EFFECTS OF HOT CRUDE OIL ON CONCRETE FOR OFFSHORE STORAGE APPLICATIONS

by

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ABSTRACT

The nature of the interaction between hot crude oil and concrete, and the effects on the mechanical properties of concrete, has been studied. The thesis is divided into three parts:

Part I gives the background information and specimen preparation prior to exposure to hot crude oil. This comprise a study of crude oil, and review of previous work concerned with the durability of concrete under different exposure conditions such as seawater, crude oil and elevated temperatures. Also included are the detailed descriptions of the present experimental investigation, apparatus, development of compressive strength and length change of test specimens during curing in seawater and at 100% RH, and the surface conditions of the specimens prior to exposure to hot crude oil.

Part II describes the effect of exposure to hot crude oil on some properties of concrete. A general form of the equation of fluid flow through concrete was established. By using this equation and applying penetration test results, an equation was obtained for the flow of crude oil through oven dry concrete. The ability of oven dry concrete to act as a molecular sieve, selectively allowing passage of the aliphatic fractions of crude oil while retaining the aromatics, was determined by means of the NMR technique. Test results of crude oil absorption, compressive strength and length change of the specimens, at elevated temperatures, are presented and discussed. Crude oil absorption of the specimens has been related to the time dependent changes in length and to compressive strength.

Part III highlights the general links between the different studies. Essentially, this section discusses the implication of the findings, in relation to existing offshore oil storage tanks.

To Mama, Papa and the Family

Best Copy Available

Variable Print Quality

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ABBREVIATIONS

ACI	American Concrete Institute
ASCE	American Society of Civil Engineers
CP110	Code of Practice 110 /31/ (UK)
H/OPC	100% RH cured opc specimens
H/PFA	100% RH cured opc/pfa specimens
S/OPC	Seawater cured opc specimens
S/PFA	Seawater cured opc/pfa specimens

CHAPTER I

INTRODUCTION

Petroleum products have been stored in concrete tanks since the turn of the century /40, 148, 150, 179/. More recently, many concrete tanks have been employed for storage of crude oil and petroleum products above ground, underground, afloat and offshore /76, 94, 114, 174/.

Concrete gravity platforms are today commonly used in offshore oil production and storage. The inception of these structures was marked with the installation in the North Sea of the Ekofisk tank in 1973. Since that time, over 20 other concrete gravity platforms have been installed in the North Sea, the Baltic Sea and offshore of Brazil. A few more are either under construction or have been proposed. A list of the various North Sea concrete platforms is given in Table (1.1). A common feature of most of these platforms is the incorporation of concrete tanks for storage of crude oil, with capacities ranging from 0.65 to 1.5 million barrels /53, 102/. The storage tanks are based at the bottom of the platforms [Fig.(1.1)] and can reach depths of up to 150m below sea level. The storage area is divided into several cells typically 30m high, 20m in diameter and wall thickness of 0.6 to 0.7m. A recent survey of tanks presently in service has shown a number of long term advantages of concrete storage platforms in terms of durability and intrinsic safety /76/.

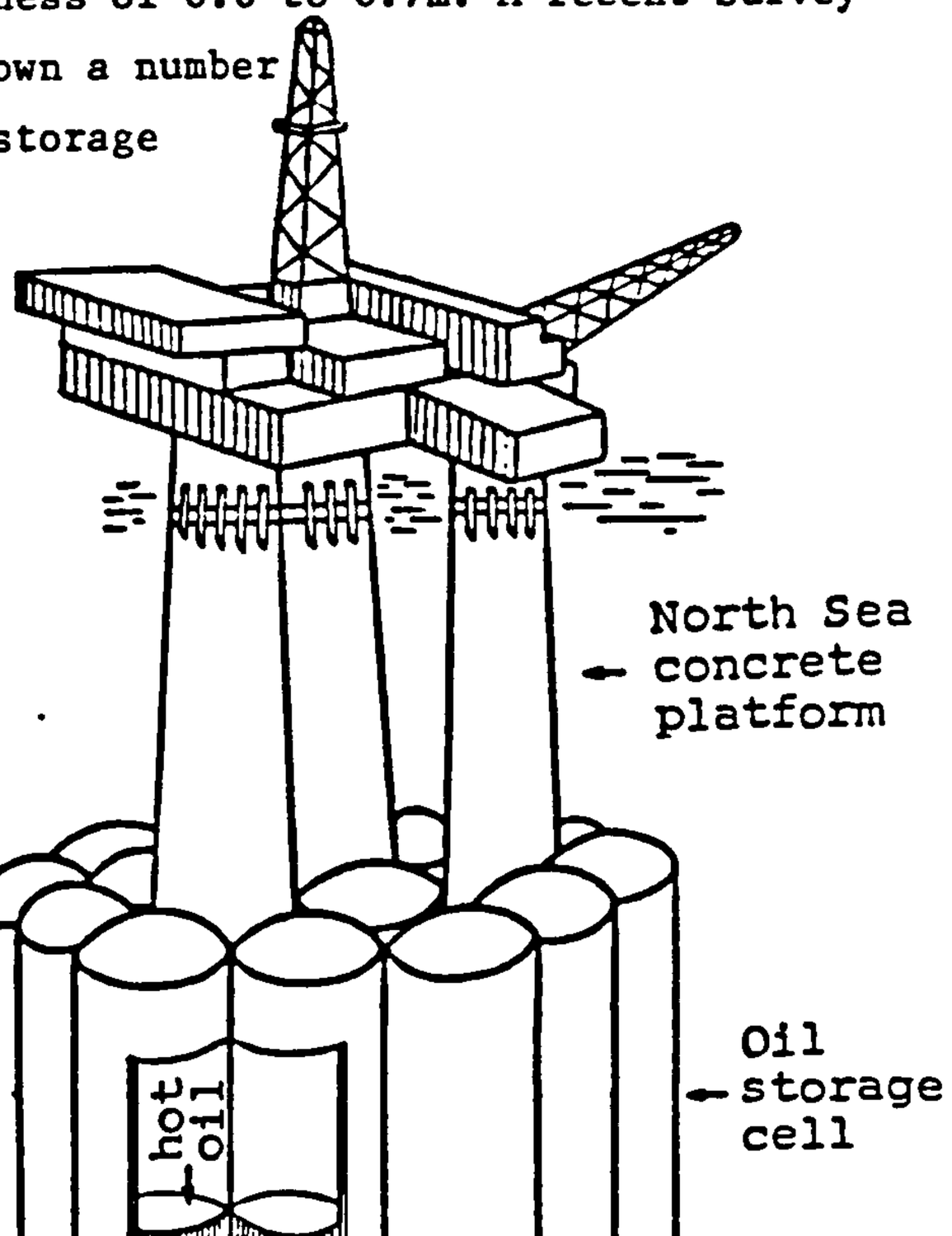


FIGURE I.I :

Diagram showing storage facility for hot crude oil at the bottom of North Sea concrete platform /76/.

TABLE 1.1: LIST OF NORTH SEA CONCRETE PLATFORMS

Field	Platform Designation	Design Type	Main Function	User	Storage Capacity (mill. barr.)	Year Installed
Beryl (UK)	A	Condeep	d,p,s	Mobil	0.93	1975
Brent (UK)	B	Condeep	d,p,s	Shell/Esso	1.00	1975
	D	Condeep	d,p,s		1.00	1976
	C	Sea tank	d,p,s		0.65	1978
Cormorant (UK)	A	Sea tank	d,p,s	Shell/Esso	1.00	1978
Dunlin (UK)	A	ANDOC	d,p,s	Shell/Esso	0.85	1977
Ekofisk (N)	Ekofisk-Centre	Doris	s	Phillips	1.00	1973
Frigg	CDP1 (UK)	Doris	d,c,p	Elf/Total	-	1975
	MP2 (UK)	Doris	c		-	1976
	TP1 (UK)	Sea tank	p		-	1976
	TCP2 (N)	Condeep	t,c,p		-	1977
Ninian (UK)	Central	Doris	d,p	Chevron	-	1978
Statfjord (N)	A	Condeep	d,p,s	Mobil	1.30	1977
	B	Condeep	d,p,s		1.50	1981

designations: d = drilling, p = production, s = storage, c = compression, t = treatment

Another advantage is the added structural stability provided by the storage tanks which more importantly, prevents costly shut-down of producing wells at times when the sea state makes tanker loading impossible.

The reliability of concrete as a construction material, based on reasonable knowledge of some of its more important properties, had led to its use in the construction of offshore structures. However, it is generally agreed that there is very limited knowledge as to the nature of the interaction of this material with the complex contents of the storage tanks /94, 105, 167, 177/. For instance, the tanks are exposed to cycles of crude oil and seawater. This subjects the uncoated concrete caisson walls to thermal cycling, since the crude oil is pumped in at temperatures of about 45-50 C, whereas the seawater 'pillow' resting beneath the oil is usually at about 5 C (Fig.1.2). These conditions also favour the growth and activity of various bacteria which produce toxic and acidic substances /68, 129/ and further complicate the system.

Concern about the durability of the material under this environment and fears that deterioration of its properties may affect the serviceability of the structures required that a thorough investigation of the problem should be made. There have been a few studies of the properties of concrete in contact with crude oil /119-121, 143/, but these have been at ambient temperatures and even then, the results reported have been contradictory. Nevertheless, no known work exists on the durability of concrete in an offshore oil storage tank at elevated temperatures. This has now been investigated and is the subject of this thesis. However, the environmental conditions relating to this study differ from those of previous investigations in the following ways:

- The internal surface of the walls of the concrete tanks are exposed to seawater before and partly during oil storage.

- The oil is stored at elevated temperatures, which exposes the concrete caisson walls to thermal cycling of between 50 C and 5 C (Fig.1.2).

- Bacterial activity enhanced by favourable conditions at the oil/ water interface causes the production of acids and hydrogen sulphide gas.

The aims of this research programme were therefore as follows:

(a) To arrive at a better understanding of the nature of the physical and chemical interaction between crude oil and concrete at ambient and elevated temperatures.

(b) To investigate the degree of crude oil penetration and the absorption that is likely to take place in the uncoated walls of the oil storage tanks at various temperatures.

(c) To ascertain whether the concrete currently being employed in North Sea oil storage tanks is likely to experience any deterioration in properties as a result of the absorption of crude oil.

(d) To determine whether oil storage temperatures can be raised from the concrete materials point of view, thus saving on the costs of cooling the oil prior to storage.

(e) To investigate the effect of bacterial activity on the acid contents of crude oil at ambient and elevated temperatures.

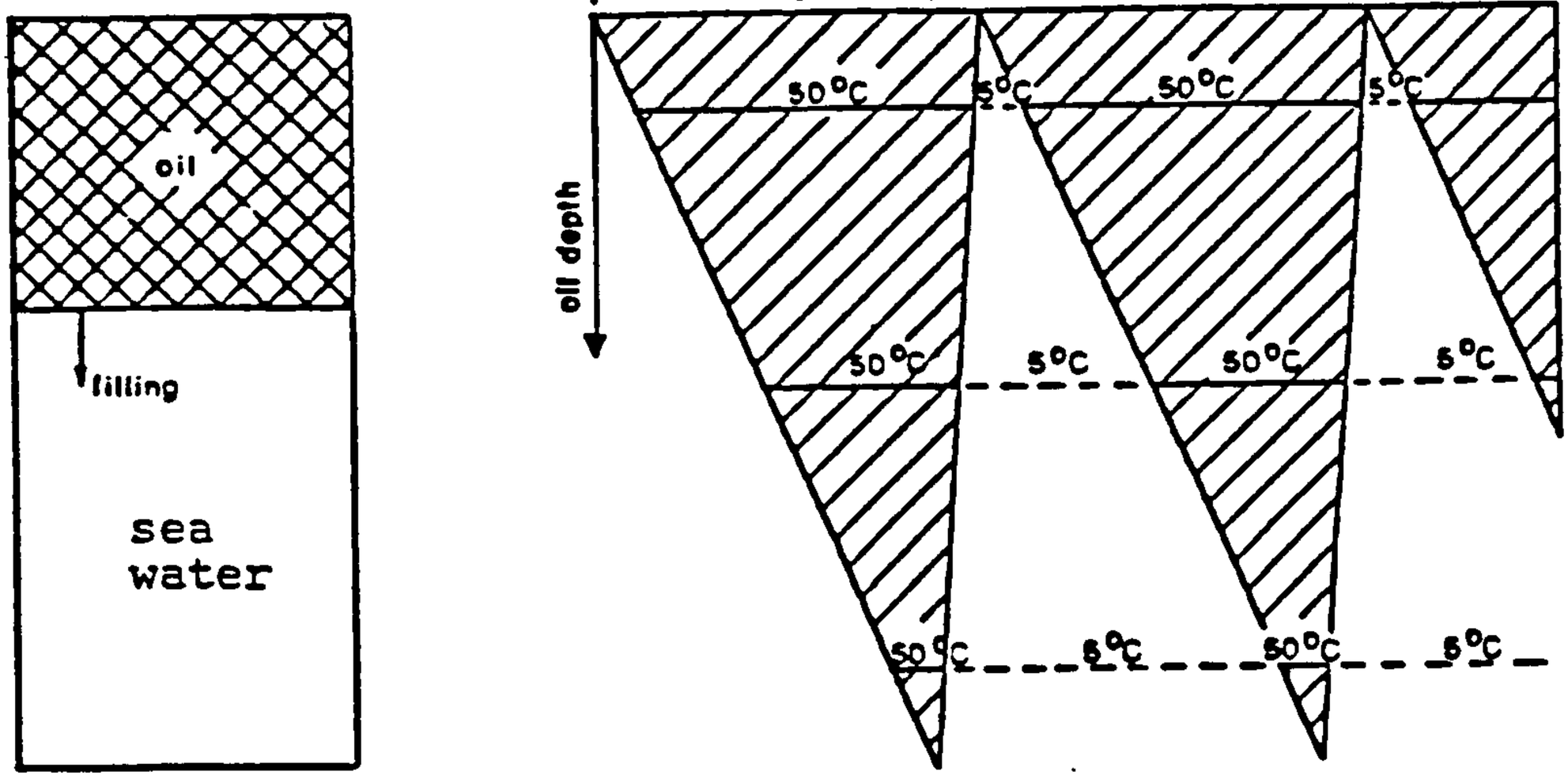


FIGURE I.2 : Thermal cycling following entry and removal of hot crude oil into the storage cell /41/.

In the investigation of mechanical properties, about two thousand mortar and concrete specimens have been tested, these comprised two mixes, opc and opc/pfa, and granite aggregates were used in the concrete mix. The specimens have been cured both in seawater and at 100% RH. Exposure to crude oil was at 4 temperature levels of 20, 45, 60 and 80 C.

It is hoped that the findings of this work would be of benefit to both the petroleum and construction industries. It is also hoped that it would serve as useful reference in the design and construction of future platform storage structures.

This thesis is divided into 3 main parts, each part consisting the following Chapters:

PART A : **BACKGROUND INFORMATION AND SPECIMEN PREPARATIONS PRIOR TO EXPOSURE TO CRUDE OIL**

Chapter 2

This chapter is a literature review in two parts. The first part is a study of crude oil through its origin and occurrence, its properties, the processes of exploration production and storage and finally the effects of bacterial activity and production of acids. The second part is a study of the durability of concrete under exposure conditions in seawater, crude oil and at elevated temperatures separately. These have been investigated with particular reference to concrete properties such as; permeability, compressive strength and volume changes.

Chapter 3

The main programme of investigation is described. The test parameters are given and justifications are made for their selection. The chapter also describes the test plans and methods and the approach to analysis of the results. Finally, details of the preparation of specimens and the testing procedures are given.

Chapter 4

The main apparatus and other items of equipment used in the test programme are described.

Chapter 5

The development of compressive strengths of concrete specimens and length changes of mortar specimens, monitored throughout the period of curing, are discussed in this chapter. The chapter also describes the surface conditions of the specimens at the end of the period of curing and prior to exposure to crude oil.

PART B : EXPOSURE TO CRUDE OIL AT ELEVATED TEMPERATURES

Chapter 6

The crude oil absorption characteristics of moist and oven dry concrete and mortar specimens are studied. In addition, the results of penetration of crude oil at various temperatures through oven dry concrete specimens, are given. Finally, the differential penetration of fractions of crude oil through oven dry concrete, as determined by the nuclear magnetic resonance (NMR) technique, are discussed.

Chapter 7

The results of compressive strengths of concrete specimens exposed to crude oil at elevated temperatures are given and discussed and are related to the trend of crude oil absorption of the specimens with time.

Chapter 8

The results of length changes of mortar bar specimens exposed to crude oil at elevated temperatures are given and discussed and are related to the trend of crude oil absorption of the specimens with time.

PART C : GENERAL DISCUSSIONS AND CONCLUSIONS

Chapter 9

This chapter contains a general discussion of all the main results and some examples are given of the findings of microstructural studies. The implications and applications of the results are also discussed.

Chapter 10

Summary conclusions, and recommendations are given for future work.

PART A: BACKGROUND INFORMATION AND SPECIMEN PREPARATION PRIOR TO EXPOSURE TO CRUDE OIL

CHAPTER II

DURABILITY OF CONCRETE IN OFFSHORE OIL STORAGE TANKS - A LITERATURE REVIEW.

This chapter is in two parts, the first is a study of crude oil, while the second is a review of the durability of concrete in seawater crude oil and at elevated temperature.

The study of crude oil is divided into four sub-sections as follows:

- brief introduction and historical background of the origin and occurrence of crude oil,
- physical and chemical properties,
- the processes of exploration, production and storage,
- bacterial activity and the production of acids in crude oil.

The second part of this chapter reviews various studies on the durability of concrete in seawater, crude oil and at elevated temperatures. Investigations of the effects under each of these conditions separately, are made on concrete properties such as permeability, penetration, compressive strength and volume changes. In addition, various test methods used by different authors are described and the advantages and disadvantages are discussed.

2.1 PETROLEUM (CRUDE OIL)

2.1.1 INTRODUCTION

Petroleum storage in concrete tanks in the United Kingdom dates back to the end of the 19th century /40, 150/. More recently, petroleum has been stored in concrete tanks offshore in the North Sea /67, 76, 167/.

There have been tremendous developments in the discovery, production and storage of crude oil in the recent past, in particular, the development of the prolific North Sea reservoirs has prompted its storage in concrete tanks offshore.

2.1.2 ORIGIN AND OCCURRENCE

2.1.2.1 Origin of Petroleum

On account of its origin, petroleum is defined as rock oil or mineral oil. In modern technical usage, it can refer to natural gas, mineral wax and bitumen, in addition to crude oil.

The problem of the genesis of petroleum has attracted attention for many years, and theories about its origin had been formulated as far back as the 19th century /12/. Berthelot (1866) was at the fore front of the earlier hypotheses which postulated the generation of petroleum from an inorganic source. It was considered that acetylene, produced by the reaction of water with a metallic carbide, was the basic material converted to petroleum at elevated temperature and pressure /12, 83, 89, 180, 182/. This idea was discarded and a new school of thought led by Engel (1911) postulated that petroleum owed its origin to organic matter. Present theories have evolved around this.

It is now amply clear that the source material was composed of organic remains of plants and animals, which accumulated in marine or near marine sediment over millions of years. These had been converted to hydrocarbons which form petroleum under the effects of temperature and pressure.

The least well understood phase of petroleum genesis is the chemistry of the transformation of organic matter into petroleum. Heat, bacteria radioactivity and low temperature catalysis have all been mentioned as possible transforming agents /83, 163, 180/. However, most of these ideas were discounted as further research had shown that the products obtained in experimental investigations using these agents, were far from matching the characteristics of petroleum.

More recently, Smith /180/ has proposed that petroleum is being formed in present day sediments, probably largely through the selection and concentration of hydrocarbons synthesised during metabolism in organisms. This is however difficult to asses given the present state of knowledge. Hobson /83/ amongst many others, is of the opinion that bacteria must have played some direct part in the process of transformation, even though experimental investigations have yet to identify this role.

2.1.2.2 Occurrence of Petroleum

Oil accumulation and the formation of oil deposits are factors dependent on geological morphology. Hanson /75/ has recognised three necessary criteria for the formation of an oil deposit, these are; source sediments, a permeable rock of sufficient porosity to serve as a 'reservoir', a 'trap' which will prevent the petroleum from migrating away and being lost and which will also facilitate accumulation. It is generally agreed that oil is not usually formed in the rock from which it is obtained, but somehow migrates into the reservoir rock. It is possible that the composition of the oil changes during this period as a result of filtration, adsorption and other physical causes. The latter may include interaction with elemental

sulphur and sulphur containing minerals, found along the path of flow /182/. An example of an accumulation within a reservoir, and of natural earth traps, are shown in Figs.(2.1) and (2.2) respectively.

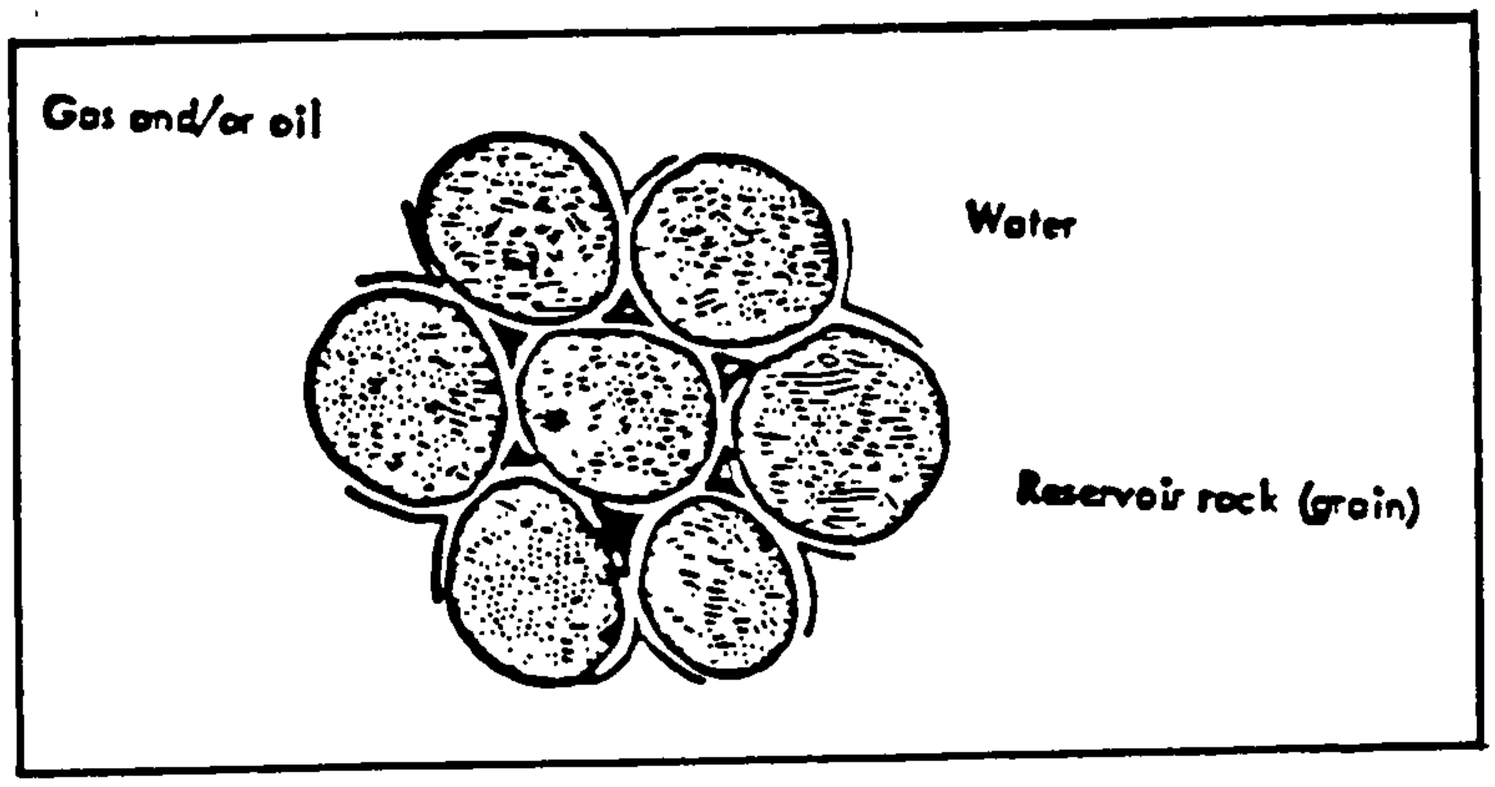


FIGURE 2.1 : Representation of oil and gas accumulation within a reservoir.

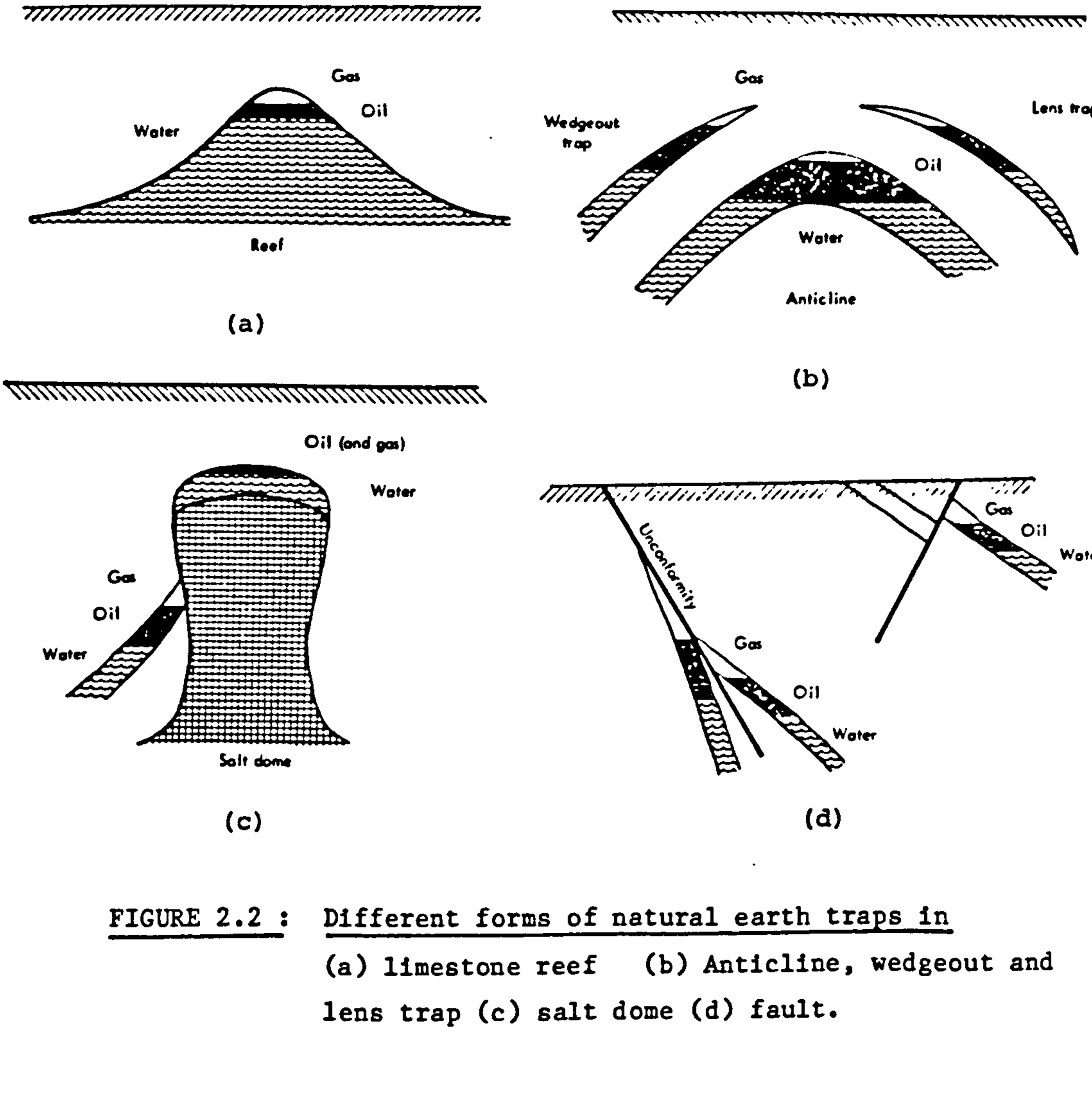


FIGURE 2.2 : Different forms of natural earth traps in (a) limestone reef (b) Anticline, wedgeout and lens trap (c) salt dome (d) fault.

2.1.3 EXPLORATION, PRODUCTION AND STORAGE

2.1.3.1 Exploration

Three periods in the history of oil and gas exploration have been identified as (i) pre-1920 (ii) 1920-1950 (iii) 1950 to present time. Prior to 1950, exploration was based on the 'hunch' of the prospector and was dependent on what could be observed on the earth's surface. Later, techniques were developed to prospect on the sub surface. Since the 1950's, however, new methods have been developed due to the availability of hi-speed computer, and the search for oil has moved increasingly offshore onto the continental shelves /89/. Methods used in oil exploration today include geological mapping, topographical and geophysical surveys.

2.1.3.2 Production

A drilled well is completed for production after casings have been cemented in place. The initial recovery of oil is by natural flow and output is controlled at the well-head by a seies of valves known as 'christmas tree'.

In the North sea where oil descoveries were made in water depths exceeding 150m, techniques of production have moved significantly to the use of giant platforms built from concrete or steel and housing production equipment. The concrete platforms also incorporate crude oil storage tanks /89, 189, 190/.

The production from a well, in addition to the liquid and gaseous hydrocarbons, include non-hydrocarbon gaseous impurities such as hydrogen sulphide gas which imparts a noticeable odour to the oil, carbon dioxide, nitrogen and Helium. The contents also include saline water containing soluble salts and solid particles such as sands and shales.

2.1.3.3 Storage

The extracted fluids are passed from the production platforms into a separation chamber where most of the sea water, gases and other impurities are removed and the temperature of the oil is reduced from over 100 C /22, 133, 168/ to about 45-50 C /167, 168/. In the North Sea, the crude oil is either piped to shore for collection by tankers or is stored in the platform storage tanks. Offshore storage is practical as it prevents shut-down of producing wells at times when the sea state makes tanker loading impossible.

The four main types of concrete platforms used in the North sea are, Sea tank/ McAlpine, Condeep, Andoc and Howard Doris. The oil wells on which these are operative have been given in Table (1.1) of Chapter I.

Crude oil along with seawater, hydrogen sulphide and other impurities which may have escaped removal in the separation chamber, are stored in the concrete storage tanks at 45-50 C. However, crude oil is continuously removed from the tanks and replenished /94, 174/, thereby allowing a rapid build up of sand and wax at the bottom and on the walls of the tanks /117/. This reduces effective storage capacity and may also provide static conditions for the development of corrosive materials leading to deterioration.

2.1.4 PHYSICAL AND CHEMICAL PROPERTIES

Petroleum is made up of a series of complex hydrocarbon compounds, ranging from a light gas, methane, through liquid petroleums, waxes, to a series of heavy solids (asphalt) with 70 or more carbon atoms (Table 2.1). The various hydrocarbons that comprise crude oil are separated by distillation under increasing temperatures. Crude oils vary greatly in their physical and chemical compositions, they are greasy or oily to the touch, may be thin, thick or viscous semi solid, and may be brownish green to black in colour. Crude oil is immiscible with water and since it has a lower density, floats on it.

2.1.4.1 Physical Properties

Crude oils are generally classified on the international markets based mainly on their specific gravities. The American Petroleum Institute (API) gravity scale is widely used in expressing quality of crude oils. In general, the lower its density the higher the API gravity (Table 2.2). Such oils usually have a lower sulphur content and therefore are of higher quality /58, 75, 163/. North Sea oil, along with Nigerian Bonny light, are classified as light crudes because of their low specific gravities (higher API) and low sulphur contents. A typical analysis of NS oil is given in Table (2.3).

Viscosity is that property of any fluid which tends to resist a shearing force and is important to fluid flow because nearly all fluid motion is accompanied by shearing forces. It can therefore be defined as a measure of the internal resistance to motion of a fluid, due to the forces of cohesion between molecules or molecular groups. Viscosity is the most important single fluid characteristic governing the motion of crude oil /83, 182/. It is reduced by increase in the amount of dissolved gas in solution and by temperature, but increases with increase in specific gravity. The two basic viscosity parameters are the dynamic (absolute) viscosity, expressed in poise or centipoise and the kinematic viscosity, which is the dynamic viscosity divided by fluid density and is expressed in stokes or centistokes.

Surface tension is another important property of crude oil and is a measure of the force acting at the boundary between a liquid and solid phase, or between a liquid and gaseous phase /182/. However, when two immiscible liquid phases are in contact (eg. crude oil and water), the attractive forces at the interface are referred to as Interfacial tension /83, 182/. These forces increase with increase in molecular weight and decrease with rising temperature, and are reduced when non hydrocarbon materials, especially polar compounds such as soaps and fatty acids, are dissolved in crude oil. Dissolved gases and even hydrocarbons cause similar effects.

Where oil-water systems are involved, the pH of the aqueous phase will have an influence on the tension at the interface, an increase in pH will cause a rapid decrease of the interfacial tension /75/. Although these tension forces are generally regarded as important and have been

studied for many years, it is felt that the narrow range of values obtained for such widely diverse components of crude oil fractions, has rendered them of little value for any attempted characterization /182/. However, it is considered that surface tension is of some importance at the interface of an acidified water/ crude oil system.

2.1.4.2 Chemical Properties

Crude oil consists basically of compounds of two elements, carbon and hydrogen, which form a large variety of complex molecular structures. But inspite of physical and molecular variations, the range in composition by (%) weight is true for all crude oils as given below /58, 75, 163/:

Carbon	83.0 - 87.0
Hydrogen	10.0 - 15.0
Nitrogen	0.1 - 2.0
Oxygen	0.05 - 1.5
Sulphur	0.05 - 8.0
Metals	0 - 0.1

(a) Hydrocarbons

Hydrocarbon components of crude oil can be divided into 3 classes: Paraffins, Naphtenes and Aromatics. A fourth class, Olefins, are not found in crude oil /163/. Some examples of members in these groups and their properties, are given in Table (2.4).

-Paraffins

They have the general formula C_nH_{2n+2}, where n is the number of carbon atoms present in the compound. They are saturated (contain maximum number of hydrogen atoms), straight or branched chained, and are inactive under most conditions. Straight chained members are known as normal-paraffins and the branch chained as iso-paraffins.

TABLE 2.1: Hydrocarbon fractions obtained from petroleum /26/

Hydrocarbon fractions	molecular size range	Boiling point °C
Natural gases	$C_1 - C_5$	-164 to 30
Liquids :		
petroleum ether	$C_5 - C_7$	30 to 90
gasoline	$C_5 - C_{12}$	30 to 200
kerosene	$C_{12} - C_{16}$	175 to 275
gas oil, fuel oil and diesel oil	$C_{15} - C_{18}$	250 to 400
Waxes :		
lubricating oils	C_{16+}	350+
greases, paraffin wax	C_{20+}	melts at 52 - 57
Solids :		
asphalt (residue)	C_{70+}	

TABLE 2.2 : API gravity scale /58/.

specific gravity at 16 C (60 F)	1.000	0.9340	0.8762	0.8251	0.7796	0.7389
API degrees	10	20	30	40	50	60

$$^{\circ}API = \frac{141.5}{\text{sp. gravity}} - 131.5$$

TABLE 2.3 : Some properties of a typical N S crude oil (Forties) /138/.

gravity, °API	36.6
sulphur (% wt)	0.30
viscosity (cSt) at	
10 C	9.6
21 C	6.8
wax (% wt)	7.0
carbon residue (% wt)	2.2
density at 20 C (kg/l)	0.838

-Naphthenes

They are saturated hydrocarbons similar in properties to the paraffins and have the general formula C_nH_{2n}. However, unlike the paraffins, the carbon atoms are arranged in closed rings, hence are also known as cyclo-paraffins. They have little tendency to react chemically and those found in crude oil have 5 to 6 carbon atoms in the ring.

-Aromatics

These are unsaturated hydrocarbons with ring compounds and general formula C_nH_{2n-6}. The basic structure is always a six member ring, with various side chains attached to form a variety of aromatic hydrocarbon compounds such as benzene, toluene, xylene and naphtalene. Aromatics are chemically active and are stable during storage /163/. They are found in all crude oils in proportions varying from 10-50 percent and sometimes even higher /182/.

(b) Non-hydrocarbons

Crude oil contains small but often important quantities of compounds of sulphur, nitrogen and oxygen, as well as metallic elements.

-Sulphur compounds

Various amounts of sulphur are found in different crude oils occurring as free sulphur, H_2S gas or as organic sulphur compounds. They are undesirable in crude oil because of their potential corrosiveness and the obnoxious smell of the H_2S. In the prescence of bacteria, hydrogen sulphide can be oxidised to sulphuric acid /65, 129, 145/.

-Oxygen compounds

Although the oxygen contents of crude oil is often less than 2 percent by weight, its influence in acidifying crude oil may be significant, especially for oils stored in steel or concrete tanks. The oxygen content of crude oil is indicated by its acid content which is usually less than 1 percent, although crude oils of naphthenic composition, including acetic and formic acids /83/, may have an acid content of up to 2 percent. In the low and medium boiling point range, oxygen is mainly present in the form of acidic compounds such as organic acids and to a limited extent, phenols /83/. Exposure to prolonged atmospheric oxidation may cause the oxygen content to increase /75/.

-Nitrogen compounds

Nitrogen, generally less than 0.1 percent by weight, is present in practically all crude oils, sometimes as part of the dissolved natural gas.

-Metal compounds

Practically all metals have been found in the ash of petroleum residues, but the amount is usually very small, often less than 5 ppm and are generally harmless. Trace metals such as Vanadium may however, pose a corrosive problem.

-Water

Saline water, saturated with sodium and potassium salts, is produced with the oil. This is because the crude oil is usually found in sedimentary permeable rocks which were laid down in water and are difficult to separate from the oil.

TABLE 2.4 : Some members of hydrocarbon series found in crude oil.

Series	Individual hydrocarbons	chemical formula	molecular weight	Boiling point, C	chemical reactivity
normal-paraffin	methane	CH_4	16.0	-161.5	very low
	ethane	C_2H_6	30.1	- 88.6	
	propane	C_3H_8	44.1	- 42.1	
	butane	C_4H_{10}	58.1	- 0.5	
iso-paraffin	iso-butane	C_4H_{10}	58.1	- 11.7	medium
	iso-pentane	C_5H_{12}	72.1	27.9	
	iso-hexane	C_6H_{14}	86.1	49.7	
naphthene	cyclopentane	C_5H_{10}	70.1	49.3	very low
	cyclohexane	C_6H_{12}	84.2	80.7	
aromatic	benzene	C_6H_6	78.1	80.1	high
	toluene	C_7H_8	92.1	110.6	
	ortho-xylene	C_8H_{10}	106.2	144.4	

2.1.5 BACTERIAL ACTIVITY AND ACID ATTACK

2.1.5.1 Bacterial Activity and Acidity

Microbial ecosystems are known to exist at the crude oil/ water interface of concrete storage tanks in offshore structures. Crude oil floating on stagnant saline waters provides suitable growth environment for aerobic oil oxidising bacteria (OOB) and anaerobic sulphate reducing bacteria (SRB). The conditions are enhanced by the favourable storage temperatures of 45-50 C /129/. The nett effect of the actions of these bacteria are the lowering of pH of water and the production of H_2S which can be converted to H_2SO_4, thereby creating a potentially aggressive environment in terms of concrete durability.

Wilkinson /209/ had found from experience offshore on Shell Petroleum installations that significant concentrations of H_2S are generated by SRB in accumulation of stagnant waters. It is believed that the formation of stagnant conditions results from growth of aerobic bacteria in large volumes of water. More often than not, these are contaminated with organic materials and sewerage discharge /129/ and can be found in the legs or storage cells of offshore structures. Once the oxygen is consumed, conditions are ideal for the growth of SRB which can use the sulphate present in seawater for their growth /209/. Morgan et al/129/ have also observed that an adequate carbon source is necessary to maintain growth of the indigenous microbial population in stagnant seawater. It seems that both conditions are suitable, as has been clarifiedby King and Stott /101/. They have observed that the usual limitation of growth of the bacteria is the carbon source, but in many oil systems with mixed population of organisms, the carbon source is not restrictive and the limitation is the sulphate. Under the circumstances, the level of sulphate in the water has a direct relationship with the level of activity of the SRB and of the sulphide produced.

Findings of a Shell research group/129/ in a recent study of microbial activities in offshore structures based on literature and experimental investigations can be summarised as follows:

- two main types of bacteria, aerobic OOB and anaerobic SRB, exist in the oil/water system.
- the environment is thought to contain both aerobic and anaerobic regions simultaneously.
- it is clear that SRB are responsible for the production of H_2S but do not make any significant direct contributions to a fall in pH and may even cause it to rise (Figure 2.3) /1, 153/.
- hydrocarbon degradation by OOB, leading to the formation of intermediate products such as fatty acids, is believed to be responsible for the lowering of pH.
- it is generally agreed that the rate at which SRB are able to grow and the levels of H_2S that are produced in the water, are greatly influenced by whether oil is present /129, 209/.

Wilkinson /209/ had monitored the fall in pH in the water filled legs of some offshore structures. It was found that in the absence of crude oil and the main carbon source on which the bacteria were growing was the stagnant seawater, the doubling time of the SRB was in the order of 6 to 8 days. The maximum amount of H_2S produced was about 5 mg/1 and pH fell from 8.2 to 6.7. However, in the presence of crude oil, the doubling time was much faster and was between 10 to 15 hours and the maximum H_2S level was 50 to 100 mg/1, while pH was reduced to 6. Findings of the Shell research group /129/ on tests on aerobic growth (Fig. 2.4) are in agreement with this.

Although SRB are responsible for H_2S production, they are unlikely to directly contribute to a fall in pH /129/. Nevertheless, in the presence of the bacteria Thiobacilli, H_2S may be oxidised to sulphuric acid (H_2SO_4) which may indirectly contribute to fall in pH.

The conditions in partially filled sewerage tanks which lead to the production of H_2S /65, 144, 145, 194/ may have some similarities with the environment created in offshore oil storage tanks. This is because growth of the Thiobacilli in sewerage tanks are encouraged by the co-existence of aerobic and anaerobic conditions /65, 129, 144, 145, 194/ and this may also exist in the oil/ water system in the storage tanks. Parker /144, 145/ had reported that given such conditions, the two bacteria Thiobacilli X and Thiobacilli Concretivorous, which thrive in such systems can cause the production of H_2SO_4 and the

lowering of pH to between 2-3 and and possibly to as low as 1.0 /145/. This has been supported by Wilkinson /209/ and Thornton /194/.

Given such possible acidic conditions in the water phase, it is not known if the crude oil is also indirectly acidified. No information could be obtained in the literature as regard this situation.

2.1.5.2 Acid attack on concrete

The attack on concrete by acids generally leads to the deterioration of concrete strength, loss of weight and reduction of the concrete to a formless mass /145/. All acid solutions attack concrete, although the extent of the attack varies with the strength of the acid which can be measured by its pH. In practice, attacks occur at pH values of 6.5 and below /170/. Lime is the primary reactant in this reaction, because it is alkaline, it tends to neutralise the acid until it is completely depleted, whereby the acid then attacks the concrete matrix. In the particular case of offshore concrete storage tanks, attack is likely to come from seawater acidified with sulphuric acid as well as organic acetic acid, produced by bacterial action /129/.

Concrete exposed to sea water acidified with sulphuric acid will deteriorate due to the following reactions:

- combination of H_2SO_4 with the free lime to form a less soluble gypsum ($CaSO_4$).
- combination of gypsum and hydrated calcium aluminate to form calcium sulphoaluminate (ettringite) which is expansive.

Both reactions cause volume increase of the concrete mass. Crystallization of the sulphate salts in the pores of the concrete result in further damage through spalling of the concrete surface /129/. Sea water acidified with acetic acid (CH_3COOH) reacts with the free lime to form a soluble calcium acetate /18, 109/, leading to rapid loss of free lime. There are also secondary reactions taking place between the cement phases and the sea water constituents. Morgan and co-workers /129/ had reported that sea water attack on typical North Sea concrete is essentially mild surface attack, greatest of which was associated

with environments where acetic acid and H_2S containing media were involved. However, since the situation in the storage tanks is not known for certain, it is impossible to predict the conditions of the concrete which may be interacting with acidified crude oil and water.

2.1.5.3 Acid intake and Determination of acidity of crude oil

The problem of the acid intake of crude oil lying on acidified sea water was unresolved /130, 191/ and no work had been done on it prior to the current investigations /99, 140/.

Studies of the inorganic and organic acid intakes of North Sea crude oil /99, 140/ are reported in Appendix A. Results have indicated that there was no intake of sulphuric acid (H_2SO_4) by the crude oil from the water phase, even at a pH level as low as 2.2 and at temperature of up to 80 C. Similarly, the intake of acetic acid from the water phase was insignificant at pH level of 5, which is the practical acid level in the storage tanks. However, at pH of 2.3, there was significant increase in the acidity of the crude oil.

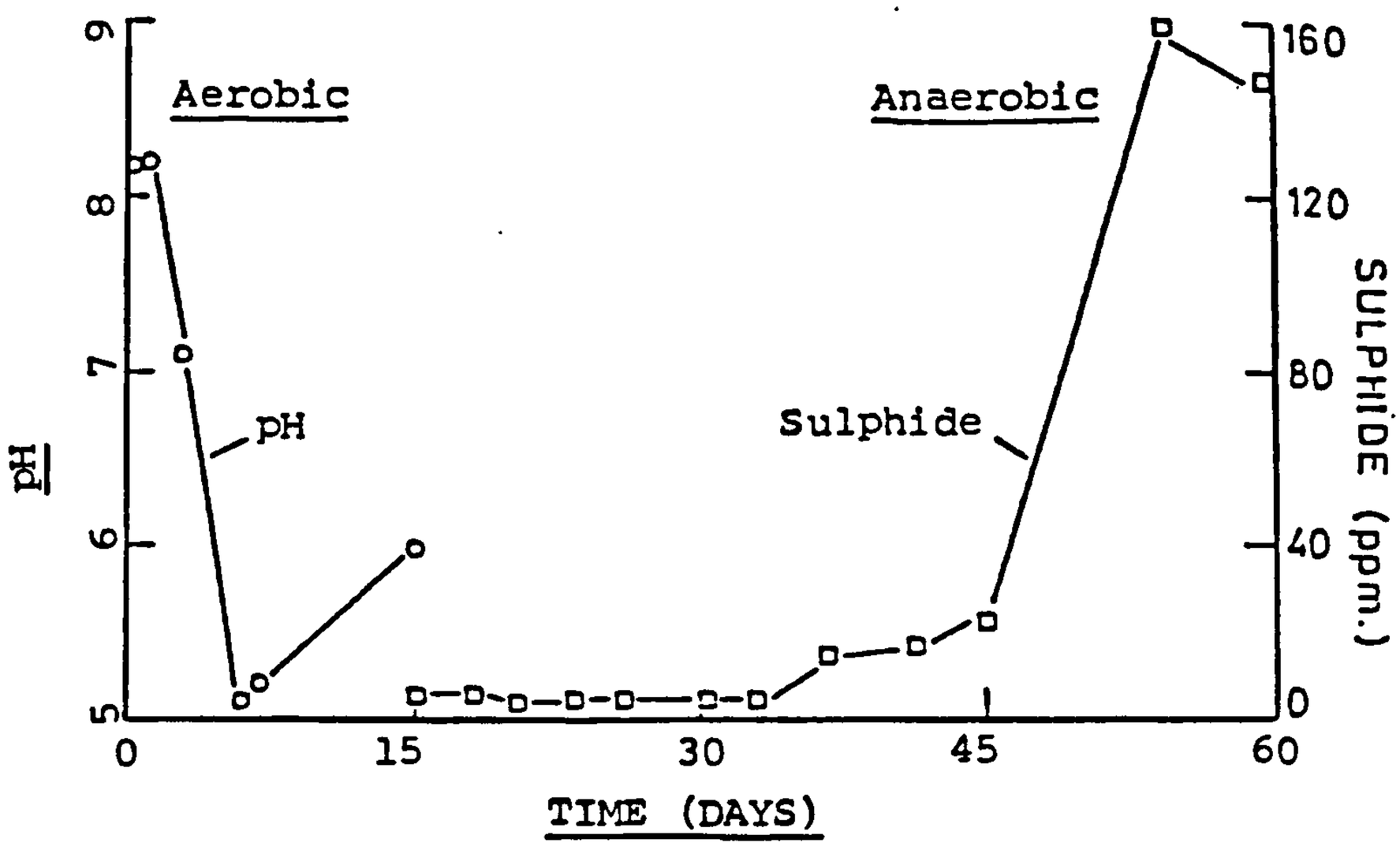


Figure 2.3: Fall in pH and production of hydrogen sulphide during aerobic and anaerobic growth with an oil/water medium /129/.

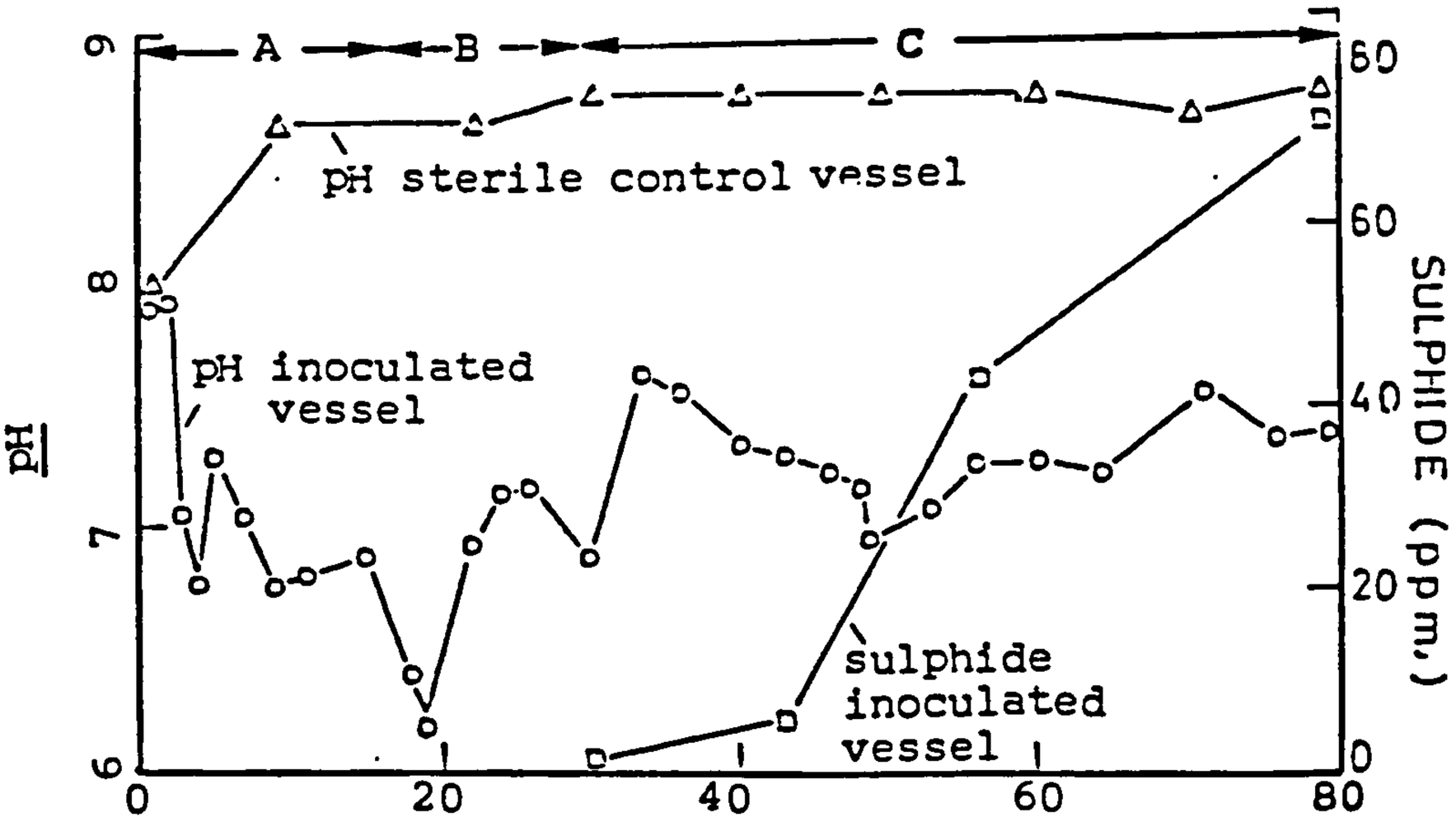


Figure 2.4: Change in pH and production of hydrogen sulphide during aerobic and anaerobic growth in an oil/water medium containing mortar test specimens /129/.

A = Aerobic conditions under forced aeration.
B = Progressive anaerobosis condition.
C = Strictly anaerobic condition. Growth of SRB.

2.2 DURABILITY OF CONCRETE

2.2.1 INTRODUCTION

The durability of concrete used in offshore oil storage tanks is influenced by its single or multiple interaction with seawater, crude oil and elevated temperature. The effects of each of these exposure conditions differ a great deal from one to the other.

A review of the durability of concrete subjected singly to sea water, crude oil and elevated temperature has been studied through changes occurring to physical properties such as permeability, penetration, compressive strength and volume changes. However, the mechanisms influencing each of these conditions will first be discussed.

This literature review does not attempt to discuss each of these subjects in full or at length. At best, an attempt has been made at highlighting relevant areas pertainining to the experimental programme in this thesis, the details of which are reported in following chapters.

2.2.1.1 PERMEABILITY

The vulnerability of concrete to external attack largely depends on its permeability, which is why most authors have considered permeability as a direct measure of concrete durability. For a mature normal weight concrete, permeability has been shown to depend on the pore structure rather than on its porosity alone /123, 137/. It is also affected by cracks and microcracks, which may have occurred as a result of improper casting and curing procedures, temperature of the surrounding and shrinkage stresses.

The porosity and pore structure of the hardened cement paste (HCP) are influenced by such factors as water/cement ratio, cement content, cement type, aggregate grading as well as the casting and curing methods. Permeability of concrete is generally of interest especially in relation to water-tightness /134/ and in its use in liquid retaining structures.

Two main methods of measuring permeability described in most national standards are the penetration and out-put (steady state) methods. The penetration method appears to be the more practically applicable /107/ although the out-put method has been more widely used, especially since it enables the calculation of the coefficent of permeability, K. This is expressed in units of metre/second and is given by Darcy's equation for laminar flow through a porous medium expressed as:

$$dQ/dt = K\,A\,dh/L \qquad (2.1)$$

where dQ/dt is the rate of flow of water in m^3, dh is the drop in hydraulic head through the sample measured in m, and L is the length of path of water flow (sample thickness) in m.

In general a large scatter of results occur, as is shown in Fig.(2.5). Critics of this method have observed that Darcy's law is not strictly applicable to concrete /38/. Glanville /72/ found that the rate of flow through concrete decreases with the duration of test even for water, indicating that there is no unique value of K. It was also observed that the applied pressure of fresh water is proportional to flow only during the initial stages of a test, flow for any pressure subsequently tended to become constant, thus supporting the view that flow through concrete is not accurately defined by Darcy's law.

According to Powers /156/, cement permeability is determined by the capillary porosity, the effect of gel porosity is negligible. However, in the low water/cement ratio range below 0.5, where capillary pores are discontinuous and separated by the gel, it is the gel porosity, although very low, which determines the permeability.

Drying concrete can increase its permeability by up to 70-fold /48/ or even higher /202/.

Powers et al /155/ attributed such increase as possibly due to the rupture of some of the gel between capillaries, through which new passages were opened for water.

Reduction in the volume of large pores in concrete reduces its permeability. Manmohan /116/ has shown that the transformation of large permeable pores to smaller and less permeable ones can be achieved by the use of pozzolans, slag and chemical admixtures. Pozzolans such as pulverised fuel ash (PFA) in particular, have been shown to reduce permeability /37, 142, 207/, through a pore-blockage phenomenon /118/.

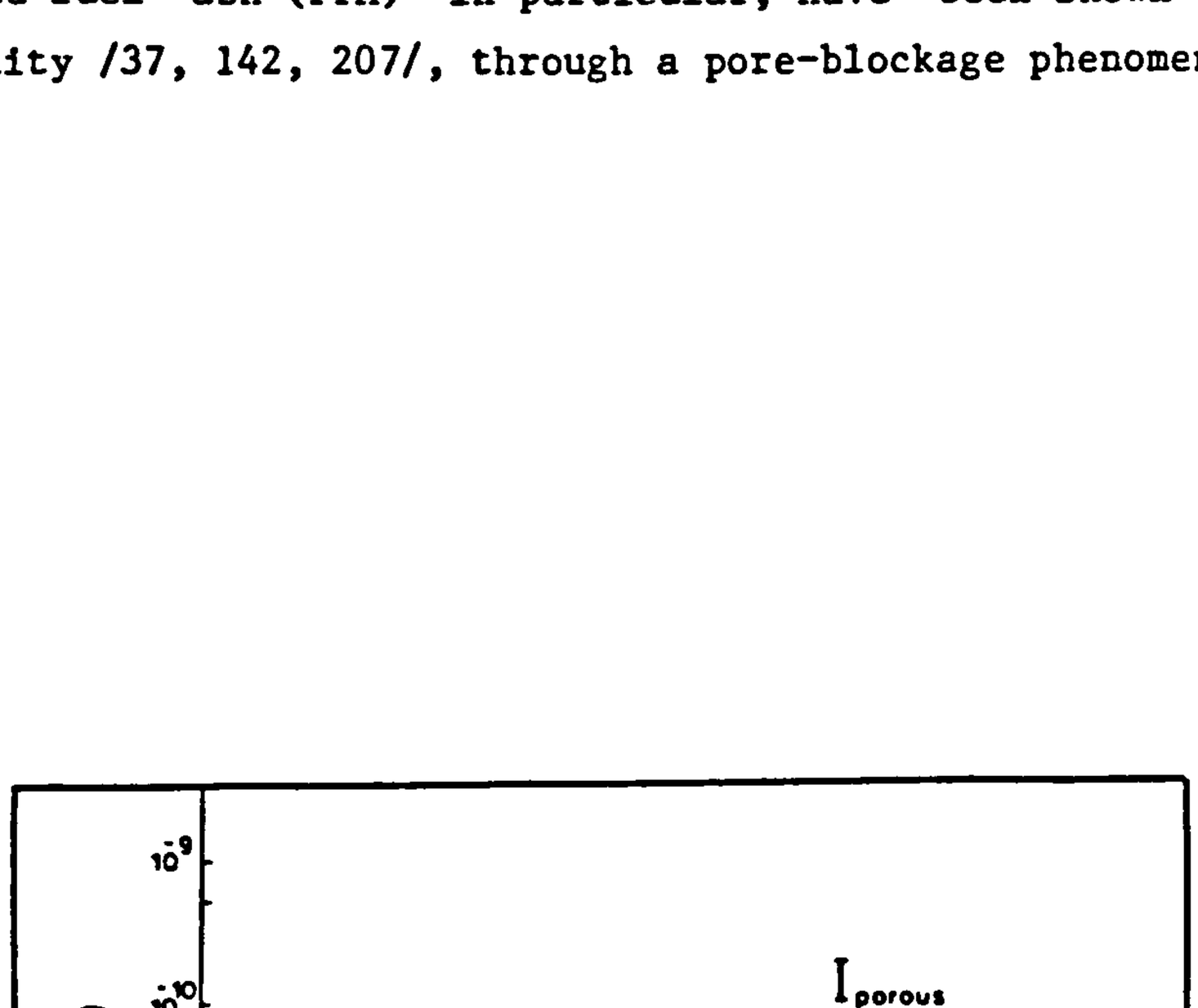


FIGURE 2.5 : Comparison of concrete permeability data. w/c = 0.4 - 0.5 in all cases /28/.

2.2.1.2 PENETRATION

Several methods have been developed to measure penetration into concrete, amongst which is the method of Murata /131/. In this test, penetration depths of water into partially dried concrete specimens at water pressure heads of 5 to 20Kg/cm3 was investigated. Pressure was applied for 24 to 48 hours and the depth of penetration was noted visually by splitting along the specimen diameter. A diffusion coefficient for the water in the concrete was then calculated. Other methods include those of Figg /63/, Valenta /198/ and the ISAT devised by Levitt /110/. In the ISAT method, the rate of absorption of water by oven dried specimens (105 deg.C) at various intervals ranging from 10min to 2hrs in water, can be determined. The method of Valenta /198/, which is discussed in some detail in section (2.2.2.2), is based on a theoretical relationship, developed for unsteady percolation of water through concrete. From this, an approximate value for the coefficient of permeability, K, can be determined. Various methods devised to determine penetration of hydrocarbons and other fluids through concrete are discussed in section (2.2.3.2).

Penetration of any fluid material into concrete depends on the permeability of the concrete surface, as well as on the properties of the fluid. Factors affecting the permeability of concrete have been previously discussed, however, it has been proposed that concrete acts as a molecular sieve /128/.

MILLS /128/ suggested that different sized molecules will penetrate differently into the concrete pore system. In particular, small sized molecules as in water (2.5Å) would penetrate the smaller inner pores (gel pores) not reached by larger molecules. Most fluids of larger molecular size will, however, be able to penetrate the capillary pores. This theory has found support from a large number of workers /46, 77, 126/, but not by others /61/.

MIKHAIL and SELIM /126/ have described the existence of gel masses with internal pores separated by an 'external'pore system within which is an 'intermediate' pore structure. The theory came about when it was found that different sized molecules of different fluids penetrated to different depths in the concrete pore system.

COOK and HAQUE/46/ similarly concluded that the inability of benzene (4.5A) and kerosene (7A) to cause any changes to the properties of concrete as compared to water (2.5A), was due to the molecular sieve effect which allowed water particles to penetrate gel pores not reached by the other fluids.

FELDMAN /61/ was less certain about the molecular sieve effect and has suggested that even fluids of similar molecular size to water such as, nitrogen (3.4A) and methanol (4A) cannot penetrate pores reached by water. The ability of water to penetrate the interlayer space is attributed to its special 'affinity'.

The effect of polarity on penetration is not very clear, Robertson and Mills /169/ appeared to have found a relationship between the reduction in strength and polarity. However, it is believed by some others /77, 126/ that dipole moment of molecules has no appreciable effect on the ability of a fluid to penetrate concrete. In penetration tests involving several organic vapours, methanol with strong dipole moment did not penetrate further than nitrogen which is non-polar and is only slightly smaller in size /126/. HANNANT /77/ had similarly found that formamide which has a high dielectric constant similar to that of water, did not penetrate a larger volume of pores than the other non-polar fluids.

It can be appreciated therefore, that penetration into concrete by any fluid, depends mainly on the fluid molecular size and probably on its polarity. Viscosity and surface tension also play a role, as would be shown in the following section. Although the special case of water as pointed out by Feldman cannot be ignored, however, it seems that the granular composition of concrete coupled with the evidences given by a number of other authors, indicate that concrete acts as a molecular sieve.

2.2.1.3 VOLUME CHANGES

Volume changes in concrete are associated mainly with the hardened cement paste (HCP) since volume changes in good concreting aggregate is so much smaller. In fact, aggregates actually restrain the amount of shrinkage that can be realised. The volume of the HCP varies with its water content.

Volume changes in the HCP are actually caused by physical factors, but may also be as a result of chemical factors such as carbonation. Under saturated conditions (100% RH), expansions occur /111, 157/, but in unsaturated air, concrete shrinks /111, 157, 181/.

Volume changes in the HCP is dependent on two factors; the intrinsic factor which is built into the mix determines the porosity and is affected by curing and storage conditions. The other is the environmental factor and it directly affects porosity. It includes such elements as; relative humidity, air movement, temperature, length of drying period and specimen size.

(i) Curing and storage conditions

The relative humidity of the medium surrounding concrete greatly affects shrinkage, as can be seen in Fig.(2.6). The expansion in water and the shrinkage in unsaturated air suggest that the vapour pressure within the paste is always less than the saturation vapour pressure. In fact, it has been reported that at 94% humidity, the paste is in hygral equilibrium with its environment /134/. In practice, however, equilibrium is considered possible only in small and practically unrestrained specimens /134/.

(ii) Porosity

The effect of porosity on shrinkage is a combination of the effects of water/cement ratio, degree of hydration, cement type and constituents. All these are extensively discussed in most concrete literature.

The question of the mechanisms causing volume change, has generated a great deal of controversy. Various mechanisms have been put forward including, capillary tension, surface energy, swelling pressure and interlayer movements. A comprehensive survey can be found elsewhere /39, 164, 181/. The models on which these mechanisms are based such as those of POWERS /159/, ISHAI /91/, FELDMAN /61/ and WITTMAN /210/ are also well documented. A summary of these mechanisms is given in Table (2.5) and is discussed below.

(a) Capillary Tension

The basis of this mechanism can be found in the relationship between the radius of curvature, r, of the meniscus and the corresponding vapour pressure, p, from Kelvin's equation as:

$$\ln (p/p_o) = 2T / R\theta\rho r \qquad (2.2)$$

where p_o is saturated vapour pressure over a plane surface, T is the surface tension of the liquid, R is gas constant, θ is temperature in Kelvin and ρ is the density of the liquid.

It is usually assumed that the mechanism of capillary tension is operative in the RH region exceeding 40 per cent, and according to Ishai /91/ most of the shrinkage occurring can be attributed to this mechanism. Feldman and Sereda /61/ considered the mechanism to be of some importance when shrinkage takes place due to drying at RH higher than 35 percent. Mikhail and Selim /126/ in their work with organic vapours, recognised the importance of capillary condensation as one of the mechanisms holding the adsorbate within the pore system. However, it was felt that the Kelvin equation did not provide for the effect of physical adsorption on the pore walls, the thickness of which should be added to the radius obtained. Powers /159/ regarded capillary tension as being of limited importance.

Table 2.5 : Shrinkage mechanisms according to four authors /181/.

Authority	*Relative humidity, %* 0 10 20 30 40 50 60 70 80 90 100
Powers	Variations in swelling pressure
	Augmentation by capillary effects
Ishai	Variations in surface energy / Capillary tension
Feldman and Sereda	Movement of interlayer water / Capillary tension and variations in surface energy
Wittmann	Variations in surface energy / Variations in swelling pressure

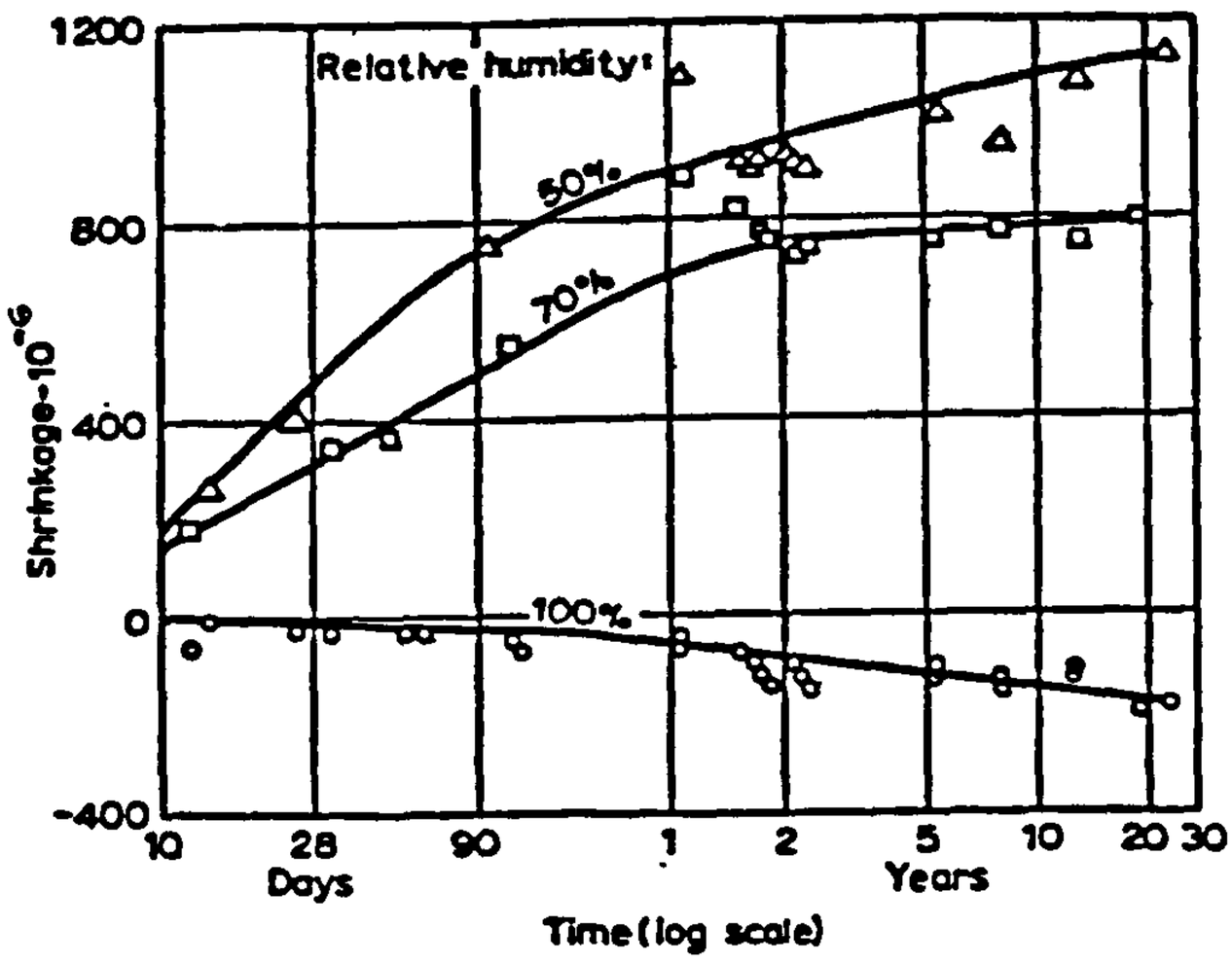


Fig. 2.6: Relations between shrinkage and time for concrete stored at different relative humidities /134/ (Time reckoned since end of wet curing at the age of 28 days).

(b) Surface Energy

Because the molecules at the surface of a material are subject to attraction forces from the body of the material, the surface tend to contract and behave like a stretched elastic skin. The resulting tension in the surface is known as surface tension and is defined as the force which acts in a direction tangential to the surface at right angles to any given line of unit length on the surface. It is measured in N/m. 'Surface energy' is defined as the amount of work required to increase the surface area by one unit, and is measured in erg/cm2.

The mechanism attributes volume changes to variations in surface tension of gel particles which are brought about by variations in the amount of the adsorbed water (only physically adsorbed water affects surface tension in this respect) /181/. Hence the mechanism is valid only at low humidities up to about 40 per cent. This is a part of the Munich model of Wittman /210/ which has been used to explain the behaviour of cement paste.

Cook and Haque /47/ extended Wittman's work by using methanol as an adsorbate, in addition to water and later, kerosene and benzene /46/. By testing compressive and tensile strengths, as well as dimensional changes of HCP's saturated with these fluids, reductions in strength caused by sorption was related to the lowering of the surface energy. This is in agreement with the work of Bangham and Fakhoury /14/, who found the relationship between the expansion dL/L of a solid and the reduction in surface energy as :

$$dL/L = \lambda(Fo - Fh) \qquad (2.3)$$

where λ is a material constant, Fo is the surface energy in the absence of an adsorbed film and Fh is the surface energy with an adsorbed film at a relative humidity, h.

Feldman found that over the range 0-100 percent RH, only 20 percent was attributable to changes in surface energy. He therefore concluded that surface energy effects are of secondary importance in volume changes /61/. Powers considered it as of even less importance and suggested that such changes affect only slightly, if at all, volume changes of cement paste /159/. Hannant /77/ dismissed surface tension of liquids in large capillaries as of any importance in the creep or shrinkage processes after examining the effect of resaturating dry

concrete with fluids of large molecular dimensions such as benzene and calcium tetrachloride.

(c) Swelling Pressure

The pressure which develops as a result of adsorbed fluid layers on adjacent sides of a pore, tends to separate the adjacent particles, thereby causing swelling. This pressure is referred to as 'swelling' or 'disjointing' pressure. The thickness of the adsorbed layer increases with RH, reaching in the case of water a maximum equivalent to a layer five molecules deep and approximately 13Å.

Powers /157/ was the first to attribute volume changes to this mechanism over the whole vapour pressure range. Wittmann's model /210/ attach some importance to the mechanism but only in the RH range beyond 50 percent. However, it is completely rejected by Feldman and Sereda /61/. Their model assumes that the interparticle bond is a solid to solid contact which will not be broken due to the adsorption of water.

(d) Interlayer Movement

Feldman and Sereda /61/ had proposed that the movement of water into the interlayer structure of the gel particles was reversible and caused volume changes. It was found that on rewetting a dry sample of concrete to 100 percent RH, over 80 per cent of the expansion was attributable to re-entry of interlayer water.

Cook and Haque /46/ stated that creep of concrete was related to interlayer movement as well as penetration of adsorbate in the gel structure. Hannant /77/ referred to interlayer water as intracrystalline or zeolithic water embedded between tobermorite crystalline layers. However, none of the publications reviewed has suggested that fluids other than water, except possibly helium /60, 61/, is able to penetrate the interlayer space.

2.2.1.4 COMPRESSIVE STRENGTH

Strength is one of the most researched and most documented property of concrete. This is probably because it serves as an indication of the overall quality of concrete and also because it is relatively easy to measure, at least in uniaxial compression. The strength of concrete at normal temperatures depend amongst others, on the intermolecular bonds (Van der Waals) within the cement paste, its adhesion to the aggregate particles,as well as on some of the aggregate properties. Multitude of factors influence the measured strength of concrete, of particular importance are :

- concrete mix constituents, mix design, type of aggregates, etc.
- shape, size, texture, etc. of aggregates.
- casting and curing conditions, age of testing.
- moisture condition at loading.
- size and shape of test specimen.
- testing apparatus, method of loading, rate of loading, platen stiffness, etc.
- history of exposure to chemical attack (seawater, etc.)
- temperature, etc.

The compressive strength of concrete has been generally determined on samples of cubes or cylinders and is defined as the maximum stress sustained by the test specimen under a load Pmax and over a cross-sectional area, A (Fig. 2.7).

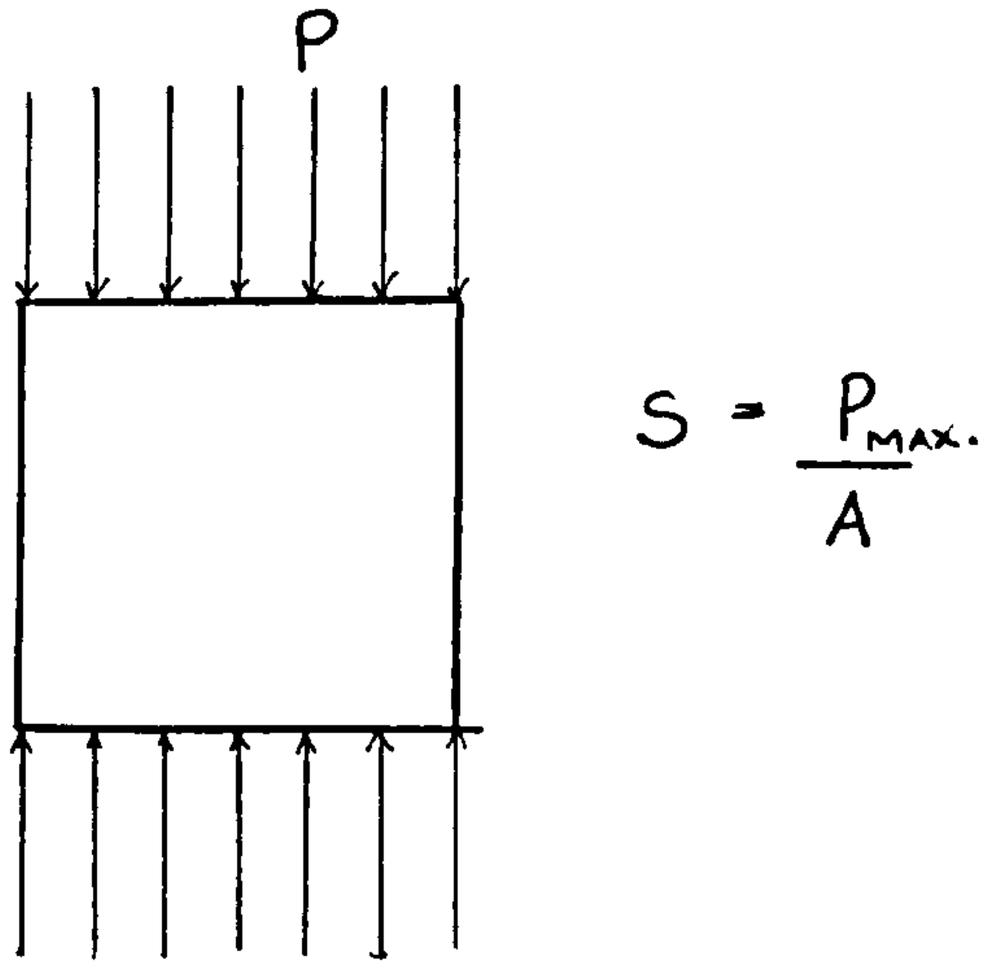


FIGURE 2.7 : Testing concrete in compression.

In practice, the conditions of testing concrete in compression are such that both ends of the test specimen should be truly plane, in order to avoid stress concentrations. This is because lack of planeness will reduce the effective contact area between the specimen and the bearing plate of the test machine, the effect of which is often a reduction in strength of the specimen. Ridges on concrete surface must also be avoided especially for small specimens as this may result in splitting and tensile effects, even while loading in compression. An even surface is usually achieved either by capping, grinding or packing with a bedding material. Grinding, using silicon carbide abrasion, has however been reported to produce the most satisfactory results /134/, its only disadvantage is its high cost.

Bearing platens of a testing machine restrain the lateral expansion of the concrete, the degree of restraint depends on the friction between the platens and the specimen. If either of the contact surfaces becomes lubricated, friction is eliminated, great lateral strains are observed and the specimen fails under a lower load. The mode of failure is often parallel to the direction of loading (along specimen length) /181/. The anomaly is that although the compressive strength so measured reflects the true strength of the concrete, this is often disregarded. This is because restraints (platens) are usually applied in practice and strength thus measured is regarded as the 'real' strength and the former only thought of as an 'apparent' measurement.

2.2.1.5 STRENGTH/POROSITY RELATIONSHIP OF HCP

As is well known, concrete strength is determined by the strengths of the aggregate, the paste and of the paste/aggregate bond. However, the strength of the paste is the main factor when considering compressive strength /181/. This is a function of the paste porosity as well as of the gel concentration, which in turn is dependent on the water/cement ratio, also an important factor in paste/aggregate bonds.

Powers and Brownyard /154/ considered that strength is related to the gel and expressed this in a 'gel space ratio'(X), defined by;

$$X = \frac{\text{gel volume}}{\text{gel volume + capillary volume + entrained air volume}} \qquad (2.4)$$

The strength S, was related to X by the equation;

$$S = AX^n \qquad (2.5)$$

where A is strength at zero porosity and n is a constant ranging from 2.6 to 3. This model indicated that maximum strength is achieved when the products of hydration fill up all the capillary space and this corresponds to a water/cement ratio of 0.38. However, the model has been found to be of limited application since it neglects the volume of unhydrated cement grains and does not account for the high strength of pastes at lower levels of water/cement ratio /39, 154/. Feldman/62/ has suggested that strength depends not only on porosity, but also on the proportions of the coarse and poor crystalline materials in a hardened paste, with the latter forming solid-solid bonds more readily.

The calcium hydroxide formed during hydration can be leached out in ponded water and it is also susceptible to chemical attack. Under such conditions, it may cause loss of strength. On the other hand, it can be used to provide additional strength when pozzolans such as pulverised fuel ash (pfa) are used as partial replacement for ordinary portland cement. The chemistry of the pozzolanic reaction which converts calcium hydroxide to C-S-H gel has been described in other publications /35, 37, 142/.

The molecular sieve concept has been used to explain the effects of the sorption of fluids of differing molecular size on the strength of concrete /46, 127, 169/. Mills /127/ had shown that the strength of dried concrete on resoaking in water reduced to the same value as that of concrete continuously moist cured. It was also reported that the resaturation of dried concretes by fluids with molecular sizes larger than water resulted in strength reductions related to the size of the molecule and probably to its polarity /127, 169/. Cook and Haque /46/ have lent support to this view and in a table, reproduced below (Table 2.6), they showed reductions in compressive strength of concrete specimens saturated with different fluids. However, it can also be seen that molecules 2 and 3 times larger than water had little or no effect on strength reductions.

These results confirm that sorption sites available to water molecules are not all available to larger size molecules. Mills /127/ attributed the increase in strength on drying to consolidation of the gel and an increase in the physical forces of attraction in the gel. Moreover, reductions in strength on saturation with water was attributed to the dilation of the gel by the adsorbed, water producing a weakening effect likened to a wedging action. Thirty nine years ago, Bangham /13/ had described this phenomenon for porous solids.

TABLE 2.6 : Effect of storage conditions on compressive strength /46/

storage conditions	approx.molecular size relative to that for water	compressive strength relative to oven-dry strength
Oven-dry	-	1.000
Water	1.0	0.740
Ethanol	1.5	0.774
Paraffin	3.0	0.984
Benzene	2.0	0.990

2.2.2 EFFECT OF SEAWATER

The mechanisms involved in the attack of concrete by seawater have been extensively discussed in several references /45, 124, 28, 166/. Discussions concerning the effects of sea water on physical properties of concrete have sometimes produced differing responses. Nevertheless, there is general agreement that the corrosive attack of mortars and concrete is complex and involves several interrelated factors of physical and chemical nature.

2.2.2.1 PERMEABILITY

It is widely believed that permeability is the most important factor determining the long term durability of concrete in seawater. In a review presented by Mehta /124/, it has been suggested that most other problems arising from seawater attack such as loss of strength and volume expansion, would become less important if the problem of permeability was solved. This is generally accepted and solutions often recommended include; the use of proper mix design, the use of pozzolan and slag cements (they contain less free lime and therefore reduce the reactivity of the cement paste), proper concreting practice and the avoidance of cracks.

It is the opinion of some /181/ that durability of normal weight concrete in seawater is dependent mainly on the density and less on cement type. It was suggested that suitable density can be attained by using the ACI recommended maximum water/cement ratio of 0.45-0.50 /4/. Although a low water/cement ratio is desirable, however, it must be appreciated that the proportions of the other mix constituents are equally important.

The findings by Conjeaud/45/ of the formation of an almost impermeable layer of brucite and aragonite on concrete, can be expected to play a significant role in future designs of concrete sea structures. These layers slow down the diffusion of sulphate and chloride ions into the

concrete and prevent further penetration after about three months. This work has found support from Haynes /81/ and also from Buenfeld /32, 33/ who measured permeability through the electrical conductivity of concrete. The finding that some concretes exhibited significant reductions in permeability on seawater immersion was associated with the formation of the surface layers.

It seems therefore, that a concrete of low permeability can be achieved by the use of a proper mix design. This would limit any chemical attack mainly to the concrete surface, as has been suggested by Gilbert and co-workers /68/. Moreover, formation of the protective layer of brucite and aragonite are likely to enhance durability.

2.2.2.2 PENETRATION

Penetration, like most other physical properties depends on concrete permeability. Both are treated together in most literature. The problem of penetration at ocean depths has been studied by Browne and Domone /27/. They investigated the performance of permanently immersed concrete oil platforms in the North sea and in particular, the factors influencing seawater penetration into concrete under pressure heads of up to 150 metres. Results indicated that penetration rate of seawater into submerged concrete decreases with time, as Marion and Mahfouz/117/ had also observed. The results obtained substantiate the theoretical relationship developed by Valenta /197, 198/, between the depth of penetration under pressure and the time.

VALENTA'S theory is based on unsteady percolation of water through concrete. It assumes that the velocity, v, of water at any stage of percolation is:

$$v = K.I = K.(hr/x) \qquad (2.6)$$

where hr is the total hydraulic head given by h-ho, h is the real water head and ho is the capillary elevation. Increase of penetration depth dx over time dt can be given as:

$$dx = v.dt = K(hr/x)dt \qquad (2.7)$$

Integrating and putting x = 0 when t = 0 gives

$$X = \sqrt{2\,Khrt} \qquad (2.8)$$

from which an approximate value for the coefficient of permeability, K, can be obtained. This relation is approximate in that it disregards the time necessary for filling up large pores on the flow channels. Nevertheless, K, thus obtained is a measure of the possibility of water percolating in concrete.

2.2.2.3 VOLUME CHANGES

Seawater attack on mortar and concrete usually manifests itself in volume increases. The nature of these expansions can be attributed to chemical factors, although physical mechanisms can also be identified. It has been concluded /45/ that volume increases are caused by the formation of expansive calcium chloroaluminate and calcium sulpho-aluminate (ettringite), formed as the respective results of chloride and sulphate attacks on the cement paste.

Regourd /166/ has attributed the mechanism causing expansion to the cement composition and in particular to the C_3A content. It has been suggested that an amount of C_3A greater than 10 percent leads to great expansions in cements rich in C_3S (Figure 2.8). This is in agreement with the limitations imposed by the British Standards /31/. It has found support from a few workers /124, 199/, but has been contradicted by others /45, 135/. Conjeaud/45/ for example had found no significant correlation between the C_3A content of cement and concrete durability in seawater.

Mehta /125/ is in support of most of the other authors and has attributed expansions to the formation of ettringite. However, the

mechanisms causing expansions were not identified. This, it is believed was because there are as yet no correlation between expansion and the amount of ettringite formed. It seems therefore, that the cause of the expansions are known, however, the mechanism by which these take place are as yet, unidentified.

2.2.2.4 *COMPRESSIVE STRENGTH*

It is generally thought that attack on concrete by seawater leads to a reduction in compressive strength. However, there have only been few attempts at explaining the mechanism by which this occur /45, 124, 166/. Gjorv /69/ was one of the many researchers who found a long-term loss in compressive strength of mortar and cement paste specimens immersed in seawater. Conjeaud /45/ also reported loss of compressive strength of mortar prisms immersed in seawater over a period of 3 years, relative to similar prisms immersed in ordinary water. However, a wide scatter of results was obtained but the indications were that the losses were larger after two years of exposure (Fig.2.9). It was concluded that strength losses cannot be attributed to crystallization of calcium chloroaluminate, since this can be accomodated by the pores and could even cause strength to increase due to the lowering of porosity. However, depletion of free lime as a result of sulphate attack can cause the loss of compressive strength /68/ as porosity increases. However, Regourd /166/ has opined that strength measurements do not serve as a good enough basis for determining concrete durability in seawater. Although this may be correct, especially when compared for example with length change measurements, it is still a useful method, for structural design purposes.

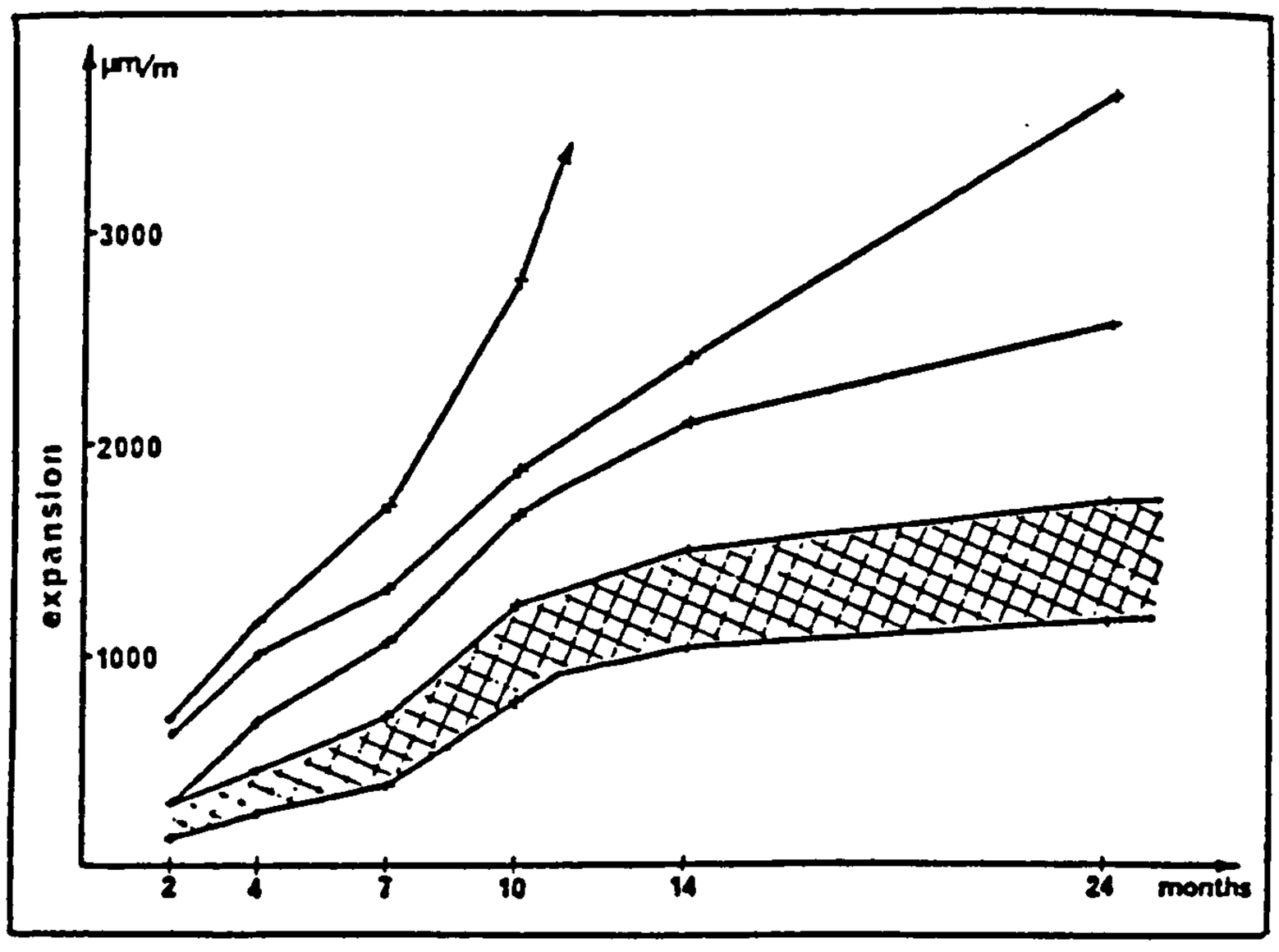


FIGURE 2.8: LINEAR EXPANSION OF ISO MORTAR SAMPLES STORED IN SEAWATER OF 13 PORTLAND CEMENTS WITH VARIOUS AMOUNTS OF C_3A. CEMENTS LOWER THAN 10% C_3A ARE ALIKE IN A NARROW RANGE SHOWN SHADED. OTHER THREE CURVES BELONG TO CEMENTS CONTAINING APPROX. 13% C_3A / 166/.

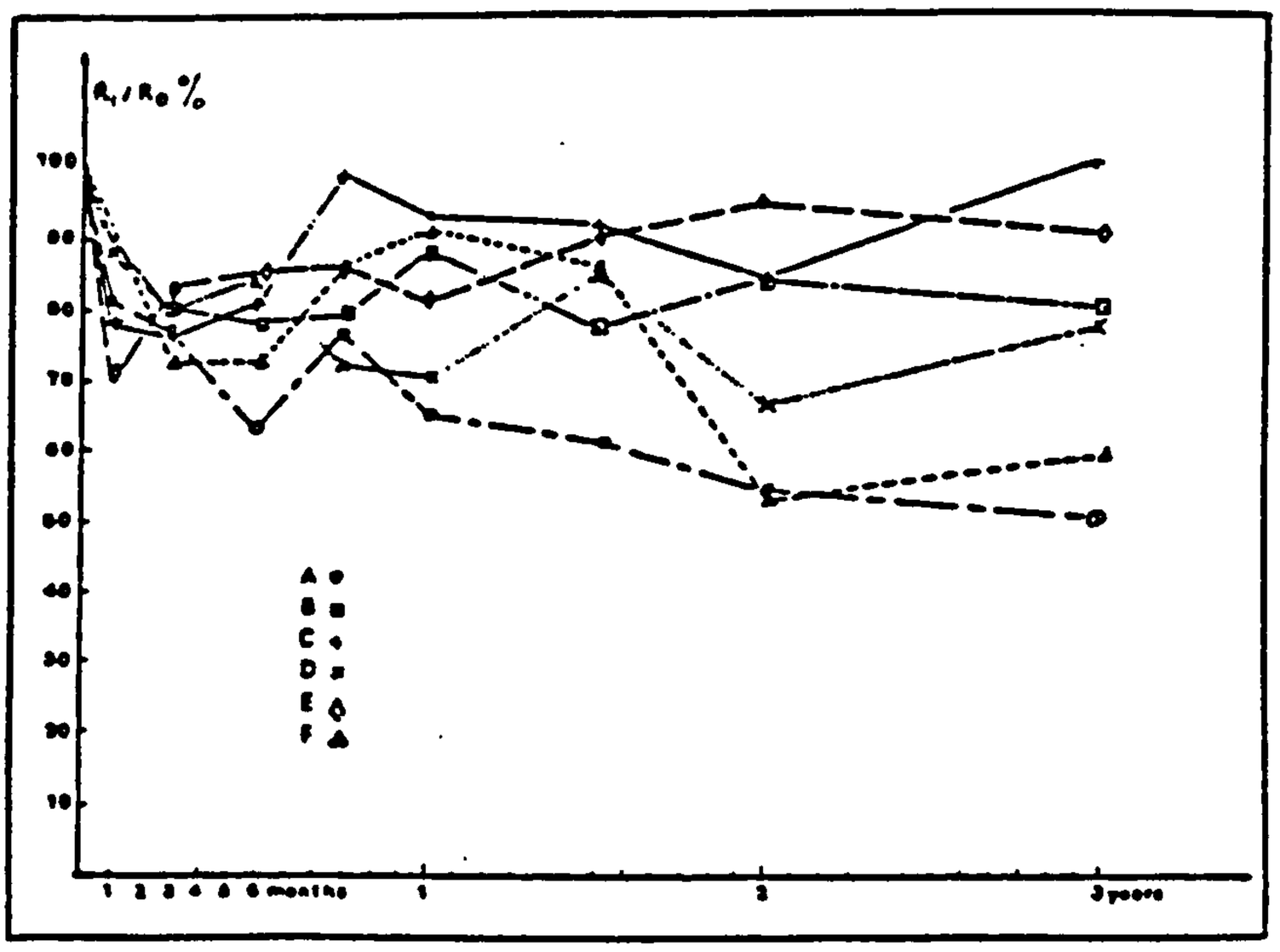


FIGURE 2.9: COMPRESSIVE STRENGTH LOSSES OF IMMERSED HALVES OF MORTARS EXPOSED TO SEAWATER / 45 /.

2.2.3 EFFECT OF CRUDE OIL

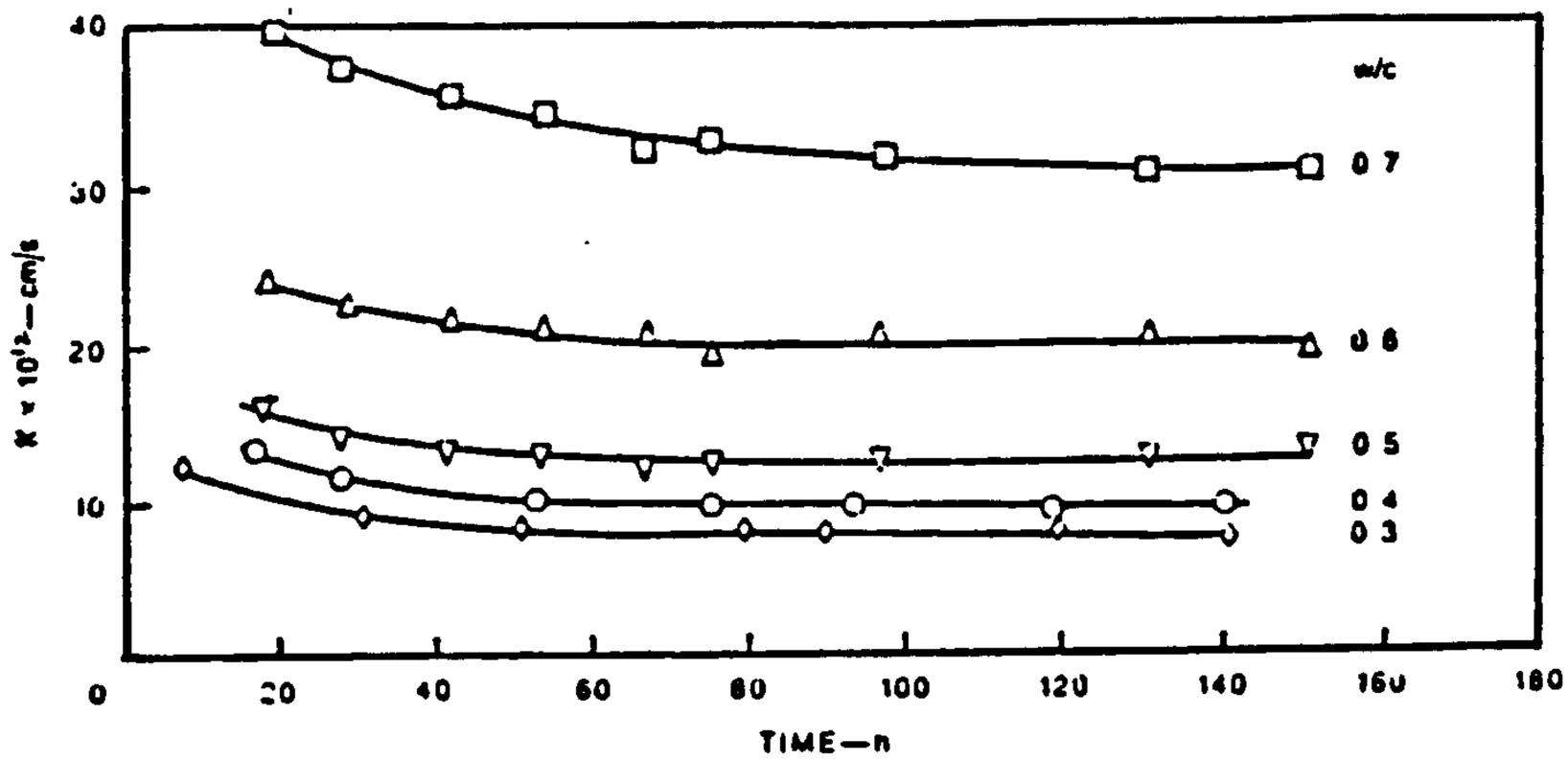
The effects of crude oil on concrete at ambient temperatures have been little investigated /119, 143/ and to date no known work exists on its effect at elevated temperatures. This review is therefore limited to the effects at ambient temperatures. Due to the lack of general knowledge of this subject, references have been made to other hydrocarbon fluids most of which, however, are fractions of crude oil.

2.2.3.1 PERMEABILITY

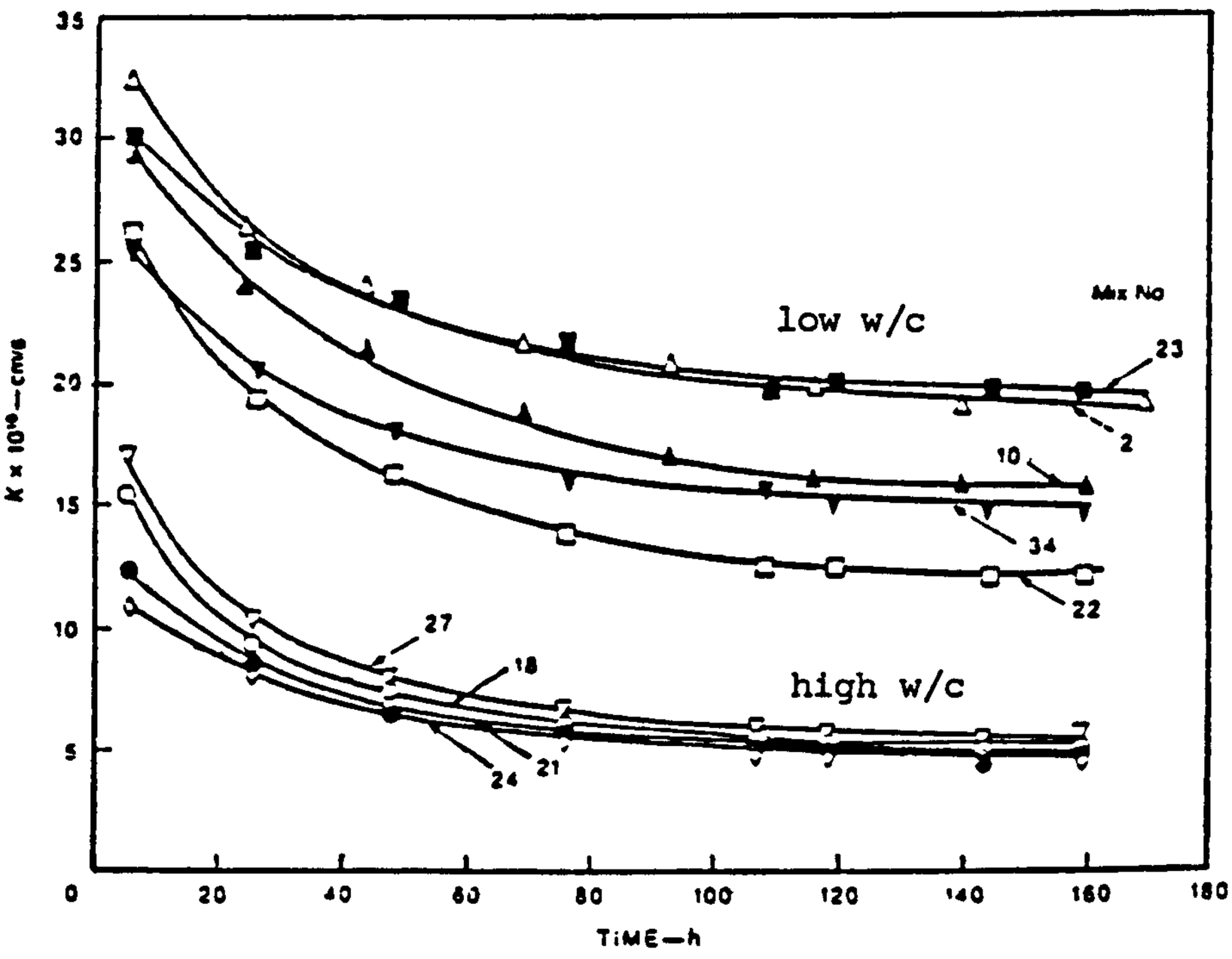
This section reviews output tests carried out with crude oil and other hydrocarbons in measuring the coefficient of permeability, K. The only available data on output tests using crude oil are those reported by OYEKA /143/ at Sheffield University, in which the flow of Kuwait crude oil through predried cement paste and concrete specimens were tested at presures of up to 1.034N/mm2. From these, the coefficient of permeability, K, was calculated using Darcy's equation and assuming laminar flow. The results can be summarised as follows:

- coefficient of permeability, K, decreased with time (Fig. 2.10), but reached an almost constant value Ks after about 120 hours.
- Ks increased exponentially with water/cement ratio and almost linearly with applied pressure (Fig. 2.11).
- for comparable specimens, K for water is greater than for crude oil, and is independent of the applied hydrostatic pressure when steady state flow is reached.

The first two conclusions are similar to observations made with the permeability of concrete to water, in that K for oil decreased with time. This is a confirmation that Darcy's law does not strictly apply to concrete. Oyeka attributed the last conclusion to differences in the molecular sizes of crude oil (18A) and water (3A), with the smaller water molecules expected to penetrate the smaller inner pores which the molecules of crude oil cannot reach.



(a)



(b)

FIGURE 2.10: VARIATION IN KUWAIT CRUDE OIL PERMEABILITY WITH TIME FOR (a) OPC PASTES WITH DIFFERENT WATER/CEMENT RATIOS AND (b) OPC CONCRETE OF DIFFERENT MIX PROPORTIONS /204/.

Maxon and Achenbach /122/ subjected moist concrete cores of low water/ cement ratios to various fluids at a pressure differential of 300 psi. Their results indicate that while pentane permeability varied from 0.007 to 0.12mm/s, flow could not be established even in vacuum saturated cores for Hutton crude oil, in tests lasting over 15 to 30 hours. It was concluded that pentane, a lighter fraction of crude oil permeates concrete more readily than crude oil.

2.2.3.2 PENETRATION

In particular, penetration of crude oil into concrete depends on the pore size range of cement paste and concrete and on the molecular size range of the fractions of crude oil. The tendency for concrete to act as a molecular sieve has been discussed in section (2.2.1.2).

Very few methods have been devised for detecting crude oil/hydrocarbon penetration into concrete and they can be classified into 3 categories;

- Ultraviolet light, Infra red and Nuclear Magnetic Resonance were methods used by **MATTI** /119/ to detect Kuwait crude oil penetration into concrete. The tests were conducted on sliced specimens at varying depths, in particular, to identify any changes in quality. His results suggested that no major chemical changes had occurred. However,the methods in themselves give only the slightest indication of quality loss or of any chemical changes.
- The dye method used by **MAXON AND ACHENBACH** /122/ to determine the penetration of pentane into moist concrete, utilised a red gasoline dye. The effectiveness of this method is difficult to assess since it seems that penetration into concrete will depend on the molecular size of the dye. If the dye is of large molecular size, its penetration will be hindered and will therefore not truely reflect the penetration of pentane which has a small molecular size (5A) and is the smallest liquid hydrocarbon.
- Weight change method has been used as a measure of the degree of penetration of hydrocarbons into concrete, through the amount of liquid absorbed /93/. The method may be effective for predried

specimens, but is likely to result in difficulties when the specimens are moist. It does not however determine the depth of penetration at any given time.

So far, no tests have been reported which studies the differential penetration of the fractions of crude oil through concrete, although Matti /119/ had obtained a relationship between the depth and rate of penetration of kuwait crude oil into concrete.

The conclusions drawn from these works can be summarised as follows:

- Penetration of crude oil/hydrocarbons into concrete decreases with increase in fluid molecular size. This suggests that concrete behaves as a molecular sieve (Figure 2.12).
- Penetration of crude oil/ hydrocarbons into moist concrete is significantly slower than into predried concrete.
- Water penetrates rapidly into hydrocarbon saturated predried concrete and seems to 'creep' along the surface of the C-S-H particles (Figure 2.13) /85/, the reverse, however, is not the case.
- The depth of penetration of these fluids increases with time and applied pressure.

