"THE EFFECTS OF IONS ON MORTAR CUBES MADE WITH KENYAN CEMENTS AND SANDS."

By

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DECLARATION

This thesis is my original work and has not been presented for a degree in any other university.

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DEDICATION

Dedicated to my mother Mrs. JOYCE WARUGURU THIONG'O whose hard work and determination to educate me has always been a great source of inspiration.

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ABSTRACT

A study of the effects of aggressive solutions on mortar cubes made from Kenyan cements and sands has been conducted. The study is important because failure of concrete structures exposed to rain water, domestic and industrial effluents is increasing.

Ordinary portland cement; sulphate resisting portland cement; and pozzolanic cement were used to make 70.7 mm cubes with British Standard sand and suitable sand samples from Kajiado and Machakos districts. The cubes were immersed in: deionised water; waste water from a factory; two concentration solutions of fluoride, chloride and sulphate prepared from the respective acids. The effect of the solutions on the cubes for a period of six months was monitored by measuring volume changes and compressive strengths of the cubes; pH, anionic and cationic concentrations of the solutions. The results for the cubes made with the standard sand were used to assess the performance of the cements. The performance of the sands was assessed by holding the different cements constant in the tests.

Kajiado sand has been found to be more coarse and to contain more silt than the Machakos one.

Machakos sand, on the other hand, has been found to be richer in mineral content . Quartz has been found to form the bulk of the two sands. Machakos sand has been found to form unworkable mixes with cements when using a W/C ratio of 0.4, and to bulk when using a W/C of 0.5. The waste water from the factory has been found to contain the following levels of anions: sulphates 361.8-2566.5 ppm; chloride 298.2-1498.8 ppm; fluoride 5.5-38.9 ppm; and phosphate 0.306-1.224 ppm.

The solutions have been found to affect the cubes differently. In environments rich in sulphate ions but combined with other ions, like industrial effluents, sulphate resisting portland cement should be used only after a careful study. The reactions of the cubes with the fluoride solutions have been found to be less deleterious than with the other ions investigated and in some cases fluoride ions were beneficial. The cement-sand combinations that were found to have performed well in the different environments are:

Environment	Cement	Sand
Deionised water	Ordinary Portland	Machakos
Industrial waste water (investigated)	Pozzolanic	Kajiado or Machakos
Fluoride	Ordinary Portland	Kajiado or Machakos
Chloride	Pozzolanic	Kajiado
Sulphate	Sulphate resisting	Kajiado

These cement-sand combinations are recommended to be used in similar environments.

EXPLANATORY NOTES

Cement chemical nomenclature and symbols.

C= CaO; S= SiO_2; A= Al_2O_3; F=Fe_2O_3; M= MgO; N=Na_2O;
K=K_2O; $\bar{S}$= SO_3; H= H_2O;

C_3S = Tricalcium silicate ($3CaO.SiO_2$)

C_2S = Dicalcium silicate ($2CaO.SiO_2$)

C_3A = Tricalcium aluminate ($3CaO.Al_2O_3$)

C_4AF = Tetracalcium aluminate ferrite ($4CaO.Al_2O_3.Fe_2O_3$)

Abbreviations used in this work.

OPC = Ordinary portland cement

SRPC = Sulphate resisting portland cement

PZC = Pozzolanic cement

BS = British Standard

ASTM = American standard for testing materials

STD sand = British standard sand

KJD sand = Sand from Kajiado district

MKS sand = Sand from Machakos district

W/C ratio = Water to cement ratio

I.R. = Acid insoluble residue

D's = The 2 litre deionised water series

W's = The waste water series

Fa's = The lower concentration fluoride solution series

Fb's = The higher concentration fluoride solution series

Ca's = The lower concentration chloride solution series

Cb's = The higher concentration chloride solution series

Sa's = The lower concentration sulphate solution series

Sb's = The higher concentration sulphate solution series

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CHAPTER 1

INTRODUCTION

It is my belief that research in the developing world should be directed towards solving the numerous problems prevalent in that world, with the aim of coming up with appropriate and tangible solutions. This is the only way we of that world can come into terms with our environments.

The problem at hand is the deterioration of concrete structures due to various deleterious chemical agencies emanating from effluents of industrial, domestic and other origins. Corrosion of concrete due to chemical effects has been observed in concrete sewer pipes, culverts,et cetera. Leaking of concrete roofs is widely experienced in the country despite the use of protective coverings like asphalt. The University of Nairobi Chemistry Building provides a vivid example.

Concrete is one of the most widely used substances in constructions and therefore, its failure and repair substantially affects the economy. Research that would minimize its deterioration is therefore important to any country. Work on the deterioration and protection of concrete systems has been done in many countries. Investigations have mainly centred on the effects of sulphates in soils, sea water, and industrial effluents, on concrete systems. Some of this work has been carried out in surveys such as 'long term study of cement performance in concrete' which was begun in 1941 sponsored by the Portland Cement Association of America. Jackson F.H. (1) in 1959 reported one of the studies whose test structures included pavements, roads, piles, parapet walls, specially designed boxes and beam specimens. Exposure conditions varied from mild to severe,with and without the use of de-icing salts; marine environments including tidal zones; and sulphated soils.

Another important survey specific to marine conditions was that organised by the 'Sea Action Committee of the Institution of Civil Engineers' (Britain) between 1929 and 1960. The cements tested were; ordinary, rapid hardening, blast-furnace, portland; high alumina, trass and artificial pozzolanic. High alumina cement gave the best performance in temperate climates and the importance of adequate cement content, low water/

cement (w/c) ratio, and proper cover to reinforcement clearly emerged (2). Work done in Belgium (3) brought out the importance of compaction, good supervision of work in addition to cement content.

Nearer home, El-Sayed et al (1981) (4) investigated the factors responsible for the premature failure of concrete and reinforcement in the pumping station at Manzala lake in Egypt. Concrete analysis showed that the water used contained a high concentration of salts. They also found out that the combined action of repeated stress due to the building vibrations during pumps operation and the corrosive environment resulted in cracking of the structure.

In Kenya very little has been done except the work by Karuu (5). Karuu used neat cement cubes to investigate the most suitable cement for: sulphate, chloride, fluoride, and phosphate environments. By comparing mass and volume changes, compressive strengths, ionic uptake and penetration, he found out that sulphate resisting Portland Cement (SRPC) was the best in sulphate environments, moderate type (II) the best in chloride and fluoride environments, while type (II) and pozzolanic cement (PZC) would be suitable in environments of low sulphate concentration. He also found out that phosphates did not have deleterious effect on any of the cements that he used.

The use of neat cement cubes is considered inadequate because 'the cement mortar has been shown to be the point of attack by most destructive agencies and the one which forms the channel by which waters can permeate into the concrete' (6). Several workers (7,8,9,10) have further ascribed deterioration of concrete to a reaction involving the cement and reactive aggregates for example the 'alkali-aggregate reaction'. A realistic investigation of the systems involved in the deterioration of concrete should therefore incorporate the aggregates.

This work uses mortar cubes instead of neat cement cubes. The coarse aggregate in a concrete is 'mostly inert, hard and impermeable' (6) and therefore the chemical state of the mortar cubes is a good representation of concrete structures. Many workers have moreover used mortar specimens to investigate concrete systems (11,12,13,14,15).

Scope of the investigation

Sand samples were collected from various locations in Kajiado and Machakos districts and their physical and mineralogical properties determined. The sands and the British Standard Sand were used to make mortar cubes with; ordinary portland cement (OPC); Sulphate Resisting Portland Cement (SRPC) and Pozzolanic Cement (PZC).

A total of 378 cube samples were prepared and stored in tap water for at least five months before exposure to aggressive solutions.

The test media consisted of deionised water, industrial waste water; sulphate, chloride and fluoride solutions of varying concentrations, made from their respective acids. A total of 72 test solutions, each with three cubes, were investigated for a period of six months. The performance of the sands and cements during the period was assessed by taking the following measurements: volumes and compressive strengths of the cubes; pH, anionic and cationic concentrations of the solutions.

It is hoped that the work will help establish a methodology for investigating chemical and other aspects of concrete research in Kenya, and also help contractors improve the durability of concrete by choosing the right constituents for specific environments.

CHAPTER II

LITERATURE SURVEY

2.1 Sand

Sands and gravels are derived from the weathering of rocks and are composed of the more resistant minerals which have withstood the destructive effects of weather and transport for a long period. Sand passes through a 3/16 inch mesh and larger particles are classified as gravel (16).

The most important mineral in sand is quartz (17). Other minerals which may be present in small quantities are as given in ASTM C294-69 and include feldspars; micaceous, carbonate, sulphate, iron sulphide, ferromagnesium and clay, zeolites and iron oxides.

Most sands used in mortars and concrete are obtained from river and glacial deposits. Other sources are crushed friable sandstones and sea sands. The latter need to be well washed on account of the presence of soluble salts.

Quartz is an unreactive crystalline form of silica having an orderly arrangement of the silicon oxygen tetrahedra (α-SiO_2). It has minor oxides of titanium, magnesium, iron, manganese, sodium and potassium. The proportion of the minor components varies from sample to sample depending on the origin of the sand. Other reactive forms of silica such as opal are different and are characterised by a random network of tetrahedra with irregular spaces between the groups of molecules (18).

A certain amount of clay ranging from almost zero to 10 per cent, or even more, is a common constituent of sands. The effect of clay in the concrete depends on the manner of distribution. It is much more injurious to the concrete if present as a film enveloping the sand grains than if distributed as fine particles throughout the mass (16).

Particle size distribution of sand affects workability and strength of a fully compacted mortar with a given w/c ratio. The distribution leads to grading which is a foremost important factor in obtaining a dense concrete. Sand and coarse aggregates are therefore graded to ensure that the voids left unfilled between the particles shall be as low as possible. This requires a progressively lower sand content in the concrete mix as the sand becomes finer (6).

BS 882 and BS 1201 of 1965 give four permissible grading zones for sand varying from coarse (zone 1) to fine (zone 4). The specification allows a sand to contain 5-50 per cent of material passing a number 52 sieve, whereas ASTM C33-67 places the maximum at 30 per cent. The main bulk of the sand which lies between a number 52 sieve and a 3/16 inch mesh should contain particles of varying sizes and not consist predominantly of any one size.

2.2 Cement

Cements are defined as "adhesive substances capable of uniting fragments or masses of solid matter to a compact whole" (19). There are basically two types of cements, hydraulic and non-hydraulic. Hydraulic cements, the most common, will set and harden on addition of water and examples include Portland Cements. Non-hydraulic cements will neither set nor harden in water, but will do so on exposure to other substances; an example is 'fat lime' which hardens on exposure to carbon dioxide.

Further classification of cements shows a gradual evolution whereby some cements which were very important at certain times have fallen partly or entirely into disuse as more sophisticated varieties were made. Presently, research is still being directed towards production of better varieties which can withstand specific or general corrosive environments. The various classes of cements are:- limes, natural cements, portland cements, high alumina cements, cements containing granulated blastfurnace slag, pozzolanas and pozzolanic cements, oil-well cements, masonry cements, sorel cements and gypsum plasters (20). Each class may have a number of varieties under it. Portland cement, for example has ordinary, sulphate resisting, rapid hardening and many others.

The discussion on the chemistry of the cements investigated in this work follows:

2.2.1 Pozzolanic Cement

The name pozzolana comes from Pozzuoli which is a name of a village near Naples in Italy. In the village, local volcanic ash has been used as a building material since the Roman times. According to ASTM D219, pozzolanas are silicaceous or silica and alumina containing materials which in themselves possess little or no cementitious value but will in finely divided form and in presence of moisture, chemically react with lime at ordinary temperatures to form compounds possessing cementitious properties.

There are natural and artificial pozzolanas. Natural ones are materials of volcanic origin consisting of glassy incoherent materials or compacted volcanic turfs arising from the deposition of volcanic dust and ash. Artificial pozzolana is mainly a product obtained by means of physical or chemical treatment of natural materials such as clays, shales, certain siliceous rocks and pulverised fuel ash.

Pozzolanic cement is a mixture of ordinary portland cement clinker and pozzolanas, containing sufficient pozzolana to combine with calcium hydroxide formed during cement hydration (21,22).

2.2.1.1 Pozzolanic activity

The phenomenon by which a mixture of pozzolana, lime and water is transformed into a compact hard material at ordinary temperatures is called pozzolanic activity. Natural pozzolanas are active because of the presence of reactive silica and alumina which react with calcium hydroxide (23).

Hydration reaction of the pozzolanic cement components:

(a) Hydration in the pozzolana-calcium hydroxide system.

The crystalline hydrates formed in the reaction between lime and pozzolana in the presence of water have been identified to be hexagonal calcium aluminium hydrate ($4CaO.Al_2O_3.XH_2O$), calcium aluminate monosulphate hydrate ($3CaO.Al_2O_3.CaSO_4.12H_2O$), and calcium silico-aluminate hydrate ($2CaO.SiO_2.Al_2O_3.8H_2O$).

The mechanism of the hydration reaction of the paste in pozzolana-calcium hydroxide system is considered to be as follows:-

On mixing pozzolana and calcium hydroxide with water, the liquid becomes saturated with calcium hydroxide within a very short time, and the solution becomes basic; water attacks pozzolana grains protonically thereby dissociating the $Si(OH)_4$ groups on the grain surface to silicate (SiO_4^{4-}) and hydroxonium (H_3O^+) ions, leaving the grains negatively charged; electrostatic adsorption of calcium ions on the grain surface then takes place; sodium and potassium ions in the pozzolana then dissolve in the liquid phase. The dissolving out of the two cations (K^+ and Na^+) accounts for the observed release of alkalis by pozzolanas and leaves a thin amorphous silica/alumina rich layer on the surface of the pozzolana grain. Silicate and aluminate ions in the layer gradually begin to diffuse to the surface.

At the surface, they react with calcium ions forming the respective silicate, and aluminate hydrates thereby increasing the thickness of the layer. Calcium silicate hydrate precipitates out more easily than calcium aluminate hydrate due to the higher electrostatic charge on silicates than on aluminates.

(b) Hydration in the pozzolana - Cement system.

Addition of pozzolana accelerates the hydration of tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and therefore the cement as a whole. The acceleration of C_3S is due to its increased dissolution caused by adsorption of calcium ions to pozzolana in the liquid phase, and the increase of the surface area. The effect on the C_2S is thought to be due to similar reasons. The acceleration of tricalcium aluminate is brought about by again the adsorption of calcium ions in the liquid phase to pozzolana surface, and the acceleration of its dissolution due to the precipitation of ettringite on the pozzolana surface.

Calcium silicate and aluminate hydrates are generally formed by the reaction between calcium hydroxide and pozzolana after one day, and the physical properties develop in stages. Alumina hydrates are formed later and the period of formation depends on the characteristics of pozzolana as far as alumina content and their solubility are concerned (24).

2.2.1.2 Effect of pozzolana on matured concrete.

During the initial stages, pozzolana serves as an inert material and the situation is equivalent to a system in which there is a reduction in the content of cementitious material. The ultimate strength developed in the pozzolanic cement concrete however may be equal to or greater than, that of plain cement concrete, as reported by Berry and Malhotra (25). This is because the active pozzolana constituents contribute to the formation of more cementitious compounds at later stages, thereby increasing the proportion of hydrated materials responsible for the strength development.

Pozzolana in pozzolanic cement raises the resistance of concrete to chemical attack significantly (21,25). This is as a result of among others, lowering of the permeability of the concrete by the hydrates formed. The heat of the hydration is also lowered significantly giving an added quality to the cement.

2.2.2 Portland Cement.

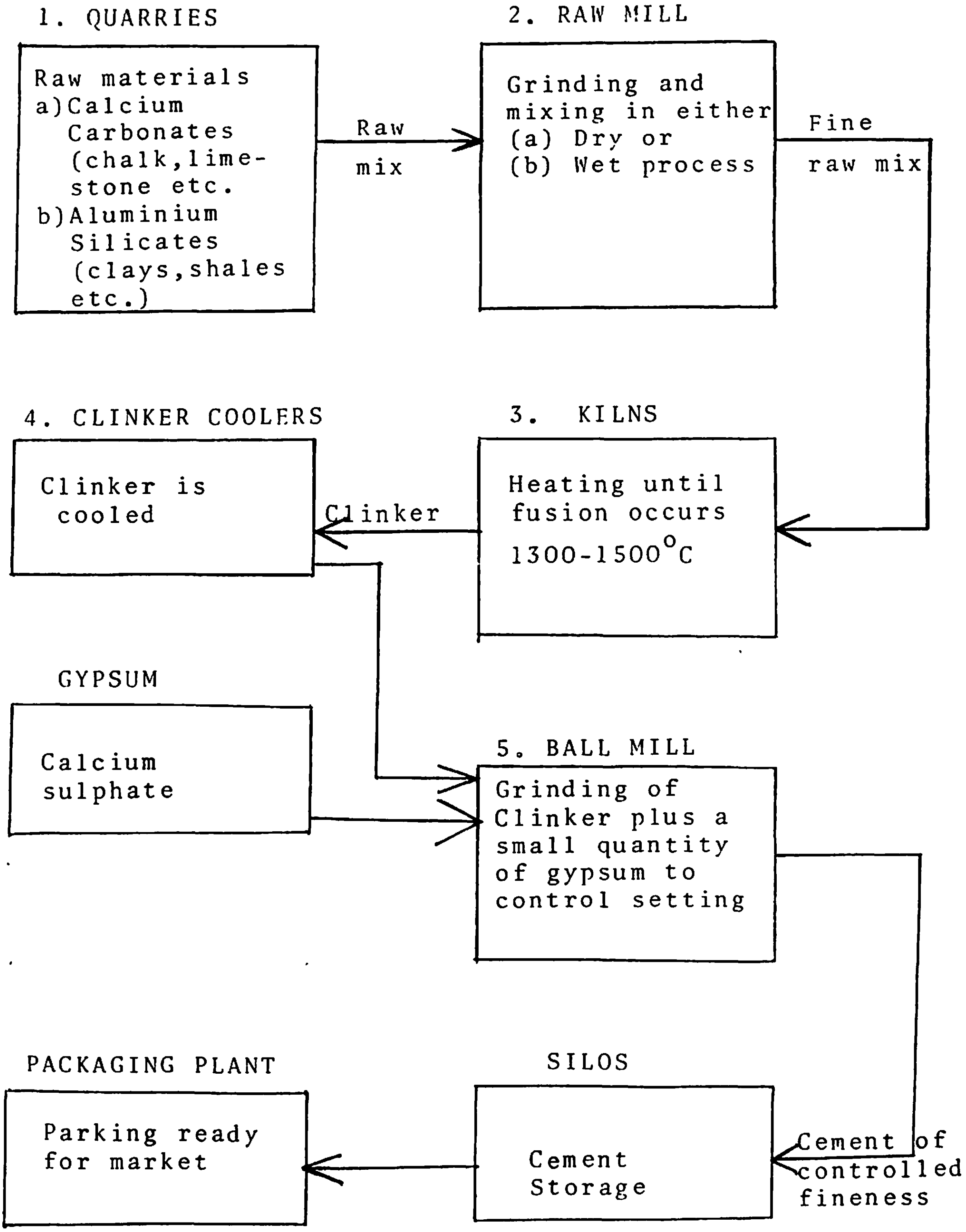
2.2.2.1 Raw materials and manufacture

Portland cement is a hydraulic cement produced by clinkering a mixture of raw materials containing lime, silica, alumina, and iron oxide (26). Table 2.1 gives the analysis of typical raw materials and a typical raw mix of portland cements (27).

Table 2.1: Composition of typical raw materials of Portland Cements (Figures in % by mass).

	Chalk	Clay	Lime-stone	Shale	Marl	Typical raw mix
SiO_2	1.14	60.48	2.16	55.67	16.86	14.30
Al_2O_3(+P_2O_5,TiO_2- & Mn_2O_3)	0.28	17.79	1.09	21.50	3.38	3.03
Fe_2O_3	0.14	6.77	0.54	9.00	1.11	1.11
CaO	54.68	1.61	52.72	0.89	42.58	44.38
MgO	0.48	3.10	0.68	2.81	0.62	0.59
S	0.01	n.d	0.03	0.30	nil	nil
SO_3	0.07	0.21	0.02	nil	0.08	0.07
Loss on ignition	43.04	6.65	42.39	4.65	34.66	35.86
K_2O	0.04	2.61	0.61	4.56	0.66	0.52
Na_2O	0.09	0.74	0.11	0.82	0.12	0.13
Total	99.97	99.96	100.00	100.20	100.07	99.99

The general manufacturing process of Portland cement can be summarised by the following flow chart:



2.2.2.2 Chemical and Mineralogical Composition of Portland Cement.

The approximate limits of chemical and mineralogical composition of portland cement are given in table 2-2 (28). The values vary as a result of the developments of the cements over the years so as to meet different challenges. The different raw materials used in different areas also contribute to the divergent compositions.

The constituents given in the table are classified as minor and major components of the cement. The major constituents are:- tricalcium silicate $3CaO.SiO_2(C_3S)$; dicalcium silicate $2CaO.SiO_2(C_2S)$; tricalcium aluminate - $3CaO.Al_2O_3$-(C_3A); and tetracalcium alumino ferrite - $4CaO.Al_2O_3.Fe_2O_3(C_4AF)$. The constituents do not exist in their pure form but contain small amounts of other oxides in solid solution. Alite (C_3S) for example contains traces of Al_2O_3, Fe_2O_3, MgO, Na_2O and K_2O.

The properties of the cements are determined by the properties of the individual constituents as well as their percentages. The percentage of C_3A in a cement, for example, determines the sulphate resisting ability of the cement (29).

Table 2.2: Approximate Oxide and Mineralogical Composition limits of Portland Cements.

Oxide	Per Cent	Constituent	Per Cent
CaO	60-67	C_3S (alite)	35-55
SiO_2	17-25	βC_2S (belite)	15-35
Al_2O_3	3-8	C_3A	7-15
Fe_2O_3	0.5-6.0	C_4AF (celite)	5-10
MgO	0.1-5.5	$CaSO_4.2H_2O$ (gypsum)	3-12.5
Na_2O+K_2O	0.5-1.3	CaO(free lime)	0.66-1.02
SO_3	1-3	MgO, K_2O, Na_2O etc.	≈3

2.2.2.3 Setting and hardening of portland cement.

The reaction of the cement with water leads to setting and hardening. This occurs in a hydration process that involves many chemical reactions that take place simultaneously.

In the hydration of alite and belite aqueous C_3S and C_2S are formed in the early stages, changing within a few hours to hydrates. Impurities affect the composition and properties of the products but they are assumed to be a CSH gel of average composition $C_3S_2H_3$ and $Ca(OH)_2$. The calcium silicate hydrate ($C_3S_2H_3$) is the main binder of hardened cement and the principal contributor to early strength development. Some of the sulphate ions from gypsum (ground with clinker) can also enter the C-S-H phase because of some degree of solid solution arising between the sulphate and silicate ions from C_3S or C_2S. The action can aid early compressive strength development. The set cement consists mainly of the alite and belite hydration products and its properties are determined accordingly. Calcium hydroxide ($Ca(OH)_2$) for example, makes cement paste to be highly alkaline (pH 12.5) and this makes concretes to be sensitive to acid attack. The high alkalinity offers protection to embedded steel in reinforced concrete against corrosion (30,31).

C_3A reacts with water too vigorously on its own and because of this, gypsum is ground with clinker to prevent quick set and control the setting reaction (29). The intermediate reactions between C_3A, gypsum and water results in needlelike crystals of a sulphoaluminate, known as ettringite ($C_3A.3CS.H_{31}$), which continue to form as far as sufficient sulphate ions are present in the solution. The ettringite crystals form a layer on C_3A grain surface and this retards further hydration of the C_3A. At this time (1-2 hours) setting is mainly dependent on the hydration of C_3S and C_2S, and so the cement remains plastic and workable. With time, diffusion causes more ettringite to form directly on the enscribed surface of C_3A. Crystallisation of the ettringite brings pressure and expansion causing the layer to crack, and this marks the end of the initial set. The cracking opens up C_3A for further hydration and the process continues until final setting takes place in about 6 hours.

The volume of the hydration products is more than twice that of the anhydrous cement and consequently, as the hydration proceeds, the products gradually fill in the spaces. Points of contact are formed causing stiffening and within 10 hours, the concentration of the hydration products and the points of contact restrict the mobility of the cement grains to such an extent that the mass becomes rigid. This is the final set and the porosity of the mass is greatly lowered.

The sulphate ions are depleted in 24 hours and further hydration of C_3A results in the conversion of ettringite into a monosulphate ($C_3A.CS.H_{12}$), or into hexagonal plate solid solution of C_4ASH_{12} and C_4AH_{13}. When the limiting composition of the solid solution is reached, the remaining C_3A hydrates to form C_4AH_{19} which depending on temperature may convert to the C_3AH_6 or by taking up silica become a hydrogarnet. Alumina and iron oxide containing phases such as $C_4A_{0.5}Fe_{0.5}H_{13}$ also begin to form at this stage. The calcium silicates continue to hydrate giving CSH particles having the shape of short fibres. The hydration products continue to fill pores reducing porosity even further.

The ferrite phase reacts in a similar manner to C_3A and the iron(III) substituted hydration products are structurally very similar. They readily enter into solid solution with their pure (C_3A) analogues (29,30).

The rate of hydration is affected by: age; cement fineness; cement composition; w/c ratio ; temperature; and admixtures (32,33). The cement paste strength is determined by the hydration process and therefore the factors cited above also affect the strength (34).

2.3 Concrete.

Concrete is composed of a coarse aggregate forming the bulk of the mix, a fine aggregate filling the voids between, and cement and water to bond the whole together (6). To obtain a dense concrete, the aggregates are graded so as to leave the least unfilled spaces between the particles. The most compatible mixes are worked out proportionately as 1 cement: x fine aggregate: y coarse aggregate by volume or by mass. The aggregate proportions and sizes may be varied depending on the products to be manufactured (35).

The quality and quantity of mortar which binds the coarse aggregate together gives the properties of the concrete (6).

2.3.1 Factors affecting concrete strength.

The quality and quantity of concrete constituents in the mix affect concrete strength. The working on the materials and supervision of the work has been found to be an important factor. If the work is carried out properly the strength is governed by the strength of the cement paste, the paste-aggregate bond, and some properties of the aggregates (36).

2.3.1.1 Aggregate Properties.

At least $\frac{3}{4}$ of the volume of concrete is occupied by the aggregate. Many properties of the aggregate depend entirely on the quality of the parent rock but the particle shape, size, surface texture and adsorption have a considerable influence on the quality of concrete. A rougher surface like that of crushed particles, porous and mineralogically heterogeneous particles result in the formation of a better bond.

Aggregate porosity, permeability and absorption not only influence the bond but also the resistance of concrete to: freezing; thawing and abrasion. The factors also influence the chemical stability of concrete (37). The aggregates' coefficient of thermal expansion, specific heat and thermal conductivity have also been found to affect concrete strength. The factors are significant especially in the hydration process.

A 'fine-grading' sand requires additional water for the workability to be preserved as compared to one of coarser grading. This results in a higher w/c ratio and hence less strength.

The suitability of zone 4 sand (finest grading) in reinforced concrete has to be tested although it usually forms good concrete especially by vibration. Presence of moisture in sand causes 'bulking' and extremely fine sand has been known to bulk as much as 40% at the moisture content of 10%. Such a sand has been found to be unsuitable for manufacture of good quality concrete. At the other extreme, a coarse sand of zone 1 produces a harsh mix, and a high sand content may be necessary for higher workability. The sand is suitable for rich mixes or for use in concrete of low workability (38,39).

Some contaminants of the aggregates are destructive to concrete. These can be classified as: impurities which interfere with the processes of cement hydration; coatings on the aggregate which prevent the development of a good paste-aggregate bond; and certain individual particles which are weak or unsound in themselves. All or part of an aggregate may be harmful due to chemical reactions between it and the cement paste.

