BNL-61651

Conf-950740--34

AGING MECHANISMS FOR CONCRETE COMPONENTS OF HIGH-LEVEL WASTE STORAGE TANKS

M. Kassir[1], K. Bandyopadhyay, S. Bush, B. Mather, P. Shewmon, M. Streicher, B. Thompson, D. van Rooyen, J. Weeks[2]

ABSTRACT

The age-related degradation mechanisms which affect the concrete and the reinforcing steel in the high-level waste (HLW) storage tanks are evaluated with respect to their potential significance to the continued performance of the concrete, and are classified into non-significant and potentially significant. A degradation mechanism is classified as non-significant if it can be shown that the concrete enclosure is either not susceptible to it or affected by it to such a small degree that its intended function, namely, providing structural stability against design and postulated loads, will be maintained during the remaining service life of the tank. An age-related degradation mechanism is defined as potentially significant when, if allowed to continue without mitigating measures, it cannot be shown that the concrete enclosure would continue to maintain its structural capability. Such degradations require mitigating measures to manage the degradation.

The identified potentially significant degradation mechanisms include the effects of elevated temperature, freezing and thawing, leaching of calcium hydroxide, aggressive chemical attack, and corrosion of the reinforcing steel. To the extent that available knowledge permits, these mechanisms are generically evaluated and quantified so that site-specific plans may be developed to verify whether significant degradation has occurred in the concrete, and, if so, to formulate mitigating measures to avoid further deterioration and possibly repair the degradation or pursue other management options.

INTRODUCTION

The age-related degradation mechanisms which may affect concrete and the reinforcing steel in the tank structures are identified from a review and evaluation of their operating history, relevant laboratory test data, analytical assessment, and related experience of similar structures in other industries [BNL Report by authors (TSIP), 1994]. The factors related to age-related degradation mechanisms include: elevated temperature, freezing and thawing, leaching of calcium hydroxide or other soluble constituents, aggressive chemical attack, alkali-aggregate reactions, creep and shrinkage, abrasion and cavitation, irradiation, and corrosion of embedded steel.

The degradation mechanisms are classified into non-significant and potentially significant. A degradation mechanism is classified as non-significant if it can be shown that the concrete enclosure is either not susceptible to it or affected by it to such a small degree that the intended function, namely, providing structural stability against design and postulated loads, may be expected to be maintained during the remaining service life of the tank. An age-related degradation mechanism

[1]Presenter

[2]The authors are members of or consultants to the Tank Structural Integrity Panel (TSIP) established by Brookhaven National Laboratory for the U.S. Department of Energy, Office of Environmental Restoration and Waste Management.

is defined as potentially significant when, if allowed to continue without mitigating measures, it cannot be shown that the concrete enclosure would continue to maintain its structural capability. Such degradations require mitigating remedies to manage the degradation.

The non-significant aging mechanisms for the concrete of the underground HLW storage tanks include, reaction of aggregates with alkalies, creep (except creep strain induced by elevated temperature) and shrinkage, abrasion and cavitation, and irradiation [BNL Report by authors (TSIP), 1994]. These mechanisms are not discussed in this paper. The following sections contain descriptions of the potentially significant degradation mechanisms and quantitative interpretations of their influences on the capability of the concrete in the HLW storage tanks.

ELEVATED TEMPERATURE

When conventional (non-refractory) concrete is exposed to sufficiently elevated temperatures, it begins to experience reactions involving loss of absorbed and combined moisture present in the cement paste, possible thermal incompatibilities between paste and aggregate, and eventual deterioration of some possible constituents of the aggregate due to phase changes if the temperature becomes high enough and suitable aggregates were not used. Typically, such degradation is accompanied by a decrease in the compressive strength and in the stiffness (modulus of elasticity) of the concrete. Also, the creep of concrete at elevated temperature and under sustained load could have an adverse effect in the concrete structure over a period of time. Generally speaking, the threshold of degradation in the concrete is at a temperature of about 95°C (200°F). The level of degradation is influenced by many variables including concrete mixing, curing age before exposure to heat, time of exposure to heat, degree of loss of moisture content, and loading conditions. A comprehensive review of the effects of elevated temperatures on degradation of concrete is available in Kassir, et al. (1993). The temperature range which is relevant for the HLW storage tanks is from ambient to 315°C (600°F).

