# THE DETERIORATION OF PORTLAND CEMENT PASTE EXPOSED TO SODIUM CHLORIDE ENVIRONMENTS

by

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# SUMMARY

The use of de-icing salts such as sodium chloride and calcium chloride on concrete surfaces has promoted a considerable amount of research interest. Despite the extensive amount of literature covering the wide ranges of investigations on the strength characteristics of cement paste and concrete subjected to chloride environments, very little has been published regarding such investigations with sodium chloride when present in different extreme environmental conditions, although sodium chloride is most widely used as a de-icing chemical. In this thesis the effects of alternate freeze/thaw and wet/dry cycles in presence of sodium chloride solutions of different concentrations on the strength and microstructure of hardened portland cement pastes of varying maturity have been investigated. Microstructural changes were detected by scanning electron microscopy, x-ray spectrometry, mercury intrusion porosimetry and differential thermal analysis. Attempts have been made to relate the observed microstructural features and their subsequent effects to the strength behaviour of the paste specimens. Ordinary portland cement paste specimens of 0.3 and 0.4 water/cement ratios were fixed for the investigations. The freeze/thaw cycles alternated between $0^{o}C$ and $-18^{o}C$. The effects of freeze/thaw and wet/dry cycles in different sodium chloride solutions on the strength of mortar specimens of different sand/cement ratios and water/cement

ratios were also studied in comparison with the effects already observed in the paste specimens.

It was noticed that cement paste of both 0.3 and 0.4 water/cement ratios cured normally for 3 and 7 days before being subjected to freeze/thaw cycles in different salt solutions suffered loss of compressive as well as flexural strengths that was not completely recoverable even after prolonged subsequent normal curing. The loss in flexural strength was more than that in compressive strength and freeze/thaw cycles in saturated solution caused maximum deterioration in strengths whereas 4% solution caused minimum. Wet/dry cycles in the solutions also caused loss of strengths in the specimens but their effects were less severe than that of freeze/thaw cycles. Comparison with similar tests on mortar specimens showed that mortar specimens were more resistant than paste specimens to freeze/thaw or wet/dry cycles in the solutions of sodium chloride.

Examination of the fracture surfaces of cement paste by scanning electron microscopy and x-ray spectrometry, and the study of the hydration characteristics by differential thermal analysis revealed that freeze/thaw cycles in the presence of sodium chloride solutions changed the morphology of cement pastes. Calcium chloroaluminates or calcium chlorosulphoaluminates formed and their needle like crystalline structures grew more with the increase in the concentration of the solution and increase of freeze/thaw cycles.

Mercury intrusion porosimetry proved to be a sensitive technique for studying the development of hydration and the changes were induced by freeze/thaw and wet/dry cycles in the solutions of sodium chloride. The freeze/thaw cycles in different solutions resulted in redistribution of pores.

The possibility of improving the cement paste to withstand freeze/thaw cycles in presence of different solutions of sodium chloride using air entraining agent was investigated. Air entrained paste specimens showed clear evidence of changes in microstructure as revealed by the scanning electron microscopy and was also found to resist freeze/thaw cycles in the solutions more effectively than the specimen without an air entraining agent. The electron micrographs of air entrained specimens also provided evidence to support the suggestion that tiny air bubbles served as escape reservoirs for the movement of solution from the capillaries during freezing cycles.

Finally several suggestions were put forward to enable this line of investigation to be extended to include other aspects of concrete deterioration.

# CHAPTER 1

# INTRODUCTION

Ever since the early stages of the development of portland cement the question of how to obtain good and durable concrete has occupied the thoughts of many research workers and practising engineers. This can be attributed to the fact that concrete has made great strides as a construction material because it lends itself so well to design and fabrication. It is a very versatile material and has brought new aspects and new techniques into structural engineering. This greatly expanded use and the demand for high quality and lasting performance from concrete have imposed corresponding demands on engineers and research workers to provide greatly increased reliability and durability in hostile environmental conditions.

In concrete the cement paste matrix forms the most important and vulnerable phase and hence, an insight into its microstructural characteristics and their relationship to its strength and other physical characteristics is of vital importance. In addition a knowledge of the interaction between cement paste and aggregates or reinforcements is vital to predict short term as well as long term responses of concrete when subjected to severe environmental stresses.

One such set of these environments occurs when concrete structures are exposed to salt action which may be presented in a variety of different ways. In coastal areas structures are exposed to sea waters containing chlorides. Concrete storage tanks are extensively used for brine in refrigeration and desalination plants. Also whenever there is frost or snow on roads rock salt is frequently scattered on the surface to act as a deicer. A complete understanding of the mechanism by which salt attacks concrete in different environments would be of great importance so that guidelines could be prepared to enable more durable concrete structures to be produced.

The main purpose of this research investigation was to study the effects of alternate freezing and thawing and also alternate wetting and drying cycles on cement pastes and mortars in the presence of sodium chloride solutions of different concentrations. This programme was initiated keeping in mind the various problems and deleterious effects that have been brought about by salt action on concrete and which have occupied the attention of research workers in many countries for several decades. It was appreciated that there already existed a considerable amount of information regarding the chloride attack on concrete and it was also noted that most of the investigations were concerned with the physical and mechanical properties of mature concrete due to action of deicers in general and calcium chloride in particular. Since sodium chloride is widely used as a deicer and since sea-water also contains sodium chloride as a major percentage of the salts in solution this present work was limited to investigating the effects of sodium chloride only on concrete.

In order to gain a fundamental understanding of this problem it was decided to begin the investigations with cement paste and to concentrate the initial attention on this phase. Later on the research was extended to include mortars in order to study the role of the aggregate phase in concrete. Under the different test conditions the microstructure of the pastes and mortars at different stages of maturity were examined. It was also decided to attempt to relate this to the observed effects on the mechanical and physical properties.

Powerful research tools such as scanning electron microscopy, x-ray spectrometry, differential thermal analysis, mercury intrusion porosimetry were used to examine the hydration procedure and the microstructure of cement pastes. An investigation into the full potential of the exploitation of these techniques was also one of the other objectives of the present work.

The author considers that the method of investigation developed in this work is a suitable procedure not only for examining the particular problems of concrete subjected to sodium chloride but also for the study of deterioration of concrete when subjected to other forms of aggressive media. The author also believes that this method of investigation is suitable for the study of different behaviours and deteriorations applied to other types of cement and grades of concrete. In the final chapter of this thesis a number of research topics which seem to be relevant and which might be conducted along lines similar to those of the present work are therefore suggested.

# CHAPTER 2

# GENERAL REVIEW OF PREVIOUS RESEARCH

## 2.1 Introduction

In this chapter the developments in the field of cement and concrete that come into the sphere of this investigation are presented.

## 2.2 Composition of Portland Cement*

The chemical composition and structure of cement have been the subjects of continuous investigation throughout the development of cement and this is well documented in various publications.(1-5) Although published more than ninety years ago, the paper of Le Chatelier(6) concerning the constitution of Portland Cement is still the basis confirmed by modern theories. Torenbohm(1, 5) checked the microscopic work of Le Chatlier and identified four distinct mineral constituents which he called Alite, Belite, Felite and Celite. Alite, the preponderating element consisted of colourless biaxial crystals, rectangular or hexagonal in outline. Belite formed round grains of no recognized crystalline character having a darker colour. Celite was recognized by its deep brownish orange colour and it formed the filling material from which Alite had separated. Felite was described as colourless and it occurred in the form of round grains, often in elongated form but without crystalline outline. Besides these minerals, Tornebohm

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* Typical composition of modern Portland cement is given in Table 2.1.

observed an isotropic colourless mass of very high refractive index which also occurred as a filling material between Alite grains. A re-examination and further analysis of Tornebohm's original slides led to the conclusion that Alite corresponded optically to $C_3S$*, Belite and Felite to two forms of $C_2S$. Celite which occurred as one of the interstitial materials between the Alite and Belite crystals was clearly a compound containing iron and is now to be identified with the $C_4AF$-$C_6A_2F$ solid solution.

Advancement in the science and technology of portland cement is closely related to the utilisation of different techniques which include microscopic examination, electron microprobe analysis, X-ray diffraction methods, differential thermal analysis and electron microscopy.(5, 7)

## 2.3 Hydration of Cement Compounds with or without Chloride Ions

When cement is brought in contact with water, the compounds mentioned in the previous section react to form hydration products with low solubilities and cementing characteristics. Several research workers and investigators have studied the mechanisms of cement hydration. Two mechanisms have been proposed, the "through solution"

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*Cement chemists use an abbreviated notation which describes each oxide by one letter, viz.: CaO = C; $SiO_2$ = O; $Al_2O_3$ = A; $Fe_2O_3$ = F. Likewise, $H_2O$ in hydrated cement is denoted by H. $SO_3$ is usually denoted by $\bar{S}$.

$$\therefore \; C_3S = 3CaO.SiO_2$$

mechanism(8) and the "solid state" mechanism.(9,10) According to the through solution mechanism the ions from the cement compounds are released into the solution and then combined to produce the hydration products. According to solid state mechanism there is a direct build up of hydration products on grains of cement compounds. Lea(5) suggests that both the mechanisms occur during the hydration process. The rate of hydration is high in the first few hours after mixing cement with water and then it decreases with time becoming quite low after 28 days.

Several research workers have also proposed models for hydrated portland cement. The early model(11) considered it to consist of an assemblage of spheres 100Å in diameter separated by films of water 6Å thick and having solid bonds. Subsequent works by Feldman and co-workers(12-15) showed that the model was inadequate to explain many physical and mechanical characteristics of cement paste and this led to the development of a new one. Figure 2.1(12) shows such a model for hydrated portland cement.

The mechanism of the action of chloride ions on the hydration of cement is not clear. Chloride ions not only alter the rate of hydration of cement minerals but may also combine with them. It also influences such properties as strength, chemical composition, morphology and pore characteristics of the hydration products.(16) To obtain a better understanding of the role of chloride ions on the hydration of cement compounds, the hydration of the individual cement minerals with or without chloride ions are discussed in a following section.

### 2.3.1 Calcium Silicates

Tricalcium silicates and dicalcium silicates react with water to produce calcium hydroxide which separates and calcium silicate hydrate gel is formed which consists of CaO, $SiO_2$ and $H_2O$, combined in a molecular ratio which several investigators have tried to determine. In the process of determination of $CaO:SiO_2$ ratio, it was necessary to establish the amount of $Ca(OH)_2$ present.

Factors such as water content, temperature, and time affect the composition of calcium silicate hydrates and so it is more convenient to denote these hydration products as C-S-H without reference to specific ratios of each constituent. Tricalcium silicate is transformed as follows if its hydration process is complete(17);

$$2(3CaO.SiO_2) + 6H_2O \longrightarrow 3CaO.SiO_2.3H_2O + 3Ca(OH)_2$$

Hence C-S-H is $C_3S_2H_3$ which stands for $3CaO.SiO_2.3H_2O$. However according to other investigators(18,19) this ratio is not stable and it changes to more stable products where the ratio of CaO to $SiO_2$ varies from 1.4 to 1.6.(5) Taylor(20) distinguished two C-S-H hydrates; one of which was observed to have a layer or foil-type structure. This type changed to a second hydrate which was the cigar shaped(21) C-S-H. Electron microscopic studies(22,23) revealed the evidence of such transition and a good number of theories have been developed to account for the effect.(24,25)

Neville(7) pointed out that although the individual layers of C-S-H are well crystallized in two axes, the distances between them are less rigidly defined and can accommodate varying amounts of lime without fundamental change. According to Steinour(26) there was a merger of solid solution and adsorption. Powers et al.(27) considered that a variety of transitional forms occurred for calcium silicate hydrate, but they all became finally converted to the fibrous form and to sheets or foils aggregated as fluffy masses. Bernal(28) indicated that calcium silicate hydrates with a short fibre repeat unit of 3.65 Å, this being interpretated to mean that there exists silicate tetrahedrons joined by hydrogen bonds. Ciach and Swenson(29) employed systematic sequential observations with the electron microscope and using x-ray analysis to interpret the morphological changes occurring during the hydration of cement compounds. According to them the first hydration product, a semicrystalline film, appeared to convert directly to the needle or cigar-like structures of calcium silicate hydrate and with time those particles developed into a three dimensional network which tended to form plates. They observed a remarkable absence of an appreciable quantity of $Ca(OH)_2$ in all cases and this suggested an accommodation within the C-S-H lattice of CaO especially when the proportion of water present was low. With high water contents, lime may be detached and crystals may then form. They also observed that the C/S ratios of the final products increased as the water/cement ratios decreased and vice versa.

In a recent review Diamond(30) distinguished four types of C-S-H gel particles. According to him the particles are as follows;

a) Type I which are best described as fibrous and they may be anywhere from 0.5 μm to about 2 μm in length and usually less than 0.2 μm across.

b) Type II particles forming a reticular network. The structure of this type involves the growth of elongated particles of roughly the same cross-sectional dimensions as the type I particles, into a continuous interconnected three dimensional reticular network.

c) Type III particles described as irregular or flattened often no more than 0.3 μm across.

d) Type IV C-S-H gel which is ascribed to the inner product within the initial outlines of the cement grains. Their grain size is only about 0.1 μm.

The main dicalcium silicate found in cement is in the $\beta$ form.(5) It is only slowly attacked by water and with the passage of time original crystals show only a surface coating of an amorphous hydrated silicate similar to that with tricalcium silicate.

With reference to the chloride effect on cement paste the original work in this field was conducted some fifty years ago by Sloane et al.(31) who observed the accelerating influence of $CaCl_2$ on the hydration and hardening behaviour of $C_3S$. These findings have been confirmed by subsequent works.(32-41) Additions of $CaCl_2$ also result in a decrease in the dormant or induction period in the hydration of $C_3S$.

The technique of differential thermal analysis has proved to be very useful in following the hydration of $C_3S$ in the presence of chloride ions.(32,33,39,42,43,47) According to Ramachandran(33) in DTA analysis the endothermal effect due to $Ca(OH)_2$ is more intense in samples containing 1% $CaCl_2$ than without it. In the presence of 4% $CaCl_2$ some of the thermal effects become more intense at earlier times than the corresponding ones hydrated in the presence of 1% $CaCl_2$.

Increasing the concentration of $CaCl_2$ up to 20% with respect to $C_3S$ has been found to influence the microcalorimetric curves.(36) Increasing the amount of $CaCl_2$ not only accelerates the appearance of the thermal peak at earlier times but also intensifies the peak.

The addition of $CaCl_2$ to $C_3S$ not only alters the rate of hydration but also influences the chemical composition of the C-S-H phase.(44) The C/S ratio depends on the water cement ratio, amount of $CaCl_2$ and degree of hydration. Collepardi and Massida(35) found that at earlier times the addition of 2% $CaCl_2$ accelerated the formation of low C/S ratio. Odler(34) found, however, that up to about 30% hydration, addition of 2% $CaCl_2$ lowered the C/S ratio of the product but beyond this stage the product formed with

$CaCl_2$ showed consistently much higher C/S values. Addition of 5% $CaCl_2$ showed even higher C/S values than those formed with 2% $CaCl_2$. A general increase in the C/S ratio for products with 0.5 to 5% $CaCl_2$ has also been reported recently, though the absolute values are not in accordance with those observed earlier.(37)

The accelerating action of $CaCl_2$ was ascribed to the formation of a calcium oxychloride hydrate.(45) In the system $CaO-CaCl_2-H_2O$ two oxychlorides, $3CaO.CaCl_2.16H_2O$ and $CaO.CaCl_2.2H_2O$ are formed, the former being stable at $CaCl_2$ concentrations of 18% or more and the latter at 34% or more.(33) Teoreanu and Munteau(37) have found a weak d-line in x-ray diffraction analysis at 3.28 Å for $C_3S$ pastes hydrated with 2% $CaCl_2$ and they have ascribed this to the presence of $3CaO.CaCl_2.12H_2O$.

In the absence of evidence for the existence of a complex it is suggested that $CaCl_2$ acts catalytically.(46) The exact mechanism by which this occurs in the $C_3S-CaCl_2-H_2O$ system is not clear. This mechanism is based on the premise that $CaCl_2$ does not go into any chemical combination. There is, however, some evidence that $CaCl_2$ may in fact be rigidly bound in the hydrating $C_3S$. Leaching with water could possibly unstabilise the complexes that may be formed. Based on the results of leaching with alcohol or $H_2O$, Ramachandran(44,47) speculated on the possible states of chloride in the hydrating $C_3S$. The chloride may be in the free state, as a complex on the surface of $C_3S$ during the dormant period, as a chemisorbed layer on the C-S-H surface, in the interlayer spaces of C-S-H and in the lattice of C-S-H.

According to Collepardi et al.(48) the accelerating action of $CaCl_2$ is due to its ability to promote the instability of the primary hydrosilicate, thus enhancing the formation of nuclei of a lower lime and a more porous hydrosilicate. This explanation is based on the observation that the addition of $CaCl_2$ to a prehydrated $C_3S$ does not accelerate further hydration.

Compared to the extensive investigations on the hydration of $C_3S$ in the presence of $CaCl_2$, only meagre work has been done on the action of $CaCl_2$ in the hydration of dicalcium silicate.(32,37,49-51) As mentioned earlier the hydration of $C_2S$ is slower compared to that of $C_3S$ even in presence of chloride ions, but calcium chloride reasonably accelerates the hydration of $C_2S$.(49)

### 2.3.2 Tricalcium Aluminate

$C_3A$ reacts very rapidly with water to form hexagonal plate crystals of mixed hydrates of $C_4AH_{19}$ and $C_2AH_8$ or a closely related solid solution of the composition $C_{2.4} \cdot A_{10.2} \cdot H_{10.2}$.(5) Feldman and Ramachandran(52) pointed out that these hydrates are not stable and gradually change to the more stable form of $C_3AH_6$ whose crystals belong to the cubic system. The rate of change from the hexagonal system to the cubic system increases with the increase in temperature and with a decrease in the amount of water. Differential thermal analysis(53) and isothermal calorimetry(54) in addition to x-ray diffraction and electron microscopy have been used to follow the hydration of $C_3A$ and the conversion of the hydrate crystals.

A study of the hydration of $C_3A$ in the presence of chloride ions is important because calcium aluminate chloride forms in the hydration of portland cement in the presence of $CaCl_2$ or NaCl.(44, 55-60) Two calcium chloraluminate hydrates are known, viz., $C_3A.CaCl_2.xH_2O$ and $C_3A.3CaCl_2.yH_2O$. It is generally believed that the low form is the main reaction product under the practical conditions of hydration. The low form may be prepared by mixing at ordinary temperature, a calcium aluminate solution with lime water and $CaCl_2$. The $Al_2O_3/CaCl_2$ ratio should be such that the $CaCl_2$ concentration level is about 3%.(4) The compound $C_3A.CaCl_2.xH_2O$ forms a series of solid solutions with $C_4AH_{13}$. The high form was obtained during hydration of tricalcium aluminate in a 23% calcium chloride solution.(55) It was also observed that the high chloride form of calcium chloroaluminate is formed preferentially at temperatures below $0^oC$. The low form crystallises as hexagonal plates and the high form as needle shaped crystals. According to Ben-yair(57) calcium chloroaluminate, which is a deterioration product of portland cement is formed by the attack of chloride solutions on two of the portland cement components: hydrated calcium aluminate and lime and results in the following reactions,

$$Ca(OH)_2 + 2NaCl = CaCl_2 + 2NaOH$$

$$3CaO.Al_2O_3.12H_2O + CaCl_2 = 3CaO.Al_2O_3.CaCl_2.10H_2O + 2H_2O$$

Whenever chloride ions are present in a solution which is in contact with cement, calcium chloroaluminate is formed and accumulates with time of exposing to the attacking solutions.(58)

### 2.3.3 Tetracalcium Aluminoferrite

Tetracalcium aluminoferrite ($C_4AF$) reacts quickly with water to form hexagonal plate crystals. Even then the cement chemists reserve their comment about the formulation of any definite reaction mechanism of $C_4AF$. However, ferric oxide can react with lime and water to give compounds analogous to those formed by alumina. The end product of the hydration reactions might be represented as follows:(3)

$$4CaO.AL_2O_3.Fe_2O_3 + 2Ca(OH)_2 + 10H_2O \longrightarrow$$
$$3CaO.Al_2O_3.6H_2O + 3CaO.Fe_2O_3.6H_2O$$

Brocard and Carlson(4) observed cubic $C_3AH_6$-$C_3FH_6$ solid solution accompanied by liberation of calcium hydroxide at a particular temperature range.

It appears that much less work has been done on the effect of chloride ions on the hydration of the ferrite phase of cement than on the other minerals.(59,61-63)

### 2.3.4 Effect of Gypsum on the Hydration of Portland Cement

As the reaction of pure $C_3A$ with water is very violent and leads to immediate stiffening of the paste, gypsum ($CaSO_4.2H_2O$) is added to cement clinker to prevent this from happening. Jones(64) has carried out a detailed investigation of the system $CaO-Al_2O_3-CaSO_4-H_2O$. The chemical nature and the stability domains of the various hydrates have been determined. Gypsum and $C_3A$ react to form insoluble calcium sulphoaluminate ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) initially. Eventually however a tricalcium aluminate hydrate is produced, although it is probable that this is preceded by a metastable $3CaO.Al_2O_3.CaSO_4.12H_2O$, formed at the expense of the original high calcium sulphoaluminate.(65) Kalousek in his papers(53,66) indicated that the first sulphoaluminate that formed was the high sulphate one. It was also considered that analogous sulphoferrite may also form. Soon, however, the high sulphate products were observed to convert to sulphate solid solution described as the solid solution of sulphoaluminate ($3CaO.Al_2O_3.CaSO_4.12H_2O$ - $3CaO.Al_2O_3.Ca(OH)_2.12H_2O$) and of the analogous $Fe_2O_3$ bearing products. Eventually this product also alters and the resultant phase is thought to be a gel consisting possibly of all the oxide constituents of cement. Lime, silica and ferric oxide are apparently required constituents for the formation of this phase. Kalousek believed that the layer structure of calcium silicate hydrate, by reasons of its large spacings provided the framework for such a composite product. Mikhailov(67) pointed out that the limited water phase hampered the growth of the high 'sulphate' formation; $C_3A(C\bar{S})_3H_{32}$ ($\bar{S}$ stands for $SO_3$), which was limited by the formation of a 'low sulphate' product, $C_3A(C\bar{S})H_{12}$. As a result a branched framework was formed of $C_3A(C\bar{S})H_{12}$, $C_4AH_{13}$ and $C_3A(C\bar{S})_3H_{32}$ lathlike splines. The last two needle like formations were completely intertwisted. The higher the water cement ratio of hydration, the more $C_3A(C\bar{S})_3H_{32}$ and the less there was of $C_3A(C\bar{S})H_{12}$ and pure gypsum. This intertwisting was rather loose during the initial period gradually becoming compacted by ions and newly formed silicate compounds, which crystallised in the aluminate and sulphoaluminate framework.

Different views exist on the role of chlorides together with gypsum in cement.(57,60,68-70) Kind and Batta(68,69) opinioned that in the presence of chloride ions formation of calcium sulphoaluminate is reduced. Van-Aardt stated in his paper(70) that up to 1959 he was also of the same opinion as Kind and Batta but as a result of further experiments he claimed that the addition of chlorides did not reduce the formation of calcium sulphoaluminate. Recently Ben-yair concluded after a series of experiments that there was the possibility of enhancing the formation of calcium sulphoaluminates in the presence of chloride solutions.(60)

## 2.4 Morphology and Microstructure of Hydrated Portland Cement Paste with or without Chloride Ions

The morphology of the hydration products of cement constituents using the light microscope have been studied by a number of research workers. Brownmiller(71) described the results of microscopic examination of hardened paste by means of reflected light and found that a close examination revealed that the cement hydrogel was not a formless mass but had an intricate structure. It was also concluded that microstructural constituents of cement paste were too small to be resolvable with the optical microscope, and attention was given to observations using the electron microscope. Using mainly X-ray techniques Bernal(72) studied hydrated calcium silicate compounds and according to him the forms of hydrated calcium silicate stable at low temperatures were related to two associated types of structures and they occurred in the form of extremely thin fibrous crystals, similar to those found in gels. He concluded this fact to be related to the setting properties of cement. Steinhour(65) also using X-ray techniques indicated similar effects like those of Bernal. The chemical reactions between components of cement and water produced new solid phases; one of them was crystalline calcium hydroxide and another, the predominant one, microscopically amorphous cement gel. Following these studies Powers(73) proposed that cement gel consisted mainly of fibrous particles with straight edges, and the bundles of the fibres seemed to form cross-linked networks containing some more or less interstitial material.

In recent years, scanning electron microscopy (S.E.M.) has been extensively used for the study of the hydrated pastes.(29, 30, 74-80) Chatterji and Jeffery(74) published the photographic results of the examination of a fractured surface of hardened cement paste and showed the three dimensional relationships between the hydrated phases and pore structure. Using the SEM Majumdar et al.(75) distinguished three types of material, a) well crystallised tabular calcium hydroxide, b) amorphous-looking material with ill defined platy form and c) fibres. They also found that there was no evidence of separate iron or aluminum bearing phases or morphologically distinct species. As minor constituents in cement they could enter into solid solution in the tobermorite (C-S-H), gel phase or form separate amorphous entities which would be indistinguishable from it.

Williamson(77) applied SEM to the study of the morphological features of portland cement paste and described the growth and distribution of hydration products in and around a single grain of cement. He found similarity in the outer hydration products around a cement grain with the columnar zones of metal castings and hence he used the term 'columnar zone' to define the outer hydration products. He assumed no single phase or chemical feature for this zone.

Diamond(30) used SEM and energy dispersive X-ray analysis (EDAX) and found that mature cement paste consisted of

a) Roughly 70% by weight of C-S-H gel (as described in section 2.3.1).

b) About 20% of well crystallized $Ca(OH)_2$ which grew in massive deposits and encapsulated other regions of the gel.

c) About 7% of the following compounds;

i) Ettringite ($C_3A(C\bar{S})_3H_{32}$) which seemed to occur as relatively long (4-5 µm) narrow rods with quite parallel sides. ii) Calcium aluminate monosulphate hydrate ($C_4A\bar{S}H_{12}$), and tricalcium aluminate hydrate ($C_4AH_{13}$), which both occurred in platy hexagonal crystals of several µm across but only about 0.1 µm or so in thickness.

d) Less than 3% of unhydrated clinker residue and other minor constituents.

Hydrated $C_3S$ obtained with chloride ions shows distinct differences in morphology from that prepared in the absence of chloride. There had, however, been a variance in the actual description of the morphology.(33,34,39,40,81-88) Odler and Skalny(34) observed hydrated $C_3S$ to form spicules or sheets rolled into cigar-shaped fibres 0.25 to 1.0 µm long in the absence of chloride ions and in pastes with 2% $CaCl_2$, the products assume a spherulitic morphology. Ramachandran(33) found that $C_3S$ hydrated without chloride ions showed needles whereas that hydrated with 1 to 4% $CaCl_2$ exhibited a platy or crumpled foil-like morphology. Collepardi and Marchese(86) as well as Berger et al.(87) obtained similar results. According to Young(85) the morphology of hydrated $C_3S$ + 0% $CaCl_2$ to hydrated $C_3S$ + 2% $CaCl_2$ occurred from needle-like C-S-H to a 'lace-like' structure. Tratterberg and Ramachandran(39) examined fractured surfaces of $C_3S$ hydrated without chloride ions at a water cement ratio of 0.5 and observed fibrous morphology and examining a corresponding sample treated with $CaCl_2$ observed dense morphology.

Chloride ions seemed not to have any influence on the morphology of the hydrated $C_2S$ as it had on the hydrated $C_3S$. The characteristic fibrous particles were observed in both $CaCl_2$ containing and $CaCl_2$-free hydrated specimens, the size being somewhat smaller in the former.(51) Using transmission electron microscopy (TEM) Lawrence et al.(89) reported some morphological differences on thin films of $C_2S$ and $C_2S + CaCl_2$ formed by evaporation and hydration.

A systematic study of the morphological and phase changes in the system containing $C_3A$, CaO, $CaSO_4.2H_2O$ and $CaCl_2$ was carried out by Gupta and co-workers.(56) In a saturated $CaCl_2$ solution, they observed $C_3A$ forming needles of $C_3A.CaCl_2.30H_2O$ which converted to the platy low form of chloride complex at 24 hours. At 3 months the product was mainly the low form. In 9% $CaCl_2$ both hexagonal C-A-H product and the low chloroaluminate formed initially and at longer time the C-A-H (hexagonal) converted to the cubic form. With 1% $CaCl_2$ hexagonal hydrate was produced initially and at 3 months the hexagonal and the cubic hydrates predominated. They also reported that the reaction in the system $C_3A$ + saturated $CaCl_2$ solution was essentially completed at 14 days, suggesting that the needle shaped chloroaluminate was not an effective barrier against $C_3A$ hydration. With 9% $CaCl_2$, foils and plates that formed did not effect complete hydration of $C_3A$.

In the $C_3A-CaO-CaCl_2-H_2O$ system in the saturated $CaCl_2$ solution initially needles and plates of $Ca(OH)_2$ were present and at longer times plates of monochloride and needles of basic calcium chloride were identified. With 9% $CaCl_2$ initial reactions were similar to those in the $C_3A$-$CaO$-$H_2O$ paste and the final products were cubic crystals of $C_3AH_6$. At 1% $CaCl_2$ the morphology was similar to that of the $C_3A$-$CaO$-$H_2O$ paste.(56)

In the system of $C_3A$-$CaO$-$CaSO_4.2H_2O$-$CaCl_2$ with a saturated solution of $CaCl_2$ needles of high chloroaluminate and calcium oxychloride hydrates formed initially. At longer periods needles of low chloroaluminate hydrate, hexagonal plates and needles of ettringite, foils and plates of calcium oxychloride hydrate together were the main products.(56)

## 2.5 Strength Behaviour of Hydrated Portland Cement Paste and Concrete with and without Chloride Ions

A large amount of research has gone into the investigation of strength behaviour of cement pastes, mortars and concretes under different conditions. The degree to which the different compounds in cement contribute to the strength is however not the same, for although the compounds $C_3A$, $C_4AF$ and $C_3S$ all hydrate rapidly, it is the last which is responsible for the major part of the strength developed. Dicalcium silicate hydrates slowly but progressively and its contribution to the strength follows a similar pattern.(5, 7) Without going into further details of strength behaviour of cement paste or concrete in normal conditions a summary is presented of the effect of chloride on the development of strength of cement pastes and concrete.

A small addition of $CaCl_2$ to portland cement is known to accelerate the setting and hardening characteristics of the cement. This is mainly attributed to the action of $CaCl_2$ on the silicate phases. Haegermann(90) observed that $CaCl_2$ accelerated the hardening process in $C_3S$ and this has since been confirmed.(33,38,39,91-93) At all times up to 28 days the strength in the paste containing 2% $CaCl_2$ was found to be higher than the specimen hydrated without the chloride.(91) The percentage increase in strength, however decreased as the hydration proceeded. The increase in strengths at earlier periods with $CaCl_2$ addition was explained by the increased amount of hydration products formed.

The hardening behaviour of $C_3S$ was found to be dependent not only on the percentage of $CaCl_2$ but also on the initial water cement ratio. Tratterberg and Ramachandran(39) observed that at a water cement ratio of 0.5, 2% $CaCl_2$ addition gave better strengths than 5% $CaCl_2$ but at a water cement ratio of 0.3, however, 5% $CaCl_2$ gave strength nearly as much as 2% $CaCl_2$ addition.

At equal degrees of hydration the $C_3S$ pastes containing $CaCl_2$ exhibited lower elastic modulii than those containing no $CaCl_2$. This was explained by assuming that in the presence of $CaCl_2$ the inner hydration products (the C-S-H phase occupying the spaces of the original unhydrated $C_3S$) had a lower density.(38)

In the system $C_3S$-$C_3A$-$CaCl_2$-$H_2O$ more $C_4AH_{13}$ was formed and better strengths were found than that without $CaCl_2$. That was explained to be related to the higher amount of $Ca(OH)_2$ formed by the accelerated hydration of $C_3S$ in the presence of $CaCl_2$.(94)

## 2.6 Behaviour of Pore Structure of Hydrated Cement Paste with or without Chloride Ions

Paste porosity is generally recognised to be the major parameter controlling the mechanical properties of concrete.(95-98) There are numerous references to the study of pore structure of cement pastes or the cement compounds in the literature. Diamond(99) using a mercury porosimeter determined the pores in the range of about 25Å - 1000 $\mu$m in diameter. He also observed variance in the pore-size distribution measured by mercury intrusion from that determined by applying adsorption-desorption isotherms.(99) The cement paste has a porosity typically in the range 30-40 Vol.% and a pore-size distribution in the range 10-0.002 $\mu$m in diameter.(85)

Porosity and pore size distribution changes in pastes of $C_3S$ with or without $CaCl_2$ are well documented.(38,39,83-85,100) At 1 day of hydration total porosity was higher in samples containing $CaCl_2$ than those without it.(83) The large increase in porosity was due to the existence of the greater amount of smaller pores of size 10-50Å in presence of chloride ions. At longer periods of curing samples of hydrated $C_3S$ of water cement ratio of 0.3 or 0.5 with 2% $CaCl_2$ showed lower porosity than the samples hydrated without chloride.(39) Presence of $CaCl_2$ resulted in the production of larger amounts of smaller pores of diameter less than about 0.03 $\mu$m.(38,85) The porosity of a $C_2S$ paste containing $CaCl_2$ was slightly higher than that without it.(51)

## 2.7 Durability of Concrete and Salt Action

When concrete is exposed to aggressive environments its successful performance is dependent to a greater extent on its durability against the environment than on strength properties. Halstead(101) defined concrete durability as its ability to withstand any influences which would render a concrete structure less fit for its designed use. Thus concrete is durable when it not only maintains its structural strength and other physical characteristics but also its good appearance, its functional dimensions, and would not develop unsightly fissures or surface defects. Some forms of construction are exposed to one or more factors of deterioration such as physical and chemical with different degrees of severity. Hence the subject of concrete durability is one of great importance and one of the most interesting aspects of this problem concerns the effect of chloride attack.

The concrete comes in contact with salt in different ways. Sea-water contains chlorides in considerable proportions together with other chemicals. Deterioration of concrete structures must be taken into consideration for coastal structures exposed to severe natural conditions, such as waves, sea-wind, abrasion by sea-shore sands together with chemical attacks such as that of chlorides.

The other destructive process that occurs during winter conditions is frost action. Surface scaling is perhaps the most easily recognised result of frost damage and this type of deterioration is noticed on concrete roads and sidewalks having slabs etc. The frost damage due to scaling is aggravated by the use of de-icing salts. Verbeck and Kleiger(102) compared the salt scaling of concrete subjected to freeze/thaw cycles using de-icers such as calcium chloride, sodium chloride, urea and ethylalcohol. They observed that a non-air-entrained concrete exposed to any de-icer showed scaling much sooner than an air-entrained concrete. The rate of scaling depended on the concentration of solution, a concentration of 2 to 4% being much more detrimental than that of 0, 8 or 16%. This observation has an important bearing on the mechanism of salt scaling. It indicates that the primary mechanics of salt scaling were not connected with any chemical reaction because increasing the concentrations of chemicals, did not intensify the attack.

Observations made by Neville(103) showed that, under steady state conditions, strong calcium chloride solutions deteriorated concrete. Both wet/dry and freeze/thaw environments had been observed to cause deterioration of de-icer exposed concrete.(104)

This particular research deals specifically with the effects of sodium chloride on cement pastes and mortars subjected to freeze/thaw and wet/dry cycles and it is the development of research in this field that is surveyed in the following sections.

## 2.8 Frost Action in Concrete and its Mechanism

The basic mechanism of salt scaling due to the presence of sodium chloride solutions is very complicated and it can best be appreciated and understood by first considering the theories concerning the freezing action of water in concrete.

In the original theories the damage caused by freezing was attributed to the expansion of about 9% in volume caused by water freezing into ice. When fresh concrete with a high water/cement ratio is cast, many of its voids are filled with water. Allowing concrete to be exposed to sub-zero temperatures in this state causes immediate damage. The mechanism may also be studied in situations where a concrete of poor quality is continuously soaked with water. The freezing mechanism of water and its solutions in hardened concrete is very complicated.

Collins(105) drew attention to typical failures of poor quality concrete, made with high water/cement ratios, which showed laminations of approximately equal thickness parallel to the cold surface. According to him cooling began at the exposed surface and extended slowly inwards. When any layer below the surface reached a sufficiently low temperature the water in the largest pores began to freeze. The ice crystals formed were in contact with unfrozen water in the surounding smaller pores, and by drawing water from them, the crystals continued to grow and a plane of weakness tended to form. As the surrounding pores became emptied, ice ceased to be formed and the cold front penetrated further until more freezable water was encountered and a new plane of ice formation arose, and so on. In subsequent freezings, ice tended to form at the same level as before. Damage to the concrete was considered to be caused primarily by the gradual growth of the ice crystals and the subsequent segregation and concentration of the ice into layers.

In concrete the cement paste matrix contains pores of various sizes, some only a few Angstorms in diameter and this adds to the complexity of the freezing process. Powers theory of frost action takes into account the size of pores.(106) The hypothesis depends on a hydraulic pressure concept. The section of an immersed specimen is shown in Fig. 2.2. When ice begins to form in region A it displaces the still unfrozen water towards the region B which is not in contact with water. If the water were free to move without resistance, no hydraulic pressure would develop. However, since the water is required to move through a fine-textured porous substance, the force causing the movement will give rise to a corresponding viscous resistance and gradients of hydraulic pressure will be present during the movement of the water according to the laws of hydraulic flow. If the reaction against the inward movement of water is high, it can be capable of damaging the specimen. The depth of saturation and the degree of permeability are very important factors that contribute to the hydraulic pressure generated which in turn brings about the disintegration of the specimen. As the number of freezing and thawing cycles increases, the thickness of region A, Fig. 2.2 increases due to the progressive increase in the amount of water absorbed by the specimen. The greater the resistance to the movement of water, the greater the hydraulic pressure becomes and the sooner disintegration starts to appear. From the hypothesis and supporting evidence Powers(107-109) expressed the influence of the different factors affecting concrete when subjected to frost action in the following formula for hydraulic pressure,

$$P = a(1.09 - \frac{1}{S}) \frac{u.R}{K} (\frac{L^3}{r_b} + \frac{3L^2}{2}) \text{ dynes/cm}^2$$

where

a = a factor depending among other things on the viscosity of water, (grams/cm.sec.)

S = saturation coefficient of the cement paste

u = amount of water, in grams per gram of cement, which freezes when the temperature falls one degree (g/g.°C)

R = rate of cooling (°C/sec)

K = permeability, (cm/sec)

$r_b$ = average radius of air bubbles (cm.)

L = spacing factor of air bubbles (cm.)

Nernst(110) discussed the controlling factors in the Powers formula and their consequences. He also concluded that the concrete should contain a large number of air bubbles, uniformly and closely spaced, into which the hydraulic pressure could easily be relieved. It is apparent from the formula that a, R and L are independent of the progress of hydration whereas S, u, K and the tensile strength of the cement paste will all change as hydration proceeds.

The hypothesis of hydraulic pressure throws more light on the aspect of frost resistance of hardened cement paste and concrete. The importance of air entraining agents is that they provide numerous discrete bubbles of air within the body of the paste. These air bubbles receive the water being forced into them during freezing, thus dissipating the generated pressure. They will also reduce the thickness of the path making it smaller than the critical depth. It follows that, for a given percentage of entrained air, increase in the number of bubbles, which means smaller average bubble diameter results in smaller distances between them, and hence better protection against frost damage. However, the percentage of air entrainment should be such that it will not significantly reduce the strength of concrete.

In a further development of this theory(108) it was postulated that at a temperature below that at which ice in a cavity was formed, the unfrozen gel water could diffuse into the cavity and cause the ice to grow and cause expansion. The cause of movement of water from the gel into cavities was ascribed to the creation of a free energy potential.

Everett(111) presented a thermodynamic model to account for crystal growth in porous structures (the model is described in Appendix A). From his model it was deduced that frost damage is associated with structures in which coarse pores are separated from one another by microporous regions. The excess pressure which can build up in a coarse pore of radius R, connected to a supply of water at the reference pressure by a capillary of radius r is proportional to $\frac{1}{r} - \frac{1}{R}$. Failure will occur if the excess pressure exceeds the strength of the porous material. For a material like hardened cement paste of certain mechanical strength, there will be a critical pore size difference which, if present may lead to frost damage.

Using a porous glass-water system, Feldman(112) made some studies on length and weight changes as a function of temperature down to -40°C. The basic mechanism of length changes in porous glass could also be applied to other systems such as hardened cement pastes, in which dilation had been explained by the movement of water from small to larger pores.(106, 111, 113) One of the conclusions of this study was that the desiccation due to cooling was controlled by the ratio $P_{o(BS)}/P_{o(SL)}$, where $P_{o(BS)}$ represents the vapour pressure of the bulk adsorbate and $P_{o(SL)}$ is the vapour pressure of the supercooled water.

Investigation by Litvan(114-116) on freezing of water in hydrated cement paste has shown some important results. He proposed a hypothesis which is based on the finding that the amount of water adsorbed in the cement paste decreases as it is cooled below 0°C.(114) According to this hypothesis at a constant temperature the amount of water adsorbed a, in a given solid, is dependent only on the relative pressure $P/P_o$, where P is the prevailing pressure of water vapour and $P_o$ is the saturation vapour pressure. The relation between a and $P/P_o$ is called the adsorption isotherm. It was found experimentally that below 0°C, the amount adsorbed has to be related to the saturation vapour pressure of undercooled water i.e. $P_{o_{u.c.w.}}$, in order to maintain the same relation between a and $P/P_o$. It was shown that with decreasing temperature below 0°C, the prevailing relative pressure $P/P_{o_{u.c.w.}}$ (where P here is $P_{ice}$), becomes smaller and smaller. Consequently a must decrease. From the results of adsorption characteristics, weight change, length change, calorimetry and differential thermograms Litvan concluded that the freezing of adsorbed supercooled water cannot be initiated by nucleation, in contrast to the bulk of supercooled water. At temperatures below 0°C, liquid water in the pores of the paste and the ice crystals on the wall co-existed. Since this cannot be in an equilibrium state, some water is exuded out of the pore system and freezes on the external surface of the specimen or on the container wall. Subsequent cooling causes more expulsion of water and more dilation. It follows that the excess water has to find its way out of the system, otherwise damage can result because of the internal pressure developed. Litvan also found in his experiments on slow cooling that the water expelled was much more than 9% of the total water present. He concluded that the amount of water that has to leave the void system exceeded 9% of the total water content primarily because of decreased adsorption capacity and not because of the volume increase experienced with bulk water. If the explanation put forward by Litvan is correct, then air entrainment is not the only method to protect hardened cement paste against frost action although Nernst(117) mentioned that by the use of suitable air entraining agent, cement paste can obtain a very large number of air voids, which reduce the critical thickness of the layers of paste as each wall of the air bubbles may serve as escape boundaries.

## 2.9 Salt Scaling in Concrete and its Mechanism

All the above mentioned theories suggest that the freezing action of water in concrete is an involved process and obviously the mechanism of freezing of salt solutions and salt scaling action in concrete must be very complex.

Any theory on salt-scaling should account for increased damage caused by freezing when salts such as NaCl or $CaCl_2$ are used as deicers to melt the ice or snow in contact with the concrete. In addition it should explain how proper air entraining improves concrete against scaling.

That the mechanism is primarily physical rather than chemical has been observed by Verbeck and Kleiger.(102) Not only inorganic salts but also organic substances such as alcohol, ethylene glycol and urea produce destructive effects. There is also firm evidence that the degree to which concrete is attacked depends on the concentration of the solution, very low and high concentrations having less severe effects. But no explanation or mechanism was suggested for such observations.(102)

Power's(106) hypothesis of hydraulic pressure throws some light on the frost resistance of hardened cement paste in the presence of salt solutions. Accordingly as NaCl or $CaCl_2$ lowers the melting point of the brine, freezing and thawing in $CaCl_2$ or NaCl brine is more destructive. Hence, during thawing, the layer surrounding the specimen will have melted before the ice inside the specimen and more liquid from outside the specimen will be absorbed thus increasing the thickness of the saturated layer, which will accelerate the deterioration process. Experimental evidence that the amount of absorption per cycle is greater in brine than it is in water is given by Hansen.(118)

Browne and Cady(119) studied the characteristics of the deicer scaling mechanism in concrete and on the basis of the findings from the experiments they concluded that a hydraulic pressure mechanism was responsible for the scaling of concrete exposed to deicer solutions under freeze/thaw conditions. The mechanism was strongly dependent upon the degree of saturation of the concrete and the deicer gradient present. A chemical reaction mechanism was responsible for deicer scaling under concentrated calcium chloride conditions and those two mechanisms were entirely independent of one another.(119) Snyder(120) also stated that a salt gradient must be present for scaling to occur. He based his statement on the observations that concrete specimens which contained salt in their mixwater were immune to deicer scaling under freeze/thaw conditions. The same type of specimens given a drying before testing, however, were quite vulnerable to attack. The deicer gradient was dependent on the water/cement ratio of the concrete.(121)

Inge Lyse(122) observed deterioration of concrete in storage tanks used for brine in refrigeration plants. The concrete began to leak and large portions of concrete in direct contact with cold brine had disintegrated while other parts not in direct contact with brine remained less damaged. He also observed $CaCl_2$ brine causing greater disintegration than the NaCl brine. After an investigation into the cause of the deterioration he came to the conclusion that the brine penetrated the concrete producing a salt solution which varied from relatively high concentration at the surface to very low concentration some distance within. Low brine temperature produced freezing of the water in the concrete except where salt concentration was sufficient to prevent it. At a certain depth from the surface salt concentration was just sufficient to give an equilibrium between freezing and no freezing of the water. Here there was a continued freezing and thawing action as the brine temperature changed a few degrees. Such action caused rapid disintegration.

In the osmotic pressure theory developed by Powers,(123) the effect of deicers is described as follows. When a salt melts ice on a concrete surface, the melt diffuses slowly into the pores of the cement. This builds up the salt concentration in the capillary spaces much more rapidly than in the smaller pores of the dense cement gel. When freezing occurs the solution is partly frozen and ice is produced in the capillaries. This results in an increased concentration of the solution in the capillary spaces. Each capillary thus becomes an osmotic pressure cell capable of drawing a weaker solution from the gel spaces. The magnitude of the pressure depends on the difference in concentration of the solution inside and outside the capillary space. The osmotic pressure developed in the capillary cavities may be sufficiently large to cause a rupture of the cement gel close to the surface of the concrete. It is also possible that de-icer salts, in addition to increasing the osmotic pressure potential, act in an opposite way by reducing the amount of ice that can form at any freezing temperature. This opposing effect may explain why destruction of concrete is maximum at some intermediate salt solution concentrations. The effect of air-entrainment is to create a number of cavities that cannot be filled with ice and concentrated solutions and to provide paths for water osmosis and thus decreases the expansion potential.

Conditions for the development of large osmotic pressures would be set up due to concentration gradient between the surface where the salt concentration is low and the areas of trapped highly concentrated salt solutions, after a number of freeze/thaw cycles. In such a system the water from the more dilute side tends to flow into the area where the more concentrated solution is present, consequently, large internal pressures develop.(104)

A second type of attack was also suggested(104) in the deep cracking and general weakening of the concrete specimens due to freeze/thaw cycles in presence of NaCl solutions. This type of attack increased with increasing solution strength and was manifested by reduced strength and the appearance of deep cracks rather than surface spalling. The dependence on concentration probably indicates a primarily chemical attack.

A factor that may enhance freezing is the sudden drop in temperature that may occur in the zone below the surface of concrete when ice is melted by de-icing salts. The melting ice on the surface, drawing heat energy from the water below, may cause this phenomenon.(124)

Another factor that may contribute to scaling is the crystallisation of a salt.(125) Hansen observed scaling generally confined to a small area immediately above the water or soil surface for piles, piers and other structures partially immersed in salt-bearing water or in salt-bearing soil. Salt-bearing water diffuses into the pores of the drying concrete whenever water evaporates from the concrete extending above the water or soil level. As evaporation proceeds, a point is reached at which salts begin to crystallize in a pore, which is slightly below the surface of the concrete. Once crystals form the solution in the pores draws salt molecules from the solutions in the smaller pores. Eventually the pores become filled with single crystals. Further growth of crystals may cause spalling of the concrete from above that pore. Spalling, of course, exposes other pores to the atmosphere, and the scaling continues to greater and greater depths.

Hansen(125) also observed scaling from the surface of a concrete structure where salts or solution come in contact with the surface. In such a case salt molecules from the solution tended to migrate into the concrete either by diffusion in the water in the pores or by diffusion through other crystals. Salt molecules could accordingly enter concrete that was saturated with water and which did not imbibe additional water. If the surface of the slab was then sealed by a layer of ice, further cooling would tend to cause crystals of salt to form in the pores. Since the separation of salt from the solution was an expansion reaction and since the solution could not escape out through the surface of the slab, the formation of crystals would force solution into pores that were not already filled. Thus each freezing drove salt-bearing solution deeper and deeper into the concrete. The process of melting ice with salt and subsequent freezing of water would cause the liquid phase of the concrete to become a solution of the deicing salt.

Either cooling or evaporation could start crystallization of salt in some of the pores of this salt bearing concrete. Under certain conditions Hansen showed that the salt crystals could grow into a single crystal and that crystal continued to grow and exert pressure on the concrete covering the pore and could cause scaling if the concrete could not resist that pressure. If the concrete was able to resist the pressure without scaling, it might instead expand and crack.

Recent data has provided some further insight into the mechanism of salt scaling.(126,127) The studies involved following dimensional and heat changes in cement pastes as a function of temperature between +15 and -70°C. Water saturated specimens immersed in different concentrations of NaCl or urea were subjected to length change and differential thermal studies. Litvan used 0, 5, 9, 13, 18 and 26% of NaCl for those studies. From the differential thermal studies he observed that at certain point of cooling the desorbed liquid from the pores of the cement paste was frozen and at further cooling the solution at eutectic composition was frozen. The temperature of the first freezing was lower than the bulk freezing point because of the time lag involved in the migration of water to the external surface and also because of supercooling. On warming, Litvan observed two processes to occur, one at about -21°C and the other at higher temperatures, increasing in magnitude with increasing salt concentration. The first process at lower temperature was attributed to the melting of eutectic mixture and that at higher temperature the melting of pure ice.

During the cooling cycle there was also an expansion of the samples particularly at lower concentrations. On warming, a significant contraction was also observed with highly concentrated salts at about -21°C (the melting point of the eutectic).

These results were discussed in terms of the theory proposed by Litvan.(115,128,129) He concluded that in the presence of a solute the degree of saturation of a porous body was higher and consequently it made the solid body less resistant to freezing action. In addition, the decreased vapour pressure of solution initiated the redistribution process at lower temperatures (at which the viscosity of the solution may be high) and enhanced the formation of crystals of solvent. Consequently, the flow of pure liquid was impeded and frost resistance was further decreased. As a consequence of these studies it was contended that reduced porosity was a better deterrent to salt scaling than air entrainment.

## 2.10 Subject of the Study

As has been shown in the above literature review, it is believed that the chlorides have a great influence with the deterioration processes of concrete specially when freezing occurs. The study of the deterioration aspect of concrete when it comes into contact with sodium chloride in different environmental conditions has been studied by very few research workers, also their investigations were mainly concerned with the physical and mechanical properties of concrete due to action of sodium chloride. A systematic study of the sodium chloride attack on the physical characteristics as well as on the microstructural features of concrete has not been covered. Since cement paste is the most important phase in concrete the author has therefore decided to examine the changes in microstructural characteristics of pastes and their relationship with the strength and other structural properties in presence of solutions of sodium chloride in extreme environmental conditions. Two major fields of investigation have been selected for study namely the effect of alternate freezing and thawing and the effect of alternate wetting and drying cycles on cement paste specimens in presence of solutions of sodium chloride of different concentrations.

Table 2.1 Approximate Compound Composition of Portland Cement Neville(7)

| Abbreviation | Percentage |
|---|---|
| $C_3S$ | 54.1 |
| $C_2S$ | 16.6 |
| $C_3A$ | 10.8 |
| $C_4AF$ | 9.1 |

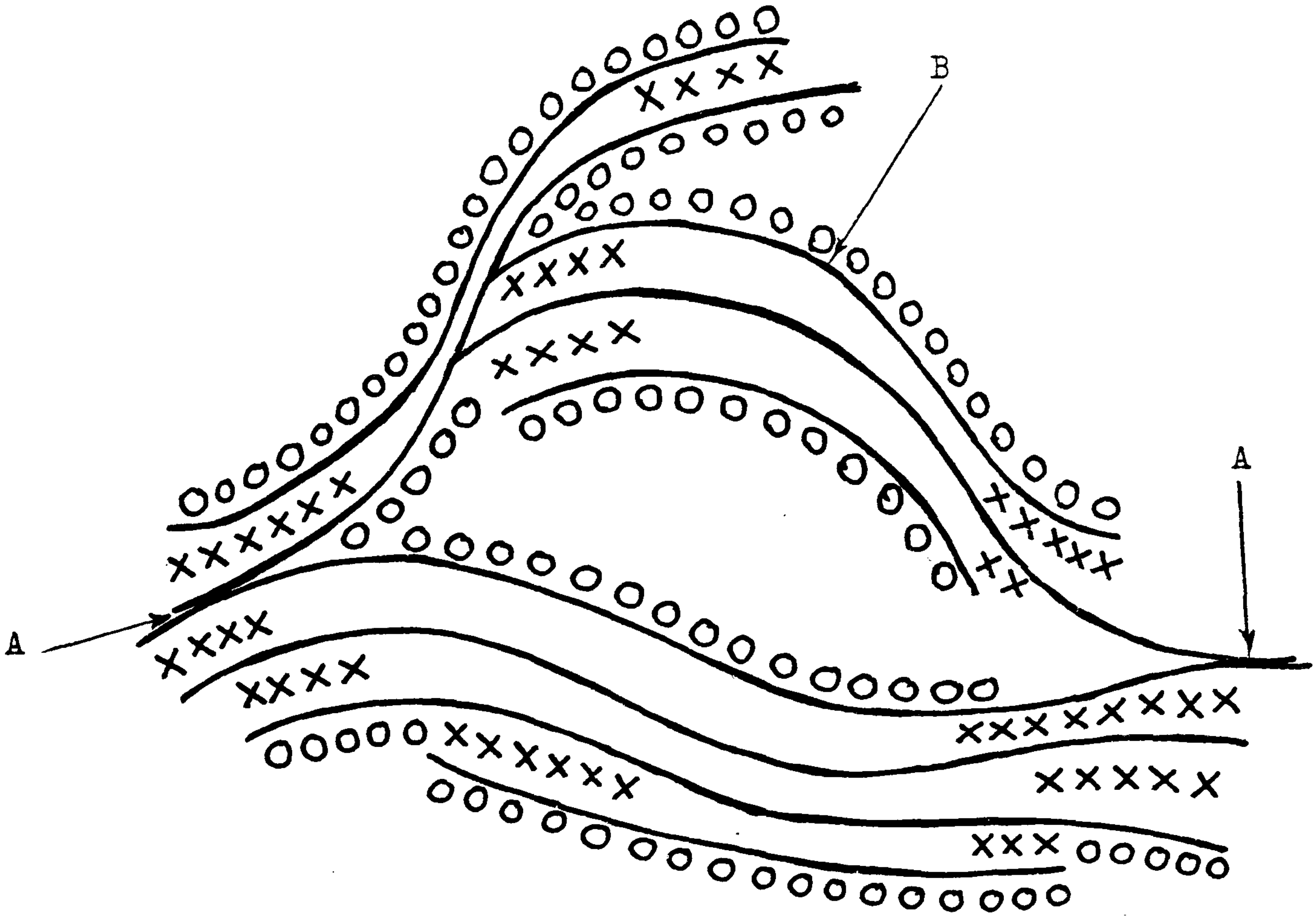

Fig. 2.1 Simplified model for hydrated portland cement. A = Inter-particle bonds, B = C-S-H sheets, X = Interlayer hydrate water, O = Physically adsorbed water.

(Feldman et al.)(12)

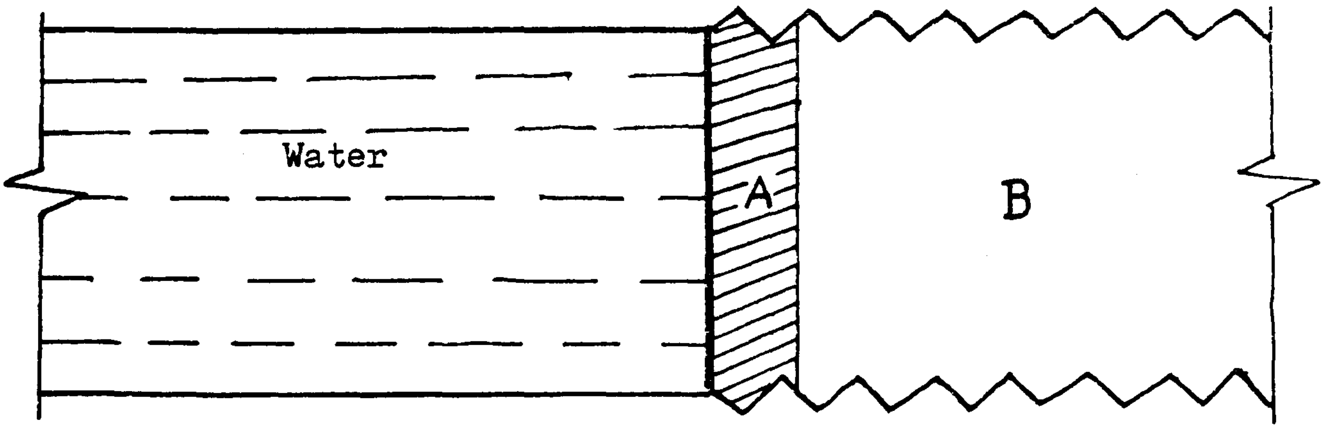

Fig. 2.2 Process of freezing and thawing of an immersed specimen.

(Powers and Brownyard)(107)

# CHAPTER 3

# MATERIALS, MIXES AND EXPERIMENTAL TECHNIQUES

## 3.1 Materials

### 3.1.1 Cement

"Blue Circle" ordinary Portland cement was used throughout this investigation. The chemical composition of a representative sample is given in Table 3.1.

### 3.1.2 Sand

Standard sand from Springbank Quarry was used. The sand was found to be of zone II according to B.S. 822 Part 2, 1973.(130) (Table 3.2)

### 3.1.3 Air Entraining Agent

A commercial liquid manufactured under the trade name of "Febcrete" by Feb, (Great Britain) Limited, was used. It was added to the mixing water at the rate of 0.31 ml per 1 Kg. of cement. The air content of the mix was determined using the method specified in A.S.T.M. C173-71(131) and was found to be 4%.

### 3.1.4 Sodium Chloride

Commercially available sodium chloride was used to make the solutions of different concentrations throughout this investigation.

## 3.2 Mixes

### 3.2.1 Cement Paste Mixes

Water/cement ratios of 0.3 and 0.4 were used to make the cement pastes throughout this investigation. Mixing was performed in "Creteangle Multiflow" mixer, which had a capacity of about 20 Kg. Mixing time was standardized at two minutes, and compaction of all the specimens was performed on a vibrating table. For making air entrained paste specimens the required air entraining agent was added to the mixing water before it was added to the cement.

### 3.2.2 Mortar Mixes

Two proportions by weight of cement to sand were chosen viz. 1:1 and 1:2 to make the mortars. The water/ cement ratios used for both the mortar were 0.4 and 0.5.

## 3.3 Specimen Preparation and Curing Conditions

255 x 50.8 x 50.8 mm beams were cast for flexural strength tests. Cube of 70.8 mm side were cast for compressive strength tests. Cubes of 50.8 mm side were also cut from the beams tested for flexural strength tests for compression tests. All these specimens were left in moulds under polythene cover at room temperature for 24 hours and then stripped off. The specimens were then placed in a curing cabinet under water at a temperature of +12°C for normal curing. After predetermined curing the specimens were brought out from the cabinet and placed in containers for freeze/thaw and wet/dry tests.

Different solutions of sodium chloride were prepared and poured in the containers so that the specimens were totally immersed. Specimens destined for freeze/thaw tests were then placed into a climatic cabinet. The climatic cabinet was a "Fisons Environmental Cabinet, model 280CT" which had two possible programmes of operation, a steady state programme and an ASTM programme. The tests were performed in accordance with the ASTM C666-75(132) alternate freeze/thaw testing procedure which involves 6 cycles of freezing and thawing every 24 hours. Each cycle consisted of 3 hours freezing when the temperature inside the cabinet was gradually lowered to -25°C, and an hour of thawing when the temperature inside the cabinet rose to +17°C. Thus the temperature of the interiors of the specimens alternated between -17.5°C and 0°C, as measured with the help of thermocouples embedded in some of the specimens during casting. The temperature variation between the interior and the surface of the specimen was recorded. It was found that the surface temperature alternated between -19°C at the end of freezing cycle to +2°C at the end of the thawing cycle. When the specimens were taken out of the cabinet at the end of the required number of cycles, those were left at room temperature for about 18 hours in order to thaw out completely. The temperatures of the interior and exterior of the specimens were both equal at that instant and had the value of approximately +15.4°C, this ensured that no ice lenses remained inside the specimens. But with the 70.8 mm side cubes the temperature of the interiors alternated between -16.5°C and -1°C during freezing and thawing cycles as measured with the embedded thermocouples. This illustrated the fact that the size of the specimens and consequently the dimensions of an actual structure may have a significant effect on the response to variations in temperature and a study of the effect of size variations with respect to different environmental conditions may be necessary.

For wetting and drying tests a cabinet was specially designed and then built in the laboratory. This cabinet allowed the specimens to be wetted and dried automatically and the time for either wetting or drying could be varied for any period. In this present investigation the alternate wet/dry testing procedure involved one cycle of wetting and drying every 24 hours. Each cycle consisted of 12 hours of wetting when the specimens were totally submerged in water or solutions of sodium chloride and 12 hours of drying when the solutions drained off from the specimens which were then dried in room temperature. To ensure proper drying of the specimens the arrangement was made to keep sufficient clearances on all sides of each specimen. But the author feels that the method of drying the specimens used could have been improved by other means and a study of the effect of drying in different ways especially at higher temperature could be an interesting and important aspect of future research.

Samples destined for porosimetry measurements were cast in plastic tubes of 50 mm height and 16 mm diameter.

The tubes were sealed after casting and were kept at room temperature for 24 hours when the plastic tubes are peeled off the hardened specimens. Those were then placed in water filled containers and subsequently placed in the curing cabinet for curing. After a predetermined number of days of curing the specimens were taken out and immersed in solutions of sodium chloride and placed either in the climatic cabinet for freeze/thaw tests or in the other cabinet for wet/dry tests.