Silt and fine dust in excessive quantities increase the amount of water necessary to wet all the particles in the mix because of their mopping up action. Salt contamination affect the quality because salt absorbs moisture from the air causing efflorescence. Unsound particles like clay lumps, wood, et cetera, lead to pitting and scaling of concrete. Free mica in the aggregate has been found to adversely affect the water requirement and strength of concrete (40).

Gypsum and other sulphates are dangerous because of the sulphate attack. Iron pyrites, mercasite and pyrrhotite react with water and oxygen to form sulphates. Glasses are expansively reactive with alkalis from cement while hard burnt lime and dolomite adventitiously incorporated in the aggregate will react with water in the fresh concrete, and carbon dioxide from the air to form hydroxides and carbonates. The products swell causing disfiguring pop-outs on the concrete (41).

2.3.1.2 Paste-aggregate bond

The bond depends on the properties of the cement paste and the aggregate. The w/c ratio is one of the important determinants and applies to concrete as it does to the paste. The roughness of the aggregate is associated with greater strength which may be due to increased surface area and improved mechanical interlocking. In some cases, the properties of the layer at the paste aggregate interface are different from those of the individual aggregate and the paste, implying that a chemical reaction takes place at the interface. While working with extrusive (lava flow) rocks, Alexander et al (42) found that the bond strength increased with increase in silica content within the range of 45-70% (silica). They attributed the phenomenon to chemical reactions between silica and lime of the cement similar to those occuring in the pozzolanic cement-water systems. With silica containing aggregates, the reactions are limited to the paste aggregate interface and these determine the bond characteristics and strength. Farran (43) found that calcareous aggregates produced stronger concrete and attributed it to slight dissolution of the calcite, and the epitaxial growth of a layer of solid solution $CaCO_3$-$Ca(OH)_2$ at the aggregate surface.

The exact nature of the paste-aggregate bond is not fully understood but the bond is characterised by the presence of a thin layer which bridges the aggregates and the paste. Soroka (44) contends that the layer is formed as a result of a chemical reaction between the cement and the aggregate, or epitaxial growth, or a combination of both. Some paste-aggregate reactions are however deleterious to concrete systems.

2.3.1.3 Deleterious concrete reactions associated with aggregates.

Most of the deleterious reactions are expansive in nature, causing failure by cracking and the associated after effects. The reactive aggregates differ and so do their respective reactive conditions.

The principal factors governing the extent of expansive reactivity of aggregates are:-

(i) nature, amount and particle size of the reactive material; and

(ii) amount of the alkali and water available.

The reactions that have been found to be detrimental to concrete are: alkali-aggregate reaction, cement-aggregate reaction, and alkali-reactive carbonate aggregate reaction (45,46).

2.3.2 Admixtures and surface treatment of concrete.

Admixtures are materials that are added to mortar or concrete when mixing in order to modify the properties of the product, either in its fresh or hardened state. Such materials are used to make expanding or non-shrinking cements; lightweight products like aerated concrete; and concretes resistant to, alkali-aggregate reaction, chemical attack, fungi, germs, and even insects.

There are a large variety of materials which are applied to the surface of concrete either to water-proof or render it resistant to attack by chemical agencies. Examples of the materials include aqueous solutions such as silicofluorides, surface covering by paints, linings and sheets; and gas treatments such as silicofluorination (47).

2.4 Chemical attack on cement and concrete.

Deterioration or corrosion of concrete due to chemical agencies is a well known phenomenon.

The agencies may either be natural like sea water, rain water, and some soils; or man made in the form of effluents from industries, sewerage systems et cetera.

Research has been done over the years to identify the agencies, and to come up with appropriate remedies. In some cases, change of cement type, use of admixtures and surface treatments has been found necessary, while in others, complete change of materials, for example, plastic for the concrete systems has been recommended.

2.4.1 Soft and pure water.

Cement paste consists of about 65% lime, part of which is present as free calcium hydroxide. The solubility of calcium hydroxide in water is about 1.7 g/l and can therefore be leached out by water. The hydrates of calcium silicates, aluminates and ferrites, are stable in aqueous solutions of a certain value of lime. Water dilutes the solution causing hydrolyses of the hydration products allowing further lime to go into solution in order to maintain equilibrium.

The effect is limited to pure and soft water because the dissolution of calcium hydroxide in hard water is rather limited. The attack is severe where continous flow occurs and this makes rain water to be among the most corrosive agents. Concrete roofing is therefore usually covered or admixed with protective substances (48).

2.4.2 Sea water

Concrete is widely used in the construction of harbours, docks, breakwaters and other structures exposed to the action of sea water. Concrete in sea water may suffer attack due to, the chemical action of the dissolved salts, crystallisation of salts within the concrete under conditions of alternative wetting and drying, and corrosion of reinforcement embedded in it. Attack in any one of these ways renders the materials more prone to the action of the remaining agents of destruction.

The pH of sea-water varies from 7.4 to 8.4. Generally chlorides make up 90% of the salts while sulphates make up the remaining 10%.

Sodium chloride does not react with the calcium hydroxide or other hydroxide products, but magnesium chloride slowly reacts with calcium hydroxide to produce magnesium hydroxide precipitate, and calcium chloride solution. Calcium chloride easily leaches out leaving a damaged structure. In dense products, the deposition of the hydroxide precipitate tends to slow down the process unlike in porous and more permeable products where leaching goes on unabated.

The sulphate concentration in sea-water is equivalent to a sulphur trioxide (SO_3) concentration of over 2000 ppm. Given that only as low as 500 ppm (SO_3 equivalent) is required to cause appreciable damage, extensive damage would be expected from sea water due to sulphates. Experience has however shown that less deterioration occurs. The exact reason for the reduced aggressiveness of the sulphate in sea water is not clear and has been attributed to various reasons. The greater solubility of gypsum and calcium sulphoaluminate in chloride solutions is thought to reduce the effect of the volume increase associated with sulphate attack (49). Another theory is that the presence of sodium chloride slows down the formation of ettringite which is completely inhibited in the presence of magnesium chloride (50). Locher (51) however argues that the presence of chlorides hardly affects the formation of ettringite, attributing the reduced rate of its formation to the presence of carbon dioxide.

2.4.3 Acids and acidic solutions.

Highly acidic conditions may exist in agricultural and industrial wastes particularly from the food and animal processing industries. For example lactic and butyric acids arise from the souring of milk and butter, acetic acid from vinegar processing, and oleic, stearic and palmitic acids are encountered as constituents of various oils and fats. Some domestic, agricultural and commercial sewage systems have been reported to be capable of producing sulphuric acid microbiologically (52).

Most acids attack the cement by converting its constituents into readily soluble salts. Attack by hydrochloric acid, for example, leads to the formation of chlorides of calcium, aluminium and iron all of which are soluble in water. A similar effect is produced by most strong acids such as sulphuric acid and nitric acids. Exceptional in this respect are oxalic, tartaric and hydrofluoric acids which produce almost insoluble salts. Of some special interest are salts of fluorosilicic acid which are sometimes used to protect concrete against mild attack (48).

Moskvin et al (53) in a study of corrosion of cement stone and concrete in acid media using 0.001-0.1M aqueous solutions of HCl, H_2SO_4, H_3PO_4, HF, HBr, HNO_3, H_2SO_3, H_2SiF_6, and $(COOH)_2$, showed that the acid corrosion media may be divided into three groups: those which form a permeable gelling layer of the corrosion products (HCl, HBr, HNO_3) with the highest rate of corrosion; those which depending on the concentration and cement stone composition, form a gel or crystalline layer of the products (H_3PO_4, H_2SO_4 and H_2SO_3) having medium rate of corrosion; and those which form a mixed gel-crystalline layer of the corrosion products (HF, H_2SiF_6 and $(COOH)_2$) as the least corrosive.

2.4.4 Sulphate solutions.

Most sulphates attack hardened concrete very severely. The attack causes expansion which then results in disruption and cracking. An exception is barium sulphate (barytes) which is almost insoluble in water and is therefore not aggressive. As low as the equivalent SO_3 concentration of 500 ppm can cause considerable damage.

Calcium hydroxide and tricalcium aluminate hydrate react with sulphate in solution to form solid products which have a larger volume. The equations below represent the reactions in the attack.

$$Ca(OH)_{2(aq)} + SO^{2-}_{4(aq)} + 2H_2O_{(l)} \longrightarrow CaSO_4.2H_2O_{(s)} - + 2OH^-_{(aq)} \quad ---2.1$$

theoretical expansion, 2.2 times.

The calcium aluminate hydrates react with sulphates in solution to form one of the two possible calcium sulphoaluminates,

$$3CaO.Al_2O_3.6H_2O_{(s)} + 3CaSO_{4(aq)} + 26H_2O_{(l)} \longrightarrow$$

$$3CaO.Al_2O_3.3CaSO_4.32H_2O_{(s)} \text{ ----------- } 2.2$$

Expansion 4.8 times

$$3CaO.Al_2O_3.6H_2O_{(s)} + CaSO_{4(aq)} + 6H_2O_{(l)} \longrightarrow$$
$$3CaO.Al_2O_3.CaSO_4.12H_2O_{(s)} \text{ -------- } 2.3$$

Expansion 2.1 times

Magnesium sulphate is more efficient because of the possibility of additional corrosive reactions due to the presence of magnesium ions which decompose both calcium silicate hydrate (C-S-H) and the calcium sulphoaluminates.

$$3CaO.2SiO_2.3H_2O_{(s)} + 3MgSO_{4(aq)} \longrightarrow$$

$$3CaSO_4.2H_2O_{(s)} + 3Mg(OH)_{2(s)} + 2SiO_2.XH_2O_{(s)}$$
$$\text{------- } 2.4$$

$$3CaO.Al_2O_3.CaSO_4.12H_2O_{(s)} + 3MgSO_{4(aq)} \longrightarrow$$

$$4CaSO_4.2H_2O_{(s)} + 3Mg(OH)_{2(s)} + Al_2O_3.3H_2O_{(s)} \text{-----} 2.5$$

The insoluble and expansive brucite ($Mg(OH)_{2(s)}$) is thus also produced (54). The silica gel formed in equation 2.4 may react with magnesium hydroxide to form a crystalline magnesium silicate which has no cementing properties (49).

Sulphate attack occurs on the C_3 A hydration products and so susceptibility of portland cement to the attack will decrease with a decrease in C_3 A content (55). This is the basis of production of sulphate resisting portland cement (SRPC). The ferrite phase also reacts with sulphates in a similar manner but the effect is less than that on the C_3 A (56).

2.4.5 Chloride solutions.

Chloride solutions are deleterious because they form soluble salts that leach out of the concrete. The chloride ions also penetrate the concrete systems endangering any reactive reinforcement especially steel.

In an investigation of the effect of chlorides on concrete in hot and arid regions, Ben Yair (57) studied the effect of chlorides on the physicochemical properties of cement and concrete exposed to chloride solutions for 8 years. He found that the penetration and absorption of the ions into portland cements was much higher than that of sulphate ions, and that climatic factors had a decisive influence on the character and magnitude of corrosion.

Gjørv and Vennesland (14) in a study of the diffusion of chloride ions from sea water into concrete found out that 'the diffusion of chloride ions into concrete is not just dependent on permeability and the capacity of chloride binding but also on the ion-exchange capacity of the system. For blended cements like pozzolanic, the pore solution has a lower concentration of hydroxyl ions hence the capacity for exchanging anions with the permeating solution is also lower'.

Calcium chloride is used as a deicing agent on the roads and its aggressiveness against portland cement has been attributed by Chatterji (58) to:-

(i) Crystallisation of complex salts containing calcium chloride hydroxide and/or carbonate;

(ii) Leaching of calcium hydroxide from the cement paste thereby making the paste porous and susceptible to subsequent action of frost.

Other work by Ono et al (13) has shown that the chloride ions in the early stages quickly penetrate deeply into a specimen as compared to sulphate ions, react with calcium hydroxide, and convert calcium ions into extractable species in the aqueous phase thereby, making the specimens very porous, although some chloride is retained as Friedel's salt, $3CaO.Al_2O_3(Cl_2,SO_4).12H_2O$.

2.4.6 Fluoride solutions.

Fluorides have been associated with increasing desirable properties to concrete systems.

In a study of the corrosion of unreinforced and reinforced concretes, Shypynova et al (59) found that hydrofluoric acid decomposed calcium hydroxide and calcium hydrosilicates to form calcium fluoride (CaF_2), Calcium silicofluoride ($CaSiF_6$) and sodium silicofluoride ($NaSiF_6$). Silicofluorides have been reported to form protective systems (48). Birilenko et al (60) have also reported that an aqueous 50-70% Na_2SiF_6 suspension was used as a hardening initiator to increase mechanical strength and homogeneity of concrete in making acid resistant concrete.

Silicofluorination as a surface treatment, in a process called Ocrate, has been used to protect sewer pipes and concrete exposed to aggressive conditions in industries in Holland, Germany, Australia and U.S.A. among others (47).

2.5 Resistance to chemical attack by some cements.

After mechanically making a high quality concrete the cement and/or the aggregate used may not be suitable for the physico-chemical environment, to which the product would be exposed. The choice of the constituents for different environments is therefore very important. This would mean using, for example, acid resistant cement and aggregates for an acidic environment.

The resistance of sulphate resisting cement (SRPC) and pozzolanic cement (PZC) vis a vis that of ordinary portland cement (OPC) to chemical attack is discussed below.

2.5.1 Sulphate resisting portland cement (SRPC)

SRPC has a lower content of C_3A than OPC. In most standards the C_3A content in SRPC is limited to 5% or less while some standards, for example ASTM C150, also limits the C_4AF content. The reduction in C_3A reduces the heat of hydration and the rate of the strength development.

The C_3A hydrates are the most susceptible compounds to sulphate attack in OPC and reduction of C_3A greatly reduces the vulnerability of cement to the attack. OPC with 15% C_3A would be expected to be at least three times more reactive than SRPC. In an investigation of the corrosion of SRPC vis a vis OPC, Fukuchi et al (61) found that SRPC had a better resistance to sodium sulphate solutions among others.

In chloride solutions, an experiment revealed little difference between mortars made of the cement and OPC. The SRPC was however found to have a higher chloride content throughout the period of study (14). This shows that SRPC takes up more chloride ions than OPC and would be expected to be more susceptible to chloride attack (62).

2.5.2 Pozzolanic cement (PZC).

Pozzolanic activity removes or reduces the calcium hydroxide necessary for gypsum, ettringite, and brucite formation (equations 2.1-2.5). Even if ettringite would be formed, it would be unstable in solutions which are deficient in lime, and therefore PZC is highly sulphate resistant. Free lime of PZC has been found to decrease rapidly after the seventh day while that of OPC increases upto the 180th day (21).

The activity brings about more calcium silicate hydrates which have a lower CaO/SiO_2 ratio than those of OPC. The hydrates therefore become more resistant to the action of soft water and consequently suffer low leaching. The presence of abundant calcium silicate hydrate phases further present an effective barrier, protecting other phases that are more sensitive to aggressive solutions.

Concrete permeability is directly related to the amount of hydrated cementitious materials present in the concrete. Inclusion of pozzolana as a partial replacement for OPC reduces permeability to water, due to an increased proportion of the hydrated cementitious materials (25).

Collepardi et al (63) while investigating penetration of chloride ions into cement pastes and concretes found out that PZC offered a higher resistance to the flow of chloride ions than the OPC pastes and concrete samples. Gjørv and Vennesland (14) came up with similar findings and found that chloride penetration in OPC may be as much as two to five times that in cements like PZC. For such cements the pore solution has a lower concentration of hydroxyl ions, hence the capacity for exchanging anions with the permeating solution is also lower.

CHAPTER III

EXPERIMENTAL

3.1 Analytical techniques

Several analytical techniques were used depending upon the nature of the analysis required. Some of the techniques, considered to be less commonly used are discussed below.

3.1.1 Potentiometric analysis

Potentiometric technique is an easily adaptable method to different circumstances. It can be used to determine a wide range of concentrations, with only a minimum of procedural variations. The technique uses ion selective electrodes and within the last few years a wide variety has become available.

Species now commonly determined by such electrodes are: sodium in pure water; fluoride and nitrate in potable waters; sulphide and cyanide in industrial effluents; potassium, calcium and carbon dioxide in biological fluids; and chloride and ammonia in a variety of media (64).

The technique depends on the relationship between concentration of the determinand and the emf of an electrochemical cell in which the determinand is one of the components of the equilibrium system (65). The ideal system is the one which utilizes the Nernst equation expressed as:

$$E = E^{o} + K \log C \text{ ----------- } \quad 3.1$$

Where E is the measured potential, E^{o} the standard reduction potential for the particular species; C the concentration of the determinand and K a constant.

$$(K = \frac{RT}{nF} \log 10)$$

Digital meters can read to 0.1 millivolts or 0.0001 pH units over a range of 999.9 mv or 0-14 pH units. Most of these meters display the polarity sign automatically on the millivolt scale. The technique has been developed over the years so as to display the determinand concentrations directly.

Specific ion membrane electrodes are used and complexing substances affect the accuracy of the ion in question. Such effects are removed from the solution by buffering, and addition of chemicals which free the ions in question. When compared to other available methods, potentiometric analysis of chlorides and fluorides has been found to be far much superior (66).

3.1.2 Turbidimetry.

Small amounts of some insoluble compounds may be prepared in a state of aggregation such that moderately stable suspensions are obtained. The optical properties of each suspension will vary with the concentration of the dispersed phase. When light is passed through the suspension, part of the incident light is passed through the suspension, part of the incident radiant energy is dissipated by absorption, reflection and refraction while the remainder is transmitted. Measurement of the intensity of the transmitted light as a function of the concentration of dispersed phase is the basis of the turbidimetric analysis.

For the cloudiness or 'turbidity'to be reproducible, utmost care must be taken in its preparation. The precipitate must be very fine so as not to settle rapidly. The following conditions should be carefully controlled in order to produce suspensions of reasonably uniform character.

(a) The concentrations of the two ions which combine to produce the precipitate.

(b) The manner, the order, and the rate of mixing.

(c) The amounts of other salts and substances present, especially protective colloids.

(d) The temperature.

The barium sulphate technique for sulphate determination is the most common (67).

3.1.3 X-ray diffractometry.

The phenomenon of X-ray diffraction by crystals results from a scattering process of X-rays by the electrons of the atoms without change in wavelength. A diffracted beam is produced by such scattering only when certain geometric conditions are satisfied which may be expressed in either of two forms; the Bragg law, or the Laue equations. "The resulting diffraction pattern of a crystal, comprising both the positions and intensities of the diffraction effects, is a fundamental physical property of the substance serving not only for its speedy identification but also for the complete elucidation of its structure" (68).

Bragg gave a very simple geometrical interpretation of diffraction by a crystal grating. Using an analogy to specular reflection he showed that the conditions for a diffracted beam of X-rays are given by the relation:

$$n\lambda = 2d \sin \theta \text{ ----------------- } 3.2$$

where η is an integer, the order of diffraction; λ the wavelength of X-rays; d the interplanar spacing between successive atomic planes in the crystal; and θ the angle between the atomic plane and both the incident and diffracted beams. This fundamental relation is the Bragg law.

If a crystal is mounted with a face on an axis of a rotating or oscillating table, and a narrow beam of monochromatic X-rays strikes the face, the conditions of the Bragg's law will be met at certain definite values of the angle θ, and the beam will produce a spectrum of several orders on a photographic plate (69).

In the Laue method a polychromatic beam is required and it is not strictly parallel but more or less divergent (70). The analysis of the positions of the diffraction effect leads immediately to a knowledge of the size, shape and orientation of the unit cell. To locate the positions of the individual atoms in the cell, the intensities must be measured and analysed.

In powder diffraction technique, a beam of monochromatic X-rays impinges upon a crystalline powder composed of fine randomnly oriented particles. Under these conditions, all the diffracted rays from sets of planes of spacing, say d_1, generate a cone of angle $2\theta_1$; planes of spacing d_2 generate one of $2\theta_2$ and so on. A pattern of concentric rings is thus produced and they intersect a film placed perpendicular to the undeviated beam at a certain point (71).

Interplanar spacings are then derived from the observed angles, with the aid of the Bragg equation (3.2). The process consists of:-

(a) a linear measurement on the film,

(b) conversion of the measurement to the equivalent Bragg angle θ, and

(c) calculation of d values from the Bragg equation.

Diffractometer stripchart records are particularly easy to interpret, since the chart paper is printed in such a way that 2θ values can be read directly. By using the data for the construction of d-scales for measuring photographic patterns, it is very easy to construct cardboard scales for the direct measurement of d spacings from the strip-chart records.

The mineral is identified by matching the d-values obtained to existing mineralogical d values data available from 'International Centre for Diffraction Data' (72,73).

3.2 Experimental

3.2.1 Materials.

Deionised water and analar grade reagents were used in all the preparations.

3.2.1.1 Cements.

Table 3.1 gives the cements and the chemical compositions which were generously provided by Bamburi Portland Cement Company limited (Mombasa).

Table 3.1: Chemical composition (main components) of cement samples (%).

Substance	OPC	SRPC	PZC
SiO_2	19.34	19.15	18.96
I.R	0.7	0.26	4.01
Al_2O_3	5.64	5.00	5.98
Fe_2O_3	4.21	6.78	3.20
CaO	62.23	63.28	59.45
MgO	0.75	0.79	0.90
SO_3	2.95	2.26	2.63
Na_2O	0.33	0.22	0.39
K_2O	0.54	0.43	0.68

3.2.1.2 Sands.

Sands were sampled from the primary sources of the suppliers to the concrete and the general construction industry.

The sources from Machakos district were:-

(a) Thwake river

(b) Syuuni river

(c) Kasinga river

and from Kajiado were:-

(a) Sajiloni area
(b) Ngoire area
(c) Olkejuado river
(d) Mbilo/Sajiloni

The samples were put in labelled pre-washed bags.

3.2.1.3 Waste waters.

These were sampled from a factory in 'Athi-river' town. The factory locations from where the water was collected were:-

(a) filter samp
(b) waste-water drain gutters
(c) waste water storage reservoirs

The samples were put in labelled plastic bottles which had been thoroughly cleaned with 0.1M HNO_3 acid followed by plenty of deionised water.

3.2.2 Analysis of the sand.

3.2.2.1 Sampling.

The sands were dried overnight in an oven at 100°C. The dried sand was then sampled by use of a sample divider (rifle box) as stipulated in B.S 812: Part 1: 1975 Clause 5.

3.2.2.2 Silt analysis.

The 'Field settling technique' as explained in B.S 812: Part 1, 1975 Clause 7.2.5, was used to obtain the amounts of silt as per cents in the sands.

3.2.2.3 Sieve analysis.

About 200g of the sample was put in preweighed sieves arranged in the order; 3/16", Numbers, 7, 14, 25, 52, 100, 200 and the collecting pan. The top sieve 3/16" was covered with the top pan and the series fixed to a 'Test Sieve Shaker Model E.F.L. 1' which was run for about 10 minutes. Each sieve (plus the collecting pan) with its contents were weighed and the masses recorded. The sieves were emptied and any stuck sand particles brushed off. The procedure was carried out three times for all the samples.

The masses of the samples retained in each sieve was obtained by substraction and the average of the three values recorded. The percentage passing each sieve was calculated by:-

(a) taking the cumulative sum of the masses of the samples retained in the sieves,

(b) Subtracting the above figures from the total masses of the samples taken, and

(c) dividing the result by the total mass of sample and multiplying by 100%.

The percentages obtained were plotted in British Standard Zones 1 to 4.

3.2.2.4 Mineralogical analysis.

Different grains in the sand samples were identified and separated using a binocular microscope. Similar grains were ground using an agate mortar with acetone. The sample powder was mounted in a cell and run in the Phillips X-ray diffractometer, Model 1710.

The data obtained (d-values) from the resulting film or strip-chart was matched to the existing data and the minerals identified. McClunes et al's Search Manual and Data Book were used for the identification (72,73).

3.2.3 Analysis of the waste waters.

The concentration of sulphate, chloride, fluoride and phosphate, in the effluent was determined using the appropriate methods described below.

3.2.3.1 Sulphate analysis.

Apparatus: Turbidimeter, HACH Model with its standards.

Reagents:

(a) Conditioning reagent; 50 ml glycerol was mixed with a solution containing 30 ml concentrated hydrochloric acid, 300 ml distilled water 100 ml 95% isopropyl alcohol and 75g sodium chloride.

(b) Barium chloride crystals 20-30 mesh.

(c) Standard sulphate solution.

147.9 mg anhydrous sodium sulphate was dissolved in distilled water and diluted to 1000ml. This was 100 ppm solution and from this solution, 5-25 ppm standard solutions were made.

Procedure:

50ml of the sample, or a suitable aliquot made up to 50 ml was measured into a 250 ml conical flask. Exactly 2.5ml conditioning reagent was added and stirred. The turbidity of the mixture was determined and recorded as turbidity without barium chloride.

The sample was put back into the flask and while stirring, a spatula of barium chloride (which was in excess of the sulphate equivalent) was added, the mixture stirred for exactly 1 minute, and the turbidity determined immediately.

A calibration curve was drawn by plotting turbidity versus concentration of 0-25 ppm standard solutions and the slope determined. The concentration of the sulphate in the sample was obtained as:-

$$\text{Concentration (ppm)} = \text{dilution factor} \times \left[\frac{\text{Turbidity with } BaCl_2 - \text{Turbidity without } BaCl_2}{\text{slope}} \right]$$

3.2.3.2 Fluoride analysis.

Apparatus:

(a) Orion ionalyser model 801

(b) Eil ionalyser model 7035

(c) Orion fluoride electrodes 94-09

(d) Orion double junction reference electrodes with the filling solutions.

(e) 100ml plastic beakers.

Reagents

(a) Standard fluoride solution A (100 ppm).

0.2210 g of anhydrous sodium fluoride (Analar) was dissolved in water and diluted to one litre in a volumetric flask. The solution was immediately transferred into a one litre plastic bottle.

(b) Standard fluoride solution B (10 ppm).

100 ml of solution A was pipetted into a litre flask, made up to the mark, and stored in a labelled plastic bottle.

(c) TISAB (total ionic strength adjustment buffer).

58g of sodium chloride, 57 ml of glacial acetic acid, and 4.5g of 1,2-diaminocyclohexanetetraacetic acid (CDTA) were added to 500ml of deionised water in a one litre beaker. 120 ml of 5M sodium hydroxide solution was slowly added with constant stirring to the mixture until all the solids dissolved. The beaker was cooled to room temperature (23 ± 2°C) by placing it in a cold water bath. Both the pH and the reference electrode were placed into the solution. More of the hydroxide solution was added slowly while stirring until a pH of 5.0-5.5 was obtained. The solution was then transferred to a one litre volumetric flask where the volume was made up to the mark with the washings from the beaker.

Procedure

25 ml of solution A (concentration S_1) was pipetted into a 100ml plastic beaker. 25ml of TISAB was added into the beaker and stirred. The fluoride and reference electrodes were rinsed with deionised water, dried with tissue paper and immersed into the solution being stirred. After stabilisation, a readout in millivolts was recorded as E_1.

The procedure was repeated with solution B (S_2) and the potential recorded as E_2. A calibration slope (K) was calculated using the formula

$$K = \frac{E_1 - E_2}{\log S_1 - \log S_2} \quad \text{-----------} \quad 3.3$$

The value of K was -57 ± 2 mv. The procedure was repeated with a sample solution whose potential (E_x) was read out. The difference between E_x and E_1 (ΔE) was calculated and the concentration (C) of the fluoride ions calculated using the formula (87)

$$C = S_1 \text{ anti log } (\Delta E/K) \quad \text{---------} \quad 3.4$$

The determination was repeated using EiL model 7035 ionalyser. In this case the concentration was read directly on the instrument.

3.2.3.3 Chloride analysis.

Apparatus.

(a) Orion ionalyser model 801.

(b) Orion chloride electrode 94-17B.

(c) Double junction reference electrode with accompanying filling solutions.

(d) 100ml plastic beakers.

Reagents.

(a) Stock chloride solution (1000 ppm).

Analar sodium chloride was dried in an oven at 150°C for four hours. 1.649g of the salt was dissolved in a litre flask using deionised water. This gave a chloride solution of 1000 ppm.

