# "THE PRODUCTION
# OF
# SULPHATE-RESISTING AND MARINE CEMENTS
# FROM
# LOCAL RAW MATERIALS"

Submitted by:

Dennis Le Sar, B.Sc., M.S.A.Chem.I., F.R.I.C.,

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Dedicated to:

The Burners of De Hoek, who "suffered in the cause of Science."

# PREFACE

"It is not always sufficiently realised that nothing man can do is proof against the forces of nature. In other words, nothing which is man-made is permanent. Some works are slowly destroyed by the disintegrating forces of time and weather. Others are suddenly destroyed by natural phenomena such as earthquakes, tidal waves, and storms. The effect of time on common materials is well known, and an engineer cannot be excused for using a material which experience has shown to have a useful life of shorter duration than that required of the structure in which it is used" (1)

"Durability of concrete is defined as its resistance to deteriorating influences of internal and external factors to which it is exposed within the duration of life required of the structure" (2).

Some Roman structures have survived the ravages of time and weather to the extent that their "useful life" continues after 2,000 years of service. Some Portland cement structures, in corrosive environments, have disintegrated in less than 20 years.

Portland Cement caters to Mankind's modern craze for "speed". Roman Cement satisfied his age-old desire for "immortality". The Marine Cement described herein combines the best features of Portland and Roman cements, as another step towards the goal of "durability".

The last word has not been spoken, and the work goes on. Perfection is an unrealisable ideal, but must remain the goal. What has been achieved so far is the production of special cements which will help to 'lengthen the useful life of concretes' in conditions where 'experience' has shown ordinary cement to be unsatisfactory.

Footnotes.

(1) Quotation from Editorial Notes on "The Force of Waves", Concrete and Constructional Engineering, August 1947.

(2) Quotation from a discussion on the "Durability of Concrete in Service" by Zoldners & Malthora - ref. 20.4D.

# NOTES

The decimal system has been used for numbering chapters, sections, paragraphs, and sub-paragraphs. In order to save space, time, and typing, the paragraphs in each section are started simply with "1". When a paragraph or sub-paragraph is referred to within its own section, it is just designated "2" or "2.3", as the case may be. When referred to from a different section or chapter, paragraphs and sub-paragraphs are designated thus: paragraph 3.5-2, or 3.5-2.3, as the case may be.

References have also been numbered by decimals, to save specifying the titles of journals and periodicals in full each time. For example, all the "20.'s" refer to the "Journal of the American Concrete Institute". Within the text of the report, references to the literature are given in brackets solely as numbers, without qualification, thus : (20.19).

# LIST OF ABBREVIATIONS USED

$RCO_3$ = Calcium + Magnesium Carbonate.

LSF = Lime Saturation Value

LCF = "Combined-lime" Saturation Value

TDS = Total Dissolved Solids

OPC = Ordinary Portland Cement

RHC = Rapid Hardening Portland Cement

SRC = Sulphate Resisting Portland Cement

LHC = Low Heat Portland Cement

PBFC = Portland Blastfurnace Cement

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| NAMES OF COMPOUNDS | "STANDARD" SYMBOLS & FORMULAE | "SIMPLIFIED" SYMBOLS & FORMULAE |
|---|---|---|
| Silicon dioxide, Silica | $SiO_2$ | S |
| Calcium oxide, Lime | CaO | C |
| Aluminium oxide, Alumina | $Al_2O_3$ | A |
| Ferric oxide, Iron oxide | $Fe_2O_3$ | F |
| Magnesium oxide, Magnesia | MgO | M |
| Sulphur trioxide | $SO_3$ | $\bar{S}$ |
| Sodium oxide, Soda | $Na_2O$ | N |
| Potassium oxide, Potash | $K_2O$ | K |
| Hydrogen oxide, Water | $H_2O$ | H |

| NAMES OF COMPOUNDS | "STANDARD" SYMBOLS & FORMULAE | "SIMPLIFIED" SYMBOLS & FORMULAE |
|---|---|---|
| Calcium sulphate | $CaSO_4$ $(CaO.SO_3)$ | $C\bar{S}$ |
| Calcium sulphate di-hydrate, "Gypsum" | $CaSO_4.2H_2O$ | $C\bar{S}H_2$ |
| Tri-calcium silicate, Alite | $3CaO.SiO_2$ | $C_3S$ |
| Di-Calcium silicate, Belite | $2CaO.SiO_2$ | $C_2S$ |
| Tri-calcium aluminate | $3CaO.Al_2O_3$ | $C_3A$ |
| Tetra-calcium-alumino-ferrite, Celite | $4CaO.Al_2O_3.Fe_2O_3$ | $C_4AF$ |
| Di-calcium-ferrite | $2CaO.Fe_2O_3$ | $C_2F$ |
| Calcium hydroxide, Slaked lime | $Ca(OH)_2$ $(CaO.H_2O)$ | CH |
| Calcium silicate hydrate, Tobermorite | $3CaO.2SiO_2.3H_2O$ | $C_3S_2H_3$ |
| Calcium-tri-sulfo-aluminate, Ettringite | $3CaO.Al_2O_3.3CaSO_4.32H_2O$ | $C_3A.3C\bar{S}.H_{32}$ |
| Calcium-mono-sulfo-aluminate, Low-sulphate Calcium Aluminate | $3CaO.Al_2O_3.CaSO_4.12H_2O$ | $C_3A.C\bar{S}.H_{12}$ |
| Aluminate hydrate, Hydro-calumite | $3CaO.Al_2O_3.Ca(OH)_2.12H_2O$ | $C_3A.CH.H_{12}$ |
| Tri-calcium-aluminate hydrate | $3CaO.Al_2O_3.6H_2O$ | $C_3A.H_6$ |
| Calcium-ferrite hydrate | $3CaO.Fe_2O_3.6H_2O$ | $C_3F.H_6$ |
| Sodium Sulphate | $Na_2SO_4 = Na_2O.SO_3$ | $N\bar{S}$ |
| Sodium Hydroxide | $(2)\ NaOH = Na_2O.H_2O$ | NH |
| Aluminium Hydroxide | $(2)\ Al(OH)_3 = Al_2O_3.3H_2O$ | $AH_3$ |

# SUMMARY

Portland Cement has been in use for just over a hundred years, and has proved to be a first-class construction material when used in concrete and re-inforced concrete that is not exposed to abnormally aggressive conditions.

Sulphates (in solution) and marine environments, however, can play havoc with "ordinary" cement concretes, and oversea investigators have found that "special" cements are required to make concrete structures "durable" under the onslaughts of these "aggressors".

"Ordinary" Portland cement generally contains a fair proportion of the mineral tri-calcium-aluminate ( "$C_3A$"), and this is the constituent which is most susceptible to attack by sulphates. By altering the chemical composition of cement its $C_3A$ can be reduced to a safe minimum level, and this can be done by using particular raw materials in the proper proportions. The first part of this project is concerned with producing low-$C_3A$ cement from materials available locally.

Sea water contains sufficient sulphate in solution to attack ordinary Portland cement. In addition, it has sufficient Magnesium in solution to affect sulphate-resisting Portland cement, and the best defence found against this (so far) is to incorporate an active pozzolanic material in the cement. No naturally active pozzolan is available locally, and the second part of this paper deals with the activation of a local shale and its subsequent incorporation in a "Marine Cement".

The results of a series of tests have been reported, in the third part, as an indication that these special cements will be more resistant than ordinary Portland cement to the specified aggressive agents.

DLS/RC.

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# CHAPTER I

## HISTORICAL INTRODUCTION

### 1.1. ORIGINS OF CEMENTS.

1. The earliest known buildings and structures were made of stone blocks placed together without the aid of any adhesive material.

2. In some countries, particularly those with dry climates, mud was used as a building material and, in fact, is still used today by primitive peoples.

3. As civilization developed men probably found it convenient to use mud to fill up the interstices in their stone structures and thus progressed to building with blocks cemented together.

4. Calcined gypsum ("Plaster of Paris") was used as a cement by the Egyptians some 6,500 years ago. Calcined limestone does not appear to have been generally used until somewhat later, but it was well known to the ancient Greeks and Romans. Bogue and Czernin have suggested that these calcareous cements were probably discovered as a result of men making fires next to pieces of gypsum or limestone, which would become powdery, and then harden again after rain.

5. Gypsum cements are limited in usefulness because of their solubility in water. Hardened lime-mortars, which have been able to absorb carbon-dioxide, are water-resistant, but the best "hydraulic" cements known to the Ancients were mixtures of lime and materials now known as "Pozzolans".

6. References : 1.1, 2.1, 3.1, 4.1, 5.1.

1.2 Pozzolanic/....

## 1.2. POZZOLANIC CEMENTS.

1. Crushed potsherds were used in admixture with lime to produce a water-resistant mortar during the time of the Minoan Civilisation which flourished in Crete about 2,000 B.C.

2. Both the Greeks and the Romans knew that certain volcanic deposits, as well as powdered tiles and pottery, when finely ground and mixed with lime and sand, yielded strong mortars which were resistant to fresh and sea waters.

3. The Greeks used volcanic tuff from the island of Thera (now called Santorin), and this material (known as "Santorin Earth") still has a high reputation in Mediterranean countries. It is included in current Greek standard specifications for cement.

4. The most famous Roman material of this type was the volcanic tuff found near Naples. The best variety came from the neighbourhood of Pozzoli or Pozzuoli (in Latin "Puteoli"), and acquired the name of "Pozzolana" . This designation was ultimately extended to the whole class of minerals having similar properties.

5. The incorporation with limes of certain siliceous materials, both raw and processed, to improve their cementitious properties, has been practised in India from times "immemorial".

6. References : 1.1, 12.1, 17.1, 18.5 - 1, 18.5 -2.

1.3 The Middle/....

## 1.3. THE MIDDLE AGES.

1. The quality of building materials declined after Roman times, and from time to time Engineers have thought that the Roman builders possessed some "secret" process which was not handed down. Recent analyses and physical examinations of old mortars and concretes, however, have indicated that careful preparation of materials, thorough mixing and intensive ramming (compaction) were the essentials of this secret. Pliny, describing the construction of cisterns in about 70 A.D., wrote "the bottom and sides should be well-beaten with iron hammers" .

   The benefits of long-continued ramming were also known to the Indians who kept up the tamping of "concrete" for several hours until "on scooping a hole and filling it with water, this is not absorbed". In spite of numerous "re-discoveries" of this "secret" (including several times within the present century), it appears to remain a secret to many!

2. During the 9th, 10th and 11th centuries the art of making good cement was almost completely lost, the lime being used in the form of badly burnt lumps and without the addition of pozzolans. From about the 12th century onwards the quality improved again.

3. References : 1.1, 2.1.

## 1.4. JOHN SMEATON

1. In more recent times the most outstanding investigation was that carried out by John Smeaton before he erected the "new" Eddystone Lighthouse in 1757. He found that a "hydraulic" lime could be obtained only from a limestone which contained

a considerable/....

a considerable proportion of clayey matter, and that the incorporation of a Pozzolan produced an under-water cement of superior hardening properties. His use of a hydraulic lime seems to have been the first major advance made on the old Roman cements (paragraphs 1.2-2 and 1.2-4) for which "high-grade" limes were specified.

2. Thirty years after the lighthouse was completed (and still standing up well to wind and wave), Smeaton wrote a book about the building of it (see below). The following quotations illustrate some of his ideas, problems and difficulties: "In this respite from sea operations, I seriously began to to consider the great importance that it was likely to be to our work, to have a Cement the most perfect that was possible, to resist the extreme violence of the sea". (Nothing resinous or oily could be used, as they required dry surfaces). "It seemed that nothing in the way of Cement would answer our end, but what would adhere to a moist surface and become hard, without ever becoming completely dry. ...... for I plainly saw from the manner of working the moorstone (granite), already described, that not only much of the beauty and neatness of the work, but its real solidity too, would depend upon getting a Cement that would, in despite of water almost continually driven against it with every degree of violence, become of so firm a consistence in itself, and adhesion to the stone, that it should lie fair and flush in the joints, and so as to compose one even regular surface with the stone; and without needing hoops of iron or copper to surround the horizontal joints ............. I was so fortunate as to succeed in this part of the business entirely to my satisfaction ........ "

3. His ambition/....

3. His ambition to build a lighthouse so durable "that it would remain permanent through the ages" was not realised, however, as the structure was dismantled about 130 years later because its rock foundation had become insecure. The upper sections of the lighthouse were, however, rebuilt on the Hoe at Plymouth.

4. The "research" work done by Smeaton was, by modern standards, very primitive, and to some extent he was lucky in that the pozzolan which he ultimately selected for his cement (and which was only available as a result of purely fortuitous circumstances) had already been proved in Roman times. The effects have, however, been far-reaching as Portland Cement is virtually a "direct descendant" of Smeaton's Cement (see next paragraph) and may yet be of still greater significance as the generally superior qualities of Portland-Pozzolanic cements are only now coming to be accepted.

5. Smeaton wrote: "With regard to those balls that were kept constantly under water, they did not seem inclined to undergo any change in form, only to acquire hardness gradually, insomuch that I did not doubt but to make a cement that would equal the best merchantable Portland Stone in solidity and durability ....."

Davis comments on this remark: "The substitution of this new hydraulic cement for, or its resemblance to, Portland stone no doubt laid the origin of the name Portland cement, and this seems clearly due to Smeaton, but he patented neither the material nor the name".

6. References: 1.1, 2.1, 2.2, 5.1, 6.2, 6.4./ 17.2 & 9.1. (Smeaton, John : "A Narrative of the Building, and the method

of construction/.....

of construction, of Edystone Lighthouse, with stone" (1st Ed. 1791), 2nd Ed. 1813, Printed by T, Davidson (Lombard St., Whitefriars), for Longman, Hunt, Rees, Orme & Brown (Paternoster Row, London)...)

## 1.5. EARLY 19TH CENTURY.

1. L.J. Vicat, an eminent French engineer, co-ordinated the fragmentary chemical knowledge that had been obtained up to 1818, and he emphasized what had been stated (though not practised) by Smeaton, namely, "that, in the absence of clay or shale occurring naturally in the rock, the same effect may be brought about by the artificial admixture of argillaceous rock with the limestone". He found, however, that the best way of preparing artificial hydraulic lime was "to mix clay in certain proportions with rich lime and calcine the mixture. This he called artificial lime twice kilned".

2. Joseph Aspdin is often credited with inventing Portland Cement, but his real claim to fame is that he was the first to patent the NAME "Portland Cement", in 1824. The method described in his patent, however, is virtually that used by Vicat for his "artificial lime twice kilned" and the name was, of course, originally suggested by Smeaton (paragraph 1.4-5) The good reputation acquired by Aspdin's cement, which later (about 1850) commanded a higher price than its competitors, has led to speculation that certain features of his manufacturing process were not revealed - a belief encouraged by Aspdin (and afterwards by his son) who used to go alone into the kiln to scatter some "secret" materials over the

dried slurry /.....

dried slurry and coke mixture. The temperature of the final burning remains doubtful, although the general belief is that it was not substantially above ordinary lime-burning temperatures. In this case the superior quality of his cement could be due to the thorough mixing of the lime and "artificial pozzolan" which must have been produced in the kiln, and also, possibly, to "low-temperature" (800 - 1100$^{\circ}$C) reactions, now known to take place between lime and argillaceous material. On the other hand, it was suggested by Reid, in 1877, that Aspdin's kiln, because of its design, may have given him much higher temperatures (1200-1300$^{\circ}$C). Probably the truth lies between the two extremes as, in fact, is suggested by Aspdin himself, where, in a letter to G.R. Redgrave, he says he made his cement from a mixture of "tender and hardburned clinker". Certainly during the 1850's, when William Aspdin was running the cement works there must have been a fair proportion of hardburned clinker as the cement set hard quickly.

3. References: 1.1, 2.1, 5.1, 6.2.

## 1.6. PORTLAND CEMENT.

1. I.C.Johnson, Manager of a Works producing Roman Cement, Keene's Plaster and Frost's Cement, started about 1845 to try and copy "Portland Cement". He was, at first, badly misled, because the "celebrated analyst", to whom he took a sample of Aspdin's cement, reported sixty per cent phosphate of lime. Ultimately, however, after experimenting on his own, he discovered the correct raw materials to use, but accidentally clinkered some of the mix. Finding that this

gave him/.....

gave him an even better cement he experimented further and ultimately arrived at a formula consisting of 5 parts of chalk with 2 parts of Medway clay. Johnson, who died in 1911 (his 101st year) claimed to be the real inventor of Portland cement (as at present understood) and this claim was supported by the eminent German chemist, Michaelis, in 1905. Davis states, however, that this claim has not been acknowledged.

2. In America the development of Portland Cement appears to have been influenced largely by the widespread occurrence of "natural cement rock". In 1818 Canvas White took out a patent for the manufacture of natural cement. This patent was later sold to the State of New York. Manufacturing restrictions were then removed and the natural cement industry expanded rapidly, largely on account of the demand for hydraulic cement for canals. Being burned at comparatively low temperatures this "natural cement" was, in point of fact, really "hydraulic lime". From about 1865 America began to import Portland Cement for its "superior" qualities. Then David Saylor, who had been making natural cement since 1850, found by analysis that Portland cement had a similar composition. After further experimentation he discovered that he could make an excellent Portland type cement by burning his rock to sintering temperature and grinding the clinker. Saylor took out a patent for the "new" cement in 1871. By 1890 there were seventeen plants producing this type of cement in the U.S.A.

3. The invention of the Rotary kiln (1877), which was developed and improved upon rapidly in England and America,

gave a terrific fillip to the production of Portland cement and resulted in considerable improvements in uniformity and quality.

4. References: 1.1, 2.1, 5.1, 6.2, 7.6.

# CHAPTER II

# THE PROBLEM

## 2.1. DURABILITY AND PERMANENCE.

1. After sheer "survival", Man's greatest ambition, both individually and nationally, seems to be to achieve "immortality". All Ages and all Nations leave their "monuments to posterity". Some of these are useful, others merely a source of wonder. The achievement of immortality, by this means, depends largely on the "durability" of the building materials used.

2. The most permanent man-made structures ever erected are almost undoubtedly the Pyramids of Egypt. Built of massive blocks of sandstone cemented together with a gypsum plaster, sheer bulk and a dry climate have been major factors in their six and a half centuries of existence.

3. The Romans were pioneers in the use of a semi-fluid, or "plastic", building material which could be moulded to the desired shape and then left to harden. This early "concrete" consisted of a mixture of hydrated lime, a pozzolan, water, sand and various coarse aggregates - including broken stone. These lime-pozzolan mortars and concretes have 2,000 years of proven durability. Roman monuments, bridges, arches and aqueducts bear witness to this. Maritime works, such as those built by Trojan at Ancona and at Civita-vecchia, which are still in use today, stand as a tribute to their "permanence".

4. Concrete and steel are the most important and widely used structural materials in South A frica. Used together, as "reinforced concrete", they may be considered THE structural

material of our Century. Portland cement has been in use for only 100 years and reinforced concrete for little more than half that period.

5. Rock is proverbially the most durable of building materials but even rocks are subject to the disruptive effects of "weathering" and different rocks have different degrees of durability. Water penetrates through cracks, crevices and capillary passages. Soluble salts are leached out, enlarging the passages and weakening the rock. Sometimes salts in the water react with rocky constituents to produce other salts, which may crystallise, expand and so crack open the rock. In cold climates similar disruption is caused by water freezing in the passages. It is obvious, therefore, that other things being equal, the least permeable rocks will be the most durable.

6. Concrete is artificial rock and is subject to the same type of attack and disruption as described above. Other things being equal, the more impermeable a concrete, the more durable it is. Where conditions are favourable for attack, soluble salts may be leached out and other constituents may be attacked by salts in solution.

7. In the early years of this Century it was the general opinion that "the durability of concrete (made with Portland cement) was, by and large, unlimited", and the American Portland Cement Association chose as their slogan "Concrete for Permanence" (20.1) Research was aimed mainly at improving strengths, but some unexpected and costly "failures" provided a rude awakening. It was slowly realised that Portland cement had some hitherto unsuspected weaknesses,

and that/.................

and that "durability had to be regarded as a separate characteristic of as great importance as the strength" (Jessing - 11.3). With the "special" cements now available, and the greatly increased knowledge of aggregates and of aggresive agents and conditions, there is little excuse these days for a concrete structure not giving the service expected from it, but "Permanence" remains the goal for which to strive.

8. References : 1.1, 1.6, 1.7, 2.1, 3.1, 3.3, 4.1, 7.10, 11.3, 20.1

## 2.2. CORROSION IN GENERAL.

1. Corrosion of concrete is generally due to the cumulative effect of several factors. In some instances, such as "rapid" failures due to alkali-aggregate reaction, there may be only one main cause, with comparatively minor effects from things like weathering and rusting of reinforement. Cases of "slow" marine corrosion, on the other hand, may have several major causes, and often a multiplicity of secondary ones. The whole problem is, therefore, somewhat complicated, with apparently contradictory observations (and subsequent "arguments") all too frequent.

2. Moskvin (10.2) has listed three basic "types" of corrosion as an aid to investigating problems:

Type I : is illustrated by water with a low temporary (carbonate) hardness - concrete components are dissolved and carriedaway, particularly where seepage occurs;

Type II : where water contains chemical agents, such as acids, magnesium salts, etc., and

Type III: "low-soluble" salts in pores and voids, which crystallise and expand - exemplified by sulphate attack.

He points out that cases of marine corrosion may conform to one, two or all three types listed. For prevention of corrosion, however, as much knowledge and as full an understanding as possible of the various aggressive agents and their mode of attack is desirable.

3. The following list includes most of the aggressive agents and/or "susceptible conditions" recognised to date;

3.1. Sulphate attack, sometimes associated with "biological corrosion";

3.2. Magnesium - ions in solution (this must be considered quite apart from sulphate attack);

3.3. Leaching out of soluble constituents;

3.4. Rusting of reinforcing material;

3.5. "Permeability" - this is what I call a "susceptible condition", as it accelerates attack by aggressive agents. I have listed it here because it can be controlled, to some extent, by using cements with special ingredients;

3.6. Frost action or, rather, cycles of freezing and thawing;

3.7. Alkali-reactive aggregates;

3.8. Shrinking aggregates;

3.9. Acid attack; and

3.10. Other "man-made" industrial agents, effluents, etc., including ammonium-salts and sugar.

4. References/............

4. References : 1.10, 2.7, 3.3, 4.3, 5.2, 6.3, 6.4, 7.10, 8.4, 10.2, 11.1, 19.1, 20.1, 20.2, 20.4, 20.5, 20.7, etc.

## 2.3. CONSTITUTION AND HYDRATION OF PORTLAND CEMENT:

1. Knowledge of cement constituents and hydration products is an essential prerequisite to the understanding of the sulphate and other corrosive reactions which occur. No more than a brief outline is possible here and the whole subject is, in any case, continuously under review as new facts come to light and theories are modified.

2. "Ordinary" Portland cement clinker normally has four main constituents:-

tri-calcium-silicate : $3CaO.SiO_2$ or "$C_3S$"
di-calcium-silicate : $2CaO.SiO_2$ or "$C_2S$"
tri-calcium-aluminate : $3CaO.Al_2O$ or "$C_3A$"
tetra-calcium-alumina-ferrite : $4CaO.Al_2O_3.Fe_2O_3$ or "$C_4AF$"

There are also a number of "minor" constituents and, in fact, it is generally recognised that even the "major" compounds are not nearly as simple as portrayed above, but these formulae suffice for discussions of general principles. Portland Cement is made by intergrinding such clinker with about 3 - 6% calcium-sulphate, usually in the form of $CaSO_4.2H_2O$ (gypsum).

3. There is reasonable agreement that hydration of the calcium silicates can be represented approximately by the equations:-

(1) 2 (3 $CaO.SiO_2$) /.........

(1) $2\,(3\,CaO.SiO_2) + 6\,H_2O = 3\,CaO.2\,SiO_2.3\,H_2O + 3\,Ca(OH)_2$

or

$2\,C_3S + 6\,H = C_3S_2H_3 + 3\,C\,H$

and

(2) $2\,(2\,CaO.SiO_2) + 4\,H_2O = 3\,CaO.2\,SiO_2.3\,H_2O + Ca\,(OH)_2$

or

$2\,C_2S + 4\,H = C_3S_2H_3 + C\,H$

$3\,CaO.2\,SiO_2.3H_2O$ ($C_3S_2H_3$) is similar to the natural mineral "Tobermorite" and a whole series of "tobermorite-like" hydrates have been prepared. It is noteworthy that there is a fair amount of "free" Calcium hydroxide liberated during the hydration of the calcium silicates.

4. The hydration mechanisms of tri-calcium-aluminate are rather more complicated and still the subject of much controversy. Conditions of hydration (particularly temperature-which may vary from just above freezing to "autoclave-temperatures" ) have considerable influence on the end product. There is evidence, however, that under "normal" concreting conditions, the following products may be found in hydrated Portland cements:-

4.1 Calcium-tri-sulpho-aluminate or Ettringite :

$3\,CaO.Al_2O_3.3\,CaSO_4.32\,H_2O$, or $C_3A.3\,C\,\bar{S}.\,H_{32}$

This is formed during setting and hardening by the interaction of tri-calcium-aluminate and calcium-sulphate, thus:

$$3\,CaO.Al_2O_3 + 3\,CaSO_4.2H_2O + 26\,H_2O = 3\,CaO.Al_2O_3.3\,CaSO_4\,32\,H_2O$$

or

$$C_3A + 3\,C\,\bar{S}.H_2 + 26\,H = C_3\,A.3C\bar{S}.\,H_{32}$$

**Notes:** 1. There is normally only sufficient $CaSO_4$ to react with about ¼ to ½ the $C_3A$.

2. Eitel (20.3) considers Ettringite to be only

"meta-stable" in/.......

"meta-stable in the hydration of Portland cement.

3. There is general agreement that Ettringite is also formed when hardened cement pastes are "attacked" by sulphates.

4.2. Calcium-mono-sulpho-aluminate, or "low-sulphate-aluminate"

$3\ CaO.Al_2O_3.\ CaSO_4.\ 12\ H_2O$ or $C_3A.\ C\ \bar{S}.\ H_{12}$.

This salt was unknown before 1929. It appears to be formed, to some extent, during the setting and hardening of cements. Bogue maintains that it is not stable in the presence of ettringite nuclei. Eitel (20.3) considers the reaction

"$3\ CaO.Al_2O_3.CaSO_4.12\ H_2O + 2\ CaSO_4$ = ettringite"

to be completely reversible.

4.3. Aluminate hydrate, or hydro-calumite:

$3\ CaO.Al_2O_3.\ Ca\ (OH)_2.12\ H_2O$ or $C_3A.CH.H_{12}$

This salt is isomorphous with the "low-sulphate" aluminate and forms crystalline solutions with it. The formula is sometimes written:

$4\ CaO.Al_2O_3.\ 13\ H_2O$ or $C_4A.H_{13}$

It is generally considered to be only meta stable.

4.4. Recent research has indicated the existence of a whole series of solid solutions:

$3\ CaO.Al_2O_3.3\ Ca(OH)_2.nH_2O = 3\ CaO.Al_2O_3.3\ CaSO_4.32\ H_2O$

" "

$3\ CaO.Al_2O_3.Ca(OH)_2.12\ H_2O = 3\ CaO.Al_2O_3.CaSO_4.12\ H_2O$

"

$3\ CaO.Al_2O_3.\ 12\ H_2O$

or

$C_3A.\ 3\ C\ H.\ H_n = C_3A.\ 3\ C\ \bar{S}.\ H_{32}$

" "

$C_3A.\ C\ H.\ H_{12} = C_3A.\ C\ \bar{S}.\ H_{12}$

"

$C_3A.\ H_{12}$

4.5. Several/.......

4.5. Several writers, including Czernin (4.3), consider the salt $3\ CaO.Al_2O_3.6\ H_2O$ ($C_3\ A\ H_6$) to be the final, stable, end-product of the hydration of tri-calcium-aluminate. It may be the result of intermediate reactions such as:-

(1)a. $3\ CaO.Al_2O_3 + 9\ H_2O = 2\ CaO.Al_2O_3.8H_2O + \underline{Ca(OH)_2}$

b. $3\ CaO.Al_2O_3 + \underline{Ca(OH)_2} + 18\ H_2O = 3\ CaO.Al_2O_3.Ca(OH)_2.18\ H_2O$

by "adding" these equations we get:

(2) $2\ (3\ CaO.Al_2O_3) + 27\ H_2O = 2\ CaO.Al_2O_3.8\ H_2O + 3\ CaO.Al_2O_3.Ca(OH)_2.18\ H_2O$

With "dehydration" these products may react further:

(3) $2\ CaO.Al_2O_3.8H_2O + 3\ CaO.Al_2O_3.Ca(OH)_2.18H_2O - 15\ H_2O = 2\ (3\ CaO.Al_2O_3.6H_2O)$

In "simplified" symbols, the above becomes:

$$C_3A + 9\ H = C_2\ AH_8 + \underline{CH}$$

$$C_3A + \underline{CH} + 18\ H = C_3A\ .CH.H_{18}\ (\text{or } C_4AH_{19})$$

by "adding", we get:

$$2\ C_3A + 27\ H = C_2\ AH_8 + C_3A.CH._{18}$$

and then with "dehydration":

$$C_2AH_8 + C_3A.CH.H_{18} - 3\ H = \underline{2\ (C_3AH_{12})} - 12\ H = 2\ C_3AH_6$$

The simplified, general equation for the whole reaction is, of **course**.

(4) $C_3A + 6\ H = C_3\ A\ H_6$

5. The hydration of teta-calcium-alumino-ferrite is virtually "sub-judice" and I feel the best I can do here is to quote Czernin (4.3)..... "the formulation of any definite reaction mechanism should be treated with some reserve. If, however, one considers that ferric oxide can react with lime and water to give compounds analogous to those formed by alumina, the end product of the hydration reactions might be represented

as follows:-/..........

as follows:

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

or:

$$(1) \quad C_4AF + 2\ CH + 10\ H = C_3AH_6 + C_3FH_6$$

The $Ca(OH)_2$ of course, comes from the hydration of the silicates and only a small proportion of the amount set free is required for this reaction (see next paragraph, equations 1, 2 & 4).

6. The "complete" hydration of a typical, ordinary Portland cement, with weights of reacting materials and products, can be represented thus:

| Composition of Cement: | | | |
|---|---|---|---|
| | $C_3S$ | : | 50 |
| | $C_2S$ | : | 24 |
| | $C_3A$ | : | 12 |
| | $C_4AF$ | : | 9 |
| | $C\bar{S}H_2$ | : | 5 |
| | Total | : | 100 |

## Hydration Reactions (simplified)

(1) $2\,C_3S + 6\,H = C_3S_2H_3 + 3\,CH$

$50.0 + 11.8 = 37.5 + 24.3$

(2) $2\,C_2S + 4\,H = C_3S_2H_3 + CH$

$24.0 + 5.1 = 23.9 + 5.2$

(3) a. $C_3A + 3\,C\bar{S}\,H_2 + 26\,H = C_3A.3\,C\bar{S}.H_{32}$

$2.6 + 5.0 + 4.5 = 12.1$

(3) b. $C_3A + 6\,H = C_3A\,H_6$

$9.4 + 3.8 = 13.2$

(4) $C_4AF + 2\,CH + 10\,H = C_3A\,H_6 + C_3F\,H_6$

$9.0 + 2.75 + 3.3 = 7.0 + 8.05$

---

Adding: (& changing the + 2 CH on the L.H.S. of equation (4) to − 2 CH on the R.H.S.):

---

**L.H.S.** : $2\,C_3S + 2\,C_2S + 2\,C_3A + C_4AF + 3\,C\bar{S}\,H_2 + 52\,H =$

$50.0 + 24.0 + 12.0 + 9.0 + 5.0 + 28.5 =$

**R.H.S.** : $= 2\,C_3S_2H_3 + C_3A.3\,C\bar{S}.H_{32} + 2C_3AH_6 + C_3FH_6 + 2\,CH$

$= 61.4 + 12.1 + 20.2 + 8.05 + 26.75$

| Left Hand Side | | | | Right Hand Side | | | |
|---|---|---|---|---|---|---|---|
| | grams | | % | | grams | | % |
| $C_3S$ | 50 | = | 38.9 | $C_3S_2H_3$ | 61.4 | = | 47.8 |
| $C_2S$ | 24 | = | 18.7 | $C_3A.3\,C\bar{S}.H_{32}$ | 12.1 | = | 9.4 |
| $C_3A$ | 12 | = | 9.3 | $C_3AH_6$ | 20.2 | = | 15.7 |
| $C_4AF$ | 9 | = | 7.0 | $C_3FH_6$ | 8.05 | = | 6.3 |
| $C\bar{S}\,H_2$ | 5 | = | 3.9 | CH | 26.75 | = | 20.8 |
| H | 28.5 | = | 22.2 | - | - | | - |
| Totals | 128.5 | = | 100.0 | Totals | 128.5 | | 100.0 |

**N.B.** 1. Each 100 g. cement liberates about 27g. $Ca(OH)_2$; i.e. the hydrated product contains about 20% "free" calcium hydroxide.

2. These reactions (at ordinary temperatures) take years for completion.

3. The volume of the water reacting with the clinker is reduced to about three quarters of its original value.

7. Magnesium Oxide, which is usually present to the extent of about 1% to 4% in Portland cement, has been completely ignored in the above discussion.

It is known to play a part, possibly catalytic, but research workers are virtually only just beginning to investigate it.

8. References: 1.4, 1.5, 2.5, 4.3, 7.1, 7.2, 7.4, 7.5, 7.7, 7.9, 20.3, 20.6, etc.

## 2.4. SULPHATE ATTACK

1. Sulphate attack has been a problem virtually since Portland cement was first made. It may even have been a problem long before then, as some pozzolans have been found to be susceptible to sulphates and the fact that many structures have survived for 2,000 years does not necessarily mean that none "fell by the wayside". In the words of Gilkey (20.1): "Darwinian law, 'Survival of the Fittest,' applies to concrete as surely as it does to crustacea." So much research work has been done and so many conflicting views put forward, that a complete volume could be written on this subject alone. I shall only touch on the most practical aspects.

2. Eitel (20.3) said : "Discovery of an apparent 'cement bacillus' (circa 1892) was a real sensation, but not before 1917 was this renowned compound identified in deteriorated concrete. This 'cement bacillus' has the same composition as the natural mineral ettringite which is also identical with the synthetic product $3\ CaO.Al_2O_3.3\ CaSO_4.32\ H_2O$....."

3. It has been found, however, that bacteria do sometimes play a part in corrosion, by converting sulphides to sulphates. Lea (1.10) mentions that bacteria probably play a part in the corrosion of concrete in the Black Sea. Sewage disposal systems are the main "sufferers". Van Aardt (6.4.D and elsewhere) and Zoldners and Malhotra (20.4 D) refer to Parker, who isolated Thiobacillus Concretivorus. Rigdon and Beardsley (20.5) explain the destructive characteristics of "autotrophes" (one-cell organisms or bacteria)

4. The simplest/........

4. The simplest mode of sulphate attack which has been postulated is illustrated by the equation:

$$(1)\ Ca\,(OH)_2 + Na_2\,SO_4 + 2H_2O = CaSO_4.2H_2O + 2\,NaOH$$

or

$$CH + \overline{NS} + 2\,H = C\,\bar{S}\,H_2 + N\,H$$

According to Lea (1.6), this reaction will only go to completion "in flowing waters, with a constant supply of sodium sulphate and removal of the sodium hydroxide." Under other conditions, however, the NaOH will accumulate until an equilibrium is reached and the reaction will then stop. Disruption of the concrete is supposedly caused by the crystallization of $CaSO_4.2H_2O$ in the pores, as this salt has a molecular volume of 74 cc, compared with 33 cc for the molecular volume of the $Ca(OH)_2$ which it replaces. Under the condition of flowing water, however, $CaSO_4.2H_2O$ should also be removed in solution,and although that would tend to weaken a structure, it seems doubtful whether this reaction is of much importance <u>by itself</u> (see, however, paragraph 6, equations (2) a and b). Hydrated sulphate-resisting("Tyre V") Portland cement also has a high calcium-hydroxide content, and would be just as susceptible as ordinary Portland cement to this mode of attack.

5. Long term investigations, in several countries, have established that Portland cements with high tri-calcium-aluminate contents (10-20%) are generally very susceptible to attack by sulphate solutions, whereas cements containing less than 5% $C_3A$ are usually highly resistant. The "form" in which the $C_3A$ is present also seems to have an influence, "glassy" $C_3A$ usually being less susceptible than "crystalline" $C_3A$.

6. It is now/.............

6. It is now generally accepted that the attack by <u>sulphates</u> is mainly on the tri-calcium-aluminate hydrates in hardened cement paste, as illustrated by the equations:

(1) $3\,CaO.Al_2O_3.12\,H_2O + 3\,Ca.SO_4 + 20\,H_2O = 3\,CaO.Al_2O_3.3CaSO_4.32\,H_2O$

or

$C_3A\,H_{12} \quad + \quad 3\,C\,\bar{S} \quad + \quad 20\,H \quad = \quad C_3A.3\,C\bar{S}.H_{32}$

(2)a. $3\,Ca(OH)_2 + 3\,Na_2SO_4 + 6\,H_2O = 3\,(CaSO_4.2\,H_2O) + 6\,NaOH$ (see paragraph 4) which, coupled with equation (1) above gives:

b. $3\,CaO.Al_2O_3.12\,H_2O + 3\,Ca(OH)_2 + 3\,Na_2SO_4 + 20\,H_2O$
$= 3\,CaO.Al_2O_3.3\,CaSO_4.32\,H_2O + 6\,NaOH$

or

$C_3\,AH_{12} + 3\,CH + 3\,N\bar{S} + 20\,H = C_3A.3\,C\bar{S}.H_{32} + 3\,NH$

By omitting the metallic ions from the above attacking sulphate salts, and treating the sulphate ions as the sole "aggressors", the <u>general</u> equation is obtained:

(3) $3\,CaO.Al_2O_3.12\,H_2O + 3\,Ca'' + 3\,SO_4'' + 20\,H_2O$
$= 3\,CaO.Al_2O_3.3\,CaSO_4.32\,H_2O$

There is usually ample $Ca(OH)_2$ available (paragraph 2.3-6 note 1 ) as a source of Ca'' ions, but the absence of Ca'' will not stop sulphate attack - although it may slow it down - as Lea (1.6) also indicates the following possible reaction:

(4)a. $2\,(3\,CaO.Al_2O_3.12\,H_2O) + 3\,Na_2SO_4 + 14\,H_2O$
$= 3\,CaO.Al_2O_3.3\,CaSO_4.32\,H_2O + 2\,Al(OH)_3 + 6\,NaOH$

or

$2\,C_3AH_{12} + 3\,N\bar{S} + 14\,H = C_3A.3\,C\bar{S}.H_{32} + AH_3 + 3\,NH,$

which can be written in the <u>general</u> form:

b. $2\,(3\,CaO.Al_2O_3.12\,H_2O) + 3\,SO_4'' + 14\,H_2O$
$= 3\,CaO.Al_2O_3.3\,CaSO_4.32\,H_2O + 2\,Al(OH)_3 + 6\,OH'$

7. The main product/..........

7. The main product in the above equations is, in all cases, $3\ CaO.Al_2O_3.\ 3\ CaSO_4.32\ H_2O$ ($C_3A.\ 3\ C\ \bar{S}.\ H_{32}$), known as calcium-tri-sulpho-aluminate, high-sulphate-calcium-aluminate-sulphate, or ettringite. (There seems to be some doubt as to the correct number of molecules of $H_2O$ to use in the formula-possibly they vary with conditions of formation, but most writers now use 32). According to Eitel (20.3) ettringite will crystallise out if a water containing as little as 4 mg $CaSO_4$/litre, and saturated with $Ca(OH)_2$ - as it usually is in concrete - comes in contact with the $C_3A$ hydrates in set Portland cement. Even when no free $Ca(OH)_2$ is present, as on the surface of aged mortars and concretes - where absorption of atmospheric $CO_2$ has changed it to $CaCO_3$ - a solution containing only 8 mg $CaSO_4$/litre will cause crystallisation of ettringite. These low critical concentrations of 4 and 8 mg $CaSO_4$/ litre illustrate the great danger of using cements with high $C_3A$ contents in situations where water or ground water is likely to contain sulphates in solution.

8. Ettringite has a high molecular volume (about 720 cc), and it has been generally thought that this was the major cause of expansion and disruption of concretes and mortars. Thorvaldson (6.4.), however, says : "While the formation of crystals of sulpho-aluminate and gypsum in Portland cement mortars during disintegration in sulphate solutions is well established, many experimental observations throw doubt on the assumption that physical forces of crystallization are the primary cause of expansion and loss in strength. A few examples might be mentioned. Lean mortars made with $C_3S$ and $C_2S$ and stored in a solution of $Na_2SO_4$ showed the presence

of masses of/..................

of masses of gypsum crystals long before there was any abnormal expansion and while the strength of the specimen was rapidly increasing. Mortar bars (1 : 5) made with a laboratory clinker ($C_3S$, 25%; $C_2S$, 50%; $C_3A$, 24% ) disintegrated in a 2% solution of $Na_2SO_4$ with very little expansion (0.06%) although microscopic examination showed very large quantities of tri-calcium sulpho-aluminate present.
Many observations such as these suggest that volume changes in the mortars are controlled by osmotic forces concerned with the swelling and shrinkage of gels, that the chemical reactions condition the gel system and destroy cementing substances while the formation of crystalline material is incidental to these chemical reactions and that the increased resistance to volume change with increased richness of mix may not be primarily due to decreased permeability but rather to the more prolonged maintenance of conditions within the mortar unfavourable to the swelling of the gels." My own experiments, (see **Chapter IX** ) with sulphates mixed in with the cement and sand, as well as present in the curing water, have shown that:

(1) Strength can increase while expansion is occurring;

(2) Transverse strength usually starts to decrease before compressive strength - the latter may continue to increase for some months after transverse strength (probably the tensile component thereof) has started dropping; and

(3) "Lean" concretes have shown decrease in strength earlier than "rich" concretes.

I feel that these results, by and large, are in accordance with Thorvaldson's suggestions, but it must not be forgotten that conditions of attack have an influence, and it may well be that alternate wetting and drying, as occurs in the inter-tidal zone with marine structures, can lead to disruption by expansive crystallization.

9. The low-sulphate double salt, $3\ CaO.Al_2O_3.CaSO_4.12\ H_2O$ may be formed under certain conditions:

(1) $3\ CaO.Al_2O_3.Ca(OH)_2.12\ H_2O + SO_4'' = 3.CaO.Al_2O_3.CaSO_4.12H_2O + 2\ OH'$

and Eitel (20.3) considers the reaction

(2) "$3\ CaO.Al_2O_3.CaSO_4.12\ H_2O + 2\ CaSO_4$ = ettringite"

to be completely reversible.

A complete series of solid-solutions of the various hydrates and sulphates of tri-calcium-aluminate is now known to exist - see paragraph 2.3 - 4.4. The low-sulphate salt doubtless has deleterious effects, on concrete, similar to those of ettringite (paragraph 8.)

10. According to Bogue (2.3) the calcium-ferrite hydrates are also susceptible to sulphate attack. The compounds $3\ CaO.Fe_2O_3.3\ CaSO_4.32\ H_2O$ ($C_3F.3\ C\bar{S}.\ H_{32}$) and $3\ CaO.Fe_2O_3.CaSO_4.\ H_2O$ ( $C_3F.\ C\bar{S}.\ H$ ) have been prepared and described. The ferrites, however, seem to be much less dangerous than the aluminates. There are two possible reasons:

10.1 the $C_4AF$ has to be "broken down" before $C_3F\ H_6$ can be formed; and

10.2 a fair proportion of the $C_4AF$ is in the form of a "glass", and therefore even slower to react.

11. References : 1.6, 1.10, 2.3, 2.6, 3.3, 4.3, 5.2, 6.4, 6.4D, 7.1, 7.2, 7.3, 7.10, 8.4, 18.1-1, 19.1, 19.2, 19.4, 20.1, 20.3, 20.4D, 20.5, 20.7, 20.8, 21.1, etc.

2.5 Magnesium Attack/.............

## 2.5. MAGNESIUM ATTACK

1. Corrosion of concrete by the sulphate-ions in sea water was initially ascribed to "Calcium-sulphate" and later to "Magnesium-sulphate". To blame "Sodium-sulphate" would be equally, or even more, logical. Actually, of course, it is the "ions" in solution which must be considered. The sulphate ions initiate one form of attack (section 2.4, particularly paragraph 6, equations (3) and (4b) ); the metallic ions may initiate a completely different form of attack, or may interact with and modify the sulphate-ion reactions.

2. Whereas sulphates attack only the tri-calcium-aluminate hydrates, magnesium-ions ultimately strike at the calcium-silicate hydrates, as illustrated by the following series of equations:

(1)a. $Ca(OH)_2 + MgSO_4 = Mg(OH)_2 + CaSO_4$

or

b. $Ca(OH)_2 + MgCl_2 = Mg(OH)_2 + CaCl_2$

Using A to designate the Anion, this may be written in the general form:

c. $Ca(OH)_2 + Mg^{\cdot\cdot} + 2A' = Mg(OH)_2 + Ca^{\cdot\cdot} + 2A'$

This reaction takes place because of the low solubility of $Mg(OH)_2$ - only about 0.01gm/Litre. When all the $Ca(OH)_2$ has been used up, the pH of the solution drops to that of a saturated $Mg(OH)_2$ solution, which is about 10.5. This is lower than the pH required to stabilise hydrated calcium silicate, which then starts to liberate lime to the solution, in an attempt to re-establish its equilibrium pH, thus:-

(2) 3 CaO. 2 $SiO_2$/..................

(2) $3\ CaO.2\ SiO_2.3H_2O \quad = \quad 3\ Ca(OH)_2 \quad + \quad 2\ SiO_2.\ aq$

or

$C_3\ S_2\ H_3 \quad = \quad 3\ CH \quad + \quad 2\ S.\ aq$

The liberated $Ca(OH)_2$ is again, of course, removed by reaction (1)c, so more hydrated calcium silicate is decomposed, and so the reaction proceeds.

3. The above reactions do not represent the end of the attack, however, for Steopoe (1.6) has found that the precipitated $Mg(OH)_2$ reacts very slowly with the silica-gel liberated according to equation (2) above, to form a hydrated magnesium silicate:

(1) $Mg\ (OH)_2 \quad + \quad SiO_2.nH_2O \quad + \quad H_2O \quad = \quad MgO.SiO_2.8\tfrac{1}{2}\ H_2O$

This material has an X-ray pattern not unlike the aluminate hydrate $4\ CaO.Al_2O_3.12\ H_2O$.

It has no binding power whatsoever.

4. When sulphate attack is combined with magnesium attack, as it is in sea water, even the ettringite formed is not safe from the magnesium. The pH of the saturated $Mg\ (OH)_2$ solution is too low to stabilise the ettringite, which then decomposes and reacts thus:

(1) $3\ CaO.Al_2O_3.3\ CaSO_4.32\ H_2O + 3\ MgSO_4$

$= \quad 2\ Al(OH)_3 \ + 6\ CaSO_4 \ + 3\ Mg(OH)_2 \ + 26\ H_2O$

or

$C_3A.\ 3\ C\bar{S}.\ H_{32} \quad + \quad 3\ M\bar{S} \quad = \quad AH_3 \quad + 6\ C\bar{S} \quad + 3\ MH \quad + \quad 26H$

5. The deposition of $Mg(OH)_2$ in the pores of the outer "skin" of a concrete does tend to hinder penetration by more solution, and consequently slows up the attack somewhat, but apparently does not stop it altogether.

6. References : 1.6, 3.3, 5.2, 6.4, 19.4, 20.2, 22.1, etc.

2.6. Leaching of/..........

## 2.6. LEACHING OF SOLUBLE CONSTITUENTS.

1. Very pure soft water corrodes hardened concrete by dissolving out the $Ca(OH)_2$. This is not important when the concrete is impermeable and/or the water "stagnant", but when water is flowing through a porous structure it can be disastrous. When all the "free" lime has been dissolved the pH will drop and hydrated calcium silicates will start decomposing (compare Magnesium attack - paragraph 2.5 - 2, equation (2) ).

2. A high carbon-dioxide content in the water will make matters worse, and the $CO_2$ content in excess of that required to stabilise the equilibrium:

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca(HCO_3)_2$$

is called "aggressive carbon-dioxide". The higher the the aggressive carbon-dioxide, the faster the solution of calcium.

3. Humic acid also increases the aggressiveness of a water - but usually not as much as $CO_2$.

4. References : 1.6, 3.3, 7.10, 12.1

## 2.7. RUSTING OF REINFORCEMENT.

1. Rusting of reinforcement, accompanied by staining, cracking, and spalling of concrete, is one of the main sources of failure of reinforced concrete structures in marine environments.

2. Under most conditions Portland cement concrete provides good protection of reinforcing steel as a result of the

"passivating" effect which the alkaline calcium hydroxide constituent has on iron. According to Copenhagen a protective film of gamma ferric oxide is formed on the steel surface, due to the high pH of $Ca(OH)_2$.

3. Hydrated Portland cement is subject to chemical reaction with the carbon-dioxide of the atmosphere. The calcium-hydroxide is converted to calcium-carbonate, the pH reduced and the steel-protective mechanism is vitiated. In good quality concrete carbonation cannot penetrate deeply, and it is only in relatively porous concrete, and where reinforcement is too close to the surface, that corrosion may become a problem from this cause.

4. Chlorides are particularly dangerous to reinforced concrete. They are always present in marine environments, not only in and next to the sea, but are often also wind-borne for quite a considerable distance inland. If only a small quantity of chloride penetrates the concrete as far as the reinforcement it will destroy the protective film at that spot and permit oxidation to proceed uninhibitedly.

5. "Differential permeability" in different parts of a reinforced concrete member can result in different concentrations of electrolytes (usually salt) at various points in it. These set up natural "cells" in the member, with micro-currents of electricity flowing from "high-concentration" areas to "low-concentration" areas and consequent corrosion (and weakening) of the steel. As the corrosion products occupy a larger volume than the original iron, their continued production will eventually develop sufficient pressure to rupture the concrete cover, whereafter corrosion proceeds apace.

6. References : 1.6, 3.5, 19.1, 20.2, 20.4, 22.2.

## 2.8. PERMEABILITY.

1. Possibly the only thing on which all cement and concrete "people" agree is that, no matter what special cements, materials, or processes may be used, high-quality "impermeable" concrete is essential for longevity, particularly in corrosive environments. This is especially so in the case of reinforced concrete in marine surroundings.

2. In a "long-time study" (20.9), which was aimed mainly at evaluating the performance of different types of cements, reinforced concrete piles were exposed to sea-water. After about fifteen years exposure it was found that differences in cement compositions had, thus far, been overridden by differences in permeability of the concrete. Where the reinforcement was well protected the piles had undergone little or no deterioration, but where sea-water had penetrated to the steel it had rusted, cracked the concrete, and, in some cases, led to complete disintegration of the pile. The piles made with low-heat cement seemed to have slightly better than average performance - possibly due to fewer "temperature-of-hydration" cracks (see paragraph 6, below).

3. As Scholer (20.10) said in 1936 "Concrete is composed of the cement, water, aggregate, time, temperature and energy which went into the mixing and placing ......."
Each and every one of these "components" can, and does, influence the permeability of concrete. Too much water leads to "water voids". Too little water and/or too little compaction results in "air voids".

4. By its very nature all concrete is "permeable" to a greater or lesser extent:

4.1. The water used by the cement for hydration is "compressed" by the chemical reaction into about three-quarters of its original volume (paragraph 2.3-6), resulting in some "intrinsic" shrinkage of the concrete, and also in the formation of some "empty space".

4.2. Segregation of the components, while the concrete is still wet, results in "bleeding", and consequent formation of flow-channels.

4.3. After setting, water not required for cement hydration evaporates and leaves open capillary passages in the structure.

5. Leaching out of soluble constituents, like calcium hydroxide, enlarges passages already extant.

6. Cracks are open "free-ways to the interior" for corroding solutions. Some causes are:-

6.1. Temperature rise during hydration, with subsequent differential cooling-shrinkage, is a source of cracks which has long been recognised in the case of mass-concrete edifices, but sadly underrated in smaller structures. Davis and co-authors (20.12) wrote in 1937 : "If this temperature change is large, stresses due to these thermal changes are likely to produce cracks. Even in walls having a thickness no greater than 2 or 3 feet where standard Portland cements have been employed, in many cases cracks of considerable frequency and magnitude have been observed soon after forms were removed." Recordings of temperatures reached during hydration in mortar and concrete specimens indicate that concrete members of 12" x 12" cross-section (or even less) will be liable to have small, but significant temperature of hydration cracks. The use of rapid hardening cement and/or "rich" concrete mixes aggravates matters. It is probably significant that, in the test series mentioned in paragraph 2 above, the piles made with low heat cements had a slightly "better than average" performance in the <u>rich</u> mixes.

6.2. Shrinkage, and expansion, cracks also result from alternate wetting and drying, particularly if the aggregates have abnormal characteristics. Temperature fluctuations are another source of cracking.

6.3. Cracks are also sometimes caused by high loads, especially if fluctuating and/or if the structure has been "underdesigned" for its purpose.

7. References: 3.8, 4.3, 11.2,/ 20.2 20.9, 20.10, 20.12, etc.

## 2.9. FROST ACTION

1. "Frost action", better described as "cycles of freezing and thawing" is of little or no practical importance in our climate, but causes considerable damage to concrete in northern countries with freezing winters.

2. Water penetrates into the concrete, through cracks, crevices and capillaries, then expands and disrupts the concrete as it freezes. (See also paragraph 2.1-5). The use of salt and other chemicals for de-icing roads often causes further deterioration.

3. References: 1.10, 20.4, etc.

2.10 Alkali-reactive/......

## 2.10. ALKALI-REACTIVE AGGREGATE.

1. Whilst investigating concrete structures in California, in 1940, Stanton (2.6.) reported that some structures, made of apparently sound aggregate and satisfactory cement, were showing excessive expansion.

2. Investigation revealed that some aggregates reacted with cements containing more than a critical amount of $Na_2O$ and/or $K_2O$. If the $Na_2O$ + 0.658 $K_2O$ in a cement was less than 0.6%, the aggregates did not react, but if the $Na_2O$ and/or $K_2O$ exceeded this value, then expansion resulted. (Some examples of reaction with low-alkali cement have since been found, and investigations are continuing in several countries) "High-alkali" cements, however, were quite satisfactory with other aggregates.

3. Opal, chalcedony, tridymite, cristobalite, rhyolites and andesites have all provided examples of alkali reactive aggregates. Opaline silica is believed to react with the alkali hydroxides to form a voluminous alkaline silicate, thus:

$$SiO_2 + 2\,NaOH = Na_2\,SiO_3 + H_2O$$

4. It is noteworthy that the effect of these aggregates can usually be nullified by incorporating a pozzolan in the cement, and the best pozzolans for this purpose are often prepared from the aggregates themselves. Fulton likens this to the use of vaccines in preventive medicine.

5. Alkali-reactive aggregates are not of great importance in South Africa (3.4), although they have been found in Barkly West, Carolina, and one or two other places.

6. References: 1 (p 494), 2.6, 3.4, 3.6, 20.11, etc.

2.11 Shrinking/..........

## 2.11. SHRINKING AGGREGATES.

1. First described by Stutterheim (19.1), "shrinking" aggregates, in contrast with alkali-reactive aggregates, have been of considerable importance in South Africa, but practically negligible elsewhere.

2. Investigation revealed that certain aggregates, particularly some fine-grained sandstones and shales derived from the Beaufort Series, exhibited abnormally high dimensional changes with change in moisture content. This led to shrinkage movements in concretes up to seven times larger than those which occur in similar concretes containing normal aggregates. As these dimensional changes are to some extent reversible, subsequent wetting causes unduly large expansions. In some cases reinforced beams buckled because the upper portion shrank on drying, while the lower section, restrained by reinforcing steel, remained virtually the same length.

3. The only real "cure" for this trouble appears to be not to use these aggregates ! Fortunately other suitable materials are also available in or near the districts where they occur.

4. References: 3.6, 3.7, 19.1.

## 2.12. ACID ATTACK.

1. "Since hydraulic cements are basic materials, it can be expected that they will be vulnerable to strong and even weak inorganic and organic acids". (van Aardt 7.10)

2. In purely "acid" attack, $Ca(OH)_2$ (or $CaCO_3$) is neutralised and the resulting salt dissolved out. The

consequent drop/.......

consequent drop in pH leads to decomposition of the cement hydrates (compare paragraphs 2.6-1 and 2.5-2) and so the reaction continues until either the acid or the cement is exhausted. The more concentrated the acid the faster the attack. If the acid is dilute and the concrete dense, attack may be limited to the surface layers only, unless other factors are present.

