, whereas a 168-hour California tilt oven test simulates 8-year field aging (in typical Florida conditions).

To enhance the predictive capabilities of the aforementioned accelerated aging methods, Ishai (76) proposes extending them to include a wide range of both time and temperature. As they exist now, these methods are known as "single-point" evaluations, in that they artificially age a material by exposing it to a single level of temperature for a single length of time. Although the results from such procedures can be correlated with those of a specific asphalt in a given location and season, they do not adequately reflect the inherent variability in environmental conditions or material characteristics. If, however, these methods were to incorporate data for numerous time and temperature combinations rather than rely on only single-point determinations, they would establish a family of aging curves, applicable to a number of different environmental and material conditions. Ishai suggests that proper interpretation of these aging curves would enable laboratory aging methods to be calibrated based on field aging.

3.2.4 Wood

3.2.4.1 Introduction (77)

A heterogeneous cellular material, wood consists primarily of three main polymeric components: cellulose, hemicellulose, and lignin. Cellulose, which comprises about 50 percent of most woods, is a linear polymer formed from glucose monomers. About 25 percent of wood is hemicellulose, a pentose and hexose polysaccharide without a high degree of polymerization. Lignin, the remaining 25 percent, is a three-dimensional, strongly bonded polymer that acts as a binder for the other two components.

Although a method to accelerate the growth of trees (and thus the availability of wood products) would be useful, the main application for wood accelerated aging techniques is currently for durability prediction. Like all other materials, wood deteriorates over time, with the rate of deterioration dependent on the levels of exposure to degrading factors. The two main categories of wood degradation factors are weathering (light, air, heat, and moisture) and biological (fungal, insect, and animal) effects. Unlike most other materials that are more prone to the effects of weathering, wood is predominantly susceptible to biological attack. Without exposure to these biological factors (i.e., weathering alone), wood would experience primarily a surface deterioration, only ranging from 6-13 mm per century (77). When biological and weathering effects are coupled, however, wood can experience significant deterioration and decay, especially when the weathering environment provides favorable conditions for fungal attack.

3.2.4.2 Deterioration Mechanisms (25, 45, 77, 78)

The mechanisms resulting from weathering can be divided into those caused by light, air, heat, and moisture. Exposure of wood to UV light triggers an absorption of the radiation energy, causing polymer chain scission and often contraction of the cell walls. The most common impact of radiation on wood is a visible color change, but radiation can also cause structural degradation. Exposure to oxygen causes oxidation reactions, which likewise cause the breakage of polymer chain bonds. Exposure to temperature causes a thermal degradation known as pyrolysis, resulting from the degradation of the cellulose and hemicellulose polymers and breakage of the lignin side chains. For the most part, moisture causes wood to shrink and swell as a result of water absorption and hydrolysis reactions. In addition, water can also facilitate leaching and cause color changes.

While each of the weathering factors has an individual effect on wood, the factors most often work in combination to enhance the individual mechanisms and create new ones. Both photodegradation and oxidation, for example, are accelerated by increasing temperatures. In addition, since exposure to high temperatures often activates hydrolysis (among other chemical reactions), pyrolysis is accelerated by increasing relative humidity. Perhaps most importantly, the combination of the weathering factors (especially moisture and air) facilitate biological degradation.

As noted above, deterioration of wood over time is primarily a result of biological factors, from fungi and bacteria to insects and animals. Most fungi cause chemical reactions and/or degradations in wood. Some fungi, such as molds, live only on the material surface so as to produce color changes or staining, but not to affect material strength. Others, such as rots, attack the interior cellular structure; the enzymes they secrete cause chemical decomposition, which results in structural decay. The impact of such decay fungi is highly dependent on the environmental conditions, as noted previously. Fungi have four basic requirements to live: air, water, moderate temperatures, and a food source. Of these, moisture is the most significant; wood kept entirely dry will never decay from fungal attack.

Less dependent on the surrounding environment, insects and animals are predominantly responsible for mechanical degradation of wood. Most insects and animals attack wood by boring tunnels through it. These tunnels weaken the structural integrity of the wood and can cause partial or full structural collapse. Some of the creatures, such as termites, larva, and shipworms, actually consume the wood for food as they tunnel. Others, such as carpenter bees, require the tunnels for shelter only, and deposit rather than eat all tunnel excavations. Woodpeckers and rodents cause similar mechanical damage to wood in their attempts to excavate nests and dwellings.

3.2.4.3 Accelerated Deterioration Methods

One way to accelerate the weathering of wood is to use controlled humidity and temperature tests. Two ASTM standards, D 1037 and D 2164 (79, 80), outline a series of accelerated aging procedures that comprise a multiple-cycle test for wood samples. In each of the six complete cycles, the samples are immersed in hot water, exposed to steam and water vapor, stored in cold air, and heated in dry air, then steam/water vapor, and then dry air again. These tests are intended to simulate the aging of wood samples under severe exposure conditions, such as those experienced after several years of extreme weathering. Material properties of the artificially aged samples are measured and compared with those from unaged samples.

A variant on the aforementioned tests, the ASTM D 2898 test (81) is intended specifically for fire-retardant-treated wood. The two methods that comprise this test simulate accelerated weathering degradation by leaching, drying, temperature, and UV light. In the first method, developed for larger specimens, the treated wood samples are subjected to 12 1-week cycles that each consist of exposure to water spray followed by drying in a hot air flow chamber. The second test subjects samples repeatedly to a 24-hour cycle that alternates wetting and drying twice and then a period of rest. The wetting process is the same as the uniform spray in the first method, but the drying segment relies on direct radiation from UV sunlamps to elevate the temperature. Upon completion of the aging procedure, the fire resistance of the artificially aged samples is evaluated.

Accelerated tests can also simulate biological attack over time. The ASTM D 2017 test (82), for example, was designed to determine the natural decay resistance of wood through accelerated fungal decay. In this test, wood blocks are conditioned with steam and then exposed to pure cultures of decay fungi in a decay chamber. The percent weight loss of the blocks, a measure of decay susceptibility, is recorded over time. Since this test is primarily quantitative, its results are not intended for comparison with long-term aged samples. Rather, the test is useful to determine more rapidly the relative decay resistance of different wood samples.

3.2.4.4 Results/Correlations

Recognizing the possibility of low pH environmental conditions, Williams (83) investigated the effects of acids on wood subject to accelerated weathering. He used a weathering chamber with xenon arc radiation to simulate natural solar radiation and dilute acid solutions to create the low pH environment. (His choice of radiation as a weathering method was based on the fact that previous accelerated weathering studies that had used accelerated xenon arc weathering produced lab results in good correlation with those of naturally aged samples.) In his test method, samples were repeatedly immersed in one of five acid solutions of different pH levels (or in the control solution of distilled water) for 1 hour and then placed in the xenon arc weathering chamber for 25 hours.

The sample weight loss was monitored over time, as a measure of surface erosion. Results from the experiment show that the surface erosion of wood can be accelerated with a decrease in pH. Specifically, specimens immersed in a sulfurous acid solution of pH 2.0 weathered twice as quickly as the control group, a difference noticeable within the first 100 hours of the experiment. Upon further investigation, Williams concluded that the acid solution caused both polymer degradation of the lignin and hydrolysis of the hemicellulose, leading to accelerated material deterioration. Hence, wood is susceptible to low pH environments, and may experience accelerated weathering in regions with acid rain or additional acidic moisture.

3.2.5 Masonry

3.2.5.1 Introduction

Traditionally referring to structures made of natural stone, the more current definition of masonry encompasses all structural assemblies of rock, brick, and concrete pieces both with and without mortar. Many masonry structures are closely related to concrete ones, for they contain concrete blocks and chunks and/or are bound together by portland cement or lime cement mortars (25) Details on the development and degradation processes and associated accelerated aging techniques for these materials can be found in chapter 4 on concrete. This section will address all masonry products that do not contain any cement or cement-based materials.

Excluding cement and concrete materials, the main application for accelerated masonry aging is durability prediction. Masonry is susceptible to many environmental and exposure factors and does indeed deteriorate over time. Since this deterioration process is often extremely slow, perhaps even imperceptible on a human time scale, determination of durability and service life of masonry requires the use of either accelerated aging techniques or good extrapolated data predictions.

3.2.5.2 Deterioration Mechanisms (25, 84-87)

The majority of, and often most damaging, masonry deterioration mechanisms are in some way a result of water. One such mechanism that is most pronounced in porous masonry is freeze-thaw (or frost) action. Either in its liquid form or as a condensed or adsorbed gas, water penetrates the pores of the material and then expands (about 9 percent at 0 °C) when it freezes. The expansion creates pressure in the pores that often induces cracking. Susceptibility of masonry to freeze-thaw damage is dependent on material porosity and pore structure. Materials with a low porosity may be fairly resistant (at least initially) to freeze-thaw damage, whereas those with a large number of primarily fine pores are the most at risk.

A second deterioration mechanism that necessitates water is salt crystallization. Soluble salts are dissolved in the water, which penetrates into the masonry pores and then recrystallize when the water evaporates. Some hygroscopic salts will absorb water when the surrounding relative humidity is high but then recrystallize if the relative humidity drops. In addition, the solubility of most salts is a function of temperature; salts often redissolve when temperature is increased and then the salts recrystallize when temperature is decreased. In all cases, the crystallization of the salt exerts pressure on the pores and causes cracking, as occurs in the freeze-thaw case.

The deterioration caused by acid rain is closely related to salt crystallization for some stones, such as limestone and marble. In this deterioration mechanism, sulfur dioxide gas combines with water and oxygen in the air and calcium carbonate in the rock to form calcium sulfate as gypsum. This process is damaging to the stone primarily because it destroys the stone's calcite matrix; crystallization of the gypsum can also cause the stone to crack. Gypsum attack and acid rain effects are greater in seaside areas in part because the solubility of gypsum is increased in salt water, and also because the greater surface moisture from the hygroscopic salts promotes sulfur dioxide deposition.

In addition, some masonry materials have components that are soluble in water, such that the repeated application of water will slowly dissolve away the material. The calcium carbonate in limestone, for example, can be dissolved by rain water that contains dissolved carbon dioxide.

Masonry is also susceptible to deterioration factors that do not include water. When masonry is exposed to abrasive particles carried by the wind, it suffers a surface mechanical deterioration called wind erosion. Some masonries experience thermal degradation when exposed to increased temperatures; marble crystals, for example, expand longitudinally and contract transversely with increased temperatures, causing compressive stresses and tensile cracking. In addition, many masonries undergo mechanical degradation and cracking as a result of animal burrowing and plant and tree root growth. Although these factors can each cause masonry deterioration in its own right, their primary significance is that they facilitate further decay from water-based mechanisms. Likewise, cyclic processes, such as wet/dry or heating/cooling cycles, are unlikely to cause material failure, but instead aid other deterioration mechanisms.

3.2.5.3 Accelerated Deterioration Methods

The ASTM methods for accelerated deterioration of stone were designed specifically for erosion-control rock, an application for which material ability to resist weathering is crucial. Both ASTM D 4992 and D 5313 (88, 89) outline wet-dry accelerated weathering tests intended to simulate cycles of rainfall and drying sunshine common in summer. In these tests, rock samples are subjected to repeated cycles of soaking in water and then drying by infrared heat lamp or oven. Specific temperatures and times for the cycles should be varied to reflect the conditions of the test site. Evaluation of the artificially aged samples includes percent weight loss calculation and a visual examination.

Similar tests, but for winter conditions, are provided in the ASTM D 4992 and D 5312 (90) freeze-thaw test methods. In these tests, alcohol-soaked rock samples are subjected to alternating cycles of freezing and thawing. Again, appropriate temperatures and times will vary for different climatic conditions, and should be decided by the user. ASTM D 4992 also contains a variant on the aforementioned freeze-thaw test that uses sodium or magnesium sulfate. In this cyclic test, rock samples are repeatedly immersed in saturated solutions of sodium or magnesium sulfate and then oven dried. Although not a freeze-thaw test, this test is intended to simulate indirectly the accelerated freeze-thaw deterioration of rock. Evaluation of the artificially aged samples, as described above, may be conducted upon completion of the aging procedures.

According to Carr et al. (91), employees of Wiss, Janney, Elstner Associates suggested a "Proposed Accelerated Weathering Test for Stone." In this accelerated test method, stone samples are subjected to 100 rapid freeze-thaw cycles while immersed in a 4.0 pH sulfurous acid solution. The samples' length change, fundamental transverse frequency, and various mechanical properties are measured periodically throughout the procedure. Although submitted as a potential new standard to the ASTM C 18-07 Committee on Environmental Properties, Behavior, and Cleaning in 1991, the proposed method has yet to be officially accepted. Initial concerns about this test included the difference between the accelerated and actual weathering procedures and the impact of immersing calcareous stone in sulfurous acid.

3.2.5.4 Results/Correlations

In addition to durability prediction, another use for accelerated aging tests of masonry is to determine the compatibility between new materials and already aged materials. This is particularly significant for monuments, in which old bricks or stones must be replaced with aesthetically and structurally compatible new ones. To this end, Binda and Baronio (92) performed two accelerated aging tests on new bricks. In a freeze-thaw test they subjected new brick samples to cycles of immersion in 35 °C water for 3 hours and then exposure to -10 °C air for another 3 hours. In the salt crystallization test, the dried samples were immersed in a saturated sodium sulfate solution and then left to dry in 20 °C conditions, first at 85 percent and then 50 percent relative humidity. Based on strength tests of the old and artificially aged bricks, Binda and Baronio were able to choose replacement bricks with durabilities compatible with the bricks already in the structure.

3.3 Considerations and Problems

Intended to accelerate both development and deterioration processes, accelerated aging techniques have been applied to many materials in numerous situations. The preceding sections have highlighted the use of such techniques for several fundamental engineering materials. Perhaps more importantly, however, these sections have also identified several important lessons regarding the applicability, or lack thereof, of accelerated aging practices.

A fundamental component of accelerated aging practices is a strong understanding of the material's development and/or degradation mechanisms. A large portion of the preceding sections was devoted to explaining possible mechanisms for each material, to show how they vary for different materials and situations. Prior to developing or applying an accelerated aging technique, one must identify the governing mechanisms for that particular situation, for one cannot easily accelerate a process that one does not understand!

Once knowledgeable of the mechanisms, one should develop and apply the accelerated aging techniques so as to accelerate these, and only these, same mechanisms. In other words, accelerated aging practices should neither incite any reactions that would not ordinarily occur, nor impede those that would. To ensure such results, one must recognize that reaction rates are not always directly related to exposure severity; accelerated aging practices have limits. This lesson is particularly relevant to thermal testing, for increasing temperatures too far will alter the deterioration or development mechanism.