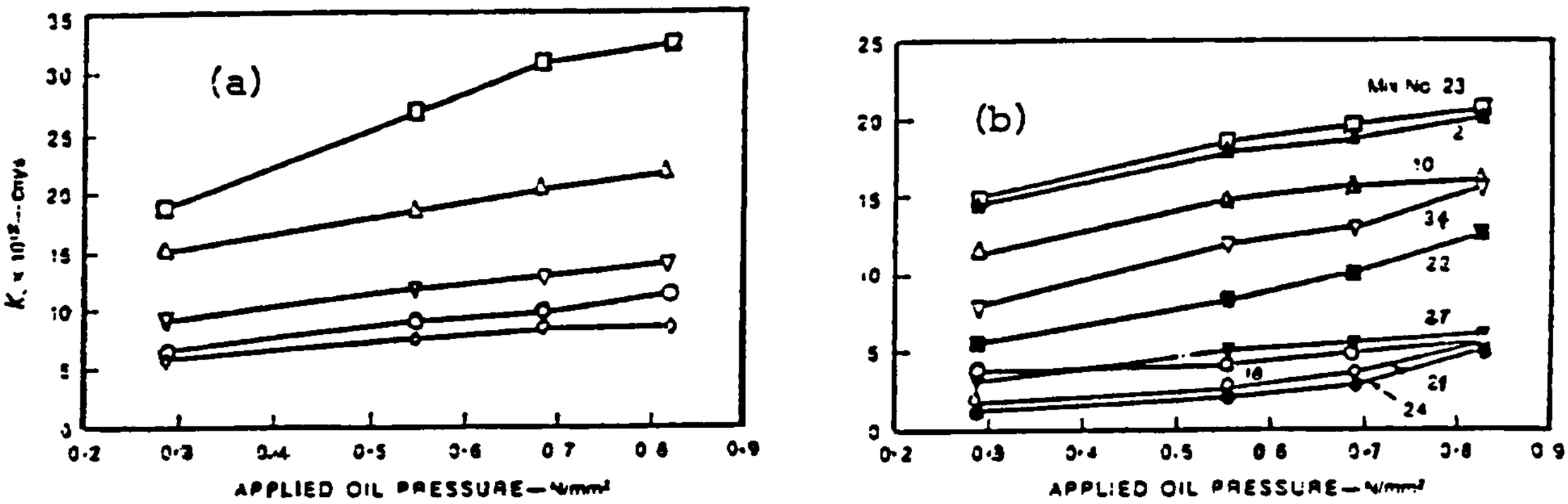


FIGURE 2.11: VARIATION IN THE COEFFICIENT OF PERMEABILITY WITH APPLIED KUWAIT CRUDE OIL PRESSURE FOR (a) OPC PASTES OF DIFFERENT WATER/CEMENT RATIOS AND (b) OPC CONCRETE OF DIFFERENT MIX PROPORTIONS /204/.

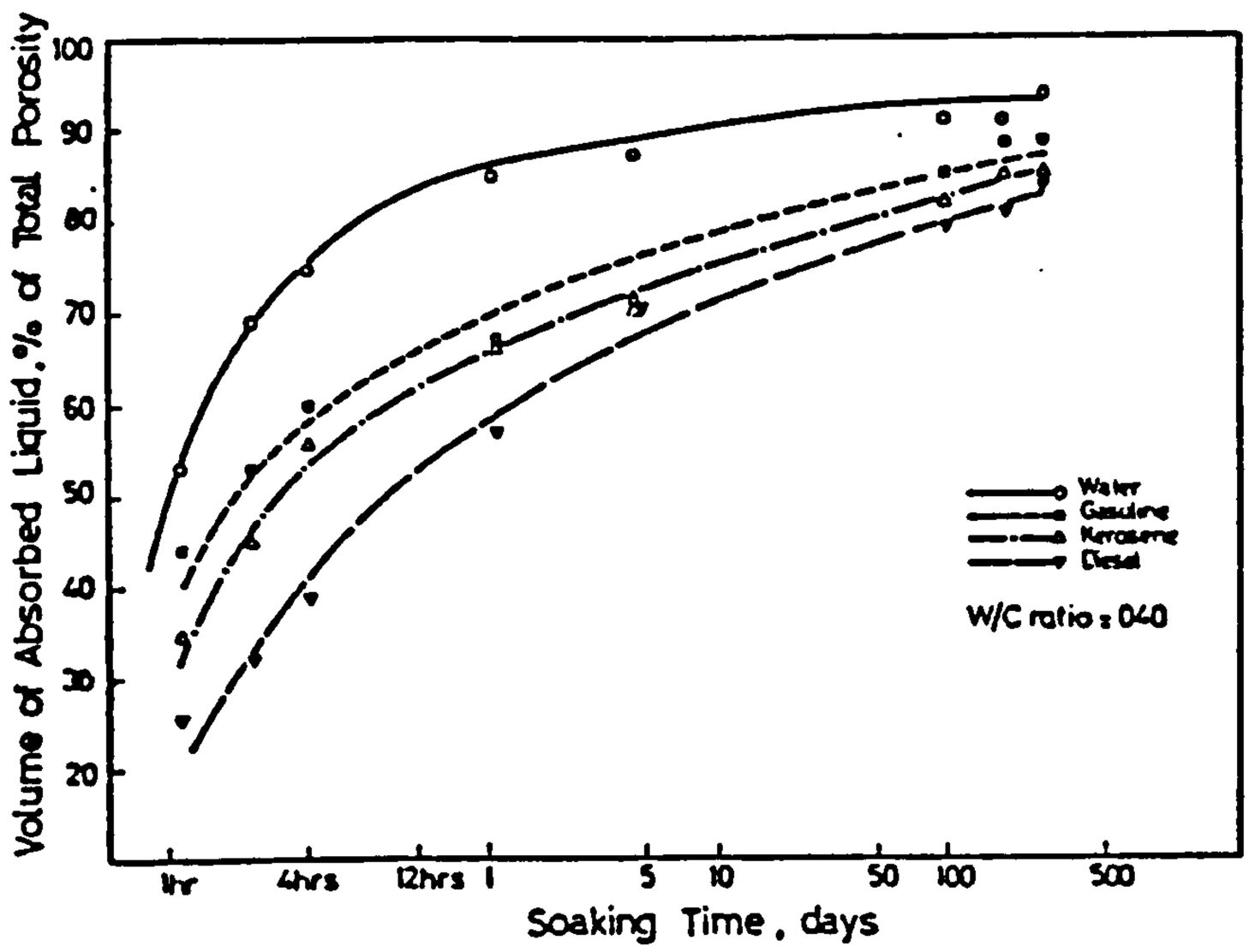


FIGURE 2.12: THE RATE OF AESORPTION OF FOUR FLUIDS BY CONCRETE PRISMS (70x70x280mm) PREDRIED AT 105°C /93/

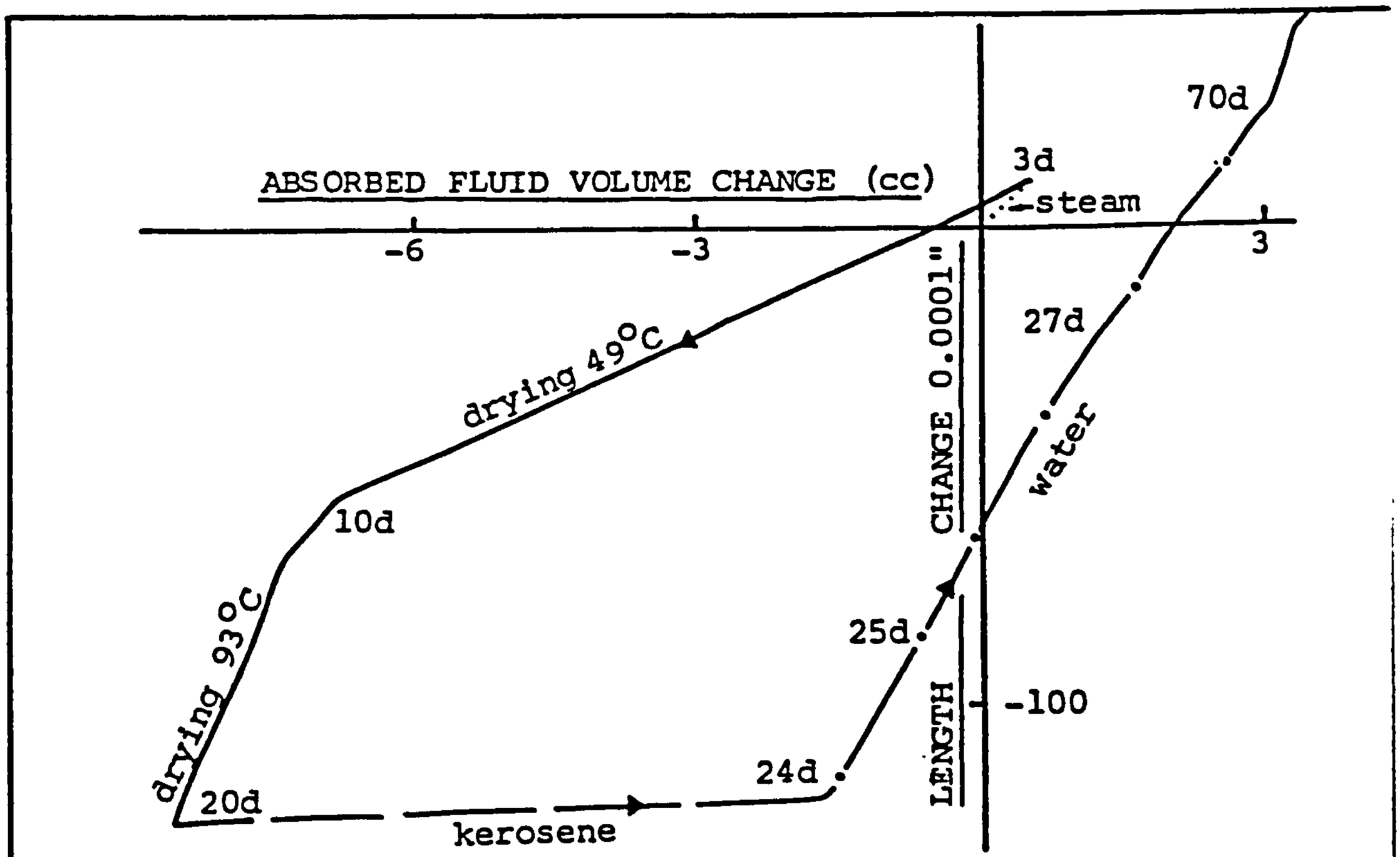


FIGURE 2.13: EFFECT OF SOAKING PREDRIED CEMENT PASTE IN KEROSENE THEN WATER ON THE VOLUME CHANGES. LUBRICATING OIL (NOT SHOWN HERE) SOAKED SPECIMENS EXPAND MUCH MORE SLOWLY IN WATER /85 /.

2.2.3.3 VOLUME CHANGES

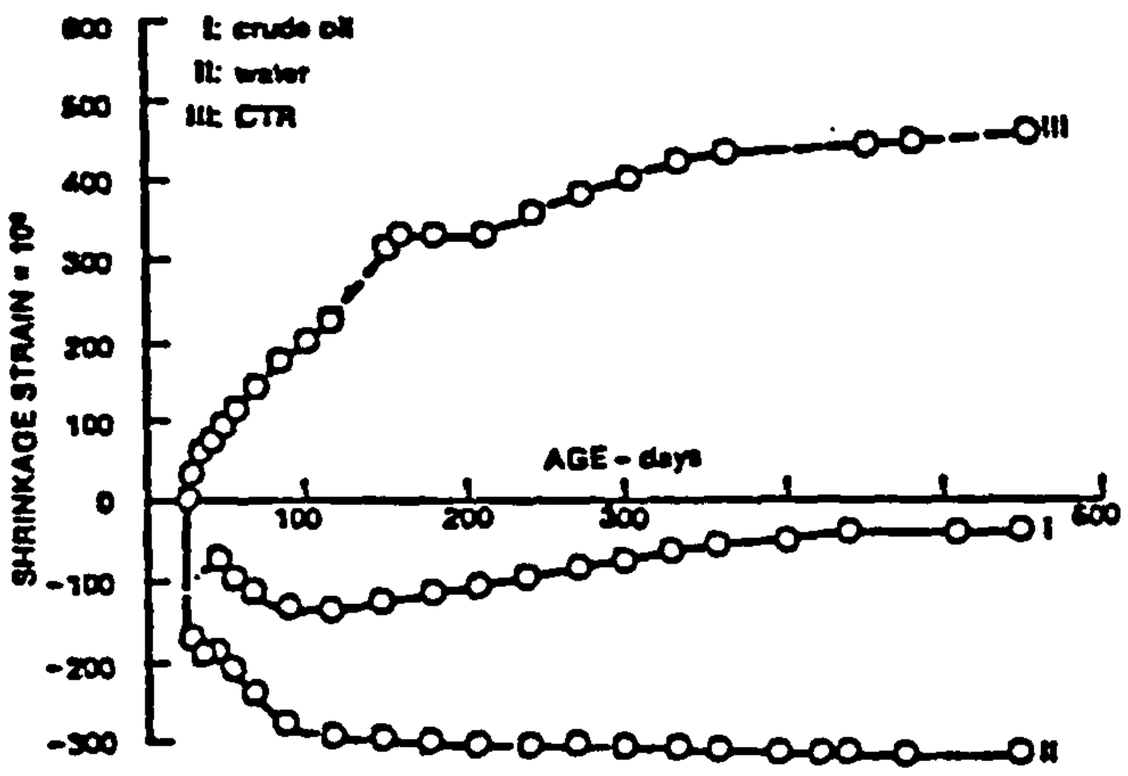
The mechanisms causing dimensional changes in concrete have been described in section (2.2.1.3). Since crude oil is believed to consist of inert hydrocarbons /119/, it is generally assumed that any interaction with concrete would be physical only.

Matti /119, 121/ has investigated the shrinkage of concrete in direct contact with crude oil at ambient temperatures, his findings were as follows:

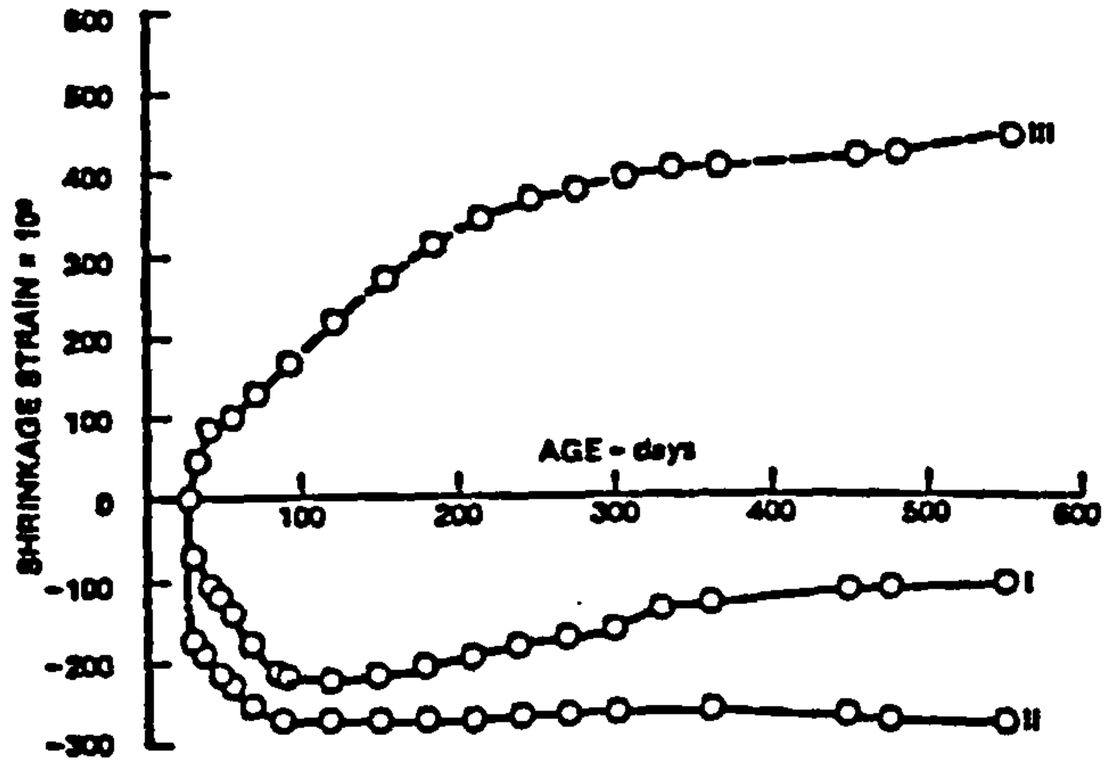
- Oil soaking does not prevent shrinkage in concrete, but evaporation of moisture is prevented. The resulting shrinkage is autogenous and is largely dependent on moisture content prior to crude oil exposure.
- The amount of shrinkage is largely dependent on the water/cement ratio and on the initial curing conditions (Fig.2.14). Shrinkage had increased with increase of water/cement ratio and also as the moisture content of the specimens prior to oil soaking.
- Predried concrete initially expanded (100-200 microstrains) after about 12-16 weeks of oil soaking and then began to shrink (Fig. 2.14).
- Saturated moist concrete specimens soaked in crude oil shrank continuously (Fig.2.15). This was regarded as autogenous shrinkage.

Matti's results were based on experimental tests using 100x100x500mm concrete prisms. To serve as controls were specimens kept under a controlled environment of constant temperature and humidity (CTR).

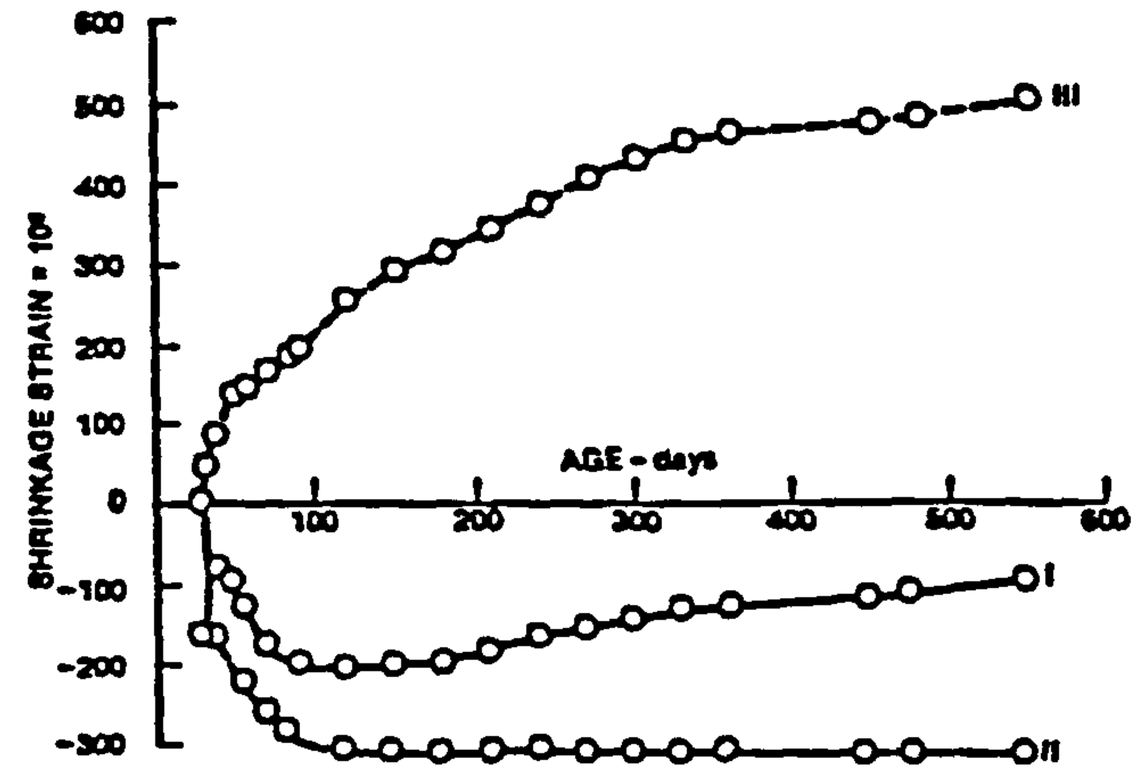
In tests performed by **HRENNIKOFF** /85/, it was found that predried concrete expanded by only a very small amount over a short period of time when saturated with kerosene or lubricating oil, although the volume of absorbed liquid was comparable to that vacated by water on drying. However, it was also found that when the hydrocarbon saturated specimens were placed in water, they absorbed the water without displacing the hydrocarbon and at the same time began to swell significantly (Fig.2.13). The total volume of fluid absorbed and the final specimen lengths both exceeded the values before drying. Hrennikoff had suggested that water entered the cement paste not through its voids but by creeping along the surface of the C-S-H particles.



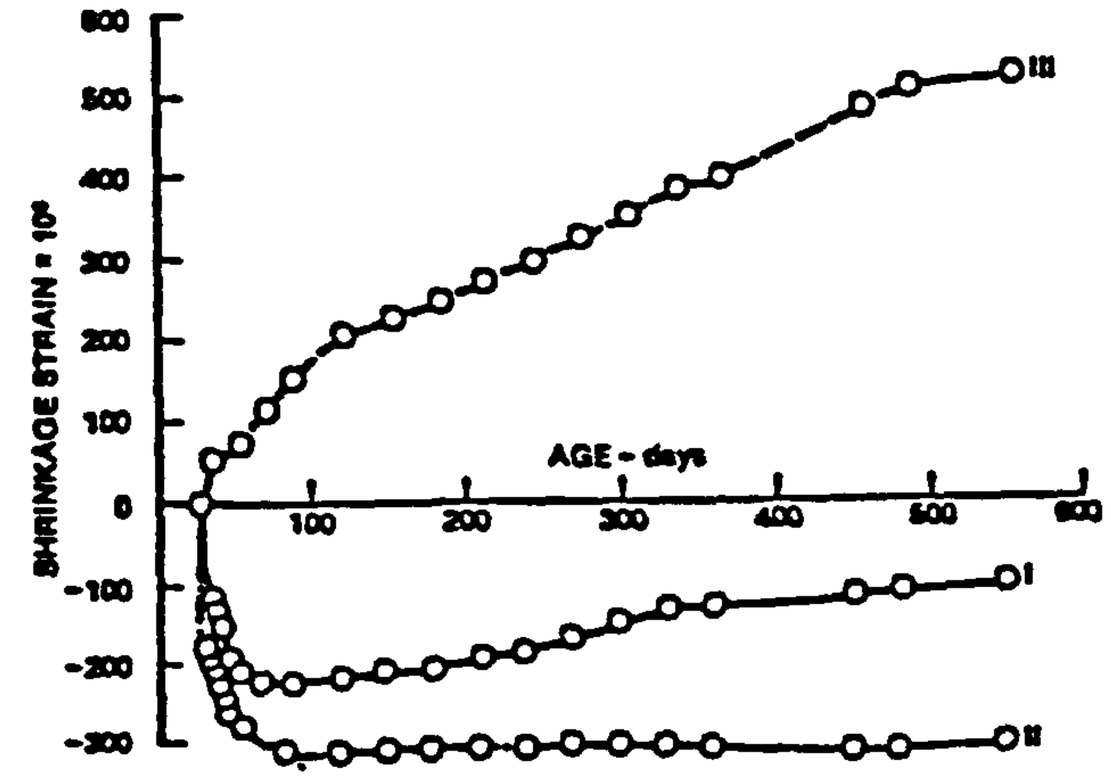
(a) Mix M1, w/c = 0·40



(c) Mix M3, w/c = 0·55

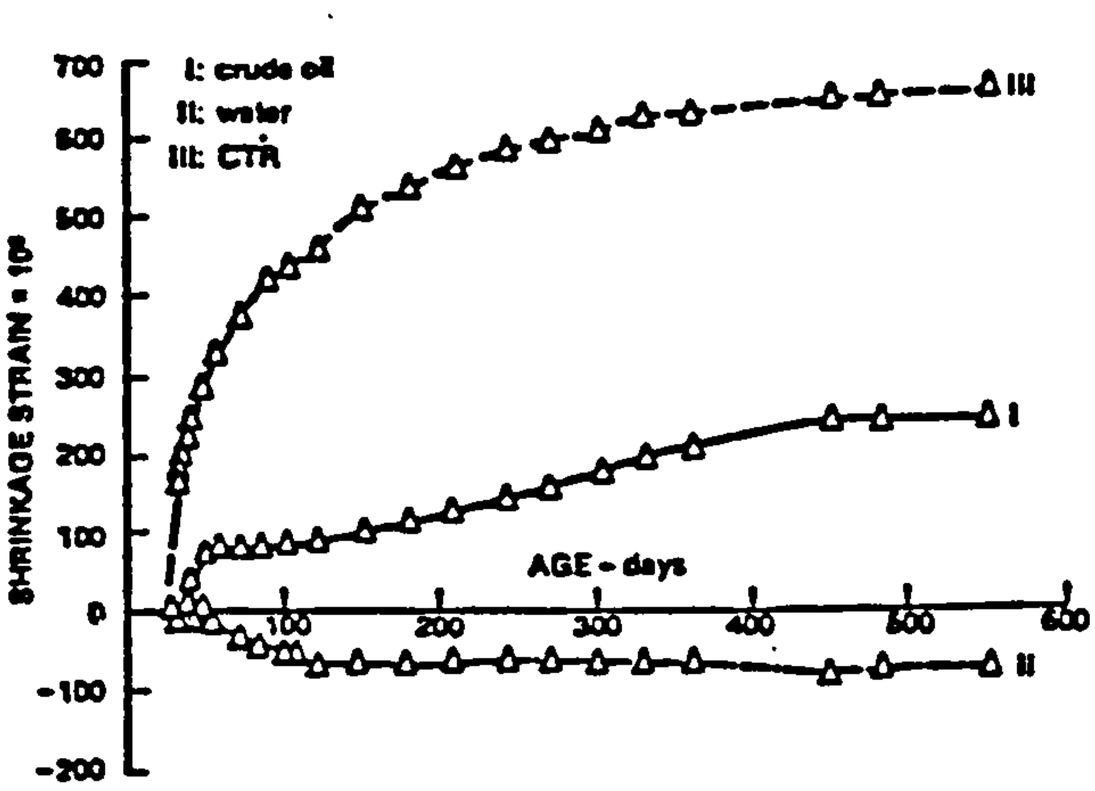


(b) Mix M2, w/c = 0·50

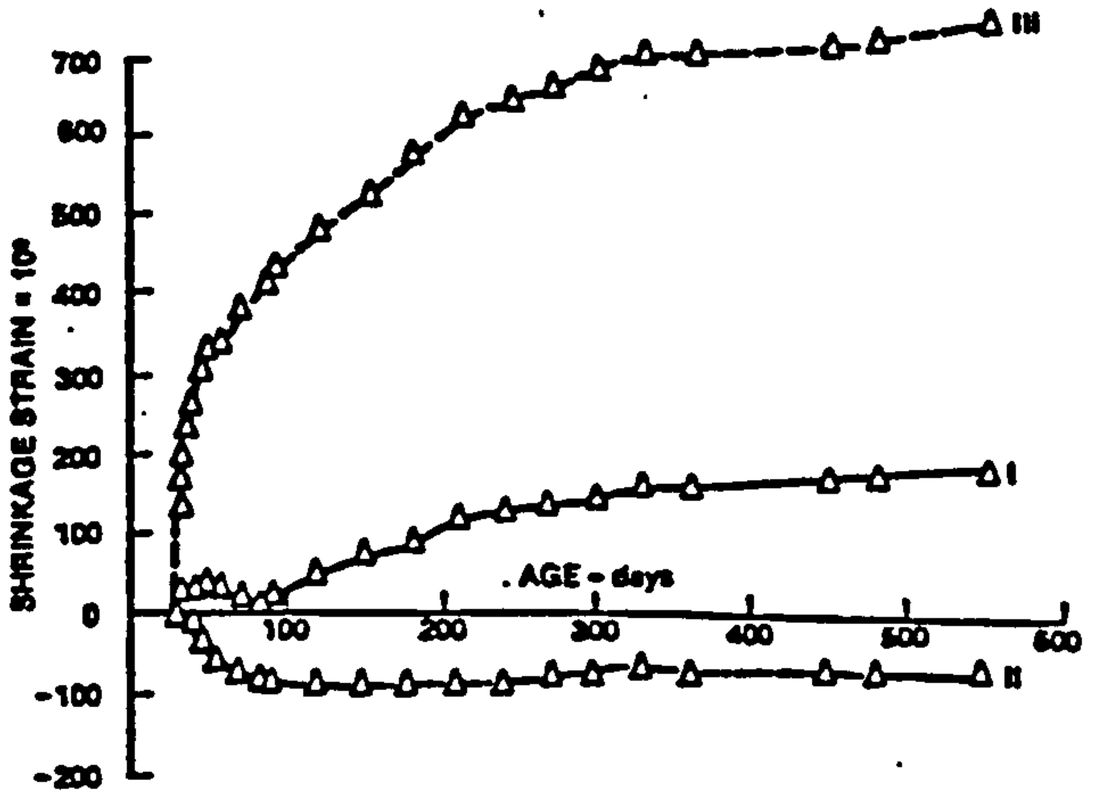


(d) Mix M4, w/c = 0·60

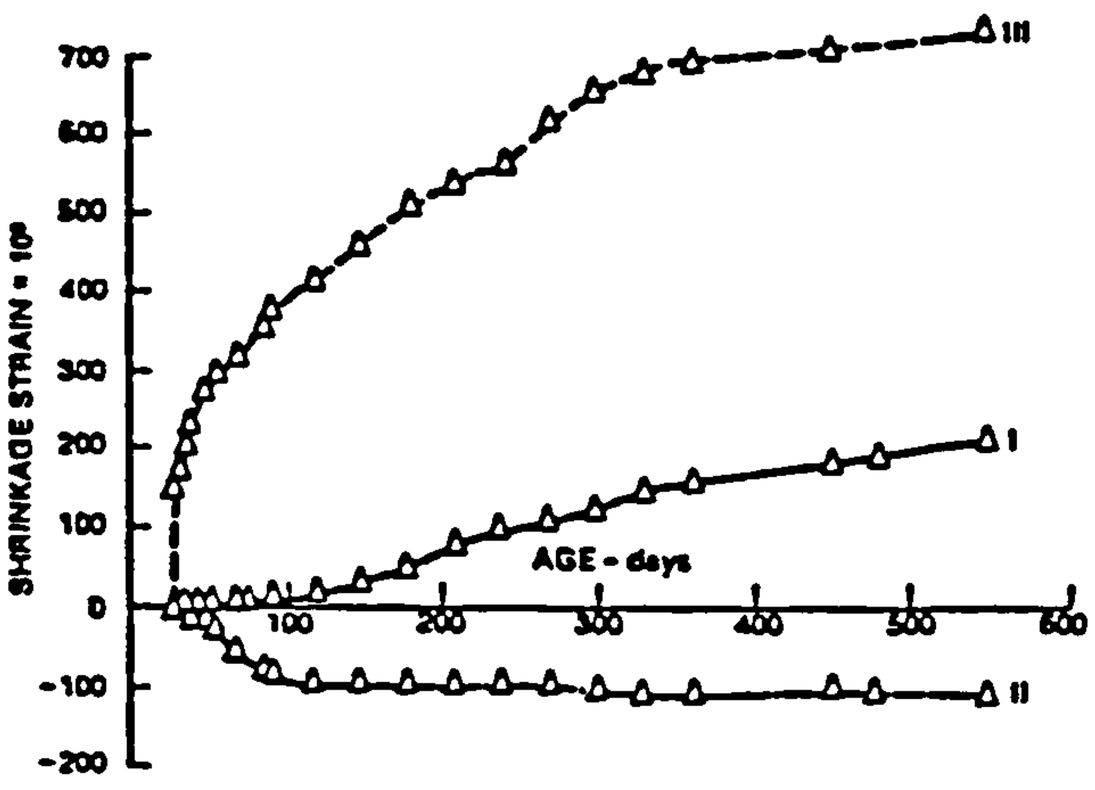
Fig. 2.14: Effects of water/cement ratio upon shrinkage after the age of 28 days (concrete cured one week in water, three weeks in CTR). Stored in: (I) crude oil (II) water (III) CTR /121/.



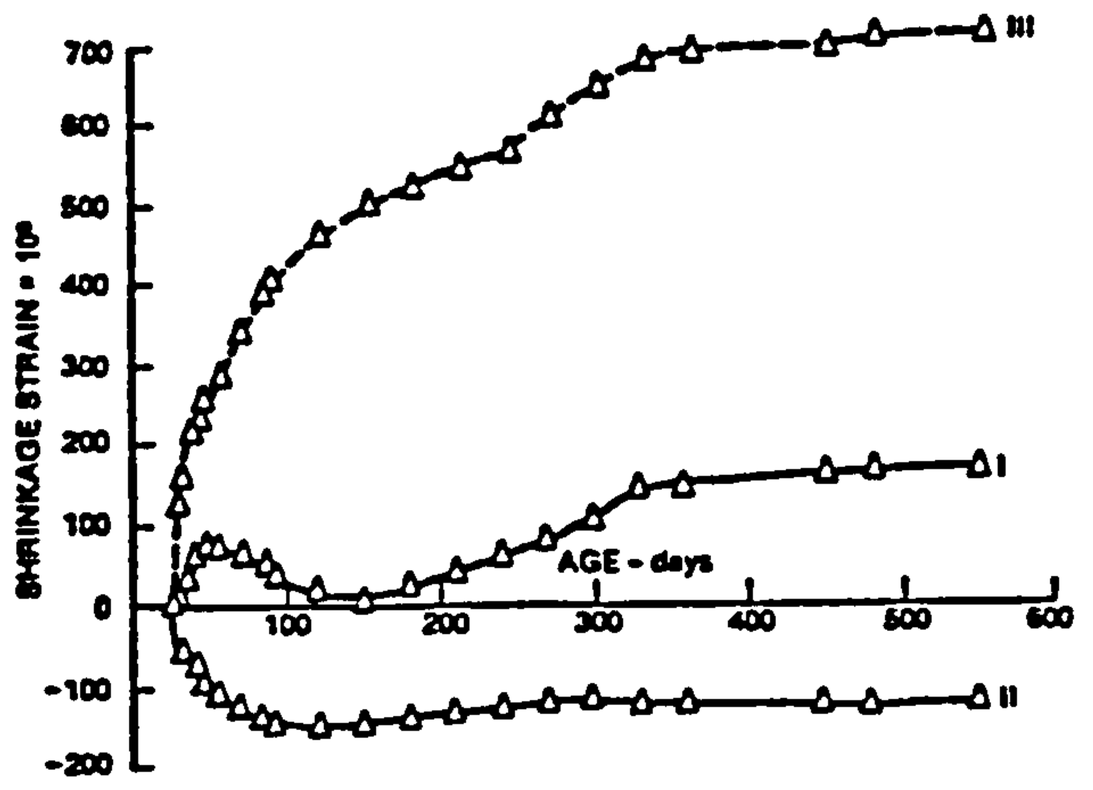
(a) Mix M1, w/c = 0·40



(c) Mix M3, w/c = 0·55



(b) Mix M2, w/c = 0·50



(d) Mix M4, w/c = 0·60

Fig. 2.15: Effects of water/cement ratio upon shrinkage of concrete (saturated with water) after the age of 28 days. Stored in:(I)crude oil (II)water (III)CTR /121/.

2.2.3.4 COMPRESSIVE STRENGTH

Factors affecting the compressive strength of concrete have been discussed in previous sections. In an extensive report, **KHOURY** /97/ had reviewed the influence of liquid hydrocarbons and crude oil on the compressive strength of concrete. Table (2.7) gives a summary of the contributions of different authors to this subject as well as their interpretation of the results. Two lines of thougth exist; those who believe there was reduction in strength on crude oil/hydrocarbon exposure, thereby speculating on concrete deterioration and others who felt that no significant strength changes had occurred.

In studying the works of the different investigators, three important factors were identified which had helped to correlate the differences in opinion. These are (a) the effect of single interaction (b) the effect of multiple interactions and (c) the 'apparent' effect.

(a) Single Interaction

In most of the works reviewed, the test specimens were dried prior to exposure in the test fluid /46, 71, 93, 105, 143/. The intention, in addition to accelerating the process of soaking to saturation, was to isolate any changes occurring in specimen property, in order that this may be attributed to the test fluid alone (in the absence of any moisture). The influence of any fluid on the compressive strength of predried concrete will depend on its ability to penetrate into the small gel pores. The difficulty involved in achieving this has been explained by the molecular sieve theory. This of course is based on the assumption that any such interactions are purely physical, with no chemical reaction taking place.

JAEGERMANN/93/ had tested predried concrete specimens saturated with kerosene, diesel oil and water and found initial early strength reductions (Fig. 2.16). However, strength recovery had occurred in all specimens by 720 days of exposure.

Author	Reference	pre-soak condition	max. soaking period	soaking medium	Interpretation of results of strength
Jaegermann	93	predried (105 C)	720 days	w,g,k and di	initial reductions after 4 days. Not significant.
Matti	119,120	moist as-cured	180 days	w and co	Reductions
Steinbach	183	moist as-cured	360 days	w,a,g,di and ho	No remarkable reduction.
Mills	127	predried (110 C)	1 day	w,ea,p and b	Not significant.
Cook and Haque	46	predried (112 C)	7 days	fr,k,b and m	Reduction not significant.
Maxon and Achenbach	122	moist as-cured	56 days	w,co and pe	Not significant.
Gjorv	71	predried (105 C)	?	w and co	Not significant.
Lacroix	105	-	-	hydro-carbon	Reduction.
Hansen	78	predried	?	ho	Reduction.
Oyeka	143	predried	58 weeks	co	Significant reduction.

Abbreviations:

a	ambient air	ea	ethyl alcohol	k	kerosene	di	diesel
b	benzene	fr	fog room	m	methanol	ho	heavy oil
co	crude oil	g	gasoline	p	paraffin	pe	pentane
w	water						

TABLE 2.7 : Variations in test parameters of concrete specimens soaked in different media.

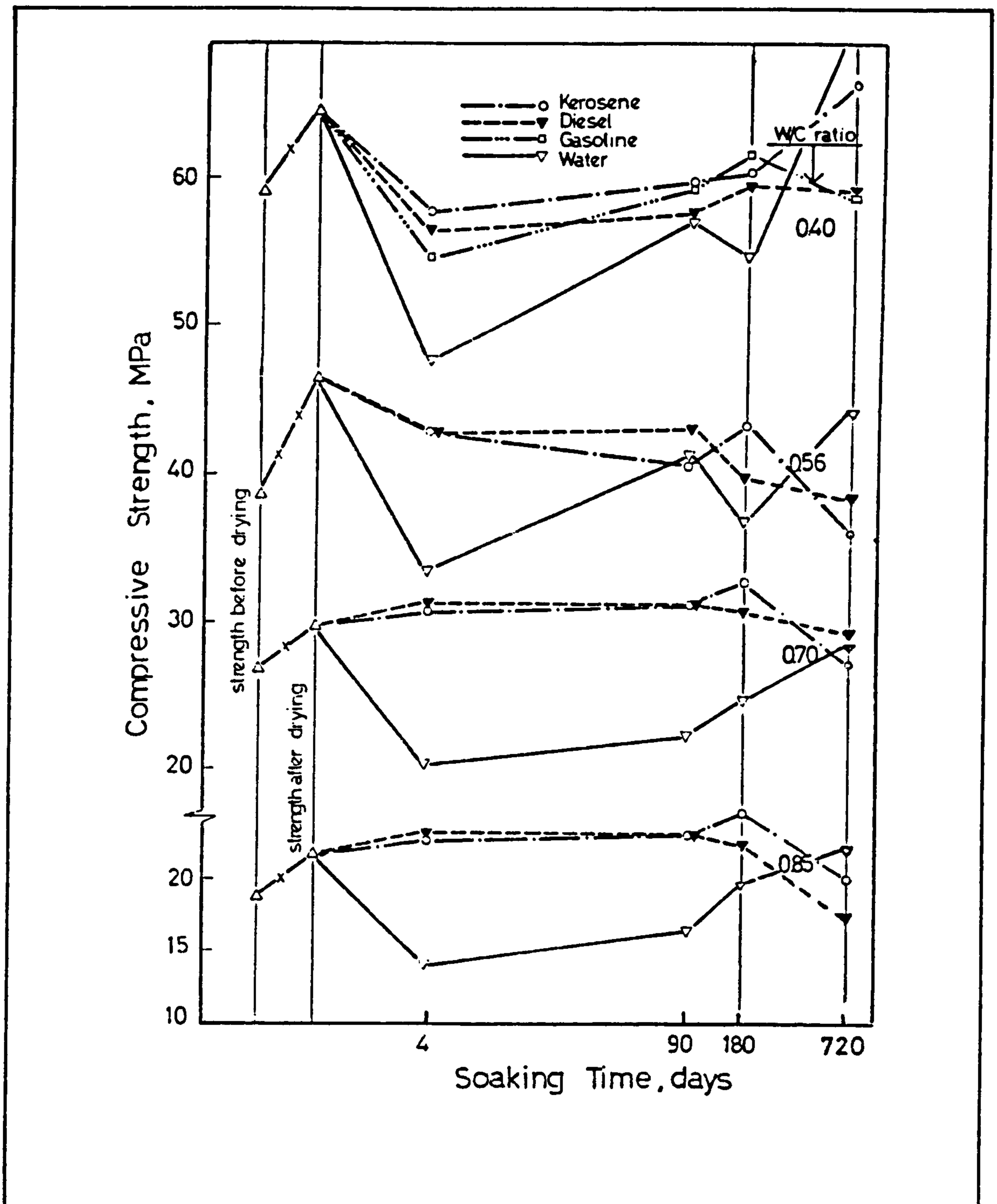


FIGURE 2.16: CHANGE IN COMPRESSIVE STRENGTH OF PRE-DRIED CONCRETE SPECIMENS AFTER SOAKING IN KEROSENE, DIESEL, GASOLINE AND WATER /93 /.

GJORV /71/ found strength reductions of 1-9 per cent for concrete specimens soaked in crude oil. The reduction was up to 40 per cent for the control specimens soaked in water (all specimens were oven dried). From these results (Table 2.8), it was concluded that the reductions in the oil soaked concrete specimens were negligible.

OYEKA /143/ tested oven dried (105 deg.C) concrete and cement paste specimens soaked in Kuwait crude oil and found reductions in compressive strength varying by between -2.5 and 6 per cent (the minus indicates an increase), at all ages. He concluded that this indicated a marked deterioration in strength. The results were in comparison with control specimens continuously cured in water (Table 2.9).

The difference in the strength reductions between predried specimens soaked in crude oil and those soaked in water can be attributed to the difference in molecular size of the fluids. Crude oil with its large molecules cannot enter spaces where water can exert disjoining pressure and does not attenuate the solid-solid bonds to the same extent as water does. It therefore, does not have the same weakening effect /169/. The difference can also be attributed to the surface energy effect which according to Cook and Haque /46/, reduces the amount of external work necessary to propagate cracks.

(b) Multiple Interaction

When moist concrete is soaked in another fluid, the interactions within the concrete skeleton are of a multiple nature. The multiple interaction of crude oil, water and concrete is complex and makes the interpretation of results very difficult. The first difficulty here is that of achieving saturation with the new fluid, at ambient temperature and pressure, this has proved impossible. MATTI /120/ found that even after 180 days of soaking moist concrete specimens in Kuwait crude oil at fluid pressures of up to 275 KN/m2, full saturation was not achieved. Similarly, MAXON and ACHENBACH/122/ had found it very difficult to saturate moist concrete specimens with liquid pentane even at pressures of up to 300 psi (2 MN/m2). They could only manage a penetration of about 1.5mm into concrete specimens 150mm in diameter.

TABLE 2.8: REDUCTION IN COMPRESSIVE STRENGTH OF PRE-DRIED CONCRETE SPECIMENS ON SATURATION WITH WATER AND CRUDE OIL /71/.

Water/cement ratio	Strength - percent of oven dry	
	water	crude oil
0.45	62%	91%
0.47	60%	99%
0.60	62%	98%
0.65	58%	98%

TABLE 2.9 : Reduction in Compressive strength (per month) due to crude oil saturation /.143/.

CEMENT TYPE	W/C RATIO	24TH WEEK		40TH WEEK		58TH WEEK	
		+Reduction N/mm^2	+% Reduction	•Reduction N/mm^2	•% Reduction	••Reduction N/mm^2	••% Reduction
OPC	0.40	1.38	6.2	0.70	3.4	0.18	0.9
	0.50	1.00	5.7	0.68	4.1	0.08	0.5
	0.60	0.38	2.7	1.05	7.9	0.30	2.4
	0.70	0.75	6.6	0.83	7.3	0.43	4.0
SRPC	0.40	0.83	3.9	0.83	4.0	0.43	2.2
	0.50	1.00	5.7	1.20	7.2	0.23	1.5
	0.60	0.58	5.0	0.58	5.2	0.43	4.1
	0.70	0.48	5.3	0.70	8.3	0.38	4.8
OPC	0.40	1.23	4.8	1.05	4.7	0.15	0.7
+	0.50	1.63	7.8	1.18	6.1	0.45	2.5
4%	0.60	1.20	7.4	0.68	4.5	0.40	2.8
Admix	0.70	1.05	8.1	0.50	4.2	0.40	3.5

+ Reduction and % reduction over CTR
• Reduction and % reduction over 24th week oil sat.
•• Reduction and % reduction over 40th week oil sat.

Interpretation of the results obtained under these conditions have been complicated by a number of factors:

(1) In cases where the control specimens were continuously cured in water, hydration can be expected to continue and further strength increases are likely to take place. This would make comparative studies difficult.

(2) Hydration would continue in moist specimens soaked in crude oil and may result in further strength increases.

(3) The degree of crude oil penetration has so far been difficult to determine.

These complications are evident in the manner of interpretation of the results reported by a few of the authors reviewed. Matti /119/ for example, concluded that there was about 8-15 per cent comparable reduction in compressive strength of concrete specimens soaked in crude oil, relative to those soaked in water. Even though this was the case, however, the moist concrete specimens had increased in strength by the end of the period of soaking of 180 days (Fig.2.17). The results also indicated that the compressive strength of specimens had continued to increase through out the duration of soaking, confirming that hydration had continued.

STEINBACH /183/ obtained similar relative strength reductions after 12 months of soaking moist mortar specimens in heavy oil, diesel and gasoline, while the control specimens were stored in air and in water (Table 2.10). But again real increases in strength were observed for some of the specimens.

(c) Apparent Effect

In the discussion on 'end conditions' in section (2.2.1.4), it was observed that the lubrication of specimen ends prior to compression testing would result in 'apparent' strength reductions. Crude oil and most of its components have a lubricating effect /117/, therefore, specimens exposed to crude oil would be lubricated, even after wiping the surfaces dry. The lubrication is due to the presence of wax in crude oil, the particles of which block surface and sub-surface pores in concrete and are difficult to remove. Under compression loading,

the wax can seep out to the surface of the specimens. In none of the studies was consideration given to this effect, although Oyeka /143/ had noted the possibility that oil may seep to the surface of the specimens under load and it was felt that this may have influenced the results. However, the problem was not investigated any further.

It is possible that the lubricating effect of crude oil and other hydrocarbons, could have affected the results of compressive strengths in the previous investigations. It is necessary therefore, that future tests should recognise this problem.

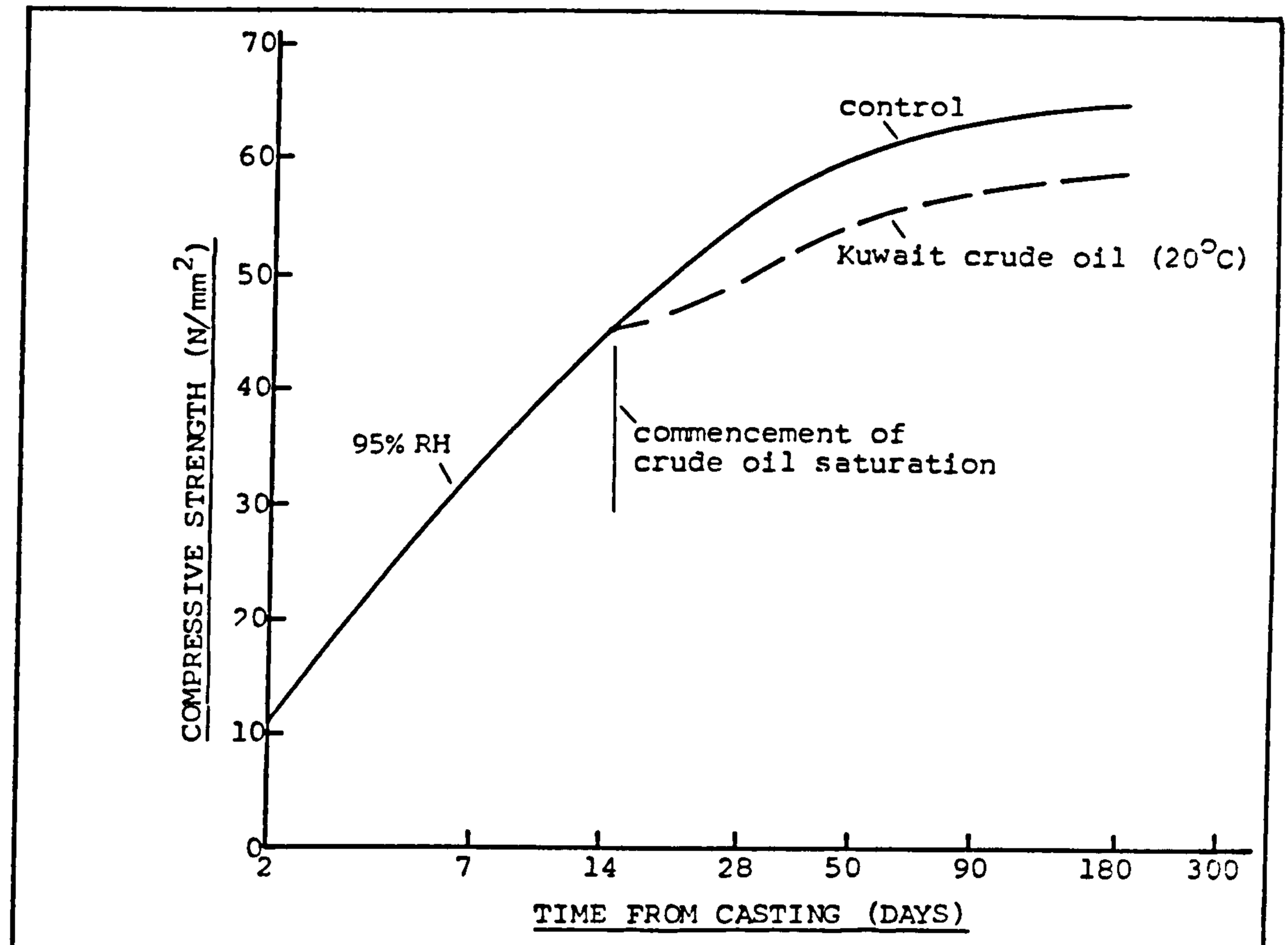


FIGURE 2.17: EFFECT ON COMPRESSIVE STRENGTH OF SOAKING MOIST CONCRETE SPECIMENS IN KUWAIT CRUDE OIL AT AN EARLY AGE OF 14 DAYS AND TEMPERATURE OF 20°C /119,120/

TABLE 2.10: COMPRESSIVE STRENGTH OF INITIALLY AIR-DRIED MORTAR AFTER SOAKING IN VARIOUS FLUIDS /183/.

W/C ratio	Cement type	Soaking time	Compressive strength % of air-dried strength prior to soaking				
			Heavy oil	Diesel	Gasoline	Water	Air
0.50	Portland	7 days	99	98	95	87	100
		3 months	93	98	95	105	103
		12 months	95	99	89	107	104
0.80	Portland	7 days	97	94	93	82	104
		3 months	85	87	97	109	109
		12 months	88	92	86	108	114
0.50	Blast furnace	7 days	94	102	98	95	94
		3 months	99	103	108	121	104
		12 months	105	113	117	136	110
0.80	Blast furnace	7 days	97	101	103	93	98
		3 months	89	97	129	138	109
		12 months	94	102	133	150	116

2.2.4 EFFECT OF TEMPERATURE

Exposure of concrete to elevated temperatures has been known to cause deteriorations in the properties of concrete. Kasami et al/96/ had reported significant damage to concrete structures exposed to elevated temperatures below 80 C.

The effect of temperature on concrete is influenced by a number of factors including (a) rate of heating and cooling (b) upper temperature limit (c) duration of thermal exposure (d) number of thermal cycles (e) loading regimes (f) temperature and load history (g) casting conditions and curing regime (h) age of concrete (i) moisture content (j) types of aggregates and cement (k) type of admixtures (l) mix proportions, water/cement ratio (m) size and shape of concrete member (n) mode of testing.

These factors have been studied by a number of different workers such as Sullivan /186/, Bazant /16/, Bertero /17/, Khoury /98/ and many others /21, 15, 96, 136/ who had investigated different properties of concrete at elevated temperatures. However, Bertero has highlighted 3 factors which influence the mechanical characteristics of concrete subjected to thermal treatment, these are: moisture condition, number of temperature cycles prior to testing and/or duration of test, and the temperature at which the concrete is tested.

In the practical case of structures such as crude oil offshore storage tanks, the inner face of the tank wall is likely to remain under moist conditions even at the maximum expected temperatures of 80-85 C, due to the great depth at which they are submerged and the effect of hydrostatic pressure (Fig.2.18). This section will therefore behave as under sealed conditions.

This study reviews the effects of elevated temperatures (up to 150 C) on sealed and unsealed concretes as reported by different workers. However, the aim is to relate the studies to the different sections of concrete caisson walls used in oil storage tanks. The concrete can be regarded as mature prior to the introduction of hot crude oil, hence, problems associated with heating fresh or immature concrete will therefore not arise.

2.2.4.1 PERMEABILITY AND PENETRATION

It has very often been said that permeability of concrete is dependent on the permeability of the cement paste, which in turn is a function of the pore structure. At elevated temperature, differential expansion of the cement paste and the aggregate may result in cracks and this will affect permeability.

(a) Unsealed Concrete

Elevated temperature accelerates the loss of capillary water. At temperatures of up to 110 C, gel pore water is lost and the loss of chemically combined water will have begun. These cause changes to occur in the pore structure of the cement paste and porosity increases significantly. **BAZANT** /16/ had stated that permeability increases a hundred-fold when temperature passes 100 C, but appears to change relatively little above 150 C. There seems to be evidence to support this view /98/. The expected increase in pore size alone is insufficient to explain a jump in permeability of this magnitude. However, a tentative explanation in terms of the widening of 'necks' of the flow passage has been offered /16/. It has been suggested that this allows for rapid flow of free water and steam as opposed to only adsorbed water.

(b) Sealed Concrete

It is now clear that elevated temperatures above 100 C initiate hydro-thermal reactions in sealed concrete /98/. This reaction occurs between the CH and C-S-H phases of cement paste as a result of the build up of vapour within the pores due,to the high temperature /17/. Scanning Electron Micrographs (SEM) are reported to have clearly shown that hydrothermal reactions result in significant increase in porosity of the cement paste and also cause changes in the microstructure. Build up of pore pressure may not be as destructive as would be expected/98/. Significantly, pore pressure is dependent on the initial moisture content of the concrete and in particular, on the rate of heating. The highest measured pore pressures found by Khoury /98/, were in the order of 0.8N/mm2, which is lower than the tensile strength of ordinary concrete.

2.2.4.2 VOLUME CHANGES

Volume changes in concrete at high temperatures often result in shrinkage. Drying shrinkage of concrete is seated in the cement paste and is restrained by aggregates. Heating increases the mobility of water and accelerates the rate of drying, consequently it increases the rate of shrinkage. Furthermore, the equilibrium moisture content, decreases with increase in temperature and this leads to higher ultimate shrinkage strain. **BLUNDELL** et al /21/ showed that temperature affects shrinkage in so far as it affects the rate and level of moisture loss. However, should hydrothermal reactions occur, expansion, rather than shrinkage is more likely to take place /98/.

(a) Unsealed Concrete

Heating of unsealed concrete causes loss of moisture, initially from the capillary pores and eventually from the gel pores as the temperature increases to over 105 C. The loss of gel pore water contributes significantly to drying shrinkage (it may be that shrinkage is related to moisture loss at various temperatures (Fig.2.19) /21/). In other words, temperature affects shrinkage in so far as it affects the level and rate of moisture loss.

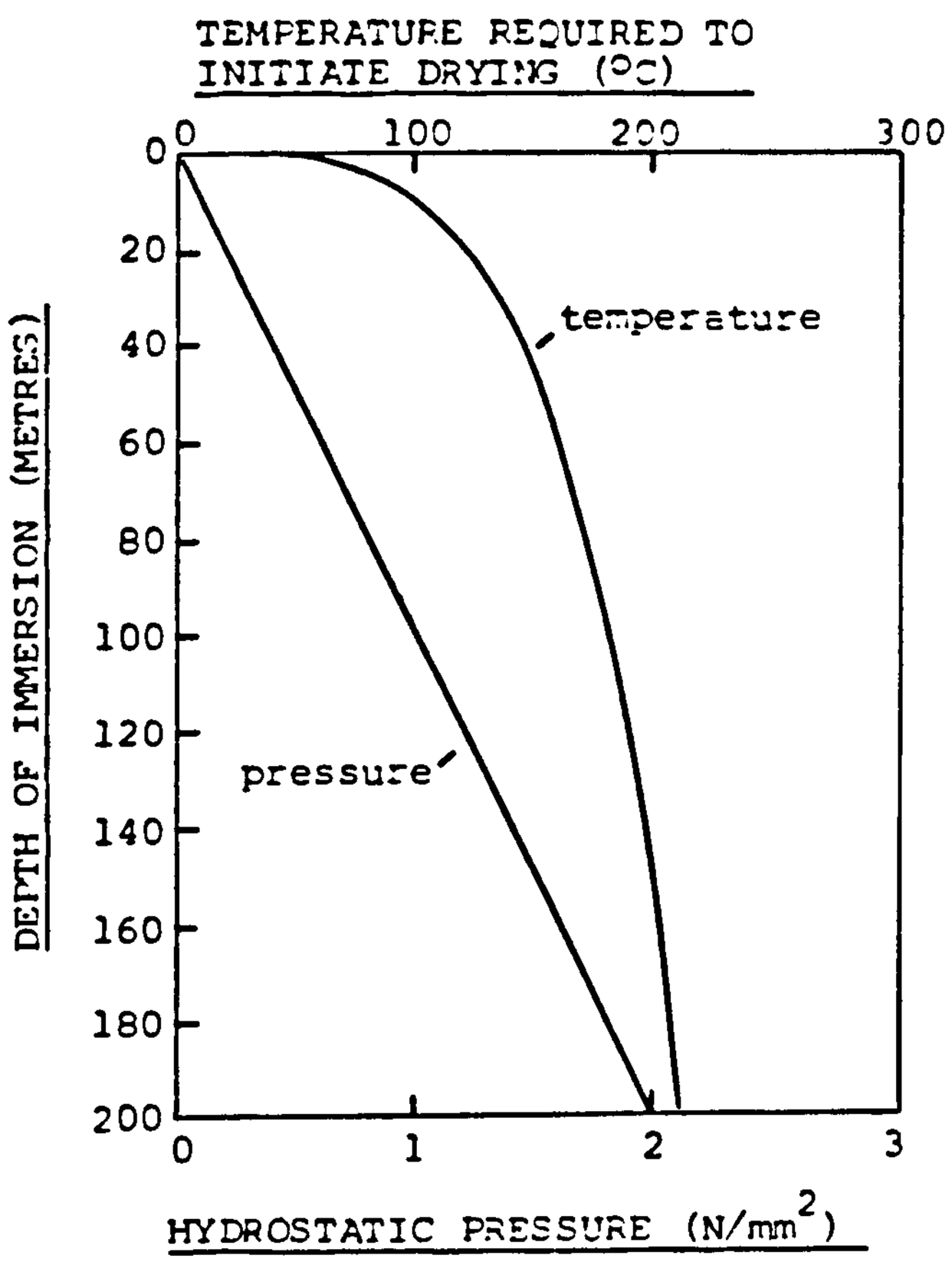
(b) Sealed Concrete

It is believed that although drying shrinkage is unlikely to occur in moist sealed concrete, significant degree of autogenous shrinkage may take place due to self-dessication /97/. Even at ambient temperatures, autogenous shrinkage seems to occur in the main body of mass concrete, remote from the outside. These strains are normally in the range of 65 microstrains after 5 years /15/ and 35 microstrains after 10 months at 45 C /17/.

At around 100 C hydrothermal reactions may occur. This normally causes time dependent expansions concurrent with the progress of the reactions. In tests on sealed moist concrete exposed to heat at 150 C, significant residual expansion was experienced which was found to increase with the number of thermal cycles and also with the duration of thermal exposure. It was found to cause cracking /17/.

FIGURE 2.18:

EFFECT OF DEPTH OF IMMERSION ON HYDROSTATIC PRESSURE AND TEMPERATURE TO INITIATE DRYING



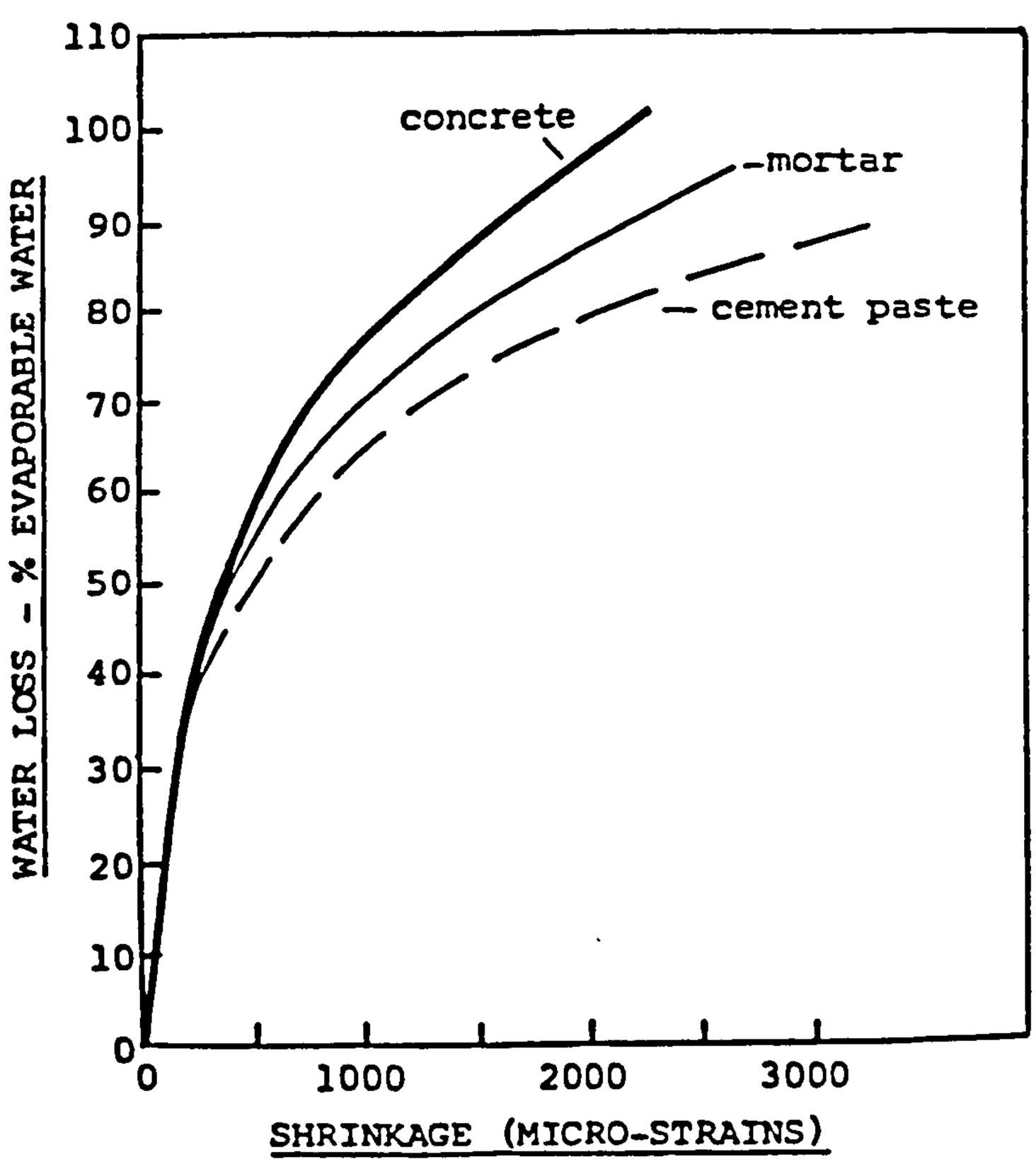


FIG. 2.19 : EFFECT OF MOISTURE LOSS FOR TEMPERATURES BETWEEN 20°C and 300°C ON THE DRYING SHRINKAGE OF CEMENT PASTE, MORTAR AND CONCRETE BASED ON DATA FROM SEVEN AUTHORS /21/.

2.2.4.3 COMPRESSIVE STRENGTH

The effects of elevated temperature on concrete strengths has been widely investigated. It is generally agreed that exposure to elevated temperature results in deterioration of strength (compressive, tensile and bond). Some of the factors liable for such deterioration include: (a) differential expansion of cement and aggregates (2) changes in porosity and build up of vapour pressure (3) cracks and microcracks (4) hydrothermal reactions (5) detrimental chemical reactions between some aggregates (e.g limestone) and the $Ca(OH)_2$ /16, 17, 96, 98, 186/.

(a) Unsealed Concrete

The compressive strength of unsealed concrete declines on heating to reach a minimum at a temperature of about 80 C regardless of the type of aggregate used (Fig.2.20) /21/. KHOURY /98/ had suggested that this weakening effect is due to increased dilation on heating of relatively incompressible gel pore water, which cannot escape until the temperature is high enough to overcome its binding energy to the solid phase. It was suggested that changes in porosity, increased micro-cracking and thermal reactions may all contribute to loss of strength /96/. However, it was previously observed that changes in chemical composition in cement paste were not noticeable at temperatures below 110 C /96/. The pattern of strength variations on heating unsealed concrete is similar in compression, tension and bond to reinforcement as can be seen in Figure (2.21).

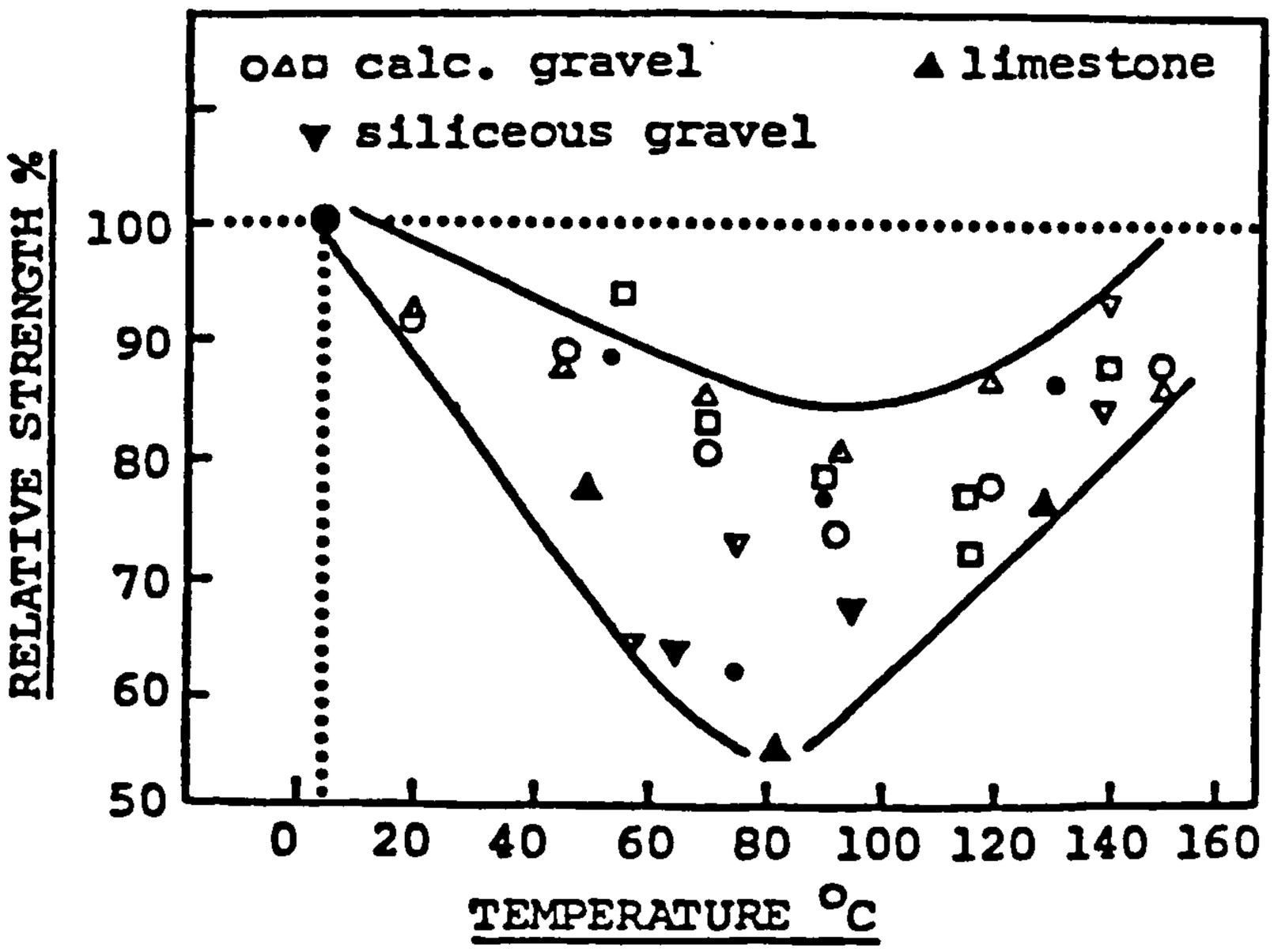


FIGURE 2.20: EFFECT OF TEMPERATURE ON COMPRESSIVE STRENGTH OF UNSEALED CONCRETES /21/.

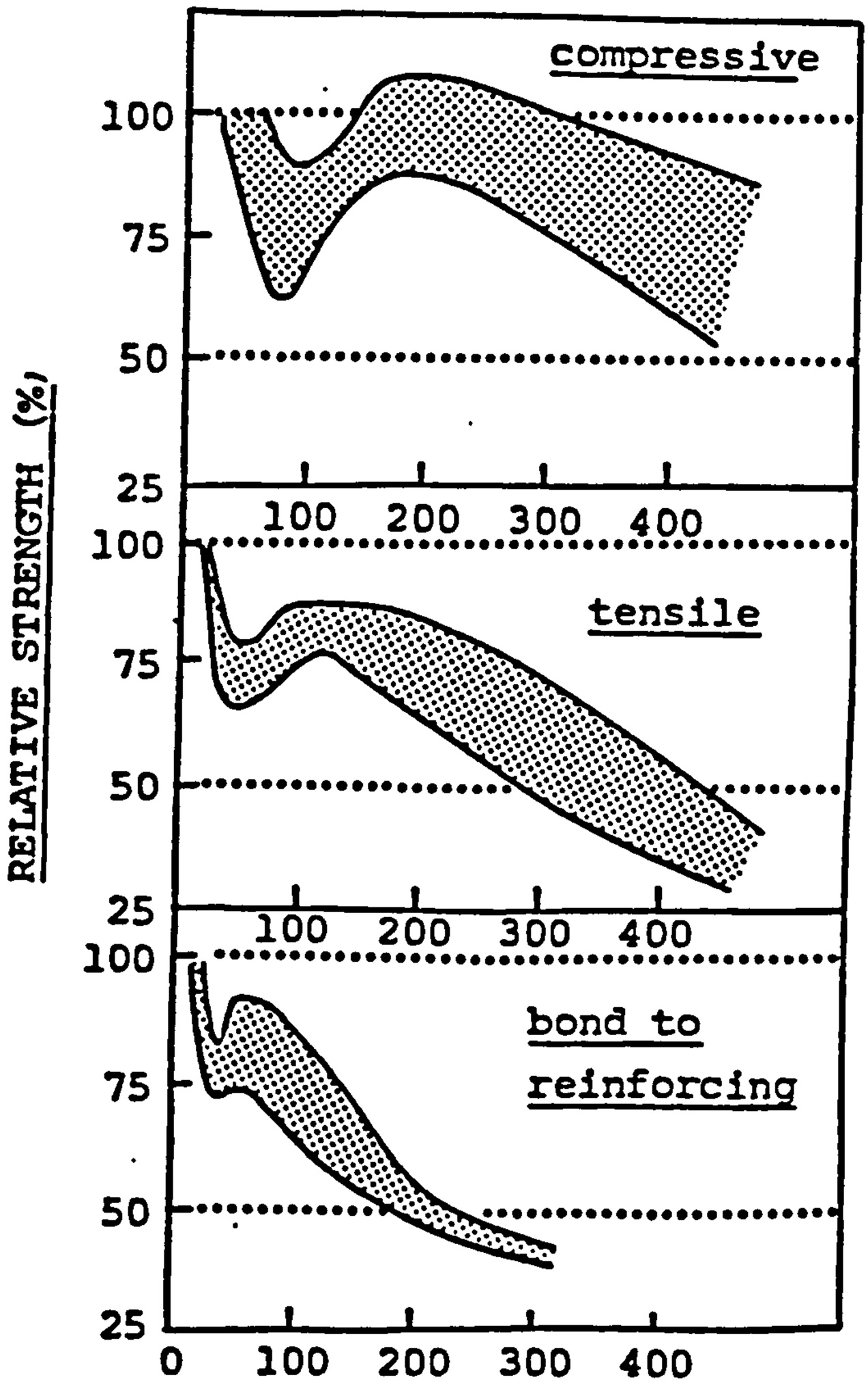


FIGURE 2.21 :
Effect of temperature on the compressive, tensile and bond to reinforcing strength of unsealed concrete /21/.

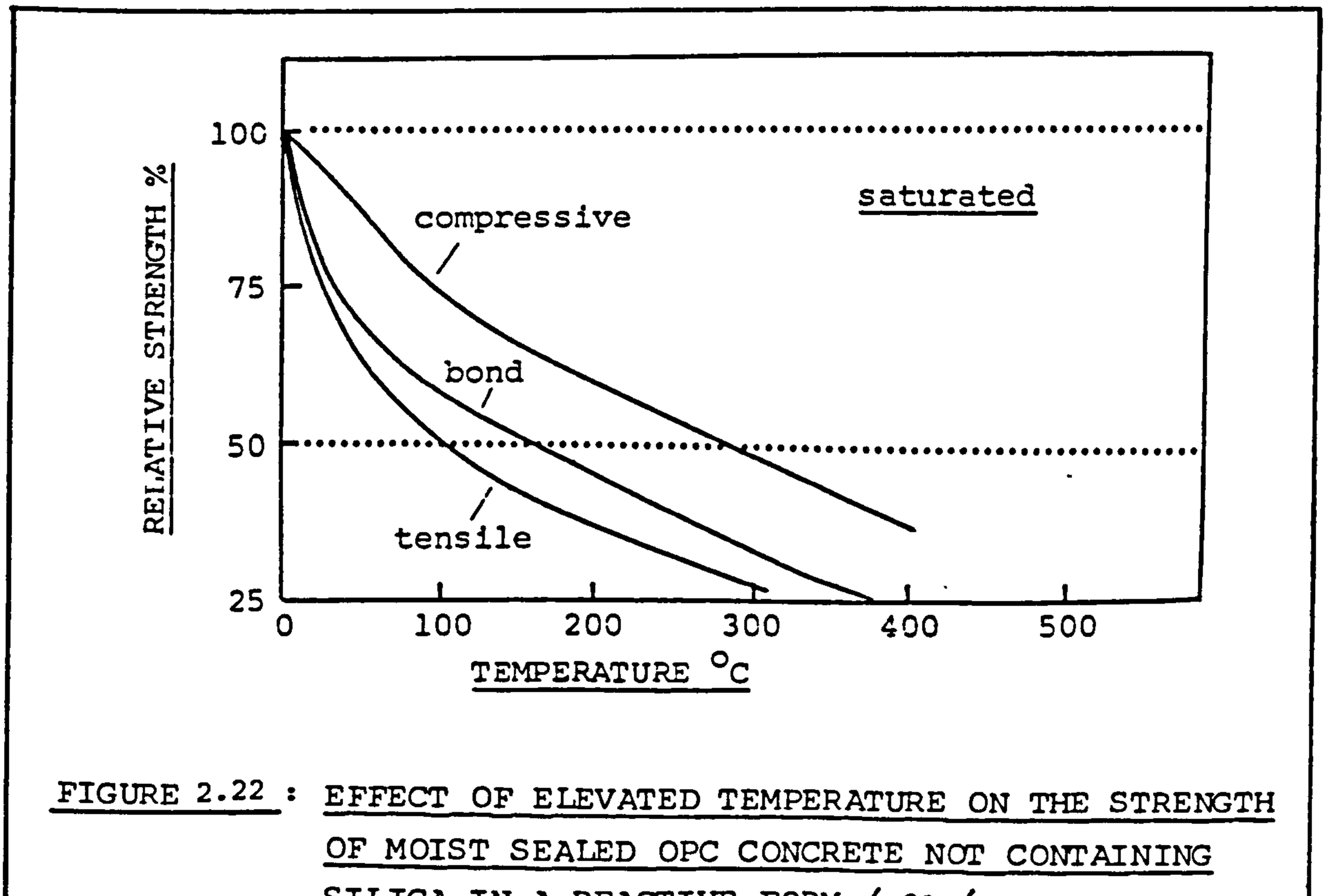


FIGURE 2.22 : EFFECT OF ELEVATED TEMPERATURE ON THE STRENGTH OF MOIST SEALED OPC CONCRETE NOT CONTAINING SILICA IN A REACTIVE FORM / 21 /.

(b) Sealed Concrete

The strength of sealed concrete declines sharply and continuously on heating, as shown in Figure (2.22). The loss in compression was least, while loss of bond to reinforcement was most severe /96, 136, 186, 187/.

NISHIZAWA /136/ found that the compressive strength of sealed concrete specimens stored at elevated temperature after water curing for up to 300 days, decreased soon after storing. It was found that the higher the storage temperature, the higher was the strength loss. At storage temperatures of 90 C, compressive strength results were found to be about 12% less than those of the control water cured specimens at 20 C. Loss in compressive strength due to elevated temperature can be much higher /98/. However, there seemed to have been recovery of strength with duration of storage (Figure 2.23).

BERTERO AND POLIVKA /17/ had observed reductions of up to 71% in the compressive strength of moist concrete specimens subjected to a temperature of 150 C. They found that strength reduction increased with duration of exposure to temperature (30% and 71%, at 7 and 25 days respectively). In addition, it was found that there was greater loss of strength in the specimens subjected to thermal cycles than in those maintained at constant temperature. Strength reduction had increased with the number of thermal cycles, although the duration of exposure appeared to have been an even more important factor /17/.

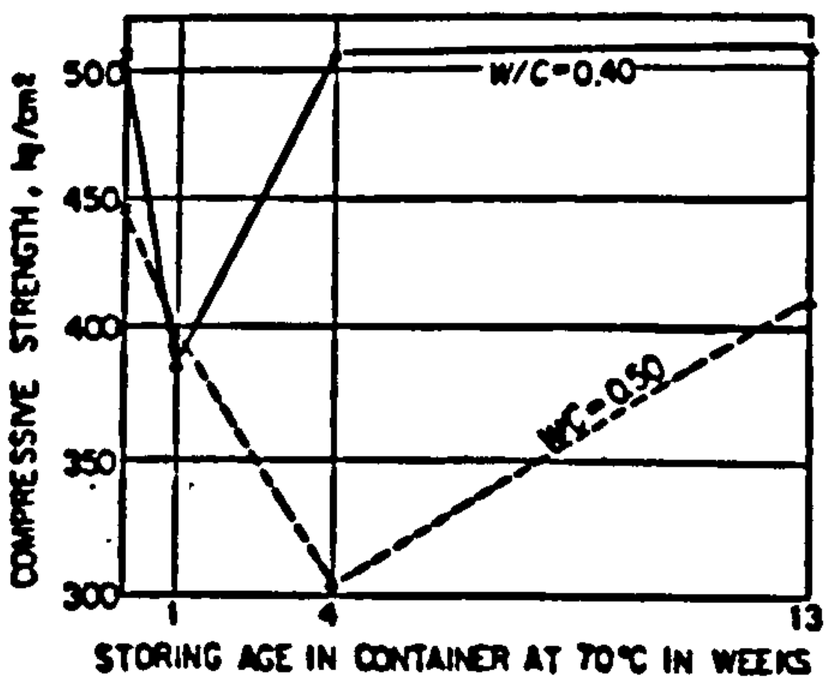


FIGURE 2.23 : Compressive strength of concrete stored in sealed container at 70 C after curing in water of 20 C for 300 days.

CHAPTER III

DESCRIPTION OF THE EXPERIMENTAL PROGRAMME

3.1 INTRODUCTION

From the literature survey presented in Chapter 2, it is clear that very few tests have been conducted on the effect of crude oil on the properties of concrete and these were all at ambient temperature. However, there have been many more tests on the effects of refined oil products and other organic liquids on concrete, but these were also all carried out at ambient temperature. Previous tests using crude oil were of relatively short duration, involving moist concretes with which full oil saturation was never achieved. The investigators did not have as one of their aims the study of differential penetration of fractions of crude oil into concrete and the depths to which these could penetrate. Given these circumstances, the effect of chemical reaction between concrete and crude oil on the physical properties of concrete, has been difficult to ascertain. Furthermore, since chemical and physical processes are often accelerated by increase in temperature, it can be expected that the reactions between any harmful substances in crude oil, and concrete, will be enhanced at elevated temperatures.

Because of its application to offshore oil storage tanks, typical of those used in North Sea oil platforms, this study differs a great deal from previous investigations in the several ways described in Chapter I. The conditions of concrete exposure which were described are complex and involve multiple physical and chemical interactions. The nature of these interactions would prove difficult to unravel unless the test programme is designed such as to isolate single interactions, in order that the combined effects can be assessed. The set up of a test programme to achieve this aim is described in this chapter. Also described are test parameters and justifications for their selection,

the test plan, preparation of test specimens, experimental procedures and the method of analysis of the results.

3.2 TESTING APPROACH

Predictions of the behaviour of concrete under any given condition can be studied by examining the effect on the constituent materials and synthesising the results. Looking at the separate behaviour of the constituent materials however, does not necessarily give their interaction, since other factors such as bond between constituents for example can also influence its properties. Indeed, an idealisation of concrete as consisting of (a) hard particles of different sizes coated with cement paste or (b) particles predominantly of one size coated with a sand cement mortar matrix, has been suggested /186/. Although both idealizations are valid for practical concrete mixes, the latter seem to have gained more acceptability, probably because it is easier to test, especially at higher temperature where mortar is more stable. Cement paste is recognised as the basic material surrounding every particle, nevertheless, a mortar using the finer sand can fairly represent the matrix. However, tests in which mortar is used to describe the behaviour of concrete must also recognise the influence of other factors such as the bond between constituents.

Concrete tests often give a considerable scatter in results, depending not only on the testing technique and the equipment used, but also on the intrinsic heterogeneity of the material and other interrelated factors which are difficult to separate. The decision about which of the mechanical properties of concrete should be tested depends most of all on the purpose of the investigation. In the practical case of offshore oil storage tanks, it was thought that of the properties which were most relevant to the serviceability of the structure, durability was the most significant.

Several properties of concrete can be investigated for durability, however, permeability and penetration are the two most important factors which govern the ingress of fluids into the material. Compressive strength is universally accepted as a measure of durability since it is the factor on which the design strength is based. It is very useful since it can be related to all the other modes of stress such as, bending, shear and torsion. Deformation of concrete is of prime importance to engineers who require information on its properties,to enable them to design and assess the performance of their structure under working load /173/. Shrinkage is of particular importance, since it may cause stresses and cracks in a structure when boundary conditions do not allow free movement. These properties were investigated in this programme.

3.3 TEST PARAMETERS

The test parameters used in this experimental programme are described below. Justifications for their selection are discussed in section (3.4).

3.3.1 Materials

The materials used in this test programme are typical of those used in the North Sea oil concrete platforms. These are a granite aggregate/ opc mix similar to that employed in phase II of the Concrete-in the-Oceans (CIO) programme /53/ and a second mix, consisting of 30% pulverised fuel ash (PFA) as opc replacement. Concrete and mortar test specimens were used. Properties of the materials and the source from which they were obtained are as follows :

3.3.1.1 Cement

Blue Circle ordinary portland cement (OPC), ex. CMC North Fleet works. Properties are given in Table (3.1).

3.3.1.2 Pulverised Fuel Ash (PFA)

ex.Pozzolanic Ltd. Properties are given in Table (3.2).

3.3.1.3 Aggregates

Coarse : crushed granite, 20mm single size 10mm single size, ex. Redland Roadstone Ltd. Mount Sorrel (Budden Quarry)

Fine : concreting sand, zone 2 grading, ex. Hall aggregates (Thames Valley) Ltd. Chertsey pit.

All the materials were stored at a constant humidity of 30 per cent and temperature of about 20 C. Coarse and fine aggregate gradings are given in Tables (3.3) and (3.4) and shown in Figure (3.1).

3.3.2 Mix Design

3.3.2.1 Mix proportions

The mix proportions for the two concrete mixes (Table 3.5) were identical to that employed in the CIO programme /97, 185/ and typical of that used in the North Sea concrete platforms /53/.

3.3.2.2 Results of Slump and As-cast densities of the concretes

An analysis of slumps from all the castings is given in Table (3.6). The total average of 47mm for the OPC mix (I) is comparable with the CIO /53/ recommendation of 50mm. Although slump is not a suitable measure of PFA concrete workability, it was determined for all mix II castings. However, the average of 65mm which was obtained is exactly the same as the CIO recommended average /53/.

Table 3.1: Analysis of Ordinary Portland Cement from CMC Northfleet /20/.

Compound Composition	Chemical Formula	Percentage by weight
Silica	SiO_2	19.7
Insoluble residue		0.4
Alumina	Al_2O_3	5.8
Ferric Oxide	Fe_2O_3	3.2
Lime	CaO	64.6
Magnesium Oxide	MgO	1.2
Sulphur Trioxide	SO_3	2.7
Alkalis	Na_2O & K_2O	0.23 & 0.47
Loss on ignition		1.4
Free lime		1.7
Lime Saturation Factor	L.S.F.	
Tricalcium Silicate	C_3S	55.2
Dicalcium Silicate	C_2S	14.8
Tricalcium Aluminate	C_3A	9.9
Tetracalcium Alumino-ferrite	C_4AF	9.7
B.S. 12 tests:		
3 day strength		22.7 N/mm^2
7		33.0 N/mm^2
28		47.0 N/mm^2
Surface area		325 m^2/kg

Table 3.2: Typical chemical analysis of Pulverised Fuel Ash (PFA) from British Bituminous Coals, to the proposed BS 3892 Part 1, 1982 /160/.

Compound Composition	Chemical Formula	Percentage by weight
Silica	SiO_2	50.00
Alumina	Al_2O_3	30.00
Iron	Fe_2O_3	8.50
Lime	CaO	2.00
Magnesia	MgO	1.50
Soda	Na_2O	1.00
Potash	K_2O	3.00
Sulphite	SO_3	0.50
Water	H_2O	0.25
Loss on Ingnition	mostly as carbon	3.25
		100.00

Table 3.3 : Coarse Aggregate Grading

(a) Granite - 10 mm size

Sieve Size		Percentage Passing	B.S. Requirement
in.	mm		
3/4	19.0	100	100
1/2	12.7	100	100
3/8	9.52	87	85-100
3/16	4.72	0.6	0-20
no. 7	2.40	0	0-5

(b) Granite - 20 mm size

Sieve Size		Percentage Passing	B.S. Requirement
in.	mm		
$1\frac{1}{2}$	38.0	100	100
3/4	19.0	85	85-100
3/8	9.52	0	0-20
3/16	4.72	0	0-5

Table 3.4 : Fine Aggregate Grading

Sieve Size		Percentage Passing	B.S. Requirement
in.	mm		
3/8	9.52	100	100
3/16	4.72	99.5	90-100
no.7	2.40	86.8	75-100
14	1.20	71.5	55-90
25	0.60	54.7	35-90
52	0.30	12.4	8-30
100	0.15	0.6	0-10
200	0.075	0	0

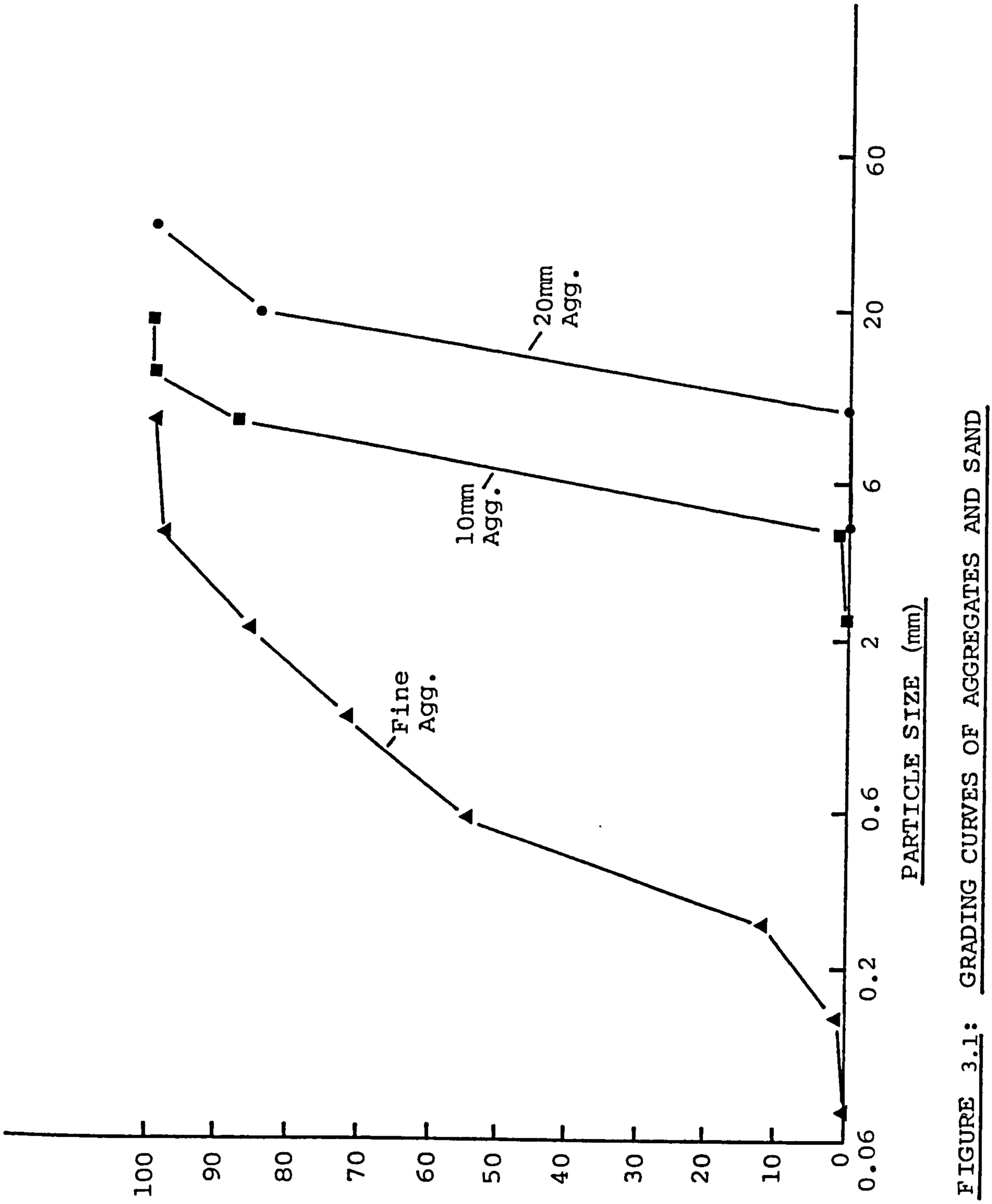


FIGURE 3.1: GRADING CURVES OF AGGREGATES AND SAND

Analysis of the as-cast densities of 6 cube specimens per casting, for all castings is given in Table (3.7). The range of densities for all 100mm concrete cube specimens, for both the OPC and PFA mixes, fall within the specific gravity range of 2.37-2.68 recommended by the CIO /53/.

3.3.2.3 Results of Flow, As-cast densities and 28-day Compressive strengths of the mortars.

Flow measurements of the mortar mixes given in Table (3.8) showed that flow was greater in the PFA than in the OPC mixes. The average flows were 98.2 and 89.1mm respectively. The difference between the two can be attributed to the improved workability in the former for the same water content.

The range of as-cast densities for both mixes was 2228-2270 Kg/m3. Averages are given in Table (3.9).

Results of the 28-day cylinder compressive strengths of the mortar specimens are given in Table (3.10). It showed that the OPC specimens had average strengths which were about 24% more than for the OPC specimens. This trend was not unexpected, as would be explained in Chapter 5.

3.3.3 Curing Conditions

All test specimens were initially cured at 100% RH for 14 days at about 20 C, by which time it was expected that the capillary pore system would have become discontinuous. The specimens were then further cured in two groups: in seawater and at 100% RH. The control specimens similarly prepared were cured in fresh water. Curing was maintained for 365 days, within which period the compressive strength of the concretes and length change of the mortars were monitored.

TABLE 3.5 : Proportion of concrete mixes I and II

Material	proportion by weight	
	Mix I (OPC)	Mix II (PFA)
cement (opc)	1.00	0.70
pozzolan (pfa)	-	0.30
aggregates		
(20mm size)	1.70	1.70
(10mm size)	0.80	0.80
sand	1.50	1.50
water	0.45	0.45
water/blend ratio	0.45	0.45
blend content (Kg/m3)	435	435

TABLE 3.6 : Concrete Slumps

	Mix I (OPC)	Mix II (PFA)
no. of castings	16	16
range of slump (mm)	28 - 74	45 - 90
average slump (mm)	47	65
std. deviation (mm)	11	14
CIO recommended average (mm) /53/	50	65

TABLE 3.7 : As-cast densities of concrete cubes

	Mix I (OPC)	Mix II (PFA)
no. of specimens	96	96
range (Kg/m3)	2413 - 2431	2363 - 2400
average (kg/m3)	2420	2385
std. dev. (Kg/m3)	12	13
CIO recommended range of specific gravity	2.37 - 2.68	

TABLE 3.8: Mortar Flows

	Mix I (OPC)	Mix II (PFA)
no. of castings	6	6
range of flow (mm)	80.5 - 106	91 - 105.5
average (mm)	89	98
std.deviation (mm)	10	5

TABLE 3.9: As-cast densities of mortar cylindrical test specimens.

	Mix I (OPC)	Mix II (PFA)
no. of specimens	30	30
range (Kg/m3)	2228 - 2270	2229 - 2261
average (Kg/m3)	2259	2246
std. deviation	15	15

TABLE 3.10: 28-day Cylinder compressive strength of mortar samples.

	Mix I (OPC)	Mix II (PFA)
no. of specimens	18	18
range (N/mm2)	51.2 - 57.8	36.0 - 44.8
average (N/mm2)	54.0	41.0
std. deviation	2.0	2.1

TABLE 3.11: Ionic concentration of seawater

Compounds	conc. (g/l)	(%) of total
Chloride	18.85	51.9
Sodium	12.21	33.6
Sulphate	2.21	6.1
Magnesium	1.98	3.5
Calcium	1.26	2.7
Potassium	0.65	1.8
Bicarbonate	0.15	0.4

The seawater used in the curing process was from the North Sea and was obtained by courtesy of Regents Park Zoo. Analysis of its ionic concentration as obtained from tests at Imperial College are given in Table (3.11). The seawater was changed regularly once every month.

3.3.4 Moisture condition of the specimens prior to oil soaking

At the end of the period of curing and prior to soaking in crude oil, half of the specimens were oven dried at 105 C for use in the 'single interaction tests', while the other half were kept saturated moist as intended for the 'multiple interaction tests'. Similarly conditioned specimens were also prepared to serve as controls, for soaking in water at elevated temperatures.

3.3.5 Test Temperatures

Tests were carried out in crude oil and in water at four temperatures of 20, 45, 60 and 80 deg.C.

3.3.6 Types of tests

Broadly, tests were undertaken to investigate the physical properties of concretes exposed to crude oil at elevated temperatures as follows;

(a) Penetration tests were carried out at ambient and elevated temperatures to determine the depth of penetration of crude oil into concrete with time.
(b) Studies were carried out to investigate the differential penetration of the different fractions of crude oil through concrete.
(c) Crude oil absorption of the specimens was studied by measuring the weight changes in crude oil.
(d) Mechanical tests were carried out to measure the compressive strengths of concrete specimens and the length changes of the mortar specimens on exposure to crude oil. These measurements were monitored at intervals over a period of 12 months.

Chemical tests were carried out to determine the organic and inorganic acid intake of crude oil from the acidified water phase. Results are given in Appendix A.

3.3.7 Test specimens

Appropriate specimens were designed and cast to measure the physical properties, these comprised of ;

1. concrete cylindrical specimens, 63.5mm diameter x 63.5mm length and 100mm concrete cubes, for compressive strength tests.
2. mortar prisms (25 x 25 x 285mm), to investigate length change.
3. concrete cylindrical specimens (63.5mm diameter x 63.5mm length) to study crude oil penetration and permeability.

3.3.8 Duration of Tests

All specimens were cured for 12 months. Specimens tested for 'single interactions' were oven dried for 12 days at 105 C. Exposure to crude oil lasted for 12 months.

3.3.9 Crude oil

The crude oil used was from the Fortis field, North Sea and was supplied by courtesy of British Petroleum (BP) /25/. Its acid contents were measured at Imperial College and were found to be insignificant (see Appendix A).

3.4 JUSTIFICATIONS FOR SELECTION OF TEST PARAMETERS

Part of the aims of this programme was to establish if concrete currently being employed in North Sea oil storage tanks is likely to experience any deterioration in properties. In designing the experimental programme therefore, it was necessary that practical conditions existing in the tanks should be simulated as closely as possible. On this basis, justifications for the selection of test parameters are as follows :

3.4.1 Materials and Mix Design

The materials, as well as the mix proportions had to be typical of those used in the existing structures. The CIO recommended mix /97, 185/ for use in North Sea structures was therefore employed. However, the recommended ratio of 80:20 for OPC:PFA was not adopted rather, a ratio of 70:30, which was in line with the more recent recommendations of BS 3892 part I, 1982 /29/, was utilised.

3.4.2 Curing conditions

The caisson walls of the platform storage tanks are said to be exposed to seawater at a very early age/97/. For at least the first year after casting and prior to the introduction of crude oil, the bare concrete walls are exposed to seawater under hydrostatic pressure at a temperature of about 5 C /97/. The concrete is, therefore, under saturated conditions throughout its life. However, concrete in the central region of the caisson wall is likely to remain unaffected by seawater (Fig.3.2), especially since the rate of penetration of seawater may have been reduced significantly with time. This can result from two factors;

- discontinuity of the capillary pore system achieved after the initial curing at 100% RH,
- the formation of relatively impermeable layers of brucite and aragonite on the surface of the concrete, as a result of chemical reactions with seawater.

The above conditions were simulated by initially curing all specimens at 100% RH for 14 days after casting. Curing was then simulated as follows (Figs. 3.2 and 3.3):

- curing specimens in seawater for one year after casting to simulate conditions on the surfaces of the caisson walls.
- curing specimens at 100% RH for one year after casting, to simulate conditions in the central region of the caisson wall unlikely to be affected by seawater.

3.4.3 Moisture condition of the specimens prior to oil soaking

Exposure of the concrete walls to hot crude oil may cause cracking at the inside face of the oil storage cells /41, 42/, especially during the first thermal cycle. It may also result from direct physical impact on the caisson walls due to several possible causes, as has been reported by Roren and co-workers /172/.

The depth and width of the cracks which may result will depend on a number of factors, including the arrangement of reinforcements, the rate of heating, the rate of cooling and the upper temperature limit of the oil. If the cracks penetrate into the concrete (Fig.3.3), hot oil will permeate into concrete cured in seawater (zone A), as well as that unaffected by seawater (zone B). Heat will furthermore conduct from the oil into both zones. Four types of exposure will result:

- moist cured (100% RH) concrete exposed to hot crude oil.
- seawater cured concrete exposed to hot crude oil.
- moist cured (100% RH) concrete exposed to elevated temperature.
- seawater cured concrete exposed to elevated temperature.

The most complex of these conditions would be the exposure to crude oil at elevated temperature of concrete saturated with seawater. This would involve multiple physical and chemical interactions between the concrete, moisture, sea salts, crude oil and elevated temperature. The effects of these will be difficult to unravel or explain, unless the basic mechanisms involved are understood. The first task, therefore, would be to investigate the nature of the interaction between concrete and each of the fluids separately at ambient temperature. Explanation of the multiple interactions would then follow.

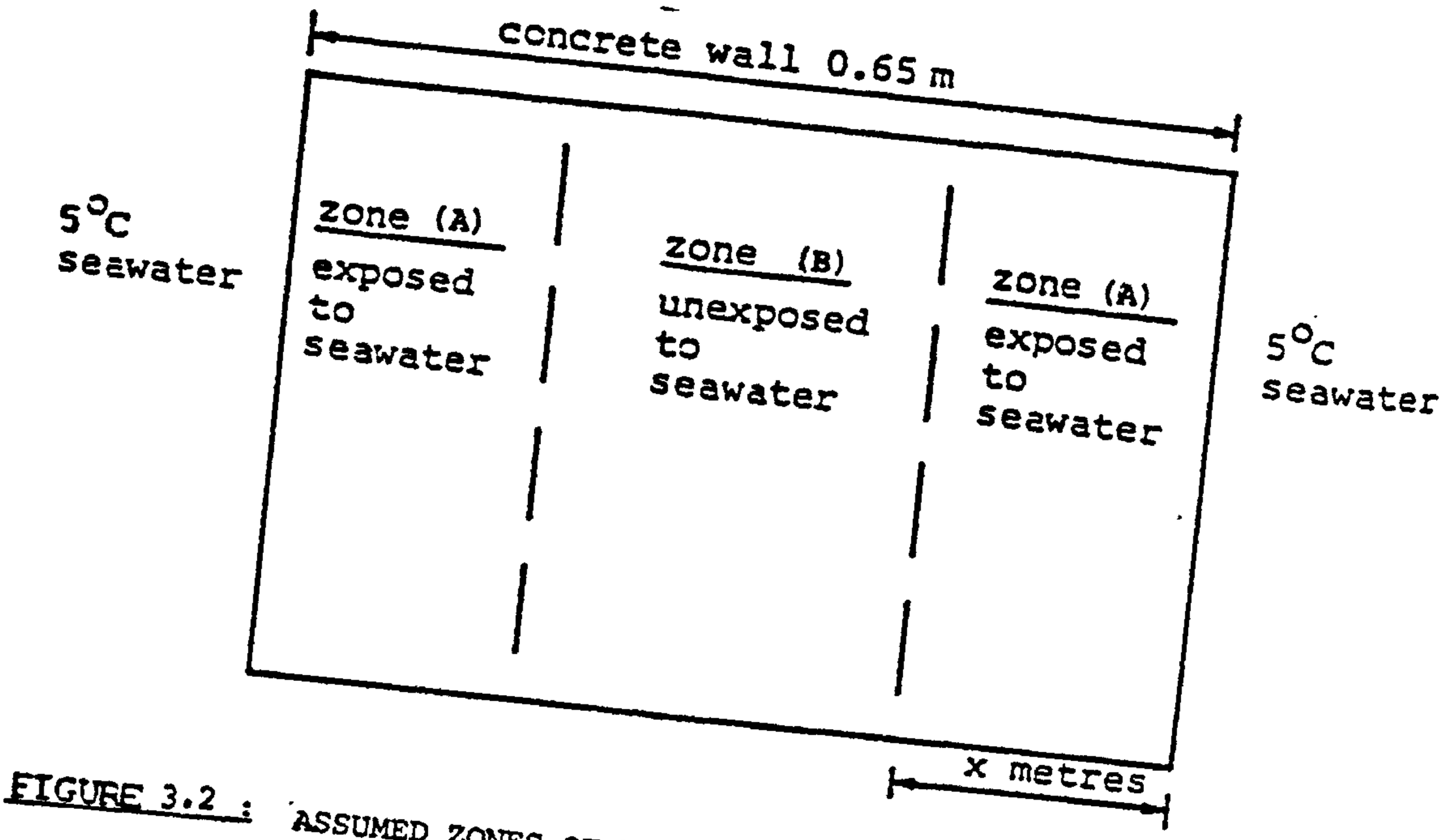


FIGURE 3.2 : ASSUMED ZONES OF EXPOSURE TO SEAWATER IN AN OIL STORAGE TANK PRIOR TO EXPOSURE TO HOT CRUDE OIL, BUT AFTER EXPOSURE TO SEAWATER FROM BOTH ENDS AT 5 deg.C.

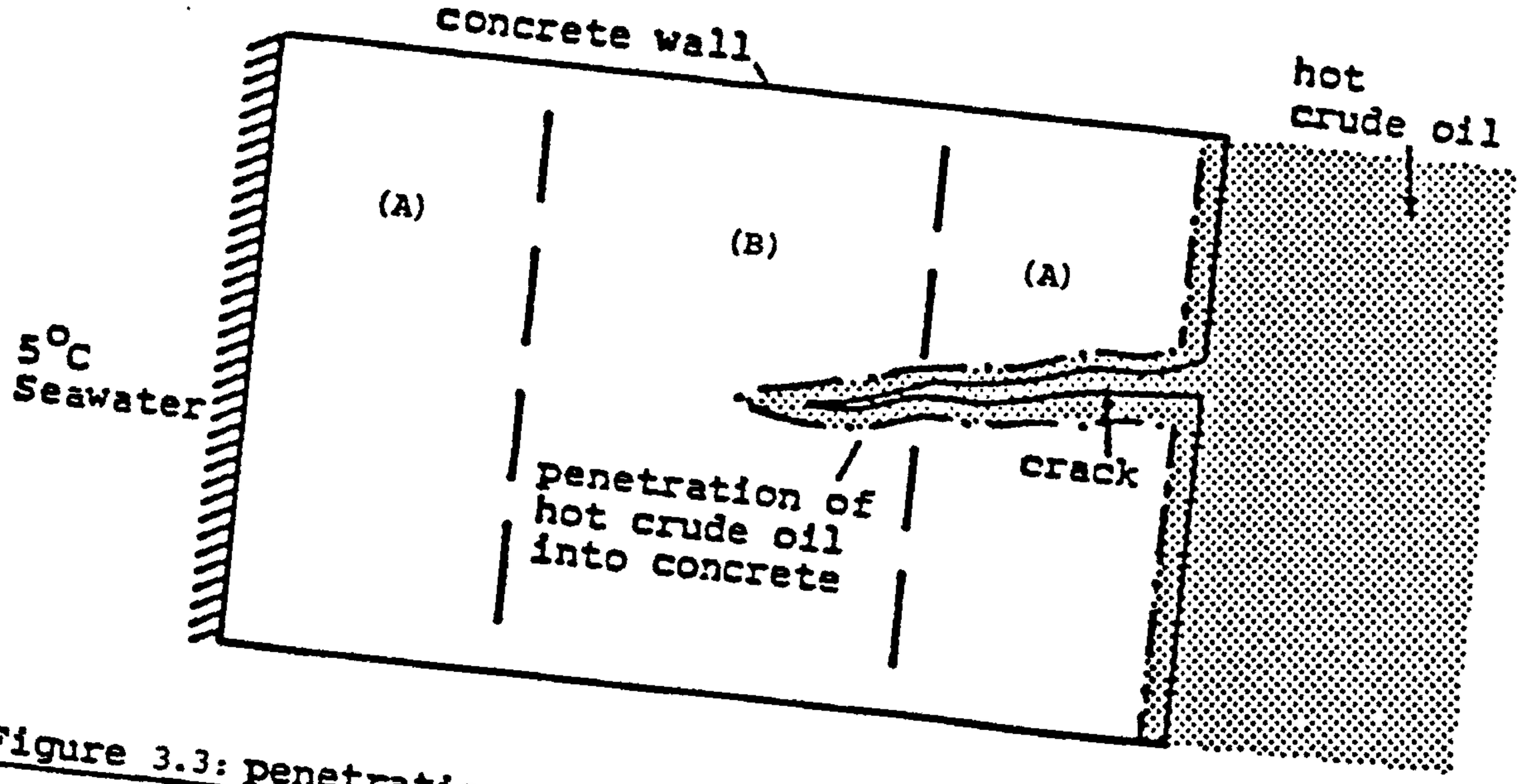


Figure 3.3: Penetration of hot crude oil into (a) surface concrete affected by sea water and (b) internal concrete cured at 100% RH.