3. If the cement is also susceptible to the anion of the acid, as in the case of sulphuric acid, then attack even by dilute acid may be severe.

4. In some portions of sewers sulphuric acid is formed by bacterial action on sulphides. If ordinary Portland cement was used for the concrete portion, then the two-fold attack destroys it comparatively rapidly, because the sulphate-expansion keeps spalling off the surface and exposing fresh surfaces for acid attack. The use of sulphate-resisting cement, although it does not prevent the acid attack as such, slows down corrosion considerably. Acid soluble aggregates, such as limestone, have also been used with success to slow down this mode of attack.

5. Some anions, on the other hand, afford protection from acid attack. Oxalic acid gives the almost insoluble calcium oxalate, tartaric acid yields calcium tartrate, and hydrofluoric acid is actually used to <u>protect</u> concrete.

6. References: 3.3, 4.3, 6.4, 7.10, 8.4, 20.7.

2.13. Other Corrosive/.......

## 2.13. OTHER CORROSIVE AGENTS.

1. Other materials to which concrete is sometimes susceptible include: vegetable and animal oils and fats, silage, sugar solutions, strong solutions of caustic alkalis and of calcium chloride, and some wet coals.

2. Ammonium salts, especially the nitrate and sulphate, are particularly deleterious to hardened concrete. Their mode of attack is illustrated by the general equation:

$$2\ NH_4A + Ca^{''} + 2\ OH^{'} = Ca\ A_2 + 2\ NH_3 + 2\ H_2O$$

The ammonia gas gets dissipated into the air, the pH drops and the cement hydrates decompose as explained under Magnesium and acid attack.

3. References: 1.11, 4.3.

## 2.14. CONCRETE CORROSION IN SOUTH AFRICA

1. The great majority of concrete structures in South Africa have stood up well to the ravages of time and weather. However, a few failures have occurred, and corrosion has been serious and costly enough to warrant thorough investigation and research.

2. The four major causes of trouble in this country are:

   2.1. Shrinking aggregates;
   2.2. Sulphate salts in ground waters;
   2.3. Sulphuric-acid formation in sewers;
   2.4. Sea-water and salty atmospheres.

3. The shrinking aggregate problem is fairly localised.

It has been/............

It has been solved by members of the C.S.I.R. staff, who discovered the cause, identified aggregates to avoid, and recommended alternative materials. (See also section 2.11.)

4. In many areas, including the Cape Flats, there are sulphate salts present in the soil and/or ground water. The particular circumstances of each new project need to be taken into consideration, but as a general rule sulphate-resisting cement should be used for making concrete which is to be placed in a soil containing more than ½% $SO_4''$ or a water containing sulphates in excess of 400 ppm. The use of special cements never precludes the necessity of making good, sound, impermeable concrete.

5. Corrosion in sewers is a problem in all warm countries. "Typical" corrosion occurs only above the water line, and is most severe immediately above the average daily level. Under suitable conditions, aided by warmth, $H_2S$ is generated in sewers and converted by some varieties of thiobacilli to sulphuric acid. No basic material, like cement, can withstand acid attack indefinitely, but the useful life of sewers can be extended by good design, acid-soluble aggregate, and sulphate-resisting cement.

6. Marine corrosion of concrete can be the result of any or all of a number of factors, some of which are:

6.1. Sulphate attack - "average" sea-water contains 2760 ppm $SO_4''$ ;

6.2. Magnesium attack - there are 1330 ppm $Mg^{\cdot\cdot}$ in sea-water

6.3. Leaching of soluble constituents - enhanced by the continual movement of the water;

6.4. Rusting of /...........

6.4. Rusting of reinforcement - the high chloride content of the sea (nearly 20,000 ppm) makes it very aggressive to iron, and the danger extends inland as far as the salt can be carried by the wind;

6.5. Wave action often causes cracks, which allow penetration of the corrosive elements, and mechanical attrition bares new surfaces for attack.

The cement used for making "marine concrete" should therefore:-

6.6. Be sulphate- and magnesium-resisting;

6.7. Contain, after hydration, a minimum of "soluble" material;

6.8. Assist in making the concrete as impermeable as possible;

6.9. Endow the concrete with "shock-resistant" qualities and, preferably, also improve its abrasion resistance.

7. References: 3.3, 3.5, 6.4, 7.10, 19.1, 19.3, 22.1, 22.2.

## 2.15. THE PRODUCTION OF SPECIAL CEMENTS FOR THE CAPE.

1. Special cements are required for some concrete structures in the "Cape" because:-

1.1. In some areas the concentration of sulphate salts in the soil and/or ground-water is sufficiently high to attack ordinary Portland cement (see Table 1 for typical analyses);

1.2. The climate is conducive to the formation of sulphuric-acid in sewers;

1.3. ~~The Climate~~/...........

1.3. Structures in and near the sea are subject to severe marine corrosion - see photographs of Muizenberg Pavilion on page 1 of the supplement, p 324.

TABLE NO. 1

SOME ANALYSES OF CAPE GROUND-WATERS

| CONSTITUENT | APPROXIMATE ORIGIN OF SAMPLE | | | | |
|---|---|---|---|---|---|
| | CLAREMONT | FORESHORE | SOMERSET WEST | | CAPE FLATS |
| pH | - | 7.45 | 7.6 | 7.3 | 7.0 - 7.5 |
| | ppm | ppm | ppm | ppm | ppm |
| T.D.S. | 4668 | 1810 | 4900 | 3300 | - |
| $SO_4''$ | 2292 | 617 | 205 | 115 | + 3000 |
| $Cl'$ | 840 | 170 | 1160 | 245 | + 4000 |
| $HCO_3'$ | 168 | - | - | - | - |
| Nitrates | - | - | trace | present | - |
| $Mg^{\cdot\cdot}$ | 294 | - | not detectable | 137 | - |
| $Ca^{\cdot\cdot}$ | 457 | - | 336 | 304 | - |
| $Na^{\cdot}$ | 617 | - | - | - | - |
| $NH_4^{\cdot}$ | - | - | not detectable | not detectable | |
| Total Hardness | - | - | 840 | 1320 | - |

2. Sulphate-resisting and Marine cements are available from oversea countries (England, Denmark, Italy, etc), but the high transport costs make them expensive. This research project was instituted, therefore, to find out whether similar cements could be produced economically from local materials.

3. The general/............

3. The general "programme" followed was:-

3.1. Survey of the literature to learn as much as possible about the nature of concrete corrosion;

3.2. Consultation with various authorities to establish the main causes of corrosion in South Africa generally and the Cape in particular;

3.3. Survey of the literature, in conjunction with an investigation of the raw materials available locally, to decide on the most suitable types of cement to make;

3.4. Laboratory investigation of : materials; methods of treating and testing; and imported cements. Calculation of mix proportions; laboratory-scale production of cements (when possible); and investigation of "accelerated" test-methods; and

3.5. Plant-scale production trials, followed by testing of material made, then manufacture of "full-scale" production batches and subsequent thorough testing of the cements with accelerated techniques and, where possible, under "natural" conditions.

4. References : 26.1, 26.2 & 26.3.

# CHAPTER III

# SPECIAL CEMENTS AND ADDITIVES

## 3.1 GENERAL CONSIDERATIONS.

1. Apart from improvements in the design and manufacture of concrete itself, methods which have been developed for combating corrosion may be classified thus:

1.1. Protective coatings and surface treatments;
1.2. "Special" cements;
1.3. Additives to cement and/or concrete.

2. Protective coatings, particularly water-proof coatings, have been used on concrete structures with varying degrees of success. In many cases, such as foundations for instance, it is impossible to apply coatings and in other cases they have proved less durable than the concrete they covered. Plastic coatings are being used in sewer pipes for protection against $H_2SO_4$ and are fairly successful, but "pin-holes" in coatings have caused some trouble. The "ocrating" process of treating concrete surfaces has also been successful in reducing corrosion in some applications. Such methods, however, are outside the scope of this report. (8.4. & 20.13.)

3. Special cements which have been developed for use when conditions are deleterious to concrete made with "ordinary" Portland cement include:

3.1. High Alumina Cement or "Ciment Fondu";
3.2. Supersulphated Cement;
3.3. "Modifications" of Portland Cement, such as Sulphate-resisting Portland Cement (ASTM Type V), low-heat Portland Cement, etc.

4. "Additives"/...............

4. "Additives" can be classified in different ways, but in this case I shall include:

   4.1. Pozzolanic Materials;
   4.2. Granulated Blastfurnace Slag;
   4.3. Air-entraining agents.

5. References: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 18, 19, 20, 21, 22, 23, 24, 25, 26.

## 3.2. HIGH ALUMINA CEMENT.

1. High Alumina Cement, also known as "Ciment Fondu", was developed in France after a series of failures of Portland cement concrete in grounds containing large amounts of Gypsum. It is manufactured from limestone and bauxite, usually by heating them to above fusing temperature. The resulting material is very hard to grind, and the cement is usually black.

2. Vicat suggested in 1846 that a cement in which the ratio of (silica + alumina) to (lime + magnesia) was greater than unity would be resistant to sulphate action, and Bied followed this up in the early 1900's. In 1908 a cement, with the approximate formula $CaO.Al_2O_3 + 2\ CaO.SiO_2$, was patented, but a number of manufacturing and other difficulties were experienced, and it was only after 1918 that Ciment Fondu became generally available.

3. High Alumina Cement is now manufactured in several countries, including the U.S.A., by a variety of different methods. It is similar in many ways to Portland cement and has about the same setting time, but hardens much more rapidly -

reaching 80-90% /...............

reaching 80 - 90% of its ultimate strength within 24 hours of mixing with water. Its total heat of hydration is about the same as that of Portland cement but, because the heat is evolved so rapidly, the hydration temperature is generally higher and sometimes gets out of hand, with adverse effects on strength and sulphate resistance. Aluminous cement is more "sensitive" than Portland cement, to impurities (chlorides, etc.) and curing conditions.

4. Ciment Fondu, properly used and cured, does have a high resistance to sulphates and to sea-water. It is at its best in cold countries, where the rapid liberation of heat of hydration is an advantage during freezing conditions, but has not been very successful in warm climates. "High alumina cement concrete should not be used in places where it will be both moist and at a temperature of 85°F or higher....." (3 - p.620 ).

5. Lack of a suitable aluminium ore, difficulties of manufacture and use, and doubts about its value in our climate, were the reasons that no attempt was made to produce this type of cement during this research project.

6. References: 1.9, 2.2, 3.3, 3.4, 3 - p.620, 19.2, 22.1, 23.1.

## 3.3. SUPER-SULPHATED CEMENT.

1. "Super-sulphated Cement is composed essentially of granulated blastfurnace slag, calcium sulphate and a small percentage of Portland cement or lime. In Belgium it is known as 'Cement Métallurgique Sursulfaté ' and in France by

this term, or, /.............

by this term, or, more shortly, as 'Cement Sursulfaté' "(1.2). In South Africa it is also known by the trade name "Sealithor".

2. For super-sulphated cement the slag used must have a moderately high $Al_2O_3$ content. The cement is made by intergrinding about 80% granulated slag, 15% "dead-burnt" gypsum, and 5% Portland cement.

3. Advantages of super-sulphated cement are:

3.1. Low heat of hydration;

3.2. High sulphate resistance (but low resistance to Magnesium sulphate ).

Disadvantages are:-

3.3. Deterioration during storage owing to the effects of carbonation;

3.4. Greater sensitivity than Portland cement to curing conditions - if insufficient care is taken then sulphate resistance can be destroyed.

4. There is no blastfurnace slag available locally. The slag available from ISCOR has a high magnesia content, and, although this has not proved detrimental in Portland Blastfurnace Cement, it is as yet untried and unproved in supersulphated cements. These factors, coupled with the disadvantages listed above (paragraphs 3.3 & 3.4), were the reasons for not including supersulphates cements in this investigation.

5. References: 1.2, 1.8, 2.2, 3.3, 7.11, 19.4, 23.4

## 3.4. MODIFIED PORTLAND CEMENTS.

1. Soon after it was found that sulphate attack was most severe on cements with high tri-calcium-aluminate contents, attempts were made to produce low $C_3A$ Portland cements.

2. The Metropolitan Water District of Southern California initiated studies on the subject in the early 1930's because some soils and waters in the Colorado River basin contain sodium sulphate in amounts which present a hazard to the permanence of ordinary concrete structures.

2.1. According to Tuthill (20.14) the effort to answer the question "What changes in cement composition could be made which would give the greatest assurance of permanent resistance to sodium sulphate in typical ground water concentrations? " soon became the most significant part of the investigation.

2.2. Various types of "acceptance tests" were tried out in an effort to find one which would give a reliable indication of sulphate-resistance within 28 days, but it was decided that the most dependable results would be assured by specification of a cement having a composition known to be effective. Acceptance tests would then only involve routine chemical analysis, and long time tests in sodium sulphate solutions confirmed that this method was satisfactory.

2.3. It was also felt, however, that a dependable 1-month acceptance test would be of great value under some circumstances, and the "slab-warping" test was developed.

2.4. The following specification was ultimately decided

upon/....................

upon for sulphate resistant cement being purchased by the Metropolitan Water District of Southern California:

| | |
|---|---|
| $C_3A$, not more than | 4% |
| $C_3A$ plus $C_4AF$, not more than | 12% |
| $C_3S$, not more than | 50% |
| $C_2S$, not less than | 30% |

Fineness and strength were also specified.

3. Miller & Manson (2.6.) investigated the sulphate resistance of 106 commercial cements by the storage of concrete cylinders in a natural sulphate-bearing lake, and by the storage of similar cylinders and mortar briquettes in $MgSO_4$ and $Na_2SO_4$ solutions in the laboratory. The predominating factor in determining resistance appeared to be the $C_3A$ content, and all cements containing less than 5.5% potential $C_3A$ (by calculation) had high resistance. These results were confirmed by Dahl (20.15), who also found that rich mixes (with low water/cement ratios) and air-entrained concretes had improved resistance. Numerous other investigators have had similar results, and have also determined the nature of the attack and the reactions involved - see section 2.4.

4. Largely as a result of the work of Miller & Manson, the American Society for Testing Materials and the U.S.A. Federal Specifications Board adopted a limiting potential value of 5% $C_3A$ (calculated by the formula $C_3A = 2.65\ A - 1.69F$) for sulphate-resistant cements (2.7.). $C_4AF$ also has some susceptibility to sulphate attack, and is therefore limited, and up till 1960 there was a maximum limit of 50% on the $C_3S$ as well. The present specification for ASTM Type V Sulphate-

resisting Portland Cement includes the following limitations on compounds:

Potential $C_3A$ : max. = 5%
Potential $C_4AF$ + 2 x potential $C_3A$ : max = 20%

This specification does prevent the use of some Portland cements with high sulphate resistance <u>and</u> high potential $C_3A$ (possibly in the form of a non-reactive glass), but it appears to be effective in excluding cements with low sulphate resistance.

5. Other specifications which place limits on compound compositions are:

5.1. ASTM Type II cement "for use in general concrete construction exposed to moderate sulphate action, or where moderate heat of hydration is required" (18.1- 1). Limits for potential compounds are:

| | | | |
|---|---|---|---|
| $C_3A$ | : | max | 8% |
| $C_3S$ + $C_3A$ | : | max | 58% |

5.2. ASTM Type III "High Early Strength Cement" for general purposes may not contain more than 15% $C_3A$. When moderate sulphate resistance is required the limit is 8% and if high sulphate resistance is required the $C_3A$ may not exceed 5%

5.3. ASTM Type IV cement "for use when a low heat of hydration is required". Limits on potential compounds are:

| | | | |
|---|---|---|---|
| $C_3A$ | : | max. | 7% |
| $C_3S$ | : | max. | 35% |
| $C_2S$ | : | min. | 40% |

Because of/............

Because of the limit on $C_3A$ this type of cement also has moderate sulphate resistance.

6. The possibility of producing low-$C_3A$ Portland cement for the local market, for use in sulphate-bearing soils and waters, was considered to be worthwhile investigating thoroughly for the following reasons:

6.1. A considerable amount of research work and widespread utilisation in the United States and Europe had already proved the value of such cements;

6.2. There was a recognised specification (ASTM Type V) to which the cement could be produced;

6.3. Suitable raw materials appeared to be available within reasonable distances of the factory;

6.4. No particularly abnormal production difficulties need be anticipated;

6.5. Builders and Contractors would have no unusual difficulties using it because the rules for making concrete from Portland cement also apply to Sulphate-resisting Portland cement, and it is no more sensitive to curing conditions than O.P.C.

6.6. Sulphate-resisting cement of this type had already been imported and used successfully in some local concrete structures.

7. References: 1.3, 1.6, 1.10, 2.6, 2.7, 3.3, 5.2, 6.4, 6.5, 7.10, 7.11, 7.12, 8.1, 8.4, 10.1, 10.2, 10.3, 10.4, 18.1-1, 19.1, 19.2, 19.4, 20.3, 20.4, 20.7, 20.8, 20.14, 20.15, 20.16, 20.17, 20.18, 20.19, 21.1, 21.4, 22.1, 23.1, 23.4, 24.5.

3.5. Pozzolanic/..........

## 3.5. POZZOLANIC MATERIALS AND CEMENTS.

1. A pozzolan may be defined as: "A siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties". (18.1-5 ).

The calcium hydrosilicates ultimately produced by the Pozzolanic "cold process" are substantially the same as the ones formed during the hydration of Portland cements, and may be generally represented by the formula $3CaO.2SiO_2.5H_2O$ ·($C_3S_2H_3$).

2. Lime-pozzolan cements are the products obtained by grinding together a mixture of lime, pozzolana, and, sometimes, a setting time regulator. As already mentioned, they are known to have been in use since before 2,000 B.C. (Paragraph1.2-1) and some Roman marine structures made with lime-pozzolan cements are still in use today (paragraph 2.1-3)

3. Portland - Pozzolan Cements, sometimes (incorrectly) just called "Pozzolanic Cements", "are the products obtained by grinding Portland clinker and pozzolana with the amount of gypsum necessary to regulate the set". (18.5-1)

4. Lime- pozzolan cements generally "went out of fashion" when the "superior" qualities of Portland cement became known, particularly in Britain and America. The main reason for this was the comparatively rapid strength development of Portland cement concrete, but the Italians continued to use Pozzolanic materials, both in conjunction with lime and with Portland cement. Portland-pozzolan

cements with/.............

cements with a 30-40% Pozzolana content are widely used in the same mix proportions as Portland cement for concrete in general building construction, for dams, and for reinforced concrete in sea-water for which the lime-pozzolana concretes are too slow in hardening.

5. There is no doubt that ordinary Portland cement is a wonderful construction material, of high strength and with adequate durability for most purposes under most conditions, but the never ending demand for higher early strengths has resulted in cements with higher tri-calcium-silicate contents. The result is a potential 20% "free" calcium hydroxide in the hydrated cement (paragraph 2.3-6), of which about half is generally released into the concrete pore water or pore space within the first month of setting and hardening. This lime contributes virtually nothing to the strength of the structure; because of its solubility it can be leached out by moisture, adversely affecting the permeability of the concrete; and it reacts readily with many aggressive agents. However, when an active pozzolanic material is present along with the Portland cement, it combines with the calcium hydroxide released from the latter forming relatively insoluble compounds with cementitious properties, which result in increased strength and impermeability of the hardened material.

6. Characteristics of Portland-Pozzolanic cements, as compared with "straight" Portland cements, are, generally:-

6.1. Reduced heat of hydration;
6.2. Reduced permeability;
6.3. Improved resistance to aggressive waters;
6.4. Improved "extensibility"
6.5. Higher "ultimate" strengths;

6.6. Expansion/......

6.6. Expansion with alkali-reactive aggregates is often reduced or eliminated.

These factors all result in improved general durability of the resulting product.

7. In Great Britain, in 1909, Potter described a material consisting of ground burnt clay and Portland cement (known as "Potters Red Cement") and stated that over 5,000 tons of it were used in fresh-water and sea-water constructions. Blount, writing in 1920 (5.2), stressed the valuable properties of pozzolans.

Denmark and France have also pioneered the use of Portland Pozzolan cements, particularly for marine work, and India and Australia have recognised their advantages for some time now.

Portland-Pozzolanic cement was first used in the U.S.A. in 1910, but was largely neglected until the 1940's when the discovery that it often reduces alkali-reactive aggregate expansion, [redacted] as well as better realisation of its other advantages, gave it quite a fillip. It has become almost "standard" for large dams and is being used in large amounts at the Glen Canyon Dam (see paragraph 9.2 below), where placement of the concrete was started in June, 1960.

## 8. "MODERN" POZZOLANS

8.1. The ASTM gives a quite comprehensive list of materials, which may be used either in the production of Portland-Pozzolan Cement or as Admixtures in Portland Cement Concrete. They are:

8.1.1. Natural pozzolans, such as some diatomaceous earths, opaline cherts and shales, tuffs, and volcanic ashes or pumicites, any of which may or may not be processed by calcination;

8.1.2. Various/..........

water per second. During the highwater period of 1948 the actual flow rate reached nearly 1 million c.f.s., producing theoretically about 5 million horse power in the stilling basin. During 17 years operation, from 1938 - 1955, the average flood discharge of the river at Bonneville was 543,000 cu.ft. per second

9.1.2. Bonneville Dam was one of the first major structures in which a pozzolanic replacement was used in the cement and at the time of construction it was criticized as being unsuited to this type of structure. The cement used consisted of 3 parts of Portland cement of modified composition interground with 1 part of calcined shale.

9.1.3. During the planning period, based on experience with Portland cement, the board of consulting engineers stated that it would be necessary to replace the baffles in the stilling basin at about 15 year intervals. After 17 years service half the stilling basin was dewatered, and found to be in better condition than expected even from divers' reports. Repairs were carried out, but it was decided that repairs to the other half, which had not been damaged by large pebbles and boulders during the construction period, could be deferred until annual divers' surveys indicated their necessity

### 9.2. Glen Canyon Dam - U.S.A.

9.2.1. Placing of the concrete in this dam was started on the 17th June 1960. It is not expected to reach completion until about 1967.

9.2.2. A new cement factory was built to supply the 12,000,000 pockets of Portland cement (Type II, low

alkali/...........

alkali), and a separate plant erected to process the 4,700,000 pockets of pozzolanic material, which will be required for its 5 million cubic yards of concrete.

9.2.3. The dam wall, a concrete arch type, will be 710 feet high, 1,500 feet long, 300 feet thick at maximum section, and 35 feet thick at crest. When full, the dam will be 186 miles long and will cover 230 square miles, impounding some 28,000,000 acre-ft. of water.

9.2.4. Pozzolanic material is being used in the concrete for the following technical reasons:

9.2.4.1. To improve workability of wet concrete;
9.2.4.2. To reduce the heat of hydration; and
9.2.4.3. To reduce permeability.

9.2.5. Specifications were written for "natural pozzolans" (including calcined materials) and "fly ash", and contractors invited to tender. 97 Samples of pozzolan, from 74 sources, were tested. Shales and clays were nearest, but most costly to process as they required calcining as well as grinding. Fly ash, which needed no processing, was the cheapest, but furthest from the site and most costly to transport.

9.2.6. When all job materials were available, samples were obtained for a comprehensive concrete mix test programme. The investigations were to determine the most desirable mix proportions for both interior and exterior Glen Canyon Dam concretes, based on workability, strength development, elastic and thermal properties, creep, permeability, drying and autogenous shrinkage, and durability. Test specimens ranged in size up to 18" x 36" cylinders.

## 10. OTHER MODERN APPLICATIONS.

### 10.1 In the U.S.A.

10.1.1. In two major structures, the Arrowrock Dam and the Elephant Butte Dam, built in 1912 - 1916, so-called "sand-cement" mixtures were used. The respective proportions and materials were: 45% granite interground with 55% portland cement and 48% sandstone interground with 52% portland cement. Judged by present-day standards these materials are relatively "inactive" (see, however, paragraph 8.6 above) and their proportions excessive, but the sand-cement mixtures had to pass portland cement specification tests before acceptance. Although their early tensile strengths were lower than those of comparable portland cements, at 1 year they were equal, and at 5 years had greater strength. The concrete in both dams was in good condition after 33 years of service, was remarkably free of cracks, and compared favourably in watertightness with other dams built about the same period.

10.1.2. The Santa Cruz Portland Cement Co., California, has been producing a Portland-pozzolan cement containing calcined Monterey shale since 1929. It was used in 1932 in several structures and in a stretch of experimental highway. As a result of these and other experiments about 1.3 million bags of this type of cement were used in the San Francisco

Bay Bridge and in the pier and fender of the Golden Gate Bridge. The main reason for permitting this material to be used in structures exposed to sea-water was its proven resistance to alkali soils and sulphate waters, together with the favourable heat generation characteristics it possessed for these massive blocks of concrete.

10.1.3. Other U.S.A. structures, and the pozzolans used were

- 10.1.3.1. Friant Dam, 1940 - 42, using Fresno pumicite;
- 10.1.3.2. Davis Dam, circa 1949, using calcined Puente shale;
- 10.1.3.3. Hungry Horse Dam, circa 1948, using Fly Ash;
- 10.1.3.4. The Tecolate Tunnel, circa 1955, using an oil-impregnated shale, the oil in which was used to calcine it;
- 10.1.3.5. Mackinac Bridge Pier, circa 1956, using Fly Ash; and
- 10.1.3.6. South Saskatchewan River Dam, circa 1961, using a Type V cement with a pozzolan.

10.2. <u>In India</u>.

10.2.1. Bhakra Dam, circa 1957, using calcined shale;

10.2.2. Rihand Dam, circa 1960, using fly ash.

10.3. <u>In Australia</u>.

10.3.1. Koombooloomba Dam, circa 1961.

10.4. The Russians and Europeans have also made extensive investigations into, and use of, natural and artificial pozzolans (see also paragraph 3.5 - 4 above).

11. Specifications/.......

## 11. SPECIFICATIONS.

The following countries have official specifications for Portland pozzolan cements:
Bulgaria, China, Czechoslovakia, France, Germany, Greece, Hungary, Italy, Japan, Mexico, Netherlands, Portugal, Rumania, Spain, U.S.A., U.S.S.R., and Yugoslavia.

12. In conclusion, I feel I can do no better than to quote Mr Wolf G.Bauer (25.1) : "Seldom has a material in industry been so greatly needed and also made so readily and economically available by nature or by-product as the lime-eliminating reactive materials we call pozzolans. By the same token, seldom has such a material been grouped and identified with a more dangerously over-simplified singular name, such as the designation 'pozzolan' would suggest. All pozzolans will, more or less, 'mop up' the free lime present or released by the portland cement. However, the fact that many of these pozzolans can be treated to act in addition as stabilizers for excess soluble alkalis released from either or both the hydrating cement or the wetted aggregate, further enhances their ultimate value; and this fact fulfills even more their potential role of helping eventually to achieve a universal safety cement for concrete of utmost permanency in general use. The relative rate and efficiency with which a pozzolan can reduce the inevitable lime content from concrete made with general-purpose amount is shown in Figure 1" (Page 60 )
" It should be further noted that chemical stability in a concrete or mortar is gained not only through removal of reactive lime, but evidently also through the mechanism of shielding and inactivating reactive aluminate hydrates which become film coated or encased by the stable gels of pozzolan-

lime-silicates."* (See footnote)

"No one material in this complex chemistry of hydraulic cementing reactions can ever be considered a cure-all. However, nothing so far has come along, either in cement manufacture or concrete additives, that can match the growing success story of properly applied pozzolans to special and general-purpose concrete and its products. To the writer, this relatively recent and widespread interest and research activity into pozzolan buffers reveals an apparent dissatisfaction with today's general-purpose concretes under other-than-normal service conditions of exposure to chemical influence from outside, as well as from aggregate and cement sources."

12. References: 1.1, 1.2, 1.7, 1.10, 2.1, 2.2, 2.6, 3.4, 4.2, 4.4, 5.2, 6.1, 6.4, 7.14, 7.15, 7.16, 8.1, 8.2, 8.4, 9.1, 10.1 - 10.5, 11.2 - 11.4, 12.1 - 12.5, 13.1 - 13.5, 18.1-2, 18.1-5, 18.1-7, 18.1-8, 18.4, 18.5-1, 18.5-2, 19.3, 20.2 D, 20.3, 20.8 D, 20.10, 20.11, 20.12, 20.14, 20.16, 20.20 - 20.37, 23.1 - 23.4, 24.1 - 24.4 25.1 - 25.5.

* According to an ingenious theory advanced by Chatterji and Jeffrey (23.4) sulphate expansion is caused by the conversion of $C_4AH_{13}$ to $C_3A.C\bar{S}.H_{12}$ in the presence of $Ca(OH)_2$. In the absence of $Ca(OH)_2$ the reaction products of sulphate attack can be "accommodated" in the structure.

# Relative Rates of Lime Release and Absorption of Portland Cement + Pozzolans

(From : Pit + Quarry, June 1959, p. 94)

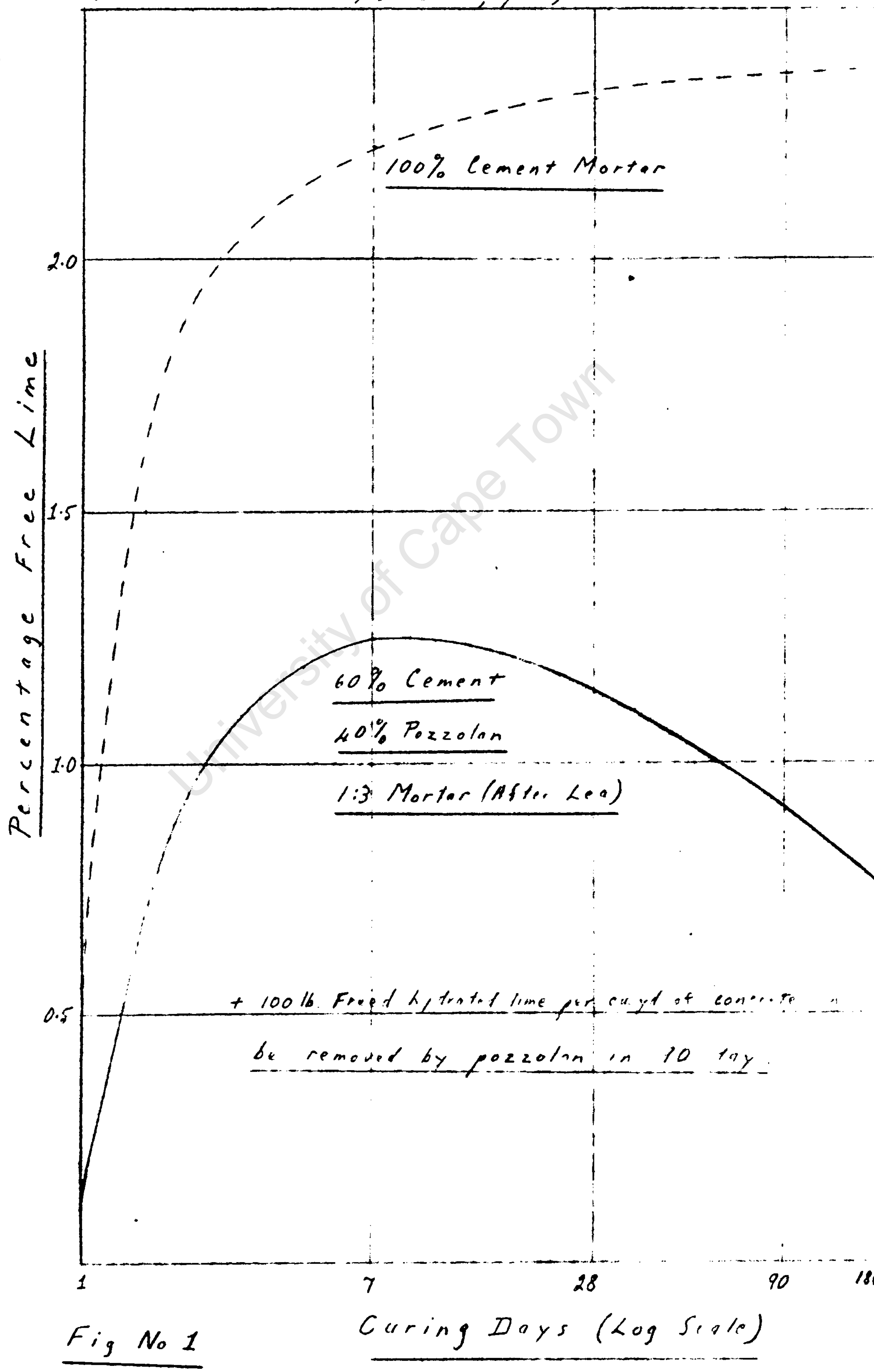


Fig No 1

## 3.6. PORTLAND BLASTFURNACE CEMENT.

1. Although also manufactured from Granulated Blastfurnace Slag, Portland Blastfurnace Cement does not have the same properties as Super-sulphated Cement. It is more like Portland cement, the proportion of which is generally about 50%, although it may range from 15% to 85%. Uncalcined gypsum is used as a setting time regulator, and generally does not exceed about 5% of the mixture.

2. Slag is sometimes classified as a Pozzolan, because it does react with hydrated lime to some extent, but the usual practice is to treat it separately, as a different type of material.

3. When interground with Portland cement, granulated blastfurnace slag does confer several of the beneficent properties of pozzolans on the product, such as reduced heat of hydration, improved resistance to chemical attack and reduced permeability. Early strengths of "P.B.F.C." are generally lower, and ultimate strengths higher, than those of the Portland cement fraction by itself, subject of course, to proportions and fineness of grinding of the mixtures.

4. Portland blastfurnace cement has not been included in this research project because there are no local sources of blastfurnace slag.

5. References: 1.8, 2.5, etc.

## 3.7. AIR - ENTRAINING AGENTS.

1. "Air present in voids in the cement paste of unhardened concrete is derived from several sources:

(1) "Air originally present in intergranular spaces in the cement and aggregate; (2) air originally present within the particles of cement and aggregate but expelled from the particles before hardening of the concrete by inward movement of water under hydraulic and capillary potential;
(3) air originally dissolved in the mixing water and
(4) air which is in-folded and mechanically enveloped within the concrete during mixing and placing." (20.45 - I). The amount of air which is entrapped in the concrete, and the size of the bubbles, can be controlled by the use of "air-entraining agents". These are chemical substances of various types; and generally amounts of less than 0.05% of the weight of cement are needed to entrain the amount of air required.

2. It was discovered, in America in the late 1930's, that air-entrained concrete is much more resistant to the action of frost (i.e. cycles of freezing and thawing) than ordinary concrete is. This discovery is generally considered to have been accidental, as a result of oil from a mill leaking into the cement at a particular factory, but Hansen maintains that "the fact that certain materials caused entrainment of air and the effects produced by this air were observed as results of systematic researches. Hence, the only accidental feature was that the investigators had not realised previously that these results would be observed" (20.47) Probably the two accounts, taken together, tell the whole story.

3. Further investigation and experience revealed that the use of air entraining agents can also reduce the susceptibility of concrete to attack by sulphates, to marine corrosion, and,

in fact/...............

in fact, generally increase its durability by a substantial factor. These benefits are not due to any chemical action, but are solely due to physical causes, such as:-

3.1. Improved "workability" of wet concrete, which enables the water/cement ratio to be reduced;

3.2. The small, discrete bubbles of air tend to break up capillaries in the concrete, and so reduce its permeability; and

3.3. A "cushioning" effect is provided which reduces the damage caused by expansion within the structure, such as that due to the freezing of capillary water and the crystallization of salts.

4. "In the realm of practical concrete mixtures air entrainment may be defined as the incorporation in the concrete of innumerable* bubbles of air having average diameters of the order of 25 to 50 microns (0.001 to 0.002 in.) aggregating a total volume not in excess of 6 or 8 percent of the concrete" (20.44)

* According to Fulton (3.4) "laboratory tests have shown that there are between 400 and 600 billion air bubbles in each cubic yard of normal air-entrained concrete, and at optimum air content the bubbles should be about 0.02 in. apart."

5. In fresh concrete these air bubbles constitute an additional fine aggregate. Their complete flexibility of shape relieves internal friction, so that they function virtually as a "lubricant" with the result that less water

is required for equal workability. Experience has shown that the sand content can be reduced by an amount approximately equal to the volume of air entrained and that the water content can be reduced by 2 to 4% for each 1% of air entrained, without loss in slump. In fact, many workers have observed that an air-entrained concrete has a "fattiness" which also enables slump to be reduced without loss of workability. Bleeding and segregation of wet concrete are both reduced by air-entrainment.

6. In a long-time study of cement performance, after fifteen years exposure of reinforced concrete piles, the beneficial effects of air-entraining outweighed differences in cement composition as far as protection of reinforcement was concerned. Numerous other tests have confirmed these findings. A distinction must be made between the micro-bubbles of deliberately entrained air and accidentally entrapped air. An improperly consolidated concrete will contain macro pockets of entrapped air which increase permeability and contribute little or nothing toward relief against disruptive pressures.

7. When air-entrainment is used in rich concrete mixes there is generally some loss of strength, but in the case of lean mixes the reduced water/cement ratio may actually result in higher strength. Bond strength between cement paste and reinforcement is only significantly affected by excess air-entrainment - more than about 8% air in the concrete.

8. Air-entraining agents have been included in this study, although they do not occur "locally", because the amounts required are very small (paragraph 1 above) and the potential benefits are large.

9. References: 1.2, 1.10, 3.2, 3.4, 4.3, 6.3, 6.5, 7.13, 8.2,
20.1, 20.4, 20.7, 20.9, 20.11, 20.27, 20.38-20.47
27.2 - 27.5.

# CHAPTER IV

## SULPHATE - RESISTING PORTLAND CEMENT - PART I

## PRELIMINARIES

### 4.1. STANDARD SPECIFICATIONS.

1. In Table No.2 (Page 66 ) I have given, for comparison purposes, a summary of the requirements of the following standard specifications for Portland cements:

1.1. B.S.12 : 1958, for Portland Cement;

1.2. S.A.B.S.471 : 1959, for Portland Cement;

1.3. ASTM : C 150, for Type I Portland Cement, "for use in general concrete construction when the special properties specified for types II, III, IV and V are not required" ;

1.4. ASTM : C 150, for Type II Portland Cement, "for use in general concrete construction exposed to moderate sulphate action, or where moderate heat of hydration is required" ; and

1.5. ASTM : C 150, for Type V Portland Cement, "for use when high sulphate resistance is required".

Table No.2
Summary of the/.................

2. B.S.12 : 1958 and S.A.B.S.471 : 1959 are the standard specifications generally used in South Africa, and it is desirable, therefore, that any special cements should comply with their requirements as nearly as possible, particularly with regard to the physical requirements of setting-time, strength, etc.

3. ASTM : C 150, for Type I Portland Cement is generally similar to the B.S. & S.A.B.S. specifications in its requirements but the methods of testing for strength are different, and the strength requirements cannot be directly compared. I included it, therefore, to indicate the differences between the requirements for O.P.C. and for sulphate-resisting cements.

4. References : 18.1 - 1, 18.2, 18.3.

## 4.2. RAW MATERIALS.

1. At the factory where the sulphate-resisting cement is now produced, Portland cement is normally made from "high-grade" and "low-grade" limestone, and shale. The low-grade limestone is, in effect, a mixture of high-grade limestone and shale, often in just about the correct proportions for Portland cement. Sulphate-resisting Portland cement has approximately the same proportions of lime and silica as the ordinary variety, but must have less alumina and/or more ferric oxide. The raw materials required are:-

(1) high grade limestone;

(2) silica and ferric-oxide-bearing materials with a comparatively low alumina content.

If all these materials are very low in alumina then the mix may be difficult to "burn" in the kiln and in such cases some aluminous material (such as shale) may have to be added as well.

2. Investigation and enquiry revealed that a nearby river sand would be a suitable source of silica, and that iron-oxide is obtainable in the form of "spent-oxide" - waste material from the manufacture of sulphuric-acid from iron-pyrites. It was later found that nearby deposits of iron-ore are equally suitable. Limestone is available at the works, and also shale (mainly aluminium-silicate) if required. "Typical" analyses of these materials are given in Table No.3.

TABLE NO. 3

"TYPICAL" ANALYSES OF RAW MATERIALS AVAILABLE FOR THE PRODUCTION OF SULPHATE-RESISTING PORTLAND CEMENT

| Material | Percentages of Constituents | | | | | | Loss on Ignition |
|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | |
| High-grade Limestone ( ± 90% $RCO_3$ [1] ) | 6.7 | 1.7 | 0.3 | 48.7 | 1.0 | - | 41.0 |
| Low-grade Limestone ( ± 76% $RCO_3$ ) | 14.2 | 4.6 | 1.9 | 41.8 | 0.9 | - | 35.5 |
| Shale | 60.2 | 17.4 | 8.0 | 2.0 | 1.0 | - | 8.4 |
| River Sand | 93.5 | 3.5 | 1.0 | 0.5 | - | - | 1.0 |
| Dry Spent-Oxide | 10 | 10 | 75 | - | - | 2 | 2 |
| Iron Ore | 14 | 9 | 73 | - | - | - | 3 |
| Fuel Ash | 43 | 29 | 6 | 13 | 2 | 7[2] | - |

Note 1 : "$RCO_3$" indicates $CaCO_3$ + $MgCO_3$

Note 2 : This includes the sulphur, in the coal, which is burnt to $SO_2$ and "picked up" by the clinker as $SO_3$.

## 4.3. TESTS FOR SULPHATE RESISTANCE

1. The "Sulphate Susceptibility Test" of Bogue and Taylor was selected for initial checking of sulphate-resistance of the Type V sulphate-resisting cements made because the results can be available within 12 hours.

### 1.1. Basis of the Test.

As already mentioned (paragraph 2.3 - 4 and section 2.4), tri-calcium aluminate and calcium-sulphate react to form ettringite - $3\ CaO.Al_2O_3.3\ CaSO_4.32H_2O$. This double salt is highly insoluble and can reduce the concentration of dissolved sulphates to 0.001 g. $SO_3$ per 100 ml. in saturated lime water (1.4 & 2.7) In this test sufficient lime-water is added to the cement sample to dissolve all the $CaSO_4$ present, ettringite is allowed to precipitate and then filtered off, and the amount of $CaSO_4$ remaining in solution is determined. Subtracting the $SO_3$ remaining in solution from the amount originally in solution gives the amount of $SO_3$ "used up" to form ettringite, and hence indicates the quantity of "susceptible" aluminate present in the cement.

### 1.2. Test Method according to Taylor & Bogue:

Full details of the test method are given in Appendix No.1.

The $SO_3$ used up, expressed as a percentage of the $SO_3$ originally present, is called the "Sulphate Reaction Value", or "S.R.V.".

### 1.3. Significance of the S.R.V. (Sulphate Reaction Value)

S.R.V's, obtained by the above method, were

correlated by/................

correlated by Bogue & Taylor with the performances of over one-hundred commercial cements immersed in magnesium and sodium sulphate solutions over a long period. Expansion and loss of strength of specimens in the sulphate solutions were measured. From these correlations Bogue concluded that:

SRV below 50: indicated a cement relatively resistant to sulphate attack. The lower the SRV the better;

SRV 50 - 65: should be considered of doubtful value in sulphate conditions; and

SRV above 65: indicated a cement relatively non-resistant to sulphate attack.

## 1.4. Defect in the Test

As it stands the test cannot be used for Portland cement clinker, which contains little or no $SO_3$. Even with cements the value obtained will depend upon the amount of $SO_3$ in the cement, as illustrated below:

Suppose two cements each contain $13\frac{1}{2}$% $C_3A$, but the one has 1.8% $SO_3$ and the other 2.7% $SO_3$.

If we assume that the $C_3A$ will react with the same amount of $SO_3$ in each case, and that 1g. $C_3A$ reacts with [illegible] g $SO_3$, then:

For Cement A:

$SO_3 = 1.8\%$

$\therefore$ Weight of sample $= \frac{5.4}{1.8} = 3.0$ g.

Weight of $SO_3$ in sample $= \frac{3 \times 1.8}{100} = 0.054$ g

Weight of $C_3A$ in sample $= \frac{3 \times 13.5}{100} = 0.405$ g.

Weight of $SO_3$ reacting with $C_3A$ $= 0.405 \times a$ g.

$$\underline{SRV} = \frac{0.405 \times a \times 100}{0.054} = \frac{405\,a}{0.054} = \underline{750\,a}$$

For Cement B:

$SO_3 = 2.7\%$

$\therefore$ Weight of sample $= \frac{5.4}{2.7} = 2.0$ g.

Weight of $SO_3$ in sample $= \frac{2 \times 2.7}{100} = 0.054$ g.

Weight of $C_3A$ in sample $= \frac{2 \times 13.5}{100} = 0.27$ g.

Weight of $SO_3$ reacting with $C_3A$ $= 0.27 \times a$ g.

$$\underline{SRV} = \frac{0.27 \times a \times 100}{0.054} = \frac{27a}{0.054} = \underline{500\,a}$$

By this method, then, any cement with an $SO_3$ content of 1.8% will have an SRV 50% higher than it would have had with an $SO_3$ content of 2.7%

Davis (23.5) also noticed this defect and, by varying $CaSO_4.2H_2O$ from 3% to 7%, obtained SRV's ranging from 64 to 24 on a clinker containing 10% $C_3A$. Increasing the $CaSO_4.2H_2O$ to 7% certainly does NOT make a cement sulphate-resistant; in fact, a high $SO_3$ is the basis of the ASTM "Performance Test for the Potential Sulphate Resistance of Portland Cement" (see paragraph 3 below).

## 1.5. Modification of Test Method:

In order to overcome the above-mentioned defect in the test, and to make it applicable to clinker, I eventually introduced the following modification:

"After determining the $SO_3$ content of the cement, calculate the weights of cement and $CaSO_4.2H_2O$ required to make a 1.8 gram sample containing 3% $SO_3$. (I prepared a table showing the weights of cement and $CaSO_4.2H_2O$ required for any sample, from a clinker with zero to a cement with 3% $SO_3$ - the maximum permitted.

This table/................

This table, and full details of the modified method, are given in Appendix No.2 ) Then proceed as before.? The advantage of this method is that the same weight of clinker is always tested in the same concentration of sulphate and the results are independent of the $SO_3$ content of the cement sample.

## 1.6. Conversion of Test Results:

Provided the $SO_3$ of the cement sample is known, as well as the SRV, values obtained by the Bogue method can be converted to Modified method values by calculation, according to the formula:

$$SRV_{Mod.} = SRV_{Bogue} \times \frac{14.5 \times \% SO_3}{46.5 - \% SO_3}$$

For the derivation of this formula, and its justification in practice, see Appendix No.3.

## 1.7. Significance of SRV's obtained by Modified Method:

A table is given in Appendix 3 showing Modified SRV's calculated from Bogue SRV's at various $SO_3$ levels. The cements tested by Bogue and Taylor mostly had $SO_3$ contents in the range 1.7% to 2.0%, so modified values of 30 and 40 may be taken as approximately equivalent to Bogues values of 50 to 65. We may reasonably assume, therefore, that when a Portland cement is tested by the Modified method:

SRV below 30 : indicates satisfactory potential sulphate resistance (the lower the SRV the better).

SRV above 40 : indicates that the cement will be susceptible to sulphate attack.

1.8. Some test/................

1.8. Some test results obtained:

| Cement | $C_3A$ % | $SO_3$ % | Sulphate Reaction Values | | |
|---|---|---|---|---|---|
| | | | Bogue | Converted[x] | Modified |
| Imported Sulphate-resisting cement. | 0.7 | 2.0 | 18 | 12 | - |
| Ordinary Portland Cement (a) | 11.5 | 2.6 | 74 | 64 | - |
| Ordinary Portland Cement (b) | 8.5 | 2.3 | 40 | 30 | 31 |
| Second batch of "Local" SR Cement | 1.8 | 2.2 | 31 | 22 | - |
| Last batch of "Local" SR Cement | nil | 1.8 | 21 | 12 | 13 |

[x] Converted means Bogue values converted by the formula given in paragraph 1.6 above.

The results for Ordinary Portland Cement (b) are of interest, because the Bogue SRV puts it in the sulphate resisting class, whereas the Modified SRV puts it in the "intermediate" class - this is more likely where it belongs, judging by its $C_3A$ content.

1.9. The test was initially used, for this work, in its original form, but is now used in the modified form. For purposes of this report, when only Bogue values are available I shall report them as determined and also converted. To be on the safe side a Modified Sulphate Reaction Value of <u>25</u> is regarded as the maximum permissible for Sulphate Resisting Cement. It does not seem advisable to use the test for "mixed" cements, such as Portland-Pozzolanic cements, because the clinker content is generally unknown, and, in my

opinion/.................

opinion the test is only applicable to "pure" Portland cement anyway.

2. The "Slab-Warping Test" (an improved version of the "Merriman Test") was developed by the research laboratory of the Metropolitan Water District of Southern California.

2.1. Method of Test (brief outline)

"The slab-warping test which finally evolved from experimentation consisted in the preparation of neat cement slabs having dimensions of 2 x 4½ x ⅛ inch, one face being coated with a water-repellent paint and the other carefully scraped to provide a fresh surface for attack. Slabs are cured under water for 7 days, then immersed in a 10% sodium sulphate solution for the remainder of the 28-day period. Due to exposure of only one face, expansion resulting from the sulphate attack causes the slab to warp, and the extent of the attack is reflected in the degree of warping.

"A spherometer was devised for measuring the extent of the warping, and it was found that the rate of the warping rather than the absolute magnitude was the best measure of the susceptibility of the cement to the sulphate action. Accordingly, the difference between the 21-day and the 7-day readings is called the warping index and is used as the basis of comparison".(20.14.p.102)

2.2. Test results were found to correlate well with long term tests in the case of Portland cements, not so well in the case of Portland-pozzolanic cements. This was to be expected, of course, because some of the protection given by pozzolans is "physical" and the "chemical"

protection/.............

protection only really starts after 28 days.

2.3. The test method appears to have been dropped in favour of the more reproducible "expansion" test described next, so it was not included in this test series.

3. The "Performance Test for the Potential Sulphate Resistance of Portland Cement", developed by the ASTM, looked most promising as a means of checking the sulphate resistance of cement within 28 days, so it was tried on a few selected samples. Time has confirmed the value of the test, which itself provides a useful long-term check on the sulphate-resistance of cements because it is "non-destructive" except in the case of cements with very low-resistance. By introducing some modifications the test-method can also be used for determining the effect of various cations, such as $Mg^{\cdot\cdot}$, on cements, in conjunction with either sulphates or other anions.

3.1. History and broad basis of test.

The test was developed by the ASTM Working Committee on Sulphate Resistance. The lengths of mortar bars containing excess calcium sulphate were measured at intervals (up to 1 year), and the percentage expansions were compared with the results of long-time field tests on concretes exposed to sulphate soils. The Working Committee claimed that: "(1) significant expansion occurs within 28 days, (2) reproducible results can be obtained in different laboratories, (3) the expansions discriminate between different cements, (4) there is a general relationship between the 28-day expansion of the mortar prisms and the $C_3A$ content of the cement and

(5) there is a relatively good relationship between the 28-day expansion of the mortar prisms and the performance of concretes exposed to sulphate soils".(21.1).

## 3.2. Brief description of the test method:

Determine the $SO_3$ content of the cement, and use this result to calculate the weights of cement and calcium sulphate powder ($CaSO_4.2H_2O$) required for a 400 gram mixture containing 7% $SO_3$. Mix the cement, calcium sulphate, 1100 grams of sand, and water in a mechanical mixer. (Sufficient water to give a standard flow-table consistency must be used - it is usually about half the weight of the cement). Place in moulds 1" x 1" x 11¼" and insert stainless steel studs in the ends - the effective gauge length between the studs is 10". Demould after about 23 hours, place the specimens in water for at least 30 minutes and then measure the length; this is the "initial reading". Replace in water and remeasure periodically. Calculate the expansion at each age to the nearest 0.01% of effective gauge length.

## 3.3. Investigation of Test Method:

Test specimens were made up from three samples of cement; expansions determined at various ages; and results compared with the ASTM results for various types of cement (21.1).

Cements used:

| Designation | Description of Sample |
|---|---|
| OPC/1 | Commercial Portland Cement-"high" potential $C_3A$ |
| OPC/2 | Commercial Portland Cement- "moderate" potential $C_3A$. |
| I/SRC | Imported Sulphate Resisting Cement(Sulfacrete) |

The analyses and potential compound contents are given in Table No.4 on Page 77.

Table No.4 /.....................

## TABLE NO.4

## ANALYSES OF CEMENTS USED FOR INITIAL TRIALS OF POTENTIAL SULPHATE-RESISTANCE TEST

| CONSTITUENT | OPC/1 | OPC/2 | I/SRC |
|---|---|---|---|
| OXIDES: | % | % | % |
| $SiO_2$ | 20.0 | 22.9 | 21.4 |
| $Al_2O_3$ | 7.1 | 4.9 | 3.9 |
| $Fe_2O_3$ | 2.9 | 2.3 | 5.7 |
| CaO | 63.2 | 63.4 | 62.8 |
| MgO | 1.7 | 1.7 | 1.2 |
| $SO_3$ | 2.6 | 2.3 | 2.0 |
| POTENTIAL * COMPOUNDS: | | | |
| $C_3S$ | 46.0 | 41.2 | 52.7 |
| $C_2S$ | 22.7 | 34.6 | 21.7 |
| $C_3A$ | 13.9 | 9.1 | 0.7 |
| $C_4AF$ | 8.8 | 7.0 | 17.3 |
| $CaSO_4$ | 4.4 | 3.9 | 3.4 |

* The ASTM "Bogue" method was used for calculating these compounds. The "Newkirk" method, which takes alkalies into account, has advantages for some purposes but would only confuse the issue here because the alkali compound $NC_8A_3$ reacts with $CaSO_4$ to form $C_3A$ and $Na_2SO_4$ (Ref. 1, page 74 )

### 3.4. Results of Investigation.

Expansions of the specimens are reported in Table No.5, to the nearest 0.005%, at 7, 14, 21, 28, 84 and 364 days. Expansions at 28 and 364 days are compared in Table No.6 with some of the expansions reported by the ASTM (21.1). The expansions found were of the same order of magnitude as those reported by the ASTM. The ASTM Committee found that;

(1) variations were lower at 28 days than at 7 days; and

(2) reproducibility was better for sulphate resistant cements than for ordinary cements.

The standard deviations reported in Table 5 generally confirm these findings.

## TABLE NO.5

### EXPANSIONS AT VARIOUS AGES OF CEMENT MORTAR BARS CONTAINING EXCESS $CaSO_4$

| AGE IN DAYS | PERCENTAGE EXPANSION OF SPECIMENS | | | | | STANDARD DEVIATION | COEFFICIENT OF VARIATION |
|---|---|---|---|---|---|---|---|
| | No.1 | No.2 | No.3 | No.4 | Average | | |
| For Cement OPC/1 ($C_3A$ = 13.9%) | | | | | | | |
| 7 | - | - | - | - | - | - | - |
| 14 | 0.125 | 0.15 | 0.13 | 0.16 | 0.14 | 0.017 | 12.1 |
| 21 | 0.175 | 0.20 | 0.185 | 0.215 | 0.195 | 0.018 | 9.0 |
| 28 | 0.225 | 0.24 | 0.245 | 0.26 | 0.24 | 0.015 | 6.2 |
| 84 | 0.495 | 0.525 | 0.495 | 0.515 | 0.505 | 0.015 | 3.0 |
| 364 | 1.015 | 0.965 | 0.895 | 1.005 | 0.97 | 0.05 | 5.6 |
| | | | | | | Av. | 7.2 |
| For Cement OPC/2 ($C_3A$ = 9.1%) | | | | | | | |
| 7 | 0.02 | 0.08 | 0.13 | 0.085 | 0.08 | 0.045 | (56.0) |
| 14 | 0.085 | 0.105 | 0.12 | 0.10 | 0.10 | 0.015 | 14.7 |
| 21 | 0.095 | 0.12 | 0.12 | 0.12 | 0.115 | 0.013 | 10.9 |
| 28 | 0.115 | 0.14 | 0.17 | 0.145 | 0.14 | 0.023 | 16.2 |
| 84 | 0.195 | 0.215 | 0.20 | 0.21 | 0.205 | 0.009 | 4.4 |
| 364 | 0.465 | 0.435 | 0.42 | 0.425 | 0.435 | 0.020 | 4.6 |
| | | | | | | Av. | 10.2 |
| For Cement I/SRC ($C_3A$ = 0.7%) | | | | | | | |
| 7 | 0.05 | 0.045 | 0.045 | - | 0.045 | 0.003 | 7.8 |
| 14 | 0.05 | 0.05 | 0.05 | - | 0.05 | 0 | 0 |
| 21 | 0.06 | 0.055 | 0.055 | - | 0.055 | 0.004 | 6.3 |
| 28 | 0.055 | 0.045 | 0.055 | - | 0.05 | 0.006 | 12.2 |
| 84 | 0.08 | 0.075 | 0.09 | - | 0.08 | 0.008 | 9.9 |
| 364 | 0.13 | 0.115 | 0.13 | - | 0.125 | 0.009 | 6.9 |
| | | | | | | Av. | 7.2 |

Table No.6/...............