A prime example of these limits is compost. The result of organic matter decomposing, the development of compost is facilitated by microbial action. These microbes perform best in moist, warm, and anaerobic conditions, but beyond this set of optimum conditions, their performance does not increase. In fact, if the temperature is elevated too high, the microbes will simply die and the compost development process will halt (93). As such, accelerated aging techniques for compost must acknowledge the necessary limitations of exposure parameters.

Since deterioration and development mechanisms are material specific, two materials may behave quite differently under the same exposure conditions. As such, an accelerated aging technique that is appropriate for one material may be completely unsuitable for another. Organics and inorganics, for example, behave quite differently, as evidenced by misapplication of a salt spray test (30). The ASTM B 117 salt spray test was originally developed for durability prediction of metallic coatings on metal. Since its results were promising for metal, its application was extended to organic coatings. The deterioration of exterior organic coatings, however, is caused by light, temperature, and oxygen, and not by corrosive salt solutions (as is the case for metal). No wonder, then, that when Skerry and Simpson (94) tested several organic coatings using the salt spray test and other metal-corrosive solutions, they found that their test results did not match those of the natural environment.

In addition to simulating the specific development or deterioration mechanisms for a given material, accelerated aging practices must also reflect the specific exposure conditions for a given site. Indeed, a salt spray exposure test of metal corrosion is much more relevant for a marine or industrial site than it is for a rural, landlocked location.

Likewise, the polymer degradation from exposure to severe relative humidity may be indicative of field performance in Florida, but not nearly so for Arizona. Environmental conditions not only vary by location, but they also change over time, making the simulation of long-term weather patterns very difficult. As such, lab tests that accelerate deterioration from exposure should always be correlated with field aging, to ensure accuracy of results.

In short, there is no universal accelerated aging technique applicable for all materials, nor can any single technique perfectly accelerate material behavior. The best accelerated aging practices are those that consider the material's development or deterioration mechanisms, the relevant factors, and location, but results from even these tests should still be correlated with actual field data. Despite the inherent difficulties in their creation and limitations in their application, accelerated aging techniques are an important part of material research and development. They can be used to hasten the development of a material, so that it can be put into service more quickly. They can also be used in durability prediction, by accelerating the deterioration of test samples to simulate long-term behavior. And, as the production of materials and products begins to overwhelm the earth's capacity, accelerated aging techniques may increasingly be used to speed material deterioration, so as to minimize landfill waste. The bottom line is that no material is immutable, and all experience changes over time. As long as there is a need to control or predict these changes, accelerated aging techniques will remain a valuable asset to engineering materials research.

4. Aging of Concrete

4.1 Introduction

Since concrete experiences time-dependent hydration of cement and the resultant development of microstructure, accelerated aging methods include those that speed up such developmental processes, as well as methods that accelerate subsequent degradation. Accelerated aging therefore, facilitates prediction of both long-term development and long-term degradation.

To accelerate microstructural development, an understanding of the factors governing the rate of formation of the microstructure is necessary. The development of the internal microstructure in concrete is a physical consequence of the hydration of cement particles and the reactions of supplementary cementing materials. The reaction products, insoluble hydrates, form a cohesive matrix or microstructural skeleton. The progressive development of this microstructure is caused by the continued growth of the resultant hydrates, occurring within the initially porous skeleton. Like most chemical reactions, the rate of hydration of cement depends on the concentration and the temperature of the reactants (see equation 3). The rate of reaction is sped up at high temperatures and slowed down at low temperatures. As a consequence, concrete temperature greatly influences the rate of formation of the internal microstructure. As will be discussed later in this section, temperature may also chemically and physically alter the microstructure.

The acceleration of degradation mechanisms in concrete is often achieved via several different accelerated tests, all of which intensify the exposure of concrete to one or more degradation mechanisms. Some of these tests are included in ASTM standards, accelerating several degradation mechanisms, as listed below: (95-108)

- Frost Resistance – ASTM C 666 and ASTM C 672
- Resistance to alkali-silica reaction – ASTM C 227, ASTM C 289, ASTM C 1260, and ASTM C 1293
- Resistance to alkali-carbonate rock reaction – ASTM C 586 and ASTM C 1105
- Sulfate resistance – ASTM C 452 and ASTM C 1012
- Abrasion resistance – ASTM C 418, ASTM C 779, ASTM C 944, and ASTM C 1138

Other degradation mechanisms not included in ASTM, such as biological attack, leaching, chemical attack of other natures, or mechanisms that enhance another degradation mechanism, like carbonation, can be evaluated via newer tests (not yet standardized). Most of these degradation procedures are performed after the matrix has achieved a certain degree of development, so that any further internal development of the material during the test will not significantly influence the final results.

This section presents current accelerated aging methods, covering both internal development and degradation mechanisms of various types. To understand the efficacy of such methods, an overview of the development processes of the microstructure formation of concrete is presented. The artificial accelerated aging tests being used in industry are reviewed and discussed.

4.2 Microstructural Formation of Concrete Materials

Concrete is a construction material that gains strength with time and shows a reduced porosity given appropriate conditions to sustain development. Concrete's transition from a semi-fluid material to a hardened material is schematically represented in figure 22 (after 109). After all materials are mixed, concrete is in a semi-fluid state, with a decreasing plasticity or workability occurring over the period known as the dormant period. A transition phase, called setting, follows. In this phase, concrete stops behaving as a liquid but does not yet respond as an elastic solid (it is more a viscous solid at this point). As soon as concrete possesses sufficient strength to support externally applied loads with acceptable and stable deformation, the hardening period starts. Concrete continues to gain strength during the hardening period.

The setting/hardening processes are observed physical consequences of the early chemical activity in the mixture. This gradual stiffening process is caused by continuous cement hydration, in which cement components combine with water to produce a porous solid often defined as a rigid gel (109). These hydrated products arrange themselves to form the fundamental matrix, or microstructure of the hardened material. The mixture develops its mechanical properties as more hydration products are formed.

Immediately after water is introduced to a cement-based mixture, a short period of intense chemical activity occurs as cement components begin to hydrate and $Ca(OH)_2$ (also called portlandite) is liberated. At the end of this short period, the dormant or induction period begins. This period is characterized by the near absence of chemical activity, with the mixture maintaining its plasticity. The existence of this period allows proper mixing, placement, and consolidation to be performed before concrete hardens. The dormant period ends when there is a marked increase in the rate of hydration (110), which can be related to the beginning of microstructure formation. Hydration products continue to be formed. Eventually, the microstructure is fully developed, with interconnected hydrated products.

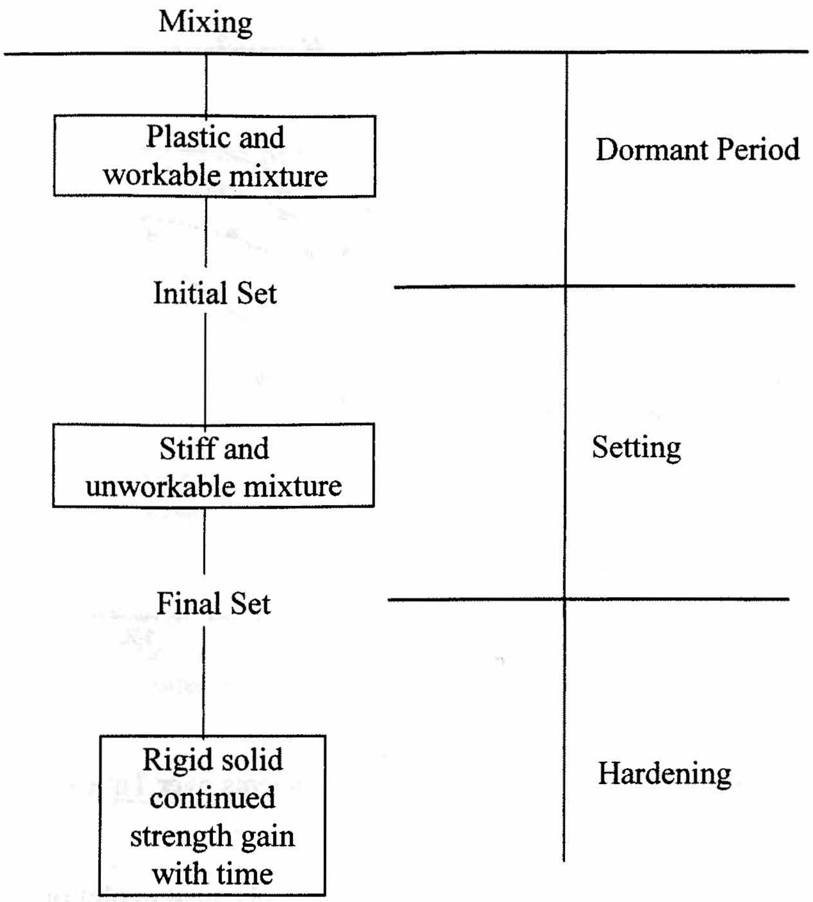

Figure 22 - Schematic Description of Setting and Hardening
(after 109)

Portland cement is itself a blend of at least four cementitious minerals, referred to in the cement literature as C_2S, C_3S, C_3A, and C_4AF[1]. Portland cement hydration is the overall summation of the hydration of each of its individual components, and includes complex reactions with many interactive possibilities (111). Each of the four components hydrates differently at different rates, as shown in figure 23 (112).

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[1] $C_2S = 2CaO \bullet SiO_2$
$C_3S = 3CaO \bullet SiO_2$
$C_3A = 3CaO \bullet Al_2O_3$
$C_4AF = 4CaO \bullet Al_2O_3 \bullet Fe_2O_3$

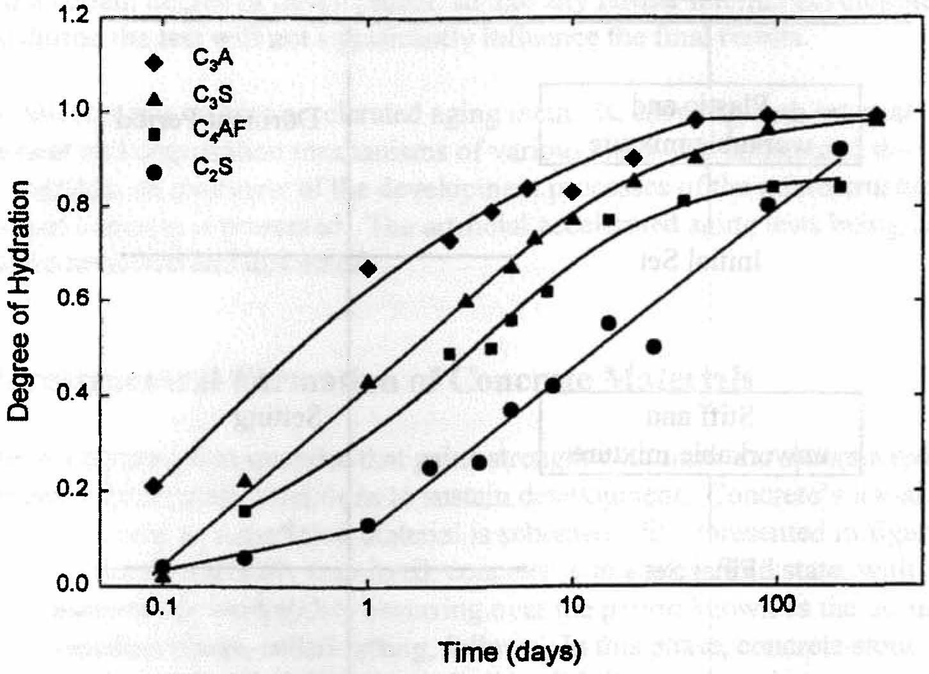

Figure 23 – Degree of Hydration of Cement Components over Time (after 112)

Since portland cement hydration is an exothermic process, the heat evolution can be easily measured by a calorimeter. The utilization of heat-evolution curves is a convenient way to follow the overall progress of cement hydration. As long as the resultant products are assumed to be essentially of constant composition at all times, the degree of hydration may be directly correlated to the heat of hydration (113). Thus, the progress of cement hydration can be followed by the use of heat-evolution curves, as shown schematically in figure 24 (after 114). This curve is the overall response to a set of chemical reactions, rather than to individual processes.

Numerous researchers have studied portland cement hydration (110-116 among others). Five distinct stages have been characterized, as schematically shown in figure 24. The first stage (→) is of short duration, being characterized by a large amount of heat liberated as the first hydrated products are formed. An ion exchange takes place between solids and the liquid with Ca^{2+} ions passing through the solution. Hydration products begin to cover the surface of C_3S and C_3A particles, the first components to react. In the hydration of C_3A, an intermediate component called ettringite is formed. A period of low chemical activity follows (✱ - the dormant period) in which continued dissolution of C_3S occurs, with C-S-H beginning to be formed. Several theories have been presented attempting to describe the origin of the dormant period and the process terminating it (110). Bye (110) concluded that the initiation of the dormant period is caused by the formation of a strongly inhibiting membrane on the surface of the C_3S particles. Taylor (115) suggested that this membrane would have an average thickness of one nm. During the dormant period the rates of hydration are low although never zero. The amount of hydration at the end of the dormant period is very low. Research using nuclear magnetic resonance showed that only 2 percent of C_3S had hydrated at the end of the dormant period (117). The dormant period ends when there is a marked increase in the rate of hydration of cement components, with a corresponding increase of the rate of heat liberated.