A review of the technical data, based mostly on laboratory testing, reveals that the compressive strength of concrete decreases with a rise in temperature. The following observations should be noted:

(a) There is less strength degradation in laboratory specimens tested under "hot" conditions compared to those tested under "cold" conditions. In "hot tests" the specimens are gradually heated to the specified level, allowed to stabilize at that level for a prescribed time and then tested while hot at that temperature. In "cold tests," the specimens are heated to the specified temperature, allowed to stabilize at that temperature for a prescribed time, cooled down slowly to room temperature, and then tested to determine the mechanical properties.

(b) Sealed specimens lose more strength than unsealed ones. This is because the moisture is not allowed to escape during heating and subsequent testing.

(c) The type of aggregates and mixture proportions influence the degradation in the strength of heated concrete. In particular, lean concrete (low cement content) shows smaller reduction in the compressive strength than rich concrete. Also, limestone aggregates degrade less than siliceous ones when the specimen is heated.

(d) The period of sustained heating and level of temperature rise affect the degree of degradation of concrete.

(e) Conditions of loading during exposure to heat, i.e., whether the concrete specimen is unaxially or multiaxially loaded and whether it is restrained during heating.

Based on these observations, the variation of the residual compressive strength of concrete (expressed as % of the initial strength) with rise in temperature up to the 600°F level is shown in Figure 1. The experimental data were obtained for specimens tested under both cold and hot conditions. The upper and lower bound strength curves represent the full spread of the data base. The variations of the mean and 84% compressive strengths (based on standard log-normal distribution of the data) with rise in temperature are also shown in Figure 1. It is clear from this figure that ***the upper bound of the test data indicates almost no reduction in the concrete strength for elevated temperatures through almost 600°F. The lower bound data, however, indicate a reduced strength for temperatures above 100°F. For example, for specimens tested at 300°F, the lower bound reduced strength is 60% of the initial compressive strength at room temperature while the mean reduced strength is about 85% of its original value.***

The stiffness or modulus of elasticity, E_c, which is the ratio of stress to strain, is an important parameter to describe the structural behavior of concrete components. At elevated temperatures, the modulus experiences a permanent reduction in its value. Like the strength parameter, several factors influence the value of the modulus of elasticity in laboratory specimens tested at high temperatures. The major factors include the method of test conditions (hot or cold) and prevention of moisture loss (sealed or unsealed specimens).

Figure 2 shows the variation of the modulus of elasticity (expressed as % of the initial room temperature value, E_c) with increase in temperature. The upper and lower curves envelope the data obtained from specimens tested in hot and cold conditions and at various moisture paths. The curves representing the mean and 84% values of the degraded moduli of elasticity are also available in Figure 2. It is clear that the degradation in the modulus of elasticity is more pronounced than that in the compressive strength, especially in the high-temperature range. At 100°F, the upper bound envelope indicates no reduction in the modulus while the lower bound curve reveals a reduction of about 5%. ***At 300°F, the upper bound curve indicates a modulus of 0.9 E_c, the lower bound curve shows a modulus of 0.45 E_c, and the mean reduced modulus is 0.7 E_c***

The creep, which is defined as an increase in strain with time under a constant stress, also affects the degradation of concrete. Since creep in concrete is a function of the evaporable water and reduces to zero when no evaporable water is present, it increases with rise in temperature. The increase in creep is due to the diffusion of solid particles and moisture into the gaps of the material. In the temperature range of interest, i.e., from ambient to 315°C (600°F), the effect of elevated temperature on creep deformation can be accounted by multiplying the predicted creep at ambient temperature by a factor, TF, given by

$$TF = 1 + 0.5\left(\frac{T}{70}\right), \quad 100 \le T \le 600$$

where T is the concrete temperature in F. The creep at ambient temperature may be predicted using the approach of ACI committee 209 [ACI 318, 1993]. Further discussion is available in [Kassir, et al., 1995].