## TABLE NO.6

## COMPARISON OF 28 DAY AND 1 YEAR EXPANSIONS WITH SOME ASTM RESULTS ON AMERICAN CEMENTS

| DESIGNATION AND TYPE OF CEMENT | | % $C_3A$ | % EXPANSION AT: 28 DAYS | 1 YEAR |
|---|---|---|---|---|
| OPC/1 | OPC - Type I | 13.9 | 0.24 | 0.97 |
| OPC/2 | OPC - Type I | 9.1 | 0.14 | 0.435 |
| I/SRC | SRC - Type V | 0.7 | 0.05 | 0.125 |
| **ASTM RESULTS** | | | | |
| 18 | OPC - Type I | 12.2 | 0.225 | (0.74 at 3 months) |
| 33 | RHC - Type III | 9.2 | 0.09 | 0.25 |
| 14 | OPC - Type I | 7.1 | 0.055 | 0.17 |
| 21 | Mod.SRC - Type II | 5.1 | 0.05 | 0.145 |
| 5M | SRC - Type V | 1.7 | 0.05 | 0.09 |
| 5P | SRC - Type V | 1.4 | 0.025 | 0.05 |
| 3L | RHC - Type III | nil* | 0.015 | 0.03 |

* This cement contained 3.6% $C_2F$ - i.e. the $Al_2O_3/Fe_2O_3$ ratio was less than 0.64.

3.5. These tests have been continued, and expansions at 2½ years of age confirm that expansions at 28 days give a good indication of the potential sulphate-resistance of a cement. The expansions at later ages, and the modifications introduced to check the effect of other solutes, are all presented in a later chapter. It has proved a most valuable method for confirming the improved stability of the special cements produced.

4. A Strength/.................

## 4. "A Strength Test for Sulphate Resistance".

4.1. Several other workers have tried using strength as a criterion of sulphate resistance. Specimens were made up, cured in various sulphate solutions, and then tested for strength. Various degrees of success have attended these efforts, but, in general, only fairly long-term tests have given significant results, and large numbers of specimens have to be made up.

4.2. Van Aardt (19.2) overcame the difficulties of strength testing very neatly by using a non-destructive procedure. The National Physical Laboratory developed an apparatus for measuring the natural frequency of vibration, and van Aardt used this to test 1" x 1" x 11¼" mortar bars, in addition to measuring their length. He found that "quality", as measured by natural frequency of vibration, generally deteriorated as expansion increased.

4.3. As cement is generally used for making concrete, consumers are more readily impressed when test results on concrete specimens are quoted and, indeed, it seems logical to use concrete strengths for assessing cement quality whenever possible.

4.4. Cembureau introduced a mortar strength test, as a tentative international standard, which has much to commend it in that three strength results are obtained from each specimen made. The bars, 4 x 4 x 16 cm, are first broken in flexure and then the broken ends are tested separately in compression. The British Standard Specification (BS 12) introduced a concrete compression test in 1959, but the 4" cubes are on the large size and only one test result is obtained per specimen.

4.5. After discussions with the staff of the local branch of the Portland Cement Institute I decided to try making concrete specimens, using small-size aggregate, in Cembureau-size moulds. These were also tested first in flexure, and then in compression. Some were cured in water, and some in various sulphate solutions. Results on specimens of up to 9 months age have been most encouraging and are fully reported in a later chapter. In general the results tend to confirm the expansion test findings, but are likely to carry more weight with construction engineers and contractors. Means of improving the test still further with the aid of mechanical mixers etc., are currently under consideration. Although accelerated techniques were used, no significant results were obtained under six months and the test is likely to have most value as a long-term method.

5. References: 1.4, 2.7, 18.1-4, 18.2, 18.3,
19.2, 21.1, 23.5.

## 4.4. PROPORTIONING OF MATERIALS.

1. The chemical requirements of Sulphate-resisting cement (ASTM Type V ) were given in section 4.1, and the analyses of the available raw materials in section 4.2, above. Experience has shown that, for the kiln used, about 1½% of the clinker produced comes from the coal ash, and this

must be taken into account when calculating the proportions in which to mix the raw materials. The composition of the first mixture used is shown in Table No.7. "Undetermined" oxides include $Na_2O$, $K_2O$, and other minor constituents. The clinker composition was determined by reducing the "total" raw mix to a "loss-free" basis, and the Bogue formula used for calculating the potential compounds. This clinker complies with all the chemical requirements of S.A.B.S.471 : 1959, B.S.12 : 1958, and ASTM Type V Portland cement standards. The three basic raw materials should, therefore, be mixed in the proportions 85½ : 9 : 4.

### TABLE NO.7

### PROPORTIONS OF MATERIALS, AND ANTICIPATED COMPOSITION OF CLINKER, FOR SULPHATE-RESISTING CEMENT

| CONSTITUENTS | LIME-STONE | SAND | SPENT-OXIDE | ASH | TOTAL | CLINKER |
|---|---|---|---|---|---|---|
| Proportions | 85½% | 9% | 4% | 1½% | 100% | - |
| % $RCO_3$ | 77.0 | - | - | - | 77.0 | - |
| % Oxides | | | | | | |
| $SiO_2$ | 5.7 | 8.4 | 0.4 | 0.65 | 15.15 | 23.4 |
| $Al_2O_3$ | 1.45 | 0.3 | 0.4 | 0.45 | 2.6 | 4.0 |
| $Fe_2O_3$ | 0.25 | 0.1 | 3.0 | 0.1 | 3.45 | 5.3 |
| CaO | 41.6 | - | - | 0.2 | 41.8 | 64.6 |
| MgO | 0.85 | - | - | - | 0.85 | 1.3 |
| $SO_3$ | - | - | 0.1 | 0.1 | 0.2 | 0.3 |
| "Loss" | 35.1 | 0.1 | 0.1 | - | 35.3 | - |
| Undetermined | 0.55 | 0.1 | - | - | 0.65 | 1.1 |
| TOTALS | 85.5 | 9.0 | 4.0 | 1.5 | 100.0 | 100.0 |
| "Ratios" : | | | | | | |
| L.S.F. | | | | | | 0.87 |
| $Al_2O_3/Fe_2O_3$ | | | | | | 0.75 |
| % Potential Compounds: | | | | | | |
| $C_3S$ | | | | | | 49.7 |
| $C_2S$ | | | | | | 29.6 |
| $C_3A$ | | | | | | 1.6 |
| $C_4AF$ | | | | | | 16.1 |
| $C_4AF$ + 2 x $C_3A$ | | | | | | 19.3 |

"Loss" means Loss on Ignition.

2. In practice/............

**For the method of calculating the proportions of the raw materials see Appendix 4**

2. In practice it is seldom possible to adhere to the proportions calculated for several reasons:

2.1. Raw materials are not of constant composition and feed rates to the mill vary with the physical nature of the material, so periodic analyses of the product must be made, and the proportions of the materials readjusted to correct for the variations.

2.2. The production rate of the mill is 30 - 40 tons per hour, and it is not possible to do complete analyses frequently. One or two parameters must be selected for hourly control, by rapid methods of analysis, and the other constituents determined once per shift and/or once per day.

2.3. In order to make the product as uniform as possible, the raw grind is first put into "blending silos", which hold about 500 tons of material each, and then transferred, with constant mixing, to "storage silos" (of about 1,000 ton capacity), from whence it is fed to the kiln. Periodic analyses are made of the kiln-feed, to check that the composition is correct, but no adjustments can be made to it at that stage.

2.4. It is, unfortunately, not possible to empty the silos completely, and varying amounts of the ordinary "raw meal" get intermixed with the special mixes. Allowance must be made for this, particularly during the first few hours of grinding, but the first lot of clinker produced usually has to be rejected for special purposes- fortunately it can be intermixed with the ordinary clinker.

3. Taking/................

3. Taking the three materials, limestone, sand, and spent-oxide, in the proportions $85\frac{1}{2}$ : 9 : 4, the feed-rates required for a mill output of 35 tons per hour, are:

Limestone : 30.4 tons per hour.
Sand : 3.2 " " "
Spent-oxide : 1.4 " " "

4. As limestone is generally the most variable material used, and $CaCO_3$ the most important constituent to maintain at a constant level, the usual method of mix control is to determine the $RCO_3$ content of the mill product every hour. This is done by dissolving a fixed weight of raw grind in a known amount of acid, boiling off the $CO_2$, and back-titrating with standard NaOH solution. If the percentage of $RCO_3$ falls outside the pre-set limits, the feeders are readjusted accordingly.

5. After burning, the cement clinker must be interground with gypsum. For this type of cement the $SO_3$ content must not exceed 2.3% (paragraph 4.1 ) and a minimum of 1-$1\frac{1}{2}$% is required to regulate setting time and to prevent undue drying shrinkage. The clinker was expected to contain about 0.3% $SO_3$, so I decided to add a further 1.5%. The gypsum available usually contains about 80% $CaSO_4.2H_2O$ and $CaSO_4.2H_2O$ has an $SO_3$ content of 46.5%, so the proportion of gypsum required was:

$$1.5 \quad x \quad \frac{100}{80} \quad x \quad \frac{100}{46.5} \quad = \quad 4.0\%$$

# CHAPTER V

## SULPHATE RESISTING PORTLAND CEMENT - PART II
## PRODUCTION

### 5.1. FIRST TEST BATCH

1. The materials available for the first trial batch of local SRC, together with their analyses and the proportions in which they should be used, were given in the previous chapter. It was pointed out, however, that the materials are variable and that analytical controls are, therefore, required. The ideal, of course, would be a complete analysis two or three times per hour, but the expensive apparatus required for this is not yet justified here. As the strength and other properties of cements are largely dependent upon the CaO content, it is important to keep the % $CaCO_3$ in the raw mix as constant as possible.

2. The $RCO_3$ is determined hourly, and a record kept of the results and of the "moving average". When necessary, alterations are made to the mill feeders to change the proportions of the materials going into the mill. A simplified "sequential analysis" method is used to ensure that the kiln feed falls within preset $RCO_3$ limits.

3. The % $RCO_3$ calculated for this particular batch, including coal ash as a raw material, was 77.0%, but for the materials fed to the raw mill it should have been

$$77.0 \div 0.985 = 78.2\%$$

Unfortunately I did not spot this at the time and set the $RCO_3$ limits at 76.9 - 77.3%. This resulted in a potential $C_3S$ content about 5% lower than intended, but did not cause any untoward difficulties.

4. Control/................

4. Control of the $RCO_3$ content of the raw mix was effected by varying the feed rates of the limestone and sand, but the total of the two was kept constant. The feed rate of the spent-oxide was also kept constant, at 1.4 tons per hour.

5. No abnormal problems were encountered during the "burning" of this mix in the kiln. It was a bit on the "soft" side, i.e. easy to burn, and the uncombined, or "free" lime in the clinker was kept below 1% with difficulty.

6. The actual analysis of the clinker produced, compared with the intended analysis and composition, is given in Table No.8. As already stated, the potential $C_3S$ was about 5% lower than intended and the $C_2S$ correspondingly higher. In addition to this, the $Al_2O_3/Fe_2O_3$ ratio came out lower than intended, resulting in a "negative" $C_3A$ content - which actually means that some $C_2F$ was formed (reported in the form of a "solid-solution" with $C_4AF$, viz. $C_6AF_2$ ). There were two reasons for the low A/F ratio:

6.1. The particular batch of limestone used had an $RCO_3$ content of about 93%, which meant it had a lower $Al_2O_3$ content than anticipated and also that less was used - the balance being made up with sand (para.4 above) resulting in an extra 0.9% $SiO_2$ in the clinker.

6.2. The spent-oxide was generally of slightly higher quality than the sample analysed. It was also in the form of a very fine powder which tended, at times, to "flush" through the feeder at a faster rate than intended.

Table No.8 /...................

## TABLE NO.8

### ACTUAL ANALYSIS AND COMPOSITION OF FIRST BATCH OF SRC CLINKER, COMPARED WITH INTENDED ANALYSIS

| CONSTITUENT | ACTUAL | INTENDED |
|---|---|---|
| OXIDES: | | |
| $SiO_2$ | 24.3 % | 23.4 % |
| $Al_2O_3$ | 3.1 % | 4.0 % |
| $Fe_2O_3$ | 6.2 % | 5.3 % |
| CaO | 64.3 % | 64.6 % |
| MgO | 1.2 % | 1.3 % |
| $SO_3$ | 0.2 % | 0.3 % |
| "Undetermined"* | 0.7 % | 1.1 % |
| | 100.0 % | 100.0 % |
| RATIOS: | | |
| LSF | 0.85 | 0.87 |
| $Al_2O_3/Fe_2O_3$ | 0.50 | 0.75 |
| POTENTIAL COMPOUNDS: | | |
| $C_3S$ | 45.0 % | 49.7 % |
| $C_2S$ | 35.8 % | 29.6 % |
| $C_3A$ | (-2.3)% | 1.6 % |
| $C_4AF$ | (18.8)% | 16.1% |
| $C_6AF_2$ | 17.0 % | - |
| $C_4AF + 2 \times C_3A$ | (14.2) % | 19.3 % |

* Includes "Loss on Ignition".

7. The clinker/................

7. The clinker passed the ASTM Type V cement chemical requirements satisfactorily. It did not comply with the minimum $Al_2O_3/Fe_2O_3$ ratio (0.66) specified in S.A.B.S. 471 and B.S.12, but this was of minor importance and, in fact, the modern tendency with Sulphate-resisting cements is to keep the A/F ratio below 0.66 deliberately in order to ensure complete absence of $C_3A$ in the clinker. (See Section 5.5.

8. When the clinker was ground, part of the cement was recirculated through a second mill in order to increase its fineness. This was done in case the strengths of the "once-ground" fraction were not up to B.S.12 requirements. Test results on the cements are given in Table No.9.

9. The once-ground cement (specific surface 3800 $cm^2/g.$) had satisfactory strengths and complied with the physical requirements of B.S.12 : 1958 in all respects with a comfortable margin to spare. The $SO_3$ content was just on the ASTM Type V maximum limit of 2.3% - one of the difficulties of making small experimental batches is that all the material is sometimes used up before the machines can be properly adjusted ! However, the chemical requirements of ASTM Type V cement and the physical requirements of B.S.12 were satisfied, and the Sulphate Reaction Values indicated good potential sulphate resistance.

Table No.9/.................

## TABLE NO. 9

## TEST RESULTS ON THE TWO BATCHES OF SULPHATE RESISTING CEMENT GROUND FROM THE FIRST BATCH OF S.R.CLINKER PRODUCED

| PROPERTY | TEST RESULTS FOR: | |
|---|---|---|
| | "COARSE" GRIND | "FINE" GRIND |
| PHYSICAL TESTS: | | |
| Setting Times: | | |
| Initial | 132 mins. | 95 mins. |
| Final | 3 hrs. 3 mins. | 2 hrs. 20 mins |
| Fineness: | | |
| No.170 Residue | 4.4 % | 0.6 % |
| Specific Surface | 3800 $cm^2/g$. | 5300 $cm^2/g$ |
| Soundness: | | |
| Le Chatelier Expansion | 1 m.m. | 0 m.m. |
| Compressive Strengths: | | |
| Vibrated Mortar Cubes: | | |
| At 1 day | 1200 $lb/in^2$ | 2200 $lb/in^2$ |
| At 3 days | 3100 " | 3850 " |
| At 7 days | 3800 " | 5350 " |
| At 28 days | 6250 " | - |
| 4" Concrete Cubes: | | |
| At 3 days | 1700 $lb/in^2$ | - |
| At 7 days | 2400 " | - |
| At 28 days | 3050 " | - |
| CHEMICAL ANALYSIS: | | |
| "Oxides" | | |
| $SiO_2$ | 23.3% | |
| $Al_2O_3$ | 3.1% | |
| $Fe_2O_3$ | 6.0% | |
| CaO | 61.5% | |
| MgO | 1.4% | |
| $SO_3$ | 2.3% | |
| $Na_2O$ | 0.3% | |
| $K_2O$ | 0.2% | |
| Loss on Ign. | 1.5% | |
| Insol.Residue | 0.7% | |
| Total ... | 100.3% | |
| Ratios: | | |
| L.S.F. | 0.82 | |
| $Al_2O_3/Fe_2O_3$ | 0.52 | |
| Potential Compounds: | | |
| $C_3S$ | 37.2 | |
| $C_3A$ | (-1.9) | |
| Sulphate Reaction Values: | | |
| Bogue | 33 | |
| Converted Bogue | 25 | |

## 5.2. SECOND TEST BATCH

1. For the second batch of S R Cement the same raw materials were used, and the clinker composition aimed for was the same as that intended for the first batch.

2. This time the correct $RCO_3$ value for the raw mix was calculated (see paragraph 5.1-3), and the limits were set at 78.2% to 78.6%. In addition, analytical control of the $Fe_2O_3$ in the raw mix was instituted on a two-hourly basis, and the "target" set at 3.3% $Fe_2O_3$ on an "as received" basis, which is 5.1% on a "loss-free" basis.

3. The clinker analyses, actual and intended, are given in Table No.10. On this occasion the actual analysis bore a closer resemblance to the intended composition, although the $SiO_2$ was again higher, and the $C_3S$ about 5% lower, than expected However, the primary aim had been achieved, and the clinker complied in all respects with the chemical requirements of B.S.12 : 1958 and S.A.B.S.471: 1959 as well as those for ASTM Type V Cement.

Table No.10/..................

## TABLE NO.10

### ACTUAL ANALYSIS AND COMPOSITION OF SECOND BATCH OF S.R.C.CLINKER COMPARED WITH INTENDED ANALYSIS

| CONSTITUENT | ACTUAL | INTENDED |
|---|---|---|
| OXIDES: | | |
| $SiO_2$ | 24.1 % | 23.4 % |
| $Al_2O_3$ | 3.8 % | 4.0% |
| $Fe_2O_3$ | 5.0 % | 5.3 % |
| CaO | 64.2 % | 64.6 % |
| MgO | 1.2 % | 1.3 % |
| $SO_3$ | 0.3 % | 0.3 % |
| "Undetermined"* | 1.4 % | 1.1 % |
| | 100.0 % | 100.0 % |
| RATIOS: | | |
| L.S.F. | 0.85 | 0.87 |
| $Al_2O_3/Fe_2O_3$ | 0.76 | 0.75 |
| POTENTIAL COMPOUNDS: | | |
| $C_3S$ | 44.6 % | 49.7 % |
| $C_2S$ | 35.5 % | 29.6 % |
| $C_3A$ | 1.6 % | 1.6 % |
| $C_4AF$ | 15.2 % | 16.1 % |
| $C_4AF + 2 \times C_3A$ | 18.4 % | 19.3 % |

* Includes "Loss on Ignition".

4. The cement produced from the clinker was again satisfactory - See Table No.11. Specific surface and strengths were slightly higher, and the Sulphate Reaction Value was slightly better. The potential compound contents, particularly $C_3S$, do not agree well with the values calculated for clinker - this is due to impurities in the gypsum, and the "true" values may be taken as about 95% of those calculated for the clinker.

Table No.11/..............

## TABLE NO.11

## TEST RESULTS ON SULPHATE RESISTING CEMENT GROUND FROM SECOND BATCH OF CLINKER PRODUCED

| PROPERTY | TEST RESULTS |
|---|---|
| PHYSICAL TESTS: | |
| Setting Times: | |
| Initial | 175 mins. |
| Final | 3 hrs. 55 mins. |
| Fineness: | |
| No.170 Residue | 1.4 % |
| Specific Surface | 4170 $cm^2/g$ |
| Soundness: | |
| Le Chatelier Expansion | 0 m.m. |
| Compressive Strengths: | |
| Vibrated Mortar Cubes: | |
| At 3 days | 3450 $lb/in^2$ |
| At 7 days | 4800 " |
| At 28 days | 7000 " |
| 4" Concrete Cubes: | |
| At 3 days | 2050 $lb/in^2$ |
| At 7 days | 2750 " |
| At 28 days | 3650 " |
| Expansion with 7% $SO_3$ (ASTM S.R. Test) | |
| At 28 days | 0.05 % |
| At 1 Year | 0.10 % |
| CHEMICAL ANALYSIS: | |
| "Oxides" | |
| $SiO_2$ | 23.6 % |
| $Al_2O_3$ | 3.8 % |
| $Fe_2O_3$ | 4.9 % |
| CaO | 62.1 % |
| MgO | 1.1 % |
| $SO_3$ | 2.2 % |
| $Na_2O$ | 0.2 % |
| $K_2O$ | 0.2 % |
| Loss on Ign. | 2.3 % |
| | 100.4 % |
| Ratios: | |
| L.S.F. | 0.82 |
| $Al_2O_3/Fe_2O_3$ | 0.77 |
| Potential Compounds: | |
| $C_3S$ | 34.5 % |
| $C_3A$ | 1.8 % |
| $C_4AF + 2 \times C_3A$ | 18.5 % |
| Sulphate Reaction Values: | |
| Bogue | 31 |
| Converted Bogue | 22 |

5.3. "High lime"/.................

## 5.3. "HIGH LIME" EXPERIMENTAL BATCH.

1. After the 50% maximum limit on $C_3S$ was removed from the ASTM Type V specification, an experimental batch of SRC was made with the highest $C_3S$ content that could be obtained.

2. Iron ore, instead of spent-oxide, was used for this and subsequent batches of SRC, because the ore proved easier to handle with the equipment available here.

3. This time three lots of cement were ground from the clinker, one with ordinary cement fineness, one with rapid hardening cement fineness, and one in between.

4. The "expected" analyses of the raw materials are given in Table No.12. The limestone analysis was based on the results obtained during the production of the two previous batches.

TABLE NO.12

"EXPECTED" ANALYSES OF RAW MATERIALS FOR HIGH-LIME S.R. CEMENT

| CONSTITUENTS | LIMESTONE | SAND | IRON ORE | COAL ASH |
|---|---|---|---|---|
| $RCO_3$ | 93% | - | - | - |
| Oxides: | | | | |
| $SiO_2$ | 3.3% | 93.5% | 14% | 43% |
| $Al_2O_3$ | 0.8% | 3.5% | 9% | 29% |
| $Fe_2O_3$ | 0.3% | 1.0% | 73% | 6% |
| CaO | 51.0% | 0.5% | - | 13% |
| MgO | 1.1% | - | - | 2% |
| $SO_3$ | - | - | - | 7% |
| Undetermined | 0.2% | 0.5% | 1% | - |
| Loss on Ign. | 43.3% | 1.0% | 3% | - |
| | 100.0% | 100.0% | 100.0% | 100% |

5. Mix proportions were calculated to give an L.S.F. of 1.015 The maximum permitted is 1.02, and anything in excess of 1.00 indicates "free-lime" in the clinker. In this case the excess 1% CaO was deliberately introduced to obtain the maximum possible $C_3S$. Details of proportions, the expected contributions of each material and anticipated clinker composition are given in Table No.13.

## TABLE NO.13

### PROPORTIONS OF RAW MATERIALS USED FOR HIGH-LIME S.R.CEMENT AND INTENDED COMPOSITION OF CLINKER

| CONSTITUENTS | LIMESTONE | SAND | IRON ORE | COAL ASH | TOTAL | CLINKER |
|---|---|---|---|---|---|---|
| Proportion | 85.0% | 10.9% | 2.6 % | 1.5% | 100% | - |
| $RCO_3$ | 79.1% | - | - | - | 79.1% | - |
| Oxides: | | | | | | |
| $SiO_2$ | 2.81 | 10.19 | 0.36 | 0.65 | 14.01 | 22.3 |
| $Al_2O_3$ | 0.68 | 0.38 | 0.23 | 0.44 | 1.73 | 2.7 |
| $Fe_2O_3$ | 0.25 | 0.11 | 1.90 | 0.09 | 2.35 | 3.7 |
| CaO | 43.35 | 0.05 | - | 0.19 | 43.59 | 69.2 |
| MgO | 0.94 | - | - | 0.03 | 0.97 | 1.5 |
| $SO_3$ | - | - | - | 0.10 | 0.10 | 0.2 |
| Undetermined | 0.17 | 0.06 | 0.03 | - | 0.26 | 0.4 |
| Loss on Ign. | 36.80 | 0.11 | 0.08 | - | 36.99 | - |
| | 85.00 | 10.90 | 2.60 | 1.50 | 100.00 | 100.0 |
| Ratios: | | | | | | |
| L.S.F. | | | | | | 1.014 |
| $Al_2O_3/Fe_2O_3$ | | | | | | 0.73 |
| Potential Compounds: | | | | | | |
| Free CaO (at L.C.F.= 1.0) | | | | | | 1.0 |
| $C_3S$ | | | | | | 84.1 |
| $C_2S$ | | | | | | 0.5 |
| $C_3A$ | | | | | | 0.9 |
| $C_4AF$ | | | | | | 11.2 |

For the method of calculating the proportions of the raw materials see Appendix 4

6. In Table No.14 the intended composition of the kiln feed is shown. Control limits were set as follows:

6.1. $RCO_3$ : 79.5% - 80.5%

I deliberately set these to give an average lower, rather than higher, than the calculated value of 80.3%, because the L.S.F. was already over 1.00, and any additional lime would be "unburnable". Once again, the $RCO_3$ was controlled by varying the feed rates of Limestone and Sand.

6.2. $Fe_2O_3$ : 3.2% - 3.9%

These limits may seem a bit "wide" but experience had shown that closer control could not be maintained. Here, too, the limits favoured an average lower than the calculated value - 3.7%. This was to try and avoid an A/F ratio below 0.66. $Fe_2O_3$ was controlled by varying the Iron Ore feed rate.

6.3. $SiO_2$ : 21.5% - 22.5%

An attempt was made to control the $SiO_2$ content of the raw mix too, and the idea was to add shale if $SiO_2$ went too high. Unfortunately $SiO_2$ was on the low side, and no extra sand could be added because that would have reduced the $RCO_3$. As it turned out extra sand may have improved matters, but by the time "complete" analyses were available practically all the material had been ground.

Table No.14/................

## TABLE NO.14

### PROPORTIONS OF MATERIALS TO BE MIXED AT THE RAW MILL FOR HIGH-LIME S.R.C., AND EXPECTED COMPOSITION OF KILN FEED.

| PROPORTIONS & CONSTITUENTS. | LIMESTONE | SAND | IRON ORE | KILN FEED | |
|---|---|---|---|---|---|
| | | | | AS RECD. | LOSS-FREE |
| Proportion | 86.3% | 11.06% | 2.64% | 100% | - |
| $RCO_3$ | 80.3% | - | - | 80.3% | - |
| $SiO_2$ | 2.85 | 10.34 | 0.37 | 13.56 | 21.7 |
| $Al_2O_3$ | 0.69 | 0.39 | 0.24 | 1.32 | 2.1 |
| $Fe_2O_3$ | 0.26 | 0.11 | 1.93 | 2.30 | 3.7 |
| CaO | 44.01 | 0.06 | - | 44.07 | 70.6 |
| MgO | 0.95 | - | - | 0.95 | 1.5 |
| $SO_3$ | - | - | - | - | - |
| Undetermined | 0.17 | 0.05 | 0.02 | 0.24 | 0.4 |
| Loss | 37.37 | 0.11 | 0.08 | 37.56 | - |
| | 86.30 | 11.06 | 2.64 | 100.00 | 100.0 |

7. The raw mix was rather "hard" to burn in the kiln, and it proved impossible to get the free-lime down to a reasonable value.

8. Actual and intended clinker analyses are given in Table No.15. The two controlled constituents, $Fe_2O_3$ and CaO, came out very near to the intended values, both being slightly lower - which was in accordance with the control limits set ( see paragraphs 6.1 & 6.2 above). Unfortunately the $SiO_2$ was 2% low and the $Al_2O_3$ was 1½% high - because on this occasion the limestone had the 90% $RCO_3$ content expected for the first batch, instead of the 93% obtained for the two previous lots. The result was that this lot just missed complying with the ASTM Type V

specification/...............

specification, although its sulphate resistance was, actually, satisfactory (see paragraph 9 below).

## TABLE NO.15

### ACTUAL ANALYSIS OF HIGH-LIME S.R. CLINKER COMPARED WITH INTENDED ANALYSIS

| CONSTITUENT | ACTUAL | INTENDED |
|---|---|---|
| Oxides: | | |
| $SiO_2$ | 20.4 % | 22.3 % |
| $Al_2O_3$ | 4.2 % | 2.7 % |
| $Fe_2O_3$ | 3.5 % | 3.7 % |
| CaO | 69.0 % | 69.2 % |
| MgO | 1.4 % | 1.5 % |
| $SO_3$ | 0.5 % | 0.2 % |
| Undetermined + Loss | 1.0 % | 0.4 % |
| | 100.0 % | 100.0 % |
| Ratios: | | |
| L.S.F. | 1.07 | 1.014 |
| L.C.F. [x] | 0.99 | 1.00 |
| $Al_2O_3$ / $Fe_2O_3$ | 1.20 | 0.73 |
| Potential Compounds: | | |
| Free CaO | 4.8 % | 1.0 % |
| $C_3S$ | 71.7 % | 84.1 % |
| $C_2S$ | 4.5 % | 0.5 % |
| $C_3A$ | 5.2 % | 0.9 % |
| $C_4AF$ | 10.6 | 11.2 % |

[x] L.C.F. is the same as L.S.F. except that only COMBINED CaO is used in the calculation. Combined CaO = Total CaO - Free CaO.

9. Details of test results on the three batches of cement produced are given in Table No.16. Strengths were very good,

and the/......................

and the "medium" ground material complied with B.S.12 in all respects - thanks to the 5½% Gypsum. The fine and coarse cements had satisfactory potential sulphate resistance when tested by the ASTM "Performance Test" expansion method (section 4.3 - 3 ), both at 28 days and at 1 year, although the latter expansions were higher than those obtained with the lower $C_3A$ cements.

10. This test batch indicated that "Rapid-hardening Sulphate Resistant Cement" can be produced here if required.

TABLE NO.16

TEST RESULTS ON THE THREE BATCHES OF CEMENT GROUND FROM THE HIGH-LIME S.R. CLINKER

| PROPERTY | | TEST RESULTS FOR: | | |
|---|---|---|---|---|
| | | COARSE | MEDIUM | FINE |
| PHYSICAL TESTS: | | | | |
| Setting Times: | | | | |
| Initial | mins. | 129 | 110 | 50 |
| Final | hrs. mins. | 3-11 | 2-52 | 1-20 |
| Fineness: | | | | |
| No.170 Residue | % | 2.0 | 1.2 | 0.8 |
| Spec. Surface | $cm^2/g$ | 3400 | 3890 | 5510 |
| Soundness: | | | | |
| Le Chatelier Exp. | m.m. | 2 | 5 | 1 |
| Compressive Strengths: | | | | |
| Vibrated Mortar Cubes: | | | | |
| At 1 day | p.s.i. | - | - | 3550 |
| At 3 days | " | 4200 | 4700 | 5250 |
| At 7 days | " | 5750 | 6000 | 6550 |
| At 28 days | " | 7800 | 8250 | - |
| 4" Concrete Cubes: | | | | |
| At 3 days | p.s.i. | 2750 | 3200 | - |
| At 7 days | " | 3950 | 4300 | - |
| At 28 days | " | 5050 | 5350 | - |
| Expansion with 7%$SO_3$(ASTM S.R.Test) | | | | |
| At 28 days | % | 0.02 | - | 0.03 |
| At 1 Year | % | 0.18 | - | 0.15 |

Chemical Analyses/...........

## TABLE NO.16 CONTINUED

## TEST RESULTS ON THE THREE BATCHES OF CEMENT GROUND FROM THE HIGH-LIME S.R. CLINKER

| PROPERTY | | TEST RESULTS FOR: | | |
|---|---|---|---|---|
| | | COARSE | MEDIUM | FINE |
| CHEMICAL ANALYSES | | | | |
| Oxides: | | | | |
| $SiO_2$ | % | 20.2 | 20.1 | 20.2 |
| $Al_2O_3$ | % | 4.2 | 4.1 | 4.2 |
| $Fe_2O_3$ | % | 3.5 | 3.5 | 3.5 |
| CaO | % | 67.7 | 66.6 | 67.7 |
| MgO | % | 1.4 | 1.4 | 1.4 |
| $SO_3$ | % | 1.5 | 2.4 | 1.5 |
| Undetermined + Loss | % | 1.5 | 1.9 | 1.5 |
| | | 100.0 | 100.0 | 100.0 |
| Ratios: | | | | |
| L.S.F. | | 1.04 | 1.02 | 1.04 |
| L.C.F. | | 0.97 | 0.95 | 0.97 |
| A/F | | 1.20 | 1.17 | 1.20 |
| Composition: | | | | |
| Gypsum in Cement | % | 3.0 | 5.5 | 3.0 |
| Clinker in Cement | % | 97.0 | 94.5 | 97.0 |
| | | 100.0 | 100.0 | 100.0 |
| Potential Compounds:[X] | | | | |
| Free CaO | % | 4.6 | 4.5 (4.5) | (4.6) |
| $C_3S$ | % | 65.8 | 60.6(67.7) | (69.6) |
| $C_2S$ | % | 8.3 | 12.0 (4.3) | (4.4) |
| $C_3A$ | % | 5.2 | 4.9 (4.9) | (5.0) |
| $C_4AF$ | % | 10.6 | 10.6 (10.0) | (10.3) |

[X] The figures shown in brackets were calculated from the clinker composition and percentages present in the cement. The "differences" are due impurities in the Gypsum, and the inaccuracy of the straightforward calculation from the oxides is clearly illustrated by the $C_2S$ -

according/...................

according to the straight calculation it has increased two to threefold ! When, of course, the clinker composition is not known, there is no other way of estimating the potential compounds (except by X-rays).

## 5.4. FIRST "NORMAL" BATCH FROM IRON ORE

1. Once again the intention was to produce a cement complying with the B.S.12 and S.A.B.S.471, as well as with the ASTM Type V, specifications. Target for $C_3S$ was 55-60%, and for $C_3A$ about 1 - 2%

2. For calculating the mix proportions the "average" analyses of previous batches of limestone were used, viz.

| | | |
|---|---|---|
| $RCO_3$ | : | 91.5% |
| $SiO_2$ | : | 5.0% |
| $Al_2O_3$ | : | 1.3% |
| $Fe_2O_3$ | : | 0.3% |
| CaO | : | 49.8% |
| MgO | : | 1.0% |
| $SO_3$ | : | - |
| Undetermined | : | 0.4% |
| Loss on Ign. | : | 42.2% |
| | | 100.0 |

3. Details of the intended clinker composition, and of the proportions of materials required to obtain it, are given in Table No.17.

Table No.17/......................

## TABLE NO.17

## PROPORTIONS OF RAW MATERIALS USED FOR FIRST "NORMAL" BATCH OF S.R. CEMENT MADE WITH IRON ORE

| CONSTITUENTS | LIMESTONE | SAND | IRON ORE | COAL ASH | TOTAL | CLINKER |
|---|---|---|---|---|---|---|
| | % | % | % | % | % | % |
| **Proportion** | 84.5 | 10.5 | 3.5 | 1.5 | 100.0 | - |
| $RCO_3$ | 77.3 | - | - | - | 77.3 | |
| $SiO_2$ | 4.23 | 9.82 | 0.49 | 0.65 | 15.19 | 23.7 |
| $Al_2O_3$ | 1.10 | 0.37 | 0.32 | 0.44 | 2.23 | 3.5 |
| $Fe_2O_3$ | 0.25 | 0.11 | 2.56 | 0.09 | 3.01 | 4.7 |
| CaO | 42.08 | 0.05 | - | 0.19 | 42.32 | 66.0 |
| MgO | 0.34 | - | - | 0.03 | 0.87 | 1.4 |
| $SO_3$ | - | - | - | 0.10 | 0.10 | 0.2 |
| Undetermined | 0.34 | 0.05 | 0.03 | - | 0.42 | 0.5 |
| Loss | 35.66 | 0.10 | 0.10 | - | 35.86 | - |
| | 84.50 | 10.50 | 3.50 | 1.50 | 100.00 | 100.00 |
| **Ratios:** | | | | | | |
| L.S.F. | | | | | | 0.90 |
| A/F | | | | | | 0.74 |
| **Potential Compounds:** | | | | | | |
| $C_3S$ | | | | | | 57.7 |
| $C_2S$ | | | | | | 24.4 |
| $C_3A$ | | | | | | 1.3 |
| $C_4AF$ | | | | | | 14.3 |
| $C_4AF + 2 \times C_3A$ | | | | | | 16.9 |

4. The proportions in which the materials were to be mixed at the raw mill are given in Table No.18, and on the basis of this table the control limits were set at:

4.1. $RCO_3$ : 78.2 - 78.8%

4.2 $Fe_2O_3$ : 4.2 - 4.8% "loss-free"

Table No.18 /...................

## TABLE NO.18

### PROPORTIONS OF MATERIALS TO BE MIXED AT THE RAW MILL FOR FIRST "NORMAL" BATCH OF S.R.C. MADE WITH IRON ORE

| PROPORTIONS & CONSTITUENTS | LIMESTONE | SAND | IRON ORE | KILN FEED | |
|---|---|---|---|---|---|
| | | | | AS RECD | LOSS-FREE |
| Proportions : % | 85.8 | 10.65 | 3.55 | 100.0 | - |
| $RCO_3$ : % | 78.5 | - | - | 78.5 | - |
| $SiO_2$ | 4.29 | 9.96 | 0.50 | 14.75 | 23.2 |
| $Al_2O_3$ | 1.12 | 0.37 | 0.32 | 1.81 | 2.8 |
| $Fe_2O_3$ | 0.26 | 0.11 | 2.59 | 2.96 | 4.6 |
| CaO | 42.73 | 0.05 | - | 42.78 | 67.3 |
| MgO | 0.86 | - | - | 0.86 | 1.4 |
| $SO_3$ | - | - | - | - | - |
| Undetermined | 0.34 | 0.05 | 0.03 | 0.42 | 0.7 |
| Loss | 36.20 | 0.11 | 0.11 | 36.42 | - |
| | 85.80 | 10.65 | 3.55 | 100.00 | 100.0 |

5. Comparisons of the intended and actual analyses of the clinker, and analysis of the cement produced from it, are given in Table No.19. This time the $SiO_2$ and $Fe_2O_3$ contents came out reasonably well, but variations in limestone resulted in the alumina being 0.7% higher than intended, and the CaO was 0.6% lower. The result was a clinker with 3.5% $C_3A$, which was satisfactory, but the $C_4AF + 2 \times C_3A$ exceeded the ASTM limit of 20%. Sulphate reaction values were satisfactory. Fortunately the cement complied in all respects with the requirements of B.S.12 & S.A.B.S.471.

Table No.19/....................

## TABLE NO.19

### INTENDED AND ACTUAL ANALYSES OF IRON ORE CLINKER AND CEMENT PRODUCED FROM IT AND PHYSICAL PROPERTIES OF CEMENT

| CONSTITUENT | | CLINKER | | CEMENT |
|---|---|---|---|---|
| | | INTENDED | ACTUAL | |
| **Oxides:** | | | | |
| $SiO_2$ | % | 23.7 | 23.4 | 22.3 |
| $Al_2O_3$ | % | 3.5 | 4.2 | 4.3 |
| $Fe_2O_3$ | % | 4.7 | 4.5 | 4.7 |
| CaO | % | 66.0 | 65.4 | 63.7 |
| MgO | % | 1.4 | 1.4 | 1.4 |
| $SO_3$ | % | 0.2 | 0.3 | 1.9 |
| Undetermined + Loss | % | 0.5 | 0.8 | 1.7 |
| | | 100.0 | 100.0 | 100.0 |
| **Ratios:** | | | | |
| L.S.F. | | 0.90 | 0.89 | 0.88 |
| L.C.F. | | - | 0.88 | 0.88 |
| A/F | | 0.74 | 0.93 | 0.92 |
| **Potential Compounds:** | | | | |
| Free CaO | | - | 0.4 | 0.4 |
| $C_3S$ | | 57.7 | 51.3 | 47.0 |
| $C_2S$ | | 24.4 | 28.4 | 28.5 |
| $C_3A$ | | 1.3 | 3.5 | 3.5 |
| $C_4AF$ | | 14.3 | 13.7 | 14.3 |
| $C_4AF + 2 \times C_3A$ | | 16.9 | 20.7 | 21.3 |
| **Sulphate Reaction Values:** | | | | |
| Bogue | | - | - | 38 |
| Converted Bogue | | - | - | 23 |
| **Physical Properties:** | | | | |
| Setting Times | | | | |
| Initial | mins. | | | 140 |
| Final | hrs.mins. | | | 3-30 |
| Fineness: | | | | |
| No.170 Residue | % | | | 1.8 |
| Specific Surface | $cm^2/g$ | | | 3440 |
| Soundness: | | | | |
| Le Chatelier Expansion | m.m. | | | 3 |
| Compressive Strengths: | | | | |
| Vibrated Mortar Cubes: | | | | |
| At 3 days | p.s.i. | | | 4350 |
| At 7 days | " | | | 5300 |
| At 28 days | " | | | 6450 |
| 4" Concrete Cubes: | | | | |
| At 3 days | p.s.i. | | | 2600 |
| At 7 days | " | | | 3150 |
| At 28 days | " | | | 4100 |

6. The results of this test served to emphasize, that with the materials and control measures available, it is difficult to make cement which complies exactly with the requirements of all three specifications at the same time.

## 5.5. "FINAL" BATCHES OF S.R.CEMENT

1. The two factors which make it difficult to produce a cement that complies exactly with the chemical requirements of S.A.B.S.471 and B.S.12, in addition to those of ASTM Type V, are:

   1.1. The maximum limit of 20% for $C_4AF + 2 \times C_3A$ in the ASTM Type V specification; coupled with

   1.2. The minimum limit of 0.66 for A/F ratio in the other two specifications.

2. Since the main idea of this project was to produce cement complying with the ASTM Type V specification, the only way to get around the above difficulty was to give up the aim of trying to keep the A/F ratio above 0.66.

3. The object of specifying an alumina/iron-oxide ratio in excess of 0.66 for cements is to ensure the absence of di-calcium ferrite ($C_2F$) in the product. This mineral forms a solid solution with $C_4AF$, and the two are generally reported together as potential $C_6AF_2$.

4. The only disparaging references I could find about $C_2F$ were:

   4.1. Lea (1 - p.82 ) says, of the reaction of the "pure" compound with water, that : (1) it sets and hardens rapidly, without marked heat of hydration;

(2) hydration stops long before the material is completely hydrated; (3) when placed in water the set material disintegrates; and (4) "a continuous expansion occurs after setting which eventually disrupts the set material and reduces the strength to a small value ... The compound $C_2F$ cannot therefore be considered to have any permanent cementing value."

4.2. Moreell wrote in 1937 ( 20.17 ) : "It will be noted that the lower limit of the $Al_2O_3/Fe_2O_3$ ratio (for a U.S.A.Federal specification for cement) corresponds approximately with a $C_3A$ content of 0 per cent to 1 per cent. This assures us a cement having no dicalcium ferrite, a compound which recent researches have indicated to be unstable and which contributes nothing to the strength."

Both of the above references appear to relate to the properties of "pure" $C_2F$, and not to cements containing it. Much recent work has indicated that the properties of a cement are <u>not</u> the "sum of the properties of its constituents", and I suggest that when it is in the form of a solid solution with $C_4AF$, and in the presence of $Ca(OH)_2$ and other cement compounds, the properties of $C_2F$ are different from those of the pure compound by itself. Jones (7.2) does not appear to consider $C_2F$ deleterious, and points out that the hydrate studied by Bogue and Lerch was not positively identified.

5. Other references to $C_2F$ and $C_6AF_2$:

5.1. Czernin writes : "This example shows clearly that the sulphate resistance of Portland cement can be improved more effectively by reducing its tricalcium aluminate

content/............l.......

content than by diminishing its w/c ratio (using a richer mix). At the same time, the curves indicate that the use of low w/c ratio mixes is also a powerful means of improving the sulphate resistance of concrete. As this is true even for cements which, as distinct from the true Ferrari cement, still contain some tricalcium aluminate, a dense concrete with a w/c ratio of 0.4 to 0.45 and based on the Ferrari type Portland cement can be expected to show high immunity even under very severe conditions of sulphate attack." (4.3)

"True" Ferrari cement had an A/F ratio of about 0.44 to 0.65, but it may have since been increased (1.2, 4.3, 6.4).

5.2. Thorvaldson said, at the 1952 Symposium : "Furthermore, it was evident within the first few months that the substitution of either $C_4AF$ or $C_2F$ for the $C_3A$ in the mortar, produced a great increase in the volume stability, especially of the bars stored in solutions of $Na_2SO_4$ and $CaSO_4$, those containing the $C_3A$ with the silicate base having completely disintegrated while those with $C_4AF$ or $C_2F$ showed no visible effects and very low expansion." (6.4)

5.3. None of the ASTM Specifications for Portland Cements, Types I to V, place any limitation on the A/F ratio (18.1 - 1). There is, in fact, an implication that a solid solution of $C_4AF + C_2F$ is acceptable in cement, because the formula for calculating it is given together with the formulae for calculating $C_3S$, $C_2S$, $C_3A$ and $C_4AF$. Furthermore, although Type V cement is limited to 5% for $C_3A$ and 20% for $C_4AF + 2 \times C_3A$, no limit is expressed or implied for $C_6AF_2$.

## 6. Experimental Results:

6.1. In the tests carried out by the ASTM Working Committee on Sulphate Resistance for the "Performance Test for the Potential Sulphate Resistance of Portland Cement" (21.1), the cement which had the best resistance to $CaSO_4$ contained 3.6% $C_2F$. The expansion was 0.03% after 1 year. (See Table No.6 on Page 79)

6.2. The first trial batch of Sulphate Resisting Cement (Section 5.1), contained about 17% $C_6AF_2$ (Table No.8), made up of 15% $C_4AF$ and 2% $C_2F$. A sample was given to the N.B.R.I. for testing, and Mr Van Aardt told me, later, that : (1) the presence of $C_6AF_2$ had been confirmed by X-ray analysis, (2) mortar bars made with the sample showed no signs of attack after exposure to sulphate solutions for more than a year, and (3) he personally preferred a sulphate resistant cement to be completely free from $C_3A$.

6.3. Cement "[illegible]" (SRC/4) (see Tables 23, 24 & 25), which contained about 3% $C_2F$ and 12% $C_4AF$, when tested by the ASTM expansion method had an expansion of only 0.04% after 1 year. As a matter of fact the expansion was 0.055% after 252 days, and the bars then appeared to contract. However, the standard deviation from average found for sets of 4 bars was 0.01 to 0.02% at any age (see Table No.5), so the "contraction" cannot be considered significant.

7. Final/......................

7. Final Mix Design:

After taking the above-mentioned factors into consideration (except for paragraph 6.3 - these results were still to be obtained), it seemed reasonable to design a mix which would yield a product complying with the chemical requirements of ASTM Type V Sulphate-resisting Portland cement, and the S.A.B.S.471 : 1959 and B.S.12 : 1958 physical requirements for Portland cement. Based on the experience and results obtained to date it appeared that an A/F ratio of 0.5 to 0.7 could be maintained without undue difficulty, and this range ensures a product with little or no $C_3A$ and/or a fairly low $C_2F$ content. With 5.7% $Fe_2O_3$, and 2.8% $Al_2O_3$ (A/F = 0.49), the $C_2F$ would be 2.2%

8. The expected analyses of the raw materials are given in Table No.20, and their requisite proportions and the anticipated clinker composition in Table No.21.

TABLE NO.20

APPROXIMATE ANALYSES OF RAW MATERIALS USED FOR "FINAL" BATCHES OF S.R. CEMENT

| CONSTITUENT | LIMESTONE | SAND | IRON ORE | ASH |
|---|---|---|---|---|
| $RCO_3$ | 91.5% | - | - | - |
| $SiO_2$ | 5.0% | 93% | 14% | 43% |
| $Al_2O_3$ | 1.3% | 3% | 9% | 29% |
| $Fe_2O_3$ | 0.3% | 2% | 73% | 6% |
| CaO | 49.8% | - | - | 13% |
| MgO | 1.0 | - | - | 2% |
| $SO_3$ | - | - | - | 7% |
| Undetermined X | 0.4% | 1% | 1% | - |
| Loss on Ign. | 42.2% | 1% | 3% | - |
|  | 100.0% | 100% | 100% | 100% |

X Includes $Na_2O$ & $K_2O$ which were, actually, determined, but are omitted from these calculations for the sake of simplicity and because the ASTM specification does not take them into account for calculating potential compound composition.

Table No.21/..................

## TABLE NO. 21

## PROPORTIONS OF MATERIALS REQUIRED FOR FINAL BATCHES OF S.R. CEMENT

| CONSTITUENTS | LIMESTONE | SAND | IRON ORE | COAL ASH | TOTAL | CLINKER |
|---|---|---|---|---|---|---|
| | % | % | % | % | % | % |
| Proportion | 84.5 | 10 | 4 | 1.5 | 100. | - |
| $RCO_3$ | 77.3 | - | - | - | 77.3 | - |
| Oxides: | | | | | | |
| $SiO_2$ | 4.23 | 9.30 | 0.56 | 0.65 | 14.74 | 23.0 |
| $Al_2O_3$ | 1.10 | 0.30 | 0.36 | 0.44 | 2.20 | 3.4 |
| $Fe_2O_3$ | 0.25 | 0.20 | 2.92 | 0.09 | 3.46 | 5.4 |
| CaO | 42.08 | - | - | 0.19 | 42.27 | 65.9 |
| MgO | 0.84 | - | - | 0.03 | 0.87 | 1.4 |
| $SO_3$ | - | - | - | 0.10 | 0.10 | 0.2 |
| Undetermined | 0.34 | 0.10 | 0.04 | - | 0.48 | 0.7 |
| Loss on Ign. | 35.66 | 0.10 | 0.12 | - | 35.88 | - |
| | 84.50 | 10.00 | 4.00 | 1.50 | 100.00 | 100.0 |
| - - - | - - - | - - - | - - - | - - - | - - - | - |
| Ratios: | | | | | | |
| L.S.F. | | | | | | 0.91 |
| A/F | | | | | | 0.63 |
| Potential Compounds: | | | | | | % |
| Free CaO | | | | | | 0.5 |
| $C_3S$ | | | | | | 60.3 |
| $C_2S$ | | | | | | 20.5 |
| $C_3A$ | | | | | | (-0.2) |
| $C_6AF_2$ | | | | | | 16.3 |

9. Proportions of materials to be fed to the mill and the expected kiln feed analysis are given in Table No.22. Control limits were accordingly set at :

9.1. $RCO_3$ : 78.3 to 78.8% and

9.2. $Fe_2O_3$ : 5.1 to 5.7% (loss-free).

Table No.22/....................

## TABLE NO.22

## PROPORTIONS OF MATERIALS TO BE MIXED AT THE RAW MILL FOR FINAL BATCHES OF S.R.C.

| PROPORTIONS & CONSTITUENTS | LIMESTONE | SAND | IRON ORE | KILN FEED | |
|---|---|---|---|---|---|
| | | | | AS RECD | LOSS-FREE |
| Proportions % | 85.8 | 10.15 | 4.05 | 100.0 | - |
| $RCO_3$ % | 78.5 | - | - | 78.5 | - |
| Oxides: | | | | | |
| $SiO_2$ % | 4.29 | 9.44 | 0.57 | 14.30 | 22.5 |
| $Al_2O_3$ % | 1.12 | 0.31 | 0.36 | 1.79 | 2.8 |
| $Fe_2O_3$ % | 0.26 | 0.20 | 2.96 | 3.42 | 5.4 |
| CaO % | 42.73 | - | - | 42.73 | 67.2 |
| MgO % | 0.86 | - | - | 0.86 | 1.4 |
| $SO_3$ % | - | - | - | - | - |
| Undetermined % | 0.34 | 0.10 | 0.04 | 0.48 | 0.7 |
| Loss on Ign. % | 36.20 | 0.10 | 0.12 | 36.42 | - |
| | 85.80 | 10.15 | 4.05 | 100.00 | 100.0 |

10. The analyses and potential compositions of three batches of clinker made according to this design are compared with the intended composition in Table No.23. Clinker " a " had a slightly lower A/F ratio than desired (due to an abnormally low $Al_2O_3$ content), but it proved to have excellent potential sulphate resistance when tested by the ASTM expansion test. Otherwise all three clinkers are satisfactorily close to the intended composition, and are well within the specification limits for ASTM Type V cement.

Table No.23/...........

## TABLE NO.23

## INTENDED AND ACTUAL ANALYSES OF THREE "FINAL" BATCHES OF SULPHATE RESISTING CEMENT CLINKER

| CONSTITUENT | | CLINKER | | | |
|---|---|---|---|---|---|
| | | INTENDED | a | b | c |
| **Oxides.** | | | | | |
| $SiO_2$ | % | 23.0 | 23.1 | 24.0 | 23.0 |
| $Al_2O_3$ | % | 3.4 | 2.5 | 2.7 | 3.6 |
| $Fe_2O_3$ | % | 5.4 | 5.6 | 5.4 | 5.4 |
| CaO | % | 65.9 | 66.9 | 66.0 | 66.0 |
| MgO | % | 1.4 | 1.4 | 1.3 | 1.2 |
| $SO_3$ | % | 0.2 | 0.2 | 0.1 | 0.3 |
| Undetermined + Loss | % | 0.7 | 0.3 | 0.5 | 0.5 |
| | | 100.0 | 100.0 | 100.0 | 100.0 |
| **Ratios.** | | | | | |
| L.S.F. | | 0.91 | 0.94 | 0.89 | 0.91 |
| L.C.F. | | 0.91 | 0.92 | 0.88 | 0.90 |
| A/F | | 0.63 | 0.45 | 0.50 | 0.67 |
| **Potential Compounds.** | | | | | |
| Free CaO | | 0.5 | 1.1 | 0.7 | 0.7 |
| $C_3S$ | | 60.3 | 64.5 | 55.6 | 58.3 |
| $C_2S$ | | 20.5 | 17.6 | 26.8 | 22.0 |
| $C_3A$ | | (-0.2) | (-2.8) | (-2.0) | 0.4 |
| $C_4AF$ | | 16.2 | 11.9 | 12.9 | 16.4 |
| $C_2F$ | | 0.1 | 2.9 | 2.0 | 0 |
| SS $C_6AF_2$ | | 16.3 | 14.8 | 14.9 | 0 |
| $C_4AF + 2 \times C_3A$ | | - | - | - | 17.2 |

11. The physical properties of the cements made from the clinkers are given in Table No.24. Strengths and other attributes were good, and are comparable with the quality of most present-day South African ordinary Portland cements.

The expansion/.............

The expansion test on cement "a", and the S.R.V. test on cement "b", confirm excellent potential sulphate-resistance properties for these cements. Cement "c" has not yet been tested, but, as already stated, the clinker composition was satisfactory.

12. A copy of the "advertising pamphlet" drawn up for this "local" sulphate-resisting cement is attached to this report, see Addendum No.1

13. References: 1 - p.82, 4.3, 6.4, 7.2, 18.1-1, 20.17, 21.1.

### TABLE NO.24

### TEST RESULTS ON THREE FINAL BATCHES OF S.R.CEMENT PRODUCED

| PROPERTY | | a | b | c |
|---|---|---|---|---|
| Physical Tests: | | | | |
| Setting Times: | | | | |
| Initial | Mins. | 175 | 170 | 160 |
| Final | hrs. mins. | 3-45 | 4-00 | 3-40 |
| Fineness: | | | | |
| No.170 Residue | % | 1.2 | 1.5 | 1.5 |
| Spec. Surface | $cm^2/g$ | 3600 | 3800 | 3700 |
| Soundness: | | | | |
| Le Chatelier Expansion | m.m. | 1 | 1 | 0 |
| Compressive Strengths: | | | | |
| Vibrated Mortar Cubes: | | | | |
| at 3 days | p.s.i. | 4000 | 4100 | 4600 |
| at 7 days | " | 5200 | 5000 | 5650 |
| at 28 days | " | 7000 | 5950 | 6700 |
| 4" Concrete Cubes: | | | | |
| at 3 days | p.s.i. | 2900 | 2800 | 3050 |
| at 7 days | " | 3750 | 3450 | 3850 |
| at 28 days | " | 4500 | 4300 | 4500 |
| Expansion with 7% $SO_3$ (ASTM S.R.Test) | | | | |
| at 28 days | % | 0.03 | - | - |
| at 1 Year | | 0.04 | - | - |
| Chemical Test Results: | | | | |
| $SO_3$ | % | 2.0 | 1.8 | 2.1 |
| Sulphate Reaction Values: | | | | |
| Bogue | | - | 21 | - |
| Converted Bogue | | - | 12 | - |
| Modified Test | | - | 15 | - |

5.6. Summary/....................

## 5.6. SUMMARY OF RESULTS.

1. A complete summary of the analyses and compositions of the clinkers, and the physical properties of the cements, produced in this project is given in Table No.25.