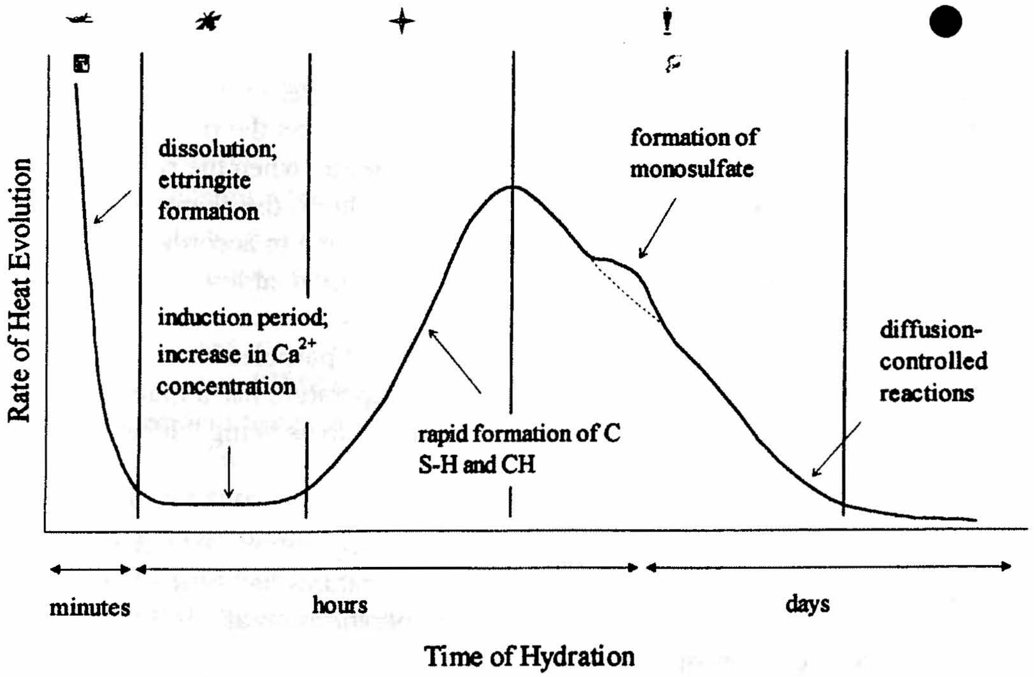

Figure 24 - Schematic Rate of Heat Evolution in Portland Cement Hydration (after 112)

An acceleratory period (✦) follows, in which permanent C-S-H begins to fill the available space rapidly. The rate of reaction increases markedly during this period. A maximum reaction rate is achieved at the end of the acceleratory period after which the rate begins to drop. The growth of hydration products and further development of microstructure continues at a slower rate in the fourth stage, the "deceleratory period." A third, smaller, peak may occur in this stage, as shown in figure 24, when there is great retardation of the C_3A hydration. The formation of the resultant C_3A hydration products (monosulfate-aluminate) occurs in this case at later stages. The level of retardation of the C_3A hydration depends on the amount of gypsum added during the manufacturing process.

Finally, a slow diffusion period due to the decrease in porosity with gradual densification of the microstructure follows. At the end of the deceleratory period, the degree of hydration may only be 50 percent or less (118). Total hydration may take up to tens of years to be completed (113).

The first three stages are chemically controlled. The last stage is fundamentally diffusion controlled, with hydration products growing inside the already formed matrix. In the deceleratory period both mechanisms occur (113, 119).

4.3 Accelerated Development by Thermal Aging

4.3.1 Overview

The development of the microstructure is accelerated at high temperatures since the rate of cement hydration increases. The influence of temperature on the rate of hydration, however, depends on the rate-limiting process. For example, when the rate of reaction is limited by the time required to transform reactants to products, the chemical reaction itself, the effect of temperature is usually significant and often in accordance with Arrhenius. This is the case in the hydration of portland cement at low degrees of hydration. As the development of microstructure becomes more advanced, diffusion of water to the unreacted and shrinking surface of the cement particles becomes the rate-limiting step, and in such latter stages of hydration, temperature has a much less significant impact on reaction rate. This phase is referred to as being "diffusion controlled" (120).

Figure 25 illustrates the effect of temperature on the C_3S hydration. At a degree of hydration greater than 40 percent, various curing temperatures had little effect on further increase of hydration. On the other hand, curing temperatures greatly influenced the rate of hydration at lower degrees of hydration.

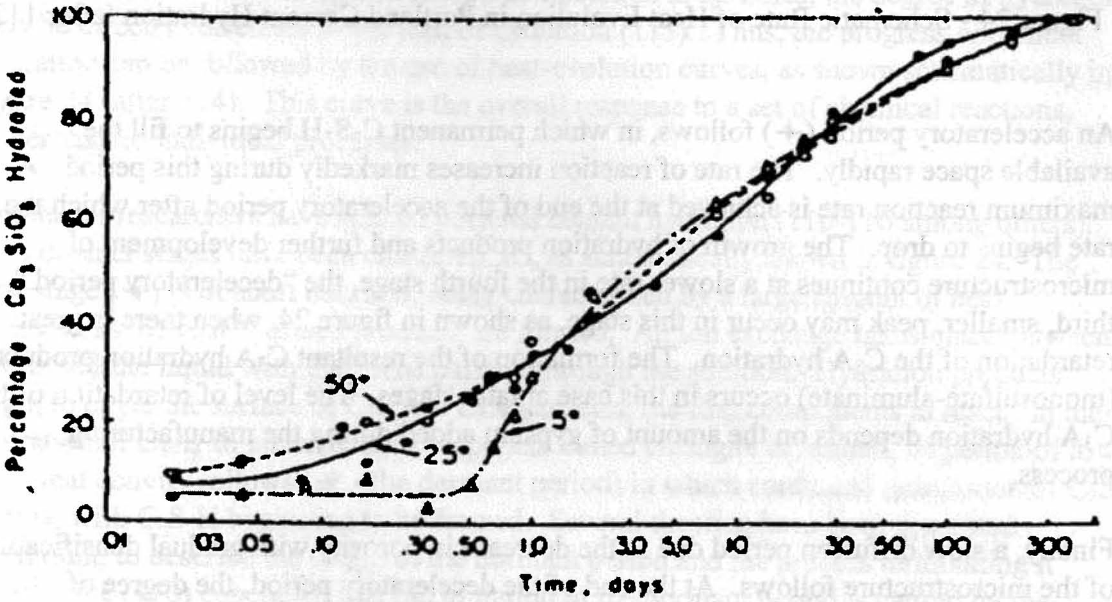

Figure 25 - Effect of Temperature on C_3S Hydration (121)

The increase in the rate of most reactions with increasing temperature was modeled by Arrhenius, and the temperature sensitivity characterized by the "activation energy E" (reviewed in chapter 2). In the case of portland cement, which is a heterogeneous blend with more than one mineral compound involved, the concept of apparent activation energy (Ea), rather than activation energy (E), is more appropriate. This concept introduces an average value of the activation energy accounting for the various hydration reactions occurring simultaneously.

Most correctly, the value of Ea should differ during the development of cement hydration depending on the predominant reactions and whether the rate is limited by chemical activity or transport phenomena. Since diffusion-controlled processes are expected to be less temperature sensitive, lower values of activation energy should apply at latter stages of hydration.. In general, then, apparent activation energy of cement hydration decreases as hydration increases. A lower value of Ea during stage ● (figure 24) would better describe temperature dependence of hydration in this phase.

The hydration of C_3S is the primary component of the early stages of hydration for an ordinary Type I or Type I/II cement, as seen in figure 23. The activation energy of C_3S hydration has therefore been the study of several researchers. Jawed et al. (114) indicate values of 40 kJ/mol during the acceleratory period, and 20 kJ/mol for the steady-state period (stage ● in figure 24). Fujii and Kondo (122) calculated a similar value of 21 kJ/mol for the diffusion-controlled period.

For portland cements, Bye (110) suggested a value of 40 to 50 kJ/mol to be applied in all stages. Copeland and Kantro (112) found values decreasing from 33.5 kJ/mol to 10 kJ/mol with increasing degree of hydration. Carino (123) suggested a value of 41 kJ/mol, while Carino and Tank (124) obtained apparent activation energies varying from 44 to 64 kJ/mol. ASTM C 1074 (125) indicates a value of between 40 to 45 kJ/mol for concrete made with Type I cement for all stages.

The apparent activation energy for a concrete mixture (i.e., mixture of portland cement, supplementary cementitious materials, chemical admixtures, aggregates, and water) is influenced by the presence of those chemical or mineral admixtures (124). Such admixtures can change the rate of cement hydration. For fly ash concrete mixtures, for example, values of 30 kJ/mol (124) up to 39 kJ/mol (126) are found in the literature.

Although it is expected that the apparent activation energy of cement hydration in concrete mixtures decreases over time as hydration proceeds, the values proposed in the literature are often applied to all stages of cement hydration. There has, however, recently been some research on varying the value of Ea (3, 127). Pinto (3) obtained a value of 40 kJ/mol for the time period before setting, a value of 38 kJ/mol during the setting period, and a smaller value of 33 kJ/mol for the steady-state period for a mixture containing silica fume. He proposed a method to take different values at Ea into account at different times.

4.3.2 Effect of High Temperature on Microstructural Development

From what has been discussed so far, one could conclude that the acceleration of microstructural formation of hardened portland cement paste (and, therefore, concrete) could be easily achieved by storing concrete at high temperatures, with appropriate investigation to determine apparent activation energies over the time being estimated. Concrete so treated would then have developed a more advanced or "mature" microstructure compared with the same material exposed to normal room temperature for the same time period. When young people develop faster than normal we often refer to them as being "mature beyond their age," and we may label an advanced student as being in the 4th grade, but "reading at an 8th grade level." Similarly, in concrete we can refer to the sample's actual clock or calendar age, or we can refer to its "equivalent age." This latter terminology refers to concrete that has been artificially aged and has a resulting behavior that is equivalent to that of a companion specimen that aged for a longer period of time under nonaccelerating conditions.

A complication arises, however, when the concrete is exposed to high temperatures during the early stages of hydration. High temperature not only affects the rate at which the hydration reactions occur, but also affects the character and arrangement of hydrated products. Thermal aging of concrete can and does result in a different microstructural formation. Verbeck and Helmuth (128) reasoned that high initial temperatures lead to a nonuniform distribution of the hydrated products within the paste, due to their rapid formation. Hydration products arrange themselves near the cement grains, impeding subsequent cement hydration. This process leads to relatively larger pores in the paste, resulting in a higher porosity and a lower ultimate degree of hydration when compared with paste cured at lower temperature.

Kjellsen et al. (129) experimentally observed this increase in porosity for mortar samples cured at 5°C, 20°C and 50°C. A much more uneven distribution of hydrated products was observed at higher curing temperatures. Patel et al. (130) compared the microstructure of concrete specimens cured according to usual practices in the precast industry (high early temperatures up to 85°C for the first 24 hours) with isothermally (20°C) cured specimens. They observed that the concrete cured at high early temperatures exhibited a coarser microstructure than the concrete cured at 20°C. They observed that microcracking formed a prominent network, predominantly infilled by ettringite.

The microstructural changes brought about by curing at higher temperatures leads to the compressive strength vs. time curves shown in figure 26 (131). As can be seen, increased temperature accelerates strength gain at early ages as would be generically expected, but the impact of the lower quality microstructure takes its toll at later ages. The apparent benefit of curing at higher temperature at early ages, followed by the relative decrease in strength at later ages is known as the "crossover" effect.

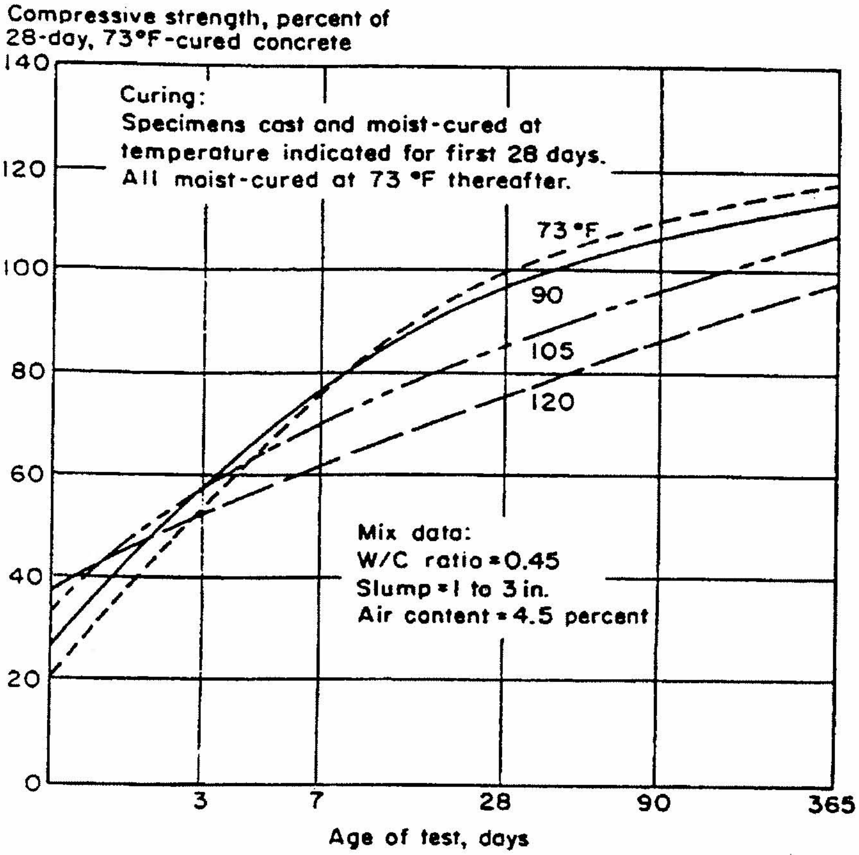

Figure 26 - Compressive Strength as a Function of Time for Various Curing Temperatures (after 131)

Further, the high early curing temperature procedures often applied in precast plants have been seen to cause a number of failures due to extensive cracking. Taylor (132) states that any ettringite formed prior to curing at temperatures of or above about 70°C is destroyed during the heat treatment, and that the damage is associated with the formation or reformation of this phase during the subsequent service at ambient temperature. The term delayed ettringite formation (DEF) is widely used to denote this problem.

In the course of heat curing in temperatures above 70°C, late formation of ettringite happens because calcium aluminate monosulfate hydrate is formed as the sole product of hydration of tricalcium aluminate, even in the presence of excessive amounts of SO_3 (133). After heat curing has been concluded and the temperature of the material drops, monosulfate may convert to ettringite, causing expansion of the hardened material, which can in turn lead to cracking.

Odler and Chen (133) have found that the renewed ettringite formation causing expansion of heat-cured cement pastes begins only after prolonged storage at ambient temperature. They suggest that the delayed expansion in heat-cured concrete may be prevented by the selection of a suitable cement and curing temperatures below which ettringite becomes unstable and thus cannot be formed.

Diamond (134) stressed that the deterioration of concrete associated with DEF is not a problem solely of concretes that had been subjected to high early curing temperatures. DEF may be facilitated by cracks formed by prior alkali-silica reaction and/or freezing and thawing mechanisms. He believed that DEF is an expansive process marked by enlargement of the affected concrete members and by development of gross cracking. The exposure of concrete to temperatures of the order of 70°C for several hours in steam curing would destroy the normal ettringite, and after cooling for some period of time ettringite would begin to form. The progressive deposition of ettringite can be the basis for DEF-induced distress. In non-steam-cured concrete, because of excessive sulfate or slow availability of C_3A or some kinetic factor, ettringite might continue to form long after the time ettringite formation is normally complete.