Thus, concrete has been modelled as comprising a solid porous 'skeleton' containing no moisture and which is capable of being saturated by one or more fluids. This could be air, moisture, seawater or crude oil. A 'normal' concrete can therefore be considered as one in which the solid skeleton is filled by moisture to the relative humidity of its surrounding. As regards the caisson wall (Fig.3.3), the concrete at the surface and within the cracks can be modelled as consisting of skeleton + multiple fluids. The skeleton can be assumed to be concrete containing no evaporable moisture, which can be achieved by oven drying at 105 C.

3.4.3.1 Single Interaction Tests

In single interaction tests, predried concrete specimens were soaked in crude oil at ambient temperature and represented as follows:

- skeleton (100% RH cured) + crude oil
- skeleton (seawater cured) + crude oil

The tests, which allowed direct contact of skeleton and crude oil were aimed at simplifying interpretations of the degree and nature of chemical reactions taking place. The absence of evaporable moisture eliminates the possibility of further hydration simultaneous with the possible reactions caused by crude oil. The tests were monitored against a background of control specimens kept oven dry.

The second phase of the single interaction tests involved the exposure of oven dry concrete specimens to crude oil at elevated temperatures. By comparing results with those at ambient temperatures, the effect of elevated temperature can be established. However, tests were also carried out to investigate the effects of elevated temperatures alone on the concrete skeleton in the absence of any fluid. This was done by reheating oven dry control specimens at the three elevated temperatures over the same periods of time as those soaked in crude oil.

3.4.3.2 Multiple Interaction Tests

These can be represented as follows:

- skeleton (100% RH cured) + moisture + crude oil + temperature
- skeleton (seawater cured) + seawater + sea salts + crude oil + temperature.

The effect of temperature in this case will be more severe, since the specimen would not have been previously exposed to it. The interactions were therefore expected to reflect in complex behaviour. However, when analysed against a background of single interactions, the effect of moisture saturation and crude oil can be identified. Further control specimens cured in water at the 4 elevated temperatures were also prepared.

3.4.4 Test Temperatures

The temperature of the crude oil flowing from a production well is between 70 and 100 C /168/, although temperatures as high as 150 C have been reported /22, 133/. The average crude oil temperature on entering the caisson wall after cooling is estimated at between 45-50C /167/. The test temperatures chosen were those which closely reflected the operating conditions and possible higher levels. These were, ambient (20), 45, 60 and 80 C. The latter two in addition to being possible upper limits, were also useful for accelerating the tests.

3.4.5 Type of Tests

The physical properties tested were standard methods of assessing the durability of concrete, as was earlier discussed (section 3.2). The penetration tests are particularly relevant since a section of the wall at the top of the storage vessel is in constant contact with hot crude oil. It becomes even more so when it is recognised that unless the crude oil penetrates the concrete, its influence is likely to be limited, if any, to chemical attack of the concrete surface. The nuclear magnetic resonance (nmr) technique was chosen to study the differential penetration of crude oil fractions into concrete, as it

is capable of separating crude oil into the aromatic and aliphatic fractions. This is significant since polar aromatics are more likely to be adsorbed differently from the non-polar saturated hydrocarbons, especially at the surface. As a matter of interest, advantage is taken of this process in the petroleum industry to separate aromatics from saturated hydrocarbons.

3.4.6 Types of Specimens

The 63.5 x 63.5mm diameter type cylinder specimens were chosen in order that quick saturation with test fluid should be achieved. It was also to minimize the use of curing space since a very large number of test specimens were cast. However, the specimens were large enough to be able to use 20mm size aggregates. The length to diameter ratio of 1:1 ensured compatibility of results with compressive strength of standard 100mm concrete cubes. The mortar specimens were chosen and prepared in accordance with standard ASTM specifications /9, 10/.

3.4.7 Duration of Tests

The test period of 12 months in crude oil was considered as a reasonable time within which the effect of exposure can be studied and understood. In effect, the specimens would be two years old since they were previously cured for 12 months.

3.5 TEST PLANS

3.5.1 Physical Tests

The plan evolved for testing the physical properties is as shown in the flow chart of Fig.(3.4). The time of test in crude oil however did not apply to the penetration tests.

The test programme was planned such that it incorporated the investigation of single and multiple interaction tests, using the two mixes: OPC mix (I) and the OPC/PFA mix (II). The other test variables involved and shown in the chart are given in Table (3.12).

3.5.2 Chemical Tests and Microscopic Investigations

To assist in the interpretation and analysis of results, chemical tests and microscopic investigations were carried out on test specimens before and after exposure to crude oil. Details are as follows:

3.5.2.1 Chemical Tests

Tests were carried out at the end of the period of curing, to investigate carbonation and lime contents in the test specimens prior to exposure to crude oil. Tests were also carried out to investigate the inorganic and organic acid intake of crude oil floating on acidified seawater, the results of which are reported in Appendix A.

3.5.2.2 Microscopic Investigations

Visual and analytic techniques were used to examine and analyse the surface and microstructure of test specimens before and after exposure to crude oil. Direct examination of the specimen surface was first by the naked eye. The formation of surface layers in the seawater cured specimens and the contrasting colouration of opc and opc/pfa specimens, were easily observed.

(a) Visual Techniques

The Reichert Zetopan reflected light optical microscope, generally at a magnification of 100X, was used to observe the layers formed on the seawater cured specimens. These layers were not found on specimens cured at 100% RH.

Scanning Electron Microscopy (SEM) was undertaken using a Hitachi S-450 scanning electron microscope at 20 kV, to study the micro-structure of samples before and after crude oil exposure. The examinations were carried out at Queen Mary College, London.

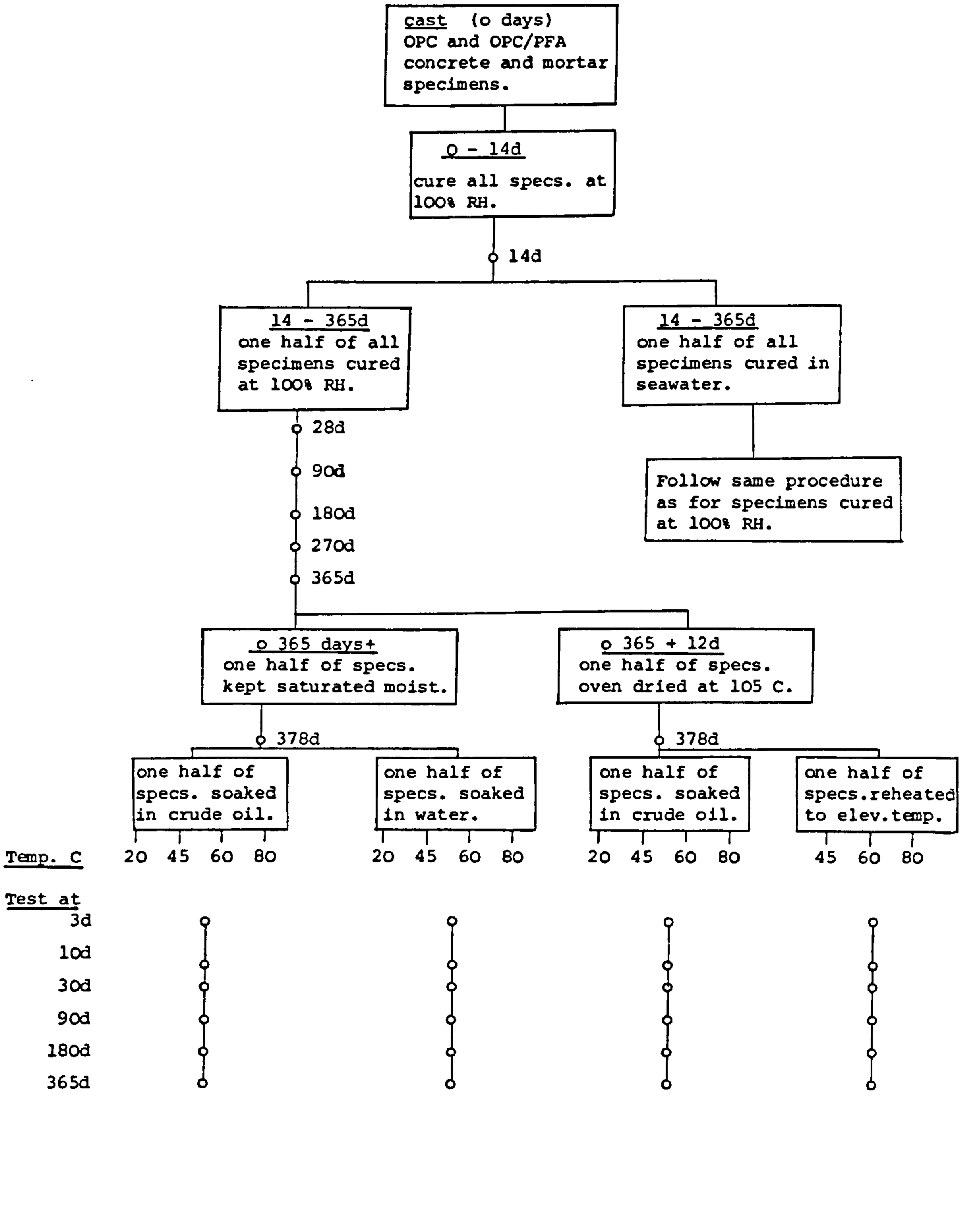
Electron-probe microanalysis was undertaken using the above scanning electron microscope with link EDS analysis. This method allows the analysis of an extremely small area of sample by identifying and quantifying elements contained within that area.

X-ray diffraction analysis was performed on the layers found, with the help of Dr. N Buenfeld of Imperial College /34/. The method allows the minerology of these layers to be identified.

TABLE 3.12 : Test variables for physical tests

VARIABLE	Degree of variation	No. oflevels
Pozzolan	0 and 30% PFA	2
curing medium	100% RH and seawater	2
Pre-soak treatment	none and 105 C	2
soak fluid	crude oil and water	2
soak temp.	20, 45, 60 and 80 C	4

FIGURE 3.4 : GENERAL TEST PLAN (Symbol o denotes test measurement of compressive strength and length and weight changes at the age indicated).



3.6 FACTORIAL METHOD OF DESIGN

3.6.1 INTRODUCTION

In the previous section, a description was given of how the isolation of single interactions can facilitate analysis of multiple interactions. This method, in general, assesses the effect of changing one variable independently of others. In a situation where many factors are being varied, it is neither sufficient nor economical to vary one factor at a time. All combinations of the different factor levels must be examined, in order to elucidate the effect of each factor and the possible ways each may be modified by the variations of the others. It is therefore possible that in the analysis of the experimental results the effect of each factor can be determined with the same accuracy as if only one factor had been varied at a time, in addition to evaluating the interaction effects. Such an experiment is known as a Factorial Experiment. The term can be extended to modified designs as in Confounding and Partial Factorial methods, full details of which can be found in some specialised texts /44, 51, 64/. Statistical significance can be improved by carrying out a full factorial analysis with replication.

The idea of this process is based on the postulate that the statistical error distribution forms the normal distribution curve. The significance tests and confidence limits which are derived from the above postulate, are used in the interpretation of experimental data.
The advantages of this method of design can be summed up as follows:
(a) When there are no interactions, it gives the maximum efficiency in the estimation of effects. By efficiency here is meant, obtaining the required information with the required degree of precision and the minimum expenditure of effort.
(b) Helps to avoid misleading conclusions when interaction exist but their nature is unknown.
(c) Allows the effect of a factor to be estimated at several levels of the other factors and the conclusions hold over a wide range of conditions.

Factorial design has been in use for many years, especially in the fields of agriculture and biological research. More recently it has found usage in the field of concrete research /90, 188/.

3.6.2 COMPLETELY RANDOMISED FACTORIAL EXPERIMENTS

Two properties of a complete factorial design able to improve its efficiency are, orthorgonality and randomization.

3.6.2.1 Orthogonality

Orthogonality is a property of the design and is the desirability of making the experiment symmetrical in all factors. This is done by testing all treatment combinations the same number of times.

In general, a full factorial design gives maximum efficiency and can be achieved with or without replication. It also ensures that all the main treatments can be independently estimated without entanglement. Its most important advantage is that the results obtained are more reliable than they would be with a partial factorial design. The experimental test programme described in the next section is an orthogonal design (Figure 3.4).

3.6.2.2 Randomization

In any experiment, the factors which cause variation of the yield are of two types: (i) those deliberately varied and (ii) those which cannot be controlled and which give rise to the residual variance, or experimental error.The uncontrolled variation or error, is treated as a random variable, meaning that it is assumed uncorrelated with any of the controlled variations. Such errors must therefore be distributed at random, or else the whole basis of the analysis and of the test of significance will be invalidated.

In the experimental programme to be described (section 3.7) it can be observed that all specimens from each of the 32 concrete castings, as well as the 10 mortar castings, were chosen randomly to be used in the different tests. However, statistical tests had earlier confirmed that the concrete specimens could be assumed to come from the same population in terms of 28 day-compressive strength.

3.6.3 Factorial design to determine the durability of concretes used in offshore oil storage tanks

The factorial method of analysis has been applied to compressive strength and length change. Factors and levels of the investigation are as follows:

A.	Cement blend	100% OPC; 70%OPC : 30%PFA
B.	Curing condition	100% RH ; seawater
C.	Pre-Treatment	saturated moist; oven dry(105 deg.C)
D.	Exposure media	freshwater; crude oil
E.	Temperature	low (20 C); high (45, 60, 80 C)

Each combination was tested with 3 replicates at 5 intervals of time: 3, 10, 30, 90, 180 days. The experiment was therefore a 2 to power 5 full factorial design. Since the three elevated temperatures were lumped together as one level, further analysis was made of the effect of the 3 different temperatures. Test results were also obtained at 365 days but were not enough for a full 5 factor analysis. This was because tests were not conducted for factor (C) at the second level at this age, as earlier explained. Nevertheless, analysis was performed on the basis of a five factor factorial incorporating missing values.

3.6.4 Computer method of evaluating Effects

The 2 x 2 x 2 x 2 x 2 factorial design involves thirty two (32) effects and interactions. The algorithms involved in the estimation of these are long and cumbersome and are best solved on the computer. To this end a specialist package called GENSTAT /3/ has been used. It is a computing language for data manipulation and statistical analysis, developed by the Rothamstead Experimental Station. By using this package, a programme given in Appendix B has been written, which is able to reduce the set of algorithms for each effect and interaction to "Mean Squares" and "Variance Ratios", from which statistical significance can be determined.

The significance of main effects and their interactions were determined based on the following statistical theory :

The variance ratio (VR) for each term is the mean square (MS) divided by the residual mean square and is the statistical **F-Value.** If a term has a larger effect than would be expected by chance given the amount of random variation in the experiment, then the VR for that term is substantially larger than unity. The probability by chance of obtaining a VR larger than the one calculated can be looked up in a **F-Table.** The variance ratio is calculated with the larger estimate of variance in the numerator and Ø1 and Ø2, the degrees of freedom in the numerator and denominator respectively. If in a single test F is greater than (say) the 5% value, it can be inferred that the experimental error is not the only source of variation and that the factor concerned had a real effect. The chance that this inference is wrong is only 5%, since in only 5% of trials could F exceed the tabulated value if the factor had no real effect. The result can therefore be considered as **SIGNIFICANT.** In some cases, it is possible that the 1% level is reached and the fact may be taken as sufficient evidence of the existence of a real effect, in such cases the result will be considered as **HIGHLY SIGNIFICANT.**

Factorial analysis is directly related to observations made from the experiment for which it was designed and cannot therefore be used as a theoretical model. It can only be used successfully when it is interpreted in conjunction with observations made. However, its limitations arise from this, in that some of the higher order interactions, especially where a large number of factors are involved, cannot be related to physical observations and therefore have to be ignored.

3.7 PREPARATIONS OF SPECIMENS

A detailed description of the methods of preparation of the concrete and mortar test specimens is given in this section.

3.7.1 CONCRETE

Concrete cylindrical test specimens (63.5 x 63.5mm diameter), were prepared for measuring crude oil penetration as well as compressive strength. In addition, standard 100mm concrete cubes were cast to serve as controls to monitor the development of compressive strength throughout the duration of curing.

3.7.1.1 Details of Moulds

Special moulds, capable of holding 55 specimens per batch were designed for casting the test specimens. The moulds were manufactured from Dura-pipes, fitted into a perspex frame. The 100mm cube specimens were cast in standard steel moulds.

3.7.1.2 Casting and curing procedures

All aggregates were dried at laboratory temperature of about 20 C and were batched by weight to the nearest gram. The dry aggregates and cement were mixed for one minute in a 0.06 m^3 horizontal pan mixer before water was added. Mixing continued for a further two minutes and the wet concrete was allowed to stand for 7 minutes before a slump test was carried out. The concrete was placed in moulds in two layers and compacted on a table vibrated for 60 seconds. The exposed face of each specimen was trowelled flat after about two hours and then covered with wet hessian and prevented from touching the trowelled face by steel mesh. The arrangement was covered with polythene sheets to minimise evaporation. The specimens were demoulded after 2-days and were cured at 100% RH and about 20 C for 14 days. The specimens were then separated into 3 equal parts, for curing in seawater, 100% RH and fresh water respectively.

3.7.2 MORTAR

Mortar prisms (25 x 25 x 285mm) were cast for the sole purpose of measuring length and weight changes in crude oil. Along with these were mortar cylinders (63.5 x 63.5mm dia.), which served as controls to monitor the development of 28-day compressive strength and density of the mortar mixes.

3.7.2.1 Details of Apparatus to ASTM standards /10/

(a) Moulds with two compartments providing for 2 No. 25 x 25 x 285mm prisms. (b) A non-absorptive, non-abrasive steel tamper with cross-section of 13 x 25 x 150mm. (c) Demoulding apparatus (d) Flow table.

3.7.2.2 Mix Design

The composition of the mortar was one part cement to 2.75 parts of graded standard sands by weight, and a free water/cement ratio of 0.45 The PFA mix had a 30% OPC replacement. The mix proportions follow specifications from ASTM C-109 /7/.

3.7.2.3 Casting and curing procedures

All fine aggregates were dried at laboratory temperature of about 20 C. Batching was by weight to the nearest gram. The paddle and bowl were placed in a horizontal mixer, water was placed and the cement added and mixed at a slow speed for 30 seconds. Aggregates were added and then mixed for a further 30 seconds at medium speed. The mortar was allowed to stand for 90 seconds, within which time all mortar adhering to the bowl were scraped into the mix and again mixed at medium speed for 60 seconds. A flow test measurement was taken immediately after. Mortar from the flow table was then remixed for 15 seconds. The mortar was placed in the moulds in three layers, each layer was tamped and vibrated at low speed for 10 seconds. The faces of the mortar were trowelled and covered with wet hessian and prevented from contact with the wet surface by steel mesh. The whole arrangement was covered with polythene sheets.

The specimens were demoulded about 24 hrs. after the addition of water to the cement during the mixing operation. The specimens were immediately placed in water and length measurements were taken. The specimens were kept in wet hessian at 100% RH for 14 days at the end of which, half the total number of specimens were further cured in this condition and the other half in seawater at about 20 C.

3.8 EXPERIMENTAL PROCEDURES

The experimental procedures for the compressive strength, length change and penetration test measurements are described below.

3.8.1 Compressive Strength

A total of one thousand concrete cylindrical specimens were prepared of which four hundred and twenty (420) were oven dried. Oven drying time extended for 12 days. The rate of heating was 5 deg.C/hour from ambient, until a steady temperature of 98 C was attained. This was maintained for 72 hours. The temperature was then raised to 105 C at the earlier rate of heating and this was maintained for another 96 hours. The specimens were then cooled to ambient at the rate of 4 deg.C/hour, surrounded with coarse silica gel.

The reason for the above procedure was to remove all capillary water while avoiding hydrothermal reactions /98, 164/ which can take place in moist concretes at temperatures above 100 C. Raising the temperature to 105 C was to ensure the removal of any remaining moisture. The slow rate of cooling was necessary to avoid the development of thermal stresses and the formation of tensile cracks.

All specimens, saturated moist and oven dried, were divided into 4 parts, one part from each alloted to one of the four thermal baths of crude oil at temperatures of 20, 45, 60 and 80 C. The arrangement in

each bath, as would be seen in the next chapter, was such that oven dried specimens were soaked separately from the moist specimens, themselves soaked in two smaller tanks, one for each mode of curing (seawater or 100% RH). Similarly prepared moist concrete specimens were soaked in water at the 4 test temperatures, while the oven dry specimens were reheated at the 3 elevated temperatures to serve as controls.

The three thermal baths at elevated temperatures were heated to temperature at the rate of 5 deg.C/hour. All specimens were maintained in these conditions until tested, after which they were removed from the tanks but maintained in the hot oil or water at temperature. They were then cooled to ambient at about 5 deg.C/hr in an insulated chamber. All specimens were weighed and their densities calculated.

The trowelled surface of all specimens were machine ground and grease lubricated at the platen ends, prior to compression testing. These method of testing is justified in Chapter 5.

3.8.1.1 Tests to assess effect of end lubrication of specimens.

A total of 12 concrete specimens (6 cylinders and 6-100mm cubes) were used in this test. All specimens were from the same batch of concrete cured in water and serving as controls. A sample of crude oil (viscosity 4.5 cSt. at 38 deg.C) and a sample of Shell Unedo grease-2 (viscosity 55.5 cSt. at 40 deg.C) were used as lubricants for the specimen ends. Three specimens were tested for each parameter. The lubricants were smeared thinly and uniformly in one continuous stroke over the specimen ends, care being taken to remove any excess grease. The specimens were then carefully placed between the platens and tested in compression.

3.8.2 Length Change

A total of 180 mortar prisms were prepared, of which 56 were oven dried as already described. The mortar specimens were soaked in crude oil and water along with concrete specimens tested for strength, separately for each moisture condition and mode of curing. The process of cooling to ambient prior to testing has been described.

3.8.3 Penetration Tests

The concrete cylindrical specimens utilised in measuring crude oil penetration were oven dried at 105 C and were prepared as follows :

- they were weighed saturated
- they were turned in a lathe and the laitance removed with coarse emery paper
- the concrete specimens were oven dried at 105 C and weighed
- all specimens were coated with 3 coats of'epoxy plus primer' of mix 5:1 (resin hardener), after which the specimens were again weighed. Each coat was allowed to dry for 24 hours in the oven at 105 C. The specimens were then fitted into the penetration caps. Jubilee clips provided the pressure required to seal the caps on to the specimens. These procedure ensured that oil seepage along the surface of the specimens was prevented.

The oil flowing through the specimens was sampled using porous plugs manufactured from felt, placed in holes drilled at 10mm intervals along the length of the concrete and staggered around its circumference. The plugs (4mm dia) which were inserted to depths of 25mm, were removed on saturation and analysed using the NMR technique. The time period over which saturation occured was recorded. Tests were concluded for each specimen when it was totally saturated. Finally,the specimens were weighed and the out-flows analysed for physical and chemical properties. Details of the technique and the method of running the nmr spectra are given in Appendix C.

CHAPTER IV

DESCRIPTION OF APPARATUS

4.1 INTRODUCTION

Standard equipment and other apparatus were purpose built at Imperial College for the test programme. These consist of two main systems; the **Thermal baths** and the **Closed Loop Inert Facility (CLIF)**, shown in Figures (4.1) and (4.2) respectively.

Three thermal baths were constructed and contained water at the 3 higher temperatures. Within each bath, three containers held crude oil for storage of concrete and mortar specimens. The CLIF rig, a schematic diagram of which is shown in Fig.(4.3), incorporated in a closed circuit a heated crude oil supply tank, penetration test rigs and a length change device which could monitor length change of mortar bars insitu. In the thermal baths, however, specimens had to be removed and cooled to ambient temperature before measurement of mechanical properties were carried out.

4.2 CRITERIA FOR DESIGN

The criteria for the design of each system were as follows:

(a) Thermal Bath

It was necessary that the system should have a controlled rate of heating, to avoid thermal shock. It should also be capable of maintaining the required temperatures throughout the period of the tests. Temperature overshoot and thermal cycling must be avoided or at least minimised to within acceptable limits. The containers holding the test specimens should be temperature resistant and chemically

inert to crude oil and its constituents. The temperature of the crude oil and water, as well as of the surface of the immersed specimens should be monitored continuously.

(b) Closed Loop Inert Facility (CLIF)

The specifications for the thermal baths were also required for the CLIF rig. To maintain the closed loop system, it was essential that it operated free of leaks by the use of appropriate seals. The construction material needed to be chemically inert to crude oil, hydrogen sulphide and acids which may be contained in the oil or included in the test. In addition, the material must be capable of withstanding temperatures of up to 80 C at high pressure.

4.3 DESCRIPTION OF APPARATUS

4.3.1 Thermal Bath

A thermal bath showing the dimensions of the inner tanks can be seen in Fig.(4.1). All 3 baths were constructed from fibre glass and were filled with water. Each contained three smaller tanks of the same material in which the specimens were stored in crude oil. The water in the main tank was heated by a 3kW supply heater and the crude oil and specimens indirectly by conduction through the tank walls.

The rate of heating was maintained by temperature control units which regulated the flow of power supply to the heating elements on the basis of the difference between set temperature and actual bath temperature. Each bath was heated at the rate of 5 deg.C/hour and a pump circulated the heated water around the bath, in order to maintain uniform temperatures. Heat loss from each bath was minimised by insulating the body of the main tank with expanded polystyrene. This was structurally protected by a purpose built hardwood box.

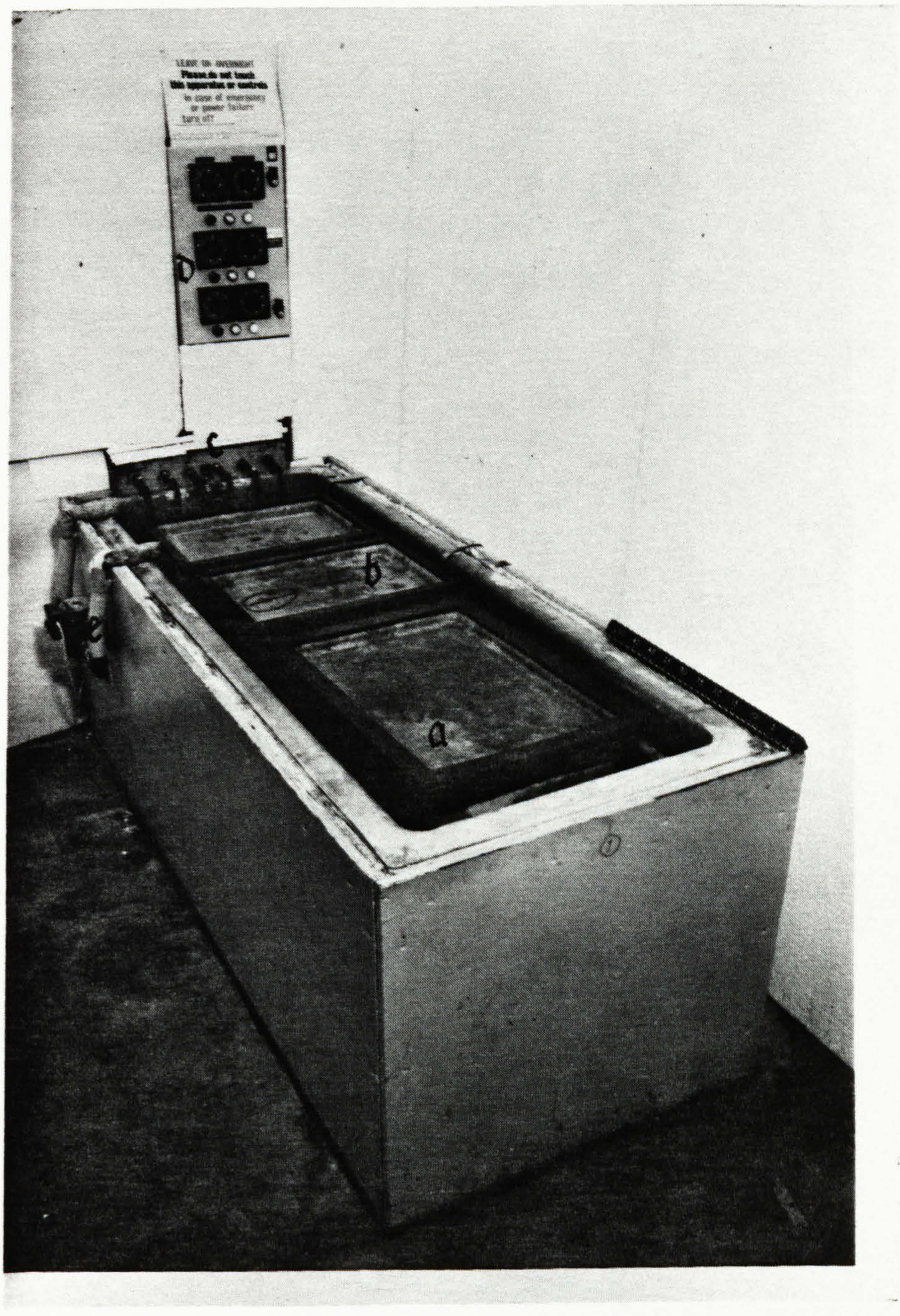


Figure 4.1: Thermal bath

(a) medium size GRP tank (61x41x38cms)

(b) small size GRP tank (46x31x31cms)

(c) heater (d) controllers (e) pump.

Each of the smaller inner tanks as well as the main tank, were covered with glass fibre lids, and the whole arrangement was covered by a wooden lid which had been insulated with expanded polystyrene. The rate of loss of heat under controlled cooling was measured as 1 deg.C/ hour. Temperatures of the water baths, the crude oil and test specimens in the smaller tanks, were monitored by chrome-alumel type K thermocouple wires connected to an Orion Data logger. The emf from the thermocouples were processed and displayed on a visual unit. A print out of all data was also obtained at four hourly intervals.

(a) Main Frame

The nominal capacity of the main thermal bath was 682 litres. Two small size GRP tanks each with a capacity of 45 litres and a medium size GRP tank with a capacity of 90 litres, were weighted down in the main tank by concrete prisms (Fig.4.1).

(b) Heaters

Each thermal bath was heated with a type HT-9, 3-phase Hedin Vat immersion heater with a total output of 9kW, although only 3kW power was used in heating the bath. The heater consisted of heavy duty tubular rod elements, formed to shape and fitted into a moisture resistant box. They were manufactured in incloy sheath material, with the heated section lying vertically. These were specially constructed with long cold vertical stems, to ensure that the heated section was positioned below the normal water level. The heaters were switched-off by means of an electrical relay, triggered-off once the water level dropped below the cold joint of the heaters.

(c) Controllers

The heaters were controlled by Honeywell controllers class CL, using type K thermocouples as sensors. The controller regulated the flow of power supply to the heating elements on the basis of the difference between set temperature and actual bath temperature. A second similar controller served as an upper temperature limit, above which the heaters were automatically switched-off.

The controllers had a selectable proportional band with a powerful overheat inhibitor and a clear process variable indication in red and green colours. They had an indication accuracy of 1% of span at set points and a scale of 0-100 C for the regulator, and 0-250 C for the upper limit control. The upper limits were set 5 C above operating temperature.

(d) Pumps

The temperature all around the water bath was uniformly maintained by pumping the heated water around the bath with a Grundfos hot water service pump, model super 4-12 DW, supplied by Grunfos Pump Ltd. The pump consists of an enclosed stainless steel chamber, which ensured contamination free supply. The ceramic pump shaft and bearing gave longer durability and ensured that it operated quietly at 1400 revs/m.

(e) Thermocouples

All thermocouples were twisted pairs, water resistant, single strand, chrome-alumel type K with PTFE sheathing, capable of withstanding temperatures of up to 250 C in continuous use. They were supplied by Lab Facility Ltd.

The thermocouples used in the thermal baths were connected to junction boxes, from which point they were connected to the data logger by compensating wire. Four thermocouple wires were used in each bath.

4.3.2 Closed Loop Inert Facility (CLIF)

This was designed and built for the purpose of circulating crude oil at constant levels of elevated temperatures of about 20 to 80 C. Flow was through a closed loop system, from a heated storage tank to a set of penetration rigs and an insitu length change device. Circulation of the oil was by means of a specially purchased pump.

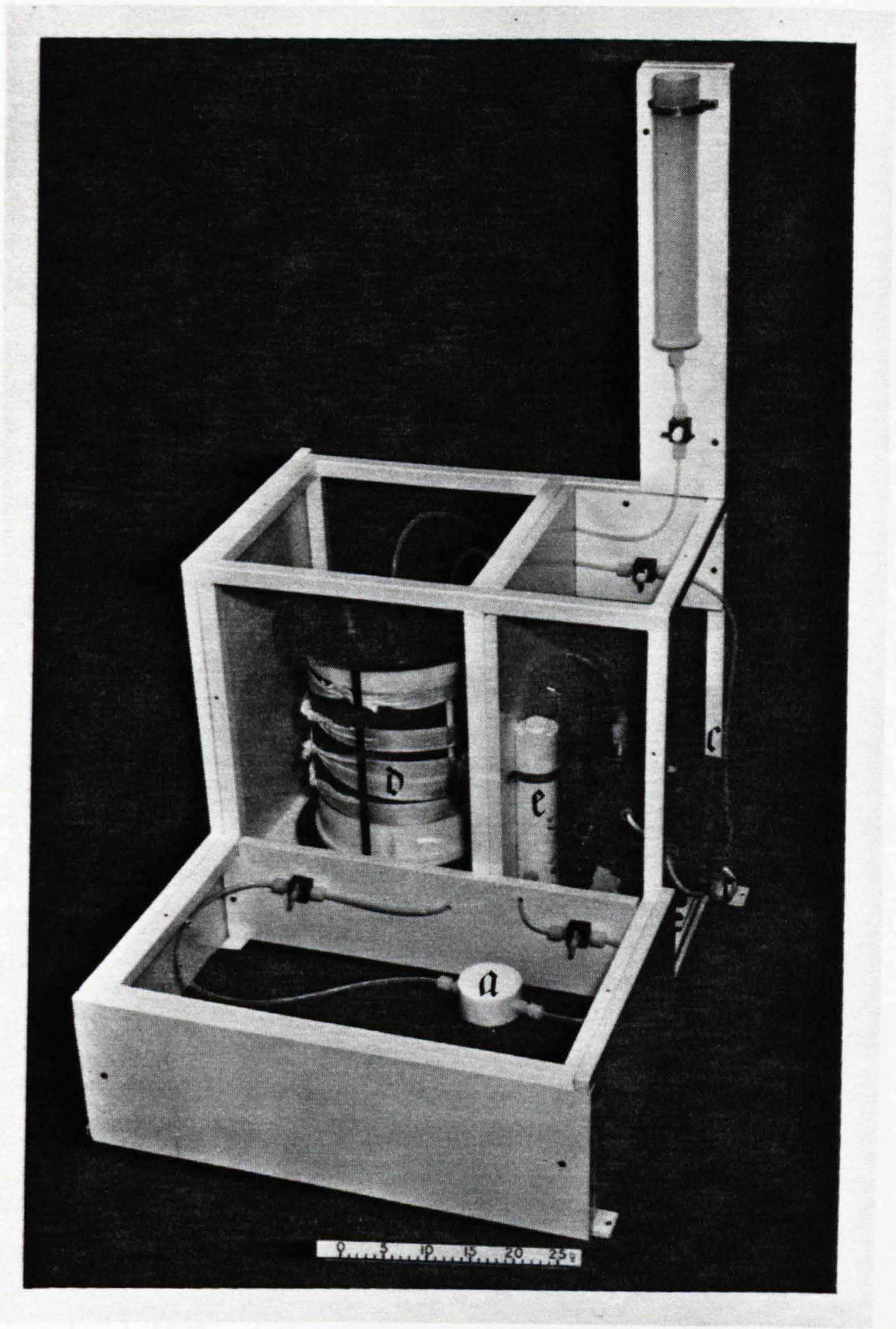


FIGURE 4.2: **CLIF apparatus**

(a) one unit of penetration rig
(b) oil storage/heating tank
(c) pump with PTFE lining
(d) heat blanket (e) sump.

The entire inner surface of the loop, including pump, filter and other ancilliary equipment, were manufactured from either polytetrafloro-ethylene (PTFE) or perfloroalkoxyl (Teflon PFA). These materials were selected as they are inert to crude oil and most other corossive substances, acids and hydrogen sulphide gas included. Tests performed on these materials at Imperial College indicated that when soaked in crude oil at 80 C over a period of two months, no changes in weight, colouration, appearance or tensile strength could be observed.

The CLIF rig consisted of three main units in addition to the pump and other peripheral items. These were the penetration rigs, insitu length change device and the oil storage heating tank.

(a) Penetration rigs

There were 4 units of these, with facilities for more when required. Each unit comprised a pressure 'cap' machined from a PTFE cylinder, through which hot crude oil was circulated under pressure of about 10 N/m^2 (I bar). The inlet and outlet fittings were of Teflon PFA. The outlet port was located at the bottom of the cap to prevent accumulation of any water which may have found its way into the system. A jubilee clip provided the pressure required to seal the cap unto the fitted concrete specimen. One such arrangement (Figure 4.4) tested to 20 psi using a high pressure air line showed no leaks or any other form of weakness.

(b) Insitu length change rig

The CLIF rig was able to measure length change insitu. However, it was not used for this purpose for a number of reasons:

- about 180 mortar prisms had been tested for length variations in crude oil at 4 temperatures, although measurements were not insitu and specimens had to be cooled to ambient temperature prior to testing.
- due to the high cost of the materials and the limited resources for this investigation , only one unit of the length change device was constructed. This was inadequate for the number of tests required and range of parameters tested.

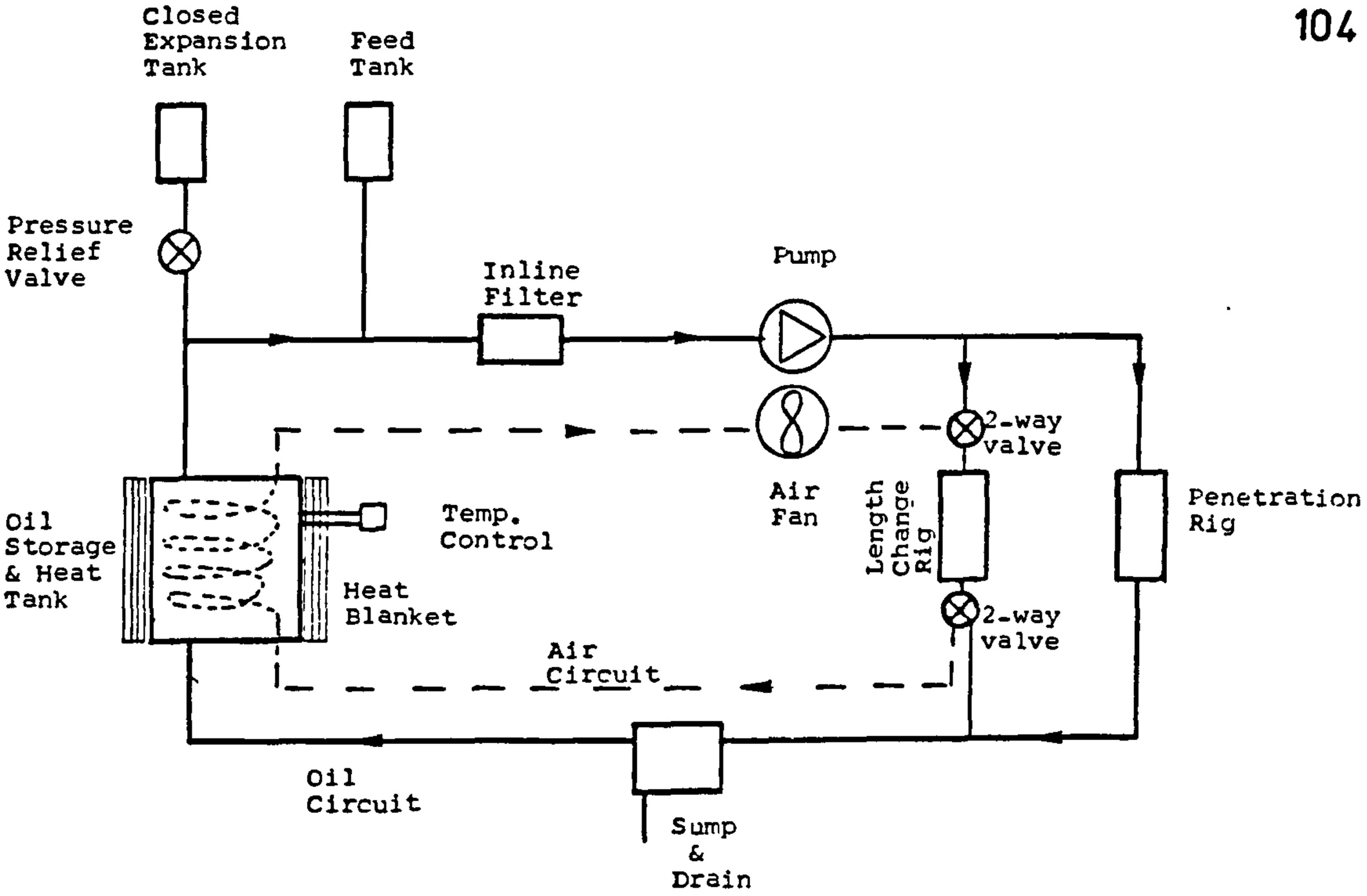
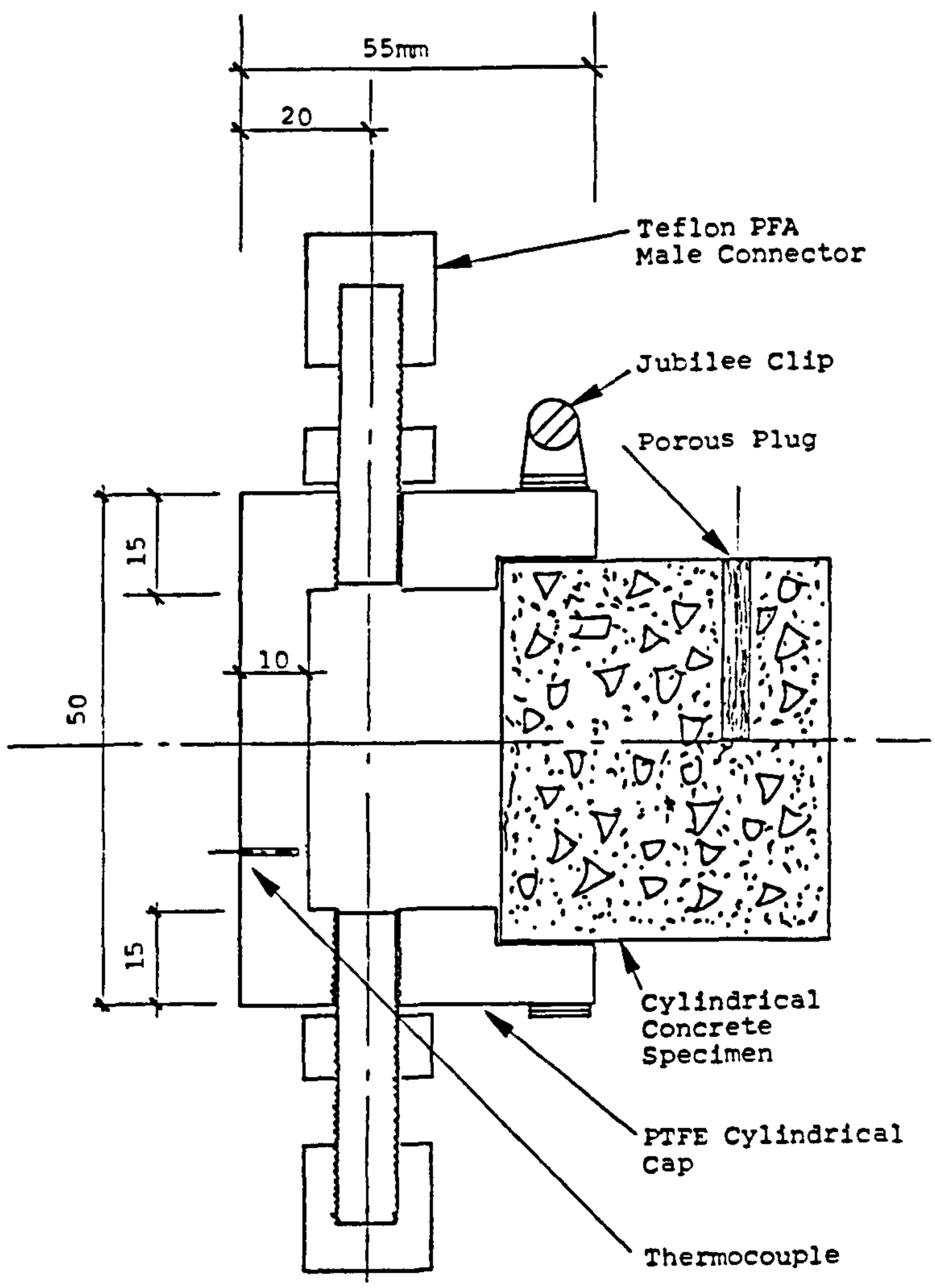


FIGURE 4.3: SCHEMATIC DIAGRAM OF CLOSED LOOP INERT FACILITY.

FIGURE 4.4:

PENETRATION RIG.



(c) Oil storage/ Heating tank

The tank consisted of an extruded hollow PTFE cylinder (245mm OD, 205mm. ID) with PTFE end caps. The seal between the caps and the cylinder was achieved by machining a ridge on the caps and a groove into the cylinder. Pressure was applied to the end caps by two mild steel end-flanges with four tie rods. All inlet and outlet ports were Teflon PFA male connectors.

The oil in the tank was heated by means of a heat blanket wrapped around the cylinder. Temperature was regulated by a controller on the basis of the difference between set temperature and the temperature of the crude oil. The heat/storage tank is shown in Figure (4.5).

(d) Ancilliary equipment

Pump, designed specially for circulating corossive or sterile liquids, with PTFE lining. The pump is suitable for use at temperatures of up to 150 C.

Heat Blanket : electro thermal flexible rubber mat heater suitable for use at up to 200 C.

Pressure Relief Valve: series PRV designed to open at a set pressure and then reset at approximately 75 per cent of the original setting.

Sump, Feed and Expansion tanks were manufactured from PTFE extruded tubing. The expansion tank was closed to prevent escape of toxic gases

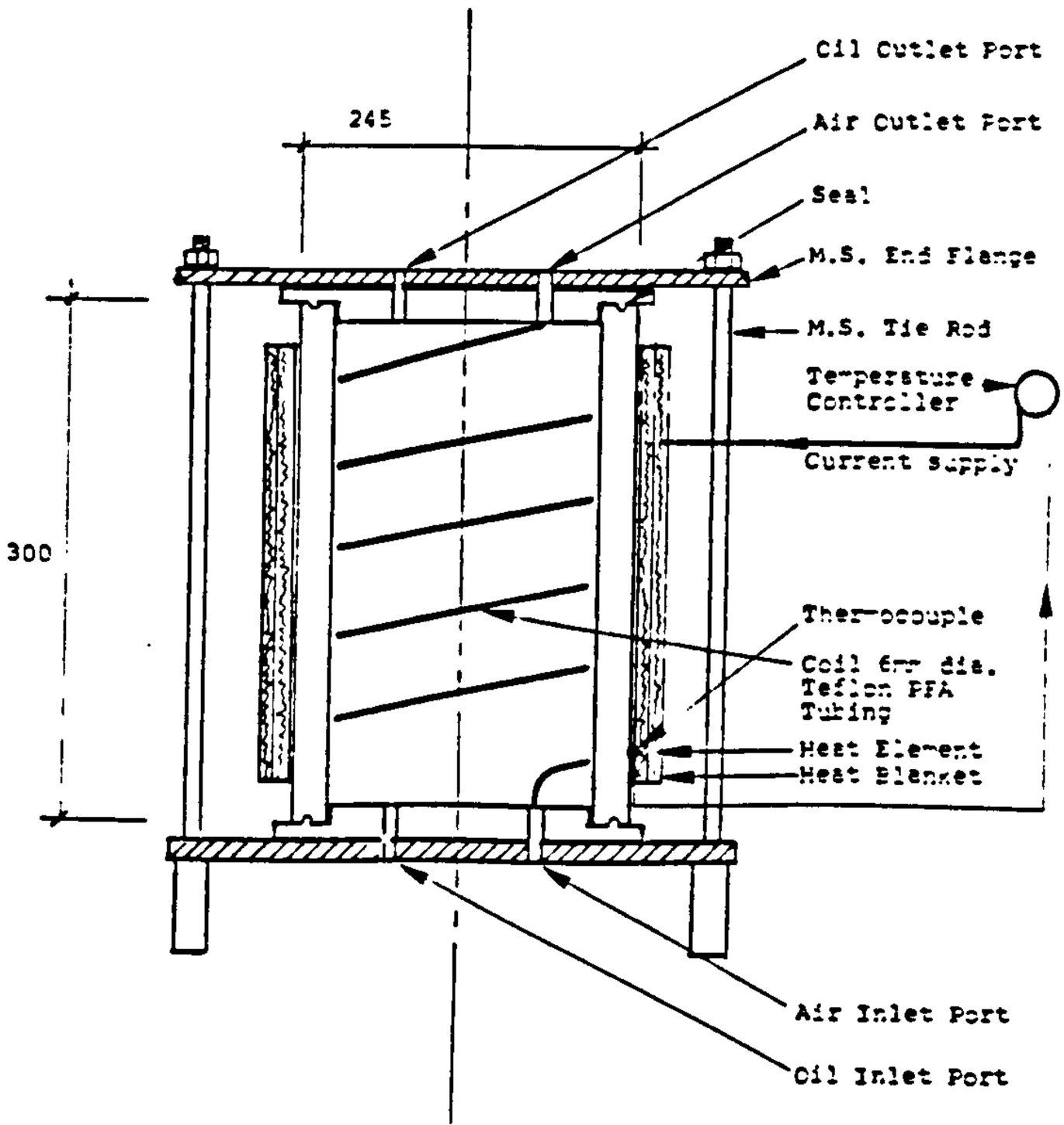


FIGURE 4.5 :

HEAT/STORAGE TANK.

4.4 DESCRIPTION OF OTHER ITEMS OF EQUIPMENT

Several other items of equipment were used in this programme, the more important are described below:

4.4.1 Data Logging Facility

A 3530 Orion data logging system incorporating a clock mechanism and capable of measuring up to 200 channels which can be allocated to 8 tasks, was used to measure signals from the thermocouples. The type of measurement to be taken through each channel was specified and the logger was activated when the task was defined and triggered. The output, displayed on the logger monitor was also obtained as a printout. One of its advantages was the ability to convert signals from thermocouples directly into temperature, through an in-built calibration and cold junction.

4.4.2 Compression Testing Machine

The compressive strength of all test specimens (100mm cubes,and 63.5mm dia. concrete cylinders) were obtained by measuring the failure loads on the compression testing machine, model GD10, obtained from Contest Instrument Ltd. The hydraulic machine had an easily controlled rate of loading.

4.4.3 Length Comparator

The length comparator used in measuring length changes of the mortar specimens (25 x 25 x 285mm) is schematically shown in Fig.(4.6). The device incorporated a dial indicator mounted on a cross bar, which was itself supported by two columns mounted on a rigid stable base. The comparator was made of invar. The indicator conforms to ASTM standards /10/ and has a high grade dial micrometer graduated to read 0.002mm units, accurate within 0.002mm in any 0.02mm range. Its range of 5mm was enough to accomodate variations in the length of test specimens. The device was checked after each set of readings against a reference bar made from invar and marked at one end. This end was placed in the instrument in the same position at all times. The terminals of the

instrument were heat treated, polished and fitted with collars. Each collar was held in place with a set screw. The instrument was obtained on a special order from Wykeham Farrance.

Accuracy of micrometer

1 unit on micrometer = 0.002mm

Initial length of specimen = 285mm

1 unit of length change on micrometer = $\frac{2\times10^{-3}}{285}$ mm/mm

= 7.0175 mm/mm

approx. **7 microstrains**

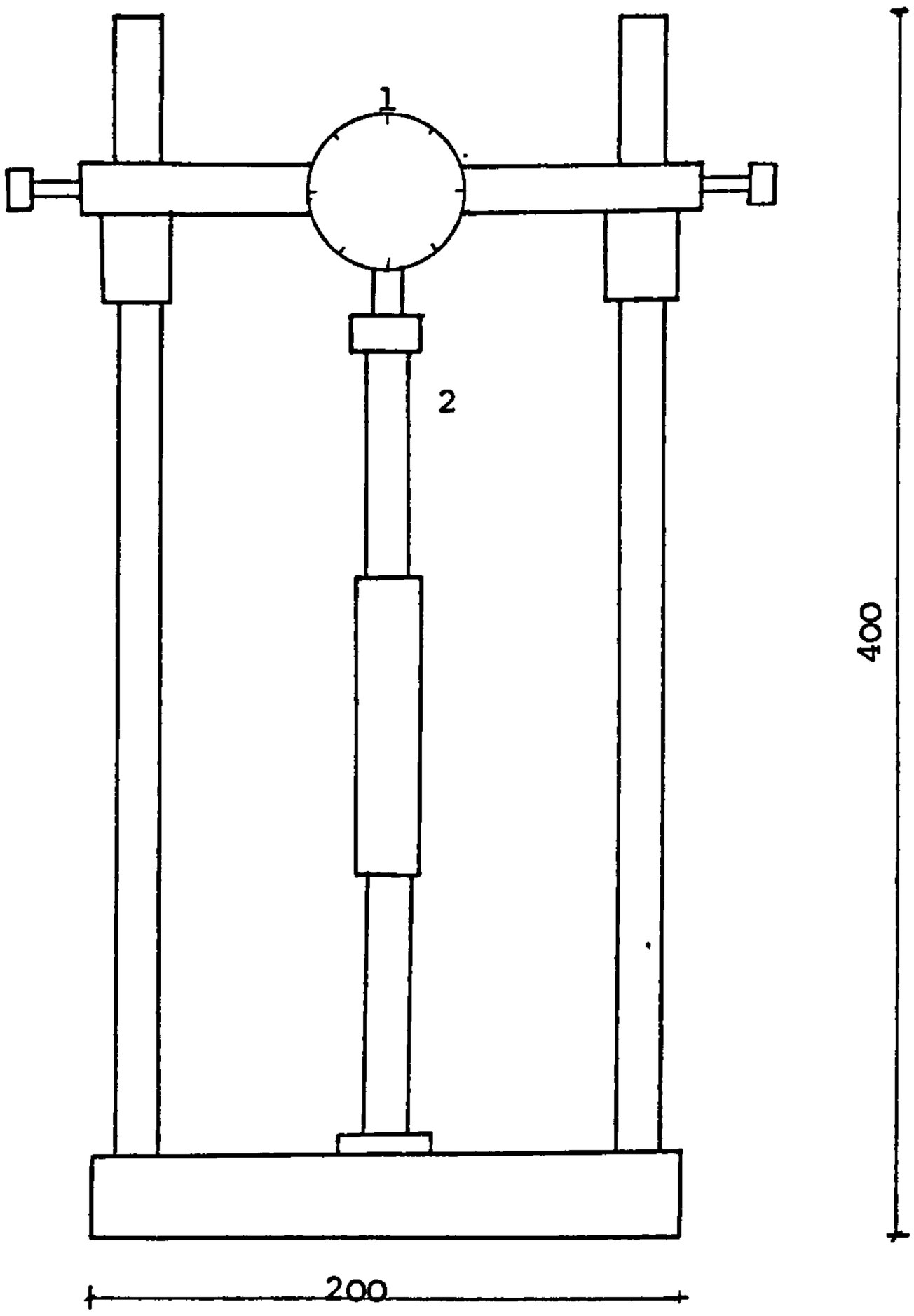


FIGURE 4.6 : Schematic view of the Length Comparator showing (1) dial gauge (2) Invar reference bar.

CHAPTER V

MATERIALS' PROPERTIES PRIOR TO EXPOSURE TO CRUDE OIL

5.1 INTRODUCTION

The compressive strength and length change of specimens were monitored throughout the 365 days of curing in seawater and at 100% RH. At the end of this, some of the specimens were oven dried at 105 C and the above properties were again measured. The results of this study are given and discussed in this chapter. Also presented are the results of tests to study 'apparent effects' on the measured compressive strength, as a result of end-lubrication of the concrete specimens. Finally, details are given of the surface properties of test specimens prior to exposure to crude oil.

The concrete cylinder specimens were used in the measurement of compressive strength and, the mortar bar specimens in the measurement of length change. In both cases, two mixes were used; 100% opc and 70:30 opc/pfa.

5.2 DEVELOPMENT OF COMPRESSIVE STRENGTH IN CONCRETES

5.2.1 INTRODUCTION

The development of compressive strengths in the two concrete mixes were monitored at about 20 C in seawater, and at 100% RH. Similarly prepared cylindrical test specimens and 100mm concrete cubes were cured in freshwater and were used as controls. In all cases, a minimum of 3 specimens were tested for each measurement. Results of the slump of each casting and the as-cast densities of 6 cubes specimens per casting have been given in Chapter 3.

5.2.2 COMPRESSIVE STRENGTH RESULTS DURING CURING

5.2.2.1 28-days cube compressive strength

Three specimens from each casting were tested for 28-day cube compressive strength after the densities had been measured. A total average compressive strength was determined for each of the OPC and PFA concrete mixes from the means obtained from all castings. These were 72.5N/mm2 for the OPC and 56.1 N/mm2 for the PFA, with standard deviations of 2.9 and 1.8 N/mm2 respectively (Table 5.1). The average for the OPC concrete specimens was in agreement with the 72.0 N/mm2 recommended by the CIO /53/. There is no parallel comparison for the PFA specimens since a different opc/pfa ratio was used (see Chapter 3).

5.2.2.2 Control specimens

The development of compressive strength of the control water cured OPC and PFA specimens throughout the duration of curing, is shown in Fig. (5.1). As expected, the PFA specimens had a lower 28-day strength compared to the OPC specimens due to the delayed pozzolanic reaction

in the former at the early age /37/. However, both had achieved similar strengths by the end of the period of curing of 365 days. The difference of about 1 percent between the two at this age, was not significant. The PFA specimens had gained strength more rapidly after 28 days, at a rate which was more than double that for the OPC specimens. The difference between the two had reduced continuously with time. This result can be attributed to the onset of pozzolanic reactions in the PFA specimens from about 28 days.

Comparison of the 28-day compressive strengths of the concrete cube and cylinder specimens given in Table (5.2) showed that similar magnitudes were achieved. The cylinder/cube strength ratio had indicated that the difference between the two, for both the OPC and PFA specimens, was only 1% which is insignificant. This justifies the use of cylinder specimens of a height/diameter ratio of 1, which were able to contain the 20mm size aggregates and as expected, had similar absolute strengths with the 100mm concrete cube specimens.

5.2.2.3 Concrete specimens cured at 100 percent RH

The trend in the development of compressive strength in concrete specimens cured at 100% RH is shown in Fig.(5.2) and is similar to those for the control specimens cured in freshwater (Fig.5.1). Direct comparison of compressive strengths of specimens under the two curing conditions indicated that similar values were achieved at all ages, as can be seen in Figs.(5.4) and (5.5), for the OPC and PFA specimens respectively. In both cases, the rate of gain of strength after 28 days for the PFA specimens was double that for the OPC specimens.

5.2.2.4 Concrete specimens cured in seawater

The concrete specimens cured in seawater were initially cured at 100% RH for 14 days, by which time it was expected that the capillary pore system would have become discontinuous.

The development of compressive strength in concrete specimens cured in seawater is shown in Fig.(5.3). Again, as has been observed under the two previous curing conditions, both the OPC and PFA specimens had achieved similar strengths by the end of the period of curing. Infact, similar strengths had been achieved by 180 days, when the difference between the two was only 1 per cent. However, it seems that the rate of strength increase of the PFA specimens in relation to the OPC, was higher in seawater than in any of the other curing conditions, as the comparisons in Table (5.3) indicate. This showed that in seawater, the rate of gain of strength of the PFA specimens from after 28 days, was about four times that for the OPC specimens. The difference, in water and at 100% RH, was by a factor of two. This development in seawater can be attributed to the greater resistance of the PFA specimens to seawater attack because they contained less lime, as compared to the OPC specimens. This is further discussed in section (5.2.3).

Furthermore, comparison of strength in specimens cured in seawater with those cured in fresh water or at 100% RH (Table 5.3), indicated that strengths in the former were consistently lower than in the latter at all ages, for both the OPC and PFA specimens. The result also showed that the rate of gain of strength of the OPC specimens was lower in seawater than in freshwater or 100% RH. However the rate of strength gain was comparable for the PFA specimens under all the curing conditions. This is confirmed by results of statistical analysis (Table 5.5), which showed that while the difference in strength of OPC specimens cured in seawater and at 100% RH was highly significant over the entire period of curing, the difference was not significant for the PFA specimens. This confirms that the relatively lime rich OPC specimens were more seriously attacked than the PFA specimens which probably had less lime content.

TABLE 5.1 : 28-day cube compressive strengths

	Mix I (OPC)	Mix II (PFA)
no. of samples	48	48
range of 28d comp. strength (N/mm2)	68.7 - 75.8	54.2 - 59.9
average	72.5	56.1
std. deviation	2.9	1.8
CIO recommendation	72.0	-

TABLE 5.2 : Comparison of 28-day compressive strengths of 100mm concrete cubes and the cylinder specimens

	compressive strength (N/mm2)		cylinder/cube strength ratio
	cube	cylinder	
Mix I (OPC)	72.5	73.5	1.01
Mix II(PFA)	56.1	56.4	1.01

TABLE 5.3 : Comparison of compressive strengths of concrete specimens cured in water, 100% RH and in seawater

mode of curing	age (days)	compressive strength (N/mm2)		change from water cured	
		OPC	PFA	OPC	PFA
water cured	28	73.5 (0%)	56.4 (0%)		
	90	82.3 (12%)	71.6 (27%)		
	180	86.7 (18%)	81.2 (44%)		
	365	91.1 (24%)	89.8 (59%)		
100% RH cured	28	74.6 (0%)	57.4 (0%)	+1.5%	+2%
	90	83.5 (12%)	72.6 (27%)	+1.5%	+1%
	180	88.5 (19%)	80.5 (40%)	+2%	-1%
	365	90.8 (22%)	86.3 (50%)	0%	-4%
seawater cured	28	67.6 (0%)	53.0 (0%)	-8%	-6%
	90	72.2 (7%)	67.3 (27%)	-12%	-6%
	180	76.5 (13%)	75.4 (42%)	-12%	-7%
	365	80.1 (19%)	76.7 (45%)	-12%	-15%

FIGURE 5.1 :
Development of compressive strength of control specimens cured in freshwater

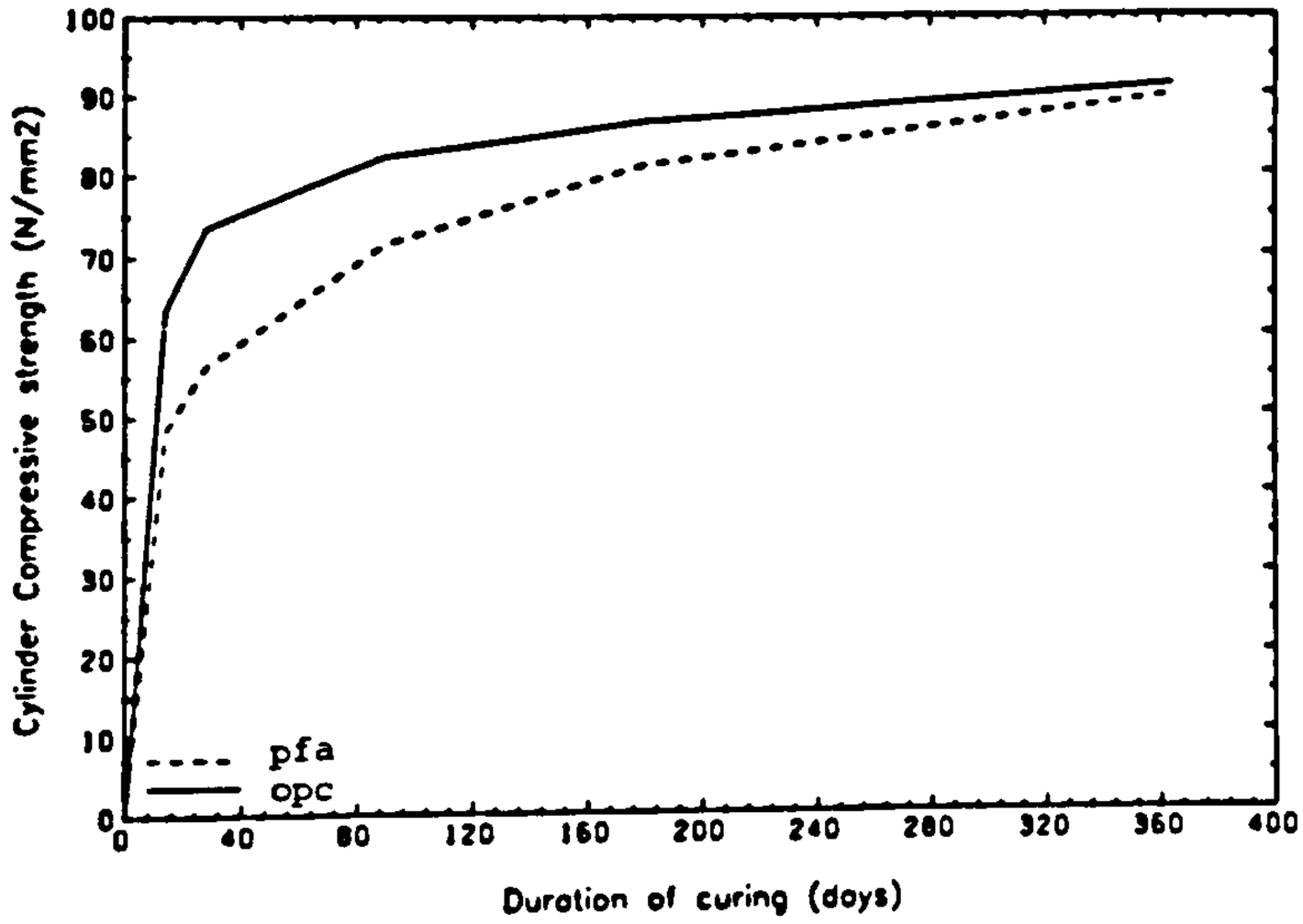


FIGURE 5.2:
Development of compressive strength of concrete specimens cured at 100 percentRH

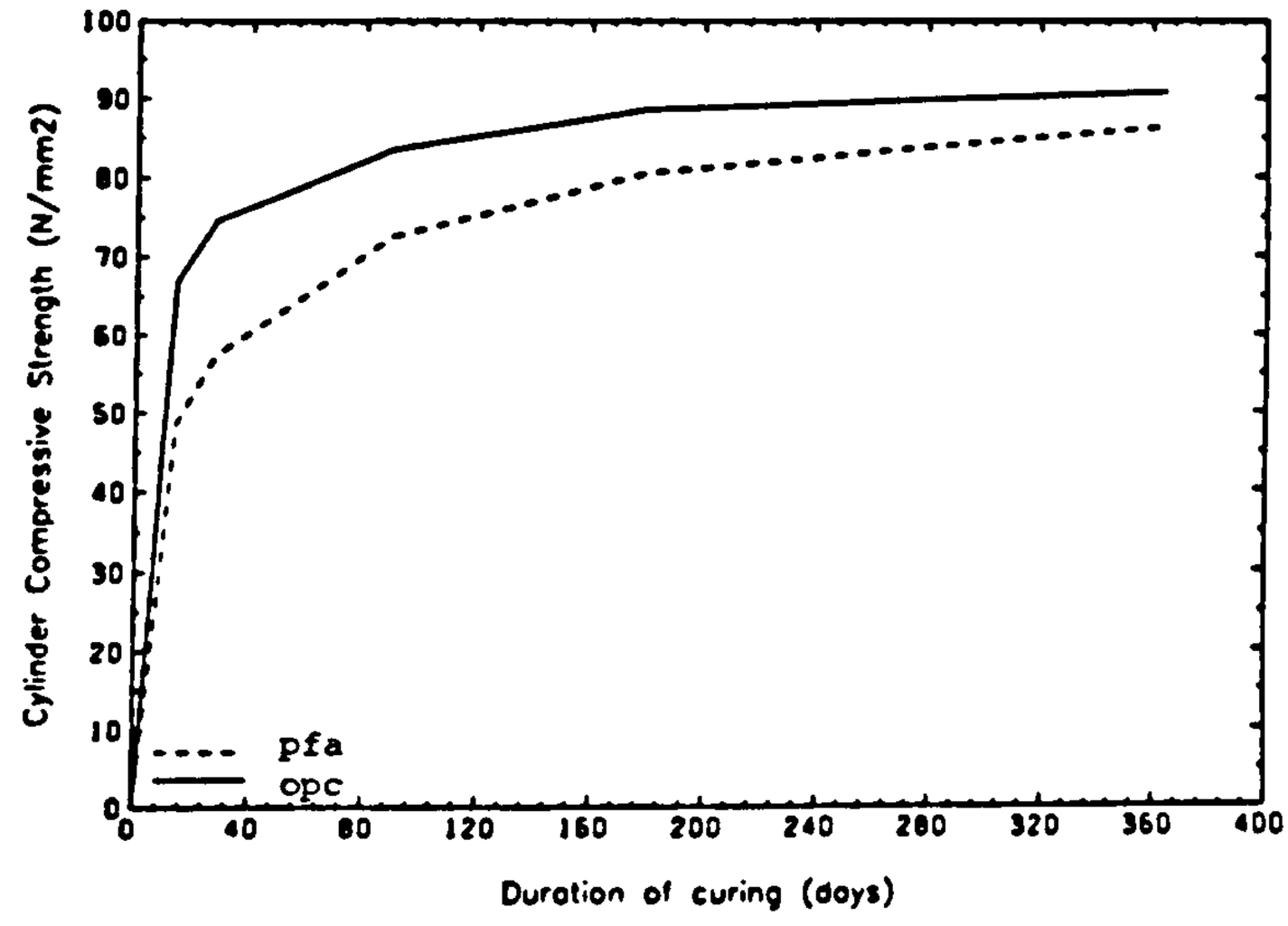


FIGURE 5.3:
Development of compressive strength of concrete specimens cured in seawater

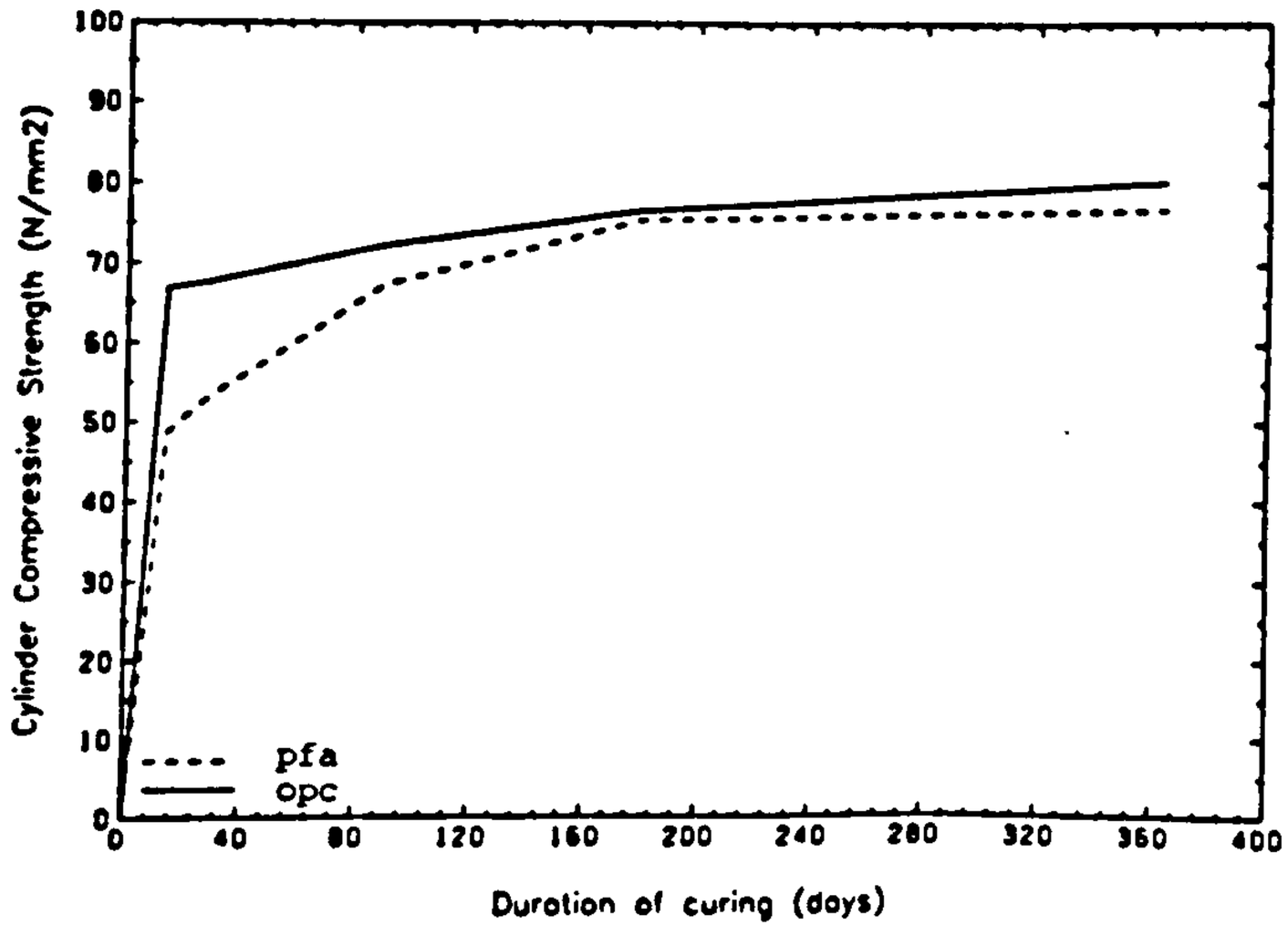


FIGURE 5.4: Comporison of compressive strengths of OPC concrete specimens

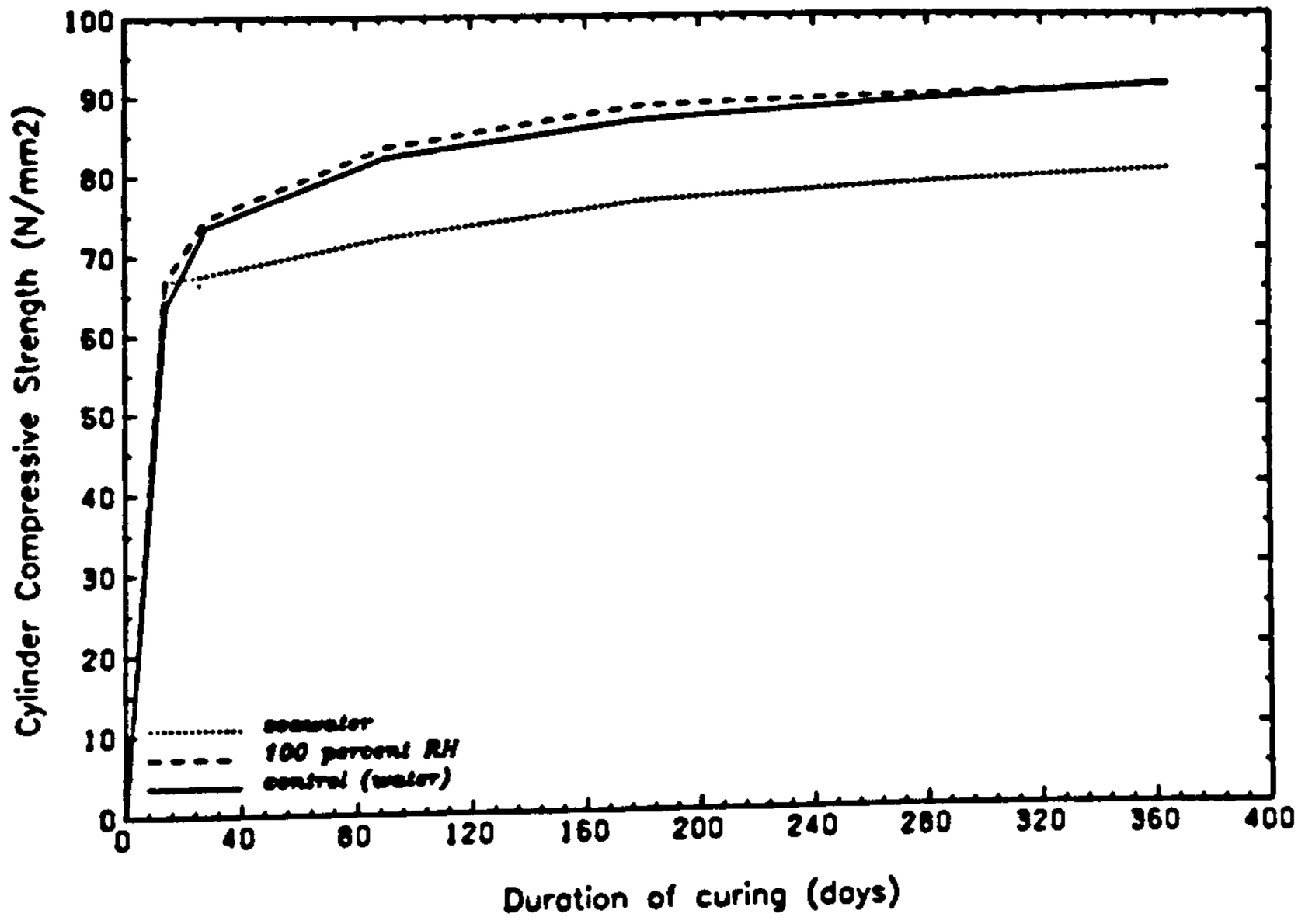
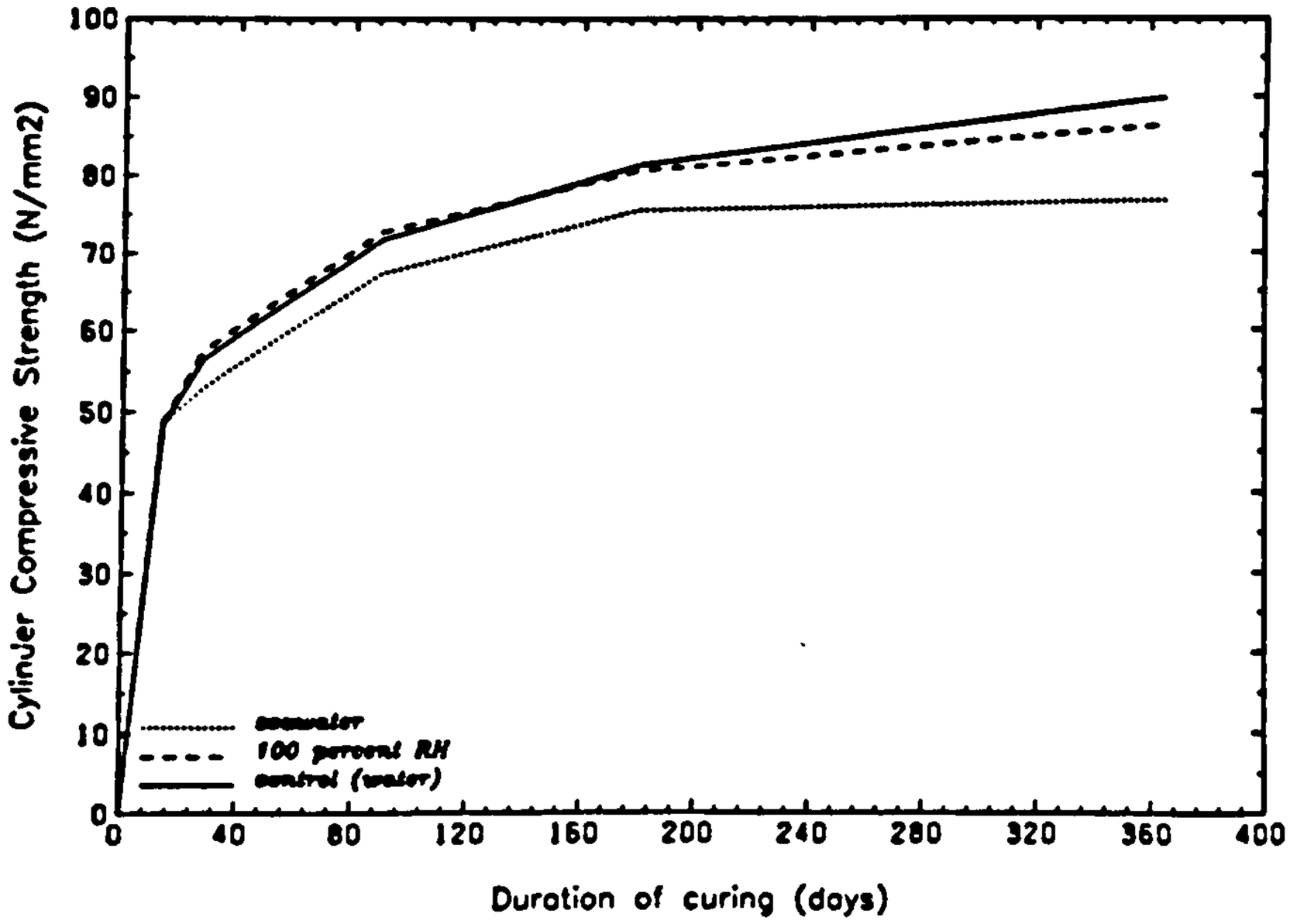


FIGURE 5.5: Comporison of compressive strengths of PFA concrete specimens



5.2.2.5 Compressive strength of oven-dried concrete specimens

Results of the compressive strength of concrete specimens which were oven dried at 105 C, after curing in seawater or at 100% RH, are given in Table (5.4). They indicate a general increase in strength of 5-6%, for all specimens, irrespective of cement blend or method of curing. This suggests that oven drying at 105 C had the same effects on all the concrete specimens.

TABLE 5.4 : Cylinder compressive strengths of concrete specimens after curing and oven drying.

curing regime	type	compressive strength (N/mm2)	
		moist	oven dried (105 C)
100% RH	OPC	90.8 (100%)	95.0 (105%)
	PFA	86.3 (100%)	90.3 (105%)
sea water	OPC	80.1 (100%)	84.5 (105%)
	PFA	76.7 (100%)	81.6 (106%)

TABLE 5.5 : t-Test of significance to compare compressive strengths of specimens cured in seawater with those cured at 100% RH.

Test	no. of samples	mean m	std. dev. s	DOF	t-value	prob. p	remark
100% RH vs.	14	83.2	7.6	27	2.96	<0.01	highly
seawater (OPC)	15	74.9	7.3				signif.
100% RH vs.	14	72.6	11.5	26	1.37	>0.10	not
seawater (PFA)	14	66.9	10.3				signif.

5.2.3 DISCUSSION OF RESULTS

5.2.3.1 Curing at 100 percent RH

The development of strength in concrete specimens cured at 100% RH is a chemical/physical process, uninfluenced chemically by the environment. The process of hydration in the cement paste leads to the formation of the C-S-H gel. The strength of the hardened cement paste (HCP) is determined by the intrinsic strength of the gel and its concentration within the paste. Gel formation is a function of the water/cement ratio and the degree of hydration. Low water/cement ratio and a long period of wet curing, help to increase concentration of the gel and therefore contribute to higher strength. As is well known, strength increases as the porosity of the paste decreases.

The partial replacement of portland cement (opc) with pulverised fuel ash (pfa), enhances the long term strength of concrete in that it increases the concentration of the gel. The mechanism by which this occur is seated in the pozzolanic reaction which converts $Ca(OH)_2$ to the strength bearing C-S-H gel, leading to further strength increases. Owen and Butler /142/ had reported increases in the compressive strength of concrete as the fly ash content increased. They seemed to have found that the greatest amount of $Ca(OH)_2$ was used up in the pozzolanic reactions involving specimens containing about 30% pfa. It was concluded that this amount of lime must be the optimum used up to form more gel. Consequently, it was assumed that the greatest increase in strength should occur with this amount of pfa. However, it is known that concretes containing high fly ash contents of up to 50%, give very high strength if appropriately designed.

For the same water/blend ratio, concretes containing pfa as opc replacement had lower average 28-day compressive strength than those made completely from opc. This is due to the slowness of the pozzolanic reaction, which is secondary to the hydration of the clinker compounds, in particular the C_2S and C_3S /37/, and occurs therefore at a slower rate. In fact, it has been reported that this reaction does not begin until about 11 days after mixing /142/. However, once it starts, the rate of gain of strength becomes rapid /141/. This can explain the lower strength of the PFA specimens up to about 28 days,

under all curing conditions, as compared with the OPC specimens. The onset of pozzolanic reactions after about 28 days, had caused the accelerated rate of gain of strength observed in the PFA specimens.

The difference in strength of about 5% between the OPC and PFA specimens at 365 days was not considered as significant, given that variations of larger amounts are usually observed in measurements of concrete strength. This result is however in agreement with that obtained for the control specimens cured in fresh water in which the difference between the OPC and PFA specimens was about 1 per cent. Both results indicated that similar compressive strengths had been achieved by the OPC and PFA specimens by 365 days of curing. However, it seemed that the PFA specimens were still gaining in strength and ultimate strength may be higher than in the OPC specimens.

The mechanism observed for the specimens cured at 100% RH would,to a large extent, also apply to specimens cured in ponded water. This is confirmed by the similarity of results obtained under both conditions of curing. However, it was thought that curing under ponded conditions could result in the leaching of lime. On this basis, all the test specimens were cured at 100% RH. The loss of lime may not in itself affect the intrinsic strength of the OPC concrete specimens, however, the early loss of lime may disrupt the pozzolanic reactions in the PFA specimens and lead to lower ultimate strength. This does not seem to have occurred as similar results were obtained under both curing conditions.

5.2.3.2 Curing in Seawater

Curing in seawater had resulted in lower compressive strengths for both the OPC and PFA specimens, relative to specimens cured in water and, at 100% RH. The strength losses that have been observed can be attributed to the attack on the cement paste by the aggressive salts in sea water, in particular to the effects of carbon dioxide and the chloride and sulphate salts of magnesium (MgCl and $MgSO_4$). Details of the reactions involved can be found elsewhere /45, 124, 166/.

Calcium hydroxide is the most vulnerable of the products of hydration of cement paste from the standpoint of reactivity. It is attacked by both MgCl and $MgSO_4$ to form products soluble in seawater, the consequence of which is the depletion of calcium hydroxide in the HCP. This phenomenon causes a high degree of porosity in concrete and is associated with the weakening of the material and loss of strength /124/. Also attacked are the calcium silicate hydrate (C-S-H) and the aluminate phases of the paste.

Sulphate attack of free lime causes the formation of gypsum. The depletion of free lime is reflected in the loss of compressive strength. The sulphate also attacks calcium aluminate hydrates (C-A-H) manifesting itself in the formation of expansive ettringite. This causes cracks in the cement paste and leads to the degradation of concrete. The chloride ions react with the aluminates to form monochloroaluminates which cause less expansion than ettringite, but also transform the C-S-H fibers into a more porous reticular network, thereby causing loss of strength /166/. The presence of carbon dioxide in seawater and, this is often found when the pH is less than 7, results in the attack of $Ca(OH)_2$. This leads to the formation of calcium bicarbonate, the solubility of which causes the loss of free lime and increased porosity of the HCP. Thus, the two principal factors causing degradation and weakening of concrete in seawater are, the dissolution of lime which leaves the structure porous, and the formation of expansive ettringite. The lower compressive strengths of the seawater cured specimens, relative to specimens cured at 100% RH, are related to these factors.

Seawater attack on concretes containing pfa is less severe. This is because such concretes contain less amounts of reactive lime which had

been used up in the pozzolanic reactions. In addition, the gel concentration is increased due to this process and therefore, strength is increased. The lower lime contents in the PFA specimens would reduce the extent of attack by the sea salts, as compared to the effects on OPC specimens. This may explain why the rate of gain of strength in the former had not been impaired, unlike in the latter.

In general, portland pozzolan blends produce less free lime on hydration than pure portland cement and have been shown to exhibit better resistance to seawater attack. Several examples of concrete structures containing pozzolan and exhibiting resistance to seawater attack, have been reported by Mehta /124/.

CONJEAUD /45/ found compressive strength losses in mortar specimens immersed in seawater over a period of 3 years (Table 5.6) using different types of cements. However, a large scatter of result was obtained for all measurements. **GJORV** /69/ also found long term loss in the compressive strengths of mortar and cement paste specimens immersed in seawater.

Conjeaud /45/ considered that calcium chloroaluminate plays a more important role in seawater attack than did ettringite, as regards loss of strength. However, this is negated by the results of SEM examinations /45/ and the findings of others /68, 125, 166/. It is felt that crystallization of chloroaluminates in the pores of HCP could lower porosity and may actually cause strength to increase, even though by only small amounts.

TABLE 5.6 : Compressive strength of immersed mortar specimens reported by Conjeaud /45/.

Age	0	1m	3m	6m	9m	12m	18m	2yrs	3yrs
water cured	69.7	73.6	75.6	78.2	78.6	78.2	83.0	81.0	79.4
seawater cured	-	57.6	57.6	63.0	77.8	72.8	76.4	70.7	80.0

5.2.3.3 Oven Drying at 105 deg.C

It is well known that the compressive strength of concrete increases on drying /46, 127, 151/. The main influence on strength gain being moisture loss. Termed drying-strengthening, Mills /127/ had considered this change in strength with the removal of moisture as the reverse of the weakening effect, caused when adsorbed water dilates the cement gel. The increase in strength has been attributed to the consolidation of the gel and also to the increase in the physical forces of attraction between particles as moisture is lost. That is, van der waal's bonds between the solid particles are strengthened. Heating of moist concrete also results in additional hydration, especially in the temperature range of 20-100 C.

Temperature in itself may cause loss of strength, especially if it results in crack formation and failure of the cement paste/aggregate bond. Nevertheless, it seems that the beneficial aspects of carefully heating unsealed concrete to temperatures of up to about 100C, outweigh the detrimental effects. Results of Table (5.4) showed a general increase in compressive strength of 5 to 6% for all specimens on oven drying at 105 C, despite the possible weakening effects of temperature.

5.3 EFFECT OF SPECIMEN-END LUBRICATION ON COMPRESSIVE STRENGTH

5.3.1 INTRODUCTION

The influence of specimen-end lubrication, resulting in apparent compressive strength, was discussed in Chapter 2. The effect has been investigated and the results are reported below.

Lubrication of concrete by crude oil increases with time under storage conditions. This is due to the build up of wax present in crude oil, on the walls of the storage tank. Marion and Mahfouz /117/ had found coatings of wax on the surface of concrete specimens soaked in Ekofisk crude oil. Similarly, Sweatman /191/ had found build up of wax on the walls of various oil storage facilities. Under experimental conditions the exposed surface of concrete specimens soaked in crude oil can be expected to be lubricated. In the situation whereby specimens are tested for compressive strength at different times, say between 3 and 365 days, lubrication of the specimens would increase with duration of storage and this would lead to inaccuracies in measurements. In order that uniformity may be achieved, it is essential that all test specimens should be uniformly lubricated prior to testing. Cleaning the specimen surface prior to testing does not necessarily eliminate this problem. This is because wax particles hiding in the pores of the specimens would come to the surface under compression loading.

In this study, the effect of grease lubrication of specimen-ends on the measured compressive strength, has been investigated. The grease used was Unedo grease-2. It is neutral, non-reactive and of high viscosity. Details of its properties are given in Appendix (A).

5.3.2 RESULTS OF COMPRESSIVE STRENGTH OF GREASE LUBRICATED SPECIMENS

The results of this study are given in Table (5.7) and trends are shown in Fig.(5.6). They indicate that when grease is used as end-lubricant, the compressive strength of a majority of specimens was reduced by between 5 and 7%. The result was independent of specimen shape or moisture condition prior to testing. An interesting observation made was that majority of the specimens had failed by splitting along the entire specimen length.

Concluding results showing the effects of oven drying and grease lubrication on the compressive strength of test specimens, are given in Table (5.8) and shown in Fig.(5.7).

5.3.3 DISCUSSION OF RESULTS

The results obtained are compatible with the mechanism of failure expected when concrete is tested in compression with ends lubricated. When unlubricated, tangential frictional forces develop between the surfaces of the specimen and the adjacent steel platens of the testing machine. These lateral forces are due to the Poisson ratio effect /134/. The vertical compressive force causes lateral expansion in the material. The lateral strain in the platen is small compared with the transverse expansion in the concrete. It has been reported that this strain is about 40% of that in the concrete at a distance from the interface sufficient to remove the restraining effect /134/. The foregoing suggests, therefore, that the platens restrain the lateral expansion of the concrete in the parts of the specimen near its ends. However, the degree of restraint excercised depends on the friction actually developed. If this is eliminated, the specimen exhibits a large lateral expansion and fails by eventually splitting along its full length under a lower load. Lubrication of specimen ends removes the friction with the platens and causes failure by splitting, as has been found in this study. The reductions of 5-7% in compressive strength observed in the concrete specimens can be related to this.

TABLE 5.7 : Effect of specimen-end lubrication on the compressive strengths of concrete specimens

Moisture condition	type of specimen	compressive strength (N/mm2)	
		no lubrication	lubrication
moist saturated	cylinder	94.3 (100%)	86.9 (92%)
	100mm cube	88.0 (100%)	82.0 (93%)
oven dry (105 C)	cylinder	101.0 (100%)	95.4 (94%)
	100mm cube	93.7 (100%)	88.0 (94%)

TABLE 5.8: Compressive strengths of concrete test specimens with ends lubricated.

curing regime	type	compressive strength (N/mm2)		
		moist (365d) unlubricated	moist (365d)	oven dried (105 C) (377d)
100% RH	OPC	90.8 (100%)	84.5 (93%)	89.7 (99%)
	PFA	86.3 (100%)	79.3 (92%)	85.6 (99%)
Sea water	OPC	80.1 (100%)	74.5 (93%)	79.1 (99%)
	PFA	76.7 (100%)	68.8 (90%)	76.8 (100%)

FIGURE 5.6: EFFECT OF END-LUBRICATION ON THE COMPRESSIVE STRENGTH OF CONCRETE SPECIMENS.

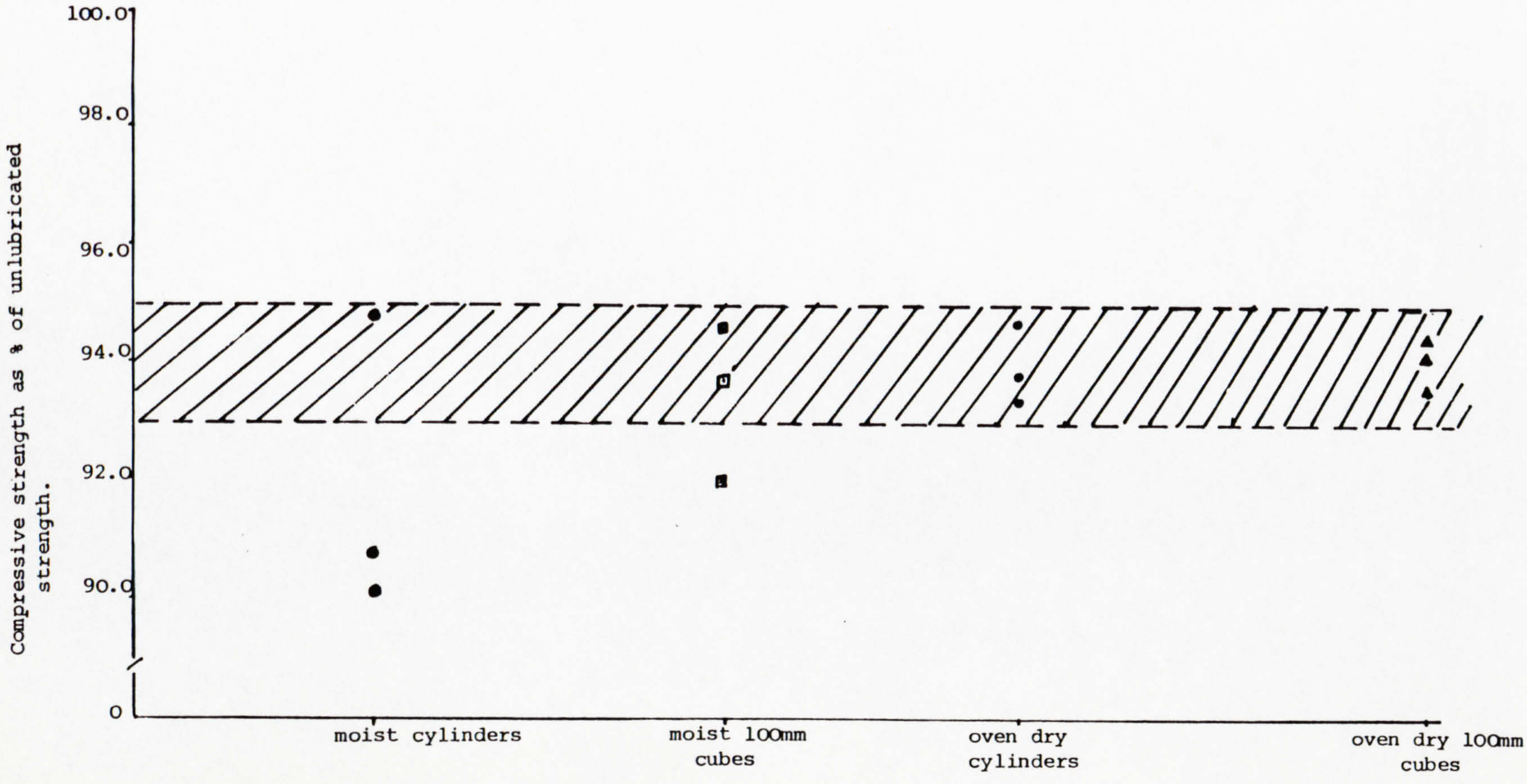
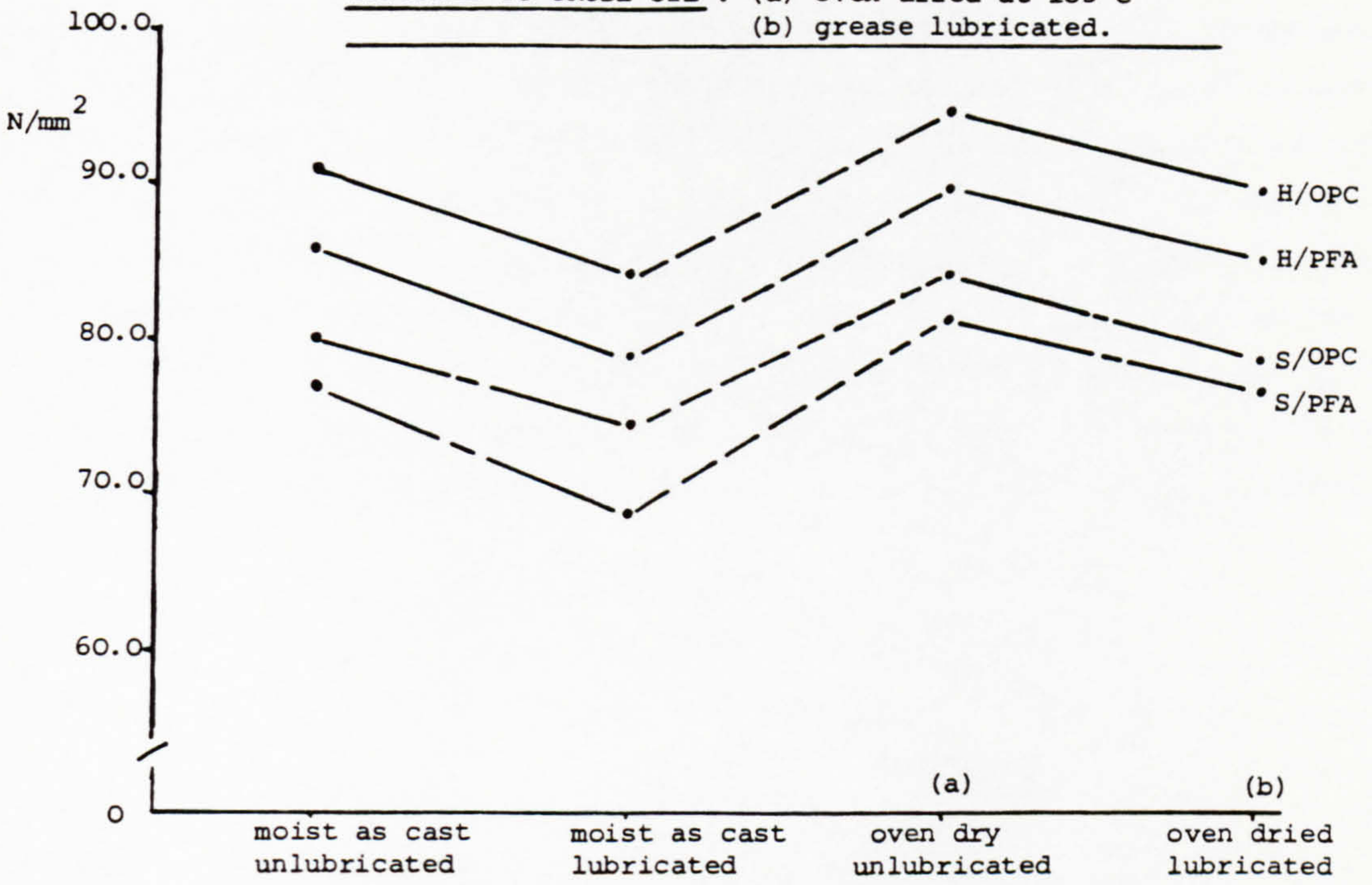
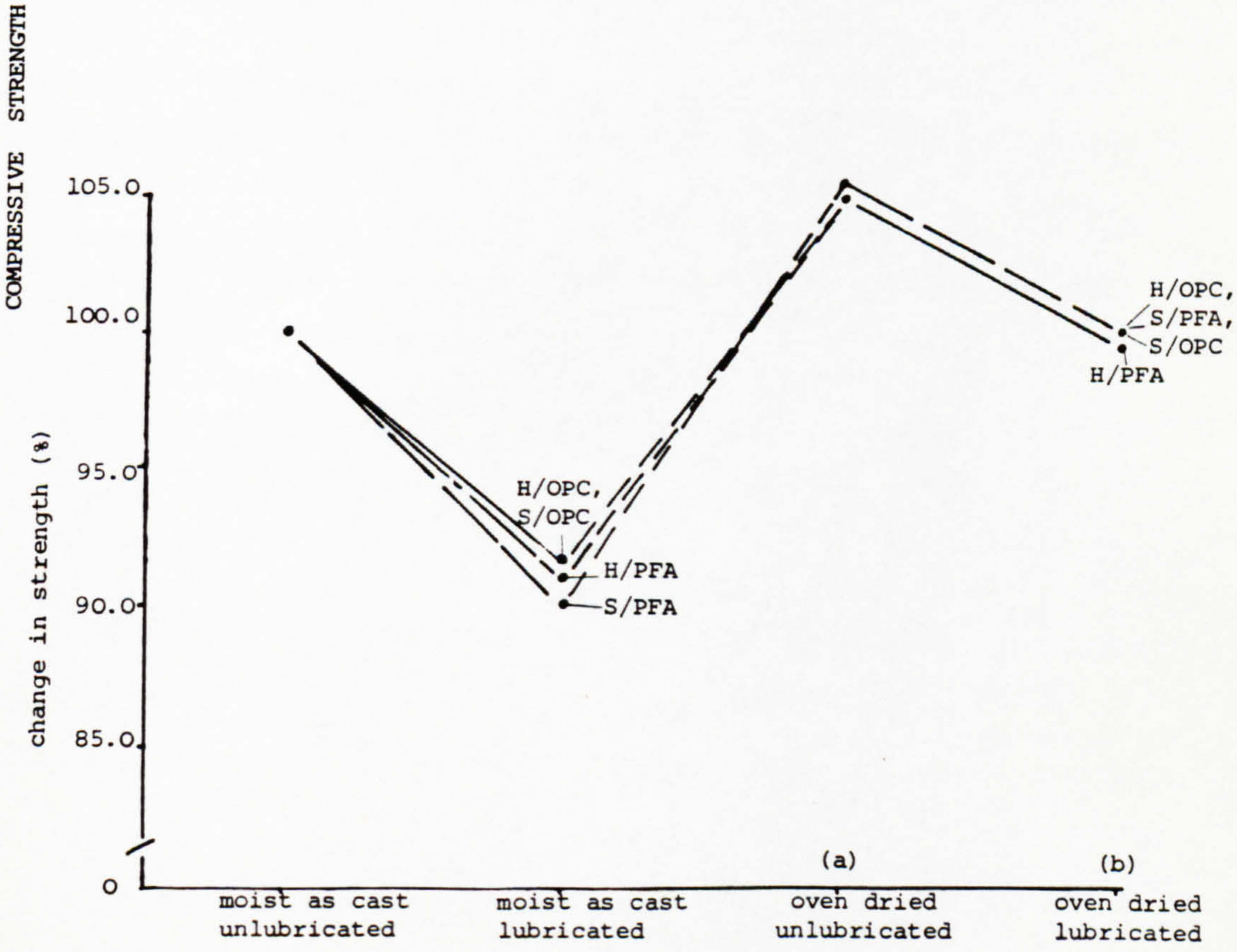


FIGURE 5.7: COMPRESSIVE STRENGTH OF CONCRETE SPECIMENS PRIOR TO EXPOSURE TO CRUDE OIL : (a) oven dried at 105 C
(b) grease lubricated.





5.4 DEVELOPMENT OF LENGTH CHANGE IN MORTAR PRISMS

5.4.1 INTRODUCTION

Length changes of mortar prisms cured in seawater and at 100% RH were monitored at about 20 C over a period of 365 days. Length measurements were obtained at various time intervals and the mean change of length of 20 specimens is reported for each test. The results are shown in Figs.(5.8) and (5.9), for the specimens cured at 100% RH and seawater respectively. Shrinkage measurements were also taken for specimens oven dried at 105 C at the end of the period of curing. Results of flow of each casting, the as-cast densities and 28-day compressive strength of cylinder specimens from the mortar mixes, were given in Chapter 3.

5.4.2 LENGTH CHANGE RESULTS DURING CURING

5.4.2.1 Mortar bar specimens cured at 100 percent RH

The trends of length changes with time for the mortar bar specimens cured at 100% RH, are shown in Fig.(5.8) from which it can be seen that similar amounts of expansion had occurred in the opc (H/OPC) and the pfa (H/PFA) specimens, throughout the duration of curing. The specimens had expanded continuously up to 180 days but had contracted slightly between 180 and 365 days. Significantly, the standard deviations between each of 20 specimens at each test period, were of similar magnitudes, for both mortar types. This varied by between 5 and 20 microstrains. Both specimen types had also achieved similar maximum expansions of 107 microstrains at 180 days, but had reduced to 89 and 87 microstrains at 365 days, for the H/OPC and H/PFA specimens respectively.