(b) Chloride buffer solution.

77.8g of analar ammonium acetate was dissolved in 250ml of water. 57ml of analar acetic acid (sp. gr. 1.05) was added and the mixture diluted to one litre.

Procedure

From the stock solution, an aliquot of 100 ppm was prepared and labelled S_1. 50 ml of S_1 was put into a 100 ml beaker. The chloride electrode which had been immersed in a 0.1M hydrochloric acid for 12 hours was removed from that solution, rinsed with deionised water and dried with tissue paper. The electrodes were dipped into the S_1 solution. 5ml buffer was added and stirred. After stabilisation, the readout (mv) was recorded as E_1. The procedure was repeated with 500 ppm (S_2) solution and the potential recorded as E_2.

The calibration slope K, (-57 ± 2 mv) and the concentration of the chloride were calculated using equations 3.3 and 3.4.

3.2.3.4 Phosphate analysis.

(i) Persulphate digestion method

Reagents

(a) Phenolphthalein indicator solution.

(b) Sulphuric acid solution.

300 ml of concentrated sulphuric acid was added to deionised water and the volume made up to a litre in a volumetric flask.

(c) Potassium persulphate solution.

5g of $K_2S_2O_8$ was dissolved in 100ml of water.

(d) 1M sodium hydroxide solution.

Procedure

100ml or a suitable aliquot of thoroughly mixed sample was taken and to it was added a drop of phenolphthalein indicator solution. If any red colour developed, sulphuric acid solution was added to just discharge the colour. 1 ml sulphuric acid solution and 15 ml potassium persulphate solution were then added.

The mixture was then boiled gently for at least 90 minutes adding distilled water to keep the volume between 25 and 50 ml. The mixture was then cooled, a drop of the indicator added, and neutralised to a faint pink colour with sodium hydroxide solution. The volume was then restored to 100 ml with deionised water.

(ii) Phosphate determination.

Apparatus

Zeiss spektralphotometer model PM 2DL.

Reagents.

(a) Combined reagent.

A 100 ml reagent was prepared by mixing; 50 ml 2.5M sulphuric acid, 5 ml antimony potassium tartrate, 15 ml ammonium molybdate, and 30 ml ascorbic acid.

(b) 0.1M ascorbic acid.

1.76g ascorbic acid was dissolved in 100 ml distilled water.

(c) Isopropyl alcohol.

(d) 2.5M sulphuric acid solution.

70 ml concentrated acid (sp.gr.1.84) was diluted with deionised water and made up to 500 ml.

(e) Antimony potassium tartrate.

4.3888g of $K(SbO)\,C_4H_4O_6.\frac{1}{2}H_2O$ was dissolved and made up to 200 ml using deionised water.

(f) Stock phosphate solution (50 ppm).

219.5 mg of potassium dihydrogen orthophosphate ($K_2H_2PO_4$) was dissolved and made up to 1000 ml with distilled water.

Procedure

From the stock solution, 1 ml, 2 ml, 3 ml, 4 ml and 5 ml were pipetted into 50 ml volumetric flasks. To each of the flasks was added 2.5 ml of propan-2-ol, 2.5ml of the working combined reagent and the volume made up to the mark with distilled water. The standards were labelled 0.02, 0.04, 0.06, 0.08 and 0.10 ppm respectively.

The wavelength was adjusted to 710 nm on the spectrophotometer. The standards were run and appropriate adjustments made on the spectrophotometer so that the concentrations would be read out as accurately as possible.

To a 20ml sample, 2ml of propan-2-ol and 2ml of the combined reagent was added and the mixture thoroughly mixed. The mixture was allowed to stand for ten minutes before reading the concentration on the spectrophotometer (74).

3.2.4 Preparation of mortar cubes.

Sand samples from each of the districts, with a silt content below 10 per cent, were mixed using mechanical concrete mixers and put in labelled bags. British standard sand was also obtained.

Mortar cubes of the three categories of sands with OPC, SRPC and PZC were made using Kenya standard KS 02-21: 1976 specifications.

Procedure

The joints of 70.7 mm cube moulds were greased, and the surfaces oiled. One such mould was fixed to a compacting vibrating machine.

For Kajiado and the standard sands the following proportions were taken. Cement 185g; sand 554g; and water 74 ml.

The sand and the cement were thoroughly mixed in a tray. The water was added and the materials were thoroughly mixed for 1 minute. The mixture was then put in the mould and the compacting machine run for two minutes.

The impregnated mould was carefully removed from the machine, and the top open side covered with a polythene paper to prevent any water loss. The procedure was repeated twice using the same ingredients. The three cubes were put in a formally wetted leakfree polythene bag and tied tightly at the edge. The bag was labelled to show the ingredients and the date, and left for 24 hours at a temperature of 27 ± 2^{o}C.

After the 24 hour period, the cubes were demoulded, labelled on their surfaces as per the label on the bag, and immersed in fresh tap water for maximum hydration. The water was changed every seven days, and the cubes stayed in it for at least five months. The procedure was repeated so that for each cement/sand combination, 126 cubes were made.

The Machakos sand/cement mixture was unworkable with the 74 ml of water and so 92.5 ml of water was used. 'Bulking' took place as well and therefore at the end of each compaction, the top of the mortar was cut off to the level of the mould.

All the cubes were made within 18 days.

3.2.5 Preparation of aggressive solutions.

Two litres of each aggressive solution, prepared as described below, were put in dessicators labelled 1x, a or b to 9x, a or b, where x was the first letter of the solution's name and 'a' or 'b' the lower or the higher concentration respectively. The fluorides were put in special fibre-glass cuboids. The waste (effluent) and deionised water were similarly sampled with the former being put in fibre-glass cuboids. The dessicators and cuboids were well covered with greased glass tops.

(a) Sulphates.

2,500 ppm sulphate solution was prepared by pipetting 2.9 ml of concentrated acid (sp.gr. 1.84) into 1900 ml deionised water in a 2 litre volumetric flask, mixing thoroughly and making up the volume to the mark. 400 ppm was prepared by pipetting 0.46 ml of the acid and repeating the above procedure.

(b) Chlorides.

1200 ppm chloride solution was made by pipetting 5.81 ml concentrated hydrochloric acid (sp.gr. 1.18) into about 1900 ml deionised water in a 2 litre flask. 500 ppm was prepared by pipetting 2.42 ml of the acid. The same procedure of dilution was used as for the sulphate solutions.

(c) Fluorides.

Plastic wares were used for the fluoride preparation. 30 and 10 ppm solutions of fluoride were made by pipetting 0.35 and 0.12 ml of hydrofluoric acid (sp.gr. 1.13) into five litres of deionised water respectively and mixing thoroughly.

3.2.6 Compressive strength, length measurements and immersion of the cubes in the aggressive media.

A cube from each pack of the three was randomnly selected and its compressive strength determined using a Denison compression machine after the five months duration in water. The average compressive strengths were calculated so as to compare the cements and the sands used. Three cubes made of the same ingredients (cement and sand) were randomnly selected and labelled a, b, and c. Lengths of the sides were determined at the middle using a vernier callipers. The average length was cubed to obtain the volume of each cube which was recorded as the first day volume.

The pH of the fresh aggressive solutions was determined and recorded (1st day pH). The cubes whose measurements were taken were immersed in the dessicators in such away that:- dessicators 1,2,3 had OPC, 4,5,6 had SRPC; 7,8,9 had PZC cubes while 1,4,7 had standard sand 2,5,8 had Kajiado sand; and 3,6,9 had Machakos sand.

Investigations were carried out on the samples in the dessicators for six months in order to compare the performances of the different cements and sands.

3.2.7 Monitoring the effect of the aggressive solutions on the cubes.

(a) pH measurements.

These were taken twice a week and the changes recorded.

(b) Volume changes.

Length measurements were taken once a week and the volume computed. After the six months, profile graphs and averages were used to assess the performance of the cements and sands based on the percent volume changes from the initial values.

(c) Ions uptake by the cubes.

Samples were taken out of the dessicators at different intervals and the respective sulphate, chloride and fluoride concentrations determined.

In the waste and deionised water samples, fresh 2 litre samples were put back after each sampling. After a sample of 100 or 50 ml was taken from the fluorides, chlorides and sulphates, the solution was readjusted by adding the respective acid until the pH was equal to the initial value. The volume was then made up to 2 litres by the addition of the appropriate volume of deionised water.

The concentration of the anions taken up by the cubes was divided by the days taken and recorded as average anion uptake per day. Analysis for each set was carried out maintaining conditions which were as identical as possible. After the six months, profile graphs of the anionic uptake per day against time in days were drawn for the anions and from these and the overall mean uptake, the performance of the sands and cements were assessed.

The volume change and anionic uptake data was analysed and the curves drawn using Instat soft-ware package (75) and the BBC microcomputer.

(d) Leaching out of the cations.

The following cations were investigated:-
(i) calcium, (ii) magnesium, (iii) iron,
(iv) silicon and (v) aluminium.

The analysis was carried out using atomic absorption spectroscopic technique. Perkin Elmer

Model 2380 and Pye Unicam SP90A series instruments were used.

A computer programme for analysing the data was written. The programme eliminated the tedious calibration curve drawing and the ensuing matching procedures. For each cation, the known absorbance (x) was entered followed by the corresponding standard concentration value (y) for the number of standards used. The unknown sample concentrations were then obtained by entering the absorbance data. The program used is given as appendix I.

(e) Compressive strengths.

At the end of the six months, the compressive strengths of the cubes from each dessicator was determined and the mean computed.

The values obtained were compared to the initial compressive strength values (before exposure) and the results recorded as percentage changes. These values together with the other data were used to assess the performance of the cements and the sands.

CHAPTER FOUR

RESULTS AND DISCUSSION

The results obtained from the experiments described in chapter three are presented. These are the results of: the physical and mineralogical analyses of the sands; chemical analysis of the factory waste waters; the pH changes of the aggressive solutions in which mortar cubes were immersed; volume changes of the cubes immersed in the solutions; anionic uptake by the cubes from the solutions; leaching out of cations from the cubes to the solutions; and the compressive strength changes that occured during the six months investigation period. From these results and their discussion the performance of the cements and the sands have been assessed.

4.1 Properties of the Kajiado (KJD) and Machakos (MKS) sands.

4.1.1 Silt content.

Results as given in tables 4.1 to 4.3 show that Machakos sand had less silt than the Kajiado one. The different types of sands used for the investigation were those whose silt content was less than 10%.

Table 4.1: Silt content of Machakos sand.

Sample	Kasinga A	Kasinga B	Thwake A	Thwake B	Syuuni
Height of silt (cm)	1.0	0.5	0.6	0.6	0.7
Height of sand (cm)	10.6	9.6	10.9	10.0	12.0
Silt percentage	9.4	5.2	5.5	7.0	5.8

Table 4.2: Silt content of the first batch of Kajiado sand

Sample	Olkejuado Valley A	Sajiloni A	Sajiloni B	Ngoire A	Ngoire B
Height of silt (cm)	0.6	2.5	2.0	2.0	1.8
Height of sand (cm)	9.8	10.3	9.9	10.9	9.5
Silt percentage	6.1	24.3	20.2	18.3	18.9

Table 4.3: Silt content of the second batch of Kajiado sand

Sample	Ngoire C	Olkejuado Valley B	Mbilo/Sajiloni
Height of silt (cm)	1.8	1.1	0.5
Height of sand (cm)	10.8	11.4	11.7
Silt percentage	16.7	9.6	4.3

4.1.2 Particle size distribution of the sands.

The results of the particle size distribution are shown in tables 4.4 and 4.5. All the sands fitted in the British standard zones and so all were suitable for concrete work. Machakos sand was the finest (ZONE 4) and was found to bulk when the mortar cubes were being made. A water/cement (w/c) ratio that gave workable mixes for the other sands gave an unworkable mix for the Machakos sand such that a higher ratio had to be used.

'Bulking', defined as the increase in volume of a given weight of sand caused by films of water pushing the sand particles apart has been known to occur upto 40% in extremely fine sand at a moisture content of 10%. Such a sand would be unsuitable for the preparation of good quality concrete (76). The results therefore indicated an inferiority of the Machakos sand.

Table 4.4: Kajiado sand particle distribution zones.

Sample	Zone fitting
Olkejuado valley A	2
Olkejuado valley B	3
Mbilo sajiloni	2

Table 4.5: Machakos sand particle distribution zones.

Sample	Zone fitting
Kasinga A	4
Kasinga B	4
Thwake A	4
Thwake B	4
Syuuni	3

4.1.3 Mineralogical contents.

Similar minerals were found in all the sand samples. This was expected because the two districts are in a similar geological area. Machakos sand was however found to be richer in mineral content.

The minerals identified in Kajiado sand were: quartz (α-SiO_2); mica (muscovite) clinoamphibole (hornblende) and goethite (iron oxide hydroxide). Quartz content was the highest, followed by mica to a small degree while the other two were in traces. Those identified in Machakos sand were: quartz, feldspar, magnetite, amphibole and mica. Quartz content was the highest while the rest were in traces.

Quartz which formed the bulk of both sands is known to be inert (18). The mica and feldspar families have been associated with deleterious reactions while the other minerals are normal trace components of sands (77,78).

4.2 Anionic analysis of waste waters.

The results of analysis of the waste waters for sulphate, chloride, fluoride and phosphate content were used to decide the anions and the concentration levels to be used in the six month investigation.

4.2.1 Sulphate content

Results as given in table 4.6 show that the sulphate levels were very high. The average results of samples 1 and 4 were used to make sulphate solutions of lower concentration while those of 2 and 3 determined the higher concentration levels for the laboratory investigation.

Table 4.6: Sulphate concentration of the waste waters.

Sample number	Concentration (ppm)		
	a	b	mean
1	361.78	377.04	369.41
2	2566.16	2566.50	2566.33
3	2414.95	2414.86	2414.91
4	378.98	362.05	369.52

4.2.2 Chloride content

The levels as given in table 4.7 are very high. The average results of samples 2 and 4 were used to make solutions of lower concentration while those of 1 and 3 were used for the higher concentration solutions.

Table 4.7: Chloride concentrations in the waste waters.

Sample number	Concentration (ppm)			
	a	b	c	mean
1	843.7	854.0	860.9	852.9
2	670.0	691.9	680.8	680.9
3	1480.7	1498.8	1492.8	1490.8
4	298.2	309.3	303.1	303.5

4.2.3 Fluoride content.

Tables 4.8 and 4.9 give the results obtained using Orion Ionalyser model 801 and EIL analyser model 7035 respectively. The latter analyser and a different set of electrodes were used to counter-check the suitability of the Orion model which was to be used for the investigation.

The two instruments gave very similar results and so any of them could be used for further analysis. The fluoride levels were lower than those of the chlorides and sulphates but quite significant. Samples 2 and 3 had the highest concentration levels and the average values were used in the preparation of the corresponding fluoride solutions. Average values of samples 1 and 4 were used to prepare the fluoride solutions of lower concentration.

Table 4.8: Fluoride concentrations (determined by Orion Ionalyser Model 801).

Sample number	Concentration (ppm)			
	a	b	c	mean
1	8.272	8.241	8.303	8.272
2	38.443	38.874	38.730	38.683
3	15.225	14.944	15.112	15.094
4	6.544	6.477	6.520	6.512

Table 4.9: Fluoride concentrations (determined by EIL Ionalyser Model 7035).

Sample number	Concentration (ppm)		
	a	b	mean
1	6.7	6.5	6.6
2	38.0	38.0	38.0
3	13.0	13.8	13.4
4	5.5	5.5	5.5

4.2.4 Phosphate content.

The phosphate levels as given in table 4.10 were so low that they were taken to be insignificant. While investigating the effect of upto 20 ppm phosphate solutions on neat cement cubes for six months, Karuu (79) found very little deleterious effect. No further investigations on phosphates were carried out.

Table 4.10: Phosphate concentrations.

Sample number	Concentration (ppm)		
	a	b	mean
1	0.306	0.459	0.383
2	1.224	1.224	1.224
3	0.306	0.306	0.306
4	0.459	0.459	0.459

4.3 Monitoring the effect of the aggressive solutions on the cubes.

4.3.1 pH changes.

Table 4.11 shows the pH of the solutions at the beginning of the investigation and the pH before the ions were replenished at various stages upto the end of the investigation. The figures represent the average pH of the same aggressive solutions contained in 9 dessicators.

The results for deionised water showed that the pH (always) rose from about 6 to approximately 12 after fresh water had been added. The observation indicated that the hydroxide ions leached out from the cubes in an attempt to establish an equilibrium between the concentration in the cube and the water. Cement paste has a pH of 12.5 and so the reaction must have severely corroded the cubes. The water acted as an acid and therefore accelerated the effect.

The waste waters recorded pH rises of above 10 only at the initial stage but subsequently only between 8 and 9 were recorded. The results showed that initially leaching out of the hydroxyl ions was high but inhibition took place later on. The waters had a high ionic content and some of these could have formed precipitates, coatings or complexes on the cube surface reducing the pores through which leaching would have occured.

In the fluoride solutions, a gradual decline in the hydroxyl ions was observed especially in the higher concentrations. The results indicated that the fluoride ions reacted with the cubes forming substances that reduced the loss of the hydroxyl ions.

The chloride solutions, like the deionised water, showed pH rises of above 11 after each replenishing throughout the period. The chloride reaction with the cubes could have been forming soluble salts that were leaching out leaving exposed sites from which hydroxide ions leached out freely.

The lower sulphate concentration solutions showed pH rising to approximately 11 after each replenishing. The results indicated that leaching was the main process taking place. The pores on the surface would be left open by any reaction taking place and thus facilitate the hydroxyl ions to leach out. In the higher concentration solutions however, the pH rise declined with age and remained below the neutral level in some cases. The products formed either inhibited hydroxyl ions leaching, or the acid reacted with all the freely available hydroxyl ions, or both processes took place, leaving structures that had very little free hydroxyl ions to neutralise the acids. The acid reaction was a very remote possibility because the cubes were intact after the six months.

Table 4.11: pH of the solutions.

Solutions	pH values at different intervals						
	4/1/86	17/1/86	11/2/86	8/3/86	3/4/86	7/5/86	7/7/86
Deionised water	6.0	11.6	11.8	11.6	11.6	11.9	11.8
Waste water	7.8	11.4	10.2	8.5	8.3	8.6	8.9
Lower fluoride concentration	3.6	11.6	11.4	11.1	11.1	10.6	10.05
Higher fluoride concentration	3.3	11.4	11.5	10.8	10.6	10.1	9.5
Lower chloride concentration	2.2	11.6	11.8	11.4	11.6	11.5	11.5
Higher chloride concentration	1.7	11.6	11.1	11.0	11.3	11.3	11.7
Lower sulphate concentration	2.1	11.6	10.8	10.6	10.5	11.0	11.0
Higher sulphate concentration	1.5	11.2	10.3	9.3	6.5	6.4	8.7

4.3.2.1 Volume changes comparing the cements.

The overall mean percent changes of the volume of the cubes comparing cements, while holding the various sands constant are given in table 4.12. From the table it was observed that cubes made with Machakos or Kajiado sand when immersed in fluoride, chloride and sulphate solutions did not perform as consistently as expected in relation to the lower and higher concentrations; while the cubes made with the standard sand showed a high degree of consistency with respect to the concentrations.

The observation showed that the cubes reacted differently with similar aggressive solutions. The behaviour would occur due to disparities in the constitution of the sands themselves. The various minerals and the particle distribution of the sands may have caused the disparities. Silt in form of clay, for example has been found to cause such problems depending on its distribution (16). The observed bulking of the Machakos sand could have been non uniform within the cubes thereby causing disparities in the performance even when the sand was held constant. Kajiado and Machakos sands would therefore be unsuitable as cement testing materials as the volume measurements have shown.

The high degree of reproducibility and uniformity displayed by standard sand cubes, confirmed the superiority of the sand as a testing material for cements. The sand is the one currently being used to test cements in concrete laboratories and cement factories in the country. The performance of cements in this work was therefore assessed by using the cubes made with the standard sand.

The performance (per cent volume change) of the cements in the aggressive solutions, holding standard sand constant, for the six months is shown in figures 4.1 to 4.8. In all cases deviation from zero change was taken as a measure of deterioration. Where the residual values could not discriminate the performance of the cements, a time series analysis using the median, as explained by Boyle (80) was performed on the data and the profile graphs drawn. If the two graphs failed, then the overall averages (table 4.12) were used to assess the performances.

Table 4.12: Mean per cent volume changes of cubes made with different cements holding sands constant.

Sand held constant / Cement / Solution	Standard Sand			Kajiado Sand			Machakos Sand		
	OPC	SRPC	PZC	OPC	SRPC	PZC	OPC	SRPC	PZC
Deionised water	-0.0857	-0.373	-0.0612	-0.272	-0.182	0.0948	-0.244	-0.0550	-0.407
Waste water	-0.140	-0.415	0.120	0.0675	0.0401	-0.104	-0.135	-0.116	-0.0920
Lower fluoride concentration	-0.184	-0.0031	-0.266	0.0245	0.0184	-0.0121	-0.217	-0.266	-0.113
Higher fluoride concentration	-0.251	-0.119	0.178	-0.006	-0.0214	-0.0948	0.218	-0.0152	-0.0948
Lower chloride concentration	-0.580	-0.315	-0.104	-0.290	-0.165	-0.238	-0.202	-0.232	-0.306
Higher chloride concentration	-0.617	-0.353	-0.266	-0.156	-0.205	-0.199	-0.553	-0.350	-0.354
Lower sulphate concentration	-0.416	-0.0214	-0.144	-0.303	-0.251	-0.0336	-0.177	-0.260	-0.214
Higher sulphate concentration	0.679	0.581	0.362	0.571	0.390	0.470	0.378	0.362	0.409

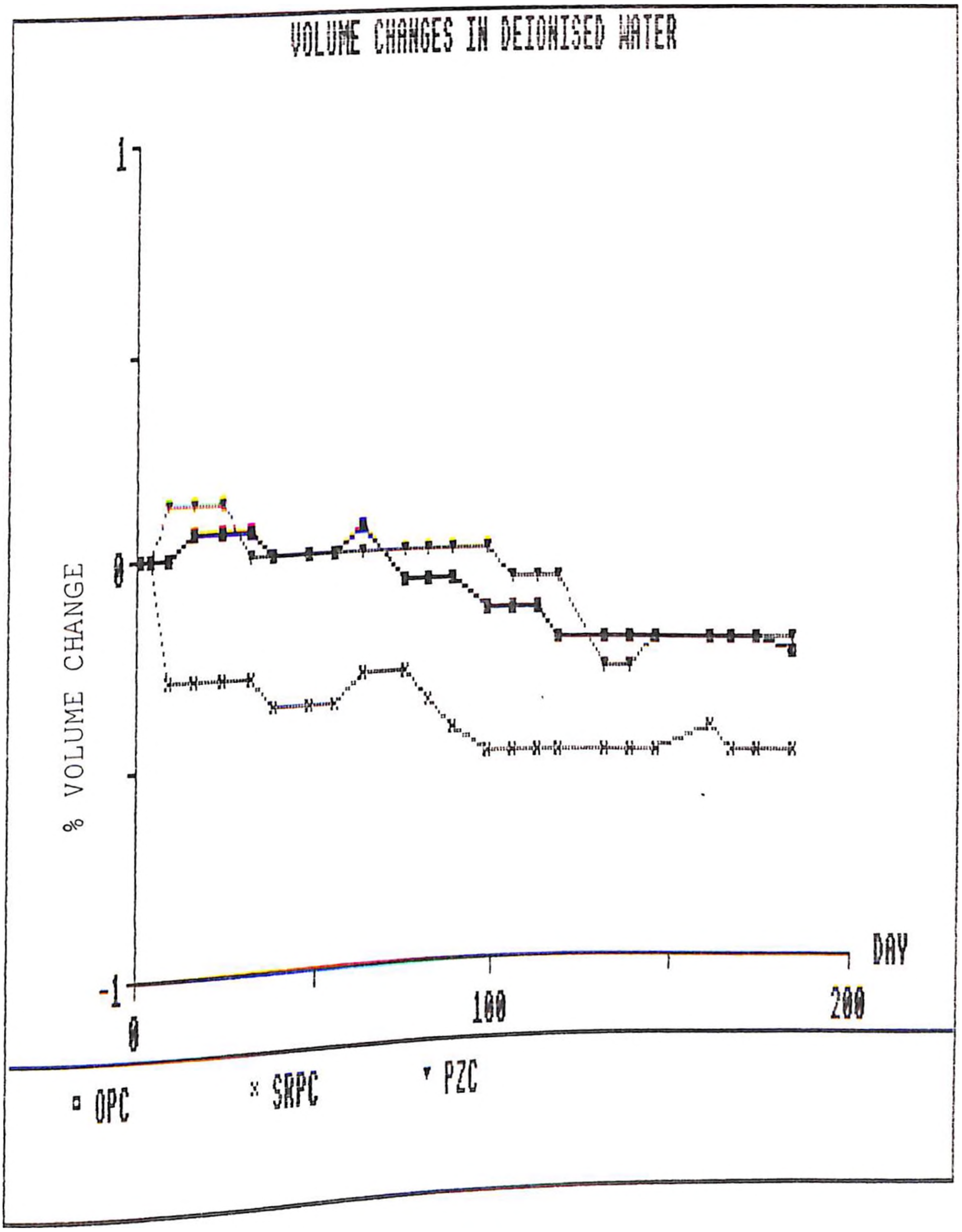
4.3.2.1.1 Performance of the cements in the aggressive solutions.

(i) Deionised water.

Figure 4.1 shows the results of volume changes with time in deionised water. The data was smoothened by a span of three using the median of every three successive points. All the cements showed an initial resistance to volume change followed by a decrease and finally a stabilisation in the volume.

OPC showed an initial resistance to change, a slight volume increase, then a return to the initial volume in the first two months. In the third month, there was a continuous decrease in volume and it finally stabilised at approximately -0.2. The slight initial increase in volume would have been caused by the cubes continuing with the hydration process thereby forming voluminous products whose effect would overwhelm the leaching out process indicated by the pH changes. The relative stability thereafter would be caused by a relative equilibrium between the processes. The decrease in the third and fourth month (DAY 75-120) could be due to the leaching out process dorminating due to more open

Fig. 4.1: Volume changes of cubes, made with STD sand and the different cements, immersed in deionised water.



sites. The stability in the final months would be due to the equilibrium between the two processes being reattained due to diminishing of the leaching out process as the reactive substances became less freely available.

SRPC cubes showed a sudden fall in volume in the first month, followed by relative stability, then a fall in the third month and finally an almost stable volume upto the final day. Calcium hydroxide, which is largely responsible for the leaching out process and hence volume decrease, is produced in the hydration of the silicates (C_3S and C_2S) and not aluminates (C_3A). SRPC has very low levels of the aluminates and so the hydroxide would be more exposed in it than in the other cements. This must have caused the early volume decrease and the lower volumes maintained throughout. The results therefore showed that C_3A and C_4AF are important components of cements. After the initial volume decrease, the trend was similar to that of OPC and so similar conclusions could be drawn. Calcium silicate hydrate has been identified as the main binder of cement (81) and so the behaviour indicated that the hydrates assumed the major role after the initial period.

PZC cubes showed a similar behaviour to the OPC cubes but offered a greater resistance to volume change. PZC has been found to react with calcium hydroxide produced in the hydration of the silicates from OPC component in the pozzolanic activity (21,22). It has further been found that PZC continues with the hydration process for a longer period than the other cements. The two factors made PZC to be less susceptible to the leaching out process characterised by calcium hydroxide and volume decreases.