Agreeing with the previous researchers, Day (135) believes that the early excessive heat treatments at temperature above approximately 70°C result in substantial amounts of sulfates being bound in an unusual form. These sulfates could be released back into the solution at later ages. He states that the current cement-production and concrete-production practices in North America are a potential for DEF-induced problems. He presents recommendations from different European organizations, in which the maximum allowable curing temperatures in concrete range from 60°C to 66°C.

4.3.3 Maturity Approach - Applications and Considerations

The application of thermal aging to concrete and the prediction of a long-term property at earlier time can be obtained by the use of the maturity approach. The maturity approach was initially developed to estimate the compressive strength of concrete based on its temperature history. In 1951, Saul (136) linked maturity to compressive strength in what he called the *law of gain of strength* with maturity:

> "Concrete of the same mix at the same maturity (reckoned in temperature-time) has approximately the same strength whatever combination of temperature and time go to make that maturity."

Thus, the utilization of the maturity approach requires previous knowledge of the strength gain over time at one temperature at least. At other temperature profiles, compressive strength is estimated at various times using "maturity functions" of both time and concrete temperature. Malhotra (137) and Carino (138) present comprehensive reviews of the maturity method.

The maturity approach, however, has a much wider application than just to estimate compressive strength development. In 1977, Freiesleben-Hanson and Pedersen (from 11) linked the concept of maturity with the development of hydration products from the following simplifying assumption:

> "The rate of hydration, $d\alpha/dt$, in a given cement paste and at a given degree of hydration α is only a function of the temperature which applies at the moment in question."

This statement can be mathematically expressed as follows:

$$\left.\frac{d\alpha}{dt}\right|_{\alpha} = f(T) \qquad [4]$$

Equation 4 can be related to the rate law of chemical reactions (equation 1), presented in chapter 2, in which the velocity v of the reaction is the rate of cement hydration ($d\alpha/dt$), in this case, or:

$$\frac{d\alpha}{dt} = f(T)\ g[\alpha(t)] \qquad [5]$$

where:

$d\alpha/dt$ = the rate of cement hydration,
$f(T)$ = rate constant, function of temperature, and
$g[\alpha(t)]$ = concentration of unreacted cement particles, being itself a decreasing function with the degree of hydration α.

Equation 5 can be rearranged as:

$$\frac{1}{g[\alpha(t)]} d\alpha = f(T)\ dt \qquad [6]$$

Since concrete temperature may vary with time, the equation can be transformed to:

$$\frac{1}{g[\alpha(t)]} d\alpha = f[T(t)]\ dt \qquad [7]$$

Integrating equation 7:

$$\int_0^{\alpha} \frac{d\alpha}{g[\alpha(t)]} = \int_0^{t} f[T(t)]\ dt \qquad [8]$$

Thus, each integral yields a different function related to α and t, as follows:

$$H(\alpha) = M(t) \qquad [9]$$

where:

$H(\alpha)$ = result of integration in α,
$M(t)$ = maturity at time t, and
$f[T(t)]$ = maturity function.

This last equation relates the development of degree of hydration as a function of the concrete temperature and time.

Kjellsen and Detwiler (127) suggested the following modification of equation 4 to incorporate the effect of temperature on the rate of hydration at increasing degrees of hydration:

$$\frac{d\alpha}{dt} = g(\alpha)\ f(T,\alpha) \qquad [10]$$

Thus, the rate constant is also a function of the actual degree of hydration.
The utilization of the maturity approach assumes that concrete temperature is the only variable affecting the rate of hydration. Materials composition, mixture proportions, moisture conditions, and other factors that may influence the development of hydration are assumed to be constant.

In using the maturity concept to predict the development of hydration as a function of temperature, a maturity function that includes the impact of both time and temperature is necessary. Some proposed maturity functions are presented here, with some background information. Other maturity functions and more detailed information can be found elsewhere (3, 137, 138, 139).

McIntosh (140), when studying the effects of electrical curing as an accelerated compressive strength test, suggested that the rate of strength gain was directly proportional to the difference between the curing temperature and the temperature below which hydration of cement stops. McIntosh introduced the concept of *basic age* as the product of time and concrete temperature above the datum temperature of -1.1°C. Nurse (141) also suggested that the product of time and temperature was able to assess the effects of steam curing. He showed that, when strength results were expressed as a percentage of 3-day strength after curing at normal temperatures, the experimental data obtained from different concretes and curing temperatures fell close to a single line. He believed that such procedure would be able to account for different aggregates and mixes. Saul (136) defined the term "maturity" as the product of time and the average temperature (above a certain datum temperature), maintained by the concrete. Recognizing that even below normal freezing temperatures the concrete would continue to harden, he recommended a datum temperature of -10.5°C.

The maturity function as defined by Saul is expressed as shown in the equation below, known as the Nurse-Saul maturity function:

$$M = \sum_{0}^{t} (T - T_o)\Delta t \qquad [11]$$

where:

M = maturity time at time t,
T = concrete temperature during interval Δt,
T_o = datum temperature, and
Δt = time interval.

Rastrup (142) introduced the term *equivalent age*. In this case, after some actual time-temperature history, the concrete in question will have reached the same level of development (or maturity) as it would have reached had it been continuously maintained at a standard or "reference" temperature for the duration equal to the equivalent age.

The Nurse-Saul function using equivalent age can be modified as follows:

$$t_e = \sum_{0}^{t} \left(\frac{T - T_o}{T_r - T_o}\right) \Delta t \qquad [12]$$

where:

t_e = equivalent age at the reference temperature, and
T_r = reference concrete temperature.

The Nurse-Saul maturity function (equation 12) tries to account for the influence of temperature on strength development by a simple mathematical equation. However, besides the datum temperature (T_o), the Nurse-Saul method makes no further connection to the actual chemical and physical processes of cement hydration. Rastrup (142), trying to model the influence of temperature on cement hydration, suggested an equation of the form below, based on the idea that the reaction rate doubles when the temperature increases 10°C:

$$t_e = \sum_{0}^{t} 2^{(T - T_r)/10} \Delta t \qquad [13]$$

Freiesleben-Hanson and Pedersen (143) proposed a maturity function based on the Arrhenius function of the dependence of the rate constant (k_t) with temperature, as presented in equation 1. The equivalent age concept, in this case, represents the ratio of the rate constant at the actual temperature to the rate constant at a reference temperature, as shown below:

$$\frac{k_t}{k_{tr}} = \frac{Ae^{-E/RT}}{Ae^{-E/RT_r}} = e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)} \qquad [14]$$

where:

k_t = rate constant at temperature T, and
k_{tr} = rate constant at reference temperature T_r.

The expression describing maturity as equivalent age (t_e) is shown below. This equation is known as Freiesleben-Hanson and Pedersen (FHP) maturity function.

$$t_e = \sum_{0}^{t} \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \Delta t \qquad [15]$$

None of the maturity functions reviewed so far take into account the actual progress of the hydration reactions, or the actual degree of hydration, as expressed by equation 5. As discussed earlier in this section, at higher degrees of hydration the rate of the hydration reaction becomes less temperature-sensitive. Therefore, E_a in the FHP maturity function should theoretically vary with degree of hydration. The FHP maturity function with a variable E_a would be consistent with the maturity function as presented by equation 5.

In the utilization of the FHP maturity function, it is assumed that the temperature dependence of cement hydration follows the Arrhenius function, and thus when ln (k_t) is plotted against 1/T (called Arrhenius plot), a linear plot is obtained with the apparent activation energy being the slope divided by the universal gas constant. If the Arrhenius plot is not linear, it is possible that the reaction does not follow the Arrhenius equation for the rate constant. In fact, according to Laidler (18) the common procedure in analyzing kinetic data in chemistry is to use the Arrhenius equation if the plot of ln (k_t) versus 1/T is linear, or a different equation if the plot is nonlinear.

4.3.4 Accelerated Aging Methods

4.3.4.1 General

Accelerated test methods in concrete have been performed for quality control and verification of long-term performance. As a quality control tool, microstructural development can be thermally accelerated to enable more timely assessment of long-term properties. Accelerated methods are widely used in the construction industry to predict the 28-day compressive strength (or any other desired mechanical property) at an age well before 28 days.

Similarly, verification that today's concrete installation will continue to survive environmental exposure for the duration of its intended service life can be achieved by an acceleration of deterioration processes. The exposure applied in these accelerated degradation tests should be more severe than the exposure expected during service. This increase in severity can be obtained by intensifying the magnitude of the potentially destructive mechanism, or increasing the duration or frequency of exposure during a period of time, or any combination of these conditions (144). Care should be taken when selecting the accelerating procedure such that the same mechanisms that take place under normal exposure conditions also occur in the accelerated process.

4.3.4.2 Accelerated Strength Testing

The compressive strength of concrete is most typically assessed by testing a standard cylinder cured under standard conditions for a period of 28 days (144). However, it is not feasible or prudent in all cases to wait 28 days to assess the material. If concrete is found to be defective (not achieving the desired 28-strength) only after 28 days after its placement, the quality control assessment of the material loses its purpose because the concrete might be buried under much other construction (144).

Accelerated strength test methods have been studied since 1915 (145). Different methods have been successfully applied in various constructions (146-149). ASTM C 684 (150) lists four methods intended to accelerate compressive strength development. Specimens exposed to accelerated curing conditions develop a significant portion of their ultimate strength within a time period of 5 to 49 hours, depending on the procedure followed.

The first of these four methods uses warm water as a medium to transfer heat to concrete. Sealed specimens are placed in warm water at 35°C for 24 hours and then tested. In the second method, 23 hours after casting, specimens are immersed in boiling water for 3.5 hours, and then tested in compression. An autogeneous curing procedure is another method presented, in which immediately after casting, specimens are placed in a thermally insulated container such that their heat of hydration serves as thermal acceleration. The last ASTM method uses both high temperature and pressure. Immediately after casting, concrete specimens are placed inside a container at a pressure of 10.3 MPa (1500 psi) and at a temperature of 150°C. The high pressure is maintained for five hours, while the high temperature is maintained for the first three hours, after which the heating element is tuned off. The specimen is tested immediately after removal from the pressure chamber, at an age of five hours after casting.

All of these methods are based on thermal exposure of concrete, with the last one also applying high pressure. Prior to the utilization of any of these accelerated tests as a predictive tool for later strength, it is necessary to establish a relationship between the accelerated strength and standard-cured strength. Appropriate statistical techniques should be used to establish a confidence interval of the estimated potential later strength (151).

Resheidat and Manadat (152) studied the application of the boiling water procedure of ASTM C 684 for use in quality control of concrete and prediction of later strength. After performing 380 accelerated tests and normal 28-day compressive strength tests, they determined a linear relationship between the accelerated tests and the normal curing results. A follow-up study in this subject (153) confirmed the previous finding for blended cements.

Other thermally accelerated methods have been proposed (154, 155). Siviero (154) presented the application of the equipment called "Speedymet," in which concrete cubes are placed inside a steam curing chamber for a curing cycle of 17 hours. The curing cycle starts with an initial temperature of 36°C, which is increased to 76°C over 5 hours. This high temperature is maintained for 5 hours, after which the curing temperature is dropped to 20°C during the next 4 hours. Finally, the 20°C temperature is maintained until the end of the test, i.e., 17 hours after casting. The compressive strength of steam-cured concrete cubes was compared with results of standard curing at 28 days for concretes made with various types of cements, with and without fly ash, with and without superplasticizer, at different cement contents, and at various water/cement ratios. Maximum aggregate sizes ranging from 9 mm to 25 mm were used. The results indicated a relationship between the compressive strength at 28 days and the compressive strength of steamed-cured cubes that depended on the type of cement and presence of cementitious material used in the mixture.

Another thermal method of accelerating strength gain in concrete, similar to the autogeneous curing method of ASTM C 684, was proposed by Das Gupta and Tam (155). Again, a relationship between accelerated curing tests and 28-day compressive strength was found. Higginson (156) studied the effect of steam curing on some properties of concrete, as practiced in the precast industry. Applying a maximum temperature of 71°C, he concluded that concrete that had been steam cured was not as well-developed as concrete that had been continuously moist cured at 23°C: steam-cured concretes had a higher permeability, lower compressive strength, and lower resistance to freeze-thaw action.

Hanson (157) tried to find an optimum combination of pre-curing and steam curing, given a fixed period of 18 hours at the end of the early curing cycle. He calculated what he considered the optimum time-temperature combination of steam curing and pre-curing, looking at compressive and tensile strengths and the modulus of elasticity at the end of the steam curing (at 18 hours) and again at 28 days. He concluded that the early application of steam curing to concrete should be avoided since it was detrimental to compressive and tensile strength and modulus of elasticity. The best 28-day results were obtained when the pre-steaming period was the longest (7 hours) at all maximum temperatures studied, 52°C, 66°C, and 79°C.

Oluokon et al. (158) showed that the steam curing caused cracks in some steam-cured concrete members. Tensile strength development appeared to have ceased even before steam curing was discontinued, resulting in lower tensile strength at the time of strand release and form stripping that might have caused the observed cracks.

4.3.5 Considerations

Thermal aging of concrete can be used efficiently to accelerate the development of the internal microstructure and consequently the physical properties of concrete materials. Care should be taken, however, in deciding when to initiate artificial aging and at what temperature concrete is to be cured, so as not to produce long-term distresses or significant changes in the resultant hydration products and their arrangement. The evaluation of the efficacy of an accelerated thermal aging process for concrete can be assessed by the use of the maturity approach with appropriate apparent activation energies at different stages of hydration. This method yields an equivalent age of the accelerated material at the end of the accelerated process.

4.4 Accelerated Degradation Mechanisms and Methods

4.4.1 Overview

Several degradation mechanisms in concrete have been investigated, with accelerated degradation tests developed. The objective of these tests is to predict long-term behavior of the material under certain conditions. Long-term field conditions are simulated with the potential degradation of the material assessed. The effects of different mixture proportions, or materials (such as another cementitious material) in the potential degradation mechanism are also investigated. A description of some degradation mechanisms and accelerated tests developed for each of them follows.