5.4.2.2 Mortar bar specimens cured in seawater

The mortar specimens cured in seawater were initially cured at 100% RH for 14 days, after casting. The trend of expansions in the specimens as shown in Fig.(5.9), indicated that the opc specimens (S/OPC) had expanded a great deal more than the pfa specimens (S/PFA), from the moment of exposure to seawater and continuously throughout the duration of curing. The difference between the two seems to have increased linearly with time, from 14 microstrains at 18 days to 237 microstrains at 365 days (Fig.5.10). The mean expansion of 453 microstrains at 365 days for the S/OPC specimens, was more than double the mean of 216 microstrains for the S/PFA specimens at the same age.

Comparison of these results with those of specimens cured at 100% RH, as shown in Fig.(5.11), clearly indicated that the expansions in sea water were significantly larger. Whereas the expansions in the S/PFA specimens were about double those observed for the H/PFA specimens at all ages, the difference was four-fold between the S/OPC and H/OPC specimens. In addition, the seawater cured specimens had shown increased repeatability of results. The trend of significant linear expansions in the S/OPC and S/PFA specimens, relative to the specimens cured at 100% RH, is comparable with the trend of compressive strength of the concrete specimens discussed earlier. The expansions observed can be related to the chemical attack by the sea salts, as will be discussed in section (5.4.3).

5.4.2.3 Length change of mortar specimens oven dried at 105 deg.C

Shrinkage of mortar specimens oven dried at 105 C are shown in Fig. (5.12). The results indicate that the seawater cured specimens which had previously expanded the most at the end of the period of curing had also contracted the most on oven drying. Although the H/OPC and H/PFA specimens had similar values of expansion throughout the duration of curing, however on oven drying, the H/PFA specimens had contracted by a larger amount than the H/OPC specimens. The difference was 56 microstrains (7%). Even though this amount is small, statistical analysis (Table 5.9) indicated that the difference was highly

significant. The difference in the total shrinkage on oven drying, between the S/OPC and S/PFA specimens,was 365 microstrains (23%).

5.4.2.4 Length change of mortar specimens dried at room RH (32%)

Mortar specimens dried at room RH of about 32% had shrunk continuously with time up to about 50 days, after which they had stabilised (Fig. 5.13). The ultimate shrinkage of about 650 microstrains, found in both the OPC and PFA specimens, was between 20% and 40% less than those observed in similar specimens which were oven dried at 105 C. This is because on heating, gel pore water begins to evaporate from about 80 C, while some of the chemically combined water may be removed at temperatures above 100 C. The loss of these cause further significant shrinkage in the HCP, which will not occur at room RH and ambient temperature.

TABLE 5.9 : t-Test of significance to compare shrinkage of H/OPC and H/PFA mortar specimens on oven drying at 105 deg.C

Test	no. of samples	mean (m)	std. dev. (s)	DOF	t-value	prob. (p)	remark
H/OPC vs.	15	781	24	28	6.788	0.005	highly
H/PFA	15	837	20				signif

FIG.5.8: Length change of mortar prisms cured at 100 percent RH

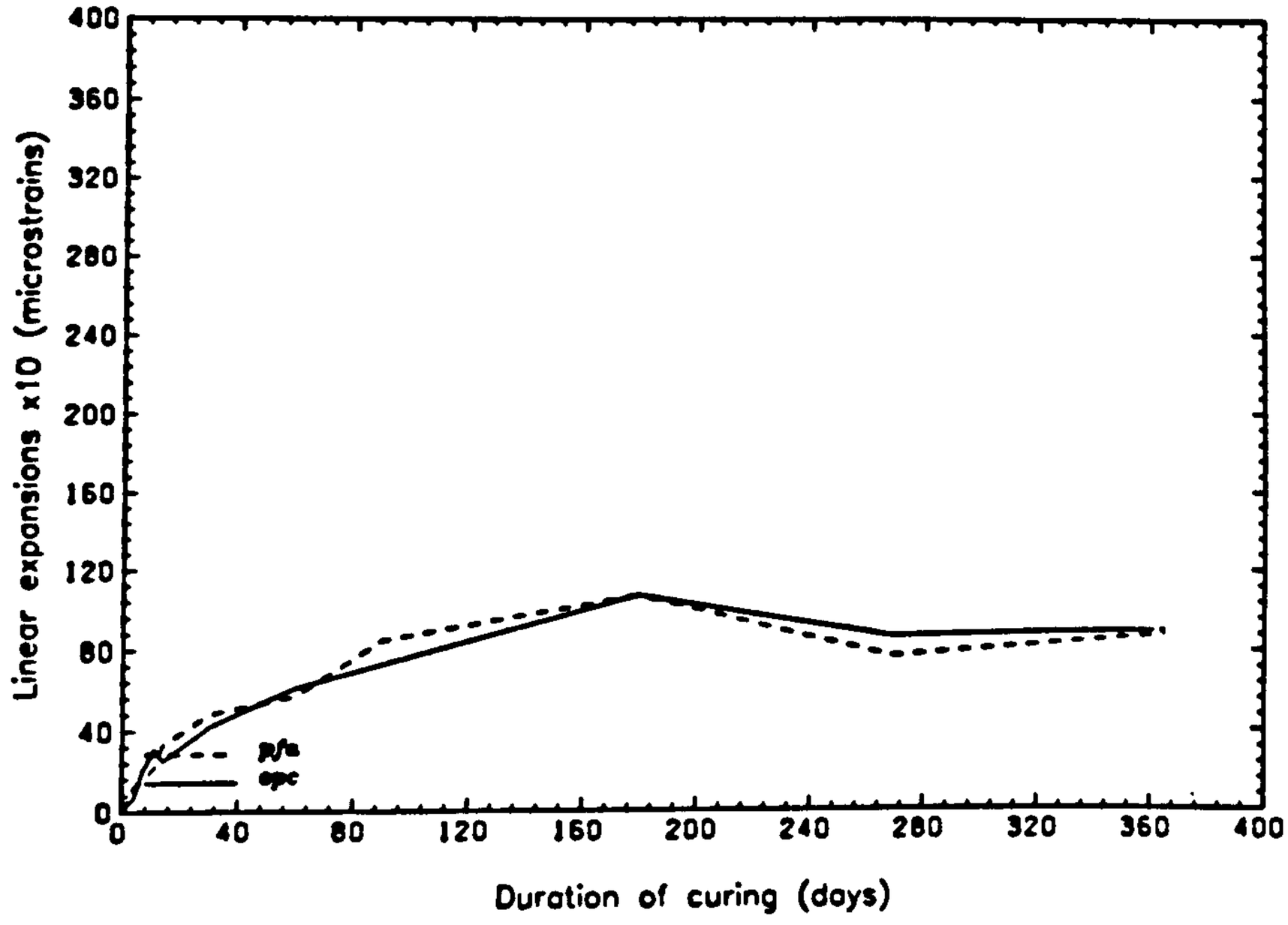


FIG.5.9: Length change of mortar prisms cured in sea water

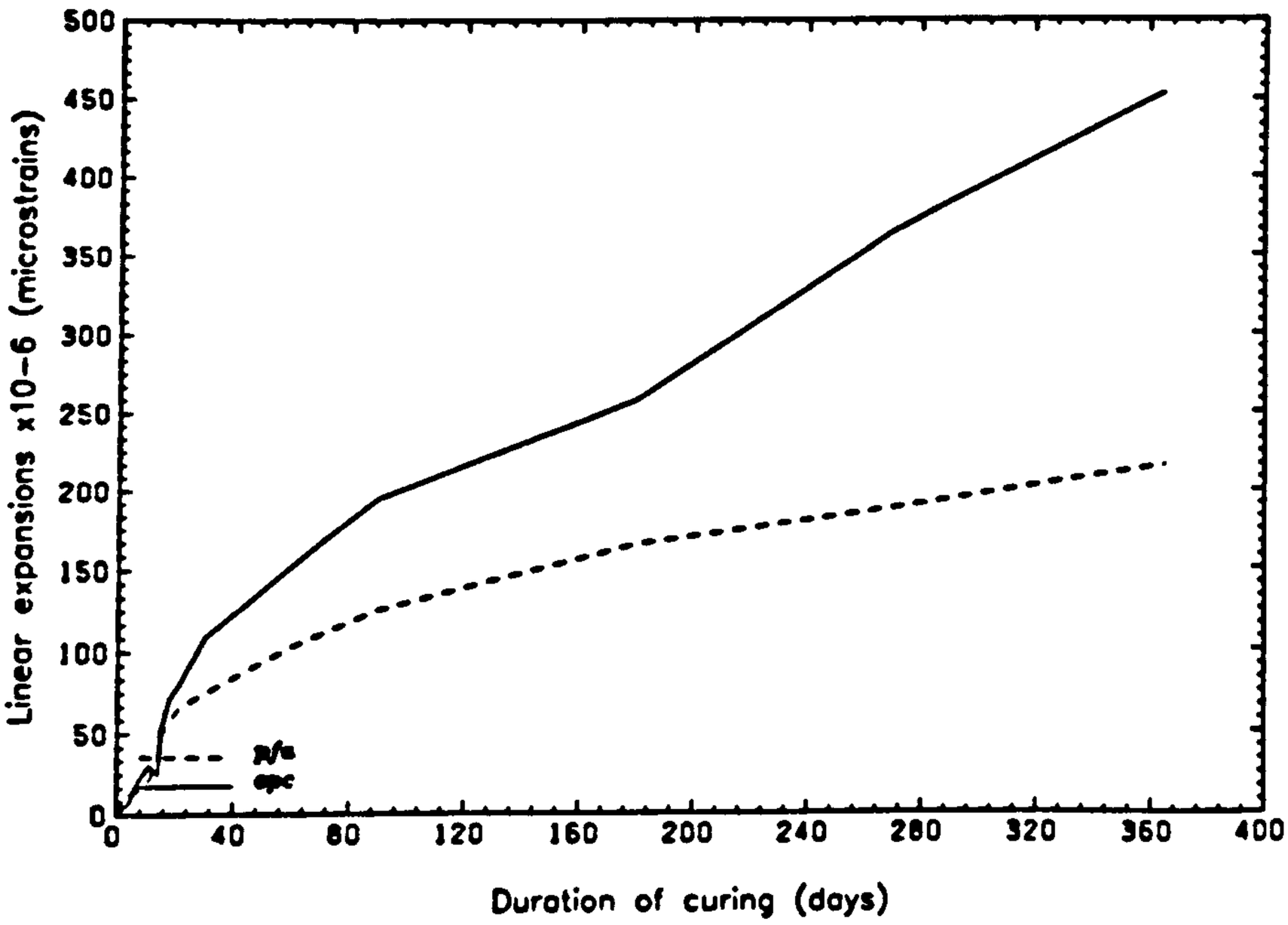


FIGURE 5.10: DIFFERENCE IN LINEAR EXPANSIONS BETWEEN S/OPC AND S/PFA SPECIMENS.

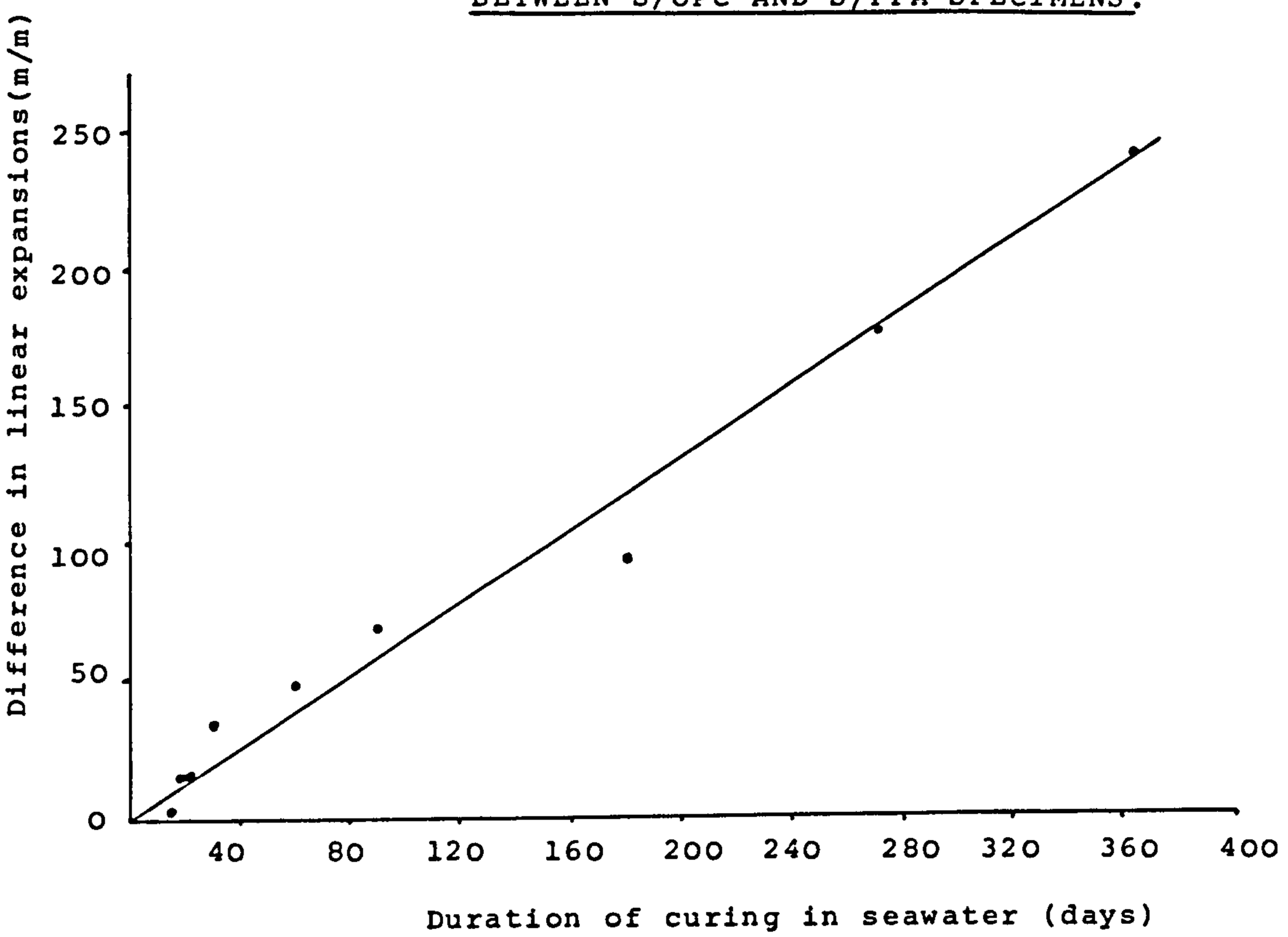


FIGURE 5.11: Comparison of length change of mortar specimens

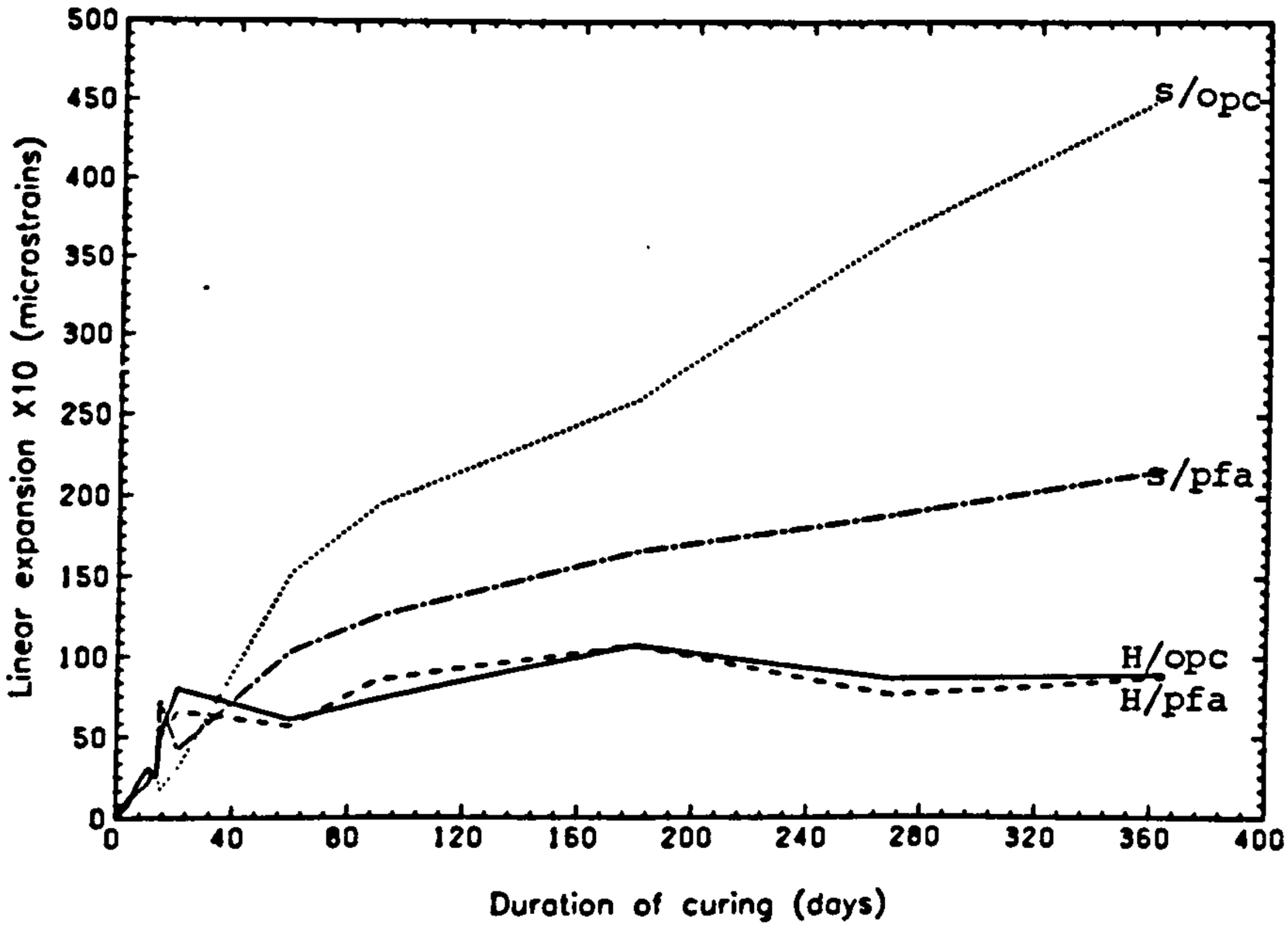


FIGURE 5.12: SHRINKAGE OF MORTAR PRISMS BEFORE AND AFTER OVEN DRYING AT 105 C.

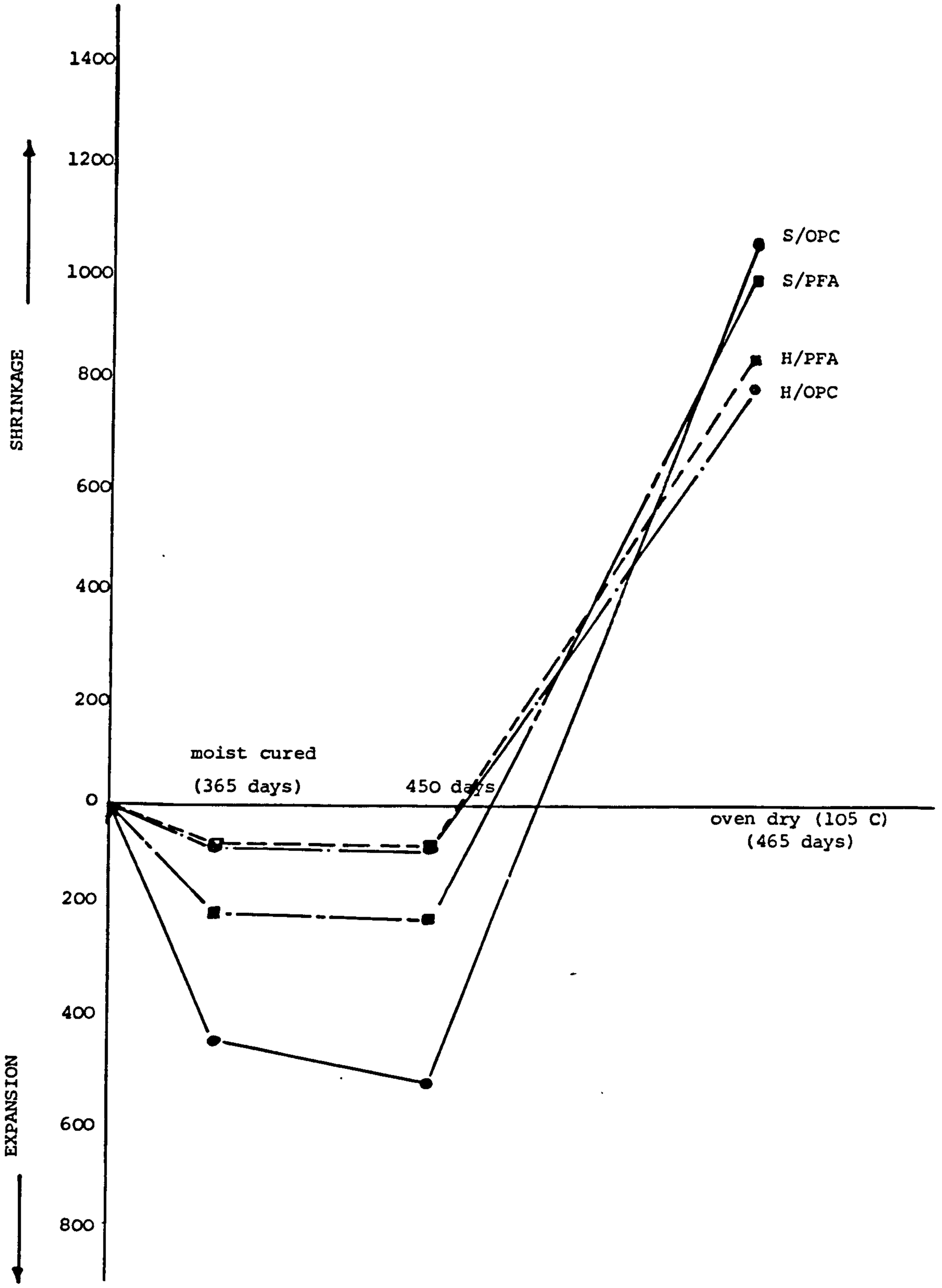
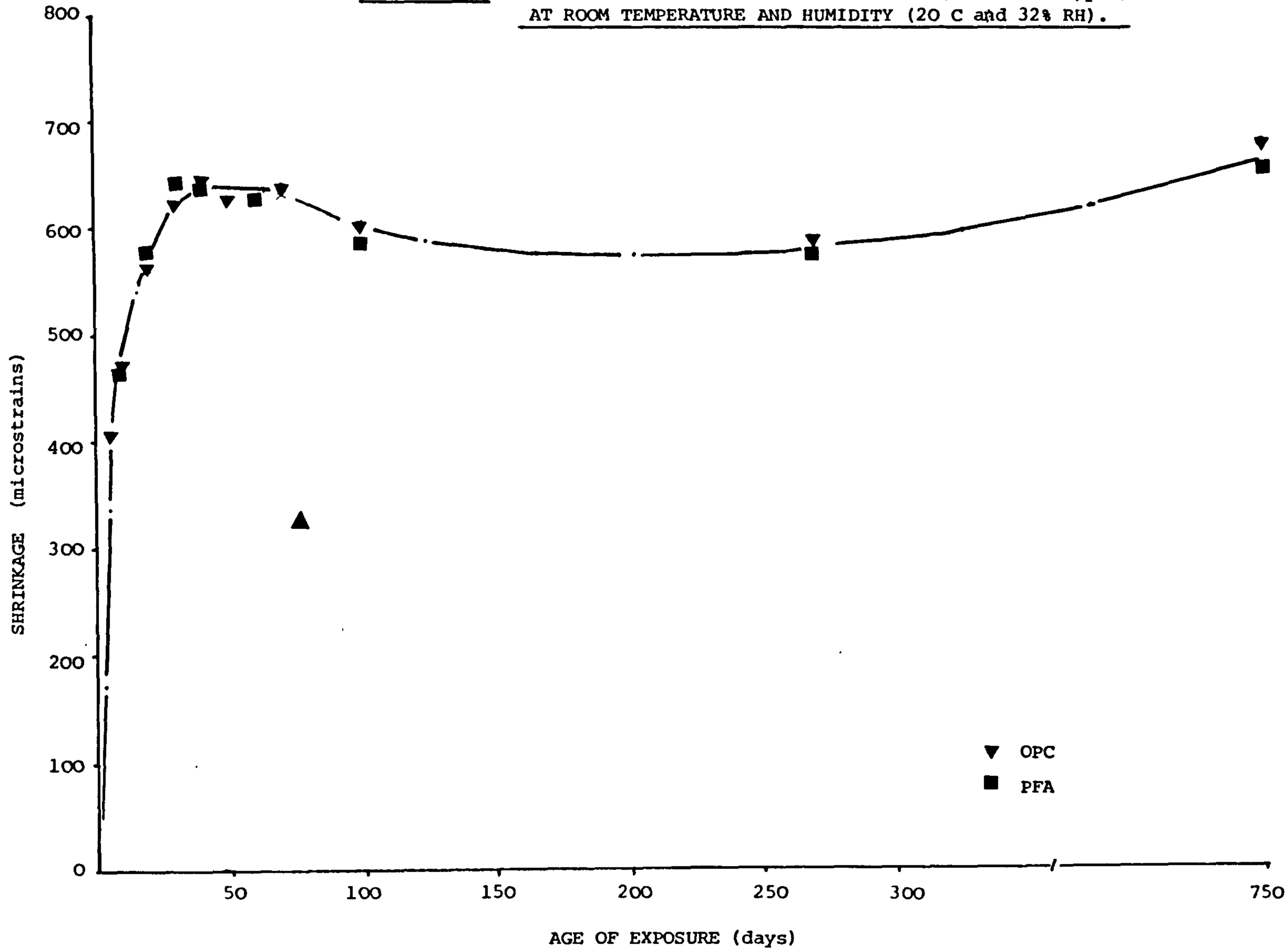


FIGURE 5.13: DRYING SHRINKAGE OF MORTAR SPECIMENS (OPC and OPC/pfa) AT ROOM TEMPERATURE AND HUMIDITY (20 C and 32% RH).



5.4.3 DISCUSSION OF RESULTS

5.4.3.1 Curing at 100 percent RH

The results of Fig.(5.8) which showed similar amounts of expansions in the H/OPC and H/PFA mortar specimens cured at 100% RH, confirms that the mechanism causing expansion in these specimens is of a purely physical nature. It is also an indication that the total pore volume susceptible to expansion mechanisms was similar in both mortar types. The well known physical mechanisms causing volume changes in concrete are; capillary tension, surface energy, swelling pressures and movement of interlayer water /91, 61, 157, 210/. These mechanisms may act singly or jointly to cause volume change.

Many workers /91, 111, 195/ have attributed expansions in the HCP to capillary forces causing elastic volume variations in the cement paste as a result of changes in the surrounding relative vapour pressure. For example, L'HERMITE /111/ had developed a theoretical relationship between the evaporable water E in the cement paste, the bound water Ec and the relative humidity θ, in the expression

$$E = Ec\,(1 - \theta)\,[\,1 - e^{-At}\,] \qquad (5.1)$$

where A is a function of dimensions (vol/area) and the coefficient of moisture diffusivity, which tends towards a constant value with age, and t is time. From this expression, it was deduced that shrinkage is a function of the surrounding relative humidity, as well as of the loss of bound water. What this means is that the relationship between water variation (relative humidity) and volume or average length variation, for each given time period, is linear.

Swelling pressure, first suggested by Powers /157/, may be another mechanism affecting length change. This develops as a result of adsorbed layers of moisture on the surfaces of two adjacent gel particles. The pressure tends to separate the particles and in so doing causes swelling. As the thickness of the adsorbed layer increases with relative humidity, the swelling pressure increases correspondingly. Hence, swelling of the cement paste increases with the increase in moisture content.

Both of the mechanisms described are seated in the C-S-H gel of hydrated cement paste and, are dependent on the relative humidity. It is the opinion of a few /60, 61/ that moisture movement in and out of the layered structure of the gel particles cause volume changes due to resulting changes in the spacing of the layers. They believe that the exit of water causes shrinkage and the re-entry of water causes swelling. This however, contradicts other models which assume that interlayer water may be removed, but will not re-enter the structure.

The maximum expansions of 107 microstrains at 180 days which was found in the H/OPC and H/PFA specimens during curing at 100% RH, falls within the range reported by L'HERMITE /111/ who had measured volume changes of cement paste,mortar and concrete prisms cured in water over a similar period of time. The results are also in agreement with those of TROXELL and co-workers /195/, who found similar values of expansion in portland cement concrete stored at 100% RH.

The shrinkages observed after 180 days in both the H/OPC and H/PFA specimens were small and may be due to a possible fall in RH over that period, although care was taken to maintain 100% RH throughout. But as L'Hermite observed, there is great difficulty in maintaining 100% RH experimentally /111/. These shrinkage values in the mortar specimens, however become insignificant, when compared with those observed for mortar specimens dried at room humidity of about 32% and 20 C, as was earlier discussed (Fig.5.13).

5.4.3.2 Curing in seawater

Similar to the observations made for the concrete specimens, the mortar prisms cured in sea water had shown characteristics which were significantly different from those of specimens cured at 100% RH. More importantly, the S/PFA specimens had reacted markedly differently from the S/OPC specimens under exposure conditions.

The expansions observed in seawater by the specimens can be attributed to a combination of physical and chemical factors, although the size of the expansions suggest the predominance of chemical factors. The possible physical mechanisms have been previously discussed. The chemical reactions between the harmful salts of seawater and the products of hydration of cement paste, in particular $Ca(OH)_2$, has also been previously discussed. The products of these reactions are the main causes of the expansions and degradations that occur in cement paste.

As was observed, the sulphate attack and in particular, attack on the tricalcium aluminate phase of HCP, results in the formation of ettringite which is most detrimental to cement paste from the point of view of expansions /111, 124, 166/. The presence of a high concentration of C_3A in cement also enhances ettringite production via the formation of chloroaluminate hydrate which, because of its instability in a sulphate environment, converts to ettringite /124/. In general, chemical expansion increases with the free lime content of cement paste.

REGOURD /166/ has reported linear expansions in mortar specimens exposed to seawater over a period of up to four years. It was observed that the C_3A content was an important factor in the resistance of portland cement to seawater because it reacts with sulphates to form ettringite. Results had shown that specimens with low C_3A contents had lower amounts of expansion. This was related to the formation of smaller quantities of ettringite. In an earlier work, L'HERMITE/111/ also attributed expansions of mortar specimens exposed to sea water to the attack on the lime aluminate by lime sulphate, which had resulted in the formation of sulphoaluminate (ettringite). The expansions observed in the current study were comparable to those reported by Regourd /166/.

The S/PFA specimens had expanded less than the S/OPC specimens probably because they contained less lime, as this is usually used up in the pozzolanic reactions. It may also be a result of the lower C_3A content of the PFA mix, since this contained 30% less portland cement. In fact, it is possibly the combination of both factors. As a result, the level of reactivity with seawater can be expected to be less, compared with the S/OPC specimens.

The role of pozzolans in reducing expansion has been reported by Bogue /23/ and others /19, 36/, who found markedly diminished swelling of cement paste and concretes containing pozzolanic material. Regourd /166/ also found that blending materials such as slag and pozzolans with portland cement generally improves resistance to sea water. X-ray diffraction (XRD) analysis showed that such blended cements contained more chloroaluminate, which causes less expansion than ettringite.

5.4.3.3 Oven Drying at 105 deg.C

Drying shrinkage of mortar is seated in the cement paste and is restrained by aggregates. Oven drying at elevated temperatures considerably increases both the rate of shrinkage and the ultimate shrinkage. The properties of concrete influencing shrinkage are water/cement ratio, the degree of hydration, cement type and aggregates.

In a properly hydrated paste of low water/cement ratio, shrinkage is intrinsic to the gel and is related to the loss of adsorbed water, especially from the smaller micropores. Shrinkage can therefore be expected to increase with increase in the micropore content of the HCP. Blending of portland cement with pfa is known to cause an increase in the finer pore content of HCP while reducing the volume of the larger pores /116/. Such a specimen can be expected to shrink more than an opc paste prepared under similar conditions. This may explain why the H/PFA specimens had contracted slightly more than the H/OPC specimens on oven drying at 105 C. However, the difference was significant, since both had previously expanded by similar amounts by

the end of curing. The result suggest that different mechanisms operate in swelling and oven drying. It seems that under saturated conditions, entry of moisture into some of the small micropores may be very difficult. These pores do not therefore contribute to swelling. However, evaporation of moisture from such pores on oven drying contribute significantly to shrinkage. This observation is in agreement with the existing theory that interlayer water may be removed, but will not re-enter the structure /91, 157, 159/, but deviates from the model of Feldman and Sereda /61/.

Shrinkage of the seawater cured specimens (S/OPC and S/PFA) was larger than in specimens cured at 100% RH (H/OPC and H/PFA). This is because total porosity in the former, due to seawater attack, had led to greater moisture absorption into the gel. The loss of this moisture on oven drying had resulted in larger relative shrinkage. In the same manner, the S/PFA specimens had contracted less than the S/OPC specimens on oven drying, since they contained less moisture. This was because the former were attacked less during curing and were therefore less porous and contained less moisture than the S/OPC specimens.

5.5 Surface condition of specimens after 365 days of curing

The surface conditions of the concrete and mortar test specimens were studied at the end of the period of curing, prior to exposure to crude oil. The studies included carbonation tests, investigation of surface cracks and the formation of surface deposits. One specimen each from the 4 types of concrete and mortar specimens tested, are shown in Figs.(5.14) and (5.15) respectively.

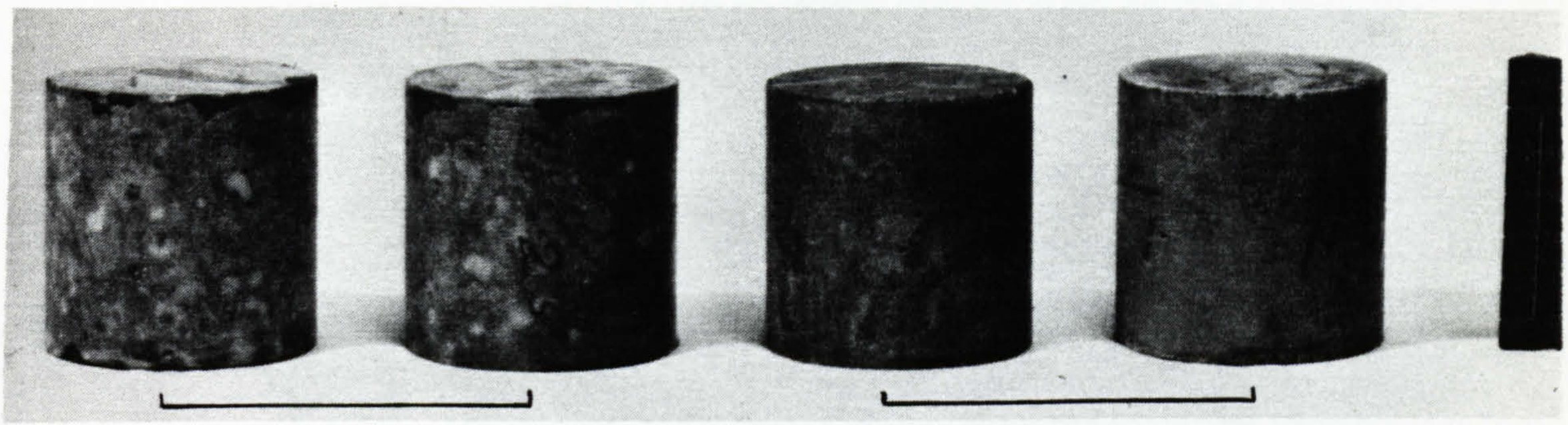
Phenolphtalein tests on the surfaces of concrete and mortar specimens cured at 100% RH (H/OPC and H/PFA) showed no evidence of carbonation. However, tests on seawater cured specimens indicated the presence of lime on the surfaces of the specimens and can be attributed to leaching, resulting from the reactions with sea water.

Direct visual observation showed the formation of a thin deposit over the entire exposed surface of the seawater cured specimens. This was not observed on the specimens cured at 100% RH. Optical microscopy was used to study polished sections of samples obtained from across the surface of concrete specimens and this confirmed that no deposits had formed on the specimens cured at 100% RH (Fig. 5.16). On the other hand, the optical microscope had shown the presence of a distinct surface layer on the seawater cured specimens. This had a thickness of about 100μm on the S/OPC specimens (Fig. 5.17a), but were thinner (about 50μm) on the S/PFA specimens (Fig. 5.17b). X-ray diffraction analysis of powdered scrapings taken from the samples /34/ had identified the layers as comprising almost entirely of brucite [$Mg(OH)_2$], with the inclusions being primarily aragonite and minor quantities of calcite. Aragonite and calcite are polymorphs (different crystalline forms) of calcium carbonate ($CaCO_3$) /33/.

Brucite [$Mg(OH)_2$] is formed as result of the reactions between the sea salts ($MgSO_4$ and MgCl) and, $Ca(OH)_2$ from the cement paste. Thinner layers were formed on the S/PFA specimens, compared to the S/OPC specimens, suggesting that there was less reaction with the sea salts in the former. This confirms that the S/PFA specimens contained less reactive lime than the S/OPC specimens, obviously as a result of the pozzolanic reactions which converts $Ca(OH)_2$ to C-S-H gel.

Buenfeld /33/ had found that the nature of the layer produced was influenced by the composition of the seawater and on its pH. Formation of the layer depends on the Mg^+ ion contents of the seawater and a high ph of about 9.3. They are thought to cause reduction in permeability, due to reduction in the ingress of sea salts /45, 33, 166/.

There was no evidence of crack formation on the exposed surfaces of concrete and mortar specimens cured at 100% RH, as observed under ultraviolet light inspections. However, a few fine cracks could be seen on the trowelled face of S/OPC concrete specimens, but not on the S/PFA specimens. There were no cracks in any of the mortar specimens.



(a) (b)

Figure 5.14: Concrete cylinder specimens

(a) seawater cured (b) 100% RH cured

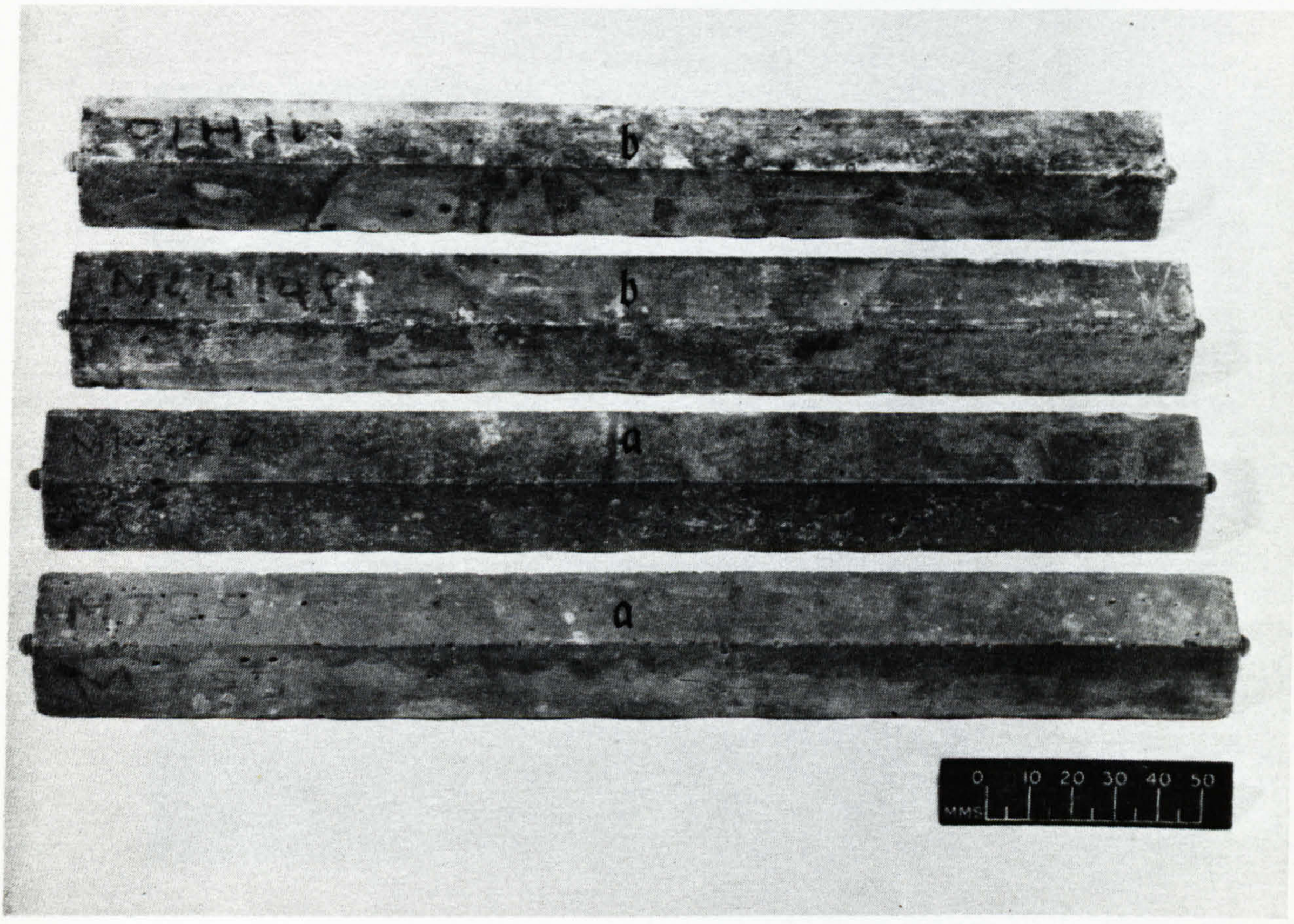
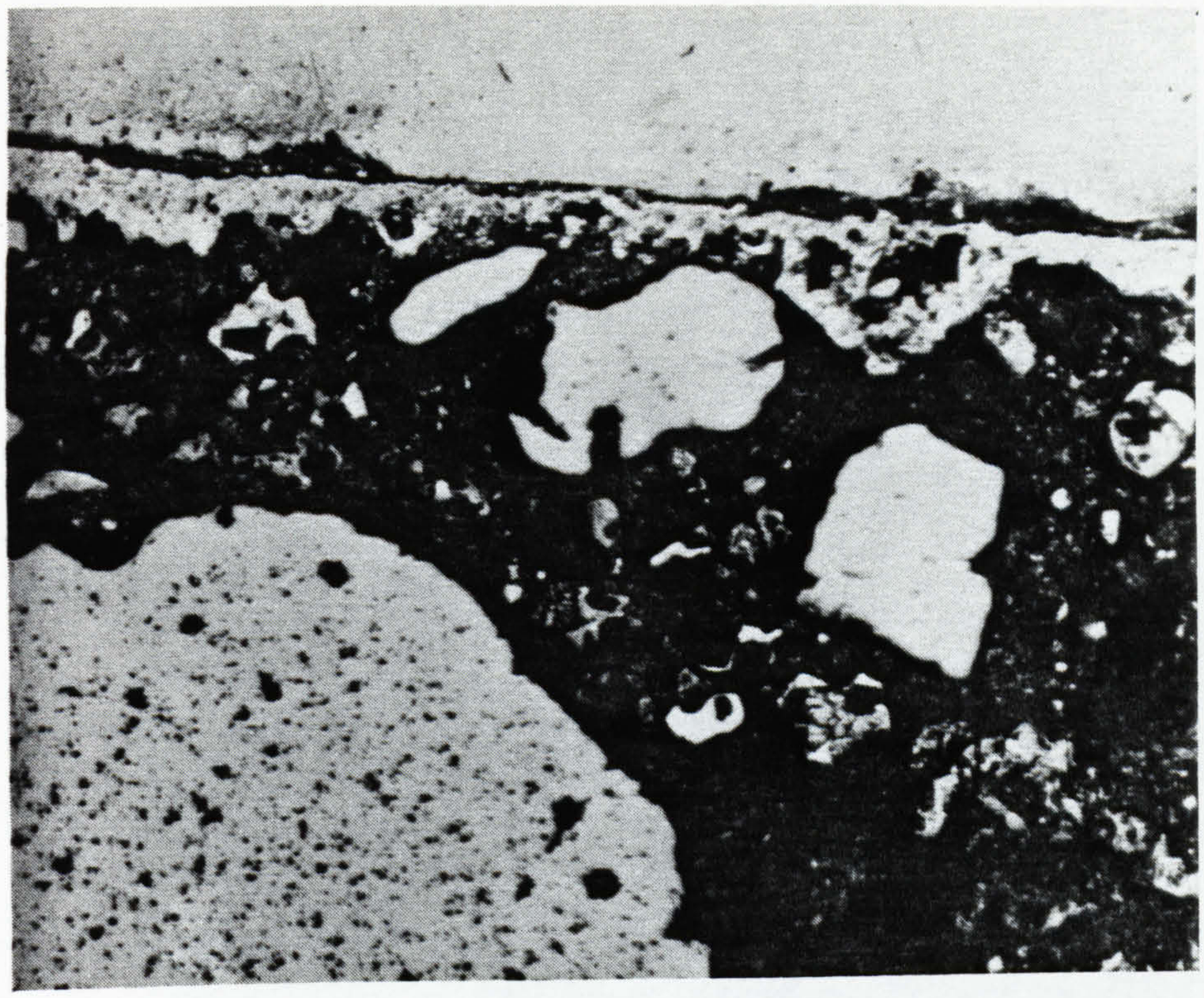
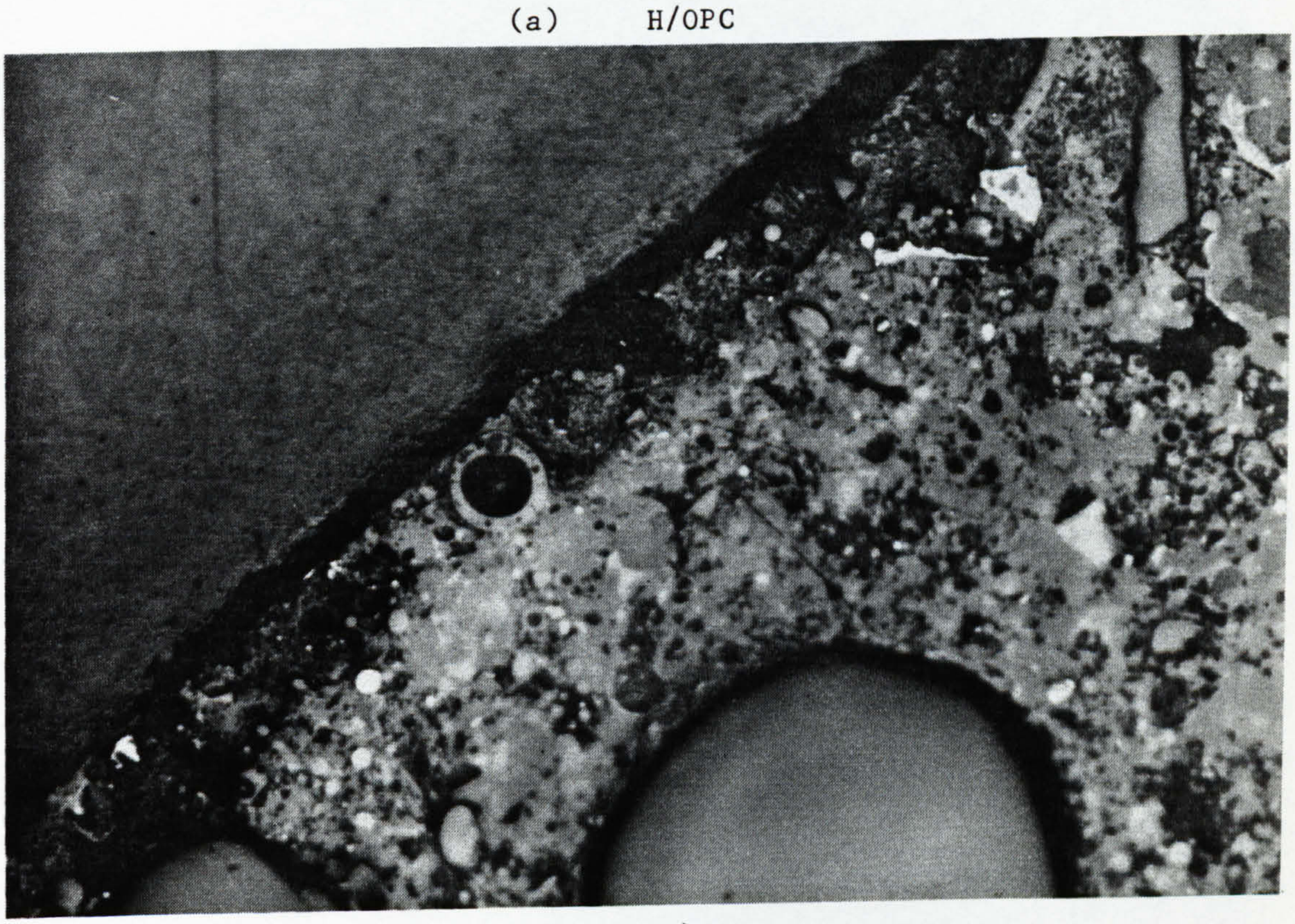


Figure 5.15: Mortar bar specimens

(a) seawater cured (b) 100% RH cured

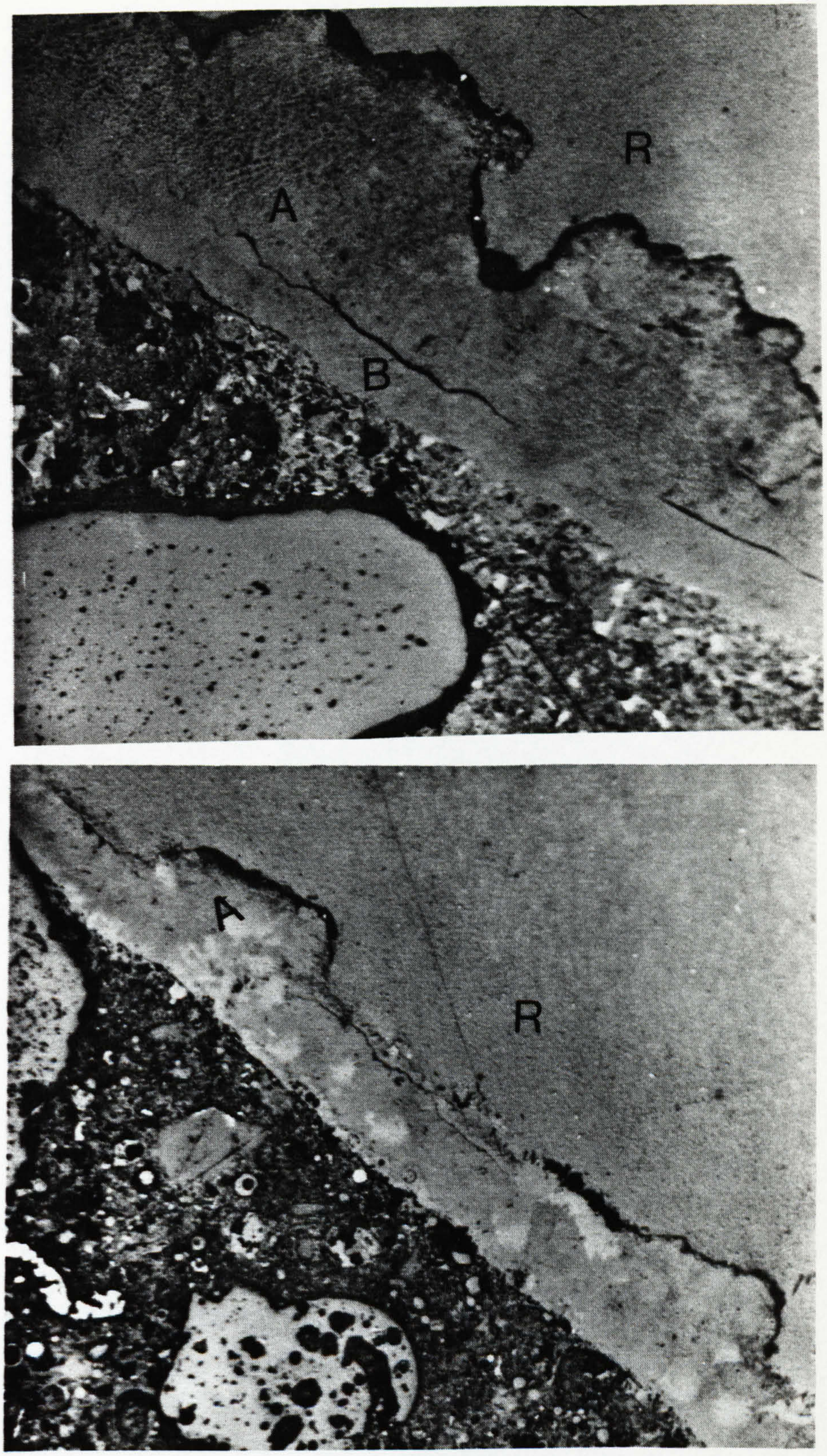


(a) H/OPC



(b) H/PFA

Figure 5.16: Polished sections of concrete specimens cured at 100% RH, showing surfaces free of any deposits.



(a) S/OPC

(b) S/PFA

100 μm

Figure 5.17: Polished sections of seawater cured concrete specimens showing surface formations.

[A = aragonite B = brucite R = resin]

5.6 SUMMARY OF RESULTS

Some of the results given in this chapter confirm reported trends on the influence of curing at 100% RH and in seawater, and of the effects of oven drying at 105 C, on the compressive strength of concretes and length change of mortar specimens. In other respects, some of the findings are new, especially those relating to the similarity in expansions of opc and pfa mortar specimens when cured at 100% RH and the difference in shrinkage on oven drying. There is also novelty in finding a relationship between brucite layer formation and the $Ca(OH)_2$ contents of specimens. Significantly, the aim at this stage was to establish the compressive strength and length change of specimens prior to exposure to hot crude oil. This has been achieved. The following have been observed:

5.6.1 Compressive Strength of concrete specimens

(1) Curing of concrete specimens at 100% RH resulted in similar compressive strengths with the freshwater cured control specimens (Figs. 5.4 and 5.5).

(2) Similar compressive strengths were achieved between the opc and pfa specimens by 365 days, under all curing conditions (Figs. 5.1 to 5.3). However, it seemed the pfa specimens may have continued to gain in strength after this period.

(3) By 365 days, the compressive strength of the H/OPC specimens cured at 100% RH had increased by 22% from the 28 day strength, while that for the H/PFA specimens had increased by about 50% (Table 5.3).

(4) The difference in compressive strengths between the specimens cured at 100% RH and those cured in seawater was statistically significant at all ages for both mixes. The compressive strengths of opc and pfa specimens cured in seawater were about 11% and 8.5% respectively lower than for similar specimens cured at 100% RH or in freshwater (Table 5.3).

(5) By 365 days, the compressive strengths of the S/OPC and S/PFA specimens cured in seawater had increased by about 19 and 45% respectively from the 28-day strength (Table 5.3).

(6) Oven drying of specimens at 105 C had increased compressive strengths by between 5 and 6% and was independent of cement blend and method of curing (Fig. 5.7).
(7) Lubrication with grease of the specimen ends, reduced the measured compressive strength of the concrete specimens by between 5 and 7%, for both moist and oven dried specimens. The results were independent of specimen shape (Fig. 5.6).

On the basis of these results, all specimen ends were lubricated with grease prior to compression testing in order to ensure uniformity of the 'apparent' effects on the measured strengths.

5.6.2 Length Change of mortar bar specimens

(1) Curing at 100% RH caused similar expansions in the H/OPC and H/PFA specimens throughout the duration of curing, and confirms that the operating mechanism under this condition was of a physical nature (Fig. 5.8). However, the H/PFA specimens had contracted by about 60 microstrains more than the H/OPC specimens, on oven drying at 105 C.
(2) In seawater, the S/OPC specimens had expanded significantly more than the S/PFA specimens throughout the duration of curing. Expansions in the former were more than double that in the latter and the difference between the two had increased linearly with time. The operating mechanism under this condition was a combination of physical and chemical factors. Chemical attack was clearly the dominant influence and depended on cement blend (Fig. 5.9). Similarly, the S/OPC specimens had contracted more on oven drying at 105 C.

PART B: EXPOSURE TO CRUDE OIL AT ELEVATED TEMPERATURES

CHAPTER VI

ABSORPTION AND PENETRATION OF CRUDE OIL AT ELEVATED TEMPERATURES

6.1 INTRODUCTION

The nature of the physical/chemical interaction between crude oil and concrete, depends on the crude oil being absorbed by the concrete and the degree with which it penetrates the pore system. It is the extent of these interactions which determine the changes that take place in the mechanical properties of the material. The results of crude oil absorption of moist and oven dry specimens, stored in crude oil at 20 C and at elevated temperatures, when measured after cooling, are presented and discussed in this Chapter. These are compared with the absorption of water by the control specimens, stored at similar test temperatures. Also presented in this chapter are the results of the investigation to establish the relationship between time and depth of penetration of crude oil into oven dry concrete at elevated temperatures. Finally, the results of the differential penetration of crude oil fractions through oven dry concrete, as obtained using the NMR technique, are presented and discussed.

6.2 ABSORPTION STUDIES

6.2.1 Introduction

Absorption studies were performed on the concrete specimens used in the compressive strength tests, and on mortar specimens used in the length change tests. The results obtained showed that in general, the trends of absorption of the concrete and mortar specimens were similar. However, details are given below of the results of tests of only the mortar specimens. This is because they reflect more accurately the variations in the trends of absorption. Test measurements were obtained continuously from the same mortar specimens at every test period, unlike the concrete specimens, for which 'new' sets of specimens were measured at every test period. This is because in the latter, the specimens were crushed in the compression tests at each test period and had to be disposed of.

Conventionally, absorption is determined by initially drying a specimen to a constant weight (often at 105 C), immersing it in a fluid and measuring the increase in weight expressed as percent of the dry weight. Most good quality concretes have absorption well below 10% /134/.

The moisture absorption by weight of the oven dry (105 C) concrete and mortar specimens are given in Tables (6.1) and (6.2) respectively. The results are averages obtained from measurements from at least 4 specimens, for each test. They show that water absorption by all specimens was less than the evaporable moisture loss on oven drying. This can be related to the "irreversible shrinkage" which takes place in cement paste on first drying (see Chapter 8 and ref./200/). The reasons for this are not very clear. However, it is believed that modifications occur within the internal structure of the HCP, which diminish the total pore volume and increases the coarsening of the pore structure. Verbeck and Helmuth /200/ found that the irreversible shrinkage component is accompanied by a corresponding irreversible loss of water content.

Comparison of the residual volume absorption of crude oil (ρ = 0.84kg/1) with the residual volume absorption of water, is made in Table (6.3), for the oven dry mortar specimens stored at 3 test temperatures, when measured after cooling. As was expected, there was less absorption of

TABLE 6.1 : Moisture absorption by weight of the concrete cylinder specimens.

Moisture condition	specimen type			
	H/OPC	H/PFA	S/OPC	S/PFA
moisture loss on drying (105 C) as % of oven dry wt.	5.5	7.1	6.7	6.7
water absorption at 20 C as % of oven dry wt.	4.5	5.6	5.2	5.5
% of moisture reabsorbed	82	79	78	82

TABLE 6.2 : Moisture absorption by weight of the mortar bar specimens

Moisture condition	specimen type			
	H/OPC	H/PFA	S/OPC	S/PFA
moisture loss on drying (105 C) as % of oven dry wt.	7.9	8.3	7.7	9.0
water absorption at 20 C as % of oven dry wt.	7.6	8.0	7.0	8.5
% of moisture reabsorbed	96	96	91	94

TABLE 6.3 : Ratio of volume absorption of crude oil to water (Aco/ Aw) of oven dry mortar specimens.

Temperature (C)	Aco/ Aw for specimens			
	H/OPC	H/PFA	S/OPC	S/PFA
20	89	77	96	77
45	97	62	99	88
60	94	89	95	93

crude oil than of water, although the difference between the residual volume absorptions of the two fluids had decreased for the specimens stored at the elevated temperatures. Furthermore, it was found that the difference between the residual volume absorptions of crude oil and of water, for the S/OPC specimens, was small. These results are discussed in more details in section (6.2.3).

Granite aggregates used in the concrete mixes were oven dried and tested for crude oil absorption at the 4 test temperatures. Results obtained after cooling indicated that no significant changes in weight had occurred even after 12 months of exposure and, there was no evidence of surface deterioration. It seems that the absorption of crude oil was based mainly in the mortar matrix of the specimens.

6.2.2 Results of crude oil absorption of mortar bar specimens.

6.2.2.1 Oven dry specimens

The residual absorption of crude oil in the oven dry mortar specimens stored at the 4 test temperatures, are shown in Fig.(6.1) as a function of time. All measurements were taken after cooling the specimens to room temperature of about 20 C. The effect of temperature is shown in Figure (6.2), for each of the specimen types. The data was statistically analysed using the t-Test of significance between means and the details are given in Table (6.4). The following observations can be made:

(1) From the results of Fig. (6.1), 3 stages of crude oil absorption can be observed. In the first stage, from the time of storage up to 3 days, there was instantaneous absorption of crude oil by all specimens. In the second stage from 3 days to about 90 days, the rate of crude oil absorption, although still rapid, was less than in the first stage. In the third stage from about 90 days to 365 days, the rate of absorption had reduced significantly and steady state seemed to have been reached.

Saturation had occurred by 90 days for the specimens soaked in crude oil at 20 C, but absorption had continued although at a slower rate, for the specimens stored at the elevated temperatures.

(2) The ultimate crude oil absorptions at 20 C were of similar amounts in all specimens (about 5-6%). These were, however, less than the residual absorptions in specimens stored at the 3 elevated temperatures (Fig.6.2). Statistical analysis showed that the difference between absorption at 20 C and at elevated temperatures was highly significant.

(3) The rate of absorption of crude oil was higher, the higher the storage temperature (Fig. 6.2), the largest amounts being in specimens stored at 80 C, at which ultimate absorptions were 7.4%, 8%, 8% and 8.5% for the H/OPC, H/PFA, S/OPC and S/PFA specimens respectively.

(4) The trend of crude oil absorption of the specimens stored at elevated temperatures had varied with the method of curing. In general, the seawater cured specimens (S/OPC and S/PFA) had larger ultimate absorptions than the specimens cured at 100% RH (H/OPC and H/PFA), as can be seen in Figs.(6.1 a and b). The difference between the two at 365 days was highly significant (Table 6.4).

(5) The residual volume absorption of crude oil by the oven dry mortar specimens was less than the residual volume absorption of water, for storage at 20, 45 and 60 C (Table 6.3).

TABLE 6.4 : Statistical t-Test analysis - Comparison of 'effects' on the ultimate absorption of crude oil by oven dry mortar specimens.

Tests	mean m	std.dev. s	no. of samples	DOF	t-value	prob. p	remark
100% RH vs.	7.11	0.55	22	43	6.48	<0.005	highly
seawater cured	8.03	0.39	23				signif.
H/OPC vs.	6.68	0.14	11	20	1.50	>0.10	not
H/PFA	6.36	0.34	11				signif.
S/OPC vs.	7.90	0.43	12	22	1.52	>0.10	not
S/PFA	7.80	0.53	12				signif.
20 C vs.	5.42	0.32	8	51	9.03	<0.005	highly
elev. temp.	7.58	0.66	45				signif.

FIGURE 6.1: CRUDE OIL ABSORPTION OF OVEN DRY MORTAR SPECIMENS.

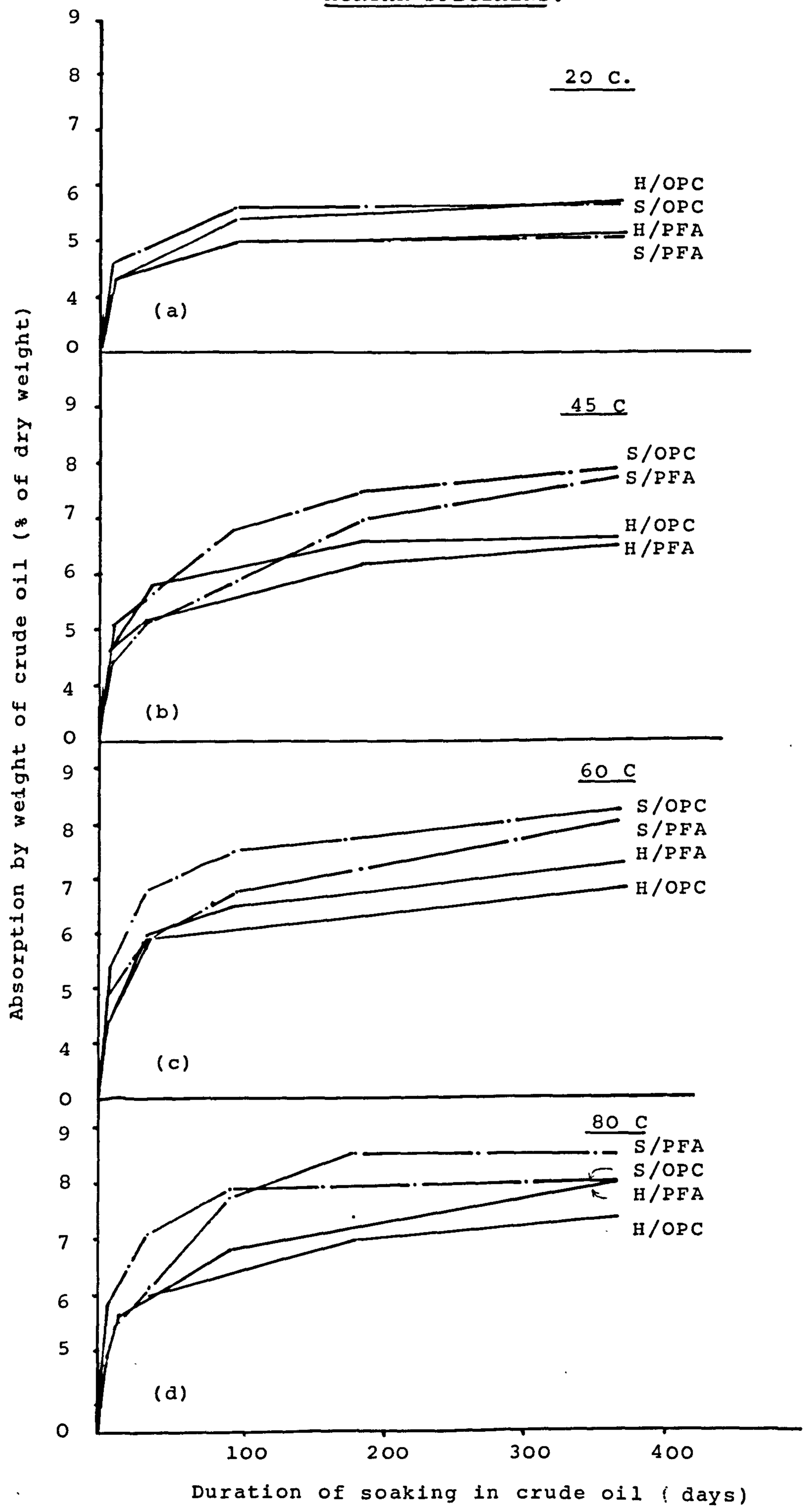
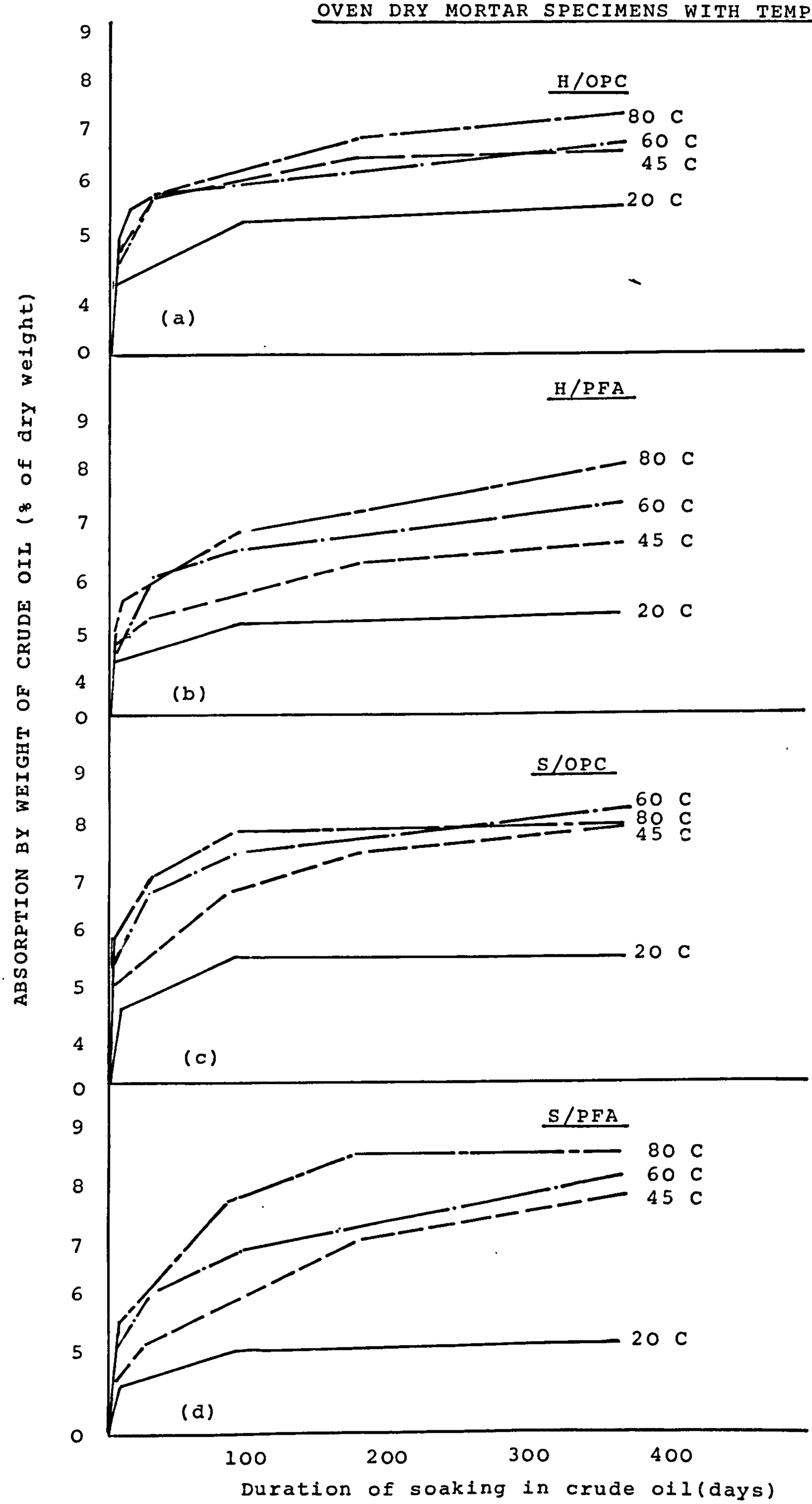


FIGURE 6.2: VARIATION OF CRUDE OIL ABSORPTION OF OVEN DRY MORTAR SPECIMENS WITH TEMPERATURE.



6.2.2.2 Moisture saturated specimens

The weight changes of moisture saturated mortar specimens soaked in crude oil at the 4 test temperatures, when measured after cooling, are shown in Fig. (6.3) as a function of time. Absorption of water by the control specimens are shown in Fig. (6.4). The results indicated that moisture saturated mortar specimens had shown no significant weight changes either in crude oil or in water, irrespective of the temperature of storage. In crude oil, weight losses were observed whereas in water, moisture absorption had taken place. The ultimate weight changes at 365 days in both crude oil and water were on average less than 0.5 percent. This amount is considered to be insignificant.

6.2.3 Discussion of the results of crude oil absorption

6.2.3.1 Oven dry specimens

The absorption of crude oil in oven dry concrete and mortar specimens is influenced amongst other factors by, (1) the viscosity and molecular size of the fluid, (2) the pore size range and pore size distribution of the specimen, (3) the volume of pores within the specimen which is accessible to the fluid and (4) the nature of the physical and chemical interaction between crude oil and the cement paste (viz. polarity, "affinity", etc.). All these factors are significantly influenced by elevated temperature.

The viscosity of the fluid would play a role in its motion through the specimen. The molecular size of some of the fractions of North Sea crude oil can be as large as 18 Å, while the gel pores in cement paste are as small as 4 Å and the "interlayer" spaces can be even smaller /61/. Furthermore, crude oil is considered to be a non-polar fluid and there are no indications of the existence of chemical interactions, or of any special affinity between cement paste and crude oil, as is known to exist between cement paste and water, and possibly with some other polar

organic liquids /169/. Saturation of the oven dry specimens with crude oil can therefore be expected to be difficult and almost impossible to achieve. At ambient temperatures, crude oil penetration of the specimens would probably be limited to the larger pores.

High temperature can significantly affect the residual absorption of crude oil in the specimens. The role of temperature can be either (a) directly through crude oil acting as a carrier of thermal energy, or (b) in the form of thermal cycling, which can lead to microcracking. The direct effect of temperature can cause expansion of the gel, widening of existing microcracks and the formation of new ones, both in the gel and at the cement paste/aggregate interface. The latter results from differential thermal expansion between aggregates and the paste. The higher the temperature, the greater is the damage to the microstructure. Since temperature also causes reduction in fluid viscosity and increases its mobility, fluid penetration of the inner pores of cement paste may increase and consequently, absorption would also increase. The effect of temperature as described, may explain why the rate of crude oil absorption and the ultimate absorptions of the specimens, were higher the higher the storage temperatures. Results have shown that temperature cycling, as a result of cooling the mortar specimens prior to testing, was not significant. Test measurements of specimens which were cycled, were comparable with those of specimens not cycled (see Chapts. 3 and 8).

The instantaneous absorption observed in all specimens during the first stage of absorption, can be attributed to the crude oil molecules occupying the larger, penetrable, moisture evacuated spaces in the oven dry specimens. The rate of absorption had reduced as the number of large penetrable spaces reduced (second stage). It is possible that the reason for the very small rate of absorption in the third stage, in which absorption had even stopped for the specimens stored at 20 C (Fig.6.1a), was because the crude oil molecules had already filled up the larger pores and were unable to penetrate the smaller pores. The expansive effects of temperature and the increased mobility of the fluid on heating, may explain the continued, though small rate of absorption in specimens stored at elevated temperatures.

Absorption of crude oil was larger in the seawater cured specimens (S/OPC and S/PFA), than in the specimens cured at 100% RH (H/OPC and H/PFA), because of the effect of curing. It was seen in Chapter 5 that the seawater cured specimens had expanded significantly more than the specimens cured at 100% RH by the end of the period of curing, and later they had contracted more when oven dried at 105 C. These suggest that relatively, the seawater cured specimens had greater gel porosity than the specimens cured at 100% RH, and is likely to be the reason why they had comparatively larger absorption of crude oil.

As expected, absorption of crude oil by the oven dry specimens was less than the absorption of water by the similarly prepared control specimens. This can be related to the smaller sized water molecule and also to the physical/chemical interaction between HCP and water (viz. polarity, affinity, hydration, etc.), which is absent between cement paste and crude oil. It is also possible that the clogging of the pores of cement paste by the large molecules of crude oil (eg. wax) may have played a part in the lower absorption by the specimens.

Oyeka /143/ and Matti /119/, had at different times investigated absorption of Kuwait crude oil by oven dried HCP and concrete at ambient temperatures. Oyeka /143/ did not obtain full replacement of water loss with crude oil and found the difference to be about 10%. However, Matti /119/, appeared to have obtained 100% crude oil replacement of water loss. This appears erroneous, since the smaller gel pores vacated by water cannot be penetrated by the crude oil molecules which are larger. The results of Oyeka on crude oil absorption are generally in agreement with the findings of this thesis.

FIGURE 6.3: WEIGHT CHANGES OF MOISTURE SATURATED MORTAR SPECIMENS SOAKED IN CRUDE OIL.

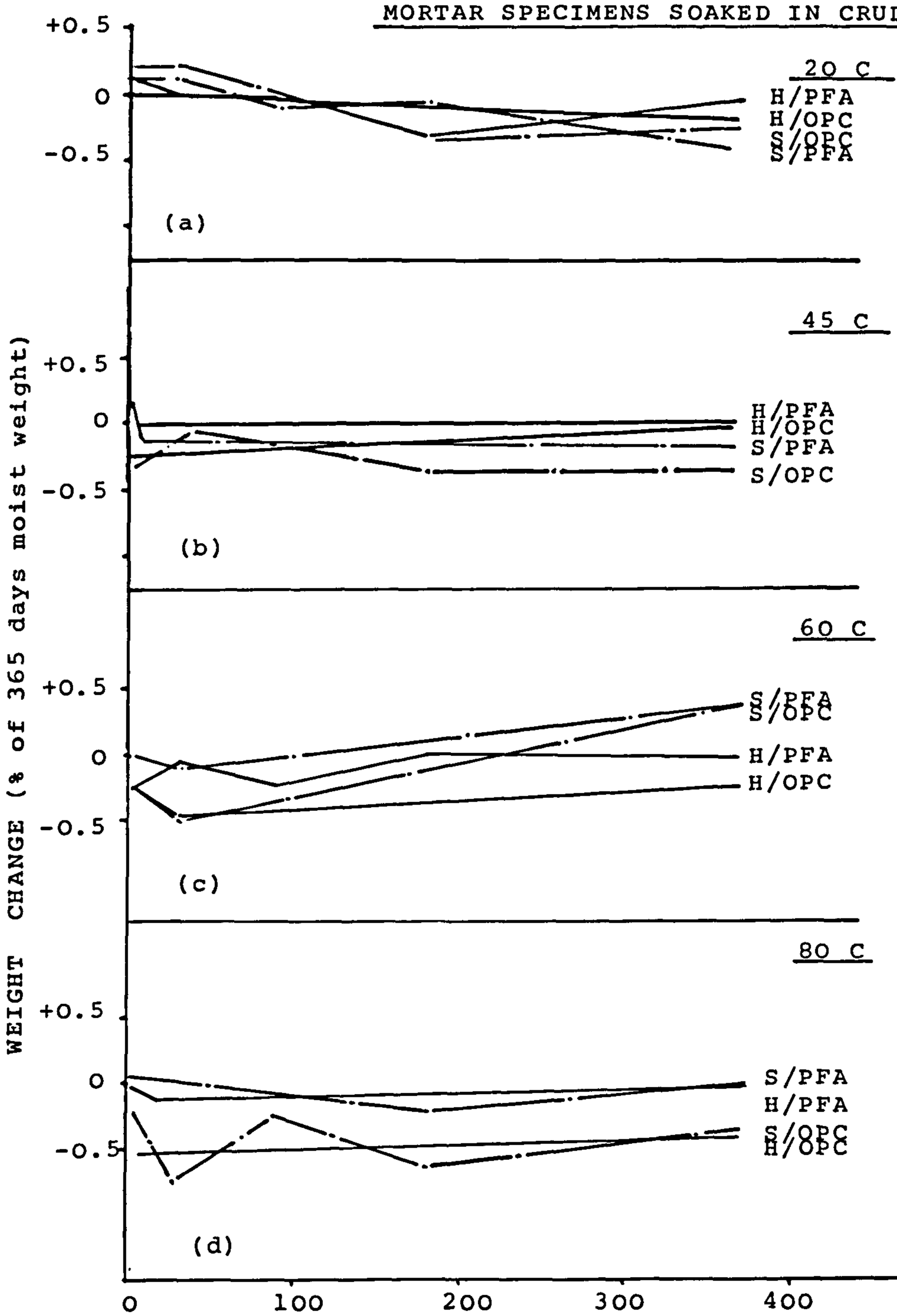
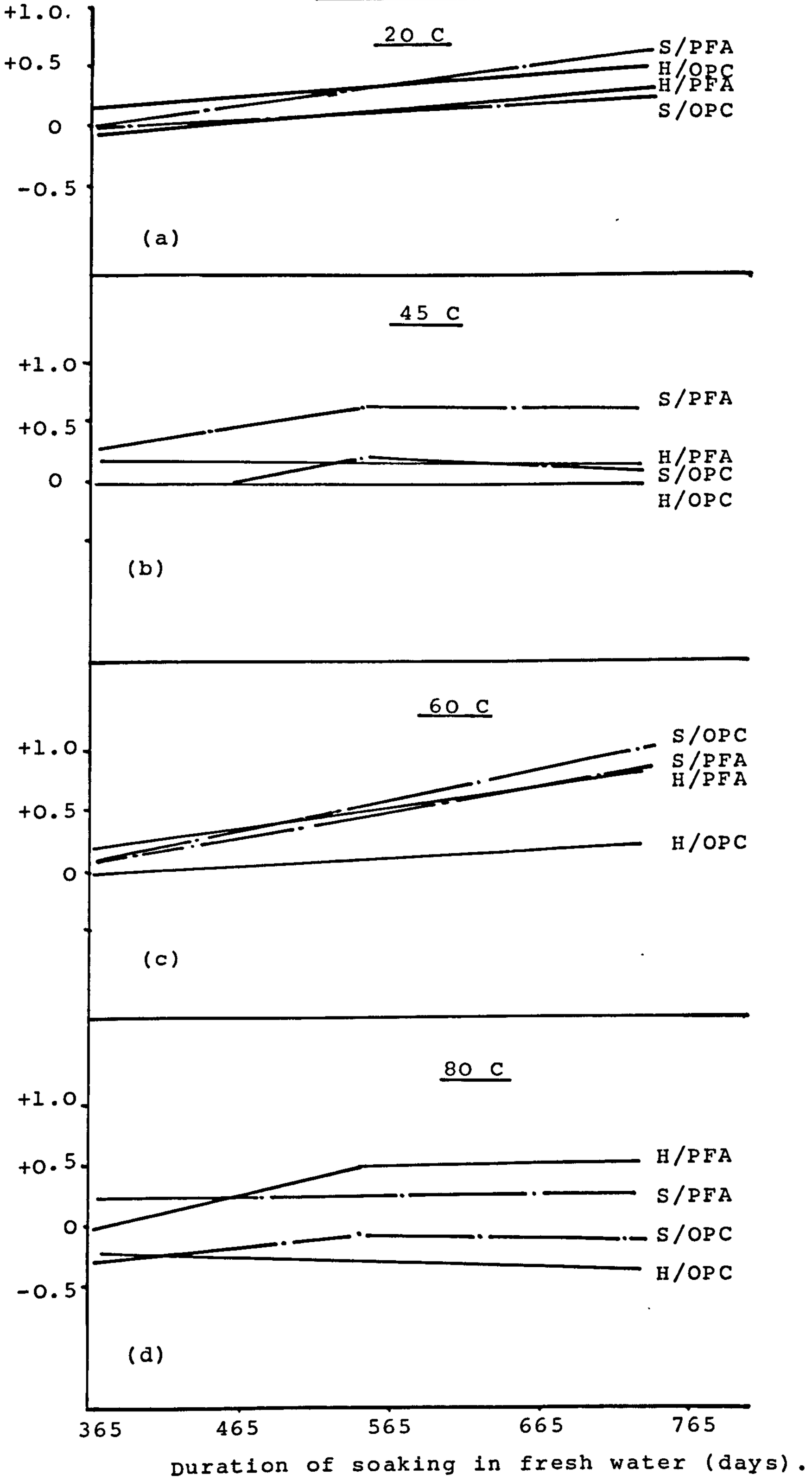


FIGURE 6.4: WEIGHT CHANGES OF MOIST MORTAR SPECIMENS SOAKED IN WATER AFTER CURING FOR 365 DAYS.



6.2.3.2 Moisture saturated specimens

Crude oil did not penetrate the moisture saturated concrete and mortar specimens, even for specimens stored at elevated temperatures. This follows from the discussions of the previous section as regards the physical/ chemical interaction between cement paste and water, and fluid molecular size. In addition, crude oil is less dense than water and being non-polar, cannot displace water (polar) from the specimen pores.

Matti /119/ did not achieve saturation with crude oil when moist 100mm concrete cubes of low water/cement ratio (0.4) were soaked in Kuwaiti crude oil, even after 6 months exposure and sometimes at hydrostatic pressures of 240 - 275 kN/m2. However, it was reported that penetration of about 19mm was achieved after 6 months, although the distribution was non-uniform and appeared to be in patches /119/. Similarly, Maxon and Achenbach /122/ did not achieve saturation when moist concrete cylinder specimens of low water/cement ratio were soaked in pentane.

Interestingly, Hrennikoff /85/ had found that when kerosene saturated concrete specimens were placed in water, they began to absorb water without displacing the kerosene and at the same time, the specimens swelled significantly. It was suggested that water had entered the cement paste by creeping along the surface of the C-S-H particles, which confirms that a special affinity exists between cement paste and water.

6.3 PENETRATION OF CRUDE OIL INTO CONCRETE AT ELEVATED TEMPERATURES

6.3.1 Introduction

The penetration of crude oil at elevated temperatures through oven dry concrete, has been investigated non-destructively by studying the relationship between the depth of crude oil percolation along the concrete vertical axis, and time. The purpose built CLIF apparatus used in this study and the method of preparation of test specimens, have been described in Chapter 4. Tests were conducted at 4 temperature levels of 20, 45, 60 and 75 C. The results are given and discussed in this section. From the relationship obtained between the depth of penetration and time [Figs.(6.6) to (6.9)], estimates of the coefficient of permeability, K, were calculated for all specimen types at each temperature (Table 6.8). The results of the investigation to determine the differential penetration of the crude oil fractions (aliphatic and aromatic) through oven dry concrete specimens, using the NMR technique, are also given in this section.

6.3.2 The penetration method of obtaining the Coefficient of Permeability

Studies of the penetration of water through concrete has resulted in the development of a mathematical relationship between the depth of penetration, x, and the coefficient of permeability, K. Valenta /197, 198/ has obtained the relationship in the form:

$$x = \sqrt{2 K h t} \qquad (6.1)$$

from which

$$K = \frac{x^2}{2 h t} \qquad (6.2)$$

where h is the hydraulic head of water sustained over a time period, t. More recently, Vuorinen /202/ has in addition considered the "open porosity" effect, for cases in which the specimen is kept immersed in water under atmospheric pressure. Equation (6.2) therefore becomes:

$$K = \frac{ax^2}{2ht} \qquad (6.3)$$

where a is the relative volume of open pores in concrete which do not become filled by capillary absorption when the specimen is kept immersed in water under atmospheric pressure. The depth of water penetration was determined by splitting the test specimens and observing the changes in colouration. Sections penetrated by water were found to be darker in colour than the rest of the surface /202/. It has been suggested that on average, the open pore space of concrete is about 80% of the air content of fresh concrete /202/.

The coefficient of permeability, K, is generally obtained by assuming Darcy's law, that flow of water is uniform through oven dry concrete. However, it is known that flow through concrete is not uniform, geometrically or otherwise and is restrained, amongst other factors, by (i) the continued hydration in the cement paste, in the case of wet concrete (ii) the physical/chemical interactions between the fluid and the cement paste (iii) the clogging of pores with particle from the fluid and (iv) the non-uniform fluid movement through surface cracks and cracks within the concrete and, through microcracks in the cement paste.

VALENTA /198/, in developing the mathematical relationship of Eq.(6.1) assumed unsteady percolation of water through concrete under a hydraulic head hr, where hr is the difference of real water head and capillary elevation (Fig.6.5). The velocity of water, v, at any stage of percolation can be given as

$$v = K.I = K.(hr/x) \qquad (6.4)$$

and since the increase of percolation depth

$$dx = v.dt = K.(hr/x).dt$$

then by integrating, the depth of percolation becomes

$$\frac{x^2}{2} + C = K.hr.t \qquad \text{at } x = 0,\ t = 0 \text{ and } C = 0$$

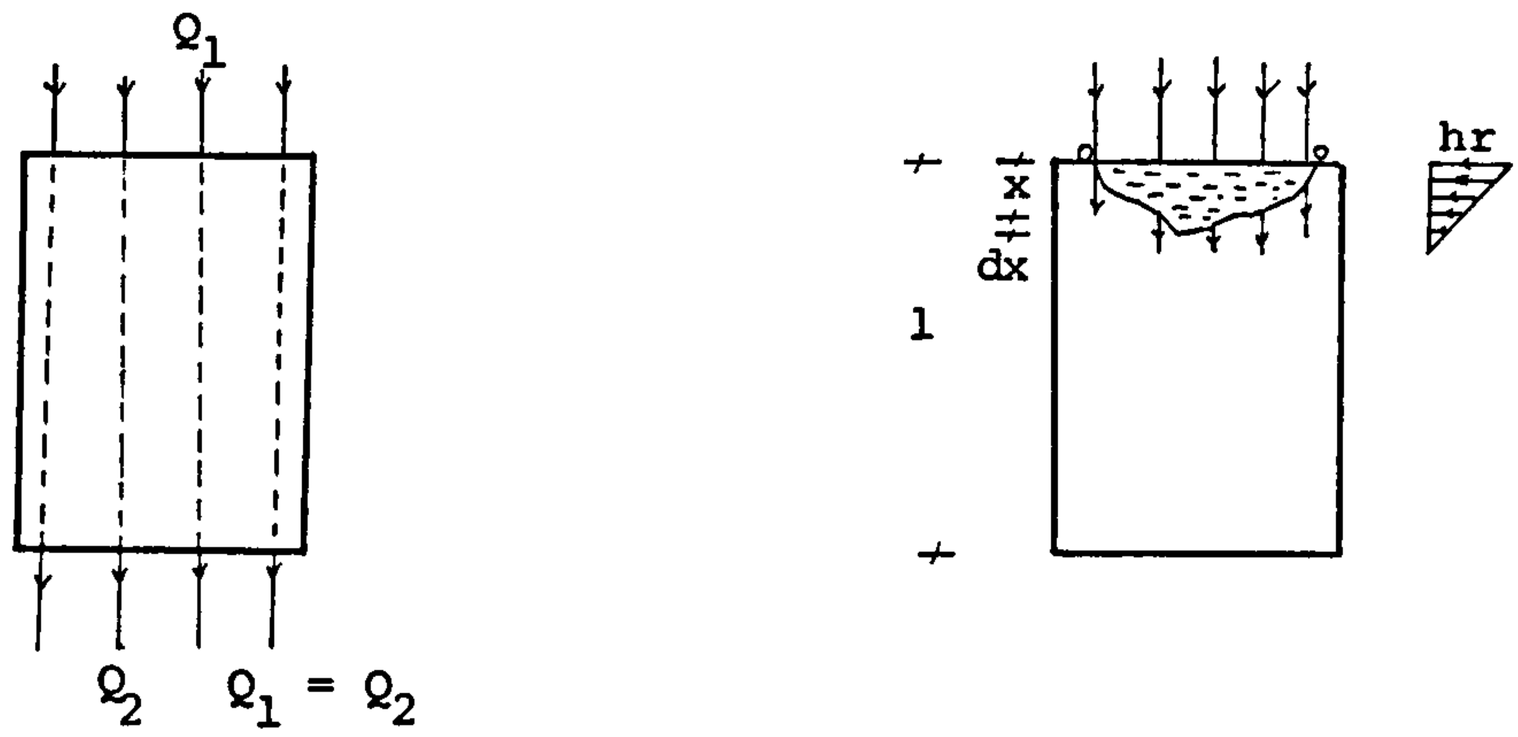
therefore;

$$x = \sqrt{2\,K.hr.t} \qquad (6.5)$$

which is Valenta's formula and from which K has been obtained as

$$K = \frac{x^2}{2.hr.t} \qquad (6.6)$$

Equation (6.6) is approximate in that it does not account for the time necessary for filling up large pores on the flow channels. It also ignores the "counterpressure" /202/ that develops within the air filled pores and which opposes and reduce the intrusion of water into the pore. Nevertheless, the method is a quick and suitable method for obtaining estimates of the coefficient of permeability.



(a) steady water percolation (b) unsteady water percolation

Figure 6.5 : Flow of water through concrete

6.3.3 Modification of Valenta's Formula

By assuming a linear hydraulic flow through concrete in Eq.(6.4), Valenta/198/ had in principle applied Darcy's law, the validity of which has often been questioned for flow through granular materials /38, 72/, especially those of low-permeability /66/. A more general form of Eq. (6.4) can be given as;

$$v = K.(hr/x)^n \qquad (6.7)$$

where n is a function of the velocity of flow of the fluid and its viscosity. The relationship assumes non-linear flow and goes beyond the

range within which Darcy's law is valid, when n is not equal to unity /66/. By integration and substitution and assuming that n = m - 1 in Eq. (6.7), a more general equation of the depth of penetration at any time, t, for flow through concrete can be obtained as:

$$x = (m.\ K.\ h.\ t)^{1/m} \qquad (6.8)$$

where $h = (hr)^{m-1}$

6.4 TEST RESULTS

6.4.1 Depth of Penetration vs Time

Insitu measurements of the depth of penetration of crude oil through the oven dry concrete specimens is plotted against time in Figures (6.6) to (6.9), at each temperature. The effect of temperature on each concrete type is shown in Fig.(6.10). The time of saturation is plotted against temperature in Fig.(6.11). The results were analysed using the t-Test of significance between the difference of means, details of which are given in Table (6.5). The following observations can be made:

(1) Penetration of crude oil through oven dry concrete was faster through the specimens cured in seawater (S/OPC and S/PFA), than through the specimens cured at 100% RH (H/OPC and H/PFA). The difference in the time of penetration between the two pairs was highly significant.
(2) The S/OPC specimens achieved the fastest rate of oil penetration, irrespective of the storage temperature. The H/OPC and H/PFA specimens had the slowest rate of oil penetration at all temperatures [Figs.(6.6) to 6.9)].
(3) The rate of crude oil penetration varied with temperature and, saturation was achieved faster, the higher the temperature (Fig.6.10). Statistical analysis showed that the difference between the rate of oil penetration at 75 C and at the lower temperatures, was significant.

(4) The relationship between the depth of penetration, x (m) and time of penetration, t (s) can be expressed as a power function of the form:

$$x = A.t^{b} \qquad (6.9)$$

values of A and b were obtained by regression analysis at each of the 4 test temperatures and are given in Table (6.6).

(5) By substituting for A in Eq.(6.9) and b = 1/m, a more general form of Eq.(6.8) from which K can be determined is;

$$x = (m.K.h)^{1/m} . t^{1/m} \qquad (6.10)$$

(6) A plot of the regression constant b (Table 6.6) against temperature (Fig.6.12), showed that b does not vary with temperature. The range of b lies between 0.3 and 0.6 for all specimens, except the S/OPC which had shown a clear deviation from the trend.

(7) Statistical analysis (Table 6.7), indicated that the difference between the values of b for the H/OPC, H/PFA and S/PFA specimens was not significant. An overall mean for all 3 specimen types, at all temperatures was obtained as **0.43**. This, essentially, is in agreement with Valenta's formula /198/ for flow of water through concrete.

6.4.2 Estimation of the Coefficient of permeability, K

The coefficient of permeability, K, has been obtained at the 4 test temperatures, for all specimen types, by applying Eqs.(6.9) and (6.10) and substituting the results of Table (6.6) at crude oil head of 300mm. The results which are given in Table (6.8) and plotted as a function of temperature in Fig.(6.13), showed a wide scatter of K, for the different specimens. It can be seen that at 20 C, the coefficient of permeability, K, was lowest for the H/OPC specimens, but the range of K was similar for the other specimen types. However, it was difficult to establish any definite trends at elevated temperatures, although it seemed that the specimens containing pfa (H/PFA and S/PFA), had lower values of K than the H/OPC and S/OPC specimens, for example at 45 and 60 C (Fig. 6.13). The values of K obtained at elevated temperatures for the S/OPC

specimens have been ignored because they fall well out of any realistic range and may be misleading.

6.4.3 NMR analysis of crude oil penetration through oven dry concrete specimens

The NMR technique is able to distinguish the two main hydrocarbon components of crude oil. These are respectively the aliphatics which are saturated and non-reactive, and the aromatics which are unsaturated and may be mildly reactive. A measure of the proportion of aliphatics to aromatics flowing through oven dry concrete specimens, was obtained by running a proton-spectrum of crude oil samples from different depths of the specimens. The results were plots of signal-Intensity (absorption), against measures of the magnetic field. The peaks obtained were integrated and represent a measure of the hydrogen contents of the organic material, rather than the quantities of aliphatic and aromatic contents (see Appendix C). The ratio thus obtained are given in Table (6.9) and were plotted against depth of penetration at each temperature (Fig.6.14) Details of the technique and the methods of running the spectra, can be found in texts on NMR Spectroscopy /2, 208/.

The results indicated an increasing presence of aliphatics relative to aromatics with increasing depth of concrete, irrespective of temperature or specimen type (i.e cement blend and method of curing). It would seem that concrete has acted as a filter, selectively retaining the aromatics while allowing passage to the aliphatics, similar to the behaviour of some clay rocks /54, 165/. The main reason for this seem to lie in the difference in the configuration and properties of the two fractions. The larger molecular size and the hexagonal shape of the aromatics makes penetration of the small pores in concrete difficult. On the other hand, the aliphatics, with smaller surface area due to the straight chain configuration, are better able to penetrate such pores. It is also possible that the mildly reactive aromatic fractions adhered to the cement paste pore structure and were not observed in the fluid flow. However, this is difficult to determine since there were no tests on the concrete specimens after crude oil penetration.

FIGURE 6.6: Depth of oil penetration into oven dry concrete vs. Time (20 C).

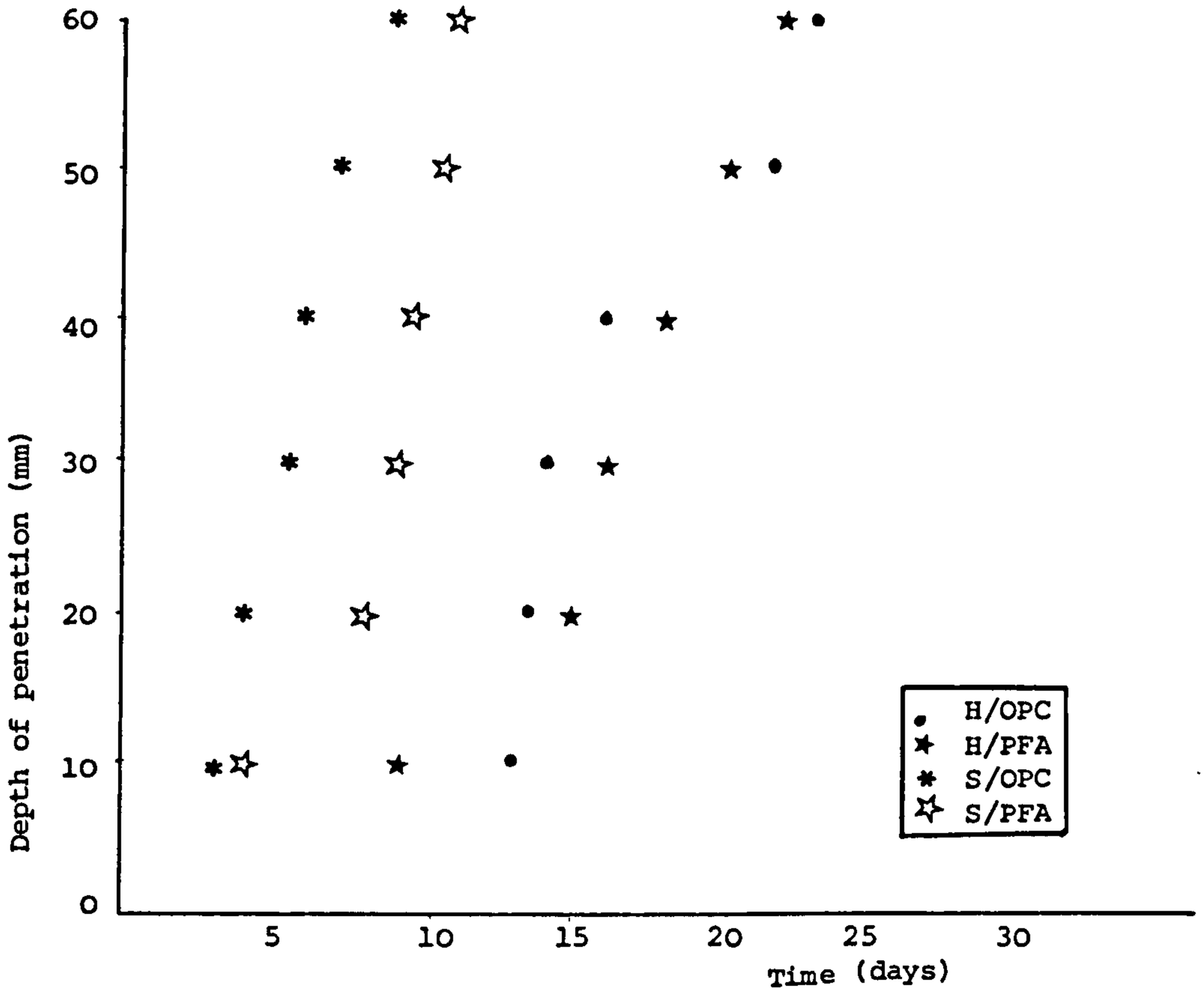


FIGURE 6.7: Depth of oil penetration into oven dry concrete vs. Time (45 C).

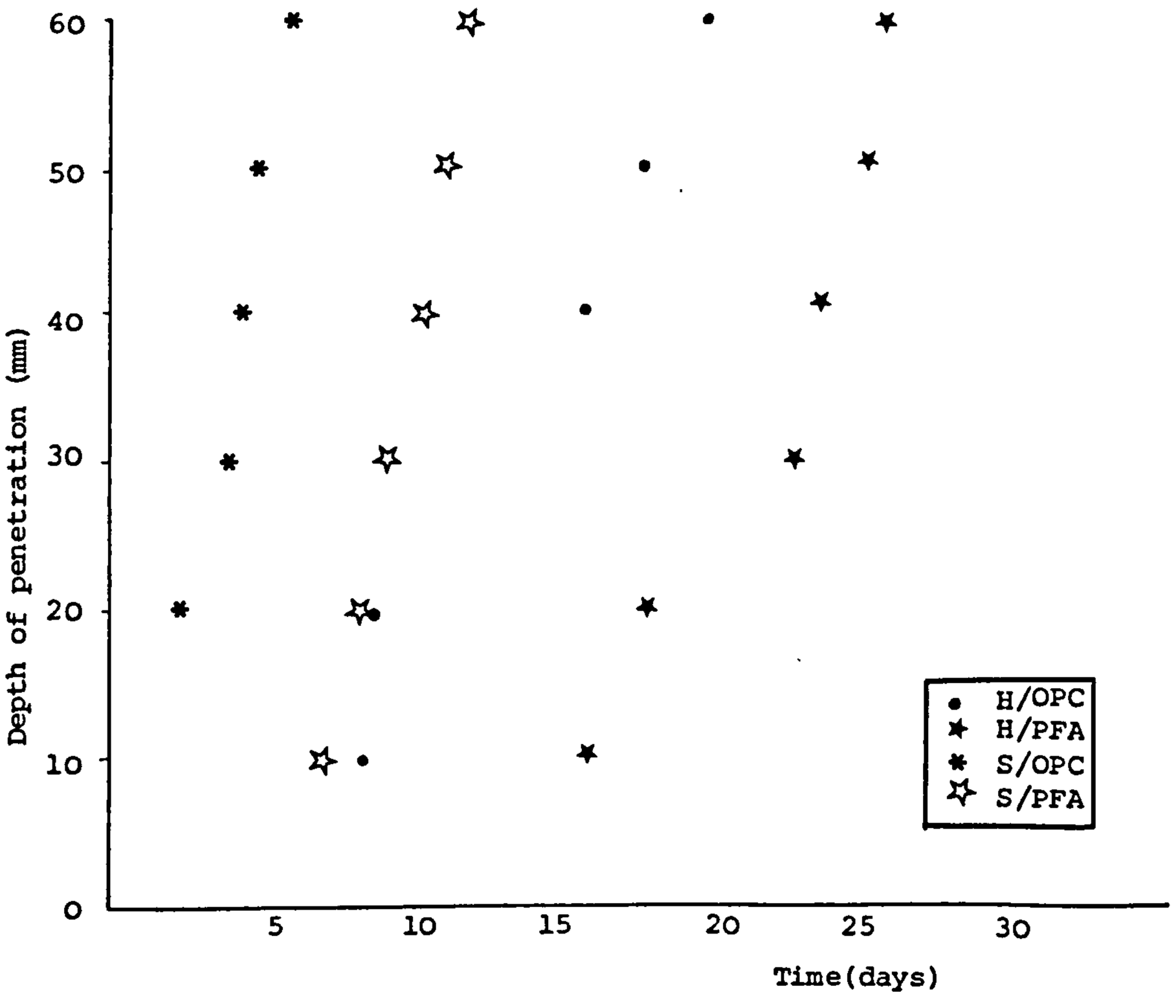


FIGURE 6.8: Depth of oil penetration into oven dry concrete vs. Time.(60 C)

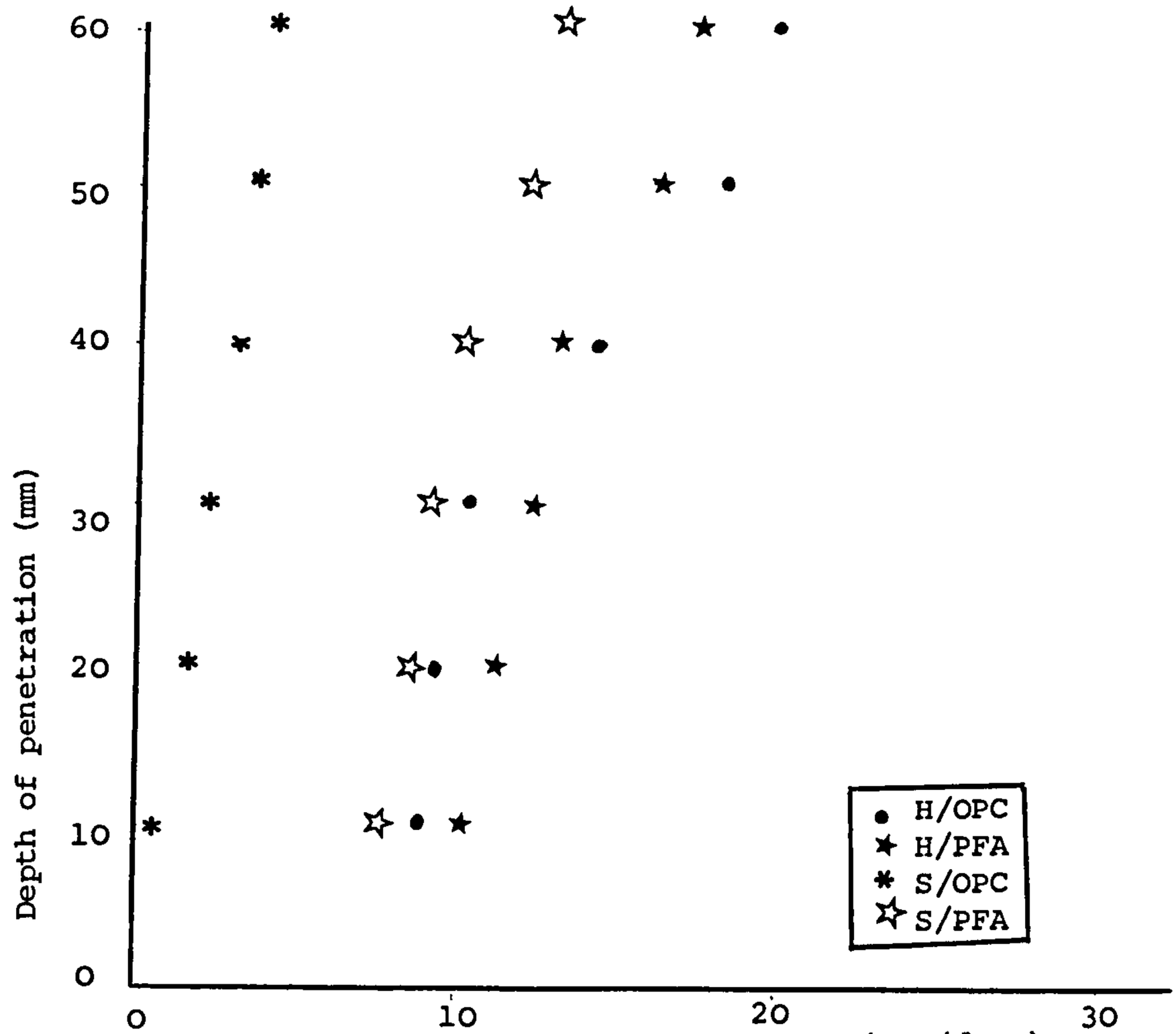


FIGURE 6.9 : Depth of oil penetration into oven dry concrete vs. Time (80 C).