The choice of the specimen size for porosimetry measurements was guided mainly by two reasons. Bigger samples could have been used but that would require much bigger dilatometer dimensions since the amount of mercury intruded would be substantial. Besides, the author opines that the results in those cases would not have been as representative owing to the fact that much of the interior parts of the specimen would have been masked by small pores whose intrusion would have required more pressure than that available. The difficulty of removing the water from the pores of bigger samples in a short period of drying would have caused another disadvantage and that would hamper to restrict uniform hydration all over the specimen.

The other choice was with the small fragments of fractured cubes to be used for porosimetry tests. That was discarded because the author felt that the process of crushing might have altered the pore size distribution. It was also considered that for comparison purposes a more or less constant shape and size of the specimens was advantageous. The chosen size of the specimens used was suitable for the amount of mercury available for the test and for the dimensions of the apparatus available in the laboratory. Moreover, the specimen was also comparable to sizes chosen by previous investigators(133) on other aspects of paste.

## 3.4 Determination of the Mechanical Properties

### 3.4.1 Compressive Strength

The compressive strength of the paste and mortar was determined by taking the average of 6 cubes of 70.8 mm side. More tests were also performed on the cubes of 50.8 mm side cut out from the beams for flexural tests. The cubes were tested by the laboratory "Avery Compression Machine, Type 7112" which had a capacity of 2500 KN. The load was applied at a rate of 14 N/mm$^2$ per minute in accordance with B.S. 1881, part 4, 1970.(134)

### 3.4.2 Flexural Strength

The flexural strength tests for paste and mortar specimens were performed on the beams of 50.8 x 50.8 x 255 mm in sizes using the machine "Avery Universal Machine Type 7110" which had a capacity of 500 KN. The beams had a total span of 228.6 mm between supports and were tested with knife edge loading at the one-third points. In each case the average load to fracture at least four specimens was taken to represent the particular condition.

## 3.5 Porosity Measurements

### 3.5.1 Total Porosity

When samples had been subjected to their various programmes of curing and exposure, they were surface dried and their weights were taken. Then they were placed in an oven at 105°C until constant dry weight was achieved. This was found to require at least 72 hours of oven drying. This method of drying was simple and quite effective and it was claimed that this method did not produce any irreversible changes in the sample.(133) After drying the dry weights were taken and the difference between the surface dry weights of the samples and their corresponding dry weights was taken as the weight of water occupying the pores. The total porosity of a specimen was taken as this value divided by the density of water (0.001 g/mm$^3$), the assumption being that evaporable water represents the water which is present in the capillaries or held by surface forces in the gel.(5) Immediately after oven drying samples were stored under vacuum in a desiccator over silica gel until the time of testing.

### 3.5.2 Measurement of Bulk Volume

A special type pycnometer was used to determine the bulk volume of the samples. The pycnometer was filled with mercury, the excess which came up through the hole of the stopper was removed. A glass plate was applied at the top of the stopper to keep the level of the mercury constant in each time it was used. At this stage the stopper was opened and the sample was inserted into the pycnometer. The stopper was then put back into position very slowly pressing on to the sample. This forced the displaced mercury to come out through the stopper and it was very carefully collected and weighed accurately. The bulk volume of the sample was calculated by dividing the weight of the displaced mercury by the specific gravity of mercury, 13.61.

### 3.5.3 Filling the Dilatometer with Mercury

Schematic details of the dilatometer and of the apparatus and a description of the procedure used to fill the dilatometer with mercury are given in Appendix B.

### 3.5.4 High Pressure Porosimetry

High pressure porosimetry was used to determine the pore sizes of paste specimens exposed to different testing conditions. Mercury was forced into the pores of the specimens at different pressures up to 15000 psi. Schematic details of the high pressure porosimetry apparatus and the operating procedures are given in Appendix C. The capacity of the apparatus was up to 40000 psi (281 $N/mm^2$).

## 3.6 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to examine the morphological changes occurring during the exposure of pastes to different testing environments as stated earlier. In addition the elements such as Ca, Si, Al, S, Cl present in the pastes during freeze/thaw and wet/dry cycles in the solutions of sodium chloride were estimated by the energy-dispersive spectrometer attached to the SEM.

### 3.6.1 Sample Preparation

Small samples of different sizes approximately 5 to 8 mm in diameter or 5 mm x 8 mm or so in sizes having a thickness of 1 to 3 mm were chosen from different parts of the representative beams and cubes after testing. These samples were then mounted on aluminium stubs using conducting glue. Care was taken to ensure that the surfaces of samples were not touched or contaminated during the process. Then the samples were coated with a thin film of copper in a vapouriser after which they were kept under vacuum in a desiccator over silica gel until the time of examination.

### 3.6.2 Sample Examination and Analysis

Examination of the samples was carried out by means of a "PHILIPS SEM 500". The range of magnification used was (20X) to (5000X). The specimen was placed in the specimen stage at an angle of $45^{\circ}$ to the beam so as to achieve maximum secondary electron collection. The accelerating voltage was normally set at 40 KV and it was found to give good resolution. After making the usual adjustments necessary to obtain clear and sharp image of the specimen on the display screen, photographs at different magnifications were taken of different features on the fracture surface by the built in camera of the electron microscope. Direct analysis of the chemical composition of the features observed in SEM was obtained by using "Link Energy Dispersive X-ray Analysis System". The beam spot was placed on the preselected site and electron beam was adjusted for efficient X-ray production. The counts of different elements were observed in the display screen. The quantities of the chemical compositions were then directly printed in the printer and kept for references.

## 3.7 Differential Thermal Analysis (DTA)

Differential thermal analysis was used to record the heat effects associated with physical or chemical changes in the cement paste samples subjected to various testing conditions in this investigation as a function of temperature. With this technique the temperature difference between the samples and a reference material ($Al_2O_3$ in this case) was continuously recorded as a function of temperature of the furnace and the reference material.

### 3.7.1 Sample Preparation

Powdered samples were extracted from the representative beams and cubes for differential thermal analysis. Hand operated driller with masonry bead was used to take out the powder from the specimens to ensure that the bead was not at all warm or hot during the drilling operations which could have significant effect on the physical or chemical changes in the paste specimens. The required quantity of the powder was weighed and placed in a small platinum rhodium crucible which was then put inside the heating furnace of the apparatus.

### 3.7.2 Sample Analysis

Thermal analysis of the samples was carried out in air by means of "Stanton Redcroft Differential Thermal Analyzer Model 673-4". The heat effects were recorded in the attached recorder as a function of temperature as the substance was heated at a uniform rate up to 900°C. The heating rate was 10°C/min.

## 3.8 Chloride Estimation

### 3.8.1 Sample Preparation and Analysis

Powdered samples were extracted by dry drilling with a masonry bead from the representative beams and cubes and those were taken at 6 mm intervals to a depth of 25 mm. Chloride was determined according to the method suggested by Building Research Station.(135)

## 3.9 Range of Tests

The various treatments which were applied to different specimens were divided into the following categories:

a) Normal curing in room temperature for different periods.

b) Normal curing for different periods and then exposure to various numbers of alternate freezing and thawing cycles in sodium chloride solutions of different concentrations.

c) Normal curing for different periods and then exposure to various numbers of alternate wetting and drying cycles in sodium chloride solutions of different concentrations.

d) As in (b) and (c) and then further exposure in water at $20^{\circ}$ for various periods.

Table 3.1 Chemical composition of the cement used throughout the investigation

| Oxide | Content % |
|---|---|
| Lime | 63.5 |
| Silica | 19.3 |
| Alumina | 6.5 |
| Oxide of Iron | 3.6 |
| Sulphates as $SO_3$ | 2.7 |
| Magnesia | 2.3 |
| Potash | 0.46 |
| Soda | 0.1 |
| Loss on ignition | 1.2 |
| Insoluble residue | 0.50 |

Table 3.2 Sieve Analysis of Sand

| B.S. Sieve Size | Wt. Retained (gm) | % Retained | Cumulative % Passing | B.S.882 Zone II |
|---|---|---|---|---|
| 5 mm (3/16") | 1.1 | 0.2 | 100 | 90-100 |
| 2.36 mm (No. 7) | 73.5 | 14.8 | 95 | 75-100 |
| 1.18 mm (No. 14) | 130.3 | 26.3 | 59 | 55-90 |
| 600 µm (No. 25) | 107.6 | 21.7 | 37 | 35-59 |
| 300 µm (No. 52) | 85.0 | 17.2 | 20 | 8-30 |
| 150 µm (No. 100) | 49.0 | 9.9 | 10 | 0-10 |

# CHAPTER 4

# THE EFFECT OF FREEZING AND THAWING CYCLES ON COMPRESSIVE AND FLEXURAL STRENGTHS OF CEMENT PASTE AND MORTAR IN PRESENCE OF SODIUM CHLORIDE SOLUTIONS OF DIFFERENT CONCENTRATIONS

## 4.1 Introduction

In assessing the deteriorating effects of freezing and thawing cycles on concrete in presence of chloride solutions the previous research workers were mainly concerned with a visual description of the various forms of deterioration such as scaling, spalling and cracking. Scaling and spalling of pavements produce uneven, unsightly surface even though the pavement may otherwise be sound and of adequate quality. Freezing and thawing in sodium chloride solutions may ultimately cause very serious damage to concrete structures. On the other hand crumbling of cement paste and exposure of aggregates can sometimes give the impression that the structure is on the verge of disintegration even though the deterioration due to freeze/thaw cycles in salt solutions has not significantly affected the structural stability and usefulness of the structure. Extensive cracking has also been reported to confirm the deterioration of concrete in freeze/thaw cycles in presence of salt solutions.

Very little is known about the deterioration of concrete as regards to its compressive and flexural strengths when it is subjected to freeze/thaw cycles in presence of sodium chloride solutions. In American practice(132,136) it has been proposed to use the measurement of the loss of dynamic modulus of elasticity and to use the observation of the surface as a measure of deterioration. Browne and Cady(119) observed increases in tensile strength followed by a steady decrease for concrete specimens subjected to freeze/thaw cycles in calcium chloride solutions. This decrease is thought to be due to the loss of effective cross section from the corrosive action of the salts. The specimens in contact with sodium chloride solutions did not show this trend. In a bid to assess the form of deterioration the technical committee of RILEM(137,138) in a more recent study suggested standard methods of carrying out and reporting freeze/thaw tests on concrete with or without deicing chemicals. In the case of deicing chemicals it suggested four types of deteriorating aspects such as surface weight loss, depth of scaling, percentage area scaled and visual description. In the case of no deicer chemical being used flexural and compressive strengths were also included to assess deterioration. The attainment of a certain degree of crushing strength before concrete is subjected to freeze/thaw cycles in water has been previously reported.(139,140)

The need to predict the effect of sodium chloride on concrete strengths led the author to begin this investigation. The change in the basic mechanical properties such as compressive and flexural strengths of cement paste when subjected to freeze/thaw cycles in presence of water and in different concentrations of sodium chloride solutions were monitored. Later on similar tests were conducted with mortar specimens to study the influence of the presence of aggregate particles in the matrix. The effect of air entrainment on the observed deterioration was also examined. This investigation was also directly related to other characteristics of the material as detailed in the following chapters of this thesis.

## 4.2 Results and Discussion

### 4.2.1 Compressive Strength

The results of compressive strength measurements made on specimens of cement pastes with water/cement ratios 0.4 and 0.3 normally cured and also when subjected to alternate freeze/thaw cycles in different concentrations of sodium chloride solutions are presented in Figs. 4.1 to 4.6. Every point on the curves represents an average value recorded from at least four specimens. Pastes of W/C 0.4, frozen and thawed after 3 days of initial curing, when subjected to a solution of any salt concentration showed an immediate drop of strength which continued to fall with the increase in the number of freeze/thaw cycles. Very soon the specimens started to show microcracks and to disintegrate when freeze/thaw cycles were stopped and test was discontinued. Among the different concentrations of the solutions the specimens in 4% solution showed the least fall of strength and those in saturated solution the most. In saturated solution the specimens disintegrated first. Similar paste specimens with 0.3 water/cement ratio exhibited a different behaviour in parallel tests. Specimens in 10% and saturated solutions showed the drop in strength like the corresponding ones with 0.4 water/cement ratio, but in other solutions such as zero, 2%, 4% and 6% the specimens gained strength before starting to fall, though, the rate of gain of strength was much lower than that of the normally cured specimens. In these cases also specimens in 4% solution showed least fall of strength at a particular number of freeze/thaw cycles.

The paste specimens of water/cement ratio 0.4 cured normally for 7 days when subjected to freeze/thaw cycles in salt solutions showed almost similar behaviour as that of 3 days normally cured specimens. The specimens in saturated solution disintegrated after 54 cycles. In all other solutions the tests were discontinued for the specimens at the end of 84 freeze/thaw cycles and it was found that specimens in the 4% solution retained maximum compressive strength followed closely by those in 6% solution at that stage. With water/cement ratio 0.3 the specimens cured initially for 7 days then subjected to freeze/thaw cycles showed significant difference in behaviour. Up to 36 cycles specimens in all the solutions showed a gain of strength except for those in saturated and 10% solutions. In these cases the specimens showed no gain or loss of strength. With further increase of freeze/thaw cycles the strength of the specimens in those solutions began to drop but in all other solutions the specimens showed further gain of strength before beginning to drop. Again the 4% solution seemed to lower the strength the least.

Specimens made with either 0.4 or 0.3 water/cement ratio behaved in a different way when cured normally for 28 days before being subjected to freeze/thaw cycles in the salt solutions. The specimens showed no loss or gain of compressive strength even after 180 freeze/thaw cycles in any solution. Some scaling and cracks were observed in some of the specimens.

Comparing all the results presented in Figs. 4.1 to 4.6 it was observed that after 3 days of initial curing the compressive strengths of the paste specimens were 33 $N/mm^2$ and 42 $N/mm^2$ respectively for 0.4 and 0.3 water/cement ratios, but when subjected to freeze/thaw cycles in different salt solutions, the specimens showed the deterioration in strength in a similar fashion. For 7 day initially cured specimens of 0.4 water cement ratio, the compressive strength was 44 $N/mm^2$ before freeze/thaw cycles and they could sustain 54 freeze/thaw cycles in saturated solution before disintegration when the strength was reduced to 26 $N/mm^2$. However the specimens in all other solutions could sustain a considerably greater number of freeze/thaw cycles even at the same reduced strength of 26 $N/mm^2$. Similar specimens with 3 days initial curing showed disintegration at 10 $N/mm^2$ after 36 and 72 freeze/thaw cycles in saturated and 10% solutions respectively. Analysis of the results led to the conclusion that paste specimens of any water/cement ratio and of an early age when subjected to freeze/thaw cycles in sodium chloride solutions deteriorates fairly quickly and the magnitude of strength attained was not the only criterion to use in the prediction of resistance to such deterioration. It was thought that the hydration procedure, morphology and pore sizes of pastes when subjected to freeze/thaw cycles in different salt solutions must play an important role in causing the deteriorations.

To observe the effect of recuring in water after a certain number of freeze/thaw cycles the specimens were taken out from the freezing chamber and immersed in water. Details of these specimens are shown in Figs. 4.7 and 4.8. After 54 cycles the specimens of 0.4 water/cement ratio in 4% and 0% salt solutions recovered about 82% and 95% of normal strength respectively at the end of another 33 days in water. At the commencement of the recuring the strengths were 22 N/mm$^2$ and 15 N/mm$^2$ for 4% and 0% solutions respectively. The gain of strength for the specimens frozen and thawed in water was even greater. The 7 day initially cured specimens experienced 54 freeze thaw cycles before they were allowed to cure normally. The specimens in saturated solution could regain only from 26 N/mm$^2$ to 34 N/mm$^2$ after 29 days of recuring. But those in 4% and 0% solutions recovered almost fully, the specimens in 0% recovering more. The specimens of 0.3 water/cement ratio having 3 days and 7 days initial curing were given recuring at the end of 54 freeze/thaw cycles in

0%, 4% and saturated solutions of sodium chloride. The specimens of 0% recovered fully, but those of 4% solution although with a greater initial strength could recover only 96% of the normal strength. The specimens of saturated solution showed significant recovery but the strengths were much below the normal strength even after 28 days of recuring. The behaviour of the strength characteristics due to freeze/thaw cycles in sodium chloride solutions and also after recuring of the paste specimens led to the conclusion that the morphology of the paste had been changed. This is further discussed in the following chapters.

Figs. 4.9 to 4.12 show the effect of freeze/thaw cycles on the compressive strength of mortars of different water/cement ratio and cement/sand ratio. A reduction in strength was again experienced after the freeze/thaw cycles. In all the mortar specimens of either 3 days or 7 days initial curing the 4% solution seemed to cause least and the saturated solution the most damage in strength similar to those observed in the paste specimens. The specimens in 4% solution started crumbling away on all the surfaces with the freeze/thaw cycles and the compression strength test was performed on the remaining core. It was also noticed that mortar specimens after 3 and 7 days initial curing could withstand more than 54 cycles before disintegration occurred. A comparison between Figs. 4.3 and 4.9 shows that 3 day initially cured cement paste which acquired a strength of 33 $N/mm^2$ could resist only 36 cycles whereas mortar specimens acquiring the same strength could resist more than 54 cycles in saturated solution. The 7 day initially cured specimens of cement paste resisted only 54 cycles whereas 7 days mortar specimens with a similar initial strength could resist more than 72 cycles. Moreover it was also noticed from Fig. 4.12 that mortar specimens subjected to freeze/ thaw cycles in different concentrations of salt solution when allowed to recure could recover the compressive strength in a better way than the paste specimens experiencing similar test conditions. The specimens of 0% recovered fully, of 4% recovered 96% and of saturated solution 80% of normal strength. From these observations it was concluded that aggregates and their characteristics must also play a significant part in determining the effects of freeze/thaw cycles, in the presence of sodium chloride solutions, on the long term behaviour of concrete.

The results of the compressive strength tests on the cement pastes of water/cement ratios 0.4 and 0.3 with air entrainment are given in Figs. 4.13 and 4.14. The figures also show the effect of freeze/thaw cycles on the strength of paste specimens in 0%, 4% and saturated solution. It was found that with the quantity of air entraining agent used in this investigation (0.31 ml per 1000 gms of cement) which produced 4% of entrained air by volume, the 28 days value of compressive strengths were approximately 8 to 10% less than those recorded for pastes of corresponding water cement ratio and having no air entrainment.

The specimens with 0.4 water/cement ratio initially cured for 3 days or 7 days showed a different behaviour from that of plain paste specimens in corresponding solutions. The specimens showed a gain of strength even where subjected to freeze/thaw cycles before beginning to drop away. Only in a saturated solution did the specimens show loss of strength after 72 freeze/thaw cycles. The 3 day initially cured specimens of 0.4 water/cement ratio gained from 30 $N/mm^2$ to 33 $N/mm^2$ and 35 $N/mm^2$ in 0% and 4% solutions respectively after 144 freeze/thaw cycles whereas similar specimens without air entrainment dropped from 33 $N/mm^2$ to 9.5 $N/mm^2$ and 21 $N/mm^2$ respectively after only 72 cycles. The specimens of 0.3 water/cement ratio showed exactly the same behaviour. They demonstrated the change of strength from 39 $N/mm^2$ to 43.5 $N/mm^2$, 45 $N/mm^2$ and 31 $N/mm^2$ after 144 freeze/thaw cycles for 0%, 4% and saturated solutions respectively. This was in comparison with from 42 $N/mm^2$ to 25 $N/mm^2$, 30.5 $N/mm^2$ after 108 cycles and to 20 $N/mm^2$ after 72 cycles respectively for 0%, 4% and saturated solutions. For the 7 day initially cured specimens of 0.4 water/cement ratio the behaviour was also similar. It was thus seen that the value of strength attained before the beginning of freeze/thaw cycles was not the only significant factor governing the ability of the paste to resist the freeze/thaw cycles in the presence of salt solutions. Rather it appeared that the microstructural characteristics of the material could be modified to provide better resistance. From Figs. 4.13

and 4.14 it also appears that air entrained specimens which were subjected to 36 freeze/thaw cycles in 0% or 4% solution and then allowed to cure normally once again could regain almost the normal strength after 21 days. In the case of specimens of saturated solution the recovered strengths were 89% and 84% of the normal strengths for 0.3 and 0.4 water/cement ratios respectively. Specimens with air entrainment and of 0.4 water/cement ratio when subjected to 72 freeze/thaw cycles in the solutions and then allowed to cure normally also showed recovery of strength in a similar fashion.

### 4.2.2 Flexural Strength

The results of flexural strength tests on cement pastes of water/cement ratios 0.3 and 0.4 subjected to alternate freeze/thaw cycles in different concentrations of sodium chloride solutions are plotted in Figs. 4.15 to 4.22. The behaviour of flexural strength was more or less similar in nature with the compressive strength pattern showing the fall in magnitude for 3 days and 7 days initially cured specimens of both water/cement ratios when subjected to freeze/thaw cycles. With 0.4 water/cement ratio, the paste specimens initially cured for 3 days or 7 days immediately suffered loss of flexural strength in all the solutions similar to the drop of compressive strength and showed sharp deterioration with the increase of cycles. Though the reduction in strength in the different solutions did not show large variations yet it was observed that in 4% solution the flexural strength was always slightly more than the specimens in other solutions at any number of freeze/thaw cycles. The maximum loss of flexural strength was always experienced with specimens in the saturated solution. The specimens of 0.3 water/cement ratio cured initially for either 3 days or 7 days showed immediate loss of flexural strength with the beginning of freeze/thaw cycles in the solutions. This was unlike the compressive strength which was found to increase before being followed by a decrease with the increase of freeze/thaw cycles. The losses in flexural strength were sharp compared to the slower rate of loss with the compressive strength. Again the specimens in saturated solution suffered the maximum loss whereas the minimum was observed for those in 4% solution.

The most dissimilar behaviour was observed with the 28 days initially cured paste specimens of both the water/cement ratios. With these specimens the loss of flexural strengths were also observed but the rate of deterioration was less than that with the 3 days or 7 days initially cured specimens. Comparing the compressive strength test results of similar specimens it was found that there was no loss or gain in compressive strengths in any solution even after 180 freeze/thaw cycles, but there was a drop in flexural strength immediately after the beginning of the cycles. The least loss was recorded with 4% solution and the most with saturated solution. This particular behaviour of 28 days initially cured specimens and also the other results points to the formation of microcracks inside the specimens due to freeze/thaw cycles in the solutions of sodium chloride. Even a large number of microcracks could not influence the resistance to compression because of the rough, interlocking surfaces of the planes of rupture. The cubes showed compressive strength almost equal to that of undamaged specimen cured for 28 days. But any microcrack could cause the loss of flexural strength.

Figs. 4.21 and 4.22 show the effect of recuring on the flexural strength of specimens of 0.4 and 0.3 water/cement ratio initially cured for several days and then subjected to freeze/thaw cycles in sodium chloride solutions. For 0.4 water/cement ratio the specimens initially cured for 3 days and 7 days were subjected to 54 cycles before being allowed to cure normally once again. In the saturated solution the recovered flexural strength after 29 days of recuring was only 40% of the normal value but in 0% and 4% solution it was up to 70%. The specimens of 0.3 water/cement ratio and 7 days initial curing when subjected to 54 freeze/thaw cycles and then allowed to cure normally once again regained almost 90% of the normal flexural strength in 0% and 4% solutions. However under similar conditions the specimens in saturated solution regained about 75% of normal value.

Comparing the nature of recovery of compressive and flexural strengths under a particular condition it was found that the rate of gain of compressive strength due to recuring was very significant and in most cases the strength regained its full normal value whereas the values of flexural strengths remained significantly below their normal values. These observations suggested that the microcracks formed due to freeze/thaw cycles must have been playing a significant role in determining the strength properties of paste specimens when subjected to freeze/thaw cycles in sodium chloride solutions. The effect of microcracks on the compressive and flexural strengths is explained earlier and is thought to be justified.

From the test results of compressive as well as flexural strengths it was noticed that the saturated solution caused maximum loss of strengths and 4% caused the minimum. Even in 0% and 2% solutions the losses were more than in the 4%. From these observations it can be argued that a chemical and a physical mechanism were both responsible for the loss of strengths of the pastes frozen and thawed in sodium chloride solutions of different concentration. The morphology and pore size distribution of pastes under similar conditions studied in later chapters confirmed such an argument.

Fig. 4.23 shows the effect of freeze/thaw cycles on the flexural strength of mortar specimens of 1:2 cement/sand ratio and 0.4 water/cement ratio in 0%, 4%, 10% and saturated solution of sodium chloride. The specimens were precured for 3, 7 and 28 days. At a particular number of freeze/thaw cycles in any solution the mortar specimens showed better resistance and the loss of strength was much less compared to the flexural strengths of similar paste specimens in similar conditions. Also the loss of flexural strength showed deterioration taking place at a much slower rate in the case of mortars compared with pastes. The fine aggregates content played an important role in reducing the losses. As mentioned earlier microcracks formed within the specimens due to freeze/thaw cycles in all the solutions, but due to the presence of the aggregate particles the propagation of the microcracks was stopped for some time and finally at a further increase of the freeze/thaw cycles the microcracks propagated. This resulted in higher values for flexural strength and less sharp deterioration compared to those obtained with the paste specimens.

Mortar specimens initially cured for 7 days were subjected to freeze/thaw cycles in 0%, 4% and saturated solution and after experiencing 54 cycles were allowed to cure normally once again. Results of flexural strength tests made on these specimens are given in Fig. 4.24. After 29 days of recuring the specimens increased in strength from 4.5 $N/mm^2$, 3.9 $N/mm^2$ and 3.4 $N/mm^2$ to 5.7 $N/mm^2$, 5.6 $N/mm^2$ and 4.25 $N/mm^2$ respectively for 4%, 0% and saturated solution. Before the beginning of the freeze/thaw cycles the flexural strength was 4.85 $N/mm^2$ for these specimens. Similar paste specimens attaining 4.8 $N/mm^2$ dropped to 2.25 $N/mm^2$, 2.1 $N/mm^2$ and 1.15 $N/mm^2$ after 54 freeze/thaw cycles and then regained the values of 4.1 $N/mm^2$, 4.3 $N/mm^2$ and 2.4 $N/mm^2$ in 4%, 0% and saturated solution respectively after 29 days of recuring.

These results show the faster rate of loss and lesser gain of flexural strength in case of paste specimens, though the initial strengths were more or less the same for both pastes and mortars. Therefore, it was concluded that the presence of aggregate particles and their characteristics must play a major part in determining the resulting effects of freeze/thaw cycles in the presence of sodium chloride solutions on the flexural strength of concrete.

Fig. 4.25 shows the effect of air entrainment on the flexural strength of paste specimens of 0.4 water/cement ratio cured normally and also the effect of freeze/thaw cycles in 0%, 4% and saturated solution of the same initially cured for 3 and 7 days. The results show that the flexural strength behaviour changed significantly due to the air entrainment. For both 3 days and 7 days initially cured specimens there was a gain of strength for a number of freeze/thaw cycles in saturated solution and only after 100 cycles did the specimens show a sharp fall of flexural strength. Compressive strength results for these air entrained specimens in saturated solution showed a similar behaviour. The only difference noticed was in the gradual decrease of compressive strength even after 100 freeze/thaw cycles. In 0% and 4% solutions the specimens gained some strength before beginning to drop due to increased freeze/thaw cycles. This was exactly the same pattern as that with compressive strength tests.

A possible explanation for such behaviour could be the formation of microcracks but formed at a delayed period due to the presence of air bubbles. At the beginning of the cycles when the internal hydraulic pressure increased some of the solution in the capillary pores could escape into the air bubbles thereby releasing some pressure. With the continuation of hydration there was also a gain of matrix strength. However as the freeze/thaw cycles were increased some of the air bubbles which had become filled with solutions could not release the internal pressure further and therefore some internal microcracks developed. This caused the sharp drop in flexural strength after a considerable number of freeze/thaw cycles. In addition to this mechanism there was some chemical reaction taking place which was responsible for the deterioration. This was confirmed by the fact that the results of compressive as well as flexural strength tests of all the specimens always showed a maximum drop in strengths with the saturated solution. This is discussed further in later chapters of this thesis.

## 4.3 Conclusions

(1) Freeze/thaw cycles in sodium chloride solution of any concentration caused significant losses in compressive as well as flexural strengths of pastes and mortars with both 3 days and 7 days initially curing.

(2) Freeze/thaw cycles in sodium chloride solution of any concentration caused very little damage in the compressive strengths of pastes and mortars after an

initial curing period of 28 days, but the flexural strengths of such specimens deteriorated significantly.

(3) Cement pastes that were cured for 3 days or 7 days disintegrated much faster than mortar specimens cured for similar period when subjected to freeze/thaw cycles in the solutions of sodium chloride.

(4) The saturated solution was found to cause the greatest damage in strengths while the 4% solution caused the minimum, even less than 0% and 2% solutions for the pastes and mortars irrespective of initial curing for 3, 7 or 28 days.

(5) The recuring procedure helped the paste and mortar to regain significantly their compressive strengths but not the flexural strengths after being subjected to freeze/thaw cycles in sodium chloride solutions of different concentrations.

(6) While initial strength is an important factor in the ability of the paste and mortar to withstand the freeze/thaw cycles in sodium chloride solutions, the results indicate that mortar was more resistant than the cement paste. Therefore other characteristics of the materials used must have some significance.

(7) Air entrained paste showed very good resistance to the freeze/thaw cycles in sodium chloride solutions.

(8) It was thought that when freeze/thaw cycles were applied, the tiny air bubbles provided escape reservoirs for the movement of salt solutions that filled the smaller capillaries, thus they reduce the effect of the internal

pressure on the walls of the capillaries which in plain paste induced their rupture.

(9) The comparison of compressive and flexural strengths of pastes and those of air entrained pastes subjected to freeze/thaw cycles in sodium chloride solutions suggested the formation of microcracks inside the specimens causing sharp deterioration in flexural strengths. The mortars behaved in a better way due to the temporary arrest of such microcracks.

(10) The mortar specimens showed gradual crumbling on the surfaces when subjected to freeze/thaw cycles in 4% sodium chloride solution though the strengths recorded for them were maximum.

* Note

For all the results of compression tests the standard deviations were less than 1 $N/mm^2$ which corresponds to between 1% and 3% of reading.

For flexural strength the standard deviations were again less than 1 $N/mm^2$ which corresponds to between 2% and 5% of reading.

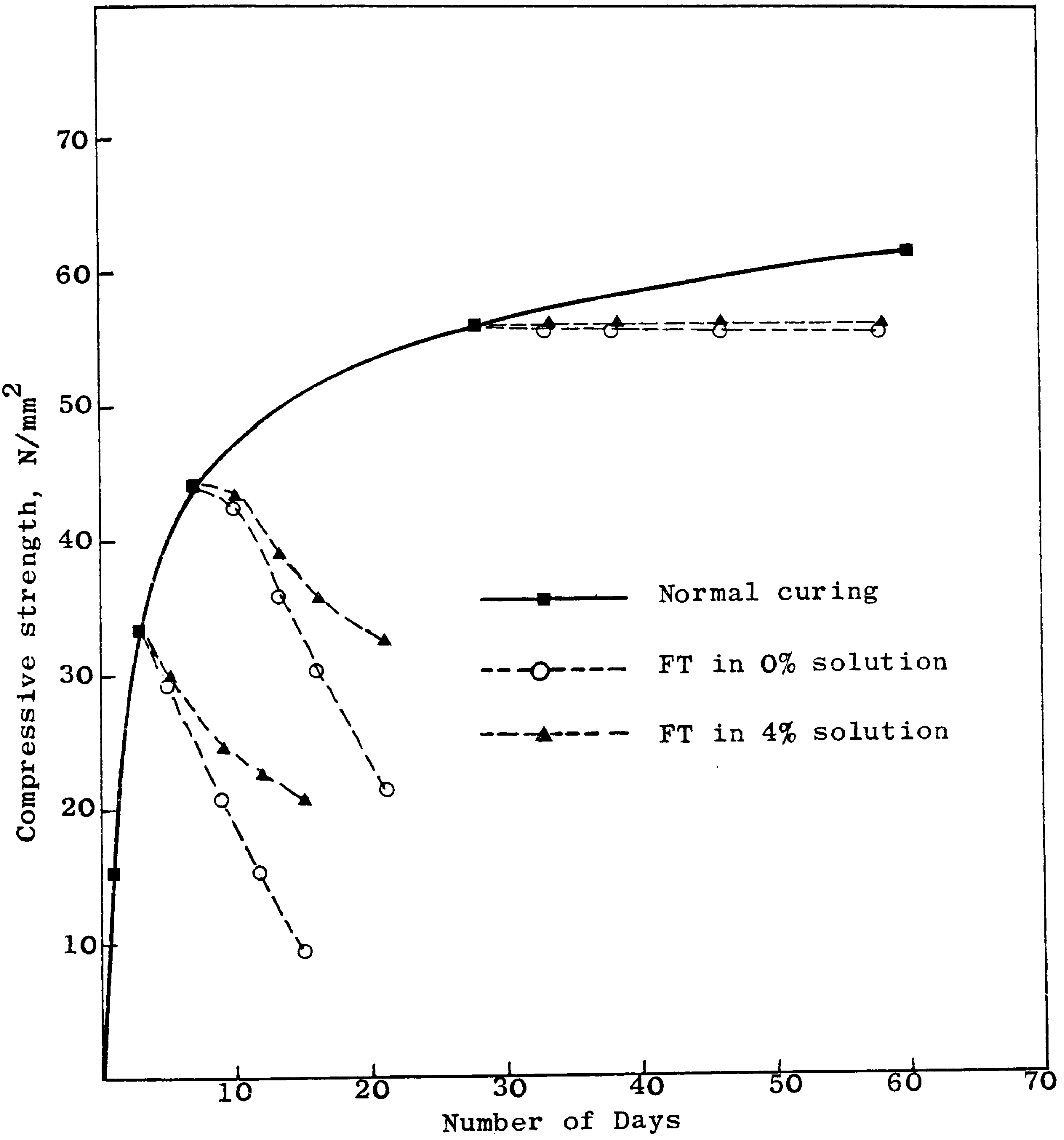

Fig. 4.1 Effect of freeze/thaw on compressive strength of cement paste (W/C = 0.4) in solutions of sodium chloride of different concentrations

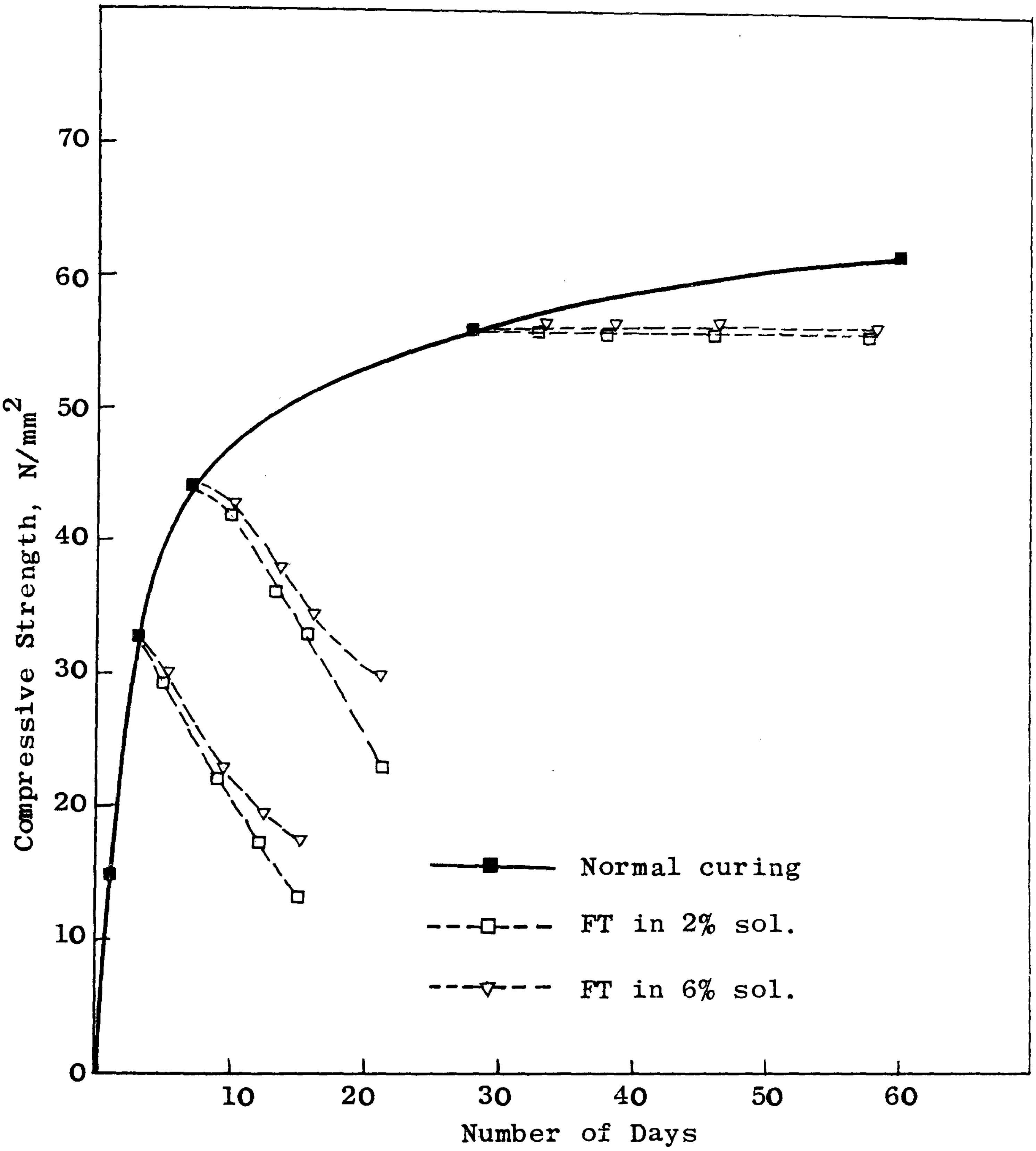

Fig. 4.2 Effect of freeze/thaw on compressive strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

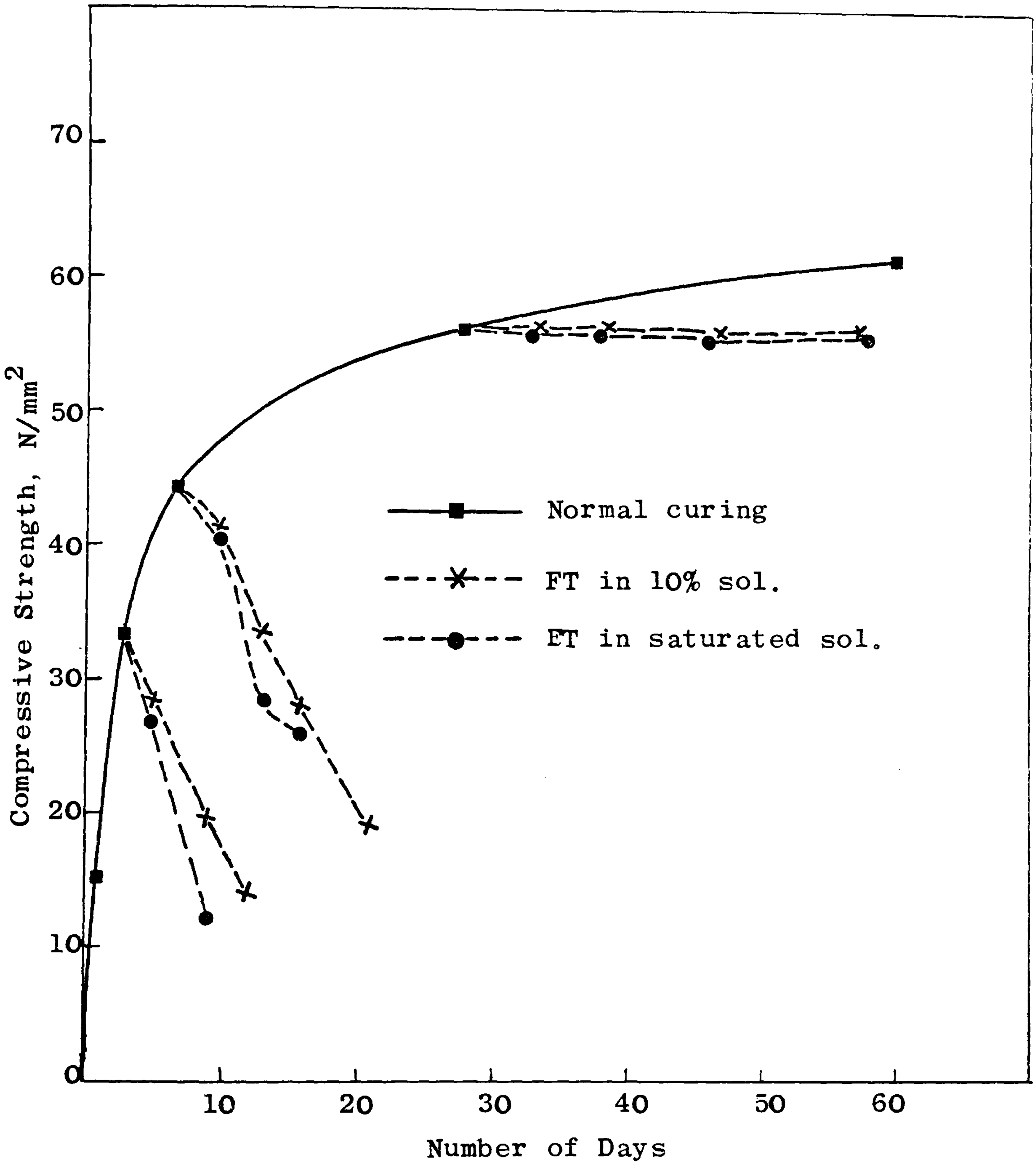

Fig. 4.3 Effect of freeze/thaw on compressive strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

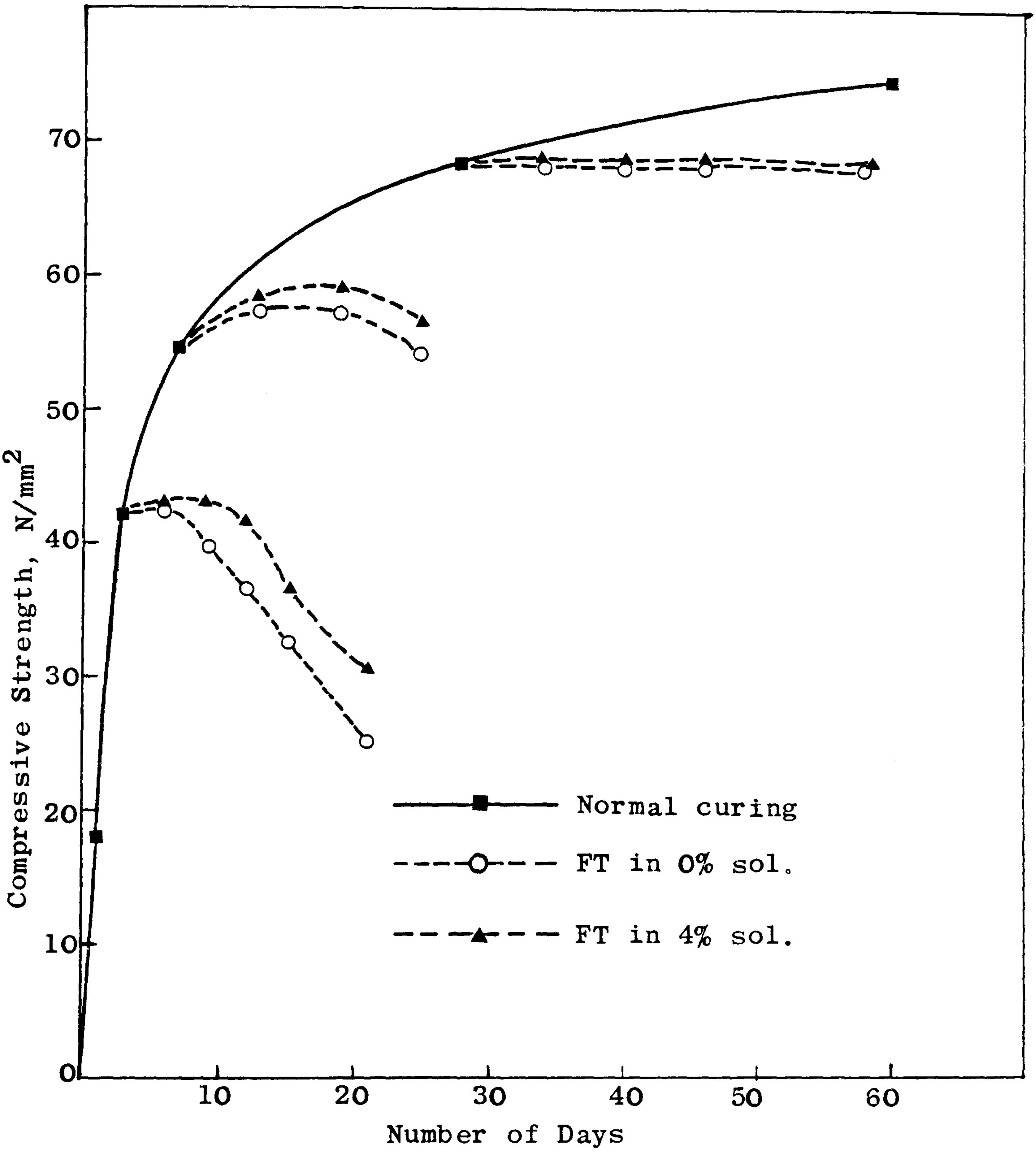

Fig. 4.4 Effect of freeze/thaw on compressive strength of cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations.

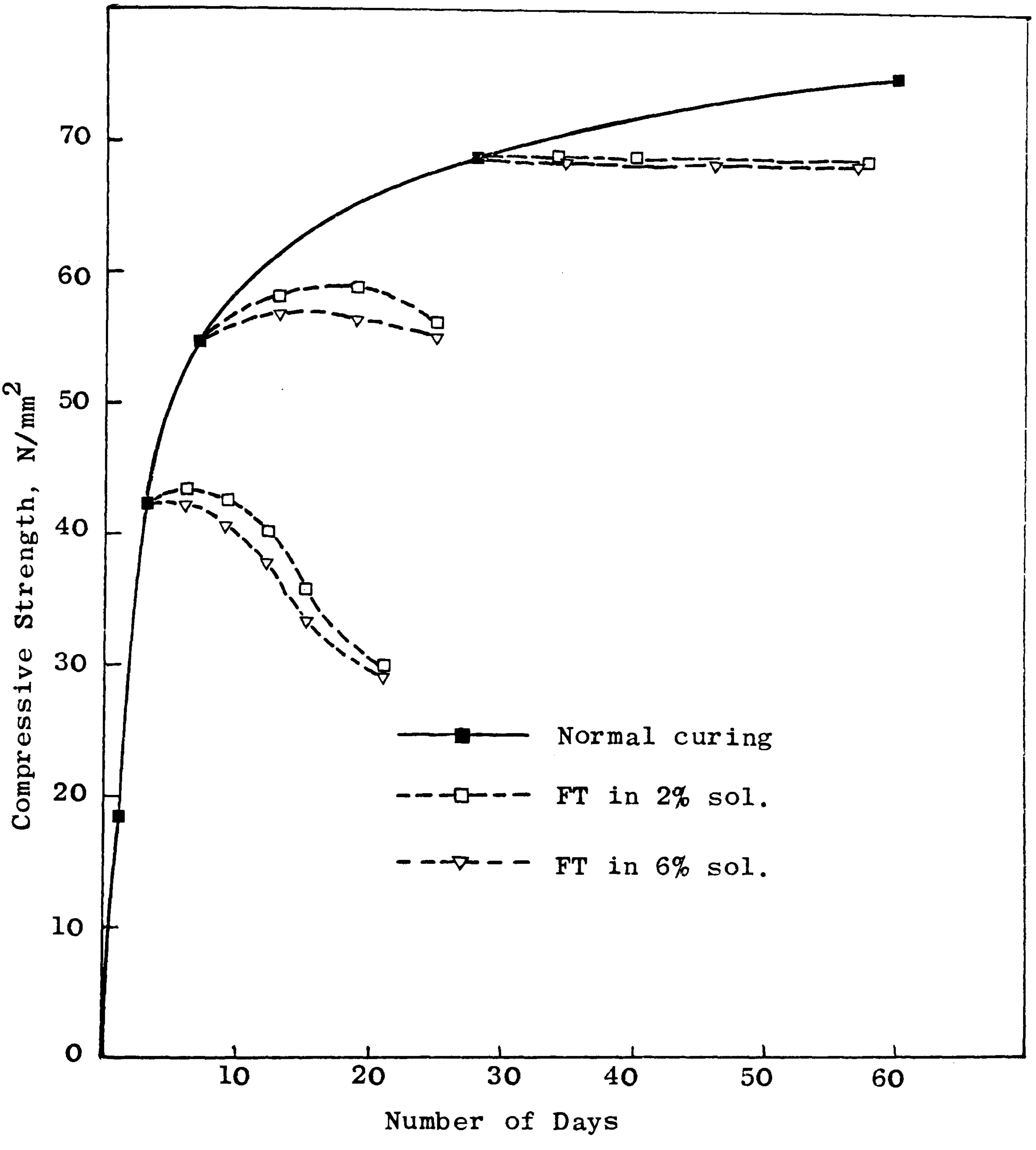

Fig. 4.5 Effect of freeze/thaw on compressive strength of cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

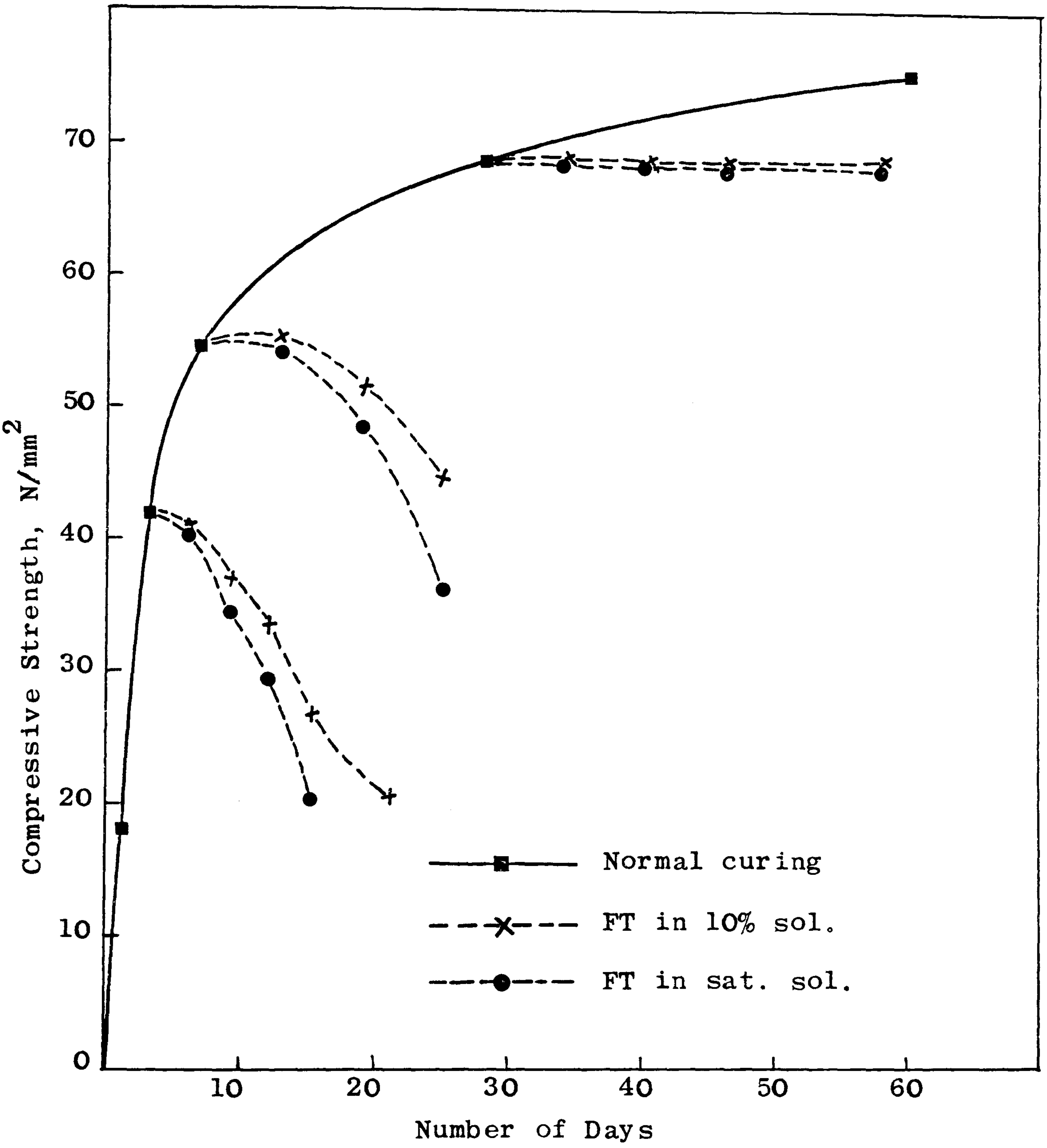

Fig. 4.6 Effect of freeze/thaw on compressive strength of cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

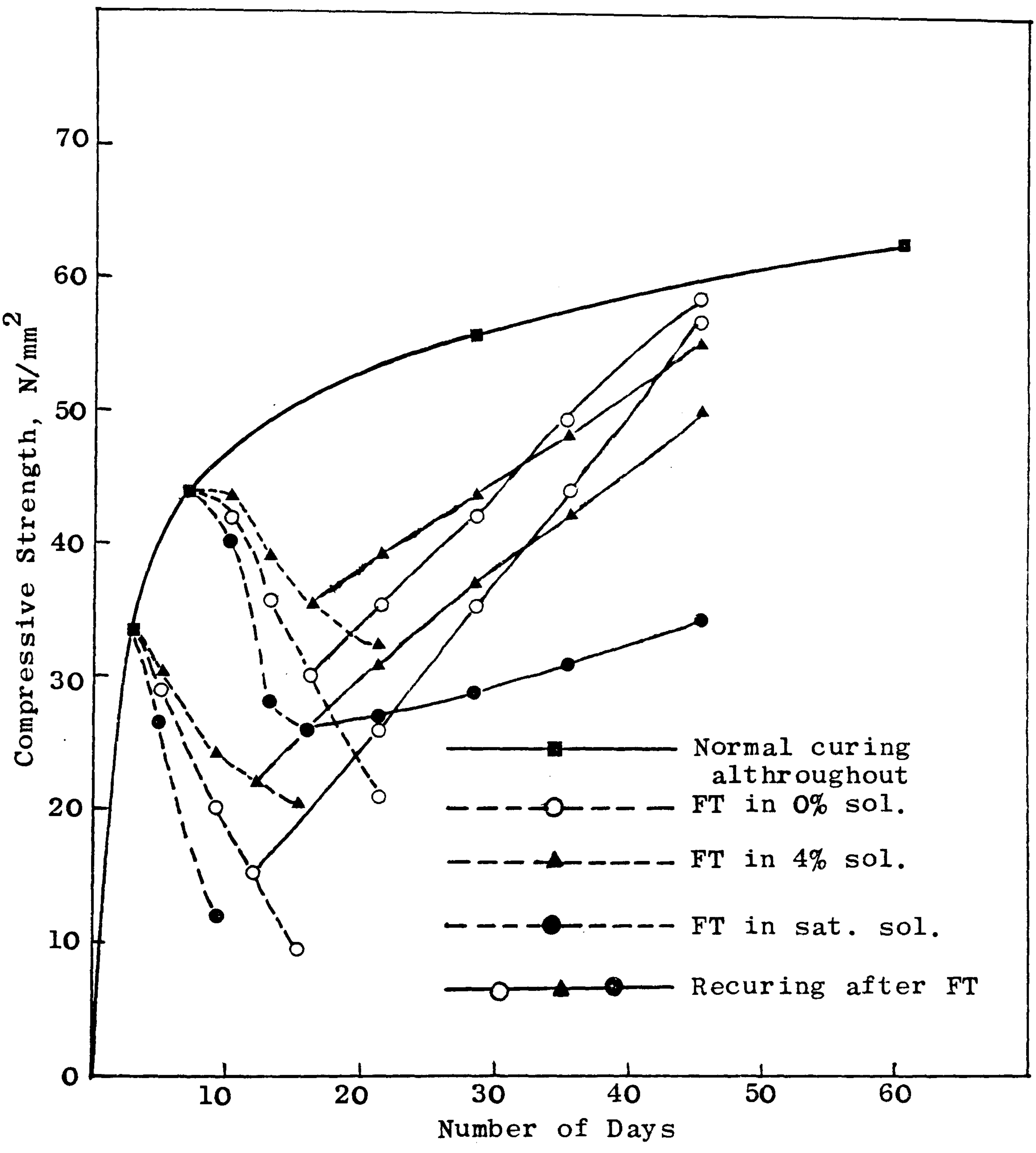

Fig. 4.7 Effect of freeze/thaw and subsequent curing on compressive strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

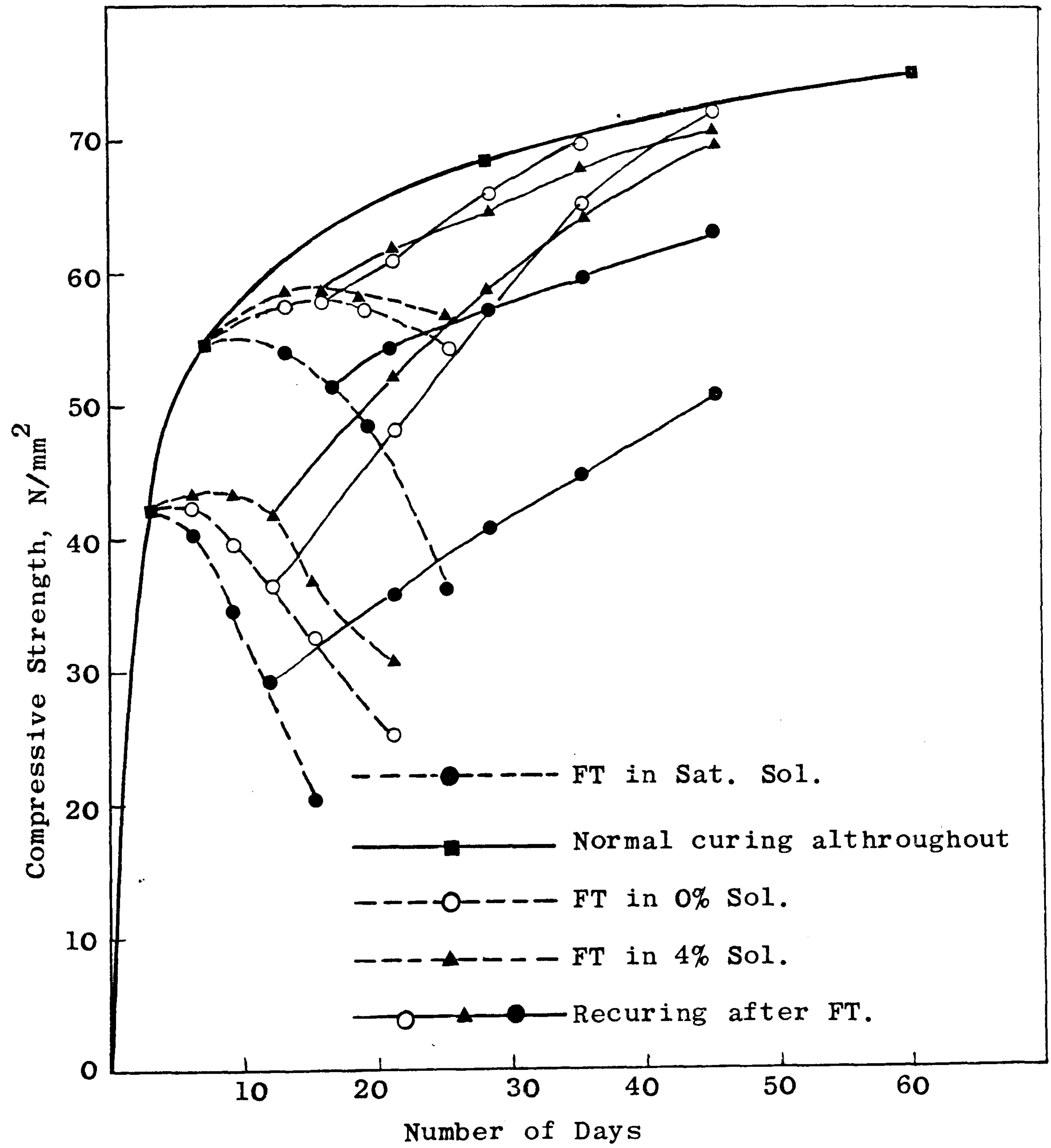

Fig. 4.8 Effect of freeze/thaw and subsequent curing on compressive strength of cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