4.4.2 Frost and Deicer Salt Resistance

Concrete when subjected to freezing temperatures may be degraded due to the pressure generated by the movement of water or ice through the pores of hardened concrete. This destructive pressure, as postulated by Powers (159) can occur due to the 9 percent increase in volume of freezing water. Saturated pores become enlarged, causing tensile stresses that can lead to the formation of microcracks. With continuous freeze-thaw cycles, the microcracks may enlarge and the concrete may expand, eventually causing the destruction of the original material.

On the concrete surface, the resultant mechanism associated with the bursting pressures generated during cycles of freezing and thawing is called scaling. Scaling of concrete is the failure of the exposed surface of concrete subjected to freezing temperatures, being enhanced in the presence of deicing salts. The frost resistance of this outer "skin" of concrete (160) is affected by the harmful pressures generated by ice formation and osmotic pressures generated by an uneven concentration of salts.

Newlon and Mitchell (161) have presented an historical evolution of accelerated tests to assess frost resistance of concrete. These acceleration methods normally subject samples of concrete to a great number of freezing and thawing cycles, in order to obtain a degree of deterioration compatible to long-term exposure. ASTM indicates two accelerated tests methods: ASTM C 666 (95) - freeze-thaw resistance, and ASTM C 672 (96) - scaling resistance to deicing salts.

ASTM C 666 method alternates cycles of freezing and thawing for concrete specimens cured for 14 days at laboratory conditions. The nominal freeze-thaw cycle consists of lowering the concrete temperature to -17.8°C followed by raising the concrete temperature to 4.4°C in not less than 2 hours and not more than 5 hours. The specimens can be either frozen in water (procedure A) or in air (procedure B), while thawing always takes place in water in both procedures.

Since the occurrence of microcracking is anticipated, freeze-thaw resistance is indirectly evaluated by changes in the relative dynamic modulus of elasticity, indicating an internal degree of microcrack formation. The relative dynamic modulus of elasticity is calculated from the following expression:

$$P_c = \left({n_1}^2 \big/ n^2 \right) \text{ x } 100 \qquad [16]$$

where:

P_c = relative dynamic modulus of elasticity, after c cycles of freezing and thawing,

n = fundamental transverse frequency at 0 cycles of freezing and thawing, and

n_1 = fundamental transverse frequency at c cycles of freezing and thawing.

The fundamental transverse frequency is calculated from the method in ASTM C 215 (162). In the calculation of P_c, it is assumed that the specimen does not change its weight or dimensions, which rarely occurs due to the loss of material caused by degradation. Despite this, the utilization of equation 16 to calculate the relative dynamic modulus of elasticity is believed to be adequate for the purpose of the test (161).

As an indication of the degree of freeze-thaw resistance, Neville (2) suggests that a decrease of more than 60 percent of the original dynamic modulus after 300 cycles indicates a poor frost resistance, while a decrease of less than 40 percent indicates that the concrete is likely to perform satisfactorily. Values between 40 and 60 percent are in the range of doubtful performance. Cordon (after 161) suggested that a concrete of poor frost resistance would suffer a decrease of more than 80 percent in its relative dynamic modulus while concrete with good frost resistance would suffer a decrease of less than 20 percent.

The rate of freezing of this method can vary widely from, 8.8 to 22.2 °C/hour, with a normal a rate of 11.1°C/hour (163). Nevertheless these rates are much higher than the ones encountered in field applications, in which a maximum cooling rate of 3.3°C/hour has been observed (164). Other important parameters influencing the results are the high degree of saturation of the specimens, the early age at which the test is initiated (14 days after casting) (161), and the rapid cooling rate applied (165). These conditions are much more severe than the natural conditions to which the concrete is likely to be exposed in service. Natural freezing of concrete in service normally occurs at lower cooling rates, at later ages, and after some period of drying.

In ASTM C 672, small slabs of concrete of at least 0.046 m^2 and a minimum thickness of 75 mm are used to evaluate scaling resistance. After 28 days of laboratory curing (first 14 days moist cured followed by 14 air cured), a solution of water and calcium chloride is placed on the top of the specimens. The specimens are placed in a freezing environment capable of lowering the surface temperature to -17.8 ± 2.8°C for 16 to 18 hours, followed by laboratory temperature of 23 ± 1.7°C for 6 to 8 hours, completing one freeze-thaw cycle. The solution is replaced at the end of each five cycles when a visual evaluation is performed. The specimens are then rated from 0 to 5 varying from no scaling (0) to severe scaling (5). Generally, 50 cycles is sufficient to evaluate the surface, although more cycles may be necessary in comparative tests.

Variations of these two methods, in which the scaled debris is collected and is dry-weighed have been used (166-169, among others). The Swedish Standard SS 13 72 44 (from 170, 171) correlates the collected mass loss per unit area with scaling potential. It is believed that scaling of less than 0.10 kg/m^2 after 56 cycles indicates good frost/scaling resistant concrete, while values greater than 1.0 kg/m^2 are often observed for nonacceptable concretes.

These two methods only indicate the potential frost/scaling long-term durability of a concrete mixture. The conditions applied in the test rarely correspond to actual conditions in the field. The number of natural freeze-thaw cycles may differ greatly from those in the tests: a different deicer salt may be used; the age of the concrete when it experiences the first freezing cycle may not be 28 or 14 days old; and the rate of freezing in the field is rarely as high as applied in lab tests (2). Therefore, these test methods only indicate potential susceptibility of a mixture to damage by freezing and thawing. Judgment is required when predicting field performance based on results of this test (161). ASTM recognizes that these methods do not indicate qualitatively the service life of a concrete structure; rather they indicate the effect of variations in properties of concrete on the frost resistance. These tests are intended for use in determining the effects of variations in the properties of concrete on the freeze-thaw resistance.

4.4.3 Resistance to Alkali-Silica Reaction

Chemical reactions between the aggregate and cement paste can result in long-term damage in concrete structures. Alkali hydroxides in pore water derived from alkalis in the cement composition (Na_2O and K_2O) may react with the active silica constituents of aggregate particles, leading to expansion and cracking. This reaction is very slow and may take many years to cause damage (2).

ASTM C 289 method can be used to test the aggregates (98). Crushed aggregate samples are placed in contact with a NaOH solution at 80°C for 24 hours, after which the reduction in the alkalinity of the solution and the amount of dissolved silica are measured. The results obtained are compared with a standard curve indicating if the aggregate tested is potentially deleterious. This method accelerates the reaction by placing the reactants at

high temperature and by allowing more surface area of material to be in contact with the alkalis.
The ASTM C 227 (97) test method evaluates the length changes in mortar samples made with the aggregate in question. After 24 hours of curing in a moist environment, mortar samples are stored over (not in contact with) water in a sealed container at 37.8°C. Length measurements are made periodically. According to ASTM C 33 (172), the cement-aggregate combination should be considered harmful if a mortar-bar expansion of more than 0.10 percent is observed after 6 months. If an expansion of more than 0.05 percent is observed after 3 months, the cement-aggregate combination should be considered potentially harmful. A similar test method, ASTM C 1293 (100), uses concrete prisms in which the alkali content of the mixture is raised to 1.25 percent.

All three of these tests have been shown to fail to identify many slowly reactive aggregates, such as gneiss among others (100, 173). Concrete made with such slowly reacting aggregates has been shown to expand 0.05 percent in the ASTM C 227 test after 2 or 3 years (174). This is a slow reaction by laboratory testing standards, but significant enough to cause problems in actual structures.

Another ASTM test method C 1260, formerly P 214, tests the potential reactive aggregate by length changes of a mortar specimen cured at high temperatures immersed in 1M NaOH solution. The aggregate to be tested is sized to a specific grading and cast in specified proportions into mortar bars with a w/c ratio of 0.47. After 1 day of laboratory curing, the specimens are demolded and immersed in tap water at a temperature of 80°C for 24 hours followed by immersion in an NaOH solution at 80°C for 14 days. Length changes are recorded during this period. ASTM suggests the following criteria to interpret the results: expansion smaller than 0.10 percent at the end of the test duration (16 days) indicates mostly innocuous behavior, expansion greater than 0.20 percent indicates potentially deleterious reactive aggregates, and expansion between 0.10 and 0.20 percent includes both potentially and nonpotentially reactive aggregates. In this case, supplemental information should be obtained, and extension of the test up to 28 days may be useful. Through exposure to an NaOH solution, the alkali content of the cement is not critical, since the alkali-silica reaction is controlled by NaOH diffusion into the mortar. Thus, this test allows the evaluation of otherwise slowly reactive aggregates. However, it does not indicate any potential cement-aggregate reactivity. Stark (174) believes that this procedure seems to be the most reliable to indicate potential reactive aggregates.

4.4.4 Resistance to Alkali-Carbonate Reaction

Reactive carbonate rocks such as dolomitic limestone and calcitic dolomites containing clay may react with the alkalis in the cement paste. According to Clifton and Knab (175), the reaction likely breaks down the structure of the rock allowing water to penetrate. The clay elements in the rock swell with absorption of water. Thus under a humid environment, expansion of concrete may occur (2).

Potential reactive aggregates can be evaluated by petrographic analysis according to ASTM C 295 (176), or by the rock cylinder method ASTM C 586 (101). In this latter accelerated method, rock cylinder specimens are prepared, water saturated, and immersed in a solution of NaOH. Length changes are measured at 7, 14, 21, and 28 days after immersion in the NaOH solution and every 4 weeks thereafter. According to ASTM C 586, expansions greater than 0.01 percent are indicative of chemical reactions, and the further utilization of the aggregate in concrete should be assessed by the test method ASTM C 1105 (102). ASTM C 1105 method is not an accelerated test, as it measures length changes in concrete specimens with the potential deleterious aggregate over time.

4.4.5 Sulfate Resistance

Concrete in contact with sulfates in solution may crack, expand, and disintegrate due to deleterious chemical reactions between the hydrated cement paste and sulfate ions. Several different reactions may occur depending on the type of sulfate and environment conditions (177). The primary mechanism of destruction is the expansive stresses resulting from the formation of ettringite, which is the product of the reaction between the sulfate ions and calcium aluminate hydrate. Sodium and magnesium sulfates also attack calcium hydroxide, forming gypsum. Expansive stresses are again induced since gypsum occupies more volume than calcium hydroxide. Gypsum may also gradually leach, leaving a more porous concrete with a higher permeability. Magnesium sulfate also attacks the calcium silicate hydrates, forming gypsum (2). This type of reaction leads to the destruction of the calcium silicate hydrate, the primary building block of hardened cement paste.

The accelerated methods to assess sulfate resistance prescribed by ASTM include monitoring the expansion at 14 days from mortar specimens mixed with additional gypsum -ASTM C 452 (103), and the length change with time of a mortar specimen immersed in a sulfate solution - ASTM C 1012 (104). ASTM C 452 estimates the sulfate resistance by the expansion observed at 14 days of water-cured mortar specimens mixed with 7.0 percent by weight of SO_3. This high amount of sulfate accelerates the reaction of calcium aluminate hydrate, causing the formation of a high amount of ettringite. However, this test method is recognized by ASTM to be not applicable to blended mixtures because of the presence of unhydrated cementitious material in such mixtures when sulfate attack is initiated (2). Results of this test generally correspond to long-term behavior of concrete exposed to aggressive sulfates (178).

ASTM C 1012, on the other hand, assesses sulfateresistance by length changes of mature specimens immersed in sulfate solutions. After the compressive strength of companion mortar cubes have reached 20 MPa, mortar prisms are immersed in a sulfate solution and length changes over time start to be monitored with readings at 1, 2, 3, 4, 8, 13, and 15 weeks after immersion. If expansion occurs, readings at 4, 6, 9, and 12 months are also prescribed. Another method to accelerate sulfate-related attack is to expose concrete specimens to cycles of wetting by sulfate water and drying (177). In this case sulfates would accumulate in the concrete surface in high concentrations.

These test methods assess sulfate resistance by intensifying environmental conditions, putting the concrete specimen in contact with a high amount of sulfates either externally or internally. However, as mentioned by Neville (2), these tests methods may take several months to give results.

4.4.6 Abrasion Resistance

The assessment of the resistance of concrete surface to abrasion or wear is a difficult task, since the damage action may vary depending on the wearing action (2). According to ACI Committee 201 (179), four main types of abrasion action can be classified:

1. Abrasion in floor and slab construction from foot traffic, cars and light truck traffic (attrition).
2. Abrasion on concrete road surface from heavy trucks and cars with studded tires and chains (attrition, scraping, and percussion).
3. Abrasion in dams, spillways, tunnels, bridge piers, and abutments from the action of abrasive materials carried by floating water (attrition and scraping).
4. Abrasion in dams, spillways, tunnels, and other water-carrying systems where high velocities and negative pressures are present due to cavitation action.

Liu (180) explained these four types of abrasive action in more detail. According to him, the first type of wear is a rubbing action increased by the presence of foreign materials; the second type adds an impact-cutting type of wear for the first type, caused by vehicles with chain-tires. The third type is essentially grinding and cutting action, while the fourth type is caused by rapid changes in the velocity and direction of water such that the pressure at some point is reduced to the vapor pressure of the water. These created vapor pockets collapse with a great impact when entering areas of high pressure, with the ability to cause holes in the concrete. ASTM presents some test methods that try to evaluate the abrasion resistance of concrete against some of these mentioned abrasion actions at a shorter duration of exposure.

ASTM C 418 (105) evaluates the abrasion resistance of concrete by sandblasting. In this method the concrete surface is exposed to a blast of a specified graded sand for a period of 1 minute. At least eight exposures are taken. The abrasion cavities caused by the blast are filled with clay, and the volume of concrete abraded is calculated. An abrasion coefficient index relating the volume abraded to the area exposed is calculated. This method simulates the action of abrasives under traffic on concrete surface and the action of waterborne abrasives (180).

ASTM C 779 (106) presents three procedures to determine the abrasion resistance of horizontal concrete surfaces. The first procedure uses revolving steel disks in an abrasive grit of No. 60 silicon carbide. Three disks are driven transversely along a circular path while being individually turned on their own axis at specific rotations per minute. The apparatus required allows a uniform total load of 22 N on the face of each disk. The test is performed for 60 minutes after which the depth of wear is evaluated. The second procedure consists of measuring the wear depth caused by a set of three steel dressing wheels riding on a circular path on the concrete surface. The test is performed for 60 minutes if long-term wear due to abrasion is to be evaluated. The last procedure involves impact and sliding friction of a rapidly rotating ball bearing under load on a wet concrete surface. The depth of wear is measured every 50 seconds after the initiation of the test for a total period of 1200 seconds, or until a maximum depth of 3 mm is achieved. ASTM recognizes that these three procedures do not provide an absolute measurement of service life from a specific concrete surface; rather they indicate variations in surface properties of concrete due to different mixture proportions, curing techniques, or surface treatments.