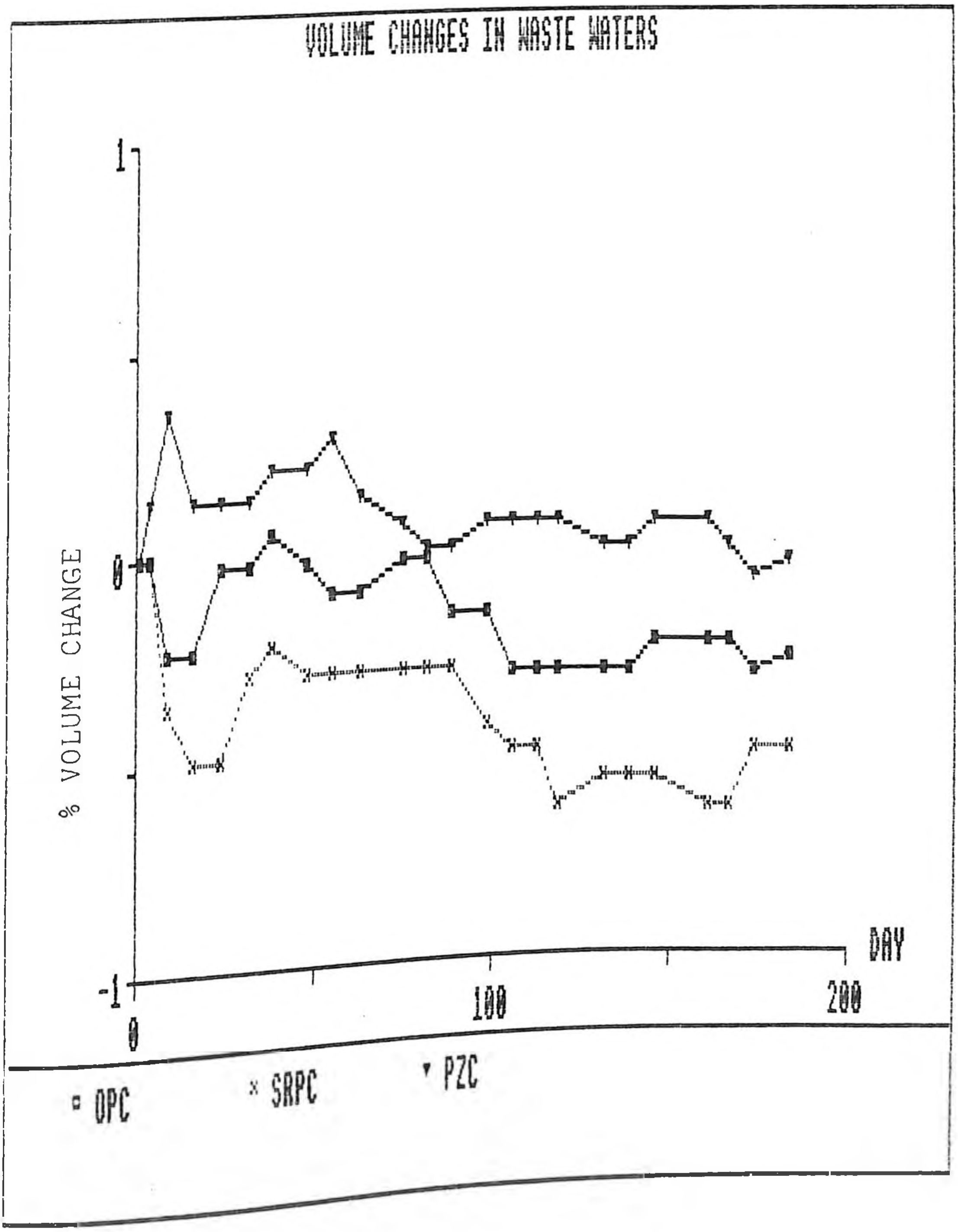
The results are significant because rain water and deionised water are very similar. From the profile graph and the table, PZC was found to be the best cement followed by OPC and SRPC respectively.

(ii) <u>Waste waters</u>

The results as shown in figure 4.2 and Table 4.12 show that PZC had the least volume change followed by OPC and SRPC. Since the effluent had various aggressive ions, the results showed the superiority of PZC over the other cements from the combined effects of those ions. This is in agreement with what has been reported earlier (14,25,63).

The concentration of sulphates was quite high but SRPC performed poorly. OPC and SRPC showed a volume decrease and therefore the sulphate attack

Fig. 4.2: Volume changes of cubes, made with STD sand and the different cements, immersed in waste waters.



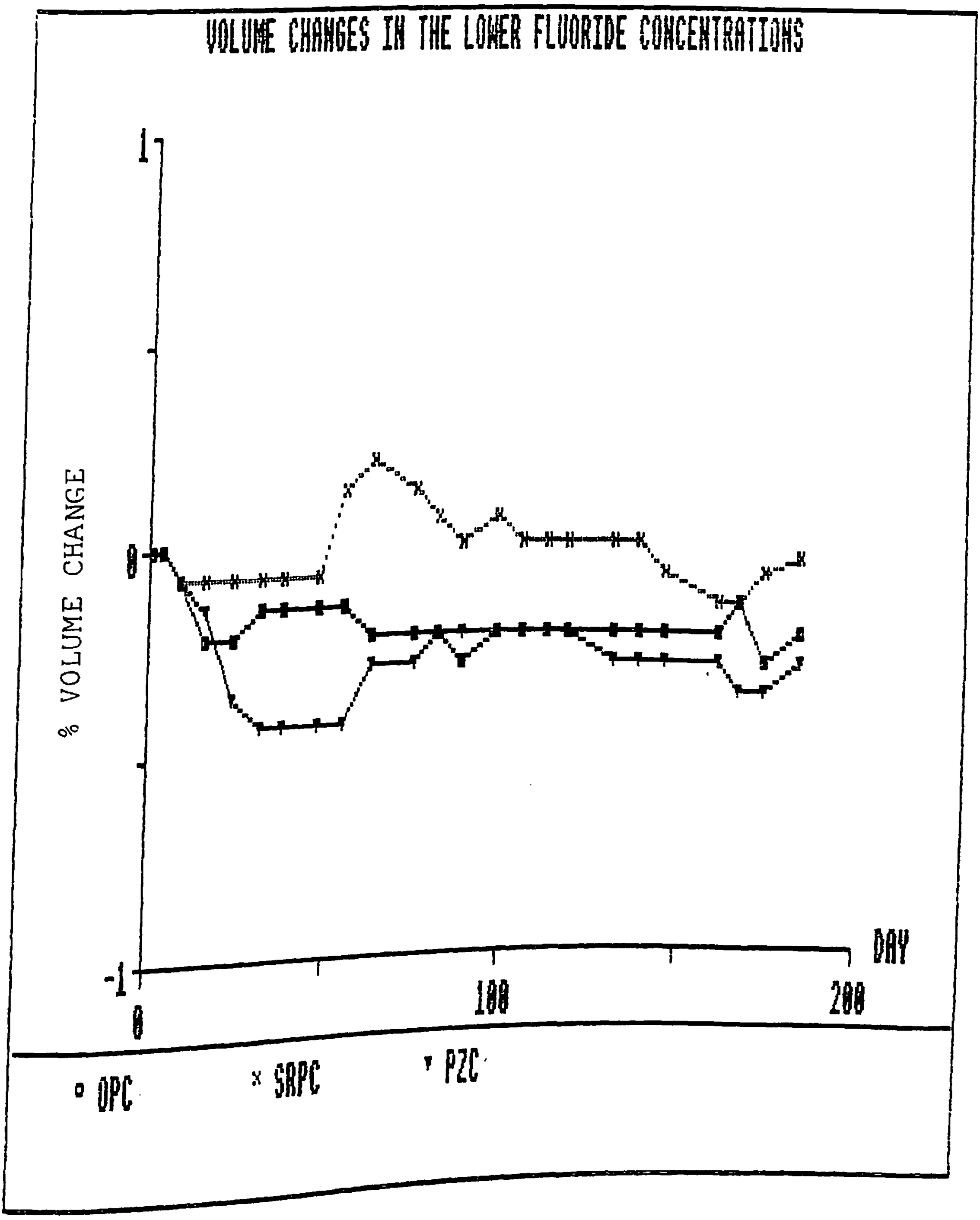
which would result in volume increase, at least on the OPC cubes, was not the dorminant reaction. The chloride ions, whose concentration was also very high, may have dorminated the reaction leading to leaching out of the soluble salts. The view is supported by the facts that SRPC has been found to be more susceptible to chloride attack than the other cements (62) while PZC resists such attack (14). The results suggest that SRPC should only be used after careful study and not just because of sulphate presence in an environment.

(iii) Fluoride solutions.

In both lower and higher fluoride concentration solutions, SRPC showed the least volume change although the results were more erratic in the latter, as shown in table 4.12 and figures 4.3 (lower concentration results) and 4.4 (higher concentration results). The erratic behaviour observed in the higher concentration solutions made it necessary to smoothen the data with a span of three. OPC and PZC exchanged positions in the lower and higher concentration solutions with PZC performing better in the higher concentration.

The lower levels of C_3A hydration products in SRPC and to a lesser extent those of C_4AF make

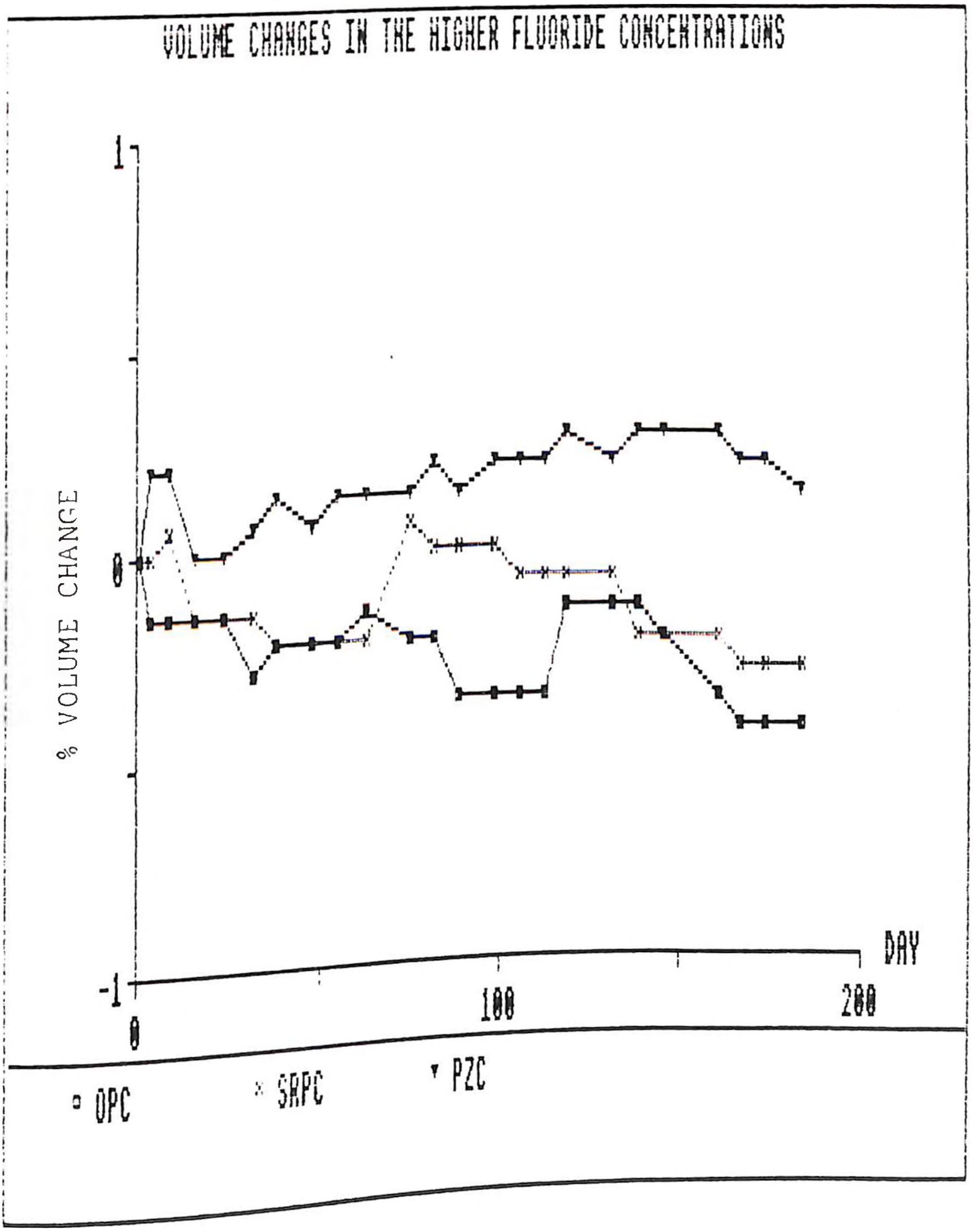
Fig. 4.3: Volume changes of cubes, made with STD sand and the different cements, immersed in the lower fluoride concentration solutions.



the silicate hydrates dorminate in the cement mortar cubes. Fluorides are known to be reactive to silicates, and the reaction would therefore be expected to be more intense on the SRPC cubes than the others. From the results however, SRPC did very well. In the lower concentration solutions, for example, it had an overall - 0.0031% volume change (table 4.12) which was the least volume change observed. The results therefore indicated that the reaction between SRPC and the fluorides was not deleterious.

The PZC cubes showed expansion in the higher concentration solutions (fig. 4.4) and volume reduction in the lower concentration solutions (fig. 4.3). Pozzolana has reactive silicate materials which could react with the fluorides. In the lower concentration solutions, the reactions would largely be confined to the surface resulting in volume reductions whereas the more concentrated ions could have penetrated the cubes via pozzolana grains and reacted internally with the calcium hydrosilicates and other materials forming expansive products. OPC cubes showed volume decreases in both solutions and so the fluorides must have attacked only the cube surface giving products that had less volume. This would have been expected because the hydrosilicates, calcium hydroxide and sand grains were available on the surface and selective

Fig. 4.4: Volume changes of cubes, made with STD sand and the different cements, immersed in the higher fluoride concentration solutions.



reaction pathways into the cubes like in the case of PZC would be less.

In a study of unreinforced and reinforced concrete, Shypyanova et al (59) found that, hydrofluoric acid decomposed calcium hydroxide and calcium hydrosilicates with the formation of calcium fluoride, calcium silicofluoride and sodium silicofluoride. They associated calcium fluoride with volume decrease while the other products were associated with expansion. The results above agree with the findings because OPC and SRPC which had plenty of calcium hydroxide, for calcium fluoride formation, showed volume decreases while PZC which had less showed slight expansion. The presence of relatively more hydrosilicates in SRPC cubes than in OPC would account for the small net volume decrease observed on the SRPC cubes as opposed to those of OPC which formed less amounts of the silicofluorides.

In conclusion therefore, SRPC and OPC cubes reacted with the fluorides forming to a large extent calcium fluoride which showed volume decrease and to a less extent silicofluorides. PZC reacted forming, to a large extent, the silicofluorides which were responsible for the volume increases.

(iv) Chloride solutions.

The results as shown in table 4.12, figures 4.5 and 4.6 showed similar trends in volume changes. The results were however more pronounced in the higher concentration solutions as would be expected. PZC had the least volume change followed by SRPC and OPC respectively. All the cubes showed a net reduction in volume. Only PZC cubes in the lower concentration solutions actually showed alternate volume increases and decreases in the first two and a half months (figure 4.5). The pH test indicated that leaching out of hydroxides was high during the investigation period. The observations in this test indicated that such leaching resulted in volume decreases because most of the chlorides formed dissolved and leached out, thereby causing shrinkage.

PZC performance was in agreement with what has been reported in the literature (14,25,63). The PZC resistance to the chloride attack can be compared to the resistance of PZC to sea water attack. In the lower concentration solutions, the volume decrease of OPC is more than five times that of PZC and this seems to agree with Gjorv and Vennesland's findings (14) that 'chloride penetration in OPC maybe as much as five times that in

Fig. 4.5: Volume changes of cubes, made with STD sand and the different cements, immersed in the lower chloride concentration solutions.

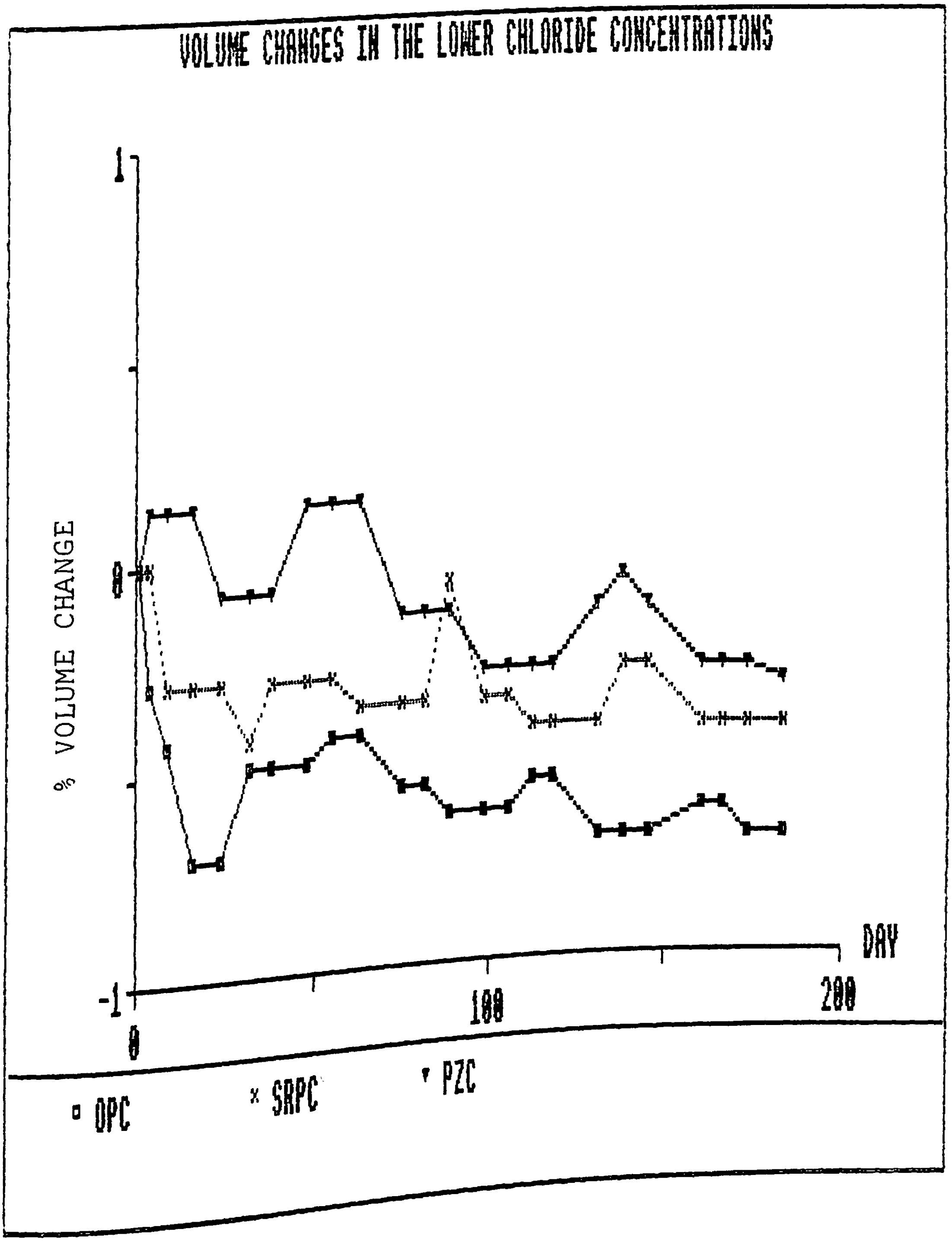
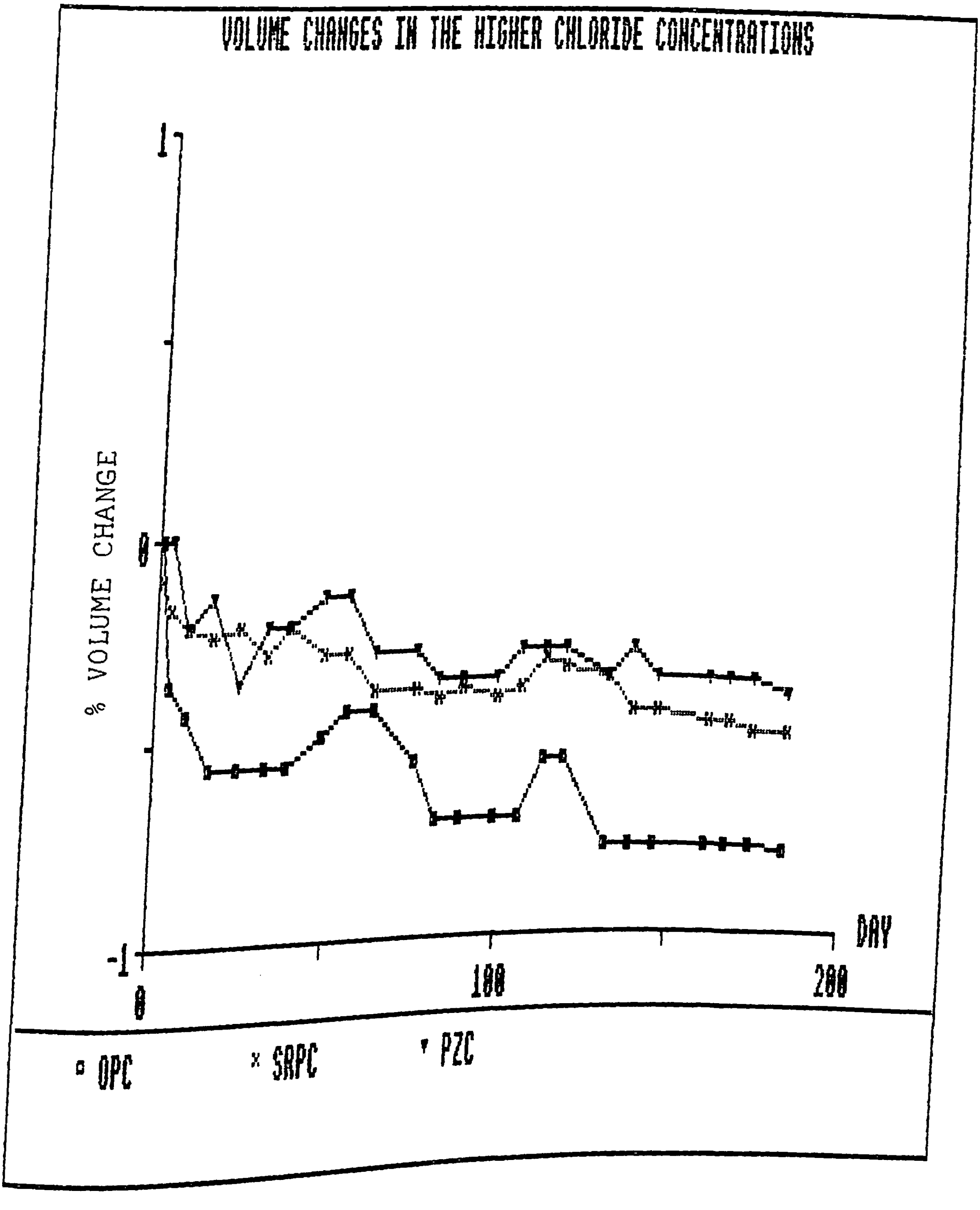


Fig. 4.6: Volume changes of cubes, made with STD sand and the different cements, immersed in the higher chloride concentration solutions.



cements like PZC'. The higher penetration caused more leaching out of chlorides such as calcium and magnesium chloride and thereby caused shrinkage.

SRPC would have been expected to perform more poorly than OPC (14), but the contrary was observed. The acid part of the solution could have effected the OPC more severely than SRPC. Such a behaviour would be expected because SRPC has relatively more exposed calcium hydroxide to neutralise the acid than OPC whose hydration products would include those of C_3A and C_4AF.

(v) Sulphate solutions.

The results are shown in table 4.12 and figures 4.7 and 4.8. In the lower concentration solutions, SRPC had the least volume change followed by PZC and OPC. There was an overall reduction in volume in all the cubes. In the higher concentration solutions, PZC had the least change followed by SRPC and OPC respectively. Expansion was observed in this case.

The results indicate that for the lower concentration solutions, either leaching occured or the reactions were confined to the surface leading to wearing out. The sulphates were in the form of sulphuric acid and so acid/base reactions

Fig. 4.7: Volume changes of cubes, made with STD sand and the different cements, immersed in the lower sulphate concentration solutions.