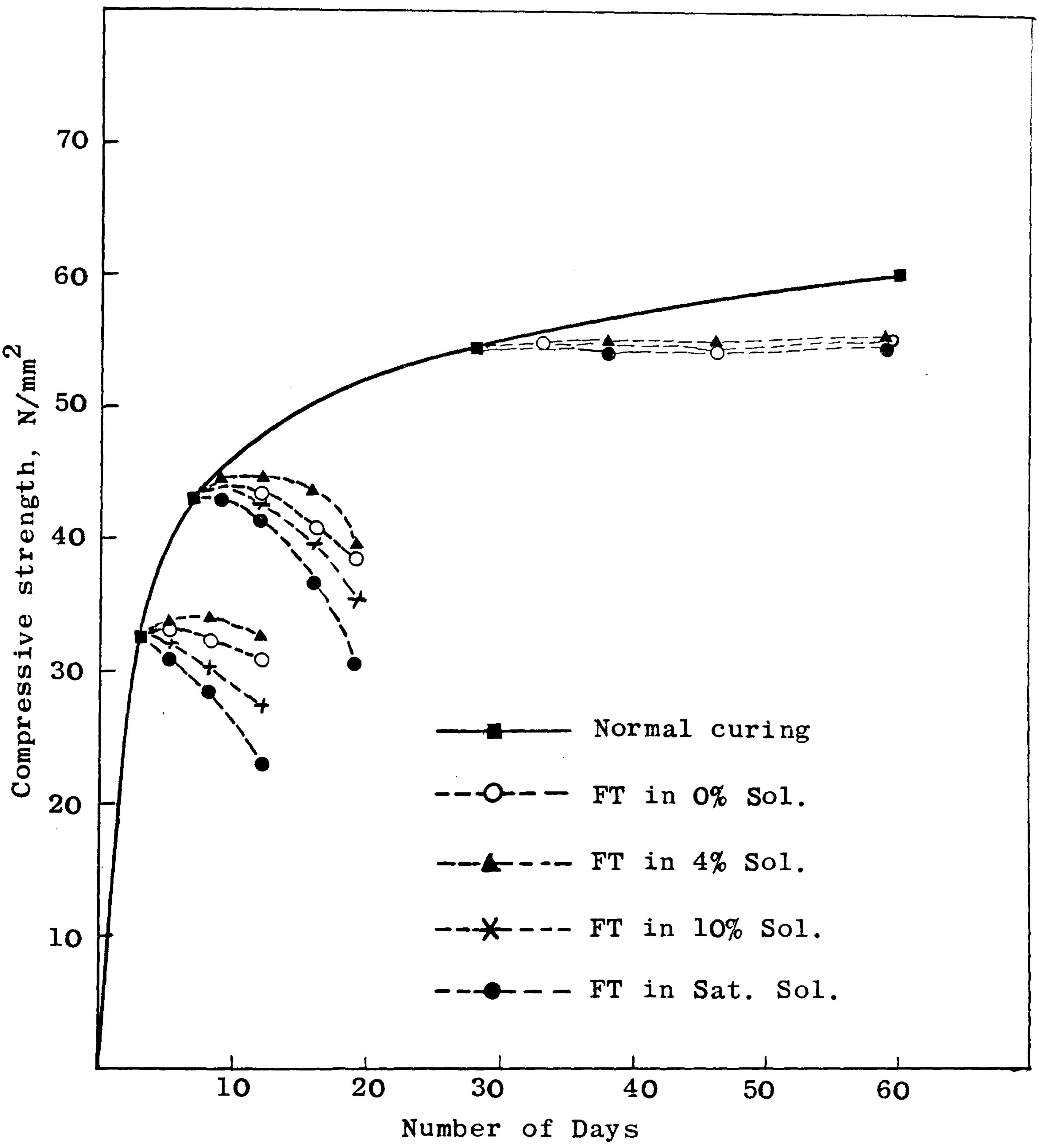

Fig. 4.9 Effect of freeze/thaw on compressive strength of mortar (cement/sand = 1:2, W/C = 0.4) in sodium chloride solutions of different concentrations

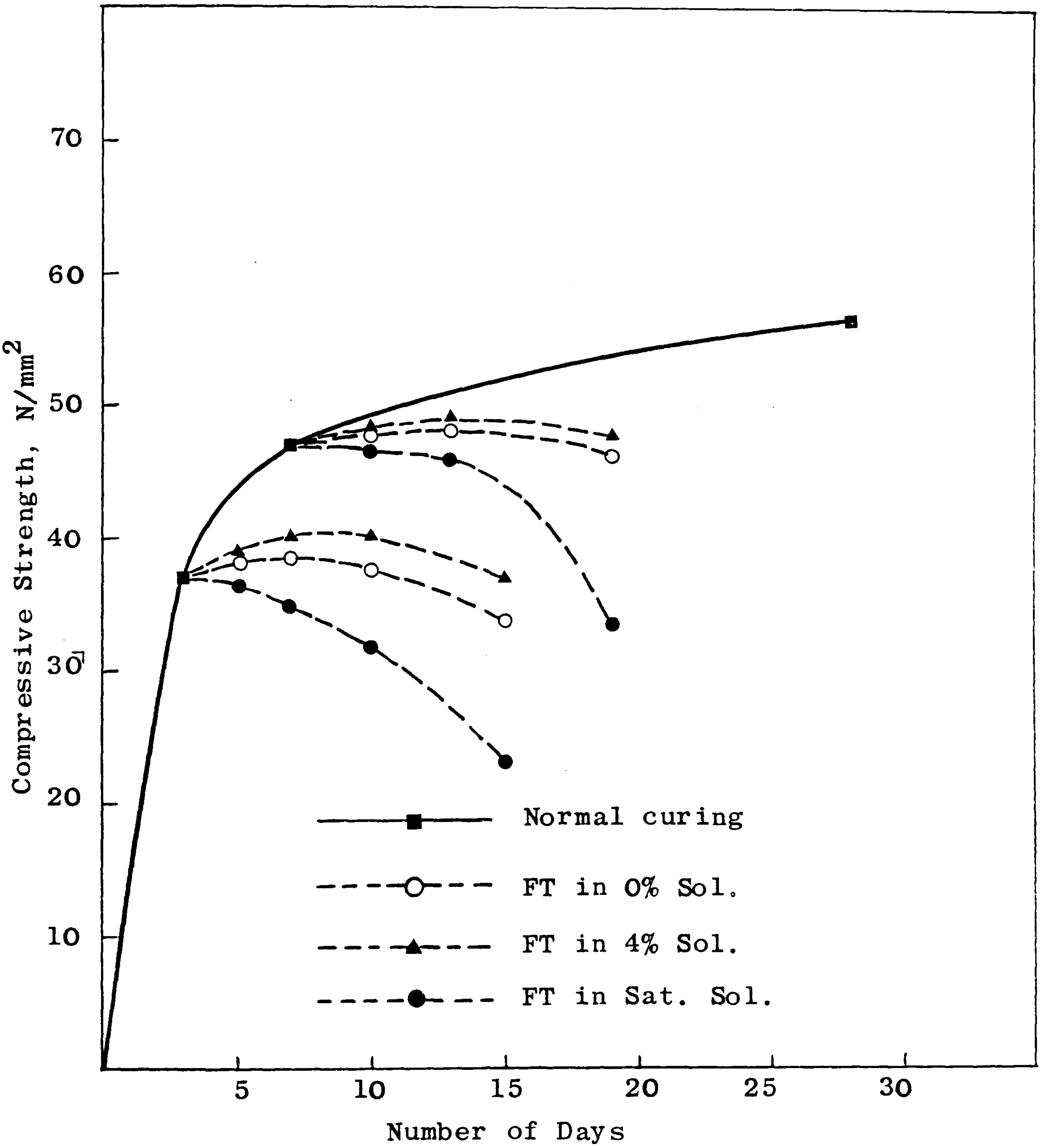

Fig. 4.10 Effect of freeze/thaw on compressive strength of mortar (cement/sand = 1:1, W/C = 0.4) in sodium chloride solutions of different concentrations

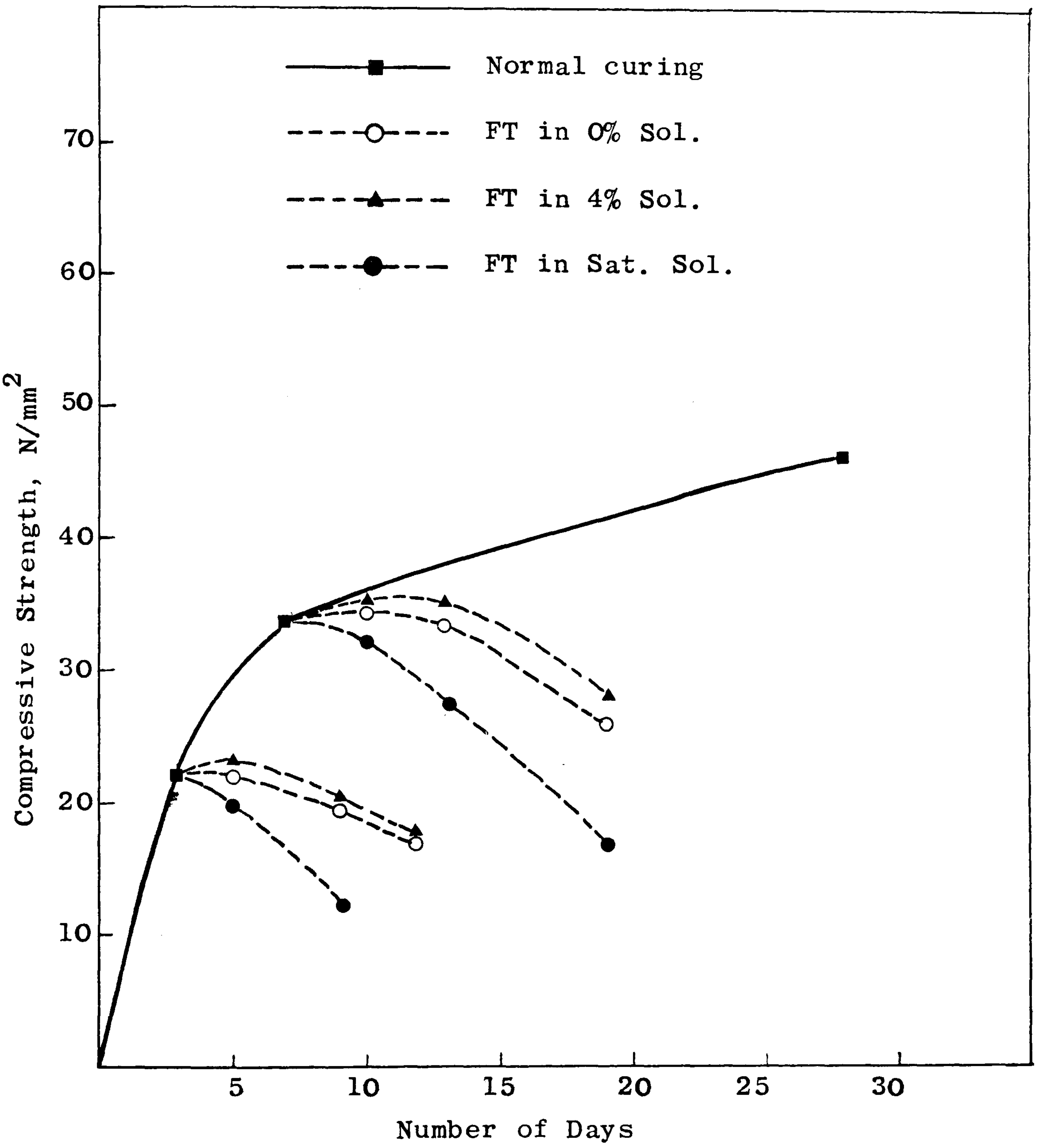

Fig. 4.11 Effect of freeze/thaw on compressive strength of mortar (cement/sand = 1:2, W/C = 0.5) in sodium chloride solutions of different concentrations

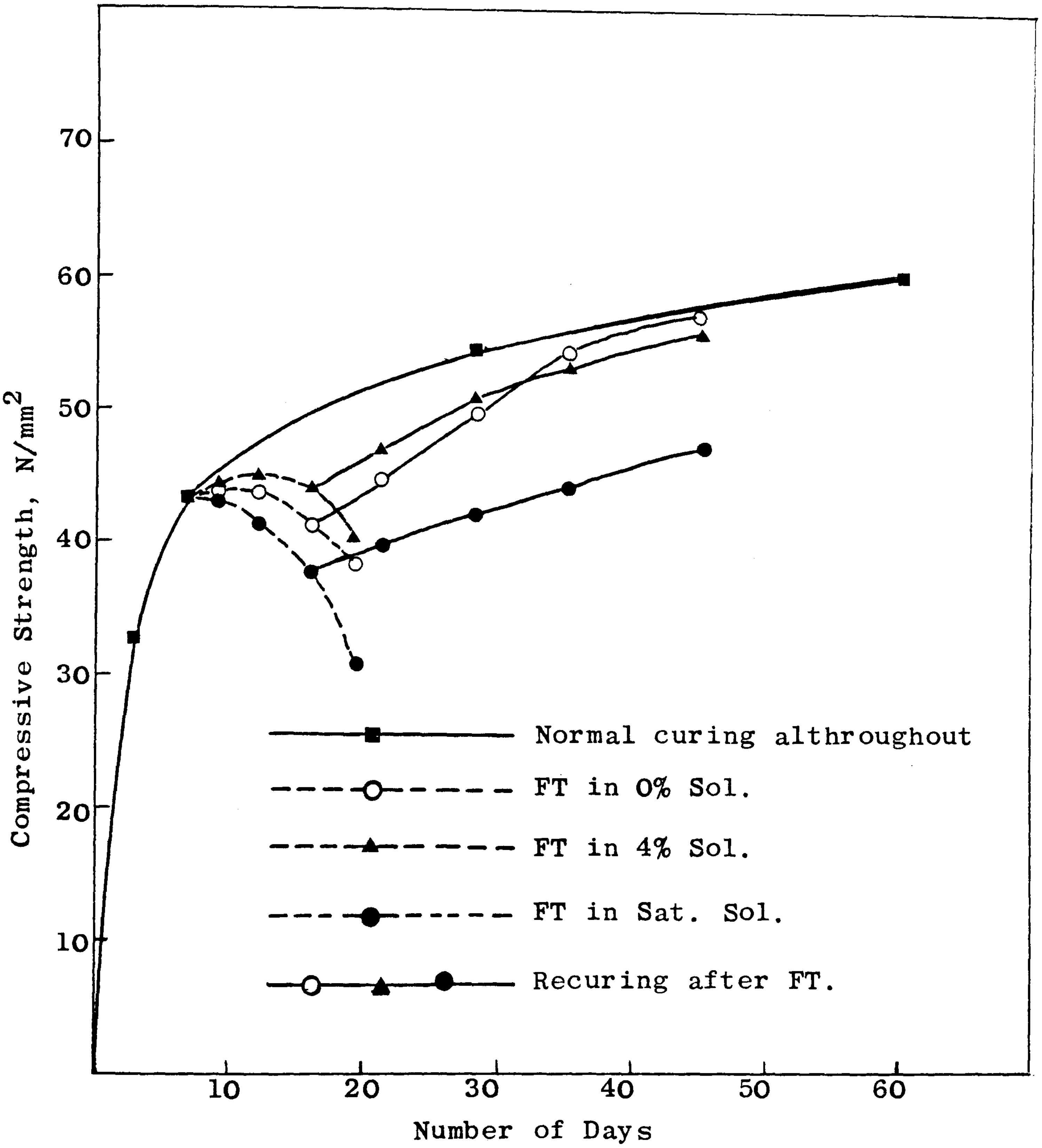

Fig. 4.12 Effect of freeze/thaw and subsequent curing on compressive strength of mortar (cement/sand = 1:2, W/C = 0.4) in sodium chloride solutions of different concentrations

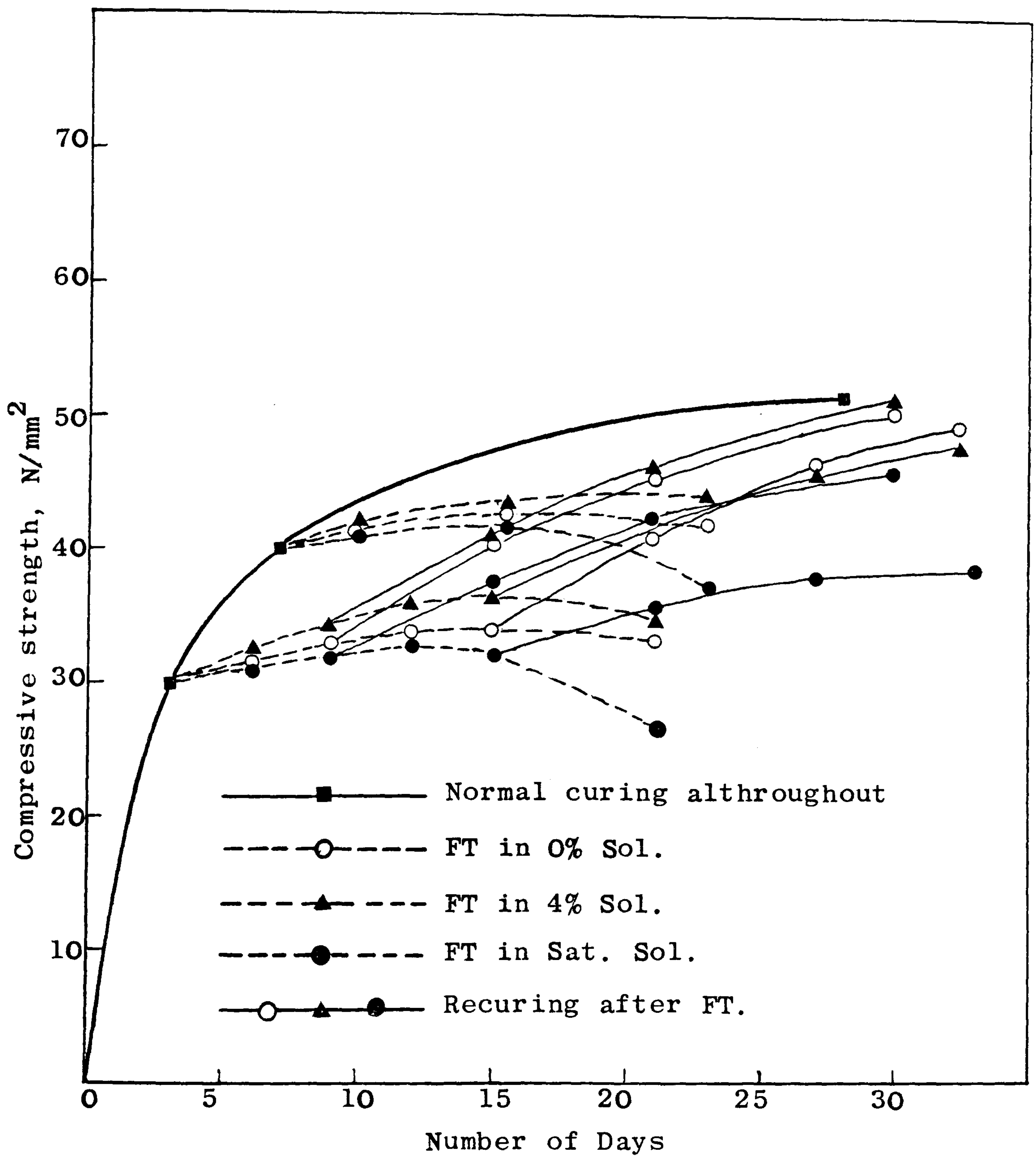

Fig. 4.13 Effect of freeze/thaw and subsequent curing on compressive strength of air entrained cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

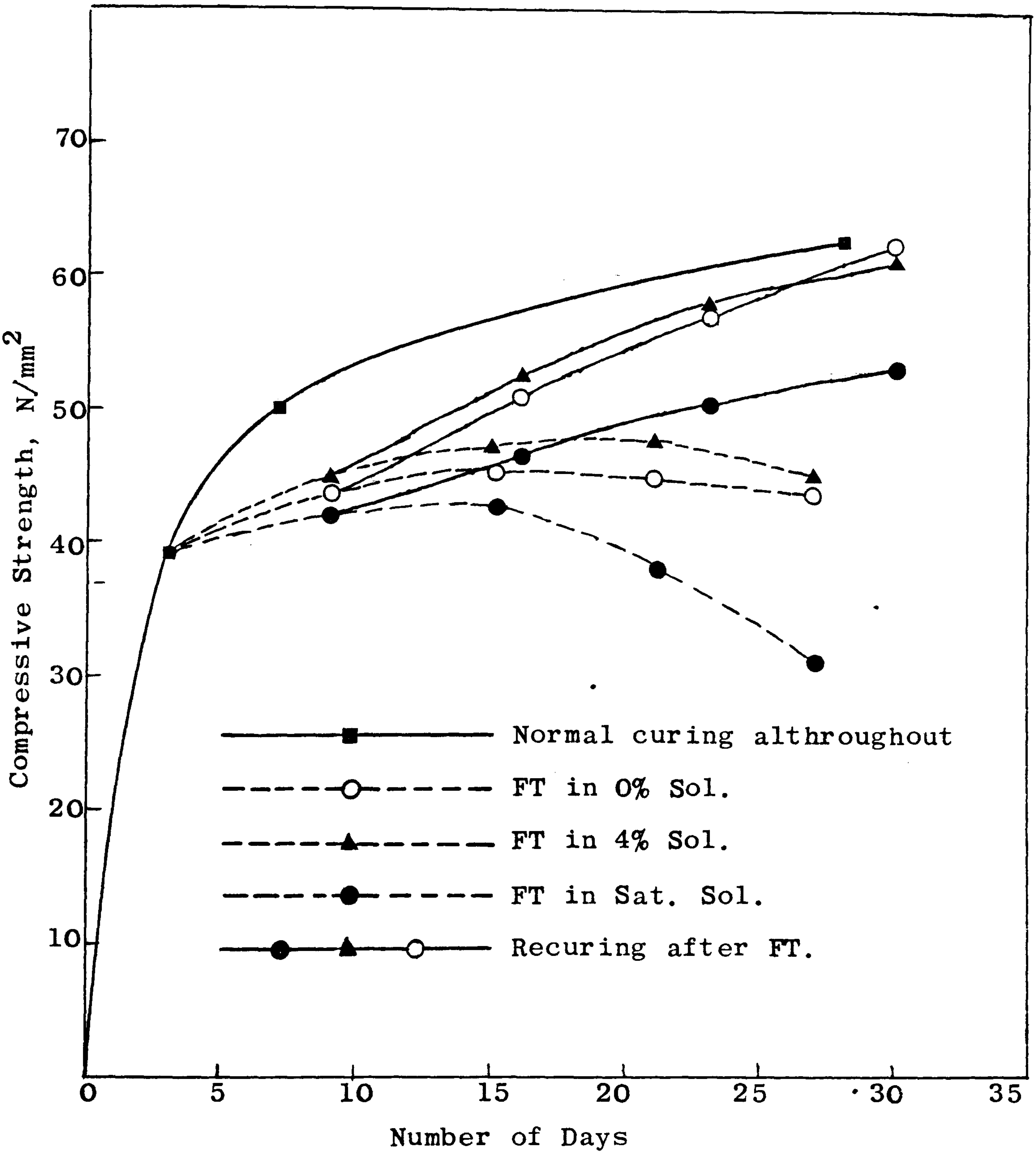

Fig. 4.14 Effect of freeze/thaw and subsequent curing on compressive strength of air entrained cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

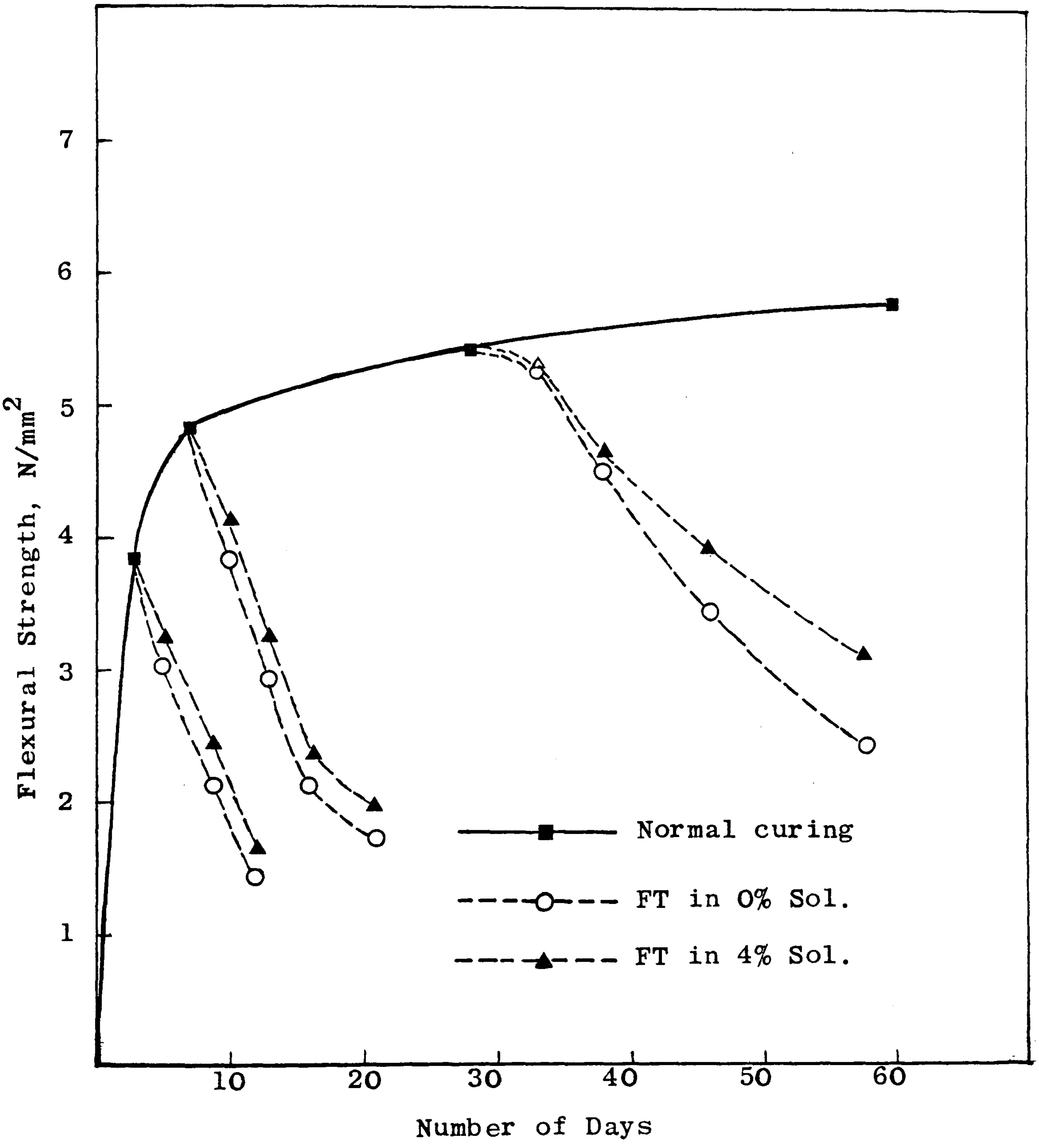

Fig. 4.15 Effect of freeze/thaw on flexural strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

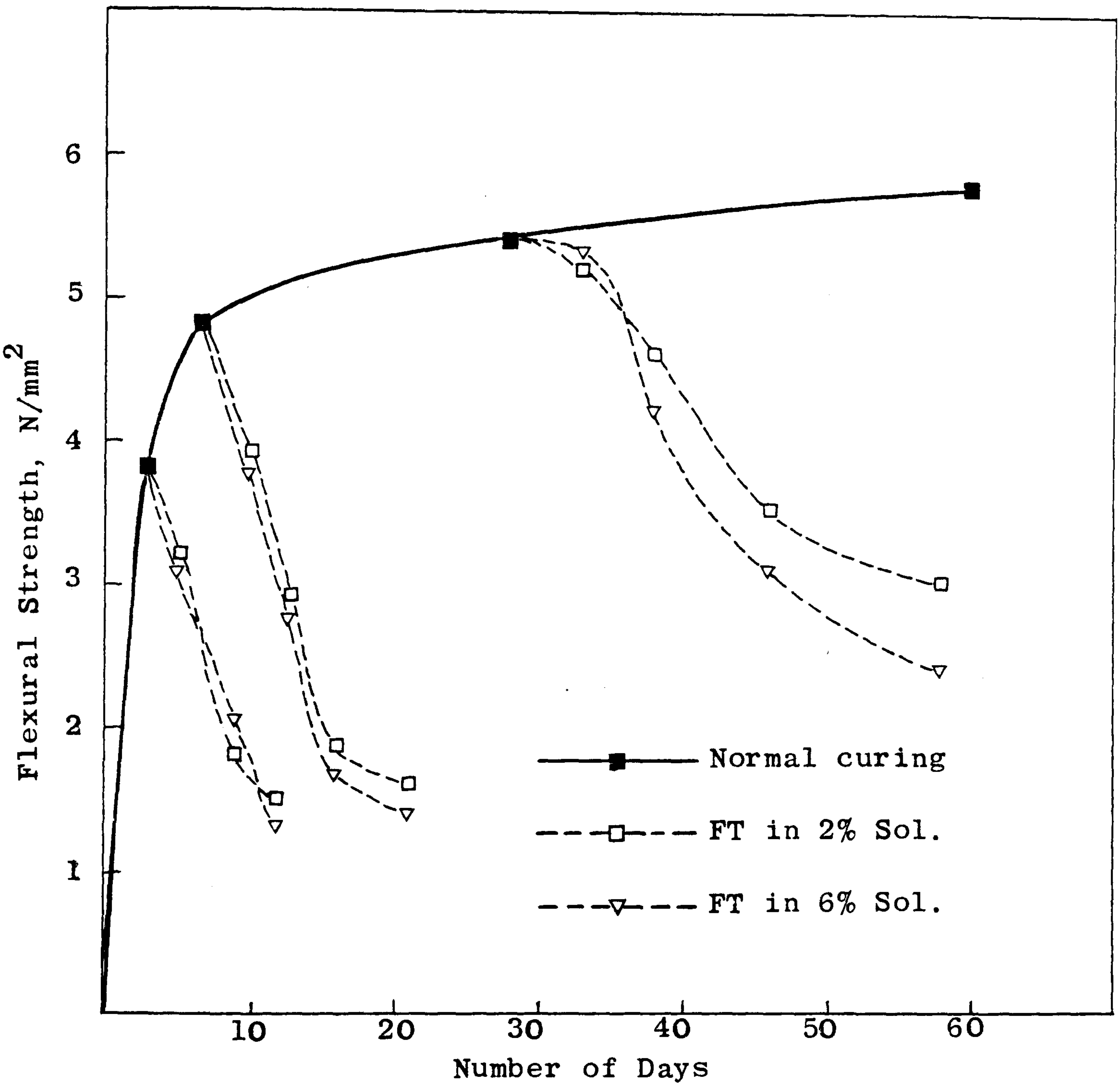

Fig. 4.16 Effect of freeze/thaw on flexural strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

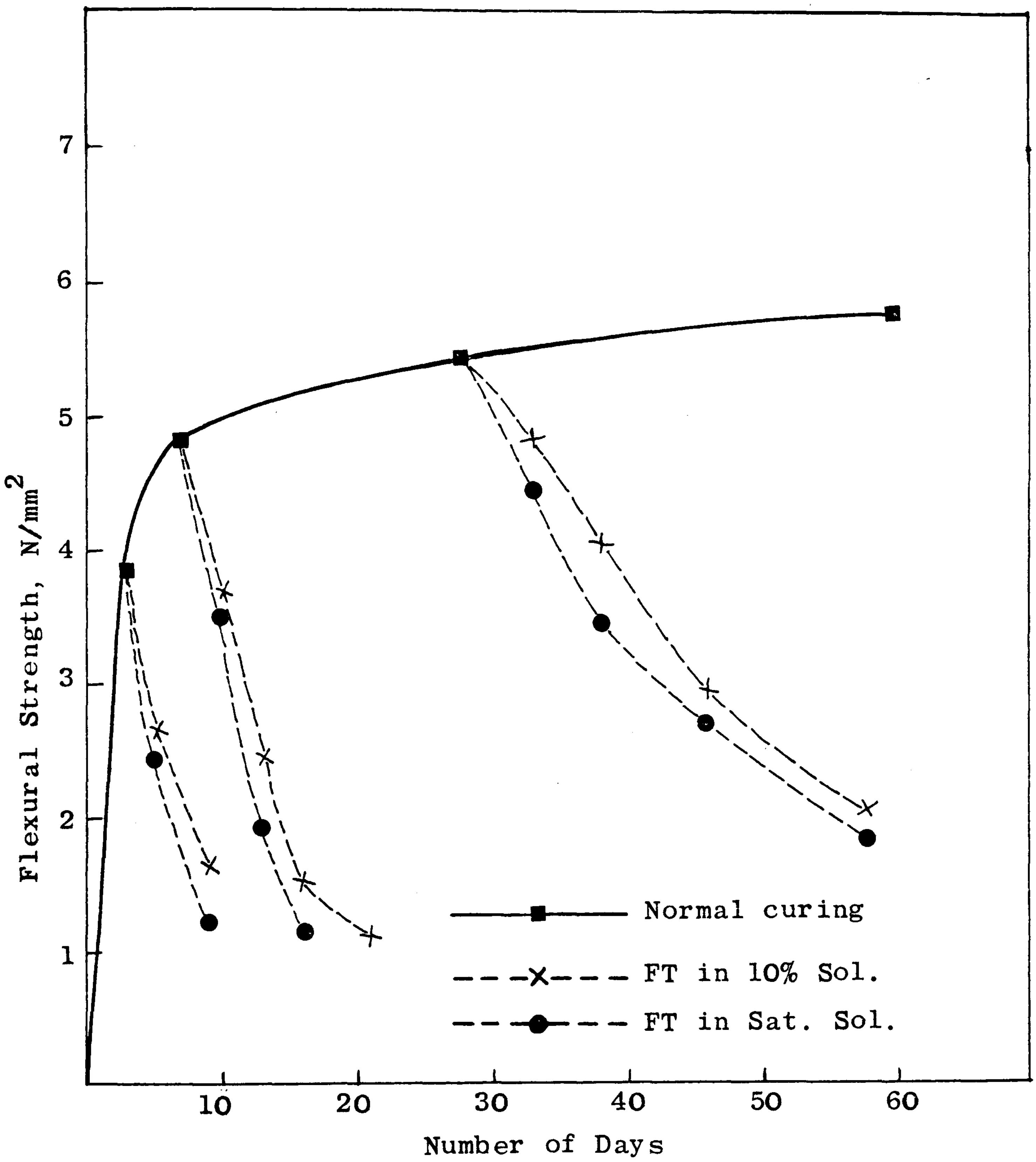

Fig. 4.17 Effect of freeze/thaw on flexural strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

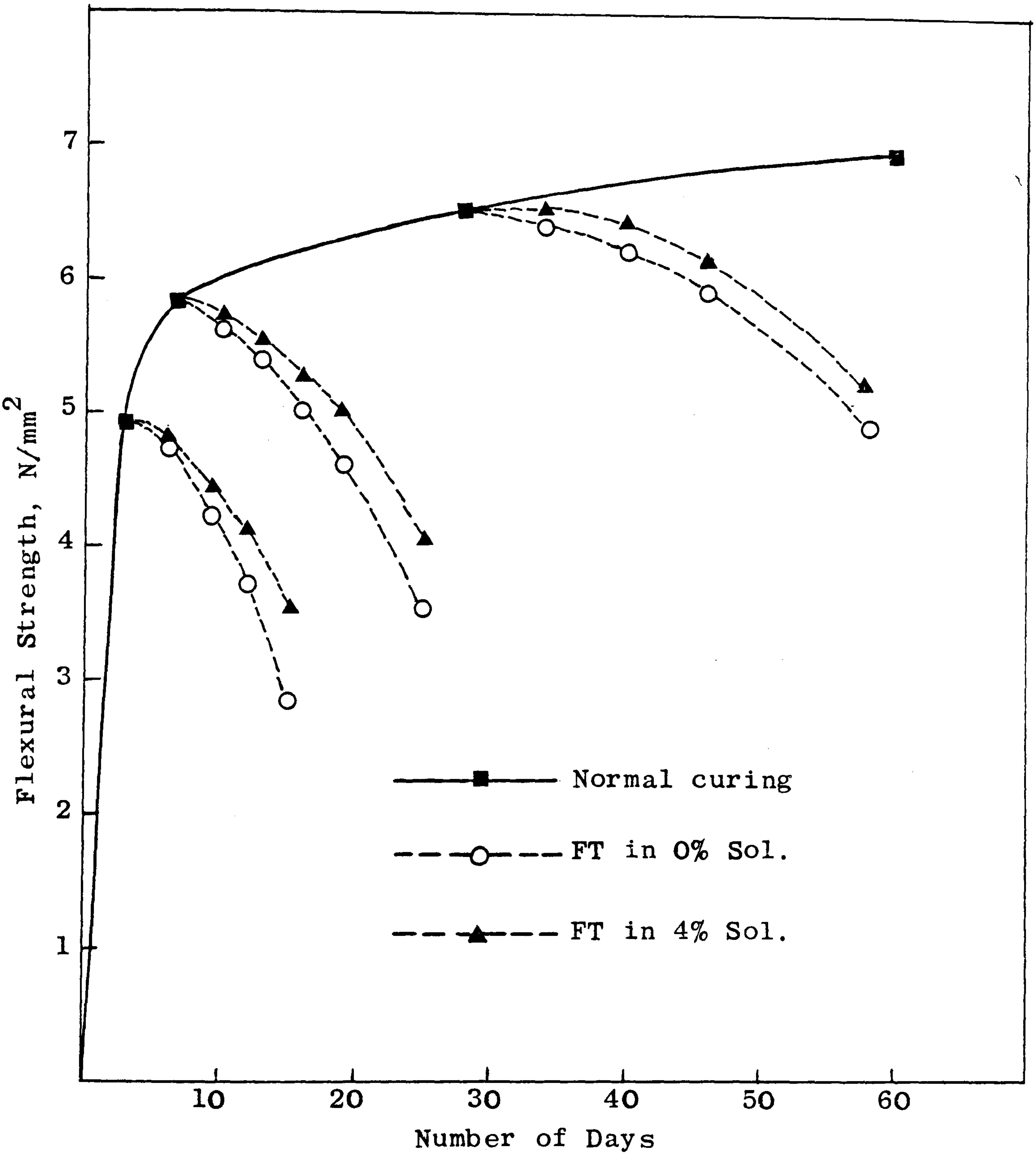

Fig. 4.18 Effect of freeze/thaw on flexural strength of cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

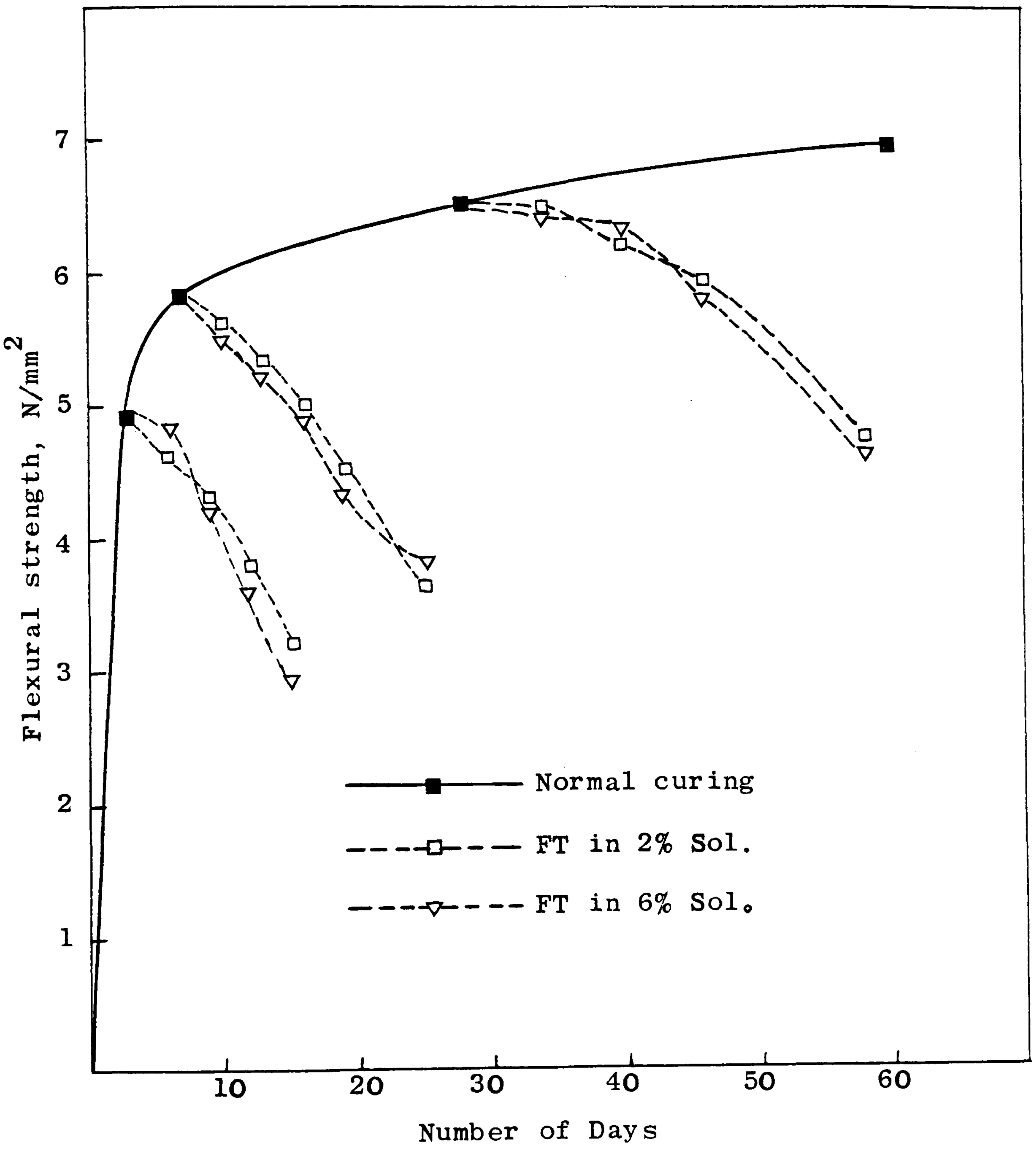

Fig. 4.19 Effect of freeze/thaw on flexural strength of cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

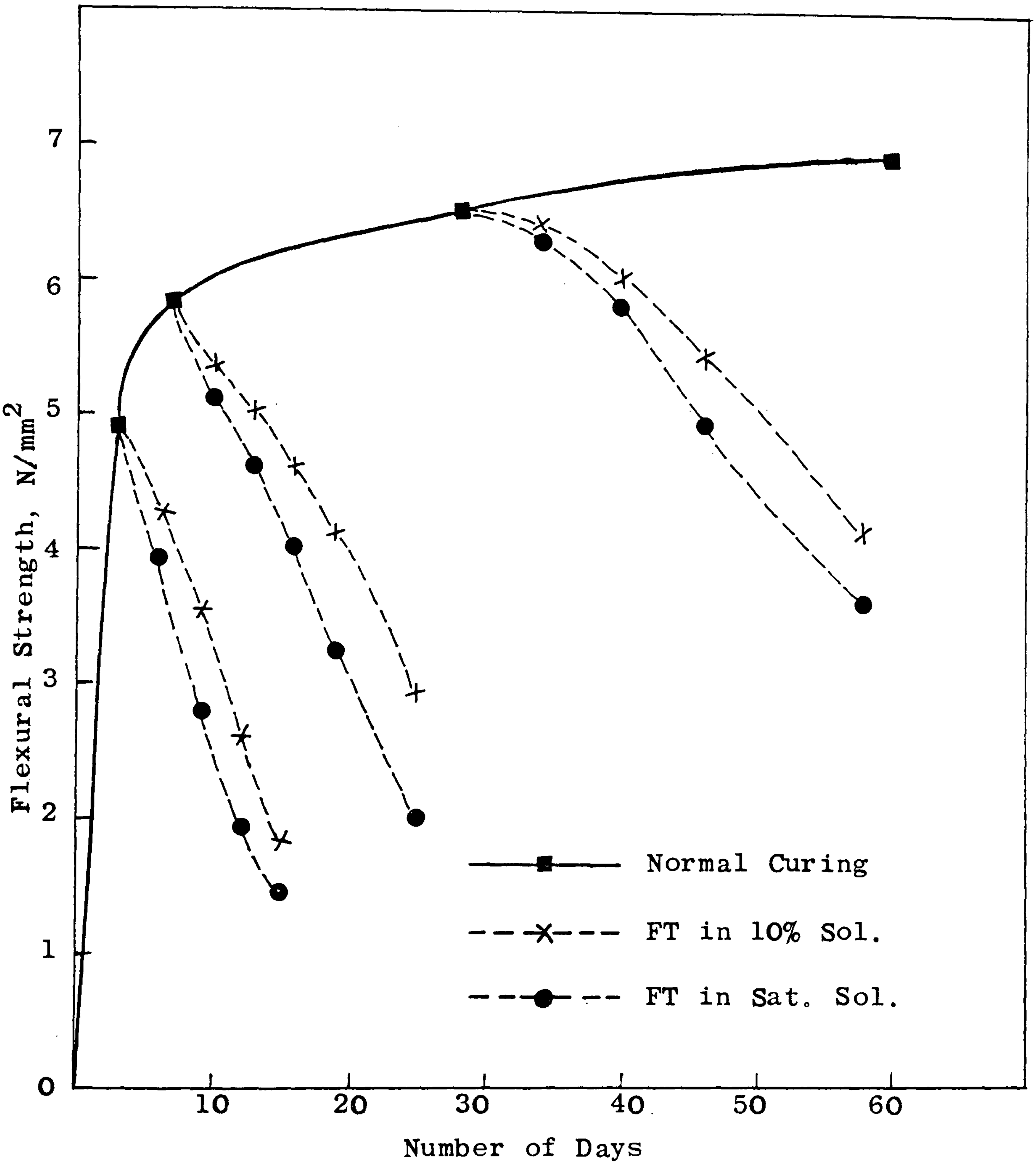

Fig. 4.20 Effect of freeze/thaw on flexural strength of cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

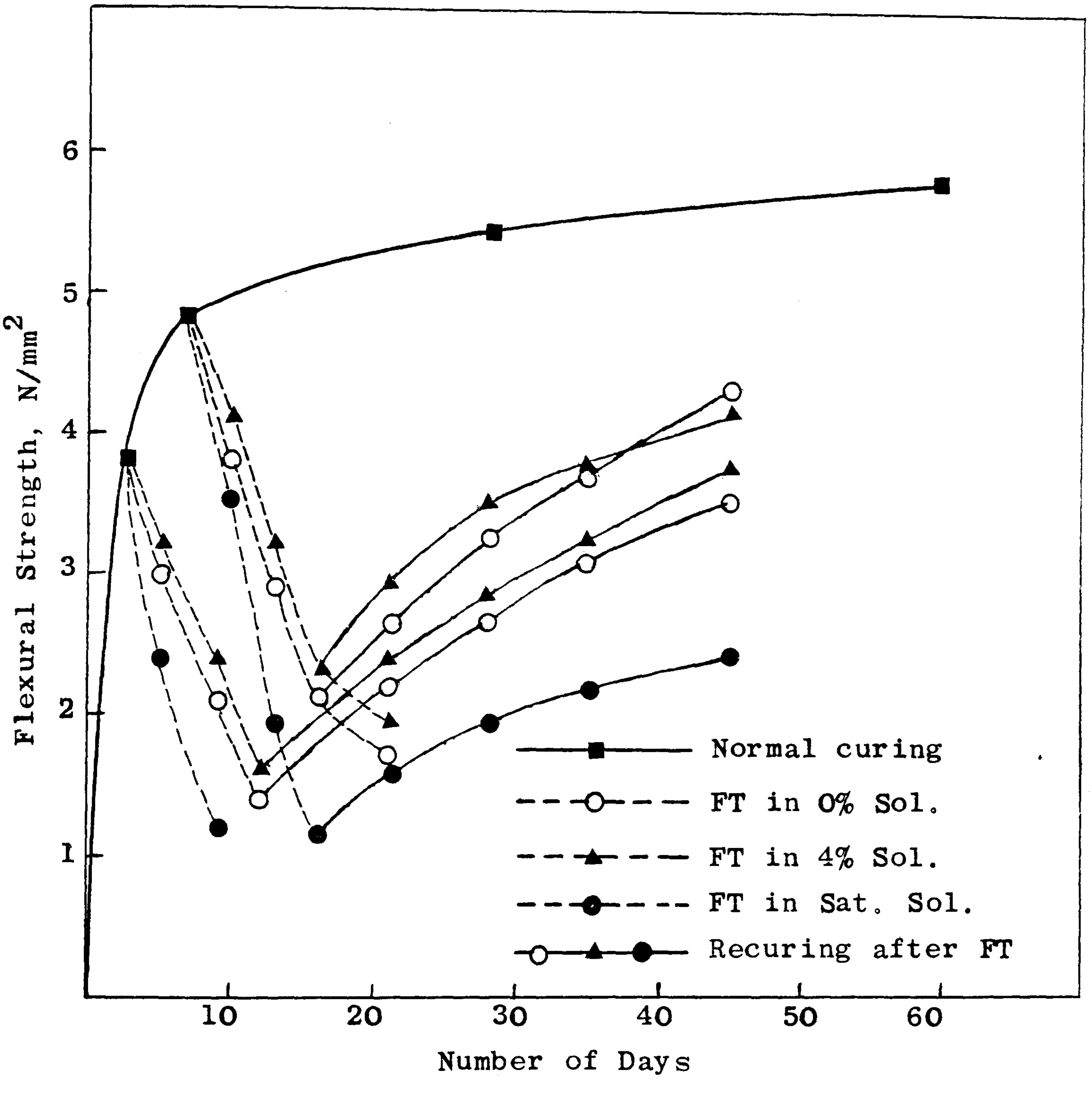

Fig. 4.21 Effect of freeze/thaw and subsequent curing on flexural strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

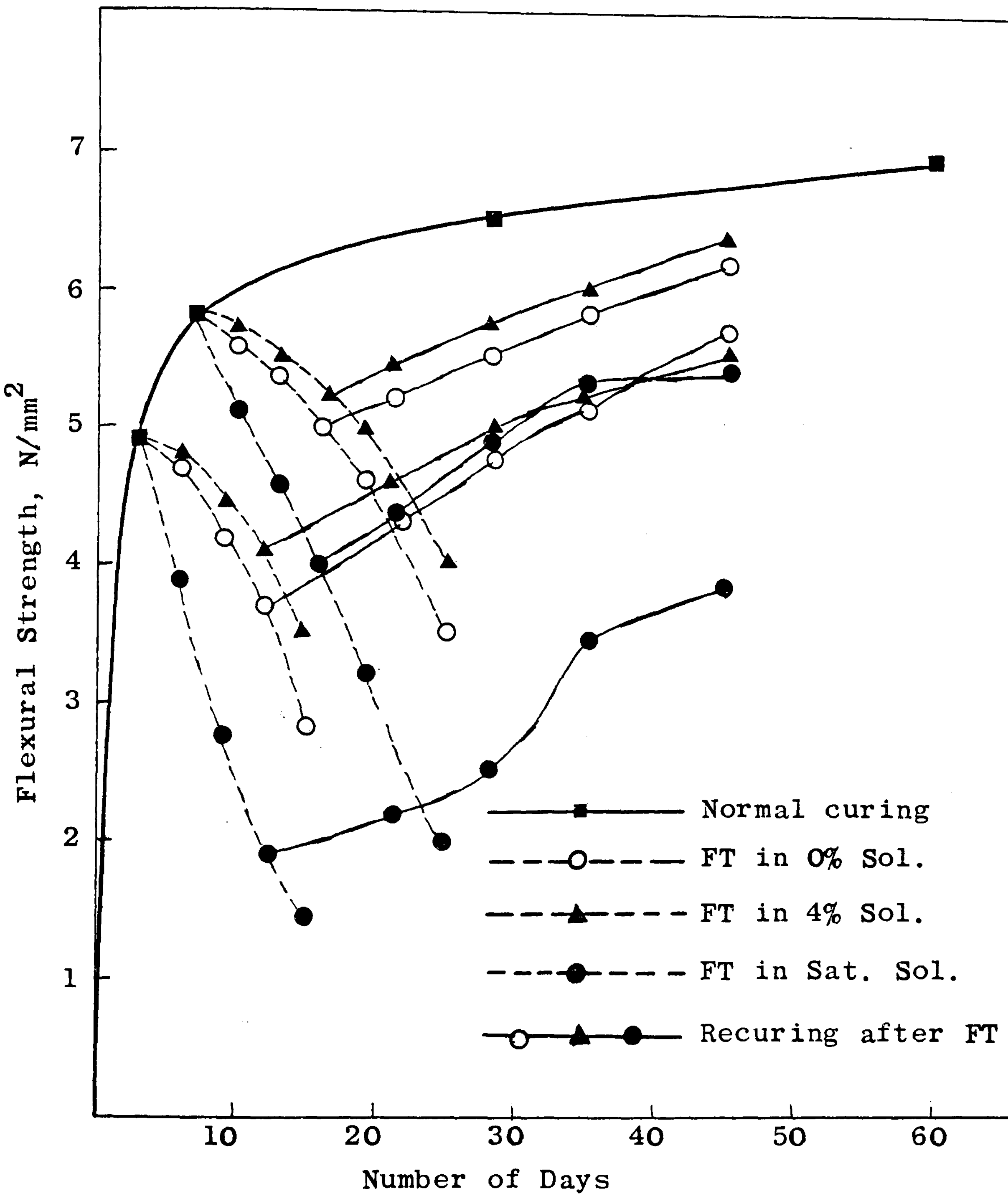

Fig. 4.22 Effect of freeze/thaw and subsequent curing on flexural strength of cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

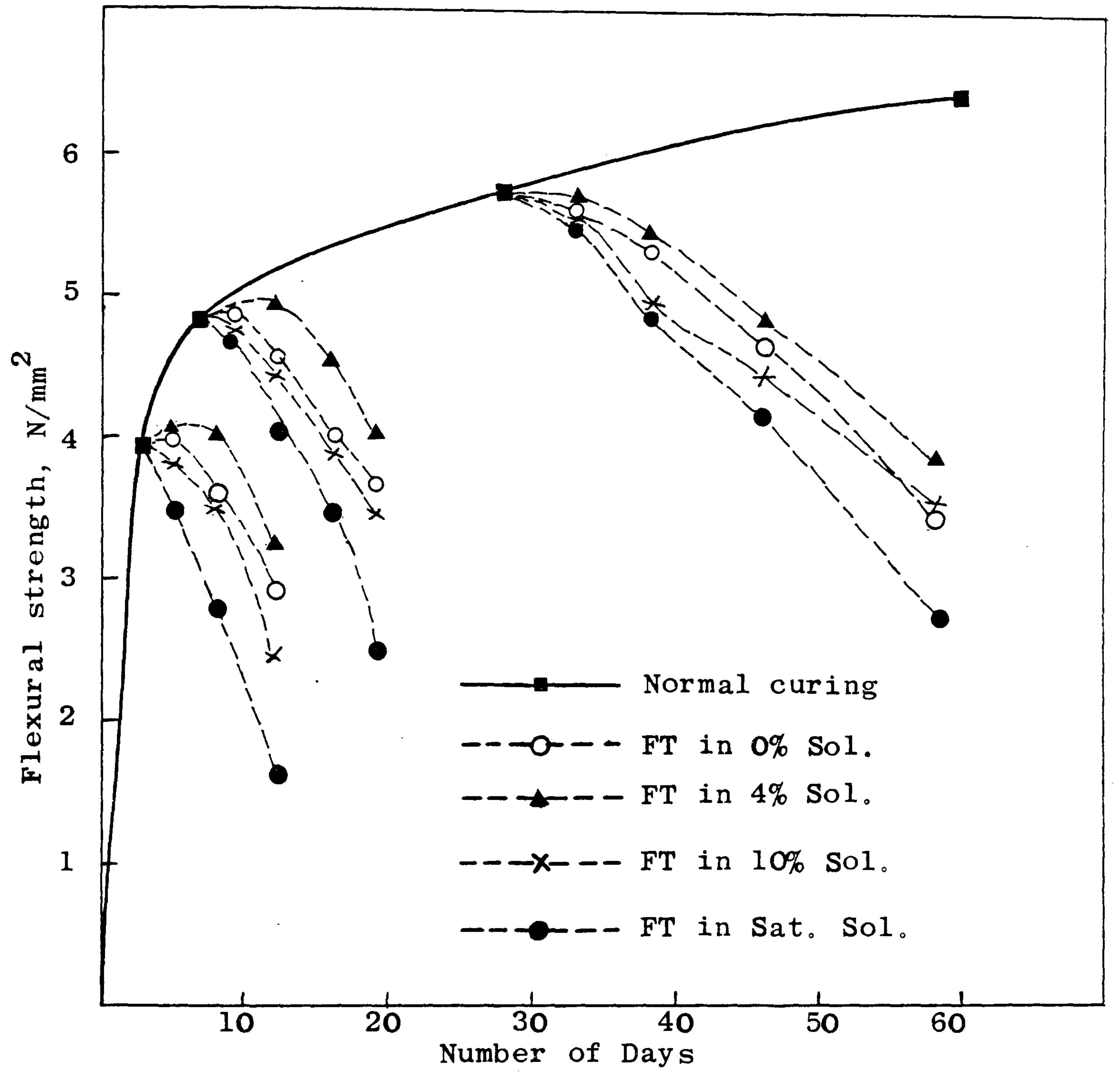

Fig. 4.23 Effect of freeze/thaw on flexural strength of mortar (cement/sand = 1:2, W/C = 0.4) in sodium chloride solutions of different concentrations

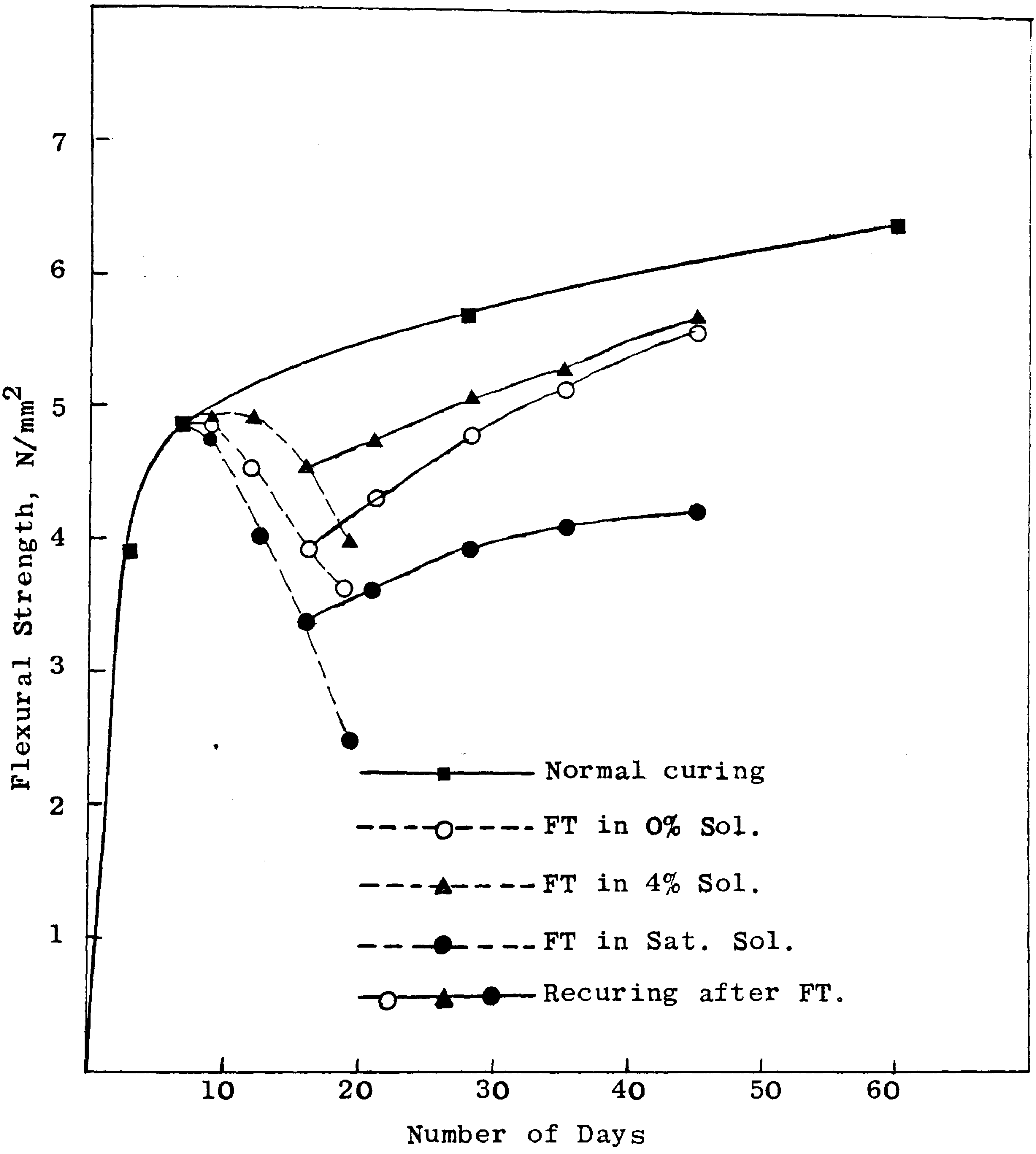

Fig. 4.24 Effect of freeze/thaw and subsequent curing on flexural strength of mortar (cement/sand = 1:2, W/C = 0.4) in sodium chloride solutions of different concentrations

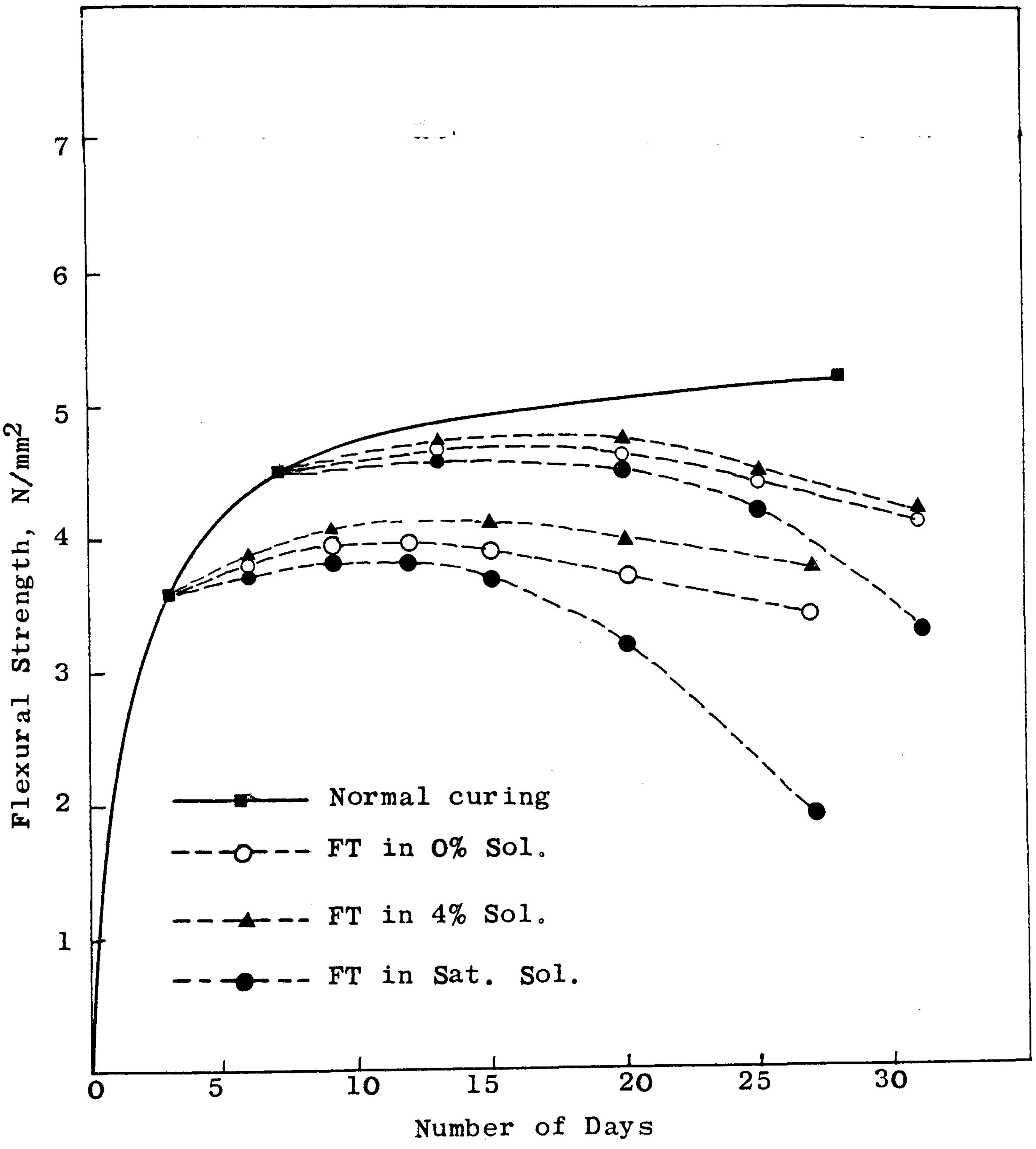

Fig. 4.25 Effect of freeze/thaw on flexural strength of air entrained cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

# CHAPTER 5

# THE EFFECT OF WETTING AND DRYING CYCLES ON COMPRESSIVE AND FLEXURAL STRENGTHS OF CEMENT PASTE AND MORTAR IN PRESENCE OF SODIUM CHLORIDE SOLUTIONS OF DIFFERENT CONCENTRATIONS.