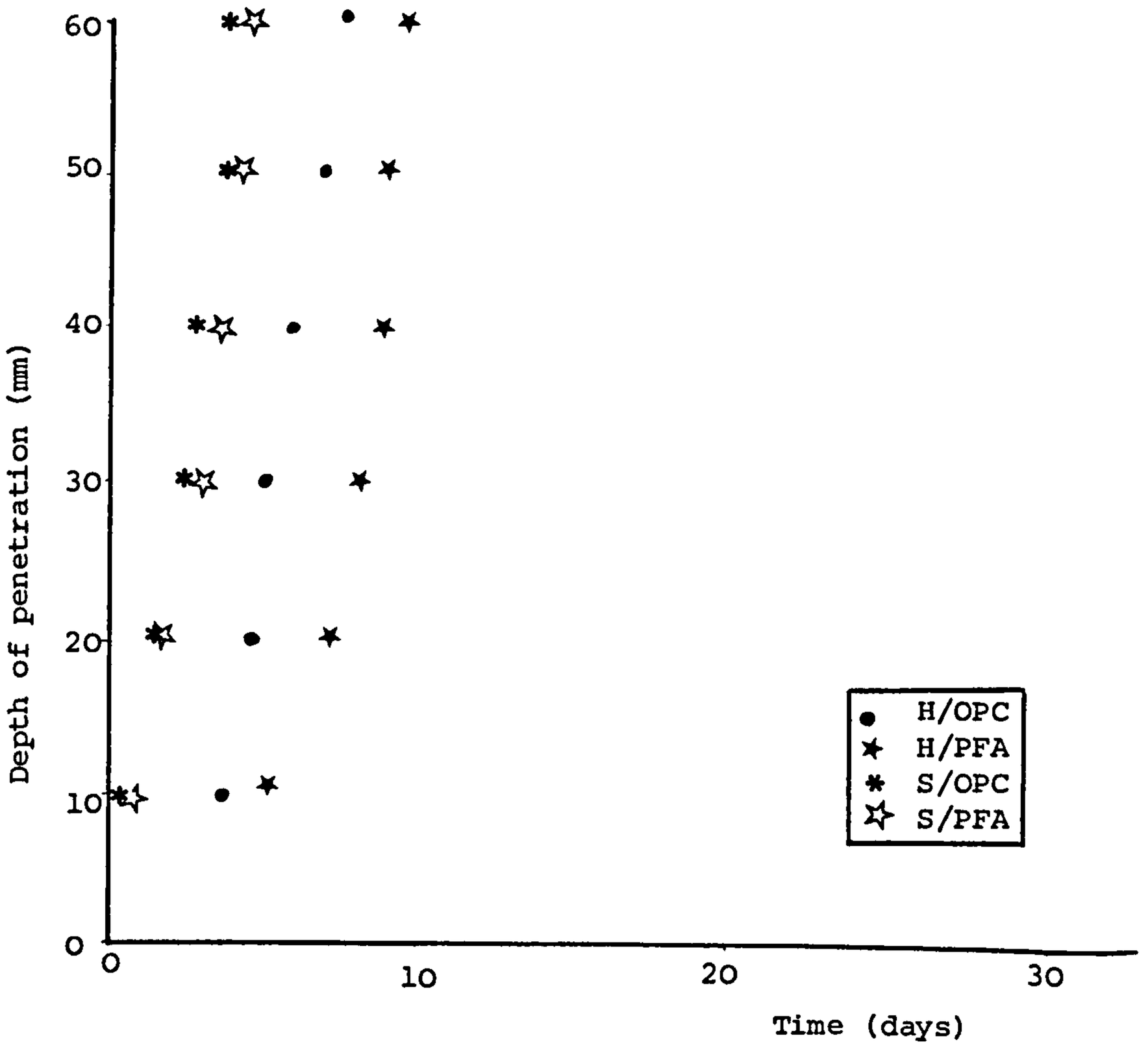


FIGURE 6.10: Effect of temperature on the depth of penetration with time for:

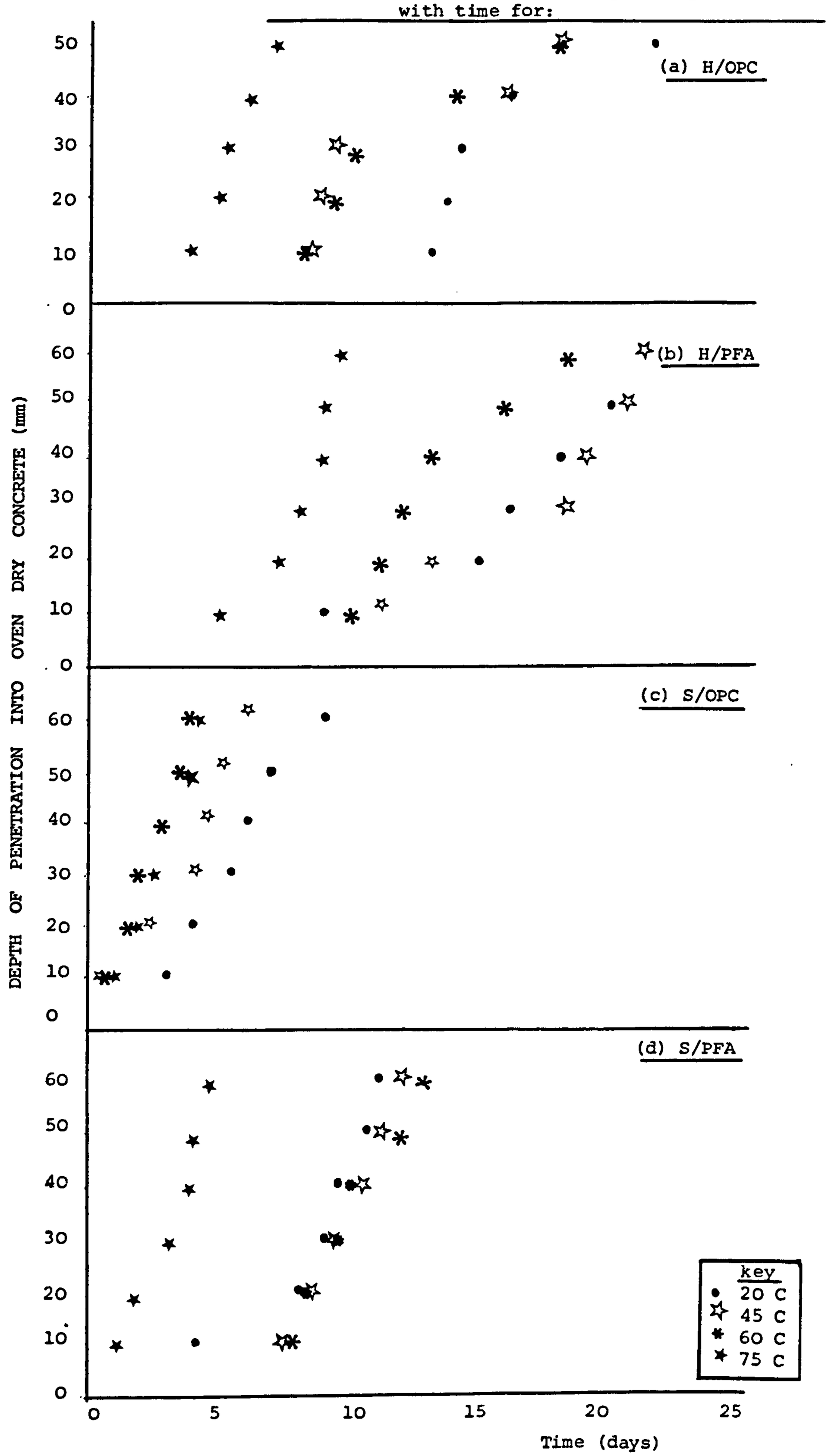


FIGURE 6.11: Time of crude oil saturation of oven dry concrete specimens vs. Temperature.

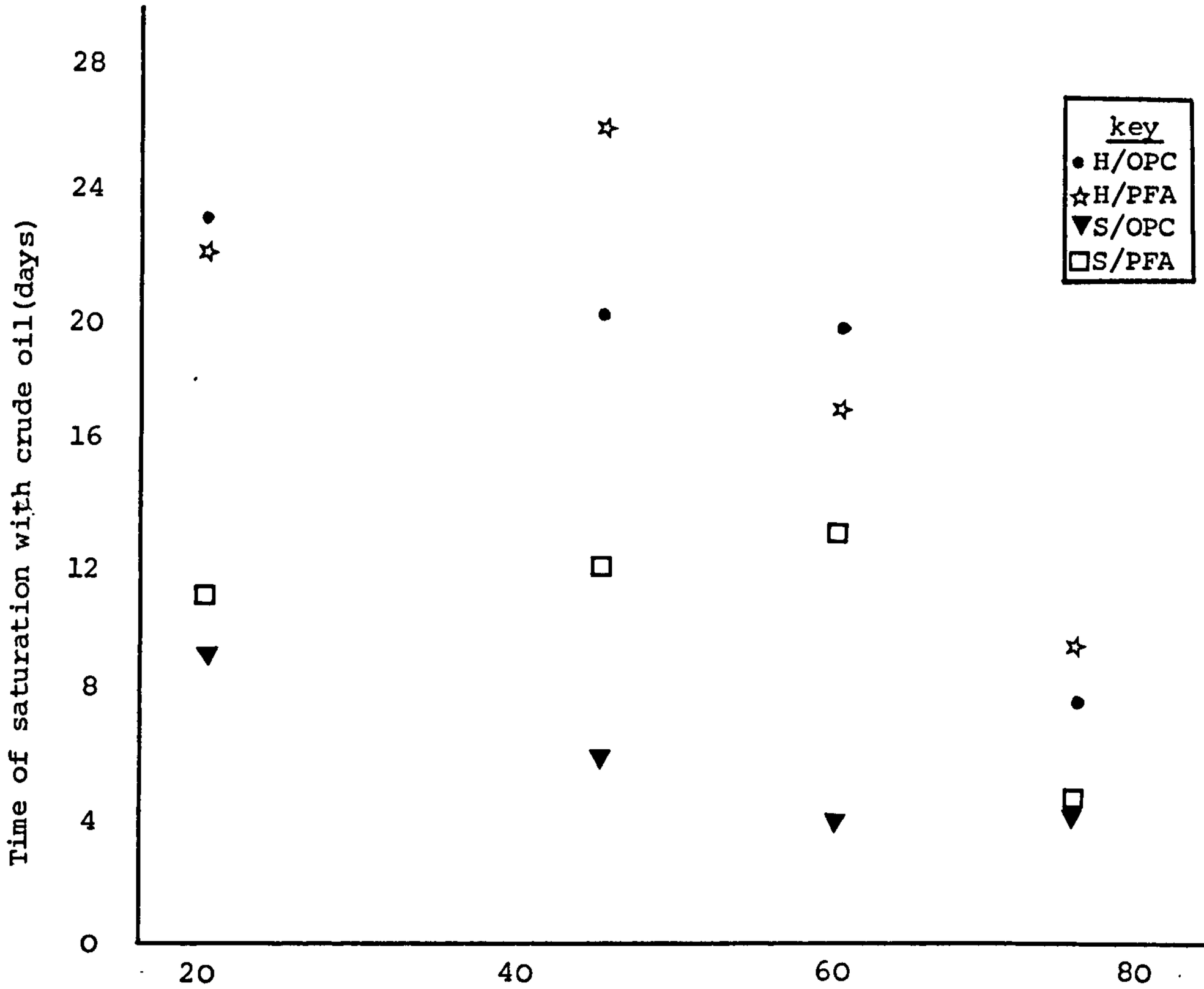


FIGURE 6.12: Variation of b(constant of regression) with Temperature.

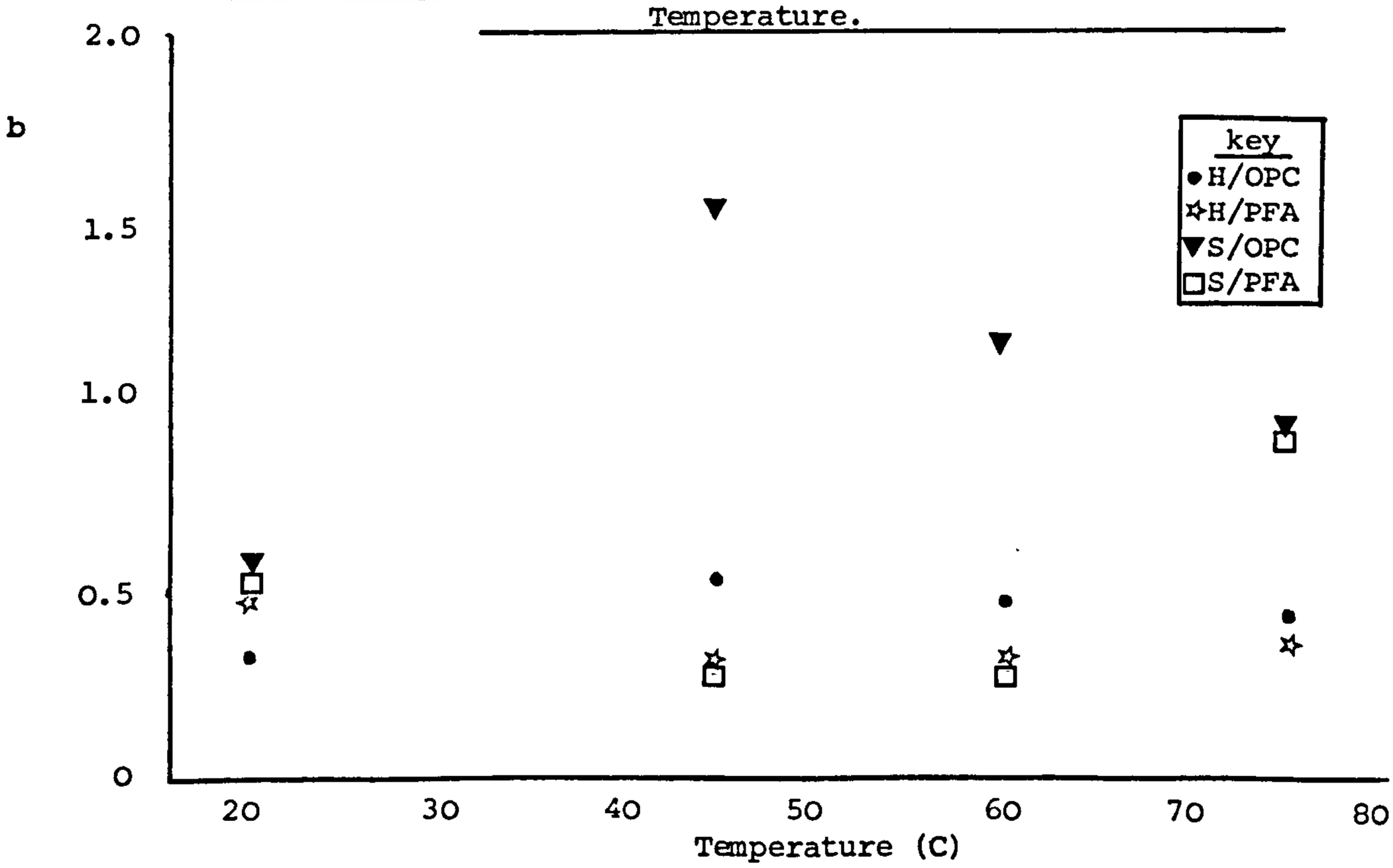


TABLE 6.5 : t-Test of significance of means of the results of Fig.(6.11) - Time of saturation of the concrete specimens with crude oil.

Test	mean m	no. of specs.	std. dev. s	DOF	t-value	prob. p	remark
100% RH vs seawater	18.06 7.94	8 8	6.49 3.76	14	3.817	<0.005	highly signif.
H/OPC vs H/PFA	17.50 18.63	4 4	6.84 7.11	6	0.228	>0.10	not signif.
S/OPC vs S/PFA	5.75 10.13	4 4	2.36 3.84	6	1.940	0.10	not signif.
Effect of temp.							
20 C vs 45 C	16.25 16.00	4 4	7.27 8.79	6	0.048	>0.10	not signif.
20 C vs 60 C	16.25 13.38	4 4	7.27 6.80	6	0.577	>0.10	not signif.
20 C vs 75 C	16.25 6.38	4 4	7.27 2.59	6	2.557	0.05	signif.
45 C vs 60 C	16.00 13.38	4 4	8.79 6.80	6	0.472	>0.10	not signif.
45 C vs 75 C	16.00 6.38	4 4	8.79 2.59	6	2.099	>0.05	may be signif.
60 C vs 75 C	13.38 6.38	4 4	6.80 2.59	6	1.924	>0.10	not signif.

TABLE 6.6 : constants of regression - Eq.(6.9) depth of penetration vs time.

Temp. (C)	constants	oven dry concrete specimens			
		H/OPC	H/PFA	S/OPC	S/PFA
20	r^2	0.73	0.96	0.97	0.90
	A (10^{-6})	4.36	7.13	3.66	4.56
	b	0.32	0.47	0.58	0.53
45	r^2	0.78	0.96	0.90	0.98
	A (10^{-6})	6.92	5.29	50.15	2.24
	b	0.53	0.30	1.53	0.30
60	r^2	0.80	0.88	0.97	0.89
	A (10^{-6})	5.68	3.16	11.04	2.41
	b	0.47	0.30	1.19	0.30
75	r^2	0.95	0.95	0.98	0.98
	A (10^{-6})	1.90	2.28	5.31	4.67
	b	0.40	0.35	0.94	0.87

TABLE 6.7 : t-Test of significance of means - comparison of b-values.

Tests	mean m	no. of specs.	DOF	t-value	prob. p	remark
H/OPC vs	0.43	4	6	1.240	>0.10	not
H/PFA	0.36	4				signif.
H/OPC vs	0.43	4	6	0.493	>0.10	not
S/PFA	0.50	4				signif.
H/PFA vs	0.36	4	6	1.032	>0.10	not
S/PFA	0.50	4				signif.
S/OPC vs	1.06	4	6	3.06	0.025	signif.
H/OPC	0.43	4				
S/OPC vs	1.06	4	6	3.45	0.02	signif.
H/PFA	0.36	4				
S/OPC vs	1.06	4	6	2.32	0.05	signif.
S/PFA	0.50	4				

TABLE 6.8 ; Calculated values of coefficient of permeability, K.

Temp. C	coefficient of permeability, K			
	H/OPC	H/PFA	S/OPC	S/PFA
20	7.32×10^{-17}	2.05×10^{-11}	5.87×10^{-10}	1.29×10^{-10}
45	2.83×10^{-10}	1.28×10^{-17}	-	7.32×10^{-19}
60	1.26×10^{-11}	2.31×10^{-18}	-	9.35×10^{-19}
75	1.21×10^{-14}	2.48×10^{-16}	-	-

FIGURE 6.13: VARIATION OF K WITH TEMPERATURE.

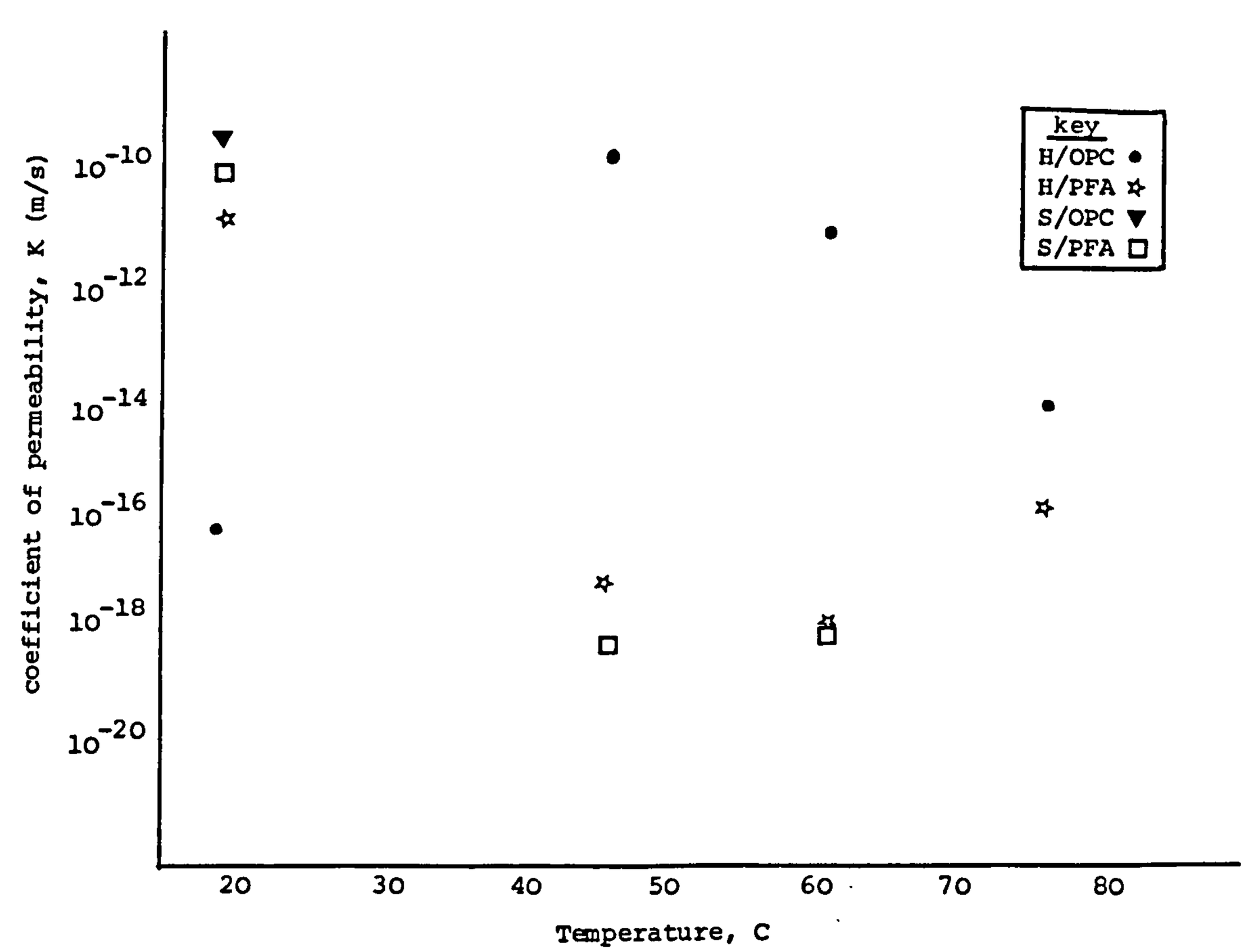
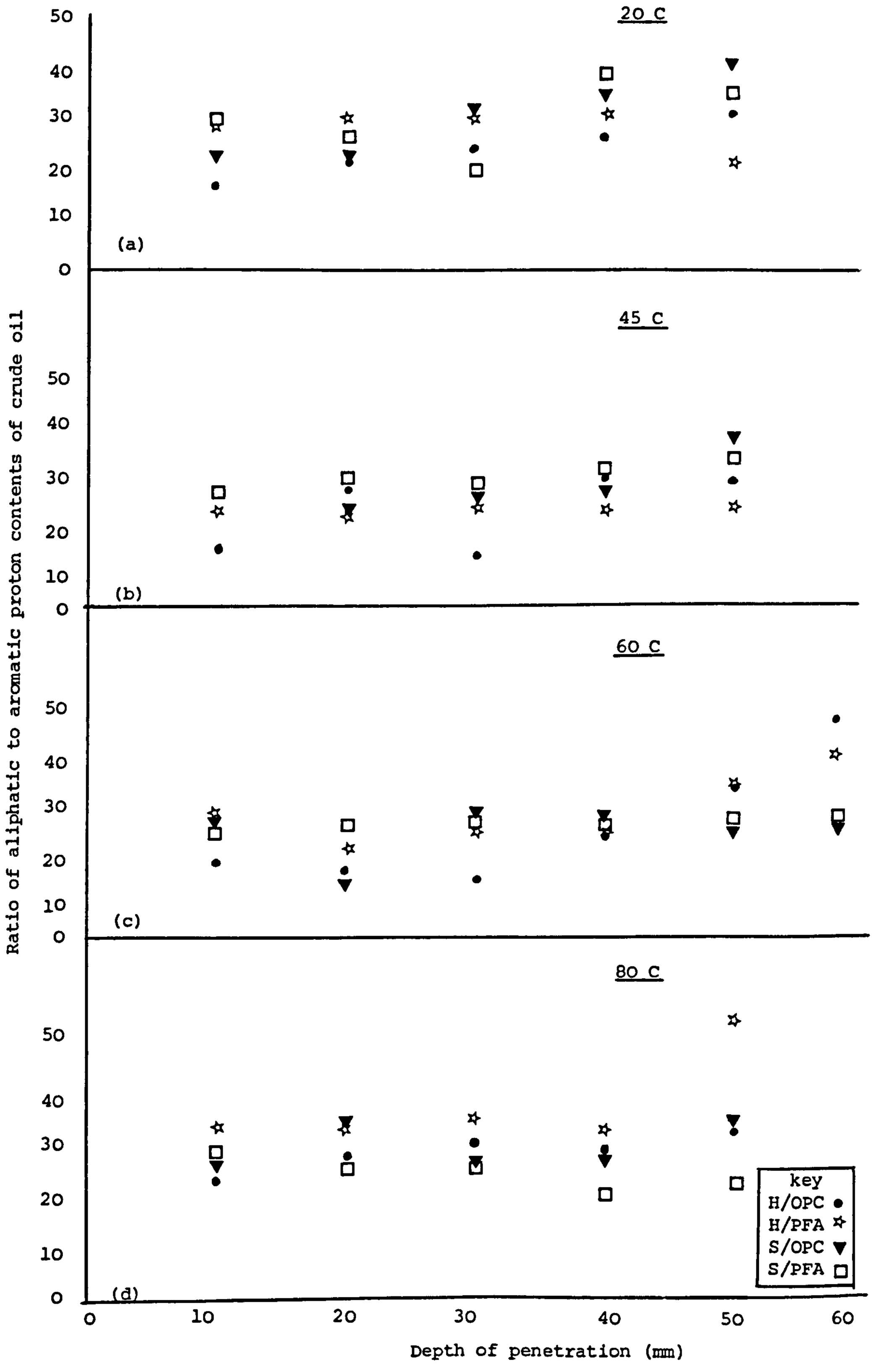


TABLE 6.9 : Ratio of aliphatic/aromatic fractions of crude oil penetrating at different depths of oven dry concrete.

Temp. C	depth (mm)	ratio of aliphatic to aromatic proton contents. H/OPC	H/PFA	S/OPC	S/PFA
		crude oil as recieved 1:25			
20	10	17.18	28.18	23.80	29.17
	20	21.05	29.59	21.36	27.36
	30	24.67	30.00	31.10	20.28
	40	25.29	30.40	34.00	42.67
	50	31.00	22.13	-	35.29
	outflow	43.20	-	52.75	-
45	10	16.60	23.24	23.05	27.22
	20	26.75	22.27	24.00	30.00
	30	15.05	23.87	25.86	27.90
	40	29.00	22.67	27.71	30.50
	50	29.00	24.45	38.43	28.07
	outflow				40.00
60	10	19.58	28.83	28.13	26.46
	20	17.89	22.18	15.30	27.38
	30	15.94	26.45	29.73	29.30
	40	25.50	26.13	28.73	25.88
	50	34.64	34.70	25.65	26.43
	outflow	47.88	41.15	26.77	27.50
75	10	22.67	32.71	26.17	27.33
	20	27.63	33.00	34.27	24.35
	30	29.88	35.40	14.59	25.42
	40	28.44	32.69	27.13	18.17
	50	32.13	54.22	-	21.60

FIGURE 6.14: RATIO OF AROMATIC TO ALIPHATIC PROTON CONTENTS OF CRUDE OIL PENETRATING INTO OVEN DRY CONCRETE.



6.5 DISCUSSION OF PENETRATION TEST RESULTS

The most important aspect of this study, has been to establish an equation (Eq. 6.8) for the flow of crude oil through oven dry concrete specimens. The relationship between the depth of penetration and the coefficient of permeability, was approximately a square root function, for which b was 0.43 (Eq. 6.10). This is similar to the finding of Valenta /198/ and also of Viruonen /201, 202/, both of whom obtained b theoretically as 0.50, for flow of water through dry concrete. Interestingly, Browne and Domone /27/ also obtained a similar relationship with b as 0.45, for flow of seawater through concrete. The differences obtained in the values for b is probably related to the differences in the fluid viscosities. The significance of these results is that the equation of flow of crude oil through oven dry concrete, is similar to that for flow of water and also of seawater through dry concrete. Matti /119/, in applying the diffusivity method of Murata /131/, had obtained a power function relationship between the depth of penetration and time, similar to that found in this study (Eq. 6.9). However, the average of 0.29 reported for b was well below the average of 0.43 obtained in this study.

The wide scatter of results obtained in estimating the coefficient of permeability, K, at elevated temperatures using Eq. (6.10), was probably an indication of the limitation of the relationship, since the effect of temperature has not been included. The inclusion of this factor requires further theoretical and experimental investigations, which is beyond the scope of this thesis. However, it is well known that the calculation of K, even at ambient temperatures, usually gives wide scatter of results /119, 134, 143, 204/. The reason for this is often attributed to several different factors, including the mix variables and the testing techniques. Oyeka /143/ and Matti /119/ investigated the permeability of concrete to Kuwaiti crude oil, the former tested specimens oven dried at 105 C and the latter tested specimens partially dried at 55 C. Matti obtained K empirically in terms of the depth of penetration, D (mm), penetration time, t (hrs) and crude oil pressure head, h (m) as:

$$K = \frac{(A^2 \; B.t^{-0.4285})}{h} \qquad (6.11)$$

where A = D/t^B and B is a constant = 1/3.4. It was found that K decreases with time. Oyeka /143/ assumed steady state laminar flow and calculated K from Darcy's law, under constant pressure heads of up to 1.034 N/mm2. K was also found to decrease with time, but increased with increase in the applied hydrostatic pressure, independent of the water/cement ratios. This was attributed to the direct effect of the pressure forcing more oil through the smaller pores,and possibly also to increased pressure breaking down some of the pore partitions, thereby creating more continuous pores.

Penetration of crude oil was found to be faster through the seawater cured oven-dry specimens (S/OPC and S/PFA) than through the specimens cured at 100% RH (H/OPC and H/PFA). This in line with the pattern of crude oil absorption earlier discussed and is related to the pore structure of the specimens, as was affected by the effect of curing (see section 6.2.3).

Penetration of crude oil through the specimens was faster the higher the temperature, due to the effect of elevated temperature (section 6.2.3). Temperature causes expansions in the specimens, often leading to microcracking. It also causes the fluid mobility to increase by reducing the viscosity, thereby speeding up the penetration.

CHAPTER VII

COMPRESSIVE STRENGTHS OF CONCRETE SPECIMENS EXPOSED TO CRUDE OIL AT ELEVATED TEMPERATURES.

7.1 INTRODUCTION

Results of the effect of crude oil at elevated temperatures, on the residual compressive strengths of concrete cylindrical test specimens, are given and discussed in this chapter. The compressive strengths prior to crude oil exposure were given in Chapter 5. The results are compared with those of similarly prepared control specimens which were soaked instead either in water (moist specimens), or reheated to the 3 elevated temperatures (oven dry specimens). Apart from serving as a basis for comparison of two different fluids, the control tests were also used in isolating separately, the effects of crude oil and of the elevated temperatures. All measurements were residual, since they were taken after the specimens had been cooled to ambient temperature. The significance of each main effect and the interactions, have been analysed by the Factorial method (see Chapter 3), which was conducted for each test period and for every temperature level. A summary of the result is given in Table (7.1).

The findings of these investigations were studied in conjunction with absorption and penetration characteristics of the specimens, reported in Chapter 6. The indications were that exposure conditions had caused changes to the specimen compressive strengths and these had varied with temperature and time, and can be related to the crude oil absorption of the specimens. The moisture condition of the specimens (moist or oven dry), prior to crude oil storage, had also influenced the results. Factorial analysis showed that this effect was significant (Table 7.1). The results of this study are, therefore, presented to reflect the moisture condition prior to crude oil storage and are given within the frame work of the single and multiple interactions.

Highlights of this study from trends observed, as well as from results of the factorial analysis were as follows:

(1) The method of curing prior to exposure to crude oil was highly significant and the effect on compressive strengths was evident throughout the duration of exposure to crude oil.

(2) The moisture condition of the specimens prior to exposure to crude oil was **significant.** The effect was prominent at the early stages of exposure up to about 10 days.

(3) Exposure of concrete specimens to crude oil at 45 and 60 C, was **highly significant** at the early stages of exposure, up to about 30 days. Exposure at 80 C was **highly significant** throughout the duration of testing.

(4) Strength losses had increased with increased crude oil absorption.

(5) The effect of blending opc cement with pfa was significant only at the early stages after soaking in crude oil. It seemed that the effect was interwoven with the method of curing.

(6) Compressive strength reductions of moist specimens soaked in crude oil were less than those of specimens which were soaked oven dry.

(7) There appeared to be no difference in compressive strength between moist specimens soaked in crude oil and those soaked in water. However, the difference in compressive strength between the oven dry specimens soaked in crude oil and those reheated at elevated temperatures was **significant** (Table 7.1).

(8) On exposure to crude oil, the S/OPC specimens (moist and oven dry) had the lowest compressive strengths. In the oven dry state, the relatively lower strength of the specimens can be related to the trend of largest crude oil absorption and fastest penetration, observed in Chapter 6.

(9) The trend of specimen compressive strengths over the entire duration of exposure in crude oil and in water fall into three periods; the instantaneous (up to 3 days), the early stages up to about 90 days and the long term, from about 180 to 365 days.

TABLE 7.1 : SUMMARY RESULTS OF THE FACTORIAL ANALYSIS.

MAIN EFFECTS	°C	3 days 20	45	60	80	10 days 20	45	60	80	30 days 20	45	60	80	90 days 20	45	60	80	180 days 20	45	60	80	365 days 20	45	60	80
CEMENT BLEND (A)		hs				-				-				-				-				-			
CURING METHOD (B)		hs				hs				hs				hs				hs				hs			
PRE-TREATMENT (C)		hs				hs				s				s				-				10			
EXPOSURE MEDIUM (D)		s				-				s				s				10				-			
TEMPERATURE (E)			hs	hs	hs		hs	hs	hs		s	hs	hs		s	-	s		-	-	hs		-	-	hs
Interactions in crude oil:																									
	AD	-				-				-				-				-				10			
	ADE		-	-	-		-	-	s		-	-	hs		-	10	-		-	-	-		-	-	10
	BD	-				-				-				-				-				10			
saturated	BDE		-	-	-		-	-	-		-	-	-		10	-	-		-	-	-		hs	-	10
moist soaked (multiple interactions)	ABD	s				-				-				s				-				10			
	ABDE																						hs		
	DE				s		hs	hs	s		s	-	s			hs			s		hs		hs		hs
	CD	s				-				10				10				s				hs			
	CDE											hs	hs				s				s				
oven dried	ACDE																								
(single interactions)	BCD																	s				10			
	BCDE				s		10	-	s								s								
	ABCD					s				-				s								s			
	ABCDE		10			s																			

key:
hs highly significant(1%) s significant (5%) 10 significant at 10% level.

note: for the different levels of main Effects, see Chapter 3.

7.2 RESULTS OF COMPRESSIVE STRENGTHS OF THE SINGLE INTERACTION TESTS

In most of the graphical illustrations given in this chapter, data points, each of which is an average of 3 measurements, have been omitted for clarity. Strength variations of individual test specimens from the mean were small and the average standard deviation was about 5.0 N/mm2, under all conditions of testing. The effect of exposure to crude oil on the residual compressive strengths of oven dry concrete specimens is shown in Figs. (7.1) through (7.4), for each temperature of storage. Reductions in strength from the oven dry strength prior to crude oil exposure had varied with temperature and time, as shown in Figs.(7.8) through (7.11) and given in Table (7.2). The results of compressive strengths of the control specimens reheated at elevated temperatures only, are shown in Figs. (7.5) through (7.7) and magnitudes of strength losses are given in Table (7.3). Comparisons are made with the results of the exposure to crude oil in Table (7.4). The relationship between crude oil absorption and the loss of strength are shown in Figs.(7.12) through (7.15), for each test temperature. Highlights of the results were as follows:

(1) The effect of crude oil on the compressive strengths of oven-dry concrete specimens stored at elevated temperatures was significant (Table 7.1), as compared with the compressive strengths of the specimens which were reheated at elevated temperatures.
(2) Three stages of strength variations were observed on exposure to crude oil. Strength losses had occurred at 3 days (first stage), these had increased gradually after this, up to about 180 days (second stage), but had increased significantly between 180 and 365 days (third stage), for specimens stored at elevated temperature (see Fig. 7.2). Strength levels had remained constant from about 30 days for the specimens stored at 20 C (Fig. 7.1).
(3) Exposure to crude oil had caused reductions in strength, which in some cases were very large and reached up to about 30% (eg. Figs. 7.2 and 7.4). Strength reductions had increased with time and the storage temperature (Figs. 7.8 to 7.11), and also as crude oil absorption had increased (eg. Fig. 7.15).

(4) The effect of temperature was significant throughout the period of storage. Factorial analysis indicated that exposure at 80 C was highly significant and was the most critical temperature of storage, while storage at 20 C was the least severe. In general, there was reduction in strength in all specimens with increasing temperature of storage, in particular, from after about 60 days. Storage at 45 and 60 C had caused similar magnitudes of strength reductions.

(5) The effect of blending opc cement with pfa did not seem to be significant, although in conjunction with the method of curing it may be significant.

(6) The H/PFA specimens had the largest average strength reductions, increasing from 13% for storage at 20 C, to 19% at 80 C (Fig.7.9). Interestingly, the S/PFA specimens had the least average reductions of between 4% and 10%, over the same storage temperature range. Average strength reductions for the H/OPC and S/OPC specimens varied by between 7% and 11%, and 10% and 12% respectively. The largest strength losses in all cases were in the specimens stored at 80 C.

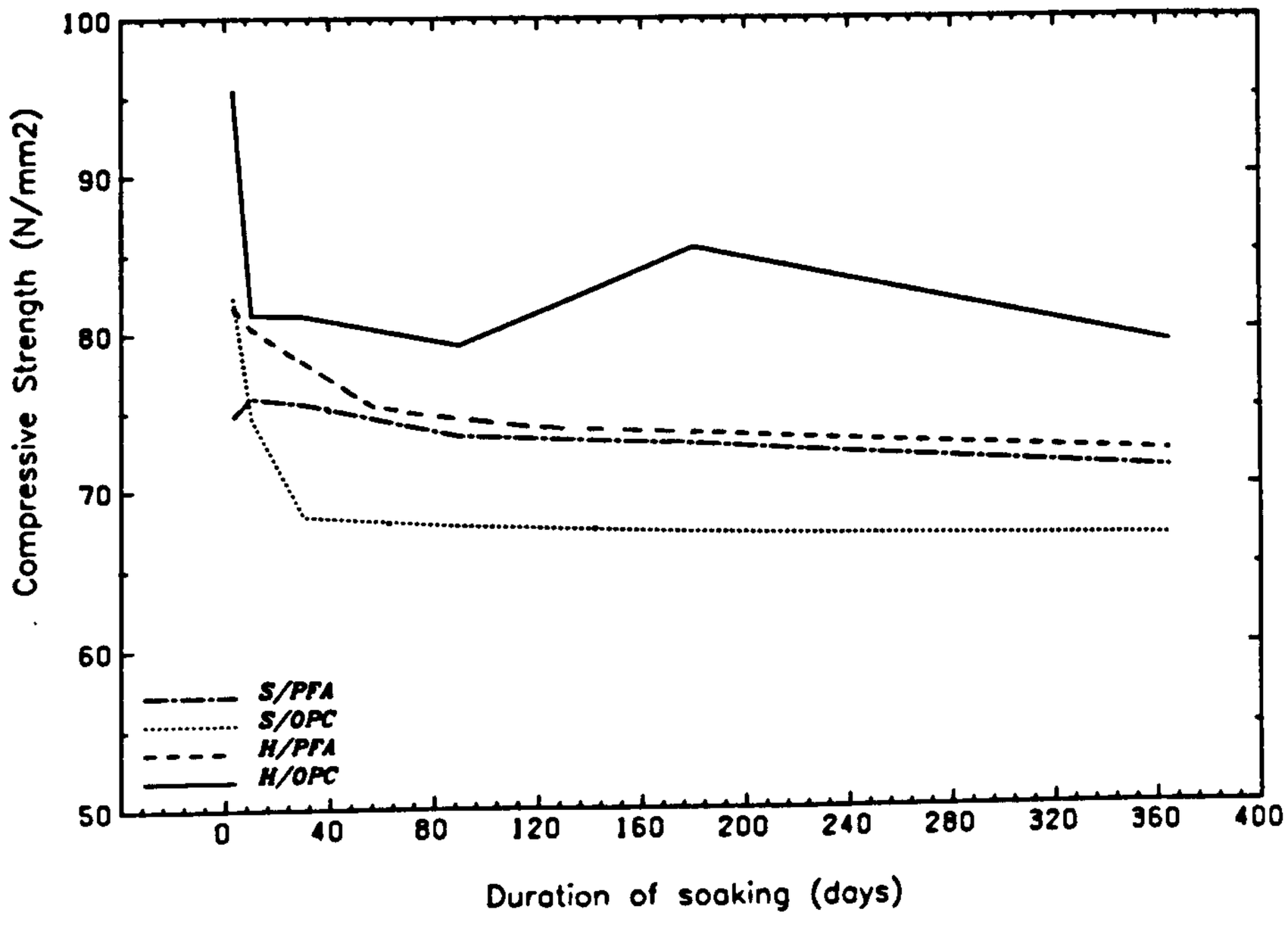
(7) A trend towards strength recovery was observed in the control specimens reheated to elevated temperatures of 45, 60 and 80 C, after large initial losses between 3 and 10 days. The losses were largest in the specimens cured at 100% RH (H/OPC and H/PFA) and did not seem to vary with temperature. On the other hand, the seawater cured specimens (S/OPC and S/PFA) had achieved strength increases the higher the storage temperature. This trend was the reverse of that observed in crude oil, in which reductions in strength had increased with increase in temperature and also as crude oil absorption had increased.

TABLE 7.2 : Compressive strength losses of oven dry concrete specimens soaked in crude oil.

Temp. (C)	Duration in crude oil (days)	Compressive strength losses (% change from oven dry strength)			
		H/OPC	H/PFA	S/OPC	S/PFA
20	3	+6.5	-4.6	+4.1	-2.7
	10	-9.5	-6.2	-5.8	-1.2
	30	-9.6	-8.8	-13.7	-1.7
	90	-11.7	-30.7	-14.4	-4.4
	180	-4.8	-14.0	-14.9	-5.1
	365	-11.7	-15.2	-15.6	-7.4
	average	-7	-13	-10	-4
45	3	-2.3	-15.1	+0.25	+0.4
	10	-0.3	-10.4	-15.0	+0.4
	30	-5.5	-8.3	-0.25	-1.6
	90	-11.0	-18.1	-10.5	+0.4
	180	-9.4	-9.4	-13.2	-7.3
	365	-25.0	-19.2	-30.2	-21.9
	average	-9	-13	-11	-5
60	3	-7.8	-19.7	-9.1	-5.7
	10	-7.2	-16.4	+0.4	-2.6
	30	-17.5	-24.0	-15.9	-11.5
	90	-2.6	-12.2	-12.1	-5.7
	180	-10.6	-13.4	-14.4	-7.3
	365	-	-	-	-
	average	-9	-17	-10	-7
80	3	0	-11.9	+1.4	-2.1
	10	-8.9	-14.8	-5.6	-3.9
	30	-4.9	-13.7	-8.0	-7.2
	90	-18.7	-25.7	-15.6	-13.0
	180	-20.4	-27.3	-26.7	-24.1
	365	-	-	-	-
	average	-11	-19	-12	-10

FIGURE 7.1:

(a) Compressive strengths of oven dried concretes soaked in crude oil at 20 deg.C



(b) Compressive strength as percent of oven-dry strength prior to soaking in crude oil at 20 C.

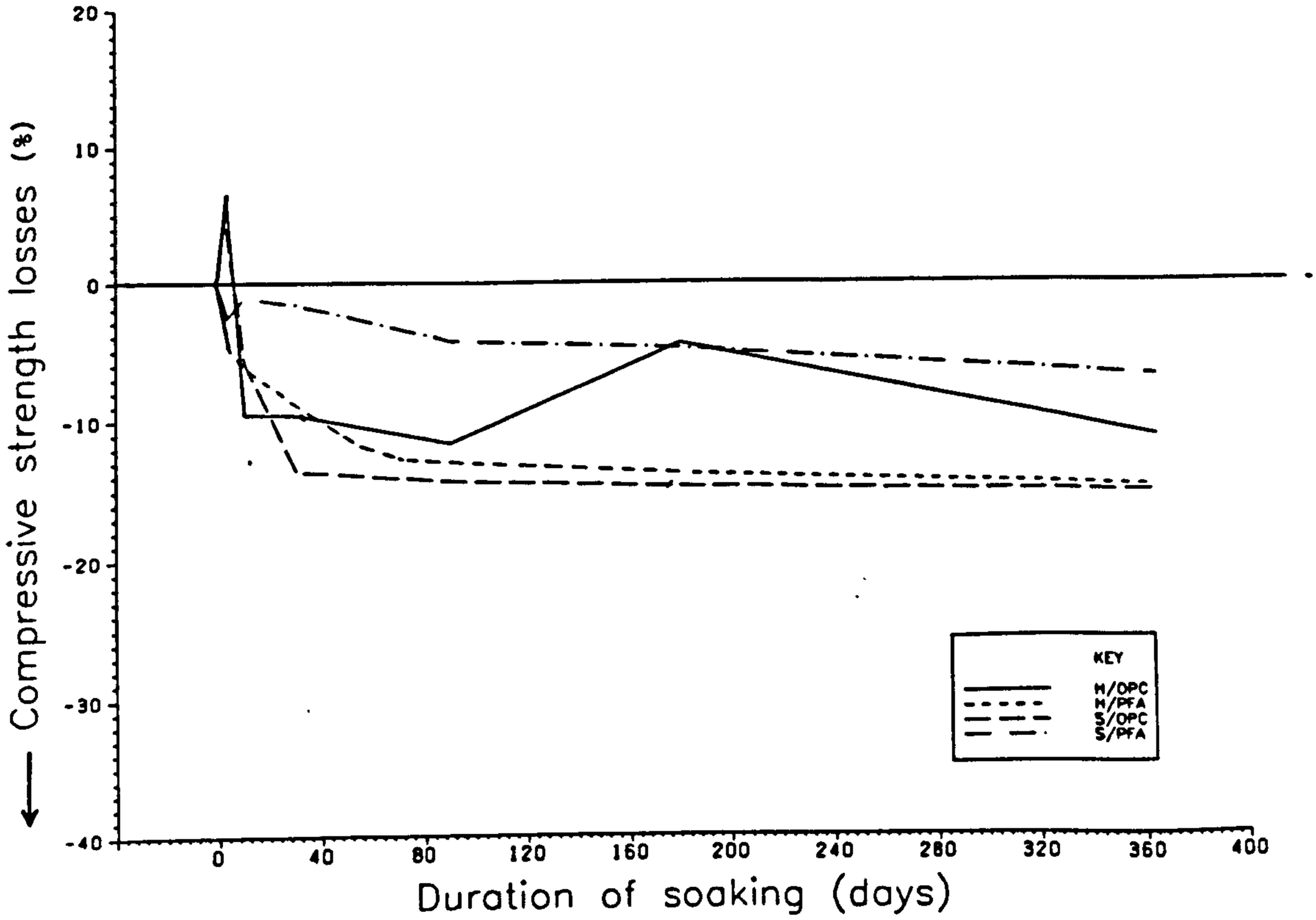
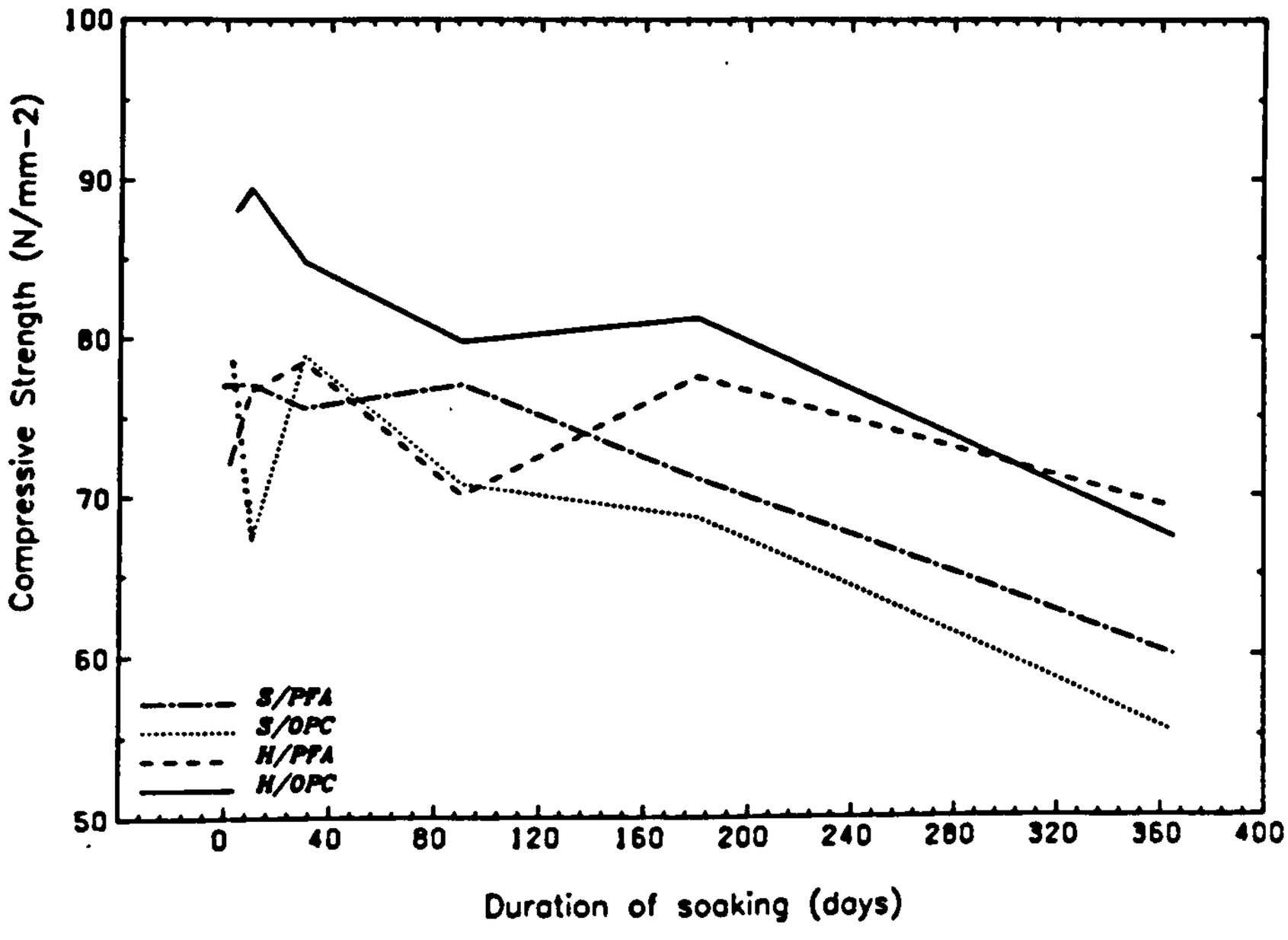


FIGURE 7.2 :

(a) Compressive strength of oven dried concretes soaked in crude oil at 45 deg.C



(b) Compressive strength as percent of oven-dry strength prior to soaking in crude oil at 45 C.

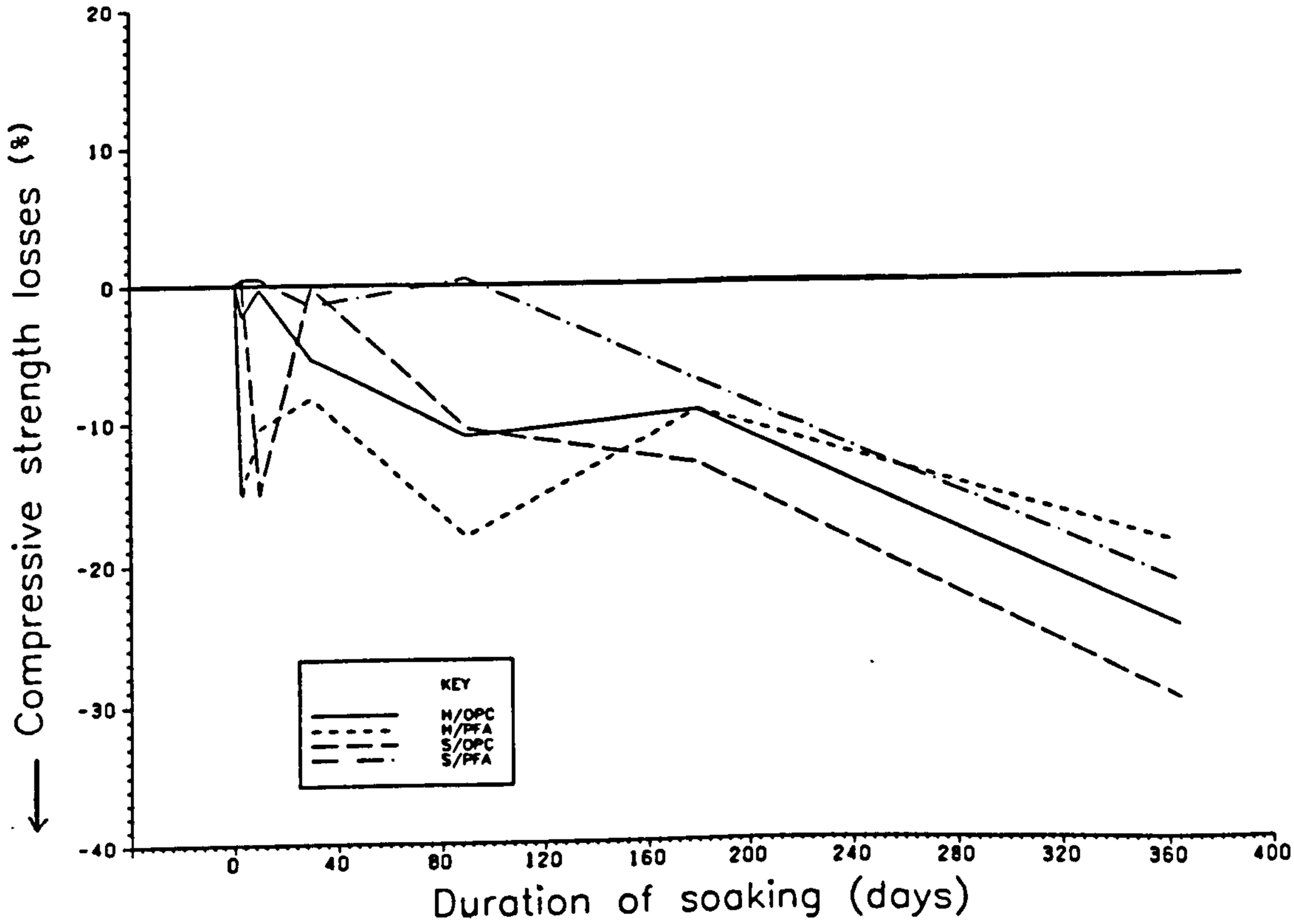
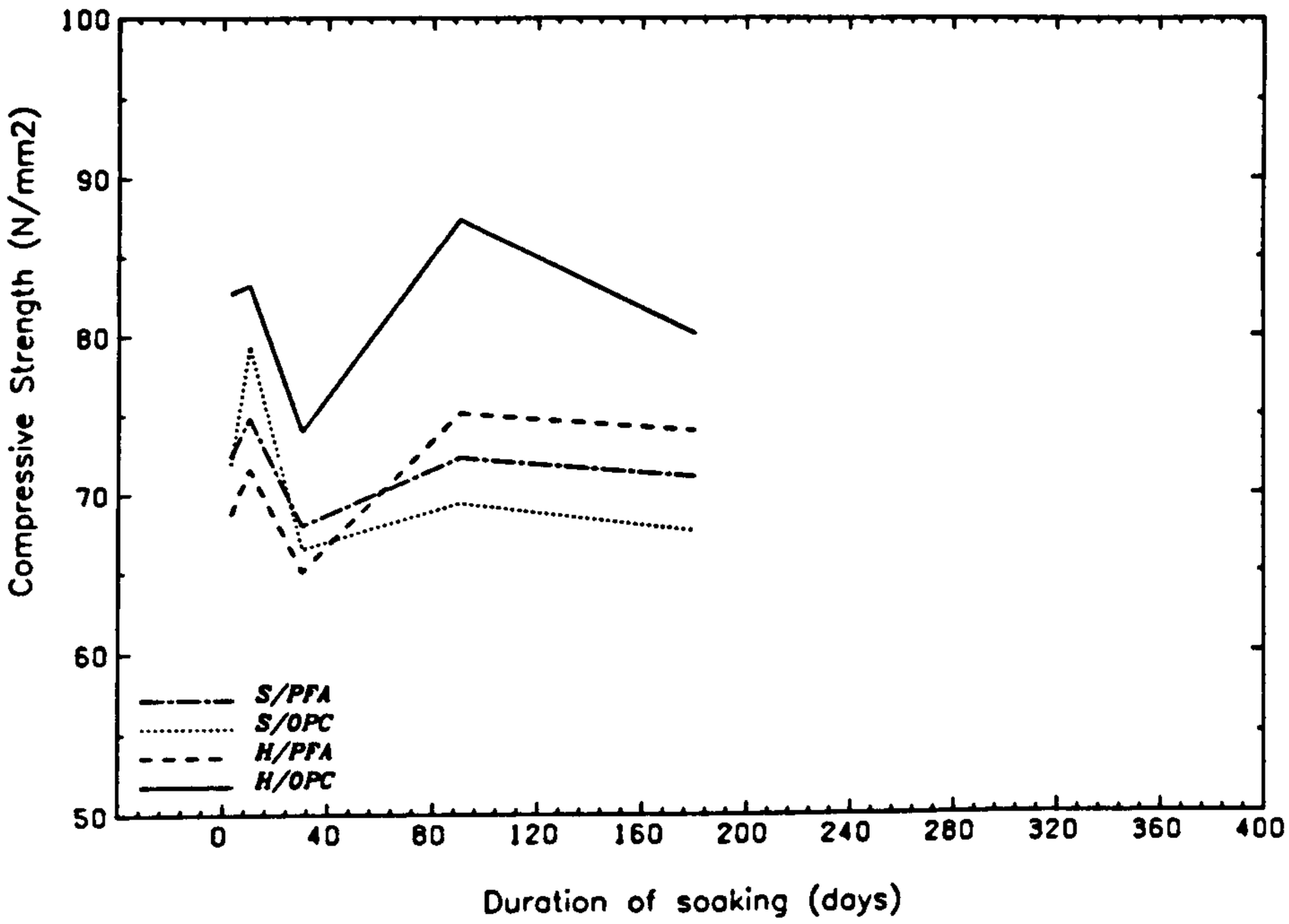


FIGURE 7.3 :

(a) Compressive strengths of oven dried concretes soaked in crude oil at 60 deg.C



(b) Compressive strength as percent of oven-dry strength prior to soaking in crude oil at 60 C.

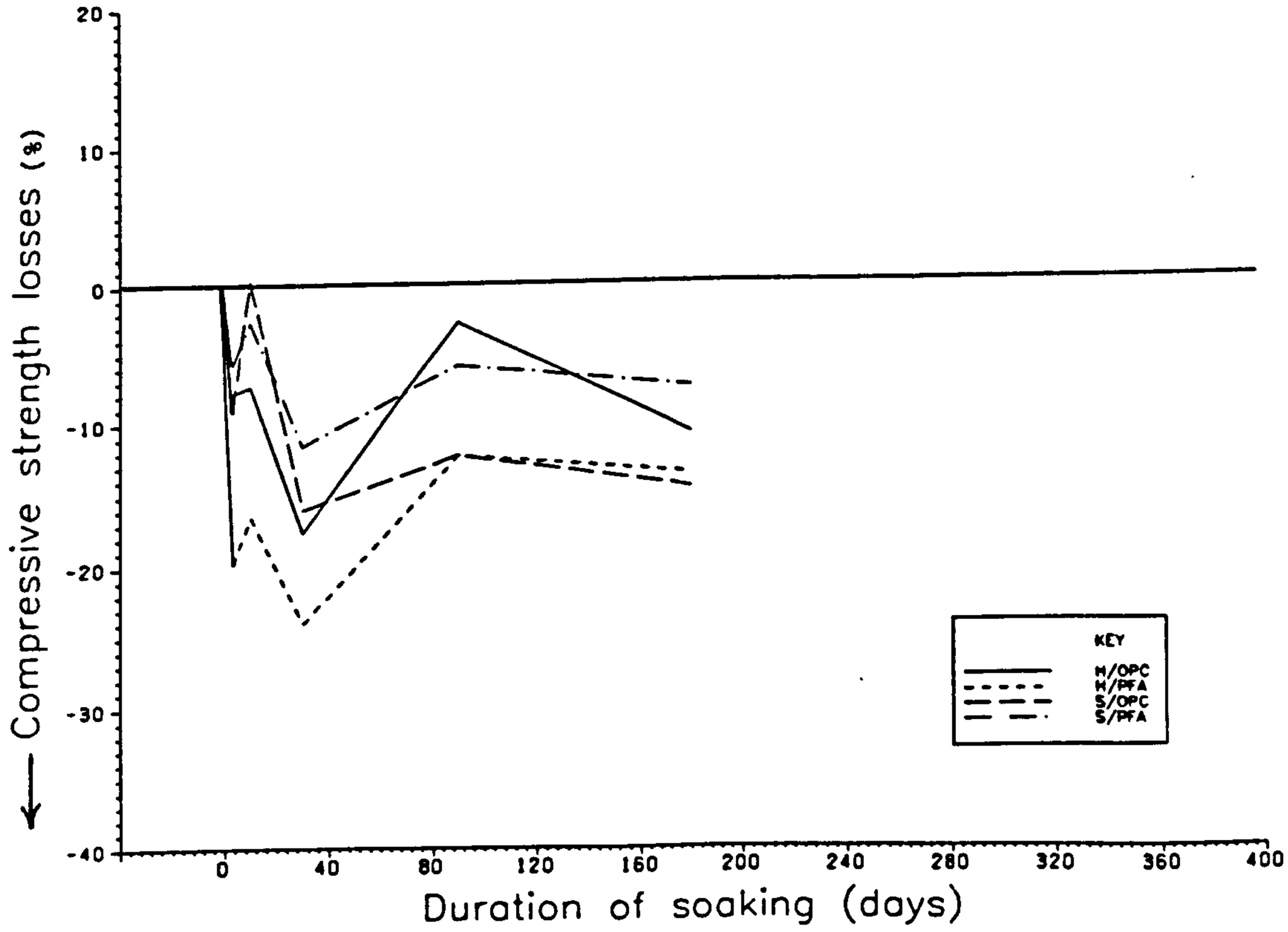
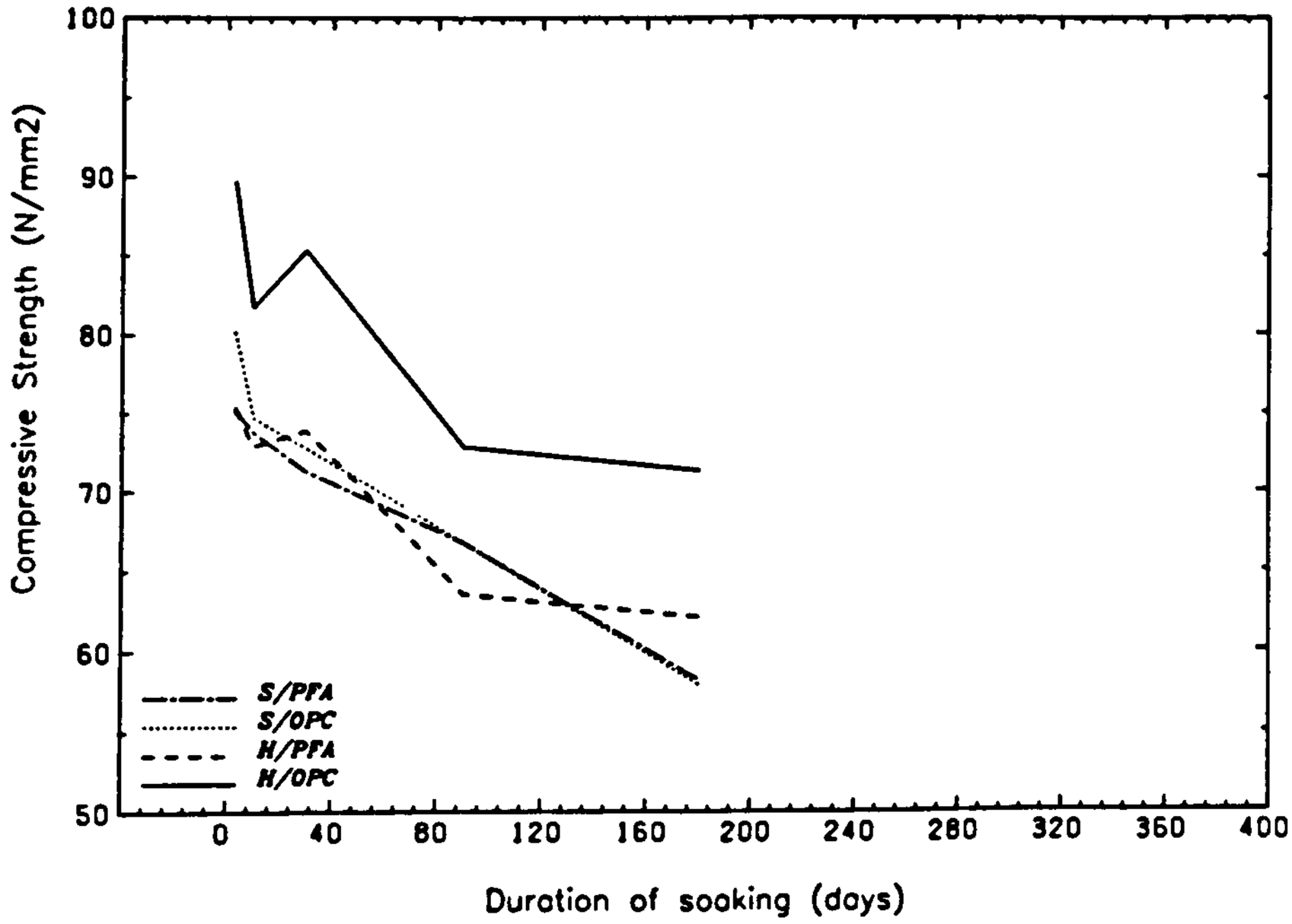


FIGURE 7.4 :

(a) Compressive strengths of oven dried concretes soaked in crude oil at 80 deg.C



(b) Compressive strength as percent of oven-dry strength prior to soaking in crude oil at 80 C.

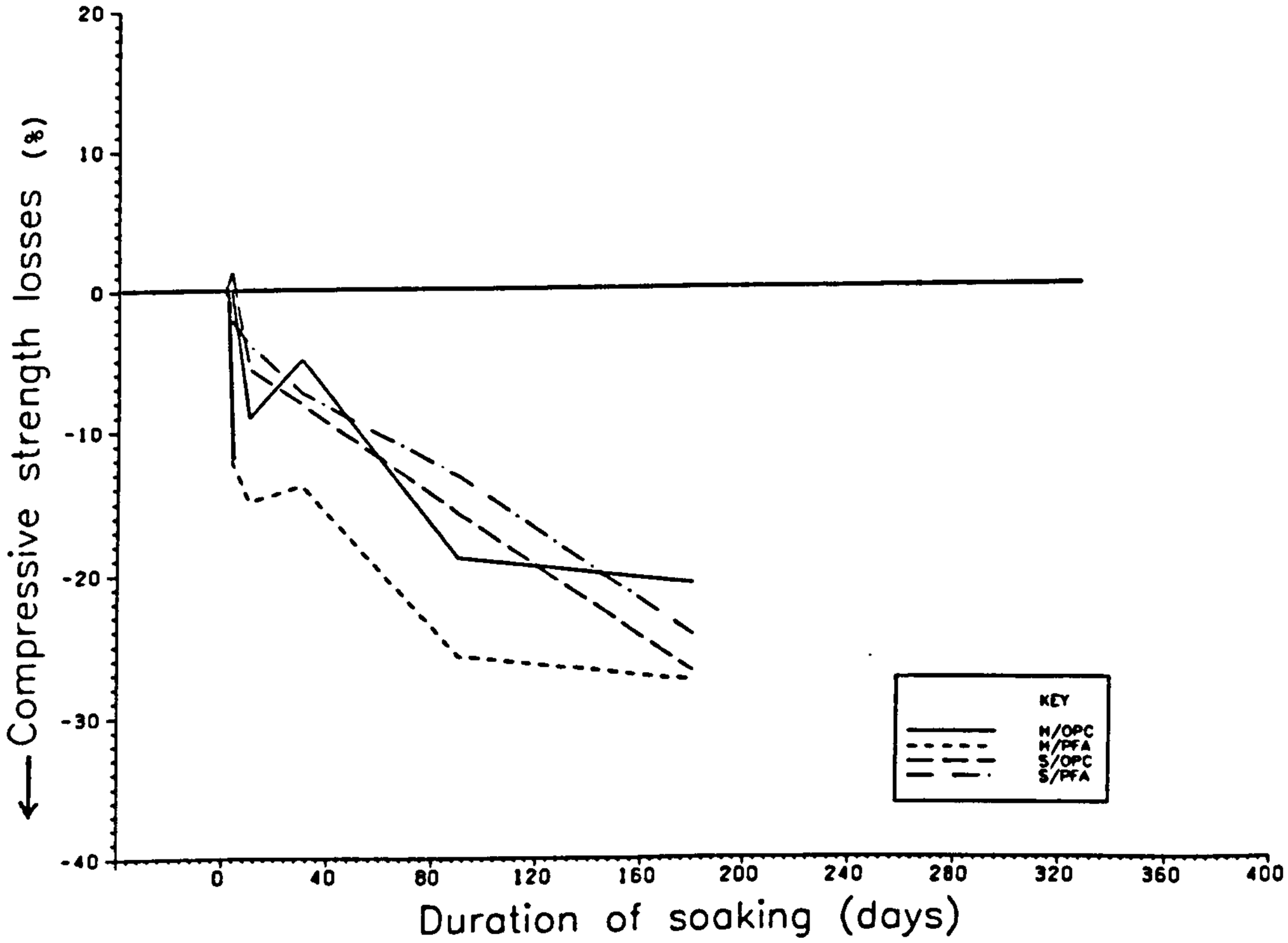


TABLE 7.3 : Compressive strength losses of oven dry concrete specimens reheated at elevated temperatures.

Temp. (C)	Duration of recycle (days)	Compressive strength losses (% change from oven dry strength)			
		H/OPC	H/PFA	S/OPC	S/PFA
45	3	-29.8	-13.1	-3.5	-5.3
	10	-19.7	-5.0	-11.0	-10.3
	30	-18.3	-13.3	-6.1	-5.6
	90	-14.2	-7.2	+2.2	+2.0
	180	-10.0	-4.8	+2.5	+4.7
	average	-18	-9	-3	-3
60	3	-27.7	-21.6	-6.2	-21.5
	10	-20.7	-21.1	-5.3	-9.0
	30	-7.1	-23.2	-1.9	+3.1
	90	-11.7	-19.6	-1.3	-3.4
	180	-11.5	-16.6	-1.9	+1.0
	average	-16	-20	-3	-6
80	3	-28.0	-27.3	-4.5	-4.6
	10	-25.0	-7.1	+2.9	-2.9
	30	-9.2	-8.8	+10.6	0
	90	-16.3	+1.1	+0.8	+3.4
	180	-9.2	-8.3	+2.8	+0.4
	average	-18	-10	+3	-1

TABLE 7.4 : Comparison of oven dry strength of specimens in crude oil with strength of specimens reheated.

Duration in crude oil (days)	Strength in crude oil/ Strength reheated											
	H/OPC			H/PFA			S/OPC			S/PFA		
	C 45	60	80	45	60	80	45	60	80	45	60	80
3	1.39	1.27	1.39	0.98	1.02	1.21	1.04	0.97	1.06	1.06	1.20	1.03
10	1.24	1.17	1.21	0.94	1.06	0.95	0.95	1.06	0.92	1.12	1.07	0.99
30	1.16	0.89	1.05	1.06	0.99	0.95	1.06	0.86	1.03	1.04	0.86	0.93
90	1.04	1.10	0.97	0.88	1.09	0.74	0.88	0.89	0.84	0.98	0.98	0.84
180	1.01	1.01	0.88	0.95	1.04	0.79	0.85	0.87	0.71	0.89	0.92	0.76

Figure 7.5: Residual compressive strength of oven dry concrete specimens reheated to 45 C as (%) of oven dry strength.

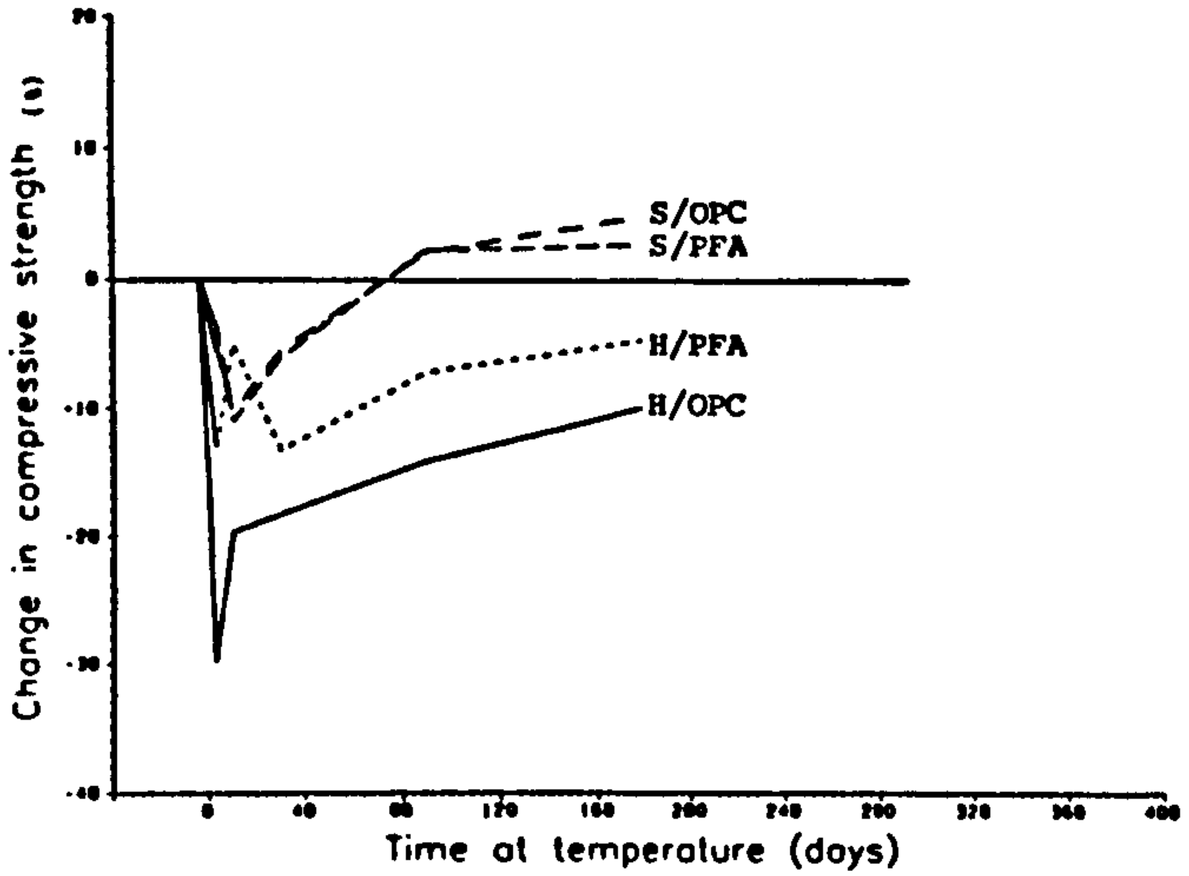


Figure 7.6: Residual compressive strength of oven dry concrete specimens reheated to 60 C as (%) of oven dry strength.

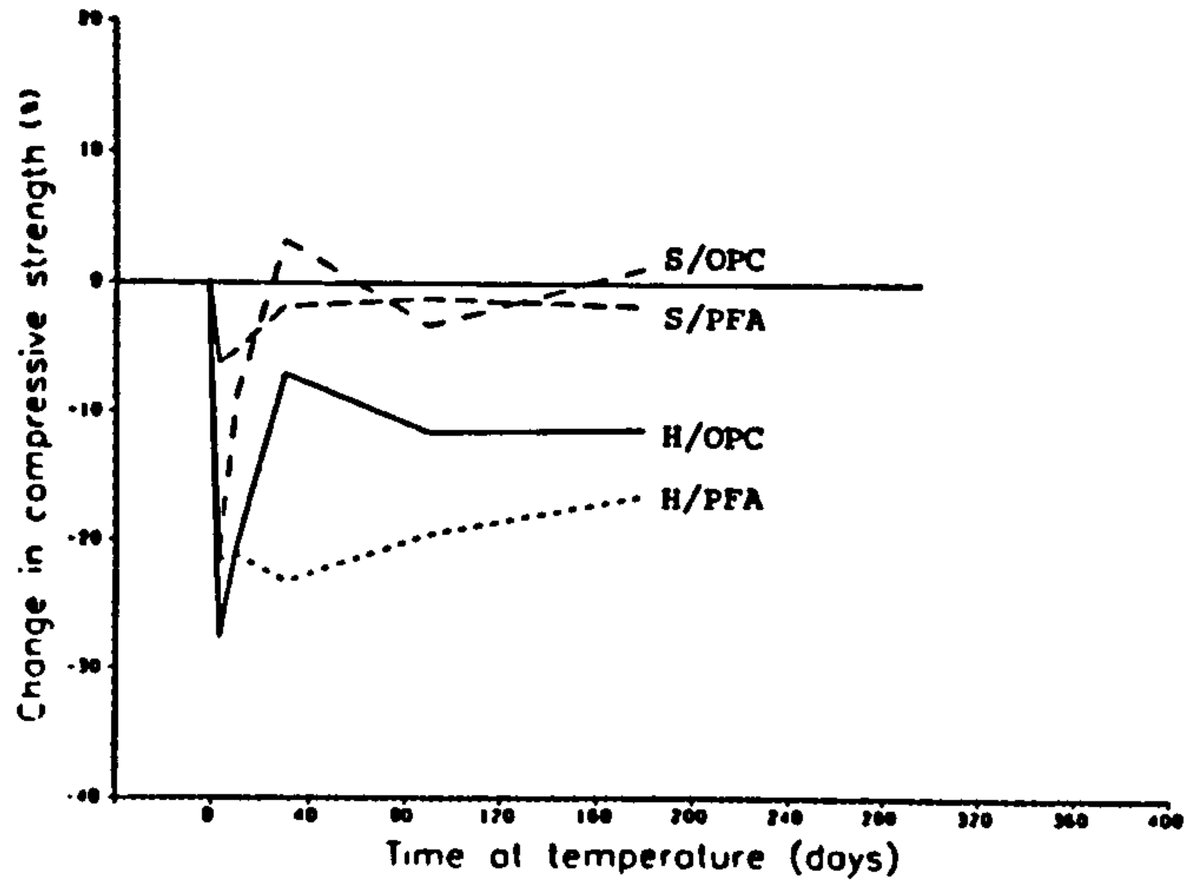


Figure 7.7: Residual compressive strength of oven dry concrete specimens reheated to 80 C as (%) of oven dry strength.

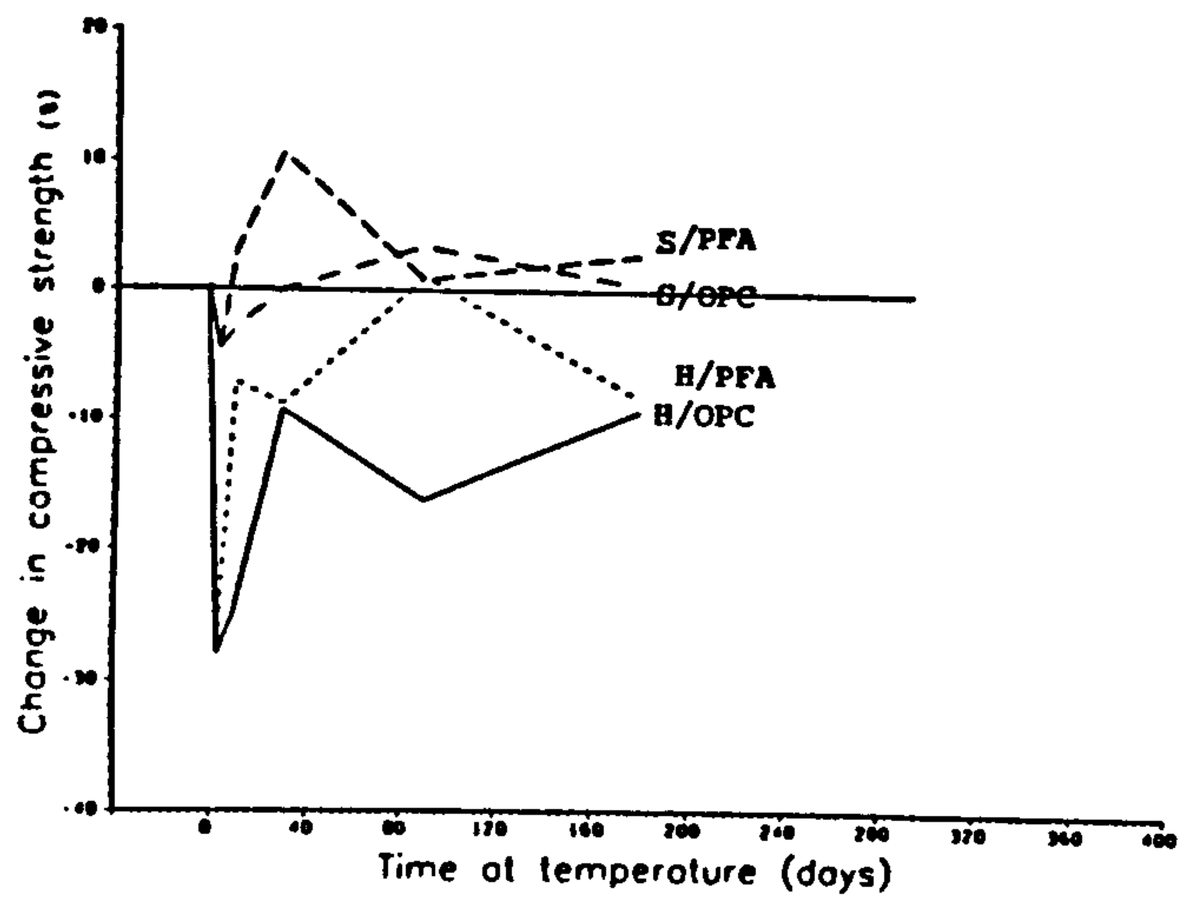


Figure 7.8 : EFFECT OF TEMPERATURE ON THE COMPRESSIVE STRENGTH OF OIL SOAKED OVEN DRY H/OPC CONCRETE SPECIMENS.

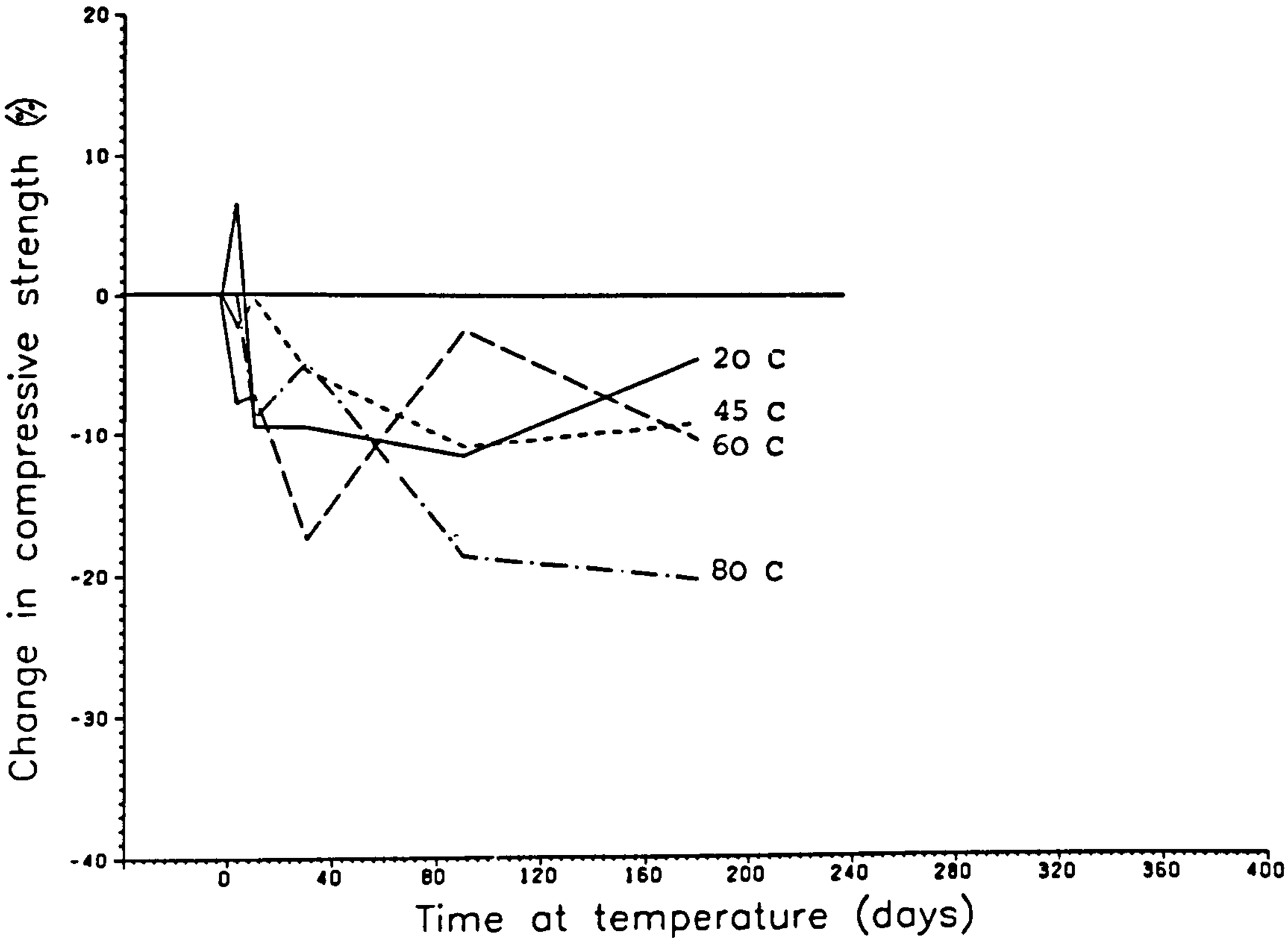


Figure 7.9 : EFFECT OF TEMPERATURE ON THE COMPRESSIVE STRENGTH OF OIL SOAKED OVEN DRY H/PFA CONCRETE SPECIMENS.

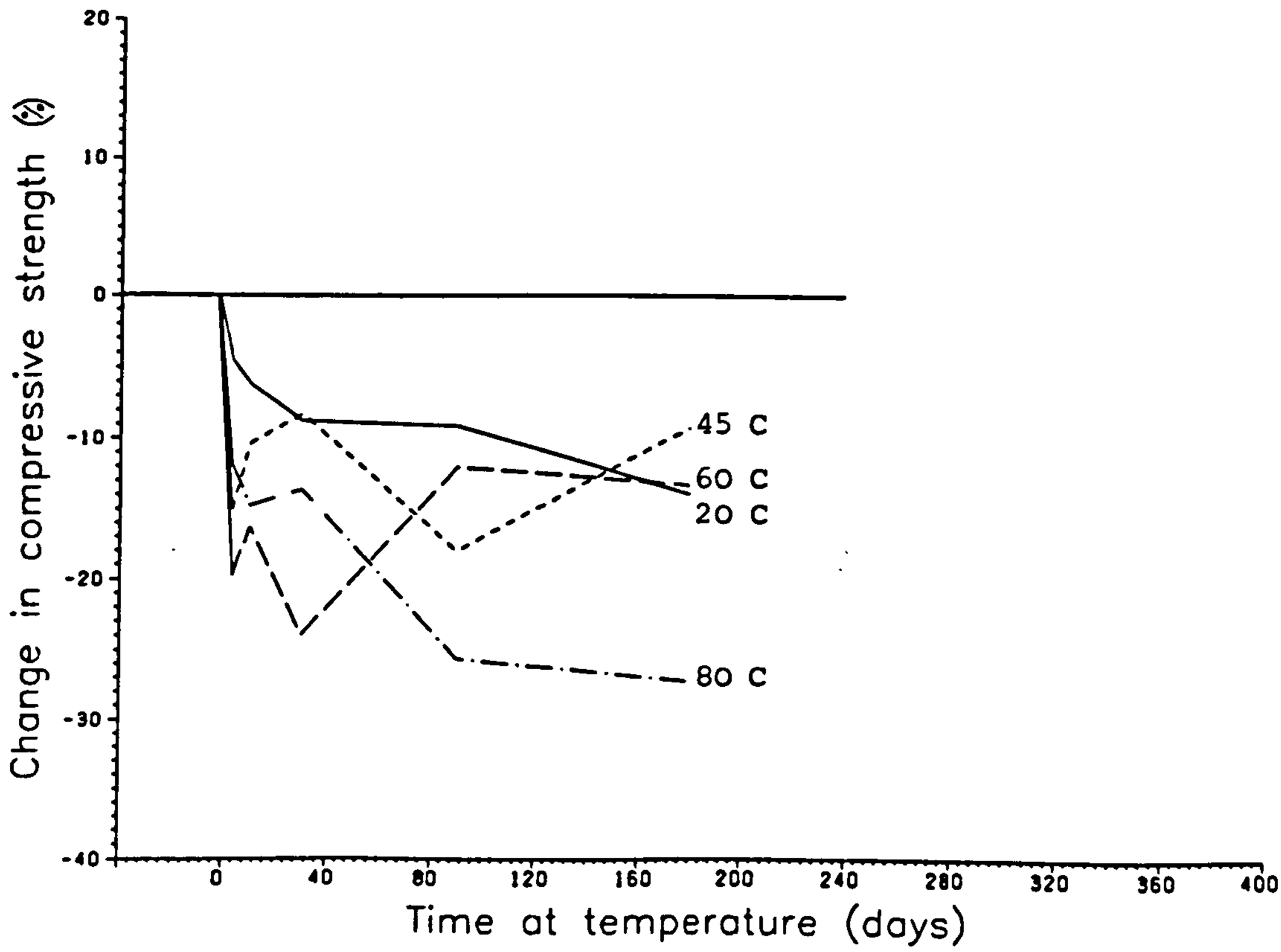


Figure 7.10. EFFECT OF TEMPERATURE ON THE COMPRESSIVE STRENGTH OF OIL SOAKED OVEN DRY S/OPC CONCRETE SPECIMENS.

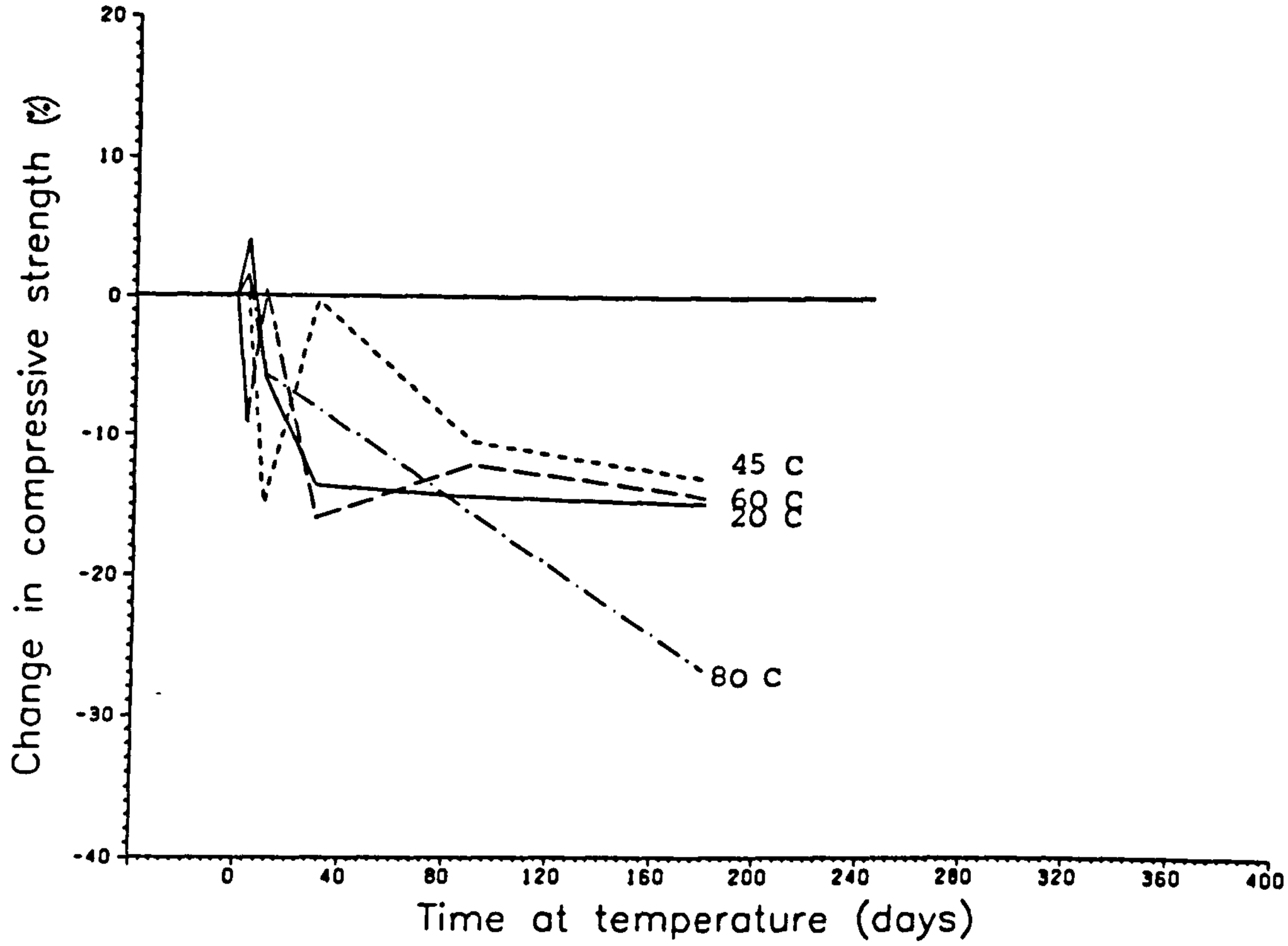


Figure 7.11: EFFECT OF TEMPERATURE ON THE COMPRESSIVE STRENGTH OF OIL SOAKED OVEN DRY S/PFA CONCRETE SPECIMENS.

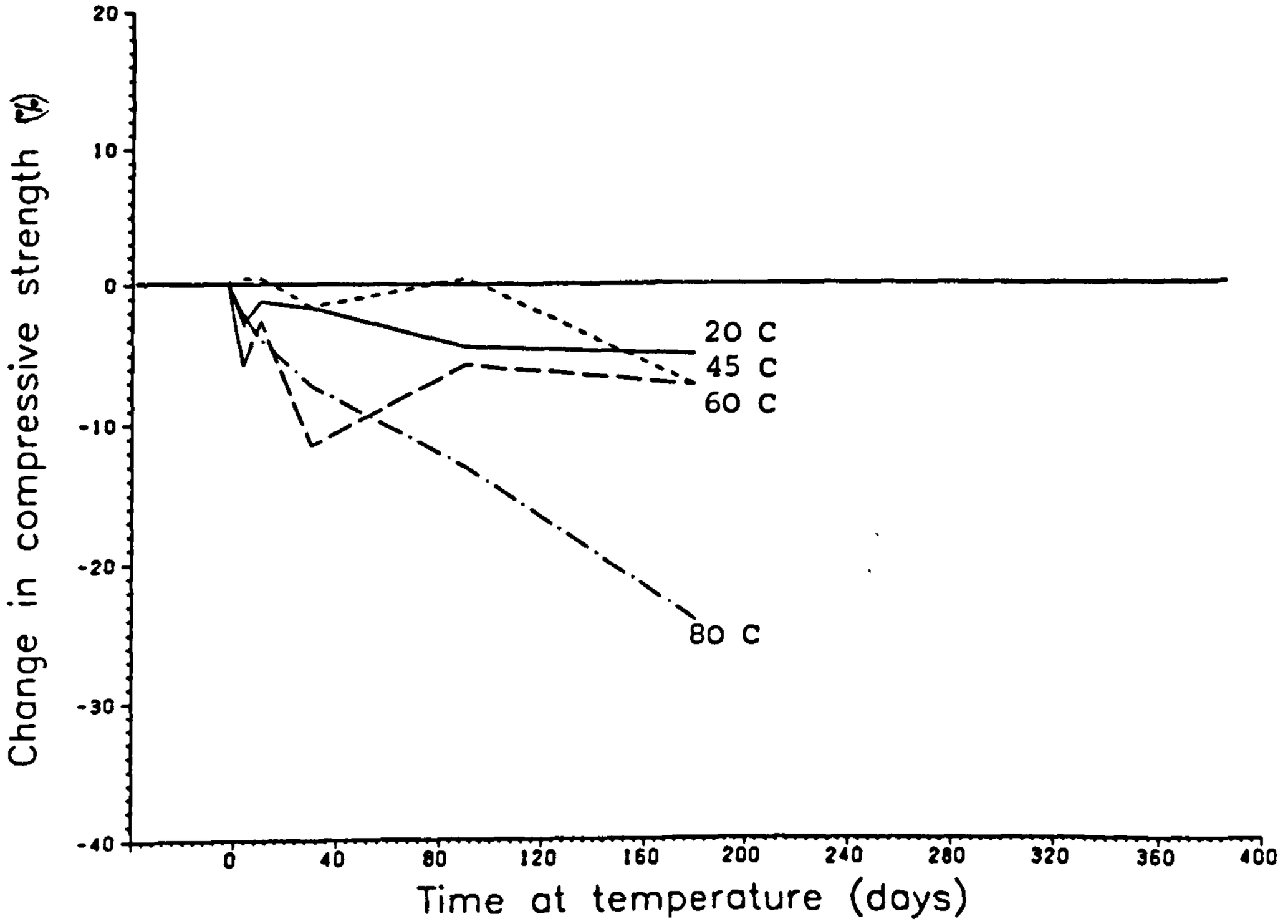


Figure 7.12: Change in strength vs crude oil absorption (20 C)

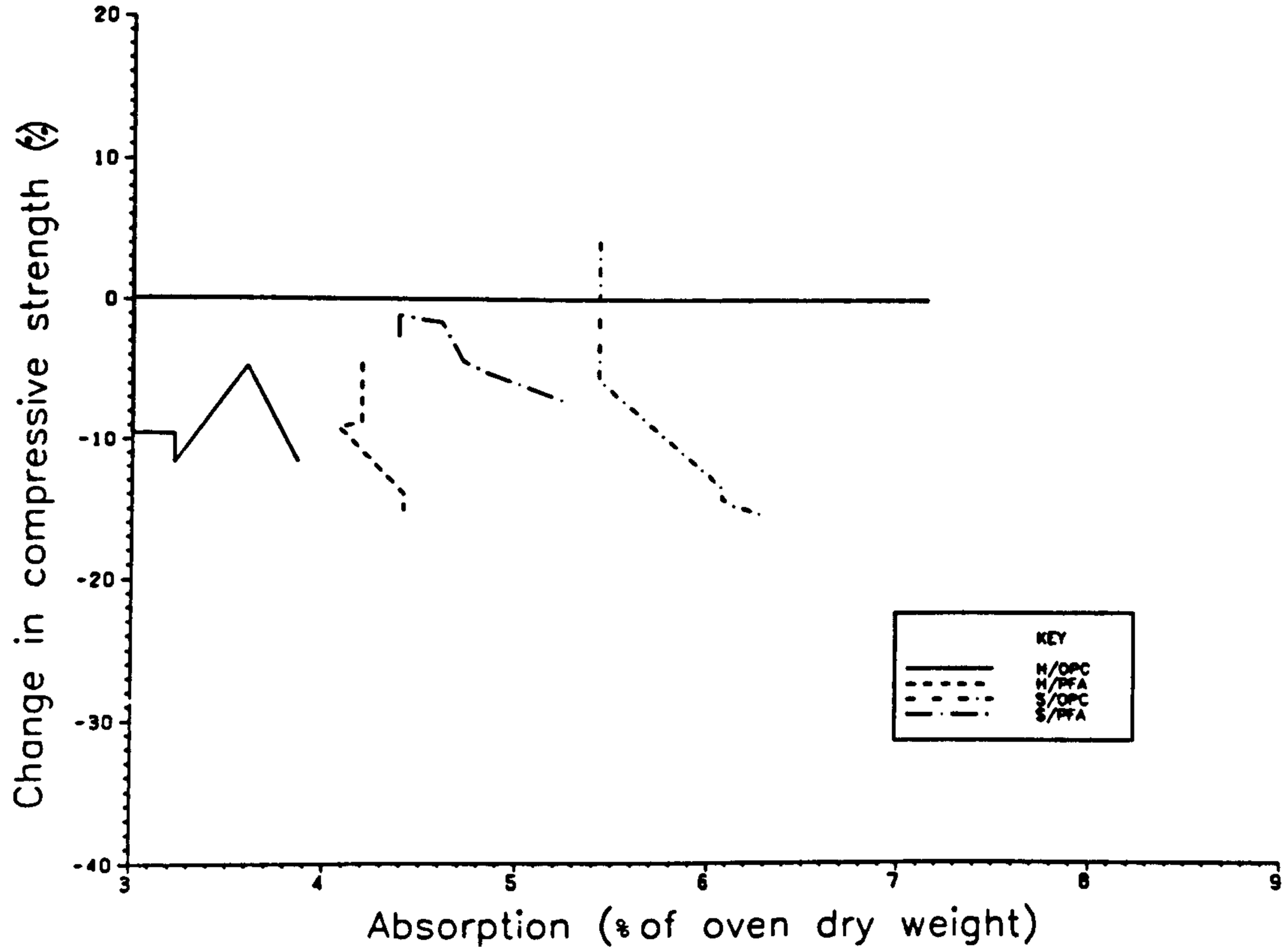


Figure 7.13: Change in strength vs crude oil absorption (45 C)

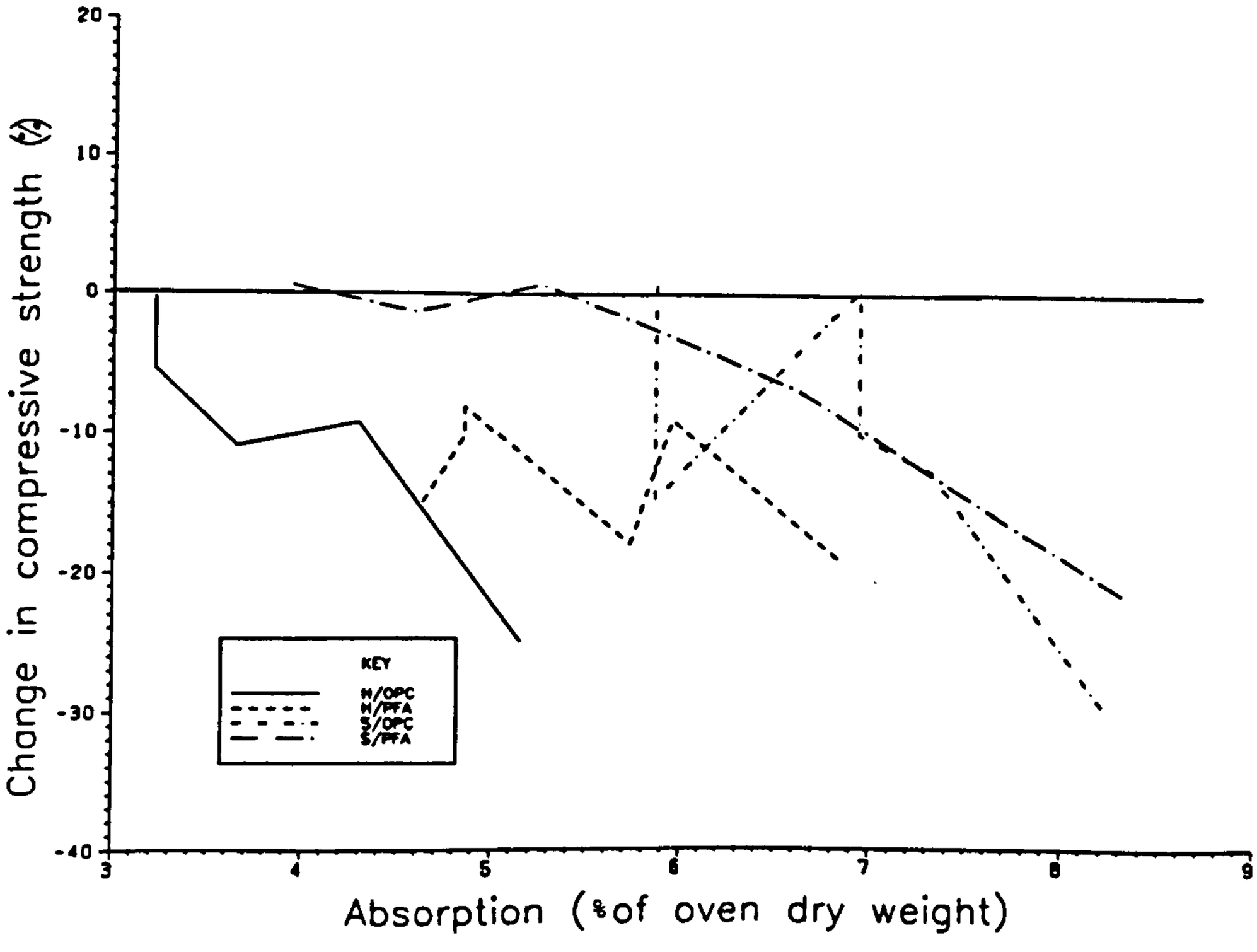


Figure 7.14: Change in strength vs crude oil absorption (60 C)

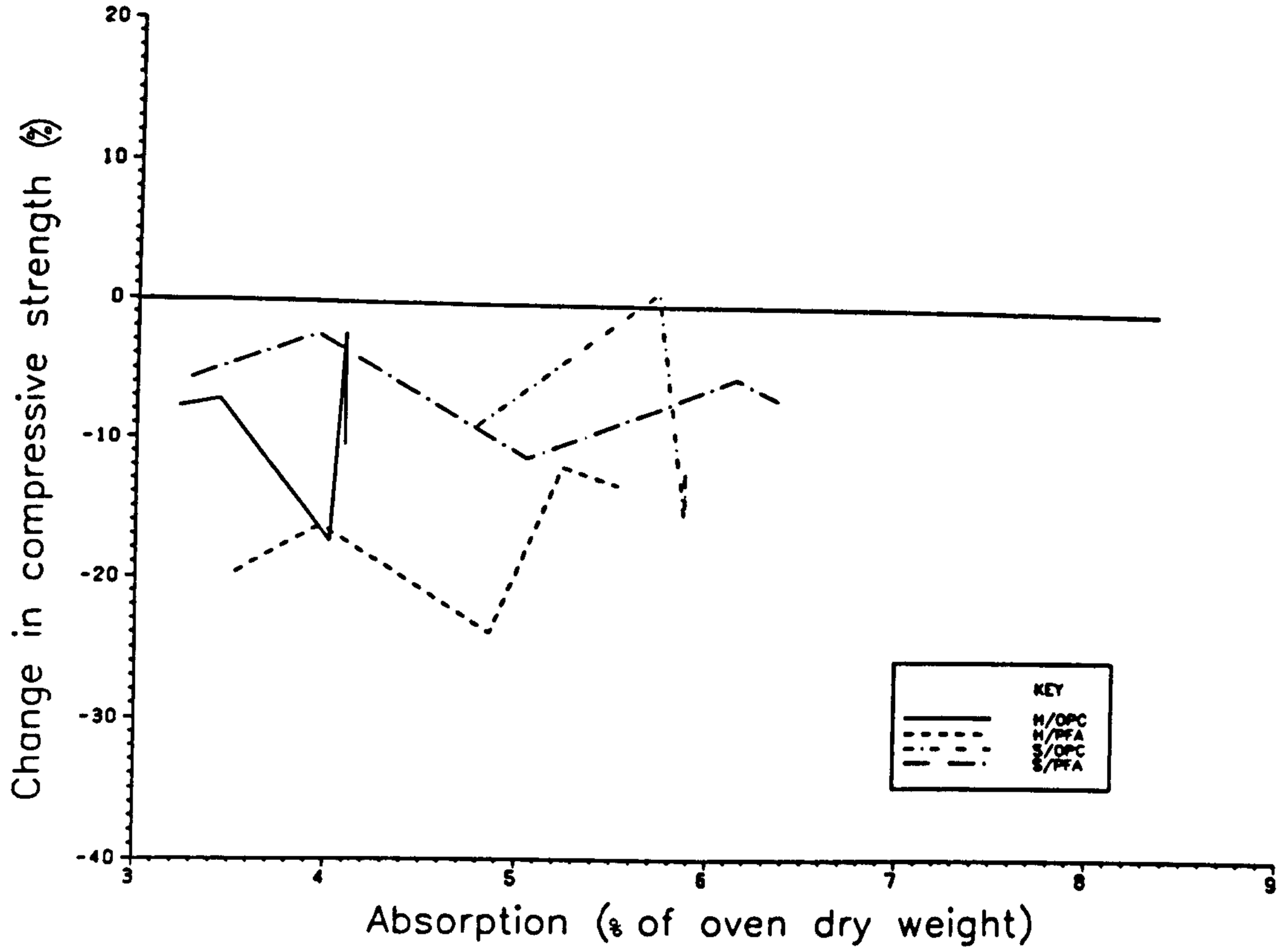
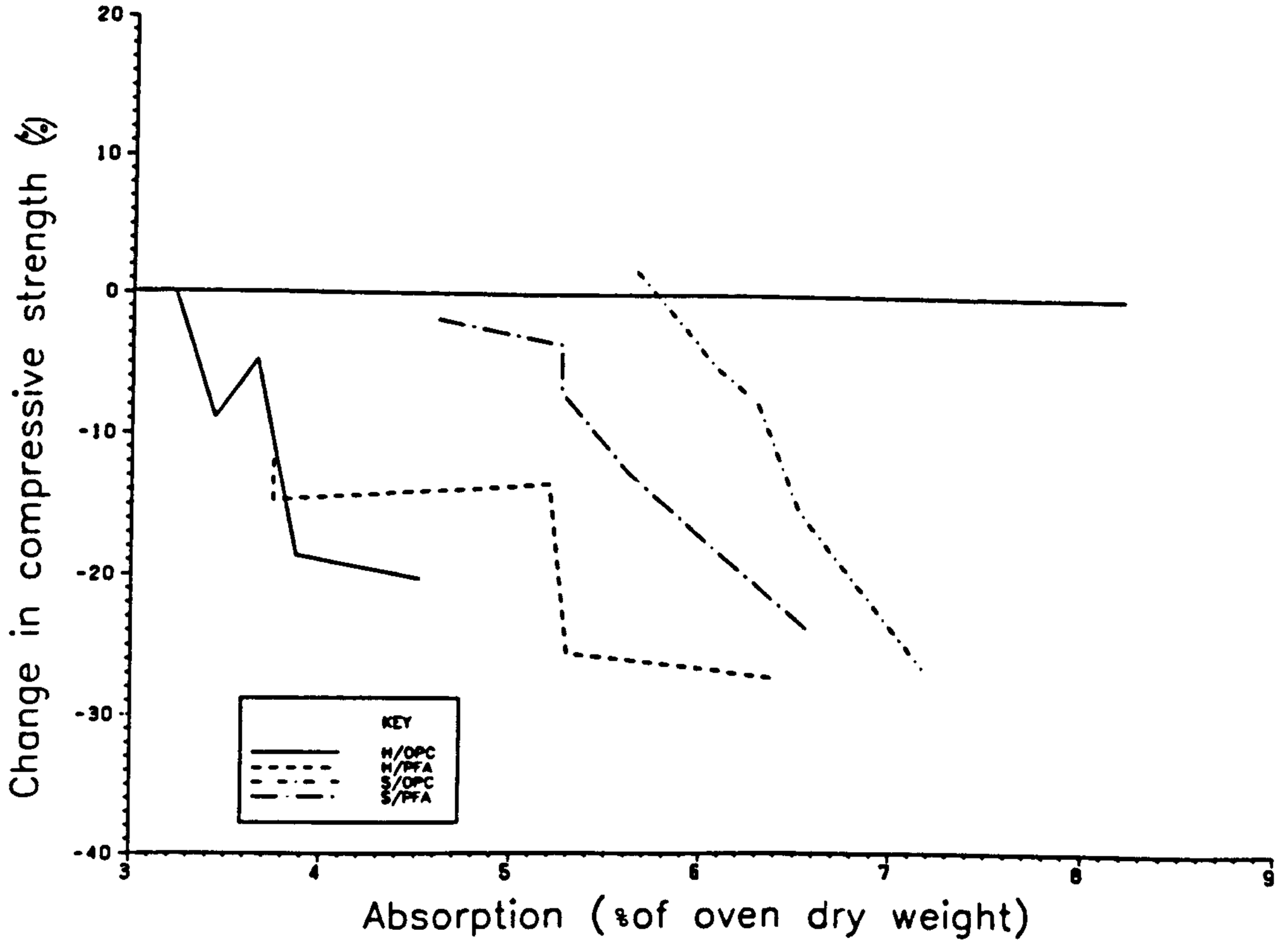


Figure 7.15: Change in strength vs crude oil absorption (80 C)



7.3 DISCUSSION OF RESULTS OF THE SINGLE INTERACTION TESTS

The reductions in compressive strength of oven dry concrete specimens exposed to crude oil, for all test temperatures, can be related to the pattern of crude oil absorption with time by the specimens, and the effect of elevated temperature. Strength losses were found to have increased as crude oil absorption increased and were higher for the the higher storage temperatures, but had remained at a constant level when steady state of absorption was reached, as was the case for exposure at 20 C (Fig. 7.1).