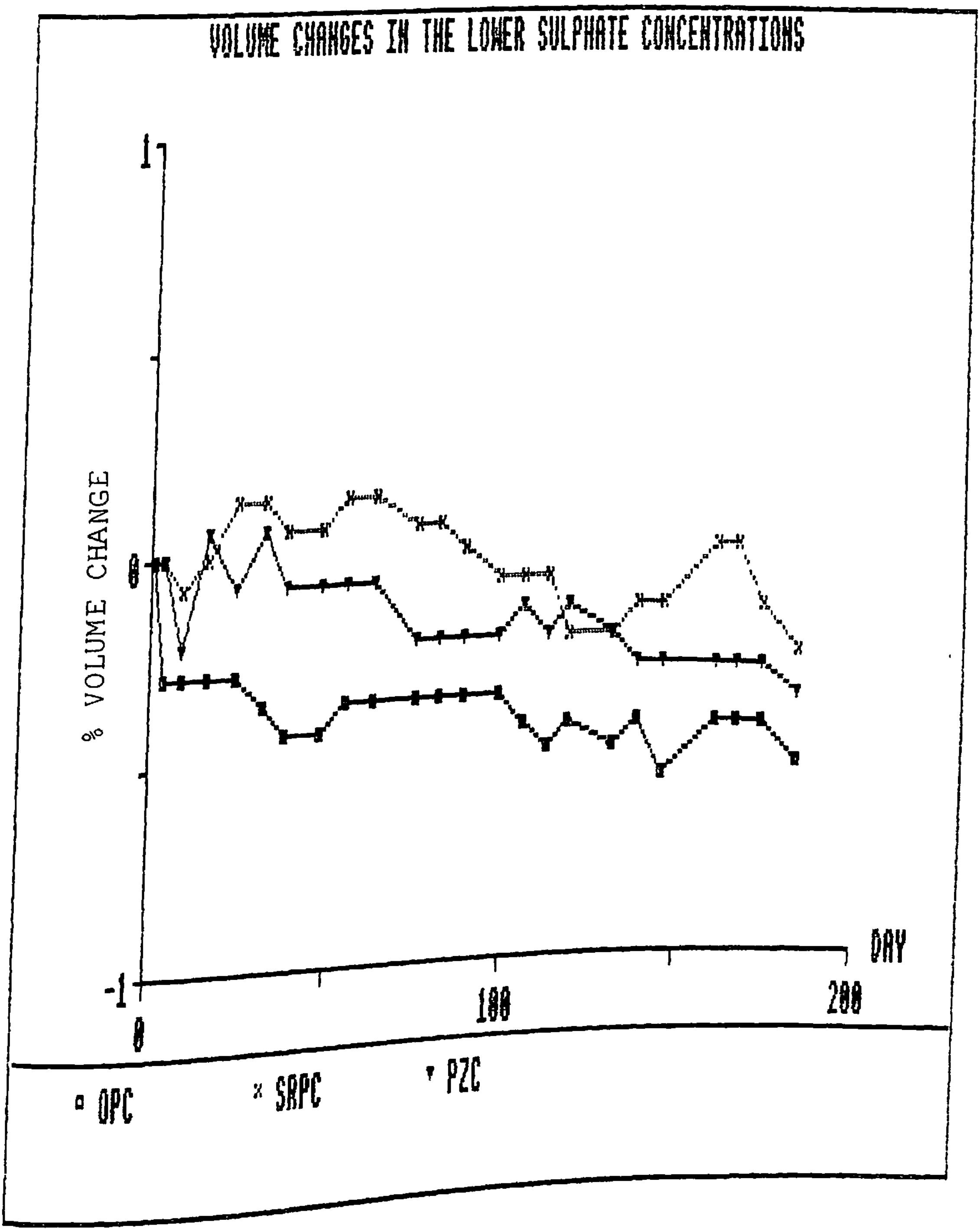
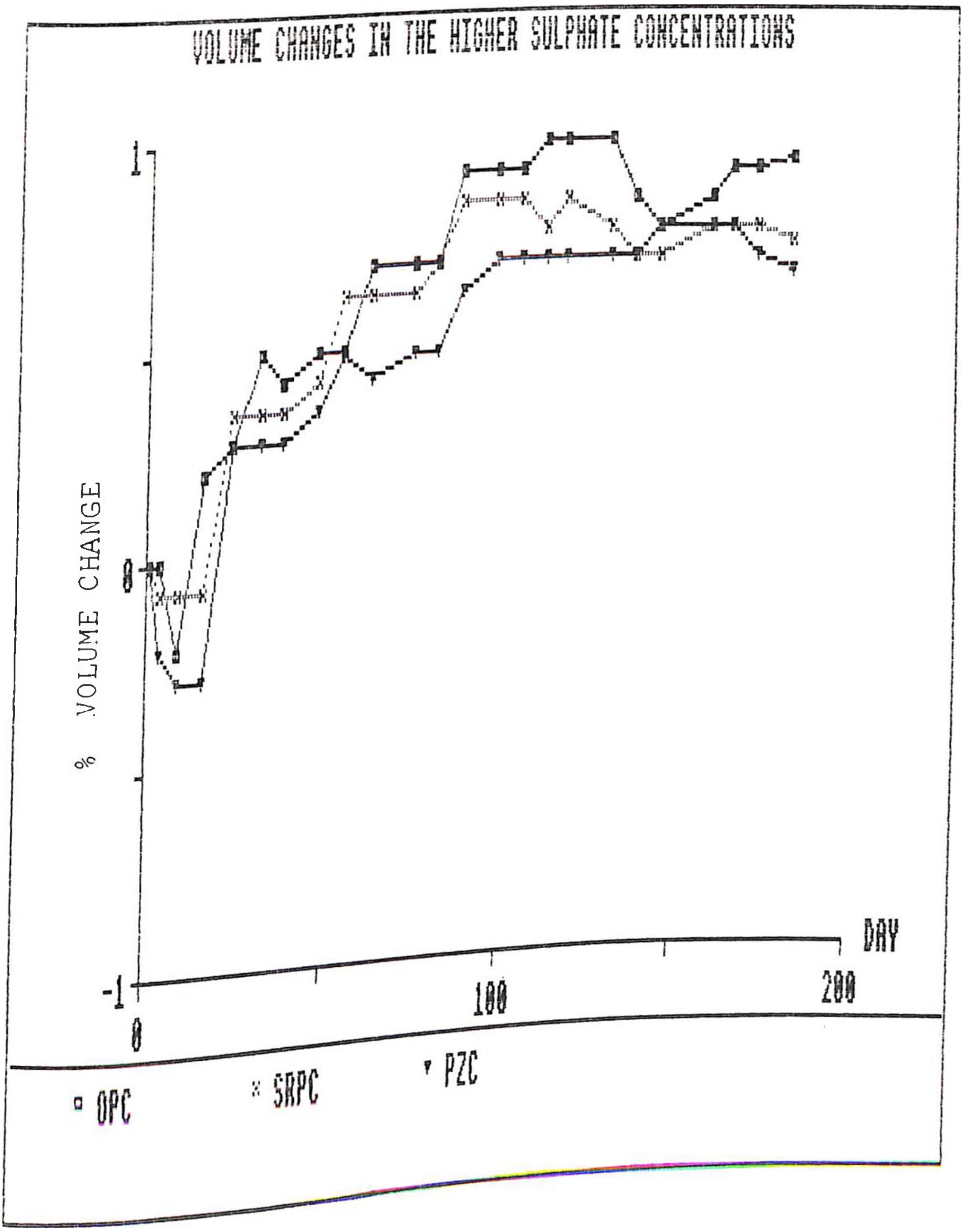


Fig. 4.8: Volume changes of cubes, made with STD sand and the different cements, immersed in the higher sulphate concentration solutions.



among others must have occured on the surface causing wearing off that resulted in volume reduction. The main product, calcium sulphate which is sparingly soluble fell as a precipitate and caused the observed shrinkage.

In the higher concentration solutions, expansive products were formed which overwhelmed the lower concentration reaction trait. The ettringite reaction (equations 2.1-2.3) would account for the behaviour. The reaction is dependent on two major cement reactants; calcium hydroxide and tricalcium aluminate hydrate. The hydroxide reacts with the sulphates to form calcium sulphate which reacts with the hydrate (C_3AH_6) to form ettringite. Both gypsum and ettringite cause expansion which lead to cracking and deterioration of concrete or mortar cubes. SRPC, to a large extent, does not react in this way because tricalcium aluminate content is too low or absent altogether. In PZC, pozzolana reacts with any calcium hydroxide formed during hydration, blocking calcium sulphate and hence retards ettringite formation. The pozzolanic activity has further been found to form protective silicate hydrate films over the vulnerable aluminate compounds

(82). Any ettringite formed in PZC cubes would furthermore be unstable in solutions of low calcium hydroxide content (21).

The results showed that PZC and SRPC performed well in the sulphate media in conformity with the theory discussed.

4.3.2.1.2 Summary of the performance of the cements under the volume tests.

'<' means 'had less volume change than' and therefore would also read "performed better than".

(i) Deionised water: PZC<OPC<SRPC
(ii) Waste waters: PZC<OPC<SRPC
(iii) Lower fluoride concentration: SRPC<OPC<PZC
(iv) Higher fluoride concentration: SRPC<PZC<OPC
(v) Lower chloride concentration: PZC<SRPC<OPC
(vi) Higher chloride concentration: PZC<SRPC<OPC
(vii) Lower sulphate concentration: SRPC<PZC<OPC
(viii) Higher sulphate concentration: PZC<SRPC<OPC

4.3.2.2 Volume changes comparing the sands.

Table 4.13 shows the volume changes when the three cements were held constant while the sands were varied. The results for any one sand were different for the different cements, showing that the cements reacted differently with the sands.

Table 4.13: Mean per cent volume changes of cubes made with different sands holding cements constant.

Cement held constant / Sands / Media	OPC			SRPC			PZC		
	STD	KJD	MKS	STD	KJD	MKS	STD	KJD	MKS
Deionised water	-0.0857	-0.272	-0.244	-0.373	-0.0182	-0.0550	-0.0612	0.0948	-0.407
Waste water	-0.140	0.0675	-0.135	-0.415	0.0401	-0.116	0.120	-0.104	0.0920
Lower fluoride concentration	-0.184	0.0245	-0.217	-0.0031	0.0184	-0.266	-0.266	-0.0121	-0.113
Higher fluoride concentration	-0.254	-0.006	0.218	-0.119	-0.0214	-0.0152	0.178	-0.0948	-0.0948
Lower chloride concentration	-0.580	-0.290	-0.212	-0.315	-0.165	-0.232	-0.104	-0.238	-0.306
Higher chloride concentration	-0.617	-0.156	-0.553	-0.353	-0.205	-0.350	-0.266	-0.199	-0.354
Lower sulphate concentration	-0.416	-0.303	-0.177	-0.0214	-0.251	-0.260	-0.141	-0.0336	-0.214
Higher sulphate concentration	0.679	0.571	0.378	0.581	0.390	0.362	0.362	0.470	0.409

(i) OPC cubes.

In the deionised water, cubes made with Machakos sand showed less volume change than those made with Kajiado sand. The 'bulking' of the cubes made with Machakos sand must have left more porous structures which allowed the dissolution and leaching of the hydration products caused by the water, to occur within the matrix of the cubes leaving the overall volume relatively unaffected. Cubes made with Kajiado sand must have formed relatively more compact structures such that the effects of the deionised water were more concentrated on the surface. This must have been mainly responsible for the higher volume reduction of the cubes made with Kajiado sand than those made with Machakos sand.

In the waste waters and fluoride solutions, cubes made with Kajiado sand showed less volume change than those made with Machakos sand. In these solutions, fluoride reactions played a key role. The reaction of the fluoride ions with the silicates and sand grains on the more compact surface of the cubes made with Kajiado sand resulted in surface deposition of calcium fluoride and other fluorosilicates which protected the cubes from further attack.

The reaction in the more porous structures of the cubes made with Machakos sand, could not produce a uniform layer and so higher volume changes were observed.

In the lower chloride concentration solutions, cubes made with Machakos sand showed less volume change than those made with Kajiado sand. Reactions leading to leaching were mainly responsible for the volume changes and so the explanation for the deionised water series equally applied in this case. In the higher chloride concentration solutions, the cubes made with Kajiado sand, however, showed less volume change than those made with Machakos sand. The more concentrated ions must have penetrated into the cubes more, thereby causing greater leaching out of products from the porous cubes. This must have caused the cubes made with Machakos sand to contract or 'crumble' to fill up the bigger voids left. Attack on the cubes made with Kajiado sand must have been maintained on the surface such that less volume change occured.

In both the sulphate solution series, cubes made with Machakos sand showed less volume change than those made with Kajiado sand. In the lower concentrations, volume decreases were observed while expansion occured in the higher concentrations. The falling off of the calcium sulphate precipitate among other products was responsible for the volume decrease in the lower concentrations. Most of the precipitate must have fallen from the more compact surface of the cubes made with the Kajiado sand, causing relatively higher volume decrease. Some of the precipitate would be deposited on the pores of the cubes made with Machakos sand, such that further attack was reduced in those cubes. This must have caused the overall volume change relatively less than that of the cubes made with Kajiado sand. The higher concentration solution reactions produced expansive materials such as ettringite. The materials must have largely filled up the pores in the cubes made with the Machakos sand, while they caused more expansion in the more compact cubes made with Kajiado sand.

(ii) SRPC cubes.

The cubes made with Kajiado sand and SRPC showed less volume change than those made with Machakos sand in most of the solutions. It was only in the higher concentration of fluoride and sulphate ions that cubes made with Machakos sand showed less volume change.

The 'bulking effect' of the cubes made with Machakos sand was mainly responsible for the observations. The effect on volume was more intense on the more porous cubes made with Machakos sand. The cubes were better in the higher sulphate concentration solutions because expansive products merely filled up the pores as explained above. Similar deposition of reaction products on the pores must have resulted in the less volume change observed for the cubes immersed in the higher fluoride concentration solutions.

(iii) PZC cubes.

The cubes made with Kajiado sand showed less volume change than those made with Machakos sand in most of the solutions. It was only in the waste waters and the higher sulphate concentration solutions that the cubes made with Machakos sand showed less volume change. As discussed above the 'bulking' effect of the cubes made with Machakos sand was mainly responsible for the observations. The filling up action by expansive products in the cubes made with Machakos sand immersed in waste waters, which had a high sulphate ions content, and higher sulphate concentration solutions made the cubes to show less volume change than in the other solutions.

On the overall, cubes made with the local sands showed less volume changes than those made with the British Standard Sand especially in combination with OPC and SRPC. This indicates that the local sands formed better bonds with the cements than those formed with standard sand. The presence of clay suspended as silt and the roughness of these sand surfaces must have been responsible for their better performance. In this work however, the emphasis is on the comparison of the two local sands. The 'bulking' effect was beneficial in the higher sulphate concentration solutions as the volume test showed. The performance of the Machakos sand was better than that of Kajiado sand in all the cubes immersed in the solutions.

A summary showing the better sand under the cement held constant in the different media is given below.

Medium	The better sand under the cement held constant		
	OPC	SRPC	PZC
Deionised water	Machakos	Kajiado	Kajiado
Waste water	Kajiado	Kajiado	Kajiado
Lower fluoride concentration	Kajiado	Kajiado	Machakos
Higher fluoride concentration	Kajiado	Machakos	-
Lower chloride concentration	Machakos	Kajiado	Kajiado
Higher chloride concentration	Kajiado	Kajiado	Kajiado
Lower sulphate concentration	Machakos	Kajiado	Kajiado
Higher sulphate concentration	Machakos	Machakos	Machakos

4.3.3 Anionic uptake.

In this work ionic uptake is defined as the total concentration reduction of ions due to:penetration into the cubes; formation of coatings and precipitates on the cube surfaces; and formation of materials which precipitated at the bottom of the dessicators.

Most of the coatings formed would have been expected to protect the cubes and so a high uptake of ions would not necessarily indicate a more damaging effect. This was especially so in the fluoride ion uptake which results in formation of protective systems (47,48,53). The performance of the sands and cements in this test was therefore assessed with respect to the reactions that were deduced to have taken place.

4.3.3.1 Ions uptake comparing cements.

The anionic uptake by cubes made with standard sand in ppm per day were plotted against the sampling day to compare the performance of the cements, in each of the aggressive solution series.

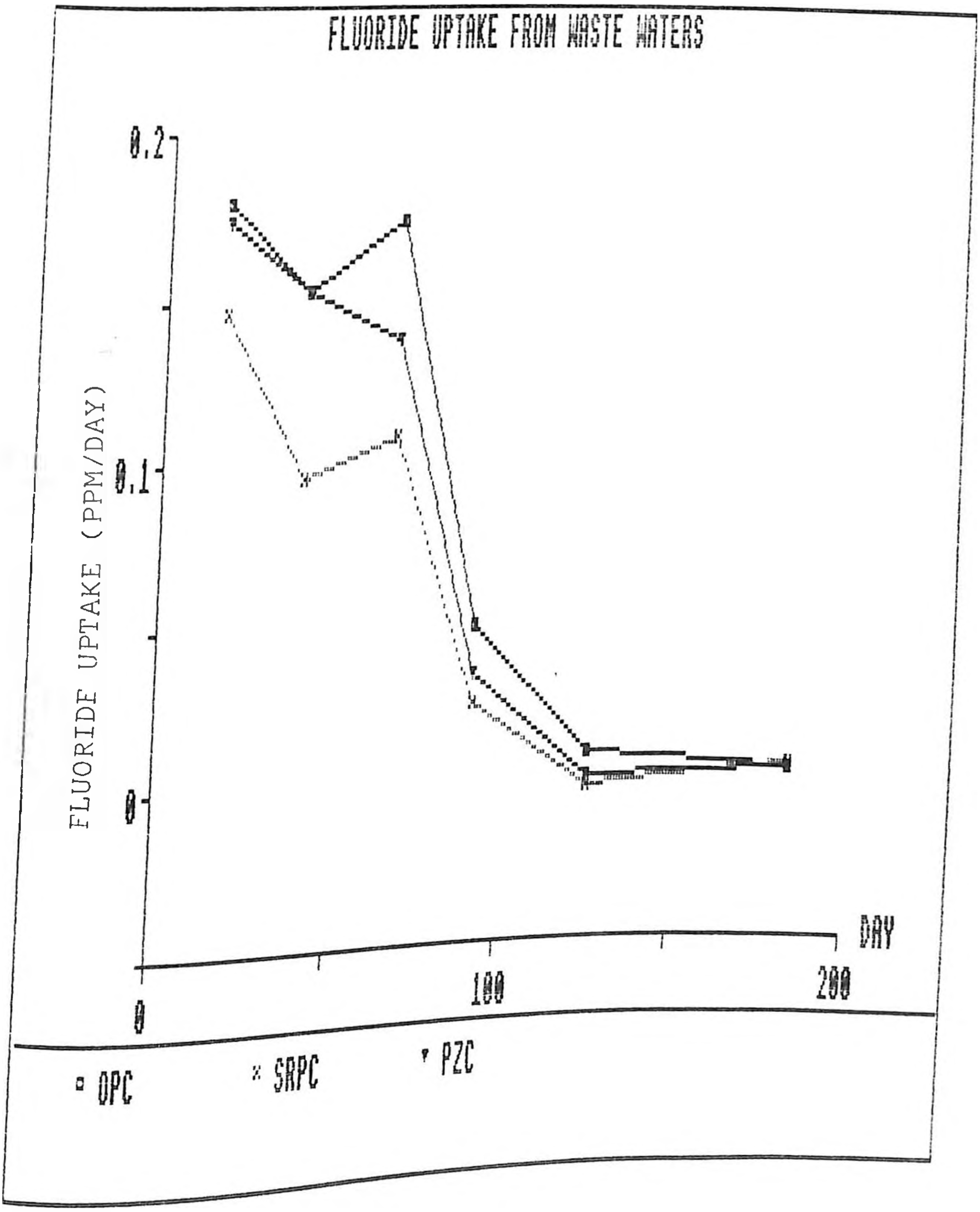
4.3.3.1.1 Fluoride uptake.

(i) Waste water solutions.

The results as shown in figure 4.9 show that the uptake was the highest in the first two months followed by a sharp decline in the third month and a very low uptake at the end of the six months.

Fluorides have been associated with the formation of protective coatings from their reactions with silicates. The high uptake at the beginning would correspond to the fluorides reacting with fresh silicate surfaces of the cubes. The slow decline in uptake especially shown by the PZC curve, shows that the silicate/fluoride reaction sites were being slowly replaced with an unreactive coating.

Fig. 4.9: Fluoride ions uptake from the waste waters by the cubes, made with STD sand and the different cements.



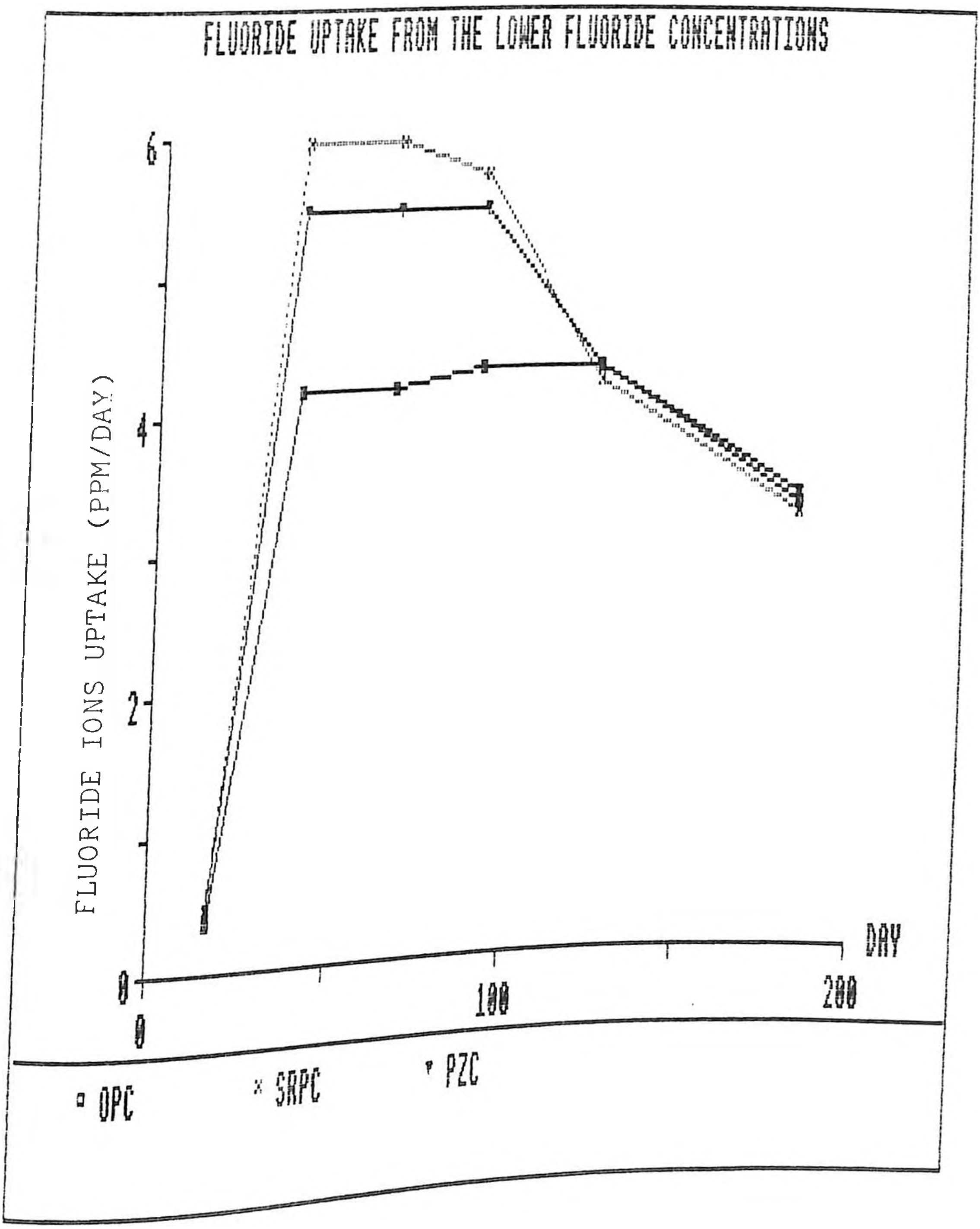
The sharp uptake decline observed in the third month (DAY 52 to 92) indicated that an effective barrier had been formed on the silicate sites which stopped further fluoride uptake. The decrease in uptake continued as the surface barrier thickened to the extent that finally, very little amounts of fluorides were taken up by the cubes.

The reaction between the fluorides and the cubes is advantageous because the products could shield cementitious compounds from further attack. Calcium fluoride and silicofluorides of calcium, magnesium and sodium formed in the reaction have been reported to give protection to concrete (48, 60,83,84). These findings explain the observations made at the end of the period that the fluoride uptake was almost zero in all cases. The SRPC formed the most effective barrier with the least uptake of fluoride ions followed by PZC and OPC, and hence it would be recommended for such an environment.

(ii) Lower and higher fluoride concentrations.

The results for the lower concentration are shown in figure 4.10. It was observed that there was an initial increase in the uptake rate followed by a steady uptake in the second and third month (40 to 92 DAY) and then decrease upto the end.

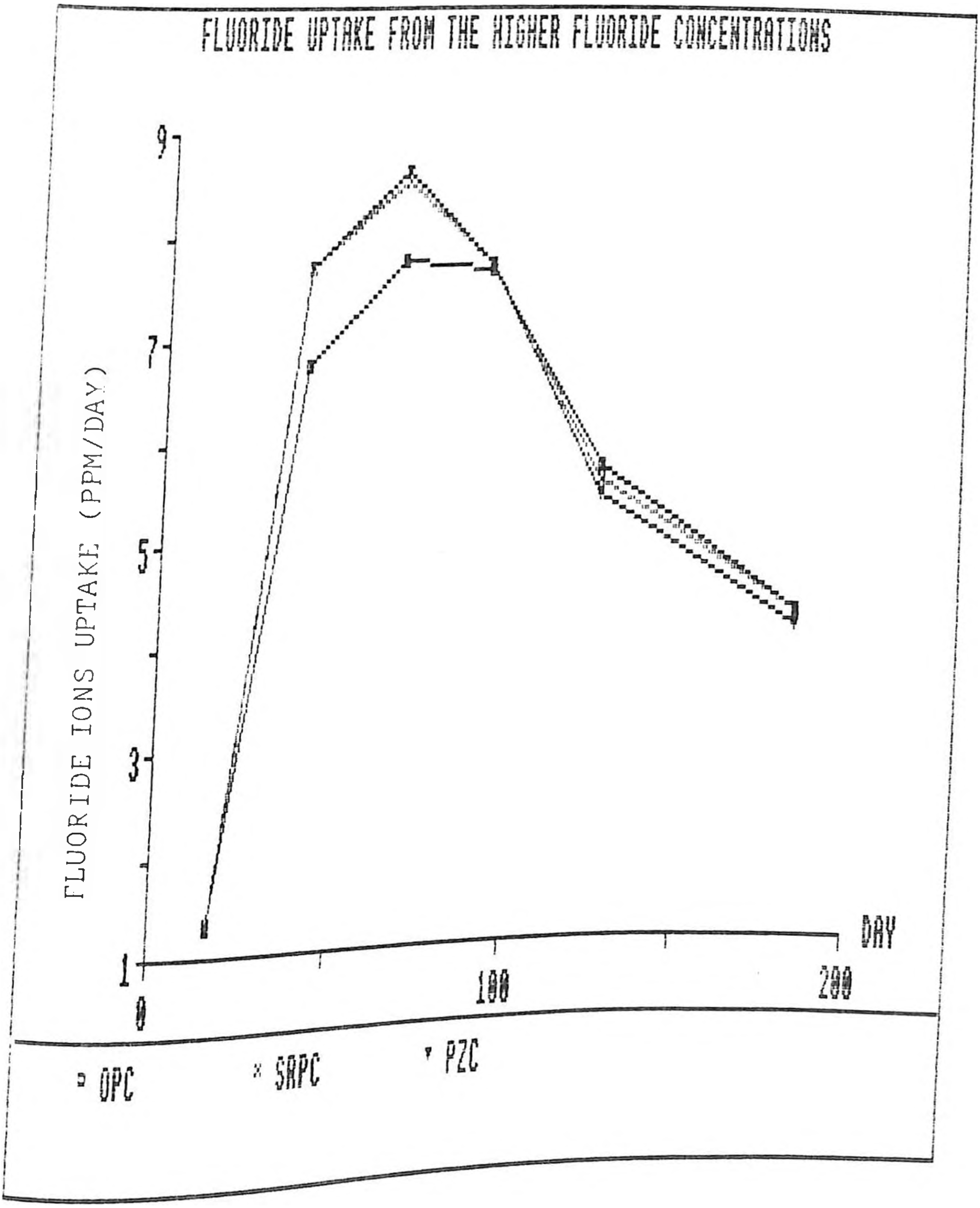
Fig. 4.10: Fluoride ions uptake from the lower fluoride concentration solutions by the cubes, made with STD sand and the different cements.



The fluorides were introduced in form of hydrofluoric acid and so, the initial increase could be due to the acid opening up the calcium hydroxide and hydrosilicate sites thereby increasing the uptake. The steady uptake could correspond to the formation of the protective coatings, made of silicofluorosilicates and calcium fluoride, until such a time that they offered effective protection to the sites when the uptake begun to decline. Further uptake increased the effectiveness of the coatings thereby minimising the uptake even further.

In this case SRPC took up the highest amount of fluoride ions followed by PZC and OPC. The decline in uptake towards the end of the six months was the same for all the cements. The cement that took up the least amount of fluorides was therefore better than the others. The presence of more hydroaluminates in the OPC which are not so reactive with the fluorides could account for the observation because the relatively less reactive sites would take up less fluorides. PZC would have been expected to show little uptake because of the lower levels of calcium hydroxide but, presence of more reactive silica and silicates in the pozzolana could have made it take up more fluorides than OPC. SRPC took up the maximum and that would be expected because of

Fig. 4.11: Fluoride ions uptake from the higher fluoride concentration solutions by the cubes made with STD sand and the different cements.



the presence of relatively higher concentration of calcium hydroxide and hydrosilicates.

An almost similar trend to the one above was observed in the higher concentration solutions as shown in figure 4.11. In this case, PZC took up slightly more than SRPC while OPC again took up the least. OPC was therefore the best.