## 5.1 Introduction

In evaluating the effects of alternate wetting and drying cycles on mortars or concrete either in water or in presence of salt solutions previous research workers have suggested several testing methods and various quantitative measures to describe progressive damage. According to their findings one of the many factors in the deterioration of concrete is the stresses set up by differential moisture movement either between different parts of the concrete as a whole, or between aggregate particles and the mortar or cement paste matrix. The extent to which wetting and drying cycles can occur under specific conditions must of course vary.

A theoretical consideration of the mechanism of shrinkage and swelling by Powers and Brownyard(11) suggested that the moisture movement in a concrete product is dominantly a property of the cement paste. The consequent expansion on wetting and shrinkage on drying depended both on the amount of cement and on the water/cement ratio. Recent studies were more or less concentrated on the need to determine minimum change in weight or change in length to prevent concrete from being damaged by wetting and drying cycles or by other means. It has been suggested(141) that failure should be assumed if any one of the following has occurred with any concrete structure: a change in weight of ± 10 per cent, a 50 per cent decrease in the square of the dynamic modulus of elasticity or a change in length of ± 0.2 per cent. According to Bellport(142) a linear expansion of 0.2 per cent shows internal disruption, but it is only at 0.5 per cent that the concrete should be assumed to have failed. Most of these existing testing methods, however, have certain drawbacks such as (1) change in weight due to wetting and drying cycles in water or in salt solutions may not reflect extensive microcracking, (2) change in length may not be reliable because expansion can be masked by surface scaling and (3) measurements of resonant frequency may not reflect extensive spalling.

Very little has been recorded regarding the effect on the physical properties of concrete or mortar when subjected to alternate wetting and drying cycles in the presence of sodium chloride solutions. Neville(103) observed leaching and loss of strength of concrete when exposed to wetting and drying cycles in saturated solution of calcium chloride. He also observed serious expansion in mixes with higher water/cement ratio. Measurements of flexural strength was found to reflect the state of corrosion in wetting and drying cycles in water.(143)

The urgency of establishing generalized and practical criteria for predicting salt action in concrete when subjected to alternate wetting and drying cycles in different solutions resulted in the examination of a very wide range of concrete mixes. The absence of any investigation into the behaviour of plain cement paste was significant. In this chapter details are given of an investigation into the effects of alternate wetting and drying cycles in water and also in different solutions of sodium chloride on the compressive and flexural strength of cement paste and comparison is made with the behaviour of mortar under similar conditions.

## 5.2 Results and Discussion

### 5.2.1 Compressive Strength

The results of compressive strength measurements on cement pastes of water/cement ratio 0.4 and 0.3 normally cured and when subjected to alternate wetting and drying cycles in 0%, 4%, 10% and saturated solutions of sodium chloride initially cured for different periods are presented in Figs. 5.1 and 5.2. Pastes of water/cement ratio 0.4 subjected to wetting and drying cycles after 3 days of initial curing showed a decrease in the rate of strength gain in all the solutions of sodium chloride. After 36 cycles the specimens in 10% and saturated solutions started dropping in strength, greatest with the specimens in saturated solution. But with the specimens in 0% and 4% solutions there was further gain of strength after 36 cycles and finally at 72 wet/dry cycles there was a tendency for the strength to drop again. In 4% solution even after 72 wet/dry cycles the loss of strength was minimum and in saturated solution it was a maximum. For the 7 days initially cured paste specimens of 0.4 water/cement ratio when subjected to wet/dry cycles in solutions of sodium chloride the behaviour of compressive strength was very nearly the same as those of 3 days initially cured specimens. The only difference was noticed in the case of specimens in 0% solutions where the samples showed gains in strength even after 72 cycles. The specimens in 0% solution showed higher values of compressive strength beyond 45 cycles than those in 4% solution which was the reverse in the case of 3 days initially cured specimens. For the 28 days initially cured specimens there was a similar gain of strength until 54 wet/dry cycles in all the solutions after which specimens in 10% and saturated solutions showed a slight drop in compressive strength, the maximum drop being again in the saturated solution. In 0% and 4% solutions the specimens exhibited the same behaviour of gaining further strength at 72 cycles.

For the paste specimens with water/cement ratio of 0.3 the behaviour of compressive strength of 3 days and 7 days initially cured specimens when subjected to wet/dry cycles in 0%, 4%, 10% and saturated solutions of sodium chloride was very much similar to that of the specimens with 0.4 water/cement ratio under corresponding conditions.

When the wetting and drying was stopped after 36 cycles in 0%, 4% and saturated solution and the specimens allowed to cure normally, the specimens whose initial curing had been for 3 days could recover significant compressive strengths after 21 days of recuring as shown in Fig. 5.3. The specimens attained a compressive strength of 33 N/mm$^2$ after 3 days of initial curing before being subjected to wet/dry cycles. At the end of 36 cycles the strengths were 47 N/mm$^2$, 48.5 N/mm$^2$ and 41 N/mm$^2$ for the specimens in 0%, 4% and saturated solution which after 21 days of recuring reached 59.5 N/mm$^2$, 58 N/mm$^2$ and 51 N/mm$^2$ respectively. This gain of strength after recuring was very similar for the specimens in all the solutions but in 0% the specimens showed the maximum recovery and almost regained its normal strength.

Fig. 5.4 shows the effect of wetting and drying cycles on compressive strength of mortar of 1:2 cement/sand ratio and 0.4 water/cement ratio. The specimens initially cured for 3 days were subjected to wet/dry cycles in 0%, 4% and saturated solutions of sodium chloride. The specimens showed a gain of strength in all the solutions similar to those with paste specimens (Fig. 5.1). But the mortars showed a greater gain of strength than the paste specimens. Attaining a strength of 33 N/mm$^2$ after 3 days of initial curing the mortar specimens reached 49 N/mm$^2$, 51.5 N/mm$^2$ and 44.5 N/mm$^2$ in 0%, 4% and saturated solutions respectively after 30 wet/dry cycles whereas for the paste specimens the corresponding values were 46.0 N/mm$^2$, 48 N/mm$^2$ and 41 N/mm$^2$ after a similar number of wet/dry cycles. After 54 wet/dry cycles the mortar specimens had compressive strength of 53 N/mm$^2$, 51 N/mm$^2$ and 43 N/mm$^2$ respectively in 0%, 4% and saturated solution which showed further increase of strength in 0% solution and drop in 4%

and saturated solution compared with the values after 30 cycles. A similar effect was also noticed with the paste specimens of both 0.3 and 0.4 water/cement ratio initially cured for 7 days and when subjected to wetting and drying for 54 cycles. From this it appears that the recuring effect caused the specimens in fresh water to recover their strength in a better way than those in salt solutions.

It was also found from Fig. 5.4 that if mortar that was initially cured for 3 days experienced 30 wet/dry cycles in 0%, 4% and saturated solution of sodium chloride and was then allowed to cure normally, the specimens were able to recover significantly. The specimens of 0% solution recovered almost fully, those of 4% solution recovered more than 95% and those of saturated solution recovered nearly 89% of normal strength after 27 days of recuring. Comparatively the paste specimens recovered less than the mortar specimens in similar conditions. It is therefore concluded that the presence of sodium chloride in young paste and mortar when subjected to wetting and drying must play a major part in the hydration characteristics and that the presence of aggregates plays an important part in providing a resistance to the attack of chlorides.

### 5.2.2 Flexural Strength

The results of flexural strength tests on cement pastes of water/cement ratios 0.4 and 0.3 normally cured and when subjected to alternate wetting and drying cycles in 0%, 4%, 10% and saturated solutions of sodium chloride are plotted in Figs. 5.5 and 5.6. The paste specimens of both water/cement ratios, initially cured for 3 days, behaved in a similar fashion when subjected to wet/dry cycles. In all the solutions except the saturated solution the paste specimens showed gain of flexural strength for a considerable number of wet/dry cycles after which the specimens showed a tendency to a drop in the flexural strength. The specimens in the saturated solution showed a reduction in flexural strength after only 12 wet/dry cycles. Comparing the flexural strengths it was noticed that the 3 days initially cured specimens of 0.4 water/cement ratio showed more drop in strength at a particular number of wet/dry cycles than the paste of 0.3 water/cement ratio. A lower initial strength and a more porous formation of structure for the 0.4 paste specimens probably caused this behaviour. From the results it was also noticed that for both the pastes the maximum drop in flexural strength was with the specimens in saturated solution and the minimum was in 4% solution at any number of wet/dry cycles up to 72 cycles.

The specimens of either water/cement ratio initially cured for 7 days when subjected to wet/dry cycles showed almost similar behaviour in flexural strength as that of the 3 days initially cured specimens. There was little gain of strength with these specimens followed by a gradual loss in 0%, 4% and 10% solutions and a steady decrease of the same in saturated solution when the wetting and drying cycles were applied. With 0.3 water/cement ratio paste specimens the minimum loss of flexural strength was noticed in the case of 0% solution after 72 cycles, but saturated solution seemed to lower the flexural strength in both the cases.

Specimens of both 0.4 and 0.3 water/cement ratios initially cured for 28 days when subjected to wet/dry cycles in sodium chloride solutions showed no loss or gain in flexural strength till 36 cycles, after that there was slow deterioration in the flexural strength. However the specimens in 0% and 4% solutions showed no loss of flexural strength even after 72 wet/dry cycles. It was also noticed that in saturated solution there was a significant loss in flexural strength of the specimens after 72 cycles. Comparing the results of specimens in saturated solution it was found that pastes of 0.4 water/cement ratio dropped 45%, 29% and 25% of their initial strength respectively for 3, 7 and 28 days of initial curing at the end of 72 wet/dry cycles. Specimens of 0.3 water/cement ratio dropped 26%, 17% and 10% of initial strengths under similar conditions. On the other hand the 4% solution seemed to lower the flexural strength least in most cases under wet/dry conditions. It was therefore concluded that the concentration of the solution had a positive role in the deterioration of pastes in terms of flexural strength. It was also concluded that the water/cement ratio had an important part in determining the effects of alternate wetting and drying on the long term behaviour of concrete in presence of sodium chloride solutions. Also, the greater tendency for deterioration in terms of flexural strength than the compressive strength of the pastes when subjected to wet/dry cycles indicated the probable formation of microcracks and a change in morphology of the specimens. The microcracks once formed could lower the flexural strength of the pastes more than the compressive strength in a similar manner as discussed in the previous chapter.

Fig. 5.7 shows the effect of recuring on the flexural strength of paste specimens of 0.4 water/cement ratio initially cured for 3 days and when subjected to 36 wet/dry cycles in 0%, 4% and saturated solutions of sodium chloride. At the beginning of the recuring the behaviour of the flexural strength changed and the specimens of all the solutions showed a significant gain of flexural strength. After 21 days of recuring the specimens of 0%, 4% and saturated solutions recovered from 4.1 $N/mm^2$, 4.25 $N/mm^2$ and 3.4 $N/mm^2$ respectively to 5.2 $N/mm^2$, 5.3 $N/mm^2$ and 4.2 $N/mm^2$. The value of flexural strength for normally cured specimens at this period was 5.7 $N/mm^2$. However comparing the recovery of the compressive strengths of similar specimens as in Fig. 5.3 it was noticed that the rate of recovery of flexural strength was lower. This confirmed the formation of microcracks inside the specimens which could not be filled up totally with the hydration products when the specimens were allowed to recure once again.

Fig. 5.8 shows the effect of wet/dry cycles on the flexural strength of mortar specimens of 1:2 cement/sand ratio and 0.4 water/cement ratio initially cured for 3 days in 0%, 4% and saturated solutions of sodium chloride. The recuring effect on the strength after 30 wet/dry cycles of the mortar specimens are also plotted in the same Fig. 5.8. The specimens in all the solutions showed a gain of strength for a considerable number of wet/dry cycles before suffering losses. Specimens in the saturated solution showed least gain of strength after 30 wet/dry cycles and after 54 cycles dropped maximum which was 21% below its initial 3 days strength and 52% below its normal value. But the specimens in 0% and 4% solutions showed more strength than the 3 days initial strength value after 54 wet/dry cycles although they were 35% and 32% below the value of normally cured specimens in 0% and 4% solutions respectively. Saturated solution seemed to cause more microcracks inside the specimens. Comparing these results with those of paste specimens of 0.4 water cement ratio as in Fig. 5.5 it was noticed that the rate of loss of flexural strength was less in case of mortar specimens. Also in saturated solution the paste specimens showed a drop in strength almost with the beginning of wet/dry cycles which was delayed in case of mortar specimens. The fine aggregate content appeared to play an important role in reducing the losses in flexural strength. The presence of aggregate particels slowed down the propagation of microcracks in mortars which showed better resistance than the paste specimens. It was therefore concluded that the presence of aggregates and their particular characteristics must play a major part in determining the effects of wetting and drying on the flexural strengths of concrete specimens in sodium chloride in both the short and long term.

Mortar specimens when allowed to cure normally for 27 days after 30 wetting and drying cycles in all the solutions gained flexural strength significantly and the values were 86%, 90% and 74% of the normal strength level for the specimens in 0%, 4% and saturated solutions respectively. The rate of gain was a minimum for the specimens in saturated solution which was also observed for the paste specimens under similar conditions. It was therefore concluded that the concentration of sodium chloride to which the specimen size subjected is a very important factor in the determination of the effects of wetting and drying cycles on the strength characteristics of concrete.

## 5.3 Conclusions

(1) Wetting and drying cycles in sodium chloride solutions of any concentration caused losses of compressive as well as flexural strengths of pastes and mortars with up to 7 days of initial curing.

(2) The compressive strengths of pastes and mortars were less affected compared with the flexural strengths

when the specimens were subjected to wetting and drying cycles in the presence of sodium chloride solutions of different concentrations.

(3) A saturated solution of sodium chloride was found to cause the most deterioration in terms of compressive as well as flexural strengths of pastes and mortars under wet/dry cycles, whereas a 4% solution of sodium chloride sometimes behaved even better than water.

(4) The behaviour of the specimens in 4% solution indicated changes in the microstructure even when the specimens were subjected to wet/dry cycles.

(5) Young paste and mortar specimens such as 3 day initially cured specimens suffered maximum losses of strengths due to wet/dry cycles in presence of sodium chloride solutions.

(6) When the pastes and mortars were allowed to recure after wet/dry cycles in solutions they could recover their compressive strengths in a much better way than the flexural strengths.

(7) Losses of strength were less in the case of mortars at a particular number of wet/dry cycles and also the recuring effect helped the mortars to regain strengths more than the pastes indicating the important role of aggregates in the mix.

(8) The comparison of compressive and flexural strengths of pastes and mortars suggested the formation of microcracks inside the specimens causing rapid deterioration in terms of flexural strength. The higher values of

flexural strengths obtained in case of mortars after wetting and drying cycles in solutions suggested the temporary blocking of microcrack propagation by the aggregate particles present.

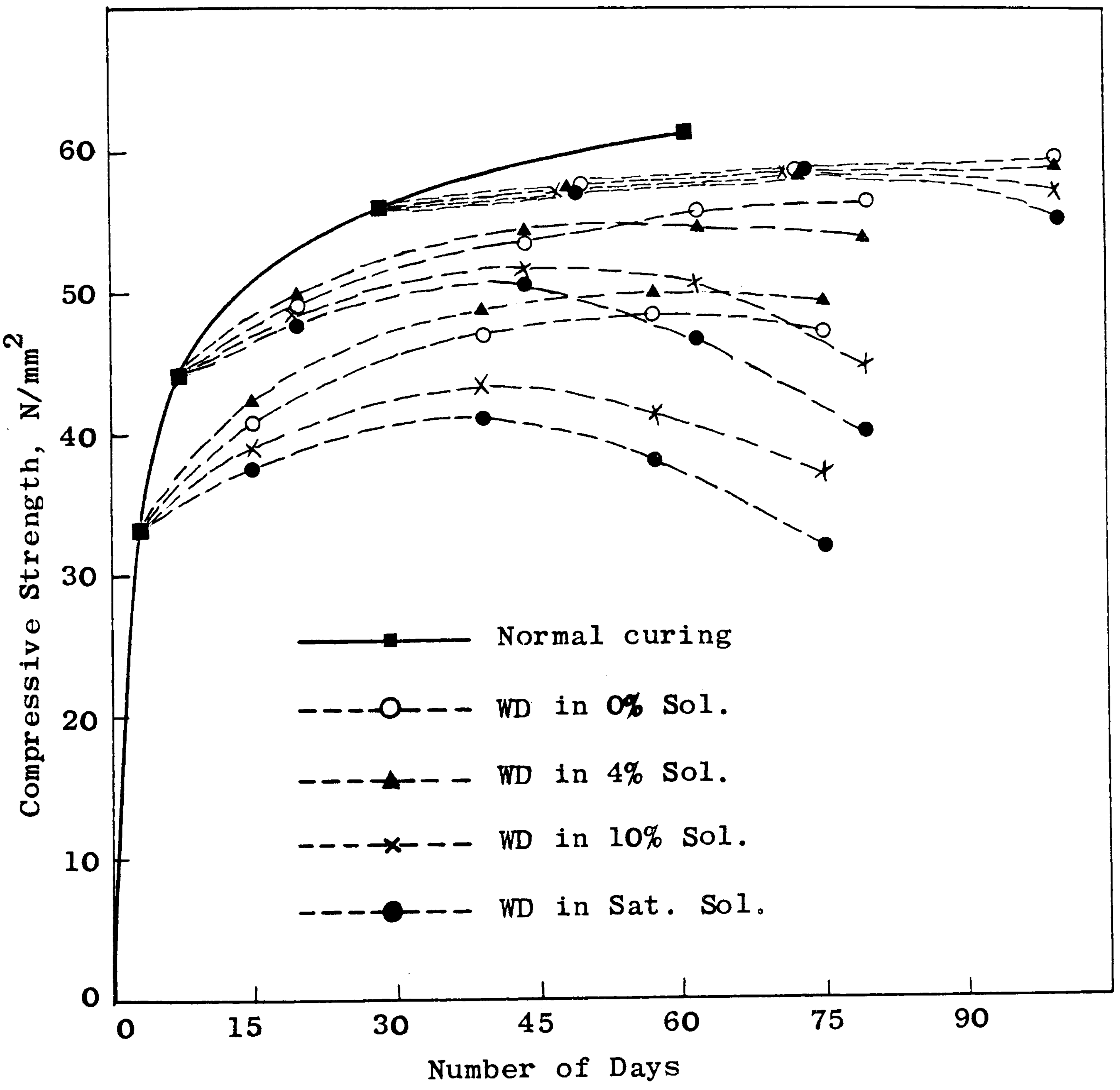

Fig. 5.1 Effect of wet/dry on compressive strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

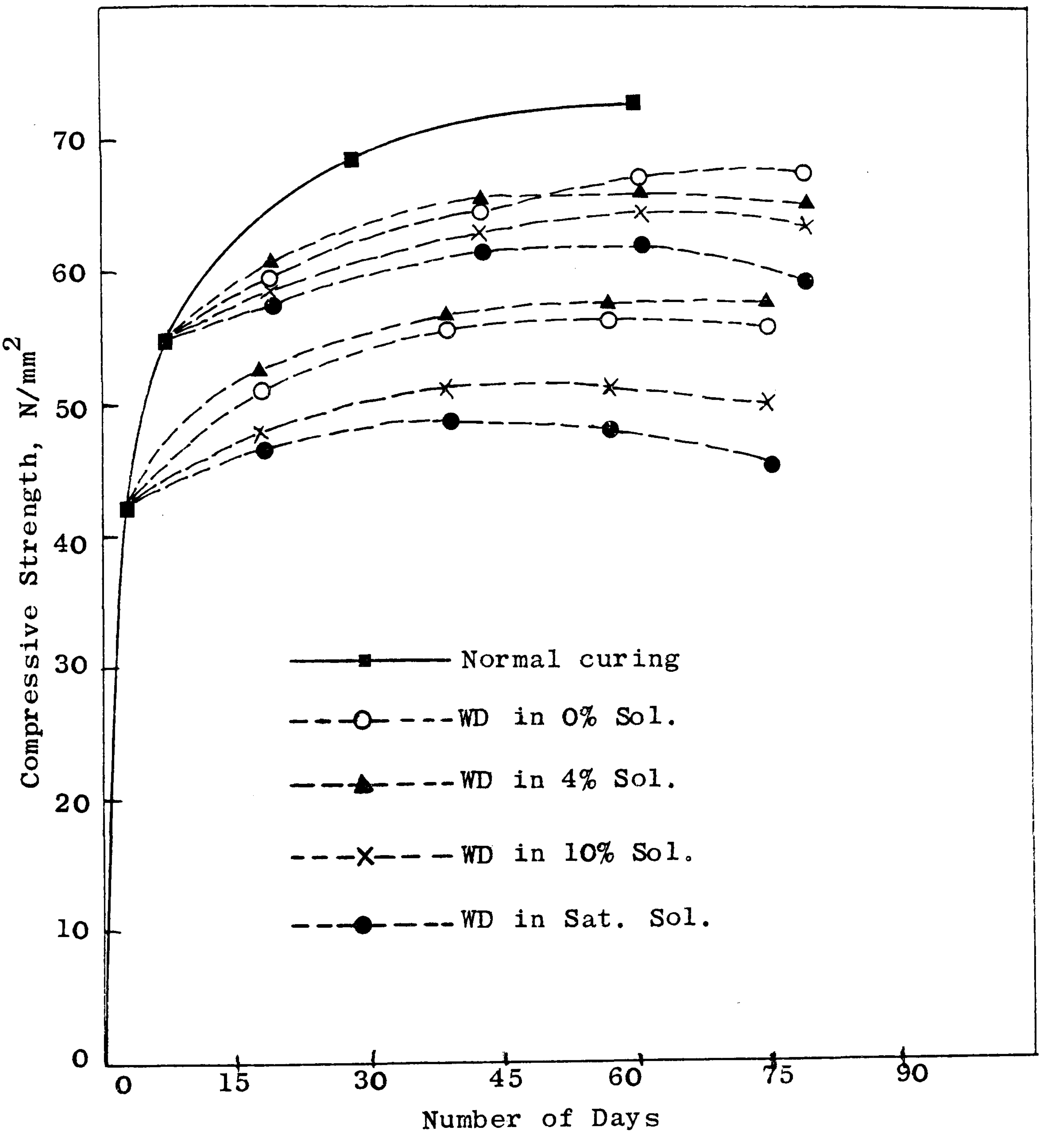

Fig. 5.2 Effect of wet/dry cycles on compressive strength of cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

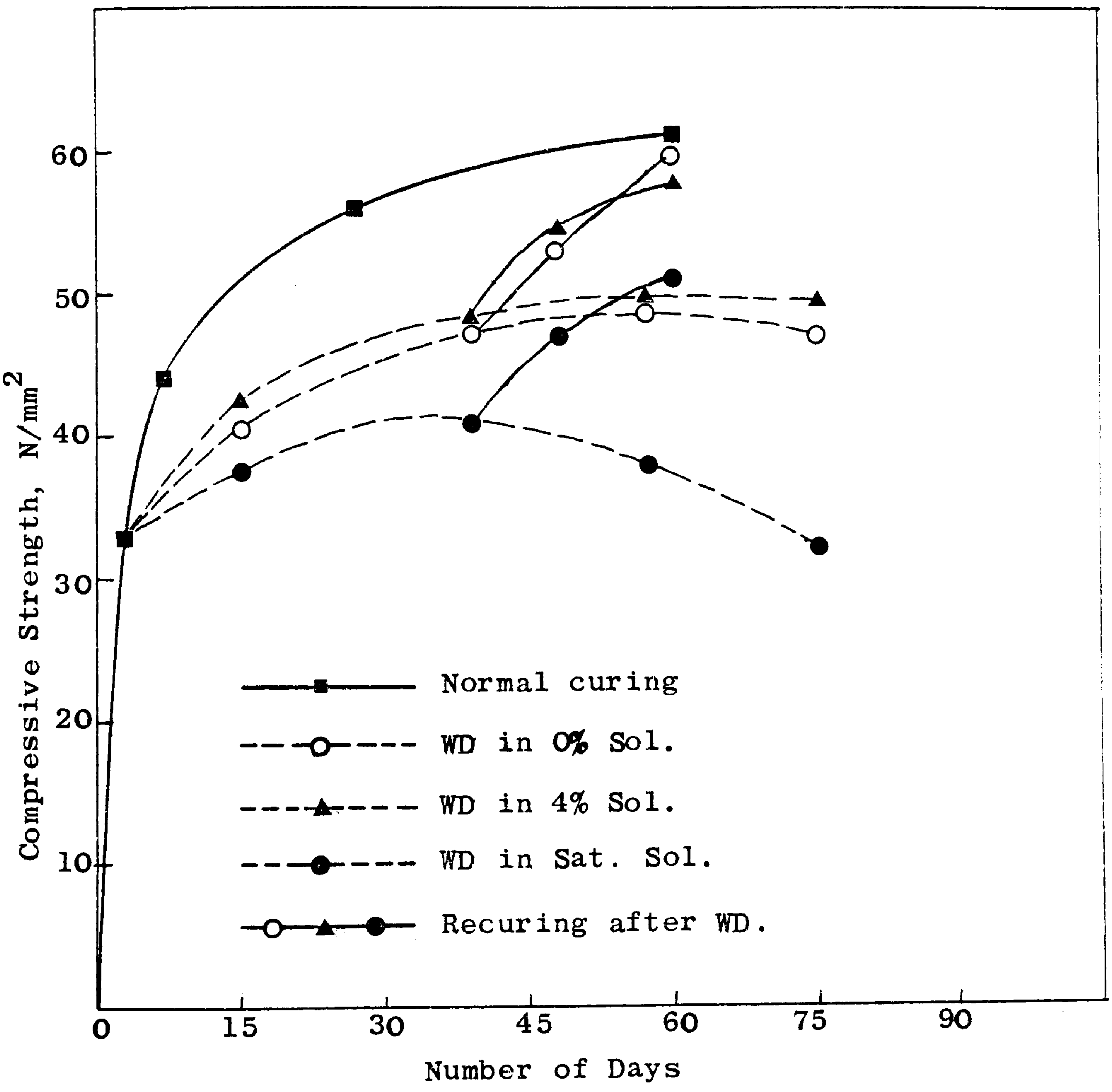

Fig. 5.3 Effect of wet/dry cycles and subsequent curing on compressive strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

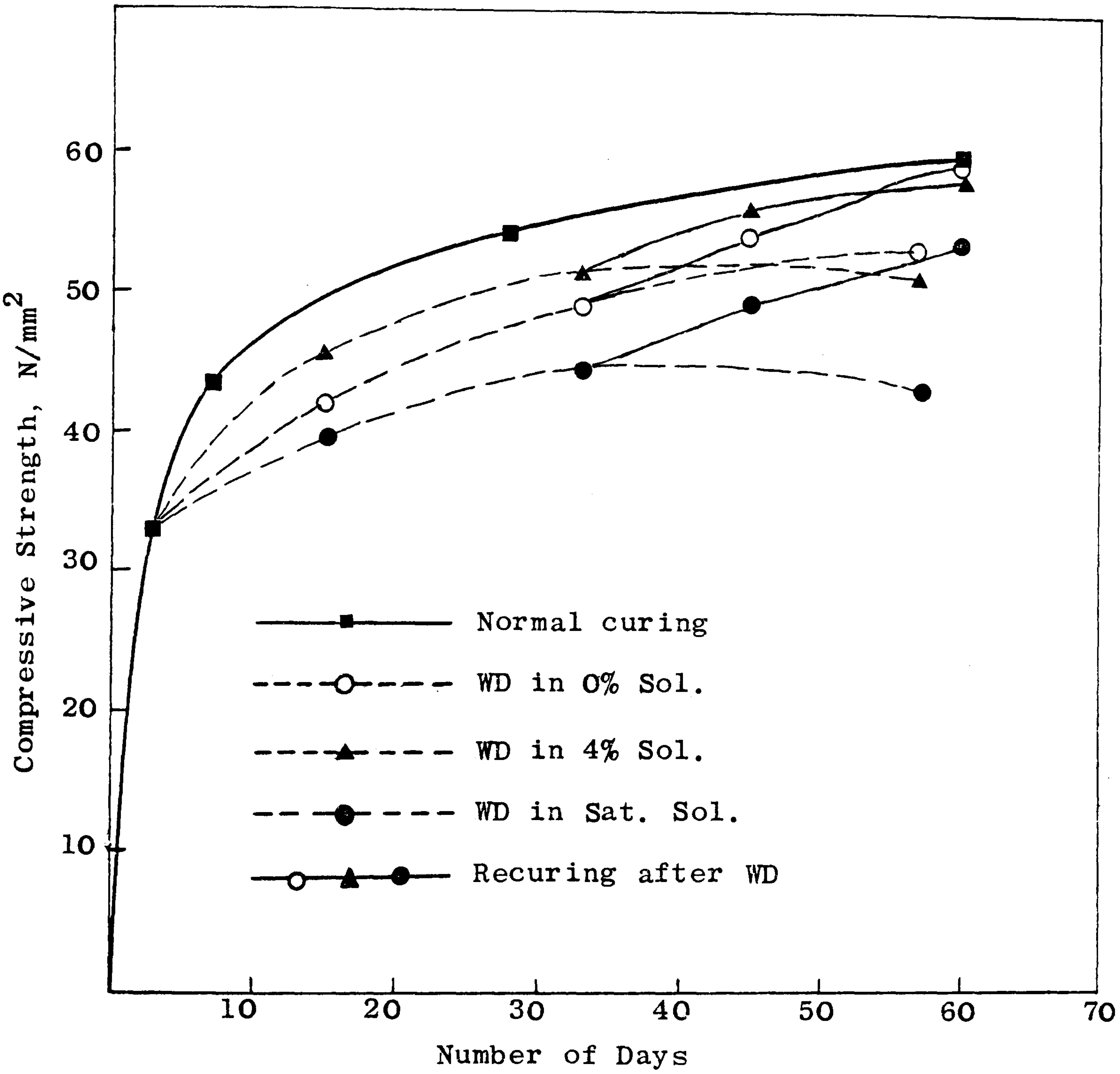

Fig. 5.4 Effect of wet/dry cycles and subsequent curing on compressive strength of mortar (cement/sand = 1:2, W/C = 0.4) in sodium chloride solutions of different concentrations

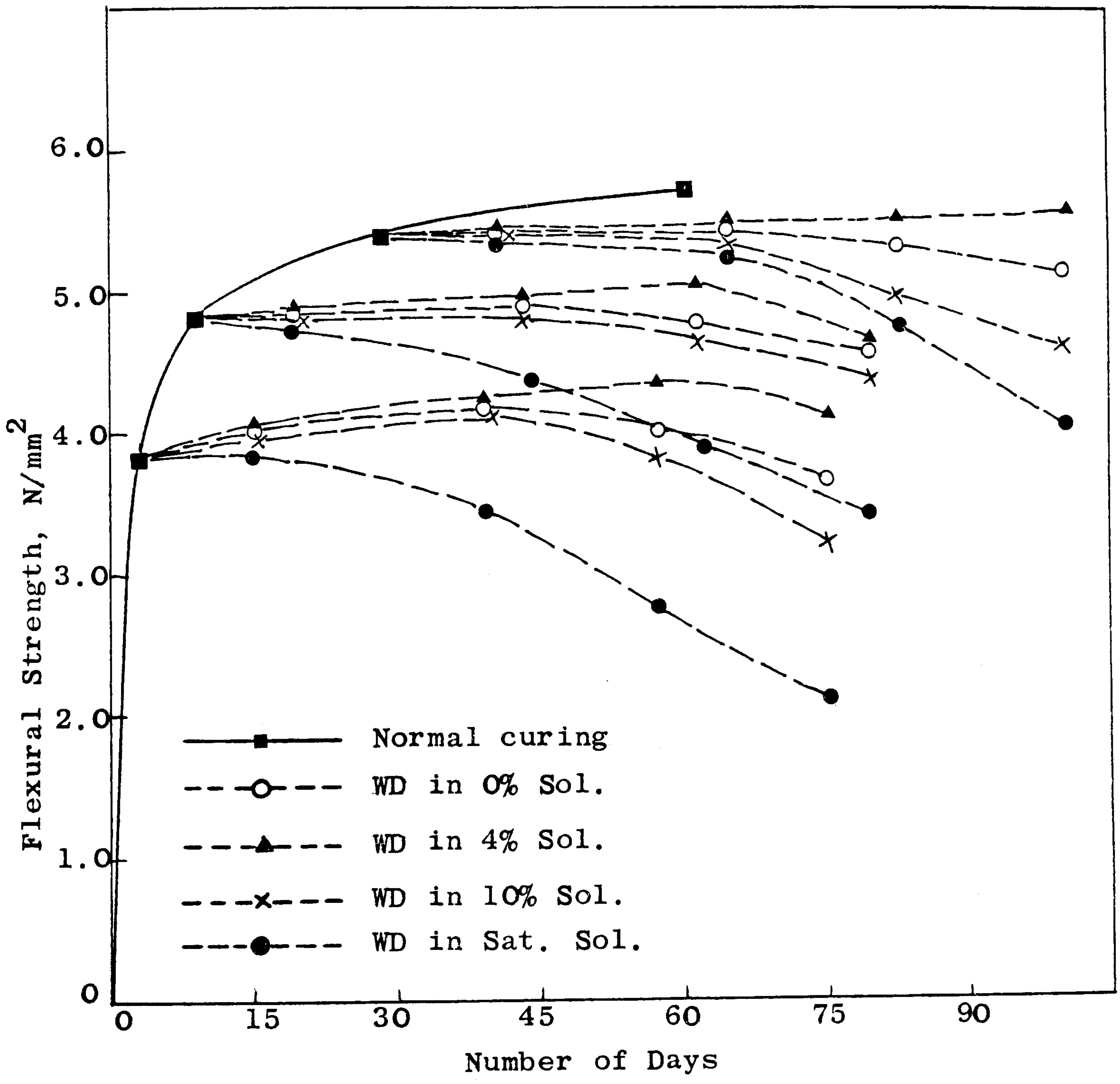

Fig. 5.5 Effect of wet/dry cycles on flexural strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

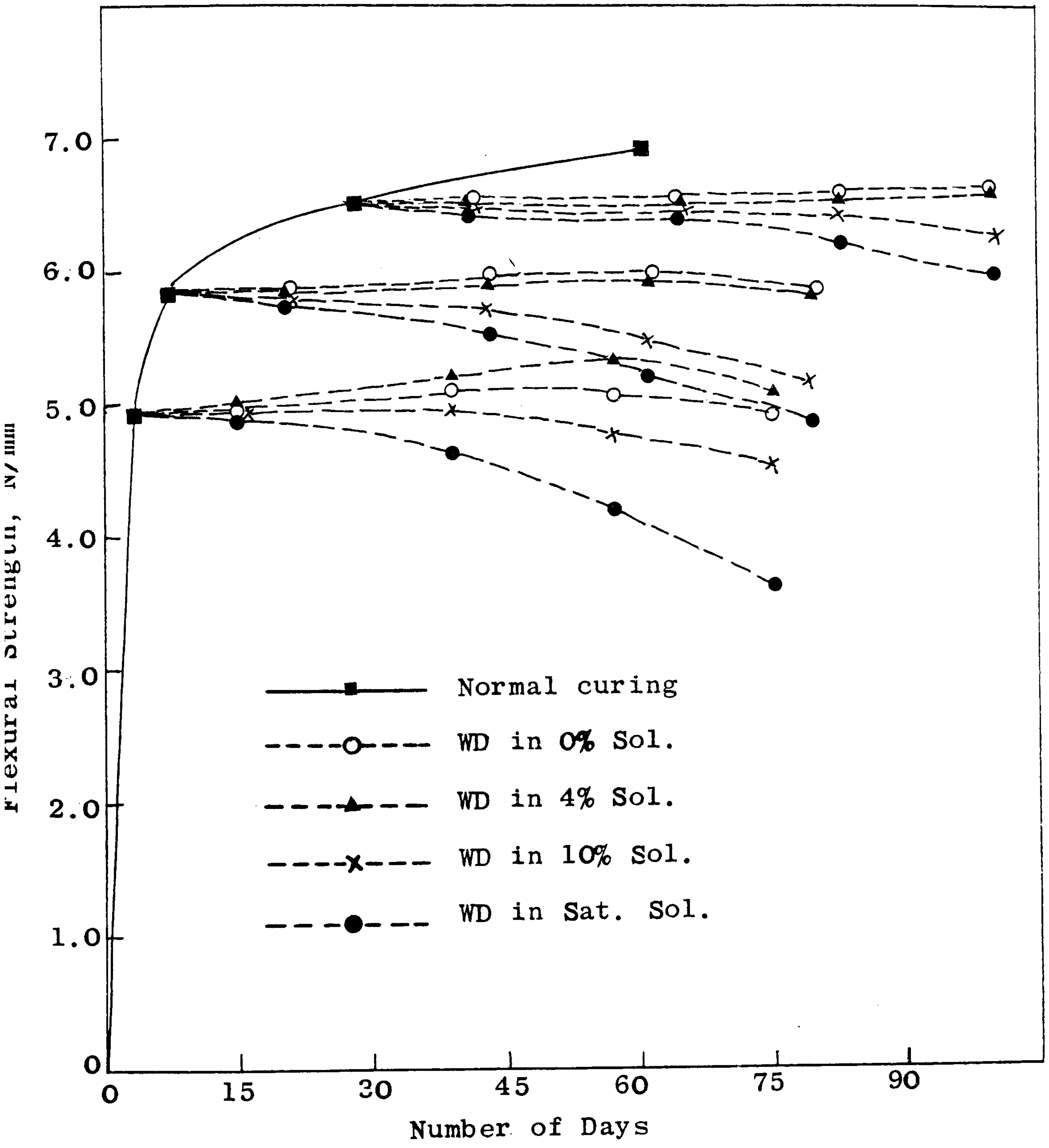

Fig. 5.6 Effect of wet/dry cycles on flexural strength of cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

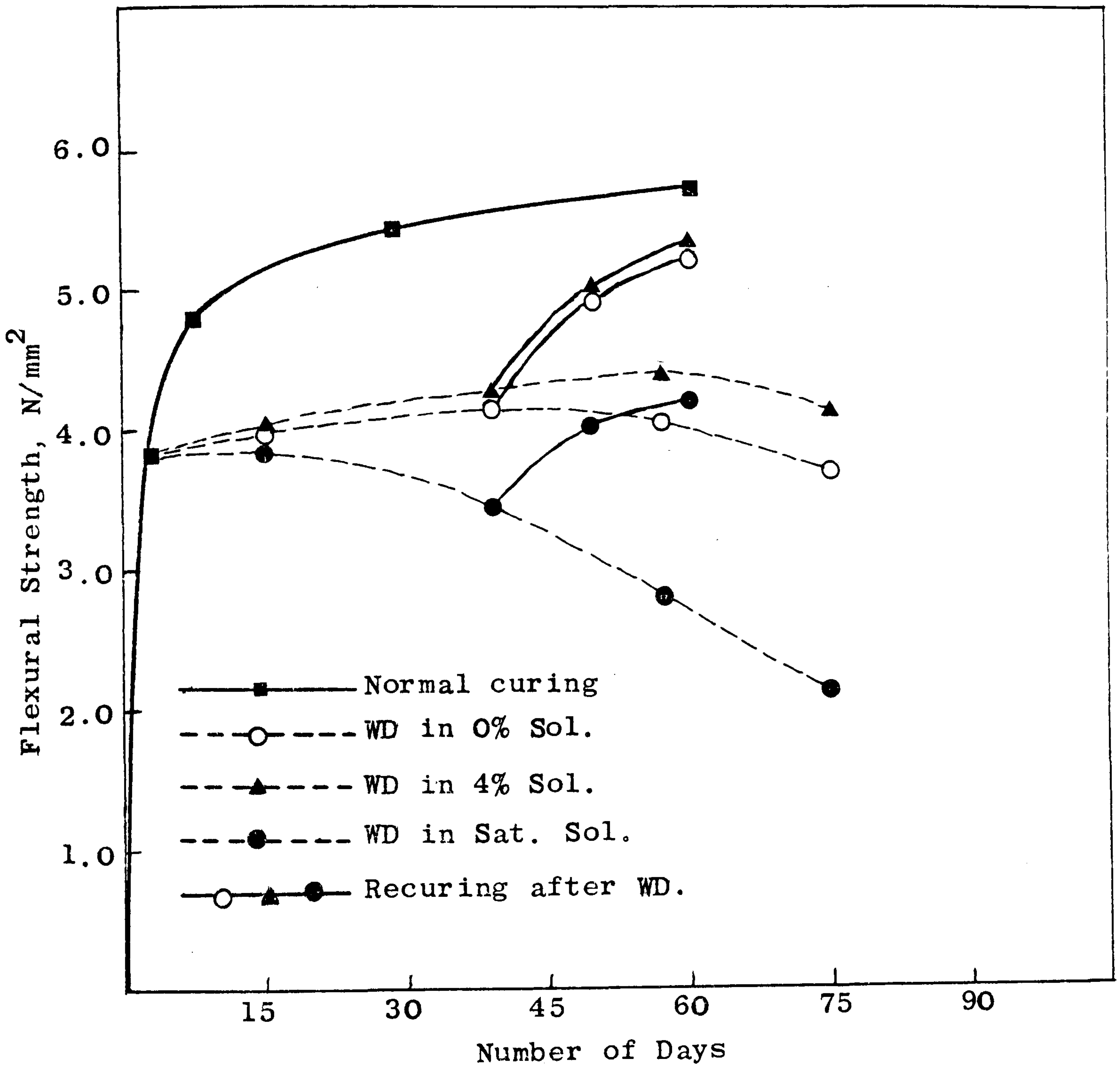

Fig. 5.7 Effect of wet/dry cycles and subsequent curing on flexural strength of cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

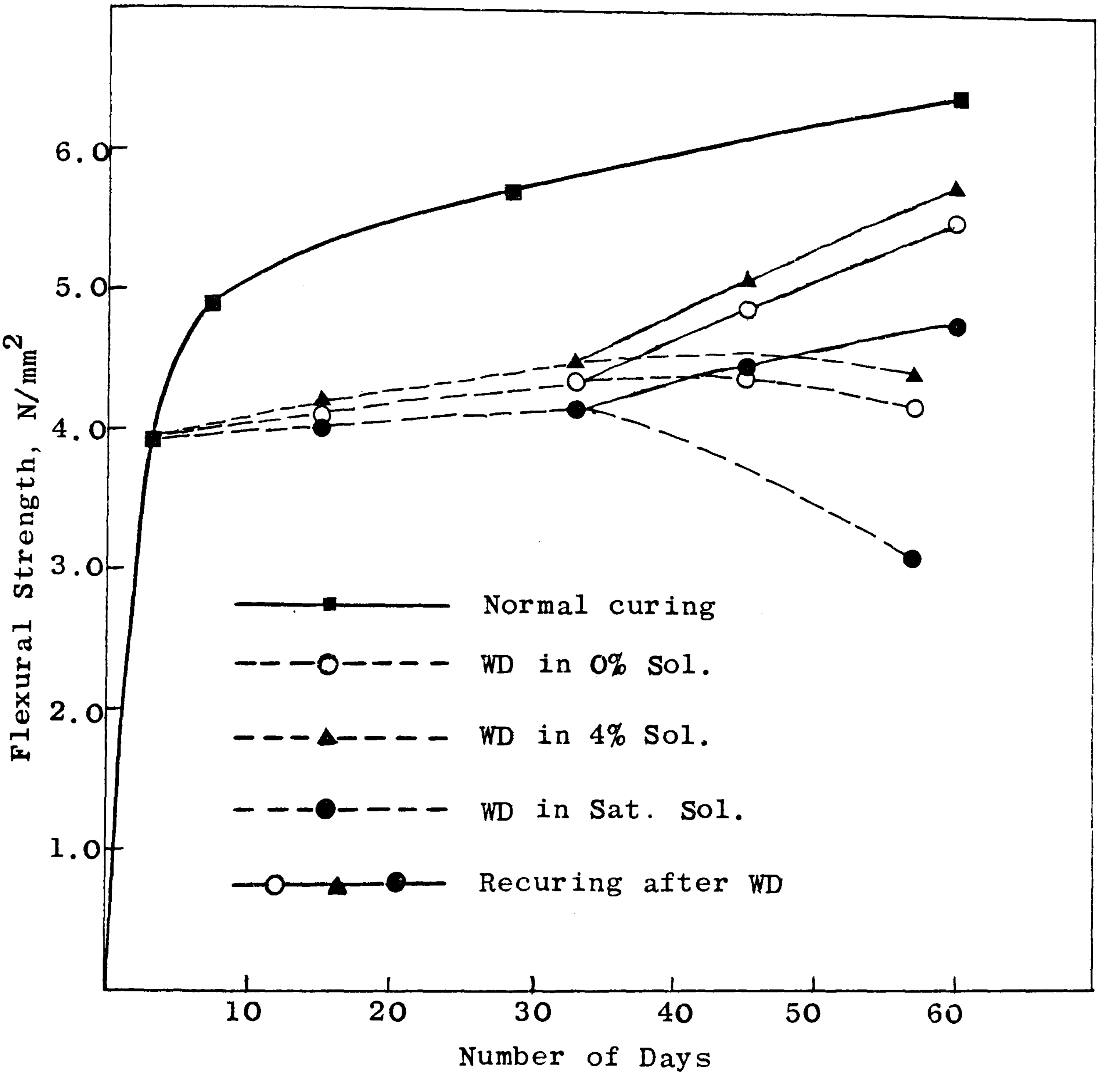

Fig. 5.8 Effect of wet/dry cycles and subsequent curing on flexural strength of mortar specimens (cement/sand = 1:2, W/C = 0.4) in sodium chloride solutions of different concentrations

# CHAPTER 6

# THE EFFECTS OF ALTERNATE FREEZE/THAW AND WET/DRY CYCLES ON THE MICROSTRUCTURES OF CEMENT PASTE IN PRESENCE OF SODIUM CHLORIDE

## 6.1 Introduction

The morphology of the hardened cement paste change with the period of hydration and also depend on the water/cement ratio, the temperature and the condition of curing. Scanning electron microscopy has provided the means of examining the morphology of cement pastes and has produced innumerable micrographs some of which are contradictory and confusing. Speculations on the origin of strength and other properties are made on the basis of these observations. Often it is questioned whether the observations are valid because of the possibility of concentrating on an interesting morphological feature that may not represent the whole system. It has been reported by many research workers that paste products consisting of well crystallised tobermorite plates are responsible for strength and that the fibres and foil like structures are poorly integrated.

The change in the morphological features of cement paste in the presence of chlorides, calcium chloride in particular, has been described by many research workers.(33,34,39,40,81-87) But most of them examined and discussed the hydrated $C_3S$ in presence of calcium chlorides and concluded that $CaCl_2$ similarly influences the microstructure in a portland cement paste. There has, however, been a variance in the actual description of the morphology.

Freeze/thaw and wet/dry cycles in the presence of sodium chloride are found to have significant influences on the mechanical properties of cement pastes and mortars as discussed in the previous two chapters. Since no work has been reported about the effect of sodium chloride on the cement pastes in terms of sequential behaviour with respect to microstructural features, it was decided that an investigation on the effects of freeze/thaw and wet/dry cycles in presence of sodium chloride on cement pastes should be carried out to examine the mechanism of chloride attack by following the progressive development of the microstructure and hydration products. In this chapter the development of hydration products from the early stages of hydration of cement paste until near maturity is followed using scanning electron microscopy. The effects of subjecting the pastes to alternate cycles of freeze/thaw and wet/dry in presence of sodium chloride solutions of different concentrations are also investigated with the aid of this technique. The effect of air entrainment in the cement pastes under similar conditions were also examined.

## 6.2 Normally Cured Cement Pastes

Figs. 6.1 to 6.6 illustrate the development of hydration products from one day to 28 days of cement paste of different water/cement ratio cured in room temperature.

The micrographs show that the hydration products around cement grains intermesh as hydration continues. Fig. 6.1 shows the columnar hydration products and small needles in between, that of C-S-H which at the later stages of hydration seemed to appear as fibres of C-S-H covering semicrystalline plates (Fig. 6.2 and Fig. 6.3). Further hydration revealed the formation of plates of $Ca(OH)_2$ (Figs. 6.4 to 6.6) among which the paste with water/cement ratio of 0.3 was found to show more dense formation of hexagonal crystals of $Ca(OH)_2$ than that of 0.4 water/cement ratio. The fracture surface in Fig. 6.1 shows that the fracture path was intergranular with the columnar zones growing around the grains. The fracture surfaces in Figs. 6.2 to 6.6 show the cleavage through plates of $Ca(OH)_2$. Williamson(77) also suggested the cleavage through what he called as primary portlandite, formed between grains and intergrew with the columnar zones and through columnar zones themselves. Walsh et al.(139) suggested that fibres bond with one another to hold the C-S-H spherulites together and that the volume between these spherulites consisted of $Ca(OH)_2$ hexagonal plates. The cleavage through the cement paste occurred mostly across the weakly bonded basal planes of $Ca(OH)_2$ and secondly through the C-S-H/$Ca(OH)_2$ interface, the strongest bonding occurring between C-S-H spherulites.

## 6.3 Effect of Freezing and Thawing Cycles in Solutions

Cycles of alternate freezing and thawing in 0%

solution i.e. in water, applied to paste specimens which had been normally cured for 3 and 7 days, caused considerable modification of the paste microstructure. The number of cycles was also important in this respect. The most notable feature of the fracture surfaces of these specimens when observed in scanning electron microscope was the presence of numerous large hexagonal crystals of portlandite which were surrounded by voids (Figs. 6.7 and 6.11). These crystals were found to be of $Ca(OH)_2$ of high purity when examined by energy dispersive X-ray spectrometry. The fibre shaped products in Figs. 6.7 and 6.8 were identified as C-S-H gel. The X-ray spectrum for the needles in Figs. 6.9 and 6.10 was consistent and suggested some form of calcium sulphoaluminate hydrates (possibly ettringite) mixed with C-S-H. Such a mixed structure gave a more general picture of the gel phase of cement pastes of young age subjected to freezing and thawing cycles. In the case of pastes which had been cured initially for 7 days at room temperature the action of freezing and thawing cycles produced changes in microstructure only after considerably greater number of cycles. Scanning electron micrographs of 7 day initially cured specimens of 0.4 water/cement ratio revealed formation of numerous hexagonal crystals on a scale comparable with that seen before only after 144 freezing and thawing cycles as in Fig. 6.11.

In the case of specimens which had been allowed to cure normally once again at room temperature after being subjected to freezing and thawing cycles when 3 days old, the fracture surfaces revealed changes in microstructural features. A scanning electron micrograph of paste of 0.4 water/cement ratio recured for 12 days after being subjected to 36 freeze/thaw cycles illustrated the changes in the microstructure as in Fig. 6.12 and it is apparent that the voids which had originally surrounded the portlandite have been largely filled by additional hydration products.

The paste specimens when subjected to freezing and thawing cycles in presence of sodium chloride solutions revealed microstructure somewhat different from those mentioned above. Fig. 6.13 shows the typical scanning electron micrograph of the fracture surface of cement paste initially cured for 3 days then subjected to 36 freezing and thawing cycles in presence of 4% solution of sodium chloride. Comparing the micrograph with those in Figs. 6.7 and 6.8 it seems that the morphology of the gel was modified to the 'lace like' structure. The outer aciculae are thought to have grown further together due to the presence of chloride ions to form such microstructure which in turn contributed to the increased strength of the paste due to the necessity of fracture through more C-S-H gels. But further increase in freeze/thaw cycles in 4% solution of sodium chloride revealed foil like structures together with long needles oriented at random (Fig. 6.14). The X-ray spectrum of the needles suggested the formation of calcium sulphoaluminate hydrates together with significant traces of chloride ions which was present in the possible formation of calcium chloroaluminate hydrates or a complex salt containing calcium, sulphur, aluminium and chlorine altogether.

Fig. 6.15 illustrates the micrograph of paste initially cured for 7 days and when subjected to 54 freeze/thaw cycles in 4% solution of sodium chloride. The lace like structure was absent, instead dense formation of C-S-H gel together with needles were present. It is thought that 7 days hydration restricted the lace like formation which was observed in case of 3 days initially cured paste specimens when subjected to freezing and thawing cycles in 4% solution of sodium chloride. In this case the aciculae grew further and probably had been engulfed by the calcium hydroxide growing within them due to more hydration. The analysis of the needles suggested the formation of calcium chloroaluminates together with calcium sulphoaluminates. Fig. 6.16 shows the micrograph of a paste specimen recured for 14 days after 54 freeze/thaw cycles in 4% solution of sodium chloride. The micrograph revealed formation of dense C-S-H together with poor crystallisation of portlandite possibly having less strength than the normally cured sample of similar age. The long needle in the middle was found to consist of calcium, sulphur, aluminium and chlorine when analysed.

The paste specimens when subjected to freeze/thaw cycles in saturated solution of sodium chloride showed considerable modification of the microstructures than those in 4% solution. The most significant feature of the fracture surface of such samples was the presence of numerous needle like crystals of calcium sulphoaluminates and calcium chloroaluminates which were not found in previous cases in such quantities.(Figs. 6.17 to 6.19). Figs. 6.17 and 6.18 represent similar specimens in saturated solution difference being with the number of freeze/ thaw cycles. The long needles were frequently observed in the scanning microscope and those were found to form with more number of freeze/thaw cycles in saturated solution as in Fig. 6.18. It was apparent from the X-ray analysis that the needle like crystals could be that of ettringite. Every crystal forming flower shape product seemed to be formed of long crystals having definite orientation. The outside surface of these crystals appeared as stepped in the direction perpendicular to the elongation axis. Chlorine was also detected in these crystals and the amount detected confirmed the possible formation of calcium chloroaluminates. But Midgley and Pettifer(140) observed such morphology what they called as long 'lath-like' crystals in the case of hydrated super sulphated cements. The saturated solution of sodium chloride together with the freeze/thaw cycles seemed to accelerate the formation of ettringites and calcium chloroaluminates in large quantities.

In case of paste specimens initially cured for 7 days when subjected to freeze/thaw cycles in saturated solution illustrated similar microstructural features together with plates of portlandite (Fig. 6.19). The voids between the portlandite crystals possibly allowed the ettringite and calcium chloroaluminate needles to grow longer when the specimens were in contact with saturated solution of sodium chloride for a larger number of freeze/thaw cycles. Comparing all these micrographs with those of specimens subjected to freeze/thaw cycles in water it was noticed that the morphology of cement paste changed considerably and needles of ettringites and calcium chloroaluminates formed due to presence of sodium chloride specially with higher concentration. Their formation in larger quantities and further growth possibly caused deterioration in the material. It was, therefore, concluded that presence of sodium chloride in large quantities in cement paste is very much deleterious especially when concrete is subjected to freeze/thaw cycles.

## 6.4 Air Entrainment and Freeze/Thaw Cycles in Solutions

Fig. 6.20 shows a general view of an air entrained cement paste normally cured for 3 days. From the micrograph the air bubbles are found to be of varying diameters. Although some of them were larger in sizes, most of the air bubbles appeared to be approximately equal in diameter and were spaced approximately equally. It was, however, noticed that the effect of the air entraining agent was not only confined to produce scattered air bubbles but also resulted to produce uniformly distributed voids. Fig. 6.21 shows a typical air bubble from those of Fig.

6.20 at a higher magnification. The hydration products appear to be of mixed nature similar to those observed in plain paste that was normally cured for 3 days.

When the 3 day normally cured specimen was subjected to 144 cycles of freezing and thawing in 0% solution the micrograph of electron microscope illustrated different microstructural features inside the voids (Fig. 6.22). The air bubble seemed to be partially filled with hydration products which was possible due to the expulsion of solution into them during the freezing cycles. X-ray analysis confirmed the formation of C-S-H gels. Besides the formation of crystalline particles with hexagonal symmetry and fibrous particles were also detected inside the bubbles. That this formation was a result of freeze/thaw application can be seen by comparing the Figs. 6.20 and 6.21 which show the microstructural features in an air bubble of a 3 day normally cured specimen with Fig. 6.22 which shows the microstructural features in an air bubble of a sample normally cured for 3 days then subjected to 144 cycles of freeze/thaw in 0% solution.

The micrograph of a similar specimen (Fig. 6.23) when subjected to freeze/thaw cycles in 4% solution of sodium chloride revealed different features from that of Fig.6.22. The air bubble was found to be partially filled with foil like structures together with long needles. Analysis of these needles showed the presence of sulphur, chlorine, aluminium and calcium in them which confirmed the formation of ettringites or calcium chloroaluminates or complex salts. The changed microstructure occurred due to the presence of 4% sodium chloride in solution and due to freezing cycles. Chlorine was also detected in the fibrous structures. Comparing the micrographs of paste specimens with and without air entrainment and with or without sodium chloride in solutions it was noticed that as the bubbles allowed the solutions to be expelled into them during freezing, the air entrained paste specimens could resist significantly large number of freeze thaw cycles compared with that of without it as discussed in Chapter 4. It is also thought that this finding may provide supporting evidence to the theory of Litvan(114-116, 126) in which it is suggested that expulsion of solution from the capillaries during freezing takes place and that the role of air bubbles is to receive the expelled solution without causing disruption in the material. The author believes that calcium hydroxide together with sodium chloride that was in solution within the capillaries has changed the morphology inside the air bubble being expelled in it during freezing cycles.

## 6.5 Effect of Wetting and Drying in Solutions

When the paste specimens were subjected to alternate wetting and drying cycles after an initial curing period the micrographs revealed almost similar microstructural features as discussed earlier. Paste specimens of one day initial curing when subjected to 72 wet/dry cycles in 0% solution illustrated hexagonal portlandite crystals surrounded by spongy looking gels (Fig. 6.24). These particles had irregular edges and had planes of cleavage through them. In presence of 4% solution of sodium chloride the paste specimens when subjected to wet/dry cycles revealed identical crystals of irregular edges together with foil like structures which was analysed to be of C-S-H (Fig. 6.25). Presence of chloride accelerated the hydration and changed the morphology, thereby showing better mechanical characteristics as was observed in the previous chapter. When the specimens were subjected to wetting and drying cycles in saturated solution numerous long needles were revealed (Fig. 6.26). Analysis confirmed those to be of ettringites and calcium chloroaluminates. Comparing the micrographs of Figs. 6.26 and 6.18 and others it was noticed that long needle like structures of ettringites and calcium chloroaluminates or both together were very frequent in the pastes in contact with saturated solution of sodium chloride, irrespective of conditions such as freeze/thaw or wet/dry cycles. They grew longer and more in number in the paste matrix being in contact with sodium chloride solutions for longer periods which might initiate microcracks thereby causing disruption of the material.

## 6.6 Conclusions

(1) Examination by scanning electron microscope and X-ray spectrometry revealed that freezing and thawing cycles with or without the presence of sodium chloride in solutions changed the morphology of the fracture surface

of hardened cement paste of young age.

(2) Normal curing produced a dense interlocked network of hydration products, gel and portlandite, whereas freeze/thaw cycles without sodium chloride gave rise to a fracture surface composed largely of hexagonal crystals of portlandite with voids between them.

(3) The presence of 4% solution of sodium chloride produced 'lace like' structure in the paste when subjected to freeze/thaw cycles, but greater number of cycles produced foils and long needles of ettringites and calcium chloroaluminates.

(4) In the presence of saturated solution of sodium chloride the paste specimens when subjected to freeze/thaw cycles numerous needles of ettringites and calcium chloroaluminates were formed which increased in numbers and grew longer with time.

(5) The formation of hexagonal lime crystals provided planes of weaknesses in the paste microstructure when subjected to freeze/thaw cycles without sodium chloride solutions and facilitated crack propagation. In case of solutions of sodium chloride the growth of numerous long needles caused stresses and expanded resulting microcracks inside the specimen.

(6) Saturated solution was found to expedite largely the formation of ettringite and calcium chloroaluminate needles which in turn grew longer and initiated the formation of microcracks.

(7) During the freezing cycles the tiny air bubbles

provided escape reservoirs for the movement of the solution that filled the smaller capillaries; thus they resisted greater number of freeze/thaw cycles than plain paste specimens with or without sodium chloride.

(8) The air bubbles when partially or completely filled with hydration products due to crystallisation of the expelled solution in them during freezing behaved similar to those without entrainment of air and suffered deterioration sharply being unable to accommodate the expelled solutions further.

(9) Wetting and drying cycles in solutions of sodium chloride was found to be less severe than freeze/thaw cycles but scanning electron micrographs illustrated similar micrographs of the fracture surfaces. Ettringite and calcium chloroaluminate crystals in needle shapes were more present in the paste specimens in saturated solution than those in 4% solution of sodium chloride during the wetting and drying cycles.

* Note:

Due to instrumental failure it was not possible to produce a set of photographs of all the specimens at the same magnification. All specimens were however observed at magnifications up to 5000.