The mechanical properties (yield strength and modulus of elasticity) of the embedded reinforcing steel are also expected to experience reduction with increasing temperatures. However, in the range of temperature under discussion, the reduction is not as detrimental as in the concrete [Kassir, et al., 1995].

FREEZING AND THAWING

Freezing and thawing degradation can occur in waste tanks exposed to cold environment and situated in sites where the water table is above the depth of frost penetration. This is because water freezing within the capillary pores of concrete creates hydraulic pressure which either increases the size of the cavities due to ice formation or forces some of the water into small voids in the surrounding areas created by entrained air bubbles. The physical manifestations of such damage include cracking, scaling, and spalling. In extreme cases, the degradation could expose the reinforcing steel to accelerated corrosion, and the resulting expansive products deteriorate the concrete further and could reduce its strength and loosen the bond between concrete and the embedded steel. The primary parameters which affect the occurrence of such degradation in the concrete vaults of the tanks include the air content of the concrete and the number, size, and distribution of the pores within the aggregate of the concrete [Mather, 1990]. The air content of the mixture needed to prevent such damage should meet the minimum requirement of Building Code ACI 318 (1994).

The following factors increase the resistance of concrete to degradation due to freezing and thawing:

(a) Adequate entrained air-void system in the cement paste (4% to 7%).

(b) Frost-resistant aggregate.

(c) Low water/cement ratio and adequate placing and curing.

Degradation due to freezing and thawing may be a significant issue for storage tanks under certain adverse conditions. For tanks where the concrete will not freeze repeatedly, the risk is not significant. This potential is almost nonexistent for underground tanks once earth backfill is put in place.

The environment to cause freezing and thawing degradation is measured in terms of "Weathering Index" which is defined as the product of the average number of freezing cycles times the average annual winter rainfall. ASTM C33 [1982] groups the U.S. into "severe," "moderate" and "negligible" weathering regions. Freezing and thawing damage potential is "severe" when the index exceeds 500 day-inches (1270 day-centimeter), it is "moderate" between 100 and 500 day-inches (254 and 1270 day-centimeter), and it is "negligible" when it is less than 100 day-inches (254 day-centimeter). If the concrete mix of the vault of the waste tank meets the air content and water-cement ratio requirements of ACI 318 [1994] then freeze-thaw damage is not a significant degradation mechanism for the "negligible" and "moderate" regions. For exposed concrete surfaces of waste tanks situated in "severe" weather regions, the degradation of affected surfaces of concrete could be significant and requires inspection and evaluation. However, such conditions may not exist for any of the high-level waste tank farms since they are underground structures.

LEACHING OF CALCIUM HYDROXIDE

Water flowing through cracks or inadequately prepared construction joints in the concrete vaults of the tanks can dissolve some calcium-containing products in concrete. The most readily soluble material is calcium hydroxide (hydrated lime). When calcium hydroxide has been leached away, other cementitious constituents become exposed to chemical decomposition, which eventually could leave behind silica and alumina gels with little or no strength [Troxell, et al., 1968]. Leaching over long periods increases the porosity and permeability of concrete, making it more susceptible to other forms of aggressive attack and eventually reducing its strength and stiffness. Generally speaking, leaching also lowers the pH of concrete and can permit corrosion in the reinforcing steel.

Concrete vaults that are exposed to ground water may be susceptible to leaching of calcium hydroxide. In order to cause leaching, the water must be flowing, not just filling a crack or a void. For tanks situated in such environment the aging degradation is plausible; otherwise it does not apply to the tank structures. Moreover, dense and well-cured concrete usually develops low permeability, so minimizing the possibility of degradation caused by leaching of the calcium hydroxide.

Quantifying the degradation is difficult. Inspection of the suspected surfaces should reveal the degree and extent of any degradation.