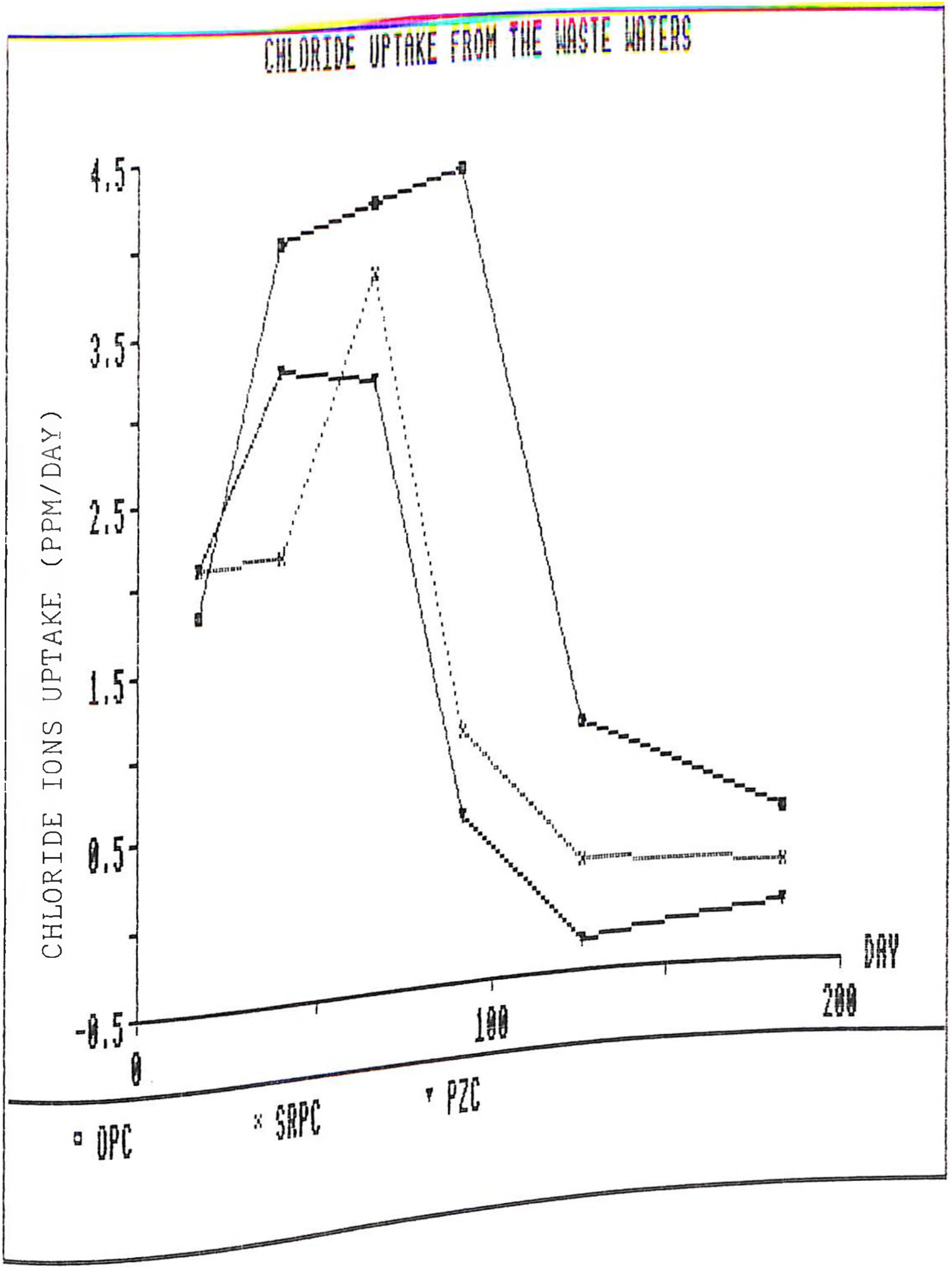
4.3.3.1.2 Chloride uptake.

(i) Waste water solutions

The results are shown in figure 4.12. OPC cubes showed a high uptake rate upto the 40th day when the rate slowed down upto the third month. A sharp decrease occured subsequently tending towards zero. PZC showed a similar trend although far much lower values were recorded. From the 40th to 67th day, the uptake was constant and then it decreased to such an extent that the chloride ions started leaching out of the cubes (marked by negative values). SRPC cubes showed an initial constant uptake level in the first month followed by a sharp rise and subsequently a fall in the uptake.

The initial increase in the uptake by the OPC cubes must have been due to formation of salts such as Friedel's $[(CaO.Al_2O_3\ Cl_2,SO_4).12H_2O]$ and calcium chloride. The latter salt subsequently leached out

Fig. 4.12: Chloride ions uptake from the waste waters by the cubes, made with STD sand and the different cements.



and therefore was responsible for the decrease in the uptake of the chloride ions. Saturation of chlorides in the cubes must have increased the leaching out process such that the stability attained at the end was due to the uptake and leaching out processes balancing out. The results seemed to agree with the observation of Mikiya et al (85) that, 'initially when mortar specimens are immersed in sea-water, most of the chloride is retained as the Friedel's salt although extractable species like calcium chloride leach out.

The observed leaching out of chlorides from the cubes made with PZC is quite interesting. PZC reacts with any calcium hydroxide formed during the hydration process and so, calcium ions are not as easily available for calcium chloride formation as in the other cements. Friedel's salt would therefore be expected to dorminate. The hydration of PZC is known to continue for a long time and the products continue filling up any pores in the cubes. The products must have 'pushed' out any unreacted chloride ions and those in the Friedel's salt.

Chlorides break up cementitions materials and leach out the resulting salts, and therefore its uptake is deleterious to the cubes. Formation of chloroaluminate is for example thought to cause disintegration of concrete, while the increased solubility of calcium hydroxide in calcium chloride solutions has also been suggested as a contributory factor (86). The less chloride ions taken up therefore, the better the cubes and hence cement involved. PZC was found to be the best followed by SRPC and lastly OPC. OPC would have been expected to offer better resistance to the chloride attack than SRPC due to its higher C_3A and C_4AF content, but in a similar experiment (14) it was found that "as much as 8.6% C_3A was not adequate for reducing the chloride penetration compared with zero content of C_3A".

(ii) <u>Lower and higher chloride concentration solutions.</u>

A similar trend was observed in the two chloride concentrations, as shown in figures 4.13 and 4.14. There was an increasing uptake trend in the first forty days followed by a decreasing trend upto the end of the investigation. PZC clearly took up the least amount of the chloride ions. SRPC and OPC curves were somehow intertwined such that it was not clear which of the two took up less ions than the other. The overall mean uptake however, as shown in table 4.14 (under standard

Fig. 4.13: Chloride ions uptake from the lower chloride concentration solutions by the cubes, made with STD sand and the different cements.

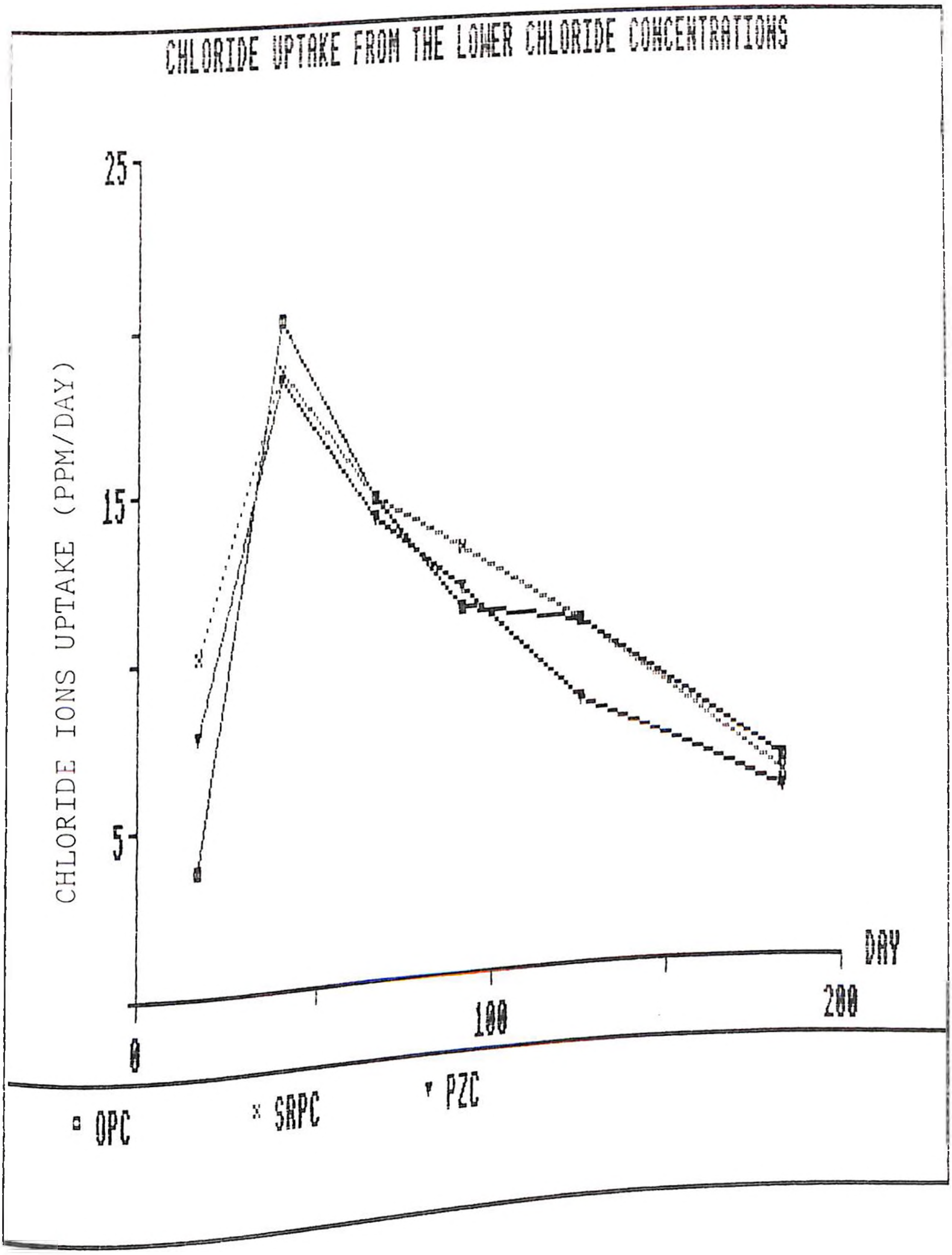
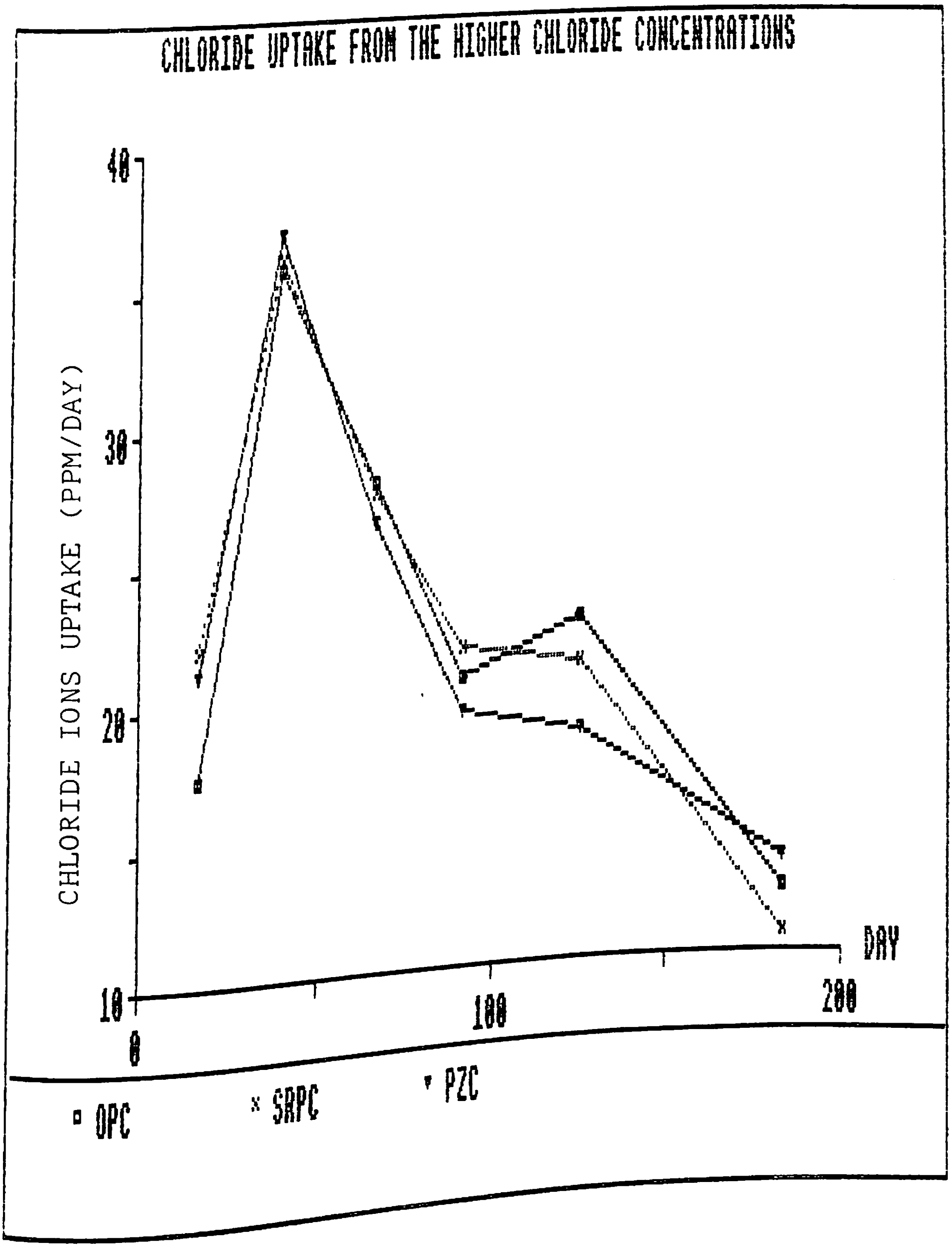


Fig. 4.14: Chloride ions uptake from the higher chloride concentration solutions by the cubes, made with STD sand and the different cements.



sand columns), show that OPC took up less amount of the chloride ions than SRPC in both cases and therefore was better than SRPC.

The reactions in this case were similar to those postulated for the waste water solutions. The results showed that C_3A is an important cementing material, and agreed with Soroka's finding (62) that SRPC is more susceptible to chloride attack than OPC. The position of PZC as the most resistant cement to chloride attack was maintained.

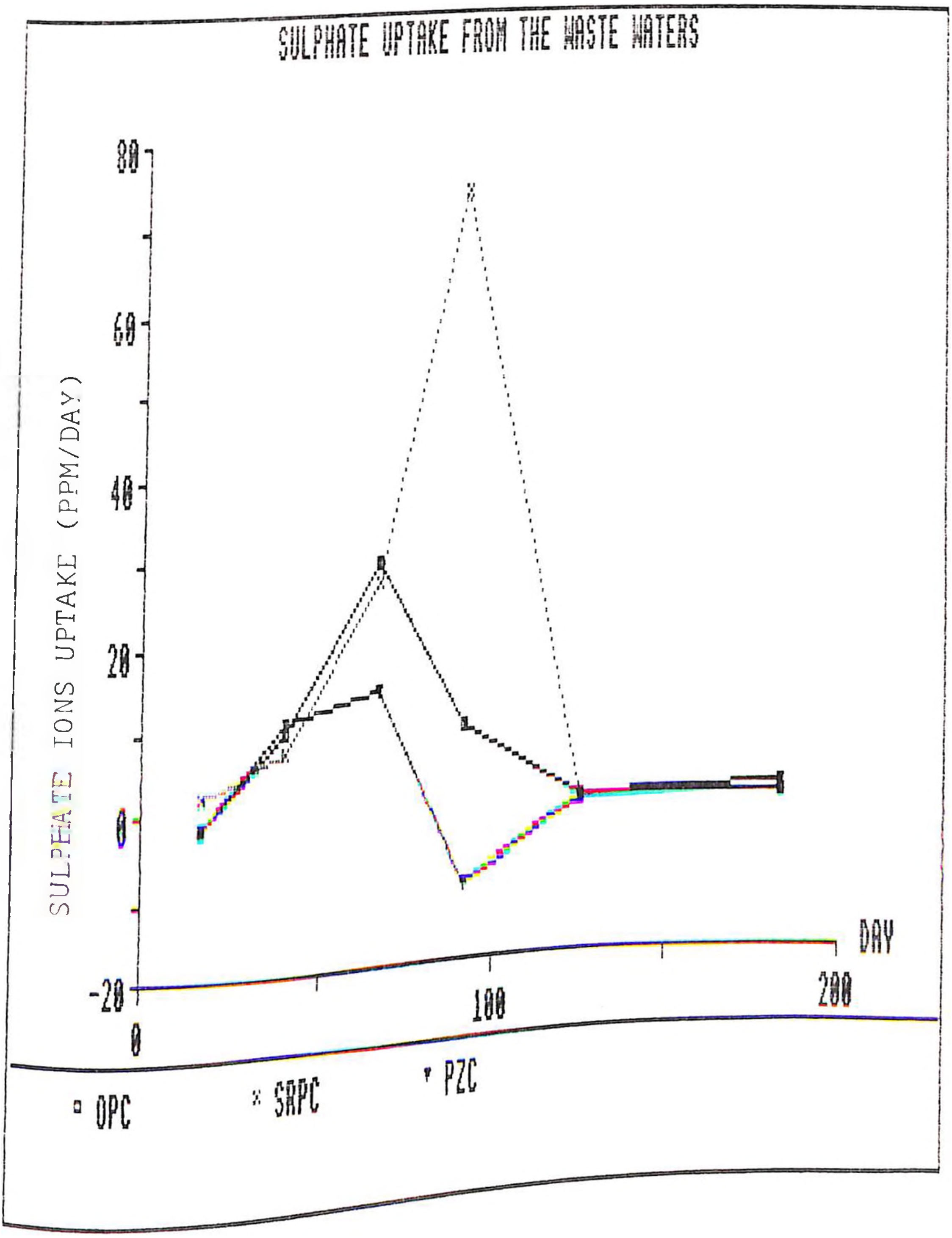
4.3.3.1.3 Sulphate uptake.

(i) Waste water solutions.

The results given in figure 4.15 show that there was an increase in the sulphate uptake upto the 67th day for OPC and PZC, and upto the 92nd day for SRPC, followed by a decrease in the uptake rate and finally a leaching out process of small amounts upto the end of the investigation. The PZC showed a high degree of leaching out from the 92nd day which eventually subsided like that of the other cements.

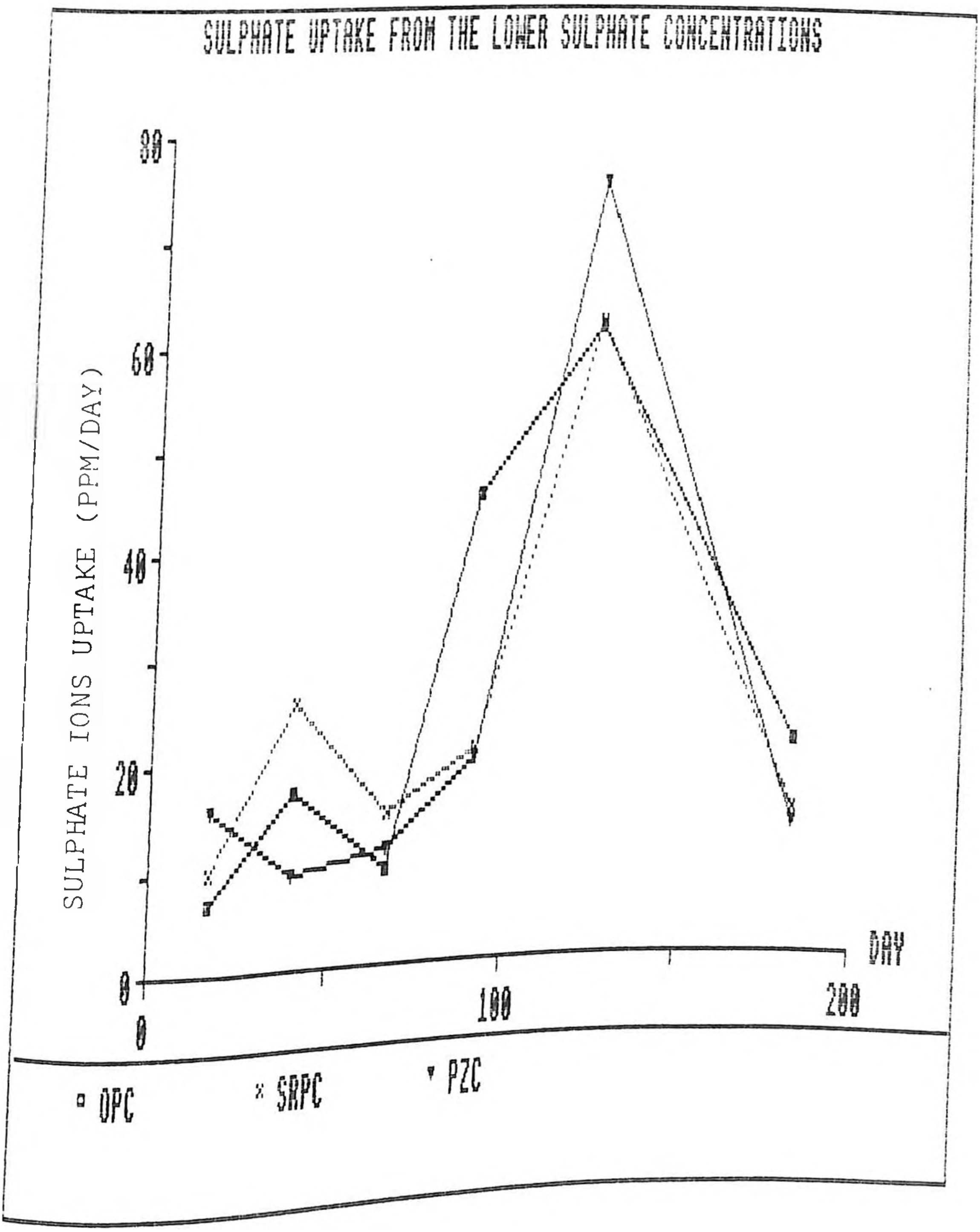
The volume test indicated that reactions leading to leaching dorminated the SRPC and OPC cubes. The sulphate reaction which would have

Fig. 4.15: Sulphate ions uptake from the waste waters by the cubes, made with STD sand and the different cements.



caused expansion seemed not to have taken place. In this test, PZC took up the least amount of ions followed closely by OPC while SRPC took up the most. The observations are in agreement with the deduction on the volume test because, had the ettringite reaction dorminated, OPC would have been expected to take up the maximum sulphate ions. The trend is probably due to leaching out of soluble salts which left porous structures through which sulphate ions diffused. Since the water also contained chloride ions, their attack was most severe to SRPC (62) and so most sulphates diffused into the SRPC structures and reacted with the reactive components. Diffusion of sulphates into the OPC cubes must have resulted in ettringite formation which filled up the pores and hence reduced uptake. PZC resisted chloride ion penetration and consequently less leaching of chloride salts resulted. The cubes made of PZC therefore took up the least sulphate ions. The leaching out of the sulphate ions observed towards the end of the investigation must have occured due to the cubes having a higher concentration of the unreacted ions than the waste waters introduced at those later stages.

Fig. 4.16: Sulphate ions uptake from the lower sulphate concentration solutions by the cubes, made with STD sand and the different cements.



The results showed PZC to be the best followed by OPC and SRPC. The results and those of volume changes agree and show that SRPC should be used with care in sulphate containing solutions.

(ii) Lower and higher sulphate concentration solutions.

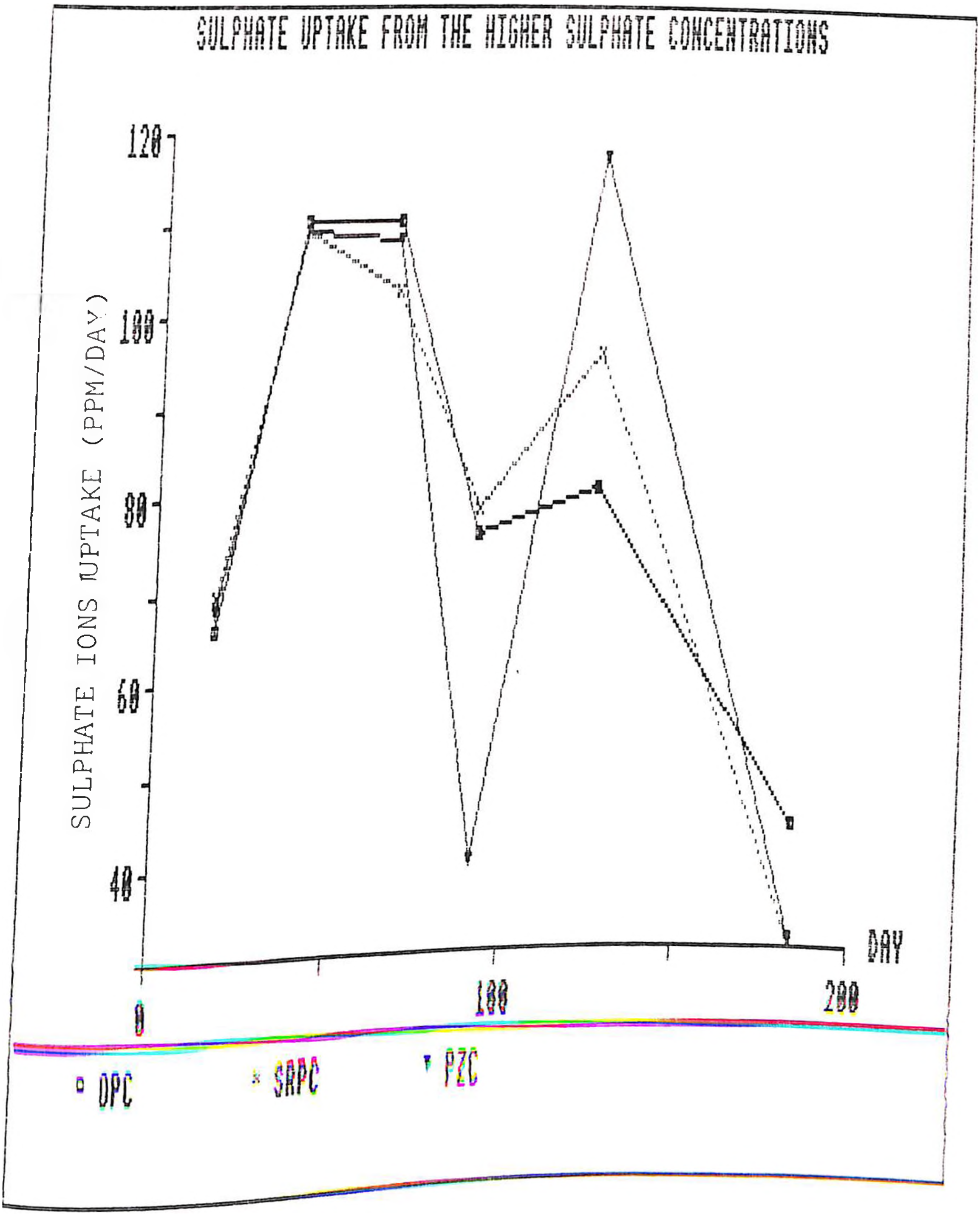
In the lower concentration solutions, figure 4.16 shows that a low uptake level was maintained upto three months (two months in the case of OPC) after which all the cements showed a rapid increase and a final fall.

The pH and volume test results indicated that the reactions took place at the surface causing volume decrease. The observation in the first three months was therefore due to availability of free calcium hydroxide which reacted with the sulphates forming, among others, calcium sulphate precipitate which fell off. The action accelerated the leaching out of the calcium hydroxide from the cubes resulting in the higher uptake of the sulphate ions. Deposition of the precipitate on the cube surface and pores must have hindered the leaching out of ions such that the sulphate uptake decreased as observed towards the end of the investigation.

In the higher concentration solutions figure 4.17 shows that there was an increase in the ionic uptake followed by a stable period and then a decrease at the end of the period. The volume test showed that there was an overall expansion for all the cements. The formation of expansive products was therefore dorminant. The products so formed were responsible for the decrease in the uptake of the sulphate ions due to expansion, depletion or shielding of the sulphate sensitive components. The reactions involved must have been those leading to gypsum and ettringite formation expressed by equations 2.1 to 2.3.

From the two figures (4.16 and 4.17), the performance of the cements could not be clearly seen but from the mean uptake levels shown in table 4.14 (standard sand columns of sulphate solutions); PZC had the least uptake followed by SRPC while OPC took up the maximum amount of sulphate ions. The results were consistent for both concentrations and the levels for the cements were very close. The proximity of the levels must have been caused by the gypsum formation which involved all the cements, such that ettringite formation failed to clearly distinguish the cements. PZC performed best because both reactions leading to

Fig. 4.17: Sulphate ions uptake from the higher sulphate concentration solutions by the cubes, made with STD sand and the different cements.



gypsum and ettringite formation are not favourable to it.

PZC would be the best suited for similar environments followed by SRPC while OPC would be the least suitable.