2. The results of potential sulphate resistance tests are also given, but analyses of cements have been omitted because, as pointed out at the bottom of Table No.16, impurities in the gypsum added result in incorrect values for potential compounds.

3. A number of tests to try and assess the potential resistance of some of the cements to sodium and magnesium sulphates have also been carried out - the results of these are given in **Chapter IX** together with the test results for Marine cements.

**Table** No. 25/........

# CHAPTER VI

## MARINE CEMENT - PART I

## GENERAL CONSIDERATIONS

### 6.1. CONCRETE AND CEMENT.

1. Blount (in 1920), Blanks, Bogue, Copenhagen, Davis, Fulton, Orchard, Stutterheim, van Aard, and, in fact, virtually everyone who has written on the subject of concrete corrosion, has emphasized that, no matter what special cements, aggregates, or other extraordinary ingredients may be used, high-quality impermeable concrete is essential as a "first line of defence". (see also paragraph 2.8-1).

2. Concerning the use of concrete in the marine environment of New York area, W.P.Kinneman wrote: "The performance of precast concrete piles under water front environment is no better or worse than the quality of concrete that goes into the piles, and of course this concrete is no better than the portland cement and aggregate that are available....."(20.2 D)

3. The object of this work is to provide "the best cement available" for marine environments.

4. References: 3, 5, 8, 12, 13, 19, 20, 22, 23, etc.

### 6.2. MARINE CORROSION AND MARINE CEMENT.

1. The principal causes of marine corrosion, and the requisite attributes of a marine cement, were listed in paragraph 2.14-6. To recapitulate, the main corroding factors are:

1.1. Sulphate ions.

1.2. Magnesium ions and

1.3. Leaching of soluble constituents, particularly $Ca(OH)_2$

1.4. Chloride ions, which attack reinforcing steel and

1.5. Mechanical attrition and cracking.

2. Marine cement should therefore:-

2.1. Be resistant to $SO_4''$ and $Mg^{\cdot\cdot}$,

2.2. Contain, after hydration, a minimum of soluble $Ca(OH)_2$,

2.3. Assist in making the concrete as impermeable and free from cracks as possible, to protect reinforcement from chloride ions and

2.4. Improve shock- and abrasion-resistance of concrete.

## 6.3. SULPHATE RESISTANCE.

1. This is best achieved by using a sulphate resisting Portland cement, as already described.

2. For other reasons, given below, it is desirable to use a pozzolan in conjunction with the Portland cement - and care must be taken that the Pozzolan used is also resistant to sulphates. Most pozzolans are resistant, but there are some exceptions - see paragraphs 6.9 - 2.3 and 7.2 - 3.2.

3. In paragraph 2.3-6, I showed how the hydration of an ordinary Portland cement can be represented. The equations show that, after complete hydration, the hardened cement paste contains (theoretically) 20.8% $Ca(OH)_2$.

4. In Appendix 6 the hydration of comparable quality low-$C_3A$ and Ferrari-type cements are shown.

5. There are significant differences in the amounts of $C_3AH_6$ formed by the 3 cement types, although not sufficient to account wholly for the differences in the resistance to sulphates. This is more likely due to the $Al_2O_3$ in the

unhydrated/.............

unhydrated S.R. cements being in combination with CF (as glass) and, therefore, extremely slow acting.

6. The total $Ca(OH)_2$ liberated is 20.3% and 19.9%, respectively, for the two S.R. types, so these cements are not likely to be more resistant than ordinary Portland cement to agents which attack $Ca(OH)_2$. About half this $Ca(OH)_2$ may be liberated during the first month of hydration. (25.1)

7. $Ca(OH)_2$ is susceptible to attack by sulphates, but does not appear to be of much importance by itself, except under special conditions - see Section 2.4, particularly paragraphs 4 and 6. There is little doubt, however, that the absence of $Ca(OH)_2$ does provide some additional protection against sulphates.

8. References: 25.1, etc.

## 6.4. MAGNESIUM RESISTANCE:

1. Magnesium attack was described in section 2.5. It can be represented by the equation:

$$Ca(OH)_2 + Mg^{\cdot\cdot} = Mg(OH)_2 + Ca^{\cdot\cdot}.$$

This reaction proceeds practically to completion because of the extremely low solubility of $Mg(OH)_2$.

2. When the conditions are such that the calcium ions are removed, in solution, the comparatively low pH of saturated $Mg(OH)_2$ solution results in decomposition of hydrated calcium silicate, with the liberation of more $Ca(OH)_2$ and this is, in turn, attacked by more $Mg^{\cdot\cdot}$ and so on.

3. According to paragraph 6.3-6 above, S.R. Portland cement should be no more resistant than O.P.C. to magnesium ions in,

say, a solution of magnesium chloride. As it happens, this does not appear to be the case - see Table No.26. Up to the age tested, and by the method used (details given in Chapter 9), the S.R.cement proved considerably more resistant than OPC to $MgCl_2$. The S.R.cement is however, not completely resistant, and something better is required for enhanced protection.

4. Pozzolans, by their very "definition", react with $Ca(OH)_2$ in the presence of water, to form insoluble compounds with cementitious properties. The experience of many investigators has been that pozzolans do improve the resistance of concrete to sea-water (see also paragraphs 2.1-3, & 3.5-10.1.2.) and improved resistance to $MgCl_2$ is confirmed by the results reported in Table No.26.

5. References: 15.2, 18.1 - 5, etc.

## TABLE NO.26

TEST METHOD : MORTAR BAR EXPANSION

TEST MATERIAL : Ordinary Portland Cement : OPC/6
Sulphate Resisting Cement: SRC/5
Marine Cement : CM/3a

TESTING MEDIA: Magnesium Chloride (6½% of cement by wt.)

CURING MEDIA: Solution of 120g.$MgCl_2$ per 1,000 ml.

| AGE IN DAYS | DAYS IN SOLN. | PERCENTAGE EXPANSION FOR | | |
|---|---|---|---|---|
| | | OPC/6 | SRC/5 | CM/3a |
| 1 | 0 | - | - | - |
| 2 | 1 | 0.03 | 0.01 | 0.01 |
| 3 | 2 | 0.055 | 0.015 | 0.015 |
| 8 | 7 | 0.095 | 0.03 | 0.03 |
| 15 | 14 | 0.115 | 0.04 | 0.03 |
| 22 | 21 | 0.13 | 0.045 | 0.035 |
| 33 | 32 | 0.145 | 0.05 | 0.035 |
| 43 | 42 | 0.145 | 0.055 | 0.035 |
| 49 | 48 | 0.15 | 0.055 | 0.035 |
| 74 | 73 | 0.175 | 0.07 | 0.045 |
| 84 | 83 | 0.175 | 0.07 | 0.045 |

## 6.5. RESISTANCE TO LEACHING.

1. The same remarks apply here as made above, and the incorporation of pozzolanic material in a cement does reduce the quantity of soluble $Ca(OH)_2$ in hardened concrete considerably.

2. This has been confirmed by numerous investigators, and also by the results reported in Chapter 9. See also paragraph 3.5-12 and Fig.1 on page 60.

3. References: 23.2, etc.

6.6 Impermeability/........

## 6.6. IMPERMEABILITY.

1. Permeability was discussed in section 2.8.

One cause is bad concreting practice, such as using too dry a mix and/or too little compaction.

2. More often the trouble is too much water, resulting in the formation of water voids and channels due to partial segregation and bleeding, while the concrete is wet. After hardening, water not required for cement hydration evaporates and leaves open capillary passages in the structure.

3. There are two ways of assisting concrete constructors to overcome the above problem:

3.1. Incorporation of a pozzolan, particularly one that has been very finely ground, makes a concrete mix more "workable", which assists in keeping the water/cement ratio low, and it also reduces the incidence of bleeding;

3.2. The use of an air-entraining agent is of considerable benefit in this respect - details of the way in which air-entraining agents work were given in section 3.7. Adding an air-entraining agent at the actual concrete mixer has an advantage, in that the particular dosage required for a specific purpose can be controlled, but expert control and close supervision "on the job" are essential. Incorporating the air entraining agent in the cement ensures: (a) that it does go in, and (b) that an overdose is not added; which is of importance, particularly in view of the workers normally used for making concrete in this country. This is also recommended in Australia (8.2.)

4. Cracks, usually in the form of "micro" cracks which can hardly be seen, often reduce the protection which concrete gives its reinforcement to practically zero.

In a discussion on the origin of cracks in hardened concrete at the 1961 RILEM Conference (11.2), Szepesi listed the following factors:

4.1. The composition of the cement used;

4.2. The fineness of grinding of the cement;

4.3. Water/cement ratio of the concrete used;

4.4. Admixtures;

4.5. Heat of hydration;

4.6. The methods of making, placing, and finishing the concrete;

4.7. Curing the concrete.

To these must be added:

4.8. Aggregate used.

The effect of heat of hydration was described in paragraph 2.8 - 6.1. The compounds which give off heat most rapidly, during hydration, are $C_3A$ and $C_3S$. $C_3A$, the worst offender, has already been reduced to a minimum in the S.R. cement produced, but reducing $C_3S$ has the effect of reducing early strength - which upsets construction people ! Once again pozzolanic admixtures are indicated, as, judiciously used, they can reduce heat of hydration without significantly affecting early strength.

5. The "extensibility" of a concrete is improved by the incorporation of a pozzolan. Extensibility refers to the ability of a material to "take up stress" by "plastic flow" without undergoing cracking (23.2, p.131.)

6. References: 8.2, 11.2, 12.4, 20.23, 20.30, 20.34, 23.2, etc.

6.7/................

## 6.7. SHOCK AND ABRASION RESISTANCE.

1. Fluctuating, and often high, stresses are normal in marine structures, due to "live" loads and to wave action. The live loads frequently become heavier as the structure gets older, and the very long hardening period of Portland-pozzolan cement, which generally has a higher ultimate strength than straight Portland cement, is an advantage here. Air-entrained concrete has been found to be less liable than the non-air-entrained variety to cracking under shock loads, such as those due to waves. (20.2-D)

2. Abrasion resistance depends primarily on strength. "Green" concrete should never be exposed to possible abrasion, such as that due to sand particles in running or swirling water, if it is at all possible to avoid it. The higher ultimate strengths of Portland-pozzolanic cements give some slight added protection against abrasion at later ages.

3. References: 12.4, 20.2-D, 20.27, etc.

## 6.8. COMPOSITION FOR MARINE CEMENT.

1. All the foregoing leads to the inescapable conclusion that the "best cement" (para. 6.1 - 3 ) which can be made available for use in marine environments should contain:

1.1. Sulphate resisting Portland cement,

1.2. A finely-ground pozzolanic material (which must also be resistant to sulphates), and

1.3. An air-entraining agent.

2. The production of S.R.Cement to ASTM Type V specification standard has already been dealt with. Many writers seem to consider ASTM Type II cement ( max.$C_3A$ content = 8% ) good

enough/............

enough, but nothing is "lost" by using Type V cement, and, as Wakeman et al said: "The percentage-wise cost of taking full precautions, based upon the total cost of the entire structure, is usually insignificant. So, why be only 'half safe' ? We are therefore definitely in favour of 'gilding the lily'." (20.2 - D)

3. As has been shown, the inclusion of pozzolanic material in concrete confers several benefits such as:

3.1. Improved resistance to Mg¨ and $SO_3$",

3.2. Reduced heat of hydration and permeability, and greater resistance to leaching and

3.3. Improved extensibility and slightly better abrasion resistance.

Its use in Marine Cement, therefore, appeared to be a "must", and tests completed to date have confirmed this.

4. Air-entraining agents were originally developed to improve the frost resistance of concrete. Most specifications for the quantity of air to be entrained are still based on this particular application, but less air is required to "promote workability, freedom from segregation and freedom from bleeding in concrete ...... Concrete strengths are improved rather than lowered by these small additions, except in the very rich range of mixes" (6.5). The ASTM specifications for air-entraining cement require that sufficient agent be added to produce a standard mortar with 16 - 22% entrained air - I eventually decided on approximately half this amount. (Their specification for "non-air-entraining cements" limit the maximum air to 12% ! Our ordinary cements entrain 0-2% air).

5. The Danes and Italians have been making Marine Cements composed of low-$C_3A$ Portland cements and pozzolans for a number of years. The Americans have favoured low-$C_3A$ cements incorporating air-entraining agents. To the best of my knowledge this is the first time that Marine Cement incorporating all three materials is to be marketed.

6. References: 1.7, 6.5, 18.1-1, 18.1-2, 20.2-D, 26.2, etc.

## 6.9. POZZOLANIC MATERIALS AVAILABLE.

1. Two pozzolanic materials are available for the manufacture of marine cement: (1) Power Station boiler ash, and (2) Shale. The boiler ash should need only grinding, but the shale needs calcination as well, to "activate" it.

"Typical" analyses of the materials available are given in Table No.27, and the chemical requirements of specifications in Table No.28.

TABLE NO.27

"TYPICAL" ANALYSES OF BOILER ASH AND SHALE AVAILABLE AS POZZOLANS

| CONSTITUENTS AND RATIOS | BOILER ASH | | SHALE | | | |
|---|---|---|---|---|---|---|
| | | | FACTORY A | | FACTORY B | |
| | "LOCAL" | "IMPORTED" | AS RECD | LOSS-FREE | AS RECD | LOSS-FREE |
| | | | % | % | % | % |
| $SiO_2$ | 33.4 | 32.3 | 60.2 | 65.7 | 57.6 | 63.4 |
| $Al_2O_3$ | 35.8 | 30.9 | 17.4 | 19.0 | 19.4 | 21.3 |
| $Fe_2O_3$ | 3.2 | 11.0 | 8.0 | 8.7 | 7.9 | 8.7 |
| Total(S+A+F) | 72.4 | 74.2 | 85.6 | 93.4 | 84.9 | 93.4 |
| CaO | 8.9 | 7.3 | 2.0 | 2.2 | 2.0 | 2.2 |
| MgO | 3.3 | 3.5 | 1.0 | 1.1 | 1.0 | 1.1 |
| $SO_3$ | 0.3 | trace | nil | nil | nil | nil |
| Loss on Ign. | 13.7 | 13.2 | 8.4 | - | 9.1 | - |
| Ratios: | | | | | | |
| $\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$ | 0.86 | 0.77 | 2.4 | | 2.1 | |
| $\frac{Al_2O_3}{Fe_2O_3}$ | 11.2 | 2.8 | 2.2 | | 2.4 | |

N.B. Analyses done on oven-dried samples.

## TABLE NO.28

## SPECIFICATIONS FOR FLY ASH AND NATURAL POZZOLANS FOR USE AS ADMIXTURES IN PORTLAND CEMENT CONCRETE : CHEMICAL REQUIREMENTS

| MATERIAL : | FLY ASH | NATURAL POZZOLANS | |
|---|---|---|---|
| SPECIFICATION: | ASTM C350-60T | ASTM C402-58T | "LOCAL" (Self-imposed) |
| CONSTITUENTS & RATIOS | % | % | % |
| $SiO_2 + Al_2O_3 + Fe_2O_3$ : min. | 70.0 | 70.0 | 70.0 |
| MgO : max. | 5.0 | 5.0 | 5.0 |
| $SO_3$ : max. | 5.0 | 3.0 | 3.0 |
| Moisture : max. | 3.0 | 3.0 | 3.0 |
| Loss on Ignition : max. | 12.0 | 10.0 | 2.5 |
| $\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$ : min | - | - | 2.0 |
| $\frac{Al_2O_3}{Fe_2O_3}$ : max. | - | - | 3.0 |
| References | 18.1-7 | 18.1-8 | - |

2. The low loss-on-ignition requirement (2½%), and the limiting values on S/(A+F) and A/F, in the "self-imposed" specification, were inserted on the advice of Mr van Aardt of the M.B.R.I.

2.1. The "ratio" **requirements** have the effect of limiting the $Al_2O_3$ content to a maximum of 25% of $SiO_2 + Al_2O + Fe_2O_3$, which means an "absolute maximum" of 25%.

2.2. Alumina, generally, is not considered harmful in pozzolans, in fact, according to Malquori and Murakami (7.14) the presence of alumina is virtually essential for satisfactory pozzolanic quality.

2.3. The idea/............

2.3. The idea of these additional requirements (loss and ratio limits) is to provide a double protection against the possibility of using insufficiently clacined kaolinite, which has been found to cause expansion in the presence of sulphates and calcium hydroxide (see paragraph 7.2 - 3.2.). These requirements are temporary, pending the development of a suitable physical test, and, fortunately, the shale available does not appear to contain kaolinite (see Table No.29 on page 127 ).

3. Both Boiler-ash samples pass the ASTM specification for Fly-ash, except as regards "loss on ignition". This is partly due to excessive unburned carbon. Although I found no "chemical" ill-effects from this source during tests with the boiler-ash samples, the general consensus of opinion is that more than 5 - 10%C is undesirable. In a "wet" concrete mix particles of carbon were found to come to the surface and spoil the appearance of the concrete. The carbon can be removed by "re-burning" the ash.

4. The shale samples pass the ASTM chemical requirements, even without ignition. The "raw" shale is, however, inert, and requires calcination to activate it. The 2½% ignition loss (minimum) in the self-imposed specification is to ensure that the shale is properly calcined (see also para. 2.3 above). Several different tests have shown that the calcined shale used has pozzolanic activity (see Section 7.3 ) but no "standard" method of test for this attribute has yet been decided on. Each batch was thoroughly checked in several ways.

5. X-ray and/...............

5. X-ray and optical examinations of samples of the raw, partially- and fully-calcined shales available were carried out by the Geology Department of the University of Cape Town. Dr Fuller reported as per Table No.29 (23.6). In Appendix 5 I have given some notes on the minerals reported, and also some extracts from an ASTM report on the constitution and properties of a number of clays and shales, one of which appeared to be similar to the local variety.

## TABLE NO.29

## GEOLOGICAL REPORT ON SAMPLES OF RAW AND CALCINED SHALES

| Sample Number | Description & Treatment. | Constituents |
|---|---|---|
| 0 | Shale A, untreated. | Chlorite, biotite, felspar quartz and calcite. Quartz and biotite conspicuous. A small amount of ore(black opaque iron oxide) is present but was not resolved by the X-ray analysis. There is probably a small amount of illite or degraded muscovite present. |
| 1 | Shale A, heated in Kiln; temp.by thermocouple ½-way along the kiln = 300°C. | Same minerals as in 0 but calcite has decreased and biotite is slightly increased with respect to quartz. |
| 2. | As above, but temperature was 450°C. | Same minerals as in 1 but chlorite is showing signs of structural damage and has enhanced (001)reflections. |
| 3. | As above, but temperature was 600°C. | Chlorite has disappeared and biotite shows a decrease with respect to quartz. |
| 4. | As above, but temperature was 700°C. (This was the temperature decided upon for calcining subsequent batches of shale). | Calcite has disappeared and biotite still further decreased. Felspar and quartz are present. |
| 5. | As above, but temperature was 750°C. With this temp. ½-way along kiln the shale coming out was partially "bloated" and was showing signs of incipient fusion | Biotite has disappeared. Quartz and felspar remain. |

6./ ....................

## TABLE NO.29 CONTINUED

## GEOLOGICAL REPORT ON SAMPLES OF RAW AND CALCINED SHALES

| Sample Number | Description & Treatment | Constituents |
|---|---|---|
| 6 | Bloated sample "selected" from product. | Biotite has disappeared. Quartz and felspar remain. |
| 7. | Bloated and partially fused sample selected from product | Biotite has disappeared. Quartz and felspar remain. |
| 8. | Completely fused sample from first (high temperature) calcination of shale in kiln. | Cristobalite has appeared. Quartz seems to have diminished slightly. Felspar remains. |
| 9. | Shale B, untreated | Compared with sample 0 it contains no felspar or calcite and the chlorite peaks are more diffuse suggesting partial breakdown of the structure. Quartz and biotite remain. |

6. Although the boiler ash gave satisfactory results in the tests carried out, the high loss-on-ignition and the unburned carbon content precludes its use without further calcination (para.3 above). Another point against it is that, if used, when the local "dump" is finished, it will be necessary to "import" supplies, and their composition may be variable. A drilling survey, carried out at the works, indicated that there is a large reserve of shale available "on the spot", and that its composition is reasonably uniform.

7. References: 1.7, 3.4, 7.14, 8.2, 12.5, 18.1-7, 18.1-8, 19.3, 20.12, 20.20, to 20.37, 23.2, 23.6

# CHAPTER VII

## MARINE CEMENT - PART II

## PRELIMINARY INVESTIGATIONS

### 7.1. TESTS FOR POZZOLANIC ACTIVITY

1. There are three general methods of testing pozzolanic materials:

    1.1. Chemical - usually based on the solubility of the pozzolan in acid or alkali, or on its reactivity with $Ca(OH)_2$;

    1.2. Strength tests - in which the strength of a mixture of lime or cement with the pozzolan is determined at a given age under specified curing conditions; and

    1.3. "Reduction-in-Expansion" - the mortar bar test developed by the ASTM to evaluate the efficiency of pozzolans in reducing expansion due to the alkali-aggregate reaction.

    This reduction-in-expansion test is an example of a test devised to check the suitability of a pozzolan for the particular use to which it is to be put. Another such test is the Swedish "leaching" test, in which the lime extracted by distilled water from hardened cement is measured, because the principal use for pozzolans in Sweden is to increase the resistance of concrete to the action of soft waters.

2. The tests based on solubility in acid and alkali are mostly the results of attemps to find rapid methods for checking pozzolanic activity. They have not been very successful, and it did not seem to be worthwhile trying any during this investigation. A "variation" of the solubility-in-acid

method is/...........

method is the "heat of solution" in acid method, which Ruiz appears to have used successfully (21.2)

3. Various methods have been developed for determining reactivity with $Ca(OH)_2$, usually in saturated solution. These are more logical, as most of the beneficial properties of pozzolans depend on their reacting with the calcium hydroxide liberated by hydrating cement. Unfortunately the reaction is slow at ordinary temperatures. It can be speeded up by autoclaving, but this generally alters the nature or mechanism of the reaction and so the results do not always correlate with those obtained in practice. In several of the tests described temperatures of 40 - 60°C are used to achieve some acceleration of the reaction without changing its nature. As most of the benefits desired from the pozzolanic material to be incorporated in the marine cement would derive from its ability to combine with $Ca(OH)_2$, I rather concentrated on this aspect, and used in all five different tests based on reactivity with calcium hydroxide. The conditions varied from autoclaving at 24 hours, to ambient-temperature curing for 1 year.

3.1. First Method.

For comparing the activities of samples of shale calcined at different temperatures and ground to various degrees of fineness, I used boiling at atmospheric pressure to accelerate the reaction. Initial tests were done in nearly saturated lime water, but I decided afterwards that it would be better to use distilled water, and an appropriate weight of cement as a source of $Ca(OH)_2$. Descriptions of the method and of the work leading up to it are given in Appendix 7. This proved a useful method for determerming the optimum calcining temperature for our shale and the requisite fineness of grinding. It was also of some value as a quality check during manufacture. The test does not appear to be valid for comparing different pozzolans, e.g. pulverised fuel ash did not give results comparable with those obtained for the calcined shale (para 7.3-3.7) although strength tests indicated that the ash is also an active pozzolan (Table No.30).

### 3.2. Second Method.

Frantini found that Portland cement gives up sufficient $Ca(OH)_2$ during its first week of curing (wet) to saturate the contact solution. In the case of a good Portland-pozzolanic cement, however, he found that the curing water was not saturated, despite the fact that the cement paste contained free $Ca(OH)_2$. Malquori considers that this corroborates suggestions that at least part of the $Ca(OH)_2$ released by pozzolanic cements is enclosed by protective films of newly formed products which passivate the crystals. Frantini proposed a test, based on this phenomonem, to check whether a cement had satisfactory "pozzolanic" properties - the reaction to be accelerated by curing at 40°C. (7.14, pages 994 & 995). An adaptation of this method was used as a check on the first "production-test" batch of shale produced, and also to try to determine the lowest proportion of shale that would be likely to benefit the cement. Details of the test, as used, are given in Appendix 8, and of the results obtained in paragraph 8.1-9.2 (Table No.40).

### 3.3. Third Method.

There was too much variation, for my liking, in the results obtained by the above test, and I felt that this was partly due to the cement lying "stagnant" during the eight days curing. Frantini, of course, devised the test for actual hardened specimens - the initial 6-hour mixing was my idea, and its purpose was to ensure "porosity" to provide the curing water with as large a surface contact as possible. What I wanted was to do was to prove that the $Ca(OH)_2$ was being made insoluble even when the water was in intimate contact with all of the cement. I therefore devised an apparatus (second page of photographs) which would keep the cement & curing water in continuous movement during the whole curing period. 10 gram samples, with 50 ml water, were put into individual plastic phials. The curing period at 40°C was extended to 28 days. A Duplicate sets of samples were cured at "room" temperature up to 3 months - these were agitated continuously for the first week and thereafter once daily. The pH of each filtrate was determined in addition to its alkalinity and $Ca^{\cdot\cdot}$ content. I used this method to compare the "activity" of the "selected" portion of the second production-scale batch of calcined shale with the "activities" of pulverised fuel ash and ground granulated blastfurnace slag, "activity", in this instance, being the test materials specific ability to make the liberated $Ca(OH)_2$ insoluble. Results are reported in paragraph 8.2 - 6.4 (Table No. 45)

## 3.4. Fouth Method : Autoclaving

This was done purely as a matter of interest. A sample of cement clinker with an abnormally high free-lime content was ground, (a) with 5% gypsum, and (b) with

5% gypsum

5% gypsum and 12½% of the third (final) production batch of calcined shale. The autoclave expansions were determined and also the water-soluble $Ca(OH)_2$ in the autoclaved specimens. Results are reported in paragraphs 8.3 - 2.3 and 8.3-5, Table No.48.

3.5. Fifth Method.

As a check on actual performance under standard curing conditions at ordinary temperature, some strength-test specimens were checked for water-soluble $Ca(OH)_2$, after breaking at 12 months age. The method used for determining "water-soluble $Ca(OH)_2$", together with the results of some tests on it, is given in Appendix 9. Results on 12-month specimens are given in Chapter IX. They have only "comparative" significance - i.e. no conclusions should be drawn from the "absolute" values. However, when specimens are made using equal weights of different cements and equal weights of the same aggregates and they are cured under identical conditions, then I feel that the amount of water-soluble $Ca(OH)_2$ found does "tell a story".

4. Strength tests developed for checking pozzolanic activity have generally followed one of two basic methods:

4.1. Mixing the pozzolan with hydrated lime, and determining the compressive strength after a given period, under standardised test conditions; and

4.2. Mixing the pozzolan with Portland cement and comparing the strength obtained with that of the "pure" Portland cement under identical conditions. Tensile, transverse, and/or compressive strength may be determined.

Either method of test (lime or cement) may be done at "ambient" temperature, or at a higher temperature (generally in the range 40°C - 60°C ) to accelerate the pozzolanic reaction. The ASTM gives both methods (18.1-8), but seems generally to favour the lime method. As the pozzolan is, in this instance, used with Portland cement, I felt that the cement method would be better, and followed the general procedure described by Lea (1.7), which has also found favour with other investigators. Details of the method as used are given in Appendix 10. This method has been in use in our laboratory for some time and has been found satisfactory within its limitations- see paragraph 7.3 - 3.4.

5. The "reduction-in-expansion" test (paragraph 1.3 above) was not tried at all during this programme because there is no reason to suspect that the cement is likely to be used in conjunction with alkali-reactive aggregates. It has, however, been earmarked for the future, as a matter of interest.

6. References: 1.7, 7.14, 13.4, 18.1-8, 18.2, 18.3, 21.2, 23.7.

## 7.2. ACTIVATION OF POZZOLANS.

1. Pozzolanic activity is essentially due to specific types of atomic structures and bonds, particularly structural "defects" that include strain in the bonds. Srinivasan (7.14 D) has compared the structural conditions required for an effective pozzolan with those required for an effective silica-alumina catalyst, although the catalytic and pozzolanic reactions are entirely different from each other. Whereas the catalyst does not change, but merely presents a surface with "active spots" where other components can interact, the pozzolan is

one of the reactants and undergoes permanent changes through new chemical bonding. On the other hand, neither silica nor alumina is as good a catalyst as a proper combination of the two together and the same rule appears to apply to pozzolans (7.14 etc). Further, to quote Srinivasan : "The silica-alumina catalysts obtained through co-precipitation have in them the $\equiv Si - O - Al \equiv$ bonds, which could not be formed if both or either of the oxides were anhydrous to begin with. In the case of clay catalysts, their modes of preparation are strikingly similar to those of clay pozzolans, both of which need acid treatment and/or dehydration. In all the preparations the Al ion is said to occupy a tetra-hedral position, which is held to be an essential condition for catalytic reaction. This structural defect has been shown to involve the movement of the O ions by a few tenths of an angstrom and consequent strain in the bonds. The $AlO_4$ part also needs an H ion to balance the electrical charge and this ion imparts the "acid" character to the catalyst. This H ion plays an important part in the reactions. Many of the said factors may also facilitate chemical bonding of the molecules with the surfaces and thus affect both pozzolanic and catalytic reactivity".

2. Some Pozzolanas are already "active" i.e. already able to combine with $Ca(OH)_2$, when found - such as volcanic ashes, opaline cherts, fly ash, etc. Others have to be treated to activate them. Three general methods are available:

2.1. Chemical treatment, with acids and alkalis;
2.2. Ultra fine grinding; and
2.3. Heat treatment.

The 1st and 2nd methods are not yet generally applicable commercially, but heat treatment has been in use for thousands

of years/...........

of years (see section 1.2). It seems, from the literature, that for each particular material there is an optimum temperature and time of treatment.

3. Careful attention to calcination temperature is essential because:

    3.1. Too high a temperature can relieve the bond strains and reduce pozzolanic activity,

    3.2. The alumina released from kaolins at 600-800 °C is in the "microcrystalline, low-temperature form of gamma-alumina with defective spinel structure", which leads to ettringite formation with calcium sulphate and subsequent disruptive expansion. At 1,000 °C the alumina released is in the high-temperature gamma form or alpha form, with reduced activity and it is unable to combine effectively with CaO and $SO_3$.

4. Time is nearly as important as temperature in the activation of pozzolanic materials, as the reactions occur in the solid-state. Comparatively low temperatures can often be used to obtain a desired effect, provided the material is maintained at the temperature for a long time, and that the temperature is above the minimum required for the particular reaction. Heating to a higher temperature will normally speed-up the desired reaction, but then care must be exercised not to go too high, or hold the temperature too long.

5. The kiln available here permits reasonably accurate temperature control (since its "modification" - see next Chapter), but does not give much scope for varying the length of time that the shale can be held at any given temperature. Fortunately, however, it has proved suitable for the particular material available.

6. Chlorites/.............

6. Chlorites, biotites, illites, montmorillonite, and kaolin are examples of "layer" silicates, and the effect of heat on their atomic arrangements is similar. They lose combined water, without distortion of their structures, at about 500 - 700°C, and this leaves them with unsaturated and strained bonds. At higher temperatures other reactions occur, such as the migration of silica tetrahedra and the formation of cristobalite and mullite. (As confirmed - See Table 29)

7. The shale available locally was found to be, as expected, inert in the raw state when checked by Lea's method - Appendix 10. As no facilities were available in our laboratory to calcine more than a few grams of material at a time, arrangements were made with the University of Stellenbosch to treat some for us. A member of their staff kindly calcined some 4 lb. of material - at 900°C for about 6 hours - along with some of his pottery specimens. Tests carried out by Lea's method gave very encouraging results - see Table No.30 - the "activity indices" being about two-thirds of those obtained with pulverised fuel ash of proven value.

8. References: 1.7, 7.14, 7.14 D, 7.15, 10.5, 12.1, 12.3, 12.4, 13.3, 20.33, 21.2, 23.2, 24.3, 25.5, 28.6, 28.7, 28.8, etc.

## TABLE NO. 30

### RESULTS OF LEA'S TEST ON SAMPLES OF SHALE CALCINED BY UNIVERSITY OF STELLENBOSCH AND SAMPLES OF PULVERISED FUEL ASH (P.F.A.)

| SAMPLE | | VIB. MORTAR COMP.STRENGTH | | PHYSICAL ACTIVITY INDEX |
|---|---|---|---|---|
| | | "COLD"CURED | "HOT" CURED | |
| Portland Cement Only | | 6800 p.si. | 7250 p.s.i. | 7% |
| **P.C. Plus:** | | | | |
| Shale A : | Raw | 2800 | 2850 | 2% |
| | Calcined | 2700 | 4100 | 52% |
| Shale B : | Raw | 2350 | 2400 | 2% |
| | Calcined | 2800 | 4400 | 57% |
| Fine Sand | | 3150 | 3650 | 16% |
| P.F.A.: | "Local" | 3280 | 5750 | 75% |
| | "Imported" | 3150 | 4900 | 56% |

## 7.3. LABORATORY INVESTIGATION OF CALCINATION.

1. In order to follow up this matter, a laboratory-size kiln was designed with the aid of our Senior Engineer, and manufactured in the factory engineering shop. A "gas-Oxygen" burner was supplied by Messrs African Oxygen & Acetylene Co., for burning "Handigas" in oxygen. This was satisfactory for the initial tests, but, with the aid of an enthusiastic assistant, a "home-made" burner was "evolved". The advantage of this burner is that, with it, coal can be burnt as well as gas, thus simulating the conditions of production in the factory kiln more closely. Photographs of the kiln, burner, and coal-feeder are shown on page 3 of the "Photographic Supplement". With this apparatus 10 - 15 lbs of material can be calcined at a time. Temperatures are measured with an "optical pyrometer".

2.First batches/..................

### 2. First batches of laboratory-calcined Shale A.

2.1. After two or three trial runs, to get accustomed to operating the kiln, four batches of shale were calcined at various temperatures - using gas and oxygen only.

2.2. Prior to calcining, the shale was ground to a fine powder and then "nodulised" with 15 to 20% of water - to reduce dust losses. The nodules averaged $\frac{1}{4}$" to $\frac{3}{4}$" diameter.

2.3. A low flame was used at first, with partial rotation of the kiln every few minutes. The flame intensity was gradually increased, and rotation made continuous, so that all the material reached the maximum temperature required within $1\frac{1}{2}$ to 2 hours.

2.4. After cooling, the material was reground in a laboratory mill for 2 hours. This period has been shown to produce a grinding effect roughly equal to that of the factory mills in the case of cement.

2.5. Results of "Lea" physical activity tests on the treated samples are given in Table No.31.

TABLE NO. 31

RESULTS OF "LEA" ACTIVITY TESTS ON FIRST FOUR BATCHES OF LABORATORY CALCINED SHALES

| Sample | Approximate Temperature of Calcination | Vib.Mortar Comp.Strength Cold Cured | Hot Cured | Physical Activity Index |
|---|---|---|---|---|
| R.H.Cement | - | 5350 p.s.i | 6050 p.s.i. | 13% |
| O.P.Cement | - | 4300 " | 4600 " | 7% |
| 50/50 Cement/Shale: | | | | |
| Shale A/B - R.H.C. | 800°C | 3450 " | 3750 " | 9% |
| Shale A/B - O.P.C. | 800°C | 2500 " | 2550 " | 2% |
| Shale A/C - R.H.C. | 950°C | 3350 " | 4000 " | 19% |
| Shale A/C - O.P.C. | 950°C | 2750 " | 3150 " | 15% |
| Shale A/A - R.H.C. | 1100°C | 3000 " | 4600 " | 53% |
| Shale A/A - O.P.C. | 1100°C | 2350 " | 3750 " | 60% |
| Shale A/D - R.H.C. | 1200-1250°C | 3650 " | 4500 " | 23% |
| Shale A/D - O.P.C. | | 2400 " | 3150 " | 31% |

2.6. The optimum/............

2.6. The optimum temperature of calcination for this shale appears to be about 1100 to 1150°C. This is somewhat higher than the general practice in other countries, but the activity indices followed the expected course - i.e. increased with increasing temperature and then declined (paragraphs 7.2.-3 and 7.2-6). The shale which was calcined at 1200-1250°C contained a fair proportion of partially fused pieces.

2.7. The good activity indices ( 52 and 57) of the samples calcined at Stellenbosch, at only ± 900°C, confirm the importance of <u>time</u> (paragraph 7.4-4). The Stellenbosch samples were held at 900°C for about 6 hours, whereas the laboratory calcined samples were raised to the temperatures reported (Table No.31), over a period of 1½ - 2 hours, and then cooled; this was done in order to simulate plant-scale conditions as nearly as possible.

## 3. First batch with coal.

3.1. One batch of shale was interground with 25% of its weight of coal, nodulised, and then calcined with gas and oxygen to 1100 - 1150°C.

3.2. After calcining the nodules of material were nearly black, and looked as if they contained unburned carbon, but their "loss on ignition" at ± 1300°C was less than 1%.

3.3. The calcined sample was split into 3 portions:

3.3.1. "A/EC" - ground in laboratory mill for 1 hour.

3.3.2. "A/EF" - ground in laboratory mill for 3 hours (specific surface 13,500 $cm^2/g$.)

3.3.3. "SRC/1/E" - 1 lb of sample was interground with 2 lb of S.R.Cement (S.R.C/1 - see section 5.2 and Table No.25; and paragraph 3.5 below for reason for proportions)

3.4. The results of "Lea" tests on A/EC and A/EF were:

| Sample | Cold Cured | Hot Cured | Physical Act. Index. |
|---|---|---|---|
| A/EC | 2300 p.s.i. | 3650 p.s.i. | 59% |
| A/EF | 3100 " | 4500 " | 45% |

The "activity Index" was slightly lower for the finely ground shale (A/EF) but the actual strengths obtained were significantly higher. Probably the fine material used a greater proportion of its "activity" in the "cold" than the coarse material did. The Chemical Activity test gave a high value for A/EF (paragraph 3.7 below).

3.5. Physical test results on "cement" SRC/1/E, compared with S.R.Cement and ordinary Portland Cement, are given in Table No.32. The strengths were lower than those of OPC and SRC, as expected, but still complied with the requirements of B.S.12 and S.A.B.S.471. The proportions in which the pozzolan and cement were mixed (1 pozzolan to 2 cement) were based on the "literature", particularly the Italian Specification for "Cemento pozzolanico" (18.5-1), which limits the CaO to a maximum equal to $SiO_2 + Al_2O_3 + Fe_2O_3$. Analyses are given in Table No.32.

Table No.32/......

## TABLE NO.32

### PHYSICAL TEST RESULTS ON CEMENT SRC/1/E, COMPARED WITH SRC/1 AND OPC/2, AND ANALYSES.

| PROPERTY | | SRC/1/E | SRC/1 | OPC/2 |
|---|---|---|---|---|
| **PHYSICAL TESTS:** | | | | |
| Setting Times: | | | | |
| Initial : | mins. | 228 | 175 | 150 |
| Final : | mins-hrs. | 4-44 | 3-55 | 3-20 |
| Fineness: | | | | |
| Residue on No.72 Screen | % | 0.0 | 0.0 | 0.1 |
| Residue on No.100 Screen | % | 0.1 | 0.1 | 0.2 |
| Residue on No.170 Screen | % | 0.6 | 1.4 | 6.2 |
| Specific Surface : | $cm^2/g$ | 5030 | 4170 | 2800 |
| Soundness: | | | | |
| Le Chatelier Expansion | m.m. | 2 | 0 | 2 |
| Compressive Strength: | | | | |
| Vibrated Mortar cubes at: | | | | |
| 3 days : | p.s.i. | 2600 | 3450 | 3850 |
| 7 " : | " | 3550 | 4800 | 4700 |
| 28 " : | " | 4500 | 7000 | 6300 |
| **CHEMICAL ANALYSIS:** | | SRC/1/E | SRC/1 | A/EF |
| $SiO_2$ : | % | 35.6 | 23.6 | 61.4 |
| $Al_2O_3$ : | % | 9.3 | 3.8 | 19.3 |
| $Fe_2O_3$ : | % | 6.1 | 4.9 | 8.7 |
| CaO : | % | 43.0 | 62.1 | 3.8 |
| MgO : | % | 1.4 | 1.1 | 2.8 |
| $SO_3$ : | % | 1.5 | 2.2 | 0.4 |
| Loss on Ignition : | % | 2.0 | 2.3 | 0.7 |
| "Undertermined" : | % | 1.1 | - | 2.9 |
| | | 100.0 | 100.0 | 100.0 |
| Ratio: | | | | |
| $\frac{SiO_2 + Al_2O_3 + Fe_2O_3}{CaO}$ | | 1.18 | - | - |

3.6. Sample/............

3.6. Sample A/EF was used to develop my chemical test (reaction with calcium hydroxide at 100°C) for activity - see Appendix 7. I then used this method to check the activities of calcined shale samples A/A, A/B, A/C and A/D, and also the two pulverised fuel ash samples. Stellenbosch calcined shale (A/US) was also used in developing the test. Test results are reported in Table No.33.

## TABLE NO.33

### CHEMICAL ACTIVITY TEST RESULTS ON VARIOUS CALCINED SHALE AND ASH SAMPLES

| Sample Designation | Approx. Calcining Temperature | Chemical "Activity" = $Ca(OH)_2$/g. Shale |
|---|---|---|
| A/Raw | - | 4 mgm |
| A/B | 800°C | 11 " |
| A/C | 950 " | 31½ " |
| A/A | 1100 " | 41 " |
| A/D | 1200 - 1250°C | 39 " |
| A/K * | 1250 - 1300°C | 39 " |
| A/U.S. | 900°C - 6 hrs | 39 " |
| A/EF | 1100 - 1150°C<br>( + Coal) | 48 " |
| PFA - | "Local" | 13 " |
| PFA - | "Imported" | 2 " |

* See paragraph 4.3 below for details of "A/K".

3.7. The results generally confirm the findings of Lea's test (Table No.31), placing sample A/A as best, and showing a drop in activity at higher calcining temperatures.

Sample A/US/....................

Sample A/US again showed up favourably (cf para 2.4 above) The ash samples did not show up well, although the "local" one had the best value by Lea's method, and has been proved satisfactory, both in practice - over a number of years - and by other laboratories. The CaO content of the ash may, of course, be responsible, because the other methods based on $Ca(OH)_2$ determinations have also shown up the ash less favourably than properly calcined shale (see Chapter VIII ) The high activity of the EF shale, as compared with A and D, is attributable to its high surface area (13,500 $cm^2/g$) whereas the other samples were ground to about 10,000 $cm^2/g$ (see also paragraph 4.4 below).

## 4. Further Laboratory-calcined batches.

4 1 Samples A/F to A/K were ground and nodulised (without coal) prior to burning.

4.2. All the above samples were calcined with gas and oxygen up to between 500 and 600°C, and then powdered coal was introduced into the burner as well. Except for sample A/F, the quantity of coal added was equal to 25% of the weight of the dry shale used.

The "practice" sample, A/F, was discarded because excess coal was used.

4.3. Burning temperatures, etc, were as follows:

| Sample | App.Calc.Temp. | Remarks |
|---|---|---|
| A/G | 1100 - 1150°C | Centres of nodules seemed slightly "underburnt". |
| A/H | ±1250°C | Slightly "overburnt" - due to coal "flushing through" and raising temperature rapidly. Sample discarded. |
| A/J | 1150°C | "As planned". |
| A/K | 1250 - 1300°C | Sample was deliberately "fused". |

4.4. Sample A/J was used to study the effects of grinding time and fineness on the Chemical Activity Index. Three pounds of A/J were put in a laboratory mill, and small samples removed at intervals during the grinding.

4.5. Grinding times and test results are given in Table No.34. I have included sample A/EF because: (1) its calcination conditions were similar and (2) its results "fit in" with the others.

4.6. Plotting all the results on a graph (Figure No.2 on p 152) indicates that increasing the grinding time beyond two hours has a comparatively small effect on the specific surface, and still less on the Chemical Activity Index.

4.7. Plotting the results on log/log paper resulted in nearly straight lines, and their slopes gave me the idea that there may be a linear relation between the square-root of the specific surface and the chemical activity index. The test for correlation gave a [redacted] positive confirmation, and the equation for the regression line was calculated (Appendix 11) and found to be:

$$\underline{i = 0.36s + 6.3}$$

where:

$i$ = chemical activity index

and $s$ = square root of specific surface.

This line and the plots of the experimental results are shown in Figure No.2 A, which confirms that the specific surface of the $1\frac{1}{4}$ hour sample appears to have been incorrectly determined - see Figure No.2.

4.8 My first thought was that the above relationship indicated that the activity had a linear relationship

to particle/.................

to particle diameter. However, the formula:

$$d = \frac{60,000}{p \times S} \text{ microns}$$

where

$d$ = mean particle diameter, in microns;

$p$ = absolute density of material, in g/cu.cm;

and $S$ = specific surface in sq.cms/g,

(see Appendix 12, for derivation of the formula) and the computed values for d (Table 34), show that particle diameter has a linear relationship to specific surface, and not, therefore, to chemical activity.

4.9. The ASTM specifies a maximum of 9.00 microns for "mean particle diameter" for pozzolans to be incorporated with Portland cement concrete. (18.1-8).
"Normal" grinding, therefore (equal to 2 hours in laboratory Mill) will satisfy the specification limit.

TABLE NO.34

| TIME OF GRINDING | | CHEMICAL ACTIVITY INDEX | SPECIFIC SURFACE | | MEAN PARTICLE DIAMETER |
|---|---|---|---|---|---|
| HOURS | MINUTES | mgm $Ca(OH)_2$ | SQUARE-ROOT | sq.cm per g. | MICRONS |
| ¼ | 15 | 25.9 | 52.4 | 2750 | 8.9 |
| ½ | 30 | 29.6 | 67.7 | 4500 | 5.5 |
| ¾ | 45 | 35.1 | 80.3 | 6450 | 3.8 |
| 1 | 60 | 37.9 | 87.7 | 7700 | 3.2 |
| 1¼ | 75 | 42.5 | 92.2 | 8500 | 2.9 |
| 1½ | 90 | 43.4 | 101.0 | 10200 | 2.4 |
| 2 | 120 | 44.4 | 107.9 | 11650 | 2.1 |
| 3 | 180 | (A/EF)48.0 | 116.2 | 13500 | 1.8 |

5. Final batches of laboratory-calcined shales.

5.1 Four more batches of shale were calcined, with gas and coal, before proceeding to the first production scale test in the factory.

5.2. Details of/................

5.2. Details of temperatures, etc.

| Sample | Approx.Calc.Temp. | Remarks |
|---|---|---|
| A/L | 1250 - 1300°C | Completely "fused" - low "yield" of product. |
| A/M | 1150°C | "Standard" product |
| A/N | 1250 - 1300°C | Completely fused - repeat of "L" in order to have sufficient material to check results obtained with K & L. |
| A/O | 1150°C | Instead of using nodulised powder, "jaw-crushed" shale, + $\frac{1}{8}$" to -$\frac{3}{4}$" size was calcined. |

5.3. Instead of using the usual 50/50 proportions of shale and cement to check the "Lea" physical activity index, "cements" were made up using 1 part pozzolan to 2 parts S.R.cement (see paragraph 3.5 above for reason for proportions). Other than "proportions", the same method as before (i.e. Appendix 10 method) was used.

5.4. Physical test results (including activity) are given in Table No.35. (Sample A/M was reserved for tests with air-entraining agents).

5.5. The "completely fused" samples showed up quite well as regards strengths, but (1) the Chemical Activity Test showed them up less favourably, and (2) it is impracticable to attempt complete fusion in the factory.

Table No.35/.............

| PROPERTY | | C/1/0 | SRC/1 | OPC/2 |
|---|---|---|---|---|
| **Setting Times:** | | | | |
| Initial : | mins | - | 175 | 150 |
| Final : | hrs. min | - | 3-55 | 3-20 |
| **Fineness:** | | | | |
| Residue on No.72 : | | - | 0.0 | 0.1 |
| Residue on No.100: | | - | 0.1 | 0.2 |
| Residue on No.170: | | - | 1.4 | 6.2 |
| **Compressive Strength:** | | | | |
| **Vibrated Mortar Cubes:** | | | | |
| At 1 day | | - | - | |
| At 3 days | | 2250 | 3450 | 3850 |
| At 7 days | | 3300 | 4800 | 4700 |
| At 14 days | | - | - | - |
| At 21 days | | - | - | - |
| At 28 days | | 5480 | 7000 | 6300 |
| At 7 days "hot" | | 5350 | 3650 | 5000 |
| "Activity Index A" | | 62% | 6% | 6½% |
| **4" Concrete Cubes:** | | | | |
| At 3 days | | - | 2050 | 1900 |
| At 7 days | | 2150 | 2750 | 2600 |
| At 28 days | | - | 3650 | 3550 |
| At 7 days "hot" | | 3050 | - | - |
| "Activity Index B" | | 42% | - | - |

* Previously done (

5.6. Sulphate resistance tests (ASTM method) on some of these cements gave the following results:

| SAMPLE | % EXPANSION AT: | | |
|---|---|---|---|
| | 7 DAYS | 28 DAYS | 84 DAYS |
| SRC/1 | - | 0.05 | 0.05 |
| SRC/1/US | 0.03 | 0.07 | 0.09 |
| SRC/1/C | 0.045 | 0.07 | 0.09 |
| SRC/1/E | 0.025 | 0.035 | 0.05 |
| SRC/1/G | 0.035 | 0.05 | 0.055 |
| OPC/2 | 0.075 | 0.14 | 56 days:0.185 |

These seemed to confirm that better resistance is obtained with the higher temperatures of calcination (para 7.2.3) - in this instance even the prolonged heating of the U.S.sample did not appear to benefit it. Long-term expansions with calcium and other sulphates are reported in Chapter IX.

5.7. On the basis of the test results reported thus **far** the decision was taken to make a trial batch of calcined shale, and then "Marine Cement", in the factory.

## 7.4. HEAT AND TEMPERATURE OF HYDRATION.

1. Both the ASTM and B.S.1370 specify methods for determining the "Heat of Hydration" of cement by determining the "heat of solution" of the dry cement powder and of its hydration products at 7 and 28 days. Whilst this information is of some value, particularly in checking compliance with specifications, little indication is given of what is likely to happen to a mass of concrete during its vital first 48 hours, when rate of hydration is at a maximum. Also, the method has been found to be inaccurate with pozzolanic and blast-furnace cements.

2. A more/................

2. A more practical method is to record the actual temperature reached by hydrating concrete (or mortar) in an adiabatic calorimeter, as this simulates conditions in the middle of a large mass of concrete.

3. As no adiabatic calorimeter was available I first tried some experiments with the calorimeter portion of a bomb calorimeter. I put the hydrating specimens into the inner container and circulated water at constant temperature through the walls of the outer container. Iron/constantan thermocouples were connected to an old "clockwork" temperature recorder, which I managed to convert to the temperature range required.

4. As my primary object was to compare the hydration characteristics of different types of cement, rather than to obtain "absolute" values, this apparatus proved suitable for the purpose. The bomb calorimeter was in frequent use for "routine" work, however, so was discarded in favour of an insulated wooden box, covered inside and out with aluminium foil. Using a thermostatically controlled fan/heater to keep room temperature constant (fortunately it was winter), surprisingly reproducible results were obtained ! I calibrated the instrument with the aid of an "ultra-thermostat".

5. Specimens were made as follows:-

| | | MORTAR | PASTE |
|---|---|---|---|
| Cement | : | 600 grams | 1000 grams |
| L.B.Standard Sand | : | 600 grams | nil |
| Water | : | 240 grams | 400 grams |

All constituents were given time to reach room temperature (30°C), and were then mixed with a Hobart mixer in accordance with ASTM Method C305 - 59T (18.1-3). All of the mortar was put

into a /......................

into a polythene plastic beaker (600 ml) and a $\frac{1}{4}$" diameter glass tube, sealed at the bottom, inserted down the middle. The beaker and contents were then put into the insulated box, and the thermocouple inserted so that its junction was at the centre of the mortar. The temperature was recorded for 24 hours.

6. Details of cements and mixtures used for initial tests are given in Table No.36, and tracings of the temperature-recorder charts in Figures 3, 4 and 5.

7. The different characteristics of the various cements are clearly indicated, and the benefits of the pozzolanic additions are obvious.