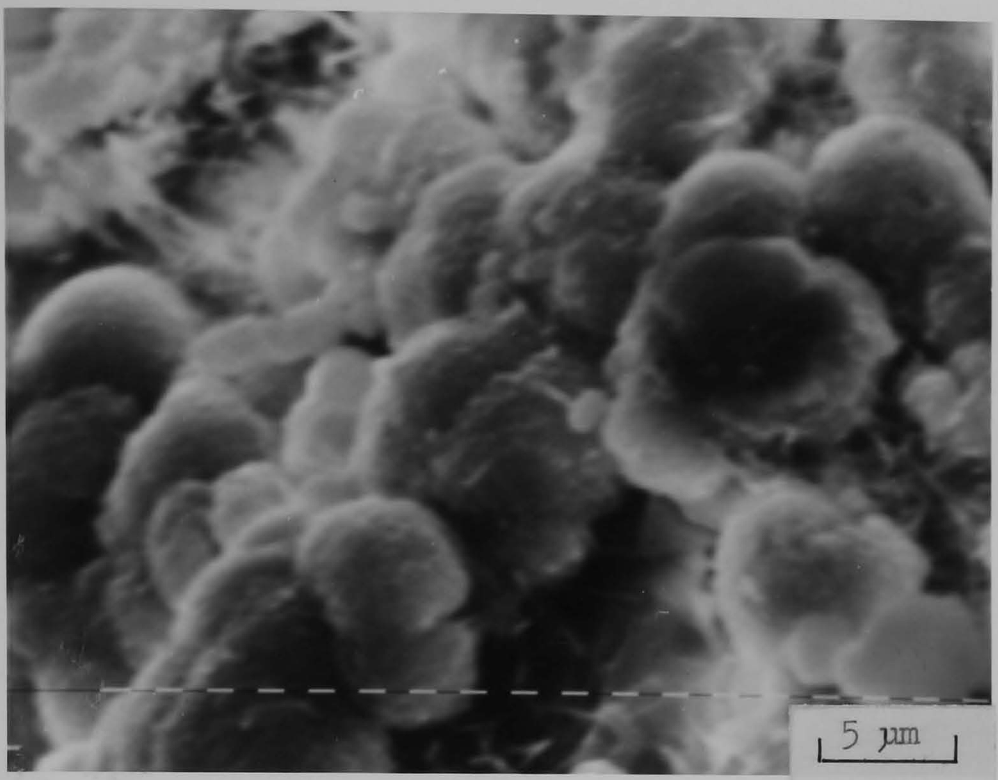

Fig. 6.1 SEM micrograph of a specimen of cement paste (W/C = 0.4) cured normally for 1 day. (Mag. 2500)

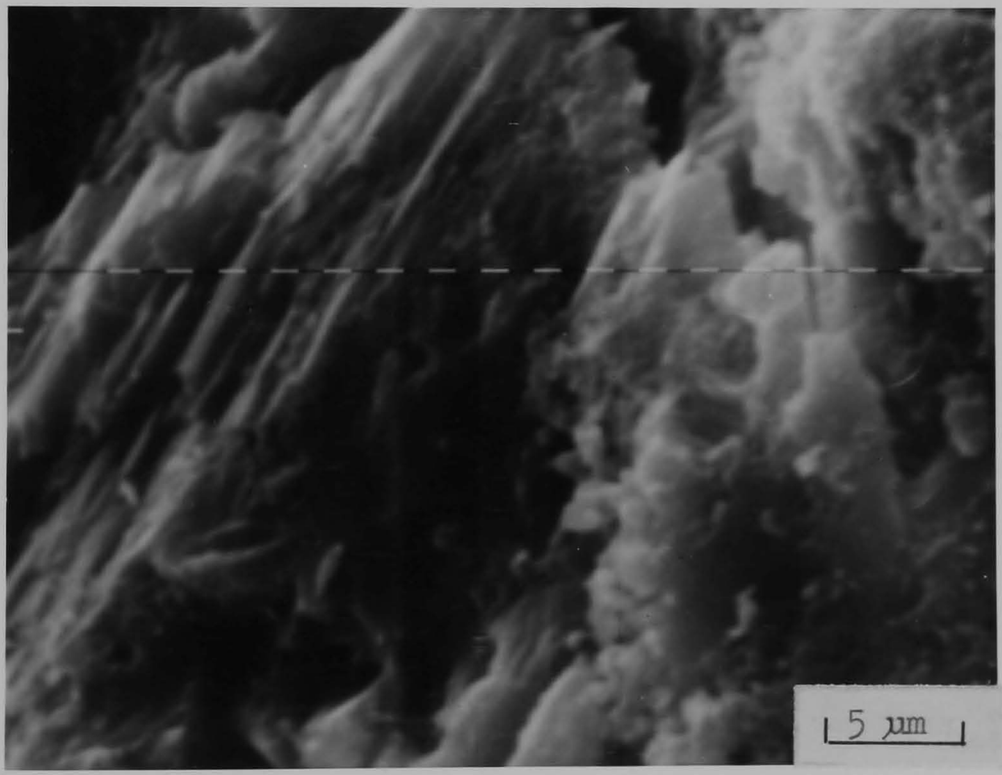

Fig. 6.2 SEM micrograph of a specimen of cement paste (W/C = 0.4) cured normally for 3 days. (Mag. 2500)

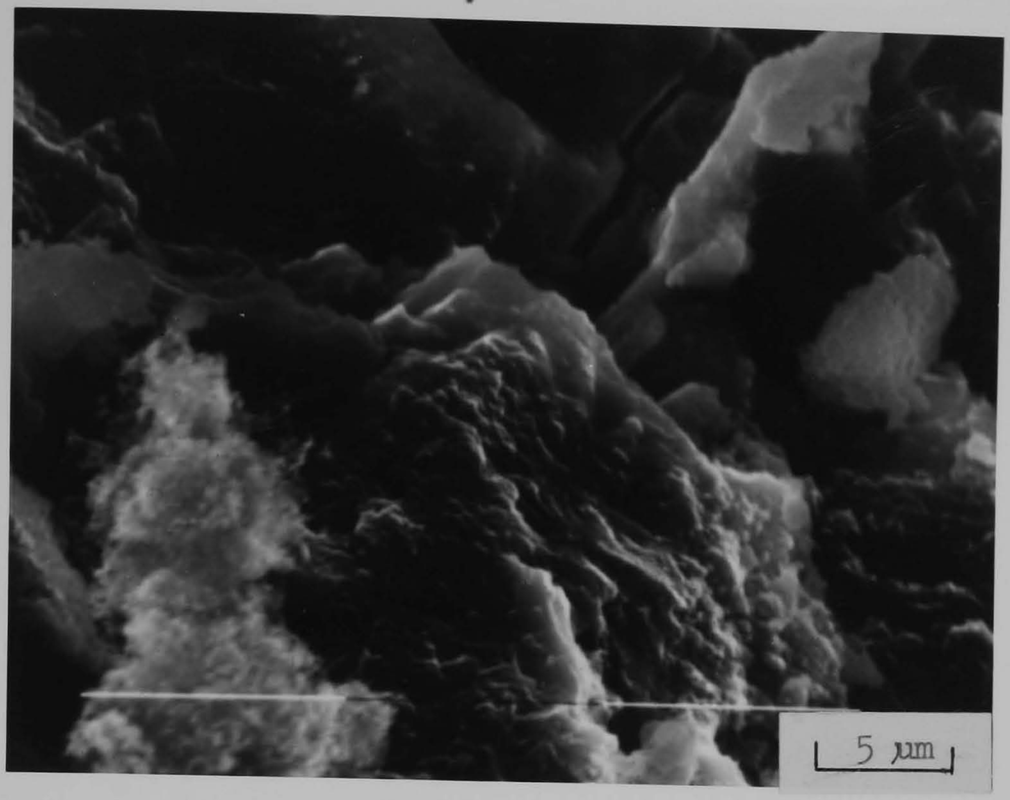

Fig. 6.3 SEM micrograph of a specimen of cement paste (W/C = 0.3) cured normally for 3 days. (Mag. 2500)

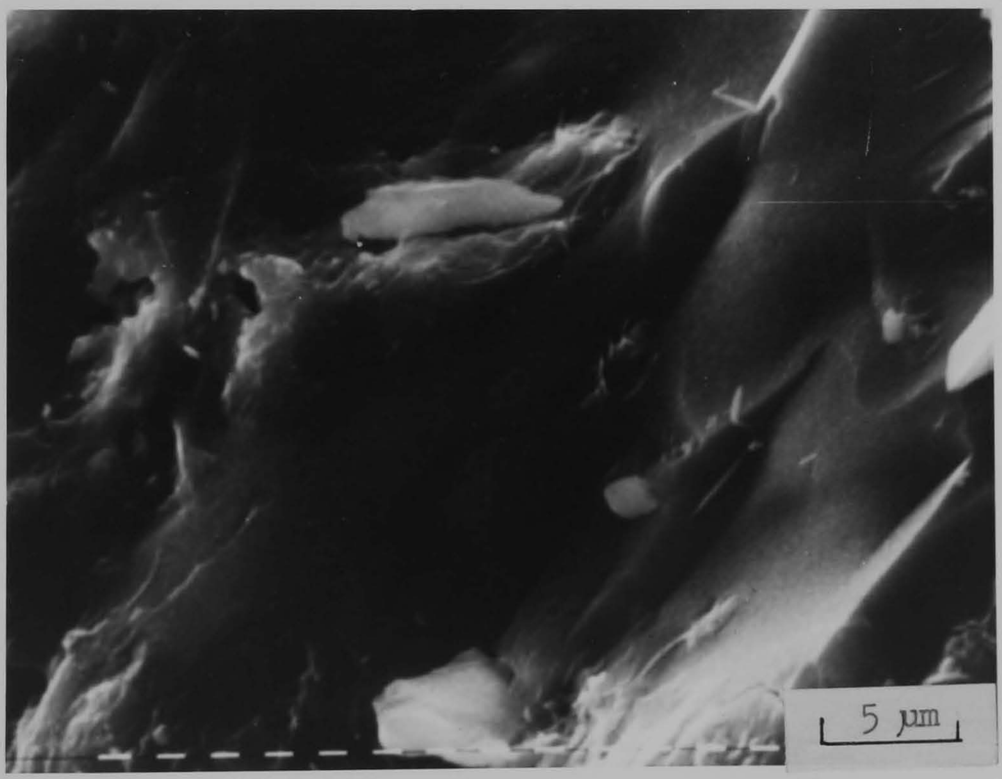

Fig. 6.4 SEM micrograph of a specimen of cement paste (W/C = 0.4) cured normally for 7 days (Mag. 2500)

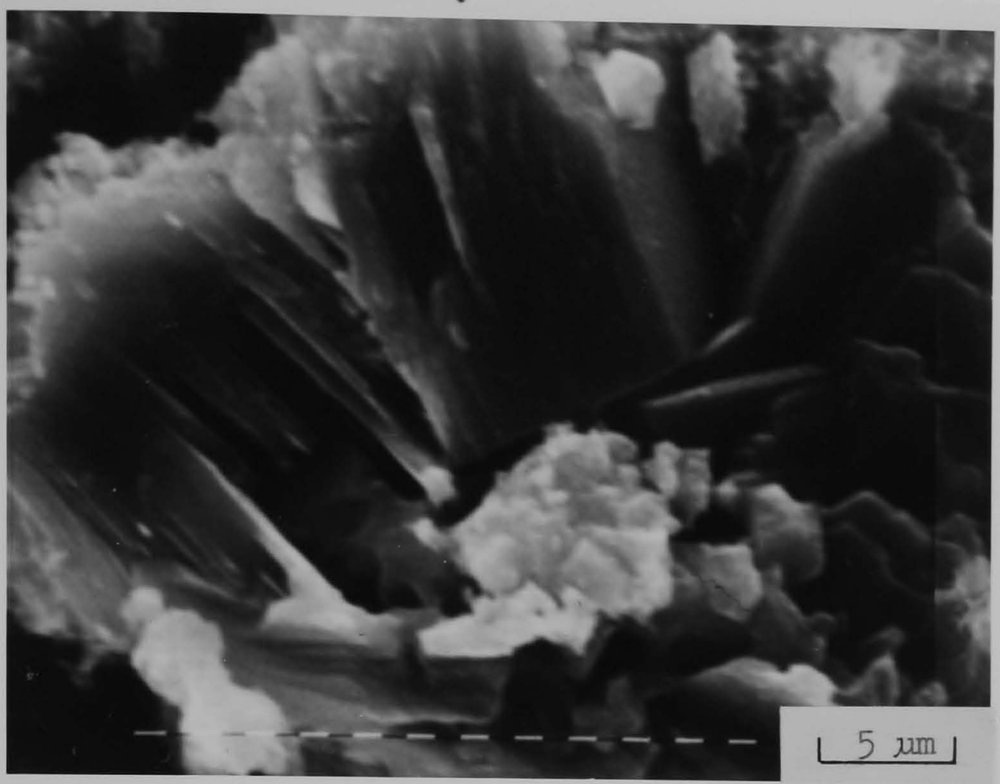

Fig. 6.5 SEM micrograph of a specimen of cement paste (W/C = 0.4) cured normally for 28 days. (Mag. 2500)

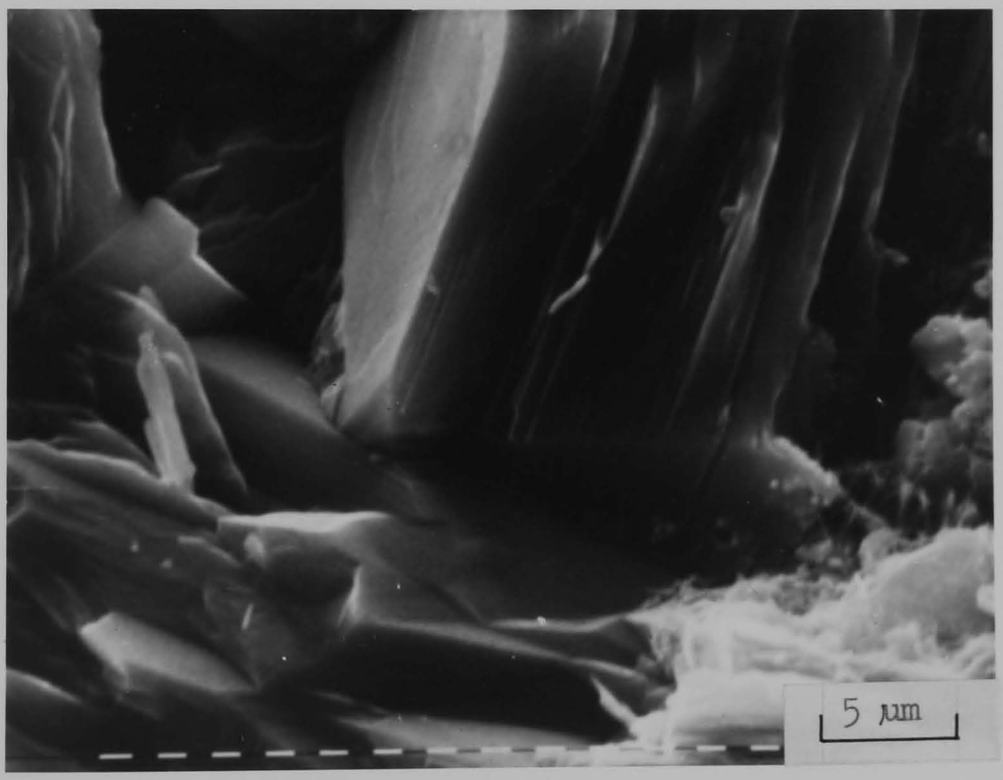

Fig. 6.6 SEM micrograph of a specimen of cement paste (W/C = 0.3) cured normally for 28 days (Mag. 2500)

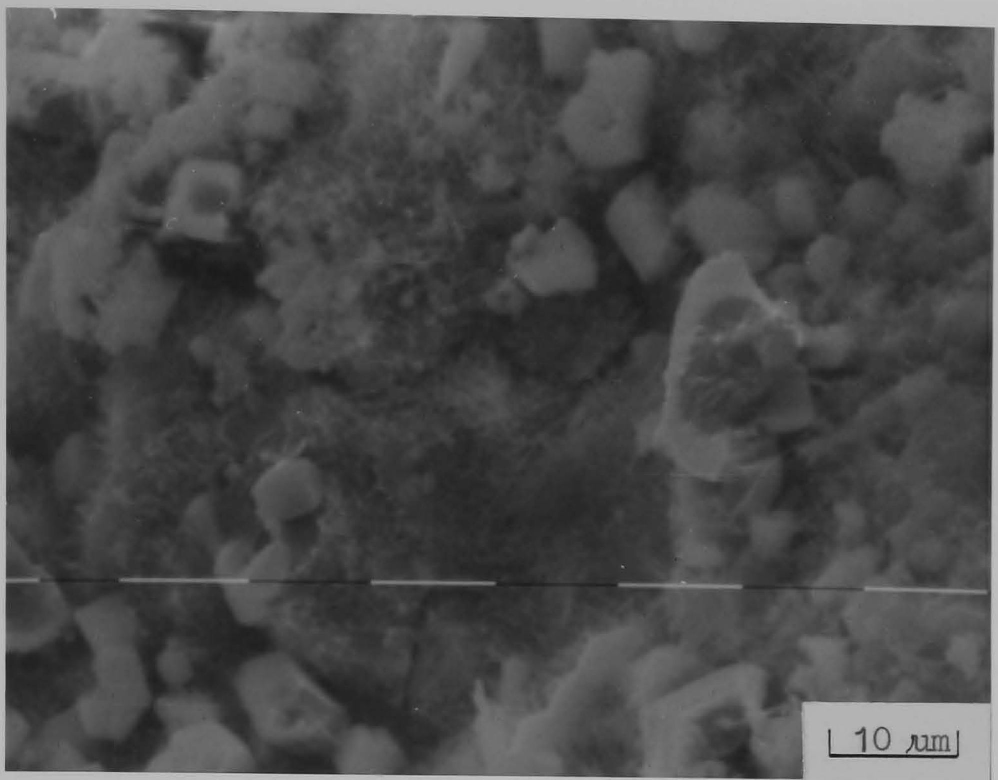

Fig. 6.7 SEM micrograph of a specimen of cement paste (W/C = 0.3) cured normally for 3 days and subjected to 54 freeze/thaw cycles in 0% salt solution (Mag. 1250)

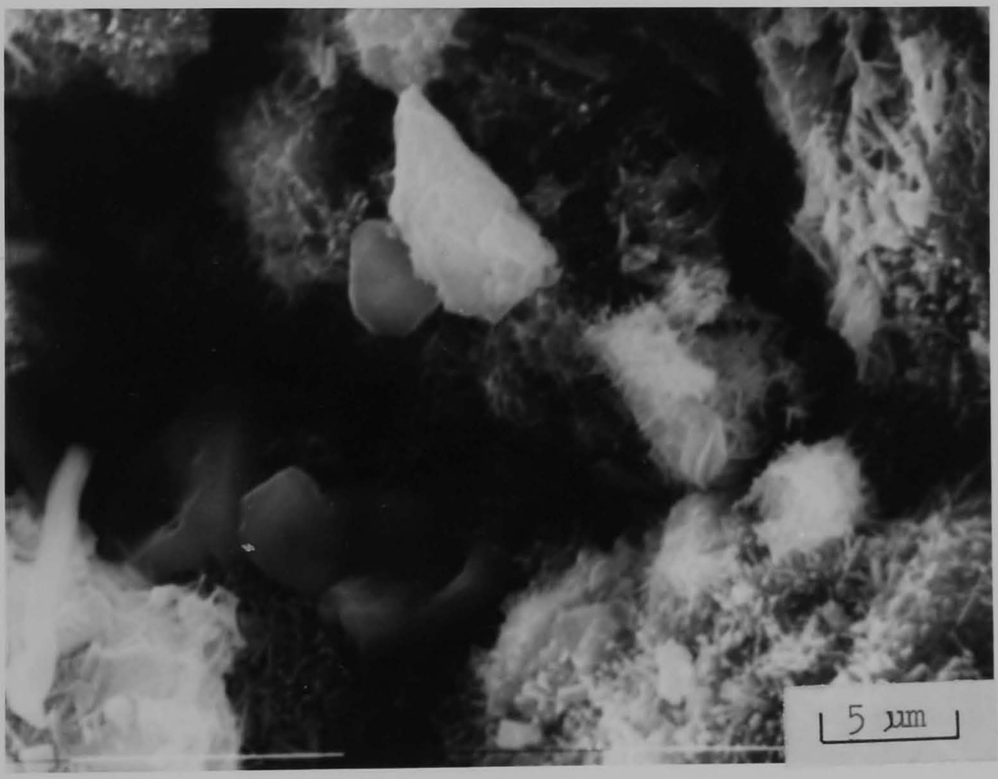

Fig. 6.8 SEM micrograph of a specimen of cement paste (W/C = 0.4) cured normally for 3 days and subjected to 54 freeze/thaw cycles in 0% salt solution (Mag. 2500)

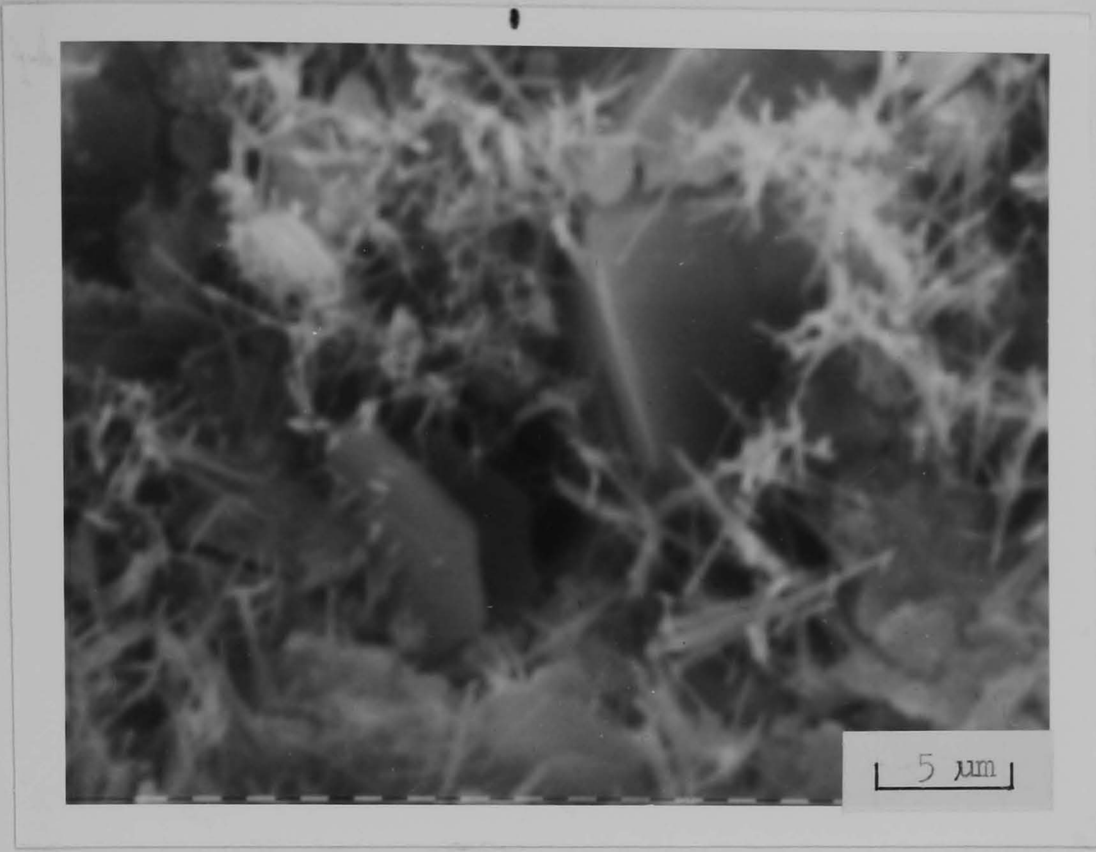

Fig. 6.9 SEM micrograph of a specimen of cement paste (W/C = 0.4) cured normally for 3 days and subjected to 84 freeze/thaw cycles in 0% salt solution (Mag. 2500)

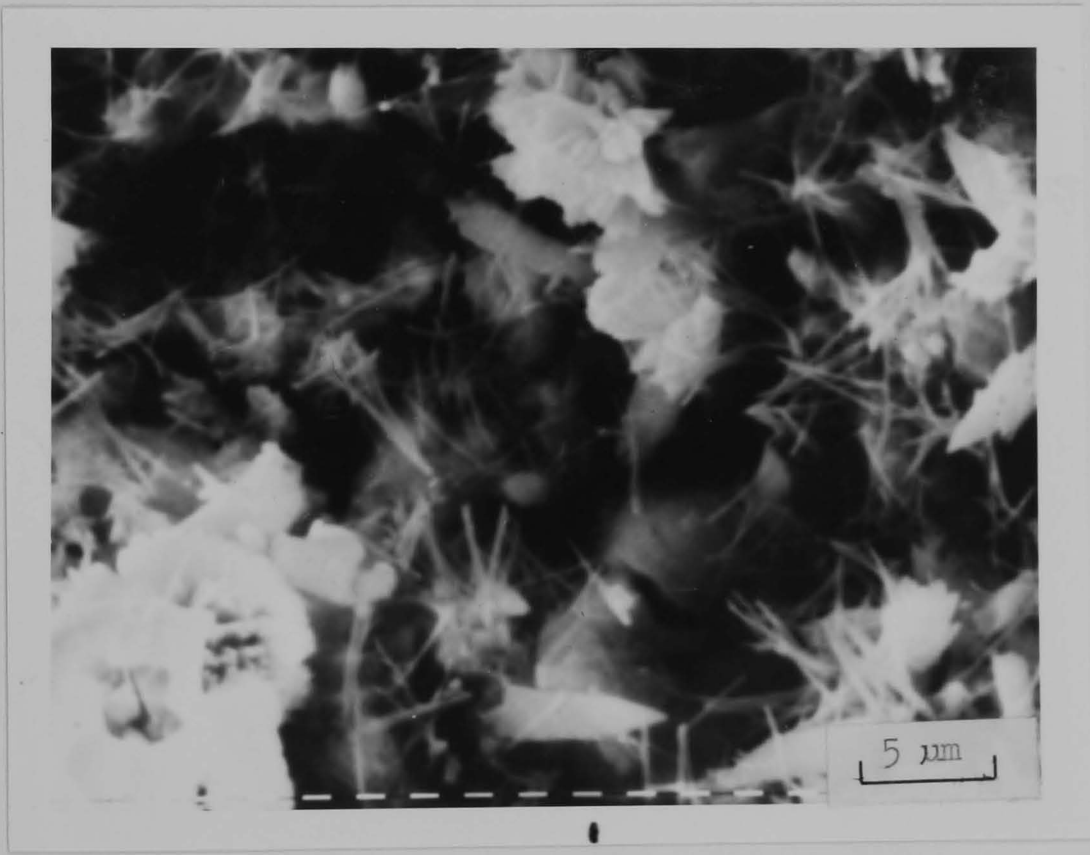

Fig. 6.10 SEM micrograph of a specimen of cement paste (W/C = 0.3) cured normally for 3 days and subjected to 108 freeze/thaw cycles in 0% salt solution (Mag. 2500)

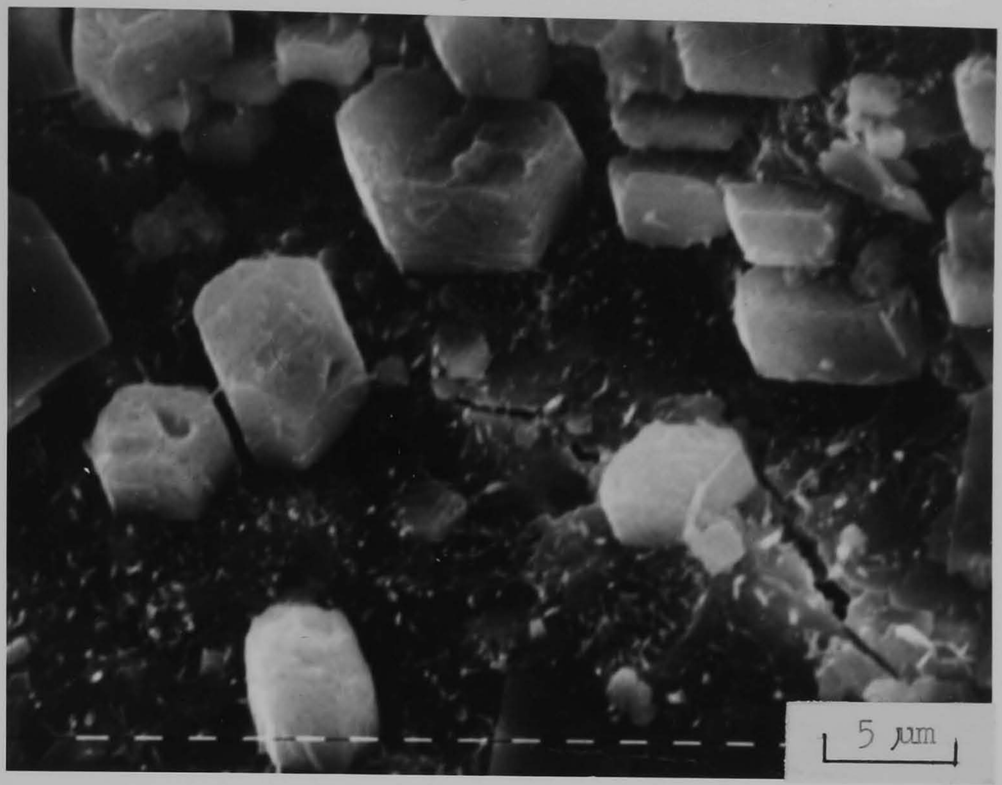

Fig. 6.11 SEM micrograph of a specimen of cement paste (W/C = 0.4) cured normally for 7 days and subjected to 144 freeze/thaw cycles in 0% salt solution (Mag. 2500).

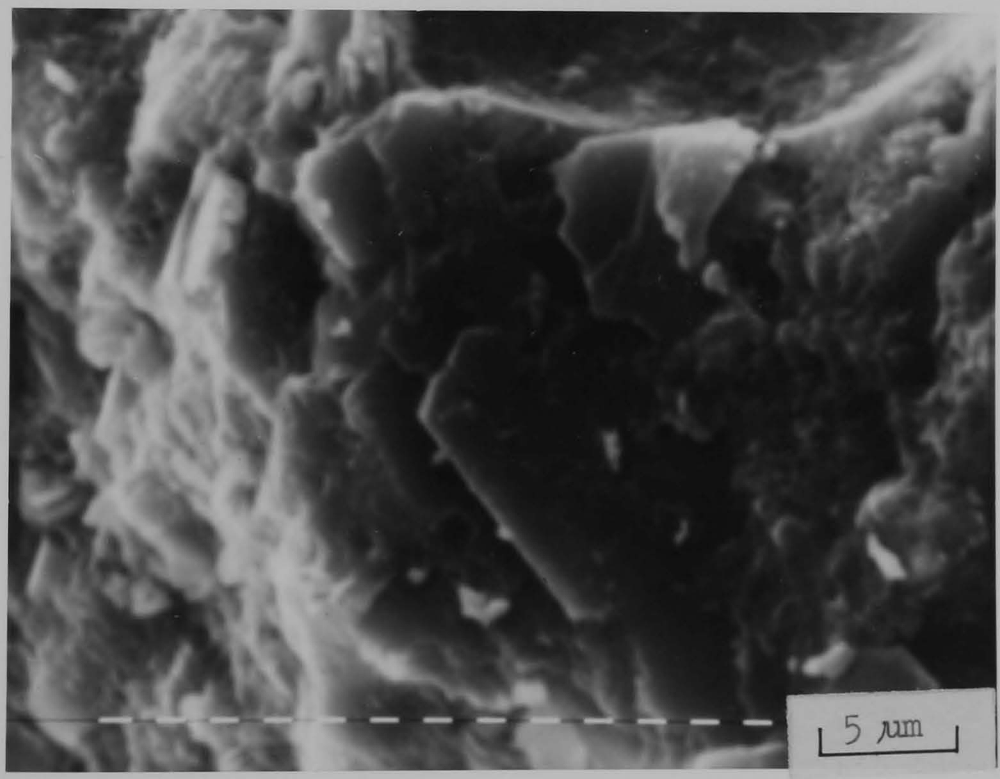

Fig. 6.12 SEM micrograph of paste specimen (W/C = 0.4) cured normally for 3 days and subjected to 36 freeze/thaw cycles in 0% salt solution then allowed to cure normally for 12 days (Mag.2500)

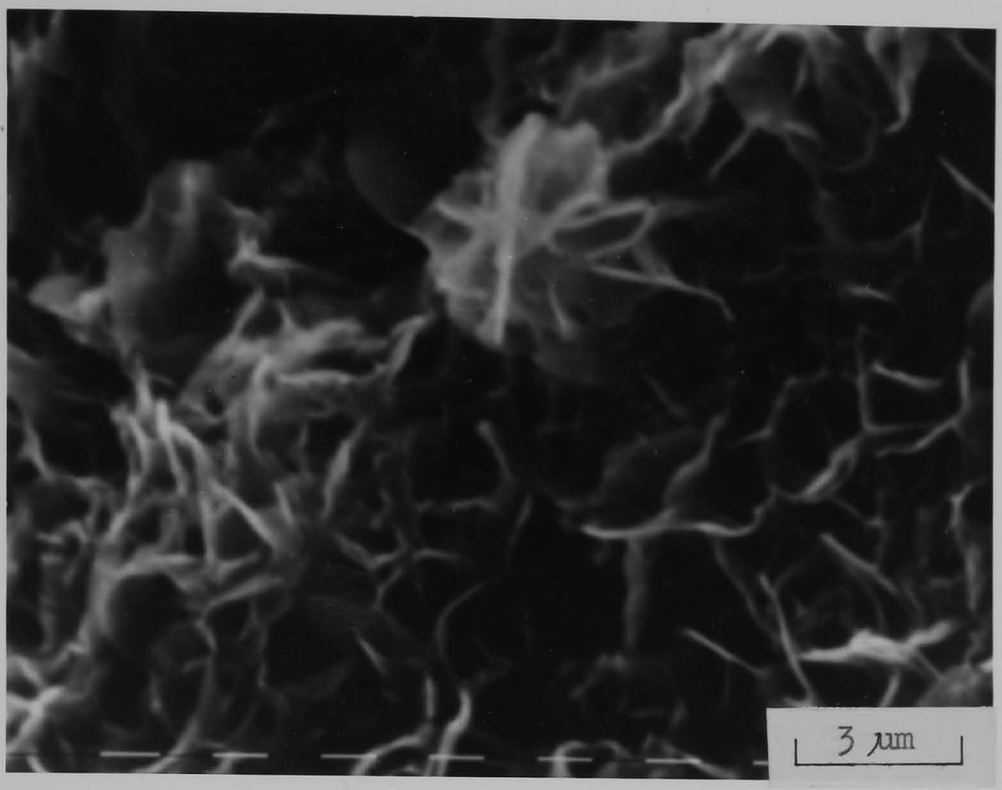

Fig. 6.13 SEM micrograph of a paste specimen (W/C = 0.4) cured normally for 3 days and subjected to 36 freeze/thaw cycles in 4% salt solution (Mag.5000)

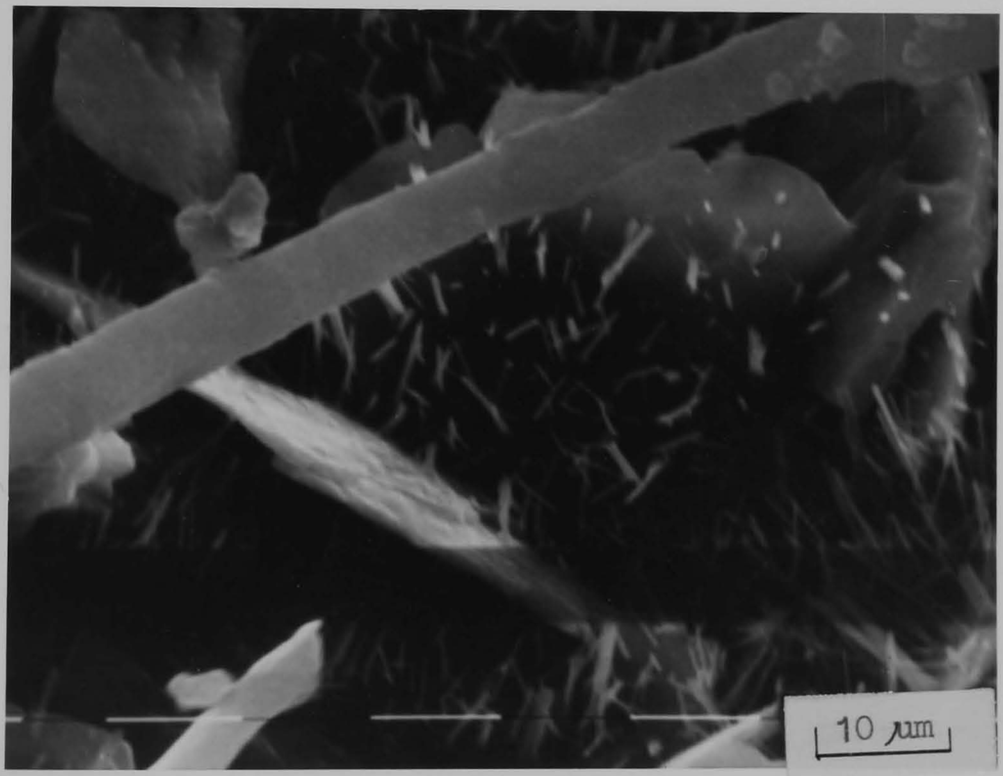

Fig. 6.14 SEM micrograph of a paste specimen (W/C = 0.4) cured normally for 3 days and subjected to 72 freeze/thaw cycles in 4% salt solution (Mag.1250)

Fig. 6.15 SEM micrograph of a paste specimen (W/C = 0.4) cured normally for 7 days and subjected to 72 freeze/thaw cycles in 4% salt solution (Mag.2500)

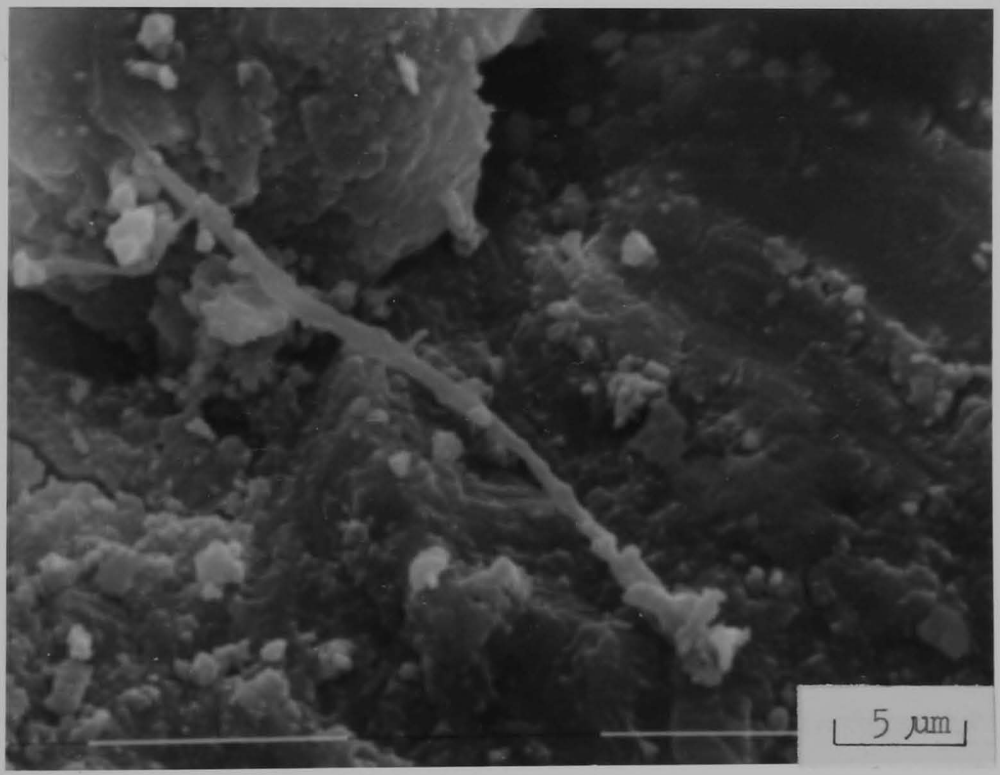

Fig. 6.16 SEM micrograph of a paste specimen (W/C = 0.4) cured normally for 3 days subjected to 54 freeze/thaw cycles in 4% salt solution and then cured normally for 12 days (Mag. 2500)

Fig. 6.17 SEM micrograph of paste specimen (W/C = 0.4) cured normally for 3 days and subjected to 36 freeze/thaw cycles in saturated solution of sodium chloride (Mag. 5000)

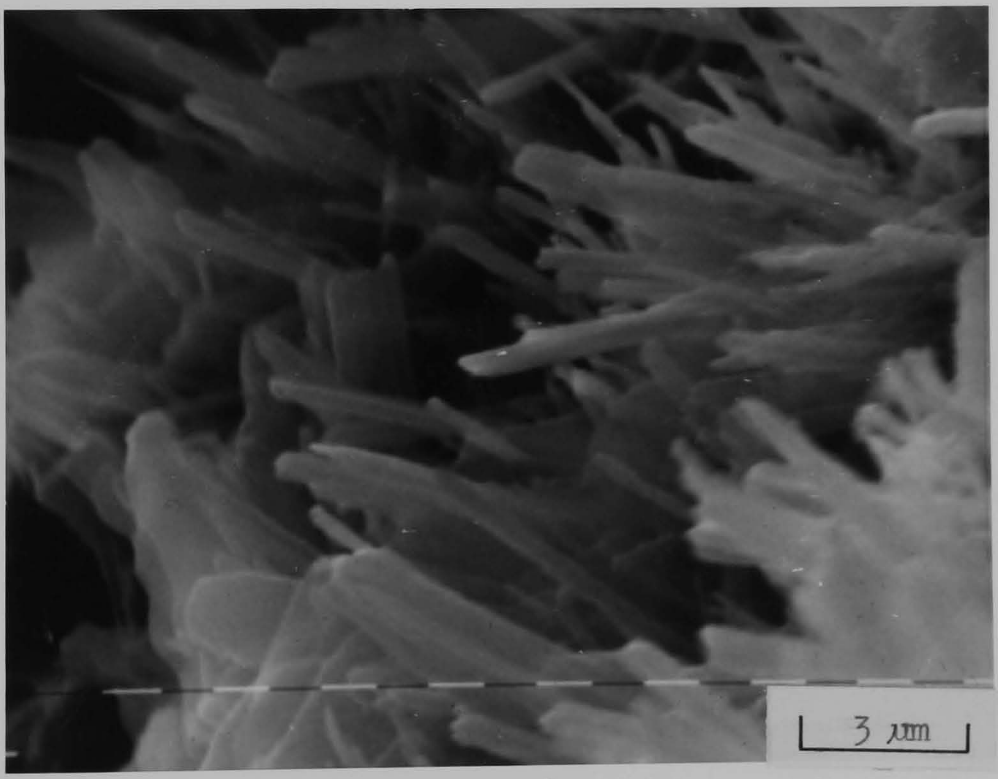

Fig. 6.18 SEM micrograph of paste specimen (W/C = 0.3) cured normally for 3 days and subjected to 54 freeze/thaw cycles in saturated solution of sodium chloride (Mag. 5000)

Fig. 6.19 SEM micrograph of paste specimen (W/C = 0.4) cured normally for 7 days and subjected to 54 freeze/thaw cycles in saturated solution of sodium chloride (Mag. 1250)

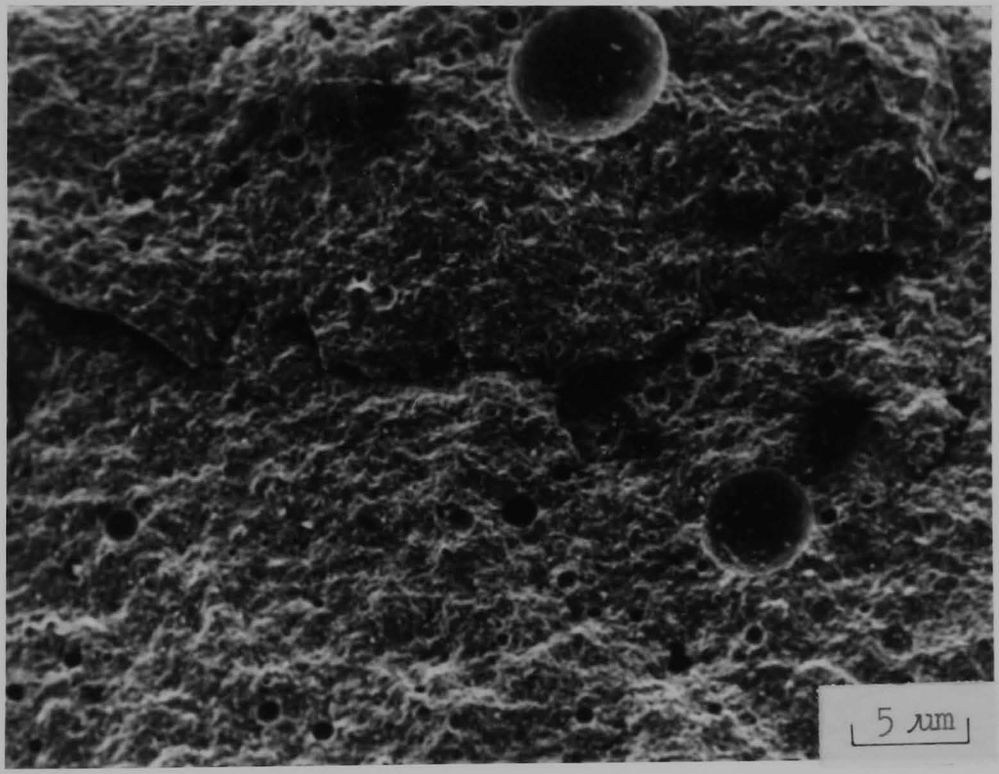

Fig. 6.20 SEM micrograph showing general view of an air entrained paste specimen (W/C = 0.4) cured normally for 3 days (Mag. 20)

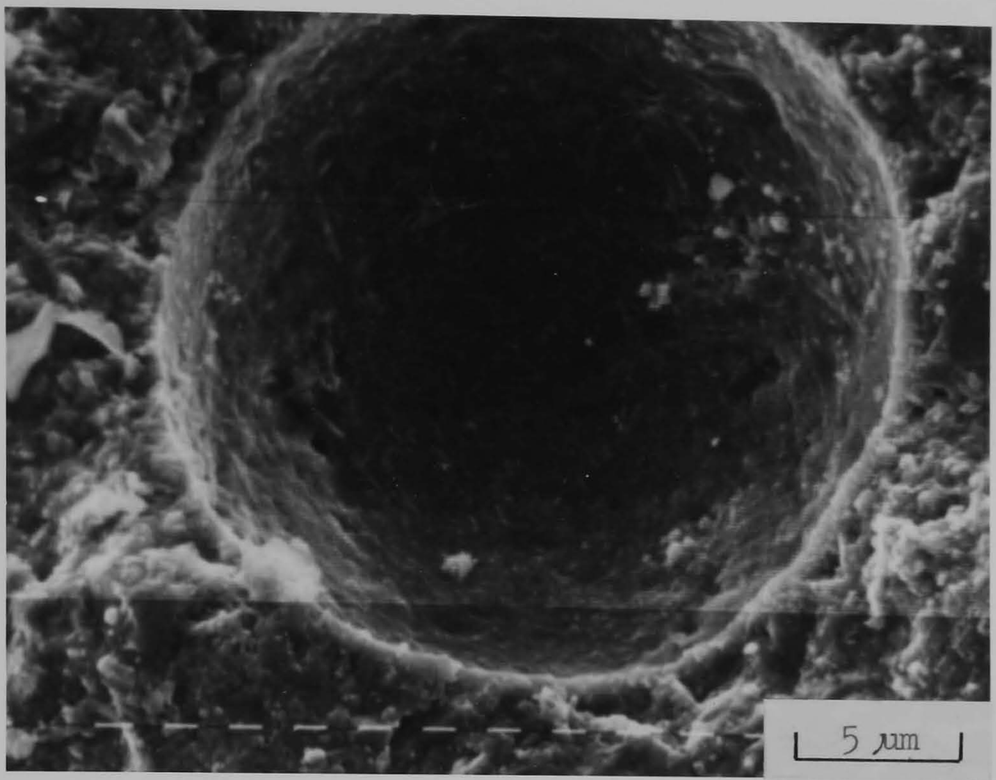

Fig. 6.21 SEM micrograph showing a typical air bubble in an air entrained paste specimen (W/C = 0.4) cured normally for 3 days (Mag. 320)

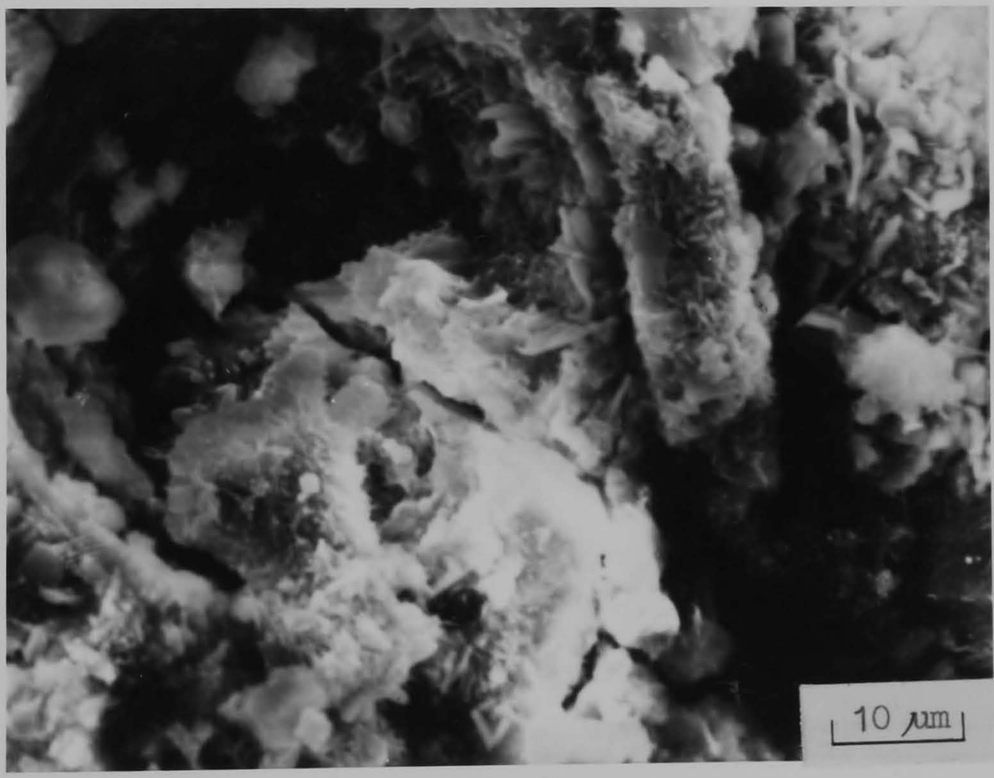

Fig. 6.22 SEM micrograph of an air entrained paste specimen (W/C = 0.4) initially cured for 3 days and subjected to 144 freeze/thaw cycles in 0% salt solution (Mag. 1250)

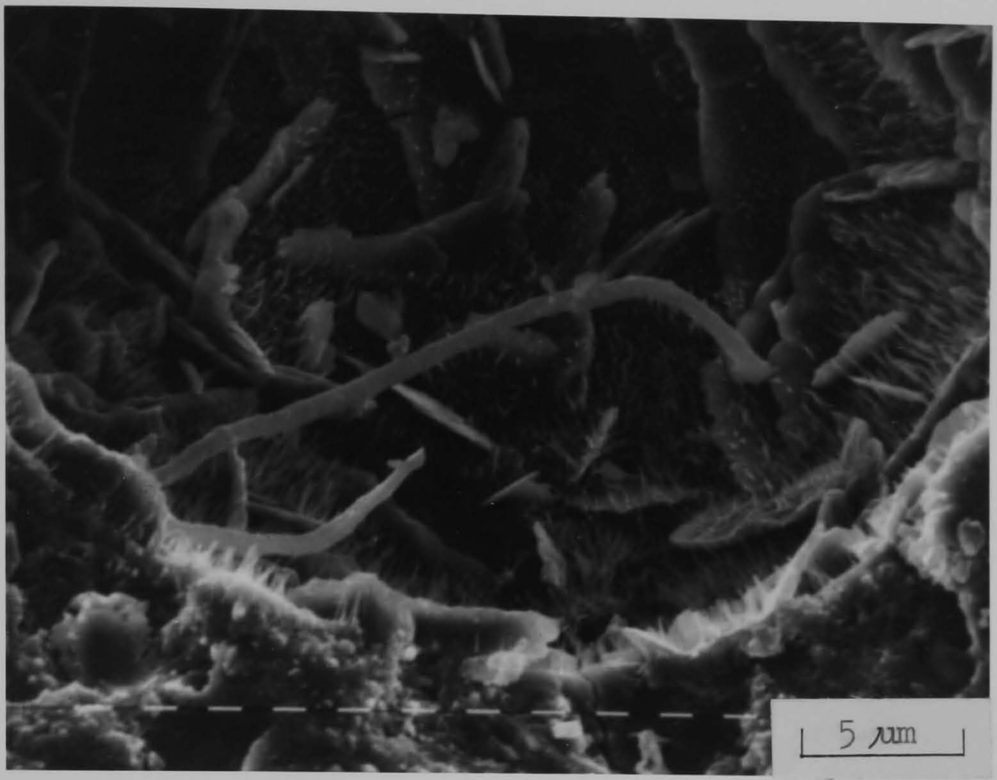

Fig. 6.23 SEM micrograph of an air entrained paste specimen (W/C = 0.4) initially cured for 3 days and subjected to 144 freeze/thaw cycles in 4% salt solution (Mag. 2500)

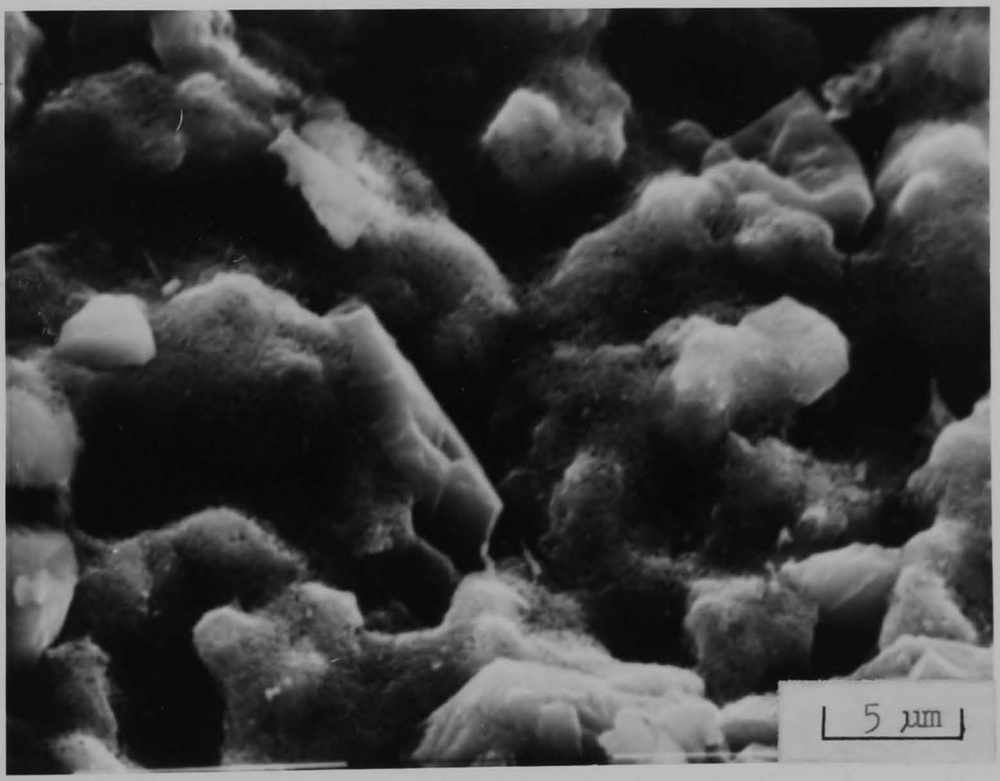

Fig. 6.24 SEM micrograph of a paste specimen (W/C = 0.4) initially cured for 1 day and subjected to 72 wet/dry cycles in 0% salt solution (Mag. 2500)

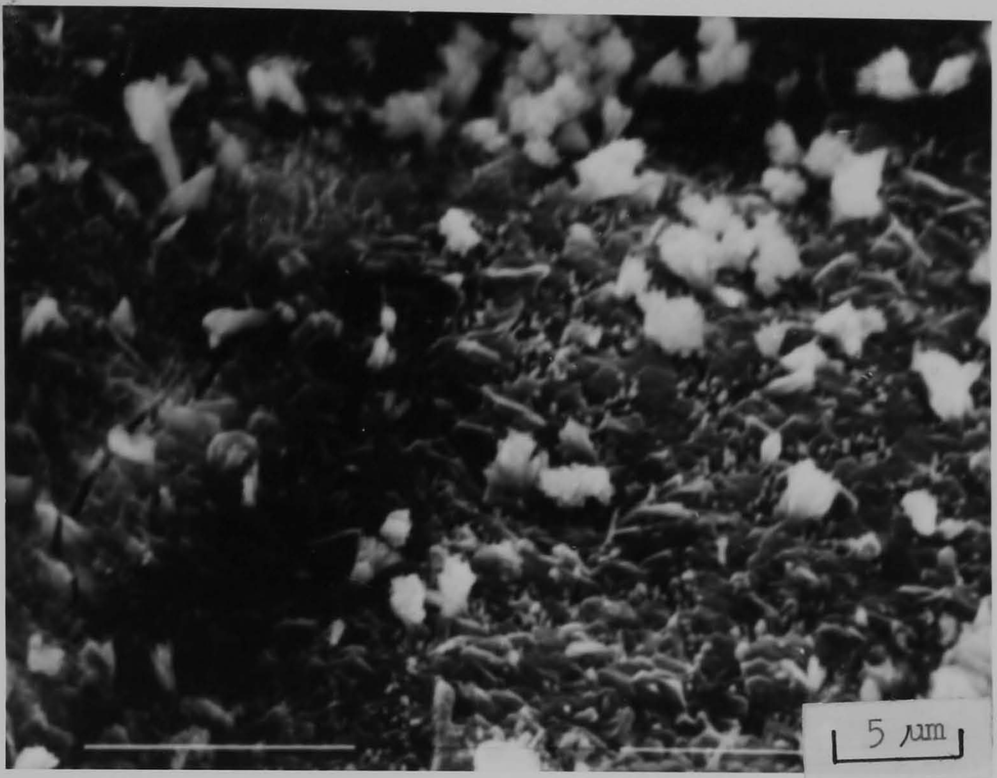

Fig. 6.25 SEM micrograph of a paste specimen (W/C = 0.4) initially cured for 1 day and subjected to 72 wet/dry cycles in 4% salt solution (Mag. 2500)

Fig. 6.26 SEM micrograph of a paste specimen (W/C = 0.4) initially cured for 1 day and subjected to 72 wet/dry cycles in saturated solution of sodium chloride (Mag. 2500)

# CHAPTER 7

# EFFECTS OF FREEZE/THAW AND WET/DRY CYCLES ON THE PORE STRUCTURE OF CEMENT PASTES IN SOLUTIONS OF SODIUM CHLORIDE OF DIFFERENT CONCENTRATIONS.

## 7.1 Introduction

Frost resistance of a material is greatly influenced by the presence of pores filled with water. Hence the structure of the pores of the material must be one of the decisive factors determining its frost resistance. Although this fact was recognised by several workers, very little effort has been directed towards a systematic investigation into the relationship between the pore structure of cement paste and its resistance to frost action.

The presence of sodium chloride adds an additional complication to the subject of the pore structure of cement paste when subjected to frost action and thus affects the durability of concrete in general. Chlorides, specially calcium chloride in certain concentrations have been found to influence the strength properties of concrete possibly by changing the pore pattern of paste matrix. The study of the pore structure of cement paste when subjected to freeze/thaw or wet/dry cycles in presence of solutions of sodium chloride has been made. In this chapter the porosity of hardened cement paste subjected to different test conditions is studied. Measurements of total porosity and of pore size distribution were performed for samples representing different stages of normal curing and samples that had been subjected to freeze/thaw and wet/dry cycles in different solutions of sodium chloride for various periods. However, owing to the importance of this subject and its possible bearing on future research into durability and strength, it is considered desirable to give a brief review of the previous works in this field and to discuss briefly the different methods used to determine pore sizes.

## 7.2 Porosity of Cement Paste - Gel Pores and Capillary Pores

The pore structure of hardened portland cement paste has great influence on its physical characteristics such as gain of strength, permeability and durability. Cement paste is interpreted as a conglomerate of cement gel, calcium hydroxide together with other coarsely crystalline hydration products, residual unhydrated cement grains and capillary pores. The most important of these constituents is thought to be cement gel which is viewed as consisting of a solid part, the finely divided or colloidal hydration products and a nonsolid part, the gel pores. The pores are treated as an intrinsic part of the gel and are said to occupy a characteristic proportion of its volume, approximately 28%.(98) Copeland and Hayes(146) found that gel porosity which is the minimum porosity of completely hydrated cement containing neither unhydrated cement nor capillary pores is 26%. The gel pores are initially filled with water, but the water can be removed by evaporation as can the water in the capillary pores. According to Powers(98) there are a range of pore sizes in the gel as a whole. The smallest size might be of monomolecular dimension, the largest would seem to be that size just smaller than the smallest in which nucleation was possible.

In contrast to the characteristic volume and size of gel pores, the capillary pores of the paste are thought to vary in volume and possibly in size depending on the water/cement ratio and the degree of hydration of the particular paste. It is also considered that in pastes of low water/cement ratio if allowed to hydrate continuously, the capillary voids will eventually be filled with gels. The size ranges of capillary pores are generally larger than gel pores, a number of inferential items of evidence are cited by Powers to this point.(98) These pores vary in shape but as shown by the measurement of permeability form an interconnected system randomly distributed throughout the paste matrix. These interconnected capillary pores are mainly responsible for the permeability of the hardened cement paste and for its vulnerability to frost. For pastes of reasonable water/cement ratios it is considered that the capillary pores become discontinuous as hydration proceeds. When this occurs transmission of fluid between capillary pores must involve passing through gel pores of very much smaller size.

## 7.3 Direct Measurement of Porosity in Cement Paste

To measure the porosity of cement paste several direct methods such as mercury intrusion porosimetry, capillary condensation and dye adsorption can be used. Mercury intrusion porosimetry was used to study the pore size distribution of the cement pastes subjected to freeze/thaw and wet/dry cycles in presence of sodium chloride solutions in this investigation, but the author considers that a brief introduction to the above mentioned techniques would be of interest.