The reductions in strength observed suggest that the oven dried concrete specimens had become weaker under the test conditions. Concrete strength is determined by the strength of its constituents in the hardened state, viz. strength of the HCP, of the aggregates and of the bond between aggregate and cement paste. The strength of the granite aggregate used in these studies was unlikely to have been affected by exposure to the hot crude oil, following the observations made in Chapter 6. The deterioration would therefore seem to be in the HCP and/or the bond to aggregate.

7.3.1 Effect of crude oil absorption

Absorption of some fluids and in particular, the absorption of water by oven dry paste, can cause dilation of the cement gel and weakening of the cohesive forces in the HCP /13, 127/. These result in a reduction in strength by a process termed the wetting-weakening effect /151/ and has been likened to a 'wedging' action /127/. Mills /127, 169/ had found a steady reduction in the strength of oven dry concrete as water content in the gel increased. The findings were supported by Cook and Haque /46/ who related the magnitude of strength reduction on sorption to the molecular size of the adsorbate. These workers concluded that fluids such as benzene and paraffin with molecular sizes 2 or 3 times greater than that for water, have little effect on strength reduction, since they are unable to penetrate the gel pores.

Furthermore, the adsorption of fluid unto the C-S-H surface can cause a decrease in surface energy and reduce the compressive stress in the material /47/. These mechanisms can be used to explain some of the strength losses observed on exposure to crude oil, in particular, for storage at 20 C. North sea crude oil has varying hydrocarbon composition, with a molecular size range of 1 to 15 Å, but mostly in the range 3.5 - 8.5 Å. The smaller fractions were therefore capable of penetrating the pore structure, causing dilation of the gel and reducing the surface energy, with the result that the compressive strength was reduced as absorption increased. The constant level of strength for specimens stored at 20 C, from about 30 days, was because saturation with crude oil had been achieved.

7.3.2 Effect of Temperature

It is generally agreed that exposure of concrete to elevated temperature results in the loss of compressive strength. The factors liable to cause deterioration include (a) alterations to the pore structure (b) bond failure at the cement paste/aggregate interface arising from differential thermal expansion and (c) formation of cracks and microcracks within the paste and at the cement paste/ aggregate bond. These factors which were discussed in the previous chapter can cause the loss of strength. The bond strength is known to be the weakest link in the concrete chain, since it is normally weaker than the cement paste which in turn is weaker than the aggregate.

Soaking of concrete in crude oil at elevated temperatures was shown earlier to lead to increased crude oil absorption. It was suggested that amongst other factors, this may have resulted from the crude oil permeating the cracks and microcracks formed in the specimens during the first drying at 105 C and/or at the crude oil elevated temperatures. If as a consequence of this the crude oil should lubricate the surface of the aggregates, then additional loss of strength would take place. Tests showing reductions in concrete strength by as high as 2.5 times when aggregates were lubricated, have been reported /98/. This

may explain part of the initial early strength losses in all specimens and particularly the reductions measured at 3 days. Although crude oil dilation of the gel may account for the remainder, especially for the specimens stored at elevated temperatures, however, it can be appreciated that crude oil penetration into the expanded gel would, indeed, be quite slow.

It seems, therefore, that the larger residual compressive strength reductions measured for the oven dry concrete specimens soaked in crude oil at the elevated temperatures and particularly at 80 C, can be explained by a contribution of factors. This can be related to the effects of elevated temperature per-se (Figs. 7.8 to 7.11) and of the penetration of the crude oil (Figs. 7.12 to 7.15), not only to the small gel pores, since this takes a longer time, but also into the bond region between the aggregate and cement paste, which may occur much faster.

The large early reductions in the residual strength of the control specimens reheated to the 3 elevated temperatures (Figs.7.5 to 7.7), was probably due to the effect of a second heat cycle, following oven drying. This may have introduced additional stresses leading to the development of cracking. Furthermore, the specimens may have absorbed moisture from the heating environment, given that the temperatures of heating were below 100 C, although care was taken to avoid this situation.

7.3.3 Effect of the method of curing

It seems that the trend of lower compressive strength of the specimens cured in seawater relative to the specimens cured at 100% RH, which was observed during the period of curing, had merely continued on exposure to crude oil at elevated temperatures. However, the S/PFA specimens had shown less strength losses than had all the other specimens, under storage conditions. It is not understood why this has been the case, however, it may be that the better response of the S/PFA specimens was intrinsic and was related to a long term effect arising from a combination of blending and the method of curing.

7.4 RESULTS OF COMPRESSIVE STRENGTHS OF THE MULTIPLE INTERACTION TESTS

Results have shown that crude oil penetration through the moist concrete specimens was insignificant. The effect of crude oil on the specimens, if any, was limited to surface interactions. The results of the residual compressive strengths of moist specimens soaked in crude oil at 20 C and at elevated temperatures, are shown in Figs.(7.16) through (7.19), for each storage temperature. The effect of each temperature is shown in Figs.(7.24) through (7.27), for each specimen type. Variations from the moist strength prior to crude oil exposure are given in Table (7.5). The trends in water of the similarly prepared control specimens are shown in Figs. (7.20) through (7.23) and magnitudes of the strength losses are given in Table (7.6). Comparisons with the trend in crude oil are made in Table (7.7). The following observations can be made:

(1) Three stages of strength variation were observed in the moist concrete specimens soaked in crude oil. Similar to the results of the oven dry specimens, 'instantaneous' strength losses had occurred at 3 days, which had increased gradually, reaching a minimum at about 90 days. Unlike in the oven dry specimens, however, strength re-gain had occurred in the moist specimens during the third stage, reaching the pre-soak values and sometimes even higher by 365 days in crude oil. These were observed for all storage temperatures (Figs. 7.16 to 7.18), except at 80 C. In the latter, strength recovery had not taken place and strength losses had continued, reaching up to about 20% in some specimens (Fig. 7.19).

(2) Exposure of moist concrete specimens to crude oil at elevated temperatures had caused significant reductions in the residual compressive strength. The reductions were higher at the higher storage temperatures (Figs. 7.24 to 7.27). Exposure to crude oil at 80 C was the most severe, causing the largest reductions in strength in all specimens.

(3) The average strength reductions in the opc specimens (H/OPC and S/OPC) were larger than in the pfa specimens (H/PFA and S/PFA). In general, the largest average strength reductions were in the H/OPC specimens and these had varied by between 4% for storage at 20 C and

20% at 80 C. Similar to the results in the single interaction tests, the S/PFA specimens had the least average strength reductions. The average strength reductions in the H/PFA specimens were less than 4% for all storage temperatures, except at 80 C when it was 18%. The average losses for the S/OPC specimens were between 8 and 12% (Table 7.5).

(4) Storage in water of the control specimens at 45 and 60 C, had caused similar strength variations with those observed in crude oil at the same temperatures. The trends at 20 and 80 C, however, differed slightly from those in crude oil.

7.5 DISCUSSION OF RESULTS OF THE MULTIPLE INTERACTION TESTS

The results of the residual compressive strengths of moist concrete specimens soaked in crude oil, for all temperatures, showed initial reductions in strength at the early stages, followed by strength recovery at later stages. Diffusion of crude oil into the specimens did not occur, but the large crude oil molecules may have partially sealed the surface pores of the specimens. The changes in strength which were observed can, therefore, be related to moisture movement with time within the specimens, accelerated at elevated temperatures. The loss of strength at the early stages can be attributed to the dilation of the gel, resulting from the increased moisture movements to this parts at high temperatures. It is well known that the strength of sealed concrete declines significantly and continuously with increase in temperature (Fig.7.28). This has also been attributed to changes in porosity and increased microcracking, due in part to the differential thermal expansions between the aggregate and cement paste /96/. The recovery of strength at the later stages was because of the increased hydration, resulting from increased moisture in the gel. Similar trends were observed in the the control specimens soaked in water (Figs. 7.20 to 7.23), for all temperatures. This indicates that similar moisture conditions were in existence in the two systems

and the effect of moisture was not significant. Nishizawa and Okamura /136/ found that compressive strength losses of sealed concrete specimens stored at elevated temperatures were higher, the higher the storage temperature. Their results also showed that there was recovery of strength after about 13 weeks of storage at 70 C (Fig. 7.29).

The fact that strength recovery did not take place in crude oil at 80 C can be attributed to the critical effect of that temperature, as Fig.(7.30) suggests. This showed that typically, the strength of unsealed moist concrete declines with increase in temperature to reach a minimum at about 80 C. On the other hand, critical strains are known to develop in sealed concrete at about 80 C (Fig.7.31), as a result of self-desiccation /6/.

Strength variations with time of the moist specimens stored in crude oil at 20 C can also be related to moisture movement within the gel structure of the concrete specimens. However, such movements can be expected to be less than at the high temperatures, which may explain why strength losses were comparatively lower at 20 C. The re-gain of strength between 180 and 365 days was due to continued hydration.

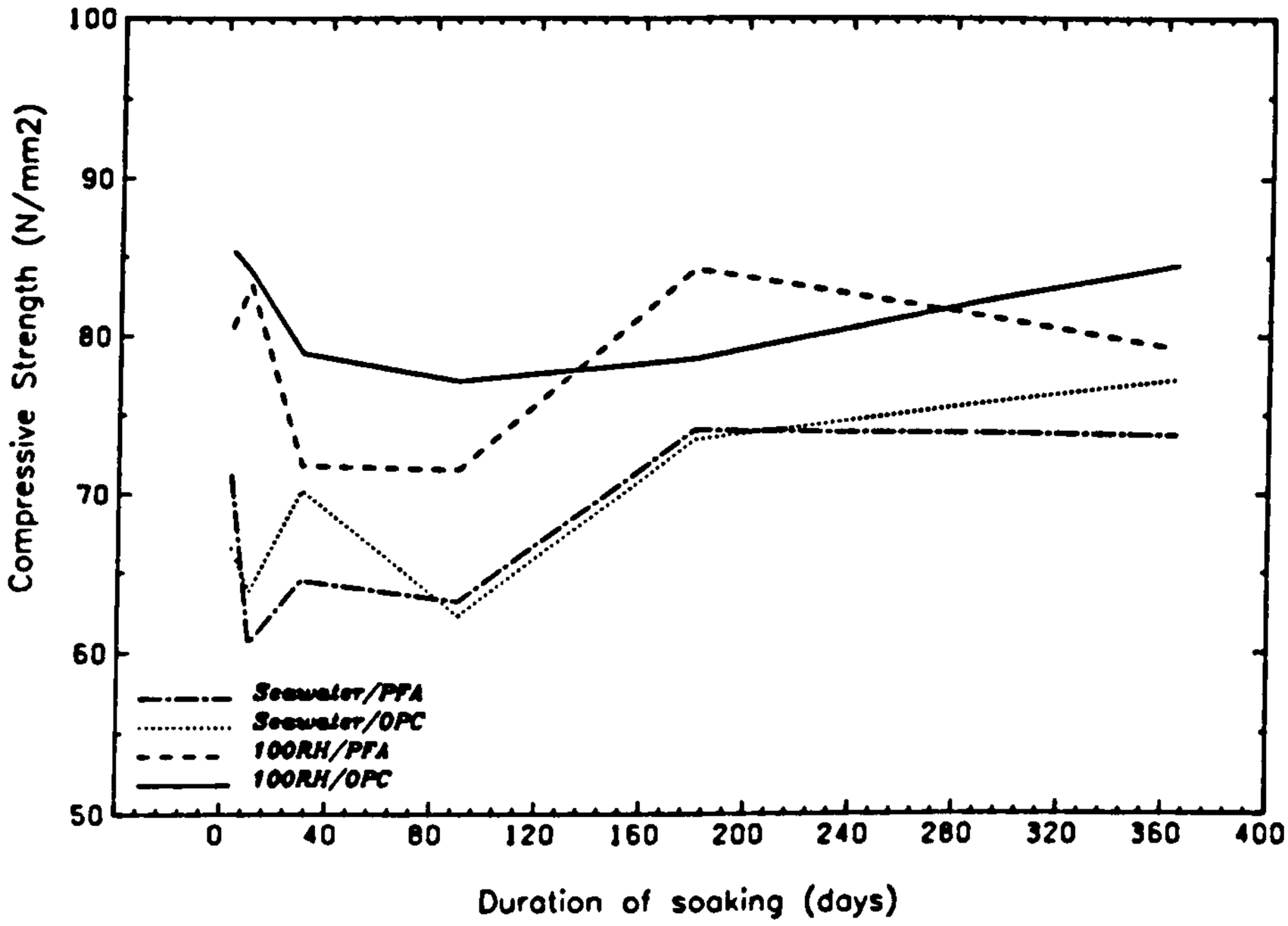
Strength reductions in crude oil were lower in the blended specimens (H/PFA and S/PFA) than in the opc concretes (H/OPC and S/OPC), as is indicated in Table (7.5). This can be attributed to continued pozzolanic reactions in the blended specimens, known to be accelerated at high temperature. It has been reported that the introduction of fly ash to opc concrete can improve the strength with time under sealed conditions, particularly between 70 and 140 C /98/.

TABLE 7.5 : Compressive strength losses of moist concrete specimens soaked in crude oil.

Temp. (C)	Duration in crude oil (days)	compressive strength losses (% change from 365d moist strength)			
		H/OPC	H/PFA	S/OPC	S/PFA
20	3	+1.1	+1.5	-10.6	+3.5
	10	-0.6	+4.9	-14.4	-11.9
	30	-6.6	-9.5	-5.8	-6.2
	90	-8.6	-9.7	-16.4	-8.1
	180	-7.0	+6.3	-1.3	+7.7
	365	0	-0.1	+3.6	+7.1
	average	-4	-1	-8	-1
45	3	-13.4	-9.2	-10.9	-4.7
	10	-17.0	-6.9	-12.6	-4.8
	30	-20.5	-11.5	-10.3	-2.5
	90	-3.9	-4.4	-8.9	-3.6
	180	-9.2	+0.4	-7.5	+6.5
	365	+5.9	+6.8	-12.4	+10.0
	average	-10	-4	-10	+0.2
60	3	-14.6	-8.6	-20.1	-6.8
	10	-15.3	-4.0	-18.9	-4.8
	30	-17.5	-2.6	-19.9	+2.3
	90	-13.7	+5.9	-9.1	+8.0
	180	-9.5	+0.1	-8.3	+13.5
	365	-4.7	-2.5	+5.1	+9.3
	average	-13	-2	-12	+4
80	3	-14.6	-8.6	+1.2	-3.2
	10	-19.6	-18.7	-12.4	-11.6
	30	-18.0	-21.6	-8.2	-10.5
	90	-23.8	-20.8	-7.7	-6.0
	180	-20.6	-18.2	-9.5	-3.0
	365	-21.7	-17.5	-11.8	-5.7
	average	-20	-18	-8	-7

FIGURE 7.16 :

(a) Compressive strengths of saturated moist concretes soaked in crude oil at 20 deg.C



(b) Compressive strength as percent of moist strength prior to soaking in crude oil at 20 C.

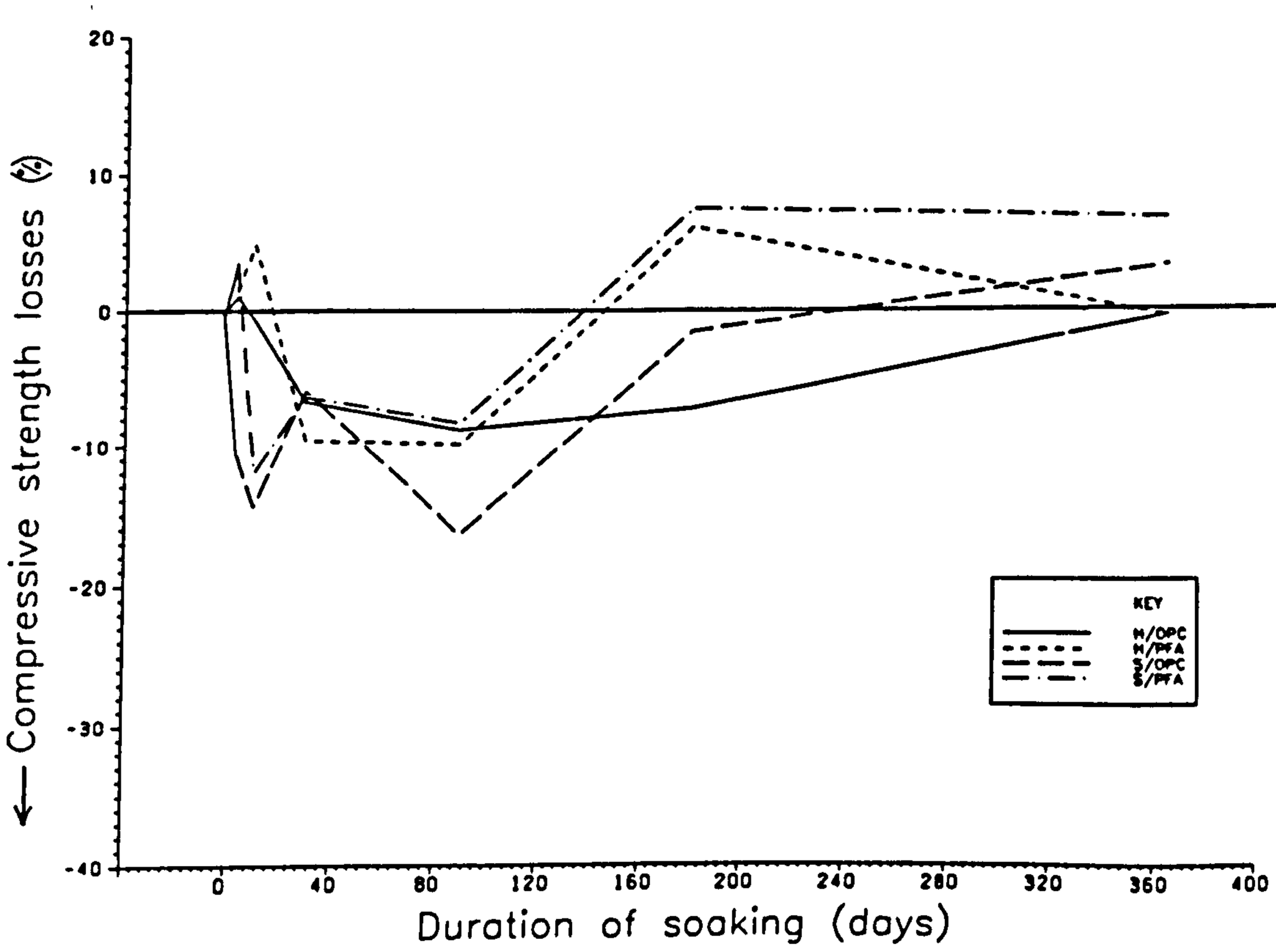
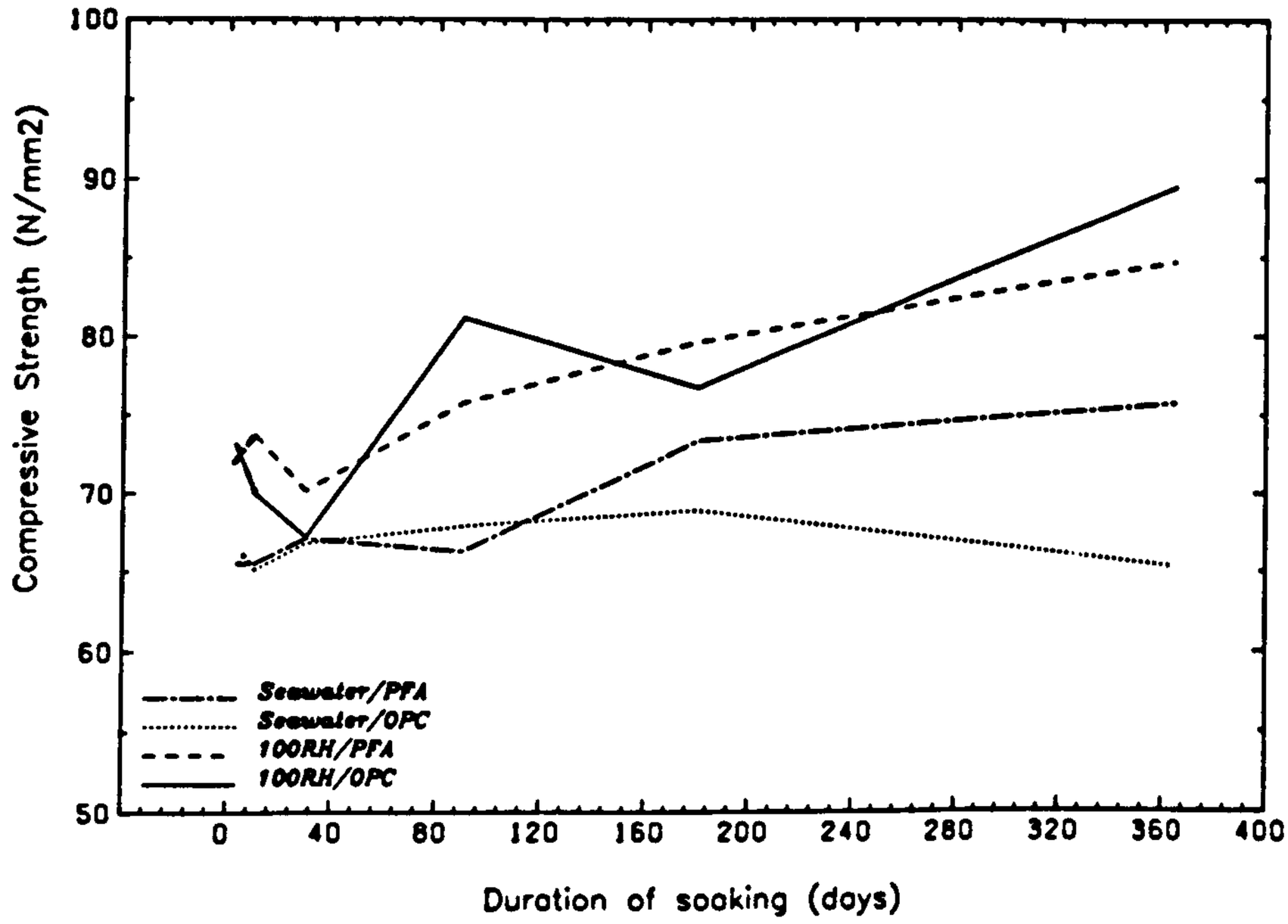


FIGURE 7.17:

(a) Compressive strengths of saturated moist concretes soaked in crude oil at 45 deg.C



(b) Compressive strength as percent of moist strength prior to soaking in crude oil at 45 C.

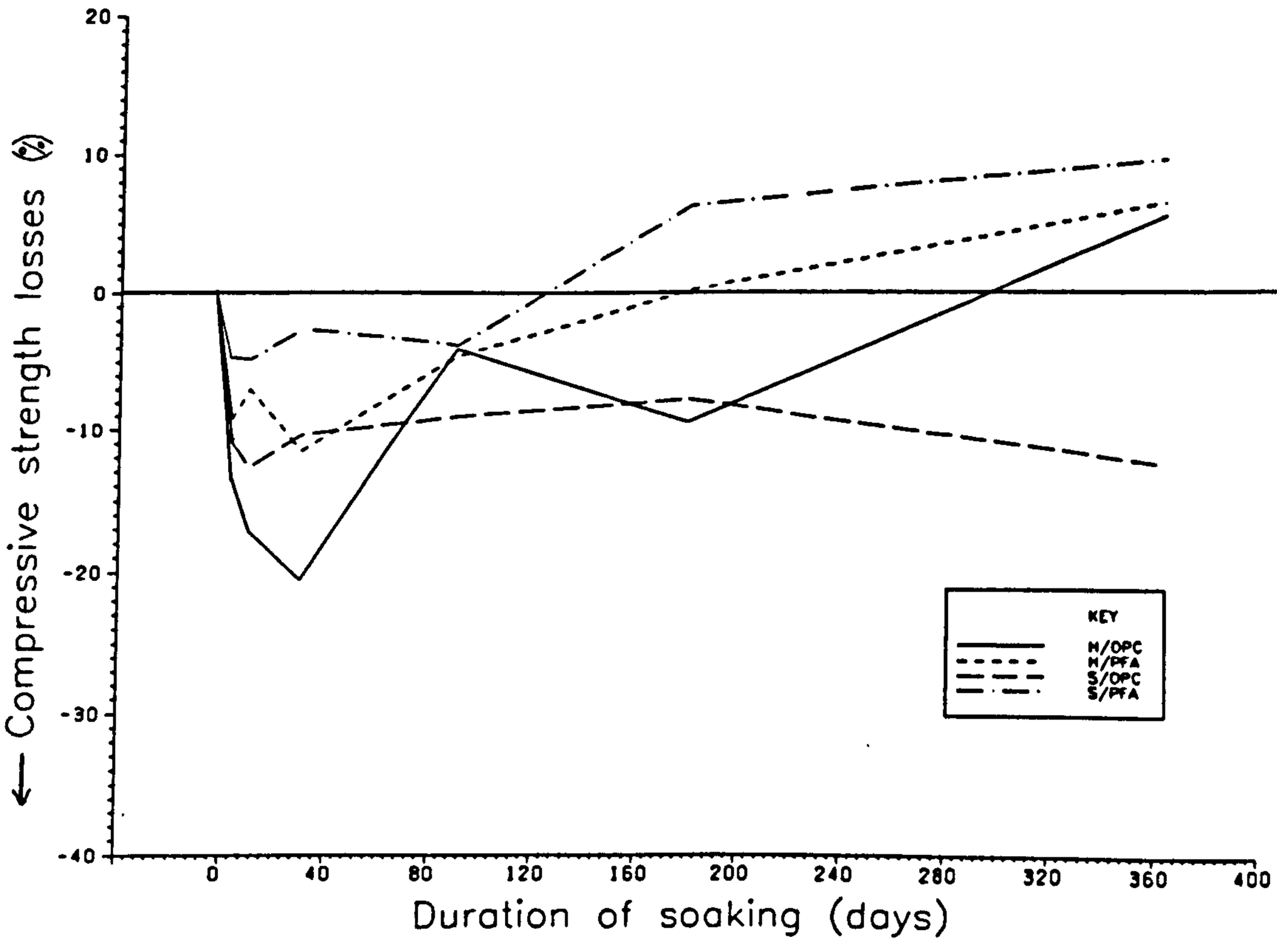
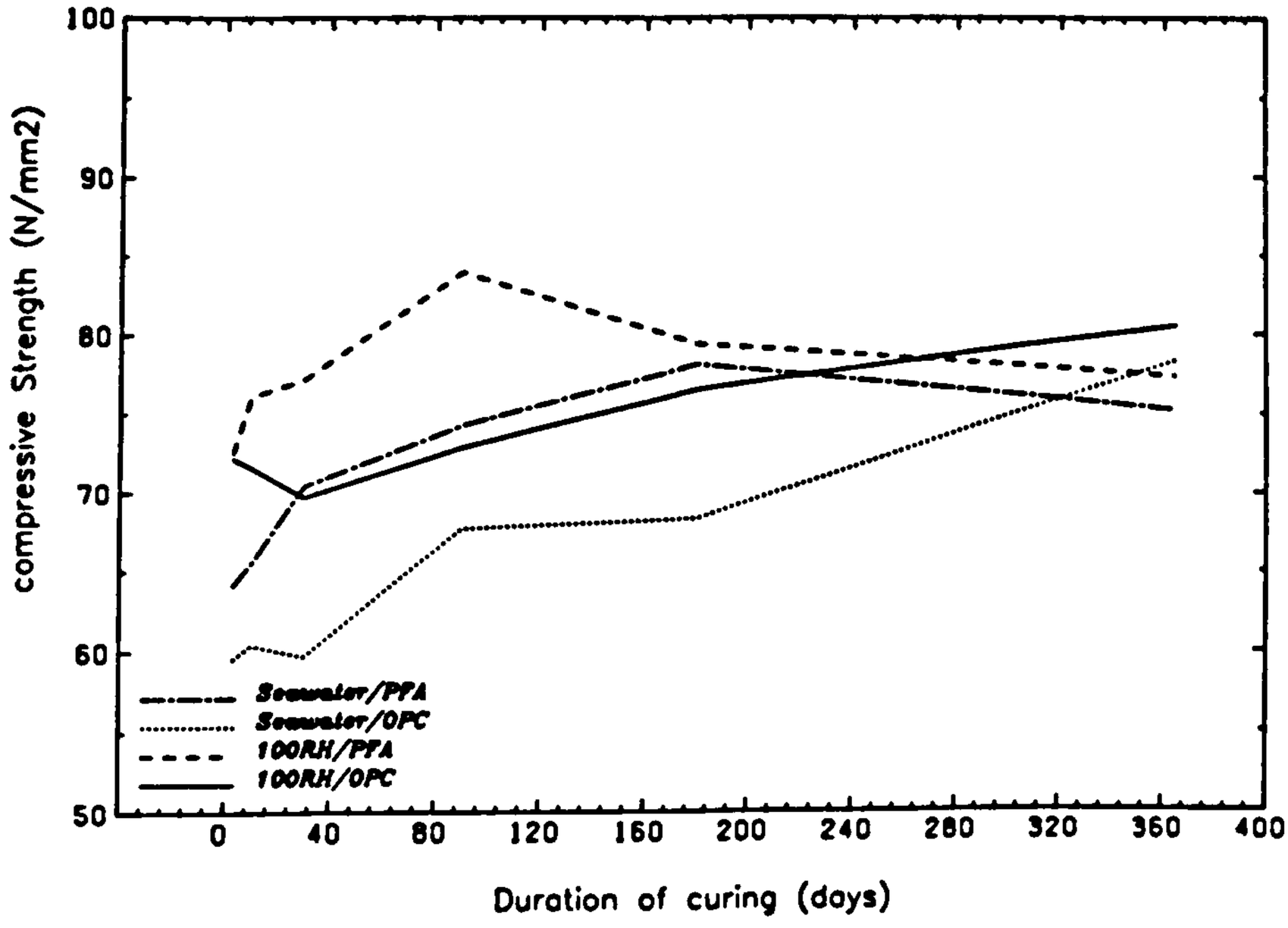


FIGURE 7.18 :

(a) Compressive strengths of saturated moist concretes soaked in crude oil at 60deg.C



(b) Compressive strength as percent of moist strength prior to soaking in crude oil at 60 C.

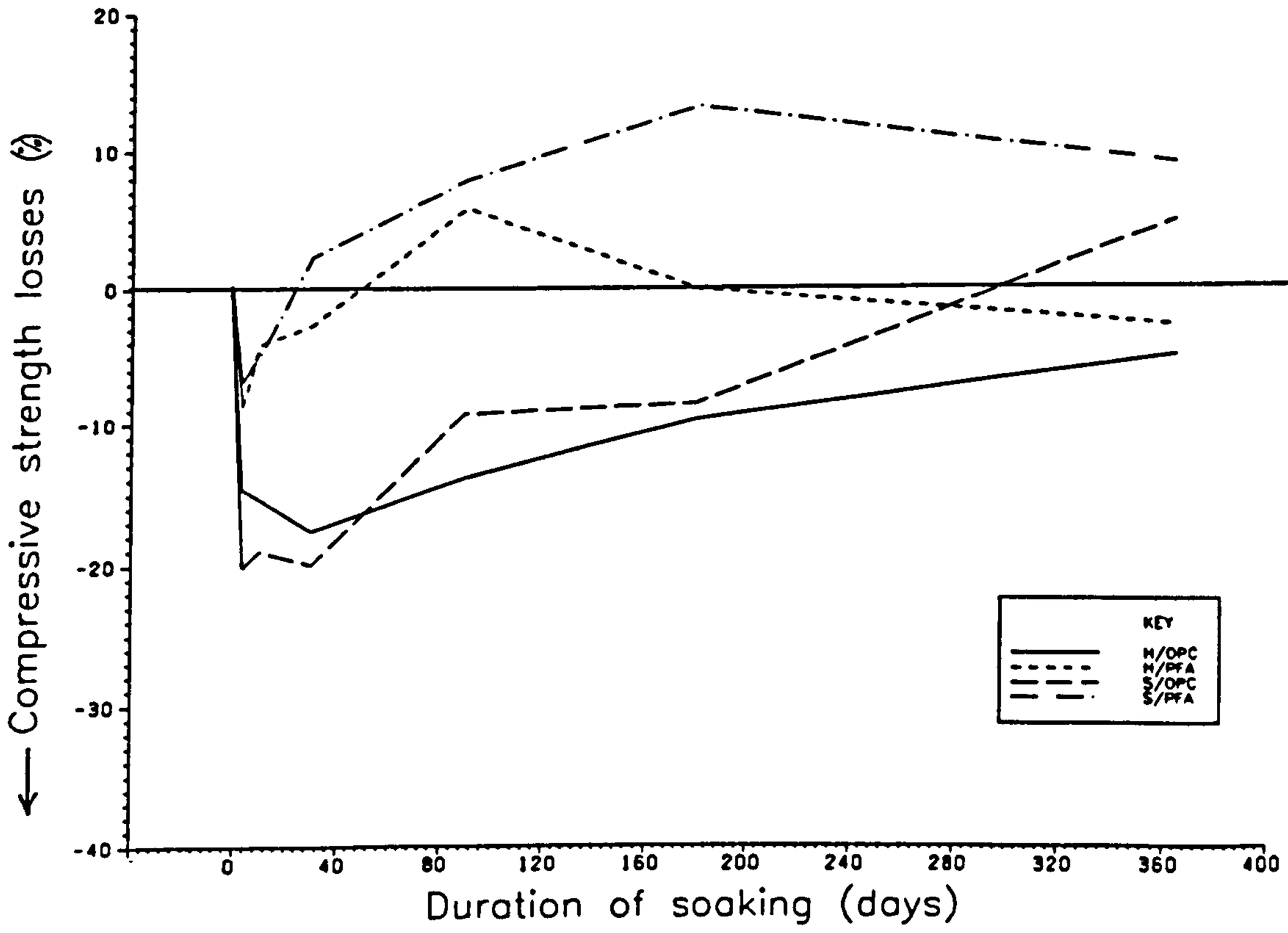
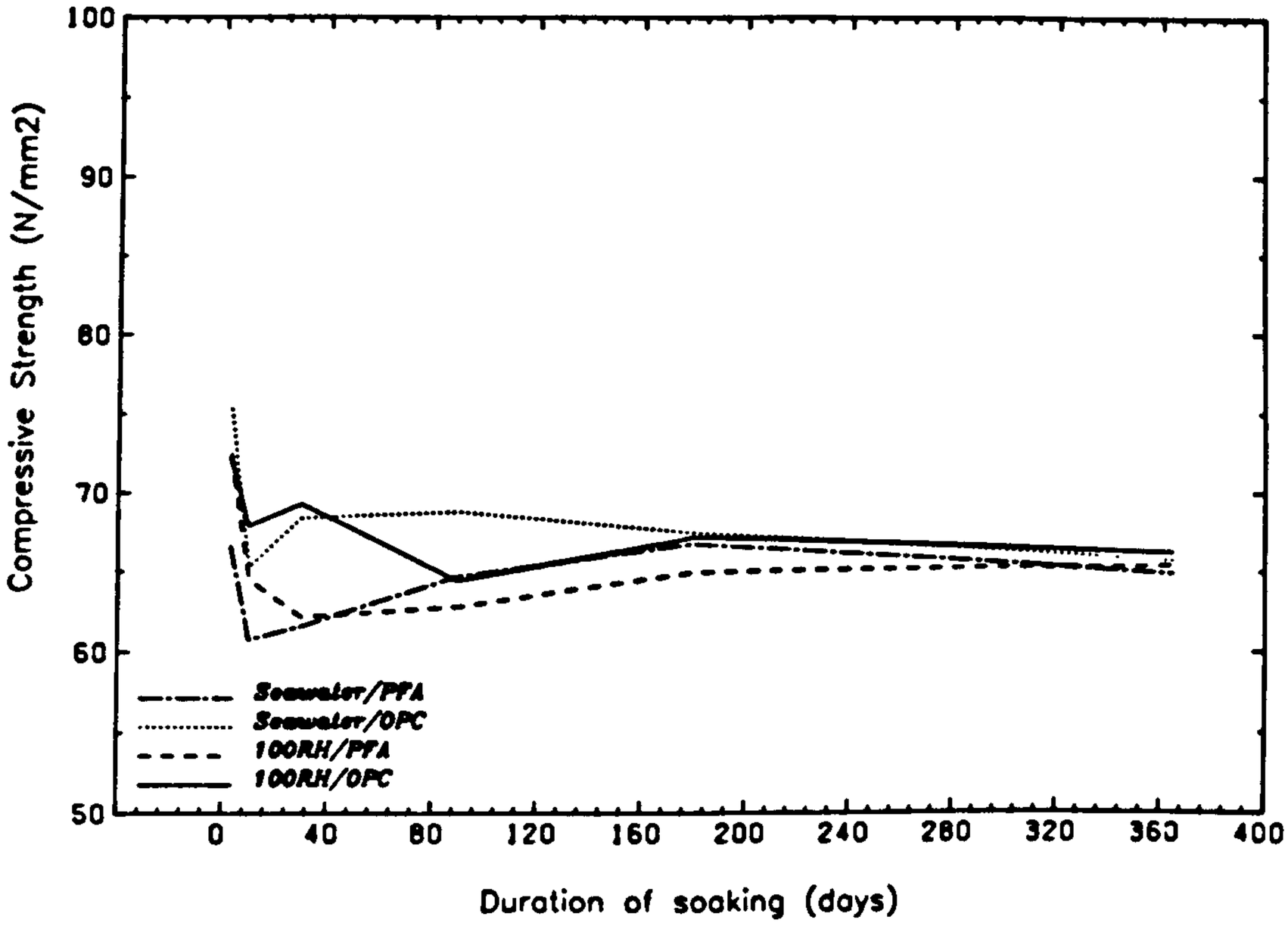


FIGURE 7.19 :

(a) Compressive strengths of saturated moist concretes soaked in crude oil at 80 deg.C



(b) Compressive strength as percent of moist strength prior to soaking in crude oil at 80 C.

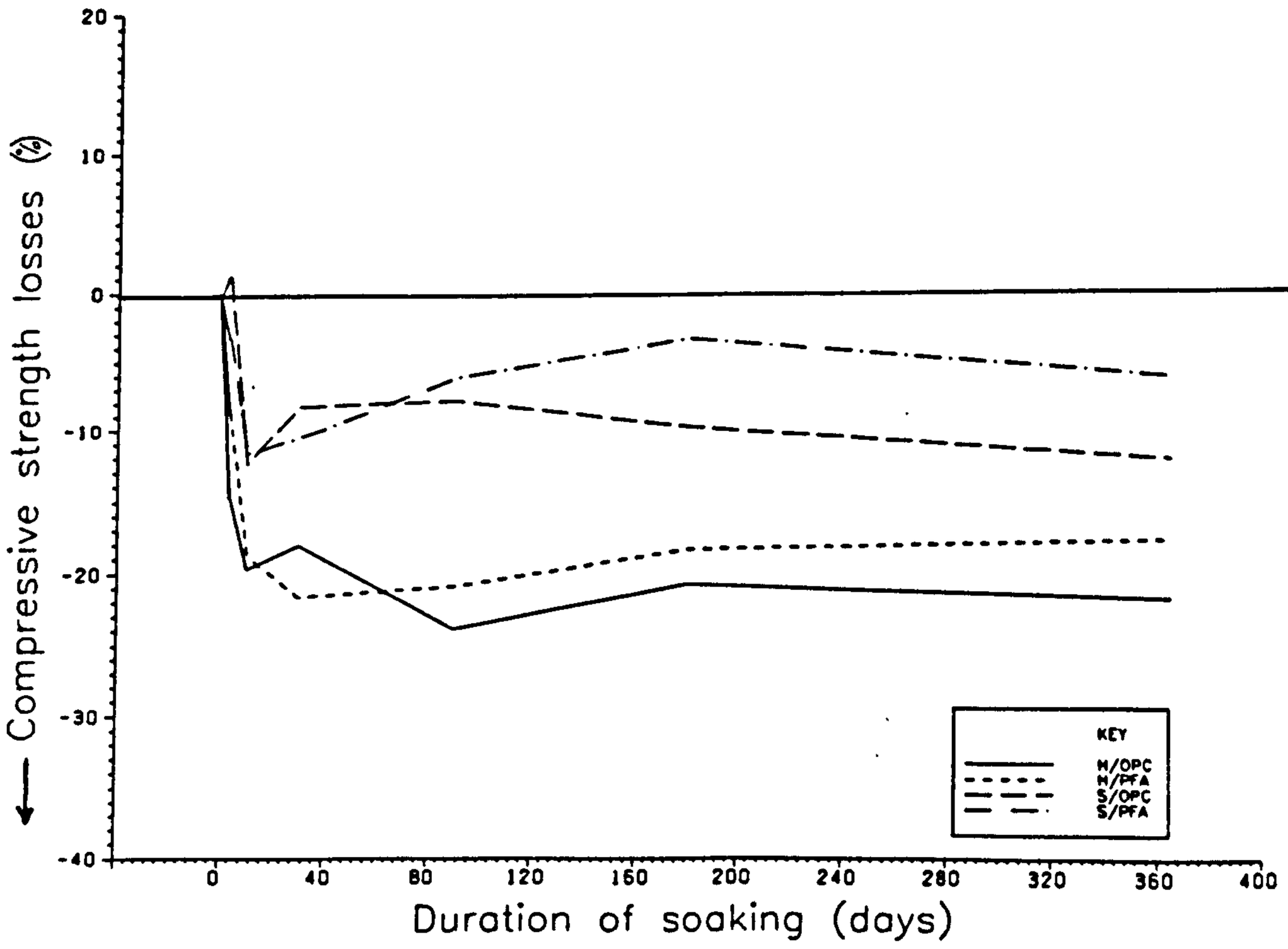


TABLE 7.6 : Compressive strength losses of moist concrete specimens soaked in water.

Temp. (C)	Duration in water (days)	Compressive strength losses (% change from 365d moist strength)			
		H/OPC	H/PFA	S/OPC	S/PFA
20	3	-	-	-	-
	10	-	-	-	-
	30	+4.1	+4.0	+3.2	+4.8
	90	-	-	-	-
	180	-8.5	-2.4	-13.7	-2.2
	365	-4.9	-3.8	-15.7	-2.2
	average	-3	-1	-8	+0.2
45	3	-10.8	-6.4	-8.6	-3.2
	10	-3.8	-15.1	-16.5	-4.8
	30	-12.0	-1.3	-8.6	-1.3
	90	-13.2	-10.6	-7.8	+7.3
	180	-7.9	+1.9	-7.7	+2.0
	365	-0.7	+13.5	+6.4	+13.8
	average	-8	-3	-7	+2
60	3	-19.4	-11.6	-14.0	-13.7
	10	-17.6	-1.9	-14.4	-3.3
	30	-13.4	-4.8	-14.1	-8.7
	90	-16.7	-3.2	-16.2	-10.6
	180	-12.1	-5.0	-18.4	+2.6
	365	-0.4	-6.1	-8.1	+2.5
	average	-13	-5	-14	-5
80	3	-17.0	-3.2	-18.0	-7.4
	10	-23.7	-15.6	-25.5	-11.2
	30	-23.3	-22.1	-24.4	-3.2
	90	-20.6	-21.3	-14.4	-13.1
	180	-12.2	-10.5	-17.1	-4.7
	365	-15.9	-2.5	-27.8	-3.6
	average	-19	-13	-21	-7

TABLE 7.7 : Comparison of moist compressive strengths of specimens soaked in crude oil and water at elevated temperatures.

Duration of exposure (days)	strength in crude oil / strength in water											
	H/OPC			H/PFA			S/OPC			S/PFA		
	C 45	60	80	45	60	80	45	60	80	45	60	80
3	0.97	1.06	1.03	0.97	1.03	0.94	0.98	0.93	1.23	0.98	1.08	1.05
10	0.86	1.03	1.05	1.10	0.98	0.96	1.05	0.95	1.18	1.00	0.98	1.00
30	0.90	0.95	1.07	0.90	1.02	1.01	0.98	0.93	1.21	0.99	1.12	0.92
90	1.11	1.04	0.96	1.07	1.09	1.01	0.99	1.08	1.08	0.90	1.21	1.08
180	0.99	1.03	0.90	0.99	1.05	0.91	1.00	1.12	1.09	1.04	1.11	1.02
365	1.07	0.96	0.93	0.94	1.04	0.85	0.82	1.14	1.22	0.97	1.07	0.98

TABLE 7.8 : Comparison of moist strength with oven dry strength on exposure to crude oil.

Duration (days)	moist strength / oven dry strength															
	H/OPC				H/PFA				S/OPC				S/PFA			
	20	45	60	80	20	45	60	80	20	45	60	80	20	45	60	80
3	.89	.84	.87	.80	.99	.99	106	.96	.81	.84	.83	.94	.95	.85	.89	.89
10	103	.78	.86	.83	104	.96	106	.88	.86	.97	.76	.87	.80	.85	.88	.82
30	.97	.79	.94	.81	.92	.89	119	.84	103	.85	.90	.94	.85	.89	104	.86
90	.97	102	.83	.88	121	108	112	.99	.92	.96	.97	103	.86	.86	103	.97
180	.92	.94	.95	.94	115	103	107	104	109	100	101	116	102	103	110	114
365	107	133	-	-	109	122	-	-	116	118	-	-	104	126	-	-

Figure 7.20 :Residual compressive strength of moist specimens soaked in water at 20 C as(%)of moist strength.

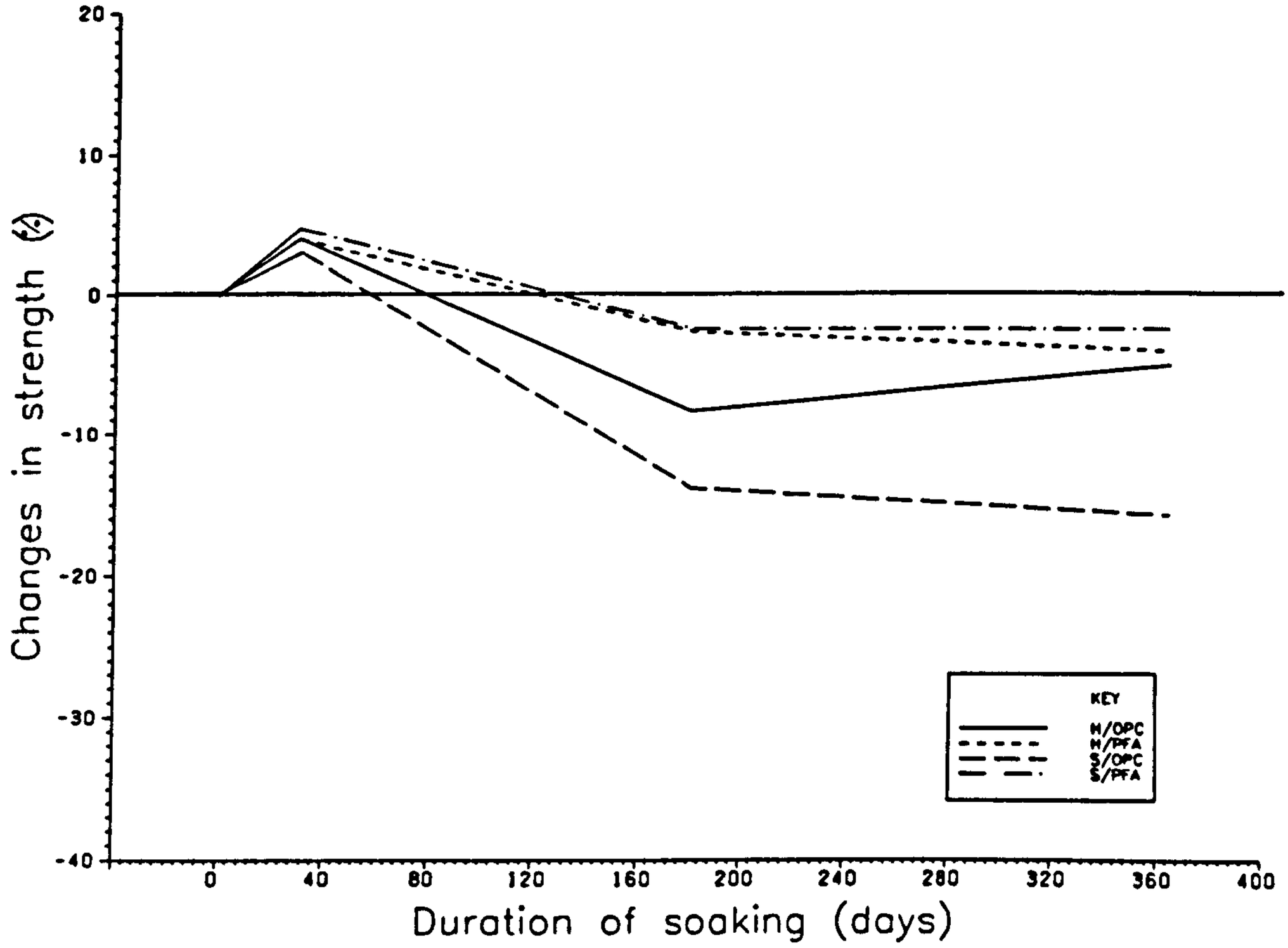


Figure 7.21 :Residual compressive strength of moist specimens soaked in water at 45 C as(%)of moist strength.

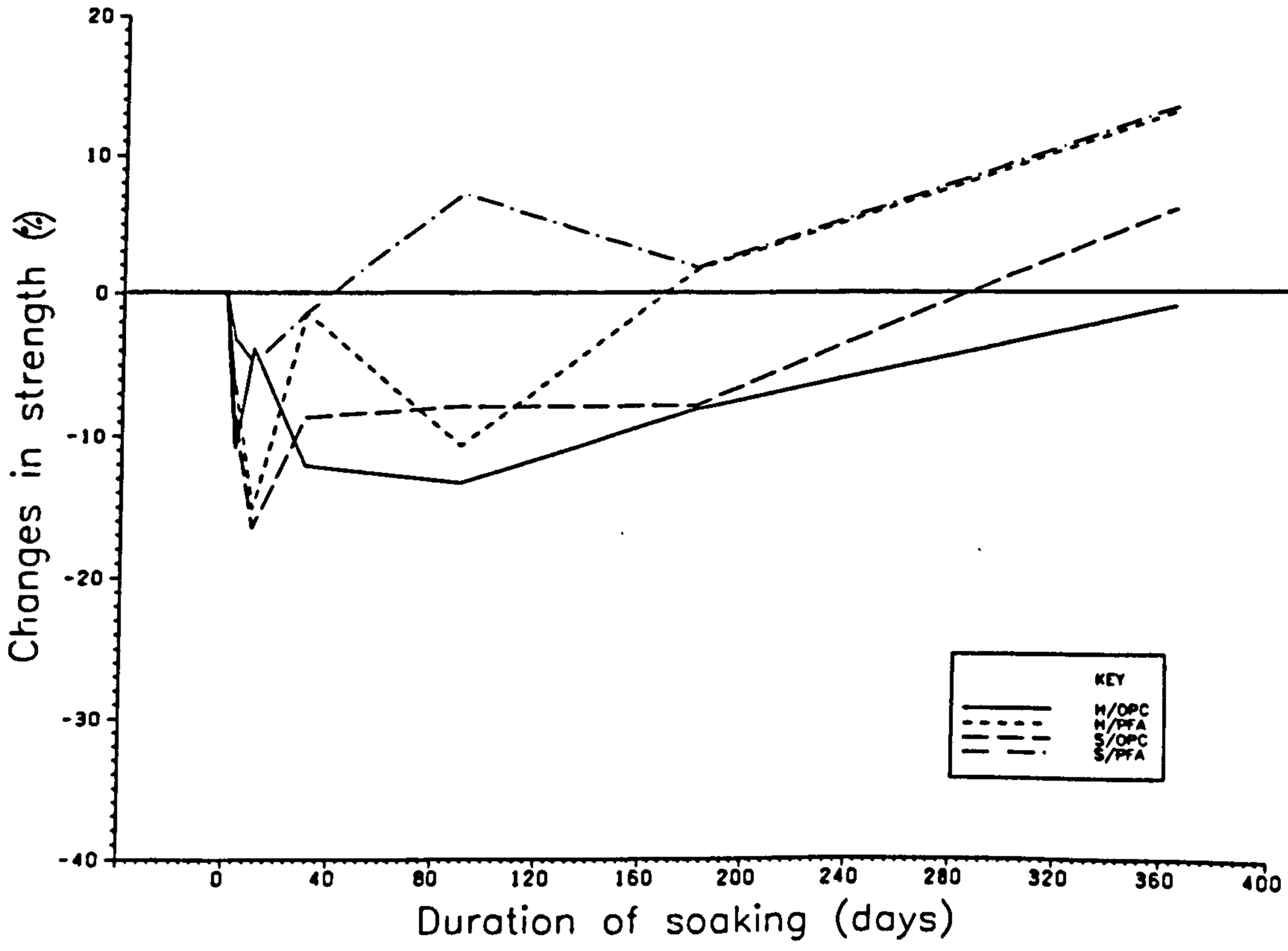


Figure 7.22: Residual compressive strength of moist specimens soaked in water at 60 C as(%) of moist strength.

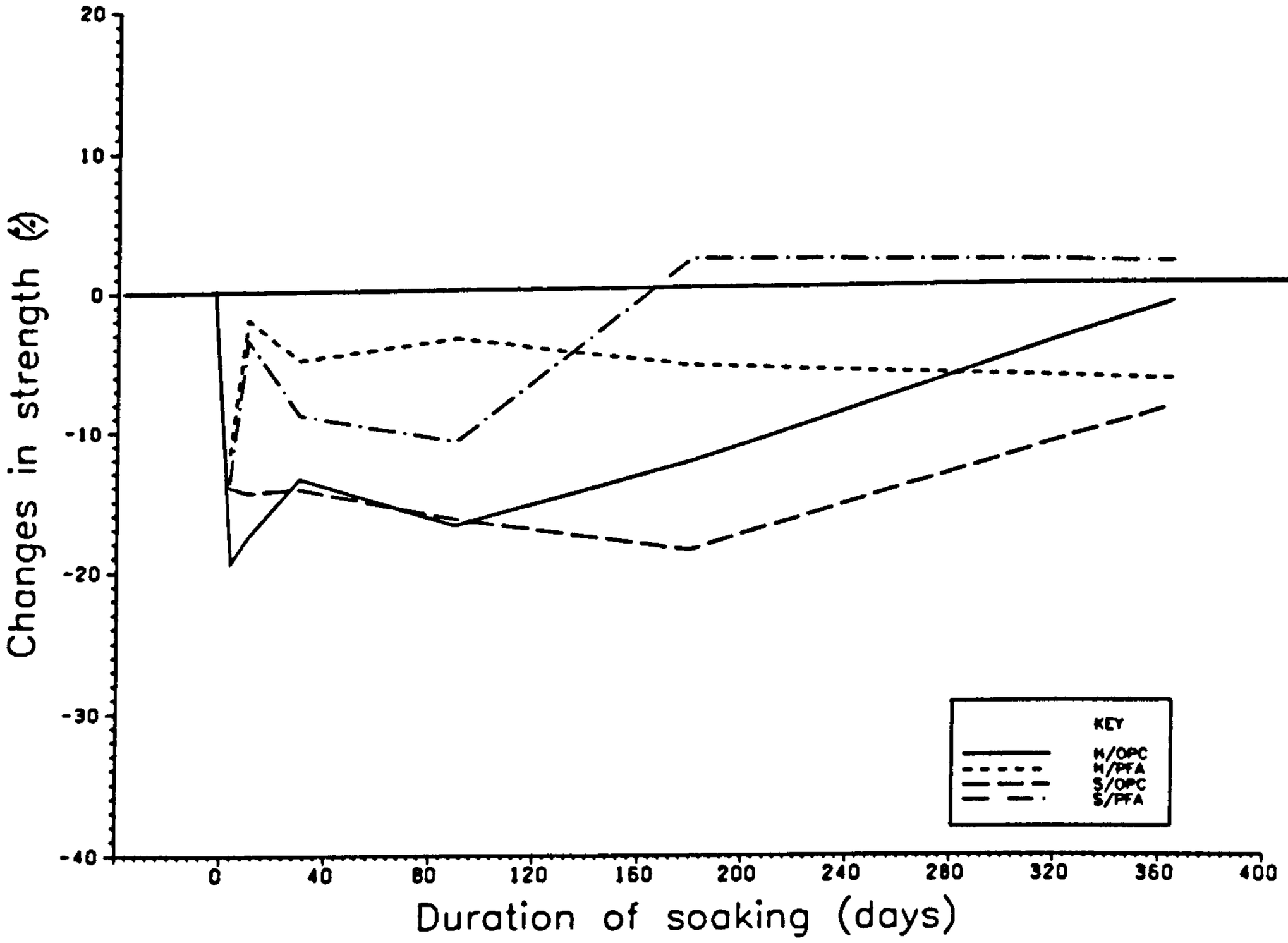


Figure 7.23: Residual compressive strength of moist specimens soaked in water at 80 C as(%) of moist strength.

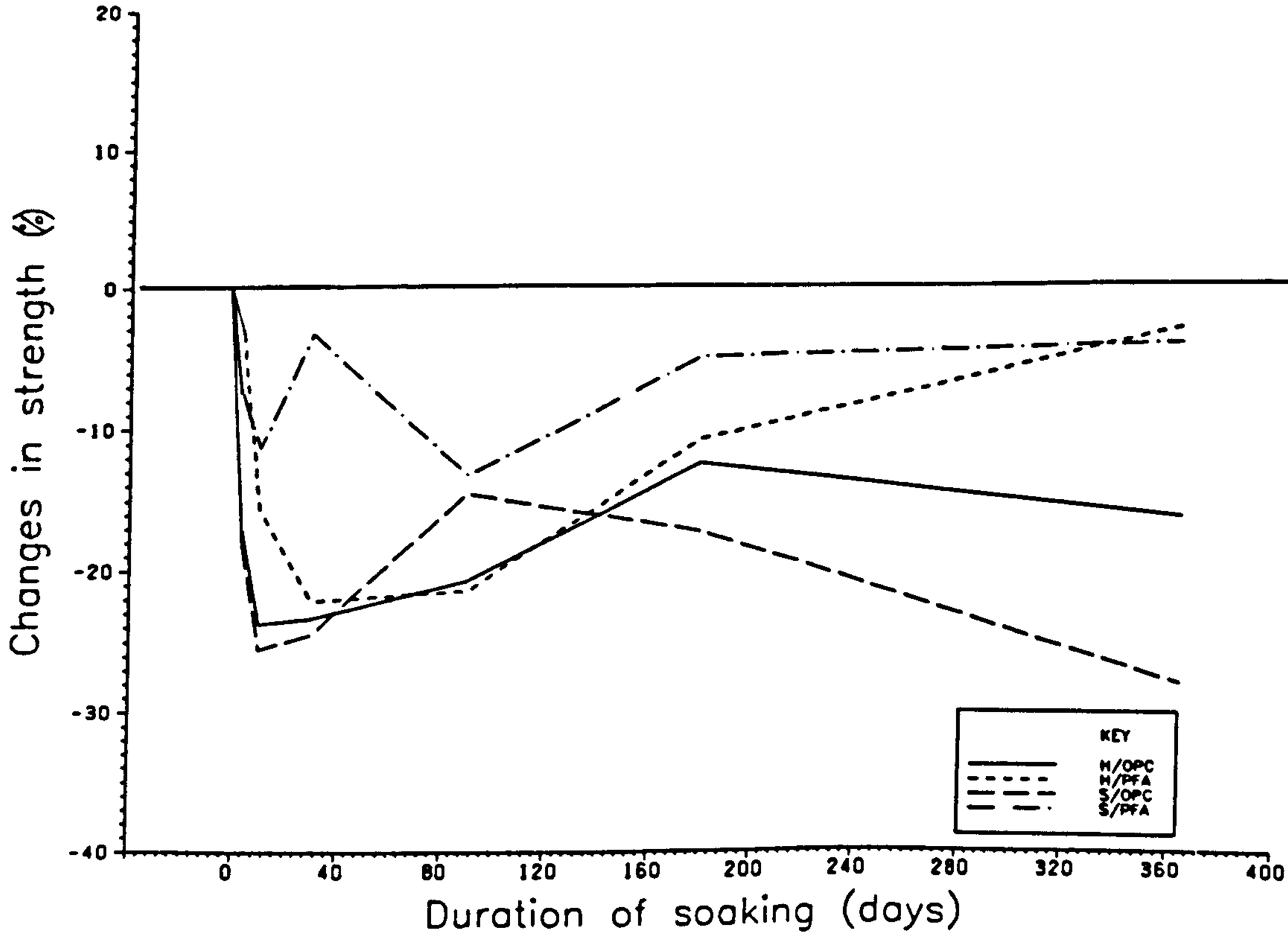


Figure 7.24: Effect of temperature on the compressive strength of oil soaked moist H/OPC concrete specimens

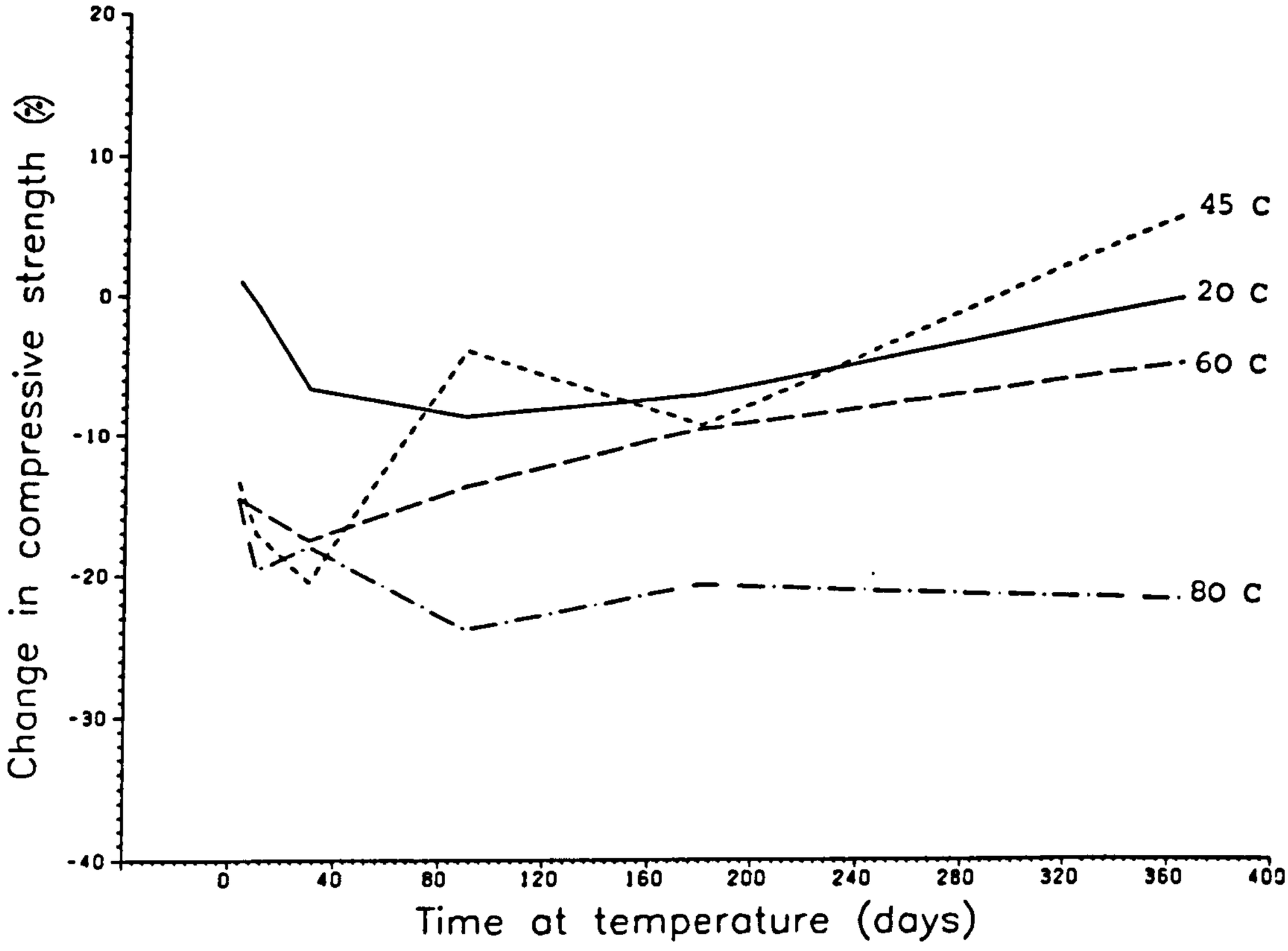


Figure 7.25: Effect of temperature on the compressive strength of oil soaked moist H/PFA concrete specimens

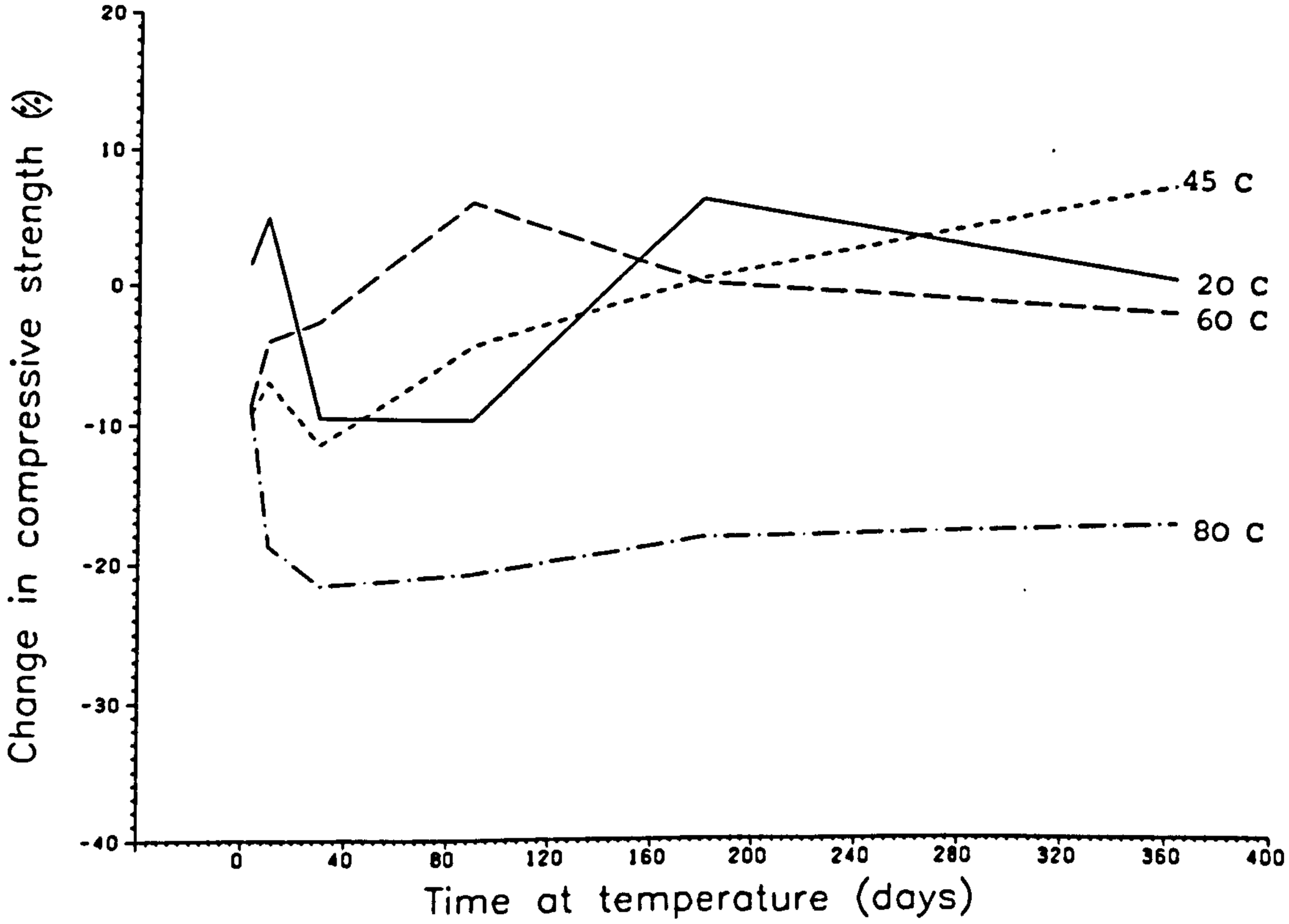


Figure 7.26: Effect of temperature on the compressive strength of oil soaked moist S/OPC concrete specimens

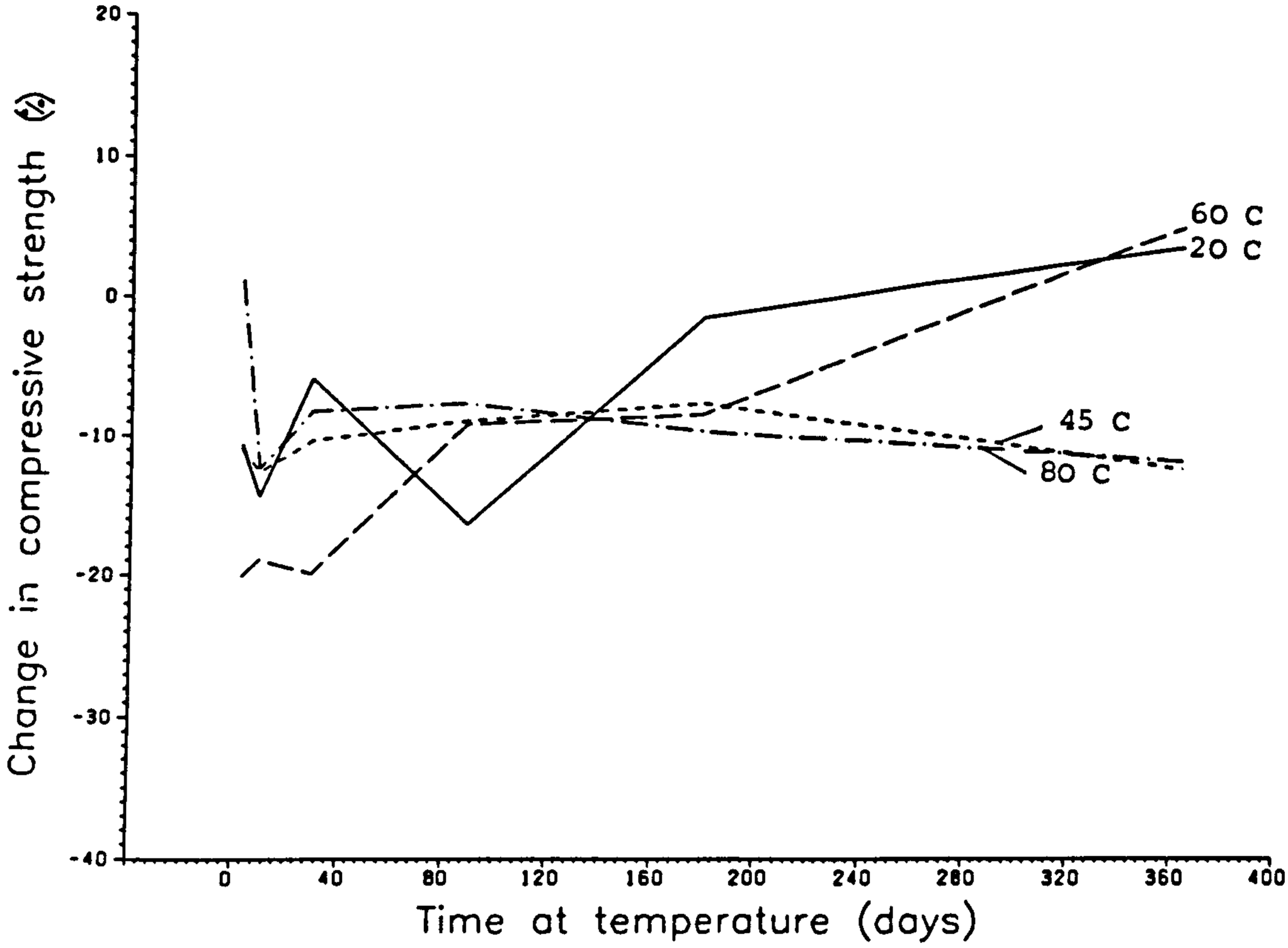
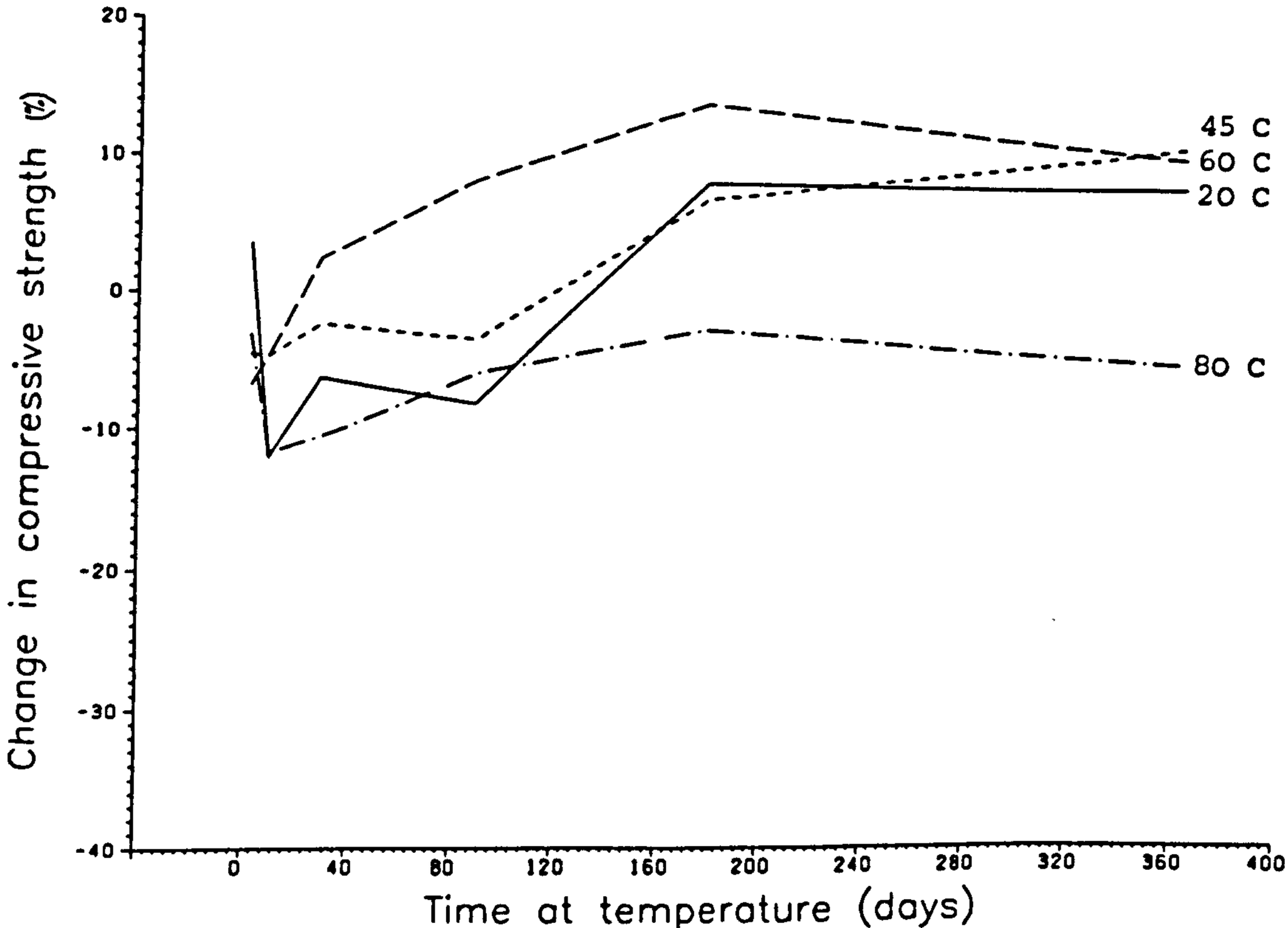


Figure 7.27: Effect of temperature on the compressive strength of oil soaked moist S/PFA concrete specimens



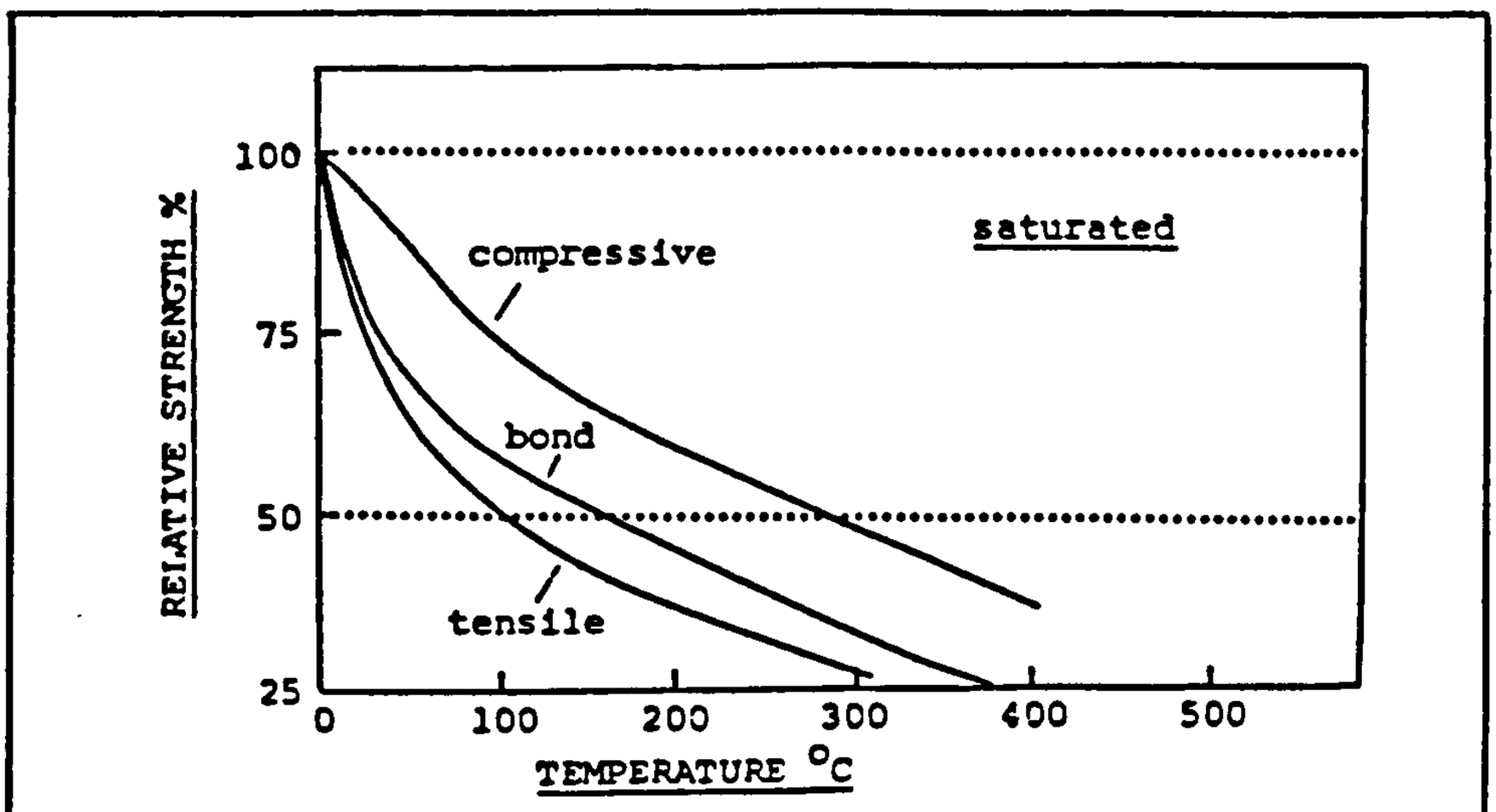


FIGURE 7.28 : EFFECT OF ELEVATED TEMPERATURE ON THE STRENGTH OF MOIST SEALED OPC CONCRETE NOT CONTAINING SILICA IN A REACTIVE FORM /21 /.

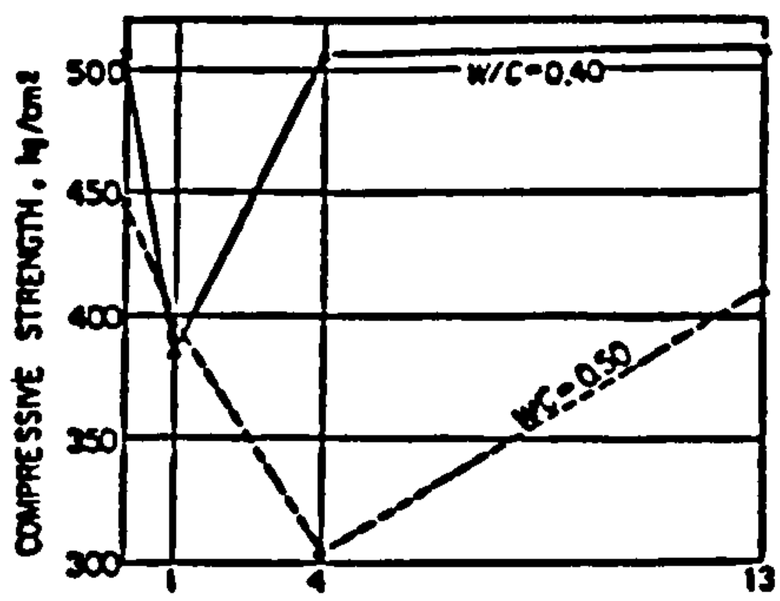


Fig. 7.29 : Compressive strength of concrete stored in sealed container at 70 deg.C after curing in water of 20 deg.C for 300 days /136/.

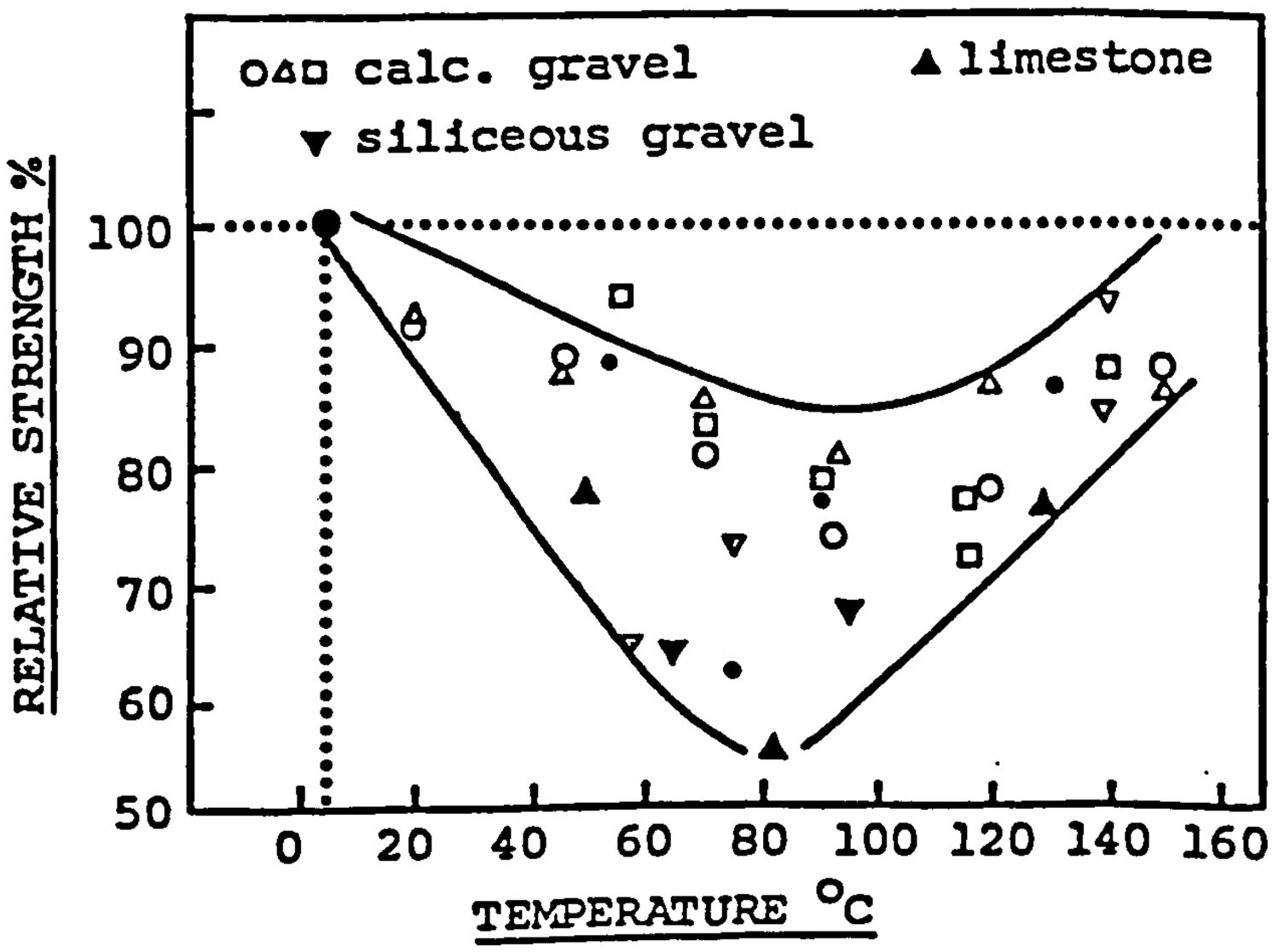


FIG. 7.30 : EFFECT OF TEMPERATURE ON COMPRESSIVE STRENGTH OF UNSEALED CONCRETES /21/.

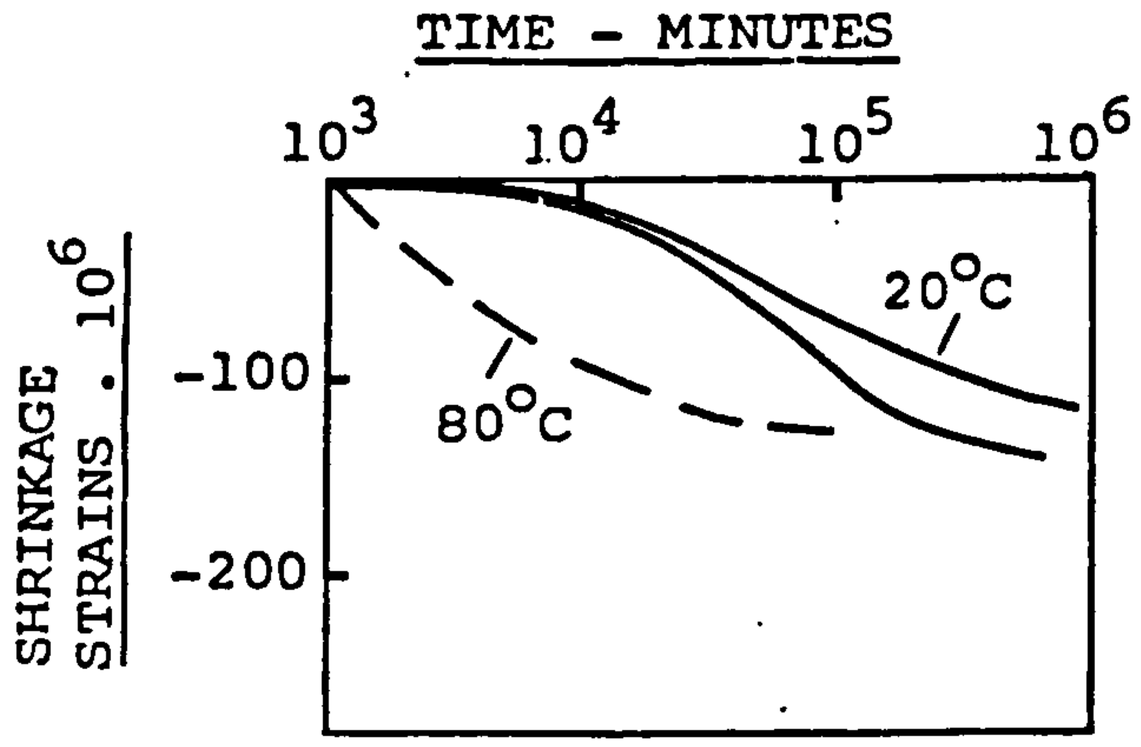


FIGURE 7.31 : SHRINKAGE OF SEALED SPECIMENS DUE TO SELF-DESICCATION ON HYDRATION AT 20°C AND 80°C /6/ .

CHAPTER VIII

LENGTH CHANGE OF MORTAR SPECIMENS EXPOSED TO CRUDE OIL AT ELEVATED TEMPERATURES

8.1 INTRODUCTION

Results of the effects of exposure to crude oil on length change of mortar prisms, at 20 C and at elevated temperatures (after cooling), are given and discussed in this chapter. They are studied in conjunction with crude oil absorption characteristics of the specimens given in Chapter 6, and compared to results of length measurements taken prior to crude oil exposure, presented in Chapter 5.

As in the previous chapter, findings of this study have been presented according to the moisture conditions of the specimens prior to exposure, oven dry or moist, to reflect the form of interaction, single or multiple, that had taken place during exposure to crude oil, respectively.

Analysis of the total data obtained was performed using the Factorial method. This had indicated that each of the 5 main factors investigated and most of the interactions, were highly significant at every test period. The analysis showed that the "residuals" or error factors were in all cases very small, resulting, therefore, in considerably large variance ratios (VR). Expert opinion /206/ sought to interpret this trend, confirmed the already held opinion that results of the analysis were an indication that the factors tested had real effects, which went beyond statistical variations. This confirms the sensitivity of length change tests and is an indication of the accuracy of the measurements.

Under the circumstances, the sums of squares (%SS) had served as the best indicator in determining which factors were most significant.

Analysis of variance showed factors C (oven drying) and D (exposure to crude oil) and their interaction (CD) to be the most significant at all test periods, and at each elevated temperature level. From the results, the following general observations can be made:

(1) The trend of length changes with time of moist specimens soaked in crude oil, differed considerably from the trends observed in the specimens which were soaked after oven drying. There was significantly more expansion in the latter than in the former, for which shrinkage had occurred in certain specimens.

(2) Linear expansions in the control specimens soaked in water, were significantly larger than in the test specimens soaked in crude oil. This was observed for both oven dry and moist specimens.

(3) The effect of exposure to crude oil at elevated temperatures on length change after cooling, was more severe on predried specimens used in the single interaction tests, than on moist specimens used in the multiple interaction tests.

It should be noted that length change measurements were taken after specimens had been cooled to ambient temperature. The results therefore represent residual measurements.

8.2 SINGLE INTERACTION TESTS

8.2.1 RESULTS

Residual length changes of oven dry mortar specimens soaked in crude oil are shown as a function of time in Figs.(8.1) through (8.4), for each test temperature. Variations of length change with temperature are shown in Figs.(8.5) through (8.8) for each specimen type,while variations with crude oil absorption are shown in Figs. (8.9) through (8.13). The following observations can be made:

(1) Length changes in crude oil at 20 C were insignificant (about 20μm) throughout the duration of exposure (Fig.8.1). However, specimens stored at elevated temperatures had shown continuous expansion with time, some of which reached over 700μm, when measured after cooling [Figs.(8.2) to (8.4)].

(2) An interesting correlation between crude oil absorption and linear expansion after cooling, was observed in the specimens stored at elevated temperatures, especially at the later stages of exposure. After the instantaneous absorptions which occurred immediately after soaking (see Fig. 6.3), but which had caused no length changes, two trends in the absorption pattern were identified which fell within the periods from 3 to 90 days and from 90 to 365 days. No significant changes in length had occurred in the first stage, but crude oil absorption in the second stage had resulted in large linear expansions.

(3) The rate of residual linear expansions within each stage was higher the higher the crude oil temperature [Figs.(8.5) to (8.8)].

(4) Ultimate (365 days) expansions in the specimens stored at the 3 elevated temperatures were of similar magnitudes in each of the S/OPC and S/PFA specimens [Figs.(8.7) and (8.8)]. However, in the specimens cured at 100% RH (H/OPC and H/PFA), this had increased with increase in the crude oil test temperature [Figs.(8.5) and (8.6)].

(5) For specimens stored at elevated temperatures, the rate of expansion and the ultimate expansions, were higher in the seawater cured specimens (S/OPC and S/PFA) than in the specimens cured at 100% RH (H/OPC and H/PFA). The difference was by about a factor of two [Table (8.1)]. The largest expansions for all storage temperatures of about 700μm, occurred in the S/OPC specimens, while the H/PFA specimens had expanded the least with a maximum of about 450μm at 80 C.

(6) Results have shown that the variation of crude oil absorption with expansion was independent of the storage temperature and was similar for all specimens, irrespective of cement blend (presence of pfa) and the method of curing (Fig. 8.13).

(7) After a period of 365 days in crude oil at elevated temperatures, the S/OPC and S/PFA specimens had each recovered about one half of the nett shrinkages which had occurred in the specimens on oven drying. However, the regain in the H/OPC and H/PFA specimens had increased with increase in the test temperature. These were about 40% each at 45 and 60 C and 60% at 80 C, for the H/OPC, and 24%, 37% and 50% at 45, 60 and 80 C respectively, for the H/PFA specimens. Interestingly, the control specimens soaked in water had recovered almost completely by 90 days at 20 C, despite the absence of the effect of elevated temperatures [Table (8.3)].

(8) The blended specimens, H/PFA and S/PFA, had expanded less than the opc specimens, H/OPC and S/OPC respectively, at all temperatures [Figs. (8.1) to (8.4)]. The difference in expansions between each pair was uniform over the period between 90 and 365 days, when steady state seemed to have been achieved [Table (8.2)].

(9) The difference in linear expansions between S/OPC and S/PFA specimens was larger than between H/OPC and H/PFA specimens. Statistical t-test analysis (Table 8.2) showed that the difference between the pair of differences, over the period from 90 to 365 days, was significant. This suggests that curing in seawater had caused more deterioration in the S/OPC than in the S/PFA specimens. It also suggests that differences in microstructure prior to soaking in crude oil between the opc and pfa specimens, were greater for those cured in seawater than for those cured at 100% RH.

FIG. 8.1:

Residual length change of oven-dry mortar specimens soaked in crude oil at 20 deg.C

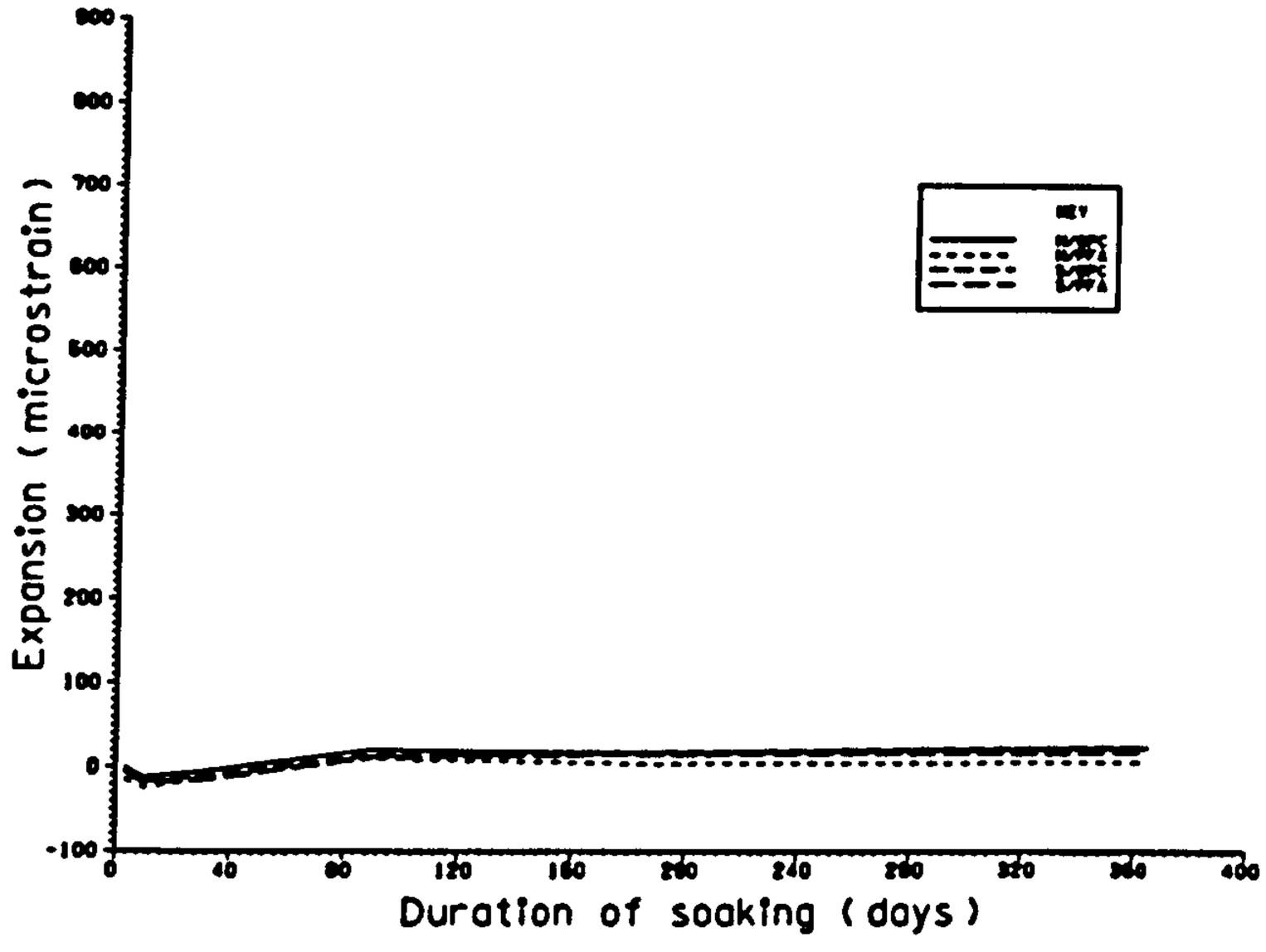


FIG. 8.2:

Residual length change of oven-dry mortar specimens soaked in crude oil at 45 deg.C

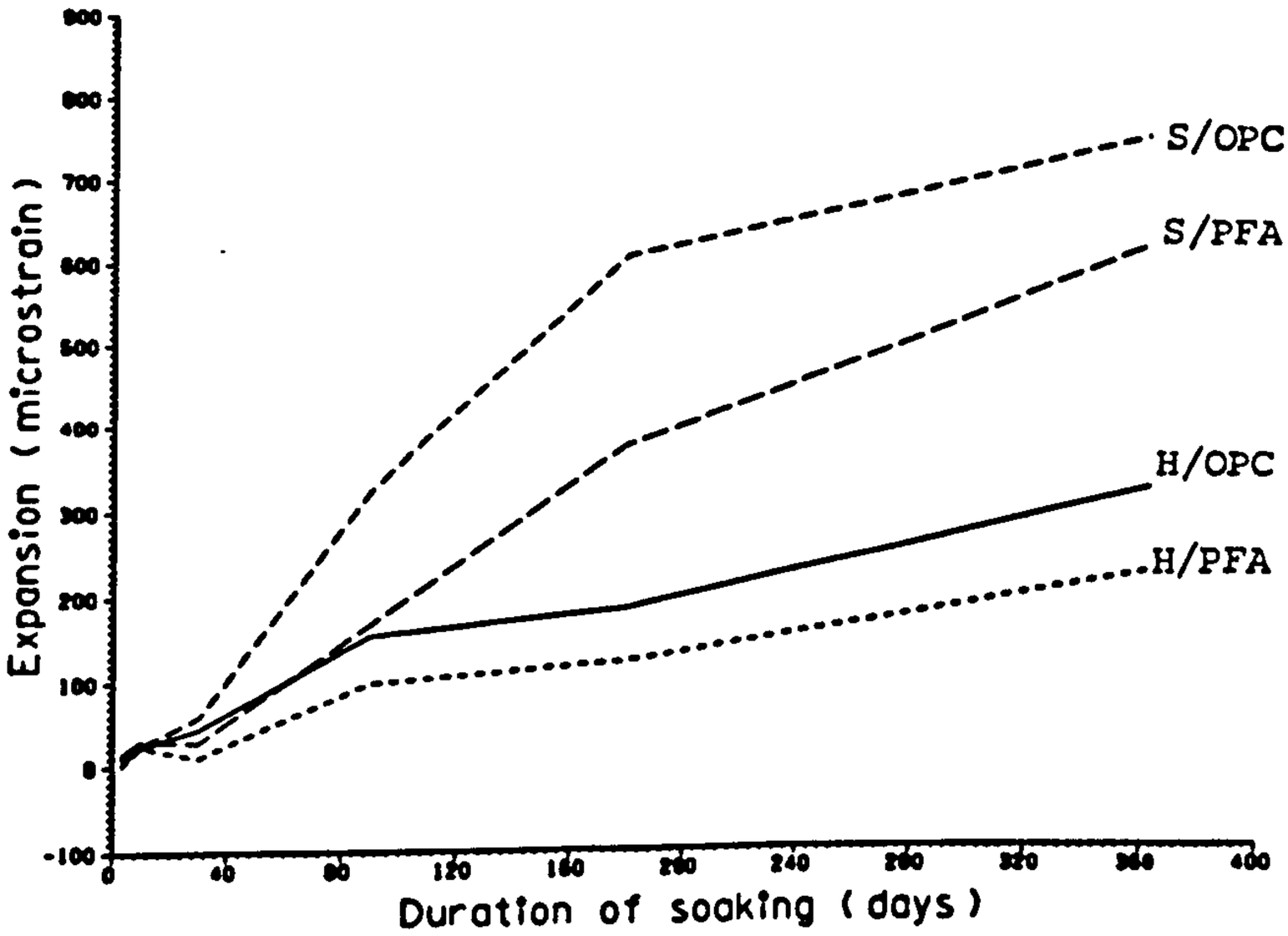


FIG. 8.3 :
Residual length change of oven dry mortar specimens soaked in crude oil at 60 deg.C.