8. References: 18.1-3, 20.48.

TABLE NO.36

| NUMBER OF TRACING | TYPE OF CEMENT | MORTAR | | PASTE | |
|---|---|---|---|---|---|
| | | MAX. TEMP. | TIME TO MAX. | MAX. TEMP | TIME TO MAX. |
| | | °C | hrs. | °C | hrs |
| 1 | R.H.Cement | 49 | 5 | - | - |
| 2 | O.P.C/1 high $C_3A$ | $46\frac{1}{2}$ | $6\frac{3}{4}$ | 55 (estimated) | $6\frac{1}{2}$ |
| 3 | O.P.C/2 mod. $C_3A$ | $42\frac{1}{2}$ | $7\frac{1}{2}$ | 46 | $5\frac{3}{4}$ |
| 4 | S.R.C/1 | 41 | 7 | - | - |
| 5 | 75% O.P.C. 25% Ash | $43\frac{1}{2}$ | $5\frac{1}{2}$ | - | - |
| 6 | 100% O.P.C + nil Calc.Shale | $52\frac{1}{2}$ | $6\frac{1}{2}$ | 55 | $6\frac{1}{4}$ |
| 7 | 70% " + 30% " " | 46 | $7\frac{1}{2}$ | $48\frac{1}{2}$ | $6\frac{3}{4}$ |
| 8 | 50% " + 50% " " | - | - | $44\frac{1}{2}$ | $6\frac{1}{2}$ |
| 9 | 30% " + 70% " " | 38 | $7\frac{1}{2}$ | 39 | 6 |

7.5. Preliminary/...........

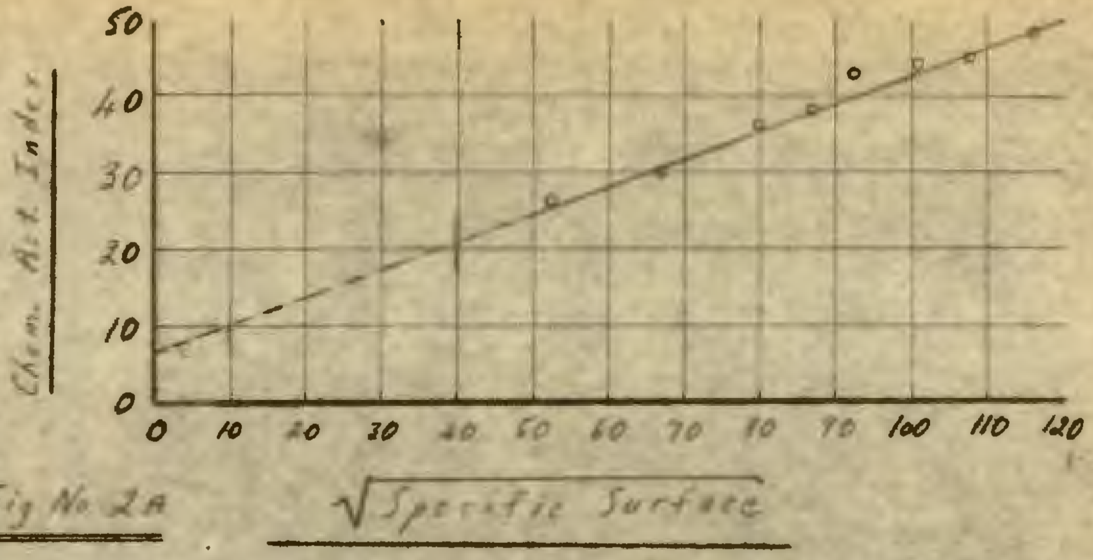


Fig No. 2A

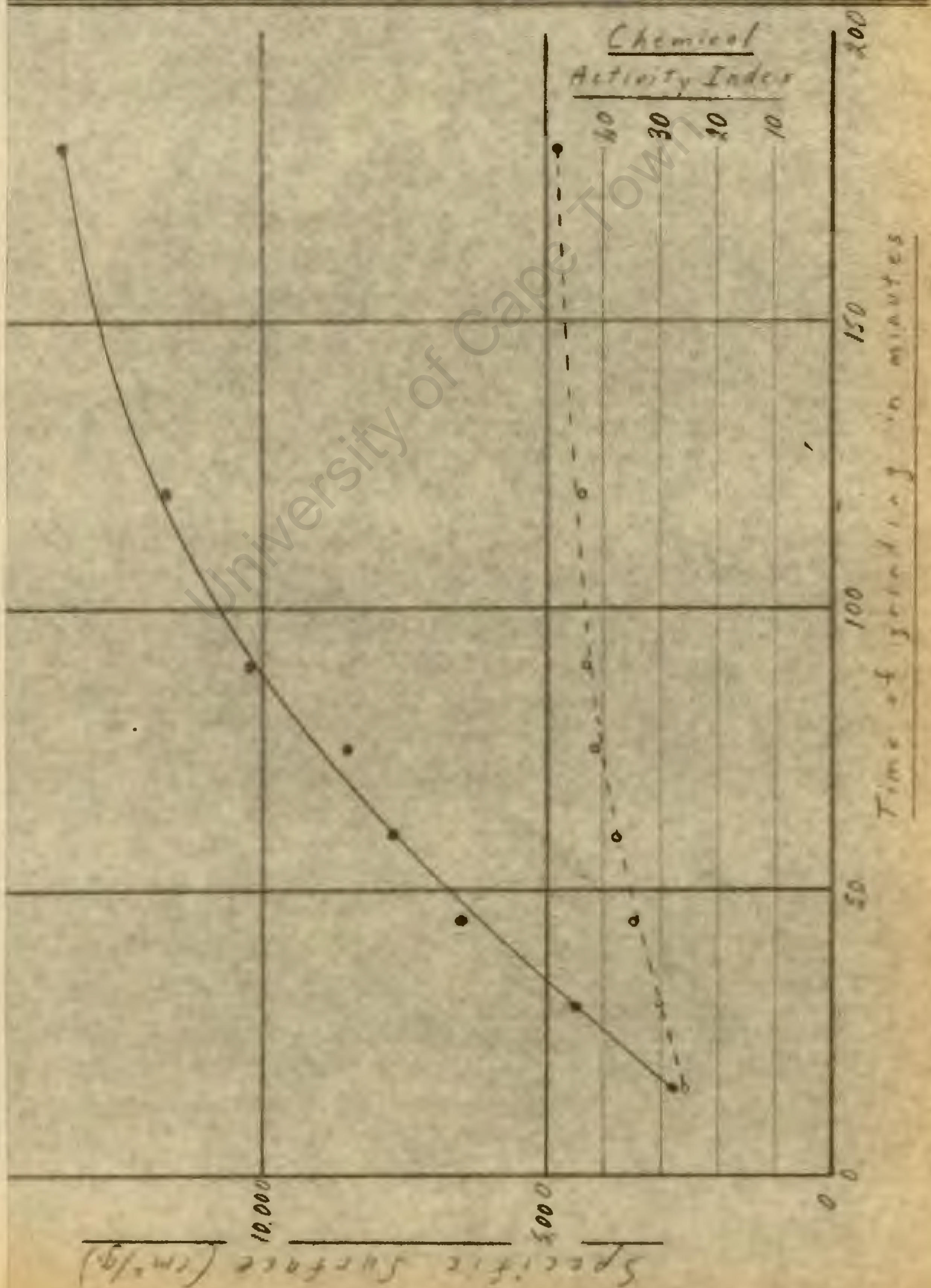


Fig. No. 2 Relationships amongst: Grinding Time, Specific Surface & Chem. Activity

Fig. No. 3

Hydration Temps. of Cement Mortars

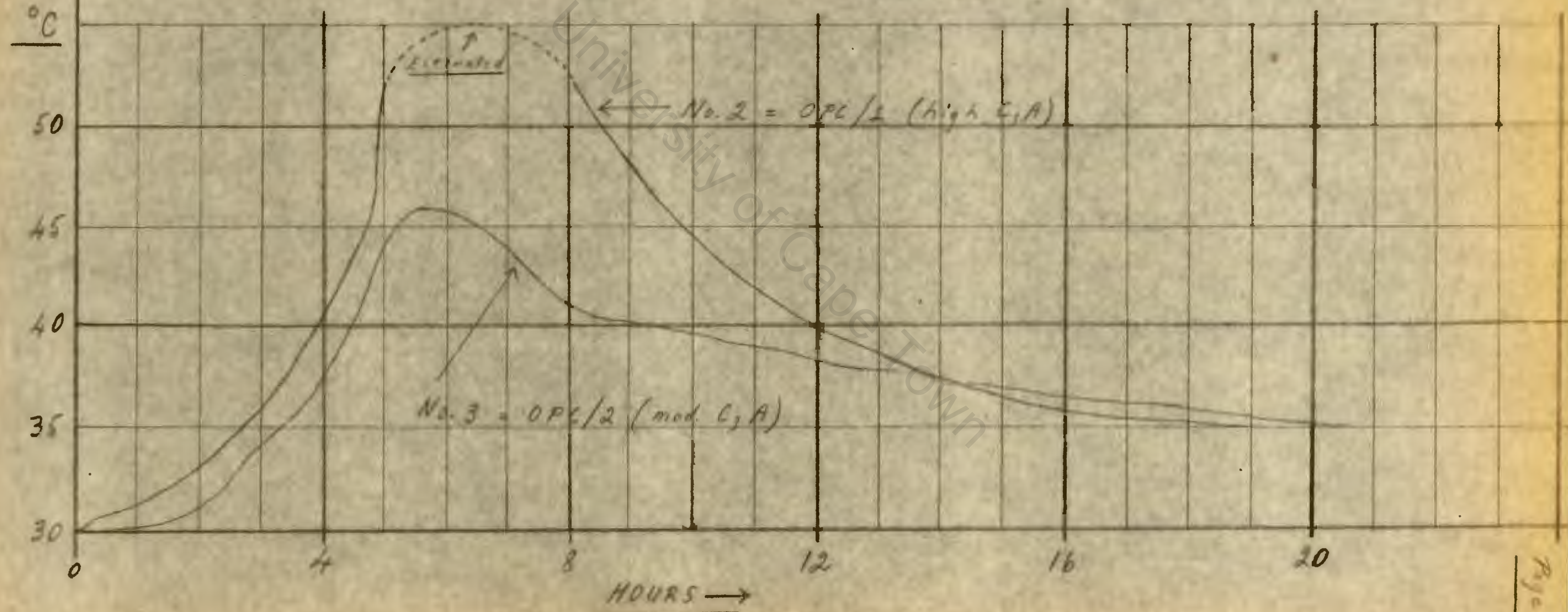


Fig. No. 4 Hydration Temps. of Cement Pastes

# TEMPERATURES OF HYDRATION

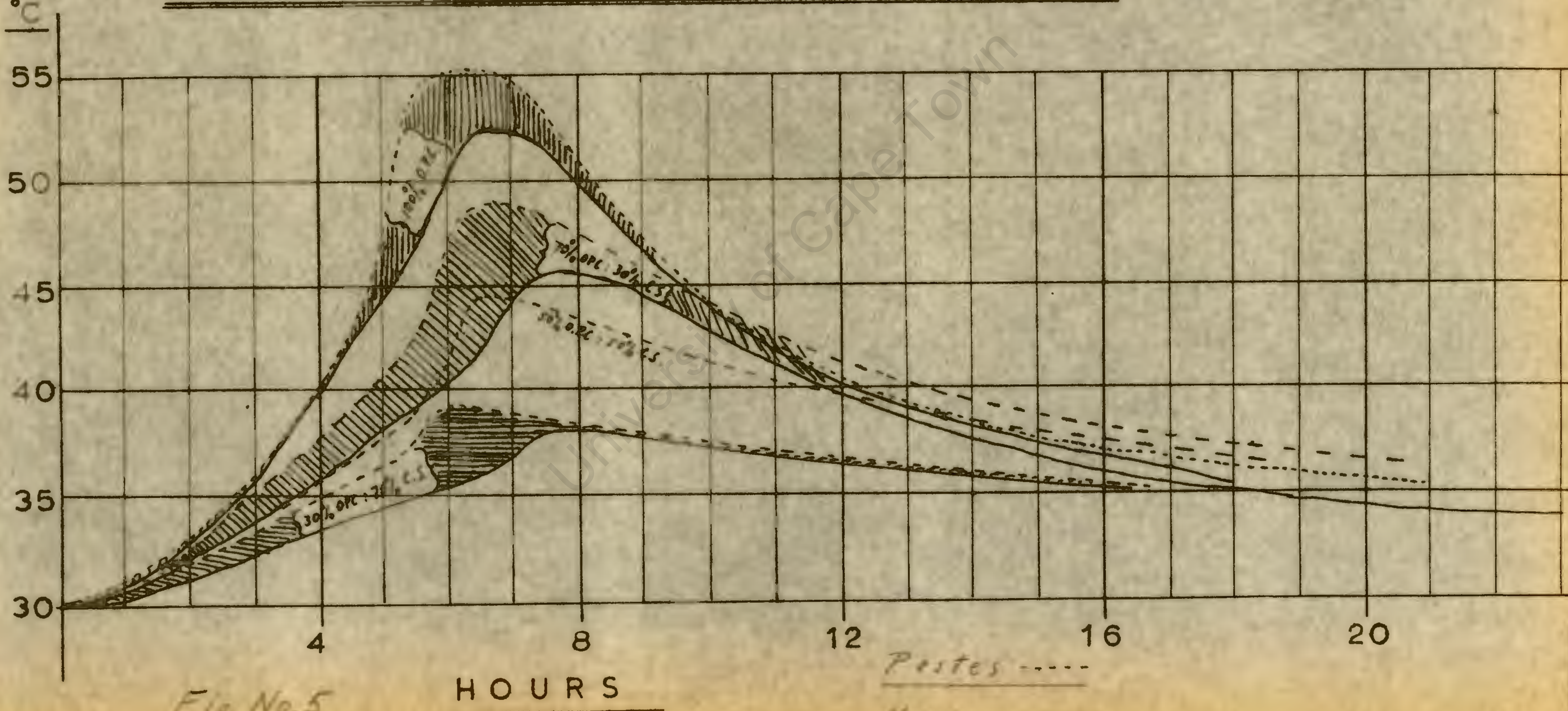


Fig. No. 5

## 7.5. PRELIMINARY TESTS WITH AIR-ENTRAINMENT.

1\. The first tests were done with a "Soluble Oil", which was highly recommended as an air-entraining agent by the suppliers, and which was already in use at the factory for another purpose.

2\. For all tests the ASTM method C185-59 was used for determining the air content of standard mortar.

3\. Initial trials were carried out to determine the amount of soluble oil required to entrain 19% air : (1) when added to the mixing water, and (2) when interground with the cement.

4\. Findings were:

4.1 For Portland cement (and S.R.cement), very little more oil was required when interground than when added to the mixing water;

4.2. About twice as much oil was required for pozzolanic cements (SRC/1/M) as for Portland cements (SRC/1), when the oil was added to the mixing water. This is in accordance with published data.

4.3. Considerably more oil was required when it was interground with the Portland-pozzolanic cement.

5\. In the laboratory mills the cement gets only slightly warm during grinding (a temperature rise of about 10°C), but in the factory mills it gets so hot that water cooling is required, and even then the ground cement has a temperature of about 100°C as it comes out of the mill and goes into the storage silos. By actual measurement the temperature in a storage silo was still 90°C after a week, so I felt that we should find out whether this would be likely to affect the air-entraining agent.

6. Some/............

6. Some specimens of cements, with and without interground soluble oil, were put into a laboratory oven at 90°C for varying periods and then tested for air-entrainment.
No significant differences were found in the case of the Portland cements, but the pozzolanic cements were found to entrain considerably <u>more</u> air than previously. This effect was noticeable after 24 hours, rose to a maximum after about a week, and then remained constant up to a month - the longest period tested.

7. With this treatment not much more oil was needed for intergrinding with Portland-pozzolanic cement than was required for adding to the mixing water.

8. The suppliers of the oil were unaware of the above phenomonem, and were unable to trace any other references to it.

9. I ultimately decided to add sufficient oil to the cement to entrain 14 - 18% air in standard mortar, and found that freshly-ground cement entrained approximately half this amount - it only entrained the required amount after the heat treatment.

10. Control limits of 7% to 9% air were accordingly set for the first batch of Marine Cement, as milled.

# CHAPTER VIII

## MARINE CEMENT - PART III

## PRODUCTION

### 8.1 FIRST TEST BATCH.

1. The first 50 ton batch of shale treated in the factory was ground to a fine powder (as in the laboratory tests) and then calcined, but without preliminary nodulising. This was the only way of doing it with the equipment available for the experiment.

2. Three major difficulties were encountered:

2.1. The amount of fine dust "exuding everywhere" made life in the neighbourhood unbearable, particularly on the burner's platform.

2.2. It was impossible to keep the kiln alight at the calcination temperature desired and the shale fused at the temperature required to keep the kiln alight. Ultimately a mixture of powder and fused lumps of various sizes was achieved.

2.3. The mechanical conveying equipment after the kiln, designed for handling clinker nodules, could not cope with the finely powdered calcined shale, and choked up continuously.

3. An "average" sample of the calcined material was taken, and designated "Y". Laboratory test results on Y are given in Table No.37

Table No.37/...............

## TABLE NO.37

### LABORATORY TEST RESULTS ON FIRST BATCH OF FACTORY CALCINED SHALE - "Y"

A. Chemical Activity Index: 35 mgm $Ca(OH)_2$/g.

B. Cement SRC/1/Y : (2 SRC/1 to 1 Y)

Setting Times:

Initial : 232 mins.
Final : 4 hrs 29 mins.

Fineness:

No. 72 residue : 0.0 %
No.100 residue : 0.0 %
No.170 residue : 1.6 %

Compressive Strengths:

Vibrated Mortar Cubes:

At 3 days : 2050 p.s.i.
At 7 days : 3050 p.s.i.
At 28 days : 4450 p.s.i.

7 days "hot" cured : 4000 p.s.i.

Physical Activity Index A : 31 %

4" Concrete Cubes:

At 3 days : 1550 p.s.i.
At 7 days : 2300 p.s.i.
At 28 days : 3600 p.s.i.

7 days "hot" cured : 3200 p.s.i.

Physical Activity Index B : 39%

---

4. The Activity Indices were not as good as those of some of the laboratory-calcined samples, but they did indicate definite pozzolanic properties, so an experimental batch of "Marine Cement" (CM-1) was manufactured to gain experience.

5. In order to keep the proportions of cement to shale at 2 to 1, control limits of 41 to 43% were set for CaO. An apparatus was rigged up for adding the air-entraining agent

(soluble oil)/..............

(soluble oil), and control limits for the freshly ground cement were set at 7 - 9% air in standard mortar (see section 7.5)

6. Considerable difficulty was experienced with the apparatus for adding soluble oil. It kept blocking up, and did not appear to be able to feed sufficient oil into the cement, because the highest test figure obtained indicated only 6% air, and most of the samples entrained only 3 - 4%. But within 24 hours of grinding, samples of cement taken from the storage silo entrained more than 20% air, and after 48 hours test results of 28 - 30% were obtained - the highest measurable with the method and apparatus used. The soluble oil had behaved differently in the large mill, and too much air-entraining agent had been added!

7. Test results on cement CM-1 are given in Table No.38. The low strengths were mainly due to the excessive amount of air entrained by this cement. The strengths did not comply with the physical requirements of O.P.C. specifications, but did comply with those specified for Low-Heat Portland Cement - B.S.1370. Temperature of hydration was particularly low - see Figure No.6.

Table No.38/.............

## TABLE NO.38

## TEST RESULTS ON EXPERIMENTAL MARINE CEMENT : CM-1

### PHYSICAL TEST RESULTS:

**Setting Times.**

| | | |
|---|---|---|
| Initial | : | 119 mins. |
| Final | : | 3 hrs. 20 mins. |
| Room Temperature | : | 68°F |
| Water Used | : | 25.5% at 73°F. |

**Fineness:**

| | | |
|---|---|---|
| Specific Surface | : | 5740 $cm^2/gm$ |

**Soundness:** :

| | | |
|---|---|---|
| Le Chatelier Expansion | : | 0 m.m. |

**Compressive Strength:**

| | | | B.S.1370: Low-heat Cement |
|---|---|---|---|
| Vibrated Mortar Cubes: | | | |
| At 3 Days | : | 1150 $lb/in^2$ | min : 1100 $lb/in^2$ |
| At 7 Days | : | 2500 " | min : 2000 " |
| At 28 Days | : | 4950 " | min : 4000 " |
| 4" Concrete Cubes: | | | |
| At 3 Days | : | 900 $lb/in^2$ | min : 500 $lb/in^2$ |
| At 7 Days | : | 1400 " | min : 1000 " |
| At 28 Days | : | 2450 " | min : 2000 " |

### CHEMICAL ANALYSIS:

| | | | |
|---|---|---|---|
| Silica | $SiO_2$ | : | 34.8% |
| Alumina | $Al_2O_3$ | : | 10.0% |
| Iron Oxide | $Fe_2O_3$ | : | 4.6% |
| Calcium Oxide | CaO | : | 41.8% |
| Magnesia | MgO | : | 2.2% |
| Sulphur Trioxide | $SO_3$ | : | 1.8% |
| Loss on Ignition | @ 900°C | | 2.7% |
| Undetermined | | : | 2.1% |
| | | | 100.0% |

**RATIO:**

$$\frac{SiO_2 + Al_2O_3 + Fe_2O_3}{CaO} : 1.18$$

Figure No.6/.......1....

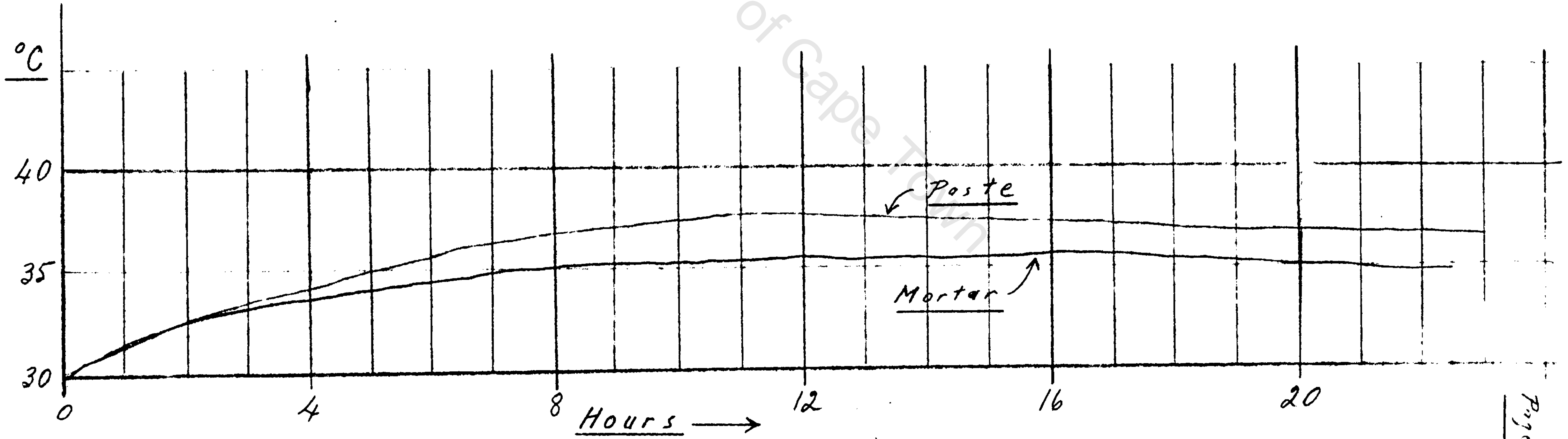


Fig No. 6

Hydration Temps of CM-1

8. This cement was used for constructing concrete furrows at the factory. For comparison purposes, three concrete mixes were used:

8.1. OPC - "low" slump,

8.2. CM-1 - "high" slump, and

8.3. CM-1 - "low" slump.

Mix 8.2 had approximately the same water/cement ratio as mix 8.1 - the high slump was due to the entrained air. Advantage was taken of this air to reduce the water/cement ratio, in mix 8.3, whilst retaining approximately the slump (workability) of mix 8.1.

After 9 - 10 months a "Concrete Test Hammer" was borrowed to check the strengths of the three concretes "in situ". Results were:

8.4. OPC - "low" slump mix - 3600 lb/in$^2$

8.5. CM-1 - "high" slump mix - 3700 "

8.6. CM-1 - "low" slump mix - 4400 "

These results confirm:

8.7. The strength-giving properties (at later ages) of the calcined shale which raised the strength of the CM-1 mix from about half that of OPC at 3 - 7 days, to equal to it at 9 - 10 months (with equal w/c ratio), and

8.8. The improvement in strength which can be obtained by taking advantage of the entrained air to reduce the water/cement ratio. The strength of mix 8.3 was 20% higher than that of the other two, at 9 - 10 months,

8.9. It was also found, whilst "placing" the concrete , that "bleeding" was reduced to nearly zero by the air - even in the sloppy "high" slump mix 8.2.

9. No matter what long-term resistance a cement may have to the

elements, engineers and contractors tend to look askance at any cement which does not comply with the 3- and 7- day strength specifications of B.S.:12 and SABS:471. Pozzolanic strength only starts developing properly after 3 - 4 weeks, and the early strengths obtained with the 2 Cement : 1 Calc.shale Cements all appeared to have been affected by the shale (see previous chapter).

Although the production-test shale had not been calcined "according to plan", and did not have the high activity indices required, it had the overwhelming merit of being available in "quantity", and was therefore used for a further two series of tests, to determine (1) the maximum amount of shale which could be incorporated without unduly affecting early strengths, and (2) the minimum amount of shale required for sufficient chemical activity (reaction with $Ca(OH)_2$ in the cement. Owing to the fairly high proportion of hard, fused lumps of material in this shale, it was given preliminary grinding, in the production test, before being interground with the cement. Some of this "½ ground" material was used for these tests, and was designated "YP" to distinguish it from the laboratory ground product.

9.1. Mixtures of calcined shale "YP" and cement were made up as follows:

| Shale YP | Portland Cement |
|---|---|
| 70% | 30% |
| 50% | 50% |
| 30% | 70% |
| nil | 100% |

9.1.1. The intention was to include mixtures containing 20% and 10% of shale as well, but the exigencies of time and routine work prevented this. However, the plant scale test - see next section - using 20-25% Shale, confirmed the conclusions drawn from this series.

9.1.2. O.P.C✓...................

9.1.2. O.P.C. was used because these tests were done at the other factory laboratory.

9.1.3. Test results are given in Table No.39 and illustrated by Figure No.7. Except for the 30% shale-mixture's 28-day strength, which appears to be "out of place", the results indicate that up to 30% shale can be incorporated with this cement without affecting the early strengths significantly.

TABLE NO.39

PHYSICAL TEST RESULTS ON MIXTURES OF CALCINED SHALE "YP" AND PORTLAND CEMENT

| % Calcined Shale | 100 | 70 | 50 | 30 | nil |
|---|---|---|---|---|---|
| % Portland Cement | nil | 30 | 50 | 70 | 100 |
| Specific Surface: $cm^2/g$ | 4850 | 4150 | 3800 | 3370 | 2540 |
| V.M.Cube Strengths: | | | | | |
| At 3 days: p.s.i. | - | 1050 | 2400 | 3750 | 3900 |
| At 7 days: p.s.i. | - | 1650 | 3300 | 4650 | 4550 |
| At 28 days: p.s.i. | - | 3400 | 5200 | 5600 | 6100 |
| "Comparative" Strengths of mixes at various ages: | | | | | |
| % of 7 day strength | | | | | |
| At 3 days : % | - | 64 | 73 | 81 | 86 |
| At 7 days : % | - | 100 | 100 | 100 | 100 |
| At 28 days : % | - | 206 | 156 | 120 | 134 |

Figure 7 /............

Strengths of Cement/Calc Shale Mixtures

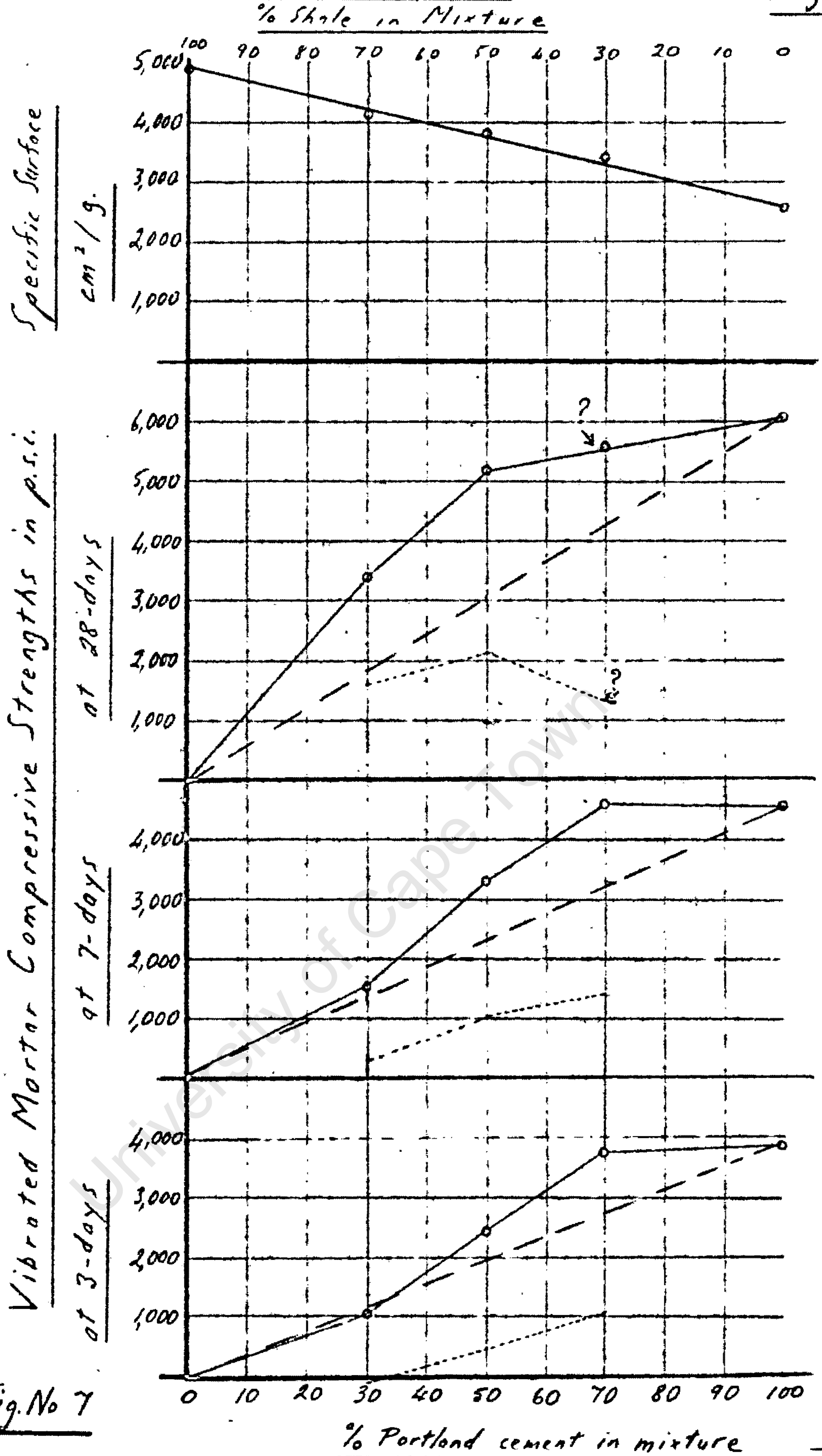


Fig. No 7

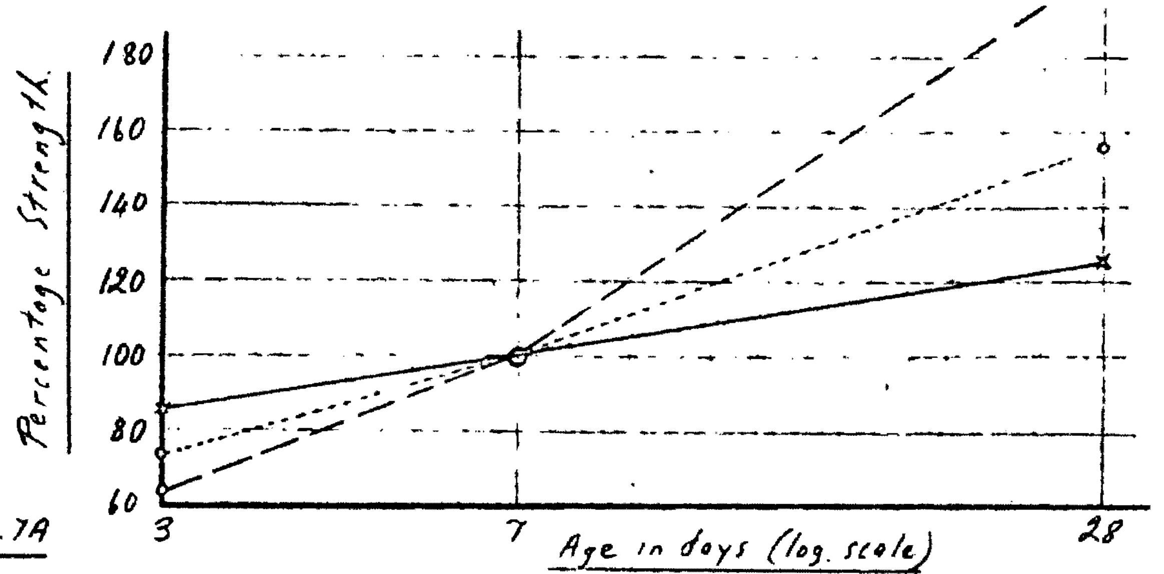


Fig. 7A

9.1.4. Assuming that the difference between the actual strength and the proportionate strength of the quantity of OPC in the mixture (dashed lines in Fig.7) is due to the calcined shale, the contribution to total strength by the shale at the various ages is noticeable. These differences are indicated by the dotted lines. The effect is most obvious in the case of the 70% shale mixture, where the shale contribution is:

Zero at 3 days age,
400 p.s.i. at 7 days age, and
1600 p.s.i. at 28 days age.

9.1.5. The effect of the shale on strength development is also illustrated by Fig.7A, where the strengths of the various mixes at 3 and 28 days have been plotted relative to their 7-day strengths taken as 100%

9.2. The "Frantini" test (see paragraph 7.1 - 3.2, and Appendix 8) was used to check the effective chemical pozzolanic activity of mixtures of shale YP and S.R. Cement, from 0 to 100% shale at 10% intervals. The activity (by this method) of "local" pulverised fuel ash was determined at the same time and some tests with cement and sand were also included. Test results are reported in Table No.40

Table No.40/.................

## TABLE NO.40

## RESULTS OF "FRANTINI" TEST ON MIXTURES OF SHALE Y AND S.R. CEMENT

| SHALE YP % | SRC/1 % | MILLIMOLS PER LITRE OF: $OH^-$ Found | $OH^-$ Av. | $Ca(OH)_2$ Found | $Ca(OH)_2$ Av. |
|---|---|---|---|---|---|
| nil | 100 | 44 | | 16½ | |
| 10 | 90 | 44 | | 15 | |
| 20 | 80 | 45 | | 12 | |
| 30 | 70 | 46 | 47 | 10 | 10½ |
| | | 48 | | 11 | |
| 40 | 60 | 47 | 47 | 8 | 8 |
| | | 47 | | 7½ | |
| 50 | 50 | 48 | 49 | 4 | 5½ |
| | | 50 | | 7 | |
| 60 | 40 | 51 | | 5 | |
| 70 | 30 | 40 | | 2½ | |
| 80 | 20 | 31 | | 1½ | |
| 90 | 10 | 20 | | 1 | |
| 100 | nil | 11 | | 0.3 | |
| **PFA** | **SRC/1** | | | | |
| nil | 100 | 46 | | 16½ | |
| 10 | 90 | 46 | | 16½ | |
| 20 | 80 | 47 | | 16 | |
| 30 | 70 | 45 | | 15½ | |
| 40 | 60 | 42 | | 13½ | |
| 50 | 50 | 38 | | 12 | |
| 60 | 40 | 33 | | 11½ | |
| 70 | 30 | 32 | | 9½ | |
| 80 | 20 | 22 | | 6 | |
| 90 | 10 | 13 | | 2 | |
| 100 | nil | 5 | | 2 | |
| **COARSE SAND** | **SRC/1** | | | | |
| nil | 100 | 44 | | 16¼ | |
| 50 | 50 | 41 | | 18 | |
| 75 | 25 | 39 | | 18¾ | |
| 75 | 25 | 40 | | 18½ | |

9.2.1. Comparing the concentrations of $Ca(OH)_2$ and $OH^-$ with the Solubility Isotherm in Figure No.8, it is seen that mixes containing from 20% and upwards of

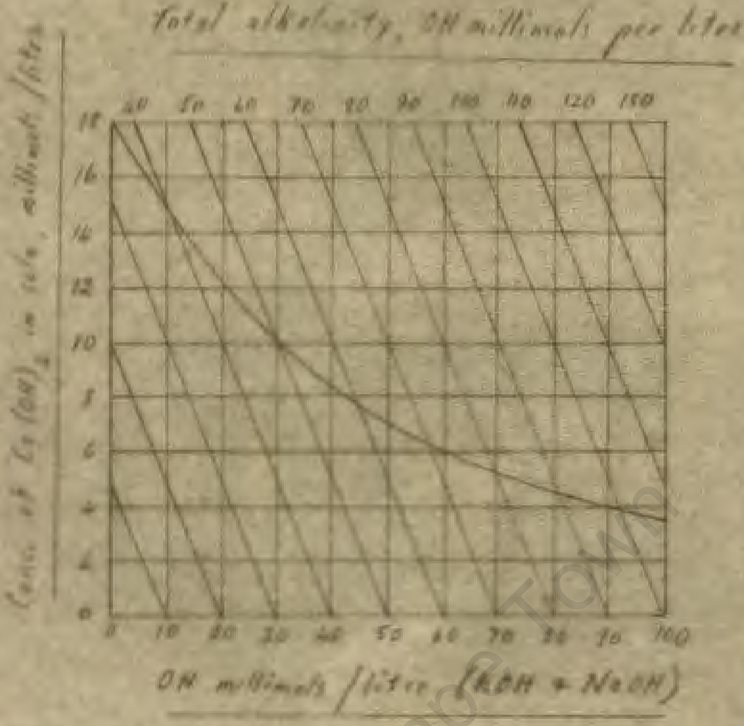
calcined/................

calcined shale do not saturate the contact water with $Ca(OH)_2$ after 8 days curing at 40°C. In the case of P.F.A. a minimum of 40% is required to fulfill this condition. This means that cements containing 20% of Shale Y P, or 40% of pulverised fuel ash, will have satisfactory chemical pozzolanic activity when judged by Frantini's standard. The sand has an apparently "negative" value - this is simply due to the lower concentration of total alkali (because of less cement in the same volume of water) allowing a higher concentration of $Ca(OH)_2$ to go into solution.

9.2.2. The differences are more strikingly illustrated by Figure No.9, where I have plotted the concentration of $Ca(OH)_2$ against the percentages of pozzolan and S.R.C. in the cements tested.

9.2.3. As a further check on the shale, cements containing 30% and 40% of sample YP were tested by this method at 4, 6, 8, 12 and 16 days. The results are given in Table No.41, and are illustrated in Figure No.10. In the case of the 30% mixture the $Ca(OH)_2$ in the contact solution was below saturation after 6 days, according to Figure No.8. The 40% mixture complied with this "standard" within 4 days. The graph illustrates the downward trend in $Ca(OH)_2$ with time.

10. References: 18.6



Solubility isotherm (40° C) for $Ca(OH)_2$, in the presence of alkalies.

After Malquori - ref 7.14, p 995.

Figure No. 8.

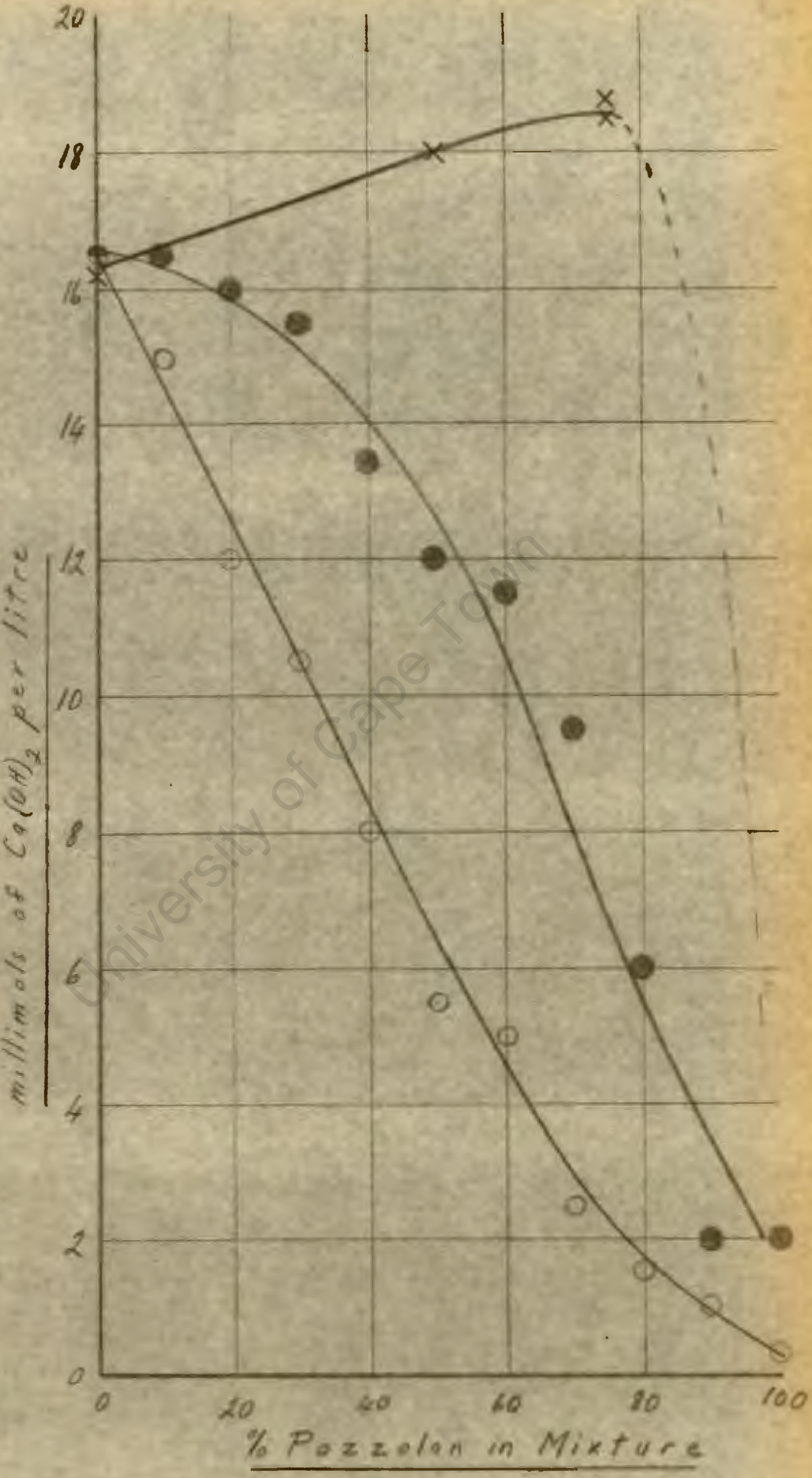

20
18
16
14
12
10
8
6
4
2
0
millimols of $Ca(OH)_2$ per litre
0
20
40
60
80
100
% Pozzolan in Mixture
Cement + Sand ×
Cement + Ash ●
Cement + Calc. Shale ○

Fig. No. 9

## Frontini Test Results :

### SRC 1 + CS

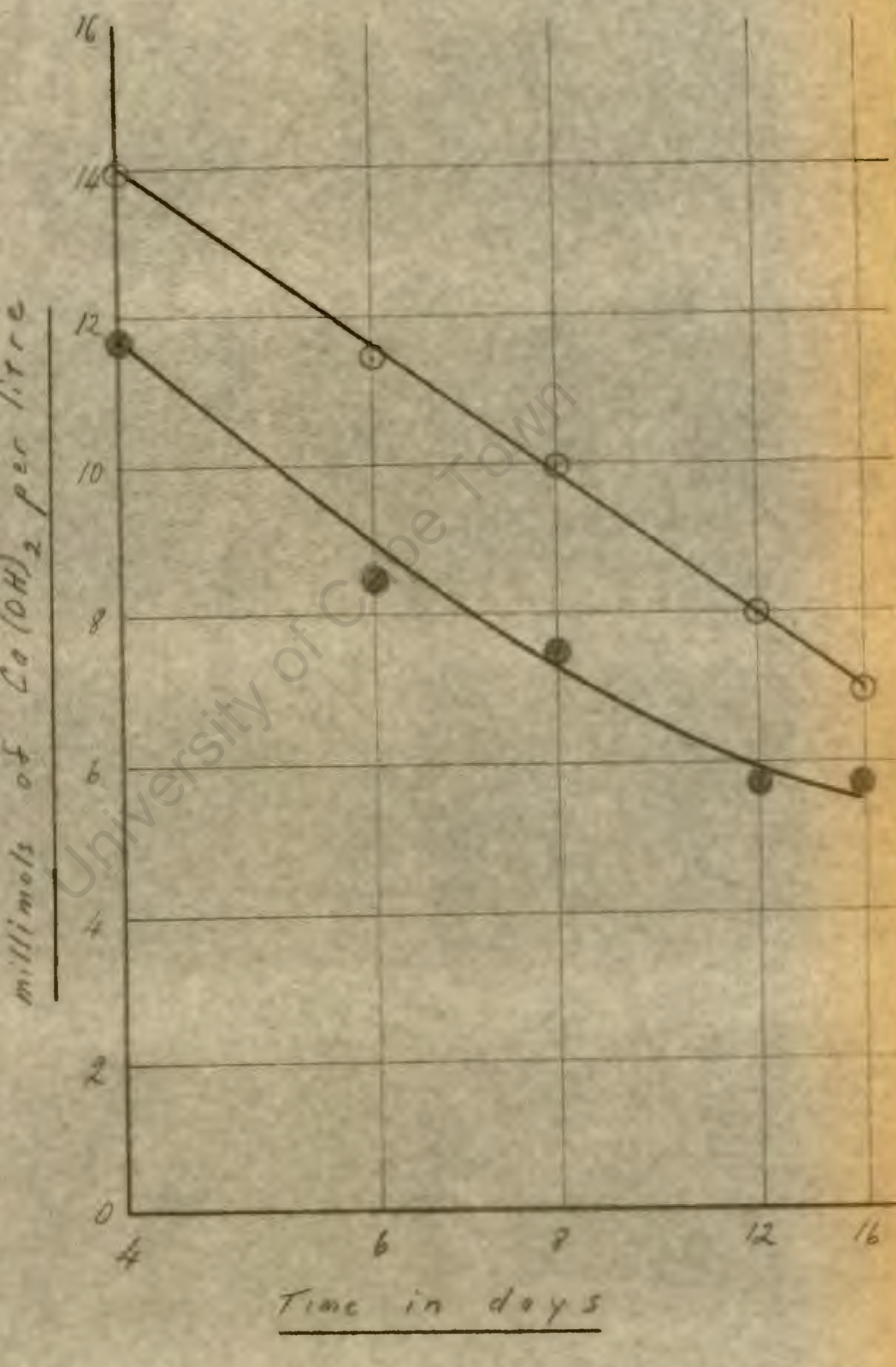


Fig. No. 10

30% Calc. Shale ○

40% Calc. Shale ●

## TABLE NO.41

RESULTS OF FRANTINI TEST ON CEMENTS CONTAINING 30% AND 40% CALCINED SHALE, AT VARIOUS AGES

| DAYS OF CURING AT 40°C | 30% MIXTURE Millimols of: | | 40% MIXTURE Millimols of: | |
|---|---|---|---|---|
| | $OH^-$ | $Ca(OH)_2$ | $OH^-$ | $Ca(OH)_2$ |
| 4 | 47 | 14 | 45 | $11\frac{3}{4}$ |
| 6 | 47 | $11\frac{1}{2}$ | 45 | $8\frac{1}{2}$ |
| 8 | 47 | 10 | 48 | $7\frac{1}{2}$ |
| 12 | 51 | 8 | 52 | $5\frac{3}{4}$ |
| 16 | 51 | 7 | 55 | $5\frac{3}{4}$ |

### 8.2. SECOND BATCH

1. Some alterations which were made to the factory and kiln, for another purpose, proved most helpful in calcining the second production scale batch of shale.

1.1. Crushed, instead of powdered, shale was fed to the kiln. A test done in the laboratory kiln had already indicated that powdering was unnecessary - Section 7.3-5; Sample A/0; Table No.35.

1.2. The rate at which the shale was fed to the kiln could be more accurately controlled, and was kept steady.

1.3. A thermocouple was installed in a "thermometer pocket" half-way along the length of the kiln. Although this did not give the temperature of the product, it did enable the temperature to be controlled.

1.4. A small oil-burner was attached to the coal burner. This provided a "pilot-flame" to keep the coal alight at the temperatures required.

1.5 Provision/..............

1.5. Provision was made for handling the material at the discharge end of the kiln cooler.

2. Five lots of shale (5 - 10 tons each) were calcined at different temperatures. According to the thermocouple readings, the temperatures half-way along the kiln were: 300°C, 450°C, 600°C, 700°C and 750°C.

2.1. The 750°C material was partially "bloated" and showing signs of incipient fusion, i.e. slightly "over-cooked".

2.2. The 700°C material was similar in appearance to the coarse material calcined in the laboratory kiln at 1100 - 1150°C. Its Chemical Activity Index of 42 mgm $Ca(OH)_2$ per gram (after 2 hours grinding in a laboratory mill) confirmed this resemblance.

2.3. Physical Activity Indices are given in Table No.42.

TABLE NO.42

PHYSICAL ACTIVITY INDICES OF SHALE CALCINED AT VARIOUS TEMPERATURES

| TEMPERATURE HALF-WAY ALONG KILN | V.M. STRENGTH AT 7 DAYS | | PHYSICAL ACTIVITY INDEX |
|---|---|---|---|
| | "COLD"CURED | "HOT"CURED | |
| 600°C | 3800 p.s.i. | 5700 p.s.i. | 50% |
| 700°C | 3700 p.s.i. | 6100 p.s.i. | 65% |
| 750°C | 3500 p.s.i. | 5350 p.s.i. | 53% |
| "Selected" partially fused lumps. | 3850 p.s.i. | 5500 p.s.i. | 43% |

2.4. The 700°C material showed up best and was selected for manufacturing the second test batch of Marine Cement

3. Before proceeding with the manufacture some preliminary tests

were carried/..................

were carried out with another two air-entraining agents.

3.1. One brand, which was highly recommended by the P.C.I., had outstandingly good properties when added to mixing water, and was also satisfactory when interground with Portland cement. When interground with cement and calcined shale, however, it exhibited the same tendency as the soluble oil to become "inactive" until heated. Although it was not as bad as the oil, I did not consider it suitable.

3.2. The oldest and best known air-entraining agent, Neutralised Vinsol Resin, ultimately turned out to be the best. It gave satisfactory results when added to the mixing water, and was practically unaffected by intergrinding. To be on the safe side, however, I specified control limits of 6 - 10% Air.

4. A preliminary batch was ground in the laboratory, consisting of 75 per cent of SRC/3 (see Table No.25) and 25% Calcined Shale "700". The CaO content was 48.4% and it entrained 9% air in standard mortar. Strength test results are given in Table No.43. Sample Designation : SRC/3/700.

4.1. The Physical Activity Indices determined by the different strength test methods were satisfyingly constant, varying only from 16% to 20%. The actual values were low, of course, because of the low shale content (25%) of the cement - in the standard test it is 50% of the total.

4.2. The cement complied with all the standard strength requirements.

4.3. Control limits for CaO in the plant scale test were set at 48% to 52%, in order to keep the shale content of the cement at 20 to 25%

Table No.43/..............

## TABLE NO.43

## STRENGTH TEST RESULTS ON LABORATORY-GROUND CEMENT SRC/3/700

| TEST | SRC/3/700 | B.S.12 & SABS.471 MINIMUM REQUIREMENTS FOR O.P.C. |
|---|---|---|
| **Vibrated Mortar Cubes** | | |
| At 3 Days | 3350 p.s.i. | 2200 p.s.i. |
| At 7 Days | 4100 " | 3400 " |
| At 7 Days "hot" cured | 4800 " | - |
| Activity Index "A" | 17% | - |
| **4" Concrete Cubes** | | |
| At 3 Days | 2000 p.s.i. | 1200 p.s.i. |
| At 7 Days | 2950 " | 2000 " |
| At 7 Days "hot" cured | 3400 " | - |
| Activity Index "B" | 16% | - |
| **SABS Mortar Transverse Strength** | | |
| (Normal $H_2O$) | | |
| At 3 Days | 510 p.s.i. | 250 p.s.i. |
| At 7 Days | 580 " | 400 " |
| (Reduced $H_2O$) * | | |
| At 3 Days | - | - |
| At 7 Days | 630 p.s.i. | - |
| At 7 Days "hot" cured | 730 " | - |
| Activity Index "C" | 16% | - |
| **Compressive Strength of ½-Prisms from SABS Transverse Test** | | |
| (Normal $H_2O$) | | |
| At 3 Days | 2200 p.s.i. | - |
| At 7 Days | 2500 " | - |
| (Reduced $H_2O$) * | | |
| At 3 Days | 3000 p.s.i. | - |
| At 7 Days | 3700 " | - |
| At 7 Days "hot" cured | 4450 " | - |
| Activity Index "D" | 20% | - |

* These specimens were made with about 10% less water - their wet mortar had the same "workability" (measured by the ASTM jolting table) as OPC specimens with the standard amount of water

5. The second production batch of Marine Cement, "CM-2", was ground without any <u>major</u> difficulties. Test results are given in Table No.44. They were satisfactory in all respects.

Table No.44/....................

## TABLE NO.44

## TEST RESULTS ON 2ND PRODUCTION BATCH OF MARINE CEMENT

| PROPERTY | TEST RESULT |
|---|---|
| PARTIAL CHEMICAL ANALYSIS. | |
| Calcium Oxide content (CaO) | 49.6% |
| Sulphur Trioxide content ($SO_3$) | 1.5% |
| PHYSICAL PROPERTIES. | |
| Air-entrainment of Standard Mortar. | |
| Immediately after production | 7% |
| After 2 weeks storage (at 100°C) | 9% |
| Setting Times. | |
| Initial | 150 minutes |
| Final | 4hrs-30 mins. |
| Fineness. | |
| No.72 Residue | 0.0% |
| No.170 Residue | 1.2% |
| No.300 Residue | 9.4% |
| Specific Surface | 5050 $cm^2/g$ |
| (Density) | (2.97 g/c.c.) |
| Soundness. | |
| Le Chatelier Expansion | 1 m.m. |
| COMPRESSIVE STRENGTH | |
| Vibrated Mortar Cubes: | |
| At 3 Days | 3200 p.s.i. |
| At 7 Days | 4300 " |
| At 28 Days | 5500 " |
| 4" Concrete Cubes: | |
| At 3 Days | 1750 p.s.i. |
| At 7 Days | 2600 " |
| At 28 Days | 4100 " |
| SABS TRANSVERSE STRENGTH. | |
| At 7 Days | 710 p.s.i. |
| At 28 Days | 840 " |
| At 56 Days | 910 " |
| COMPRESSIVE STRENGTH OF ½ PRISMS FROM TRANSVERSE TEST | |
| At 7 Days | 3400 p.s.i. |
| At 28 Days | 5100 " |
| At 56 Days | 5900 " |

6. As an additional check on the ability of Shale "700" to combine with the $Ca(CH)_2$ liberated by cement, and to render it insoluble, the Modified Frantini Test (as described in paragraph 7.1 - 3.3) was carried out on a laboratory-ground sample of this shale.

6.1. For comparison purposes, tests were run concurrently on local pulverised fuel ash and a sample of South African ground granulated blastfurnace slag ("Slagment").

6.2. In addition to determining the $Ca^{\cdot\cdot}$ and $OH^{1}$ contents of the "contact" water, the pH was measured in order to see whether this declined with the $Ca^{\cdot\cdot}$ concentration, as this would reduce the protection given to reinforcing material by concrete.

6.3. The mixtures used were:

6.3.1. 5g Cement and 5g L.B.Sand
6.3.2. 5g Cement and 5g Slagment
6.3.3. 5g Cement and 5g Pulverised Ash
6.3.4. 5g Cement and 5g Shale 700
6.3.5. 10g L.B.Sand
6.3.6. To each was added 50 ml of $CO_2$-free distilled water. Half the samples were kept at 40°C and the other half at "room" temperature (15 to 30°C)

6.3.7. They were kept continuously agitated up to 28 days and then shaken once a day up to 3 months. After the test period the samples were filtered rapidly, without washing, and aliquots taken for titration with 0.1 N EDTA, 0.1 N HCl, and the pH measured with a pH meter.

6.4. Test results are given in Table No.45 and illustrated with Figure No.11

Table No.45/....................

## TABLE NO.45

## RESULTS OF MODIFIED FRANTINI TEST ON SLAGMENT, ASH, & SHALE 700

| MIXTURE NUMBER | 6.31 | 6.32 | 6.33 | 6.34 | 6.35 |
|---|---|---|---|---|---|
| TEST COMPONENT | SAND | SLAGMENT | ASH | SHALE | BLANK |
| A TESTS AT 40°C | | | | | |
| Conc.of $Ca(OH)_2$ in mgm/ml | | | | | |
| After 1 day | 1.10 | 1.18 | 1.19 | 1.22 | - |
| After 7 days | 0.81 | 0.87 | 0.86 | 0.42 | - |
| After 28 days | 0.68 | 0.69 | 0.63 | 0.20 | - |
| Conc.of $OH^1$ in millimols/litre | | | | | |
| After 1 day | 46 | 48 | 49 | 50 | - |
| After 7 days | 46 | 52 | 47 | 49 | - |
| After 28 days | 57 | 53 | 56 | 64 | - |
| pH of filtrates | | | | | |
| After 1 day | 11.9 | 11.9 | 11.9 | 11.9 | - |
| After 7 days | 12.0 | 12.0 | 12.0 | 12.0 | - |
| After 28 days | 11.9 | 11.9 | 11.9 | 11.9 | - |
| B TESTS AT "ROOM"TEMPERATURE | | | | | |
| Conc.of $Ca(OH)_2$ in mgm/ml. | | | | | |
| After ½ hour | 2.21 | 2.22 | 2.24 | 2.26 | 0.03 |
| After 1 day | 1.63 | 1.66 | 1.69 | 1.69 | - |
| After 7 days | 1.28 | 1.17 | 1.36 | 1.19 | 0.02 |
| After 28 days | 0.96 | 0.76 | 1.08 | 0.55 | - |
| After 3 months | 0.80 | 0.56 | 0.59 | 0.18 | - |
| Conc.of $OH^1$ in millimols/litre | | | | | |
| After ½ hour | 44 | 41 | 41 | 42 | 0 |
| After 1 day | 52 | 57 | 58 | 58 | - |
| After 7 days | 52 | 51 | 57 | 52 | 0 |
| After 28 days | 51 | 48 | 55 | 47 | - |
| After 3 months | 46 | 54 | 50 | 60 | - |
| pH of filtrates | | | | | |
| After ½ hour | 11.9 | 11.8 | 11.3 | 11.3 | 8.9 |
| After 1 day | 11.9 | 11.8 | 11.9 | 11.9 | - |
| After 7 days | 12.0 | 12.0 | 12.1 | 12.0 | 8.9 |
| After 28 days | 11.9 | 11.9 | 11.9 | 11.9 | - |
| After 3 months | 11.7 | 11.8 | 11.8 | 11.8 | - |

Figure No.11/..................