### 7.3.1 Mercury Intrusion Porosimetry

This method was originally developed by Washburn(147) and it has been applied by other workers to many porous materials. Recently attention was drawn by Winslow and Diamond(133) and Diamond(99) to the usefulness of this method in the study of pore structure of hardened cement paste and it has subsequently been applied in a number of such investigations.(148,149)

The method involves the measurement of the mercury volumes penetrating the porous material under progressive increases in pressure. The pore size distribution of the material may be calculated from the well known physical relationship describing the penetration of a non-wetting fluid (whose contact angle is greater than 90° with the particular solid) as given by Washburn(147) for cylindrical pores:

$$P = \frac{-4\,\gamma \cos\theta}{d}$$

where

P = pressure required to intrude a pore

d = diameter of the intruded pore

$\gamma$ = surface energy of the liquid

$\theta$ = contact angle between the liquid and the pore wall.

Using the above equation in case of hardened cement paste Winslow and Diamond(133) considered the value of $\gamma$ to be well established as 484 x $10^{-6}$ N/mm(150) (484 dynes/cm) and determined the value of $\theta$ by performing tests using accurately known cylindrical pores. Under the conditions of these tests in which the paste specimens were oven dried at 105°C the value of $\theta$ was found to be 117°C. They used oven dried paste specimens all through their experiments on the assumption that more complete removal of water prior to intrusion of mercury was achieved by this method than by other techniques. They also showed experimentally that there was no danger of microcracking or other irreversible changes accompanying this drying procedure.

The author holds the view that this particular method of drying adopted might be of significance in determining the final results obtained and that more work is needed to establish the effect of different drying techniques. This view is strengthened by the observations of Litvan(151) on the differences obtained in the measurements by nitrogen absorption of the surface area of hardened cement paste dried by different techniques.

From their work Winslow and Diamond proposed a model of the pore size distribution in cement pastes. Their model consisted of mainly continuous veins of pores of diameter close to a value referred to as the 'threshold diameter' and of local pores of smaller sizes branching from the main continuous pores. As particulate hydration products were formed, the proportion of intermediate sized pores would be expected to increase initially as the coarse pores were subdivided and then gradually to decrease as spaces between grains of hydration products grew finer and finer. It was also found that much of the pore spaces present at all ages occurred in pores between 0.1 and 0.01 μm, i.e. between the conventional concepts of capillary and gel pore diameter. Mercury intrusion porosimetry can be applied for assessing porosity ranging from an upper limit of pore diameter around 1000 μm to a lower limit of as small as 25 Å provided the pressurizing capacity is available.

### 7.3.2 Capillary Condensation

The capillary condensation method of determining pore size distribution depends on the Kelvin equation. Basically the method involves the measurement of the uptake by the solid under investigation of a vapour, which is allowed to reach equilibrium at controlled temperature and controlled relative pressure.

Application of capillary condensation to cement paste has been performed by several workers, most of whom used nitrogen as the condensate. Diamond(99) compared mercury intrusion porosimetry and capillary condensation as applied to cement paste porosity studies and reported discrepancies in the results obtained. He pointed out that while mercury intrusion data indicated coarse size distributions with mean diameters of the order of several hundred Å, the capillary condensation data yielded mean pore diameters between 50 and 100 Å and indicated that most of the space was in the form of pores of diameter less than 100 Å.

### 7.3.3 Method of Dye Adsorption

Unlike the previous two methods, which measure the pore volume, the method of dye adsorption measures the internal surface area of the pores. It was originally devised for the measurement of specific surfaces of solids, mainly nonporous powders. Giles and his colleagues have given an account of the method and its application in several investigations.(152,153)

The application of this method to cement paste has yet to be performed but the author holds the view that such application to cement powder and paste is worthy of serious investigation.

## 7.4 Scope of Tests in the Present Work

Total porosities of the samples were measured by assessing the difference between the weights of surface dry saturated samples and their corresponding weights oven dried at 105°C until constant weight was achieved. For using mercury intrusion porosimetry the sample preparation and apparatus details are discussed in chapter 3 of this thesis. Tests were conducted on the following categories of samples.

1. Samples that were normally cured for different periods.
2. Samples that were cured in different solutions of sodium chloride.
3. Samples that were normally cured and then subjected to freeze/thaw cycles in solutions of sodium chloride.
4. Samples that were cured normally and then subjected to wet/dry cycles in solutions of sodium chloride.

## 7.5 Results and Discussion

A computer programme (given in Appendix D) was prepared to calculate the pore size distribution of the samples from the measurements of mercury intrusion and also to obtain the curves. The ICL 1904S computer at Strathclyde University was used for this purpose. Plotting was done using the "GHOST" graphical system. Two types of pore size distribution curves are presented here: (1) cumulative curves, i.e. cumulative volume of pores ($V_g$) against the pore diameter (d) and (2) frequency curves, i.e. $\frac{\Delta V_g}{\Delta \log d}$ against the pore diameter.

The pore size distribution curves for cement pastes of water/cement ratios 0.4 and 0.3 normally cured for different periods are plotted in Figs. 7.1 and 7.2. The trend of these curves as a function of curing period is similar with the findings of previous investigations.(133, 154) The curves move towards the left with a decrease in total porosity which is found to be consistent with the generally accepted concepts of the hydration of portland cement. As the hydration proceeds capillary porosity decreases as a result of the lower density hydration products growing into the original water filled spaces between the cement grains.(11) From the curves in Figs. 7.1 and 7.2 it is noticed that the average capillary pore diameter is a function of both water/cement ratio and curing period. The specimens of 0.3 water/cement ratio had less total porosity at a particular curing period than that of specimens made with 0.4 water/cement ratio. But the pore size range was quite large for the specimens of both water/cement ratios varying from a few microns at very short time to about 100 nm for well hydrated continuously cured specimens.

In order to study the effect of sodium chloride on the hydration of cement paste, specimens of both water/cement ratios were placed in 4% and saturated solutions of sodium chloride after being stripped from the moulds. The frequency curves against pore diameter of such specimens are plotted in Figs. 7.3 to 7.6. From Figs. 7.3 and 7.4 it may be noticed that when cement paste of 0.4 water/cement ratio cured in 0%, 4% and saturated solutions of sodium chloride, the pore size characteristics of the specimens differ considerably from one another. There were more pores in the range of 170 nm to 1 μm in case of normally cured specimens than those cured either in 4% or saturated solution of sodium chloride. The samples hydrated with salt solutions exhibited higher amount of microporosity in the range of 40 nm to 100 nm. This appeared to be due to the greater degree of hydration and different morphological features as observed in the previous chapter due to the presence of sodium chloride. In addition to the microporosity the samples cured in saturated solutions of sodium chloride seemed to have a greater proportion of larger pores in the range of 200 nm to 1 μm diameter than those cured in 4% solution. Similar effects were also observed with the specimens of 0.3 water/cement ratio when cured in 0%, 4% and saturated solutions of sodium chloride as in Figs. 7.5 and 7.6. The microporosity of the specimens of both the water/cement ratios cured in 4% and saturated solutions of sodium chloride in the range of 40–100 nm diameter and the formation of larger pores in the range of 100 nm and upwards in case of specimens treated with saturated solution indicated that the concentration of sodium chloride must have a significant role in the hydration characteristics of cement pastes. From the above discussion it would therefore appear that sodium chloride produces more rapid hydration as shown by the increasing microporosity. Ben-yair(60) has however suggested that with increased concentration of sodium chloride, calcium chloride is produced by reaction with calcium hydroxide. It is possible that leaching played an important part in removing calcium chloride due to its higher solubility in concentrated solution of sodium chloride resulting formation of the larger pores initially near the surface and subsequently inside the specimens.

The effects of alternate freezing and thawing cycles on the pore size distribution of the paste samples in presence of solutions of sodium chloride are shown in Figs. 7.7 to 7.10. Specimens of 0.4 water/cement ratio cured normally for 3 days when subjected to 24 freeze/thaw cycles in 0%, 4% and saturated solutions of sodium chloride showed changed pore size characteristics (Fig.7.7). Formation of larger number of pores in the range of diameters of 70–300 nm was noticed in the case of specimens subjected to freeze/thaw cycles in water. The 4% solution produced considerably more pores in the range of diameters of 15–80 nm. Saturated solutions were found to produce a greater number of pores in two distinct ranges of diameters, i.e. 15–60 nm and 80–400 nm. The 15-60 nm range is similar to that of the 15-80 nm range in the case of specimens frozen and thawed in 4% solution and the curve in 80–400 nm diameter range is also similar in nature to that of the 70–300 nm diameter range in the case of specimens cycled in 0% solution. It was also noticed that in the range of diameters 80-400 nm the saturated solution produced more bigger pores such as 160–400 nm in diameter than did the 0% solution.

When the specimens were initially cured for 7 days and subjected to 54 freeze/thaw cycles in the solutions the pore size distribution curves were almost identical in nature with those of 3 days initially cured samples when subjected to 24 freeze/thaw cycles in corresponding solutions. The greater number of pores in three different ranges of diameters were noticed for the specimens subjected to freeze/thaw cycles in different solutions as was observed previously in Fig. 7.7. But the comparison between Figs. 7.7 and 7.8 revealed that the redistribution of pore sizes took place for the specimens in 0% and saturated solution. When subjected to freeze/thaw cycles in water 3 days normally cured specimens showed the peak of pore sizes in the range 100-200 nm whereas for the 7 days normally cured specimens the peak was found to occur in the range of 45-90 nm. Freezing and thawing cycles in saturated solution changed the peak of the pore sizes from the range of 70-300 nm to 60-160 nm in diameter for the 7 day cured specimens. The other peak in the range of 30-60 nm in case of the specimens subjected to freeze/thaw cycles in saturated solution was found to be present as found earlier with the 3 days initially cured specimens. The peak of the pores for the specimens cycled in 4% solution was in exactly the same range as before. The other significant change in pore sizes was found to occur in case of specimens subjected to freeze/thaw cycles in saturated solution. A sizeable amount of pores in larger diameters in the range of 100-300 nm was noticed for both the 3 day and 7 day initially cured specimens. It is possible that the observations may reflect the leaching of calcium chloride by dissolution process due to higher concentration of sodium chloride in the solution as discussed earlier.

When the specimens were initially cured for 28 days and subjected to 84 freeze/thaw cycles in 0%, 4% and saturated solution the pore size distributions as in Fig. 7.9 were very similar to those of 3 day and 7 day initially cured specimens. The only difference noticed was in the case of specimens in saturated solution where only one peak was present instead of two peaks as in the previous cases. Higher numbers of large diameter pores were found to be formed in saturated solution indicating the formation of calcium chloride(60) and its subsequent leaching from the samples. The redistribution of pores in the comparatively smaller diameter ranges as found in case of the specimens when subjected to freeze/thaw in water or in sodium chloride solutions reflects two possible mechanisms. In the case of freeze/thaw cycles in water gradual collapse of the materials surrounding the larger pores possibly took place thereby causing the larger pores to be subdivided. When sodium chloride was present in smaller concentrations as in the case of 4% solution the hydration rate was accelerated and the hydrated products filled up the capillary pores significantly as a result of which the number of smaller diameter pores were increased. The behaviour of higher concentration of sodium chloride was possibly different as mentioned earlier and it resulted in the formation of larger pores. In addition it is possible that some complex salts were formed and grew significantly as discussed in the previous chapter due to presence of saturated solution of sodium chloride. The formation and growth of these products made the pastes microporous.

Paste specimens of 0.3 water/cement ratio initially cured for 3 days and when subjected to 36 freeze/thaw cycles in 0%, 4% and saturated solution had exactly similar pore size distribution curves as those of 0.4 water/cement ratio specimens. Fig. 7.10 compares very well with the Figs. 7.7 and 7.8 confirming the formation of pore sizes in different ranges due to the presence of 4% and saturated solution of sodium chloride. Freezing and thawing cycles together with saturated solution produced two significant peaks of pore sizes, one of which was comparatively larger than those present either in 0% or 4% solution in the diameter range of 100-200 nm. Comparing the Figs. 7.7 to 7.10 and the nature of the curves for the pore sizes in 0%, 4% and saturated solution of sodium chloride it may be concluded that freeze/thaw cycles in the presence of sodium chloride changed the pore structure of cement pastes significantly. Saturated solution was found to produce comparatively larger pores while 4% solution produced more microporous structure.

The effect of wetting and drying in different solutions of sodium chloride on the pore size distribution of 1 day normally cured cement paste of 0.4 water/cement ratio is shown in Fig. 7.11. It was noticed that 72 wet/dry cycles in 0%, 4% and saturated solutions of sodium chloride produced significantly larger numbers of pores in the 30-90 nm diameter range. Saturated solution was found to produce another peak of larger pores in the 100-250 nm diameter range. Comparing these observations and other findings in the case of paste specimens subjected to freeze/thaw cycles in saturated solution of sodium chloride it may be concluded that saturated solution produced some products which were leached out subsequently leaving behind larger pores in the paste matrix. The formation of the peak of pores in 30-90 nm diameter range in case of specimens wetted and dried in 0% solution was not observed in those specimens subjected to freeze/thaw cycles in 0% solution where the similar peak was formed in 50-110 nm diameter range. The less deleterious effect due to wet/dry cycles and the simultaneous curing effect for 72 days during wetting cycles changed the pore structure of the specimens to a microporous one. The effect of 4% solution of sodium chloride was similar again, the only difference being noticed in the case of pores of the 100-250 nm diameter range where the pores were more numerous than those in 0% solution. Saturated solution produced significantly larger amount of pores in this range as mentioned earlier. Comparing all the Figs. 7.3 to 7.11 it is therefore concluded that sodium chloride in different concentrations changed the pore size distributions of the cement pastes to a different pattern irrespective of attacking conditions i.e. freeze/thaw or wet/dry. This behaviour of pore sizes plays a significant role in determining the mechanical properties of the cement pastes. The relationship of the pore sizes with mechanical strength of cement pastes when subjected to freeze/thaw or wet/dry cycles in presence of sodium chloride solutions of different concentrations is more fully discussed in Chapter 9 of this thesis.

## 7.6 Conclusions

(1) The average capillary pore diameter of hardened cement pastes was a function of both water/cement ratios and curing periods.

(2) Sodium chloride when present in different concentration in the curing solution produced different pore size distributions of the hardened cement pastes.

(3) The rate of hydration of paste specimens was accelerated when the specimens were cured in 4% solution of sodium chloride as a result a more microporous structure than that of normally cured specimens was obtained.

(4) The saturated solution of sodium chloride also showed a higher degree of hydration. In addition it produced some products possibly calcium chloride which was leached out producing significant amount of larger pores in the paste specimens.

(5) Freeze/thaw cycles in sodium chloride of any concentration caused redistribution of pore sizes. The 4% solution produced one large peak of pores in the diameter range of 15-80 nm whereas saturated solution produced two distinct peaks, one in a similar range and the other in comparatively larger diameter range.

(6) Wet/dry cycles in saturated solution of sodium chloride did not restrict the hydration of cement pastes but at the same time it had similar leaching action that in freeze/thaw cycles on some products causing considerable amount of larger pores to occur.

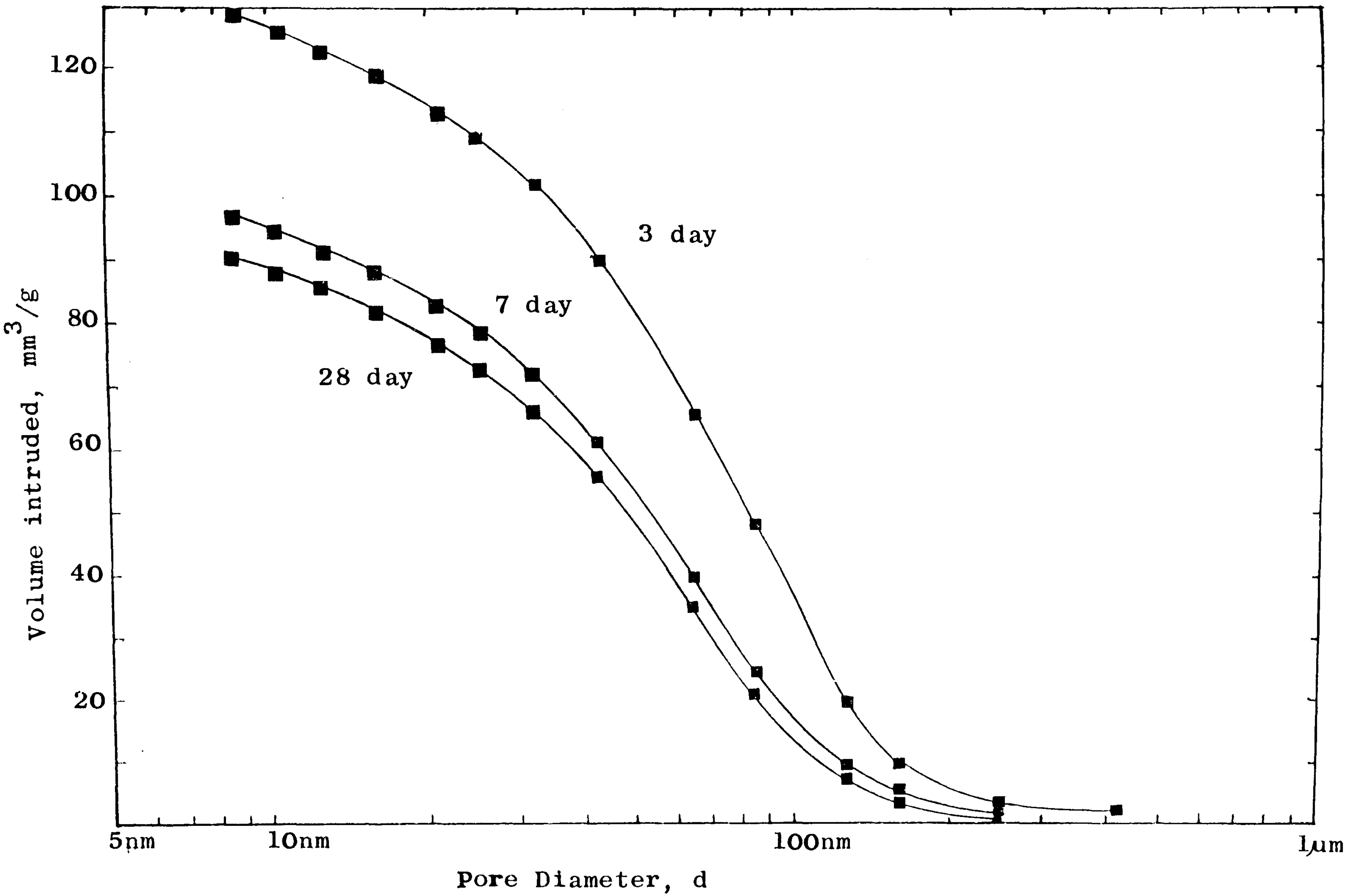

Fig. 7.1 Pore size distribution curves for paste (W/C = 0.3) normally cured for different ages

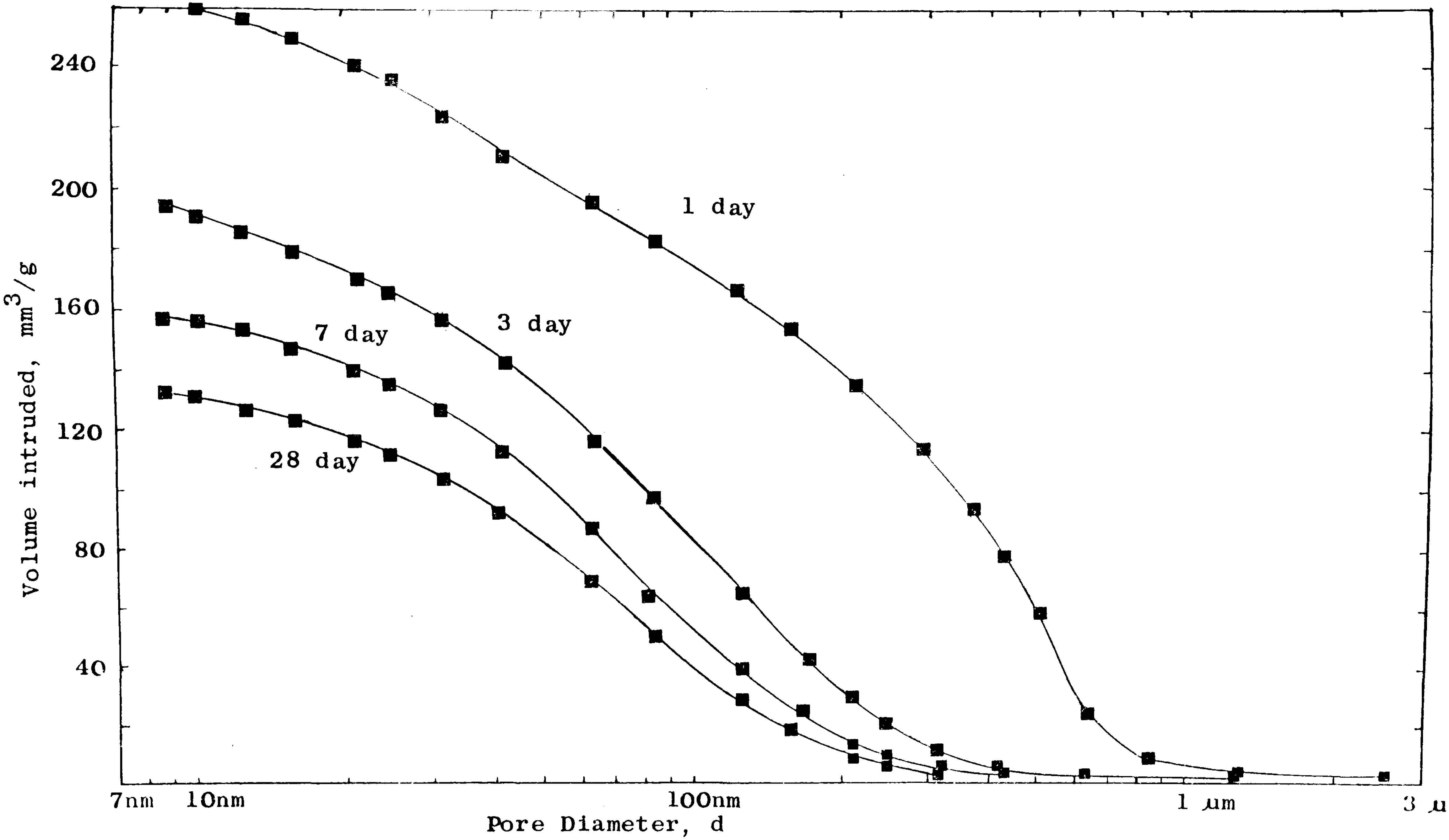

Fig. 7.2 Pore size distribution curves for paste (W/C = 0.4) normally cured for different ages

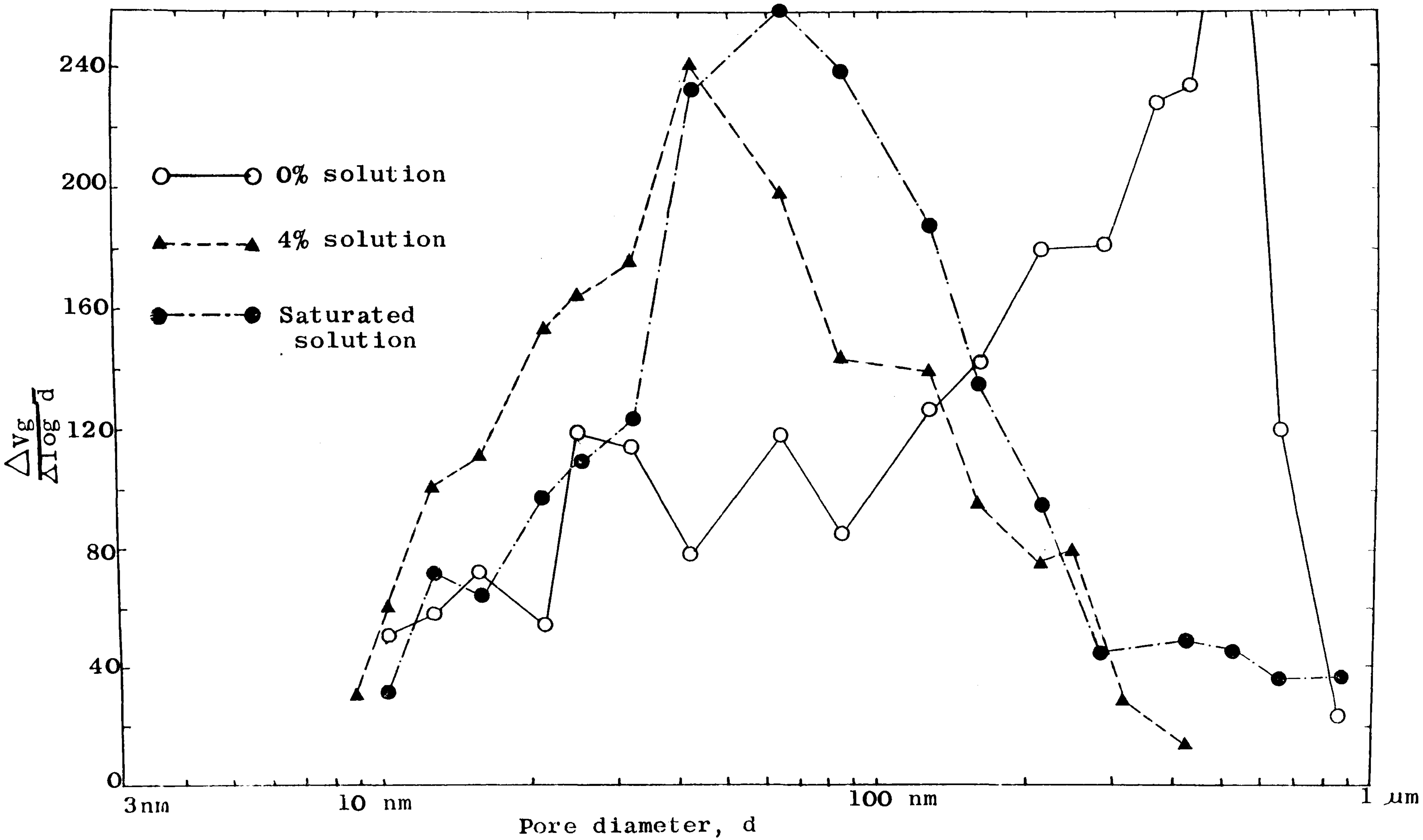

Fig. 7.3 Pore size distribution curves of cement paste (W/C = 0.4) cured 1 day in solutions of sodium chloride of different concentrations

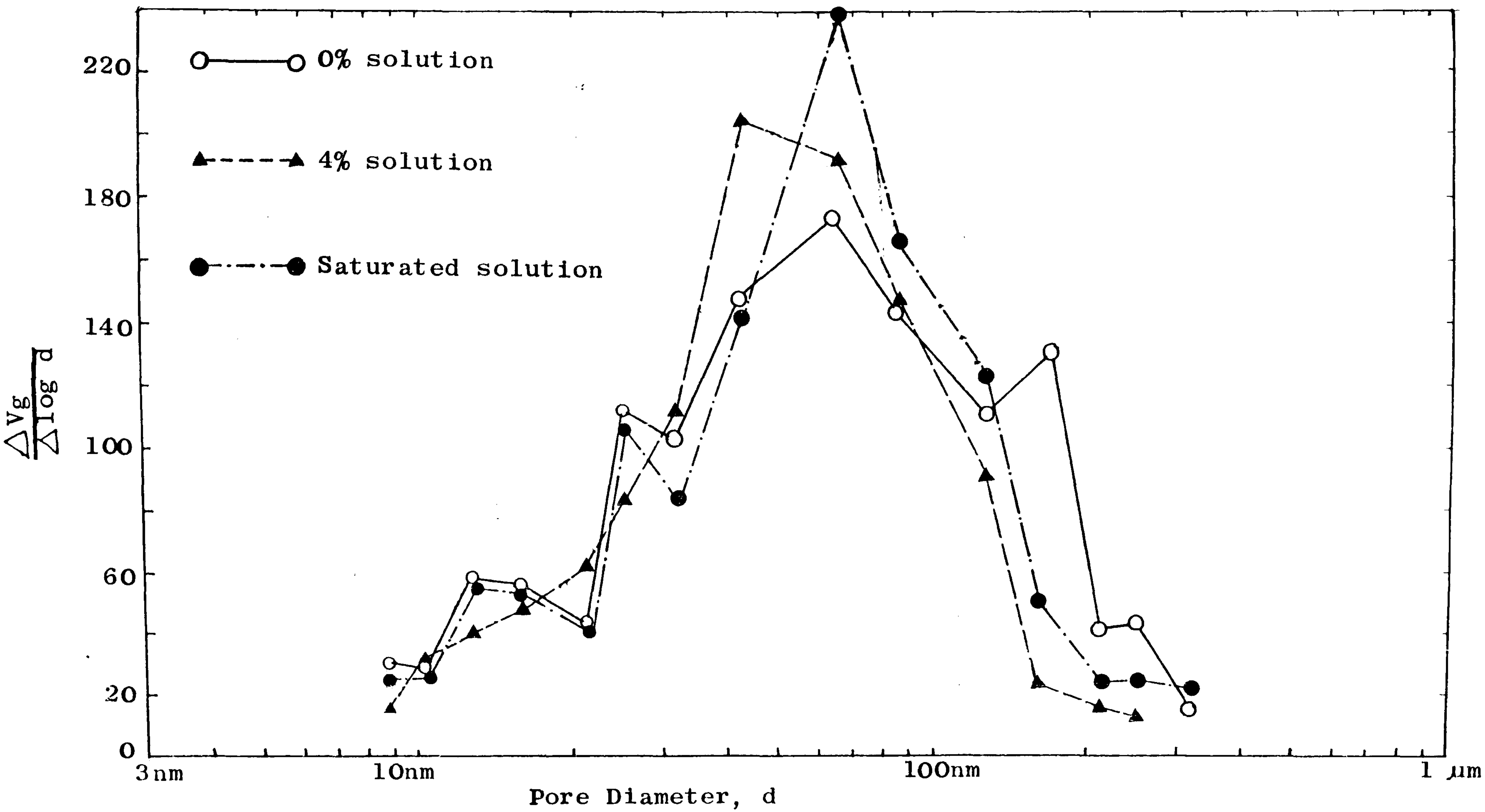

Fig. 7.4 Pore size distribution curves of cement paste (W/C = 0.4) cured 7 days in solutions of sodium chloride of different concentrations

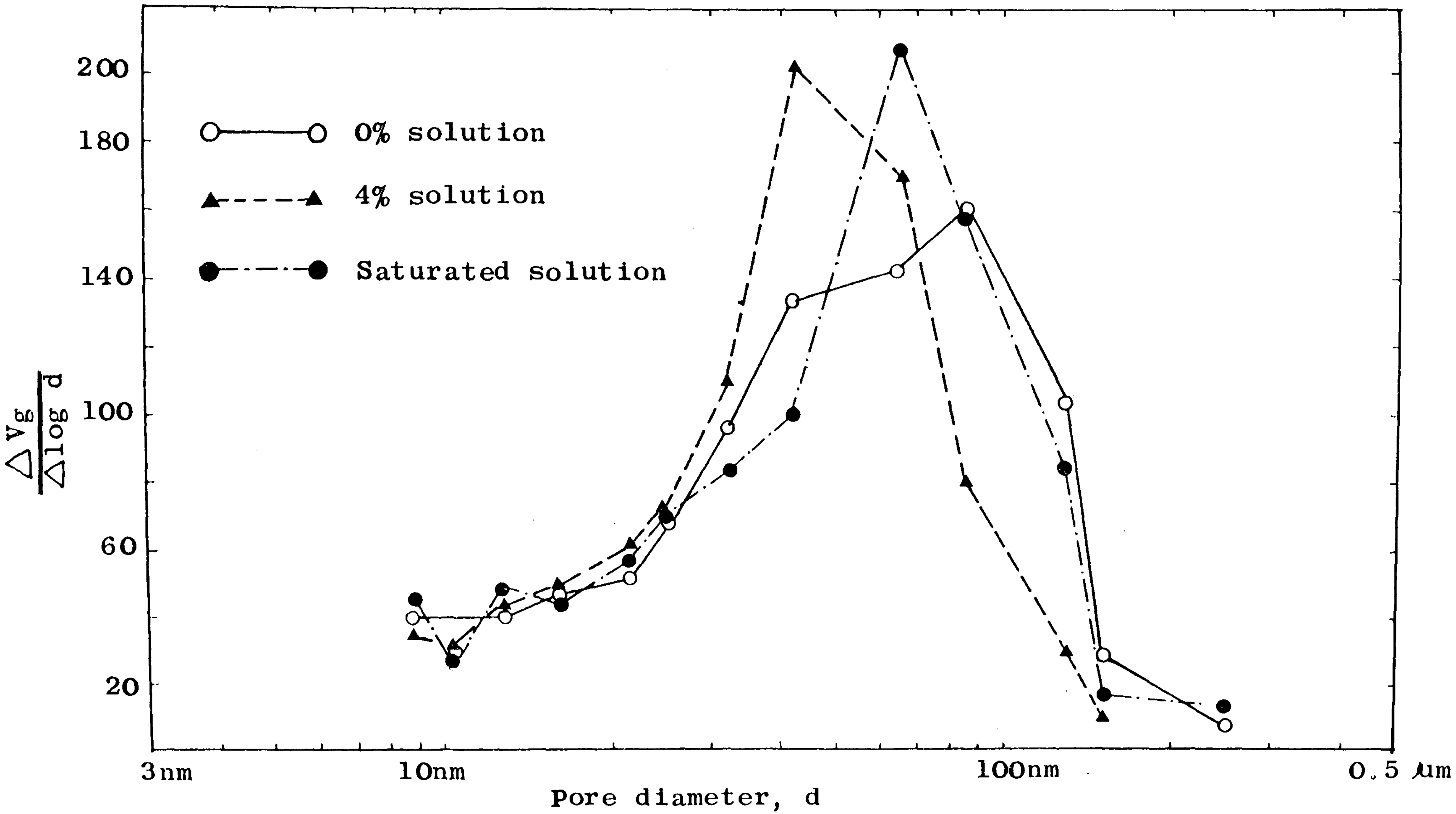

Fig. 7.5 Pore size distribution curves of cement paste (W/C = 0.3) cured 3 days in solution of sodium chloride of different concentrations

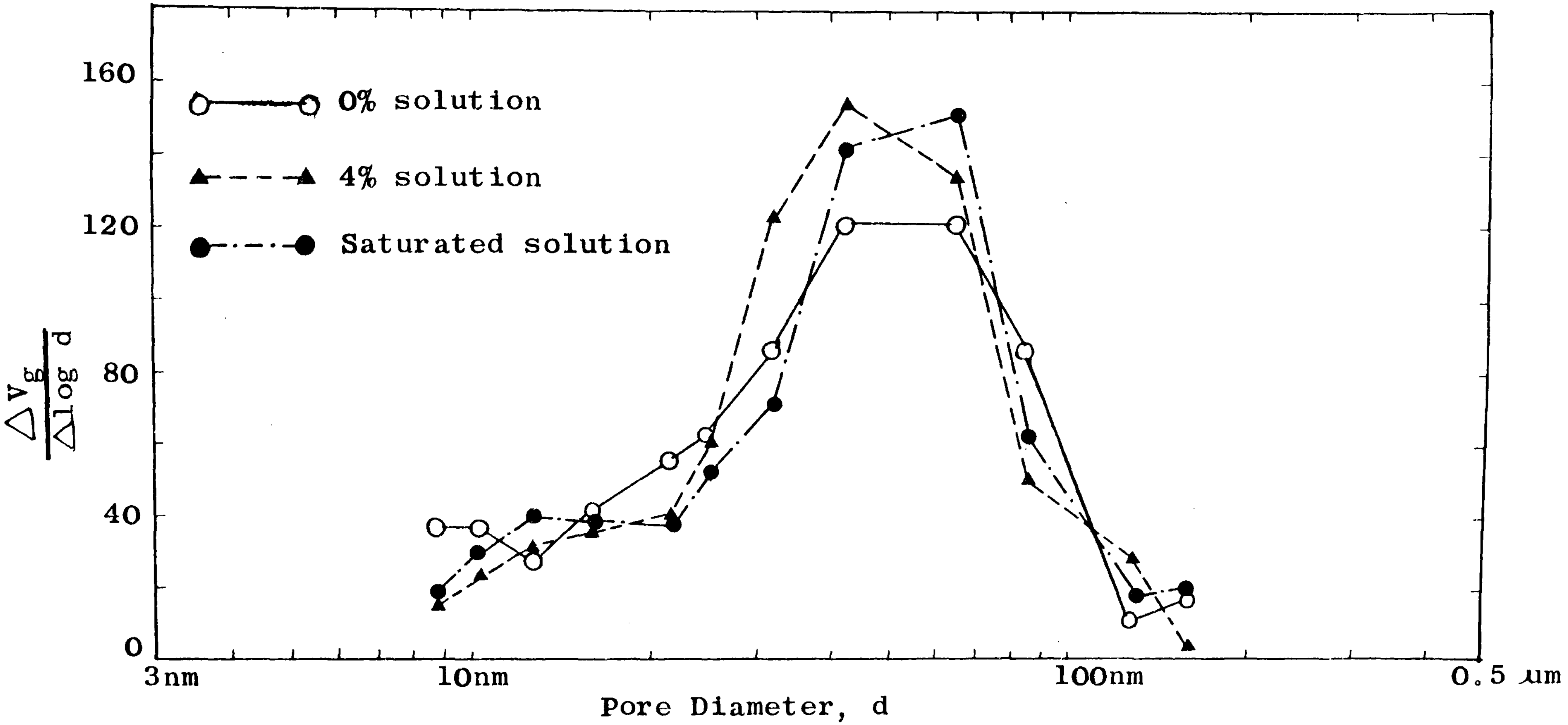

Fig. 7.6 Pore size distribution curves of cement paste (W/C = 0.3) cured 7 days in solutions of sodium chloride of different concentrations

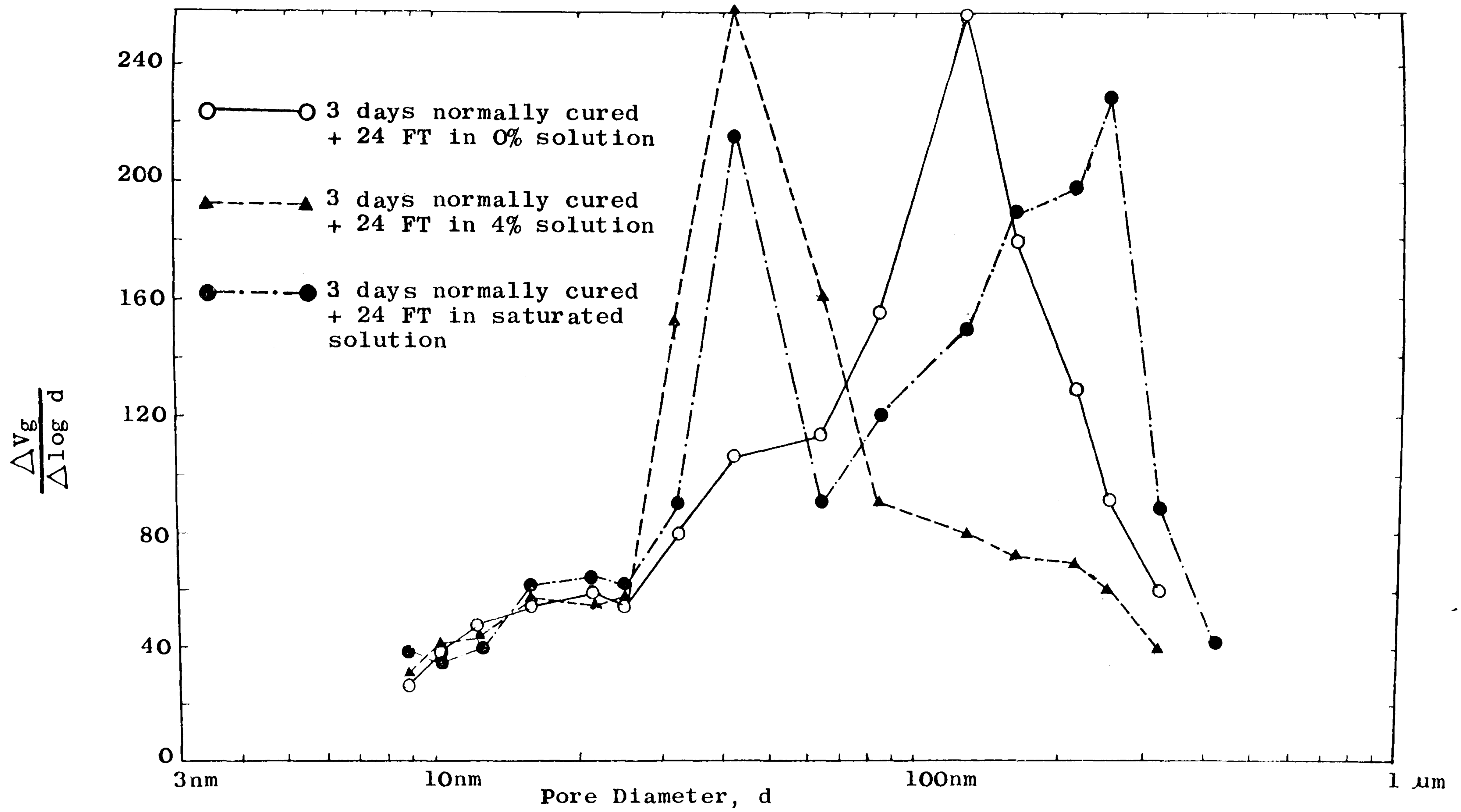

Fig. 7.7 Effect of freeze/thaw on pore size distributions of cement paste (W/C = 0.4) in different concentrations of sodium chloride solutions

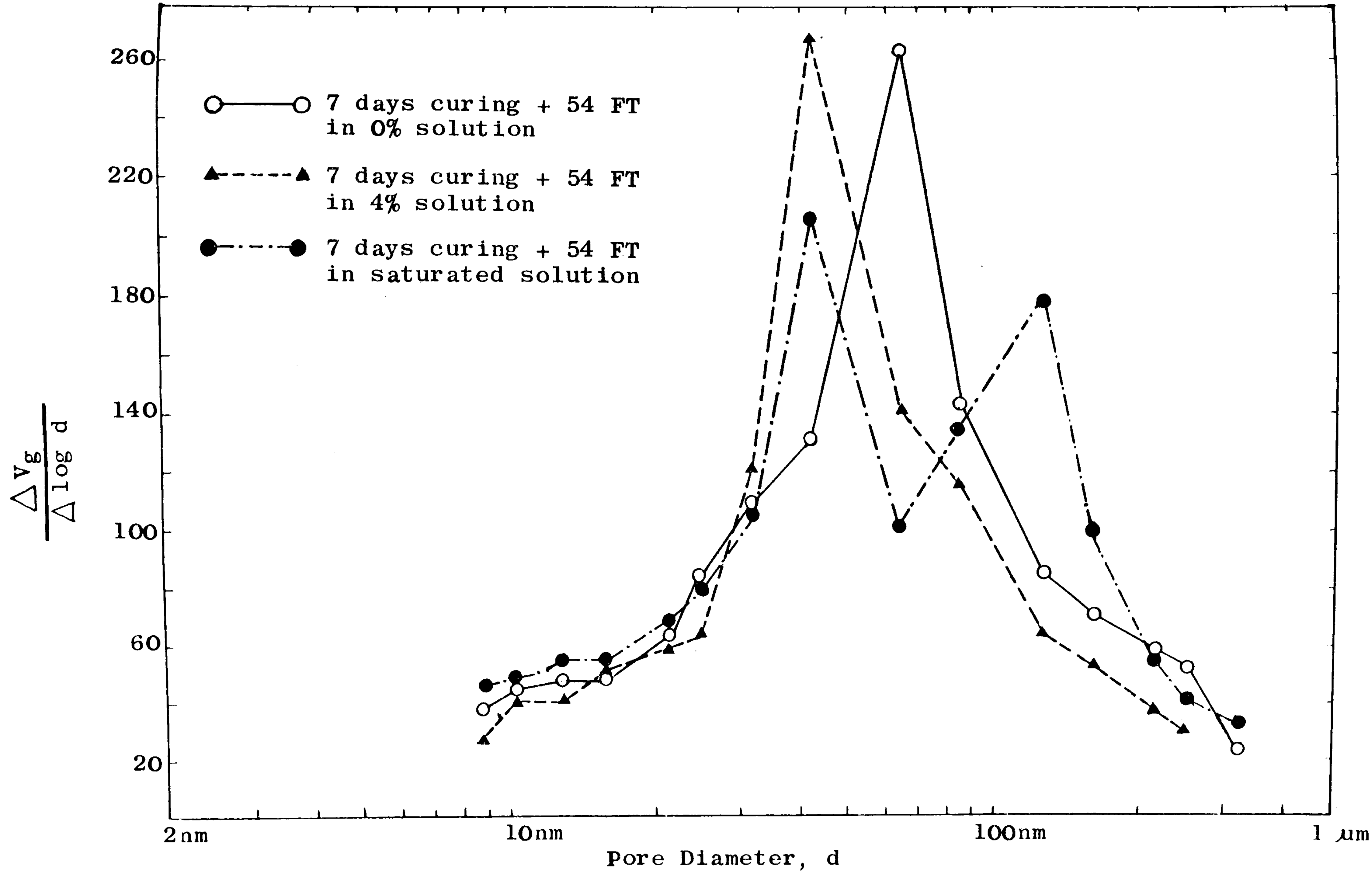

Fig. 7.8 Effect of freeze/thaw on pore size distributions of cement paste (W/C = 0.4) in solutions of sodium chloride of different concentrations

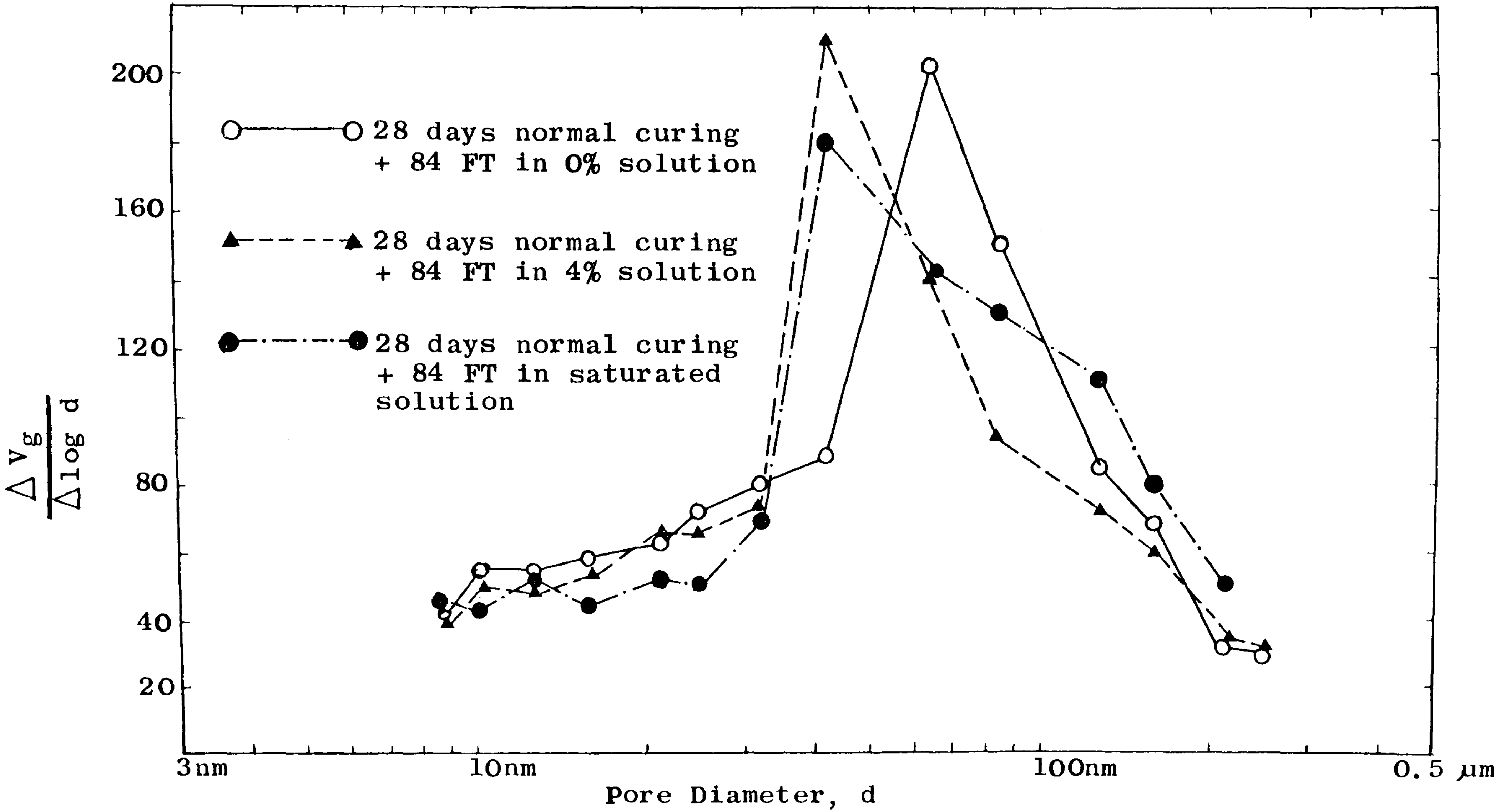

Fig. 7.9 Effect of freeze/thaw on pore size distributions of cement paste (W/C = 0.4) in different concentrations of sodium chloride solutions

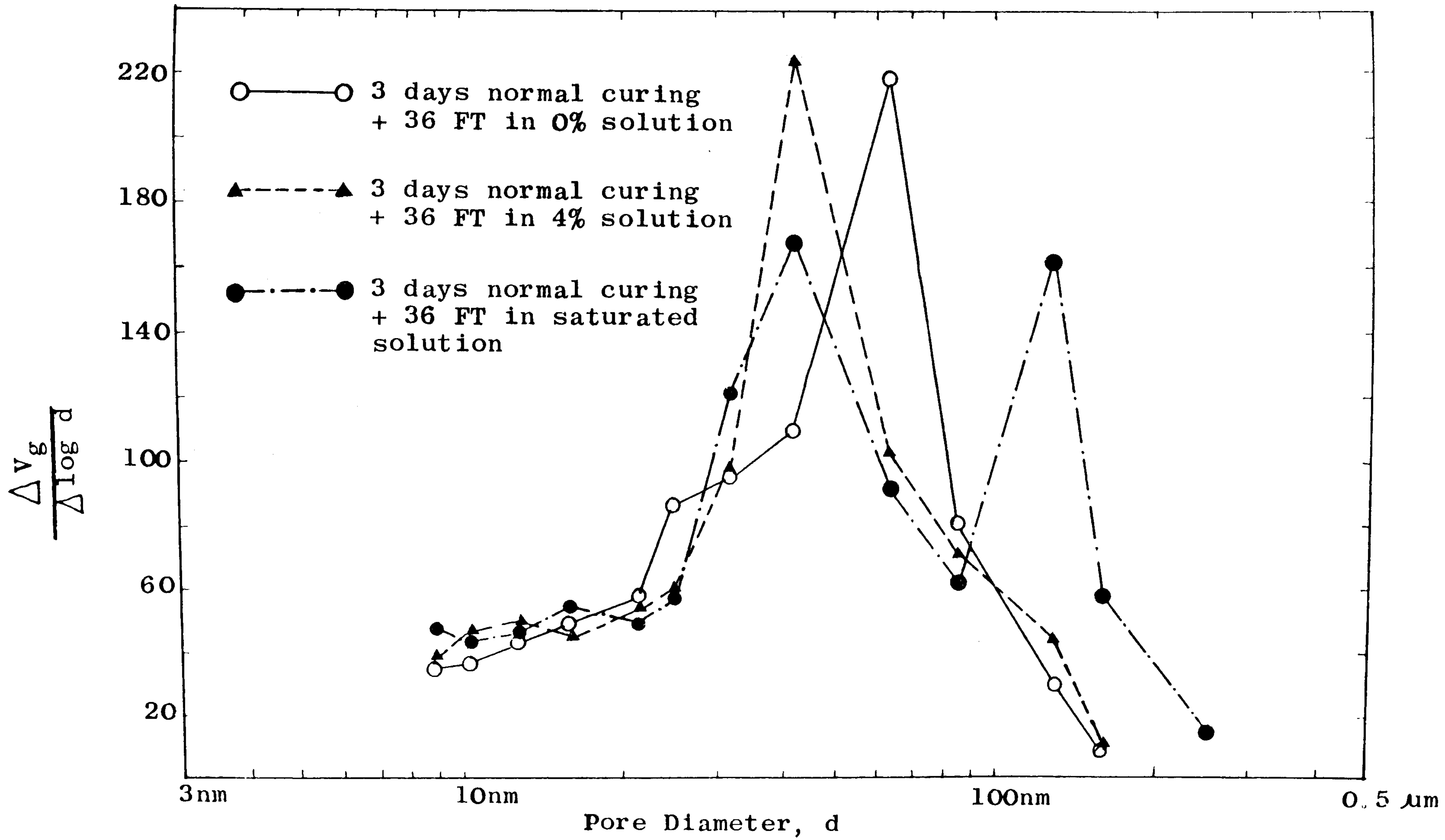

Fig. 7.10 Effect of freeze/thaw on pore size distributions of cement paste (W/C = 0.3) in solutions of sodium chloride of different concentrations

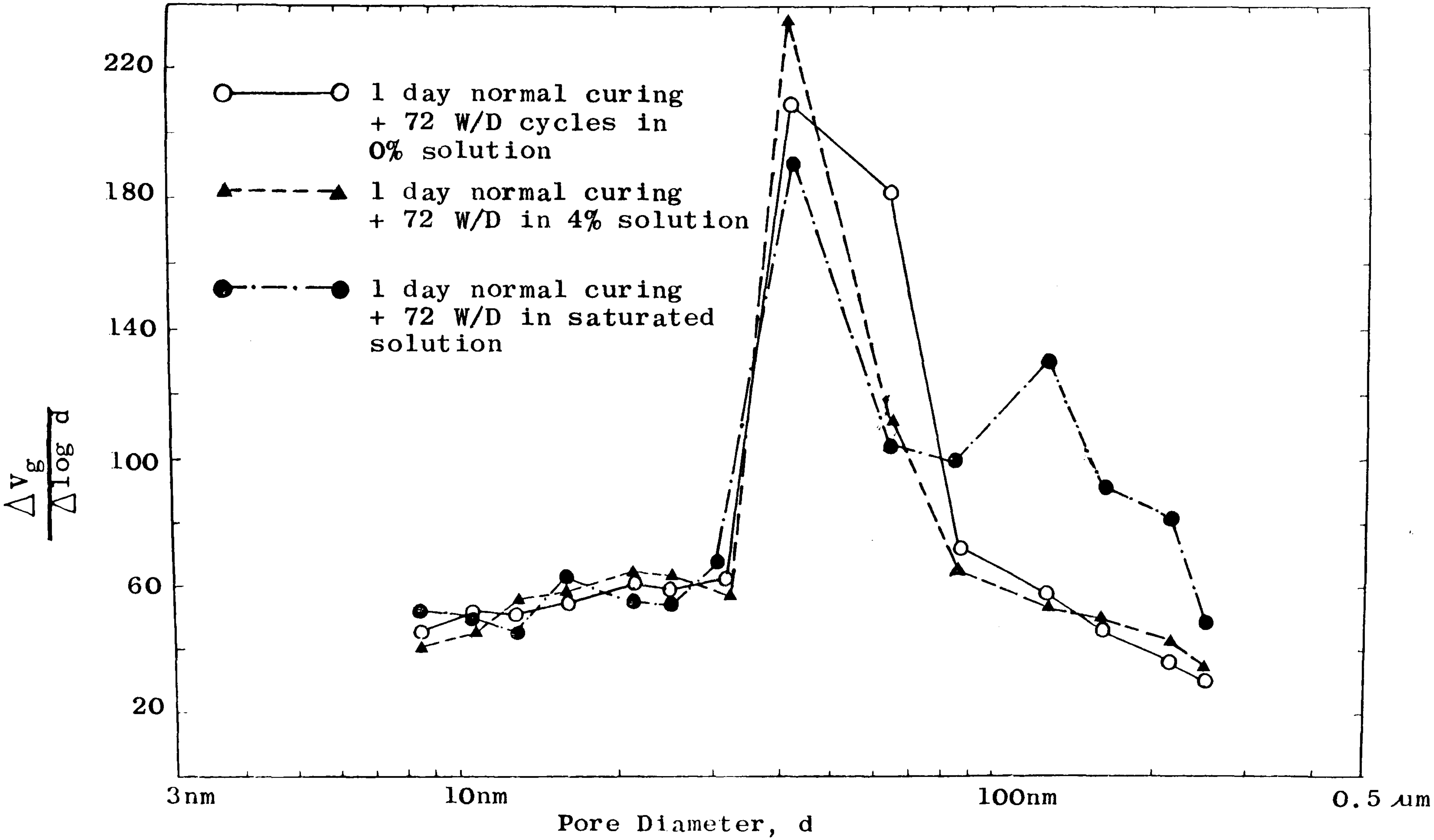

Fig. 7.11 Effect of wet/dry on the pore size distributions of cement paste (W/C = 0.4) in different concentrations of sodium chloride solutions

# CHAPTER 8

# DIFFERENTIAL THERMAL ANALYSIS OF CEMENT PASTES SUBJECTED TO FREEZE/THAW CYCLES IN PRESENCE OF SODIUM CHLORIDE SOLUTIONS

## 8.1 Introduction

The chemical reactions involved in the hydration of portland cement have been studied with increasing interest in recent years and modern techniques are gradually adding more information to that pool of knowledge. The technique of differential thermal analysis (DTA) is one of these techniques and it has provided a means of studying the hydration products of hydrating paste cured normally or subjected to any test condition.(43, 53) DTA has been applied to study the change in the hydration characteristics of cement due to the presence of chloride ions specially calcium chloride by many research workers.(32,33,39,40) Those studies were mainly concerned with the influence of calcium chloride on the hydration characteristics of the individual components of portland cement which were useful for evaluating the effect of calcium chloride on the hydration of portland cement, but similar investigations of portland cement in presence of sodium chloride are few.(58)

The freeze/thaw cycles in presence of sodium chloride solutions was found to have a deleterious effect on the strength properties, morphology and pore structure of cement pastes as discussed in the previous chapters. It was decided that DTA should be used to study the hydration mechanism of cement pastes when subjected to alternate freeze/thaw cycles in presence of solutions of sodium chloride of different concentration and an attempt made to correlate these measurements with the other properties as detailed in previous chapters. However, owing to the importance of DTA and its possible bearing on future research into the hydration characteristics of cement paste and concrete in different environments, it was considered desirable to discuss briefly the technique first and then to present the results of DTA obtained in the present investigation.

## 8.2 Thermal Analysis and Differential Thermal Analysis

Thermal analysis(155) is the name applied to a group of techniques having a common operating principle: as a sample is heated or cooled according to a predetermined programme, some physical property of the sample is recorded as a function of temperature on a thermal analysis curve. Differential thermal analysis, DTA, is one of the thermal analysis techniques which records the difference between some property of the sample and that of a standard material e.g. their temperature difference, differential measurements. The sample and a reference material are separately heated in identical environments. The reference material undergoes no thermal event in the temperature range under study, and therefore its temperature is the same as the programmed temperature throughout the heating. Hence a differential thermal curve represents the difference between the sample and reference temperatures against the furnace temperature. Recording the DTA curve of a sample is not a difficult procedure once suitable conditions are established. The interpretation of such curves involve firstly the distinction between experimental features and genuine transitions in the sample and secondly the quantification, where possible, of those transition processes. The physical processes such as reversible phase transformations (endothermic on heating) and irreversible chemical changes (exothermic) occur in DTA and are plotted in the curves.

## 8.3 Results and Discussion

### 8.3.1 Normally Cured Cement Paste

Figs. 8.1 and 8.2 illustrate the typical DTA curves of cement pastes of 0.3 and 0.4 water/cement ratios respectively, cured normally for different periods. Fig. 8.1 also illustrates a curve for the unhydrated cement used throughout these investigations. The curve for the unhydrated cement showed a typical endothermic reaction for gypsum between about 130° and 160°C. At about 475°C there was a broad endotherm for calcium hydroxide formed during exposure to the air.

After 6 hours hydration the DTA curve as in Fig. 8.1 shows double peaks around 100°C and 125°C and a small peak around 160°C. The first peak at 100°C was due to the free water present in the sample and the second at 125°C was due to the formation of tobermorite gel (CSH).

The peak near 160°C was that of gypsum as found earlier with unhydrated cement. The other peak found around 475°C indicated the start of formation of crystalline calcium hydroxide. After 1 day hydration the DTA curve showed no peak for gypsum, instead a small shoulder like formation was found to occur at around 200°C. This was due to the formation of calcium sulphoaluminate hydrate. The double peaks, i.e. those of free water and tobermorite gel became deeper. The peak of calcium hydroxide at 500°C was found to be broader than that of 6 hours hydrated sample. The 3 day, 7 day and 28 day cured samples produced similar thermal curves. The peaks for free water and calcium silicate hydrate were there as usual, the peak for the latter becoming deeper with the longer hydration period. The shoulder like formation previously noticed at 200°C grew broader with increasing hydration period. This was the calcium sulphoaluminate hydrate. There was also a marked increase in the peak for calcium hydroxide which was possibly responsible for producing a dense paste structure.

The thermal curves for 0.4 water/cement ratio paste samples (Fig. 8.2) were very similar to those of 0.3 water/cement ratio samples cured normally for similar period. These findings for normally cured paste specimens were consistent with the results obtained by other workers.(53) From all the curves in Figs. 8.1 and 8.2 it was noticed that there existed a peak like 'kinking' in the vicinity of 480°C, just before the formation of calcium hydroxide peak. The character of such 'kink' was not very clear.

### 8.2.2 Samples Cured in Salt Solutions

Figs. 8.3 and 8.4 illustrate the typical differential thermal analysis curves for cement paste specimens with 0.4 water/cement ratio cured in 4% and saturated solution of sodium chloride respectively for various periods. The specimens cured in both the solutions produced thermal curves similar in nature with those for normally cured specimens (Fig. 8.1). Differences were however noticed in the peak areas for the hydrated products such as calcium silicate hydrate, calcium sulphoaluminate, calcium hydroxide. There was also the formation of a new peak at 300-320°C.