ASTM C 994 (107) is similar to the second procedure of ATSM C 779 and is useful for concrete surfaces with not enough area required by ASTM C 779. An abrading cutter rotates on the concrete surface at a specified velocity and under uniform load of 98 N for a minimum of 6 minutes. The mass loss of the specimen is evaluated at two-minute intervals.

ASTM C 1138 (108) evaluates the abrasion resistance of concrete under water, simulating the action of water containing suspended and transported abrasion potential particles. The specimen is placed inside a steel tank after being soaked in lime-saturated water or in the water that it will be abraded for 48 hours. A set of 70 grade 1000 chrome steel grinding balls is placed on the concrete surface to be evaluated. The tank is then filled with the same water used during the soaking period, after which an agitation paddle mounted in a drill press applying 1200 rpm is immersed in the tank. The test consists of measuring the volume loss of material over 72 hours under agitating conditions at intervals of 12 hours.

All these methods revised here accelerate the abrasion resistance by physically applying more abrasion conditions over a shorter period of time. These test methods indicate the quality of concrete surface and are useful in evaluating the effect of variables such as mixture proportion, cementitious materials, finishing procedures, and coatings in the abrasion resistance (180). These methods do not indicate quantitatively the abrasion resistance of a given concrete.

4.4.7 Carbonation

Carbon dioxide in the air in the presence of moisture reacts with hydrated cement, leading to a reduced alkalinity. Carbon dioxide reacts with calcium hydroxide and to a lesser content with calcium silicate hydrate to form calcium carbonate, changing the microstructure of concrete (181).

Carbonation itself does not lead to a deterioration of the concrete. Its importance lies in the removal of the passive layer of steel bars inside the concrete. According to Neville (2), a passivity layer of oxide is formed on the surface of steel bars in concrete, giving them protection from corrosion. This state of passivation of steel bars is maintained while the pH of the pore water in contact with the passivating layer is high. Carbonation causes the pore water pH to drop from about 13 to 9 (2, 181). This reduction of pH leads to the destruction of the passivating layer, and thus corrosion may take place.

Several factors affect the rate of carbonation. The rate of carbonation increases with an increased concentration of CO_2. It depends on the moisture content of the concrete (2), being slower if the pores are fully saturated. The rate of carbonation may take many years under natural conditions (182).

Accelerated carbonation tests often increase the rate of carbon dioxide diffusion through concrete, since the other factors affecting the rate of carbonation, such as the microstructure, and the availability of reactive elements among others is mixture dependent. Studying the effect of re-alkalanization on the properties of concrete, Al-Kadhimi et al. (182) developed an accelerated carbonation test in which concrete samples previously dried to an internal relative humidity of 60 percent were exposed to a pure atmosphere of CO_2 at 15 bar pressure. They observed that specimens of a minimum dimension of 100 mm were fully carbonated after being exposed for 2 weeks. Saeki et al. (181), studying the change in microstructure from carbonation, accelerated the carbonation process by exposing concrete specimens to a atmosphere of 7 percent by volume of CO_2, at a temperature of 40°C and at a relative humidity of 50 percent. The depth of carbonation was measured over time for up to 10 weeks.

4.4.8 Leaching

Free lime can react with acids, producing soluble calcium salts, or it can be dissolved by water. This leaching process damages the material, increasing its permeability and reducing surface strength. The study of leaching is important when concrete is used as a waste container for short-life radioactive material (183), in agricultural construction (184), or when it is subjected to acid attack.

Accelerated tests can be performed by subjecting concrete samples to a low pH solution for a certain time. Belie et al. (184) studied the resistance of concrete to feed acids using solutions with pH from 2.1 to 4.5. Concrete prisms were submerged in the low pH solutions for nine days, after which the prisms were dried in air and brushed for two minutes to remove the weakened concrete layer. The concrete hydrostatic weight was measured before and after the test. A second cycle of 27 days was also applied. These repeated drying and wetting cycles also accelerated the damage since the dry concrete can absorb fresh effluent upon re-immersion.

4.5 Summary

Concrete materials can be subject to both accelerated development and accelerated degradation. Accelerated development is conducted primarily by thermal aging; exposure to increased temperatures speeds up the hydration reactions, accelerating the development of the internal microstructure. Accelerated development is desirable for assessment and prediction of long-term properties and quality control for long-term performance.

Concrete is degraded by a number of different mechanisms. The specific degradation mechanisms discussed in this chapter include exposure to freeze/thaw cycles and deicer salts, alkali-silica reactions, alkali-carbonate reactions, exposure to sulfates, abrasion, carbonation, and leaching. Accelerated degradation tests can be performed to simulate the long term effect of these varying degradation mechanisms in a shorter time period, and thus predict long-term performance.

5. References

1. Sasse, H. R., and Schrage, I. "A Proposed Method for Aging Polymers Used in Buildings Under Simultaneous Action of Artificial Weathering and Mechanical Stress," *Durability of Building Materials*, Vol. 2, 1983, pp. 45-48.

2. Neville, A. M. *Properties of Concrete*, Fourth Edition, John Wiley and Sons, Inc., London, 1996, 844 pp.

3. Pinto, R. C. *The Effect of Curing Temperatures on the Development of Mechanical Properties of Fresh and Hardened High-Strength Silica Fume Mixtures - A Maturity Approach*, Ph.D. Thesis, Cornell University, 1997, 294 pp.

4. Bisaillon, A., and Malhotra, V. M. "Permeability of Concrete Using a Uniaxial Water-Flow Method," *Permeability of Concrete*, ACI SP-108, Whiting and Walitt, eds., American Concrete Institute, 1988, pp. 175-193.

5. Keyser, J. H. "Durability of Materials and Construction," *Durability of Building Materials and Components*, ASTM STP 691, Sereda and Litvan, eds., American Society for Testing and Materials, 1980, pp. 38-55.

6. Ozol, M. A. "Alkali-Carbonate Rock Reaction," *Significance of Tests and Properties of Concrete and Concrete-Making Materials*, ASTM STP 169C, Klieger and Lamond, eds., American Society for Testing Materials, 1994, pp. 372-387.

7. Boelen, B., Schmitz, B., Defourny, J., and Blekkenhorst, F. "A Literature Survey on the Development of an Accelerated Laboratory Test Method for Atmospheric Corrosion of Precoated Steel Products," *Corrosion Science*, Vol. 34, No. 11, 1993, pp. 1923-1931.

8. Kelen, T. *Polymer Degradation*, Van Nostrand Reinhold Company, New York, 1983, 211 pp.

9. Petersen, J. C. "A Thin Film Accelerated Aging Test for Evaluating Asphalt Oxidative Aging," *Asphalt Paving Technology*, Proceedings: Association of Asphalt Paving Technologists - Technical Sessions, Vol. 58, 1989, pp. 221-237.

10. Lyon, D. E. "Degradation of Wood in Use and Wood Protection," *Wood as a Structural Material*, Forest Products Laboratory, USDA, Dietz, Schaffer, and Gromala, eds., 1982, pp. 235-266.

11. Byfors, J. *Plain Concrete at Early Ages*, CBI Research Report No. 3:80, Swedish Cement and Concrete Research Institute, 1980, Stockholm, 464 pp.

12. ASTM E 632, "Standard Practice for Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials," ASTM E 632-82, Annual Book of ASTM Standards, Vol. 14.02, American Society for Testing Materials, Philadelphia, 1991.

13. Sjöström, C. "Overview of Methodologies for Prediction of Service Life," *Problems in Service Life Prediction of Building and Construction Materials*, Masters, ed., Martinus Mijhoff Publishers, 1985, pp. 3-20.

14. Fagerlund, G. "Essential Data for Service Life Prediction," *Problems in Service Life Prediction of Building and Construction Materials*, Masters, ed., Martinus Mijhoff Publishers, 1985, pp. 113-151.

15. Mullick, A. K. "Accelerated Tests for Prediction of Service Life of Concrete Structures," *Proceedings of the 3rd International Conference on the Durability of Building Materials and Components*, Espoo, Finland, 1984, pp. 123-134.

16. Mielenz, R. C. "Significance of Accelerated Durability Tests of Concrete," Highway Research Record, No. 268, Highway Research Board, 1969, pp. 17-34.

17. Brown, T. L., LeMay, H. E., and Bursten, B. E. *Chemistry -The Central Science*, Fifth Edition, Prentice-Hall, 1991, 1045 pp.

18. Laidler, K. J. *Chemical Kinetics*, Third Edition, Harper and Row Publishers, 1987, 531 pp.

19. Ladd, M. F. C., and Lee, W. H. *Introduction to Physical Chemistry*, Cambridge University Press, Cambridge, 1986, 347 pp.

20. Stiller, W. *Arrhenius Equation and Non-Equilibrium Kinetics: 100 Years Arrhenius Equation*, Teubner-Texte zur Physik - Band 21, Leipzig, 1989, 160 pp.

21. MacDougall, F. H. *Physical Chemistry*, The Macmillan Company, 1943, 722 pp.

22. Moore, W. J. *Physical Chemistry*, Third Edition, Prentice-Hall, Inc., 1962, 844 pp.

23. Paul, M. A. *Physical Chemistry*, D. C. Heath and Company, Boston, 1962, 460 pp.

24. Krokosky, E. M. "Construction Materials," *Standard Handbook for Civil Engineers*, Merritt, ed., McGraw-Hill, Inc., NY, 1983, pp. 5.1-5.49.

25. Illston, J. M., ed. *Construction Materials: Their Nature and Behaviour*, E & FN Spon, London, 1994, 518 pp.

26. Bradford, S. A. "Corrosion," *Encyclopedia of Physical Science and Technology*, Academic Press, Inc., 1992, 354 pp.

27. Baker, A. J. "Corrosion of Metal in Wood Products," *Durability of Building Materials and Components*, ASTM STP 691, Sereda and Litvan, eds., American Society for Testing and Materials, 1980, pp. 981-993.

28. Holsworth, R. M. "Overview - On the Weathering of Organic Coatings," *Permanence of Organic Coatings*, ASTM STP 781, American Society for Testing and Materials, 1982, pp. 3-9.

29. ASTM B 117, "Standard Test Method of Salt Spray (Fog) Testing," ASTM B 117-90, Annual Book of ASTM Standards, Vol. 03.02, American Society for Testing Materials, Philadelphia, 1993.

30. Ashton, H. E. "Evaluating the Performance of Organic Coatings and Building Materials," *Permanence of Organic Coatings*, ASTM STP 781, American Society for Testing and Materials, 1982, pp. 67-85.

31. Altmayer, F. "Choosing an Accelerated Corrosion Test," *Metal Finishing*, October 1985, pp. 57-60.

32. ASTM B 287, "Standard Test Method of Acetic Acid-Salt Spray (Fog) Testing," ASTM B 287 - discontinued in 1986, Annual Book of ASTM Standards, Vol. 02.05, American Society for Testing Materials, Philadelphia, 1993.

33. ASTM B 368, "Standard Test Method for Copper - Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test)," ASTM B 368-85, Annual Book of ASTM Standards, Vol. 02.05, American Society for Testing Materials, Philadelphia, 1993.

34. ASTM D 2247, "Standard Practice for Testing Water Resistance of Coating in 100% Relative Humidity," ASTM D 2247-92, Annual Book of ASTM Standards, Vol. 06.01, American Society for Testing Materials, Philadelphia, 1993.

35. ASTM G 60, "Standard Test Method for Conducting Cyclic Humidity Tests Testing," ASTM B 60-86, Annual Book of ASTM Standards, Vol. 03.02, American Society for Testing Materials, Philadelphia, 1993.

36. ASTM D 3459, "Standard Test Method for Humid-Dry Cycling for Coatings on Wood and Wood Products," ASTM D 3459-87, Annual Book of ASTM Standards, Vol. 06.02, American Society for Testing Materials, Philadelphia, 1993.

37. ASTM D 2246, "Standard Test Method for Finishes on Primed Metallic Substrates for Humidity - Thermal Cycle Cracking," ASTM D 2246 - discontinued in 1992, Annual Book of ASTM Standards, Vol. 06.01, American Society for Testing Materials, Philadelphia, 1993.

38. ASTM B 605, "Standard Specification for Electrodeposited Coatings of Tin-Nickel Alloy," ASTM B 605-75, Annual Book of ASTM Standards, Vol. 02.05, American Society for Testing Materials, Philadelphia, 1993.

39. ASTM G 37, "Standard Practice for Use of Matteson's Solution of pH 7.2 to Evaluate the Stress-Corrosion Cracking Susceptibility of Copper-Zinc Alloys," ASTM G 37-90, Annual Book of ASTM Standards, Vol. 03.02, American Society for Testing Materials, Philadelphia, 1993.

40. ASTM G 44, "Standard Practice for Evaluating Stress Corrosion Cracking Resistance of Metals and Alloys by Alternate Immersion in 3.5 % Sodium Chloride Solution," ASTM G 44-88, Annual Book of ASTM Standards, Vol. 03.02, American Society for Testing Materials, Philadelphia, 1993.

41. ASTM G 103, "Standard Test Method for Performing a Stress-Corrosion Cracking Test of Low Copper Containing Al-Zn-Mg Alloys in Boiling 6 % Sodium Chloride Solution," ASTM G 103-89, Annual Book of ASTM Standards, Vol. 03.02, American Society for Testing Materials, Philadelphia, 1993.

42. Sato, E., Abo, H., and Murata, T. "Lifetime Estimation and Accelerated Stress Corrosion Cracking Test of Stainless Steel in a Neutral Chloride Environment," *Corrosion*, November 1990, pp. 924-928.

43. Simpson, T. C. "Accelerated Corrosion Test for Aluminum-Zinc Alloy Coatings," *Corrosion*, July 1993, pp. 550-560.

44. Drazic, D. M., and Vascic, V. "The Correlation Between Accelerated Laboratory Corrosion Tests and Atmospheric Corrosion Station Tests on Steels," *Corrosion Science*, Vol. 29, No. 10, 1989, pp. 1197-1204.

45. Lyon, S. B., Thompson, G. E., Johnson, J. B., Wood, G. C., and Ferguson, J. M. "Accelerated Atmospheric Corrosion Testing Using a Cyclic Wet Dry Exposure Test: Aluminum, Galvanized Steel, and Steel," *Corrosion - NACE*, Vol. 43, No. 12, December 1987, pp. 719-726.