Modified

Frantini

Test

Results

with

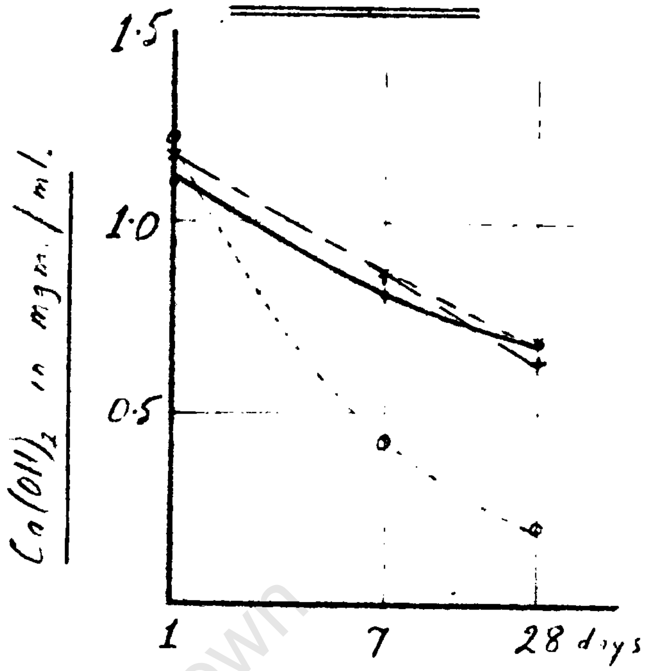
Cement

and

Various

"Pozzolans"

At 40°C



At "Room" Temperature

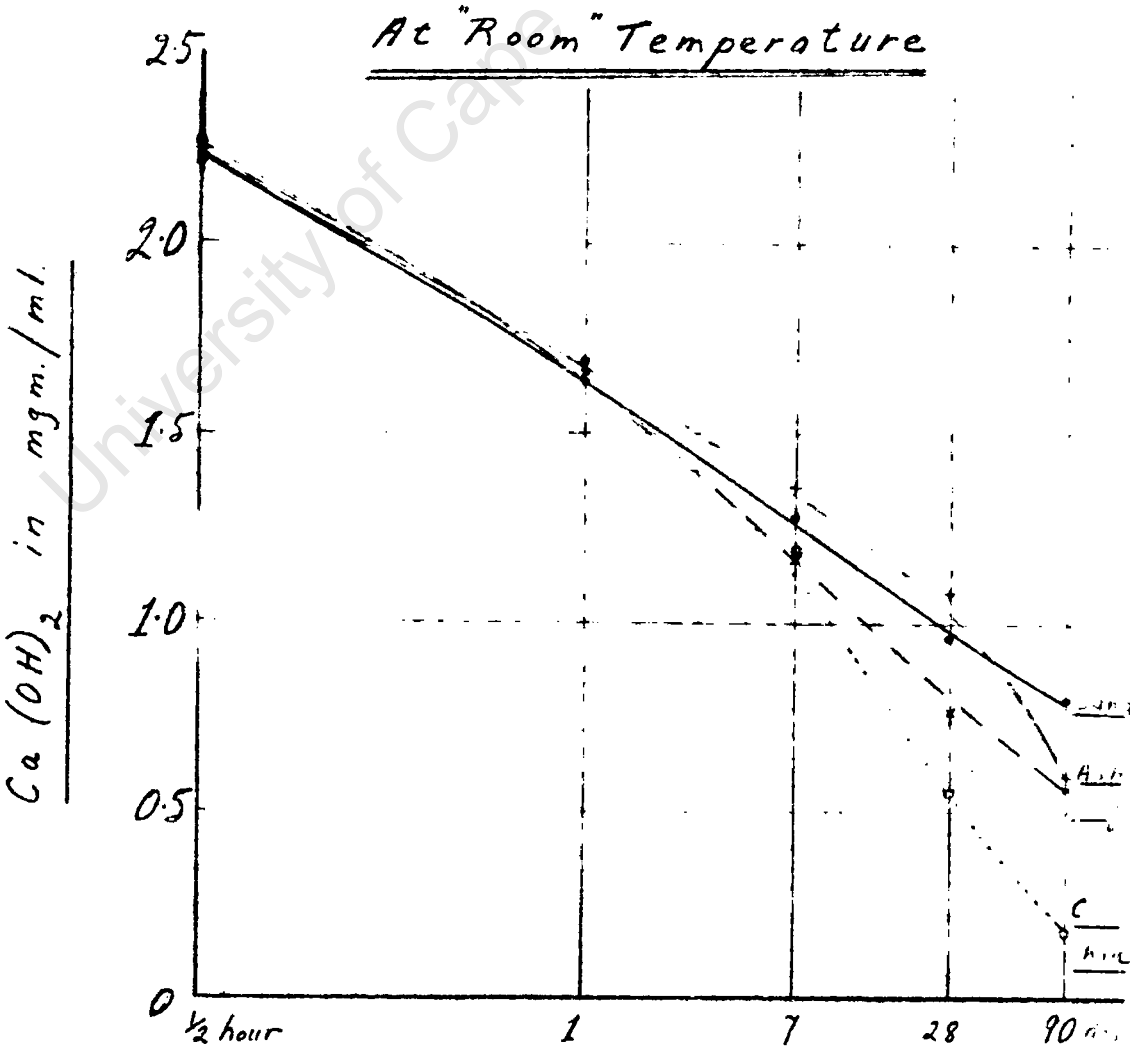


Fig. No. 11

6.4.1. The shale proved to be, chemically, the most active of the materials tested, both at ambient temperature and at 40°C. The 40°C test results at 28 days were approximately equal to the ambient temperature results at 3 months.

6.4.2. The pH of the filtrates can be considered constant - the small variations recorded were most likely due to the pH meter.

6.4.3. Variations in alkalinity (millimols of $OH^1$ per litre) seem to be random about 50. Errors were most likely due to the very small aliquots, and even smaller titration quantities, available for this test. It may be noteworthy that the shale samples ended up with the highest alkalinities at both temperatures. Further checking on these lines is to be undertaken at a later date.

7. The temperature-of-hydration test method used to date was clearly able to distinguish between "high" and "low" heat cements but Mr C.F.Zietsman (of the S.A.R & H. Research Laboratories) suggested a thoroughly "practical" test. He said that engineers would be better able to understand and appreciate a chart which showed the actual temperature reached in the centre of a cubic yard block of concrete. (See page 4 of photographs)

7.1 This advice was taken, and two concrete "specimens", 3' x 3' x 3' and weighing about two tons each, were made up in the following proportions:

| Material | O.P.C. | CM-2 |
|---|---|---|
| Cement | 94 lb | 94 lb |
| Sand, approx. | 140 " | 140 " |
| Limestone aggregate, app. | 204 " | 204 " |
| Water | 35 " | 32 " |
| Water/Cement ratio, including water in sand. | 0.43 " | 0.39 " |

A total/..........l......

A total of 8 pockets of cement, i.e. a fairly "rich" mix, was used for each block.

7.2. A sealed glass tube was cast into the middle of each block, and a chrome/alumel thermocouple inserted so that its junction was at the centre of the mass. Glass wool was used to insulate the open top of the glass tube

7.3. The thermocouples were connected to the Leeds and Northrup "Speedomax" Cement Mill Temperature Recorder, which, fortunately, had two spare recording "points" available. Temperatures were recorded for 5 days. Daily maximum and minimum ambient temperatures were also taken.

7.4. As the chart travels at a rate of 2" per hour, the temperature record was 20 feet long ! The chart range is from 0 to 200°C, and is 10" wide, so that the scale is 2°C per one-tenth of an inch. A small section of a reprint of the chart is attached to this report - Addendum No.2

7.5. The temperature recorded on the hour, each hour, was read off the chart and reported in Table No.46. I drew Figure No.12 from these readings.

7.6. The figure shows clearly the advantage of the Marine Cement. The rise in temperature above ambient was less than half that caused by the OPC, and it took twice as long to reach the maximum.

Table No.46/.................

## TEMPERAUG. 1963.

| TIME | 12.8.63. | | 18.8.63. | |
|---|---|---|---|---|
| | CM II | OPC | II | OPC |
| 1 a.m. | - | - | ¾ | 21¾ |
| 2 | - | - | ¾ | 21¾ |
| 3 | - | - | ½ | 21½ |
| 4 | - | - | ½ | 21½ |
| 5 | - | - | ¼ | 21¼ |
| 6 | - | - | ¼ | 21¼ |
| 7 | 14½ | 15 | | 21 |
| 8 | 14 | 14½ | | 21 |
| 9 | 14 | 14½ | | 21 |
| 10 | 15 | 15½ | | 21 |
| 11 | 15 | 15½ | | 21 |
| 12 noon | 16 | 16½ | | 21 |
| 1 p.m. | 17 | 17½ | | 21 |
| 2 | 17 | 17½ | | - |
| 3 | 18 | 18 | | - |
| 4 | 19 | 19 | | - |
| 5 | 13 | 16 | | - |
| 6 | 13 | 16 | | - |
| 7 | 13 | 17 | | - |
| 8 | 13½ | 18 | | - |
| 9 | 14 | 19 | | - |
| 10 | 14 | 20 | | - |
| 11 | 15 | 22 | | - |
| 12 m.n. | 15½ | 24 | | - |

| DAILY AMBIENT TEMPERATURES | | |
|---|---|---|
| DATE | MAX. | MIN. |
| 12th | 21 | 14 |
| 13th | 25 | 18 |
| 14th | 25 | 17 |
| 15th | 25 | 16 |
| 16th | 25 | 16 |
| 17th | 24 | 16 |
| 18th | 24 | 18 |

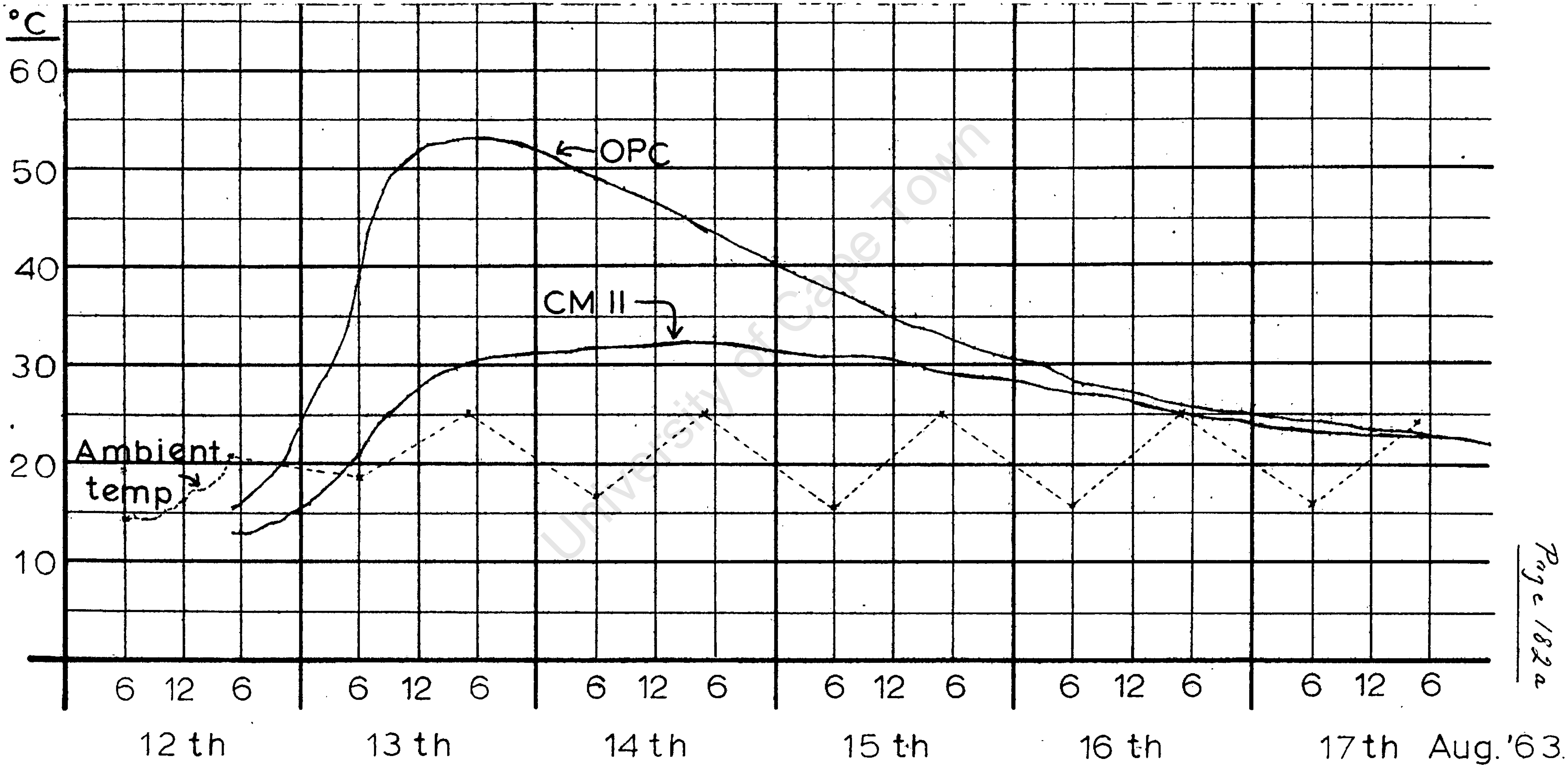

°C
60
50
40
30
20
10
OPC
CM II
Ambient temp
6 12 6
6 12 6
6 12 6
6 12 6
6 12 6
6 12 6
12 th
13 th
14 th
15 th
16 th
17 th
Aug.'63.

*Fig. No. 12*

8. The general conclusion drawn from this, second production, test was that a satisfactory product can be manufactured. The decision was taken to make a "full scale" production batch of Marine Cement and subject it to intensive testing.

## 8.3. FINAL BATCH OF MARINE CEMENT

1. About 70 tons of crushed, but not powdered, shale were calcined within temperature limits of 680°C to 730°C in the middle of the kiln. Estimated limits in the "hot" zone were some 400°C to 450°C higher. Loss-on-ignition was kept below 1%. Sample designation was "CS".

2. Activity test results were:

2.1. Chemical Activity Index : 45 mgm $Ca(OH)_2$ per gram.

2.2. Physical Activity Test results (on 50/50 mixtures of cement and shale):

| Vibrated Mortar Comp.Str. | Portland Cement | Portland Cement + Raw Shale | Portland Cement + CS |
|---|---|---|---|
| At 3 days | 5350 | 2100 | 2550 |
| At 7 days | 5900 | 2550 | 2950 |
| At 7 days "hot" curing | 6750 | 2800 | 5150 |
| Physical Activity Index | 14% | 10% | 75% |

2.3. Autoclave Activity Test: The test method was described in paragraph 7.1 - 3.4, and the method for determining soluble lime is given in Appendix 9.

| Autoclaved specimens of "neat" cement paste | O.P.C. | O.P.C. + 12½% CS |
|---|---|---|
| Loss on Ignition: | 15.7% | 14.7% |
| Water-soluble $Ca(OH)_2$: | | |
| "as recd" | 12.5% | 6.8% |
| "loss-free" | 14.8% | 8.0% |

3. The calcined/..........

3. The calcined shale was interground with the latest available batch of sulphate resisting cement, SRC/4 - see section 5.5 and Table No.25. CaO limits were set at 49 to 51%, and "air" limits at 8 to 12%. Specific surface was kept above 5,000 $cm^2/g$, and $SO_3$ at 1.3 to 1.7%. The laboratory sample was designated SRC/4/CS, and the batch was called CM-3.

4. "Ordinary" test results on this cement are given in Table No.47. CM-3 complies "comfortably" with all the physical test requirements of SABS.471 : 1959 and B.S.12:1958.

TABLE NO.47

"ORDINARY TEST RESULTS ON MARINE CEMENT CM-3 (SAMPLE SRC/4/CS)

| PROPERTY | TEST RESULTS |
|---|---|
| CHEMICAL ANALYSIS | |
| $SiO_2$ | 31.0% |
| $Al_2O_3$ | 6.8% |
| $Fe_2O_3$ | 6.4% |
| CaO | 49.4% |
| MgO | 1.9% |
| $SO_3$ | 1.4% |
| Loss on Ignition | 1.1% |
| PHYSICAL TEST RESULTS | |
| Setting Times: | |
| Initial | 155 mins. |
| Final | 3 hrs. 45 mins. |
| Fineness | |
| No.72 Screen Residue | nil |
| No.170 Screen Residue | 0.8% |
| Specific Surface | 5380 $cm^2/g$ |
| Soundness | |
| Le Chatelier Expansion | 1 m.m. |
| Compressive Strenths. | |
| Vibrated Mortar Cubes: | |
| At 1 Day | 1650 p.s.i. |
| At 3 Days | 3400 " |
| At 7 Days | 4300 " |
| At 28 Days | 5850 " |
| 4" Concrete Cubes: | |
| At 3 Days | 2050 p.s.i. |
| At 7 Days | 2900 " |
| At 28 Days | 4450 " |
| Transverse Strength. | |
| At 3 Days | 550 p.s.i. |
| at 7 Days | 650 " |
| at 28 Days | 800 " |

5. "Special" Test results are given in Table No.48.

5.1. The amount of air entrained is sufficient to reduce "bleeding" to nearly zero, and to enable the water content of most concrete mixes to be reduced by approx.10%

5.2. The ASTM expansion test with $CaSO_4$ indicates satisfactory sulphate resistance. Further test results are reported in Chapter IX.

5.3. Autoclave expansions were very satisfactory. The quantity of water-soluble $Ca(OH)_2$ in the hydrated CM-3 bars was less than half the amount in the SRC/4 bars.

5.4. The percentage of particles smaller than 10 microns in diameter was 37%, against 22% for O.P.C.

TABLE NO.48

"SPECIAL" TEST RESULTS ON CM-3, SAMPLE SRC/4/CS

| PROPERTY | TEST RESULTS | |
|---|---|---|
| AIR ENTRAINED BY STANDARD MORTAR. | | |
| (a) Immediately after production | 9% | |
| (b) After 4 weeks in storage silo | 10% | |
| A.S.T.M.SULPHATE RESISTANCE TEST | | |
| (Expansion with $CaSO_4$ - at 7% $SO_3$) | | |
| At 7 Days | 0.02% | |
| At 28 Days | 0.025% | |
| At 56 Days | 0.035% | |
| At 84 Days | 0.05% | |
| AUTOCLAVE TESTS. | | |
| (On "neat" cement) | SRC/4 | SRC/4/CS |
| Expansion of 10" bars. | 0.03% | 0.02% |
| Loss on ignition | 10.5% | 12.8% |
| Water-soluble $Ca(OH)_2$: | | |
| As recd. | 16.9% | 6.5% |
| loss-free. | 18.9% | 7.4% |
| PARTICLE SIZE ANALYSIS : (BY SEDIMENTATION METHOD) | % By Weight Undersize | % By Weight Undersize |
| Size (Microns) | O.P.C | SRC/4/CS |
| 150 | 98 | - |
| 106 | 95 | - |
| 75 | 89 | 99 |
| 53 | 79 | 94 |
| 37.5 | 65 | 84 |
| 26.5 | 52 | 72 |
| 18.8 | 41 | 60 |
| 13.3 | 30 | 45 |
| 9.4 | 22 | 37 |
| 6.6 | 15 | 28 |
| 4.7 | 10 | 19 |
| 3.3 | 8 | 13 |
| 2.4 | - | 8 |

6. Another pair of cubic yard blocks of concrete were made and their temperatures recorded. Details of the materials and mixes used are:

6.1. Coarse Aggregate: 1½" Limestone
Bulk density (loose): 101 lb/cu.ft.
S.G. : 2.66

Fine Aggregate : De Grendel Sand
Bulk density : 104 lb/cu.ft.
Moisture : 3½%
S.G. dry : 2.66

6.2. Pockets of cement per cubic yard concrete : 8

6.3.

| Material | Quantities per concrete mixer batch. | |
|---|---|---|
| | Ordinary Portland Cement | CM-3 |
| Cement | 94 lb | 94 lb |
| Sand | = ± 140 " | ± 140 " |
| Stone | = ± 204 " | ± 204 " |
| Water - added | 35 lb.) | 32 lb.) |
| Water - in sand (3½%) | 5 " )40 " | 5 " )37 " |
| Water/Cement ratio | 0.425 | 0.395 |

6.4. On this occasion the cubes were cast and cured inside the mill motor room, i.e. in a warm atmosphere, and a thermograph was used to record the ambient temperature for the whole period.

6.5. The hourly temperatures are given in Table No.49 and are presented graphically on Figure No.13.

6.6. On this occasion a Portland cement with moderate $C_3A$ (± 9%) was used as the control, but in spite of this the Marine Cement concrete had a markedly lower hydration temperature.

7. The results of long-term and other tests on some of the cements produced during this project are given in the next chapter. It is intended to carry on testing for some time to come, and to still further improve the product if possible. In the meantime a pamphlet has been drawn up listing the essential properties of the cement, as it has given every indication, to date, of being more durable than O.P.C. in Marine environments. A copy of the pamphlet is attached as Addendum No.3.

## TABLE NO. 49

### TEMPERATURES, IN °C, OF HYDRATION OF CUBIC YARD CONCRETE BLOCKS : 11th - 19th NOV. 1963

| TIME | 11.11.63. | | | 12.11.63. | | | 13.11.63. | | | 14.11.63 | | | 15.11.63 | | | 16.11.63. | | | 17.11.63 | | | 18.11.63 | | | 19.11.63. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CMIII | OPC | Amb | CMIII | OPC | Amb | CMIII | OPC | Amb | CMIII | OPC | Amb | CMIII | OPC | Amb | CMIII | OPC | Amb | CMIII | OPC | Amb | CMIII | OPC | Amb | CMIII | OPC | Amb |
| 1 a.m. | – | – | – | 47 | 61 | 30½ | 46½ | 53½ | 35½ | 41½ | 43¼ | 31 | 35½ | 36½ | 30½ | – | – | – | – | – | – | – | – | – | – | – | – |
| 2 | – | – | – | 47½ | 61¼ | 30 | 46¼ | 53¼ | 35 | 41 | 43 | 31 | 35½ | 36 | 31 | – | – | – | – | – | – | – | – | – | – | – | – |
| 3 | – | – | – | 47¾ | 61½ | 30 | 46 | 53 | 34 | 41 | 43 | 30½ | 35½ | 35½ | 30 | – | – | – | – | – | – | – | – | – | – | – | – |
| 4 | – | – | – | 48 | 62 | 29½ | 46 | 52½ | 32 | 41 | 42½ | 32 | 35 | 35½ | 29½ | 32¼ | 32½ | – | 31½ | 31½ | – | 30 | 30 | – | 29 | 29 | – |
| 5 | – | – | – | 48 | 62¼ | 29½ | 46 | 51½ | 33 | 40½ | 42 | 34 | 34½ | 35 | 29½ | – | – | – | – | – | – | – | – | – | – | – | – |
| 6 | – | – | – | 48 | 62 | 29½ | 46 | 51 | 33½ | 40½ | 41½ | 32 | 34½ | 35 | 30½ | – | – | 27 | – | – | 28 | – | – | 26 | – | – | 26 |
| 7 | – | – | – | 48 | 61½ | 31 | 45¾ | 50¾ | 35 | 40 | 41 | 30 | 34 | 34½ | 30 | – | – | – | – | – | – | – | – | – | – | – | – |
| 8 | – | – | – | 48 | 61¼ | 34 | 45½ | 50 | 35 | 40 | 41 | 31 | 34 | 34½ | 29½ | 32 | 32 | – | 31 | 31 | – | 30 | 30 | – | 28½ | 28½ | – |
| 9 | – | – | 28 | 48 | 61¼ | 35½ | 45 | 49½ | 34½ | 39½ | 40½ | 32 | 34 | 34½ | 33 | – | – | – | – | – | – | – | – | – | – | – | – |
| 10 | – | – | 32 | 48 | 61 | 38 | 44½ | 49¼ | 36 | 39 | 40 | 32 | 34 | 34½ | 34½ | – | – | – | – | – | – | – | – | – | – | – | – |
| 11 | 27 | 27 | 33 | 48 | 60½ | 39½ | 44¼ | 49 | 38 | 38½ | 39½ | 32 | 33¾ | 34¼ | 35½ | – | – | – | – | – | – | – | – | – | – | – | – |
| 12 noon | 27 | 27 | 34½ | 48 | 60 | 40½ | 44 | 48½ | 39 | 38½ | 39½ | 33 | 33¾ | 34¼ | 36 | 32 | 32 | – | 30½ | 30½ | – | 39½ | 29½ | – | 28 | 28 | – |
| 1 p.m. | 27 | 27½ | 35½ | 47¾ | 59½ | 41½ | 44 | 47½ | 40 | 38 | 39 | 33 | 33¾ | 34¼ | 36½ | – | – | – | – | – | – | – | – | – | – | – | – |
| 2 | 28 | 29 | 36 | 48 | 59 | 43 | 43¾ | 47¼ | 40½ | 38 | 39 | 32 | 33½ | 34 | – | – | – | – | – | – | – | – | – | – | – | – | – |
| 3 | 29 | 31½ | 36½ | 47¾ | 58½ | 43½ | 43½ | 47 | 41 | 38 | 39 | 33 | 33½ | 34 | – | – | – | – | – | – | – | – | – | – | – | – | – |
| 4 | 30 | 35 | 37 | 47½ | 57½ | 44 | 43¼ | 46¾ | 41¾ | 37½ | 38½ | 33 | 33½ | 34 | 38 | 32 | 32 | 40 | 30½ | 30½ | 38 | 29½ | 29½ | 34 | 28 | 28 | 35 |
| 5 | 32 | 39½ | 37 | 47½ | 57¼ | 44 | 43 | 46 | 40½ | 37 | 38 | 33 | 33½ | 34 | – | – | – | – | – | – | – | – | – | – | – | – | – |
| 6 | 34 | 46½ | 36½ | 47½ | 57 | 44 | 43 | 45½ | 39 | 36½ | 38 | 33 | 33½ | 33¾ | – | – | – | – | – | – | – | – | – | – | – | – | – |
| 7 | 36 | 53 | 36 | 47¼ | 56½ | 43 | 42½ | 45 | 38 | 36½ | 37½ | 32 | 33¼ | 33¾ | – | – | – | – | – | – | – | – | – | – | – | – | – |
| 8 | 39 | 56 | 36 | 47¼ | 56 | 39 | 42½ | 45 | 36½ | 36½ | 37½ | 32 | 33¼ | 33½ | – | 32 | 32 | – | 30½ | 30½ | – | 29 | 29 | – | 28 | 28 | – |
| 9 | 41 | 57½ | 35½ | 47 | 55½ | 40 | 42 | 44¾ | 35½ | 36½ | 37 | 32 | 33¼ | 33½ | – | – | – | – | – | – | – | – | – | – | – | – | – |
| 10 | 43 | 59 | 35 | 47 | 55 | 38 | 42 | 44½ | 34½ | 36½ | 37 | 32 | 33 | 33¼ | – | – | – | – | – | – | – | – | – | – | – | – | – |
| 11 | 45 | 60 | 32 | 47 | 54½ | 38 | 42 | 44 | 33 | 36½ | 37 | 31 | 32¾ | 33 | – | – | – | – | – | – | – | – | – | – | – | – | – |
| 12 m.n. | 46 | 60½ | 31 | 46½ | 54 | 36½ | 42 | 43½ | 32 | 36 | 36½ | 29½ | 32¾ | 33 | – | 32 | 32 | – | 30 | 30 | – | 29 | 29 | – | 28 | 28 | – |

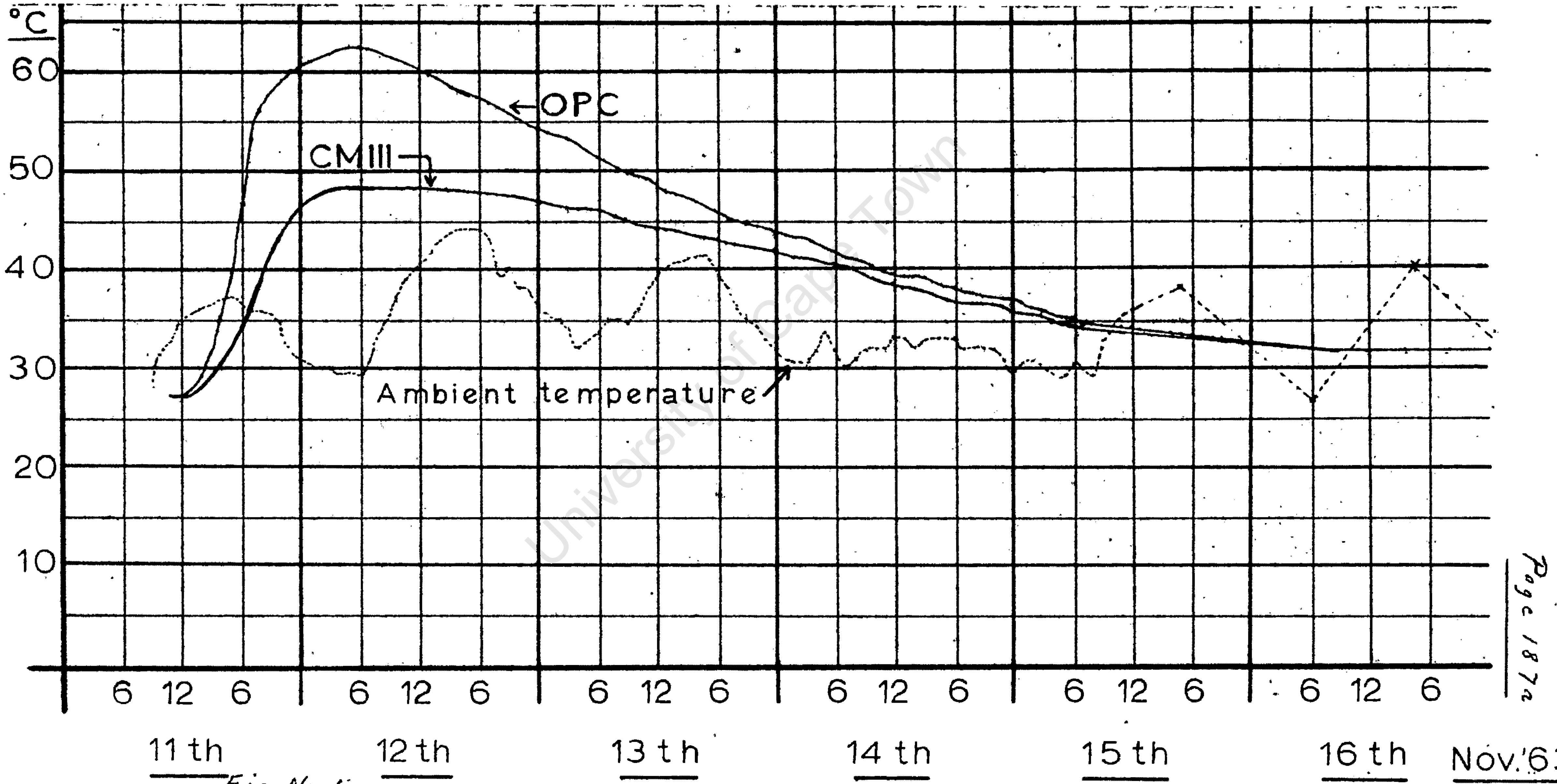

°C
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Fig No. 13

# CHAPTER IX

## COMPREHENSIVE TEST PROGRAMME

### 9.1. ACCELERATED TESTING

1. Accelerated testing techniques may be counted amongst the World's "mixed blessings". Testing a special cement in concrete, under natural conditions, would take many years. During this period: (1) inestimable damage might have been done to concretes made with ordinary cements; (2) the "formula" for making the special type would probably have been lost or destroyed; and (3) so much progress would have been made in the meantime that newer types of cement would probably be available anyway. Some form of accelerated test is therefore essential, but, once the test has been developed and the results obtained, how does one interpret them?
In the words of Scholer, "how many cycles of freezing and thawing will represent a useful life for twenty years?"
There is no answer !

2. Some writers seem to feel quite strongly on the subject. Burke claimed, in 1960, that a "universal short-time test for sulphate resistance does not exist". This is quite true, of course, because the cations in combination with the sulphates affect the susceptibility of the cement (see Chapters 2 & 4). But there is no help in adopting a defeatist attitude - one can only keep on trying and testing.

3. The Editor of Concrete and Construction Engineering wrote, in 1940, that "To be worth the name of research it must be proved that acceleration does not alter the nature of the reaction". He points out, correctly, that concentrated solutions sometimes act quite differently from weaker ones,

and can give misleading results. This warning has been heeded, and results obtained with concentrated solutions are treated with reserve. As a matter of fact, in the case of solutions of $MgSO_4 + Na_2SO_4$, I actually found the weaker solution to be more aggressive than the stronger !
He also warns against high temperatures; and other researchers have proved conclusively that autoclaving, for example, results in quite different hydration products. That is why the autoclave has [redacted] been used only once, in this project, although the temptation to utilise it more often has been strong.

4. Kind was careful not to "increase the concentration of aggressive solutions to decrease the time of experiments, as this often distorts the corrosion process" (10.3), and took years over his experiments. He was fortunate to have the time !

5. It was, apparently, agreed at the 1961 RILEM Symposium on Concrete that a "convenient unified method of testing is required" and that "such a method should accelerate the whole process of disintegration of concrete but should at the same time represent accurately the real conditions of deterioration". (11.1). Such a test is a good ideal for which to strive, but is, unfortunately, (in my opinion) impossibly impracticable.

6. The durability of concrete, as has already been implied, is a physico-chemical problem. Durability, particularly in the case of reinforced concrete, is as much dependent on impermeability as it is on chemical resistance. Although as much as possible has been done to produce a cement which

will assist contractors to make their concrete impermeable, most of the accelerated tests I have used and designed have been aimed at checking the potential chemical resistance of the cement. Instead of making the specimens with water and then immersing them in aggressive solutions, I have used the ASTM sulphate-resistance test technique of incorporating the attacking agent within the specimen. The specimens are immersed in aggressive solutions as well. This is roughly equivalent to testing the cement in a porous concrete through which an aggressive water is continually flowing. Other tests have been, and are being, designed to test specifically the permeability of mortar and/or concrete.

7. As far as "interpretation" of results is concerned, I feel that there is no "absolute" answer. In all cases I have used comparison as the basic testing technique. The special cement is always checked against an ordinary cement. When the special cement withstands the attack better, then I feel it is legitimate to say: "under similar circumstances of manufacture and use, a concrete made with the special cement will outlast a concrete made with ordinary cement".

8. References: 10.3, 11.1, 20.10, 23.9, etc.

## 9.2. MORTAR BAR EXPANSION TESTS

### 1. The ASTM "Performance Test for the Potential Sulphate Resistance of Portland Cement".

1.1. This has been fully discussed in section 4.3-3. In it, excess calcium sulphate is incorporated in the specimens, and their expansions are measured at various ages. The ASTM Working Committee on Sulphate Resistance checked test results against the actual

performance/....................

performance of cements, and concluded that the expansion of specimens during their first 28 days gave a good indication of the potential sulphate resisting properties of the cement used. Expansions at 84 and 365 days were also reported.

1.2. This test was used to check the potential resistance of the various batches of S.R.Cement produced. Some of the calcined shales produced were combined with S.R.cements and tested by this method, as a check on the sulphate resistance of the shale !

1.3. Instead of discarding the specimens they have been kept, and are still measured periodically. Some tests have now been on the go for nearly three years, and interesting results are emerging.

1.4. In the following tables some of the sets of results have been used twice - this has been done in order to facilitate the comparisons of different types of cements with one another. The same applies to the graphs. In all graphs age has been plotted on a logarithmic scale.

1.5. Table No.50 gives some of the results reported by the ASTM S.R.Test Working Committee, and they are represented graphically by Figure No.14. The influence of potential $C_3A$ content of the cement is most marked.

Table No.50/............

## TABLE NO. 50

TESTING METHOD : MORTAR BAR EXPANSION

TESTING MEDIUM : Calcium Sulphate ($CaSO_4$ added to cement to increase $SO_3$ to 7%)

CURING MEDIUM : Water.

NOTE: : The test results given below were extracted from the A.S.T.M. Bulletin for February 1956. They were amongst results reported by the A.S.T.M. Working Committee, on Sulphate - Resistance, for American Cements of various types.

| Type of Cement | $C_3A$ % | Percentage Expansion At: | | | | | |
|---|---|---|---|---|---|---|---|
| | | 7 days | 14 days | 21 days | 28 days | 84 days | 1 year |
| Type I = Ordinary Portland Cement. | | | | | | | |
| No.14="best" | 7.1 | 0.03 | 0.04 | 0.05 | 0.055 | 0.09 | 0.17 |
| No.18= worst | 12.2 | 0.085 | 0.135 | 0.18 | 0.225 | 0.74 | discarded |
| Type II = Moderately Sulphate Resisting. | | | | | | | |
| No.21="typical" | 5.1 | 0.03 | 0.04 | 0.045 | 0.05 | 0.08 | 0.145 |
| Type III = Rapid Hardening, i.e. Finely Ground | | | | | | | |
| No.33="typical" | 9.2 | 0.04 | 0.06 | 0.075 | 0.09 | 0.24 | 0.25 |
| No.3L=Special$^{x}$ | nil$^{x}$ | 0.01 | 0.01 | 0.01 | 0.015 | 0.02 | 0.03 |
| Type V = Sulphate Resisting. | | | | | | | |
| No.5P=best | 1.4 | 0.015 | 0.02 | 0.02 | 0.025 | 0.035 | 0.05 |
| No.5M="worst" | 1.7 | 0.03 | 0.04 | 0.045 | 0.05 | 0.065 | 0.09 |

---

x The cement contained 3.6% $CF_2$

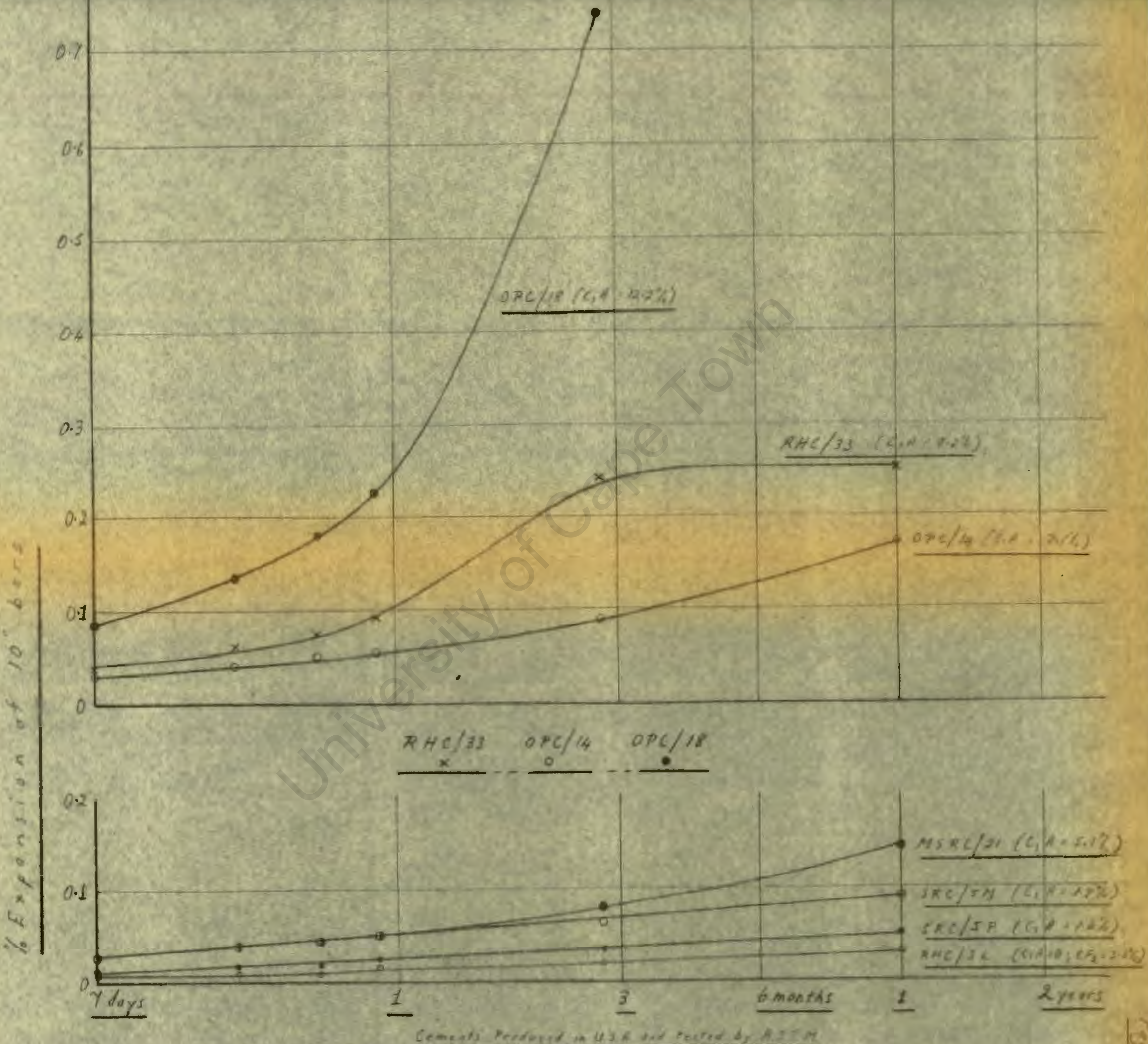

0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
OPC/18 (C3A = 12.7%)
RHC/33 (C3A = 7.2%)
OPC/14 (C3A = 2.1%)
RHC/33 ×
OPC/14 ○
OPC/18 ●
0·2
0·1
0
MSRC/31 (C3A = 5.1%)
SRC/5M (C3A = 1.7%)
SRC/5P (C3A = 1.6%)
RHC/3L (C3A 10; CF2 = 3.1%)
% Expansion of 10" bars
7 days
1
3
6 months
1
2 years
Cements Produced in U.S.A. and Tested by A.S.T.M.
RHC (CF2)/3L
SRC/5P
SRC/5M
MSRC/31
CaSO4

Fig. No. 14

1.6. In Table No.51 the expansions of:

2 "local" Portland Cements,
2 "local" S.R.cements,
1 imported S.R.cement and
1 imported Marine cement

are given, and these are illustrated graphically by Figures 15 and 16. Once again the influence of potential $C_3A$ is most marked. It is interesting to see how the expansions have "levelled out" at the later ages, particularly in the case of the high $C_3A$ cements. The Americans seem to have missed this phenomonem by not continuing their tests long enough - at any rate they have not reported it. It might be that this could lead to a method for determing the "effective $C_3A$" content of a cement, and it would be pleasing to compare a series of such tests with X-ray analyses of the cements in the series.

It is noteworthy that the "local" S.R.cements compare favourably with the imported variety, and also with the ASTM-tested American S.R.cements.

1.7. In Tables 52 and 53 and Figures 17 and 18 the following cements are reported on and illustrated:

| FIG NO. | TABLE NO. | CEMENT | REMARKS |
|---|---|---|---|
| 17 | 52 | SRC/2/OG | $C_3A$ = 5 %, cement was "coarse" ground |
| 17 | 52 | SRC/2/FG | $C_3A$ = 5%, cement was " fine" ground |
| 18A | 52 | SRC/1 | $C_3A$ = 1.6% This cement was interground with the pozzolans listed below. |
| 18A | 52 | SRC/1/BA. | Local pulverised fuel ash. |
| 18A | 53 | SRC/1/US | Shale calcined at 900°C for 6 hrs. |
| 18B | 53 | SRC/1/C | Calcined in Lab.kiln at 950°C ("undercooked") |
| 18B | 53 | SRC/1/Y | Calcined in plant kiln - mixture of powder and fused lumps("overcooked") |
| 18C | 53 | SRC/1/E | Calcined in lab.kiln,1125°C. 25%coal intermixed before calcination. |
| 18C | 53 | SRC/1/G | Calcined in lab.kiln,1125°C. 25%coal used in burning the shale. |

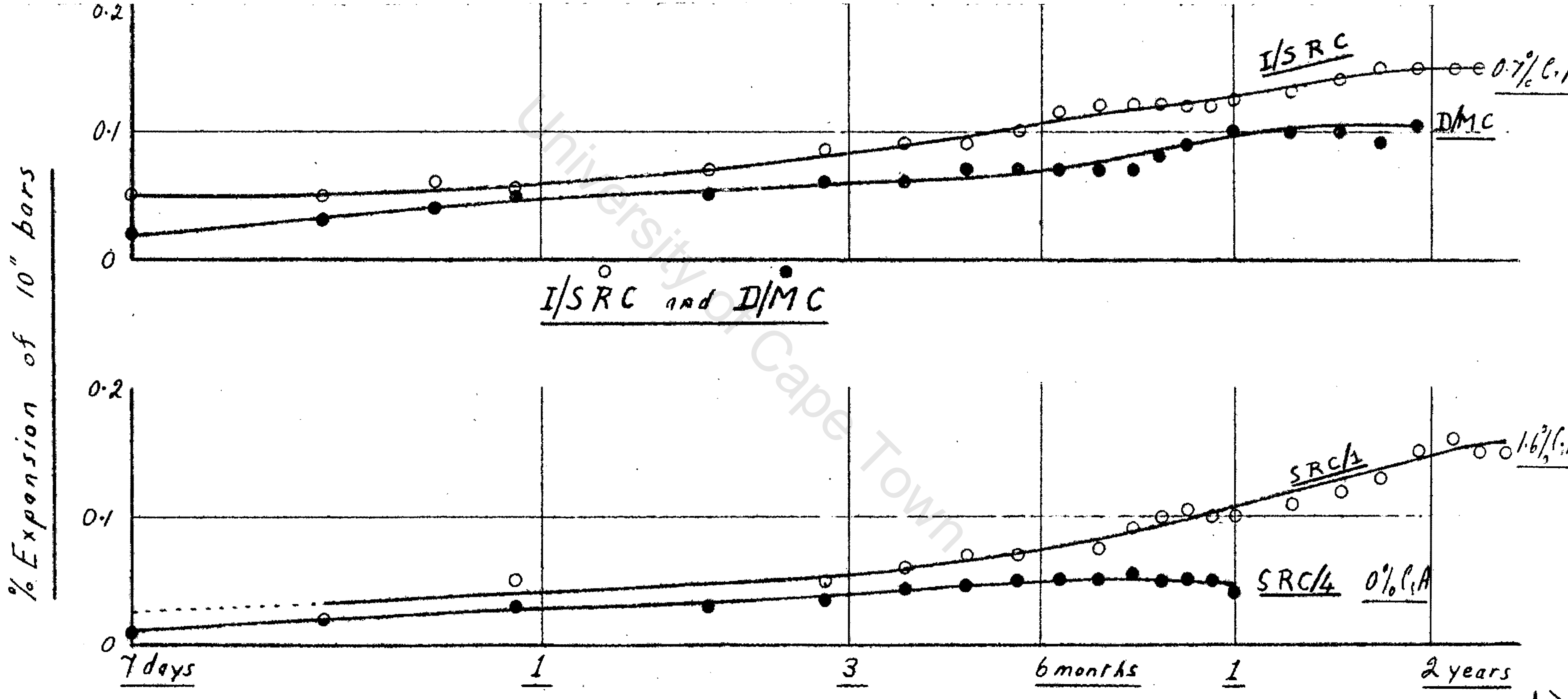
# TABLE NO. 51

TEST METHOD : MORTAR BAR EXPANSION

TESTING MEDIUM : Calcium Sulphate
($CaSO_4$ added to cement to increase $SO_3$ to 7%)

CURING MEDIUM : Water

| AGE IN DAYS | Percentage Expansion For: | | | | | |
|---|---|---|---|---|---|---|
| | OPC/1 | OPC/2 | SRC/1 | SRC/4 | I/SRC | D/MC |
| 7 | n.a. | 0.075 | n.a. | 0.01 | 0.05 | 0.02 |
| 14 | 0.13 | 0.10 | 0.02 | 0.02 | 0.05 | 0.03 |
| 21 | 0.18 | 0.11 | n.a. | n.a. | 0.06 | 0.04 |
| 28 | 0.235 | 0.14 | 0.05 | 0.03 | 0.055 | 0.05 |
| 56 | 0.34 | 0.185 | n.a. | 0.03 | 0.07 | 0.05 |
| 84 | 0.495 | n.a. | 0.05 | 0.035 | 0.085 | 0.06 |
| 112 | 0.83 | 0.26 | 0.06 | 0.045 | 0.09 | 0.06 |
| 140 | 0.95 | n.a. | 0.07 | 0.045 | 0.09 | 0.07 |
| 168 | n.a. | 0.35 | 0.07 | 0.05 | 0.10 | 0.07 |
| 196 | 0.945 | 0.35 | n.a. | 0.05 | 0.115 | 0.07 |
| 224 | 0.945 | 0.41 | 0.075 | 0.05 | 0.12 | 0.07 |
| 252 | 0.95 | 0.43 | 0.09 | 0.055 | 0.12 | 0.07 |
| 280 | 0.955 | 0.44 | 0.10 | 0.05 | 0.12 | 0.08 |
| 308 | 0.95 | 0.435 | 0.105 | 0.05 | 0.12 | 0.09 |
| 336 | 0.955 | 0.44 | 0.10 | 0.05 | 0.12 | n.a. |
| 364 | 0.955 | 0.44 | 0.10 | 0.04 | 0.125 | 0.10 |
| 448 | 0.95 | 0.44 | 0.11 | n.a. | 0.13 | 0.10 |
| 532 | 0.94 | 0.43 | 0.12 | n.a. | 0.14 | 0.10 |
| 616 | 0.95 | 0.44 | 0.13 | n.a. | 0.15 | 0.09 |
| 700 | 0.95 | 0.445 | 0.15 | n.a. | 0.15 | 0.105 |
| 784 | 0.95 | 0.44 | 0.16 | n.a. | 0.15 | n.a. |
| 868 | 0.94 | 0.435 | 0.15 | n.a. | 0.15 | n.a. |
| 952 | 0.94 | 0.44 | 0.15 | n.a. | n.a. | n.a. |
| Number of Test Pieces | 2(4) | 2(4) | 2(4) | 4 | 2(3) | 4 |

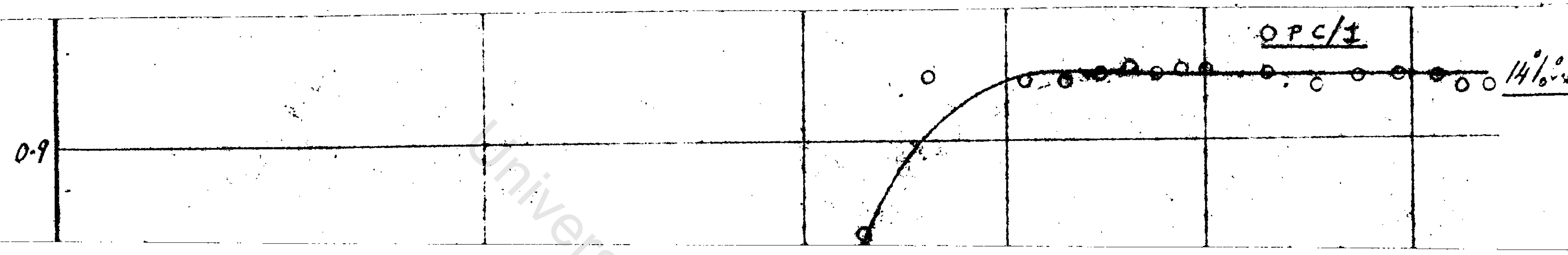


I/SRC and D/MC

Fig. No. 15

SRC/1 and SRC/4

$CaSO_4$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○ PC/1
14‰

## TABLE NO. 52

TEST METHOD : MORTAR BAR EXPANSION

TESTING MEDIUM : Calcium Sulphate
($CaSO_4$ added to cement to increase $SO_3$ to 7%)

CURING MEDIUM : Water

| AGE IN DAYS | Percentage Expansion For: | | | | |
|---|---|---|---|---|---|
| | SRC/1 | SRC/1/BA | SRC/2/OG | SRC/2/FG | SRC/4 |
| 7 | n.a. | 0.025 | 0.00 | 0.02 | 0.01 |
| 14 | 0.02 | 0.04 | 0.01 | 0.02 | 0.02 |
| 21 | n.a. | 0.05 | 0.015 | 0.025 | n.a. |
| 28 | 0.05 | 0.06 | 0.02 | 0.03 | 0.03 |
| 56 | n.a. | 0.06 | 0.04 | 0.04 | 0.03 |
| 84 | 0.05 | 0.06 | 0.06 | 0.05 | 0.035 |
| 112 | 0.06 | 0.08 | 0.07 | 0.06 | 0.045 |
| 140 | 0.07 | 0.09 | 0.08 | 0.06 | 0.045 |
| 168 | 0.07 | 0.09 | 0.10 | 0.07 | 0.05 |
| 196 | n.a. | n.a. | 0.11 | n.a. | 0.05 |
| 224 | 0.075 | 0.10 | 0.13 | 0.09 | 0.05 |
| 252 | 0.09 | 0.10 | 0.14 | 0.10 | 0.055 |
| 280 | 0.10 | 0.105 | 0.15 | 0.12 | 0.05 |
| 308 | 0.105 | 0.10 | 0.16 | 0.13 | 0.05 |
| 336 | 0.10 | 0.105 | 0.17 | 0.14 | 0.05 |
| 364 | 0.10 | 0.10 | 0.18 | 0.145 | 0.04 |
| 448 | 0.11 | n.a. | 0.195 | 0.17 | n.a. |
| 532 | 0.12 | 0.11 | 0.26 | 0.21 | n.a. |
| 616 | 0.13 | 0.115 | n.a. | n.a. | n.a. |
| 700 | 0.15 | 0.105 | n.a. | n.a. | n.a. |
| 784 | 0.16 | 0.11 | n.a. | n.a. | n.a. |
| 868 | 0.15 | n.a. | n.a. | n.a. | n.a. |
| 952 | 0.15 | n.a. | n.a. | n.a. | n.a. |
| Number of Test Pieces | 2(4) | 4 | 4 | 4(8) | 4 |

## TABLE NO. 53

TEST METHOD : MORTAR BAR EXPANSION

TESTING MEDIUM : Calcium Sulphate
(CaSO$_4$ added to Cement to increase SO$_3$ to 7% )

CURING MEDIUM : Water

| AGE IN DAYS | Percentage Expansion For: | | | | |
|---|---|---|---|---|---|
| | SRC/1/US | SRC/1/C | SRC/1/E | SRC/1/G | SRC/1/Y |
| 7 | 0.03 | 0.045 | 0.025 | 0.035 | 0.02 |
| 14 | 0.05 | 0.055 | 0.03 | 0.045 | 0.05 |
| 21 | 0.07 | 0.06 | 0.04 | 0.04 | 0.05 |
| 28 | 0.07 | 0.07 | 0.035 | 0.05 | 0.065 |
| 56 | 0.08 | 0.08 | 0.04 | 0.06 | 0.08 |
| 84 | 0.09 | 0.09 | 0.05 | 0.055 | 0.095 |
| 112 | 0.12 | 0.10 | 0.05 | 0.06 | 0.11 |
| 140 | 0.12 | 0.10 | 0.05 | 0.06 | 0.11 |
| 168 | 0.13 | 0.105 | 0.05 | 0.055 | 0.13 |
| 196 | 0.14 | 0.115 | 0.05 | 0.06 | 0.14 |
| 224 | 0.15 | 0.115 | 0.045 | 0.055 | 0.15 |
| 252 | 0.15 | 0.13 | 0.05 | 0.05 | 0.16 |
| 280 | 0.16 | 0.13 | 0.05 | 0.06 | 0.16 |
| 308 | 0.18 | 0.13 | 0.05 | 0.05 | 0.17 |
| 336 | 0.19 | n.a. | 0.045 | n.a. | n.a. |
| 364 | 0.20 | 0.14 | 0.045 | 0.045 | 0.18 |
| 448 | 0.24 | 0.18 | 0.04 | 0.05 | 0.17 |
| 532 | 0.26 | 0.18 | 0.045 | 0.06 | 0.18 |
| 616 | 0.28 | 0.17 | n.a. | 0.045 | 0.17 |
| 700 | 0.28 | 0.16 | 0.04 | 0.05 | 0.17 |
| 784 | 0.29 | n.a. | n.a. | n.a. | n.a. |
| 868 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 952 | n.a. | n.a. | n.a. | n.a. | n.a. |
| Number of Test Pieces | 4(6) | 2(4) | 2(4) | 2(4) | 2(4) |