The peak for calcium sulphoaluminate was found to form more intensely when the specimens were cured in 4% solution of sodium chloride for 1 day than that produced in normal curing for the same period of time (Fig. 8.3). In the vicinity of 320° there seemed to be the beginning of a broad peak that of calcium chloroaluminate. The peak for calcium hydroxide was deeper and its area was also increased in the case of the specimens cured in 4% solution. After 3 days of curing in 4% solution the calcium sulphoaluminate peak was increased and the formation of calcium chloroaluminate peak clearly observed. Both of these peaks were more significant in the case of the specimens cured 7 days in such solution. The 7 day cured specimens in 4% solution of sodium chloride also showed peaks of calcium hydroxide much larger in area, this increase being attributed to the presence of the chloride solution during curing.

When cured in saturated solution the DTA curves showed clear and deep peaks for calcium sulphoaluminate and calcium chloroaluminate even after 1 day (Fig. 8.4). These peaks were markedly increased in size with increasing curing period in saturated solution. The peak areas for calcium hydroxide were found to be less in such cases than those from specimens cured in 4% solution. Comparing all the thermal curves in Figs. 8.1 to 8.4 and also the formation of the calcium sulphoaluminate peaks it was concluded that the presence of sodium chloride solution enhanced the formation of calcium sulphoaluminate hydrates and also possibly formed a complex salt of calcium chloro-sulphoaluminate hydrates. It was further concluded that presence of sodium chloride in cement paste tended to produce calcium chloroaluminate hydrates but the intensity of such hydrates depended mainly on the concentrations of sodium chloride present and also on the periods of curing in such solutions.

### 8.2.3 Samples Frozen and Thawed in Salt Solutions

Fig. 8.5 illustrates the thermal curves for 3 day cured cement pastes of 0.4 water/cement ratio when subjected to 24 freeze/thaw cycles in 0%, 4% and saturated solution of sodium chloride. The thermal curve for specimens subjected to freeze/thaw cycles in water showed a broad peak of calcium sulphoaluminate hydrate at about 200°C. Such a broad peak was absent for 7 day normally cured samples and also for the samples cured normally for 28 days as in Figs. 8.1 and 8.2. The other characteristics of the curve for samples frozen and thawed in 0% solution were very similar to those of normally cured samples.

When samples of similar age were subjected to freeze/thaw cycles in 4% solution of sodium chloride, the thermal curve showed the CSH peak as usual around at 125°C, a broad deep peak of calcium sulphoaluminate at 190°C, and also a broad peak at 320°C of calcium chloroaluminate as well as the peak for calcium hydroxide at 510°C. Comparing this curve with that of 7 day normally cured sample and that of 7 day cured in 4% salt solution as in Fig. 8.3 significant differences were noticed. The peak areas for calcium sulphoaluminate and calcium chloroaluminate hydrates were increased significantly in the first curve and the peak area of calcium hydroxide was found to decrease in the curve for 3 day normally cured specimen subjected to 24 freeze/thaw cycles in 4% solution of sodium chloride.

When specimens of similar age were subjected to freeze/thaw cycles in saturated solution of sodium chloride the thermal curve differed profoundly from those mentioned earlier. The peak for calcium silicate hydrate almost vanished producing a broad single peak for loose water with a kink in the vicinity of 135°C. The peak for calcium sulphoaluminate at 190°C was intense and the peak due to calcium chloroaluminate became more intense producing a broad and deep peak at 320°C. Comparing this curve with that of specimens cured in saturated solution for 7 days, it was noticed that freeze/thaw cycles changed the characteristics of the thermal curve resulting in the formation of more calcium sulphoaluminate hydrate or possible calcium chlorosulphoaluminate hydrate and also calcium chloroaluminate hydrate. The peak for calcium hydroxide in such case was as usual in shape but with much less area than that either in normal curing or cured in 4% solution of sodium chloride.

Figs. 8.6 and 8.7 represent the thermal curves for 7 day normally cured cement paste of 0.4 water/cement ratio subjected to 54 freeze/thaw cycles and 0.3 water/cement ratio subjected to 72 freeze/thaw cycles respectively in 0%, 4% and saturated solution of sodium chloride. The nature of these curves in different solutions were very similar to the corresponding curves shown in Fig. 8.5 as mentioned above. The peaks for calcium sulphoaluminate and calcium chloroaluminate were significantly larger in area for the samples frozen and thawed in saturated solution of sodium chloride. A remarkable difference between the DTA curves for the same samples was noticed at a temperature of 580°C when the curves showed the onset of an intense exothermic peak. This type of exothermic peak was absent for samples subjected to freeze/thaw cycles either in 0% or 4% solution of sodium chloride but was present for the samples frozen and thawed in saturated solution of sodium chloride. Ramachandran(33) obtained similar effects in $C_3S$ with calcium chloride and suggested that it might have been caused by the chemisorbed chloride on the CSH surface and possibly also by chloride ions in the interlayer positions. The other interesting feature noticed was that the peak temperatures of the thermograms of different hydrates differed considerably from one another due to the variations in concentration or in composition of the chloride phase. Comparing all the thermograms in Figs. 8.3 to 8.7 it was concluded that either lower temperature or freeze/thaw cycles in salt solutions produced more calcium chloroaluminates in the cement paste, the saturated solution producing more than 4% solution. It was further concluded that calcium chlorosulphoaluminate instead of calcium sulphoaluminate was possibly the hydration product that increasingly formed due to the freeze/thaw cycles in sodium chloride solutions.

## 8.3 Conclusions

1) Calcium chloroaluminate hydrate was formed whenever cement was exposed to sodium chloride solutions of any concentration, and such hydrate increased in quantity with the increase of exposure period.

2) The formation of calcium chlorosulphoaluminate hydrate was found to increase due to the presence of sodium chloride solutions in cement pastes.

3) Freeze/thaw cycles also increased the formation of calcium chlorosulphoaluminate in cement paste and this increase was dependent on the concentration of sodium chloride solutions, higher concentration producing higher amount of such hydrate.

4) Concentration of sodium chloride had significant effect on the formation of calcium chloroaluminate in cement paste. Saturated solution produced more calcium chloroaluminate than 4% solution either in normal curing or when present in freeze/thaw cycles.

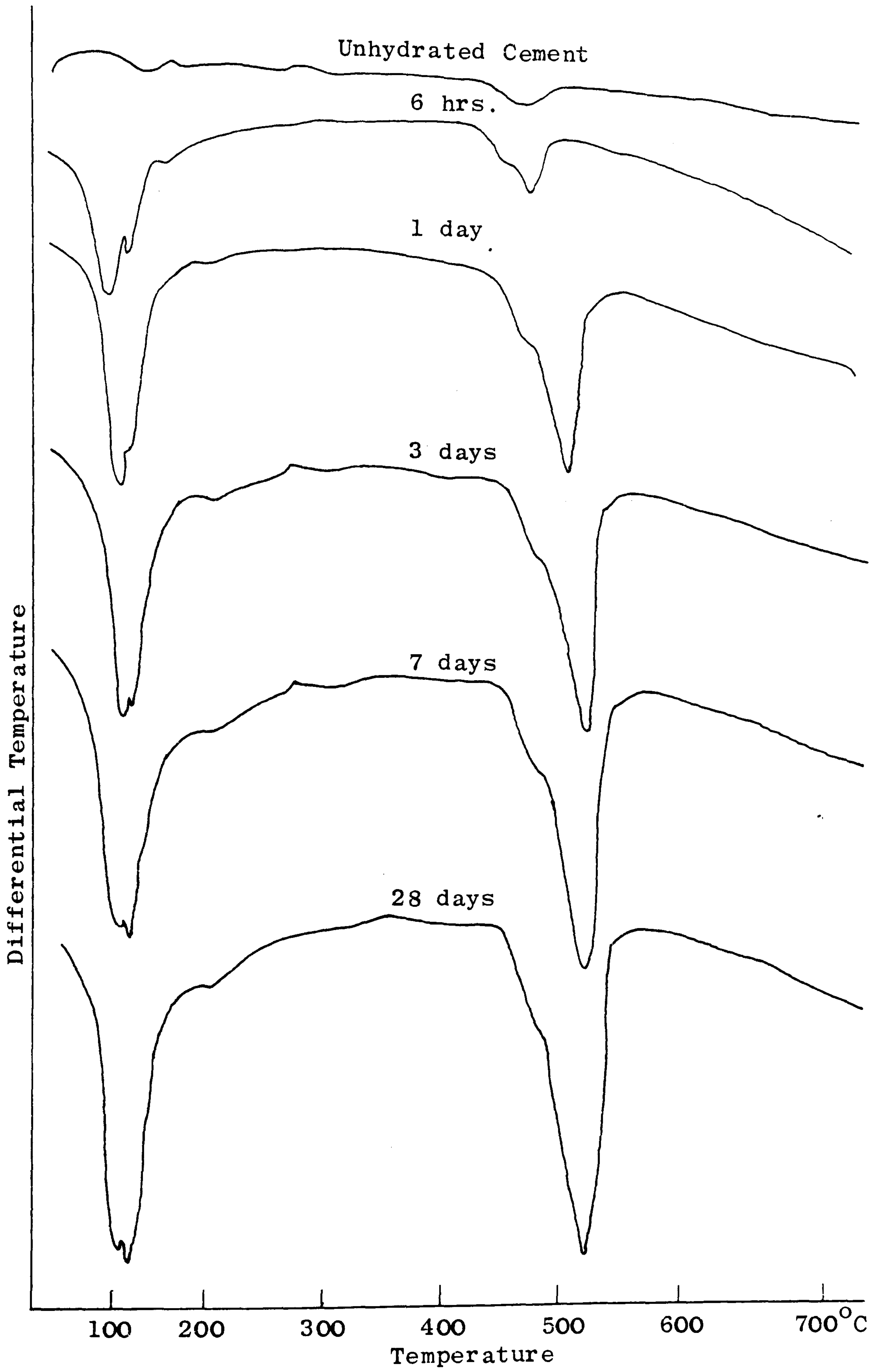

Fig. 8.1 DTA curves for normally cured cement paste (W/C = 0.3)

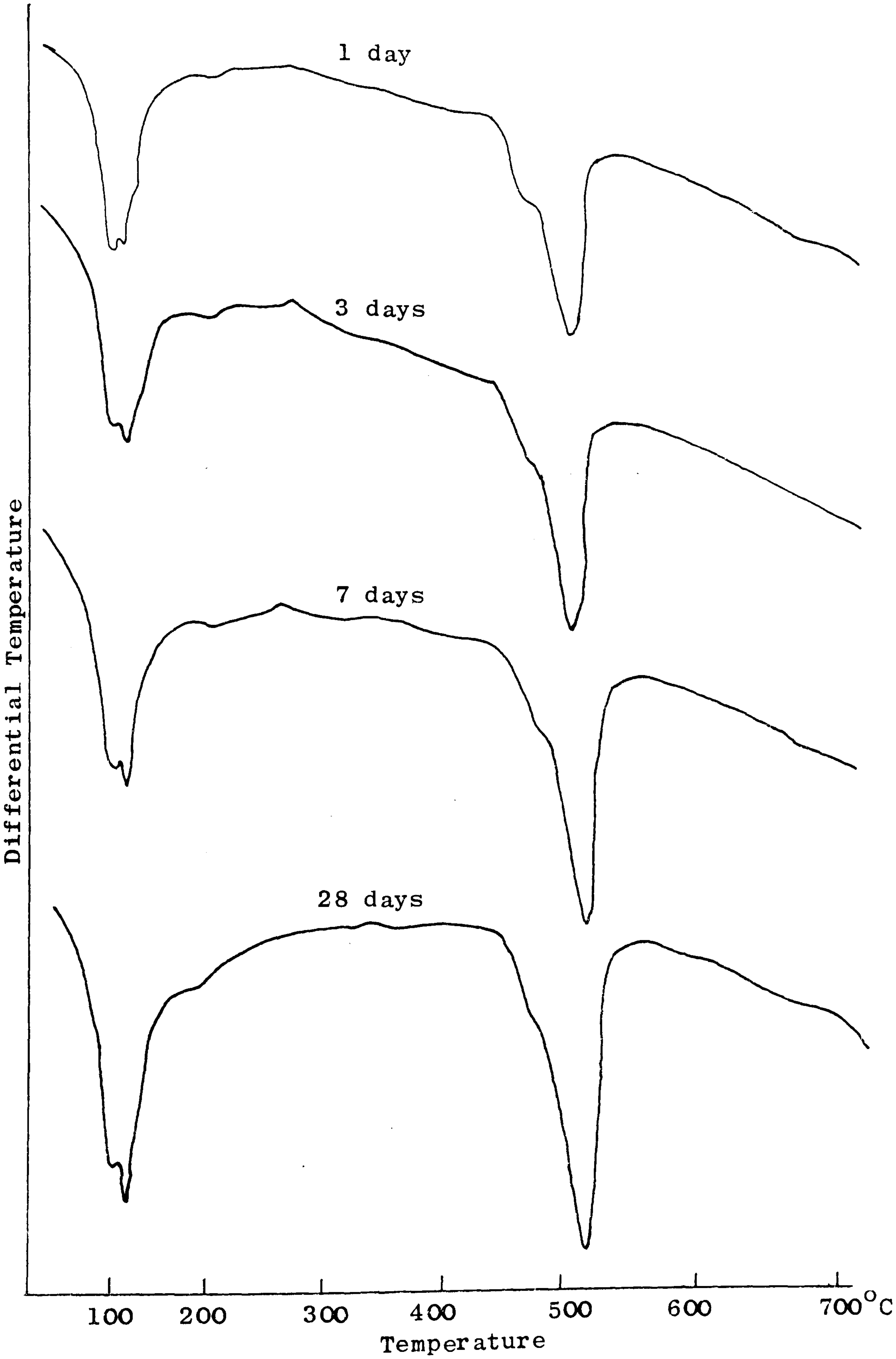

Fig. 8.2 DTA curves for normally cured cement paste (W/C = 0.4)

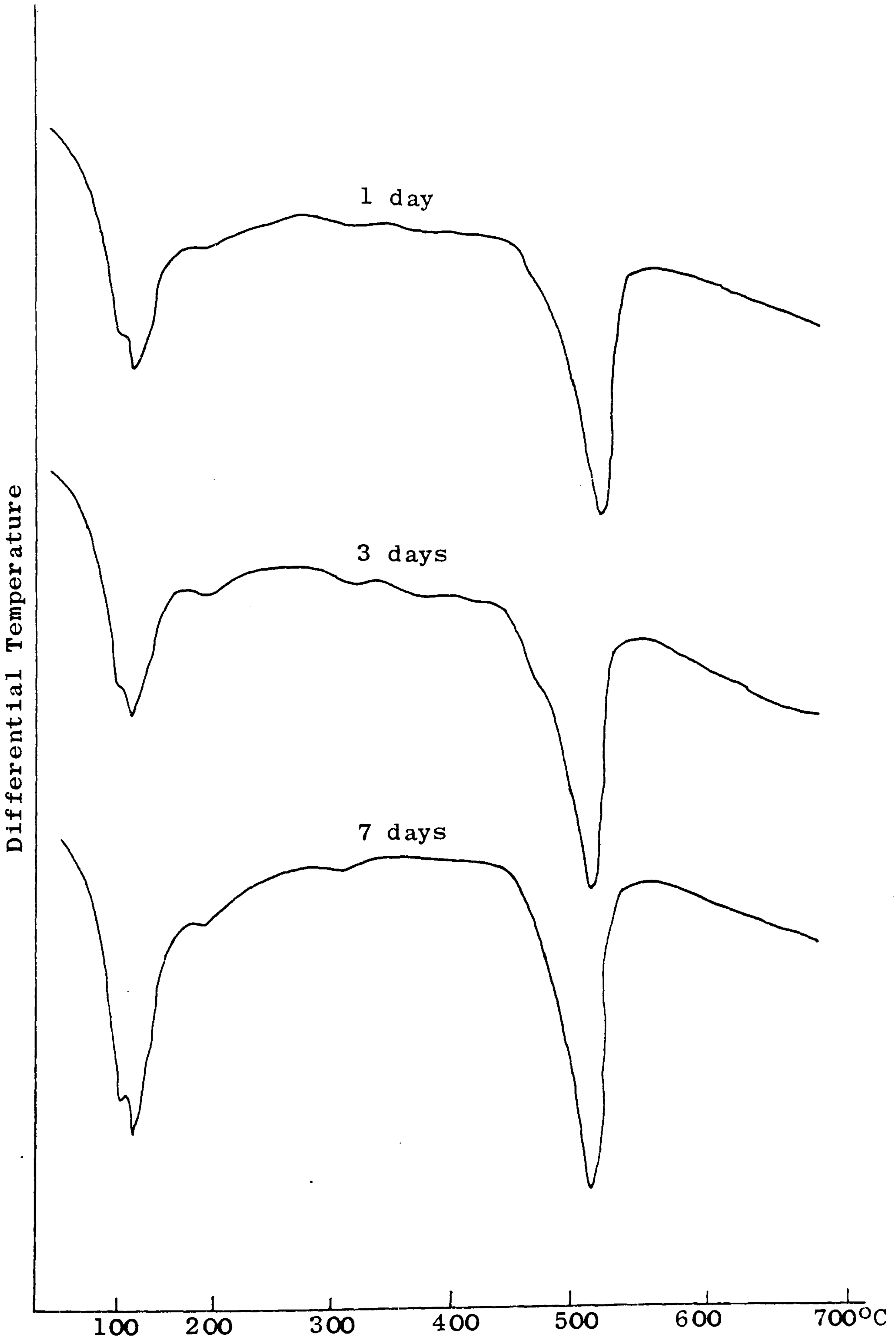

Fig. 8.3 DTA curves for cement paste (W/C = 0.4) cured in 4% solution of sodium chloride

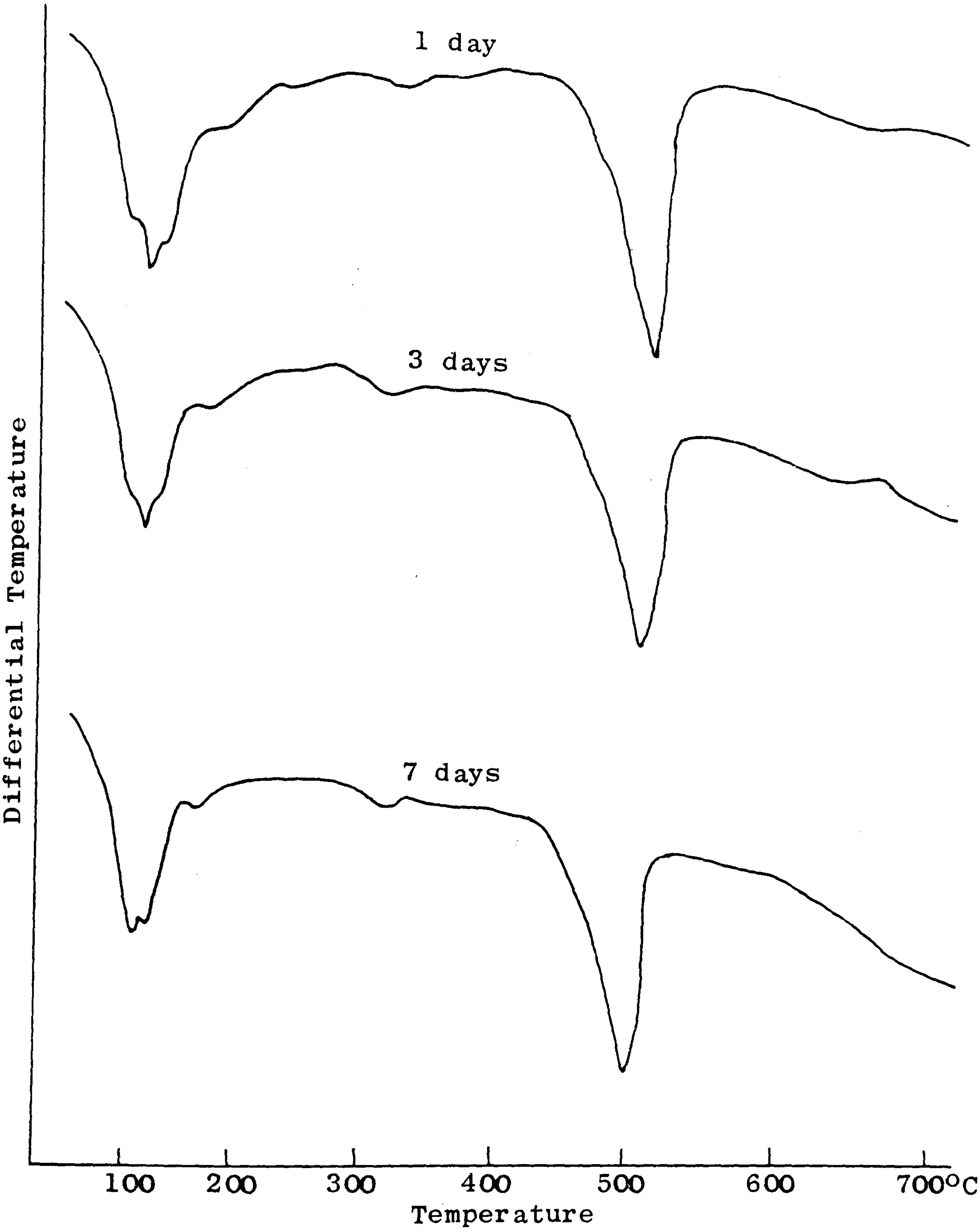

Fig. 8.4 DTA curves for cement paste (W/C = 0.4) cured in saturated solution of sodium chloride

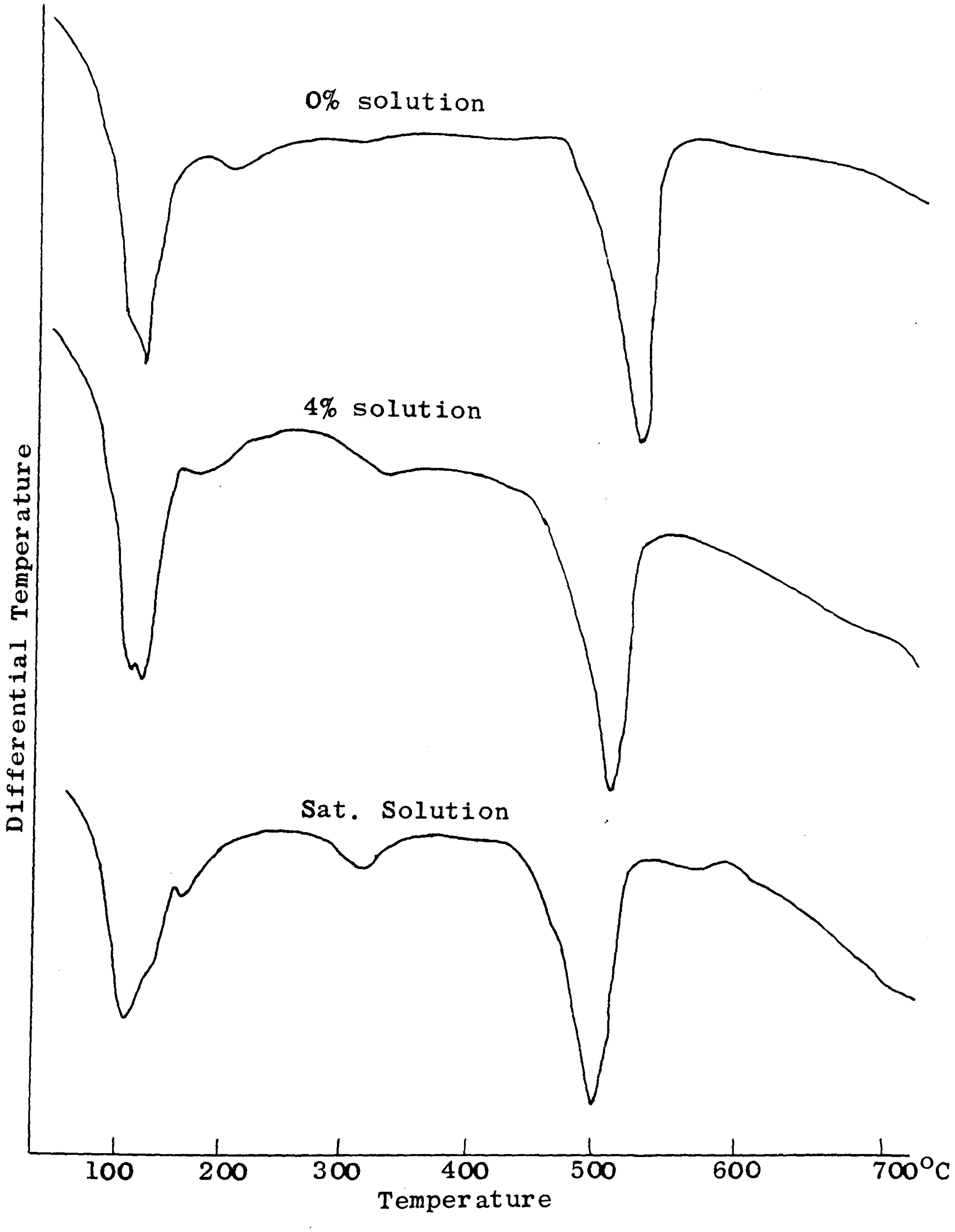

Fig. 8.5 DTA curves of 3-day normally cured cement paste (W/C = 0.4) subjected to 24 freeze/thaw cycles in different solutions of sodium chloride

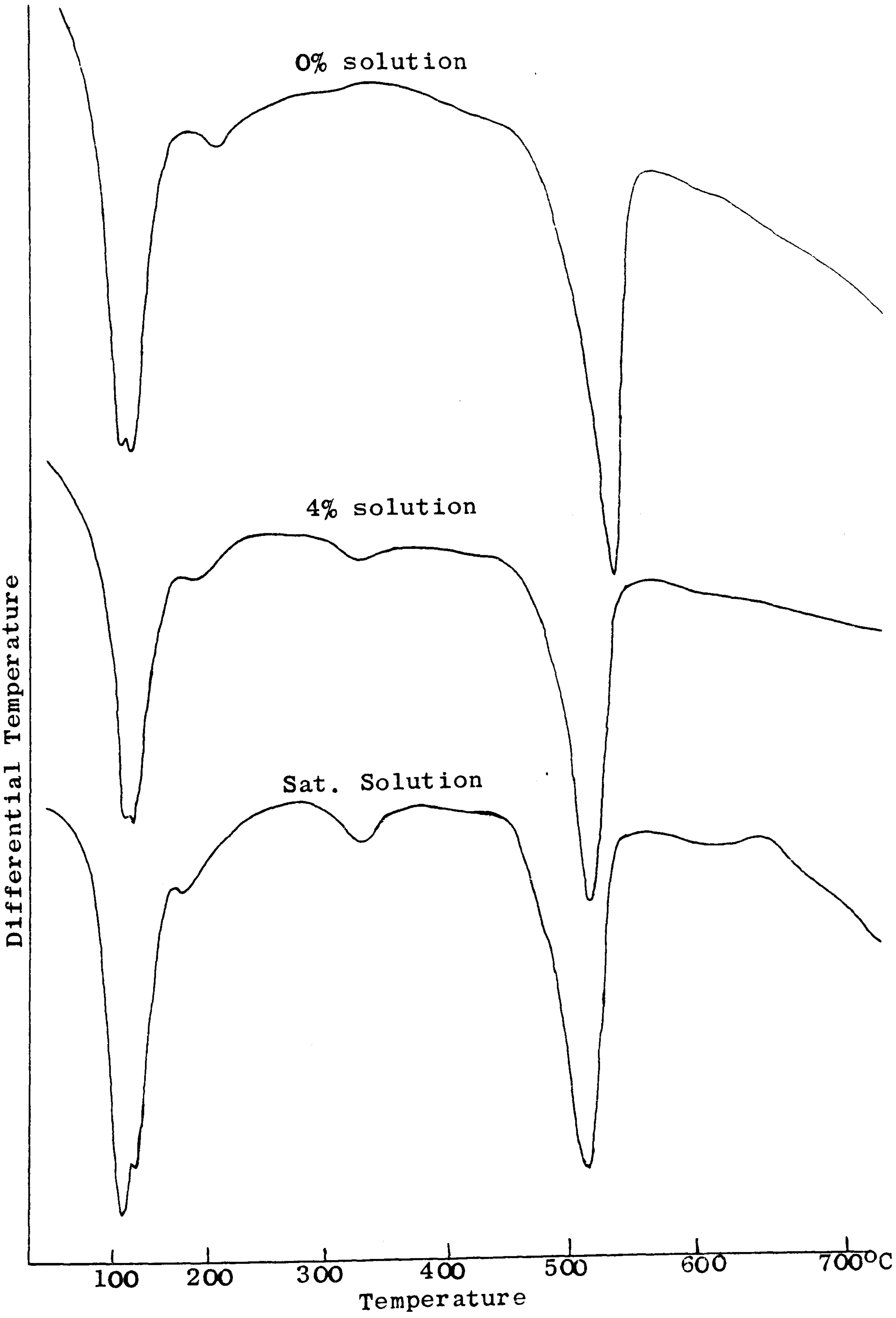

Fig. 8.6 DTA curves of 7 day normally cured cement paste (W/C = 0.4) subjected to 54 freeze/thaw cycles in different solutions of sodium chloride

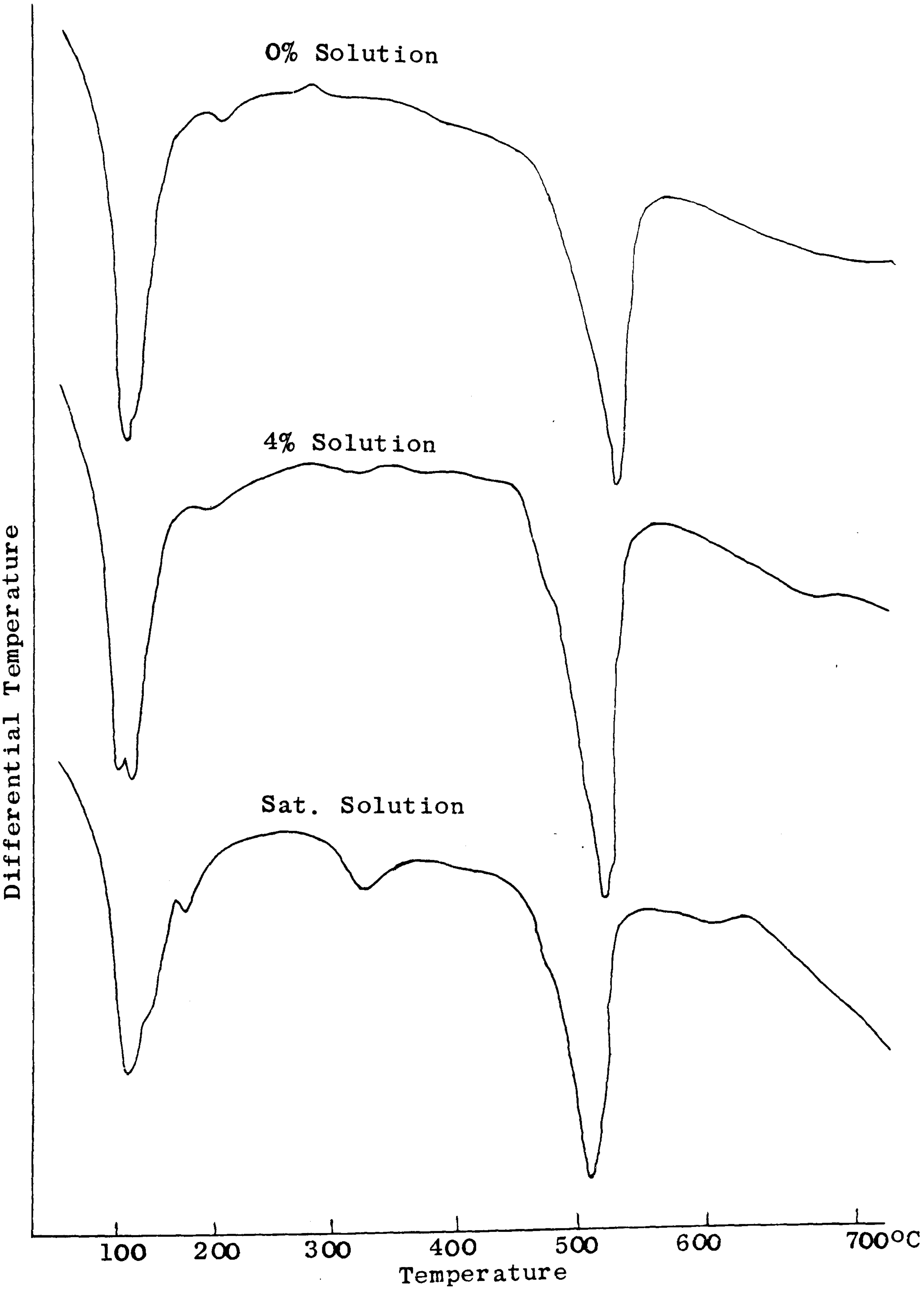

Fig. 8.7 DTA curves for 7 day normally cured cement paste (W/C = 0.3) subjected to 72 freeze/thaw cycles in different solutions of sodium chloride

# CHAPTER 9

# RELATIONSHIP BETWEEN MICROSTRUCTURAL FEATURES AND STRENGTH CHARACTERISTICS OF PORTLAND CEMENT PASTES SUBJECTED TO FREEZE/THAW AND WET/DRY CYCLES IN SALT SOLUTIONS

## 9.1 Introduction

In chapters 4 and 5 a study of the strength properties, such as compressive as well as flexural strengths of cement pastes and mortars subjected to alternate freeze/thaw and wet/dry cycles in different solutions of sodium chloride was made and the subsequent results in connection with the deterioration of the pastes and mortars have been illustrated and discussed. The subsequent chapters were concerned with the study of the microstructural features of hardened cement pastes subjected to similar testing conditions. The techniques used were scanning electron microscopy, x-ray spectrometry, mercury intrusion porosimetry and differential thermal analysis. The changes in the microstructural features as a result of freeze/thaw and wet/dry cycles in presence of sodium chloride solutions of different concentration have also been illustrated and discussed. In this chapter an attempt will be made to relate the development and changes in strength characteristics to the development and changes that occur in the microstructural features of cement pastes. This relationship has been carried out in the light of some important previous investigations and findings which the author believes to be worth mentioning in brief.

## 9.2 Effects of Pores

### 9.2.1 Everett's Thermodynamic Model

Everett(111) presented a thermodynamic model to account for crystal growth in porous structure (the model is described in Appendix A). From his model he deduced that frost damage is associated with structures in which coarse pores are separated from one another by microporous regions. For a material like hardened cement paste of a given mechanical strength, there will be a critical pore size difference which if present, may lead to frost damage.

### 9.2.2 The Concept of Hasselman and Fulrath

Hasselman and Fulrath(156) investigated the effect of stress concentrations on strength of composite materials to determine whether engineering stress concentration theories could be applied to these types of material. On the basis of the experimental work a hypothesis was developed relating the relative size of the region in the glass matrix over which stress concentrations act to the size of Griffith flaws(157) responsible for failure. Based on this hypothesis, the effect of porosity on strength can be viewed in terms of three possible conditions;

a) The pore size and resultant micromechanical stress fields are large relative to the size of the Griffith flaw.

b) The flaw size is of the order of the pore size.

c) The pore size is small relative to the flaw size.

In case (a) the pore size is substantially larger than the flaw size, so that a flaw lies entirely in material stressed to the maximum value of stress concentration. Here the stress concentration approach can be applied successfully and the strength shows a precipitous decrease after the introduction of a small fraction of pores. For case (c) the pore is considerably smaller than the Griffith flaw and it will be completely unaffected by the stress concentrations near the pores. Strength should show a monotonic decrease with increasing porosity without the precipitous decrease in strength characteristics of case (a). In intermediate case (b) the flaw size is of the order of the pore size so that only a segment of the flaw is subjected to the stress concentration. The effect of porosity on strength in this region causes a precipitous decrease in strength on introduction of the first pore but not to a value corresponding to the maximum stress.

## 9.3 Interrelation Between Mechanical Properties and Microstructural Features of Cement Pastes Obtained from various Test Conditions

Figs. 9.1 to 9.4 illustrate the percentage changes in compressive as well as flexural strengths of 3 day and 7 day initially cured cement paste specimens of both 0.4 and 0.3 water/cement ratios when subjected to different number of freeze/thaw cycles in 0%, 4% and saturated solution of sodium chloride. From all these figures it was clearly noticed that freezing and thawing in saturated solution of sodium chloride caused maximum losses of compressive and flexural strengths of cement pastes at any number of cycle whereas 4% solution caused the minimum losses of strengths even less than those in 0% solution. In chapter 4 detailed results of strength properties of the paste specimens subjected to freeze/thaw cycles in various concentrations of sodium chloride solutions were given and discussed. In Figs. 9.1 to 9.4 it may also be noticed that the rate of fall in flexural strength of paste specimens at any number of freeze/thaw cycles was greater than that in compressive strength. The 7 day normally cured paste specimens of 0.3 water/cement ratio gained 5% and 8% of their initial 7 day compressive strength after being subjected to 72 freeze/thaw cycles in 0% and 4% solutions of sodium chloride respectively. But similar specimens in the saturated solution lost 11% of their initial compressive strength after 72 freeze/thaw cycles. Similar specimens lost 21%, 14% and 45% of their initial 7 day flexural strength after 72 freeze/thaw cycles in 0%, 4% and saturated solution of sodium chloride (Fig. 9.4). Microcracking inside the specimens and the subsequent crack propagation were thought to be the causes for such behaviour. This concept was further supplemented by the results of strength properties of mortar specimens when subjected to freeze/thaw cycles in the solutions. In each solution the mortar specimens showed much better resistance than the paste specimens against freeze/thaw cycles (Figs. 4.9-4.11, 4.23, 4.24). The aggregate particles were responsible for the arrest in the crack propagation resulting in better resistance to freeze/thaw cycles. The saturated solution was once again found to cause the maximum deterioration of compressive and flexural strengths of the mortar specimens and the 4% solution caused the minimum. But an interesting feature was noticed in that the mortar specimens frozen and thawed in 4% solutions of sodium chloride showed gradual crumbling of the surfaces with increasing numbers of cycles without showing any deep cracking, scaling or spalling of the material. The saturated solution on the other hand produced cracks initially which became wider and finally at a larger number of freeze/thaw cycles separated a large portion of material altogether from the mortar specimens. These features are well illustrated in Figs. 9.5 and 9.6 which show the photographs of 3 day initially cured mortar specimens subjected to freeze/thaw cycles in saturated and 4% solution of sodium chloride respectively.

The process of surface deterioration in case of paste specimens showed different behaviour. The 4% solution did not show any gradual crumbling instead scaling and spalling were found and these were increased with the increase of cycles. On the other hand the saturated solution caused scaling and spalling comparatively in a lesser degree but large number of minute cracks were found with the increase of freeze/thaw cycles. These cracks on many occasions became continuous and separated the specimens into two or more pieces. Even 28 day initially cured paste specimens were found to break into two pieces after 216 freeze/thaw cycles in saturated solution, though no sign of scale was observed in this case. The observation of maximum surface deterioration in paste and mortar specimens when subjected to freeze/thaw cycles in 4% solution of sodium chloride was consistent with the findings of Verbeck and Kleiger.(102) Figs. 9.7 to 9.9 show the photographs of paste specimens subjected to freeze/thaw cycles in solutions of sodium chloride for different test conditions.

The morphological features of the paste specimens when subjected to freeze/thaw cycles in solutions as detailed in chapter 6 appeared to have a significant effect on the different behaviour of strength properties. Figs. 6.17 - 6.19 showed that the freezing and thawing cycles in saturated solution produced numerous long needles in the fracture surface of cement paste. These long needles of calcium sulphoaluminate hydrates or calcium chlorosulphoaluminate hydrates and calcium chloroaluminate grew longer with the increase of freeze/thaw cycles. The growth of large number of such needle like structures caused the initial microcracking inside the paste specimens which at later stages propagated at further increase of cycles. The solutions moving into the cracks also exerted pressure against the material when frozen. The 4% solution on the other hand changed the morphological features into a 'lace like' structure and also produced few needle like structures (Figs. 6.13-6.16). Study of fracture surface of paste specimens when subjected to freeze/thaw cycles in 0% solution showed broken coarse grained portlandite crystals surrounded by large voids (Fig. 6.11). Williamson(77) has also suggested portlandite crystals as one of the probable flaws in cement pastes. These cleaved portlandite crystals surrounded by large pores were responsible for the losses of strength of the paste specimens subjected to freeze/thaw cycles in 0% solution.

The pore size distributions of the paste specimens were found to have very significant effect on their strength properties. The presence of 4% solution of sodium chloride immediately produced microporous structure in pastes resulting in large volumes of smaller pores in the diameter range of 30-70 nm. The increased rate of hydration due to the presence of chloride ions at this concentration produced such a structure. This was also revealed in the micrographs from the scanning electron microscope where lace like formations of CSH hydrates were noticed. Initially these smaller diameter pores probably formed near the surface of the paste specimens. The minimum loss of strengths as found with the specimens subjected to freeze/thaw cycles in 4% solution of sodium chloride was due to the increased hydration. But in such specimens the surface deterioration in the form of scaling was found to be maximum. This discrepancy, less loss in strengths but more scaling may be explained qualitatively in terms of the theory developed by Everett.(111) The formation of smaller pores near the surfaces separated from comparatively larger pores inside the specimens caused excess pressure resulting in local failures in the form of scaling. The gradual crumbling of mortar specimens was also due to similar effects. In the case of paste specimens the excess pressure caused a crack at a particular point near the surface and the crack finally propagated removing some material in the form of scales but in case of mortars the excess pressure loosened the aggregate particles causing gradual crumbling. The formation of smaller diameter pores near the surface as detailed above can also be argued from the observations of mortar specimens when subjected to freeze/thaw cycles in 4% solution of sodium chloride. The gradual crumbling of materials was the resultant of the increase in freeze/thaw cycles. The solution produced micropores near the surface as usual separating the larger pores inside. When freezing occurred pressure was exerted and cracks were formed near the surfaces. Due to the presence of aggregate particles cracks propagated along the periphery of the aggregates as they were strong enough to be penetrated. This mechanism loosened the particles causing crumbling. Further freezing cycles acted on subsequent layers and, as a result, gradual crumbling of particles was noticed with increasing number of freeze thaw cycles. Fig. 9.6 illustrates such specimens of different freeze/thaw cycle.

The specimens when subjected to freeze/thaw cycles in saturated solution produced different pore size distributions. These specimens showed a considerably larger percentage of pores in the diameter range greater than 80 nm as discussed in chapter 7. This would appear to have a very significant effect on the strength properties of the material as discussed in chapter 4. The discrepancy in the strengths may be explained qualitatively in terms of the theory developed by Hasselman and Fulrath.(157) In the light of this theory it may be seen that large pores tend to produce a more significant fall in strength than those which are small or of the same order of size as Griffith flaws. The specimens frozen and thawed in 0% solution also produced significant amount of larger pores which again were responsible for loss of strengths.

The study of the hydration products made by DTA added further information and confirmed the mechanism which caused the deterioration in strength of paste specimens subjected to freeze/thaw cycles in different solutions of sodium chloride. The 4% solution produced comparatively larger peaks of calcium hydroxide at any number of freeze/thaw cycles in the paste specimens. The C-S-H peaks were also deeper. Such significant peaks were the result of accelerated hydration of cement pastes due to the presence of 4% solution of sodium chloride and these specimens showed better strength properties than the specimens in other solutions. Specimens subjected to freeze/thaw cycles in saturated solution produced comparatively smaller peaks of calcium hydroxide and the C-S-H peaks were also found to disappear or to form very insignificantly. The formation of calcium chloroaluminate peak at 320°C was large for the specimens subjected to freeze/thaw cycles in saturated solution and this peak was found to increase with the increase of freeze/thaw cycles. This observation was consistent with the findings of Serb-Serbina et al.(55) The peaks for calcium sulphoaluminate hydrates at about 200°C were also found to be very intense due to the presence of saturated solution of sodium chloride. The scanning electron micrographs revealed numerous needle like crystals that of calcium sulphoaluminate and calcium chloroaluminate. The growth of these crystals appeared to have significant effect on the strength properties of paste specimens subjected to freeze/thaw cycles in saturated solution of sodium chloride as discussed earlier. The calcium chloroaluminate was also formed in the paste specimens when subjected to freeze/thaw cycles in 4% solution but the amount of such hydrate, as observed in the DTA results, was much less than that in saturated solution of sodium chloride. Increased freeze/thaw cycles also caused a larger quantity of calcium chloroaluminate hydrates to be formed in 4% solution as noticed in DTA curves in Figs. 8.6 and 8.7. The significant formation of such hydrates at a greater number of freeze/thaw cycles in 4% solution appeared to have influenced the flexural strengths of paste specimens. The flexural strengths were found to drop sharply in these cases having similarity with the specimens in saturated solution.

The chloride content analyses at 6 mm intervals to a depth of 25 mm in the paste specimens subjected to freeze/thaw cycles revealed different distributions of chlorides in 4% and saturated solution of sodium chloride. The specimens in saturated solution appeared to have an almost constant distribution of chlorides throughout the depth up to 25 mm as shown in Fig. 9.10. The specimens in 4% solution of sodium chloride displayed a normal diffusion type chloride distribution, higher concentration at the surface, decreasing with depth (Fig. 9.11). This observation was further supplemented by the results of DTA of samples taken from 6 mm intervals up to 25 mm depth of the specimens subjected to freeze/thaw cycles in 4% and saturated solution of sodium chloride as in Figs. 9.12 and 9.13. The DTA curves of samples taken at different depths from the specimens subjected to 36 freeze/thaw cycles in saturated solution showed peaks of calcium chloroaluminate hydrates at 320°C which were almost equal in area. But curves for similar samples from specimens subjected to 36 freeze/thaw cycles in 4% solution showed such peaks of different sizes at around 320°C. The sample taken from surfaces up to 6 mm depth showed a considerably bigger peak for calcium chloroaluminate hydrates, but this peak was found to decrease in area with increasing depth. Microporosity of the specimens as found with 4% solution of sodium chloride reduced the diffusion mechanism whereas formation of larger pores and the microcracks formed near the surfaces of the specimens when subjected to freeze/

thaw cycles in saturated solution increased the permeability of the material to chlorine ions. As a result reactions took place at a further depth inside the specimens and calcium chloroaluminate and calcium chlorosulphoaluminate hydrates were formed as found in the electron micrographs. The growth of the crystals of such hydrates again exerted pressure initiating further cracks inside the specimens which in turn made the specimens more permeable to chlorine ions. This mechanism continued with the increase of freeze/thaw cycles and affected the strengths of paste and mortar specimens. It was therefore concluded that freeze/thaw cycles in solutions of sodium chloride of different concentration produced chemical as well as physical attack on cement pastes and mortars resulting in significant losses of strength.

The paste specimens of 0.4 water/cement ratio cured normally for 3 days and subjected to freeze/thaw cycles in different solutions of sodium chloride suffered maximum losses in their compressive and flexural strengths and the rate of such loss was also maximum. But similar specimens with 0.3 water/cement ratio were found to be more resistant and they lost less strengths. The water/cement ratio of the mix played an important role in this case and the chemical attack as mentioned above coupled with the dependence of the hydraulic pressure mechanism explains such behaviour of paste specimens of immature age. The mature specimens such as 28 day normally cured specimens of both 0.3 and 0.4 water/cement ratios showed no loss in compressive strengths even after 180 freeze/thaw cycles in any solution of sodium chloride (Figs. 4.1-4.6). But the flexural strengths of similar specimens dropped significantly (Figs. 4.15-4.20) under similar conditions because of the formation of microcracks and their subsequent propagation.

When the paste specimens were subjected to wet/dry cycles in salt solutions similar microstructural features as before were observed. The long needle like crystals of calcium sulphoaluminate and calcium chloroaluminate were seen in the micrographs (e.g. Fig. 6.26). The crystals were in abundance when the specimens were subjected to wet/dry cycles in a saturated solution of sodium chloride. These crystals caused the flexural strengths of paste specimens to fall considerably after a number of wet/dry cycles. Since freezing and thawing cycles were absent the deterioration process was slow with wet/dry cycles. It was therefore concluded that concrete should not be placed in contact with sodium chloride especially when freezing occurs, if present, the concrete should be properly cured at least for 28 days before it is subjected to any chloride environments.

Air entrained cement paste specimens were found to provide much better resistance against freeze/thaw cycles in solutions of sodium chloride (Figs. 4.14 and 4.25). After 144 freeze/thaw cycles the losses in compressive and flexural strengths of air entrained paste specimens were found to be significantly less than those of specimens without air entrainment subjected to 72 freeze/thaw cycles in solutions of sodium chloride. In the case of air entrained specimens the formation of microcracks were delayed. The air bubbles received the expelled solution without disruption of the material and the chemical reactions occurred inside the bubbles. As a result the needle like crystals could grow longer without exerting additional pressure on the walls of the bubbles. The micrographs also revealed such morphology as in Figs. 6.22 and 6.23. But at a considerably larger number of freeze/thaw cycles the needle like crystals grew much longer and started to exert pressure initiating microcracks. These in turn affected the strengths of the specimens. It was therefore concluded that air entrainment in concrete provides much better resistance against freeze/thaw cycles in sodium chloride solutions but it is not the absolute solution against such attack.

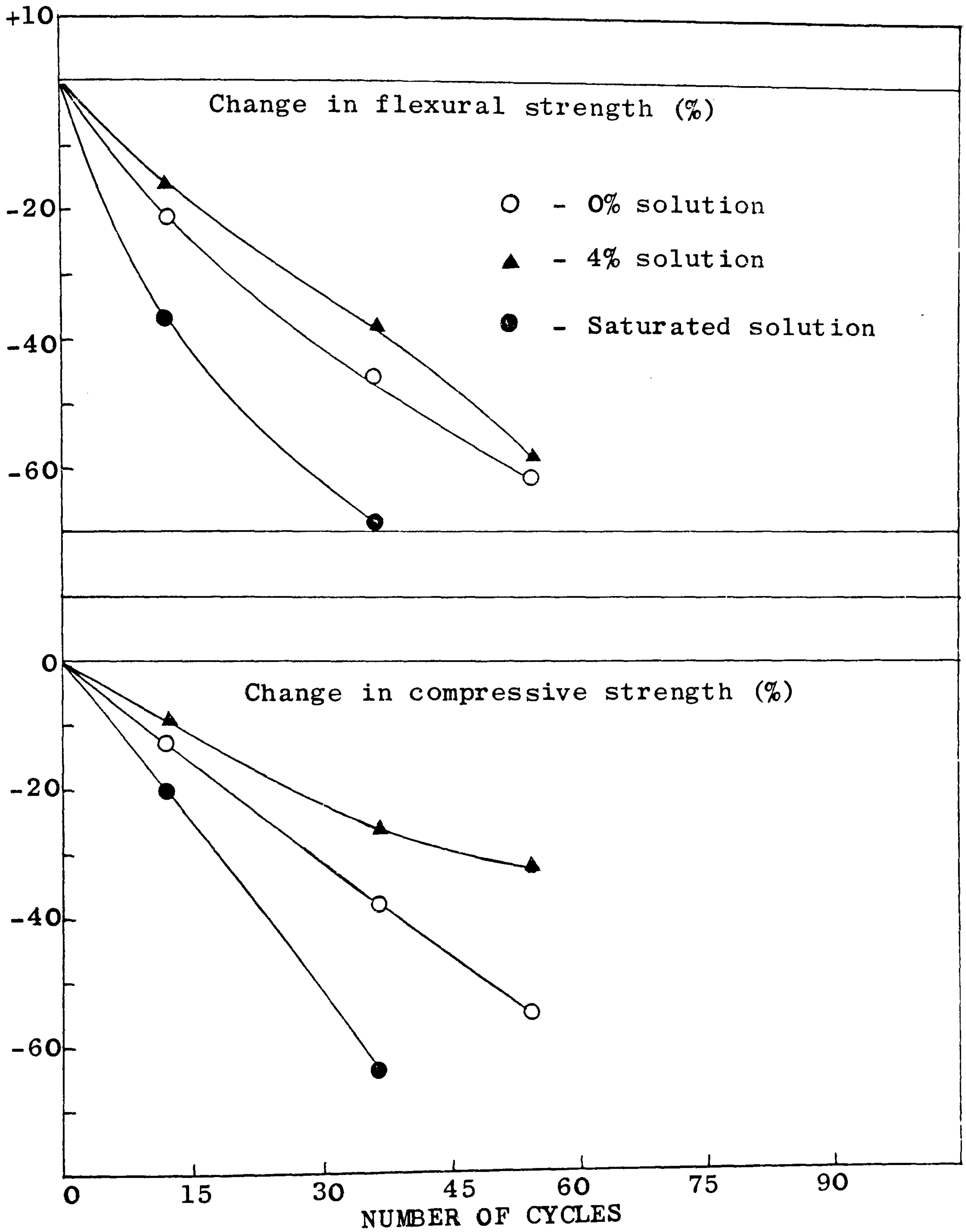

Fig. 9.1 Effect of freeze/thaw cycles on 3 day normally cured cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

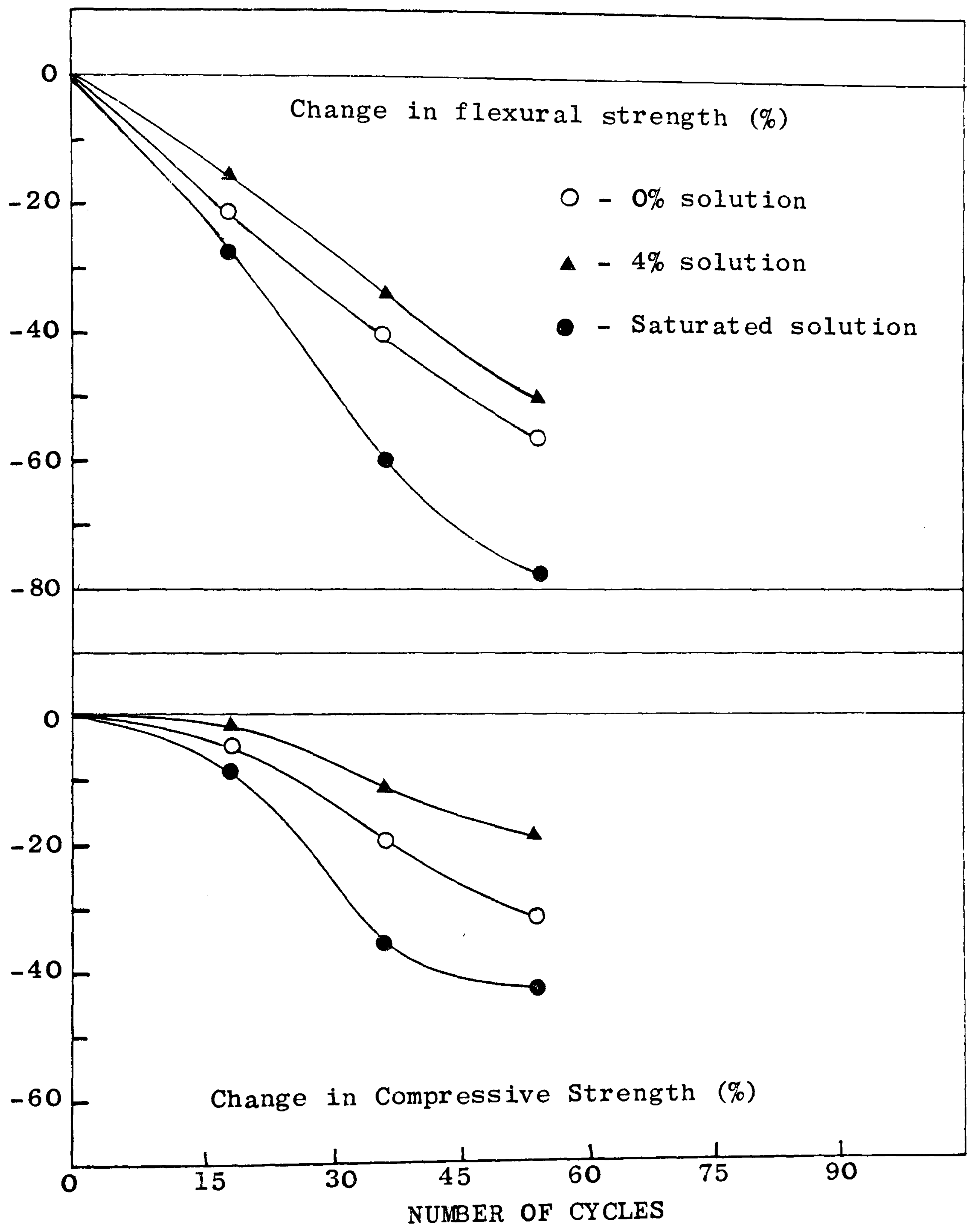

Fig. 9.2 Effect of freeze/thaw cycles on 7-day normally cured cement paste (W/C = 0.4) in sodium chloride solutions of different concentrations

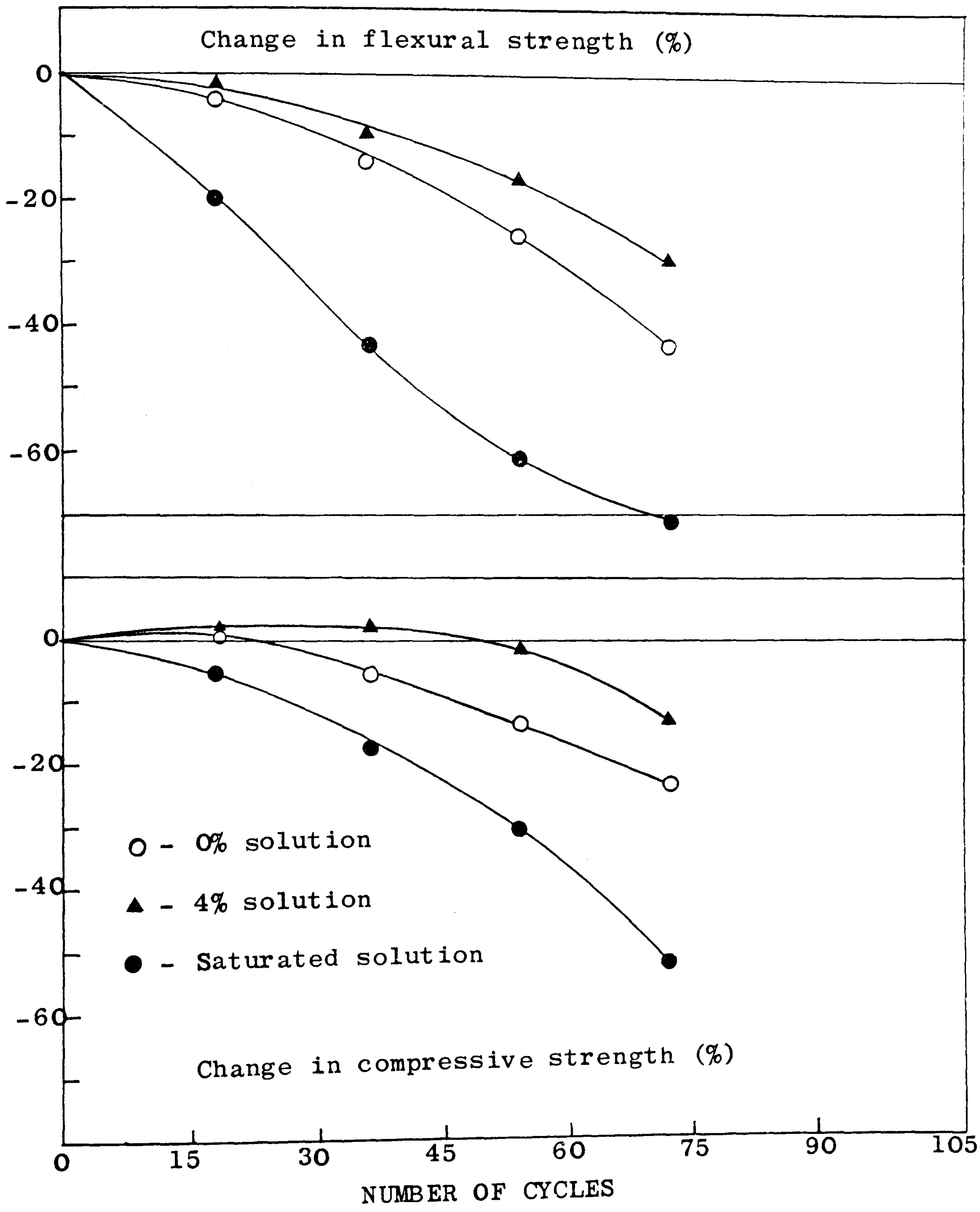

Fig. 9.3 Effect of freeze/thaw cycles on 3 day normally cured cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

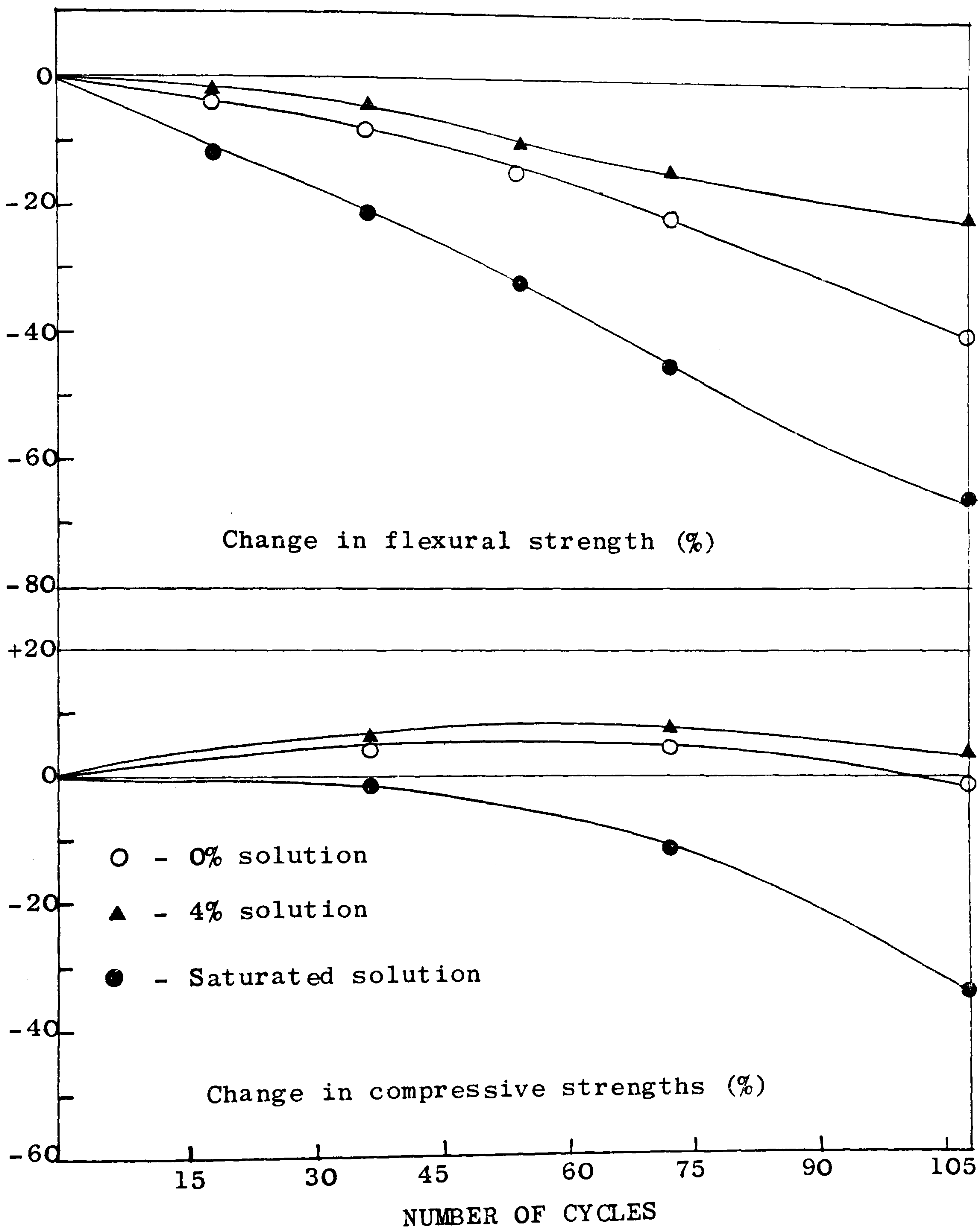

Fig. 9.4 Effect of freeze/thaw cycles on 7 day normally cured cement paste (W/C = 0.3) in sodium chloride solutions of different concentrations

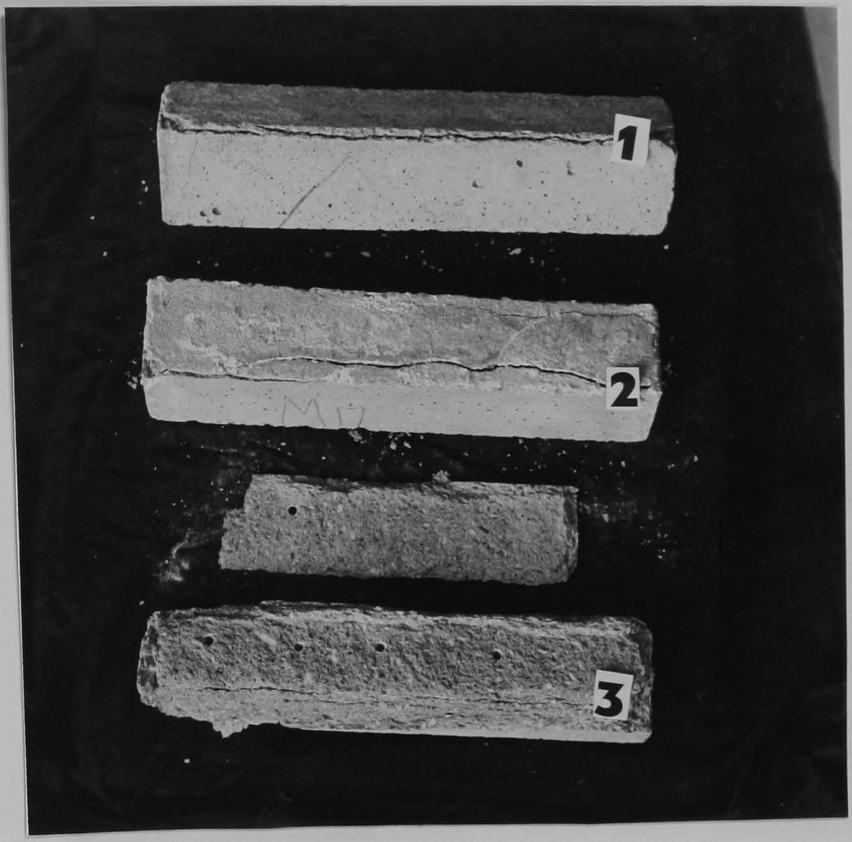

Fig. 9.5 Effect of freeze/thaw cycles on 3 day cured mortar specimens (cement/sand = 1:2, W/C = 0.4) in saturated solution of sodium chloride after (1) 36, (2) 54 and (3) 72 cycles.