AGGRESSIVE CHEMICAL ATTACK

In a recent laboratory work, which was setup to simulate a breached hazardous waste line embedded in concrete, nitric acid with 4-molar concentration was allowed to leak and react with the concrete in regions containing reinforcing steel and construction joint [Brewer, 1993]. The leaching rates of calcium from the concrete were measured, initially at 1.1 to 1.6 g Ca/day, and decaying to 0.15 to 0.5 g Ca/day after 110 days. These rates are equivalent to 0.4 to 0.7% in volume of the test cylinder after 110 days of continuous contact with 4M HNO_3. The concrete used to fabricate the test cylinders had a siliceous-calcareous aggregate, water/cement ratio of 0.5, air content of 1.5% and density of 2.2 g/cm^3 (137 pound mass/ft^3).

Because of the high alkalinity of concrete (pH > 12.5), it is degraded by strong acids whenever the concrete is exposed to such solutions [Mindess, et al., 1981]. Sulfates in the soil and groundwater are potential sources of chemical attack on concrete. Also, when the concrete comes into contact with the waste (in case of tanks which are known to have leaked) and with vapor of aggressive compositions, for example, in the under surface of the exposed domes of single-shell tanks. Chemical attack usually increases the porosity and permeability of concrete, reduces its alkaline nature and subjects it to further deterioration which can result in reduced compressive strength and stiffness. Sulfates typically attack concrete by reaction with the aluminate phase in the cement to produce internal expansion and cause deterioration if the concrete is not made using sulfate-resisting cement. Chlorides lower the pH of concrete and can cause corrosion in the reinforcing steel.

The only outward manifestation of this degradation is the appearance of a "pock marked" surface which ultimately leads to spalling and cracking. Quantifying the degradation is difficult; however, inspection should reveal the extent of the degradation. For concrete below grade level, the critical zone occurs along the exterior surface where ground water table fluctuates. The environment in contact with the concrete surface must have a pH level of less than 5.5 for this attack to occur. The minimum chloride concentration for potential corrosion of the reinforcing steel is approximately 500 ppm. A concentration of 1500 ppm sulfate is the minimum degradation threshold limit when Type II cement is used while a concentration of over 150 ppm may cause degradation when Type I cement is used in the concrete [BNL Report, 1994].

CORROSION OF EMBEDDED STEEL

Concrete is a highly alkaline material (pH > 12.5) which provides an ideal environment to protect the embedded reinforcing steel rods from corrosion. However, when the pH of the environment in contact with the steel is reduced below the threshold level of 11.5, then corrosion of the embedded steel can occur [ACI 22R-92, 1992]. In the high-level waste storage tanks, concrete surfaces which are continuously exposed to an aggressive environment are susceptible to embedded steel corrosion. This is because the corrosive agents could have access to the steel through cracks in the concrete. A reduction in the pH requires an ongoing intrusion of aggressive ions (most notably, chlorides in the presence of oxygen) and could be caused by entry of acidic materials from the waste in single-shell tanks with breached liners or from an aggressive environment surrounding tanks situated in a zone of fluctuating ground water. The chloride ions cause a breakdown of the normal passive condition of the steel in the pore solution of portland cement and cause the corrosion. Calcium chloride accelerates the corrosion more than sodium chloride. Leaching of the alkaline products in the concrete through cracks or carbonation can also result in lower pH in concrete. In addition to the corrosive agents, the severity of corrosion is influenced by the quality of concrete (cement type, properties of aggregates, and moisture content), depth of concrete cover over steel, and the permeability of concrete. Generally speaking, concrete with low permeability contains less water and hence is more likely to have low electrical conductivity and better resistance to corrosion. Such concrete also provides a barrier to oxygen which is an essential element of the corrosion process. It follows that concrete with low water-to-cement ratio and adequate air entrainment provides greater resistance to water penetration, intrusion of aggressive agents, and corrosion of the embedded steel.