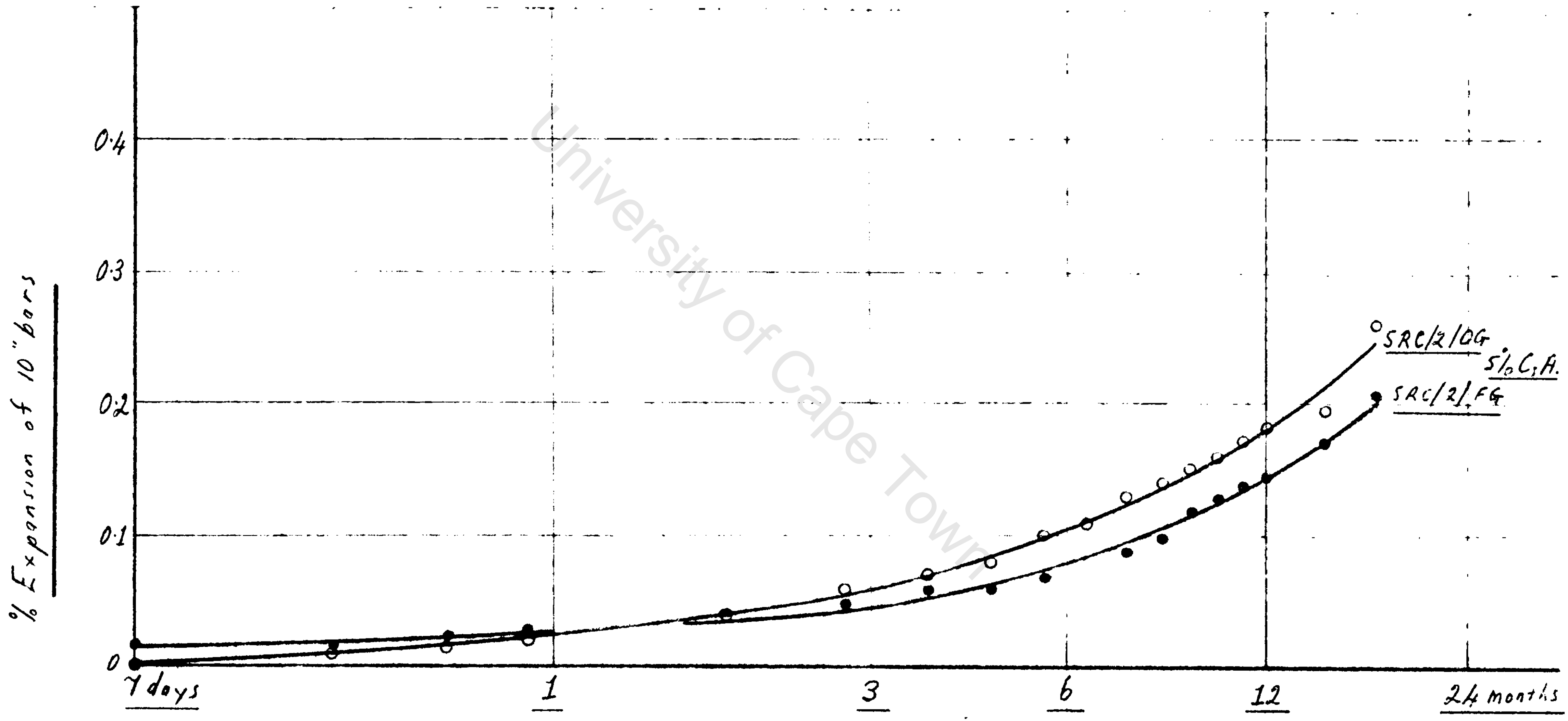


Fig No. 17

○ SRC/2/OG and ● SRC/2/FG

$CaSO_4$

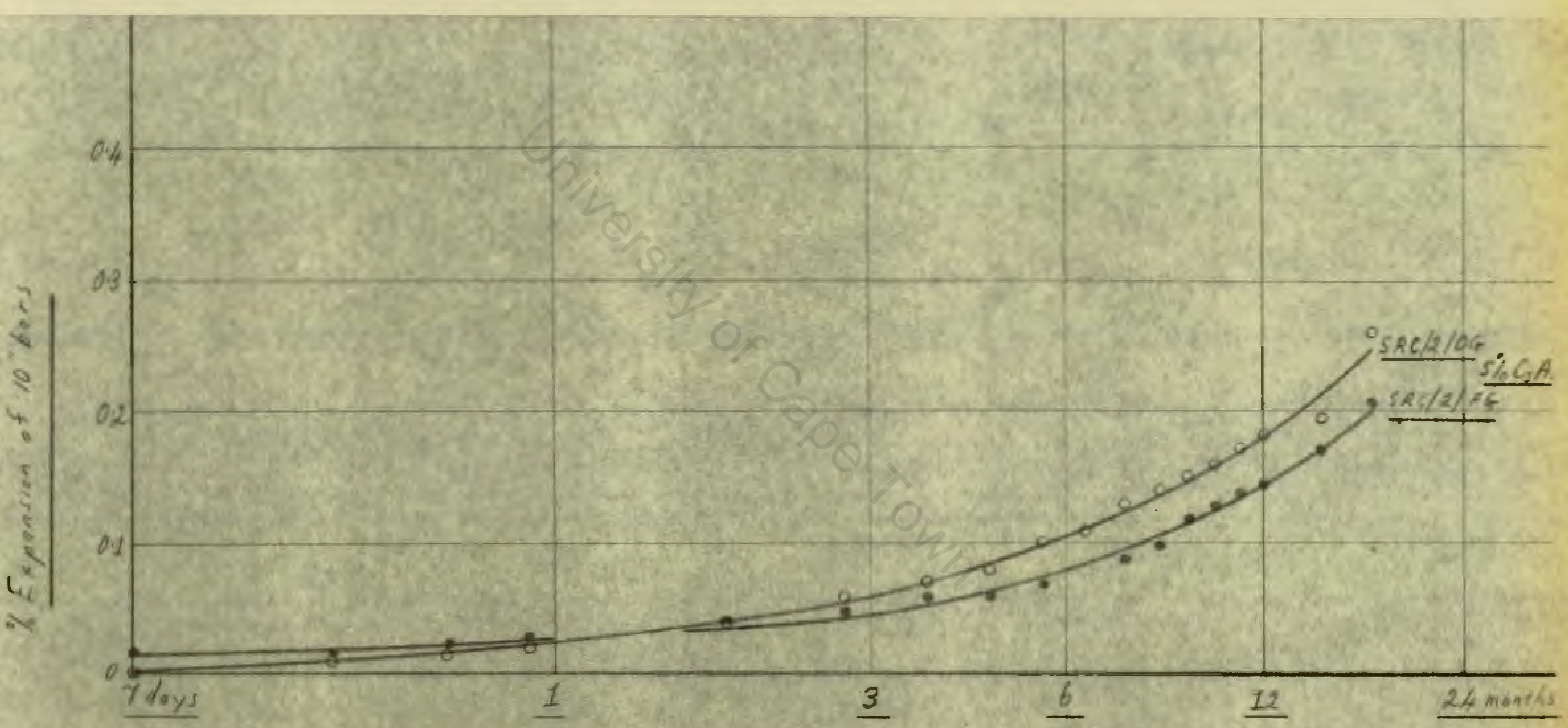


Fig No 17    ○ SRC/2/OG and ● SRC/2/FG    $CaSO_4$

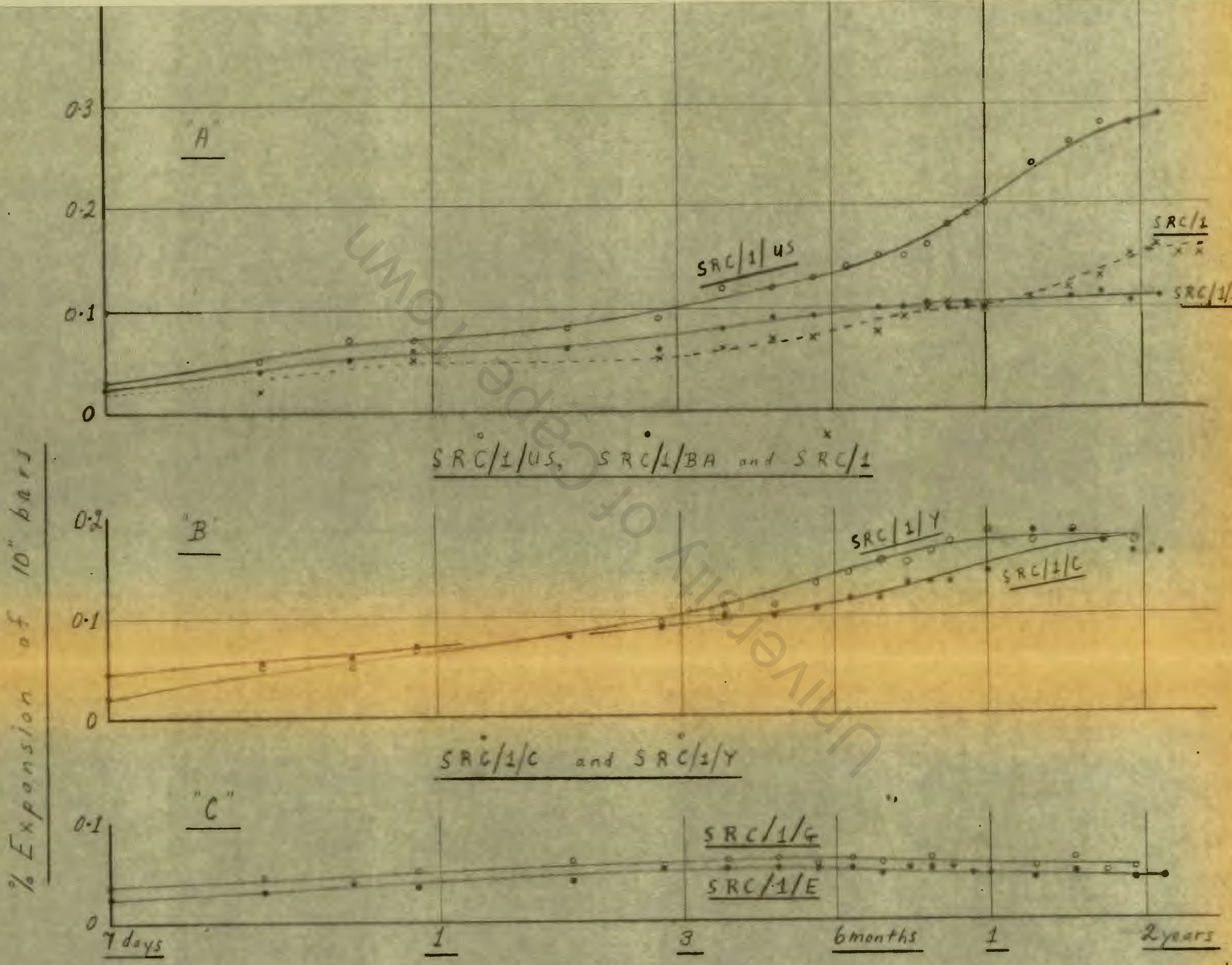


Fig. No. 18 SRC/1/E and SRC/1/G CaSO$_4$

Figure 17

(1) Confirms that with 5% $C_3A$ (the maximum permitted by the ASTM Type V specification), a cement has less resistance to sulphates than a cement with under 2% $C_3A$. Both the American and the "local" S.R.cements with zero $C_3A$ had the best resistance - Figures 14 & 15.

(2) Illustrates the "dual forces" at work in this type of test. The strength of the cement tends to prevent expansion, whereas the sulphate reaction tends to cause expansion. The more finely ground cement had the greater strength (up to 6 - 12 months), but was more susceptible to attack on account of its fineness, and therefore it had the higher expansion to start with, but later on the higher strength dominated and the coarse-ground weaker cement expanded more.

Figure 18A

(1) The U.S.shale sample was calcined at only 900°C, but its 6 hour treatment gave it both chemical and physical activities equal to those of shales calcined at 1100 - 1150°C. Its resistance to sulphates, however, was not as good.

(2) Up to 1 year the fuel ash seemed to detract from the cement's sulphate resistance, but by 2 years it had improved it.

Figure 18B

Shale Y was over calcined and shale C was under calcined- both detract slightly from the S.R. cement's sulphate resistance.

Figure 18C/..................

Figure 18C

Shales E & G were both calcined at 1100 - 1150°C, with the addition of coal. Both had good physical and chemical activity indices, and both improved the sulphate resistance of cement SRC/1.

## 2. EXPANSIONS WITH $Na_2SO_4$

2.1. To check on the resistance of cements to Sodium-sulphate, as compared with their resistance to Calcium-sulphate, I had some bars made up with an 8½% solution of $Na_2SO_4$ (i.e. one containing approx. 85,000 ppm of $Na_2SO_4$). This was equivalent to increasing the $SO_3$ content of the cement by 2½%, whereas the ASTM $CaSO_4$ method increases the $SO_3$ by about 5%. The bars were also cured in 8½% $Na_2SO_4$ solution.

2.2. Note that this solution is on the "strong" side - few ground waters are so concentrated, and concrete would normally not be made up with such a water. However, there are places in South West Africa where water with a T.D.S. as high as 60,000 ppm is the only water available - and over half of the TDS consists of sulphate salts. The test cannot, therefore, be considered entirely impractical, but I did, afterwards, have tests done with weaker sulphate solutions as well.

2.3. Test results on SRC/1/US and SRC/4 for both $CaSO_4$ and $Na_2SO_4$, and on OPC/3 ($C_3A$ = 14%) with $Na_2SO_4$ only, are reported in Table No.54 and illustrated by Figures 19 and 20

Table No.54/..............

## TABLE NO. 54

TEST METHOD : MORTAR BAR EXPANSION

TESTING MEDIA : (a) Calcium Sulphate. ($CaSO_4$ added to cement to increase $SO_3$ to 7%)

(b) Sodium Sulphate (equivalent to increasing $SO_3$ in cement by 2½% )

CURING MEDIA : (a) Water

(b) Soln.of 180-200g $Na_2SO_4.10\,H_2O$ per 1,000 ml.

| AGE IN DAYS | Percentage Expansion For: | | | | |
|---|---|---|---|---|---|
| | SRC/1/US | | SRC/4 | | OPC/3 |
| | a | b | a | b | b |
| 7 | 0.03 | 0.04 | 0.01 | 0.02 | 0.04 |
| 14 | 0.05 | 0.055 | 0.02 | 0.03 | 0.06 |
| 21 | 0.07 | 0.06 | n.a. | n.a. | 0.085 |
| 28 | 0.07 | 0.07 | 0.03 | n.a. | 0.11 |
| 56 | 0.08 | 0.08 | 0.03 | 0.05 | 0.21 |
| 84 | 0.09 | 0.09 | 0.035 | 0.06 | 0.31 |
| 112 | 0.12 | 0.12 | 0.045 | 0.09 | 0.42 |
| 140 | 0.12 | 0.14 | 0.045 | 0.105 | 0.495 |
| 168 | 0.13 | 0.16 | 0.05 | 0.13 | 0.55 |
| 196 | 0.14 | 0.17 | 0.05 | 0.15 | 0.60 |
| 224 | 0.15 | 0.18 | 0.05 | 0.16 | 0.65 |
| 252 | 0.15 | 0.18 | 0.055 | 0.17 | 0.69 |
| 280 | 0.16 | 0.195 | 0.05 | 0.175 | 0.73 |
| 308 | 0.18 | 0.20 | 0.05 | 0.18 | 0.77 |
| 336 | 0.19 | 0.205 | 0.05 | 0.20 | 0.81 |
| 364 | 0.20 | n.a. | 0.04 | 0.22 | 0.83 |
| 448 | 0.24 | 0.24 | n.a. | n.a. | 0.93 |
| 532 | 0.26 | 0.27 | n.a. | n.a. | 0.99 |
| 616 | 0.28 | 0.275 | n.a. | n.a. | 1.04 |
| 700 | 0.28 | 0.29 | n.a. | n.a. | 1.10 |
| 784 | 0.29 | n.a. | n.a. | n.a. | n.a. |
| Number of Test Pieces | 4(6) | 4(6) | 4 | 4 | 4 |

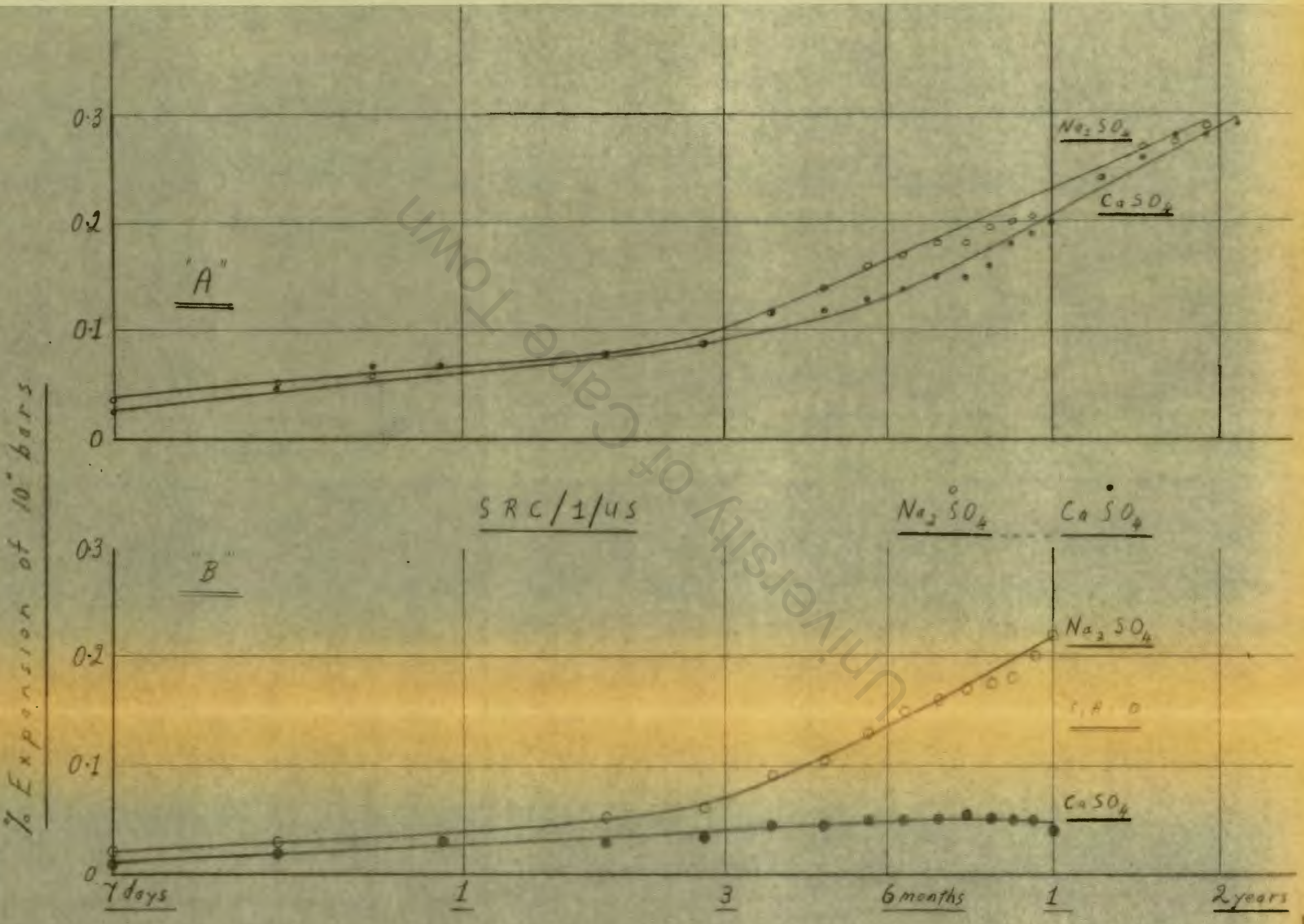


Fig. No. 19 SRC/4 ○ $Na_2SO_4$ ● $CaSO_4$

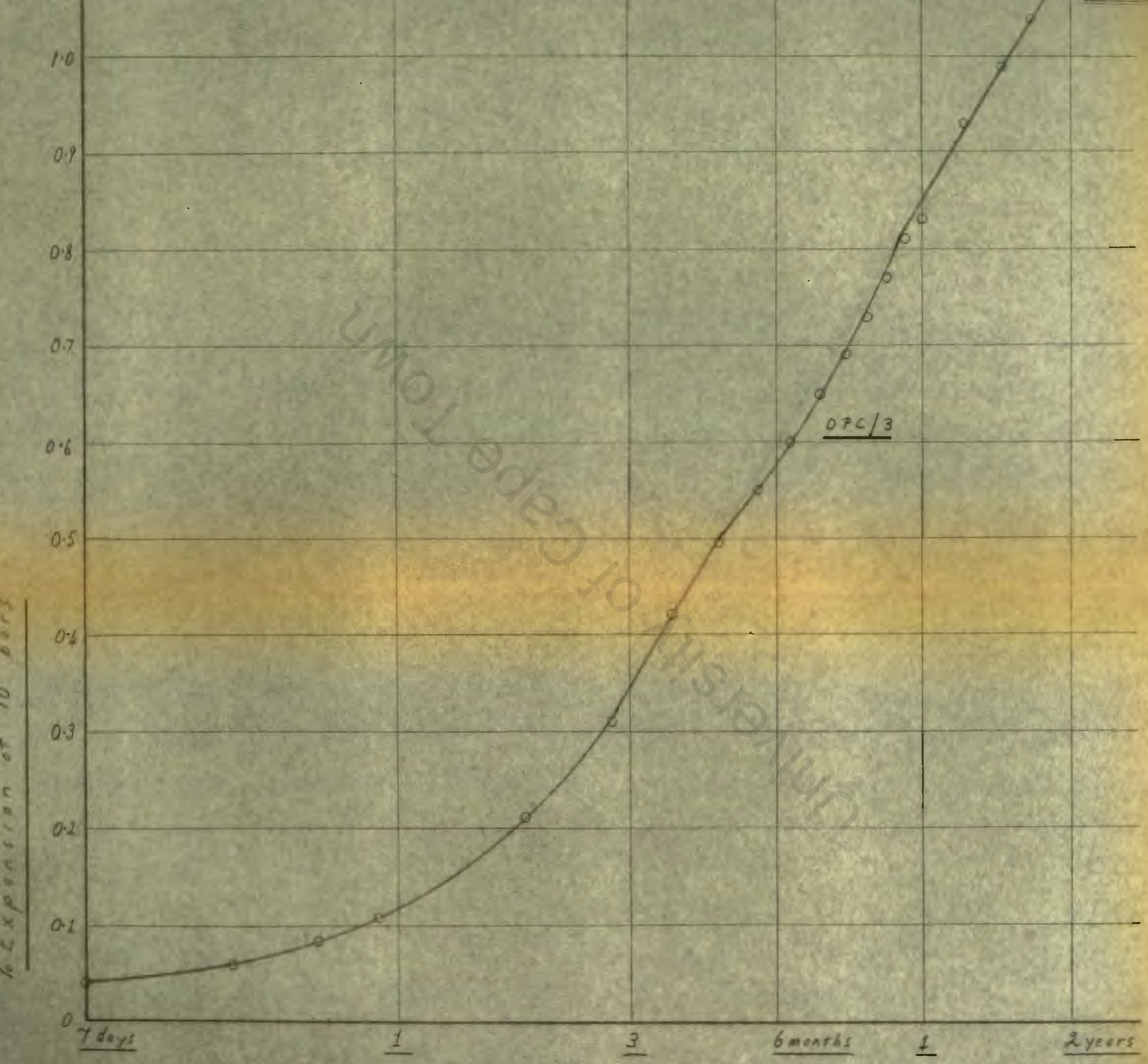


Fig No. 20 OPC/3 $Na_2SO_4$

2.4. Figure 20

Compared with the action of $CaSO_4$ on a similar cement (Figure 16), the $Na_2SO_4$ is a bit slower to react. The $Na_2SO_4$ specimens had the same length after about 18 months as the $CaSO_4$ specimens had after 6 months but the $Na_2SO_4$ specimens are continuing to expand and have not reached a maximum after 2 years exposure.

2.5. Figure 19A

The two chemicals have had the same effect on cement SRC/1/US (see section 1.7 above) up to 2 years exposure.

2.6. Figure 19B

Cement SRC/4 (with zero $C_3A$) is by no means entirely insensitive to $Na_2SO_4$, although there is no doubt that it is much less susceptible than cement OPC/3 (with 14% $C_3A$ ) - see Figure 20

2.7. Some further tests were carried out with this $Na_2SO_4$ method, on the following cements:

| CEMENT | REMARKS |
|---|---|
| OPC/4 | Contains about 13% $C_3A$ |
| SRC/3 | Contains about 3½% $C_3A$ |
| SRC/3/CS | i.e. CM-2 |
| OPC/2/BA | A cement with 9% $C_3A$ interground with pulverised fuel ash. |
| SRC/4/CS | i.e. CM-3, or "Marine Cement" |

2.8. Results are reported in Table No.55 and illustrated by Figure No.21

2.9 Figure 21A/.............

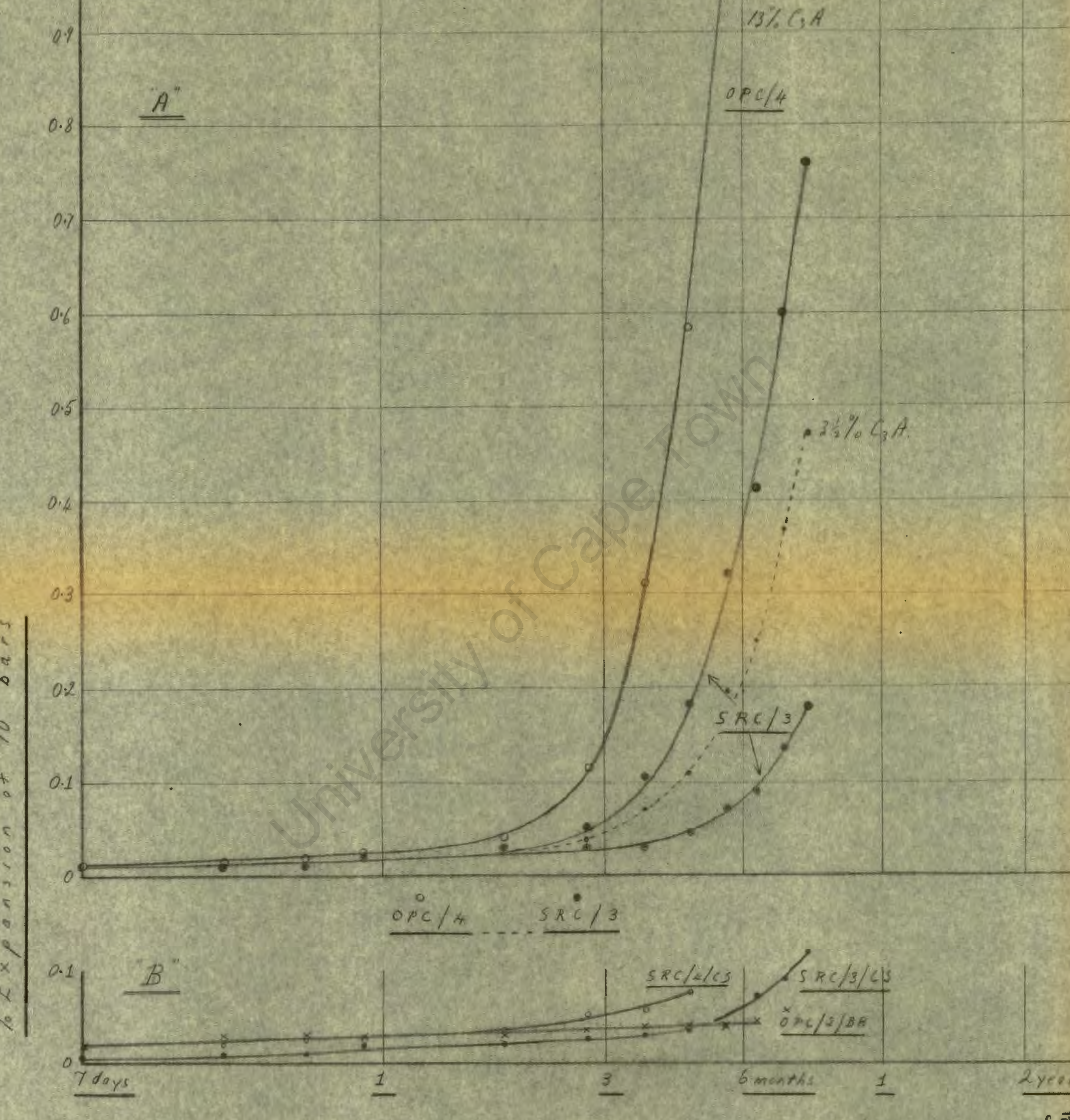

"A"
13% C₃A
OPC/4
3½% C₃A
SRC/3
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
○ OPC/4
● SRC/3
"B"
SRC/4/CS
SRC/3/CS
OPC/2/BA
0.1
0
7 days
1
3
6 months
1
2 year
% Expansion at 10 Days

Fig. No. 21

• SRC/3/CS
× OPC/2/BA
○ SRC/4/CS
Na₂SO₄

2.9. Figure 21A

(1) OPC/4 took even longer to "get going" than OPC/3 (Fig.20), and even looked "resistant" up to 2 months, but was worse than OPC/3 before 6 months were up.

(2) SRC/3 has presented a "puzzle". Four specimens (10" bars) were made up at the same time and under the same conditions. Up to 3 months they were all expanding at about the same rate, and then two of them started to expand more rapidly. The reason for this is still being sought and it is my intention to have one of each pair of bars analysed after 12 months to see if they really are the same.

2.10. Figure 21B

Calcined shale improved both S.R.cements, and fuel ash "did wonders" for OPC.

## 3. EXPANSIONS WITH $MgSO_4$

3.1. In another set of tests the same technique **was used** with Magnesium-sulphate, i.e. the specimens were made up with a solution which would increase the $SO_3$ content of the cement by about 2½%, and cured in the same solution - 7½% $MgSO_4$, or 75,000 ppm. This is also on the "strong" side.

3.2. The same cements as described in para.2.7 above were used, and the results are reported in Table No.56 and illustrated by Figure No.22.

3.3. OPC/4 again shows the least resistance, and calcined shale again appears to help the S.R.cements. This time, however, the fuel ash appears to have done little or nothing for OPC/2.

Table No.56/.................

## TABLE NO. 56

TEST METHOD : MORTAR BAR EXPANSION

TESTING MEDIUM : Magnesium Sulphate (equivalent to increasing $SO_3$ in cement by $2\frac{1}{2}$% )

CURING MEDIUM : Solution of 155 gm $MgSO_4 . 7 H_2O$ per litre (= ± 6,000 p.p. 100,000 of $SO_4''$ and 1,500 p.p. 100,000 of $Mg^{\cdot\cdot}$ )

| AGE IN DAYS | Percentage Expansion For: | | | | |
|---|---|---|---|---|---|
| | OPC/4 | SRC/3 | SRC/3/CS | OPC/2/BA | SRC/4/CS |
| 7 | 0.06 | 0.03 | 0.02 | 0.06 | 0.03 |
| 14 | 0.07 | 0.045 | 0.02 | 0.075 | 0.035 |
| 21 | 0.075 | 0.045 | 0.025 | 0.085 | 0.035 |
| 28 | 0.08 | 0.06 | 0.03 | 0.09 | 0.04 |
| 56 | 0.105 | 0.075 | 0.045 | 0.11 | 0.05 |
| 84 | 0.13 | 0.09 | 0.05 | 0.125 | 0.06 |
| 112 | 0.18 | 0.10 | 0.06 | 0.14 | 0.08 |
| 140 | 0.275 | 0.125 | 0.055 | 0.16 | n.a. |
| 168 | 0.38 | 0.15 | 0.07 | 0.20 | n.a. |
| 196 | 0.51 | 0.19 | 0.08 | 0.26 | n.a. |
| 224 | 0.63 | 0.24 | 0.10 | 0.34 | n.a. |
| 252 | 0.74 | 0.305 | 0.12 | 0.42 | n.a. |
| 280 | n.a. | n.a. | 0.16 | 0.48 | n.a. |
| 308 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 336 | n.a. | n.a. | n.a. | n.a. | n.a. |
| 364 | n.a. | n.a. | n.a. | n.a. | n.a. |
| Number of Test Pieces | 8 | 4 | 4 | 4 | 4 |

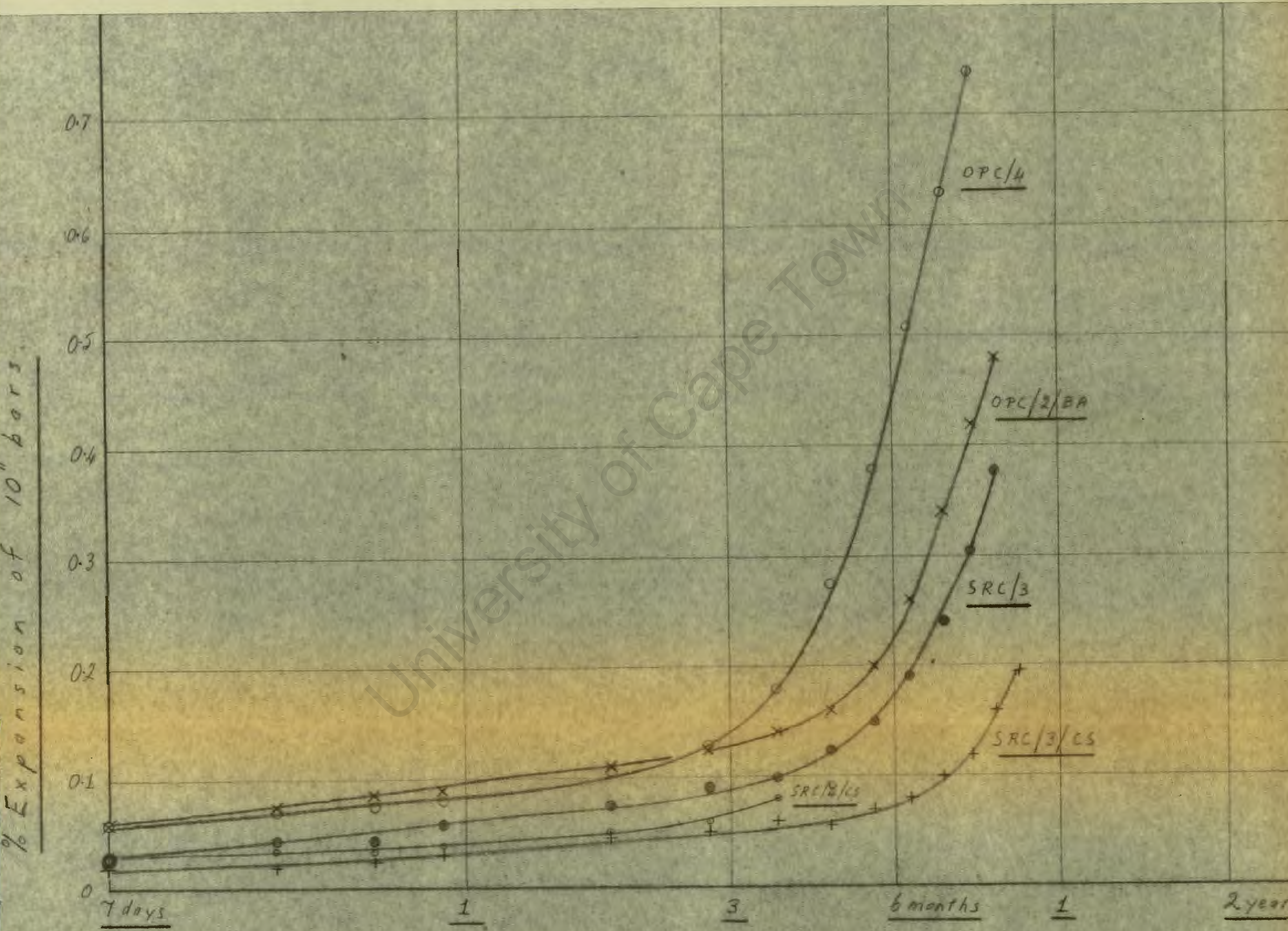

% Expansion of 10" bars.
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
7 days
1
3
6 months
1
2 years
OPC/4
OPC/2/BA
SRC/3
SRC/3/CS
SRC/4/CS
○ OPC/4
● SRC/3
+ SRC/3/CS
× OPC/2/BA
∘ SRC/4/CS
MgSO₄

Fig. No. 22

## 4. EXPANSIONS WITH "STRONG" $Na_2SO_4$ + $MgSO_4$

4.1. In a third set of tests the same cements were tested for resistance to a mixture of the two salts. Owing to a change in staff and a misunderstanding three cement were done in solutions containing the same concentration of each salt as before, which meant an additional 5% $SO_3$ in the cement (the same as in the $CaSO_4$ test), and two cements were done in solutions with the combined salts adding 2½% $SO_3$ to the cement - as in the two previous sets of tests.

4.2. The test results are reported in Table No.57 and illustrated by Figure No.23.

4.3. At the "5% $SO_3$ Level"

Cement OPC/4 has undergone "terrific" expansion, and SRC/3 is "not far behind" - in fact it looks like "over taking". Calcined shale has helped cement SRC/3 considerably. This solution definitely falls in the "abnormal" class, and not too much attention can be paid to the results.

4.4. At the "2½% $SO_3$ level"

The SRC/4/CS cement (CM-3) has been satisfactory up to 4 months, but the OPC/fuel ash mixture had even less resistance than to $MgSO_4$ only.

Table No.57/..............

# TABLE NO. 57

TEST METHOD : MORTAR BAR EXPANSION

TESTING MEDIUM : Sodium plus Magnesium Sulphate (Equivalent to increasing $SO_3$ in cement by 5% (A) or 2½% (B)

CURING MEDIUM : A : Solution of 200g $Na_2SO_4.10\,H_2O$ + 155g $MgSO_4.\,7\,H_2O$ per litre x

B : Solution of 100g $Na_2SO_4.10\,H_2O$ + 80g $MgSO_4.7\,H_2O$ per litre. xx

| AGE IN DAYS | Percentage Expansion For:- | | | | |
|---|---|---|---|---|---|
| | A<br>OPC/4 | A<br>SRC/3 | A<br>SRC/3/CS | B<br>OPC/2/BA | B<br>SRC/4/CS |
| 7 | 0.26 | 0.04 | n.a. | 0.16 | 0.01 |
| 14 | 0.51 | 0.18 | 0.04 | 0.18 | 0.01 |
| 21 | 0.59 | 0.19 | 0.04 | 0.21 | 0.015 |
| 28 | 0.66 | 0.24 | 0.03 | 0.26 | 0.015 |
| 56 | 0.785 | 0.41 | 0.04 | 0.31 | 0.035 |
| 84 | 0.89 | 0.56 | 0.045 | 0.35 | n.a. |
| 112 | 0.98 | 0.77 | 0.065 | 0.37 | 0.04 |
| 140 | 1.07 | 0.88 | 0.095 | 0.40 | n.a. |
| 168 | 1.13 | 1.01 | 0.11 | 0.43 | n.a. |
| 196 | 1.19 | 1.12 | 0.19 | 0.48 | n.a. |
| 224 | 1.24 | 1.21 | 0.24 | 0.51 | n.a. |
| 252 | 1.30 | 1.27 | 0.28 | 0.58 | n.a. |
| 280 | n.a. | 1.35 | 0.33 | n.a. | n.a. |
| 308 | n.a. | 1.42 | 0.37 | n.a. | n.a. |
| 336 | n.a. | 1.51 | 0.42 | n.a. | n.a. |
| 364 | n.a. | n.a. | 0.51 | n.a. | n.a. |
| Number of Test Pieces | 3 | 3 | 4 | 4 | 4 |

x A = ± 12,000 p.p. 100,000 of $SO_4''$; + 2,800 $Na^{\cdot}$ & 1,500 $Mg^{\cdot\cdot}$

XX B = ± 6,000 p.p. 100,000 of $SO_4''$; + 1,400 $Na^{\cdot}$ & 750 $Mg^{\cdot\cdot}$

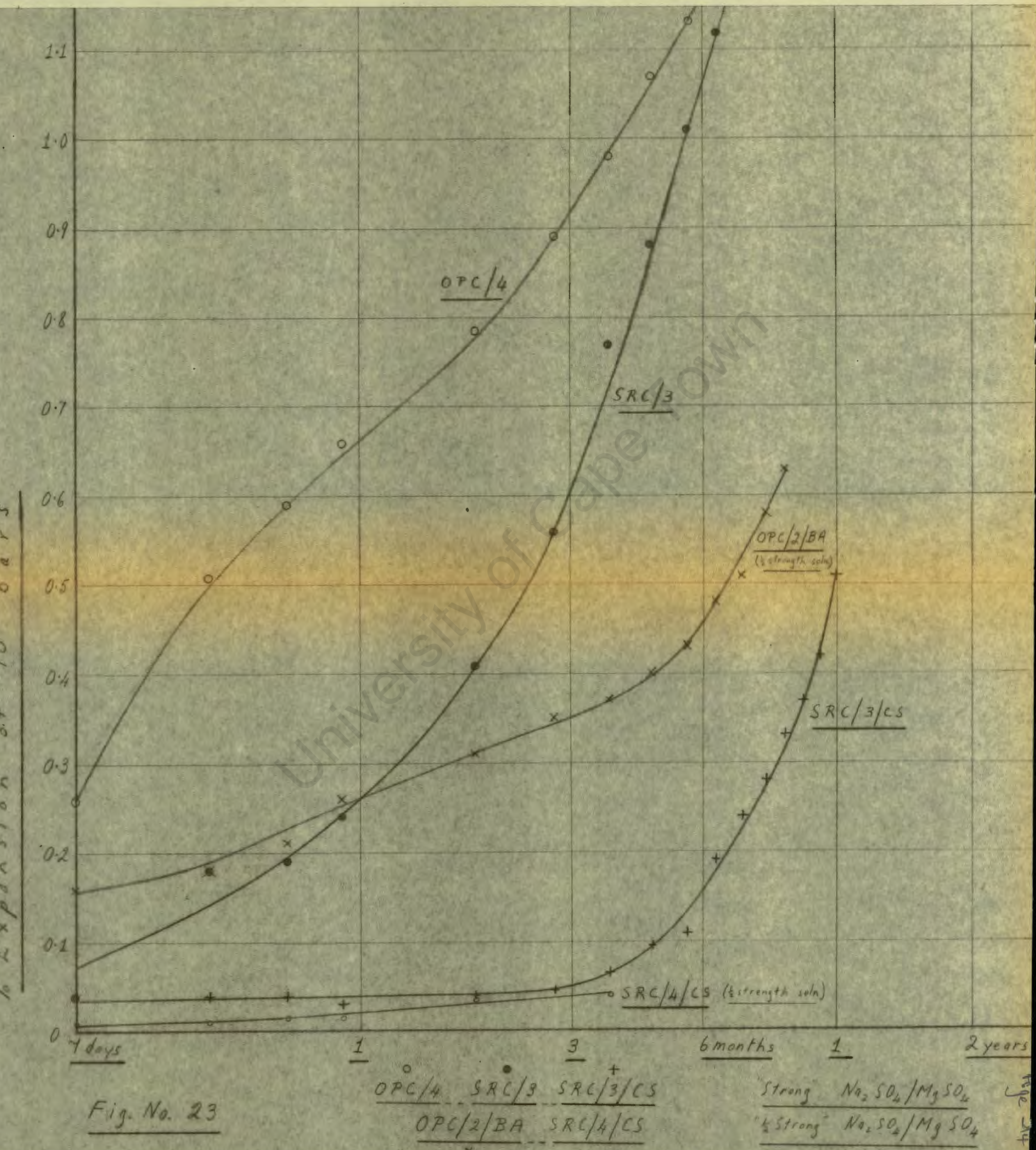

% Expansion of 10 bars
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
7 days
1
3
6 months
1
2 years
OPC/4
SRC/3
OPC/2/BA
(½ strength soln)
SRC/3/CS
SRC/4/CS (½ strength soln)
○ OPC/4 -- ● SRC/3 -- + SRC/3/CS
OPC/2/BA -- SRC/4/CS
"Strong" $Na_2SO_4/MgSO_4$
"½ Strong" $Na_2SO_4/MgSO_4$

Fig. No. 23

## 5. EXPANSIONS WITH "WEAK" $Na_2SO_4$ + $MgSO_4$

5.1. A fourth set of specimens was made up with $Na_2SO_4$ and $MgSO_4$ in equivalent proportions, and containing one-tenth of the amount of each used alone. This was equivalent to adding only 0.5% $SO_3$ to the cement, and the solution had a T.D.S. of 16,000 ppm (1.6%), which is similar to many ground waters. Incorporating the salts in the mortar, as well as curing the specimens in the solution, is (in my opinion) roughly equivalent to having water flowing continuously through a permeable concrete. This is a severe test, but not impractical.

5.2. The results are reported in Table No.58 and illustrated by Figure 24.

5.3. The specimens made with OPC/4 (13% $C_3A$) were "reasonable" up to 3 months, but then started expanding rapidly, and cracked and broke after 10 months.

5.4. After 11 months exposure there is "not much to choose" amongst the other cements, and it looks as if patience will have to be exercised for another year or two.

6. The results/...............

# TABLE NO. 58

TEST METHOD : MORTAR BAR EXPANSION

TESTING MEDIUM : Sodium plus Magnesium Sulphate (equivalent to increasing $SO_3$ in cement by 0.5% )

CURING MEDIUM : Soln. of 20g $Na_2SO_4.10\ H_2O$ + 15½g $Mg.SO_4\ 7\ H_2O$ per Litre (= ± 1,200 p.p.100,000 $SO_4$ ";+ 280 Na & 150 Mg")

| AGE IN DAYS | Percentage Expansion For: | | | | |
|---|---|---|---|---|---|
| | OPC/4 | SRC/3 | SRC/3/CS | OPC/2/BA | SRC/4/CS |
| 7 | 0.01 | 0.025 | 0.01 | 0.01 | 0.01 |
| 14 | 0.02 | 0.035 | 0.01 | 0.01 | 0.01 |
| 21 | n.a. | 0.04 | 0.015 | 0.02 | 0.015 |
| 28 | n.a. | 0.04 | 0.02 | 0.02 | 0.01 |
| 56 | 0.04 | 0.04 | n.a. | 0.02 | 0.02 |
| 84 | 0.06 | 0.04 | 0.02 | 0.02 | 0.025 |
| 112 | 0.10 | 0.045 | 0.025 | 0.02 | 0.025 |
| 140 | 0.145 | 0.045 | 0.03 | 0.02 | n.a. |
| 168 | 0.19 | 0.045 | 0.03 | 0.03 | n.a. |
| 196 | 0.27 | 0.045 | 0.03 | 0.03 | n.a. |
| 224 | 0.33 | 0.045 | n.a. | 0.03 | n.a. |
| 252 | 0.42 | 0.045 | 0.03 | n.a. | n.a. |
| 280 | 0.61 | 0.05 | 0.03 | n.a. | n.a. |
| 308 | 0.82 | 0.05 | 0.035 | n.a. | n.a. |
| 336 | All cracked &/or broken | 0.05 | 0.035 | n.a. | n.a. |
| 364 | - | n.a. | n.a. | n.a. | n.a. |
| Number of Test Pieces | 2 | 4 | 4 | 4 | 4 |

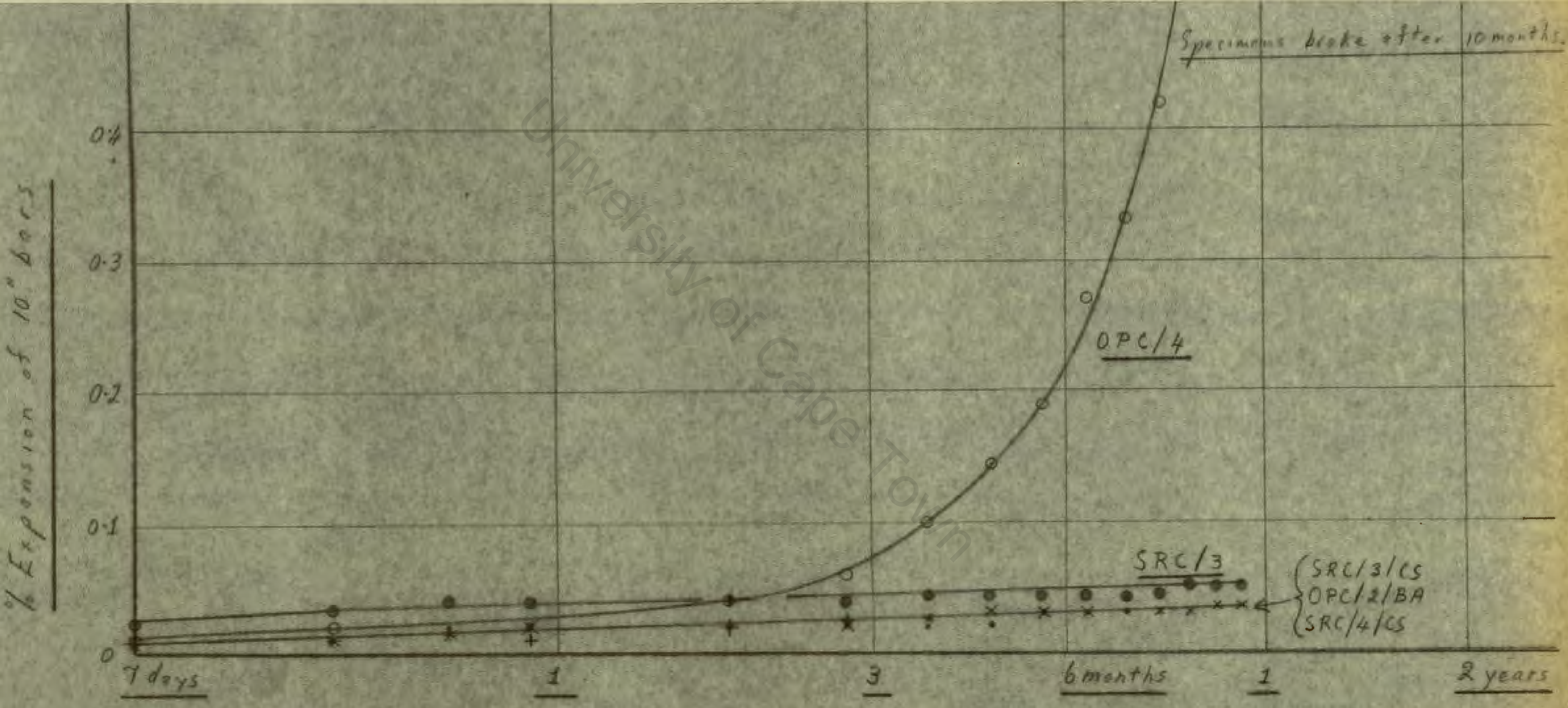


Fig. No. 24

3:1 $Na_2SO_4/MgSO_4$

6. The results presented in Sections 2 (from para.2.7 onwards), 3,4 and 5 have been "regrouped" in the following tables and figures, in order to illustrate the relative effects of the various chemicals on each cement separately.

6.1. Cement OPC/4; Table No.59, Figure No.25

The $MgSO_4/Na_2SO_4$ soln. gave higher expansions than the $CaSO_4$ with equivalent $SO_3$ content, but the bars did not break even at 1.5% expansion after 11 months. (Test is continuing). The weak mixed solution broke the bars at 0.8% expansion after 10 months exposure. The other solutions all caused high expansions after 3 months.

6.2. Cement OPC/2/BA; Table No.60, Figure No.26

Even though the "mixed" solution was only "½-strength" it attacked the cement strongly. $MgSO_4$ attacked more severely than $Na_2SO_4$ did in an equivalent "strong" solution.

6.3. Cement SRC/3, Table No.61, Figure No.27

The cement was not resistant to the strong mixed solution and was attacked by $Na_2SO_4$ and $MgSO_4$ in separate solutions after 4 months.

6.4. Cement SRC/3/CS, Table No.62, Figure No.28.

The calcined shale improved the cement's resistance to all three strong solutions.

6.5. Cement SRC/4/CS, Table No.63, Figure No.29

Up to the age tested it was about the same as cement SRC/3/CS, except that the strong $MgSO_4$ solution's attack seemed a bit more severe. Testing of this cement in actual running sea-water (dilute $Mg^{\bullet\bullet}$ solution) is now being done.

Table No.59/...........

# TABLE NO. 59

TEST METHOD : MORTAR BAR EXPANSION

TEST MATERIAL : Ordinary Portland Cement - OPC/4

TESTING MEDIA [x] : (a) $Na_2SO_4$ (b) $Mg\ SO_4$

(c) $Na_2SO_4 + MgSO_4$ - dilute solution

(d) $Na_2SO_4 + MgSO_4$ - strong solution

CURING MEDIA [x] : Solutions of a, b, c & d as above.

| AGE IN DAYS | Percentage Expansion With: | | | |
|---|---|---|---|---|
| | (a) $Na_2SO_4$ | (b) $MgSO_4$ | (c) Dil. $Na_2SO_4/MgSO_4$ | (d) Strong $Na_2SO_4/MgSO_4$ |
| 7 | 0.01 | 0.06 | 0.01 | 0.26 |
| 14 | 0.015 | 0.07 | 0.02 | 0.51 |
| 21 | 0.02 | 0.075 | n.a. | 0.59 |
| 28 | 0.025 | 0.08 | n.a. | 0.66 |
| 56 | 0.04 | 0.105 | 0.04 | 0.785 |
| 84 | 0.115 | 0.13 | 0.06 | 0.89 |
| 112 | 0.31 | 0.18 | 0.10 | 0.98 |
| 140 | 0.585 | 0.275 | 0.145 | 1.07 |
| 168 | 1.01 | 0.38 | 0.19 | 1.13 |
| 196 | 1.60 | 0.51 | 0.27 | 1.19 |
| 224 | n.a. | 0.63 | 0.33 | 1.24 |
| 252 | n.a. | 0.74 | 0.42 | 1.30 |
| 280 | n.a. | n.a. | 0.61 | n.a. |
| 308 | n.a. | n.a. | 0.82 | n.a. |
| 336 | n.a. | n.a. | All cracked at studs &/or broken | n.a. |
| 364 | n.a. | n.a. | | n.a. |
| Number of Test Pieces | 1(3) | 8 | 2 | 3 |

---

[x] Strengths of solutions as in previous Tables.

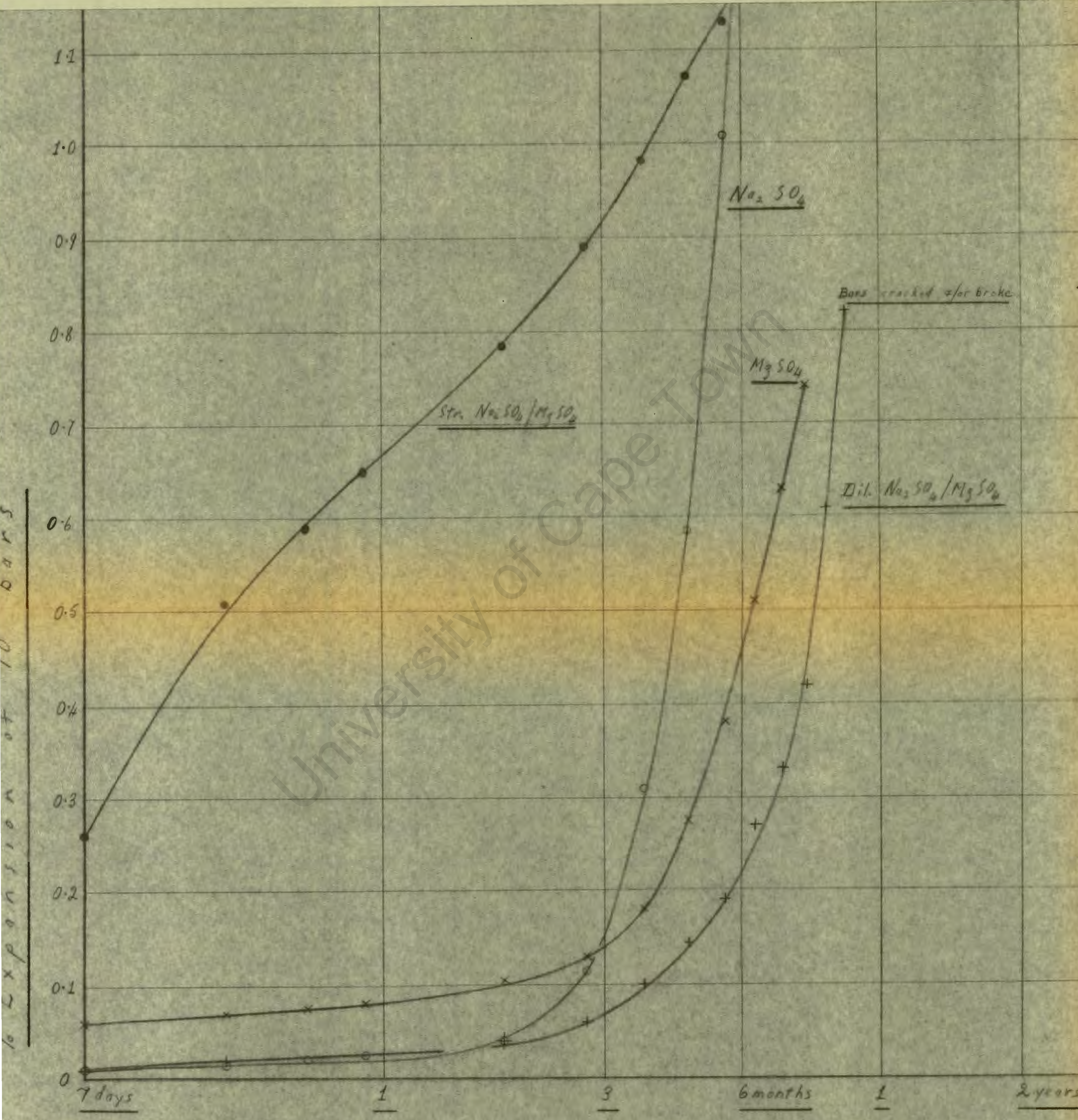


Fig. No. 25 OPC/4 $Na_2SO_4$ $MgSO_4$ Dil. $Na_2SO_4/MgSO_4$ Str. $Na_2SO_4/MgSO_4$

# TABLE NO. 60

TEST METHOD : MORTAR BAR EXPANSION

TEST MATERIAL : ORDINARY PORTLAND CEMENT + BOILER ASH - OPC/2/BA

TESTING MEDIA[x] : (a) $Na_2SO_4$ (b) $Mg SO_4$
(c) $Na_2SO_4$ + $MgSO_4$ - dilute solution
(d) $Na_2SO_4$ + $MgSO_4$ - ½ Strong solution

CURING MEDIA[X] : Solutions of a, b, c & d as above

| AGE IN DAYS | Percentage Expansion With: | | | |
|---|---|---|---|---|
| | (a) $Na_2SO_4$ | (b) $MgSO_4$ | (c) Dilute $Na_2SO_4$ + $MgSO_4$ | (d) ½ Strong $Na_2SO_4$ + $MgSO_4$ |
| 7 | 0.02 | 0.06 | 0.01 | 0.16 |
| 14 | 0.03 | 0.075 | 0.01 | 0.18 |
| 21 | 0.03 | 0.085 | 0.02 | 0.21 |
| 28 | 0.03 | 0.09 | 0.02 | 0.26 |
| 56 | 0.03 | 0.11 | 0.02 | 0.31 |
| 84 | 0.035 | 0.125 | 0.02 | 0.35 |
| 112 | 0.04 | 0.14 | 0.02 | 0.40 |
| 140 | 0.04 | 0.16 | 0.02 | 0.43 |
| 168 | 0.04 | 0.20 | 0.03 | 0.48 |
| 196 | 0.045 | 0.26 | 0.03 | 0.51 |
| 224 | n.a. | 0.34 | 0.03 | 0.58 |
| 252 | n.a. | 0.42 | n.a. | n.a. |
| 280 | n.a. | 0.48 | n.a. | n.a. |
| 308 | n.a. | n.a. | n.a. | n.a. |
| 336 | n.a. | n.a. | n.a. | n.a. |
| 364 | n.a. | n.a. | n.a. | n.a. |
| Number of Test Pieces | 3 | 4 | 4 | 4 |

[x] Strengths of solutions as in previous Tables.