46. Boelen, B., Schmitz, B., Defourny, J., and Blekkenhorst, F. "A Literature Survey on the Development of an Accelerated Laboratory Test Method for Atmospheric Corrosion of Precoated Steel Products," *Corrosion Science*, Vol. 34, No. 11, 1993, pp. 1923-1931.

47. Kamal, M. R., and Saxton, R. "Recent Developments in the Analysis and Prediction of the Weatherability of Plastics," *Weatherability of Plastic Materials*, Applied Polymer Symposia No. 4, National Bureau of Standards, Gaithersburg MD, 8-9 February 1967, pp. 1-28.

48. Blaga, A. "Deterioration Mechanisms in Weathering of Plastic Materials," *Durability of Building Materials and Components*, ASTM STP 691, Sereda and Litvan, eds., American Society for Testing and Materials, 1980, pp. 827-837.

49. ASTM D 4674, " Standard Test Method for Accelerated Testing for Color Stability of Plastics Exposed to Indoor Fluorescent Lighting and Window-Filtered Daylight," ASTM D 4674-89, Annual Book of ASTM Standards, Vol. 08.03, American Society for Testing Materials, Philadelphia, 1993.

50. ASTM D 4364, "Standard Practice for Performing Accelerated Outdoor Weathering of Plastics Using Concentrated Natural Sunlight," ASTM D 4364-84, Annual Book of ASTM Standards, Vol. 08.03, American Society for Testing Materials, Philadelphia, 1993.

51. ASTM D 865, "Standard Test Method for Rubber - Deterioration by Heating in Air (Test Tube Enclosure)," ASTM D 865-88, Annual Book of ASTM Standards, Vol. 09.01, American Society for Testing Materials, Philadelphia, 1993.

52. ASTM D 573, "Standard Test Method for Rubber - Deterioration in an Air Oven," ASTM D 573-88, Annual Book of ASTM Standards, Vol. 09.01, American Society for Testing Materials, Philadelphia, 1993.

53. ASTM D 1870, "Standard Practice for Elevated Temperature Aging Using a Tubular Oven," ASTM D 1870-91, Annual Book of ASTM Standards, Vol. 09.01, American Society for Testing Materials, Philadelphia, 1993.

54. ASTM D 454, "Standard Test Method for Rubber Deterioration by Heat and Air Pressure," ASTM D 454-88, Annual Book of ASTM Standards, Vol. 09.01, American Society for Testing Materials, Philadelphia, 1993.

55. ASTM D 572, "Standard Test Method for Rubber - Deterioration by Heat and Oxygen," ASTM D 572-88, Annual Book of ASTM Standards, Vol. 09.01, American Society for Testing Materials, Philadelphia, 1993.

56. ASTM D 395, "Standard Test Methods for Rubber Property - Compression," ASTM D 395-89, Annual Book of ASTM Standards, Vol. 09.01, American Society for Testing Materials, Philadelphia, 1993.

57. ASTM D 3137, "Standard Test Method for Rubber Property - Hydrolytic Stability," ASTM D 3137-81, Annual Book of ASTM Standards, Vol. 09.01, American Society for Testing Materials, Philadelphia, 1993.

58. ASTM D 756, "Standard Practice for Determination of Weight and Shape Changes of Plastics Under Accelerated Service Conditions," ASTM D 756-78, Annual Book of ASTM Standards, Vol. 08.01, American Society for Testing Materials, Philadelphia, 1993.

59. Kamal, M. R. "Effect of Variables in Artificial Weathering on the Degradation of Selected Plastics," *Polymer Engineering and Science*, October 1966, pp. 333-340.

60. Lemaire, J. "Predicting Polymer Durability," *Chemtech*, October 1996, pp. 42-47.

61. Pett, R. A., and Tabar, R. J. "The Oxidative Aging of a Compounded Natural Rubber Vulcanizate," *Rubber Chemistry and Technology*, Vol. 51, 1977, pp. 1-6.

62. Nichols, M. E., and Pett, R. A. "Effects of Aging on the Fracture Behavior of Chlorinated Polyethylene and Chlorosulfonated Polyethelene," *Rubber Chemistry and Technology*, Vol. 67, No. 4, September-October 1994, pp. 619-628.

63. Vicic, J. C., Cain, D., and Maligas, M. "Estimating Elastomer Failure Life Using Environmental Tests," *Elastomerics*, May 1992, pp. 16-22.

64. Vicic, J. C., Cain, D., Roldan, S., Su, L., and Chen, C. C. "Life Estimation of Elastomers Using Temperature-Stress Acceleration Techniques," *Materials Performance*, June 1991, pp. 52-54.

65. Carlozzo et al. - The Cleveland Society for Coatings Technology Technical Committee. "Correlation of Accelerated Testing and Exterior Exposure Sites," *Journal of Coatings Technology*, Vol. 66, No. 837, October 1994, pp. 49-67.

66. Carlozzo et al. - The Cleveland Society for Coatings Technology Technical Committee. "Correlation of Accelerated Exposure Testing and Exterior Exposure Sites Part II: One-Year Results," *Journal of Coatings Technology*, Vol. 68, No. 858, July 1996, pp. 47-61.

67. Stern, H. J. *Rubber: Natural and Synthetic*, Maclaren and Sons Ltd., London, 1967, 519 pp.

68. ASTM D 4818, “Standard Classification for Rubber Compounding Materials - Vulcanization Accelerators,” ASTM D 4818-89, Annual Book of ASTM Standards, Vol. 09.01, American Society for Testing Materials, Philadelphia, 1993.

69. Road Research Laboratory Personnel. *Bituminous Materials in Road Construction*, Department of Scientific and Industrial Research: Road Research Laboratory, Her Majesty's Stationary Office, London, 1962, 611 pp.

70. Stanton, T. E., and Hveem, F. N. "Test Methods for Performing Accelerated Durability Tests on Asphalts," *Symposium on Accelerated Durability Testing of Bituminous Materials*, American Society for Testing Materials, Atlantic City NJ, 30 June - 1 July 1949, pp. 84-99.

71. Oliensis, G. L. "Durability Tests - A Word of Caution," *Symposium on Accelerated Durability Testing of Bituminous Materials*, American Society for Testing Materials, Atlantic City NJ, 30 June - 1 July 1949, pp. 100-108.

72. Herrington, P. R., Patrick, J. E., and Ball, G. F. A. "Oxidation of Road Asphalts," *Industrial and Engineering Chemistry Research*, November 1994, pp. 2801-2809.

73. ASTM D 1754, "Standard Test Method for Effect of Heat and Air on Asphaltic Materials (Thin-Film Oven Test)," ASTM D 1754-87, Annual Book of ASTM Standards, Vol. 04.03, American Society for Testing Materials, Philadelphia, 1993.

74. ASTM D 2872, "Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test)," ASTM D 2872-88, Annual Book of ASTM Standards, Vol. 04.03, American Society for Testing Materials, Philadelphia, 1993.

75. Huang, S., Tia, M., and Ruth, B. E. "Laboratory Aging Methods for Simulation of Field Aging of Asphalts," *Journal of Materials in Civil Engineering*, August 1996, pp. 147-152.

76. Ishai, I. "A Suggested Methodology for the Analysis of Asphalt Age-Hardening," *Journal of Testing and Evaluation*, May 1987, pp. 127-132.

77. Schniewind, A. P, ed. *Concise Encyclopedia of Wood and Wood-Based Materials*, The MIT Press, Cambridge MA, 1989, 354 pp.

78. Singh, J. and White, N. "Timber Decay in Buildings: Pathology and Control," *Journal of Performance of Constructed Facilities*, February 1997, pp. 3-12.

79. ASTM D 1037, "Standard Test Methods for Evaluating Properties of Wood-Base Fiber and Particle Panel Materials," ASTM D 1037-93, Annual Book of ASTM Standards, Vol. 04.09, American Society for Testing Materials, Philadelphia, 1993.

80. ASTM D 2164, "Standard Methods of Testing Structural Insulating Roof Deck," ASTM D 2164-83, Annual Book of ASTM Standards, Vol. 04.09, American Society for Testing Materials, Philadelphia, 1993.

81. ASTM D 2898, "Standard Test Methods for Accelerated Weathering of Fire-Retardant-Treated Wood for Fire Testing," ASTM D 2989-81, Annual Book of ASTM Standards, Vol. 04.09, American Society for Testing Materials, Philadelphia, 1993.

82. ASTM D 2017, "Standard Method of Accelerated Laboratory Test of Natural Decay Resistance of Woods," ASTM D 2017-81, Annual Book of ASTM Standards, Vol. 04.09, American Society for Testing Materials, Philadelphia, 1993.

83. Williams, R. S. "Effect of Dilute Acid on the Accelerated Weathering of Wood," *JAPCA*, February 1988, pp. 148-151.

84. Torraca, G. *Porous Building Materials - Materials Science for Architectural Conservation*, ICCROM, Rome, 1982, 145 pp.

85. Winkler, E. M. *Stone in Architecture: Properties, Durability*, Springer-Verlag, Berlin, 1994, 309 pp.

86. Ashurst, J. and Dimes, F. G. *Conservation of Building and Decorative Stone*, Vol. 1, Butterworth-Heinemann Ltd., London, 1990, 193 pp.

87. Beard, R. "Brick Masonry," *Chemistry and Industry*, 15 December 1986, pp. 848-854.

88. ASTM D 4992, "Standard Practice for Evaluation of Rock to be Used for Erosion Control," ASTM D 4992-89, Annual Book of ASTM Standards, Vol. 04.08, American Society for Testing Materials, Philadelphia, 1993.

89. ASTM D 5313, "Standard Test Method for Evaluation of Durability of Rock for Erosion Control Under Wetting and Drying Conditions," ASTM D 5313-92, Annual Book of ASTM Standards, Vol. 04.08, American Society for Testing Materials, Philadelphia, 1993.

90. ASTM D 5312, "Standard Test Method for Evaluation of Durability of Rock for Erosion Control Under Freezing and Thawing Conditions," ASTM D 5312-92, Annual Book of ASTM Standards, Vol. 04.08, American Society for Testing Materials, Philadelphia, 1993.

91. Carr, D. D., Strickland, J., McDonald, W. M., and Bortz, S. "Review of Durability Testing of Building Stone with Annotated Bibliography," *Journal of Testing and Evaluation*, September 1996, pp. 324-328.

92. Binda, L., and Baronio, G. "Measurement of the Resistance to Deterioration of Old and New Bricks by Means of Accelerated Aging Tests," *Durability of Building Materials*, Vol. 2, 1984, pp. 139-154.

93. Young, R. F., Former President of American Soil, Inc. composting facility. Personal correspondence, November 1997.

94. Skerry, B. S., and Simpson, C. H. "Accelerated Test Method for Assessing Corrosion and Weathering of Paints for Atmospheric Corrosion Control," *Corrosion*, Vol. 49, No. 8, pp. 663-674.

95. ASTM C 666, "Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing," ASTM C 666-92, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

96. ASTM C 672, "Standard Test Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals," ASTM C 672-92, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

97. ASTM C 227, "Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations (Mortar-Bar Method), ASTM C 227-90, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

98. ASTM C 289, "Standard Test Method for Potential Alkali-Silica Reactivity of Aggregates (Chemical Method), ASTM C 289-94, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

99. ASTM C 1260, "Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)," ASTM C 1260-94, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

100. ASTM C 1293, "Standard Test Method for Concrete Aggregates by Determination of Length Change of Concrete Due to Alkali-Silica Reaction," ASTM C 1293-95, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

101. ASTM C 586, "Standard Test Method for Potential Alkali Reactivity of Carbonate Rocks for Concrete Aggregates (Rock Cylinder Method)," ASTM C 586-92, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

102. ASTM C 1105, "Standard Test Method for Length Change of Concrete Due to Alkali-Carbonate Rock Reaction," ASTM C 1105-95, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

103. ASTM C 452, "Standard Test Method for Potential Expansion of Portland Cement Mortars Exposed to Sulfate," ASTM B C 452-89, Annual Book of ASTM Standards, Vol. 04.01, American Society for Testing Materials, Philadelphia, 1993.

104. ASTM C 1012, "Standard Test Method for Length Change of Hydraulic Cement Mortars Exposed to a Sulfate Solution," ASTM C 1012-89, Annual Book of ASTM Standards, Vol. 04.01, American Society for Testing Materials, Philadelphia, 1993.

105. ASTM C 418, "Standard Test Method for Abrasion Resistance of Concrete by Sandblasting," ASTM C 418-90, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

106. ASTM C 779, "Standard Test Method for Abrasion Resistance of Horizontal Concrete Surfaces," ASTM C 779-95, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

107. ASTM C 944, "Standard Test Method for Abrasion Resistance of Concrete or Mortar Surfaces by the Rotating-Cutter Method," ASTM C 944-95, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

108. ASTM C 1138, "Standard Test Method for Abrasion Resistance of Concrete (Underwater Method)," ASTM C 1138-97, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

109. Soroka, I. *Concrete in Hot Environment*, E & F N Spon, 1993, 251 pp.

110. Bye, G. C. *Portland Cement - Composition, Production and Properties*, Pergamon Press, 1983, 149 pp.

111. Bensted, J. "Hydration of Portland Cement," *Advances in Cement Technology - Critical Reviews and Case Studies on Manufacturing, Quality Control, Optimization and Use*, Ghosh, ed., Pergamon Press, 1983, 307-347.

112. Copeland, L. E., and Kantro, D. L. "Hydration of Portland Cement at Ordinary Temperatures," *The Chemistry of Cements*, Vol. 1, Taylor, ed., Academic Press, 1964, pp. 314-370.

113. Gartner, E. M., and Gaidis, J. M. "Hydration Mechanisms I," *Material Science of Concrete*, Vol. 1, Skalny, ed., The American Ceramic Society, 1989, pp. 95-126.

114. Jawed, I., Skalny, J., and Young, J. F. "Hydration of Portland Cement Cement," *Structure and Performance of Cements*, Barnes, ed., Applied Science Publishers, 1983, pp. 461-465.

115. Taylor, H. F. W. *Cement Chemistry*, Academic Press, 1990, 475 pp.

116. Brown, P. W., "Early-Age Cement Hydration Reactions," *Transportation Research Record*, No. 1284, 1990, pp. 53-59.

117. Rodger, S. A., Groves, G. W., Clayden, N. J., and Dobson, C. M. "Hydration of Tricalcium Silicate Followed by ^{29}SiNMR with Cross-Polarization," *Journal of the American Ceramic Society*, Vol. 71, No. 2, 1988, pp. 91-96.