Solid corrosion products of steel have a volume greater than that of the original metal. When corrosion occurs, this factor will subject the concrete to stress, eventually causing hairline cracking, followed by rust staining, spalling, and more severe cracking. Such development may expose more of the reinforcing steel to the corrosive environment and the concrete to further degradation. The degradation in concrete is usually manifested by a reduction in its strength, stiffness, and other physical properties; and a loss of bond between concrete and embedded steel. A reduction in the cross sectional area of the steel can occur which ultimately could impair the structural integrity of the concrete enclosure of the tanks. For single-shell tanks and all tanks situated below ground water table, corrosion of embedded steel could be a significant age-related degradation mechanism.

Laboratory simulation indicates that the threshold for Cl^-/OH^- in the concrete pores necessary to cause corrosion is approximately 0.3 [Hsu, et al., 1993]. This is equivalent to a pore water chloride level of about 9000 ppm. In bridge deck concrete structures, corrosion is thought to occur when the chloride ion concentration reaches 0.35 to 1.0% by weight based on cement content of the concrete. Results of subjecting reinforced concrete test cylinders to direct contact with nitric acid of 4-molar concentration have been reported [Hsu, et al., 1993]. Acid penetration rates of 0 and 9.84 x 10^{-4} mm/day (0.025 in./day) were determined. The combined dissolution of the reinforcing steel and concrete created a cavity in the test cylinder which increased at a rate between 0 and 0.2 cm^3/day (0 and 0.0127 $in.^3$/day). This amounts to approximately 0.29 of the length of the reinforcing steel that was degraded after 110 days of direct contact with the acid. The quality of concrete and its permeability play a major role in its resistance to intrusion of chloride ions and the resulting corrosion. If the concrete has a water-to-cement ratio of 0.35 to 0.45 and 3 to 6% air entrainment, it will have low permeability and provide good resistance to corrosion of the reinforcement steel.

CONCLUSIONS

The potentially significant age-related degradation mechanisms which affect the concrete and the reinforcing steel in the high level waste storage tanks are identified. They include effects of elevated temperature, freezing and thawing, leaching of calcium hydroxide, aggressive chemical attack, and corrosion of the reinforcing steel. Based on review and evaluation of the operating history of the storage tanks, relevant laboratory test data, analytical assessment, and related experience of similar structures in other industries, the mechanisms are generically evaluated and, whenever possible, quantified so that mitigating measures can be planned and implemented to provide repairs and avoid further deterioration.

ACKNOWLEDGEMENT

The authors are grateful to the DOE Program Director, Mr. John Tseng, and his staff, particularly Drs. Charles O'Dell and Dinesh Gupta, for their encouragement and support. The authors sincerely acknowledge the advice, cooperation, and comments of many representatives of the DOE contractors responsible for management of the waste sites at Hanford, Idaho, Savannah River, and West Valley.

REFERENCES

ACI 209R-92, "Prediction of Creep, Shrinkage and Temperature Effects in Concrete Structure," American Concrete Institute, American Concrete Institute Manual of Concrete Practice, Part 1, Detroit, Michigan, 1993.

ACI 222R-89, "Corrosion of Metals in Concrete," American Concrete Institute, American Concrete Institute Manual of Concrete Practice, Part 1, Detroit, Michigan, 1993.

ACI 318, (Revised 1992), "Building Code Requirements for Reinforced Concrete," American Concrete Institute, ACI Manual of Concrete Practices, Part III, Detroit, Michigan, 1994.

ASTM C33, "Standard Specification for Concrete Aggregates," American Society for Testing and Materials, Philadelphia, PA, 1982.

BNL report prepared by Tank Structural Integrity Panel (TSIP), "Guidance for Development of Structural Integrity Programs for DOE High-Level Waste Storage Tanks," Draft, December 1994.

Brewer, K.N., "Effects of Rebar and Concrete Construction Joints on the Migration of 4M HNO_3 in Concrete Test Cylinders," Idaho National Engineering Laboratory, WINCO-1125, June 1993.