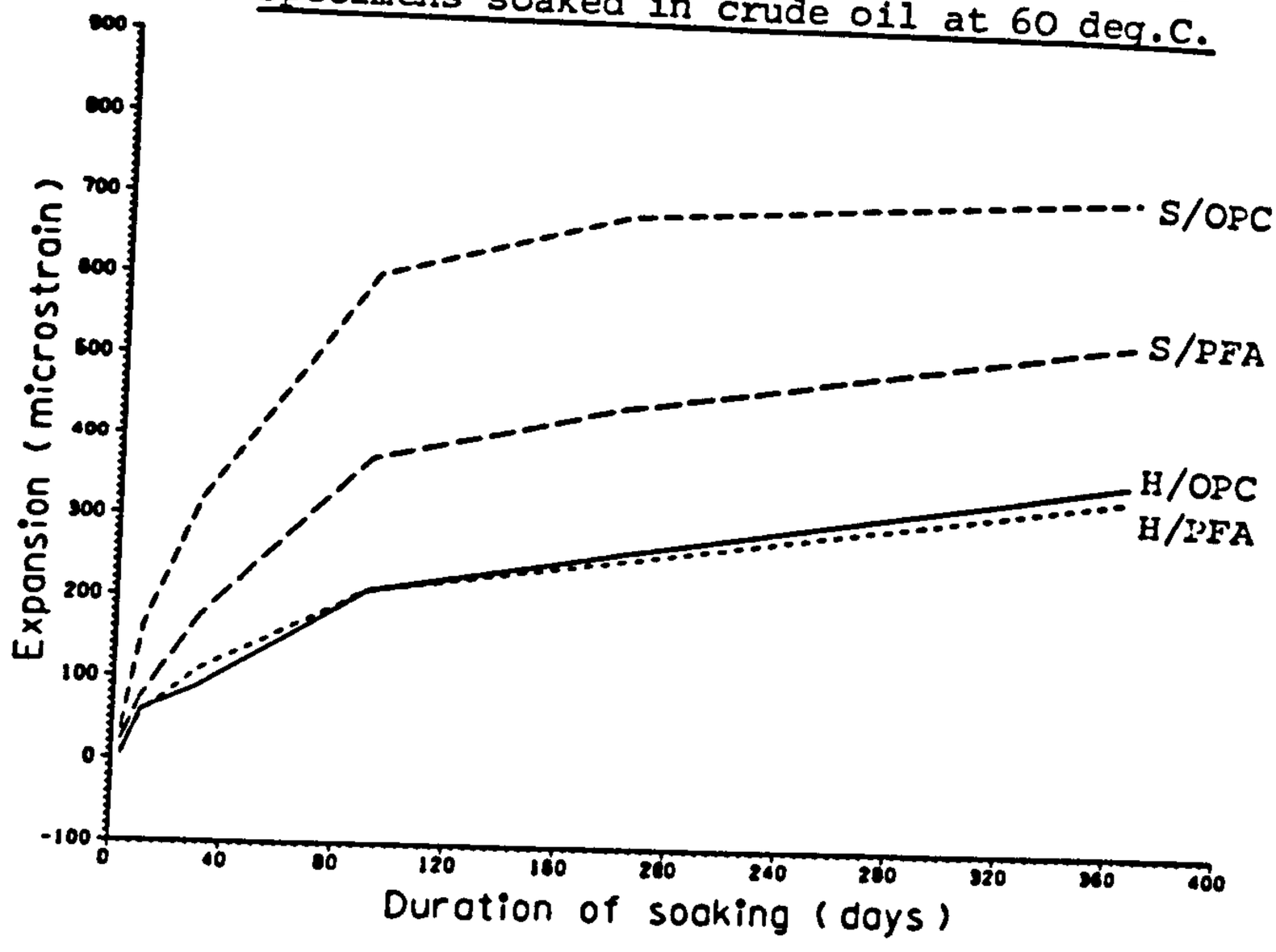


FIG.8.4 :
Residual length change of oven-dry mortar specimens soaked in crude oil at 80 deg.C.

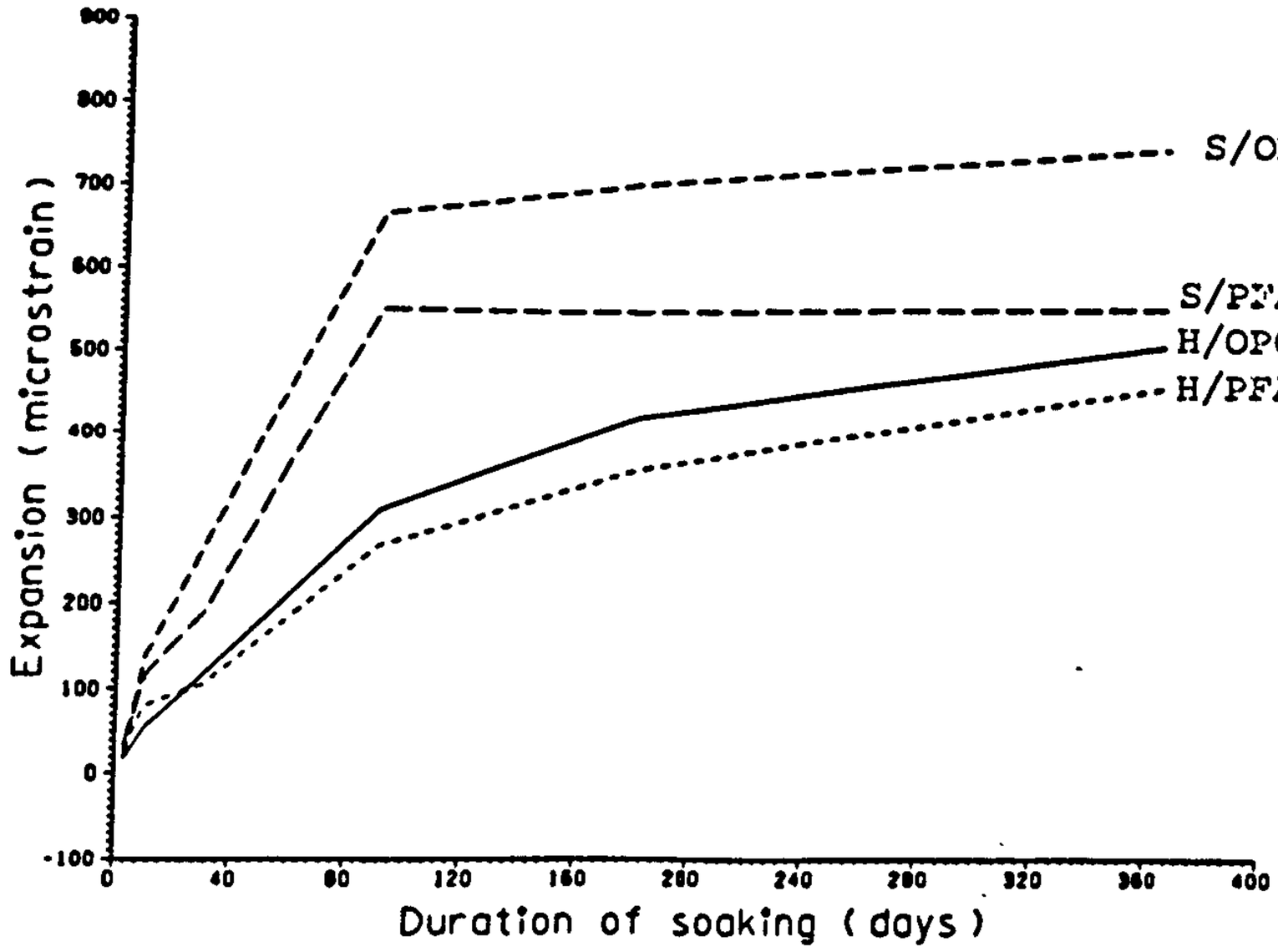


FIG.8.5:

Effect of temperature on length change of oven-dry H/OPC mortar samples in crude oil.

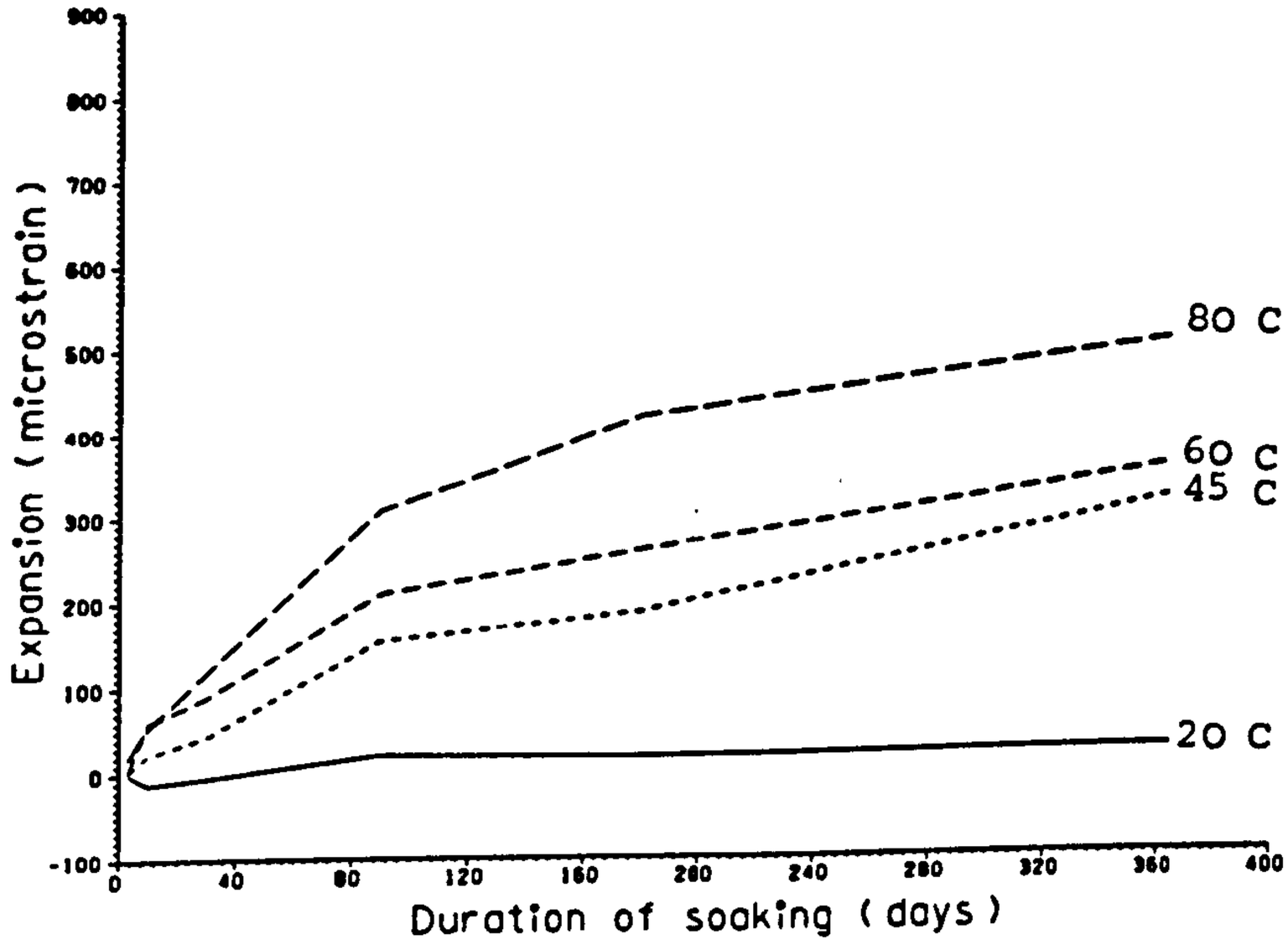


FIG.8.6:

Effect of temperature on length change of oven-dry H/PFA mortar samples in crude oil

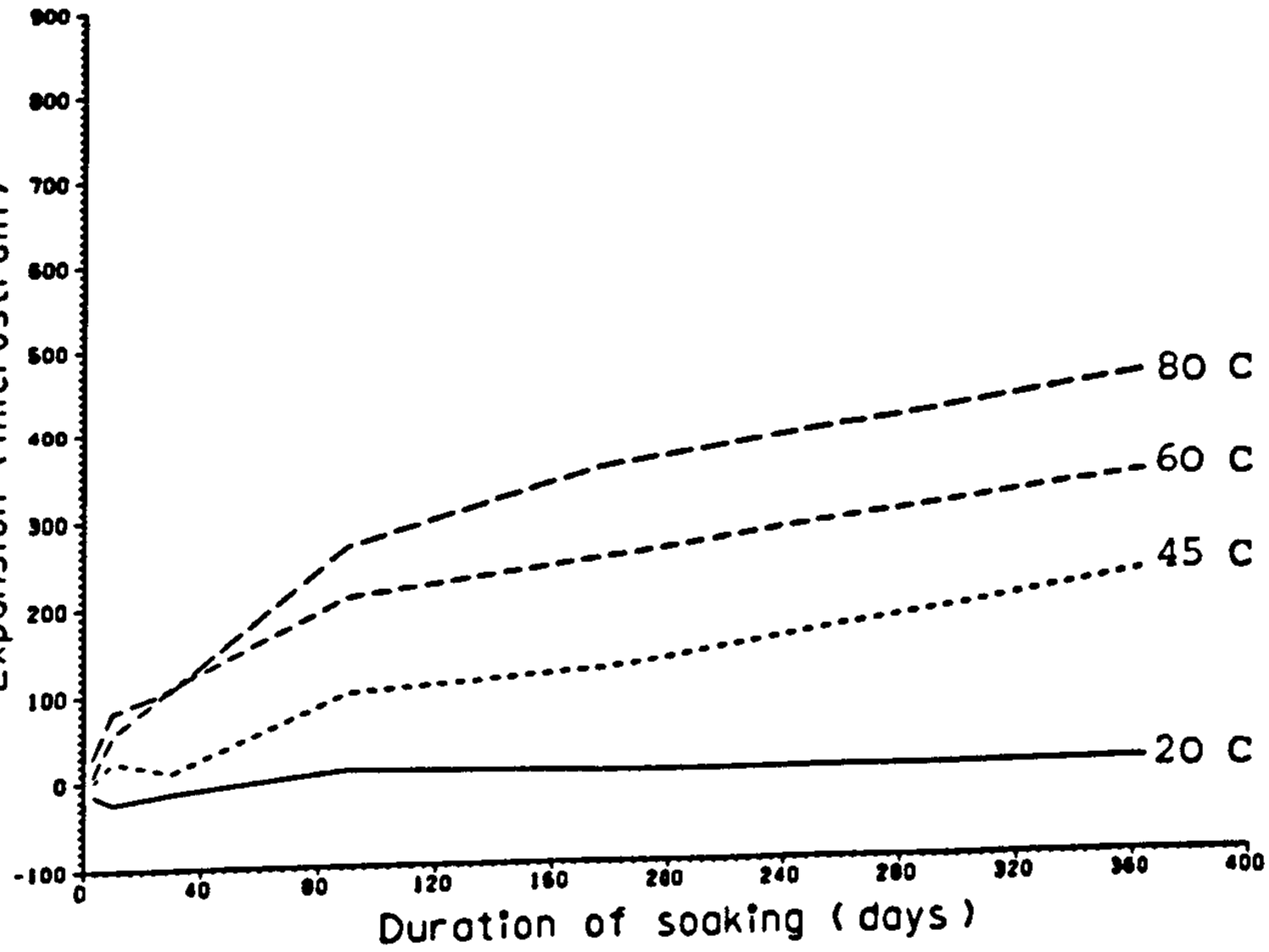


FIG.8.7:

Effect of temperature on length change of oven-dry S/OPC mortar samples in crude oil.

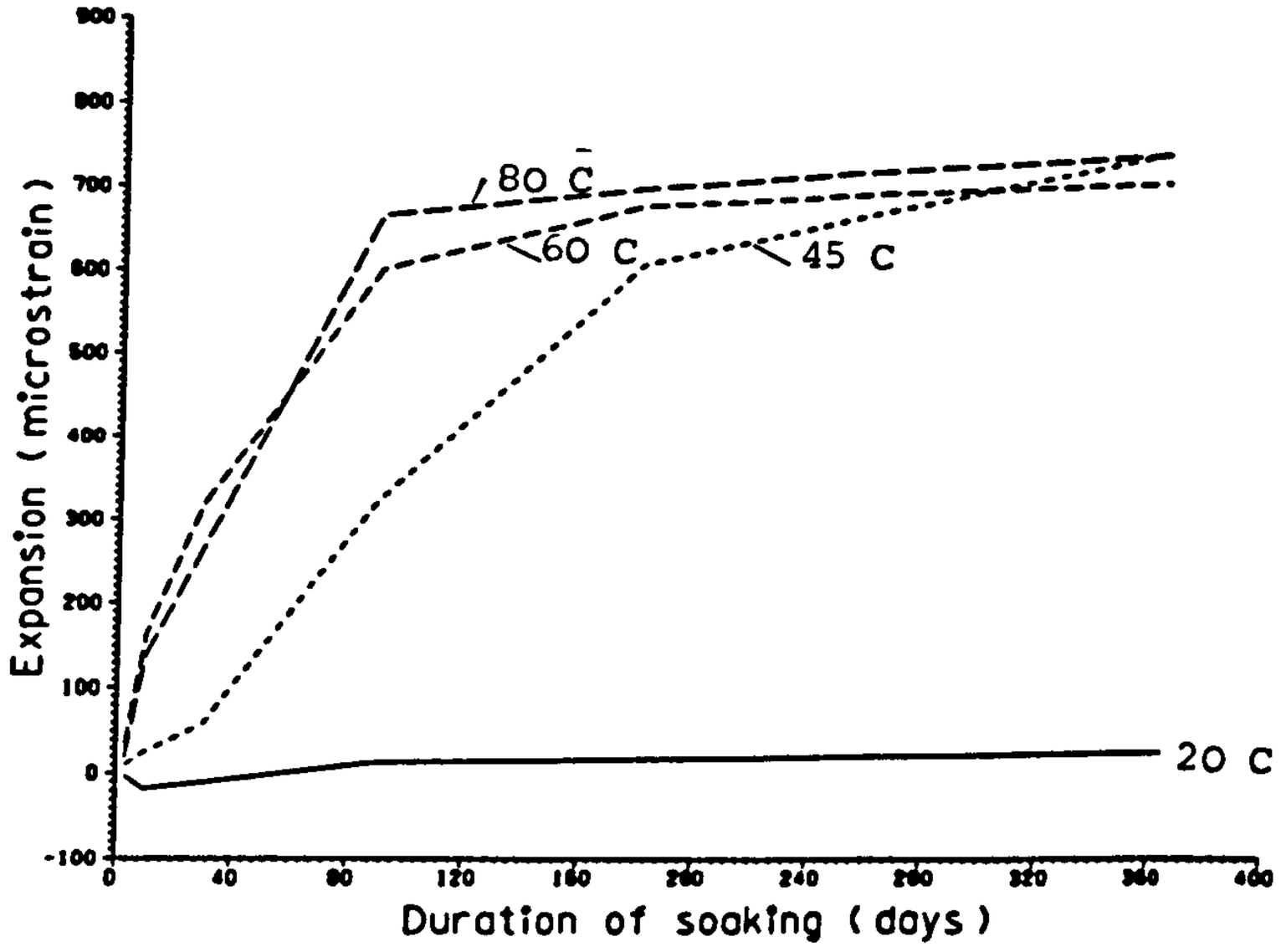


FIG.8.8:

Effect of temperature on length change of oven-dry S/PFA mortar samples in crude oil.

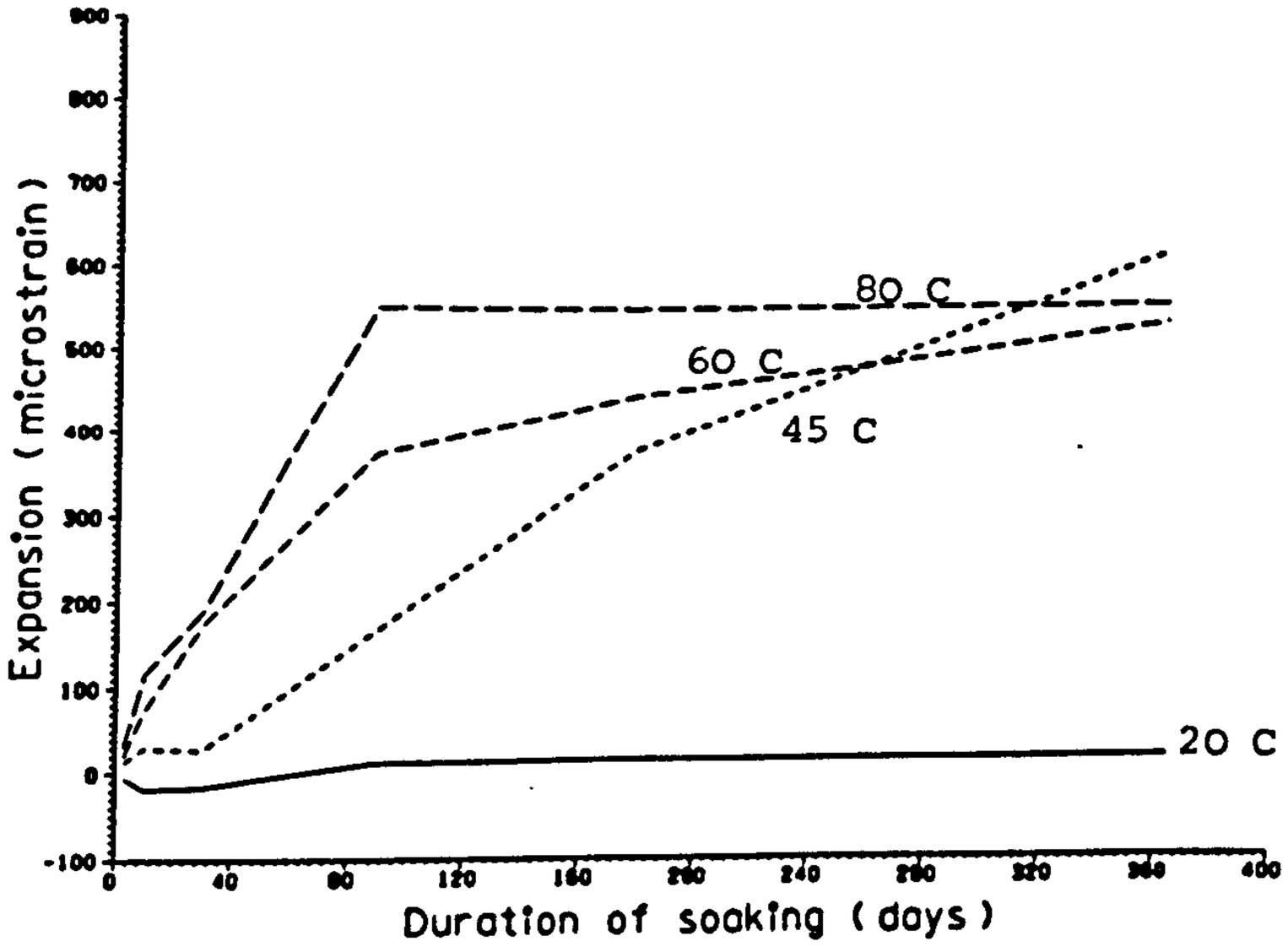


FIG.8.9: Length change vs crude oil absorption at 20 deg.C

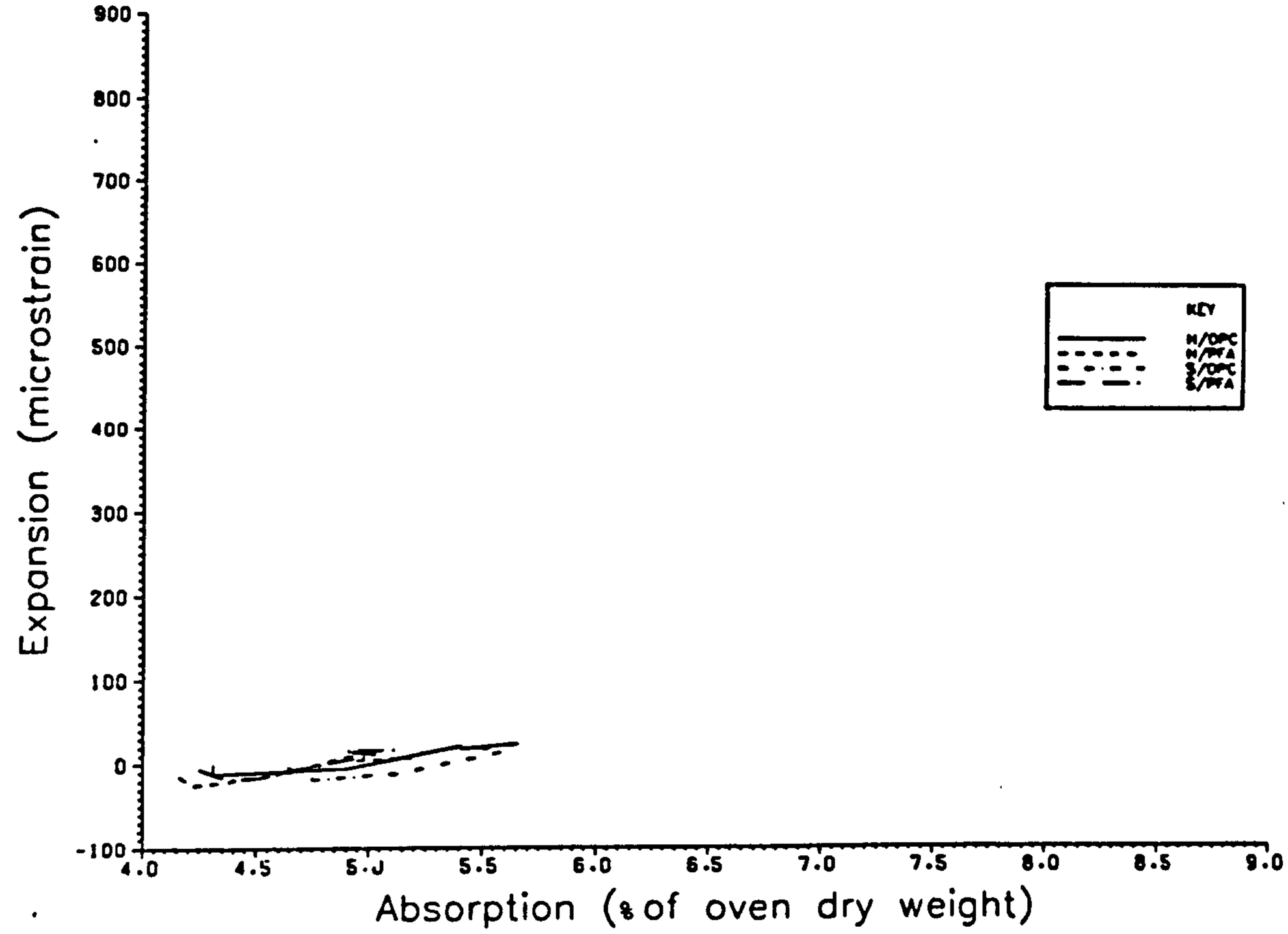


FIG.8.10: Length change vs crude oil absorption at 45 deg.C

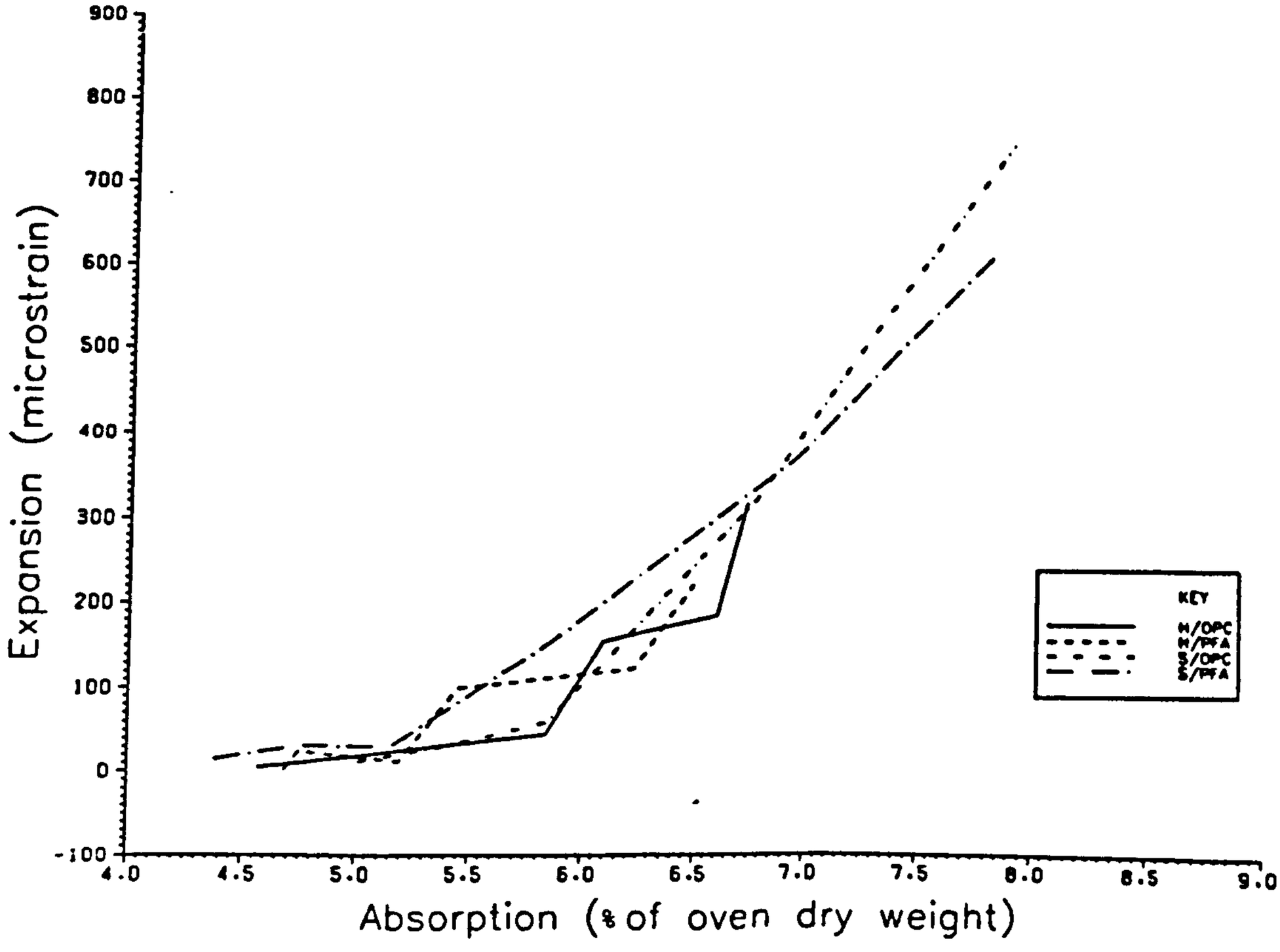


FIG.8.11 : Length change vs crude oil absorption at 60 deg.C

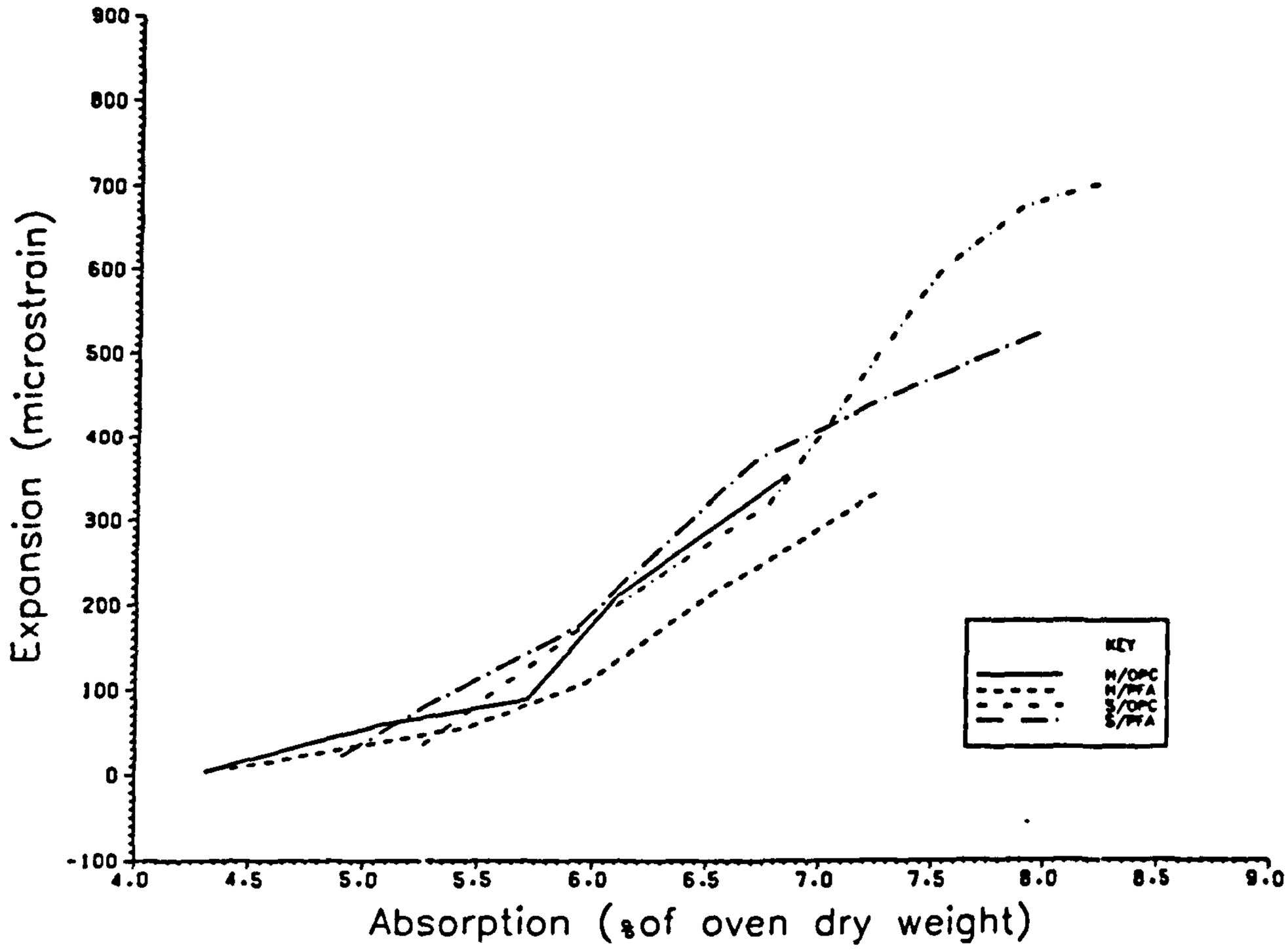


FIG.8.12: Length change vs crude oil absorption at 80 deg.C.

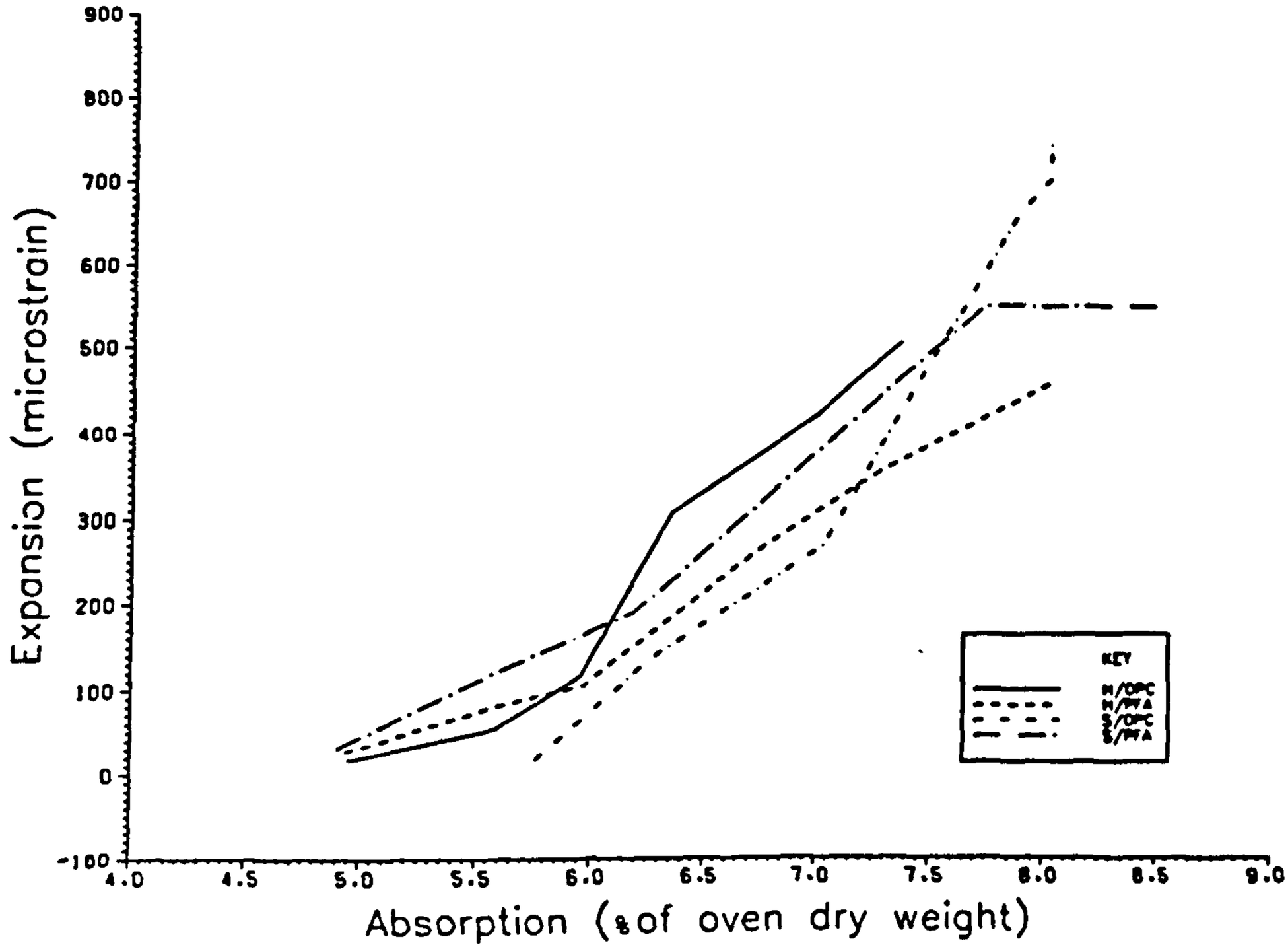


FIG.8.13: Length change vs Crude oil absorption for all elevated test Temperatures

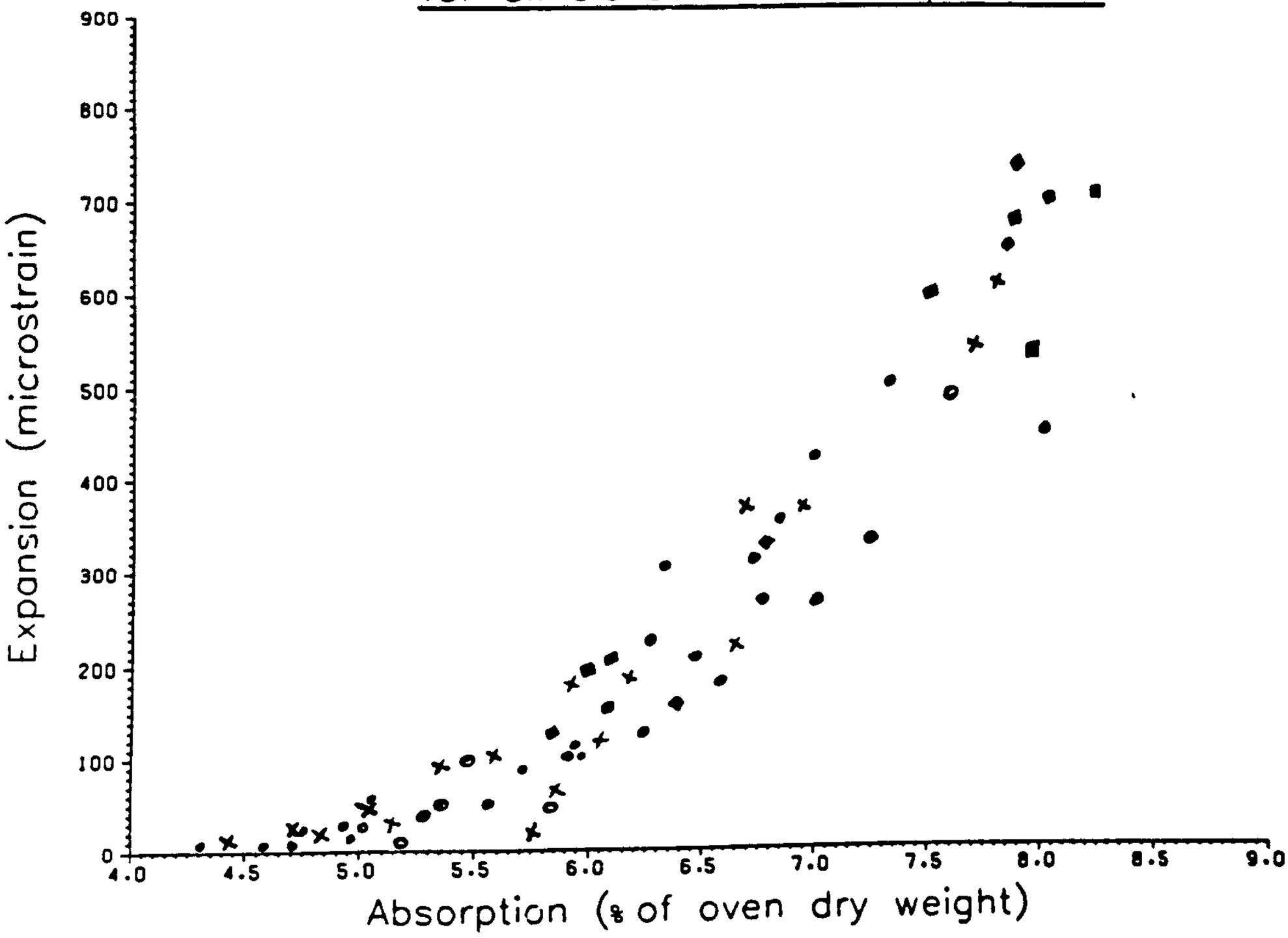


TABLE 8.1 : Comparisons of the effect of the method of curing on linear expansions of oven dry mortar specimens in crude oil.

Temp. (C)	Duration in oil (days)	ratio of expansions in specimens S/OPC / H/OPC	S/PFA / H/PFA
20	3	-	0.36
	10	-1.50	0.72
	30	2.10	-1.14
	90	0.67	1.14
	180	1.00	3.20
	365	1.09	2.50
	av.	0.67	1.13
45	3	3.00	-
	10	1.13	1.28
	30	1.32	2.67
	90	2.09	1.70
	180	3.27	3.06
	365	2.34	2.77
	av.	2.03	2.30
60	3	-	-
	10	2.72	1.34
	30	3.62	1.61
	90	2.88	1.78
	180	2.63	1.77
	365	1.99	1.57
	av.	2.77	1.61
80	3	-	-
	10	2.56	1.43
	30	2.27	1.79
	90	2.16	2.06
	180	1.67	1.54
	365	1.47	1.21
	av.	2.03	1.61

TABLE 8.2 : Comparisons of the effect of blending on linear expansions of oven dry mortar specimens in crude oil.

Temp. (C)	Duration in oil (days)	ratio of expansion of specimens H/OPC (H) H/PFA	S/OPC (S) S/PFA
20	3	-	0.70
	10	0.48	1.00
	30	0.36	0.66
	90	2.00	1.17
	180	3.60	1.13
	365	3.29	1.47
45	3	-	0.75
	10	0.98	0.87
	30	4.19	2.07
	90	1.57	1.93
	180	1.51	1.62
	365	1.44	1.21
60	3	0.50	1.67
	10	1.07	2.17
	30	0.83	1.84
	90	1.00	1.61
	180	1.04	1.54
	365	1.06	1.34
80	3	0.64	0.56
	10	0.67	1.19
	30	1.11	1.41
	90	1.15	1.21
	180	1.18	1.28
	365	1.11	1.35

Statistical t-Test to compare H and S, between the periods 90 and 365 days at the 3 elevated temperatures.		
means	1.23	1.45
DOF	16	
t-value	2.0903	
probability (p)	0.05	
remark	significant	

8.2.2 DISCUSSION OF THE RESULTS OF SINGLE INTERACTION TESTS

The results given in section (8.2.1) for the oven dry mortar specimens, clearly indicated that no length changes had occurred in crude oil at 20 C. However, significant expansions had taken place by storing in crude oil at the 3 elevated temperatures. The implication of this is that at ambient (20 C), crude oil had no significant physical or chemical effect on volume changes of the specimens. As will be explained below, heating affects both the mobility of the fluid and the microstructure of the mortar, thus contributing to the residual expansions measured after cooling.

The mechanisms associated with swelling in HCP which have been discussed in Chapter 2 are; swelling pressures, interlayer moisture movement, surface tension and capillary effects. In these mechanisms, it is the adsorption of water into the gel pores rather than into the capillary pores that causes swelling in the HCP. Evidence of this have been given in publications by Powers /157, 159/ and other workers /85, 111, 200/. The relatively limited penetration of crude oil into the gel pore system is largely due to its larger molecular size range.

Comparison of the volume absorption of crude oil with the volume absorption of water given in Chapter 6, indicated that for exposure at 20 C, there was more absorption of water than of crude oil. The difference in this absorption pattern had increased with increasing porosity for the 4 specimen types, from about 4% to 23% (Table 6.8). However, when this is related to the resulting ultimate linear expansions, it was seen that there was about 30 to 50 times more expansion in water even after only 30 days, than in crude oil at 365 days. The only explanation that can be given for this behaviour is that water molecules had penetrated parts of the HCP microstructure (C-S-H), where the chemical/physical interactions that took place had resulted in large linear expansions. On the other hand, the path of crude oil molecules into these points were limited.

The expansions in water of the control specimens can be explained by the swelling mechanisms described earlier, and are in agreement with the findings of other workers /85, 111, 119/. The inability of liquid hydro-

carbons and other fluids with molecules larger than those of water to cause swelling in HCP, has been previously reported /47, 85/. Hrennikoff /85/ had found that kerosene and light lubricating oil were unable to cause swelling in oven dry (110 C) cement paste specimens, although the volume of absorbed fluid was comparable to the volume vacated by water on drying. However, it was also found that when the oil saturated specimens were placed in water, they began to absorb water without displacing the oil or kerosene and at the same time they began to swell. The final expansion as well as the volume of fluid absorbed seemed to have exceeded the original values prior to drying. It was suggested that water had entered the cement paste not through its voids but by way of creeping along the C-S-H particles. Cook and Haque /47/ similarly found that methanol did not cause significant length changes in oven dry paste, compared to those caused by water.

Results of the studies of this thesis, as described above, are in agreement with the findings of Hrennikoff /85/ and further justify the theory of affinity of cement gel for water. These confirm that swelling is dependent on the absorbed fluid reaching the gel, and lend support to the molecular sieve theory proposed by Mills /128/.

8.2.2.1 Effect of Temperature

Quite clearly, heating has contributed to the expansions observed in the oven dry specimens, with crude oil acting as a heat carrier. The trends of residual expansions measured after cooling, were related to crude oil absorption in two stages. Significant expansions during the first stage of absorption did not occur, since crude oil was not able to reach the smaller gel pores and only remained within the larger pores. However, when the gel had been penetrated, as was presumably the case in the second stage, large movements had occurred. This reasoning is enhanced by the other results which showed that the rate of expansion increased with increase in both absorption and temperature of the oil.

The effect of temperature may have been to open up more pore space as a result of the expansion of the gel, thereby accomodating the larger crude oil molecules. The higher the temperature, the greater is the damage to the microstructure and this would cause absorption to increase. On cooling, contraction of the gel is hindered by the molecules of crude oil trapped within it and this may cause it to expand. Heating can also cause damage to the mortar, firstly through the widening of existing microcracks and secondly due to the formation of new ones, within the paste and at the paste-aggregate interface. Damage can also be caused as a result of differential thermal expansions between the aggregates and the paste. Temperature also reduces the viscosity of the penetrating fluid and increases its mobility.

The nett effect of all these factors is that fluid penetration into the gel is enhanced. Once the gel is reached, the mechanisms of swelling are activated and expansions occur. This may explain the residual expansions in crude oil when measured after cooling.

It is believed that the process of expansion as described, was primarily physical and had resulted from the expansions caused by the effect of heating. It was also due to the deeper penetration of the accelerated crude oil particles into the weakened microstructure of the oven dry mortar specimens.

The interesting trend at 365 days, in which similar ultimate magnitudes of expansion were reached at the 3 elevated temperatures, by each of the seawater cured specimens, S/OPC and S/PFA, can be attributed to crude oil saturation of the gel in these specimens. The implication of this is that for a given gel structure, there may be a limit to the amount of expansion that can take place as a result of temperature. It seems that the temperature range of 45-80 C had caused similar ultimate expansions in each of the seawater cured specimens. In the case of the H/OPC and H/PFA specimens, the ultimate expansions had followed the expected trend and had increased as temperature increased.

In Chapter 5, it was established that by the end of the period of curing, porosity in the seawater cured specimens was greater than in specimens cured at 100% RH, as a result of the curing method. This was confirmed by the trends of crude oil absorption of the specimens, as well as by

results obtained from the penetration tests given in Chapter 6. The microstructure of the oven dry seawater cured specimens was probably even more damaged when subjected to second heating on exposure to crude oil at elevated temperatures. The resulting increased porosity had made it easier for the crude oil to penetrate into the gel, which was saturated much faster than the less porous 100% RH cured specimens.

Results have shown that temperature cycle (the rate of heating and cooling were about 5 C/hour), does not significantly change length measurements. It was found that the length measurements of specimens which were cycled were comparable with those of specimens not cycled (see Chapter 3).

8.2.2.2 Effect of cement blend

There was less expansion in the blended specimens, H/PFA and S/PFA, than in the opc specimens, H/OPC and S/OPC, at all temperatures (Table 8.2). This follows the trend of crude oil absorption and can be related to the pore structures of these specimens.

It was established in previous chapters that the outcome of the pozzolanic activities in the OPC/pfa blended specimens was the formation of denser gel structure. Although total porosity may have increased, however, large pore sizes were reduced and redistributed such that penetration by the large crude oil molecules was more difficult than through the opc structure. This had reduced expansion in the blended specimens.

Manmohan and Mehta /116/ and also Marsh et al/118/ had found that pastes containing fly ash had a larger number of finer pores than the control portland cement paste. They concluded that the pore structure of OPC/pfa specimens became more compacted with the process of curing.

8.2.2.3 Effect of the method of curing

The larger expansions in the S/OPC and S/PFA specimens as compared to the H/OPC and H/PFA, were in line with the porosity of the specimens as has been determined. Table (8.1) shows that the rate of expansion and the ultimate expansions in the seawater cured specimens were double those in the specimens cured at 100% RH, at all temperatures.

The results follow the trend which had been observed during and after the period of curing, in which seawater cured specimens had expanded significantly more than the specimens cured at 100% RH during curing, and had contracted more on oven drying. The reason for this was found in the reaction of the C-S-H and CH phases of HCP with the chloride and sulphate ions in seawater /45, 124, 125, 166/. These reactions caused microstructural damage and ultimately led to increased porosity in the specimens, relative to those cured at 100% RH. The porosity of S/PFA specimens was less than of the S/OPC, since the former were influenced less by seawater. In addition, the S/PFA specimens contained less amounts of CH which had been used up in the pozzolanic reactions. Exposure to crude oil at elevated temperatures increased existing deterioration and led to greater expansions in these specimens.

TABLE 8.3 : Expansions of oven dry mortar specimens stored in water at 20 deg.C

Duration in water (days)	Expansions (microstrains)			
	H/OPC	H/PFA	S/OPC	S/PFA
3	460	434	672	305
10	580	529	865	837
30	700	637	1103	869
90	745	670	1201	937

8.3 MULTIPLE INTERACTION TESTS

8.3.1 RESULTS

Residual length changes of moisture saturated mortar specimens soaked in crude oil at 20 C and at elevated temperatures, were clearly different from those earlier observed for the oven dry specimens. Such differences were not unexpected since, unlike the oven dry specimens, the moist specimens did not absorb crude oil (section 6.2.2).

Residual length changes of moist specimens soaked in crude oil are shown as functions of time in Figs.(8.14) through (8.17), for each test temperature. The effects of temperature are shown in Figs.(8.18) through (8.21) for each specimen type. The residual length changes of similarly prepared control specimens soaked in water at the same temperatures, are shown in Figs.(8.22) to (8.25). The following observations can be made:

(1) Exposure of moist mortar specimens to crude oil at temperatures of 20, 45 and 60 C,over a period of one year, had caused residual expansion in the S/OPC specimens, but little or no ultimate length changes in the S/PFA specimens. However, it had resulted in continuous shrinkage with time in the H/OPC and H/PFA specimens [Figs.(8.14) to (8.16)].

(2) Exposure to crude oil at 80 C had caused residual expansions in all specimens except the H/PFA, after small initial early shrinkages. These values were however small, the largest of which was less than 75 micro-strains. The H/PFA specimens had contracted continuously with time, reaching just over 100 microstrains at 365 days.

(3) The S/OPC specimens had the largest residual expansions for all temperatures, reaching about 100 microstrains at 60 C. However, this amount was about 8 times less than the maximum expansion in the single interaction tests, and 3 times less than for the control specimens in water.

(4) The H/PFA specimens had the largest residual shrinkages for all temperatures, the largest of which was about 115 microstrains at 80 C. This amount of shrinkage merely offset the nett ultimate expansion of about 90 microstrains observed in the specimens at the end of curing at 100% RH.

(5) While ultimate residual shrinkage in the H/OPC specimens stored at the higher test temperatures had decreased (Fig. 8.18), the reverse was the case for the H/PFA specimens (Fig. 8.19). Residual length changes in the S/OPC specimens had not varied with temperature throughout the duration of exposure (Fig. 8.20). There was no nett length change in the S/PFA specimens stored at the 3 lower test temperatures, however at 80 C there was nett expansion of about 70 microstrains (Fig.8.21).

(6) Although the trend of length changes of the control specimens soaked in water [Figs.(8.22) to (8.24)] were similar to those for specimens tested in crude oil, the magnitudes of expansion were higher and shrinkages were smaller. In fact, the only shrinkage which had occurred was in the H/PFA specimens at 80 C and this was by only 30 microstrains. Interestingly, ultimate expansions in all specimens were lower at 80 C than at lower temperatures. This seems to suggest that the mechanisms which caused length changes in water were different from those which had caused the changes in crude oil.

(7) Seawater cured specimens (S/OPC and S/PFA) had expanded most, the largest expansions being for specimens stored at the crude oil temperature of 45 C.

(8) Expansions in water of the control moist soaked specimens were less than those observed in water for the specimens soaked oven dry.

FIG.8.14: Length change of moist mortar specimens soaked in crude oil at 20 deg.C

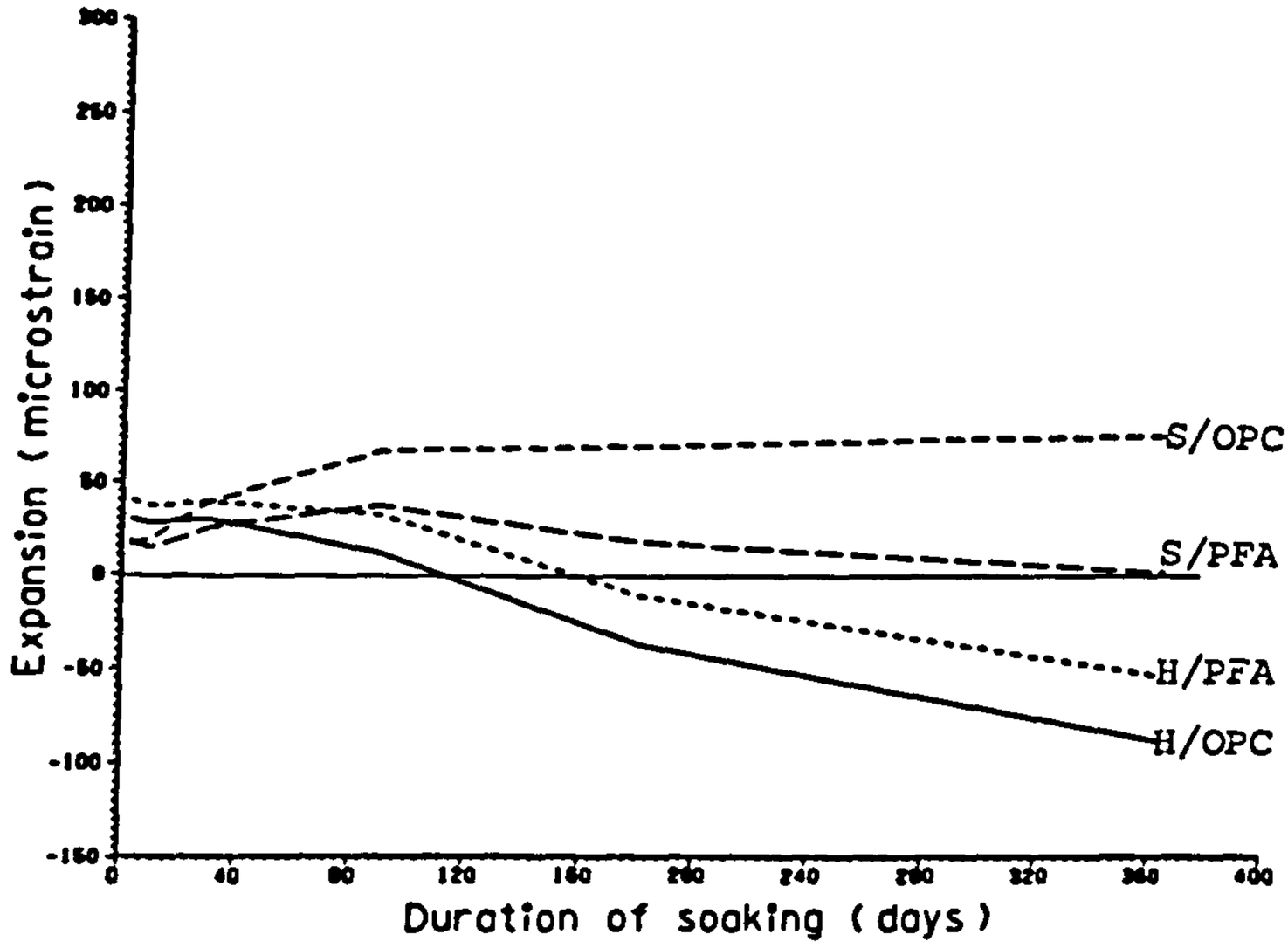


FIGURE 8.15:

Residual length change of moist mortar specimens soaked in crude oil at 45 deg.C

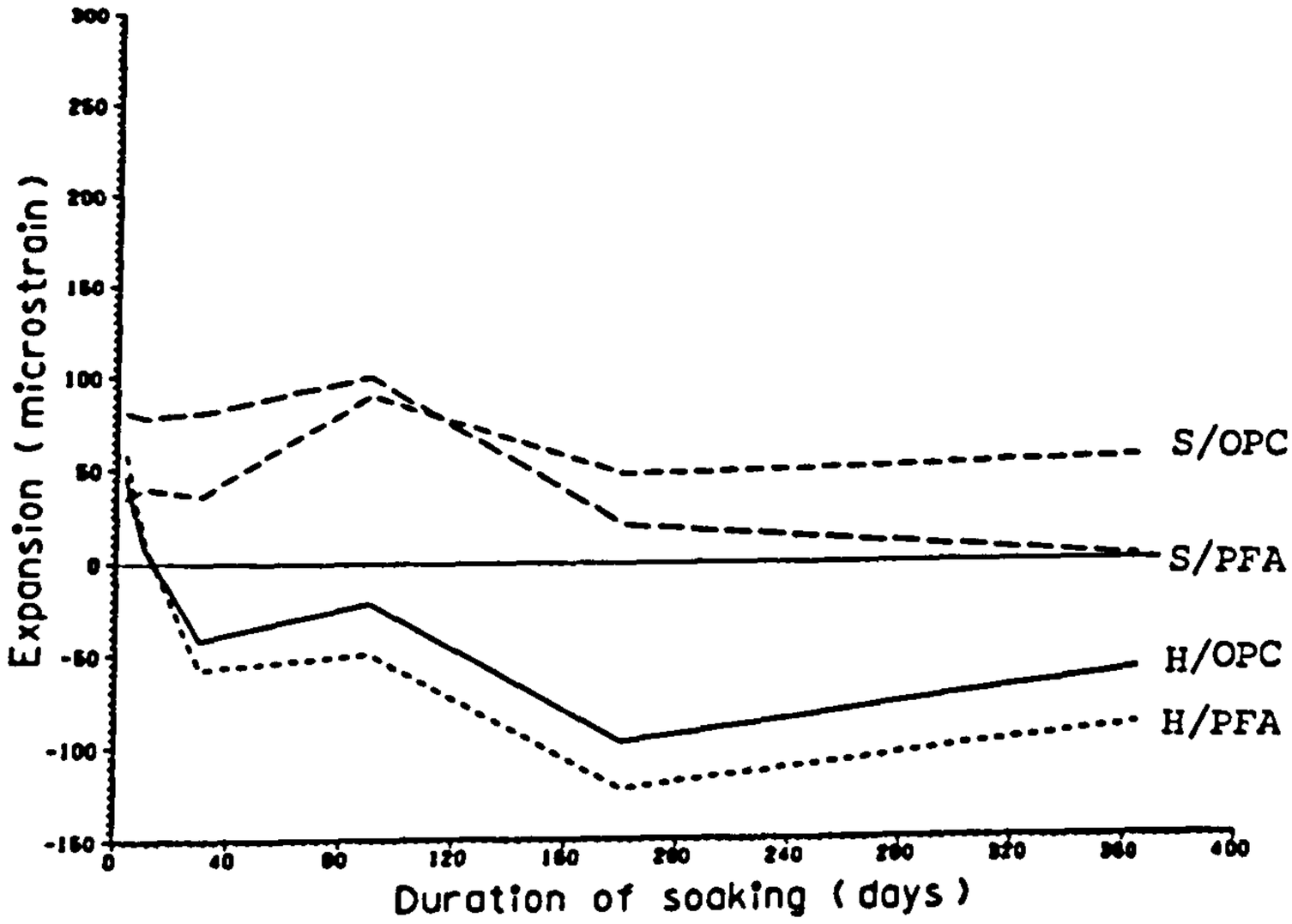


FIGURE 8.16:

Residual length change of moist mortar specimens soaked in crude oil at 60 deg.C

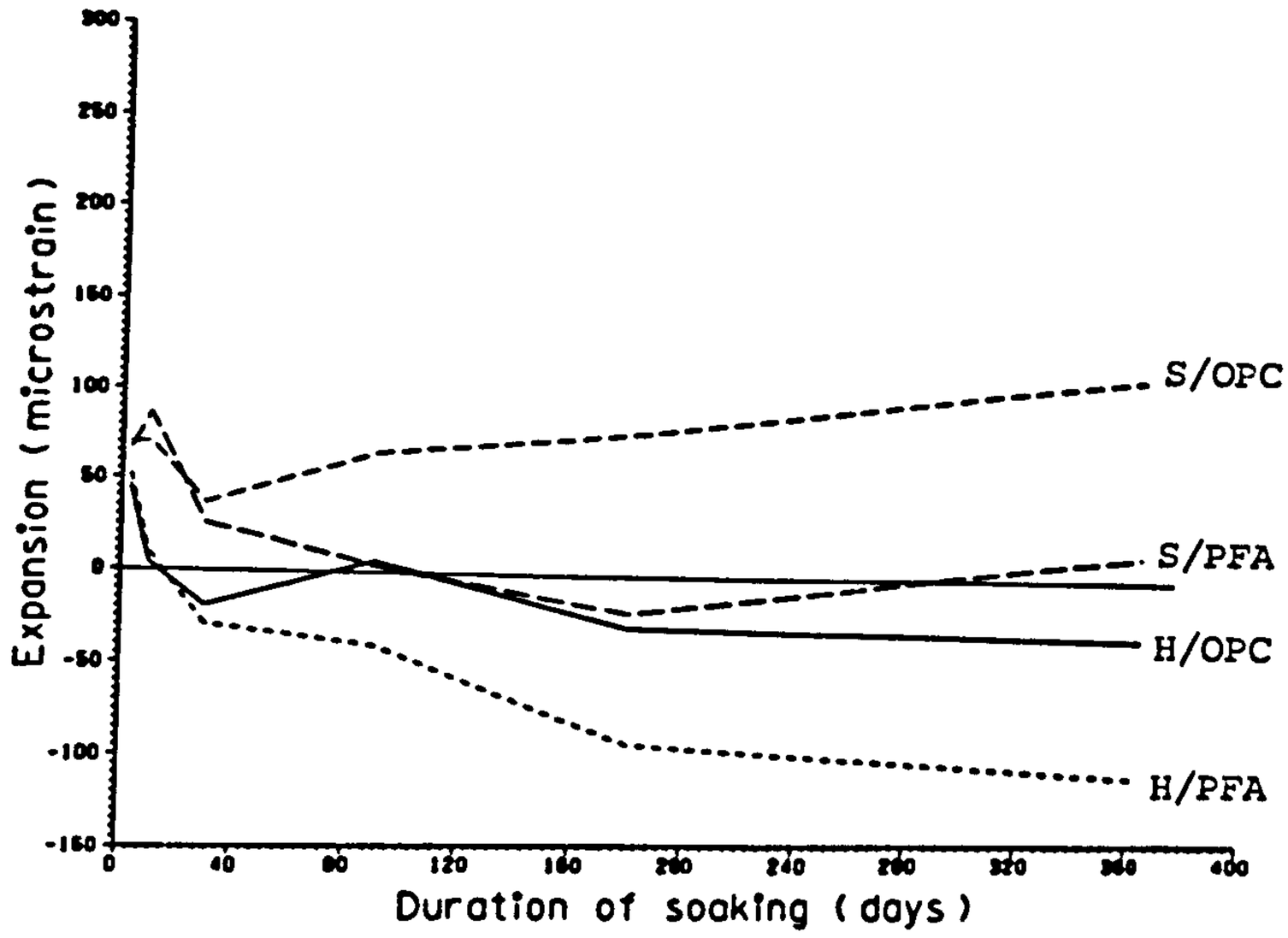


FIGURE 8.17:

Residual length change of moist mortar specimens in crude oil at 80 deg.C.

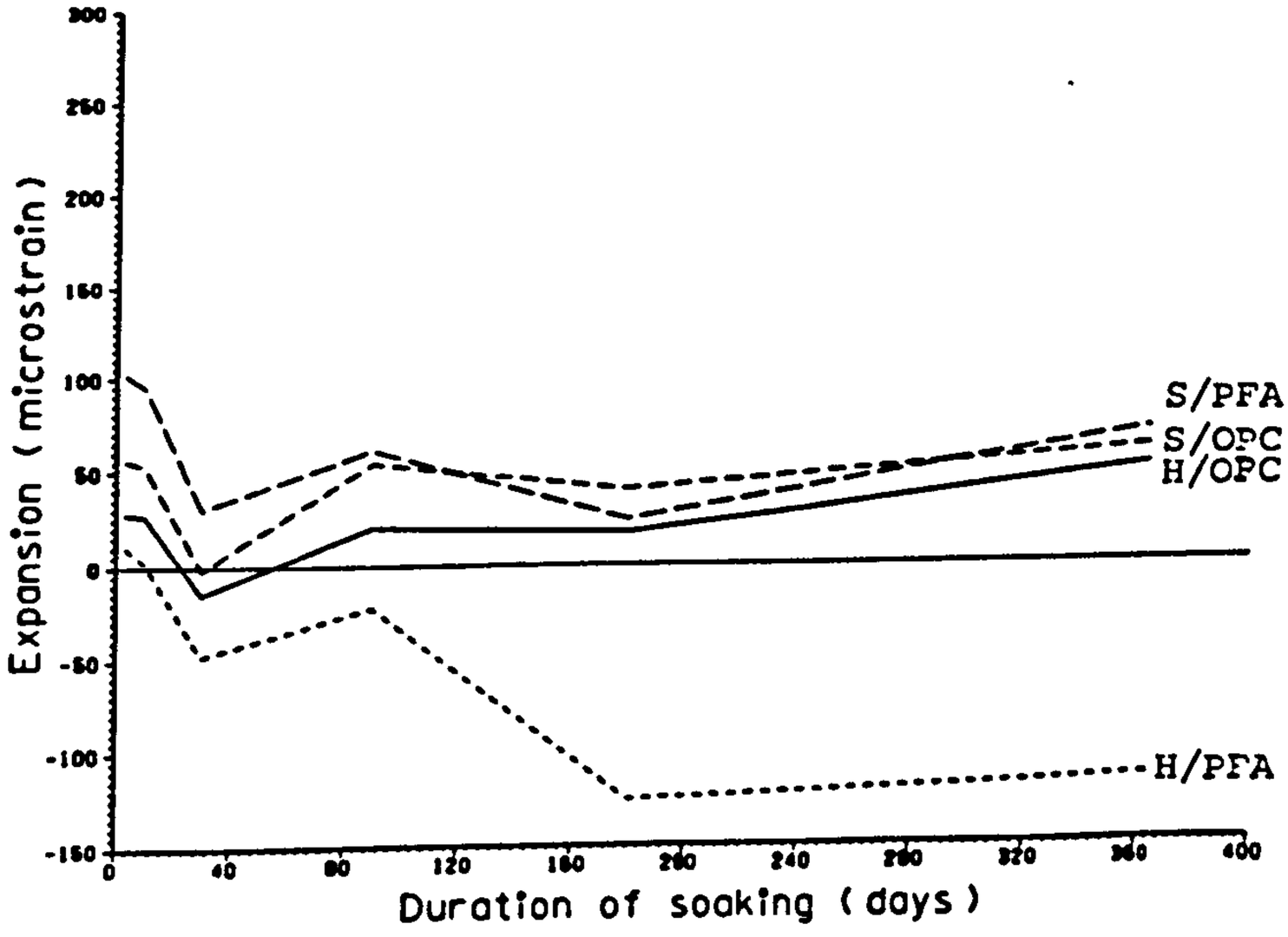


FIGURE 8.18:

Effect of temperature on length change of moist H/OPC mortar samples in crude oil.

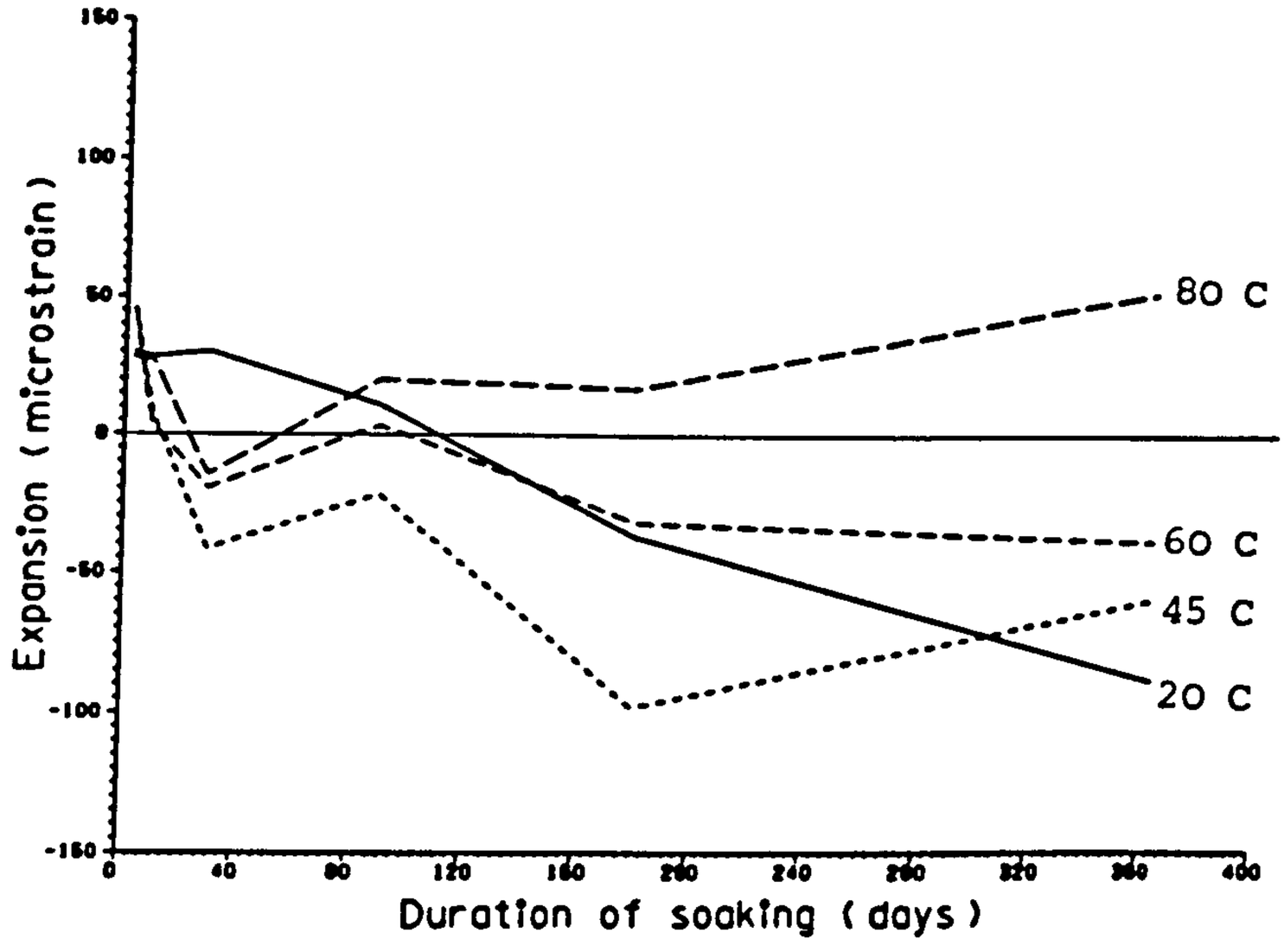


FIGURE 8.19:

Effect of temperature on length change of moist H/PFA mortar samples in crude oil

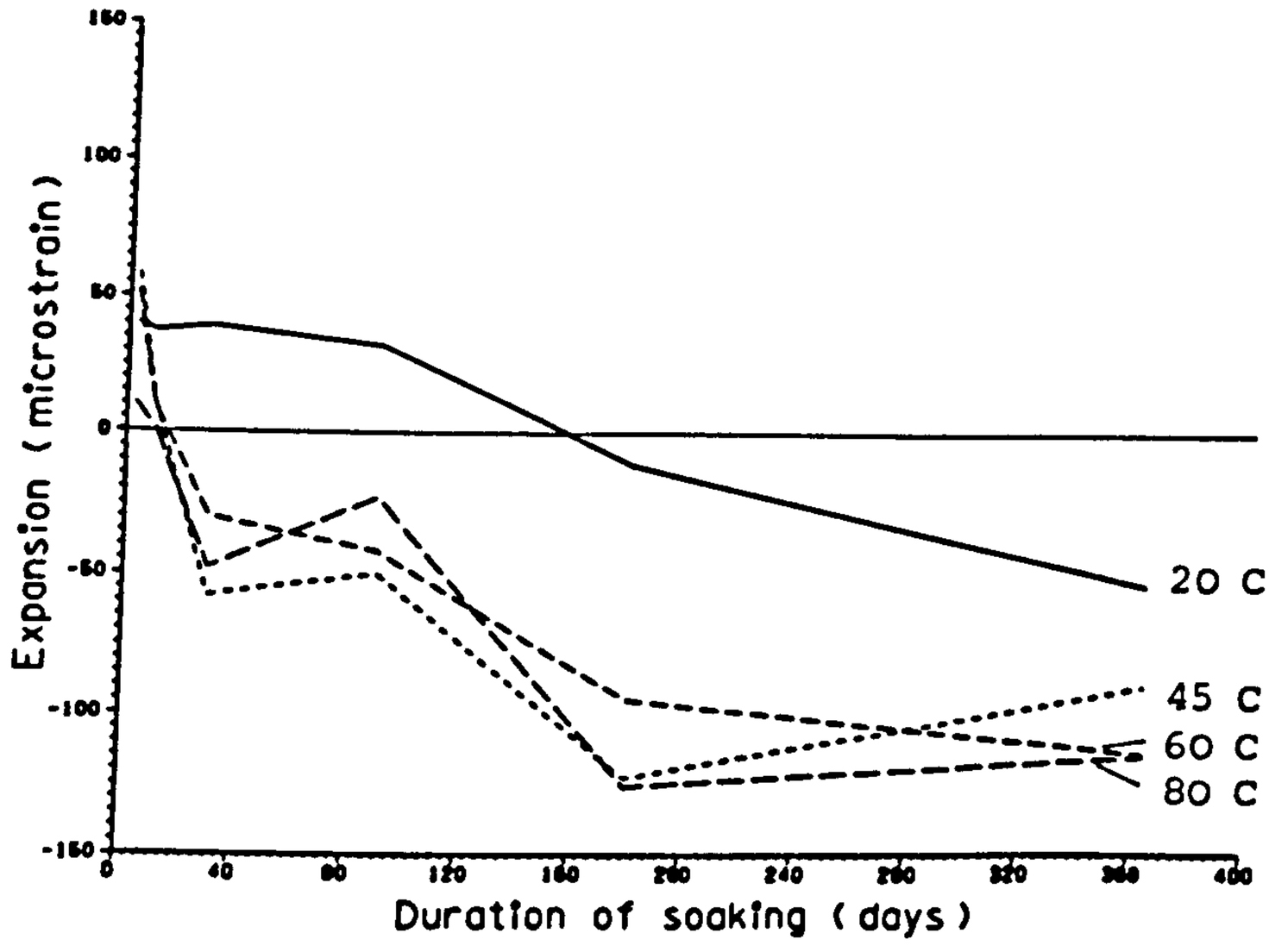


FIGURE 8.20:

Effect of temperature on length change of moist S/OPC mortar samples in crude oil.

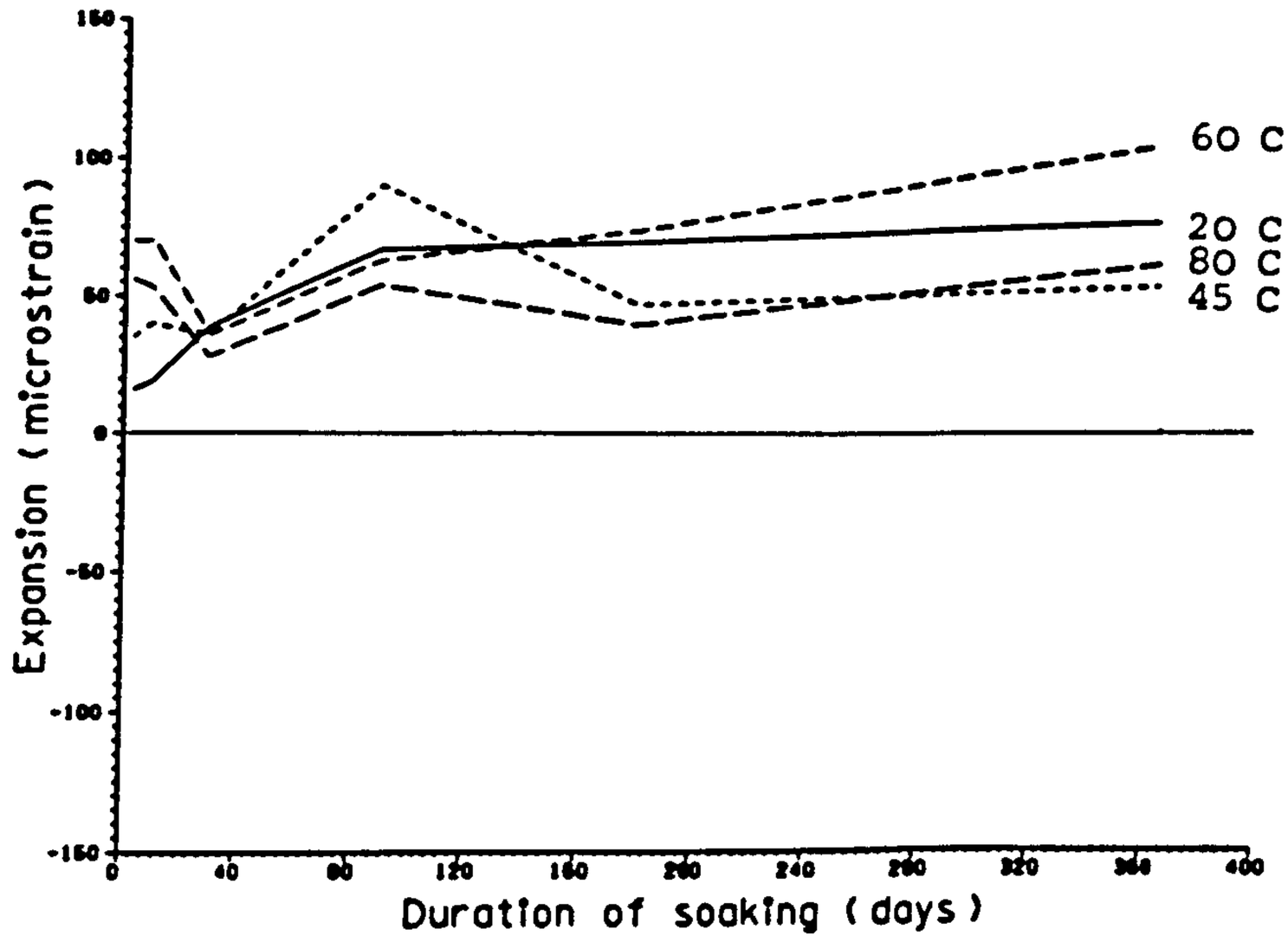


FIGURE 8.21:

Effect of temperature on length change of moist S/PFA mortar samples in crude oil.

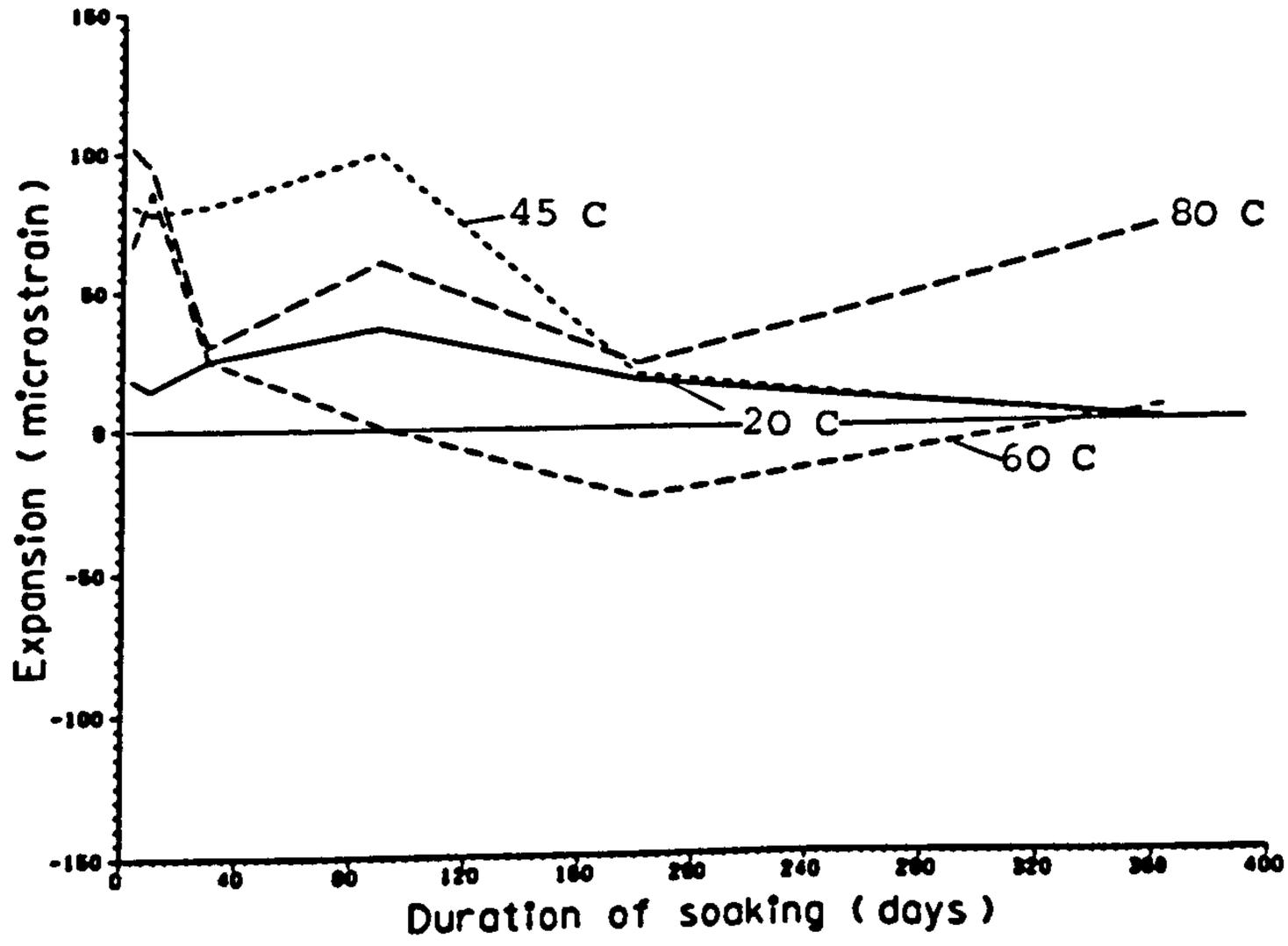


FIGURE 8.22:

Residual length change of moist mortar specimens in WATER at 20 deg.C.

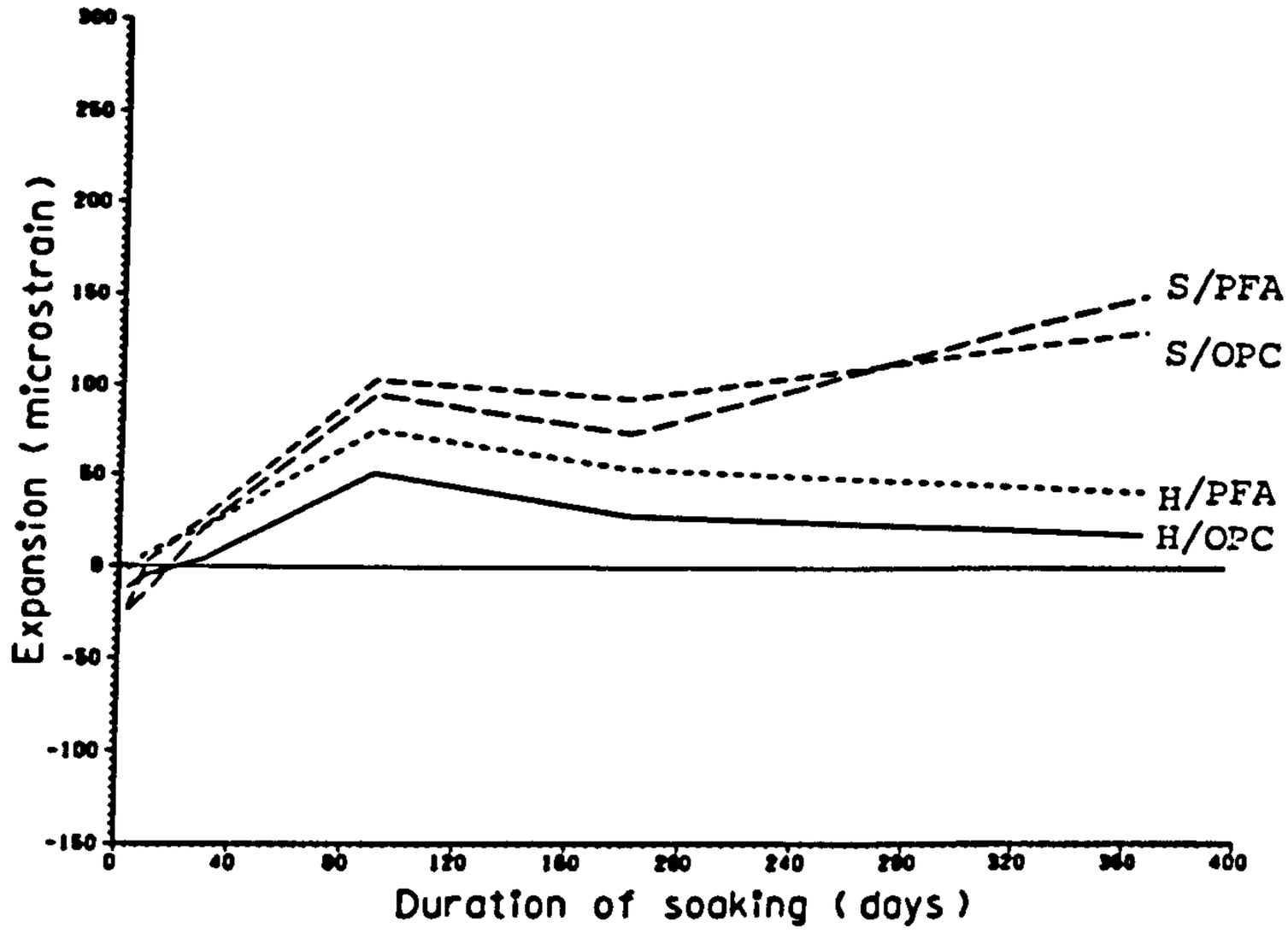


FIGURE 8.23:

Residual length change of moist mortar specimens in WATER at 45 deg.C.

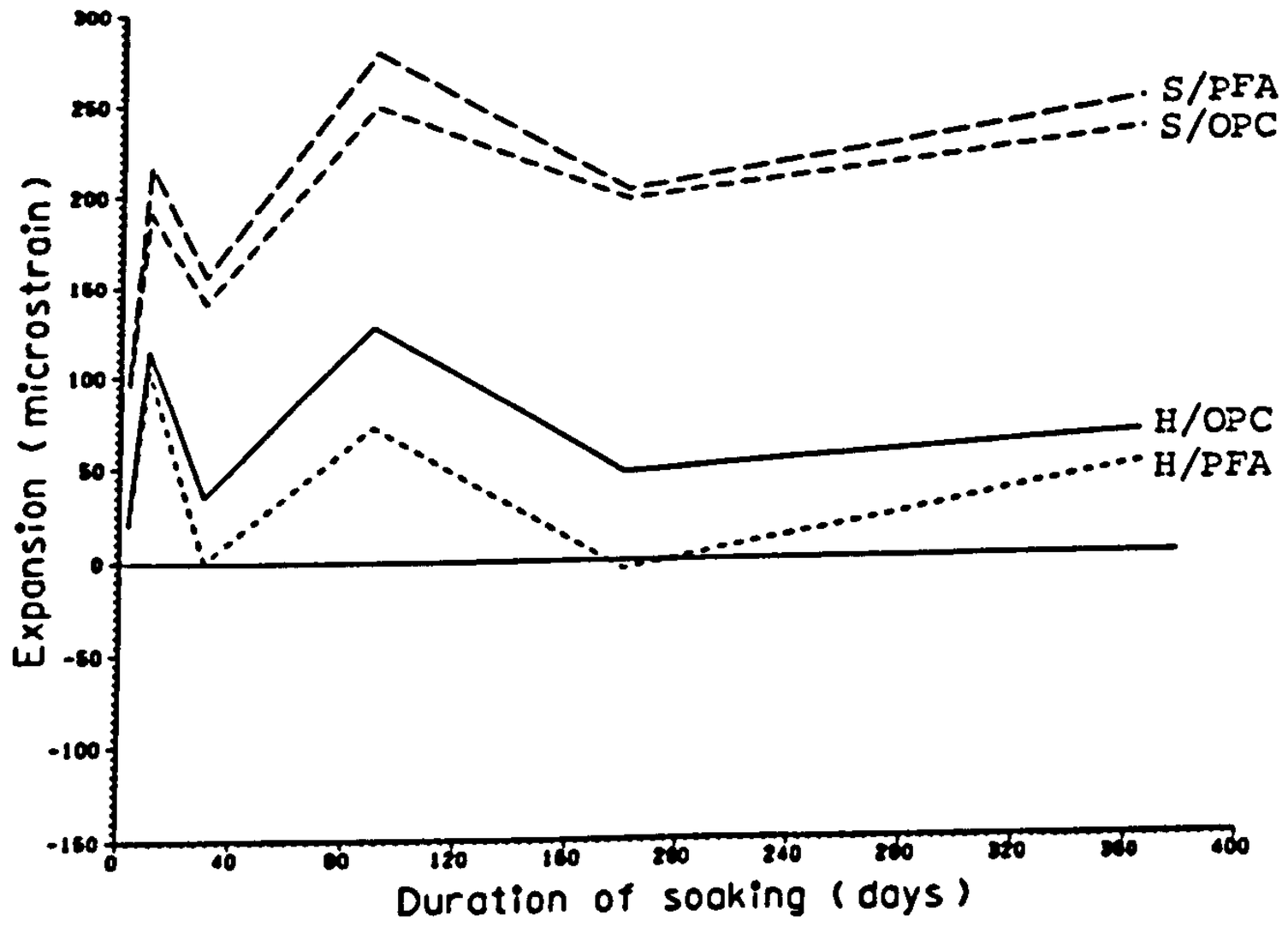


FIGURE 8.24:

Residual length change of moist mortar specimens in WATER at 60 deg.C.

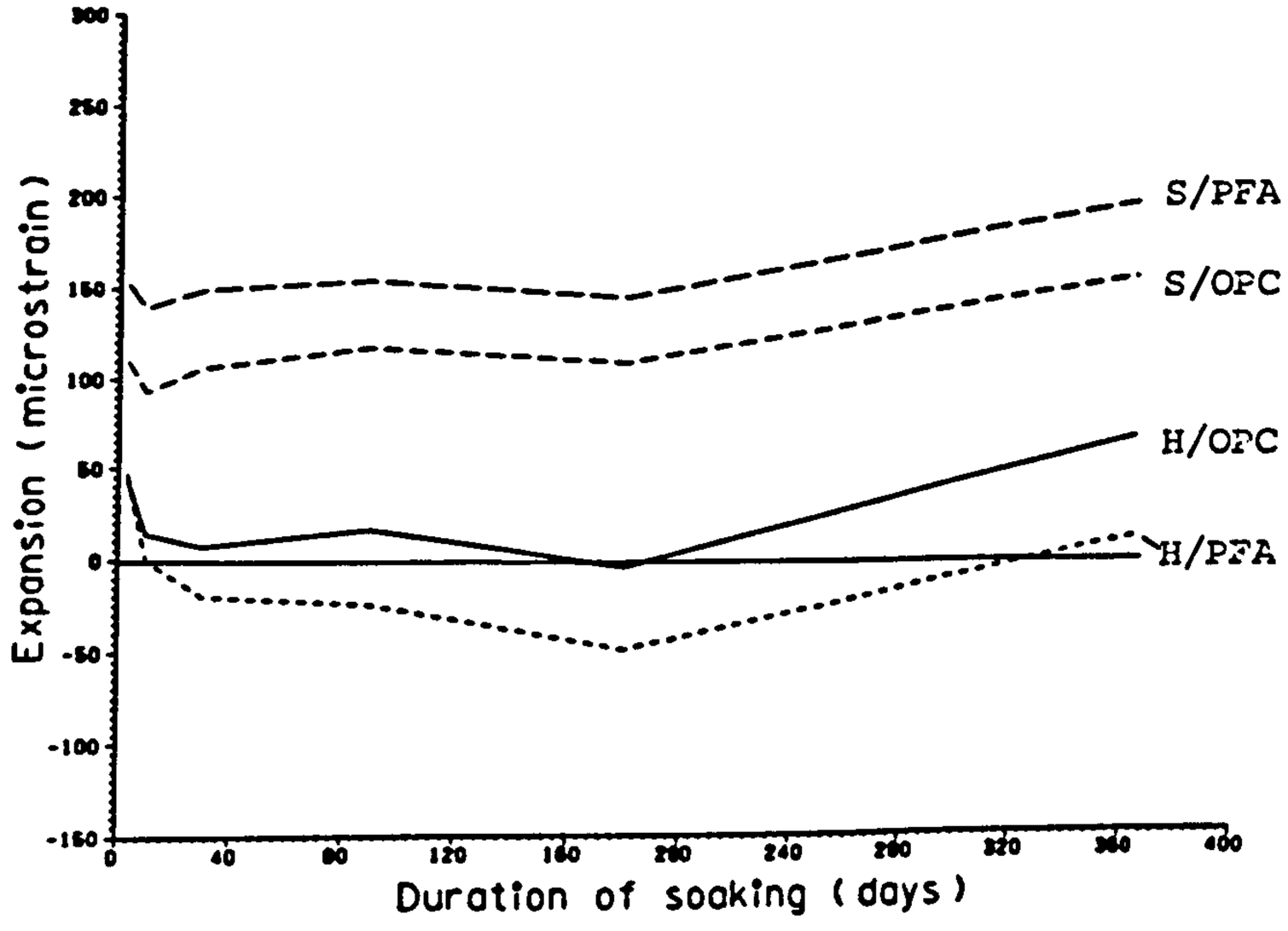
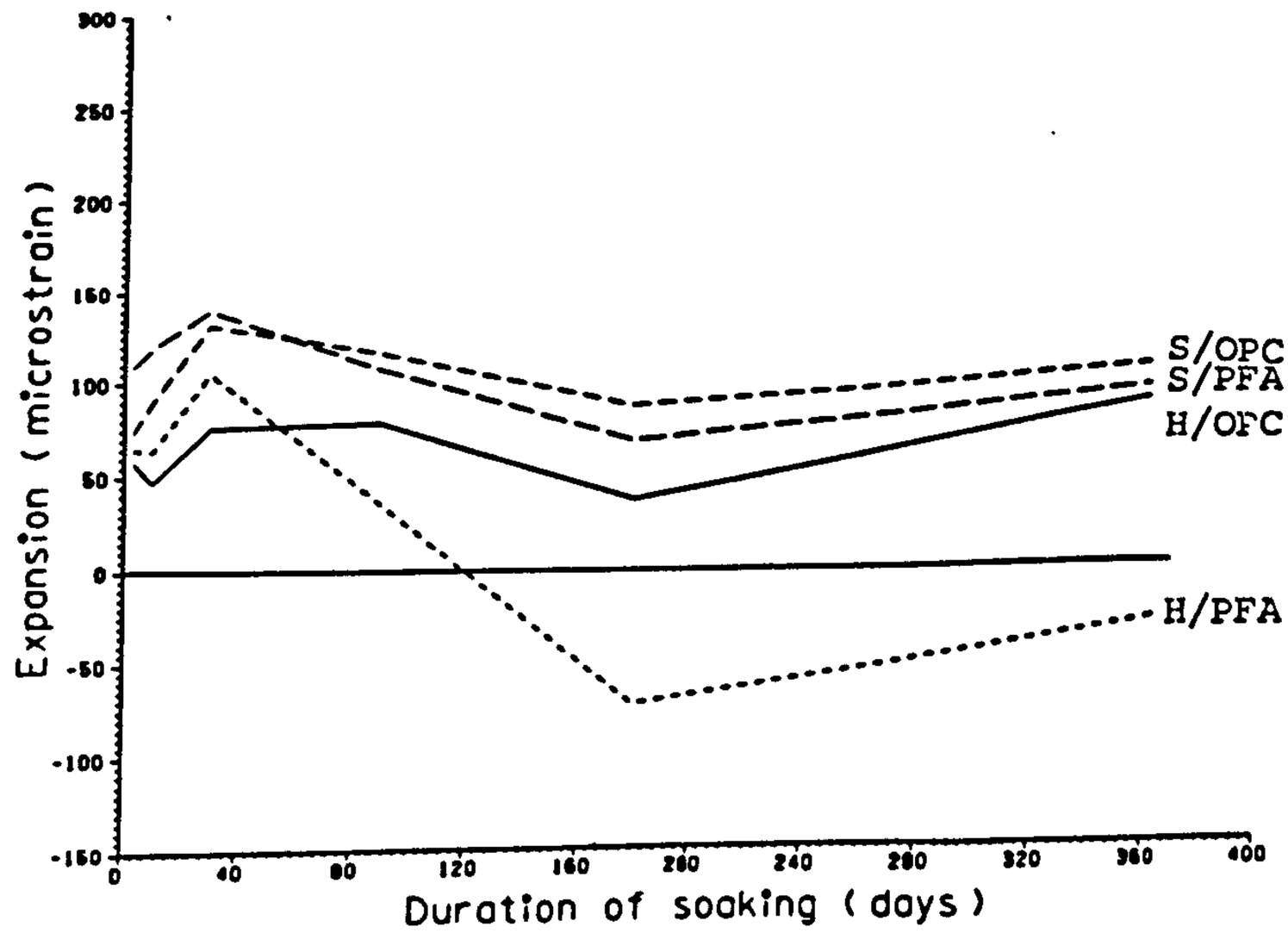


FIGURE 8.25:

Residual length change of moist mortar specimens in WATER at 80 deg.C.



8.3.2 DISCUSSION OF THE RESULTS OF MULTIPLE INTERACTION TESTS

The results have shown that the trend of residual length changes of moist specimens soaked in crude oil at elevated temperatures were clearly different from those of specimens soaked oven dry. In the latter, large expansions had occurred in all specimens soaked at elevated temperatures. In the multiple interaction tests, specimens previously cured in seawater had expanded, while those cured at 100% RH had contracted. However, the changes were relatively small for all temperatures, the largest being of the order of about 100 microstrains.

Some explanations to why the trends in the two interactions differed was given in Chapter 6 when discussing the trends of absorption of crude oil by the specimens. It was shown that while the oven dry specimens absorbed crude oil, the moist specimens did not, but had actually lost some weight. This implied that, not only had significant absorption of crude oil not occurred, but in actual fact, the specimens lost some moisture. This may have resulted from additional hydration in the moist specimens when stored in the crude oil at elevated temperatures, causing autogenous shrinkage, particularly as the moisture loss is not replenished from any external source.

Matti /119, 121/ reported shrinkage of moist concrete specimens when soaked in crude oil at room temperature. It was found that the amounts by which the specimens contracted had increased as the water/cement ratio of the specimens decreased. Shrinkage of the oil soaked specimens was attributed possibly to autogenous shrinkage, with the alternative cause being some "unknown chemical reaction" between the cement and the crude oil. The latter is very unlikely, since it has been established that crude oil does not displace water in the HCP. The inability of moist specimens to absorb crude oil as was found in this study, as well as the results of Hrennikoff /85/, are proofs of this.

The expansions in water at 20 C and at elevated temperatures, confirm that when an external moisture source is available, swelling in the HCP would occur. The results obtained are in agreement with other findings /91, 111, 119, 159/ where swelling, accelerated by temperature /173/, is attributed to continued hydration when a continuous supply of moisture is present. The small amount of shrinkage observed at 80 C in the H/PFA

specimens can be related to the critical exposure temperature of 80 C. This is discussed in section (8.3.2.3).

8.3.2.1 Effect of cement blend

Specimens blended with pfa are known to have a denser gel structure than opc specimens. These specimens are also known to have a greater number of finer pores and less large pores, more uniformly distributed within the microstructure /116, 118, 123/.

The effect of cement type on the residual length measurements of specimens exposed to crude oil at the 4 test temperatures, can be assessed by comparing the length changes of H/PFA specimens with the H/OPC, and of S/PFA with S/OPC. However, there is no clear pattern discernible from Figs.(8.14) to (8.17). The curing process probably influenced the overall behaviour. Nevertheless, the tendency for the H/PFA specimens to shrink more than the H/OPC specimens and the S/OPC specimens to expand more than the S/PFA specimens, are pointers to differences in the pore structure distribution within the specimens.

The extra amount of gel formed due to the pozzolanic reactions and the resulting reduction in the proportion of large pores, means that the H/PFA specimens can be expected to contain less moisture per unit volume of gel than the other specimens. It follows, therefore, that the specimens would shrink more during self-dessication. The same principles would apply to the S/PFA specimens, compared to the S/OPC. However in this case, the degradation experienced during the period of curing and possibly also during storage in crude oil at elevated temperatures, had resulted in expansions rather than shrinkage.

8.3.2.2 Effect of curing

It was evident that the total porosity of seawater cured specimens was greater than that of the specimens cured at 100% RH by the end of curing. The S/PFA specimens were less damaged and were therefore less porous than the S/OPC specimens, because they contained less calcium hydroxide during the period of immersion in the seawater. It is believed that the nature of the microstructures of these specimens and in particular, of the S/OPC, were such that they contained larger pores and more microcracks than the specimens cured at 100% RH. The latter had developed denser gel, with less large pores and microcracks, under the humid conditions of curing. The seawater cured specimens can, therefore, be expected to contain larger amounts of moisture, given that saturation of the pores would occur in the ponded seawater. The 100% RH cured specimens, however, had much less moisture, as the weight measurements of Table (6.2) had indicated. The onset of self-dessication on exposure to crude oil, had meant that the seawater cured specimens had ample moisture in the larger pores and microcracks to continue to replace that which was used up internally. The specimens had therefore continued to swell. It is also possible that any constituents of seawater still present in the specimens, in particular, chlorides and sulphates, may have reacted with the HCP during storage in crude oil at elevated temperatures. This may have caused additional expansions. However, the 100% RH cured specimens had lost the little amount of moisture they contained quicker and had, therefore, contracted. The expansion at 80 C in the H/OPC specimens was related to the critical effect of that temperature, as will be seen in the following section.