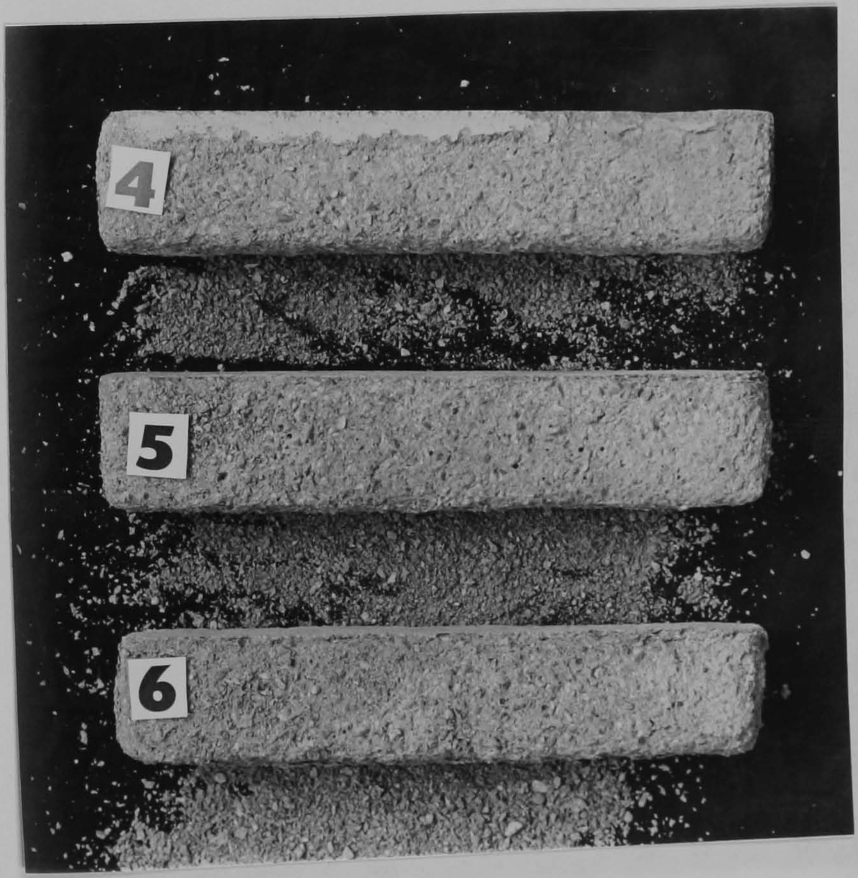

Fig. 9.6 Effect of freeze/thaw cycles on 3 day cured mortar specimens (cement/sand = 1:2, W/C = 0.4) in 4% solution of sodium chloride after (4) 36, (5) 54 and (6) 72 cycles.

Fig. 9.7 Effect of freeze/thaw cycles on 1 day cured paste specimens (W/C = 0.3) in 4% solution of sodium chloride after (9) 72 and (10) 18 cycles

Fig. 9.8 Effect of freeze/thaw cycles on 1 day cured paste specimens (W/C = 0.3) in saturated solution of sodium chloride after (7) 72 and (8) 18 cycles.

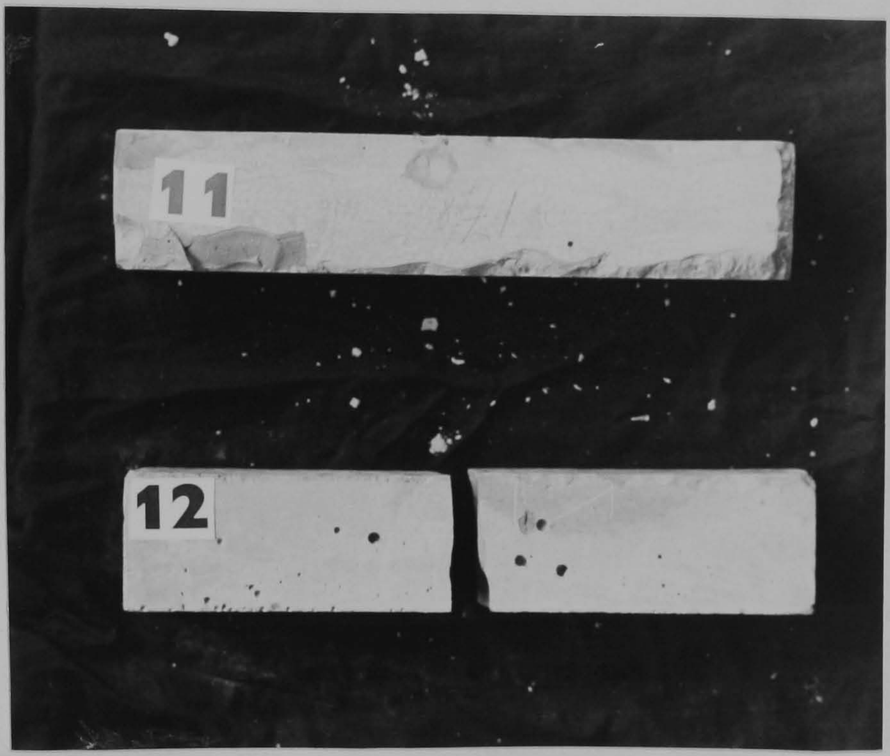

Fig. 9.9 Effect of 216 freeze/thaw cycles on cement paste (W/C = 0.4) initially cured for 28 days in (11) 4% and (12) saturated solution of sodium chloride

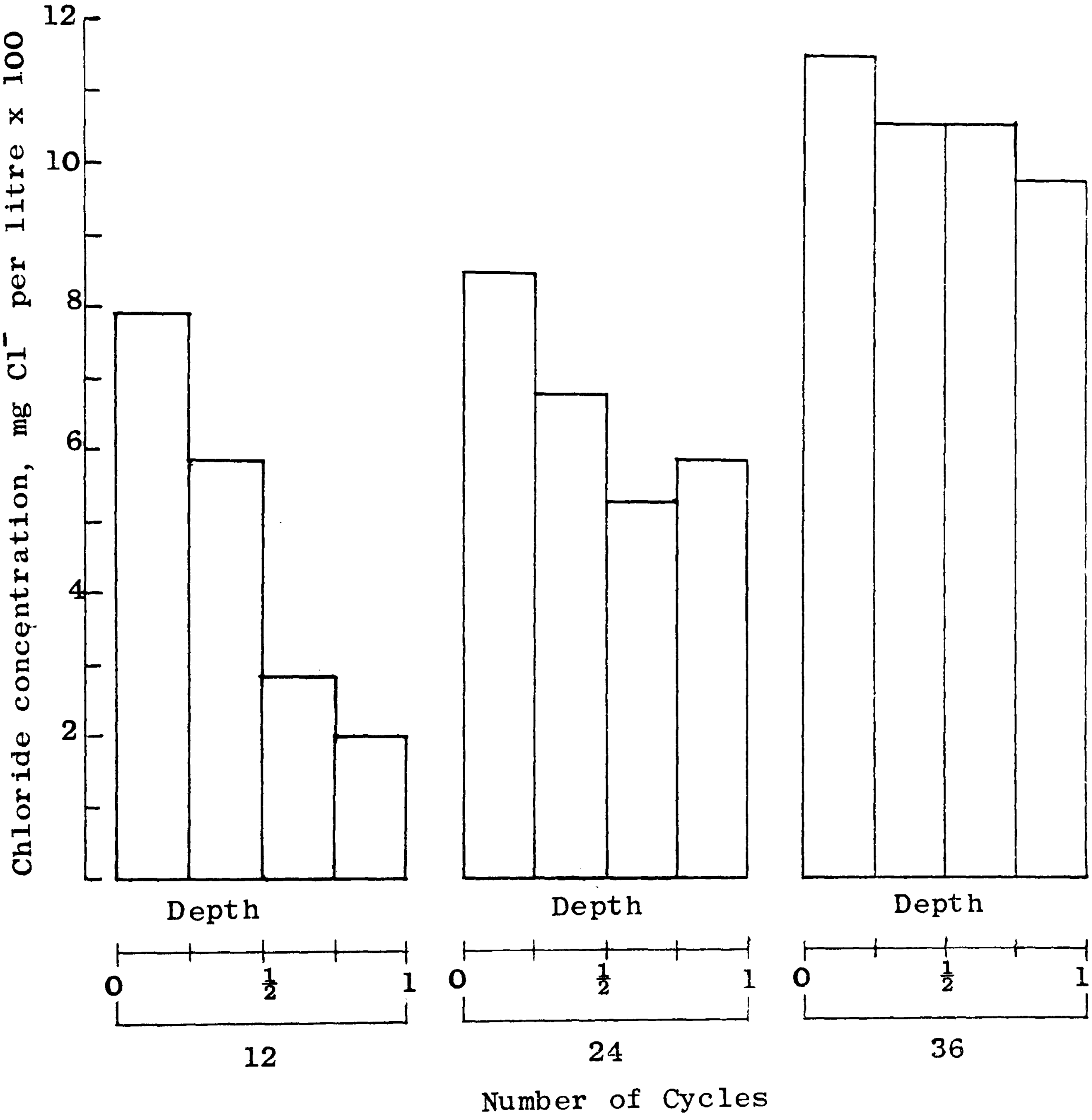

Fig. 9.10 Chloride contents of 3 day initially cured paste specimens (W/C = 0.4) exposed to freeze/thaw cycles in saturated solution of sodium chloride measured at 6 mm intervals

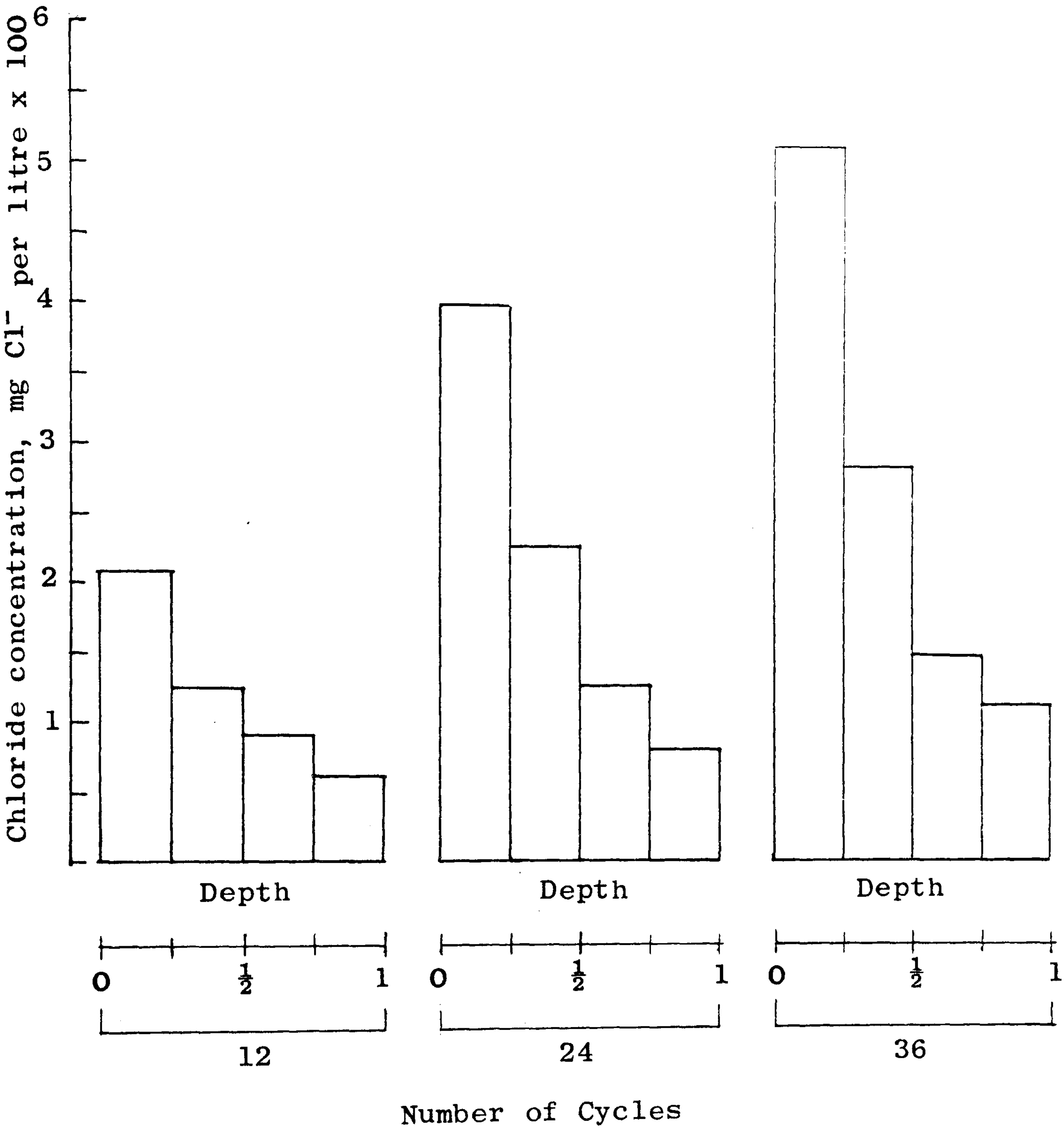

Fig. 9.11 Chloride contents of 3 day initially cured paste specimens (W/C = 0.4) exposed to freeze/thaw cycles in 4% solution of sodium chloride measured at 6 mm intervals

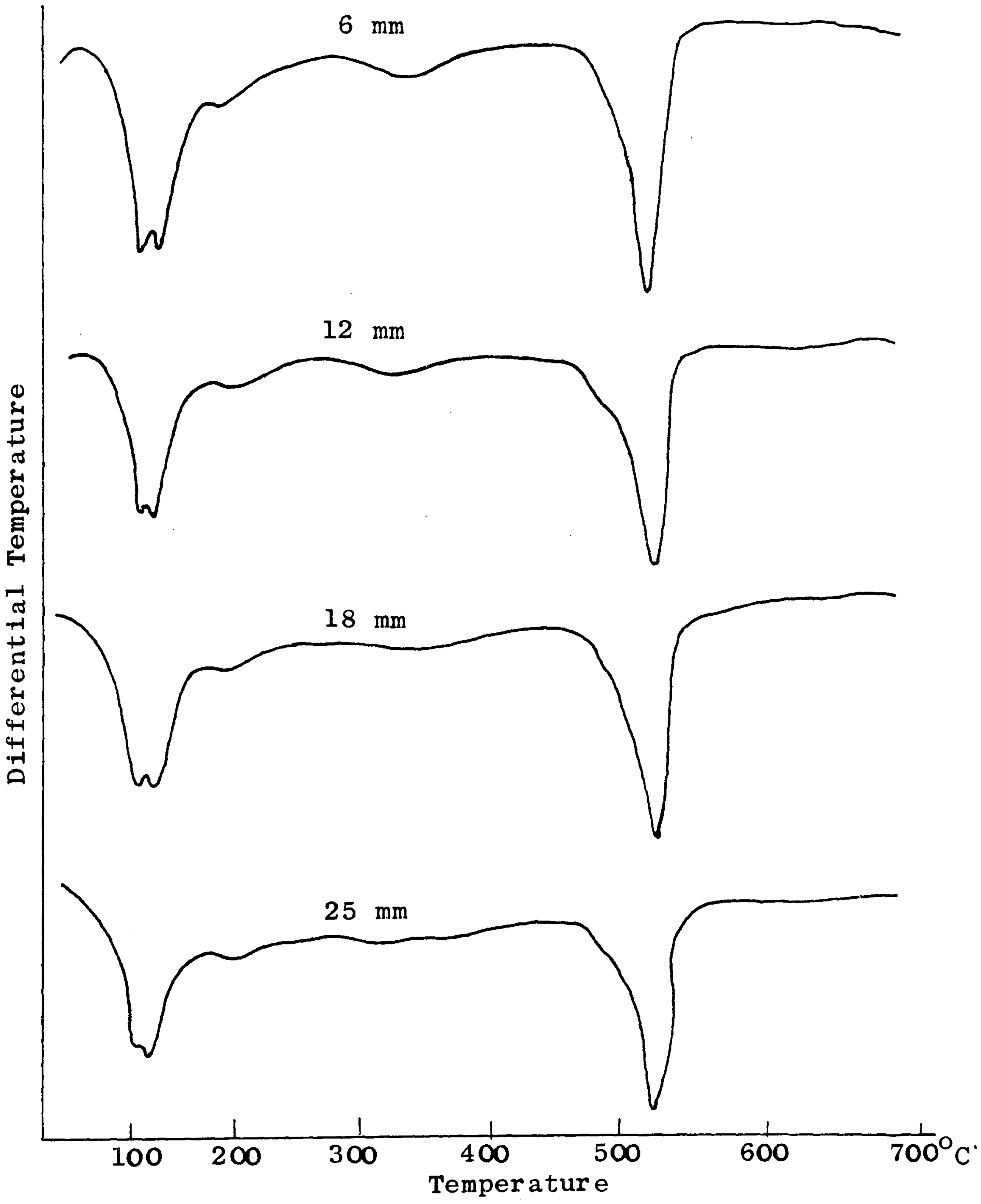

Fig. 9.12 DTA curves for samples of 3 day normally cured paste (W/C = 0.4) exposed to 36 freeze/thaw cycles in 4% solution of sodium chloride taken at 6 mm intervals up to 25 mm depth

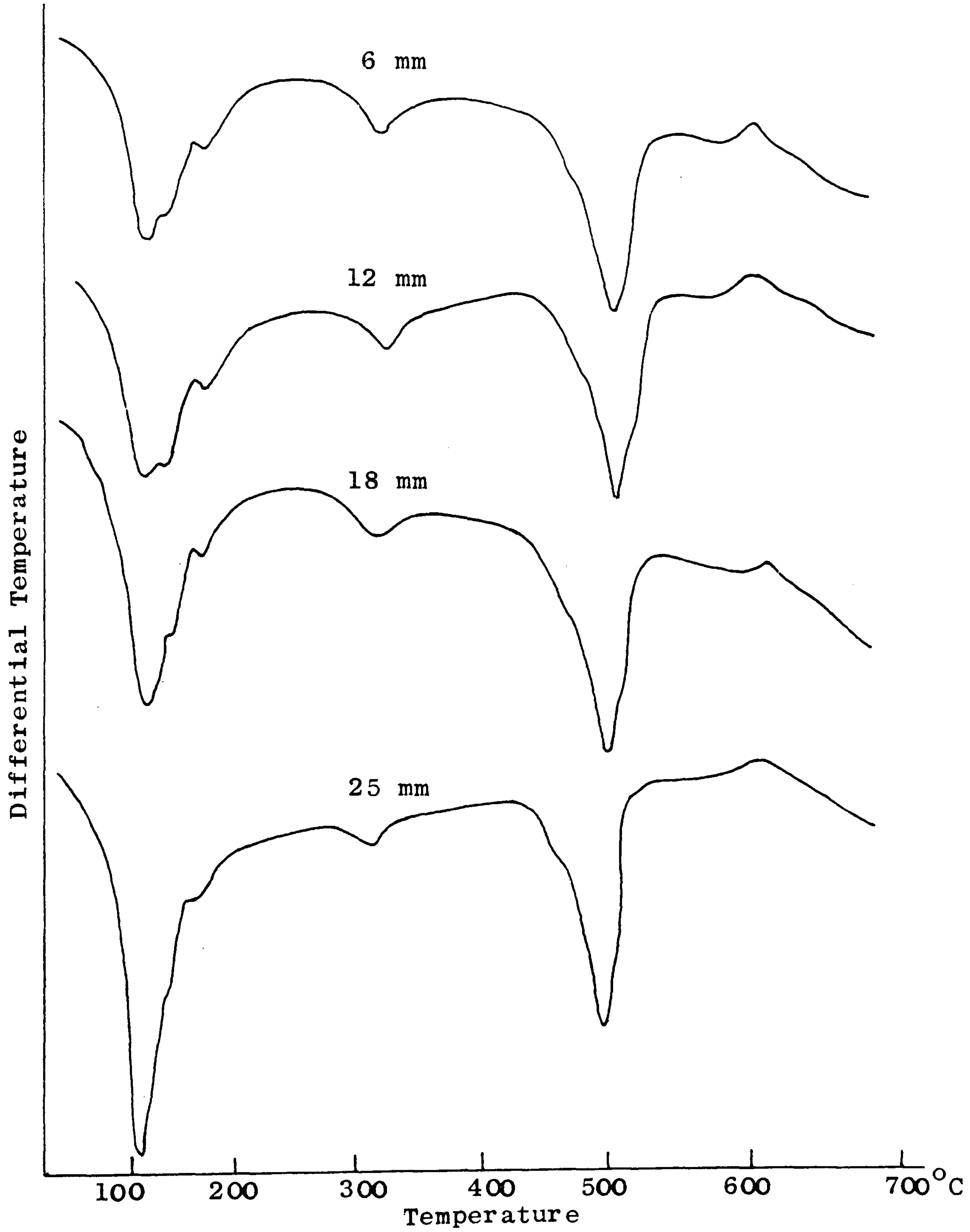

Fig. 9.13 DTA curves for samples of 3 day normally cured cement paste (W/C = 0.4) exposed to 36 freeze/thaw cycles in saturated solution of sodium chloride taken at 6 mm intervals up to 25 mm depth

# CHAPTER 10

# GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

## 10.1 General Conclusions

a) Subjecting hardened cement paste and mortar to alternate freeze/thaw and wet/dry cycles in different solutions of sodium chloride deteriorated the compressive and flexural strengths significantly. The flexural strengths dropped at a faster rate and also they suffered maximum damage compared with the rate and fall of compressive strengths in both paste and mortar specimens. The mortar specimens were more resistant than the paste specimens. These results suggested the formation of microcracks inside the specimens causing sharp deterioration in flexural strengths but the mortar specimens behaved in a better way due to the temporary arrest of such microcracks by the aggregate particles.

b) The concentration of sodium chloride in the solutions in which the specimens were subjected to freeze/thaw cycles had significant effects on the deterioration mechanism regarding the loss of strengths. The saturated solution was found to cause maximum damage whereas the 4% solution caused minimum even less than 0% and 2% solutions, however the 4% solution caused maximum surface degradation in both the paste and mortar specimens.

c) When cement paste was subjected to the alternate cycles of freeze/thaw in different solutions of sodium chloride the microstructure of its fracture surface was found to change significantly from a predominantly interlocked mass of hydration products to other patterns. In 0% solution microstructure was changed to massive well developed hexagonal crystals of calcium hydroxide with voids surrounding them. In 4% solution the micrographs showed lace like CSH products with few needle like structures of calcium sulphoaluminate or calcium chloroaluminate or both together whereas saturated solution produced numerous similar needle like structures which grew more in number due to increase in freeze/thaw cycles.

d) The author believes that the easily cleaved portlandite crystals surrounded by large pores constituted flaws in the material and the formation and subsequent growth of numerous long needle like structures with increasing freeze/thaw cycles initiated microcracks which were the cause of the loss of strength of pastes and mortars.

e) A study of the pore size distribution of the paste specimens cured normally, cured in solutions of sodium chloride and when subjected to freeze/thaw cycles in different solutions of sodium chloride with the aid of mercury intrusion porosimetry indicated a significant redistribution of pore sizes. The 4% solution in general produced microporous structure with a peak of pores in the diameter range of 15-80 nm whereas saturated solution produced two distinct peaks, one in a similar range and the other in comparatively larger diameter range.

f) The author believes that the microporosity developed in the specimens due to the presence of 4% solution was responsible for the observed effects such as maximum scaling, spalling etc., and for the least loss of strengths of the specimens when they were subjected to freeze/thaw cycles. The higher proportion of pores of comparatively larger diameters produced in the specimens frozen and thawed in saturated solution of sodium chloride were found to be associated with the initial stages of cumulative damage in the specimens.

g) A study of the hydration products of the paste specimens cured normally or in salt solutions and when subjected to freeze/thaw cycles in different solutions of sodium chloride by the technique of differential thermal analysis revealed changes in the peak intensities of different hydrates under different conditions. Calcium chloroaluminate was formed in the paste whenever sodium chloride was present in curing water or in the freeze/thaw cycles. But the intensities of the peaks of this hydrate depended mainly on the concentration of the chloride solution and the number of freeze/thaw cycles. The increase in freeze/thaw cycles together with the increase in concentration produced intense and deep peaks for calcium chloroaluminate hydrates at 320$^{o}$C. Another peak around 200$^{o}$C that of calcium sulphoaluminate together with some other form of calcium chloroaluminate was also intense due to the higher concentration of sodium chloride and increasing freeze/thaw cycles.

h) The author holds the opinion that the large quantities of calcium chloroaluminates formed in the paste specimens when subjected to freeze/thaw cycles in saturated solution of sodium chloride was responsible for the observed strength deterioration of the specimens.

i) When the paste and mortar specimens were subjected to wet/dry cycles in solutions of sodium chloride a chemical mechanism, similar to that involved in freeze/thaw cycles in the solutions of sodium chloride was responsible for the deterioration of the strengths. But the effects of wet/dry cycles were much slower compared with the effects of freeze/thaw cycles.

j) Air entrainment in cement paste was found to have changed the response of the material to freeze/thaw cycles in different solutions of sodium chloride. The accompanied changes in the morphology of such specimens were also observed in the scanning micrographs. The specimens with air entrainment could resist significantly higher number of freeze/thaw cycles in solutions of sodium chloride than the specimens without air entraining agents before showing any fall in the strengths.

k) The author considers that air entrainment was reasonably effective in helping concrete to withstand freeze/thaw cycles in different solutions of sodium chloride, but it was not the complete answer to obtaining durable concrete immune to such environments.

l) It was observed that an interrelationship existed between the strength properties and microstructural features of hardened cement paste when subjected to freeze/thaw cycles in different solutions of sodium chloride. The loss of strength was found to be associated with the formation of microcracks as a result of the growth of large numbers of calcium chloroaluminate and calcium sulphoaluminate crystals as revealed by scanning electron microscope and also by the differential thermal analysis techniques. The observed physical properties were also associated with the pore size distribution of the specimens under different test conditions.

m) Finally the author holds the opinion that the concrete used in structures which are liable to be exposed to environments similar to those used in this investigation should be a rich mix made as dense as possible to reduce the porosity and should be cured for a longer period than normal. Considering the findings of this investigation it is surprising to note that in CP110(158) Table 48 which gives the minimum cement content required to ensure durability, the value quoted for plain concrete (20 mm aggregate) is 280 kg/m$^3$ for severe exposure (alternate wetting and drying and freezing when wet) with a maximum free water/cement ratio of 0.5 whilst for concrete subjected to de-icing salts the minimum cement content is reduced to 250 Kg/m$^3$ and the maximum water/cement ratio allowed is increased to 0.55. Instead of reducing the quantity of cement in concrete exposed to salt for de-icing it should rather be increased and the maximum free water/cement ratio should be reduced to produce a more durable concrete.

## 10.2 Suggestions for Future Research

In the light of the present investigation the author believes that the following lines of research may be of value for the increase of knowledge of concrete when subjected to extreme environments.

a) More extensive research into other cement pastes subjected to the effect of freeze/thaw and wet/dry cycles in different solutions of sodium chloride and other chlorides or combination of two or more chlorides.

b) The research in (a) extended to cover mortars and concretes using different types of aggregates.

c) An investigation into the effect of sodium chloride solution or any other salt solution in different concentrations when used as mixing water in cement paste, mortar and concrete subjected to freeze/thaw and wet/dry cycles. This will enable the effect of using salt contaminated water or aggregates on strength and durability.

d) Extended research into the effect of air entrainment agents in paste, mortar and concrete coupled with the studies as mentioned above.

e) A study of other types of deterioration such as the corrosion of main reinforcement or fibre reinforcement present in pastes, mortars or concretes when exposed to solutions of sodium chloride or any other salts.

# APPENDIX A

## EVERETT'S MODEL FOR ICE CRYSTAL GROWTH

When a small crystal was immersed in and kept in equilibrium with a fluid subjected to some hydrostatic pressure the chemical potential can be expressed in the form

$$\mu = \mu(p_1) + v_s \cdot \sigma \cdot \frac{dA}{dV} \qquad \ldots (1)$$

where

$\mu$ = chemical potential of the small crystal

$\mu(p_1)$ = chemical potential of bulk solid at a pressure $p_1$

$v_s$ = molar volume of the solid

$\sigma$ = interfacial free energy between solid and liquid (or mean surface free energy of the solid)

A = area of interface

V = total volume of the solid.

For a spherical particle of radius r, the above expression becomes

$$\mu = \mu(p_1) + 2v_s \frac{\sigma}{r} \qquad \ldots (2)$$

If the pressure $p_s$ within the crystal increased, then the chemical potential of the crystal exceeds that of the bulk solid by:

$$\mu(p_s) - \mu(p_1) = v_s(p_s - p_1) \qquad \ldots (3)$$

From (1) and (3)

$$p_s - p_1 = \sigma \cdot \frac{dA}{dV} \qquad \ldots (4)$$

Equation (4) is the general formula for equilibrium.

If it is possible to subject the solid phase to an isotropic pressure different from that in the liquid phase then the shape of the interface between the solid and liquid should change such that $\frac{dA}{dV}$ will satisfy equation (4).

The above concept was presented in the following model; considering cylinders A and B as shown in Fig. A-1 to be full of water and connected by a capillary. If crystal nucleation is only allowed in B and the pistons are allowed to move, the crystal will continue to grow in B until all the water in B freezes. If temperature is depressed still further, then either one of the following two possibilities will occur;

a) Crystal growth will penetrate through the capillary.

b) The crystal in B will continue to grow over its lower surface and thus cause an upward movement of the upper piston.

If the pressures exerted by the pistons are equal and $p_l = p_s = p_{reference}$, then according to equation (4), $\frac{dA}{dV} = 0$, and the interface between the solid and the liquid will be a plane (Fig. A-2), and there will be no tendency for the ice to penetrate the capillary.

For the ice crystal to grow into the capillary, it should have a higher chemical potential such that

$$\mu_s(\text{cap}) = \mu_s(\text{bulk}) + v_s \cdot \sigma \cdot \frac{dA}{dV} \qquad \ldots (5)$$

Thus if $p_s$ remained constant, growth of the ice in B will continue until all the water has been withdrawn from A.

Such is the condition of weakly consolidated material where no large difference in pressure exists, so macroscopic ice lenses grow withdrawing the water from the surrounding material.

If $p_s$ was increased, however, while $p_l$ is maintained at $p_{ref.}$, propagation of the ice along the capillary should occur. The equilibrium state will be reached when

$$v_s(p_s - p) = v_s . \sigma . \frac{dA}{dV} \qquad \ldots (6)$$

or $$p_s - p = \Delta p_s = \sigma . \frac{dA}{dV} \qquad \ldots (7)$$

So if the upper piston is held while heat is being withdrawn from the system, $\Delta p_s$ will build up in B by the migration and freezing of water. Frost damage happens if this $\Delta p_s$ exceeds the strength of the walls.

If $p_l$ is reduced while $p_s$ is kept constant at $p_{ref.}$, the equilibrium is still controlled by the pressure difference $p_s - p_l (= p_{ref.} - p_l)$, and ice growth will commence in the capillary when

$$\Delta p_l = p_{ref.} - p_l = 2 \frac{\sigma}{r} \qquad \ldots (8)$$

which explains the reduction of heaving when the capillary water is in a state of tension. Thus heaving (growth of bulk ice) can be stopped either by applying pressure to the ice or tension to the water or both.

Everett showed that if the radius R of cylinder B is not large, then $\frac{1}{r}$ should be replaced by $\frac{1}{r} - \frac{1}{R}$.

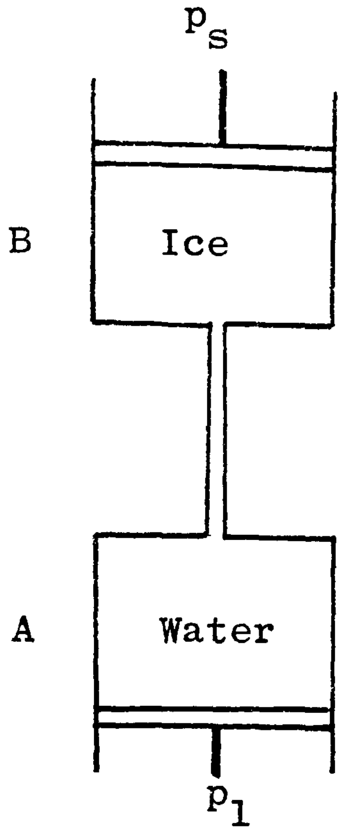

Fig. A-1 Everett's model for freezing in porous solids(111)

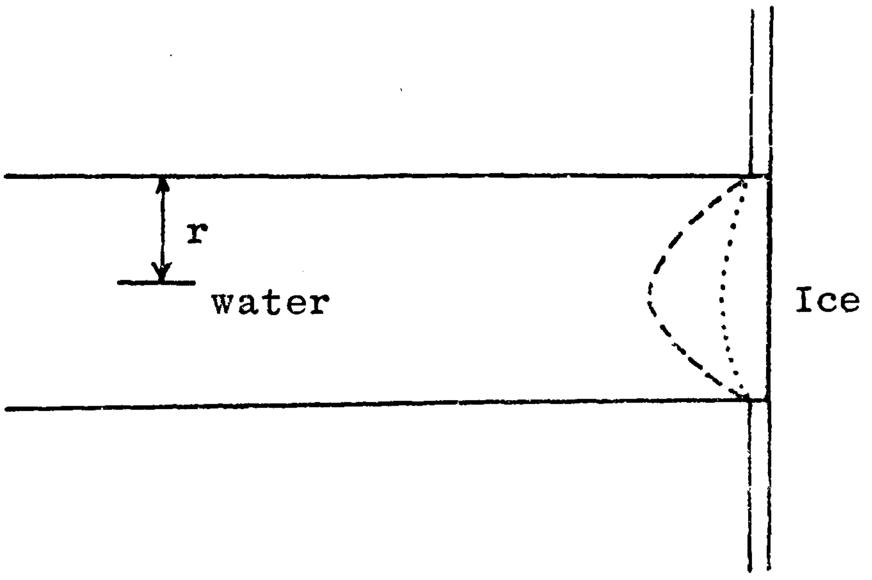

Fig. A-2 Equilibrium interface between ice and water (Everett)(111)

——————— when $p_s = p_l$

............. when $p_s - p_l < 2\sigma/r$

- - - - - - - - when $p_{s-p_l} = 2\sigma/r$

# APPENDIX B

## PROCEDURE FOR DILATOMETER FILLING

With the aid of the diagrams of Figs. B-1 and B-2 the steps to be followed are:

a) Sample is weighed accurately before placing into the dilatometer.

b) All joints are greased with high vacuum grease before joining together.

c) Small springs are attached to ensure tightness and secure the sample compartment and the stopper cap in position.

d) Dilatometer is placed above extension joint 10.

e) All taps in the system are opened except 6 and 8 which open to the atmosphere. Now taps 1 and 5 are closed.

f) The mechanical pump is operated. Tap 5 is now opened slowly so that mercury goes up slowly in the manometer.

g) When pressure becomes sufficiently low, on the vacuum gauge ( $\approx$ 0.03 mm) cold water tap is opened to circulate in the mercury pump.

h) Liquid nitrogen is now poured into the chambers and the mercury pump is put on. Pressure is checked until the desired vacuum is achieved.

i) When high vacuum is obtained tap 1 is closed so that it separates the mercury pump from the rest of the system. Taps 4 and 7 are now closed.

j) Situation is now ready for introduction of mercury. This is done by very slowly opening tap 8. This causes mercury to rise in the tube through tap 9 and into the dilatometer.

k) Mercury is allowed to continue rising until sample is completely covered and the level of the mercury in tube T is above the small bulb. At this point tap 10 is closed and tap 7 is opened. Tap 6 is slowly opened. The dilatometer is now full at atmospheric pressure.

l) Tap 9 is opened to drain the mercury down.

m) Dilatometer is removed from apparatus from below joint 10. It is put right side up, joint 10 is dismantled, excess mercury is carefully collected and joint 10 is cleaned and returned in position in the apparatus.

n) The mercury pump is switched off when it is cool and the water tap is closed.

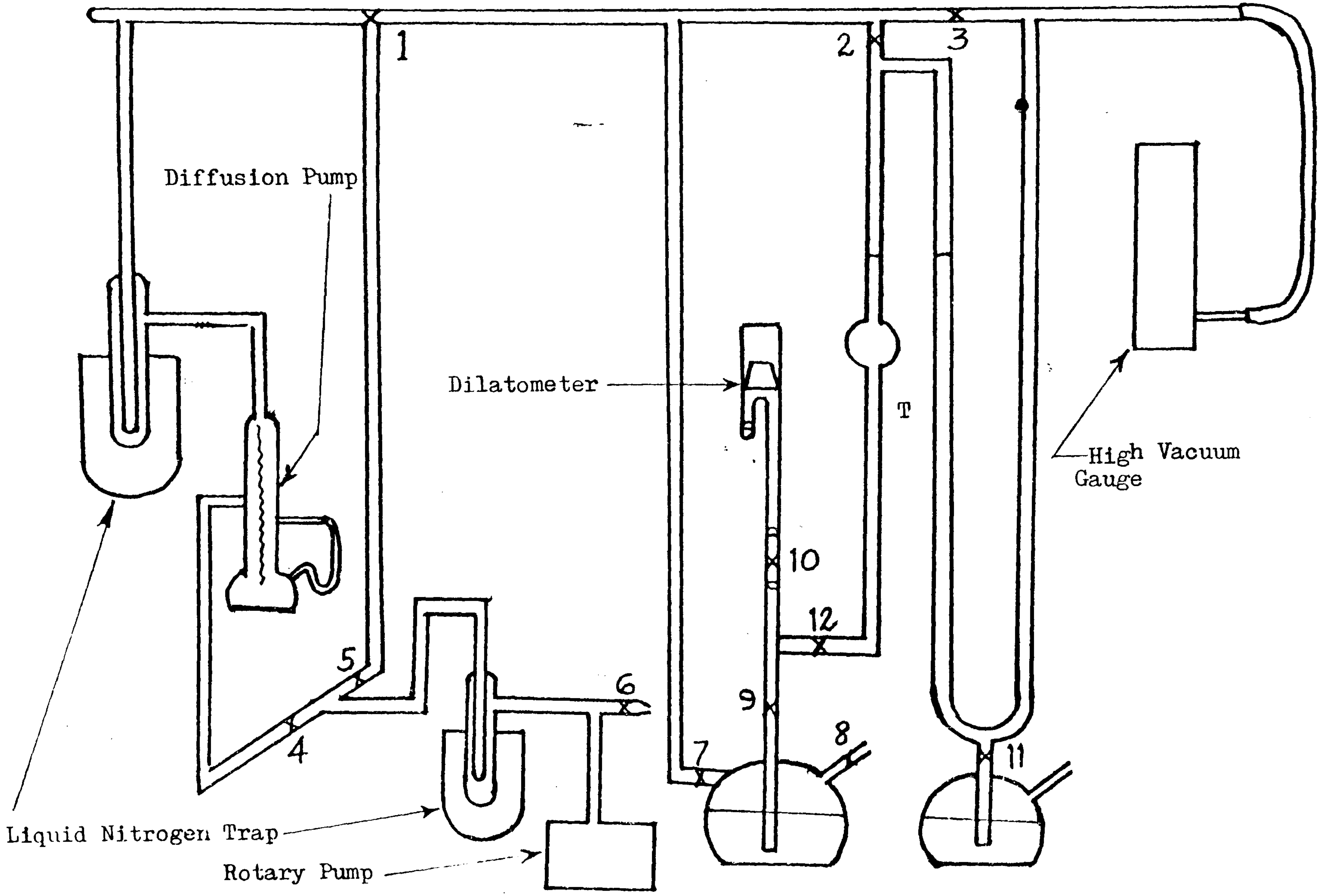

Fig. B - 1 Schematic details of Dilatometer filling Apparatus

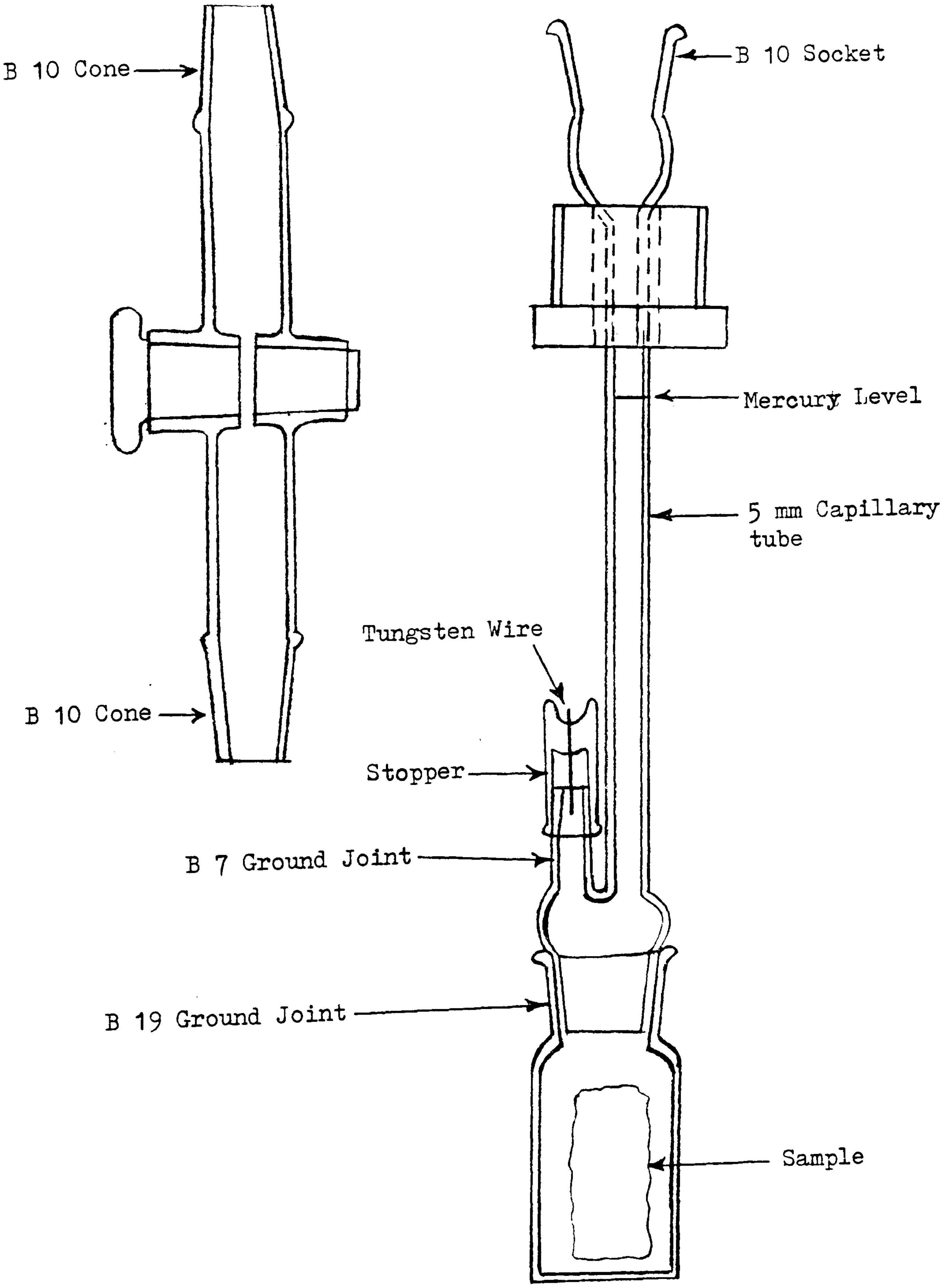

Fig. B - 2 Schematic details of the dilatometer

# APPENDIX C

## PROCEDURE FOR HIGH PRESSURE POROSIMETRY

The following procedure is carried out with the help of Figs. C-1 and C-2.

a) Before commencing the operation, the metallic scale and probe are placed in a vice at the side of the table.

b) A drop of mercury is placed in the side cap of the dilatometer in order to provide electrical conductance.

c) The dilatometer is connected to the scale by means of the fitted screw.

d) The head of the wire that is connected to the probe assembly is immersed in the mercury that is in the side cap of the dilatometer.

e) The probe assembly with the dilatometer attached to it is carefully removed from the vice and introduced slowly into the pressure chamber and screwed properly in position. Care is taken that there is sufficient oil in the chamber.

f) The electric line is connected. The hand pump is connected and the pump knob is closed.

g) Valves A, B, C, D and F are opened. Valve E is closed.

h) Pressure is applied very slowly with the help of hand pump so that the indicator needle of the probe is lowered. When it touches the top surface of mercury in the dilatometer the bulb glows. At this stage the reading is taken and recorded as the initial reading.

i) Valves D and F are closed and valve E is opened.

j) Rotate valve A clockwise till light is off.

k) Apply pressure by hand pump slowly till the light is on again. Pressure is read in gauge 3 and corresponding reading in the scale.

l) Steps (j) and (k) are continued till the pressure in gauge 3 reaches around 500 psi.

m) Valve E is closed and valve F is opened.

n) The nitrogen cylinder is opened and a pressure of 10 psi is applied.

o) Regulator is controlled so that pressure in the cylinder increases and light goes off.

p) Pressure is again applied by hand pump till the light is on again. Pressure is read in gauge 2 and corresponding reading in the scale.

q) Steps (o) and (p) are repeated till pressure reaches around 5000 psi in gauge 2.

r) Valve C is closed now and valve D is opened fully.

s) Nitrogen cylinder pressure is increased to 40 psi. Steps (o) and (p) are repeated till pressure reaches 15000 psi. But for readings of pressure it is read in gauge 1 now. The readings of the scale give the distance travelled by probe which is equal to the distance travelled by mercury. This mercury enters the sample. So knowing the diameter of the dilatometer tube, the volume of mercury that is introduced into the sample during a pressure interval can be evaluated.

t) The nitrogen cylinder is closed.

u) The valve C is opened slowly so that pressure in gauge

1 drops to around 4000 psi. At this point valve C is closed.

v) The hand pump knob is opened very slowly so that the probe gradually returns to its original position. When the probe sufficiently rises up the hand pump knob is closed. Valve C is opened completely.

w) The probe assembly is removed from the pressure chamber and is attached to the vice. The dilatometer is then removed from it.

x) Oil is washed out with heptane. Then mercury is removed and collected for purification and reuse. Dilatometer is dismantled and washed with heptane then put in an oven at 60°C to dry.

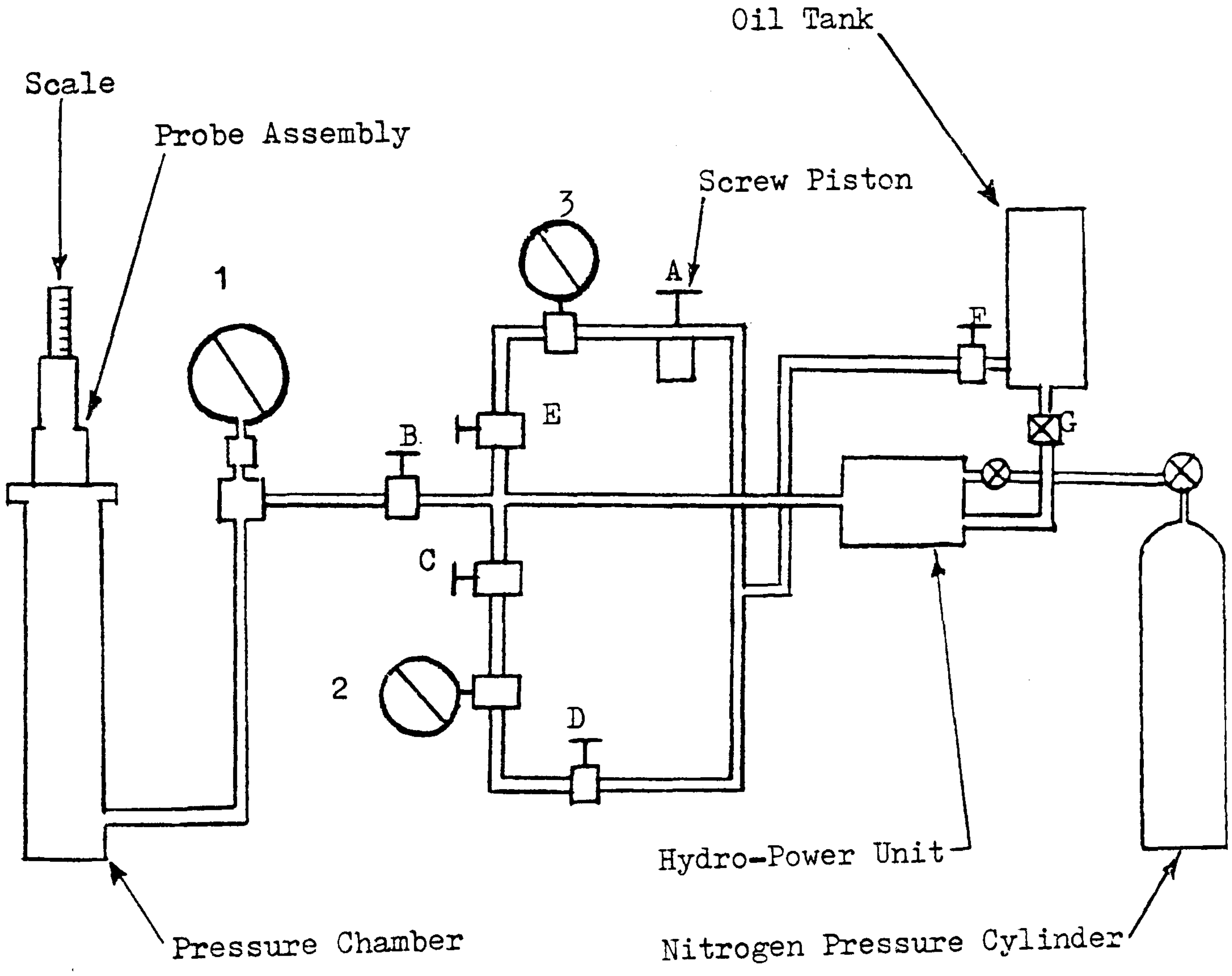

Fig. C - 1 Schematic details of the high pressure Porosimetry Apparatus

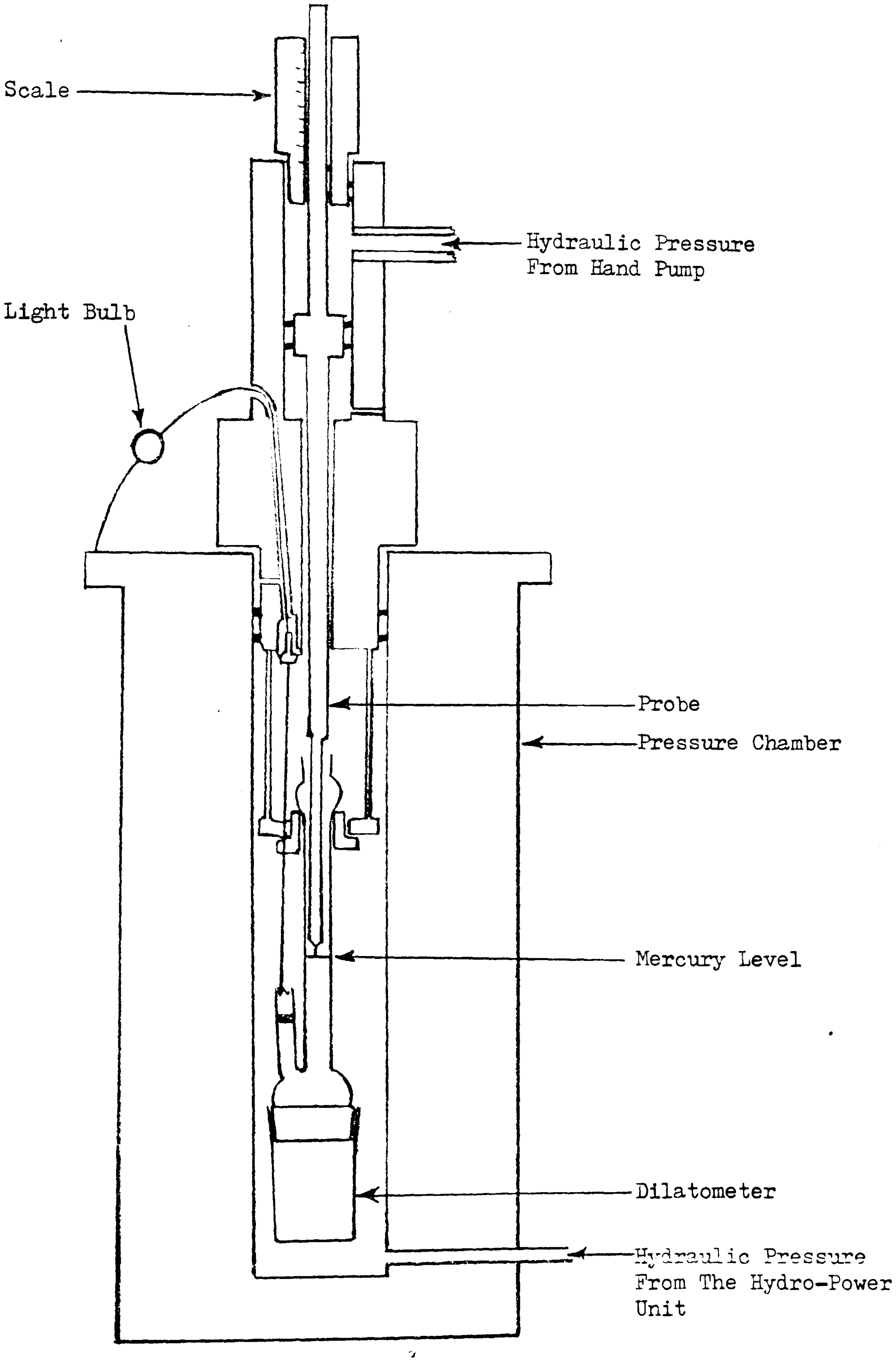

Fig. C - 2 Schematic details of the pressure chamber with the dilatometer and probe assembly in position

# APPENDIX D

## A COMPUTER PROGRAMME FOR THE CALCULATION OF PORE SIZE DISTRIBUTION DATA AND PLOTTING THE CURVES

```
FORTRAN ER=1FAIL,RUN,LIST,PLOT=PORE
      LIBRARY(ED,SUBGROUPGOST)
      PROGRAM(CMAR)
      INPUT 5=CR0
      OUTPUT 6=LP0
      COMPRESS INTEGER AND LOGICAL
      TRACE 2
      COMPACT
      END
C  THIS PROGRAMME PREPARES THE RESULT-SHEET FROM
C  POROSIMETER EXPERIMENT DATA          AND
C  PLOTS THE PORE-SIZE DISTRIBUTION CURVES.

C CHANGE THE FOLLOWING PARAMETER FOR EACH SET OF DATASHEET
C               N=NO. OF READINGS
C               HEAD1=INITIAL HEAD READING
C               SECAREA=X-SECTIONAL AREA OF SAMPLE
C               DRWT=DRY WEIGHT OF SAMPLE
C               SIGMA=SURFACE TENSION OF HG AT 20C IN DYNE
C               THETA=CONTACT ANGLE BETWEEN HG AND MAT.,DEGREE
C                PRESS IN PSI
C                POREDIAMETER IN MICRON
      MASTER SHAMIM
      DIMENSION HEAD(75),PRESS(75),VG(75),Y(75)
      DIMENSION DIFFHEAD(75),POREDIA(75),VOLINTRD(75),
     +ALPORE(75),DELVG(75),DELALP(75),FINCOL(75),X(75)
      DATA HEAD1,SECAREA,DRWT,N/23.1,20.0,8.6485,13/
      DATA THETA,SIGMA/117.0,484.0/
      DO 100 I=1,N
      READ (5,10) HEAD(I),PRESS(I)
 10   FORMAT(2F0.0)
100   CONTINUE
      WRITE (6,20)
  20  FORMAT(2X,'SL.NO.',4X,'HEAD',5X,'DIFFHEAD',7X,
     +'PRESS',6X,'POREDIA',7X,'VOLINTRD',7X,'VG',
     +7X,'DELVG',7X,'DELALP',4X,'FINCOL')

C  CALCULATION OF RESULT SHEET
      DO 200 I=1,N
      DIFFHEAD(I)=HEAD(I)-HEAD1
      POREDIA(I)=((-4.0)*SIGMA*COS(THETA)*0.145)/PRESS(I)
      ALPORE(I)=ALOG10(POREDIA(I))
      VOLINTRD(I)=DIFFHEAD(I)*SECAREA
      VG(I)=VOLINTRD(I)/DRWT

200   CONTINUE
```

```
      DELVG(1)=0.0
      DELALP(1)=0.0
      DO 300 I=2,N
      DELVG(I)=VG(I)-VG(I-1)
      DELALP(I)=ALPORE(I-1)-ALPORE(I)
      FINCOL(I)=DELVG(I)/DELALP(I)
300   CONTINUE

      DO  400 I=1,N
      WRITE(6,40) I,HEAD(I),DIFFHEAD(I),PRESS(I),
     +POREDIA(I),VOLINTRD(I),VG(I),DELVG(I),DELALP(I),FINCOL(I)
40    FORMAT(2X,I5,3F12.2,6F12.4)
400   CONTINUE


C  PLOTTING OF PORE-SIZE DISTRIBUTION CURVE
      WRITE(6,30)
  30   FORMAT(////'COORDINATES OF THE GRAF,SEMILOG PLOT '///)
      DO 500 I=1,N
      X(I)=ALPORE(I)
      Y(I)=FINCOL(I)
      WRITE(6,50)I,X(I),Y(I)
   50 FORMAT(2X,I5,2F15.5)
 500  CONTINUE
      CALL REGION(0.0,1.0,0.0,1.0)
      CALL LIMITS(0.0,6.0,0.0,8.0)
      CALL BORDER
      CALL REGION(-2.0,0.0,0.0,300)
      CALL LIMITS(0.5,5.5,0.5,7.5)
      CALL CRSET(4)
      CALL CRSIZE(0.1)
      CALL AXESSI(0.5,50.)
      DO 70 I=1,N
      CALL PLOTNC(X(I),Y(I),54)
      CALL JOIN(X(I),Y(I))
  70  CONTINUE
      CALL GREND
      STOP
      END
      FINISH
```

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