Hsu, T.C., et al., "Savannah River Site Waste Tank Corrosion Program (W)," WSRC-TR-93-373, Draft, September 1993.

Kassir, M.K., K.K. Bandyopadhyay, and M. Reich, "Thermal Degradation of Concrete in the Temperature Range from Ambient to 315°C (600°F)," BNL Report No. 52384, Revision 1, 1993.

Mather, B., "How to Make Concrete That Will Be Immune to the Effects of Freezing and Thawing," in Paul Klieger Symposium on Performance of Concrete, David Whiting, Editor, American Concrete Institute, SP-122, pp. 1-18, Detroit, Michigan, 1990.

Mindess S. and Young, J.F., Concrete, Prentice Hall, Inc., Englewood, New Jersey, 1981.

Troxell, G.E., H.E. Davis, and J.W. Kelly, Composition and Properties of Concrete, Second Edition, McGraw-Hill, 1968.

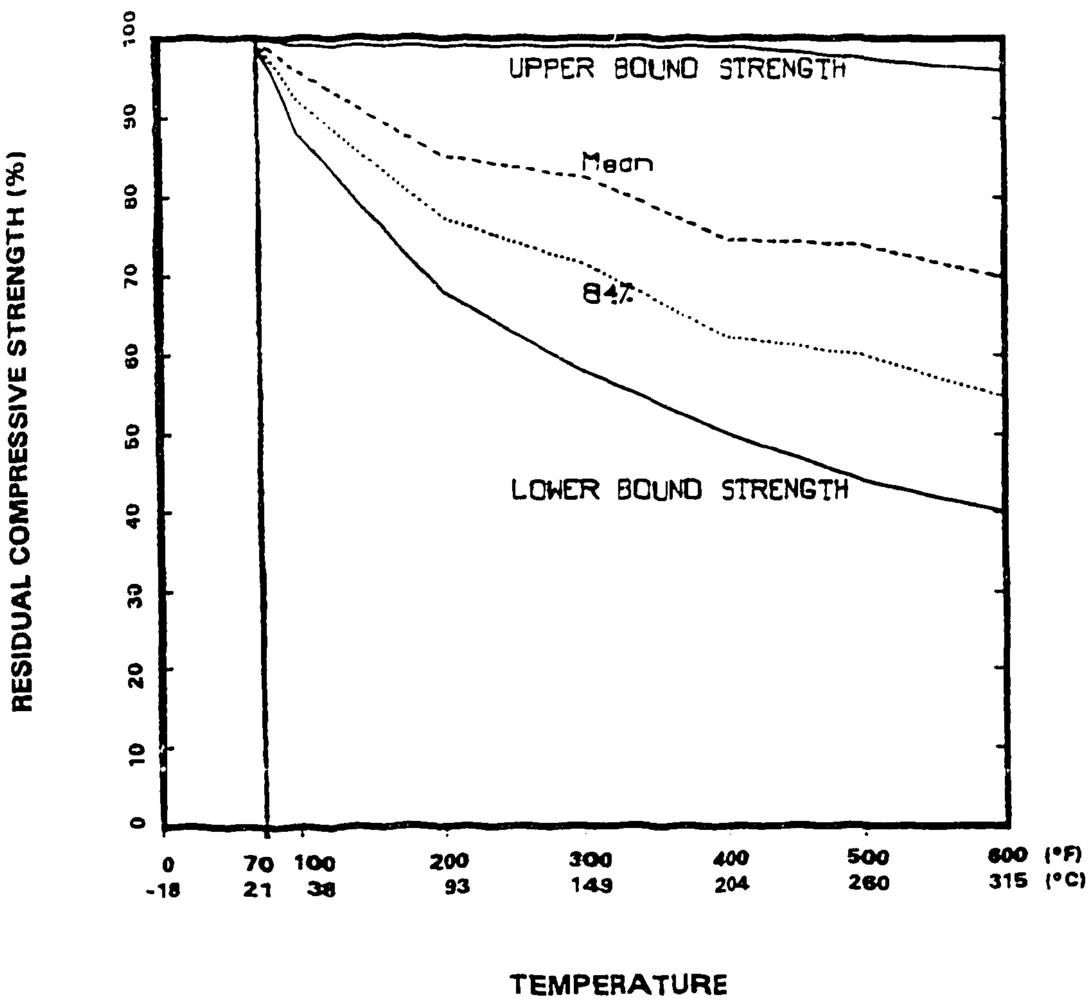

Figure 1 Reduction of Compressive Strength of Concrete at Elevated Temperature

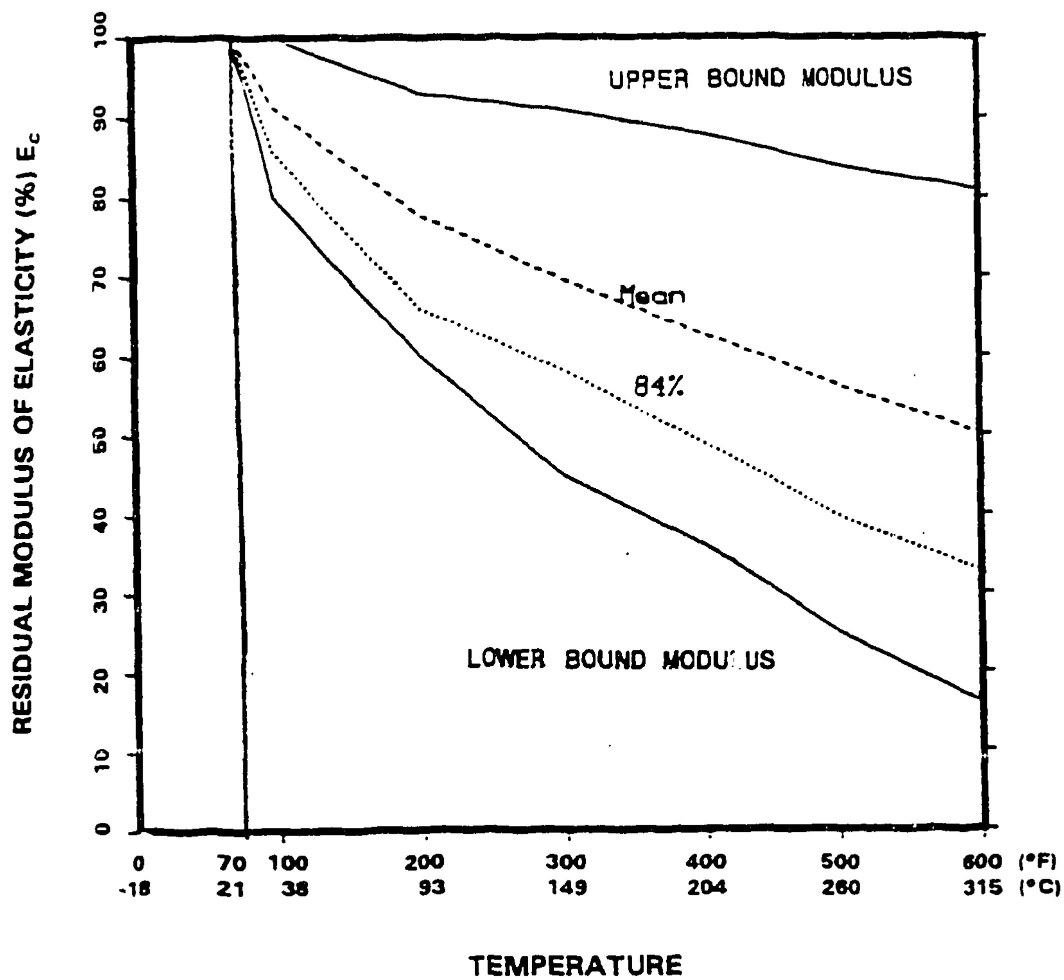

Figure 2 Variation of the Modulus of Elasticity of Concrete with Temperature