4.3.3.1.4 The summary of the performance of the cements with respect to the anionic uptake.

(i) Fluoride uptake;

Waste waters: SRPC < PZC<OPC

Lower fluoride concentration: OPC<PZC<SRPC

Higher fluoride concentration: OPC<SRPC<PZC

(ii) Chloride uptake;

Waste waters: PZC<SRPC<OPC

Lower chloride concentration: PZC<OPC<SRPC

Higher chloride concentration: PZC<OPC<SRPC

(iii) Sulphate uptake;

Waste waters: PZC<OPC<SRPC

Lower sulphate concentration: PZC<SRPC<OPC

Higher sulphate concentration: PZC<SRPC<OPC

(where '<' reads 'took up less than' which means 'was better than').

The summary shows that the results were highly consistent for lower and higher concentrations as would be expected. Except for fluoride uptake where PZC exchanged positions with SRPC the other ions showed uniformity.

Table 4.14: *Mean anionic uptake (ppm/day) holding cements constant.*

Cement held Constant		OPC			SRPC			PZC		
Ion taken up	Solution	STD	**KJD**	MKS	STD	KJD	MKS	STD	KJD	MKS
	W's	0.094	0.078	0.105	0.063	0.050	0.109	0.083	0.072	0.085
Fluoride	Fa's	3.928	4.047	3.694	4.112	4.451	4.647	4.006	3.951	3.776
	Fb's	5.330	5.645	5.786	5.842	6.344	5.897	5.943	5.524	5.455
	W's	2.645	1.810	2.773	1.544	1.460	2.747	1.422	1.214	2.153
Chloride	Ca's	11.029	9.736	11.680	12.016	11.080	12.155	10.817	10.984	12.772
	Cb's	22.784	22.315	25.937	23.210	23.408	26.797	22.628	22.766	25.193
	W's	7.188	7.668	7.866	17.916	10.410	8.125	1.640	-1.414	0.363
Sulphate	Sa's	26.802	25.780	24.702	24.490	24.513	25.855	24.087	24.178	24.587
	Sb's	81.303	77.762	79.146	81.224	82.033	81.733	79.076	81.327	81.527

4.3.3.2 Ions uptake comparing the sands.

To a great extent, the reaction of the sands with the aggressive solutions was expected to be minimal if not absent altogether. Fluoride ions were however expected to react with the silica component of the sands. The major reactions bringing about anionic uptake were expected to be between the cement component of the cubes and the aggressive solutions. The extent of that reaction would be dependent on the cement/sand bond, and that is where the quality of the sand came in. The inference that less ionic uptake into the cubes implied presence of better bonds was expected to hold true. The sands that were therefore associated with lower anionic uptake were taken to be better. Table 4.14 shows the results obtained while holding the different cements constant.

4.3.3.2.1 Fluoride uptake.

For OPC cubes, the cubes that were made with Kajiado sand took up less ions than those made with Machakos sand in waste water and higher concentration solutions, while the reverse was observed in the lower concentration solutions. For these cubes therefore, Kajiado sand was better than Machakos sand in waste water and higher concentration solutions while the reverse was deduced for the lower concentration solutions. For SRPC cubes, Kajiado sand was better in the waste waters and lower concentration solutions while the reverse was deduced for the higher concentration solutions. For PZC cubes, Machakos sand was better than Kajiado sand in the lower and higher concentration solutions while the reverse was deduced for the waste water solutions. The results as can be seen are not consistent and do not give any pattern. The reasons for such anomalous behaviour are not apparent at the moment and would need a more detailed study to determine the causes. Unfortunately the period allowed for MSc work does not allow such an undertaking now and so further work on the area is recommended.

4.3.3.2.2 Chloride uptake.

Cubes made with Kajiado sand took up less ions than those made with Machakos sand in all the cases investigated. Chloride ions attack mortar cubes by penetration, formation of salts and leaching out of soluble salts. The results show that cubes made with Machakos sand were attacked more due to a higher chloride penetration. This must have been mainly caused by the 'bulking' effect which caused the structures to be more porous.

4.3.3.2.3 Sulphate uptake.

In the waste waters, cubes made with Kajiado sand took up less ions than those made with Machakos sand. Here again the 'bulking' effect of the Machakos sand is considered to be responsible.

In the lower concentration solutions, cubes made with Machakos sand took up less sulphate ions than those made with Kajiado sand although the levels were very close. The reactions were mainly on the surface as shown by the pH and volume change tests. The cubes made with Machakos sand, which were more porous due to the 'bulking' effect, must have deposited the calcium sulphate precipitate on the pores reducing further uptake in contrast to the cubes made with Kajiado sand whose precipitate fell off more readily, due to more compact surfaces, leaving exposed sites for further attack.

In the higher concentration solutions, it was observed that cubes made with Kajiado sand took up less sulphate ions than those made with Machakos sand. The 'bulking' effect of the Machakos sand must have been responsible for a higher uptake of the sulphate ions which penetrated the cubes. The penetration into the cube structures resulted in ettringite and gypsum formation as evidenced by the volume change measurements.

SRPC and PZC cubes had uptake figures that were very close together for cubes made with Kajiado and Machakos sand. The trends were not consistent and the reasons for the observations are not very clear; although formation of gypsum in preference to ettringite could explain the observed close values of the uptake.

4.3.3.2.4 The summary of the performance of the sands with respect to the anionic uptake showing the better sand.

		OPC cubes	SRPC cubes	PZC cubes
(i)	Fluoride uptake			
	Waste water solutions (W's):	Kajiado	Kajiado	Kajiado
	Lower fluoride concentration (Fa's):	Machakos	Kajiado	Machakos
	Higher fluoride concentration (Fb's):	Kajiado	Machakos	Machakos

	OPC cubes	SRPC cubes	PZC cubes
(ii) Chloride uptake			
Waste water solutions (W's):	Kajiado	Kajiado	Kajiado
Lower chloride concentration (Ca's):	Kajiado	Kajiado	Kajiado
Higher chloride concentration (Cb's):	Kajiado	Kajiado	Kajiado
(iii) Sulphate uptake			
Waste water solutions (W's):	Kajiado	Machakos	Kajiado
Lower sulphate concentration (Sa's):	Machakos	Kajiado	Kajiado
Higher sulphate concentration (Sb's):	Kajiado	Machakos	Kajiado

4.3.4 Leaching out of cations from the cubes.

The results obtained for individual cations leached out as well as the combined mean of all the cations leached out were used to compare the cements. The performance of the sands was assessed by comparing only the combined mean of all the cations leached out of the cubes made of the same cement. The cement or sand which had the lowest leaching out of cations was considered to be the most suitable.

4.3.4.1 Leaching out of cations comparing the cements.

Table 4.15 shows the results of the cations leached out of the cubes made of different cements.

(i) Deionised water series.

OPC cubes showed the least calcium ion leaching followed by PZC and SRPC respectively. Magnesium ions leached out least from SRPC followed by PZC and OPC respectively. Iron ions showed the same trend as that of calcium. Aluminium ions leached out least from OPC followed by SRPC and PZC in that order. Silicon ions showed a similar trend to that of magnesium while the overall combined leaching (mean of all the cations) showed a similar trend to that of calcium.

Deionised water attacked the cubes by penetrating them or attacking the surface, dissolving and breaking up the cementitious materials. From the pH changes, calcium hydroxide was deduced to be a major product in the processes and so the calcium leaching column would have more weight in showing the extent of the aggressive reactions. This was shown by the overall mean column as the two columns showed the same trend. SRPC cubes

Table 4.15: Concentration of the cations leached out from cubes made with standard sand (ppms) comparing the cements.

Cation	Calcium			Magnesium			Iron			Alumimium			Silicon			Overall Mean		
Cement / Solution	OPC	SRPC	PZC	OPC	SRPC	PZC	OPC	SRPC	PZC	OPC	SRPC	PZC	OPC	SRPC	PZC	OPC	SRPC	PZC
D's	253	636	544	6.26	4.28	6.01	0.210	2.11	1.33	3.68	5.54	7.92	43.4	13.8	19.1	61.3	132	116
W's	-144	-105	-148	-31.8	-23.7	-33.1	-0.606	0.099	-0.232	1.13	0.611	0.822	39.0	20.7	31.4	-27.3	-21.5	-29.8
Fa's	98.1	235	182	4.97	4.47	3.70	0.212	0.273	0.166	0.611	1.22	2.64	79.3	47.6	52.8	36.6	57.7	48.3
Fb's	158	353	169*	4.03*	4.89	4.80	0.349	0.822	0.287	0.305*	0.916*	0.753*	71.6*	56.3	61.6	46.9	83.2	47.3
Ca's	2347	2778	2540	20.4	17.8	20.9	10.7	19.3	8.35	6.71	8.10	7.81	75.0	70.6	64.2	492	579	528
Cb's	7701	7060	6976	37.5	25.1	23.7	28.0	38.6	23.6	46.7	44.1	40.8	111	92.1	163	1585	1452	1445
Sa's	2224	2434	2437	21.2	30.8	16.3	6.70	11.8	7.82	2.39	5.62	8.42	80.9	62.6	58.4	467	509	506
Sb's	3220	3185	3786	121	57.0	105	16.9	15.0	11.3	37.3	7.06	34.6	91.0	83.5	89.4	697	670	805

experienced more leaching out because its hydration products were more exposed due to a low content of C_3A and C_4AF products. PZC cubes on the other hand were affected more than those of OPC because the pozzolana grains provided channels for the water to reach more hydration products. SRPC and PZC are moreover known to take more time to hydrate fully and so they would be more prone to the leaching out reactions than OPC as the unhydrated components would provide channels for permeation.

On the overall, OPC was found to be the best cement followed by PZC and SRPC. The result is reassuring since most of the concrete surfaces exposed to rain water are made using OPC. The leaching out levels observed show that all the cements were susceptible to attack by deionised water and hence rain water.

(ii) Waste waters.

Most of the cations were taken up from the waters instead of leaching out of the cubes. Cubes made with SRPC took up the least calcium and magnesium ions followed by OPC and PZC. A small quantity of iron leached out of the cubes made with SRPC while those of PZC took up less amounts than those of OPC. Leaching out was observed for aluminium and silicon ions and in both cases, SRPC cubes leached out the least followed by PZC and OPC. The overall mean values showed a similar trend to that of calcium and magnesium. In all the cases SRPC cubes were found to be best while PZC was found to be better than OPC from the iron,aluminium and silicon results.

The waste waters had very high levels of sulphates and the results indicated that they were dorminantly involved in the reactions resulting in the SRPC cubes' good performance. This was shown especially by the uptake of calcium and magnesium whose sulphates are well known sulphate attack reactants (equations 2.1 to 2.5).

From the overall results, SRPC was found to be the best followed PZC and OPC.

(iii) Fluoride solutions.

In the lower concentration solutions, the cation leaching out trends were different for almost all the cations. From the overall mean, OPC cubes had the least leached out cations followed by PZC and SRPC. In the higher concentration solutions, the results for calcium, magnesium, aluminium and the overall mean showed the same trend as for the lower concentration. For iron, PZC cubes lost the least followed by OPC and SRPC while silicon leaching out was least for SRPC followed by PZC and OPC.

It was observed that the higher concentration solutions did not show increased cation leaching as would have been expected. On the contrary, in some cases (marked by asterisks in table 4.15), the leaching out levels were lower for the higher concentration solutions than the lower ones. The observation was a further indication that the fluorides reacted with the cubes forming protective substances. From the observation, it seemed that the higher the fluoride concentrations, the better the protective substances were.

From the overall results, OPC was found to be the best followed by PZC and SRPC.

(iv) Chloride solutions.

In the lower concentration solutions, the leaching out trends of the cements were different for most of the cations. Only calcium and aluminium showed a similar trend where OPC cubes had the least leaching out followed by PZC and SRPC cubes. From these and the overall mean results, OPC was found to be the best followed by PZC and SRPC.

In the higher concentration solutions, calcium, magnesium,aluminium and the overall mean leaching out levels showed that PZC cubes lost the least cations, followed by SRPC and OPC. PZC was also found to be the best for iron leaching followed by OPC and SRPC. Silicon leaching however showed SRPC to be the best followed by OPC and PZC which was the reverse of the other observations. From the majority of cases and the overall mean results, PZC was found to be the best followed by SRPC and OPC.

On the overall, the results for both lower and higher concentration solutions show that PZC was the best followed by OPC and SRPC. SRPC was taken on the overall to have performed poorly because OPC's performance in the lower concentration solutions was quite good. The results agreed with what has been reported in the literature (14).

(v) Sulphate solutions.

In the lower concentration solutions, the leaching out trends were different for all the cations studied. OPC cubes leached out the least cations as shown by the concentrations of calcium, iron, aluminium and the overall mean. The overall mean results showed that the levels for SRPC and

PZC were very close together compared to those of the OPC. PZC cubes however showed a slightly lower leaching out level than that of SRPC. The results indicated that OPC was the best followed by PZC and SRPC.

In the higher concentration solutions the leaching out of magnesium, aluminium and silica showed SRPC cubes to have lost the least cations followed by PZC and OPC. The overall mean and the value for calcium showed that SRPC had the least followed by OPC and PZC. PZC had the least iron leaching out followed by SRPC and OPC. The results indicated that SRPC was the best followed by PZC and OPC.

The lower concentration results indicated that the characteristic sulphate attack reactions were not involved, otherwise the SRPC would have performed better. The results therefore reinforced earlier deductions that the reactions in this case were confined to the surface of the cubes. The predominant reaction was the precipitation of calcium sulphate. The higher concentration results however indicated that the characteristic sulphate attack reactions were dominant since SRPC and PZC performed better than OPC as would be expected.

4.3.4.1.2 The summary of the cements' performances under cation leaching test. ('<' reads, 'leached out less ions than', or 'was better than').

Deionised water: OPC<PZC<SRPC
Waste waters: SRPC<PZC<OPC
Lower fluoride concentration solutions: OPC<PZC<SRPC
Higher fluoride concentration solutions: OPC<PZC<SRPC
Lower chloride concentration solutions: OPC<PZC<SRPC
Higher chloride concentration solutions: PZC<SRPC<OPC
Lower sulphate concentration solutions: OPC<PZC<SRPC
Higher sulphate concentration solutions: SRPC<PZC<OPC

4.3.4.2 Leaching out of cations comparing the sands.

The results are shown in table 4.16.

In deionised water, OPC and SRPC cubes made with Machakos sand leached out less cations than the ones made with Kajiado sand. The results indicated that the cubes made with Machakos sand were more strongly bonded than those of Kajiado sand. Machakos sand was finer and had less silt content and this must have resulted in a higher cement paste/sand surface contact and hence stronger bonds. The PZC cubes made with Kajiado sand leached out less cations than those made with Machakos sand. The relatively

Table 4.16: Overall combined mean of the cations leached out of the cubes (ppms), holding cements constant.

Cement Held Constant / Solutions / Sands	OPC			SRPC			PZC		
	STD	KJD	MKS	STD	KJD	MKS	STD	KJD	MKS
Deionised water	61.3	34.7	32.8	132	43.3	36.6	116	44.7	46.7
Waste water	-27.3	-19.3	-35.4	-21.5	-27.1	-20.8	-29.8	-18.6	-33.0
Lower fluoride concentration	36.6	51.8	38.6	57.7	82.2	59.8	48.3	44.2	34.0
Higher fluoride concentration	46.9	66.3	42.5	83.2	99.6	78.8	47.3	39.7	64.5
Lower chloride concentration	492	597	530	579	765	516	528	564	529
Higher chloride concentration	1585	1438	1339	1452	1442	1327	1445	1451	1340
Lower sulphate concentration	467	521	532	509	477	473	506	513	518
Higher sulphate concentration	697	652	647	670	677	670	805	767	859

more silt content and less cement/sand surface area contact associated with Kajiado sand must have left relatively more space for the pozzolanic activity products. This resulted in better cubes which allowed less cation leaching.

In the waste water solutions, the cubes took up cations from the waters instead of leaching out. A better cube would take up less amounts of cations and so cubes made with Kajiado sand were better than those made with Machakos sand for both OPC and PZC while the reverse was observed for SRPC cubes.

In the fluoride solutions, the cubes made with Machakos sand were found to have lost less cations than those made with Kajiado sand except when used with PZC immersed in the higher concentration solutions. The results showed that cubes made with Machakos sand were better than those made with Kajiado sand. The fluorides reacted with the cubes forming products such as calcium fluoride (solubility = 0.0016g/100ml water), which protected the cubes from further attack. The 'bulking' effect of the Machakos sand left relatively more pores on the surface and deposition of the protective products on pores must have protected the cubes more. Deposition of the products on the smoother surfaces of the cubes made with Kajiado sand gave less protection because agitation on the surface during length measurements, for example, must have removed the protective products to a larger extent. The pozzolana in the PZC created a higher porosity in the PZC cubes, and similar deposition of the products would account for the observed better performance of Kajiado sand in the higher concentration solutions.

In chloride solutions, cubes made with Machakos sand lost less cations than those made with Kajiado sand in all the solutions. The results indicated that Machakos sand had formed better bonds with the cement pastes than the Kajiado sand. The higher silt content of the Kajiado sand must have aided the chloride attack by providing relatively more channels for the penetration into the cubes and the leaching out of the ions.

In the lower sulphate concentration solutions, cubes made with Kajiado sand showed less cationic leaching than the Machakos ones with OPC and PZC, while the reverse was observed with SRPC. The reactions in this case took place mainly on the surface. Cubes made with Machakos sand had weaker bonds due to the 'bulking' effect, and hence showed relatively more cationic leaching than the Kajiado sand counterparts.

In the higher concentration sulphate solutions, the cubes made with Machakos sand lost less cations than those made with Kajiado sand for OPC and SRPC, while the reverse was observed for PZC. The better performance of the Machakos sand showed that there were relatively less channels for sulphate ions penetration and cationic leaching. Ettringite was one of the principal products in this reaction and due to its expansion, the pores left by the 'bulking' effect must have been filled up leaving more compact structures. Formation of ettringite in the cubes made with Kajiado sand, and the relatively higher silt content, conversely, created more channels for the cationic leaching. For OPC and SRPC therefore, Machakos sand was better than the Kajiado sand. The better performance of Kajiado sand with PZC could have been due to the pozzolanic activity products filling up any of the pores and channels caused by the relatively higher silt content. The pozzolanic activity products did not fill up the pores existent in the cubes made with Machakos sand due to the 'bulking' effect and so the cubes showed a higher leaching out of cations.

A summary of the performance of the sands with respect to the cationic leaching, showing the best sand is given below.

Solution	OPC	SRPC	PZC
Deionised water;	Machakos	Machakos	Kajiado
Waste water;	Kajiado	Machakos	Machakos
Lower fluoride concentration;	Machakos	Machakos	Machakos
Higher fluoride concentration;	Machakos	Machakos	Kajiado
Lower chloride concentration;	Machakos	Machakos	Machakos
Higher chloride concentration;	Machakos	Machakos	Machakos
Lower sulphate concentration;	Kajiado	Machakos	Kajiado
Higher sulphate concentration;	Machakos	Machakos	Kajiado

Overall, the results indicated that Machakos sand was better than Kajiado sand but the specific results are more important.

4.3.5 Compressive strength tests.

The difference in the compressive strength values determined before the cubes were exposed to the aggressive solutions, and after the exposure period was expressed as percentage change and recorded. From these values the performances of the cements and sands were assessed.

4.3.5.1 Compressive strength changes comparing the cements.

The results are given in table 4.17.

(i) Deionised water series.

PZC showed the highest strength loss followed by OPC while SRPC showed a slight increase. Deionised water attacked the cubes and leached out calcium hydroxide, among other substances, formed during the hydration process. Pozzolana in PZC reacts with the calcium hydroxide to form cementitious compounds. The depletion of the calcium hydroxide by the leaching out process in the PZC cubes must have reduced the pozzolanic activity thereby resulting in weaker cubes. The increase in strength in the case of SRPC indicated that the deionised water was beneficial. SRPC had a low concentration of C_3A and this slowed down its hydration process considerably. The cement had relatively more calcium silicates and so it gave out relatively more calcium hydroxide and other calcium silicate hydration products. The calcium hydroxide must have provided the necessary environ-

Table 4.17: Percent compressive strength changes of cubes made with standard sand comparing the cements.

Solution medium \ Cement	OPC	SRPC	PZC
Deionised water	-3.76	1.18	-7.55
Waste water	1.38	11.8	-8.36
Lower fluoride concentration	6.05	4.85	3.53
Higher fluoride concentration	9.62	5.23	7.91
Lower chloride concentration	2.88	-1.00	3.13
Higher chloride concentration	6.85	-1.59	-7.29
Lower sulphate concentration	7.11	7.58	5.66
Higher sulphate concentration	-4.17	-3.79	-5.38

$$\text{Compressive strength change (\%)} = \frac{\text{C.S.(B)} - \text{C.S.(A)}}{\text{C.S.(A)}} \times 100\%$$

where C.S.(A) is the mean compressive strength (N/mm^2) before exposure to the aggressive solutions and C.S.(B) is the mean compressive strength (N/mm^2) after the six month exposure period.

ment for the continuation of the hydration process, which resulted in strength increase. The deionised water was changed periodically and so, the process just described must have outdone the leaching out effect that caused strength loss in the other cubes. SRPC was therefore found to be the best followed by OPC and PZC in the deionised water exposure test.

(ii) Waste water solutions.

SRPC was found to be the best followed by OPC and PZC. The waters had very high levels of sulphates, chlorides, fluorides and various cations. The performance of SRPC indicated that the sulphate attack reactions dorminated. PZC would have been expected to perform better than OPC due to the high sulphate levels. The presence of the fluoride ions which have been found to be more beneficial to OPC must have altered the expected order, of PZC being better than OPC.

(iii) Fluoride solutions.

OPC was found to be the best followed by PZC and SRPC. The results were consistent for both concentrations. All the values showed substantial strength increases indicating that the reactions were reinforcing the cubes. The finding is in contrast to that of Karuu (87) that the ions caused reduction of the compressive strength of neat cement cubes. His finding that SRPC performed worse than OPC and PZC is however in agreement with these results. The reinforcing action must have therefore been caused mainly by the reaction between the fluoride ions and the sand grains as discussed in section 4.4.

(iv) Chloride solutions.

The lower chloride concentration solutions showed PZC to be best followed by OPC and SRPC. The performance agreed well with work reported in the literature (14,62). In the higher concentration solutions, OPC was the best followed by SRPC while PZC performed poorly. The solutions were acidic and neutralisation reactions took place. Some of the calcium hydroxide that reacts with pozzolana could have reacted with the more concentrated acid thereby reducing the pozzolanic activity resulting in an overall strength loss. The strength increases for the other cements indicated that the leaching out reactions were confined to the surfaces such that the inner core continued gaining strength due to continued hydration. The low w/c ratios and the compaction method used must have produced too strong specimens for deep penetration by the ions.

(v) Sulphate solutions.

The results were consistent for both the lower and higher concentration solutions. SRPC was the best followed by OPC and PZC. In the lower concentration solutions there was an overall increase in strength. The observation indicated that the reaction was confined to the surface of the cubes. The reaction was the type Mehta (88) described as, 'a surface softening-spalling type of acidic sulphate attack which is associated with the conversion of calcium hydroxide to gypsum'. The formation of a small quantity of ettringite served as a reinforcing rather than a deleterious agent (89). The overall decline in the strengths for the solutions of higher concentration is most probably due to the combined effects of the acid neutralisation and sulphate attack. The performance of SRPC is in conformity with its superiority over the other cements in resisting the sulphate attack.

4.3.5.1.2 Summary of the cements' performance under compressive strength tests.

The symbol '>' means 'had higher compressive strength than' and therefore, 'was better than'.

Deionised water: SRPC>OPC>PZC

Waste water: SRPC>OPC>PZC

Lower fluoride concentration: OPC>PZC>SRPC

Higher fluoride concentration: OPC>PZC>SRPC

Lower chloride concentration: PZC>OPC>SRPC

Higher chloride concentration: OPC>SRPC>PZC

Lower sulphate concentration: SRPC>OPC>PZC

Higher sulphate concentration: SRPC>OPC>PZC

The summary shows that the results were consistent for solutions of the same ion except for the chloride solutions. Although the compressive strength is the ultimate variable of importance, it was given the same weight as the other tests because the results showed that the reactions were mainly confined to the surface. With less strong cubes or a longer exposure period, the test could have been taken to be more decisive.

4.3.5.2.1 Compressive strength changes comparing the sands.

The results are shown in table 4.18.

(i) Deionised water.

Machakos sand performed better with OPC and PZC than Kajiado sand which was however found to be better with SRPC. The results showed that cubes made with Kajiado sand were more adversely affected by the deionised water than those made with Machakos sand. Kajiado sand had a higher silt content than the Machakos sand and because dissolution and leaching was dorminant, the silt must have introduced channels through which the water permeated and facilitated further leaching.

(ii) Waste water solutions.

Cubes made with Kajiado sand were found to be better than those made with Machakos sand for all the cubes tested. The water had many ions that could have attacked the cubes. Resistance to the attack would depend on the sand/cement bond and so the results showed that Kajiado sand formed stronger bonds than Machakos sand. The 'bulking' effect of cubes made with Machakos sand must have resulted in relatively weaker bonds and this could have been the main reason for the observations made. The

Table 4.18: Percent compressive strength changes of the cubes holding cements constant to compare the sands.

Cement held constant / Sand / Solution medium	OPC		SRPC		PZC	
	KJD	MKS	KJD	MKS	KJD	MKS
Deionised water	-2.22	1.88	-4.53	-11.3	-16.5	-8.81
Waste water	7.54	5.63	0.885	-1.16	6.90	-3.76
Lower fluoride concentration	6.65	4.39	13.2	0.305	13.60	12.8
Higher fluoride concentration	13.5	12.6	3.10	5.42	12.5	11.9
Lower chloride concentration	9.86	6.67	-5.29	3.63	-0.0823	5.71
Higher chloride concentration	-0.218	-3.74	-1.20	-6.26	-4.64	-7.35
Lower sulphate concentration	-0.475	3.41	4.88	4.73	7.11	4.96
Higher sulphate concentration	-1.03	2.78	-5.06	1.59	-6.27	-2.14

cubes made with Machakos sand were found to have gained strength only with OPC. The fluoride ions must have been responsible for the observed increase in strength as has been discussed earlier.

(iii) Fluoride solutions.

It was observed that the cubes made with both the sands gained strength. This was because the reaction products of the fluoride ions with the silicates sealed up the pores and hence allowed continued hydration which increased the strength. The presence of non silicate materials in Machakos sand, due to the richer mineral content, reduced the formation of the products. This could explain why the cubes made with Machakos sand had lower strength increases than those made with Kajiado sand.

(iv) Chloride solutions.

Some cubes were found to have gained strength in the lower chloride concentration solutions. The reactions between the ions and the cubes must have taken place on the surface such that the hydration process continued in the interior of the cubes resulting in higher compressive strengths. This behaviour was observed for all the cubes made with Machakos sand while for Kajiado sand it was only observed with OPC.

In the higher concentration solutions, a decrease in the compressive strengths was observed in all cases. The deleterious reactions had therefore penetrated the cubes thereby weakening them. Kajiado sand was better than the Machakos one in all the cements. The bulking effect of the Machakos sand must have been responsible for the lower compressive strengths.

(v) Sulphate solutions.

In the lower sulphate concentration solutions an overall strength increase was observed except for the cubes made with Kajiado sand and OPC. The observation indicated that the deleterious reactions were confined to the surface of the cube leaving the interior intact where the hydration process continued unaffected. The surface softening-spalling type of reaction discussed earlier was responsible.

In solutions of higher sulphate concentration, cubes made with Kajiado sand showed strength losses for all the cements. Cubes made with Machakos sand showed strength loss only with PZC but showed strength increases with OPC and SRPC. On the overall, Machakos sand was therefore better than Kajiado sand. The bulking effect of the cubes made with Machakos sand made the cubes to be relatively more porous such that the formation of expansive products, like ettringite, made the structures more compact. This would explain the strength increases observed.