118. Scrivener, K. L., and Wieker, W. "Advances in Hydration at Low, Ambient and Elevated Temperatures," *Proceedings of the 9th International Congress on the Chemistry of Cement*, Vol. I, New Delhi, 1992, pp. 449-482.

119. Mindness, S., and Young, J. F. *Concrete*, Prentice-Hall Inc., 1981, 672 pp.

120. Scrivener, K. L. "The Microstructure of Concrete," *Material Science of Concrete*, Vol. I, Skalny, ed., The American Ceramic Society, 1989, pp. 127-161.

121. Kantro, D. L., Brunauer, S., and Weise, C. H. "Development of Surface in the Hydration of Calcium Silicates. II. Extension of Investigation to Earlier and Later Stages of Hydration," *Journal of Physical Chemistry*, Vol. 66, 1962, pp. 1804-1809.

122. Fujii, K., and Kondo, W. "Kinetics of the Hydration of Tricalcium Silicate," *Journal of the American Ceramic Society*, Vol. 57, 1974, pp. 492-497.

123. Carino, N. J. "Maturity Method: Theory and Application," *Journal of Cement, Concrete, and Aggregates*, ASTM, Vol. 6, No. 2, Winter, 1984, pp. 61-73.

124. Carino, N. J., and Tank, R. C. "Maturity Functions for Concretes Made with Various Cements and Admixtures," *ACI Materials Journal*, Vol. 89, No. 2, 1989, pp. 188-196.

125. ASTM C 1074, "Standard Practice for Estimating Concrete Strength by the Maturity Method," ASTM C 1074-93, Annual Book of ASTM Standards, Vol. 04.02, Philadelphia: American Society for Testing Materials, 1997.

126. Ma, W., Sample, D., Martin, R., and Brown, P. W. "Calorimetric Study of Cement Blends Cointaining Fly Ash, Silica Fume, and Slag at Elevated Temperatures," *Cement, Concrete, and Aggregates*, Vol. 16, No. 2, 1994, pp. 93-99.

127. Kjellsen, K. O., and Detwiler, R. J. "Later-Age Strength Prediction by a Modified Maturity Method," *ACI Materials Journal*, Vol. 90, No. 3, 1993, pp. 220-227.

128. Verbeck, G. J., and Helmuth, R. H. "Structure and Physical Properties of Cement Paste," *Proceedings of the 5th International Symposium on the Chemistry of Cement*, Vol. III, 1968, pp. 1-32.

129. Kjellsen, K. O., Detwiler, R., J., and Gjørv, O. E. "Development of Microstructure in Plain Cement Pastes Hydrated at Different Temperatures," *Cement and Concrete Research*, Vol. 21, 1991, pp. 179-189.

130. Patel, H. H., Bland, C. H., and Poole, A. B. "The Microstructure of Concrete Cured at Elevated Temperatures," *Cement and Concrete Research*, Vol. 25, No. 3, 1995, pp. 485-490.

131. Kosmotka, S. H., and Panarese, W. C. *Design and Control of Concrete Mixtures*, Thirteenth Edition, Portland Cement Association, 1988, 205 pp.

132. Taylor, H. F. W., Guest Editorial. *Cement & Concrete Composites*, Vol. 18, No. 3, 1996, pp.157-159.

133. Odler, I. and Chen, Y. "On the Delayed Expansion of Heat Cured Portland Cement Pastes and Concretes," *Cement & Concrete Composites*, Vol. 18, No. 3, 1996, pp.181-185.

134. Diamond, S. "Delayed Ettringite Formation - Processes and Problems," *Cement & Concrete Composites*, Vol. 18, No. 3, 1996, pp. 205-215.

135. Day, R. L. "The Effect of Secondary Ettringite Formation on the Durability of Concrete: A Literature Analysis," Research and Development Bulletin RD108T, Portland Cement Association, 1992, 115 pp.

136. Saul, A. G. A. "Principles Underlying the Steam Curing of Concrete at Atmospheric Pressure," *Magazine of Concrete Research*, Vol. 2, No. 6, 1951, pp. 127-140.

137. Malhotra, V. M. "Maturity Concept and the Estimation of Concrete Strength - A Review," *Information Circular IC 277*, Department of Energy, Mines and Resources (Canada), November 1971, 43 pp.

138. Carino, N. J. "The Maturity Method," *CRC Handbook on Nondestructive Testing of Concrete*, Malhotra and Carino, eds., CRC Press, 1991, pp. 101-146.

139. Johnson, G. L. *Concrete Testing on the Kroch Library Project: Thermometry, Maturity, and Calorimetry*, M. Sc. Thesis, Cornell University, 1993.

140. McIntosh, J. D. "Electrical Curing of Concrete," *Magazine of Concrete Research*, Vol. 1, No. 1, 1949, pp. 21-28.

141. Nurse, R. W. "Steam Curing of Concrete," *Magazine of Concrete Research*, Vol. 1 No. 2, 1949, pp. 79-88.

142. Rastrup, E. "Heat of Hydration in Concrete," *Magazine of Concrete Research*, Vol. 6, No. 17, 1954, pp. 79-92.

143. Freiesleben-Hanson, P., and Pedersen, E. J. "Maturity Computer for Controlled Curing and Hardening of Concrete," *Nordisk Betong*, Vol. 1, 1977, pp. 21-25.

144. Abdun-Nur, E. A. “Accelerated, Early, and Immediate Evaluation of Concrete Quality,” *Accelerated Strength Testing*, American Concrete Institute, SP-56, 1978, pp. 1-13.

145. Ramakrishnan, V. “Accelerated Strength Testing - Annotated Bibliography,” *Accelerated Strength Testing*, American Concrete Institute, SP-56, 1978, pp. 285-312.

146. Sanchez-Trejo, R., and Flores-Castro, L. “Experience in the Use of the Accelerated Testing Procedure for the Control of Concrete During the Construction of Tunnel “Emmisor Central” in Mexico City,” *Accelerated Strength Testing*, American Concrete Institute, SP-56, 1978, pp. 15-28.

147. Bickley, J. A. “Accelerated Concrete Strength Testing at the CN Tower,” *Accelerated Strength Testing*, American Concrete Institute, SP-56, 1978, pp. 29-38.

148. Ferrer, M. M. “Quality Control of Concrete by Means of Short-Term Tests at La Angostura Hydroelectric Project, State of Chiapas, Mexico,” *Accelerated Strength Testing*, American Concrete Institute, SP-56, 1978, pp. 51-74.

149. Rodway, L. E., and Lenz, K. A. “Use of the Modified Boiling Water Method in Manitoba and Alberta, Canada,” *Accelerated Strength Testing*, American Concrete Institute, SP-56, 1978, pp. 129-148.

150. ASTM C 684, “Standard Test Method for Making, Accelerated Curing, and Testing Concrete Compression Test,” ASTM C 684-96, Annual Book of ASTM Standards, Vol. 04.02, Philadelphia: American Society for Testing Materials, 1997.

151. Carino, N. J. “Prediction of Potential Concrete Strength at Later Ages,” *Significance of Tests and Properties of Concrete and Concrete-Making Materials*, Klieger and Lamond, eds., ASTM STP 169C, American Society of Testing Materials, 1994, pp. 140-152.

152. Resheidat, M. R., and Manadat, O. N. “Accelerated Strength and Testing of Concrete in Jordan,” *Materials and Structures*, Vol. 25, 1992, 79-83.

153. Resheidat, M. R., and Ghanma, M. S. “Accelerated Strength and Testing of Concrete Using Blended Cement,” *Advanced Cement Based Materials*, Vol. 5, No. 2, 1997, pp. 49-56.

154. Siviero, E. “Evaluation of Early Concrete Strength,” *Materials and Strictures*, Vol. 27, 1994, pp. 273-284.

155. Das Gupta, N. C., and Tam, C. T. "Controlled Tropical Curing Method for Accelerated Concrete Strength," *The International Journal of Cement Composites and Lightweight Concrete*, Vol. 11, No. 1, 1989, pp. 29-36.

156. Higginson, E. C. "Effect of Steam Curing on the Important Properties of Concrete," *Proceedings: Journal of the American Concrete Institute*, Vol. 58, 1961, pp. 281-298.

157. Hanson, J. A. "Optimum Steam Curing Procedure in Precasting Plants," *Proceedings: Journal of the American Concrete Institute*, Vol. 60, 1963, pp. 75-100.

158. Oluokon, F. A., Burdette, E. G., and Deatherage, J. H. "Concrete Physical Property Development at Early Ages: the Influence of Steam Curing," *Transportation Research Record*, No. 1284, Transportation Research Board, 1990, pp. 31-36.

159. Powers, T. C. "The Air Requirement of Frost Resistant Concretes," *Proceedings: Highway Research Board*, Vol. 29, 1949, 184 pp.

160. Kreijer, P. C. "Inhomogeneity in Concrete and Its Effect on Degradation: a Review of Technology," *Protection of Concrete*, Dhir and Green, eds., E & F.N. Spon, London, 1990, pp. 31-52.

161. Newlon, H. Jr., and Mitchell, T. M. "Freezing and Thawing," *Significance of Tests and Properties of Concrete and Concrete-Making Materials*, ASTM STP 169C, American Society for Testing Materials, Klieger and Lamond, eds., 1994, pp. 153-163.

162. ASTM C 215, "Standard Test Method for Fundamental Transverse, Longitudinal, and Torsional Frequencies of Concrete Specimens," ASTM C 215-91, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

163. Vanderhost, N. M., and Jansen, D. J. "The Freezing-and-Thawing Environment: What is Severe?" *Paul Krieger Symposium on Performance of Concrete*, Whiting, ed., SP-122, American Concrete Institute, 1990, pp. 181-200.

164. Lin, C., and Walker, R. D. "Effects of Cooling Rates on the Durability of Concrete," *Transportation Research Record*, 539, 1975, pp. 8-19.

165. Pigeon, M., Prevost, J., and Simard, J. "Freeze-Thaw Durability Versus Freezing Rate," *Journal of the American Concrete Institute*, Vol. 82, 1985, pp. 684-692.

166. Siebel, E. and Reschke, T. "Three Different Methods for Testing the Freeze-Thaw Resistance of Concrete with and without Deicing Salt - European Round Robin Test," *International Workshop on the Resistance of Concrete to Scaling due to*

Freezing in the Presence of Deicing Salts, Centre de Recherche Interuniversitaire sur le Béton (CRIB), Université de Sherbrooke - Université Laval, 1993, pp. 75-92.

167. Janssen, D. J., and Snyder, M. B. "Mass loss experience with ASTM C 666: with and without Deicing Salts," *International Workshop on the Resistance of Concrete to Scaling due to Freezing in the Presence of Deicing Salts*, Centre de Recherche Interuniversitaire sur le Béton (CRIB), Université de Sherbrooke - Université Laval, 1993, pp. 137-152.

168. Narayanan, G. *Further Investigations into the Deicer Scaling of Slag Cement Concrete with Emphasis on Surface Properties*, M. Sc. Thesis, Cornell University, 1997, 199 pp.

169. Gagne, R., Pigeon, M., and Aitcin, P. C. "Deicer Salt Scaling Resistance of High Performance Concretes," *Paul Krieger Symposium on Performance of Concrete*, Whiting, ed., SP-122, American Concrete Institute, 1990, pp. 29-44.

170. Marchand, J., Gagné, R., Jacobsen, S., Pigeon, M. and Sellevold, E. J. "La Résistance au Gel des Bétons a Haute Performance," *Canadian Journal of Civil Engineering*, Vol. 23, No. 5, 1996, pp. 1070-1080.

171. Jacobsen, S., and Sellevold, E. J. "Frost Testing of High Strength Concrete: Scaling and Cracking," Fourth International Symposium on the Utilization of High Strength/High Performance Concrete, Paris, 1996, pp. 597-606.

172. ASTM C 33, "Standard Specification for Concrete Aggregates," ASTM C 33-93, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

173. Stark, D. "Alkali-Silica Reaction in Concrete," *Significance of Tests and Properties of Concrete and Concrete-Making Materials*, ASTM STP 169C, American Society for Testing Materials, Klieger and Lamond, eds., 1994, pp. 365-371.

174. Stark, D. "Alkali Silica Reactivity: Some Considerations," *ASTM Cement, Concrete, and Aggregates*, Vol. 2, No. 2, 1980, pp. 92-94.

175. Clifton, J. R., and Knab, L. I. "Service Life of Concrete," *NISTIR 89-4089*, 1989, 119 pp.

176. ASTM C 295, "Standard Guide for Petrographic Examination of Aggregates for Concrete," ASTM C 295-90, Annual Book of ASTM Standards, Vol. 04.02, American Society for Testing Materials, Philadelphia, 1997.

177. Clifton, J. R. "Predicting the Remaining Service Life of Concrete," NISTIR 4712, 1991, 73 pp.

178. DePuy, G. W. "Chemical Resistance of Concrete," *Significance of Tests and Properties of Concrete and Concrete-Making Materials*, ASTM STP 169C, American Society for Testing Materials, Klieger and Lamond, eds., 1994, pp. 263-281.

179. ACI Committee 201, *Guide to Durable Concrete*, American Concrete Institute, 1992, 39 pp.

180. Liu, T. C. "*Abrasion Resistance, Significance of Tests and Properties of Concrete and Concrete-Making Materials*, ASTM STP 169C, American Society for Testing Materials, Klieger and Lamond, eds., 1994, pp. 182-191.

181. Saeki, T., Ohga, H., and Nagataki, S. "Change in Micro-Structure of Concrete due to Carbonation," *Concrete Library of JSCE*, No. 18, 1991, pp. 1-12.

182. Al-Kadhimi, T. K. H., Banfill, P. F. G., Millard, S. G., and Bungey, J. H. "An Accelerated Carbonation Procedure for Studies on Concrete," *Advances in Cement Research*, Vol. 8, 1996, pp. 47-59.

183. Carde, C., and François, R. "Aging Damage Model of Concrete Behavior During the Leaching Process," *Materials and Structures*, Vol. 30, 1997, pp. 465-472.

184. Belie, N. D., Debruyckere, M.m Nieuwenburg, D. V., and Blaere B. D. "Concrete Attack by Feed Acids: Accelerated Tests to Compare Different Concrete Compositions and Technologies," *ACI Material Journal*, Vol. 94, No. 6, 1997, pp. 546-554.

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