Matti /119/ stated that 'the pore characteristics of concrete determines the amount of evaporable and non-evaporable water (capillary and gel pore water) held in the pores. This controls the exchange of moisture between the concrete and its surrounding' and accordingly, determines the extent of volume change. This generally summarises the relationship between pore structure and volume changes in the HCP as has been reported /60, 61, 91, 157, 159, 173, 200/. It also lends support to the explanations given above.

8.3.2.3 Effect of Temperature

The effect of temperature on volume changes in the multiple interaction tests was not as clear as it had been in the single interaction tests. However, statistical analysis has shown that in most cases, exposure to elevated temperatures had a significant effect on the residual strains (Table 8.4). The difference in the results between the two series of tests can be attributed to (a) difference in initial moisture contents of the specimens prior to soaking in crude oil and (b) differences in thermal history, since the specimens used in the single interaction tests were pre-heated at 105 C.

The initially moist specimens can be regarded as unsealed when soaked in crude oil since moisture escape is not prevented. Comparisons can therefore be made with published data on the effect of heating on initially moist unsealed concrete, particularly since significant absorption of crude oil had not taken place (see Chapter 6).

It was noted earlier that the length change of specimens in the multiple interaction tests were significantly less than those obtained in the single interaction tests, even after exposure to elevated temperatures. Interestingly, the residual expansions and shrinkages of the various specimen types, were not markedly affected by temperature level attained during soaking in crude oil (eg. Fig. 8.20). The possible exception was specimens soaked at 80 C (eg. Figs.8.18 and 8.21). Published data suggests that heating unsealed initially moist concrete specimens to about 80 C may cause changes to the microstructure. A minimum in porosity of cement paste was measured by Kasami and co-workers /96/ at 80 C, within the pore size range 75Å to 75 000Å. This may be related to the loss of adsorbed and interlayer water which is believed to take place at this temperature range /164/. In addition, a peak in the thermally stimulated luminescence (glow curves) was found at 80 C /162/. Essentially, it seems that the effect indicated a phase transition and is interpreted as the point when liberation of strongly bound water occurred. Furthermore, results of Chapter 7 have shown that exposure of moist concrete specimens to crude oil at 80 C had caused the largest compressive strength reductions in all specimens.

The similarity in results at lower temperatures can be attributed to two

factors. Firstly, the specimens were heated and cooled very slowly such that significant microcracking may have been avoided. Secondly, the loss of adsorbed and interlayer water, both of which cause dimensional changes, may not have taken place. By contrast, the loss of these types of water and the greater differential thermal movement between the aggregate and cement paste for specimens cooled from 80 C, may have affected the results.

TABLE 8.4 : t-Test of significance between means to determine the effect of temperature on length changes of moist mortar specimens soaked in crude oil.

Tests	no. of specimen	mean m	std. dev. s	DOF	t-value	prob. p	Remark
H/OPC:							
20 C vs.	12	-4.7	46	29	1.904	>0.05	not
45 C	19	-37.2	46				signif.
20 C vs.	12	-4.7	46	26	1.241	>0.10	not
60 C	16	-20.6	19				signif.
20 C vs.	12	-4.7	46	29	2.146	0.05	signif.
80 C	19	22.3					
H/PFA:							
20 C vs.	12	13.7	38	64	4.278	<0.005	highly
elev. temps.	54	-58.2	55				signif.
S/PFA:							
20 C vs.	12	18.7	13	29	2.949	0.01	highly
45 C	19	53.8	38				signif.
20 C vs.	12	18.7	13	25	0.208	>0.10	not
60 C	15	16.1	41				signif.
20 C vs.	12	18.7	13	29	4.290	<0.005	highly
80 C	19	65.0	36				signif.

PART C: GENERAL DISCUSSIONS AND CONCLUSIONS

CHAPTER IX

GENERAL DISCUSSIONS AND CONLCUSIONS

9.1 INTRODUCTION

The findings in this thesis have shown that the conditions in a concrete offshore oil storage tank are such that the material properties can change with time. For instance, it was found that the effect of the method of curing and the presence of pfa in concrete, had each significantly affected the behaviour of the material when exposed to hot crude oil. However, the extent of the deterioration in properties which was caused, depended on the moisture condition of the specimens prior to exposure and on the temperature of the crude oil. It was found that storage temperatures of about 80 C can cause significant loss of strength. Deterioration was assessed by measuring absorption, penetration, compressive strength and length changes. The results provided indications of the state of the material at various periods during storage in crude oil. They hopefully form useful data which can be employed in the design of concrete offshore structures and for other practical purposes.

Replicates were used in the experimental investigations to improve the significance in the statistical analysis. The overall average standard deviation of about 5 N/mm2 obtained in the compressive strength tests and the increasing repeatability of the length change measurements, confirmed that test methods, as well as instrumentation, were adequate to meet the demands of the test programme and provided added confidence in the results.

The discussions that follow are essentially to highlight the main results, the general links between different studies and the implications of the findings, in relation to existing structures.

9.2 GENERAL DISCUSSION OF MAIN RESULTS

9.2.1 Mix Proportions

The imposition of the mix design for the concrete in the oceans programme (CIO) /97/, had meant that both mix I (OPC) and mix II (OPC/pfa) contained the same quantity of water by weight. In practice, advantage is taken of the increased workability of the OPC/pfa mix and the amount of water used is reduced, to reflect the lower proportion of portland cement. Nevertheless, the mix proportion has been shown to be adequate and the PFA specimens had achieved similar 365-day compressive strengths with the OPC specimens under all curing conditions. The pfa mixes also exhibited better durability on exposure to crude oil at elevated temperatures.

9.2.2 Crude oil Absorption and Penetration studies (Chapter 6)

Regardless of the method of curing and the storage temperature, crude oil absorption by the moist concrete and mortar specimens was insignificant. Although this is the more practical condition as regards the offshore oil storage tanks (section 9.4), the absorption of crude oil by the concrete skeleton (oven dry state) was also investigated, in order that the effect of crude oil alone on the properties of concrete can be understood.

Crude oil absorption by the oven dry concrete and mortar specimens, determined by weight change measurements, had occurred in 3 stages; (i) 'instantaneous' absorption within 3 days (ii) less rapid rate of absorption and (iii) relatively slow rate of absorption. Absorption of crude oil was a function of the storage temperature and was related to the method of curing. The residual absorption was higher at the higher storage temperatures and was faster and greater for specimens cured in seawater, compared to those cured at 100% RH. Earlier results (Chapter 5) had shown that the seawater cured specimens were less dense than the

specimens cured at 100% RH. The density can, therefore, be related to the porosity of the specimens.

The rate of crude oil penetration into the oven dry concrete specimens was also determined by a novel method (Chapter 3) using the purpose built CLIF apparatus (Chapter 4). The results indicated similar trends to those obtained in the absorption studies.

A more general equation of flow through dry concrete which does not assume Darcy's law, has been obtained. It was found that the equation of flow of crude oil through oven dry concrete was similar to the theoretical formula obtained by Valenta /198/ and also by Vuorinen /202/, for flow of water through dry concrete. Despite the differences in viscosity, molecular size and other physical properties of the fluids the result suggest that the equation of flow of crude oil, water and seawater /27/ through dry concrete, were similar.

It has been found that oven dry concrete acts as a molecular sieve, selectively allowing passage to the aliphatic fractions of crude oil, while retaining the aromatics, similar to the behaviour of some clays /54, 165/. This has been related to the molecular configuration, as well as to the physical and chemical properties of the different crude oil fractions.

9.2.3 Crude oil Absorption vs Compressive strength (Chapter 7)

The changes in residual compressive strength reduction with time of the oven dry concrete specimens was related to the absorption of crude oil, for storage at elevated temperatures (Figs.7.12 to 7.15). It was found that as crude oil absorption had increased with the temperature of storage, so had the loss in compressive strength. However, when absorption of crude oil had stopped, as for example beyond 30 days, for storage at 20 C (Fig.7.1), strength losses in the specimens had ceased. The strength reductions were probably due to the combination of two factors namely, (i) oil lubrication of the aggregates due to crack

formation at the cement paste/aggregate interface and (ii) dilation of the gel as crude oil began to penetrate those parts. The first is likely to occur faster and may explain parts of the initial early strength losses, especially those found at 3 days. The second factor would take place more slowly, depending on the temperature of the crude oil. This would cause further loss of strength.

Moist concrete specimens did not absorb crude oil and the changes in strength which were observed cannot, therefore, be related to chemical interactions between crude oil and concrete, but can be related to the effect of elevated temperature. The reductions in strength at the early stages were due to (i) the incompatibility of expansion between cement paste and the aggregates and (ii) the increased moisture content in the gel. The recovery of strength in the later stages was due to the resulting increase in gel content as hydration had continued.

9.2.4 Crude oil Absorption vs Length Change (Chapter 8)

The residual linear expansions in the oven dry mortar specimens stored in crude oil at elevated temperatures, were directly related to the crude oil absorption of the specimens (Figs. 8.9 to 8.12). These had occurred in 3 stages; the 'instantaneous' absorption within 3 days caused no length changes, while the relatively less rapid absorption in the second stage caused only very little expansion, relative to the significant expansions in all specimens in the third stage of crude oil absorption. The 3 stages, respectively correspond to absorption into the cracks and microcracks, the capillary pores and into the gel pores. The absorption into the gel pores which had caused the linear expansions, had occurred only in the specimens stored at elevated temperatures (Figs.8.5 to 8.8). The relationship between linear expansions and crude oil absorption was similar, irrespective of (i) the method of curing, (ii) the cement blend or (iii) storage test temperatures (Fig.8.13).

Moist mortar specimens did not absorb crude oil which, however, had partially sealed the surface pores of the specimens, possibly causing inward moisture movement into the gel. Autogenous volume changes had occurred and these were related to the nature of the pore structure of the specimens and also to the moisture content and chemical composition (sea water or freshwater), prior to crude oil exposure.

9.2.5 Compressive strength vs Length change

From the discussions of sections (9.2.3) and (9.2.4), a relationship can be deduced between the residual compressive strength and length change of oven dry specimens stored in crude oil at elevated temperatures. Both were functions of crude oil absorption and the effect of elevated temperatures. The latter, however, seemed to have been the governing factor since it causes cracking and expansions, especially of the gel, and had also allowed the penetration of crude oil into parts which otherwise it could not have reached. 'Instantaneous' absorptions within 3 days, was into cracks and microcracks. This caused no variations in length, but by lubricating the aggregates at the cement paste/ aggregate bond, had caused initial strength reductions. Absorption into the capillary pores had not significantly affected either strength or length change. However, absorption into the gel caused significant expansions and, its dilation had resulted in further strength losses.

For the moist specimens soaked in crude oil at elevated temperatures, the autogenous changes which had resulted from increased hydration and self-dessication, had caused increased strength and length reductions.

9.3 MICROSTRUCTURAL STUDIES

Microstructural studies were carried out on test specimens before and after exposure to crude oil, by examining polished and fractured surfaces under the scanning electron microscope (SEM). Although some interesting observations were made, it was believed that a more comprehensive study is needed before definite conclusions can be drawn from such studies. Nevertheless, examples of some of the findings are shown in the micrographs of Figs.(9.1) to (9.5). The first two are images obtained from fractured surfaces, while the other three are back-scattered images of polished surfaces. Figure (9.1) shows a sample which was soaked in crude oil with features suggesting the erosion of some of its sharply crystalline phases, as compared with Fig.(9.2) for example, for a sample which was not exposed to crude oil. In Fig.(9.3), the extent of crack formation and bond failure at the cement paste/aggregate interface can be seen. This was an observation typical of the oven dry specimens stored in crude oil at the elevated temperatures. Figure (9.4) shows that the 'packing' effect of the unreacted pfa spheres in the cement paste microstructure may, for example, explain the relatively denser pore structure of the PFA specimens, as compared to the OPC specimens (Fig. 9.5).



FIGURE 9.1: SEM of the surface(microstructure) of oven dry H/OPC concrete specimen after soaking in crude oil for 365 days.

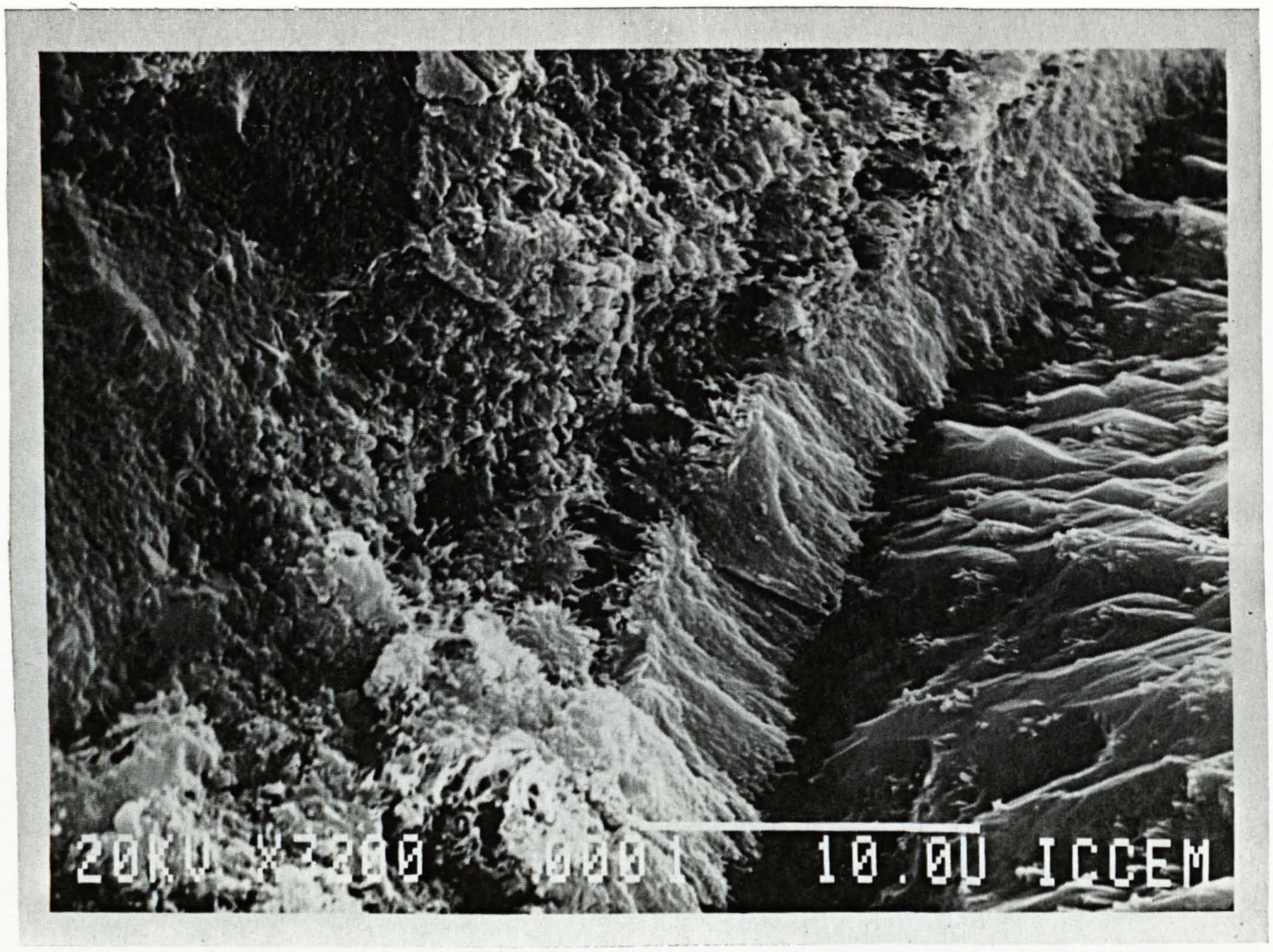


FIGURE 9.2: SEM of the surface (microstructure) of moist H/OPC concrete specimen after soaking in hot water for 365 days.

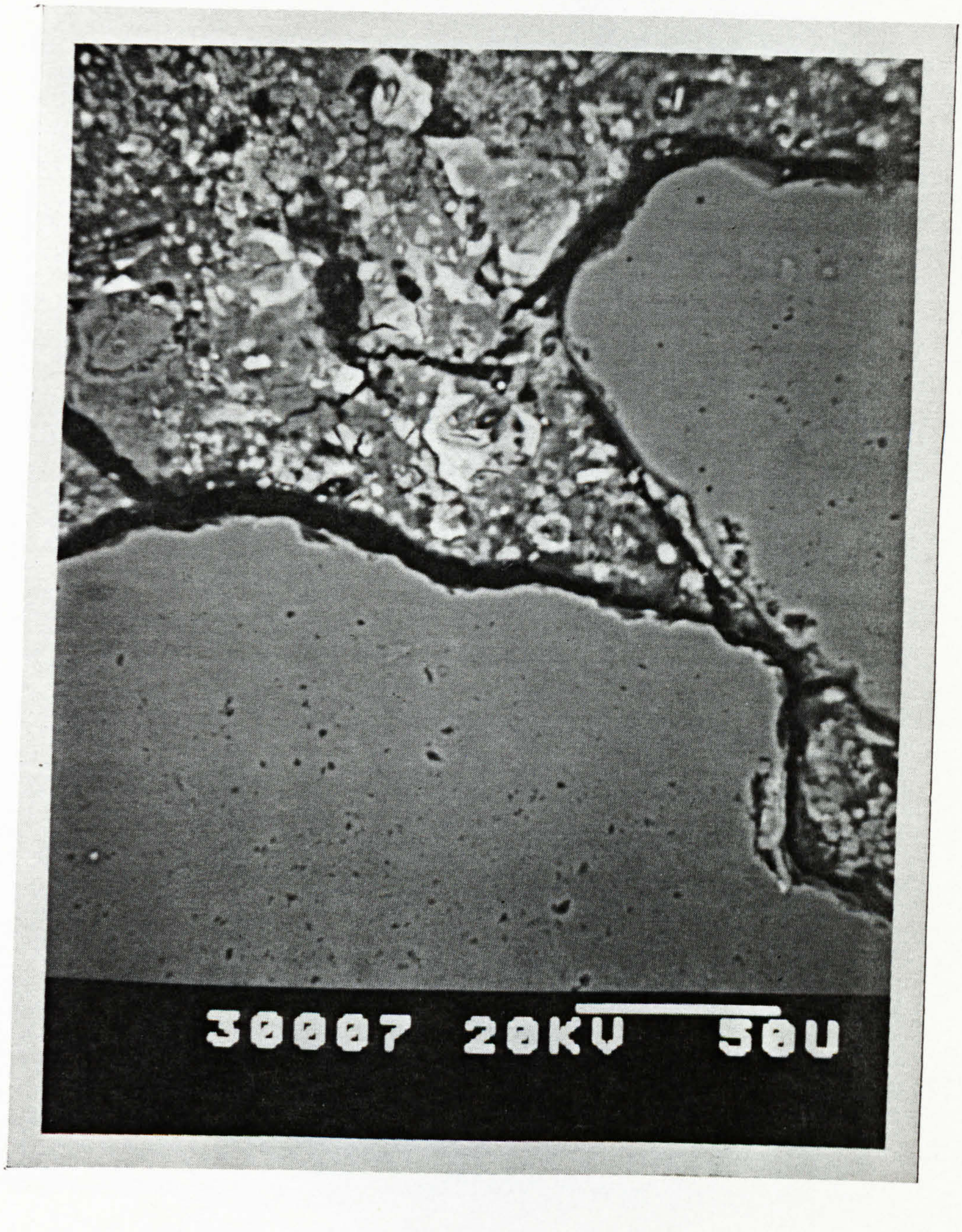


FIGURE 9.3: Crack formation at cement paste/aggregate interface in crude oil soaked oven dry H/OPC mortar specimen.



FIGURE 9.4: Unreacted pfa spheres in crude oil soaked H/PFA mortar specimen (2 years after casting).



FIGURE 9.5: Microstructure of polished surface of crude oil soaked S/OPC mortar specimen (2 years after casting).

9.4 IMPLICATIONS OF THE RESULTS

9.4.1 Introduction

In Chapter 3, the concrete wall of an offshore oil storage tank was modelled as comprising 3 zones of curing (Fig. 3.2), which was simulated in the laboratory. The exposed faces of the caisson wall was considered as cured in seawater (zone A), while the central region which was unlikely to be penetrated by seawater (zone B), was considered as cured at 100% RH. It was believed that due to the different cycles of hot crude oil and cold seawater (see Chapter 3), cracking may occur. In fact, that such cracks may have formed has now been confirmed from the results of tests performed at the Cement and Concrete Association (C&CA) /43/. The findings, which are as yet unpublished, showed that "map" cracking, visible to the naked eye, had occurred on the inside face of the scaled model which was tested. However, there were no indications as to the depth of tranverse cracks into the caisson wall. This result lends support to earlier assumptions that the formation of cracks in the caisson wall, may allow crude oil to permeate into both zones A and B (Fig. 3.3). However, immersion of the caisson below sea level ensures that the concrete is at all times under saturated conditions. Even after exposure to hot crude oil, there is unlikely to be any evaporation of moisture (Fig. 9.6). Therefore, it is only the results of the multiple interaction tests which are strictly practically applicable in this discussion.

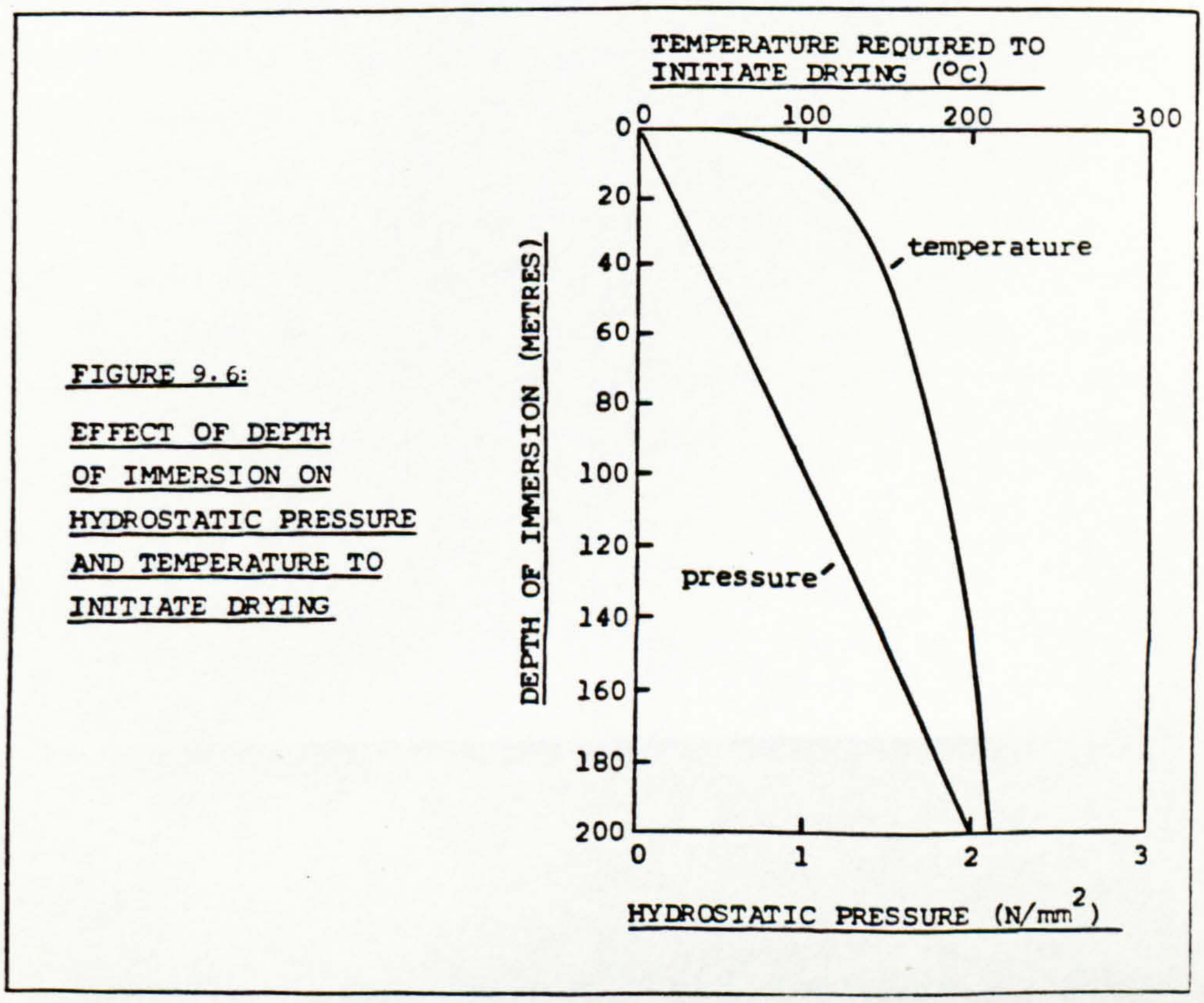


FIGURE 9.6:

EFFECT OF DEPTH OF IMMERSION ON HYDROSTATIC PRESSURE AND TEMPERATURE TO INITIATE DRYING

9.4.2 Absorption and Penetration of crude oil

As results have shown, the moist concrete specimens did not absorb crude oil. The implication of this, therefore, is that the inner surface of the caisson wall, cured in seawater, is unlikely to be permable to crude oil. Furthermore, the protective layers of brucite and aragonite formed at the surface during curing may even prevent the entry of crude oil molecules into the surface pores. However, if cracks should form as a result of the temperature gradient across the caisson wall, as well as the effect of temperature cycling, penetration of crude oil into the inner zones may still take place.

9.4.3 Compressive strength

Significant reductions in compressive strength may occur across the entire section of the caisson wall and at the roof of the storage cells, especially at the early stages when hot crude oil is introduced. The losses may fall below the design strength (28-day strength), particularly at the inner section which was cured in seawater and was in continuous contact with hot oil (Fig. 9.7). The changes in compressive strength throughout the period of curing and on exposure to crude oil relative to the 28-day strength, are shown for the OPC and PFA concretes in Figs.(9.7) and (9.8) respectively. The most critical temperature of storage was 80 C and the least critical 20 C. Without doubt, storage of crude oil at temperatures above 60 C can cause loss of strength and weakening of the concrete. More important is the fact that the slow early strength gain of the PFA concrete mix is a significant advantage in its use over the OPC mix, since even for storage at 80 C, the compressive strength at any time period can be expected to be reasonably higher than the 28-day strength (Fig.9.8), unlike for the OPC concrete (Fig. 9.7).

The disparity in the rate of gain of strength in the different sections of the caisson wall during the period of curing in seawater or at 100% RH, means that strength would not be uniform across the entire thickness

of the wall. This may lead to cracking, the amount and extent of which is difficult to determine. It is therefore advisable that curing of the caisson walls is allowed to reach an advanced stage prior to slipforming, and exposure to seawater.

9.4.4 Deformations

The length changes with time during curing and on exposure to crude oil, are shown in Figs. (9.9) and (9.10), for the OPC and PFA mortar specimens respectively. Length changes were most critical at temperature of exposure of 80 C and were least critical at 20 C. Quite clearly, length changes on exposure to crude oil were small irrespective of the storage temperature and the method of curing. This is good news from the point of view of cracking across the thickness of the caisson wall. However, the most important factor for length change as it was for compressive strength, was the effect of blending portland cement with pfa. The presence of pfa in the mix had reduced the amount of expansion during curing in seawater to less than half the amount found in the opc specimens (Figs. 9.9 and 9.10). This is very significant as it can reduce the extent of cracking that may form at the interface between sections cured in seawater and those cured at 100% RH (Fig.9.10) and is important for the service performance of the structure.

FIG. 9.7: COMPRESSIVE STRENGTH CHANGES RELATIVE TO 28-DAY STRENGTH OF MOIST OPC CONCRETE.

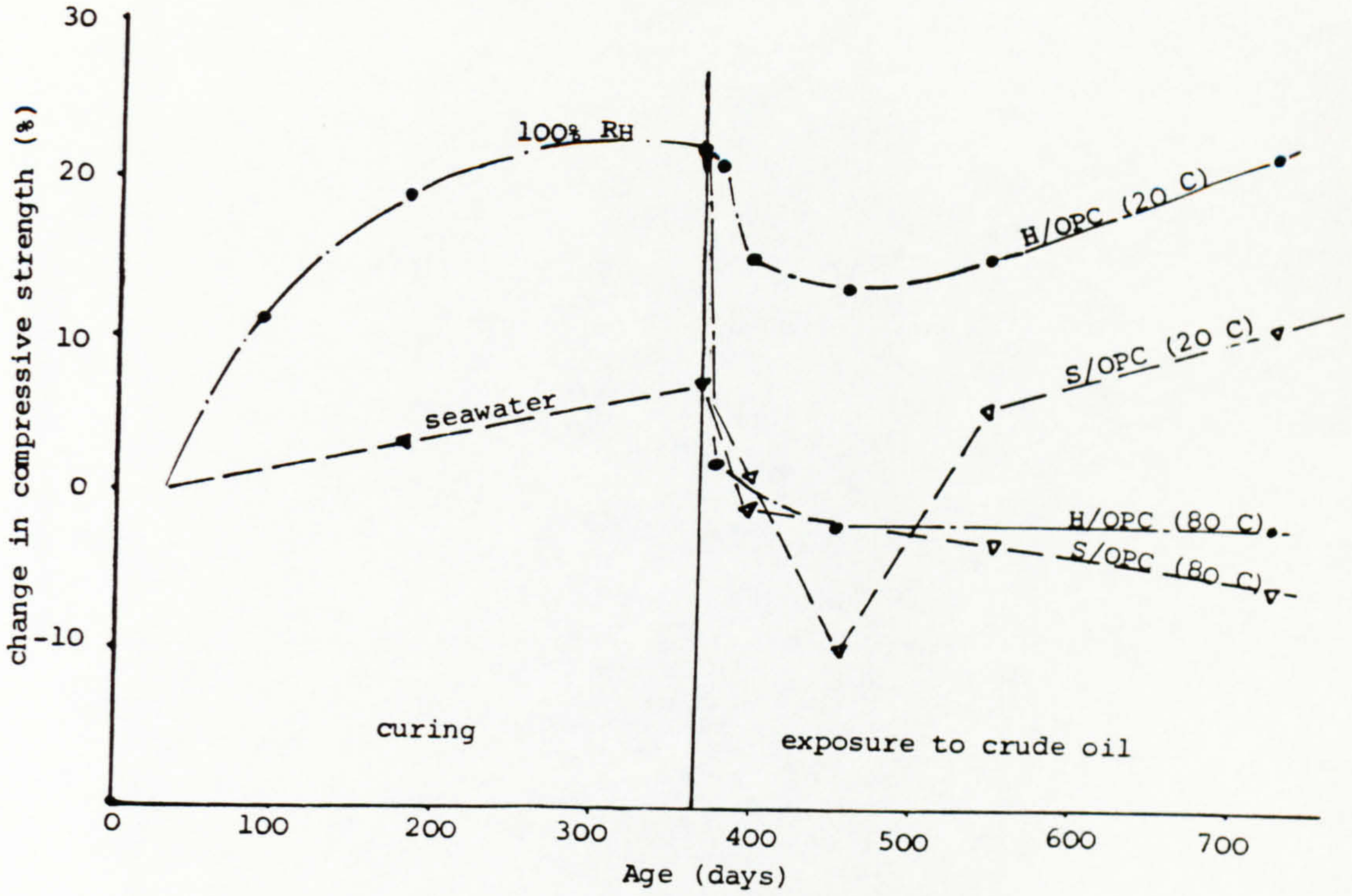


FIG. 9.8: COMPRESSIVE STRENGTH CHANGES RELATIVE TO 28-DAY STRENGTH OF MOIST PFA CONCRETE.

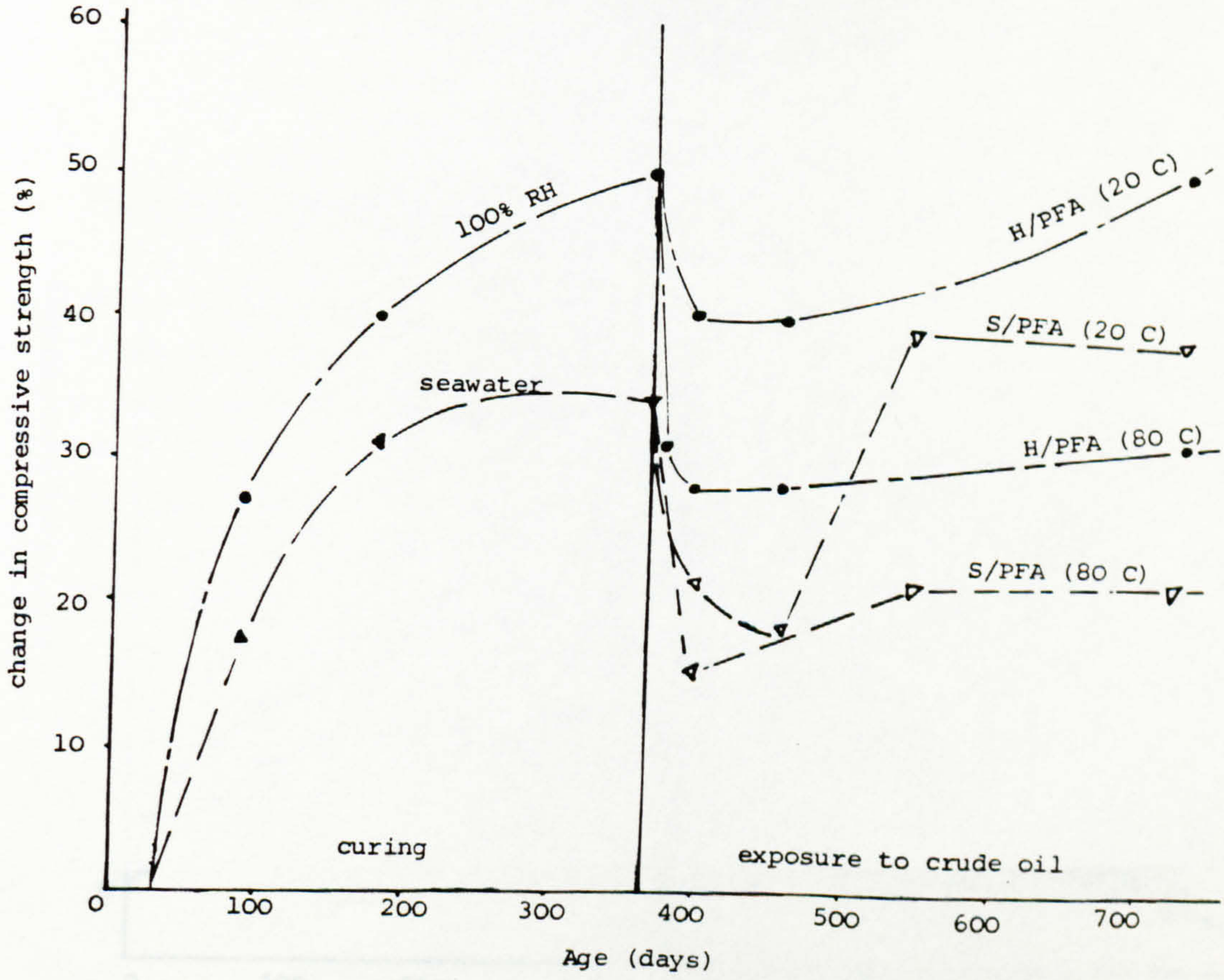


FIG. 9.9: LENGTH CHANGES OF MOIST OPC MORTAR FROM AFTER CASTING.

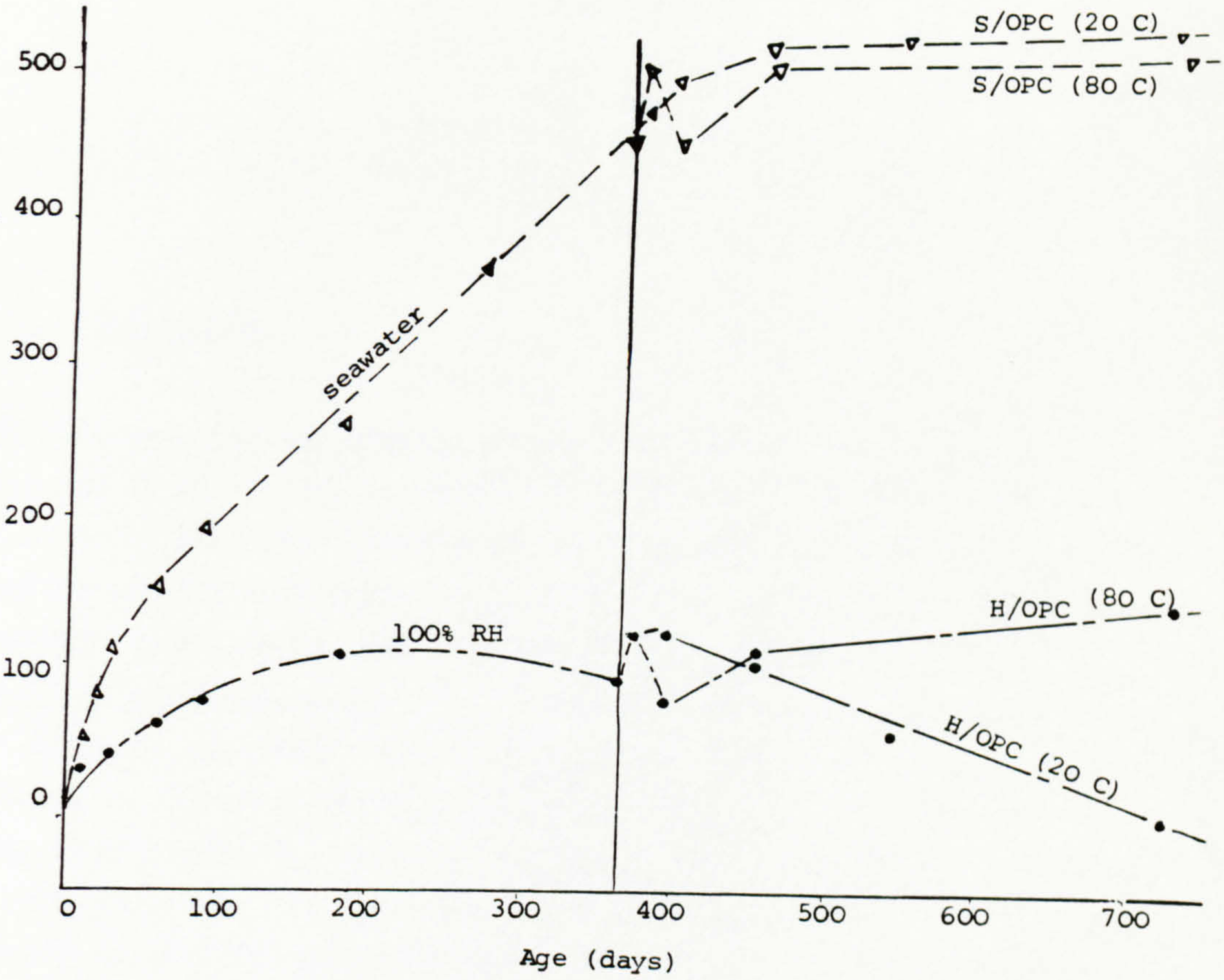
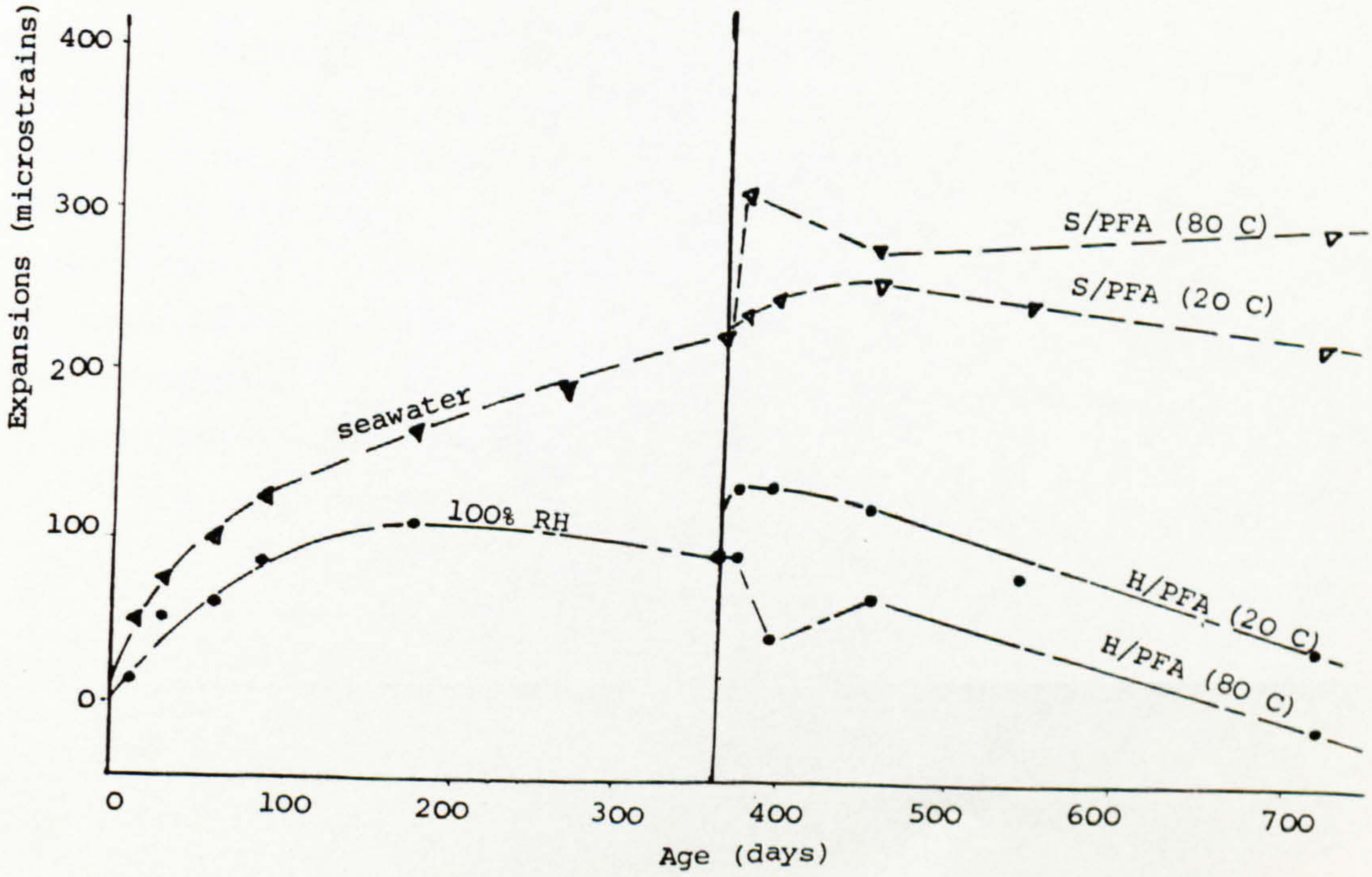


FIG. 9.10: LENGTH CHANGES OF MOIST PFA MORTAR FROM AFTER CASTING.



CHAPTER X

SUMMARY CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

10.1 CONCLUSIONS

The aims of this research programme as were set out in Chapter I, have been achieved. As was pointed out in Chapters I and 2, very little could be found in the literature on studies of the properties of concrete in contact with crude oil at elevated temperatures. Even then, some of the few results reported were contradictory. In particular, there was a gap in knowledge as to the form and nature of the interaction between concrete used in platform storages and the complex contents of an oil storage tank. It is believed that to a large extent, this gap in knowledge has now been partially bridged as a result of this study. For instance, it has now been ascertained that there is no significant uptake of acids, inorganic or organic, by crude oil stored on stagnant seawater which has been acidified as a result of bacterial activity. However, organic acetic acid may be absorbed by the crude oil, if the pH at the crude oil/seawater interface falls below the expected level of about 5.

The method of curing the concrete prior to exposure to hot crude oil had a significant effect. Curing can influence the mechanical properties of the concrete throughout its service life, even after curing has ceased. For example, it was found that the concrete specimens cured in seawater were less dense than the specimens cured at 100% RH, which also had higher compressive strength and less length variations. This was observed throughout the 365 days of curing and also throughout the 365 days of exposure to hot crude oil.

Most importantly, the intention to arrive at a better understanding of the nature of the physical and chemical interaction between crude oil and concrete, at ambient and at elevated temperatures, has been achieved. Essentially, it is now known that:

(a) The absorption of crude oil by oven dry concrete is a time dependent process and increases with increase in storage temperature. It is also related to the method of curing of the concrete prior to exposure to crude oil.

(b) Crude oil absorption at elevated temperatures can significantly affect the mechanical properties of oven dry concrete such as compressive strength and length change.

(c) The absorption of crude oil by moist concrete is not significant, even at elevated temperatures. However, the conditions of exposure may significantly affect the mechanical properties of the concrete.

(d) The effect of the storage temperature is highly significant. Storage temperatures above 60 C can cause serious weakening of the concrete and storage at about 80 C is the most detrimental, in the range of test temperatures.

(e) Partial replacement of portland cement (opc) with pulverised fuel ash (pfa) can significantly improve the durability of the concrete during curing and on exposure to crude oil. Designing concrete oil storage structures to the 28-day compressive strength of PFA concrete will provide adequate margin of safety.

It would be highly desirable that further work is done in the following areas of interest:

(1) Study of the effects of bacterial activity which takes place in the water phase of an oil/ water system,in an oil storage tank, on the properties of concrete. This would include the effects of the combined inorganic sulphuric acid and the organic acetic acid formed during the various metabolisms.

(2) Time related studies of the physical and chemical changes taking place in the microstructure of hardened cement pastes and concretes, when exposed to crude oil at elevated temperatures.

(3) Studies of the permeability of concrete exposed to crude oil at elevated temperatures, subjected to high pressure heads.

(4) Creep studies of oil saturated concrete at elevated temperatures.

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8. **ASTM C157-75** Standard test method for length change of hardened cement mortar and concrete.

9. **ASTM C305-65(75)** Mechanical mixing of hydraulic cement pastes and mortars of plastic consistency.

10. **ASTM C490-74** Apparatus for use in measurement of length change of Hardened Cement paste, mortar and Concrete.

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APPENDICES

APPENDIX A

(i) INORGANIC ACID INTAKE OF CRUDE OIL

(ii) ORGANIC ACID INTAKE OF CRUDE OIL

(iii) PROPERTIES OF UNEDO GREASE-2

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The Institute acquired its crest, designed by the College of Heralds, in 1949. Its motto, 'Conjunctione Potiores' (strength through unity), supports a shield portraying the Archaeopteryx, an avian fossil which was found in Jurassic strata similar in age to important oil-bearing formations in the North Sea.

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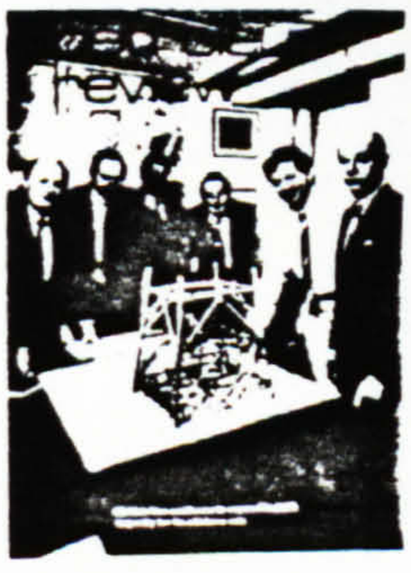
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Cover: British Gas exploration and research directors and managers: (from left to right) Dr Harold WD Hughes, Dr Ernest Shannon, Peter Hinde, Graham Cribb, Noel Fitzgerald and Nicholas Townsend, have given an interview on their work. Article p6. Photo by Jon Whitbourne

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Technical paper

Inorganic acid content of N S oil: effect of anaerobic bacterial activity in tanks

By OA Onabolu, GA Khoury, PJE Sullivan and R Sterritt, Imperial College of Science and Technology, Civil Engineering Department, University of London

1 Introduction

The crude oil in the North Sea oil storage tanks in offshore concrete platforms rests on relatively stagnant saline waters rendered acid by microbial activity.[1] Since acid can be harmful to concrete, it is important to ascertain whether any of the acid in the water phase is transferred to the crude oil, and if so to what extent it is retained.

Bacterial activity is enhanced by the favourable storage temperature between 45°C and 50°C at the oil water interface. Since the temperature of the oil issuing from the production well may often be between 70°C and 100°C, research should be designed to include a broad temperature range. It is known[1] that anaerobic sulphate reducing bacteria (SRB) are active under North Sea storage conditions and such activity leads to the production of H_2S which is in turn converted to H_2SO_4, thus contributing to a decrease of the pH value of the seawater pillow to 5.

Other than in oil storage for offshore platforms, the propagation of SRB and hence acidic conditions can take place in:

- Crude oil carriers which contain only a small amount of water resulting in pH values as low as 2–3.
- Sewers, where the production of H_2SO_4 has led to serious damage to concrete pipes.[2–5]
- In dams situated in the Middle East where the relative quiescent water at elevated temperatures is conducive to accelerated production of bacteria.

The objectives of this work, part of which was instigated by Shell UK Exploration and Production, were, therefore, to examine the effects of mixing crude oil with water acidified with H_2SO_4 over a range of pH values on the acidity of the oil fraction and to ascertain whether this would be influenced by temperature level and degree of mixing.

2 Materials and Methods

2.1 Crude oil

The crude oil used in this work was supplied by BP (UK) Ltd, Sunbury, England, from the Forties North Sea field. A summary of some of its properties is given in **Table 1.**

2.2 Determination of acidity of the oil fraction

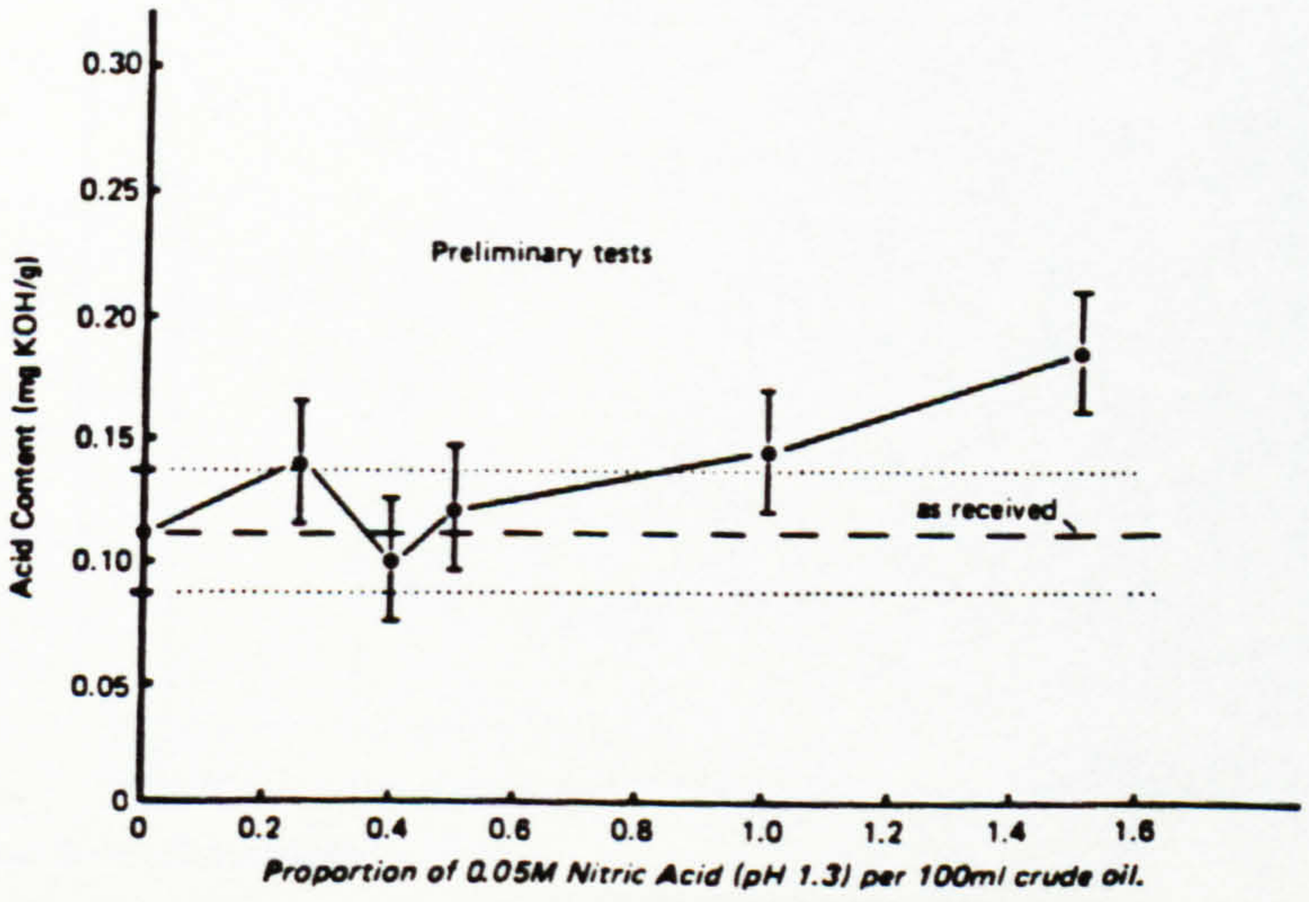
Acidity of the oil fraction was determined by titration with alcoholic KOH solution using alkali blue indicator (BDH Ltd., Poole) to an end point comparable with the colour of a 10 per cent (W/V) solution of colbaltous nitrate, according to the method described in British Standard 2000, part 1: 1982.[6] Total acidity was expressed as mgKOH per g of oil with an accuracy of ± 0.025 $mgKOHg^{-1}$.

Table 1: Properties of crude oil — Forties North Sea field

Crude Inspection Data	
Gravity, °API	36.6
Specific gravity (15°C)▽	0.8403
Sulphur content (% by wt.)▽	0.30
Moisture content (% by vol.)▽	0.40
Wax content (% by wt.)	7.0
Carbon residue (% by wt.)	2.2
Melting point of wax (°C)	55.6
Viscosity cSt. at	
10°C	9.60
21°C	6.81
38°C	4.50
Acidity* (mg KOH/g)	0.05

*Acidity value is a Dec 1975 average.[6]
▽Measured properties of sample supplied.[7]
All other results are based on averages from the Forties field as at June 1983.[8]

Figure 1: Acidity of crude oil after addition of various percentages by volume of acid at ambient temperature.



2.3 Determination of the acidity of the water fraction

Acidity was determined by titration of the sample to pH 8.3 with 0.023M NaOH using phenolphthalein indicator, and was expressed as mg CO_2l^{-1}.

PH was determined using a Pye model 292 pH meter standardised against buffer solutions of pH 4.0 and pH 7.0.

3 Experimental and results

3.1 Preliminary tests

A series of 'calibration' tests were performed

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in which acid (pH 1.3) was added to crude oil in increasing amounts by volume in order to ascertain the acid intake of the crude oil as determined by this method of testing.

A known volume of 0.05M nitric acid, pH 1.3, was mixed with 100ml of crude oil and the total acidity was measured as 0.9mg. $KOHl^{-1}$. The acid was then added in several small proportions by volume to 100ml samples of crude oil, thoroughly mixed and tested for acidity. The measured acidity is given in **Figure 1** and indicates that a four-fold increase in the amount of acid added has not produced any significant increase in the measured acidity of the oil. The variations in the measured acidity of the oil are within the limits of experimental error. However, it appears that an increase in the acidity of the oil takes place when the proportion of 0.05M acid exceeds about 1–1.5 per cent by volume. Although these preliminary tests were performed using nitric acid, the rest and bulk of the testing was performed using sulphuric acid.

Table 2: Tests for acidity of crude oil and water fractions at ambient temperatures

Parameters	*Acidity of water fraction*			*Acidity of oil fraction*		
	1d*	7d	14d	1d	7d	14d
w (pH = 3)	198	195	195	—	—	—
w (pH = 5)	100	80	70	—	—	—
co	—	—	—	0.11	0.14	0.11
w (pH = 3) + co + a (1:1:0)	195	197	196	0.11	0.11	0.14
w (pH = 5) + co + a (1:1:0)	98	90	70	0.14	0.14	0.11
w (pH = 3) + co + a (1:1:1)	198	195	195	0.11	0.17	0.11
w (pH = 5) + co + a (1:1:1)	98	80	80	0.11	0.11	0.11
w (pH = 3) + co + a (3:1:0)	198	198	196	0.11	0.14	0.17
w (pH = 5) + co + a (3:1:0)	90	80	80	0.11	0.14	0.17

w = water, co = crude oil, a = air, acidity of water — mg CO_2/l, acidity of oil — mg KOH/g *time in days after mixing for 15 minutes

3.2 *Tests using sulphuric acid*

3.2.1 *Ambient temperatures (20°C)*

One sample of tap water (pH 8.4) was acidified with a few drops of concentrated sulphuric acid and brought to pH 3. The sample was thoroughly mixed in a 250 ml conical flask with a known volume of crude oil by means of a magnetic stirrer for 15 minutes within which time only the colour of the crude oil could be observed. Three tests were conducted for different sample ratios of crude oil: acidified water: air pocket in flask; as follows:

(a) 1:1:0 (b) 1:1:1 (c) 3:1:0

The flasks were then sealed and left to stand for periods of 1 day, 7 days and 14 days in order to study the effect of time on the degree of separation and consequently on the acidity of the oil fraction.

Similar tests were performed with water acidified to pH 5. The results are given in **Table 2** while the individuals results for the crude oil and water fractions are given in **Figures 2 and 3** respectively.

3.2.2 *Effect of duration of mixing*

A sample of 100ml of crude oil was thoroughly mixed by means of a magnetic stirrer with a 100ml sample of water acidified to pH 5. Mixing was for 5 minutes, after which the samples were allowed to settle and separate before testing each fraction for acidity after 24 hours. The experiement was repeated using similar samples but varying the duration of mixing to 10, 15 and 20 minutes. The results are given in **Table 3**. They show that there is no variation in the acidity of the crude oil and water fraction with duration of mixing.

3.2.3 *Effect of temperature level*

Several tests were carried out at three levels of elevated temperature of 45, 65 and 85°C using acidified waters of pH 2.2 and pH 5.

(a) Effect of temperature without mixing

Crude oil and acid water samples were heated separately at 45, 65 and 85°C for two days and tested for acid content. The acid content of the crude oil was 0.11 mg.KOH/g before and after heating. Similarly, the acid contents of the water samples of pH 2.2 and 7.0 remained constant at 28,000 and 70 mg.CO_2/l irrespective of temperature level. The pH values also remained unchanged.

(b) Mixing at 20°C and subsequent heating

A sample of crude oil was mixed with a sample of acidified water (pH 2.2) in a 1:1 ratio with no air gap for 15 minutes using a mechanical stirrer. Three samples were then immediately placed in ovens at temperatures of 45, 65 and 85°C respectively for 2 days after which they were tested. The tests were repeated using acidified water of pH 5.

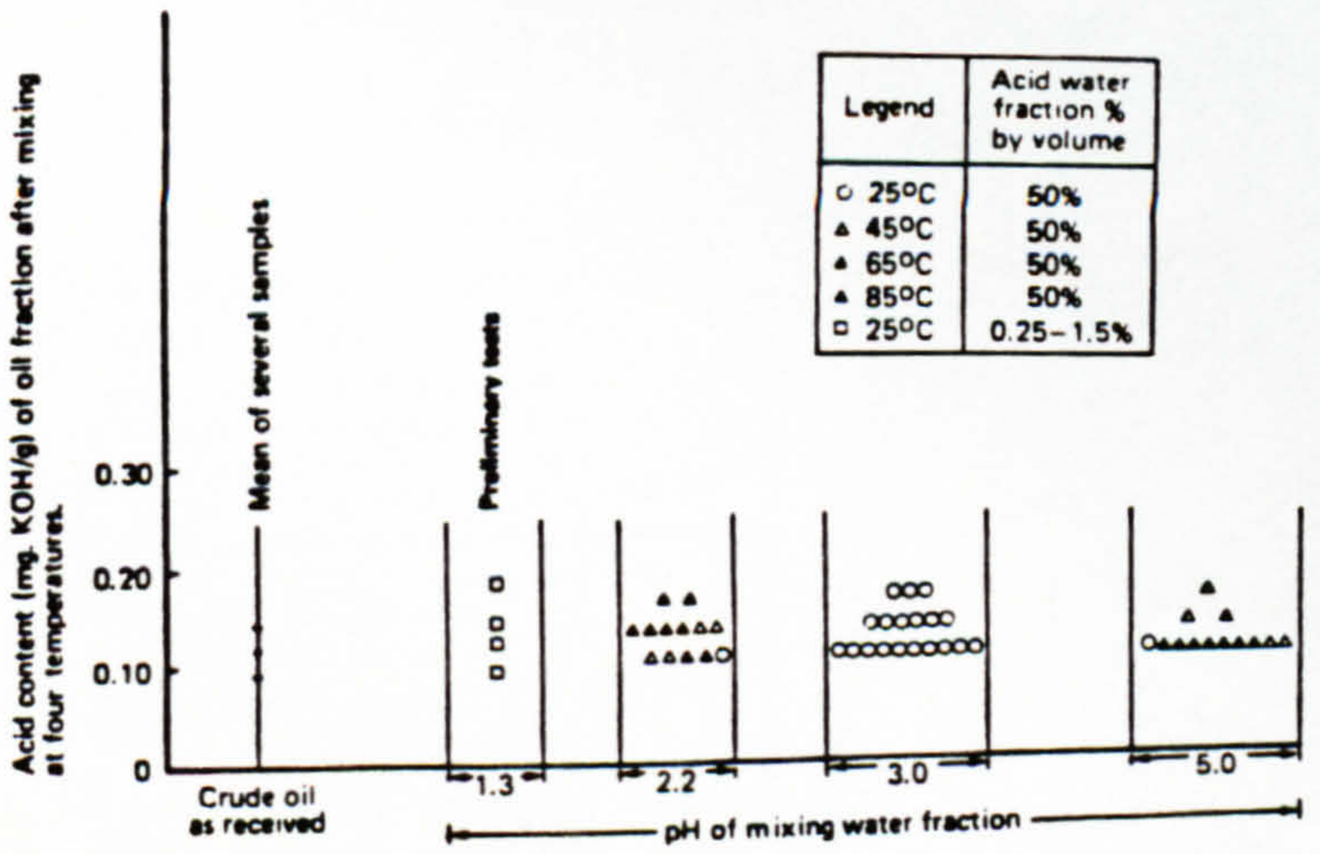
(c) Mixing hot crude oil and acidified water at 20°C and subsequent heating

Samples of crude oil heated to 45, 65 and 85°C were mixed with samples of acidified water (pH 2.2 and 5) which were at ambient temperature. The mixed samples were then heated to the temperature of the original mixing oil for two days before testing.

(d) Mixing hot crude oil and hot acidified water prior to heating

Similar tests to (c) were conducted but using samples of crude oil and acidified water heated to the same temperature (45, 65 and

Figure 2: Acidity of oil fraction after mixing with acid water at four temperatures.



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85°C respectively), mixed and maintained at their respective temperature levels for two days before testing.

(e) Mixing of hot crude oil and hot acidified water and cooling to ambient temperatures

The tests were similar to those described in (d) except that the samples were cooled to ambient immediately after mixing and were tested 2 days later.

The results of these tests are given in **Figures 2 and 3** for the oil and water fractions respectively. Only those relating to mixing with acidified water at pH 5 are, however, tabulated here in **Table 4.**

4 Discussion and Conclusions

The results clearly indicate that there was no retention of acid in the crude oil. It was also interesting to discover that temperature level, duration of mixing and length of time after mixing prior to testing had no effect on the acid level of 0.11 mg KOH/g present initially in the crude oil sample. It can, therefore, be concluded that in practice, the crude oil in the North Sea oil storage tanks is unlikely to absorb any inorganic acid from the water pillow on which it rests. The preliminary tests confirm that negligible amounts of acid are taken up by the crude oil even when it is directly mixed with acid.

The following conclusions can also be drawn from the results:

a Separation takes place after crude oil is mixed with acidified water.

b Separation is almost instantaneous after 5 pH water is mixed vigorously with crude oil. It is, however, slightly slower when 2.2 pH water is employed.

c A very thin layer of water soluble fraction was formed after separation at the oil-water interface. It is estimated to be about 0.05mm for pH 5.5 and 0.1mm for pH 2.2 water.

d Although separation was complete after crude oil was mixed with 5.5 pH water, globules of oil were observed in the water fraction after mixing at higher acid levels of pH 3 and 2.2.

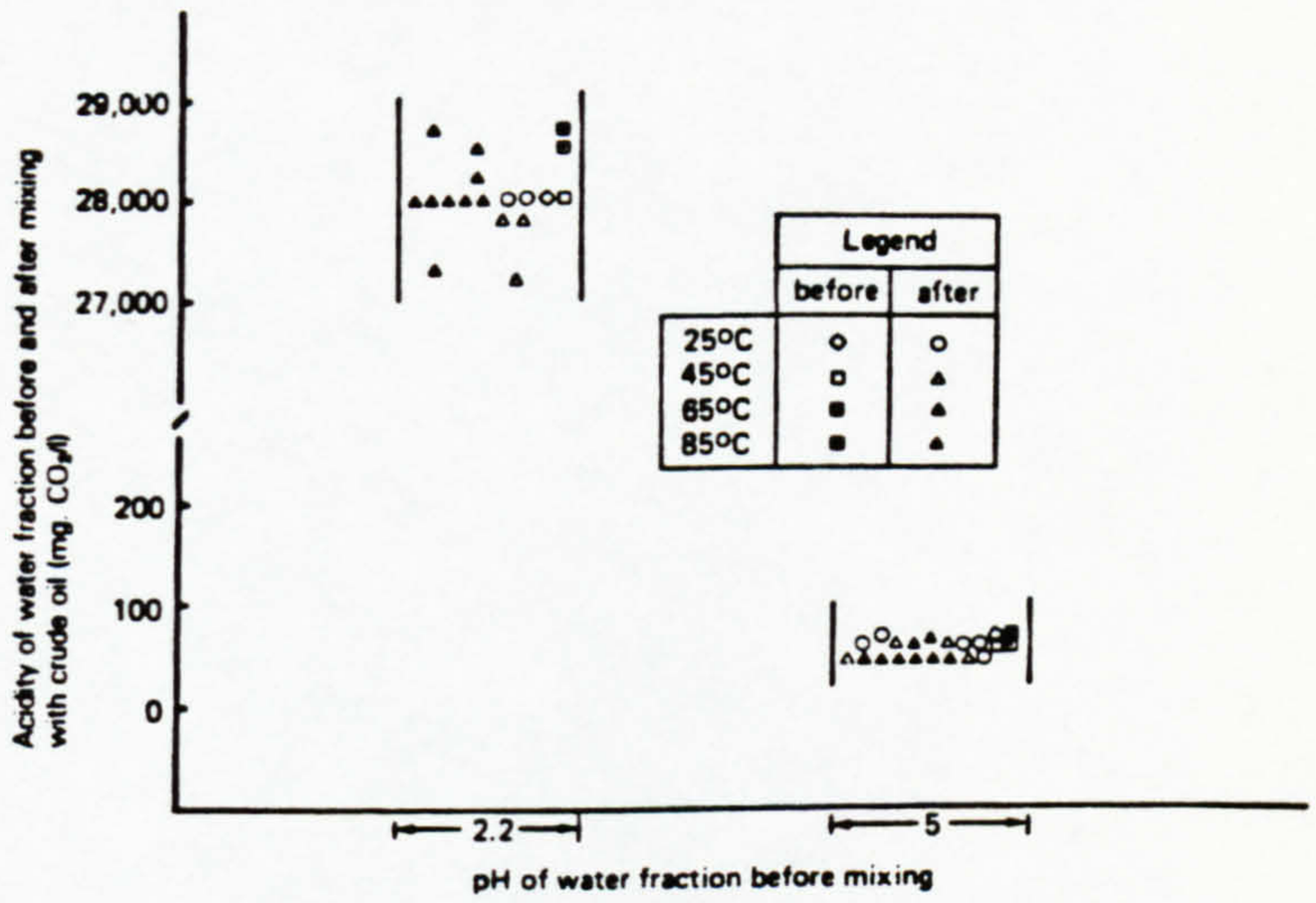
e The duration of mixing up to 20 minutes had no influence on the results.

f The presence of an air pocket above the crude oil also had no noticeable effect on the results.

g However, the presence of an air pocket over 5.5 pH water has, it seems, reduced its acidity after exposure of 1–2 days due possibly to the effect of dissolution of CO_2.

h The temperature level, up to 85°C, of the various fractions had no effect on the results regardless of whether exposure to temperature has taken place before or after mixing.

Figure 3: Effect of mixing with crude oil at four temperatures on the acidity of water fraction.



5 Acknowledgements

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Table 3: Effect of duration of mixing on the acidity of crude oil and water fractions

Duration of mixing (mins)	*Acidity of water (mg CO_2/l)*	*Acidity of crude oil (mg.KOH/g)*
0 (prior to mixing)	100 (pH = 5)	0.11
5	98	0.11
10	100	0.11
15	100	0.11
20	90	0.11

Table 4: Acidity of oil fraction following mixing with water at 5 pH and storage for 2 days at 4 temperatures.

Temperature (°C)			*acidity of oil fraction (mg.KOH/g)*
crude oil	*water (5 pH)*	*after mixing*	
20	20	20	0.14
45	20	45	0.17
45	45	45	0.11
45	45	20	0.14
65	20	65	0.11
65	65	65	0.11
65	65	20	0.11
85	20	85	0.14
85	85	85	0.11
85	85	20	0.11

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Technical paper

Organic acid intake of crude oil in North Sea oil storage tanks as affected by aerobic bacterial activity

by Gabriel A Khoury, Patrick J E Sullivan, Rafic A Dahan and OluKunle A Onabolu,
University of London, Imperial College of Science and Technology

Introduction

The presence of oil, and elevated temperatures, in North Sea oil storage tanks can favour the growth and activity of aerobic and anaerobic bacteria in the seawater 'pillow' beneath the oil.[1] Some aerobic bacteria can produce organic acids which can reduce the pH level of the water pillow, while anaerobic sulphate reducing bacteria (SRB) can generate H_2S which subsequently can be microbially converted to H_2SO_4.[1]

Since acids attack concrete, it is necessary to ascertain whether any of the acid in the water phase is transferred to the crude oil, and if so to what extent it is retained. It has been shown in the first stage of this study[2] that the crude oil is unlikely to absorb inorganic sulphuric acid from the water phase even if the pH level is as low as 2.2. The aim of this investigation,[3] which is part of a wider research programme into the effect of hot crude oil and bacterial activity on concrete,[4-8], is to examine the acid content of crude oil after it is mixed with seawater acidified with acetic acid over a range of pH values. Other effects studied include temperature level of the oil and water fractions before and after mixing, duration of mixing and time after mixing.

The bacterial problem

Growth of indigenous microbial population (restricted in stagnant seawater by the amount of carbon present) is enhanced in the oil storage tanks by the presence of oil and by the elevated temperatures resulting from oil storage. The oil-water system is likely to contain both aeorobic oil oxidising bacteria (OOB) and anaerobic sulphate reducing bacteria (SRB).[1]

Since oxygen is a primary requisite for hydrocarbon degradation,[9] growth of OOB on oil is likely to take place before growth of SRB will occur in the presence of oil, which suggests some form of nutritional interaction between the two bacterial groups.[1,10,11]

Fatty acids are one of the major metabolic intermediates of the degradative pathway of the hydrocarbons found in oil.[12,13] Fatty (eg acetic[14]) acids are present in the aqueous medium outside the bacterial cell during growth of OOB on oil.[15,16] A rapid fall in pH to a minimum of 5.1 was found to take place after 6 days when a culture containing OOB was grown aerobically on atmospherically stabilised Brent crude oil.[1] However, a less marked erratic reduction in pH reaching a minimum of 6.2 after 19 days has taken place in the presence of mortar due to leaching of alkaline $Ca(OH)_2$ which had the effect of increasing the pH of a sterile sample to 8.7.

The onset of anaerobic conditions and growth of SRB follows partial oxidation of the oil by OOB. It is, however, unlikely that hydrocarbons present in the oil will provide a direct carbon source for SRB[17] although some of the organic acids produced by OOB may provide a growth substrate for SRB.[1] Whilst SRB is responsible for the production of H_2S in oil-water sytems, it is unlikely to make a significant direct contribution to a fall in pH. In contrast, the pH may rise slightly during growth of SRB,[18,19] although it should be noted that aqueous H_2S solutions are mildly acidic. However, if Thiobacilli are present, the H_2S may make an indirect contribution to the fall in pH by providing an energy source for these bacteria which oxidise sulphide to sulphuric acid.

Table 1: As received acid content of crude oil and after heating at 80°C for 3 days in air

Acid content of crude oil (mg KOH/g)		
As received		After heating at 80°C in air for 3 days
0.095		0.158
0.056		0.153
0.100		0.156
0.095		
0.076		
0.084	Average	0.156

Acid attack on North Sea concrete

The unlined internal concrete walls of North Sea oil storage tanks are in direct contact with the oscillating hot oil-seawater environment in which acids generated by bacterial activity form a potentially aggressive constituent.

North Sea concrete consists of some two-thirds by volume of 'inert' aggregate (crushed igneous rocks, eg: granite and basalt) and sand, held together by hydrated Portland cement 'paste'. The main constituent of cement paste is its binding agent, calcium silicate hydrate which is an insoluble, porous (~ 30 per cent porosity) structure of colloidal dimensions. Interspersed with this structure are soluble calcium hydroxide ($Ca(OH)_2$) crystals comprising 24 per cent of cement paste by weight, and smaller amounts of other minor phases.

The concrete is in a continuous state of moisture saturation. Its pores are filled with saturated $Ca(OH)_2$ solution rendering the concrete alkaline with pH of about 12.5, and therefore particularly vulnerable to acid attack. Although $Ca(OH)_2$ is the constituent most readily attacked by acids, none of the other hydrated cement compounds is completely resistant to a solution with pH value below 10–11 since they tend to lose calcium to the solution. In practice, however, damage is expected to take place at pH values below about 6.5.[20] For pH values between 3 and 6, attack progresses at a rate approximately proportional to the square root of time.[20] The rate of attack, however, also depends on other factors which include the solubility of reaction products, mobility of the attacking medium and ambient temperature, as well as factors relating to the concrete such as porosity, cracking, $Ca(OH)_2$ content, reactivity of the aggregate and the presence of any surface protection.

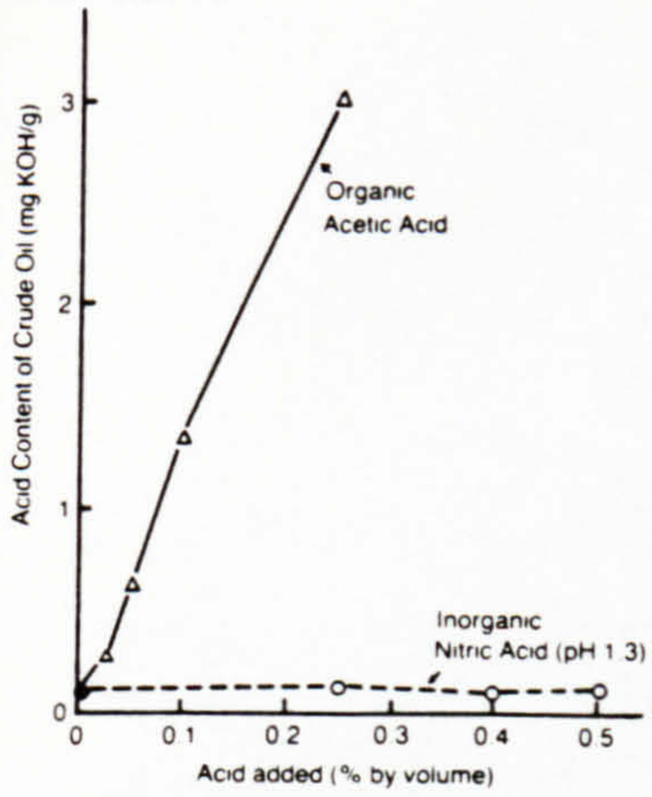
Both sulphuric and acetic acids are classified as causing rapid rate of attack on concrete at ambient temperature.[21] Even H_2S, which by itself does not harm concrete,[22] forms a weak acid in aqueous solution and reacts detrimentally with concrete.[23] The three main products of aerobic and anaerobic bacterial activity in North Sea oil storage tanks are, therefore, harmful to concrete.

Chemical reactions with concrete involving sulphuric acid, acetic acid or H_2S solution form water-soluble calcium compounds[23,24] which are leached away, rendering the concrete weaker and more porous. In the case of sulphuric acid attack, additional or accelerated deterioration results by the expansive ettringite formed. If acids or salt solutions are able to reach the reinforcing steel through cracks or pores in the concrete, corrosion of the steel can result which will in turn cause cracking and spalling of the concrete.[21]

The rate of acid attack on concrete in North Sea oil storage tanks is likely to be influenced by a number of beneficial and detrimental factors. The concrete being dense is of low permeability to both seawater and acids. Although the concrete was not provided during construction by a protective coating, the reaction of the concrete surface during curing with the seawater environment results in the formation of an 'impermeable' layer of aragonite ($CaCO_3$) and brucite ($Mg(OH)_2$)[25,26] which offers the concrete some protection. An additional wax lining may form after entry of crude oil into the tanks.[4] The acids, therefore, need to consume these 'natural' barriers first before attacking the concrete thus retarding the erosion rate. However, thermal cycling resulting from entry and removal of hot crude oil may cause the development of surface cracks,[27] while the elevated temperatures enhance both bacterial activity and chemical reactions with the concrete. The mobility of the oil-water system also helps transport concentrations of reaction products from the concrete surface. Concrete factors also come into play. Since pozzolan or slag cement replacements were not included in the mix, the concrete possesses a relatively high concentration

Technical paper

Figure 1: Acid content of crude oil as a function of amount of acid added



of $Ca(OH)_2$ with the implications that this may have on both seawater and acid attack. Due to the non-reactivity of the aggregate, erosion of mainly the cement paste matrix is likely to result in an irregular rough 'pebble-dash' surface. A reactive aggregate would have produced a smoother surface and a provided a greater volume of neutralising material.[28]

Coating of concrete is recommended when acid attack is likely to take place.[29 30] However, the acid levels in the North Sea oil storage tanks are not as yet known and it is not certain that such a protective measure is required.

Materials, methods and test procedure

Crude oil

North Sea crude oil from the Forties field supplied by BP was used in this work details of which have already been published.[2]

Determination of crude oil acidity

Acidity of the crude oil was determined by titration with alcoholic solution using alkali blue indicator to a consistent potassium hydroxide (KOH) end point[3] in accordance with the method described in British Standard 2000, part 1: 1982.[31] Total acidity is expressed as mgKOH per g of oil to the nearest 0.05 mgKOH g.

Determination of water acidity

Water acidity was determined[3] by titration of the sample to pH 8.3 with 0.023 NaOH using phenolphthalein indicator, and was expressed as mg CO_2 l.

pH was determined using a Pye model 292 pH meter standardised against buffer solutions of pH 4.0 and pH 7.0.

Test procedure

The acidity of both seawater and crude oil were first determined separately after addition of increasing amounts of acetic acid. The main tests involved mixing for 15 minutes of a sample of crude oil (as received) with seawater acidified with acetic acid at pH levels of 2.5 and 5.0 and temperatures of 20 C and 80 C. The majority of tests were performed with sea-

Table 2: Acid content of crude oil as function of volume of acetic acid added

Volume of acetic acid added	*Acid content of crude oil (mg KOH/g)*					
	Individual Results					*Average*
0.0	0.095	0.056	0.10	0.095	0.076	0.084
0.01	0.16	0.14	0.16	0.14	0.15	0.15
0.015	0.15	0.15	0.16	0.17	—	0.16
0.025	0.26	0.25	0.28	0.25	—	0.26
0.025	0.31	0.26	0.27	—	—	0.28
0.05	0.61	0.61	0.65	—	—	0.63
0.1	1.34	1.35	1.36	—	—	1.35
0.2	2.77	2.73	2.73	—	—	2.74
0.25	3.00	3.00	—	—	—	3.00
0.5	5.33	5.22	5.10	5.05	4.88	5.12
5.0	54.00	51.90	54.70	—	—	53.53

water to simulate conditions found in practice, although tap water was also used to allow comparisons to be made with results obtained with seawater. Other parameters examined included the duration of mixing (15 or 30 minutes), time of testing after mixing (up to 21 days) and oil/water volume ratio (1:1 and 2:1).

Results

Acidity of crude oil

(a) As received: The average acid content of the crude oil as received was 0.084 mgKOH/g **(table 1)** which appears less than the value obtained in the previous tests (0.11).[2] However, the two series of tests were performed a year apart using different samples and when the results are expressed to the nearest 0.05 mg KOH/g, as specified in BS 2000, they both give a value of 0.10 mg KOH/g.

(b) After heating: The average acid content increased to 0.156 mg KOH/g after heating in the presence of air for 3 days **(table 1)** due to oxidisation. Such an increase was not obtained after heating without an air pocket.[2]

(c) After adding acetic acid: Considerable increase in acidity of the crude oil occurred after addition of acetic acid **(table 2 & figure 1)** Adding 0.5% by volume of acetic acid increases the acidity of the crude oil to 5 mg KOH/g while adding the same amount of inorganic sulphuric acid results in no measurable increase in acidity **(figure 1)**.

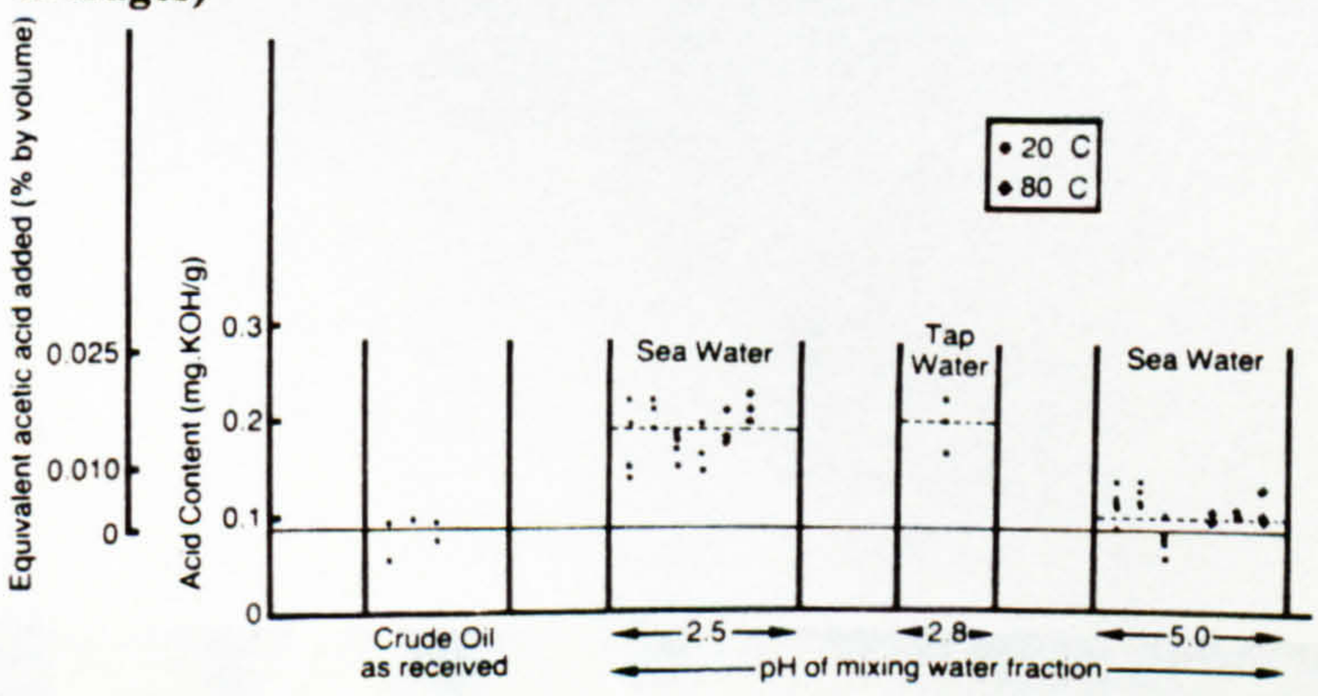
(d) After mixing with acidified water: Details and results of the crude oil acid content tests performed at various times after mixing for 15 minutes of crude oil and water acidified with acetic acid at pH levels 0.25 and 5.0 and temperatures of 20°C and 80°C are given in **table 3.** The acid contents of the crude oil fraction were determined after a fair degree of separation from the water phase has taken place. The value for each test being the average of at least 4 readings **(table 3)**.

The results **(figures 2–4)** indicate that, unlike the case with sulphuric acid[2], the acid content of the crude oil increases with decrease in pH level of the mixing water. The increase at pH 5.0 is marginal (0.84 to 0.1 mg KOH/g) but at pH 2.5 the crude oil acid content is more than doubled (2.26 times the value as received).

The pH level of the mixing water seems, however, to be the main factor influencing the results since the acid content of the crude oil was not affected by mixing temperature, oil/water volume ratio or whether the water phase was seawater or tap water. Readings taken at various times after separation **(table 3 & figure 3)** indicate that the acetic acid is retained in the crude oil for at least 7–20 days after mixing.

The results of the various treatments are compared in an 'equivalence' diagram **(figure 4)** with acid contents obtained after direct addition of acetic acid to the crude oil. Heating in the presence air for 3 days at 80°C and mixing with pH 2.5 water appear to be equivalent to adding about 0.0125 per cent and 0.0175 per cent by volume of acetic acid respectively.

Figure 2: Acidity of oil fraction after mixing with water acidified with acetic acid at two temperature levels (dashed lines represent averages)



Technical paper

Table 3: Acid content of crude oil fraction after mixing with water acidified with acetic acid

Test no	*Details**	*Time after mixing*	*Acid Content (mg KOH/g) Individual Results*					*Averages*		
a1	S:2.5/1/20–20:20	9d	0.20	0.22	0.14	0.15	—	0.18		
		19d	0.22	0.21	0.19	—	—	0.21	0.19	
		21d	0.17	0.18	0.18	0.15	—	0.17		
a2	S:2.5/2/20–20:20	9d	0.20	0.16	0.15	—	—	0.17	0.17	0.19
a5	S:2.5/1/80–80:20	3h–1d	0.17	0.18	0.21	0.17	—	0.18	0.18	
a6	S:2.5/1/80–80:80	1h	0.21	0.20	0.22	0.23	—	0.21	0.21	
b	T:2.8/1/20–20:20		0.20	0.16	0.22	0.22	—	0.20	0.20	0.20
c1	S:5.0/1/20–20:20	2d	0.11	0.12	0.08	0.11	0.13	0.11		
		7d	0.13	0.13	0.11	0.11	—	0.12	0.10	
		11d	0.07	0.10	0.08	0.05	0.07	0.07		
c2	S:5.0/1/80–20:20	5h–1d	0.09	0.09	0.10	0.10	—	0.10	0.10	0.10
c3	S:5.0/1/80–80:20	3h	0.10	0.11	0.10	—	—	0.10	0.10	
c4	S:5.0/1/80–80:80	1h	0.13	0.09	0.10	0.10	—	0.10	0.10	

S = Seawater, T = Tap water, d = days, h = hours.
**Interpretation*
S:2.5/1/80–80:20 = Seawater:pH 2.5/oil to water ratio = 1/temp. oil = 80°C, water = 80°C: mix = 20°C.

Acidity of water

(a) After adding acetic acid: Addition of 0.05 g of acetic acid to 100 ml of seawater reduced the pH level from 7.8 to 3.8 **(table 4 and figure 5)**. Increasing the acid content from 1 to 1.5g/100 ml caused a reduction in pH from 2.48 to 2.45 and lower levels were not attained. The corresponding minimum value for tap water was pH 2.8.

(b) Before mixing with crude oil: The test pH levels of 2.5 and 5.0 were obtained by adding 8g and 6–7 drops of acetic acid per litre of seawater respectively. The corresponding acid levels were 7945 and 15–47 mgCO_2/l respectively **(table 5)**.

(c) After mixing with crude oil: The acid levels of the water fraction following separation after mixing with crude oil reduced to 7595–7855 and 0–20 mgCO_2/l for initial pH levels of 2.5 and 5.0 respectively **(table 5)**.

Mode of separation of crude oil and acidified water

The first acid content reading was taken at a time following mixing **(table 3)** when sufficient separation was deemed to have taken place which allowed testing of oil and water fractions. Separation was slower at lower pH levels, for tap water than seawater, at lower temperatures and for longer mixing times. Separation was also slower and less well defined than when inorganic sulphuric acid was used.[2] Mixing at 80°C with pH 5.0 water provided the only test in which no trace of oil in the water phase was left after separation. It was possible to take the first reading 1 hour after mixing. In contrast, mixing at 20°C resulted in a 3 layer system (oil, mixed and oily water) even after 2–4 days following mixing. The 3 layer system was more prolonged for longer mixing times (30 minutes) and lower pH levels. Given sufficient time following mixing, separation into two phases equal in volume to the initial values occurred except that traces of oil were still visible in the water fraction. Such separation using pH 2.5 water was attained 2 weeks after mixing for 15 minutes. The various factors considered such as temperature level, stirring time, pH level and type of acid, therefore, affected both the speed and clarity of separation.

Figure 3: Effect of time after mixing on the acid content of crude oil mixed with seawater acidified at two pH levels with acetic acid
Note: limits are not those for scatter but represent accuracy of test method.

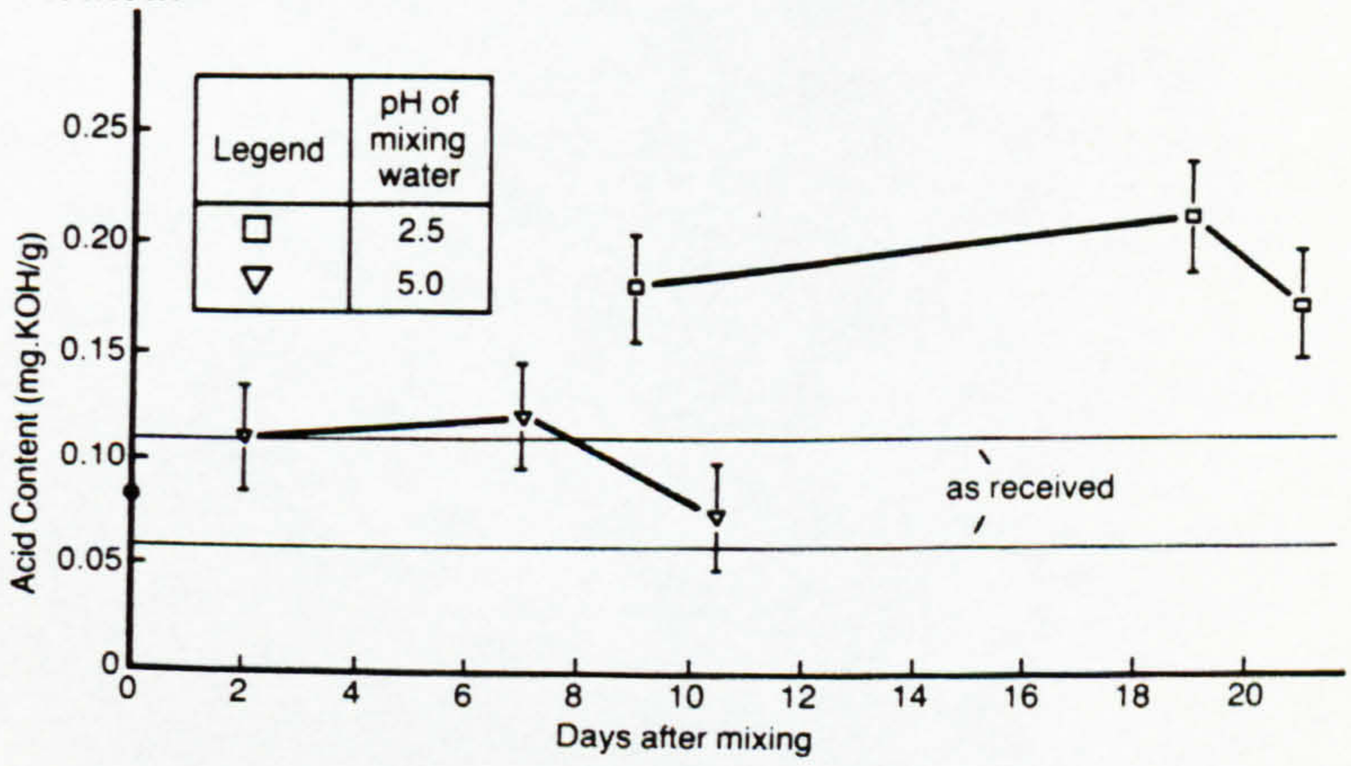


Table 4: pH level of seawater as a function of amount of acetic acid added

Volume of seawater (ml)	*Amount of Acetic acid added*	*pH*
100	0.0	7.8
200	2 drops	4.8
200	0.05g	4.3
200	0.1g	3.8
100	0.6g	2.95
100	0.7g	2.55
100	0.8g	2.51
100	0.8g	2.50
100	1.0g	2.48
100	1.5g	2.45

Figure 4: Summary graph showing acid content of crude oil following various treatments

Technical paper

Discussion and conclusions

The test results indicate that an uptake of organic acids (such as acetic acid generated by aerobic bacterial activity) by the crude oil in North Sea oil storage tanks could take place. This is in contrast with the conclusions drawn previously[2] for inorganic acid where no retention of acid was deemed likely to take place. It is also probable that the acetic acid will be retained in the crude oil for some time after being absorbed. Mixing crude oil with pH 5.0 seawater results in about 20 per cent increase in the acid content of the crude oil fraction after separation when compared with the acid content as received. Mixing with pH 2.5 seawater results in doubling of the acid content and the increase is equivalent to the addition of about 0.0175 per cent by volume of acetic acid. A reduction in the acid content of the water fraction was measured following separation after mixing. Such a reduction did not occur when sulphuric acid was employed.[2]

The following conclusions can also be drawn from the results:

(a) Adding increasing amounts of acetic acid to tap water and seawater reduces the pH levels to a minimum of 2.8 and 2.45 respectively.

(b) Adding increasing amounts of acetic acid to crude oil results in a significant increase in acid content. Adding 0.5 per cent by volume of acetic acid increases the acid content of the crude oil by 61 times whereas adding the same amount of inorganic acid results in no measurable increase in acid content.

(c) Heating crude oil in the presence of air at 80°C for 3 days results in an increase in acid content equivalent to adding 0.0125 per cent by volume of acetic acid.

(c) The pH level of water acidified with acetic acid appears to be the main factor affecting the acid content of the crude oil following separation from the water phase. Mixing temperature, oil/water ratio, period after separation up to 21 days and type of water (tap or sea) did not significantly influence the results.

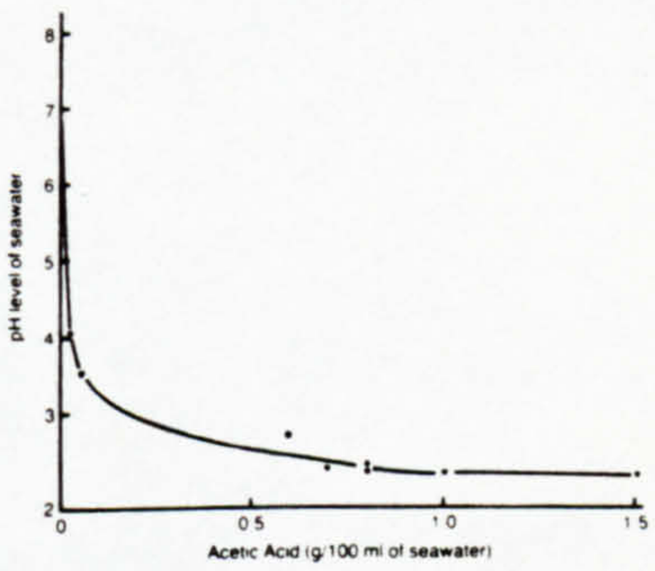
(d) The speed and clarity of separation were, however, influenced by all the test parameters. Separation was slower and less clear for lower temperatures, longer mixing times, lower pH levels, acetic rather than sulphuric acid and tap- rather than sea water.

Table 5: Acidity of water fraction before and after mixing with crude oil

Test*	Acidity of water fraction ($mg\ CO_2/l$)	
	Before mixing	*after mixing*
a5	7945	7855
a6	7945	7595
c1	47.5	20 (7d) 0 (11d)
c3	15	0
c4	15	0

**Test details are given in table 3.*

Figure 5: PH of seawater as affected by amount of acetic acid added



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Shell Unedo Greases have good resistance to water washout by immersion or spray.

Stability

Poor mechanical stability can lead to grease softening which results in a reduction in lubrication performance and a tendency to leak.

Shell Unedo Greases have good resistance to mechanical working without significant changes in consistency. They will not alter in consistency during storage and can withstand operating temperatures up to 55°C without hardening or forming deposits.

Typical physical characteristics of Shell Unedo Greases

Shell Unedo Grease		1	2	3
Colour		Yellow	Yellow	Yellow
Base		Calcium	Calcium	Calcium
NLGI Consistency		1	2	3
IP Penetration, worked, IP 167		310–340	265–295	220–250
Dropping Point, IP 132, °C		100	100	100
Base Oil Viscosity, kinematic cSt, IP 71				
	at 40°C	55.5	55.5	55.5
	at 100°C	5.9	5.9	5.9

@ 15°C 3>>.0

Health and safety

Shell Unedo Greases present no significant health and safety hazards providing they are properly used. The booklet 'Shell Petroleum Products, Guide to Health and Safety' outlines the main precautionary measures to ensure that Shell petroleum products will be safe and without risk. Copies are obtainable from your Shell Representative.

APPENDIX B

GENSTAT PROGRAM

```
1.   "REFERENCE"  CSTR
2.   "TITLE"
3.   "UNITS" $  96
4.   "FACTORS"  REP $ 3 : A, B, C, D, E $ 2
5.   "GENERATE" REP, E, D, C, B, A
6.   "HEADING" H
7.   "DESCRIBE" CSTR $ ; H
8.   "INPUT" 2
9.   "READ"
10.  "INPUT" 1
11.  "BLOCKS" REP
12.  "TREATMENTS"  A*B*C*D*E
13.  "ANOVA/ORTH = Y, LIMA = 5" CSTR
14.  "RUN"
15.  "CLOSE"
16.  "STOP"
```

APPENDIX C

DETAILS OF RUNNING THE NMR SPECTRA

The crude oil was extracted from the plug with CCl_2-D_2 (deutero-dichloromethane), an unreactive, inert solvent. This dissolves the oil to give a sample solution. The sample was placed in the NMR machine and a proton-spectrum is ran. The machine used was a conventional NMR spectrometer, type Bruker WM-250. No calibration was needed, in a routine way the machine measures frequency, and the result is given as a plot of intensity of signal, versus the measure of magnetic field.

The basic principles are as follows:

- Protons have quantised magnetic moments which can only adopt either a relaxed or an excited energy state.
- A certain magnetic frequency in the radio frequency band will cause the proton to move from the relaxed to the excited state. This is the resonant frequency of the proton.
- The resonant frequency is proportional to the strength of an externally applied magnetic field.
- The resonant frequency of a proton is altered by the surrounding electron cloud. Protons in different molecules are surrounded by different electron fields and therefore their resonant frequencies are different.
- As a proton falls from the excited state to the relaxed energy state, it generates a high frequency signal corresponding to its resonant frequency.

The signals emmited by the protons falling from their excited energy state, provide an indication of the composition of the sample tested. A chart giving the frequencies obtained for a range of chemicals is shown in Figure (C.I). An example of a nmr spectrum of an oil sample from a concrete specimens, is shown in Figure (C.2).

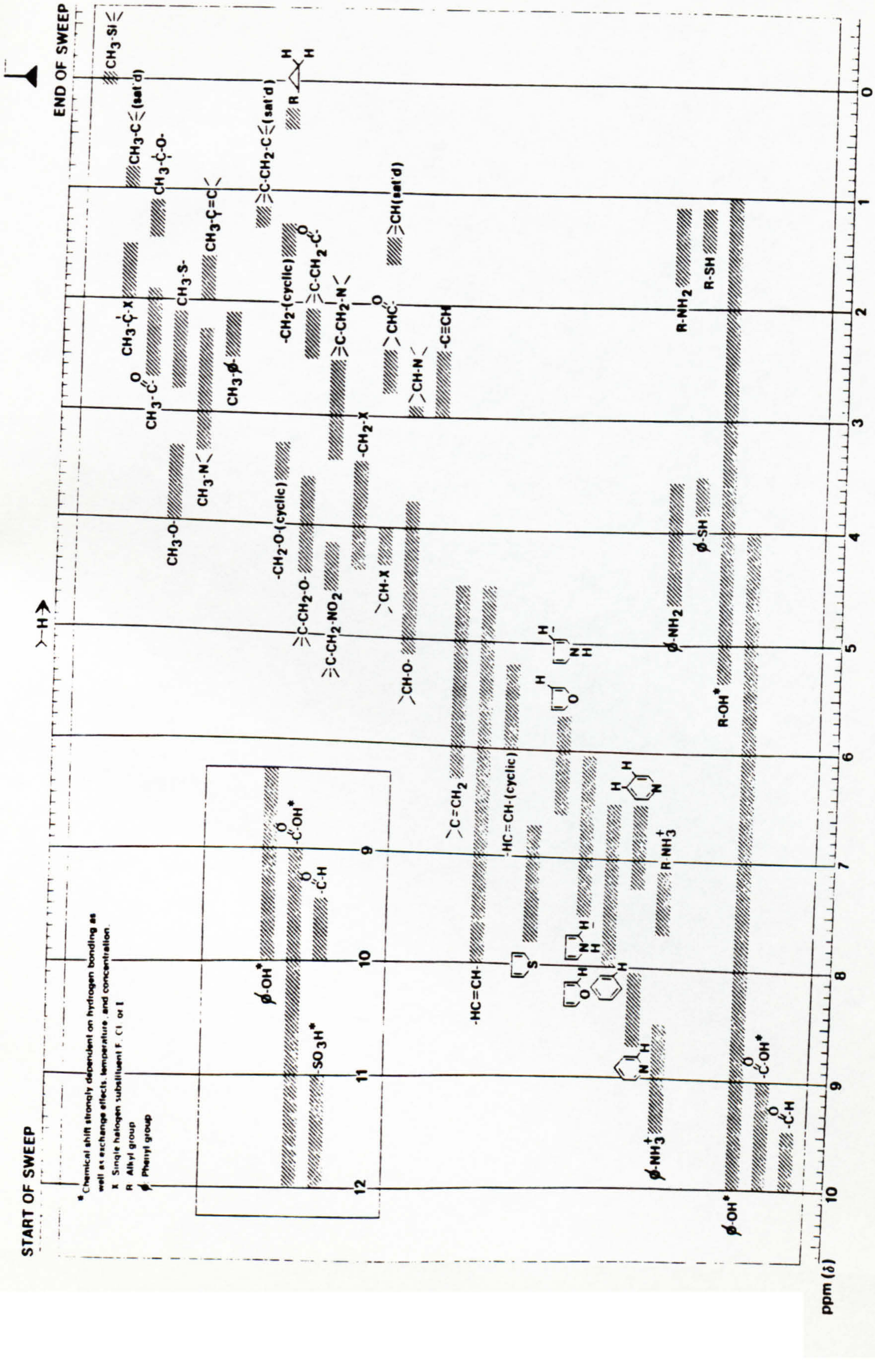


Figure C.1: Proton NMR chemical shift chart

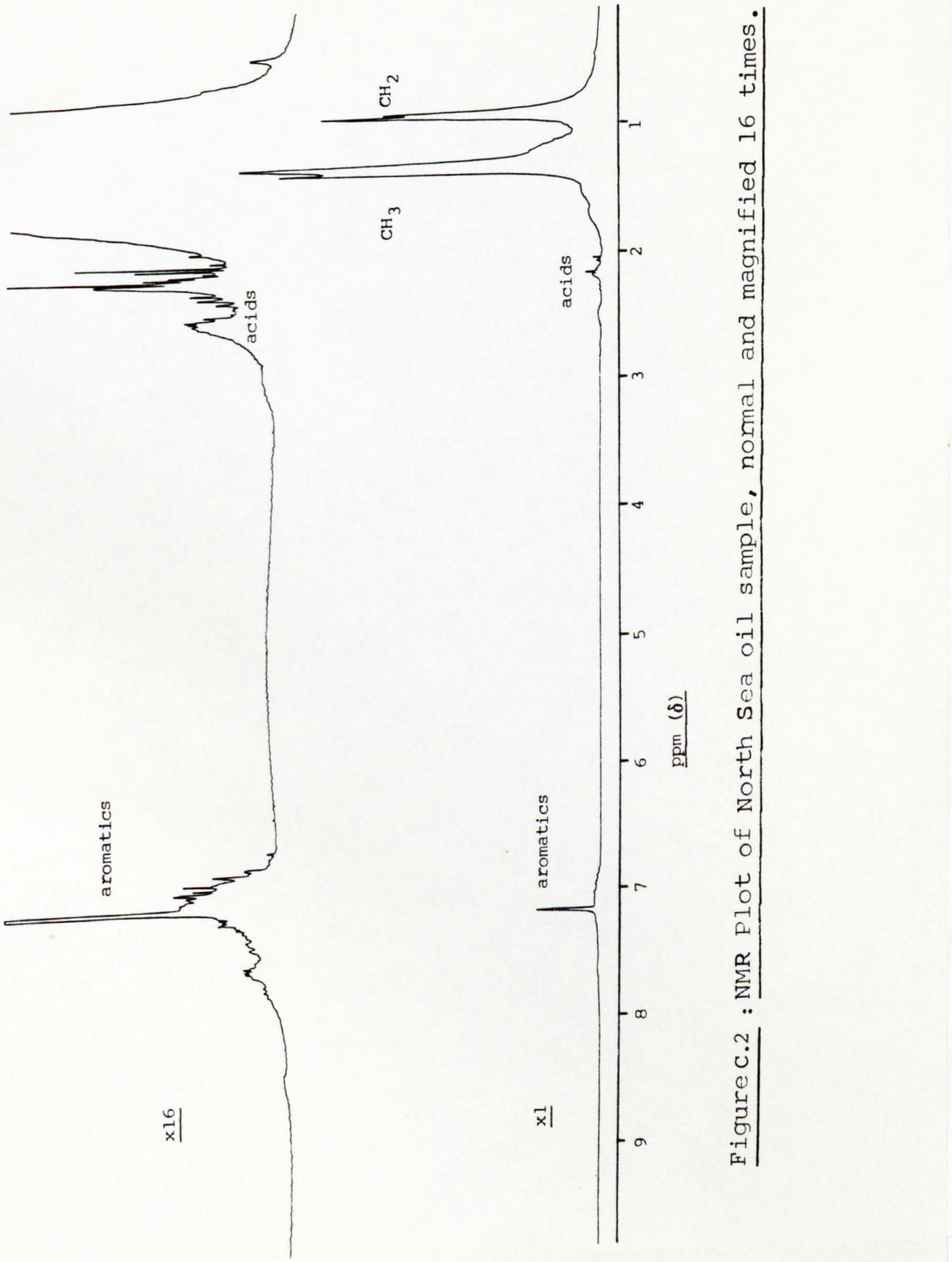


Figure C.2 : NMR Plot of North Sea oil sample, normal and magnified 16 times.