4.3.5.2.2 Summary showing the best sand under compressive strength test.

Test solution medium	The best sand for the different cements		
	OPC	SRPC	PZC
Deionised water	Machakos	Kajiado	Machakos
Waste water	Kajiado	Kajiado	Kajiado
Lower fluoride concentration	Kajiado	Kajiado	Kajiado
Higher fluoride concentration	Kajiado	Machakos	Kajiado
Lower chloride concentration	Kajiado	Machakos	Kajiado
Higher chloride concentration	Kajiado	Kajiado	Kajiado
Lower sulphate concentration	Machakos	Kajiado	Kajiado
Higher sulphate concentration	Machakos	Machakos	Machakos

4.4 The summary of the effects of the test solutions on the cubes.

On the basis of the results the following reactions were proposed to have taken place. From these results, the performance of the different cements, different sands and their combination were assessed.

4.4.1 The effect of deionised water on the cubes.

The reactions between deionised water and the cubes resulted in dissolution, surface wear and leaching as evidenced by pH, ion exchange and volume changes. One of the most leached out cation was calcium. This was basically as a result of dissolution of lime formed during the hydration process.

$$Ca(OH)_{s(s)} + H_2O_{(aq)} \longrightarrow Ca^{2+}_{(aq)} + OH^-_{(aq)}$$

solubility $(ca(OH)_2) = 1.7g/l$

The dissolution exposed more hydration products which broke down by hydrolysis to maintain the equilibrium each time fresh water samples were put in the dessicators (48). The process must have not only increased the porosity of the cubes, but also surface wear and hence volume decreases.

The combinations that performed the best under the various tests were:

Test	Combination in order of performance	
Volume changes:	PZC/KJD;	OPC/MKS
Cation leaching:	OPC/MKS;	PZC/KJD
Compressive strength:	SRPC/KJD;	OPC/MKS

On the overall, OPC and Machakos sand were therefore found to be the best cement and sand respectively. OPC with Machakos sand would therefore be recommended for making concrete structures exposed to rain water.

4.4.2 Waste waters.

From the pH changes, it was concluded that there was little base dissolution from the cubes. Cations and anions were taken up by the cubes, but from the volume test, only PZC cubes showed expansion. Many reactions were involved and calcium ions from calcium compounds, which formed the bulk of the cement component of the cubes, reacted as follows:

$$Ca^{2+}{}_{(aq)} + SO_4^{2-}(aq) \longrightarrow CaSO_{4(ppt)}$$

$$Ca^{2+}_{(aq)} + 2F^{-}_{(aq)} \longrightarrow CaF_{2(s)}$$

$$Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \longrightarrow CaCl_{2(aq)}$$

The calcium sulphate produced must have proceeded with some or all of the following processes:

(i) falling as a precipitate at the bottom of the dessicators and leaving more exposed sites for further reactions;

(ii) closing the pores on the surface of the cubes thus offering protection;

(iii) reacting further with calcium aluminate hydrate to form ettringite.

The calcium chloride leached out leaving a more porous system, with exposed sites for further attack. Penetration of the chloride ions into the matrix of the cubes would result in the formation of complex salts such as Friedel's $[(3CaO.Al_2O_3Cl_2.SO_4).12H_2O]$.

The calcium fluoride formed would seal the pores on the cube surfaces and thus protect the cubes from further corrosion. Other fluoride reaction products with the silicates such as fluorosilicates would also seal the pores and form protective layers on the cubes.

The volume test indicated that precipitation and leaching dorminated the OPC and SRPC cubes, resulting in volume decreases. Ettringite formation which could take place on the OPC cubes was either minimal or the expansive effect was reduced by the processes just cited. The OPC cubes were however found to have taken up more fluoride ions than the others and so the calcium fluoride and fluorosilicates must have protected the cubes considerably from severe sulphate attack. The relatively higher volumes of the OPC cubes than that of the SRPC however, indicated that ettringite formation took place albeit in a small way.

The slight expansion exhibited by the PZC cubes was due to the pozzolana reacting with the various anions that had diffused into the cube matrix. The pozzolana grains initially offered channels through which the ions passed.

The best combinations for the different tests were:

Test		Best cement/sand combination
Volume		PZC/KJD
anionic uptake	(1. Fluoride:	OPC/MKS
	(2. Chloride:	PZC/KJD
	(3. Sulphate:	PZC/MKS
cationic leaching:		SRPC/MKS
compressive strength:		SRPC/KJD

On the overall, PZC with Kajiado or Machakos sand would be recommended for such or similar environments.

4.4.3 Fluoride solutions.

It has been observed in this work that the cubes that were immersed in fluoride solutions were better off at the end of the investigation than those immersed in the other solutions. This was amply shown by compressive strength tests, especially when comparing the sands (table 4.18). The results indicated that fluorides in form of hydrofluoric acid can be used to protect or strengthen concrete. Further research should be carried out to determine the nature of the phenomena and the various ways in which the acid can be applied.

The reaction between hydrofluoric acid and silica has been shown to proceed as follows (90,91):

$$SiO_{2(s)} + 4HF_{(aq)} \longrightarrow SiF_{4(g)} + 2H_2O_{(aq)}$$

If the silicon tetrafluoride gas is not allowed to escape freely, the following reactions take place.

$$SiF_{4(g)} + 2HF_{(aq)} \longrightarrow H_2SiF_{6(aq)}$$

The fluorosilicic acid could then react with any base or other compounds in the cubes forming among other salts fluorosilicates (fluates) which are reportedly (83,84,92) used in the building industry as waterproofing compounds and for protecting concrete against corrosive attack. An example of such a reaction would be:

$$Ca(OH)_{2(s)} + H_2SiF_{6(aq)} \longrightarrow CaSiF_{6(s)} + 2H_2O_{(aq)}$$

The silicon tetrafluoride gas could react directly with the cubes like it does in the 'Ocrate' or silicofluorination process forming a coating of hydrated silica and alumina, along with calcium fluoride which resists many aggressive agents. The process ('Ocrate') is actually used to treat sewer pipes and concrete exposed to aggressive industrial conditions in Holland, Germany, Australia and the U.S.A. (47,83).

The silicofluorination process has been shown to double acid resistance and to increase concrete resistance to other chemical attack upto ten-fold for shale-sand concrete (93). Of the fluorosilicates, an aqueous 50-70% sodium fluorosilicate suspension has been used as a hardening initiator to increase the mechanical strength and homogeneity of concrete in the production of acid resistant concrete (60).

The combinations that gave the best results were:

Test	Lower fluoride concentration	Higher fluoride concentration
volume	SRPC/KJD	SRPC/MKS
anionic uptake	OPC/MKS	OPC/KJD
cationic leaching	OPC/MKS	OPC/MKS
compressive strength	OPC/KJD	OPC/KJD

On the overall therefore, OPC with either of the sands would be recommended for such fluoride environments.

4.4.4 Chloride solutions.

Leaching out reactions were predorminant as shown by pH, volume and cation leaching tests. One of the major reactions that resulted in the leaching of calcium ions is:

$$Ca(OH)_{2(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + 2H_2O_{(aq)}$$

Other reactions such as the formation of Friedel's salt ($3CaO.Al_2O_3Cl_2.SO_4).12H_2O$) are possible (85).

The combinations that gave the most resistance to the attack under the different tests were:

Test	Lower chloride concentration	Higher chloride concentration
volume	PZC/KJD	PZC/KJD
anionic uptake	PZC/KJD	PZC/KJD
cationic leaching	OPC/KJD	PZC/MKS
compressive strength	PZC/MKS	OPC/KJD

On the overall therefore, PZC with Kajiado sand would be recommended for chloride environments.

4.4.5 Sulphate solutions.

The pH changes showed that base dissolution and leaching took place. In the lower sulphate concentration solutions, the cubes showed a reduction in volume while they expanded in the higher concentration solutions. The main reactions that must have taken place are:

(i) $Ca(OH)_{2(s)} + H_2SO_{4(aq)} \longrightarrow CaSO_{4(s)} + 2H_2O_{(l)}$

(ii) $3CaO.Al_2O_3.6H_2O_{(s)} + 3CaSO_{4(aq)} + 26H_2O \longrightarrow$

$3CaO.Al_2O_3.3CaSO_4.32H_2O_{(s)}$

Calcium sulphate precipitates more due to the presence of lime, and its deposition on the surface of the cube protected the cubes in the lower concentration solutions as indicated by the compressive strength increases. Accumulation of the precipitate and perturbation during volume measurements however, resulted in falling of the precipitate in the solution leaving exposed surfaces. The process therefore continued as the sulphates were replenished and hence caused volume reductions.

In the higher sulphate concentration solutions, the ettringite forming reaction must have dorminated as indicated by the high degree of expansion. Lower compressive strengths were recorded and so, the ettringite must have disrupted the inner matrix of the cube.

The combinations that gave the best results under the different tests were found to be:

Test	Lower sulphate concentration	Higher sulphate concentration
volume	SRPC/KJD	PZC/MKS
anionic uptake	PZC/KJD	PZC/KJD
cationic leaching	OPC/KJD	SRPC/MKS
compressive strength	SRPC/KJD	SRPC/MKS

On the overall, SRPC with Kajiado sand would be recommended in such sulphate environments.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

From the results of this work, the following conclusions and recommendations were made:

5.1 Conclusions.

1. Sand from Machakos district had less silt and was more fine than that from Kajiado district.
2. The sand from Machakos district was richer in mineral content than that from Kajiado district.
3. The sand from Machakos formed unworkable mixes with cements when a w/c ratio of 0.4 was used, and showed a "bulking" effect when a w/c ratio of 0.5 was used.
4. Both the Machakos and Kajiado district sands, under test, are not suitable materials for testing cement(s).
5. SRPC may not be the best cement to use in factory waste waters containing a combination of ions, such as sulphates, chlorides, fluorides etc.
6. The fluoride solutions were not deleterious to the cubes made with the cements investigated.

7. The action of deionised water on the cubes resulted in dissolution, leaching and surface near.
8. The action of chloride solutions on the cubes produced mainly soluble salts which leached out of the cubes.
9. In the lower sulphate concentration solutions, reactions took place mostly on the surface of the cubes forming mainly precipitates.
10. In the higher sulphate concentration solutions, expansive products were formed.
11. The "bulking" effect of the Machakos sand was found to be beneficial in sulphate environments whose reaction with the cubes formed expansive products.
12. PZC is superior to OPC and SRPC in resisting attack from chlorides, and solutions with a combination of many ions such as the factory waste waters.
13. In sulphate solutions, SRPC and to a lesser degree PZC are superior to OPC in resisting sulphate attack.
14. On the overall, most of the reactions between the cubes and the solutions took place on the surface of the cubes.

15. The low w/c ratios and the compaction method used produced strong specimens which resisted extensive deleterious reactions within them in the six month period of investigation.

The cement-sand combinations which were found most suitable for the different media are summarised in table 5.1.

Table 5.1: The best cement-sand combinations for the media investigated.

Medium	Cement	Sand
Deionised water	OPC	MKS
Waste waters	PZC	KJD or MKS
Fluoride solutions	OPC	KJD or MKS
Chloride solutions	PZC	KJD
Sulphate solutions	SRPC	KJD

5.2 Recommendations.

1. Sand samples from other parts of the country should be investigated in order to determine their suitability for testing cements.
2. Before making concrete structures for environments rich in sulphates, chlorides, fluorides,

etc. such as those found in some factory waste waters, a careful study should be carried out to determine the most suitable cement.

3. Further research should be carried out to determine the effect of the fluoride ions and hydrofluoric acid on cements, sands and concrete products, and if the reactions can be used to protect the products against chemical attack.

4. Further research on the effect of ions on mortar or similar cubes should be done with weaker more porous cubes. This can be achieved by using a higher w/c ratio. A longer investigation period would also be recommended in order to get results of a longer duration.

5. The cement-sand combinations given in table 5.1 would be recommended for use in environments similar to those investigated.

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APPENDIX 1

Computer programme for A.A.S. data analysis(by A.R. Tindimubona)

```
 5 CLEAR
 10 DIM X0(100),Y0(100)
 20 PRINT "This program will require you to enter your data item by item."'"",
"When it is ready for you to enter a number it will type a '?'"'"follow this by
the value of your item and then depress the button,"
 30 PRINT "on the right, labelled RETURN."
 40 PRINT
 50 PRINT "Where your values are x,y pairs, enter the x-value followed by a co
mma"'"then the y-value followed a depression of the RETURN key."
 60 PRINT
 70 PRINT
 80 TIME = 0
 90 IF TIME > 500 GOTO 120
100 GOTO 90
120 PRINT "LINEAR REGRESSION"
130 PRINT
140 PRINT "NUMBER OF KNOWN POINTS"
150 INPUT N
160 REM - LOOP TO ENTER COORDINATES OF POINTS
170 FOR I=1 TO N
180 PRINT "X,Y OF POINT";I;
190 INPUT X,Y
200 X0(I)=X
210 Y0(I)=Y
220 REM - ACCUMULATE INTERMEDIATE SUMS
230 J=J+X
240 K=K+Y
>
```

APPENDIX 1 (CON'D)

```
250 L=L+X^2
260 M=M+Y^2
270 R2=R2+X*Y
280 NEXT I
290 REM - COMPUTE CURVE COEFFICIENT
295 B=R2/L
296 A=0
300 REM B=(N*R2-K*J)/(N*L-J^2)
310 REM A=(K-B*J)/N
320 PRINT
330 PRINT "For the equation:    y = a + bx"
340 PRINT
350 PRINT "a = ";A;
360 PRINT "b = ";B;
370 REM - COMPUTE REGRESSION ANALYSIS
380 J=B*(R2-J*K/N)
390 M=M-K^2/N
400 K=M-J
410 PRINT
420 R2=J/M
430 PRINT "COEFFICIENT OF ";
440 PRINT "DETERMINATION";
450 PRINT "(R^2)= ";R2
460 PRINT
470 PRINT "COEFFICIENT OF ";
480 PRINT "CORRELATION=";SQR(R2)
490 PRINT
500 PRINT "STANDARD ERROR OF ESTIMATE=";
510REM PRINT SQR(K/(N-2))
520 PRINT
530 PRINT "DO YOU REQUIRE A GRAPHICAL PLOT OF YOUR DATA AND FITTED LINE?"
>
```

APPENDIX 1 (CONT'D)

```
LIST540 540,820
  540 PRINT "TYPE Y FOR YES AND N FOR NO";
  550 ANS$=INKEY$(10000)
  560 IF ANS$ = "Y" GOSUB 810
  580 REM - ESTIMATE Y-COORDINATES OF POINTS WITH ENTERED X-COORDINATES
  590 PRINT "INTERPOLATION: ";
  600 PRINT "(ENTER X=0 TO END)"
  610 PRINT "X =";
  620 INPUT X
  630 REM - RESTART OR END PROGRAM? USER INPUT REQUIRED
  640 IF X=0 THEN 680
  650 PRINT "Y =";A+B*X
  660 PRINT
  670 GOTO 610
  680 PRINT "DO YOU WISH TO ENTER ANOTHER SET OF DATA (Y or N)?"
  690 ANS$=INKEY$(10000)
  700 IF ANS$="Y" GOTO 5
  710 PRINT "DO YOU WISH TO USE A DIFFERENT STATS PROGRAM (Y or N)?"
  720 ANSW$ = INKEY$(10000)
  730 IF ANSW$="Y" CHAIN "S.PROGS"
  740 MODE 1
  750 PRINT
  760 PRINT "Now exiting to BASIC"
  770 PRINT "If you have finished, please"'"remove the stats disk and"
  780 PRINT "switch off the computer."
  800 GOTO 1100
  810 MODE 2
  820 XMAX = 0
 >
```

APPENDIX 1 (CONT'D)

```
830 YMAX = 0
840 FOR I = 1 TO N
850 IF X0(I) > XMAX THEN XMAX = X0(I)
860 IF Y0(I) > YMAX THEN YMAX = Y0(I)
870 NEXT I
880 XFACT = 1000/(XMAX)
890 YFACT = 800/(YMAX)
900 XMAX0 = XMAX*XFACT
910 YMAX0 = YMAX*YFACT
920 GCOL 0,1
930 MOVE 0,0
940 DRAW 0,YMAX0
950 MOVE 0,0
960 DRAW XMAX0,0
970 MOVE 0,A*YFACT
980 GCOL 0,3
990 DRAW XMAX*XFACT,A*YFACT+B*XMAX*YFACT
1000 FOR I=1 TO N
1010 GCOL 0,4
1020 PLOT 69,X0(I)*XFACT,Y0(I)*YFACT
1030 NEXT I
1040 PRINT TAB(20)"y = ";A;" + ";B;"x"
1045 PRINT
1050 PRINT "Type C to continue"
1060 ANS$=INKEY$(10000)
1070 IF ANS$ <> "C" GOTO 1050
1080 MODE 4
1090 RETURN
1100 END
1110 FOR I = 1 TO N
```

APPENDIX 2: PERCENT VOLUME CHANGES DATA (FOR FIGURES 4.1-4.8)

DAY	OPC	SRPC	PZC
1	0	0	0
4	0	0	0
9	0	-0.281	0.141
16	7.05E-2	-0.281	0.141
24	7E-2	-0.281	0.141
32	7.05E-2	-0.281	0
38	0	-0.352	0
48	0	-0.352	0
55	0	-0.352	0
63	7.05E-2	-0.281	0
75	-7.05E-2	-0.281	0
82	-7.05E-2	-0.352	0
89	-7.05E-2	-0.422	0
99	-0.141	-0.492	0
106	-0.141	-0.492	-7.05E-2
113	-0.141	-0.492	-7.05E-2
119	-0.211	-0.49	-7.05E-2
132	-0.211	-0.492	-0.282
139	-0.211	-0.492	-0.282
146	-0.211	-0.492	-0.211
161	-0.211	-0.422	-0.211
167	-0.211	-0.492	-0.211
174	-0.211	-0.492	-0.211
184	-0.246	-0.492	-0.211

Volume changes in deionised water.

DAY	OPC	SRPC	PZC
1	0	0	0
4	0	0	0.141
9	-0.225	-0.351	0.353
16	-0.225	-0.492	0.141
24	-1.42E-2	-0.492	0.141
32	-1.42E-2	-0.281	0.141
38	5.62E-2	-0.211	0.212
48	-1.42E-2	-0.281	0.212
55	-8.46E-2	-0.281	0.283
63	-8.46E-2	-0.281	0.141
75	-1.42E-2	-0.281	7.07E-2
82	-1.42E-2	-0.281	0
89	-0.155	-0.281	0
99	-0.155	-0.422	7.07E-2
106	-0.296	-0.492	7.07E-2
113	-0.296	-0.492	7.07E-2
119	-0.296	-0.632	7.07E-2
132	-0.296	-0.562	0
139	-0.296	-0.562	0
146	-0.225	-0.562	7.07E-2
161	-0.225	-0.632	7.07E-2
167	-0.225	-0.632	0
174	-0.296	-0.492	-7.07E-2
184	-0.261	-0.492	-3.52E-2

Volume changes in waste waters.

Volume changes (%) of the cubes in:

(i) Lower fluoride concentration solutions.

DAY	OPC	SRPC	PZC
1	0	0	0
4	0	0	0
9	-7.05E-2	-7.05E-2	-7.04E-2
16	-0.211	-7.05E-2	-0.141
24	-0.211	-7.05E-2	-0.352
32	-0.141	-7.05E-2	-0.422
38	-0.141	-7.05E-2	-0.422
48	-0.141	-7.05E-2	-0.422
55	-0.141	0.141	-0.422
63	-0.211	0.211	-0.281
75	-0.211	0.141	-0.281
82	-0.211	7.04E-2	-0.211
89	-0.282	0	-0.211
99	-0.211	7.04E-2	-0.211
106	-0.211	0	-0.211
113	-0.211	0	-0.211
119	-0.211	0	-0.211
132	-0.211	0	-0.281
139	-0.211	0	-0.281
146	-0.211	-7.05E-2	-0.281
161	-0.211	-0.141	-0.281
167	-0.141	-0.141	-0.352
174	-0.282	-7.05E-2	-0.352
184	-0.212	-3.53E-2	-0.282

(ii) Higher fluoride concentration solutions.

DAY	OPC	SRPC	PZC
1	0	0	0
4	-0.141	0	0.212
9	-0.141	7.05E-2	0.212
16	-0.141	-0.14	0
24	-0.141	-0.14	0
32	-0.282	-0.14	7.04E-2
38	-0.211	-0.211	0.141
48	-0.211	-0.211	7.05E-2
55	-0.211	-0.211	0.141
63	-0.141	-0.211	0.141
75	-0.211	7.05E-2	0.141
82	-0.211	0	0.212
89	-0.352	0	0.141
99	-0.352	0	0.212
106	-0.352	-7.02E-2	0.212
113	-0.352	-7.02E-2	0.212
119	-0.141	-7.02E-2	0.282
132	-0.141	-7.02E-2	0.212
139	-0.141	-0.211	0.282
146	-0.211	-0.211	0.282
161	-0.352	-0.211	0.282
167	-0.422	-0.281	0.212
174	-0.422	-0.281	0.212
184	-0.422	-0.281	0.142

Volume changes (%) of the cubes in:

(i) Lower chloride concentration solutions.

DAY	OPC	SRPC	PZC
1	0	0	0
4	-0.281	0	0.141
9	-0.422	-0.281	0.141
16	-0.702	-0.281	0.141
24	-0.702	-0.281	-7.05E-2
32	-0.492	-0.422	-7.05E-2
38	-0.492	-0.281	-7.05E-2
48	-0.492	-0.281	0.141
55	-0.422	-0.281	0.141
63	-0.422	-0.352	0.141
75	-0.562	-0.352	-0.141
82	-0.562	-0.352	-0.141
89	-0.632	-7.04E-2	-0.141
99	-0.632	-0.352	-0.282
106	-0.632	-0.352	-0.282
113	-0.562	-0.422	-0.282
119	-0.562	-0.422	-0.282
132	-0.702	-0.422	-0.141
139	-0.702	-0.281	-7.05E-2
146	-0.702	-0.281	-0.141
161	-0.632	-0.422	-0.282
167	-0.632	-0.422	-0.282
174	-0.702	-0.422	-0.282
184	-0.702	-0.422	-0.317

(ii) Higher chloride concentration solutions.

DAY	OPC	SRPC	PZC
1	0	-9.4E-2	0
4	-0.352	-0.16433	0
9	-0.422	-0.21133	-0.211
16	-0.562	-0.23467	-0.141
24	-0.562	-0.21133	-0.352
32	-0.562	-0.28167	-0.211
38	-0.562	-0.21133	-0.211
48	-0.492	-0.28167	-0.141
55	-0.422	-0.28167	-0.141
63	-0.422	-0.37533	-0.281
75	-0.562	-0.37533	-0.281
82	-0.703	-0.39867	-0.352
89	-0.703	-0.37533	-0.352
99	-0.703	-0.39867	-0.352
106	-0.703	-0.37533	-0.281
113	-0.562	-0.305	-0.281
119	-0.562	-0.32833	-0.281
132	-0.773	-0.35167	-0.352
139	-0.773	-0.44533	-0.281
146	-0.773	-0.44533	-0.352
161	-0.773	-0.46867	-0.352
167	-0.773	-0.46867	-0.352
174	-0.773	-0.49233	-0.352
184	-0.788	-0.4925	-0.387

Volume changes % of the cubes in:

(i) Lower sulphate concentration solutions.

DAY	OPC	SRPC	PZC
1	0	0	0
4	-0.282	0	0
9	-0.282	-7.05E-2	-0.211
16	-0.282	0	7.04E-2
24	-0.282	0.141	-7.04E-2
32	-0.352	0.141	7.04E-2
38	-0.422	7.04E-2	-7.04E-2
48	-0.422	7.04E-2	-7.04E-2
55	-0.352	0.141	-7.04E-2
63	-0.352	0.141	-7.04E-2
75	-0.352	7.04E-2	-0.211
82	-0.352	7.04E-2	-0.211
89	-0.352	0	-0.211
99	-0.352	-7.05E-2	-0.211
106	-0.422	-7.05E-2	-0.141
113	-0.492	-7.05E-2	-0.211
119	-0.422	-0.211	-0.141
132	-0.492	-0.211	-0.211
139	-0.422	-0.141	-0.281
146	-0.563	-0.141	-0.281
161	-0.422	0	-0.281
167	-0.422	0	-0.281
174	-0.422	-0.141	-0.281
184	-0.528	-0.247	-0.352

(ii) Higher sulphate concentration solutions.

DAY	OPC	SRPC	PZC
1	0	0	0
4	0	-7.04E-2	-0.211
9	-0.211	-7.04E-2	-0.281
16	0.211	-7.04E-2	-0.281
24	0.282	0.353	0.282
32	0.494	0.353	0.282
38	0.423	0.353	0.282
48	0.494	0.424	0.352
55	0.494	0.636	0.492
63	0.706	0.636	0.423
75	0.706	0.636	0.492
82	0.706	0.707	0.493
89	0.919	0.849	0.635
99	0.919	0.849	0.705
106	0.919	0.849	0.705
113	0.989	0.778	0.705
119	0.989	0.849	0.705
132	0.989	0.778	0.705
139	0.848	0.707	0.705
146	0.777	0.707	0.776
161	0.848	0.778	0.776
167	0.919	0.778	0.776
174	0.919	0.778	0.705
184	0.949	0.743	0.67

APPENDIX 3

Ionic uptake (ppm/day) data (for Figures 4.9-4.17)

Fluoride ions uptake (ppm/day) in:

(i) waste waters.

DAY	OPC	SRPC	PZC
17	0.179	0.146	0.173
40	0.152	9.6E-2	0.152
67	0.174	0.107	0.137
92	4.8E-2	2.5E-2	3.3E-2
126	8E-3	-2E-3	0
184	4E-3	5E-3	4E-3

(ii) lower fluoride concentration solutions.

DAY	OPC	SRPC	PZC
17	0.391	0.472	0.482
40	4.161	5.979	5.469
67	4.161	5.979	5.49
92	4.332	5.724	5.469
126	4.332	4.221	4.303
184	3.29	3.24	3.397

(iii) higher fluoride concentration solutions.

DAY	OPC	SRPC	PZC
17	66.176	69.824	68
40	110.44	103.15	108.44
67	110.44	103.15	108.44
92	80.647	95.647	108.44
126	76	78.64	39.864
184	62.315	63.194	74.489

Chloride ions uptake (ppm/day) in:

(i) waste waters.

DAY	OPC	SRPC	PZC
17	1.835	2.118	2.118
40	4	2.13	3.261
67	4.222	3.778	3.148
92	4.4	1	0.48
126	1	0.147	-0.324
184	0.41	9E-2	-0.151

(ii) lower chloride concentration solutions.

DAY	OPC	SRPC	PZC
17	3.871	10.153	7.765
40	20.074	18.617	18.226
67	14.548	14.463	13.993
92	11.02	12.848	11.632
126	10.506	10.397	8.132
184	6.153	5.619	5.153

(iii) higher chloride concentration solutions.

DAY	OPC	SRPC	PZC
17	17.576	22.276	21.294
40	35.73	36.026	36.97
67	27.785	27.419	26.27
92	20.492	21.732	19.252
126	22.479	20.921	18.479
184	12.431	10.884	13.505

Sulphate ions uptake (ppm/day) in:

(i) waste waters.

DAY	OPC	SRPC	PZC
17	-1.824	1.824	-1.824
40	8.957	6.783	10.478
67	29.074	26.444	13.222
92	8.88	73.68	-10.8
126	-1.235	-1.235	-1.235
184	-0.724	0	0

(ii) lower sulphate concentration solutions.

DAY	OPC	SRPC	PZC
17	7	9.765	15.824
40	16.909	26	9.565
67	9.307	14.493	11.456
92	44.88	20.612	19.452
126	61.559	62.059	75.353
184	21.155	14.01	12.872

(iii) higher chloride concentration solutions.

DAY	OPC	SRPC	PZC
17	66.176	69.824	68
40	110.56	109.35	109.17
67	110.44	103.15	108.44
92	76	78.64	39.864
126	80.647	95.647	117.65
184	43.983	30.741	31.328