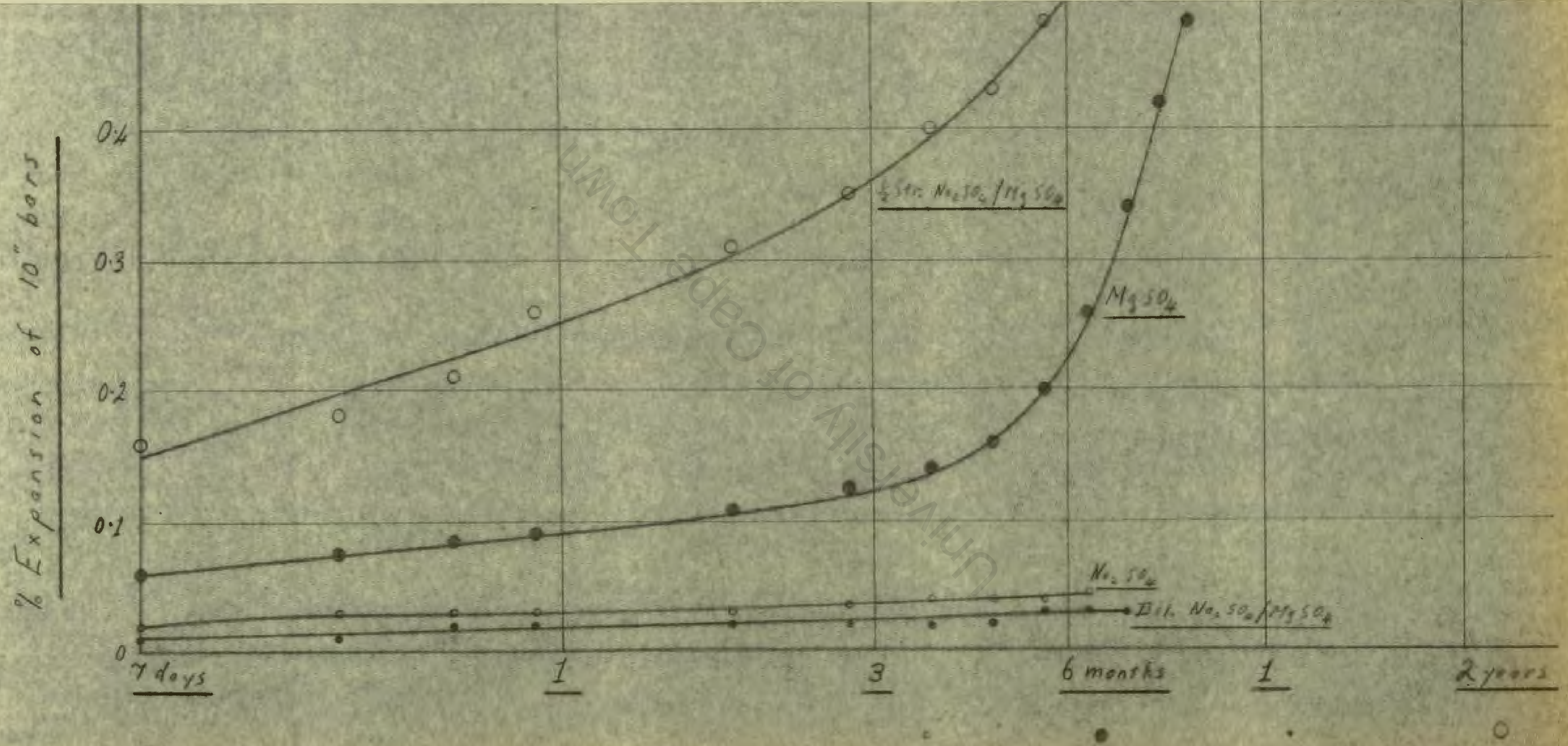


Fig: No. 26 OPC/2/BA

## TABLE NO. 61

TEST METHOD : MORTAR BAR EXPANSION

TEST MATERIAL : SULPHATE-RESISTING PORTLAND CEMENT - SRC/3

TESTING MEDIA x : (a) $Na_2SO_4$ (b) $MgSO_4$
(c) $Na_2SO_4$ + $MgSO_4$ - dilute solution
(d) $Na_2SO_4$ + $MgSO_4$ - strong solution

CURING MEDIA x : Solutions of a, b, c & d as above.

| AGE IN DAYS | Percentage Expansion With: | | | |
|---|---|---|---|---|
| | (a) $Na_2SO_4$ | (b) $MgSO_4$ | (c) Dilute $Na_2SO_4$ + $MgSO_4$ | (d) Strong $Na_2SO_4$ + $MgSO_4$ |
| 7 | 0.01 | 0.03 | 0.025 | 0.04 |
| 14 | 0.01 | 0.045 | 0.035 | 0.18 |
| 21 | 0.01 | 0.045 | 0.04 | 0.19 |
| 28 | 0.02 | 0.05 | 0.04 | 0.24 |
| 56 | 0.03 | 0.075 | 0.04 | 0.41 |
| 84 | 0.05 / 0.03 | 0.09 | 0.04 | 0.56 |
| 112 | 0.105 / 0.03 | 0.10 | 0.045 | 0.77 |
| 140 | 0.18 / 0.045 | 0.125 | 0.045 | 0.88 |
| 168 | 0.32 / 0.07 | 0.15 | 0.045 | 1.01 |
| 196 | 0.415 / 0.09 | 0.19 | 0.045 | 1.12 |
| 224 | 0.60 / 0.135 | 0.24 | 0.045 | 1.21 |
| 252 | n.a. | 0.305 | 0.045 | 1.27 |
| 280 | n.a. | n.a. | 0.05 | 1.35 |
| 308 | n.a. | n.a. | 0.05 | 1.42 |
| 336 | n.a. | n.a. | 0.05 | 1.51 |
| 364 | n.a. | n.a. | n.a. | n.a. |
| Number of Test Pieces | 2 2 | 4 | 4 | 3 |

x Strengths of solutions as in previous Tables

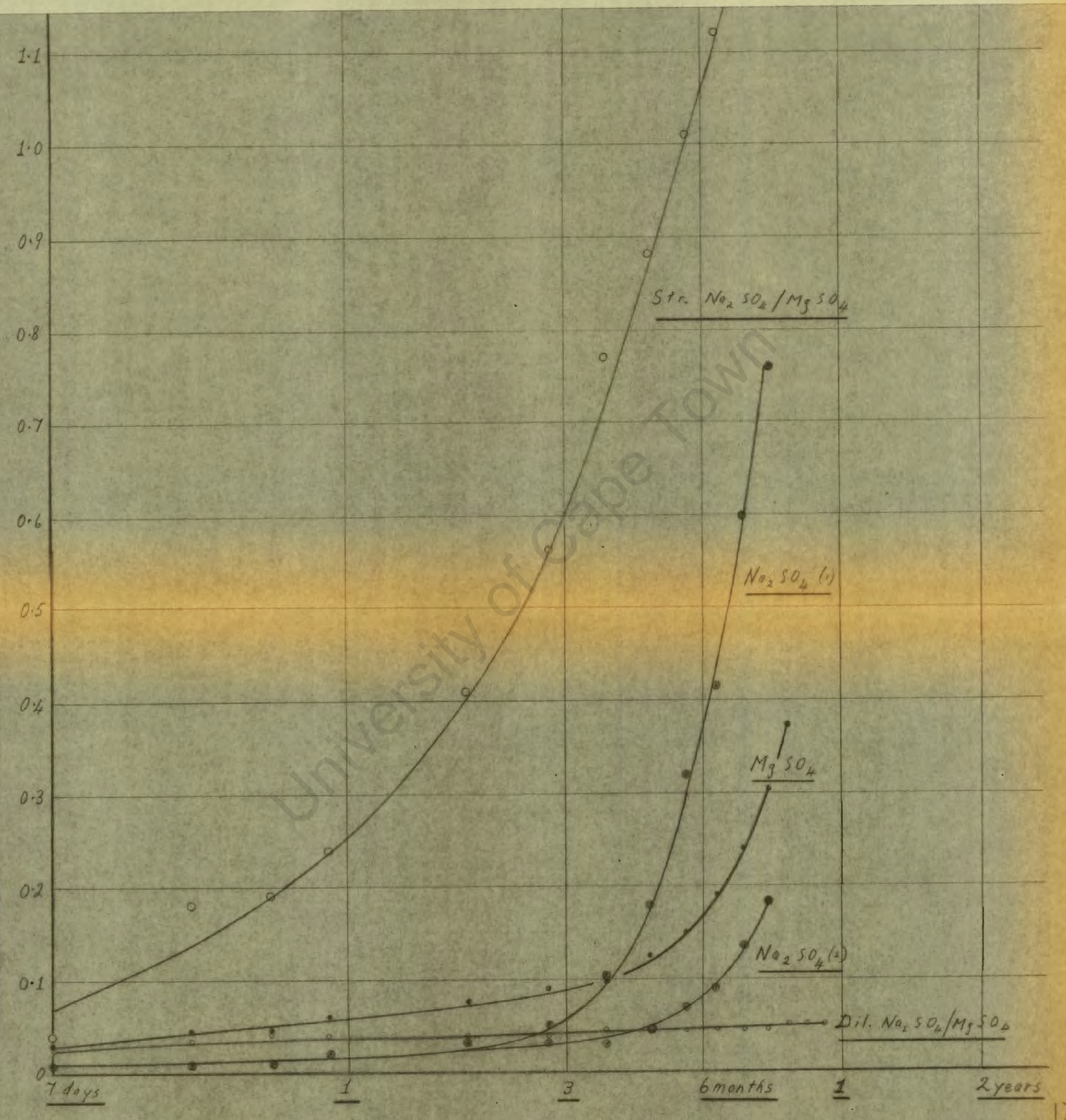


Fig. No. 27

SRC/3

● $Na_2SO_4$ — · — • $MgSO_4$ — · — ○ Dil. $Na_2SO_4/MgSO_4$ — · — ○ Str. $Na_2SO_4/MgSO_4$

## TABLE NO. 62

TEST METHOD : MORTAR BAR EXPANSION

TEST MATERIAL : SULPHATE RESISTING CEMENT + CALCINED SHALE SRC/3/CS

TESTING MEDIA x : (a) $Na_2SO_4$ (b) $MgSO_4$
(c) $Na_2SO_4$ + $MgSO_4$ - dilute solution
(d) $Na_2SO_4$ + $MgSO_4$ - strong solution

CURING METHOD x : Solutions of a, b, c & d as above.

| AGE IN DAYS | Percentage Expansion With: | | | |
|---|---|---|---|---|
| | (a) $Na_2SO_4$ | (b) $MgSO_4$ | (c) Dilute $Na_2SO_4$ + $MgSO_4$ | (d) Strong $Na_2SO_4$ + $MgSO_4$ |
| 7 | 0.01 | 0.02 | 0.01 | n.a. |
| 14 | 0.01 | 0.02 | 0.01 | 0.04 |
| 21 | 0.01 | 0.025 | 0.015 | 0.04 |
| 28 | 0.02 | 0.03 | 0.02 | 0.03 |
| 56 | 0.02 | 0.045 | n.a. | 0.04 |
| 84 | 0.025 | 0.05 | 0.02 | 0.045 |
| 112 | 0.03 | 0.06 | 0.025 | 0.065 |
| 140 | 0.035 | 0.055 | 0.03 | 0.095 |
| 168 | 0.04 | 0.07 | 0.03 | 0.11 |
| 196 | 0.07 | 0.08 | 0.03 | 0.19 |
| 224 | 0.09 | 0.10 | n.a. | 0.24 |
| 252 | n.a. | 0.12 | 0.03 | 0.28 |
| 280 | n.a. | 0.16 | 0.03 | 0.33 |
| 308 | n.a. | n.a. | 0.035 | 0.37 |
| 336 | n.a. | n.a. | 0.035 | 0.42 |
| 364 | n.a. | n.a. | n.a. | 0.51 |
| Number of Test Pieces | 4 | 4 | 4 | 4 |

x Strengths of solutions as in previous Tables.

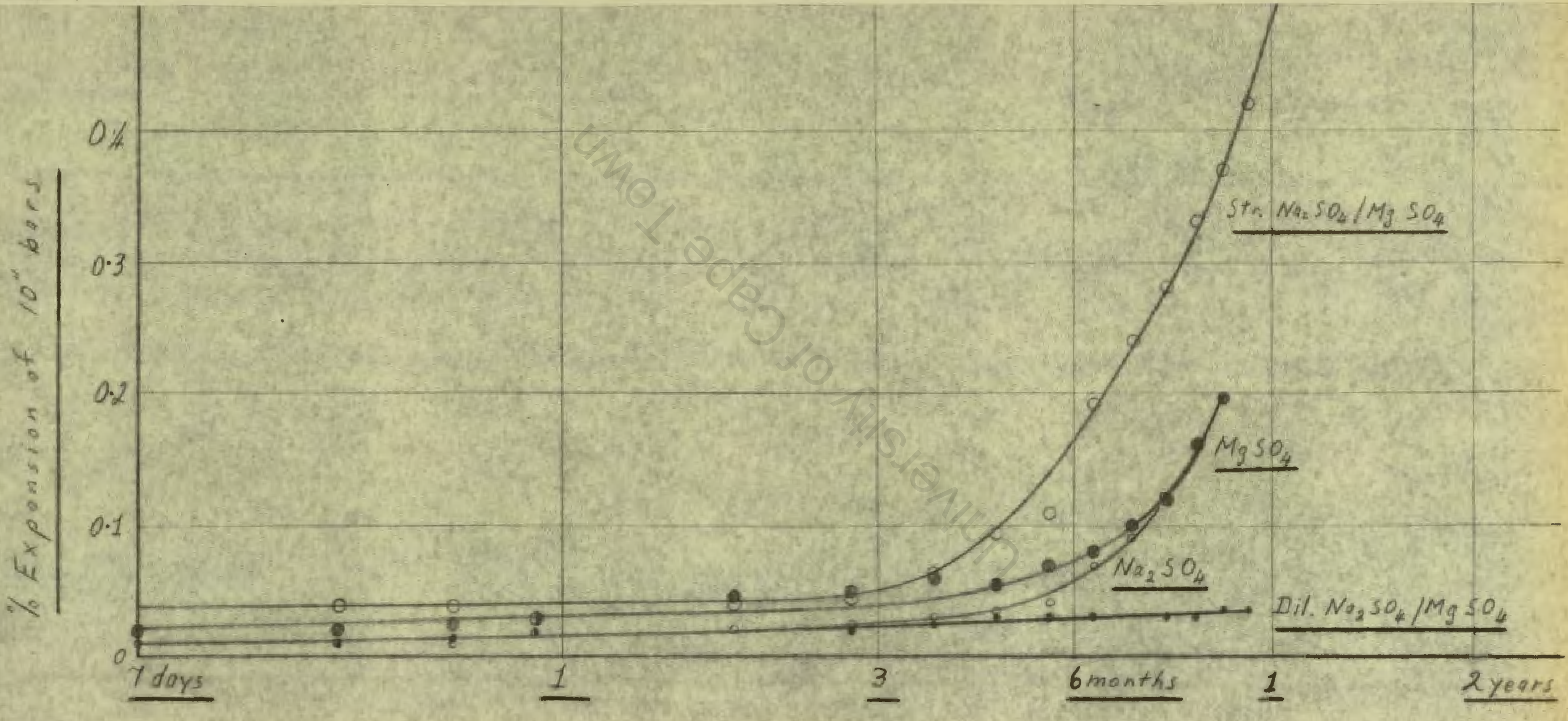


Fig. No. 28 SRC/3/CS

# TABLE NO. 63

TEST METHOD : MORTAR BAR EXPANSION

TEST MATERIAL : MARINE CEMENT - SRC/4/CS

TESTING MEDIA x : (a) $Na_2SO_4$ (b) $MgSO_4$ -
(c) $Na_2SO_4$ + $MgSO_4$ - dilute solution
(b) $Na_2SO_4$ + $MgSO_4$ - "½ strong" solution.

CURING MEDIA x : Solutions of a, b, c & d as above.

| AGE IN DAYS | Percentage Expansion with: | | | |
|---|---|---|---|---|
| | (a) $Na_2SO_4$ | (b) $MgSO_4$ | (c) Dilute $Na_2SO_4$ + $MgSO_4$ | (d) "½ Strong" $Na_2SO_4$ + $MgSO_4$ |
| 7 | 0.02 | 0.03 | 0.01 | 0.01 |
| 14 | 0.02 | 0.035 | 0.01 | 0.01 |
| 21 | 0.025 | 0.035 | 0.015 | 0.015 |
| 28 | 0.025 | 0.04 | 0.01 | 0.015 |
| 56 | 0.035 | 0.05 | 0.02 | 0.035 |
| 84 | 0.05 | 0.06 | 0.025 | n.a. |
| 112 | 0.055 | 0.08 | 0.025 | 0.04 |
| 140 | 0.075 | n.a. | n.a. | n.a. |
| 168 | n.a. | n.a. | n.a. | n.a. |
| 196 | n.a. | n.a. | n.a. | n.a. |
| 224 | n.a. | n.a. | n.a. | n.a. |
| 252 | n.a. | n.a. | n.a. | n.a. |
| 280 | n.a. | n.a. | n.a. | n.a. |
| 308 | n.a. | n.a. | n.a. | n.a. |
| 336 | n.a. | n.a. | n.a. | n.a. |
| 364 | n.a. | n.a. | n.a. | n.a. |
| Number of Test Pieces | 4 | 4 | 4 | 4 |

x Strengths of solutions as in previous Tables.

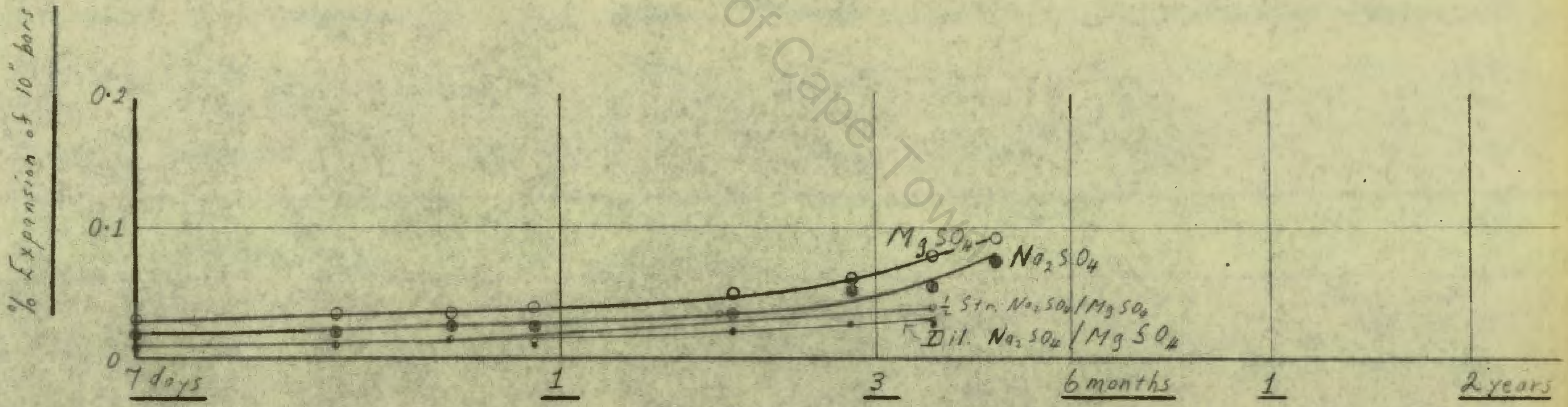


Fig. No. 29 SRC/4/CS

## 7. EXPANSIONS WITH $MgCl_2$

7.1. It has been stated in previous chapters that the free $Ca(OH)_2$ content of hydrated S.R.cements should render them liable to attack by both $SO_4''$ and $Mg^{\cdot\cdot}$, although the $SO_4''$ attack should be less severe because of the reduced $C_3A$ content of these cements. Referring back to Figures 15 and 27, it is seen that S.R.cements <u>are</u> actually liable to attack by $MgSO_4$, $Na_2SO_4$ and $CaSO_4$ after periods varying from 3 to about 15 months - although the attack is mild compared with that on O.P.C.

7.2. To determine the effect of $Mg^{\cdot\cdot}$, $SO_4''$ must be excluded, so some bars were made up with, and cured in, a 12% solution of $MgCl_2$.

7.3. The results are given in Table No.64 and illustrated by Figure No.30.

7.4. Strictly according to theory the SRC should be no more resistant than OPC to $MgCl_2$, but the test shows tha it is. The Marine cement (SRC/4/CS - "second" sample) should be more resistant than SRC, and this has been confirmed. However, the results at later ages may be more significant, and, in any case, this solution is very concentrated. Further tests are to be done with weaker solutions.

Table No.64/.......,,

## TABLE NO.64

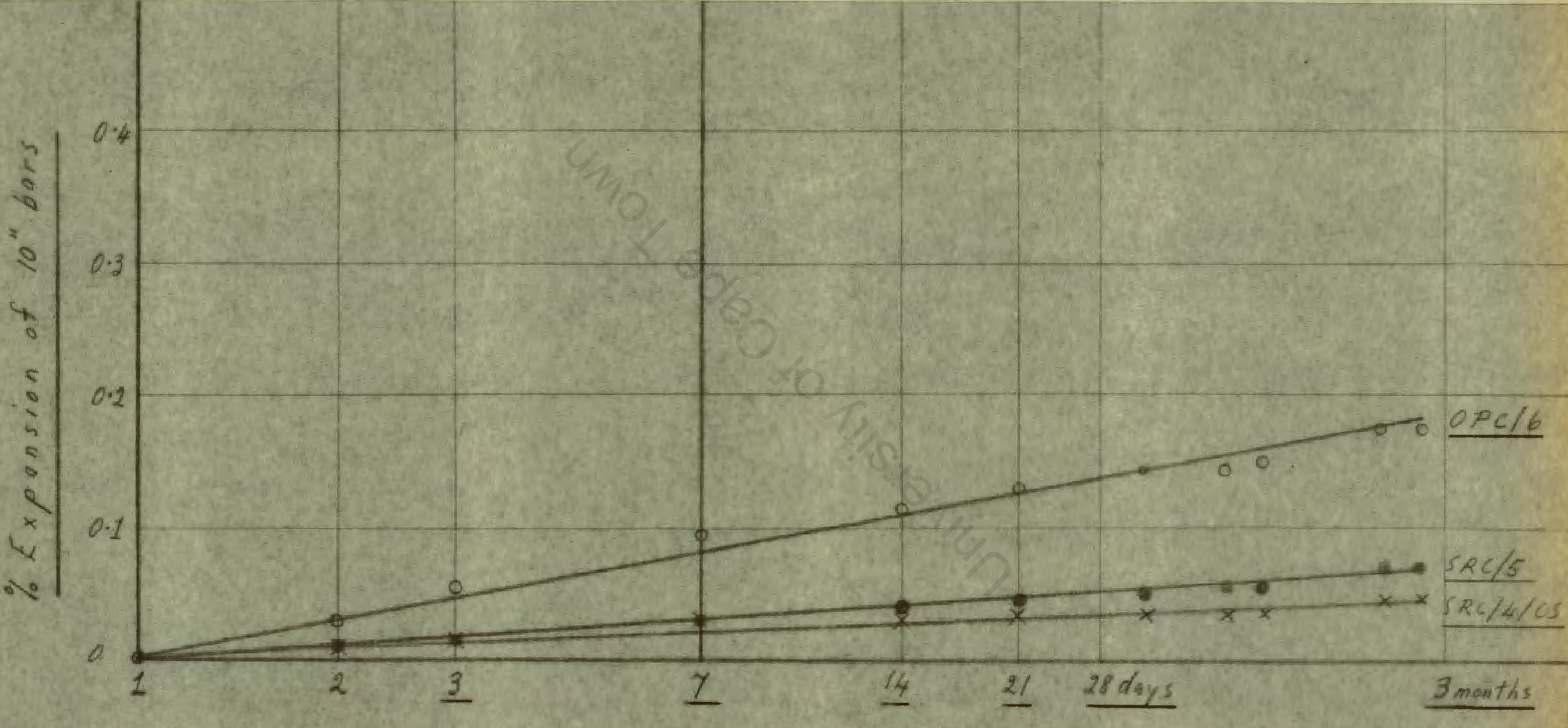
TEST METHOD : MORTAR BAR EXPANSION

| | | | |
|---|---|---|---|
| TEST MATERIAL : | Ordinary Portland Cement | : | OPC/6 |
| | Sulphate Resisting Cement | : | SRC/5 |
| | Marine Cement | : | CM/3a |

TESTING MEDIA : Magnesium Chloride (6½% of cement by wt).

CURING MEDIA : Solution of 120g.$MgCl_2$ per 1,000 ml.

| AGE IN DAYS | PERCENTAGE EXPANSION FOR | | |
|---|---|---|---|
| | OPC/6 | SRC/5 | CM/3a |
| 1 | - | - | - |
| 2 | 0.03 | 0.01 | 0.01 |
| 3 | 0.055 | 0.015 | 0.015 |
| 8 | 0.095 | 0.03 | 0.03 |
| 15 | 0.115 | 0.04 | 0.03 |
| 22 | 0.13 | 0.045 | 0.035 |
| 33 | 0.145 | 0.05 | 0.035 |
| 43 | 0.145 | 0.055 | 0.035 |
| 49 | 0.15 | 0.055 | 0.035 |
| 74 | 0.175 | 0.07 | 0.045 |
| 84 | 0.175 | 0.07 | 0.045 |



○ OPC/6 ● SRC/5 × SRC/4/CS

Fig. No. 30

$MgCl_2$

## 9.3. EFFECT OF SULPHATE ATTACK ON STRENGTH

1. It is inadvisable to judge cement quality by one criterion only, and low expansions in the above tests do not necessarily mean that the specimens are sound in all respects. Some have had their edges rounded, but are still strong. Others still look good, but are easily broken. I have decided against reporting "appearance" of specimens here, although it has been recorded, because "appearances can be deceptive", and they are in any case "subjective " criteria ! "Objective" results are to be preferred, except for strictly "ornamental" purposes.

2. The most important property of concrete is usually its strength, so a series of tests was undertaken to determine the effect of sulphate attack on strength at various ages. The "weak" solution of $Na_2SO_4$ plus $MgSO_4$ was selected for this purpose, and specimens were again made up with the solution (to incorporate the salts within the specimens), as well as being cured in it. Duplicate specimens were made with and cured in water, for comparison purposes.

3. Lacking Mr van Aardt's "natural frequency of vibration" apparatus for non-destructive testing (paragraph 4.3-4.2), I decided to use the Cembureau technique of making 16 x 4 x 4cm prisms which can be broken first in flexure and then twice in compression, thus giving three test results per specimen.

4. One set of specimens was made up with standard sand only, in accordance with the SABS : 471 method for transverse strength specimens. The rest were made up as "concrete" specimens, using ¼" chips of "Malmesbury Blue Hornfels" (from the Windmill Quarries, Agter Paarl), kindly supplied by the Cape Town P.C.I. personnel, who also advised on the mix

proportions/...............

proportions to use. De Grendel building sand was used as fine aggregate.

5. Lean, medium and rich mixes were used, and the details of these concrete mixes and also of the mortar mix are given in Table No.65

6. Strength test results available to date are given in Tables Nos. 66 and 67. The tests are being continued.

7. Figure No.31 : Mortar Mix: Transverse Strengths.

(1) Water-cured: results were not satisfactory, partly due to trouble (since rectified) with the test machine.

(2) Solution-cured: SRC strengths were significantly higher than OPC strengths. They appeared to decline after 3 months.

8. Figure No.32. Mortar Mix : Compressive Strengths.

These results were not very satisfactory either, the water-cured specimens tended to show an even greater drop in strength after a few months, than the solution-cured specimens. SRC appeared to be better than OPC in the solution.

9. Figures 33 and 34 : Concrete Mixes: Transverse Strengths.

9.1. Water cured: Except for an unexplained low 9 month strength for S.R.cement (medium mix) results were reasonably satisfactory and indicated fairly regular strength development for all the concretes.

9.2. Solution cured: there was one unduly high 9 month strength, otherwise the figure illustrates matters well:

9.2.1. All three O.P.C.mixes exhibited severe deterioration of strength after 3 months;

9.2.2. The lean SRC mix showed some deterioration after 3 months, the medium mix seemed to be "levelling out" and the rich mix gave an inexplicably high result at 9 months.

9.2.3. The Marine Cement (CM-2) - medium mix - appeared to be making satisfactory progress.

## TABLE NO.65

## CONCRETE AND MORTAR MIXES FOR STRENGTH TESTS

| TYPE OF CEMENT AND CONCRETE | POCKETS/CU.YD. | CEMENT | BUILDING SAND | STONE CHIPS | WATER OR SOLUTION | W/C RATIO |
|---|---|---|---|---|---|---|
| | | grams | grams | grams | ml. | |
| CONCRETES: | | | | | | |
| Lean Mix : | 5 | 321 | 1235 | 962 | 256 | 0.80 |
| Medium Mix | 7 | 447 | 1120 | 969 | 256 | 0.57 |
| Rich Mix: | 9 | 588 | 990 | 977 | 256 | 0.435 |
| Lean Mix + Air Entraining Agent: | 5 | 321 | 1235 | 962 | 192 | 0.60 |
| "Marine-Cement" CM-2, Med. Mix: | 7 | 447 | 1120 | 969 | 223 | 0.50 |
| MORTAR | | | Standard Sand | | | |
| "Standard" Mix : | - | 600 | 1800 | nil | 300 | 0.50 |

SOLUTION STRENGTH: $20g\ Na_2SO_4.10\ H_2O$ ) $15\frac{1}{2}g\ MgSO_4.7\ H_2O$ ) per 1000 ml.

## TABLE NO. 66

## STRENGTHS OF CONCRETE[x] MIXES

| CONCRETE MIX AND TEST AGE | TRANSVERSE STRENGTH |  |  |  | COMPRESSIVE STRENGTH |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  | Water Cured |  | Solution[xx] |  | Water Cured |  | Solution[xx] |  |
|  | OPC | SRC | OPC | SRC | OPC | SRC | OPC | SRC |
|  | psi | psi | psi | psi | psi | psi | psi | psi |
| **"LEAN"** |  |  |  |  |  |  |  |  |
| 7 days | 420 | 470 | 390 | 510 | 2000 | 2600 | 2400 | 2900 |
| 28 " | 600 | 550 | 480 | 630 | 2950 | 3050 | 3050 | 3800 |
| 3 Months | 620 | 710 | 490 | 780 | 3350 | 3550 | 3200 | 3900 |
| 6 " | 630 | 700 | 370 | 750 | 3550 | 3750 | 2950 | 4000 |
| 9 " | 660 | 700 | 190 | 720 | 3800 | 4150 | 2850 | 4150 |
| **"MEDIUM"** |  |  |  |  |  |  |  |  |
| 7 days | 880 | 850 | 710 | 830 | 4800 | 4900 | 5400 | 5300 |
| 28 " | 900 | 930 | 940 | 1060 | 5950 | 5850 | 5650 | 7100 |
| 3 months | 940 | 1100 | 960 | 1170 | 6250 | 7450 | 6450 | 7350 |
| 6 " | 870 | 1130 | 690 | 1160 | 6350 | 8300 | 6350 | 8150 |
| 9 " | 960 | 1040 | 600 | 1210 | 7100 | 8900 | 5150 | 8150 |
| **"RICH"** |  |  |  |  |  |  |  |  |
| 7 days | 1160 | 1130 | 1060 | 1200 | 8100 | 8000 | 7400 | 7450 |
| 28 " | 1250 | 1190 | 1230 | 1330 | 8650 | 9650 | 8400 | 9450 |
| 3 months | 1260 | 1320 | 1220 | 1250 | 9100 | 10350 | 8550 | 10200 |
| 6 " | 1260 | 1320 | 1030 | 1390 | 10000 | 12300 | 8850 | 12750 |
| 9 " | 1280 | 1420 | 960 | 1820 | 10300 | 12300 | 9750 | 13550 |

[x] Made with ¼" granite chips - see text for details.

[xx] Dilute solution of $Na_2SO_4$ + $Mg.SO_4$ - see text for details.

# TABLE NO. 67

## STRENGTHS OF CONCRETE[x] AND MORTAR MIXES

| CONCRETE MIX AND TEST AGE | TRANSVERSE STRENGTH | | | | COMPRESSIVE STRENGTH | | | |
|---|---|---|---|---|---|---|---|---|
| | Water Cured | | Solution[xx] | | Water Cured | | Solution[xx] | |
| | OPC psi | SRC psi | OPC psi | SRC psi | OPC psi | SRC psi | OPC psi | SRC psi |
| "LEAN + AIR" | | | | | | | | |
| 7 days | 570 | 620 | 500 | 580 | 2650 | 3100 | 2900 | 3450 |
| 28 " | 580 | 690 | 540 | 640 | 2950 | 4000 | 3400 | 4000 |
| 3 months | 590 | 810 | 640 | 700 | 3500 | 4400 | 3550 | 4350 |
| 6 " | 650 | 760 | 490 | 860 | 3550 | 4650 | 3550 | 4700 |
| "MEDIUM" | | CM | | CM | | CM | | CM |
| 7 days | | 710 | | 750 | | 3400 | | 3800 |
| 28 " | | 840 | | 910 | | 5100 | | 5000 |
| 56 " | | 910 | | 1040 | | 5900 | | 5850 |
| 3 months | | 980 | | 960 | | 6450 | | 6350 |
| 6 " | | 880 | | 1050 | | 6850 | | 6800 |
| 9 " | | 1030 | | 1110 | | 7100 | | 7200 |
| "MORTAR" | OPC | SRC | OPC | SRC | OPC | SRC | OPC | SRC |
| 7 days | 790 | 850 | 840 | 890 | 5100 | 5450 | 4600 | 4550 |
| 28 " | 950 | 960 | 920 | 1160 | 6900 | 7400 | 5900 | 7350 |
| 3 months | 950 | 1050 | 800 | 1280 | 6800 | 7600 | 6000 | 8000 |
| 6 " | 790 | 940 | 840 | 1150 | 6750 | 8200 | 5450 | 8750 |
| 10 " | 850 | 980 | 830 | 1150 | 6000 | 7300 | 6050 | 8300 |

[x] Made with ¼" stone chips - see text for details.

[xx] Dilute solution of $Na_2.SO_4$ + $Mg.SO_4$

# MORTAR PRISMS

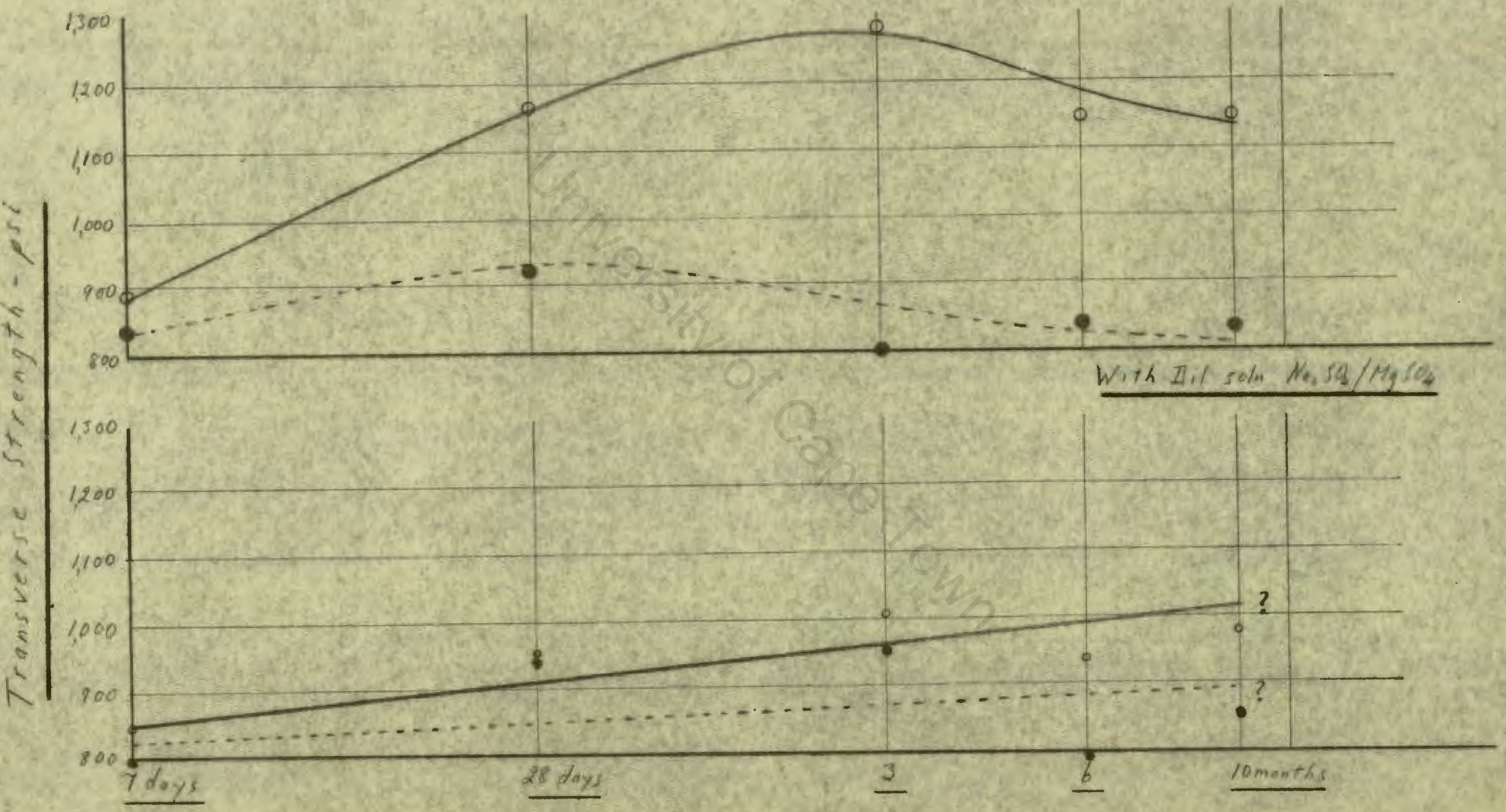


Fig. No 31

# MORTAR PRISMS

Fig. No. 32

# CONCRETE PRISMS

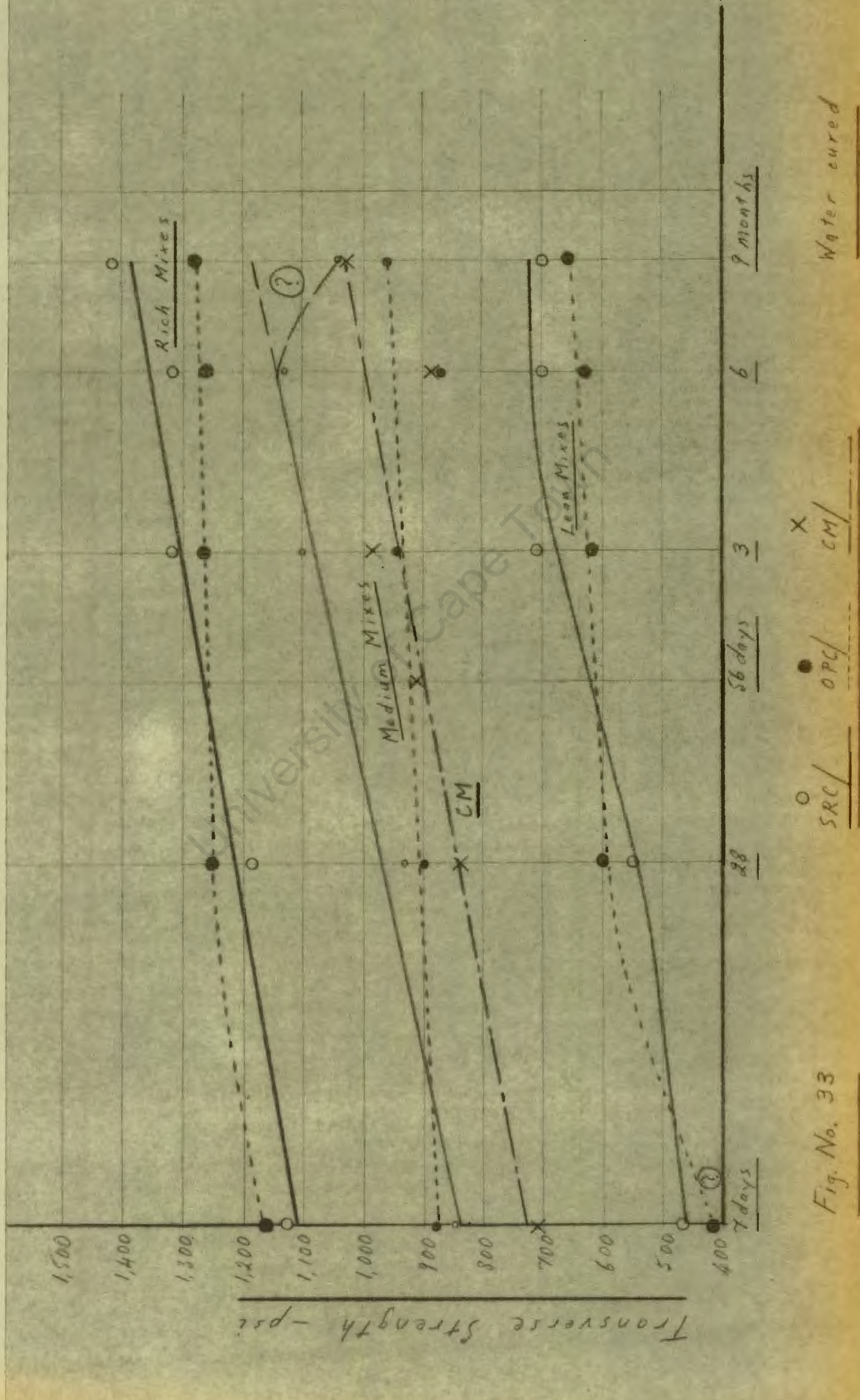


Fig. No. 33

## CONCRETE PRISMS

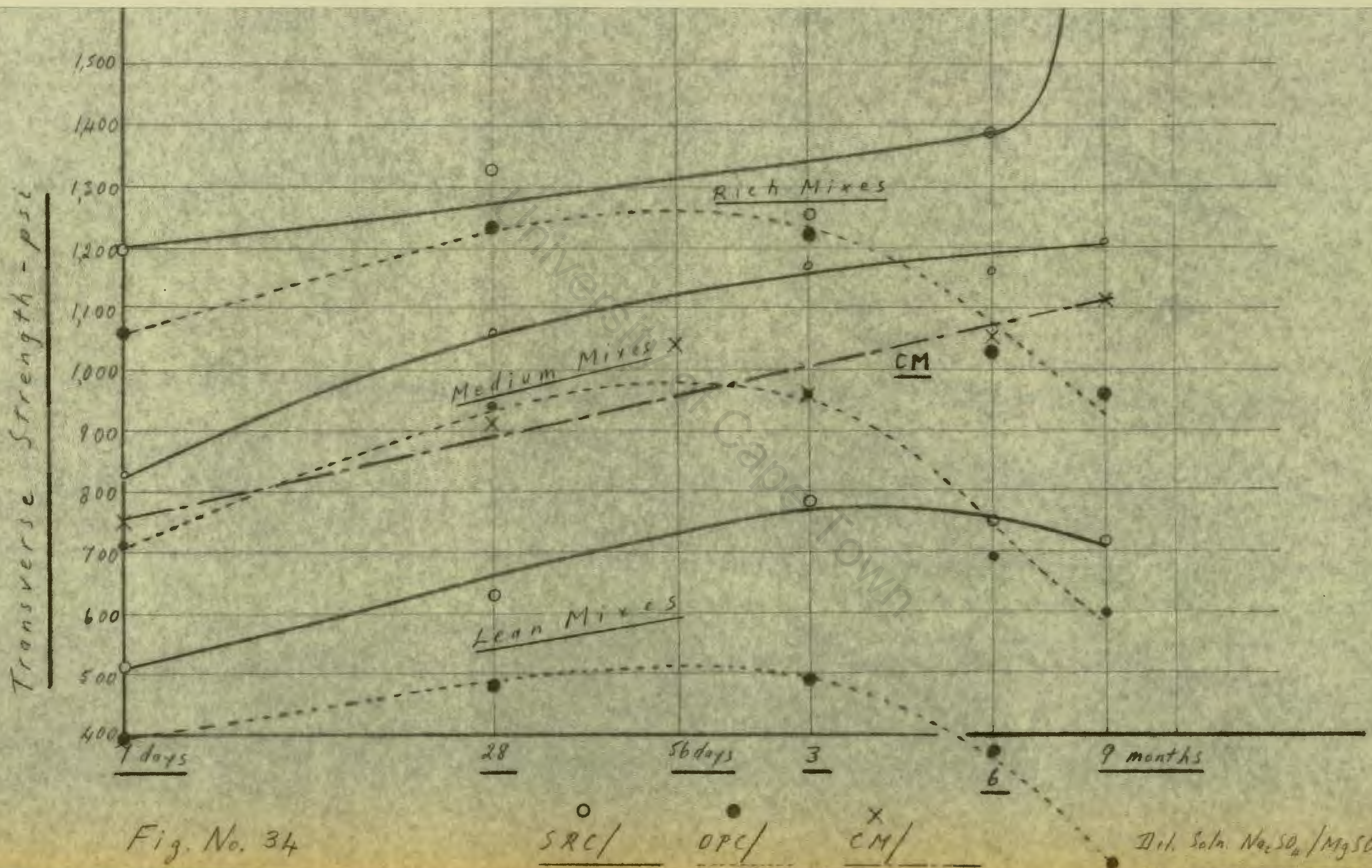


Fig. No. 34

10. Figures 35 and 36 : Concrete Mixes : Compressive Strengths

10.1 Water-cured : All the mixes showed regular strength development.

10.2 Solution-cured:

10.2.1. The lean and medium OPC mixes declined in strength after 3 months. The rich mix was still "holding its own", but its transverse strength declined after about 2 months(Fig.34)

10.2.2. All three SRC mixes continued to increase in strength up to 9 months. The rich mix seemed to be "accelerating" but not sufficiently to account for the "freak" high transverse strength at that age.

10.2.3. The Marine Cement exhibited "exemplary" progress.

11. Figures 37 and 38 : Lean, Air-entrained Concrete Mixes:

11.1 Transverse Strengths: Both water-cured concretes appeared to behave normally. The solution-cured OPC concrete decreased in strength after 3 months, whereas the S.R.C. still increased.

11.2 Compressive Strengths: All specimens were still tending to gain strength up to 6 months, although the OPC solution-cured concrete seemed to be "levelling off"

## CONCRETE PRISMS

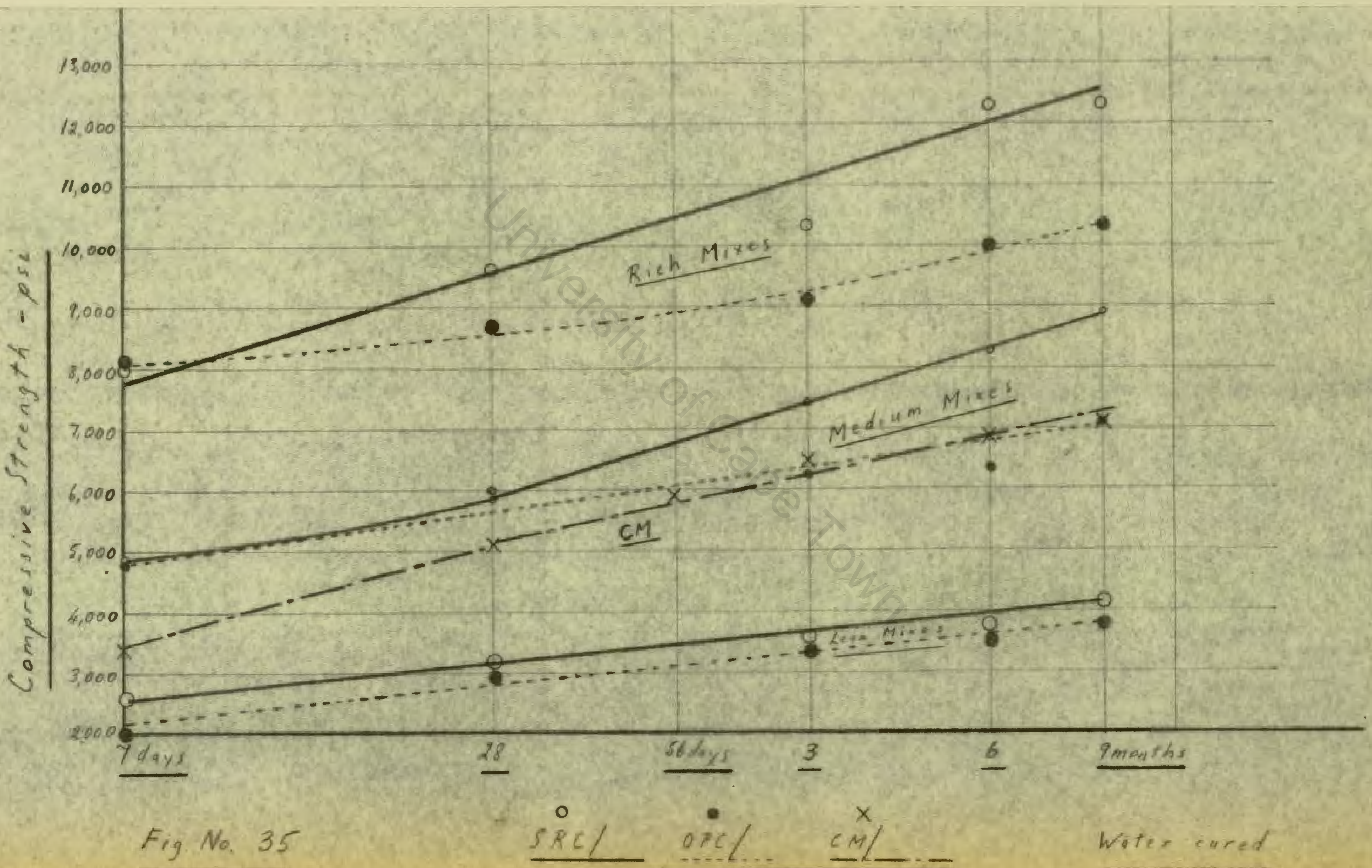


Fig. No. 35

Water cured

## CONCRETE PRISMS

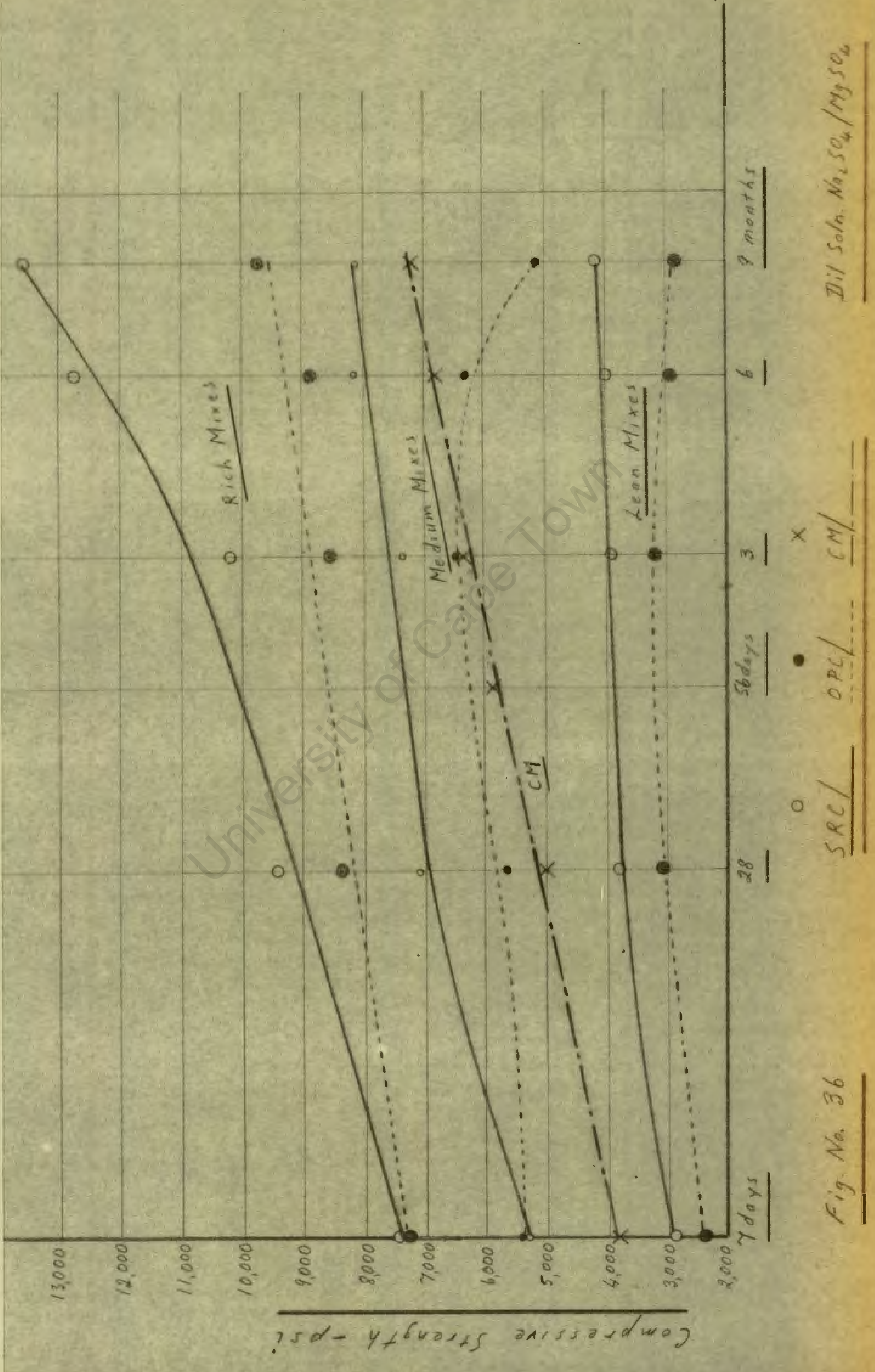


Fig. No. 36

# CONCRETE PRISMS

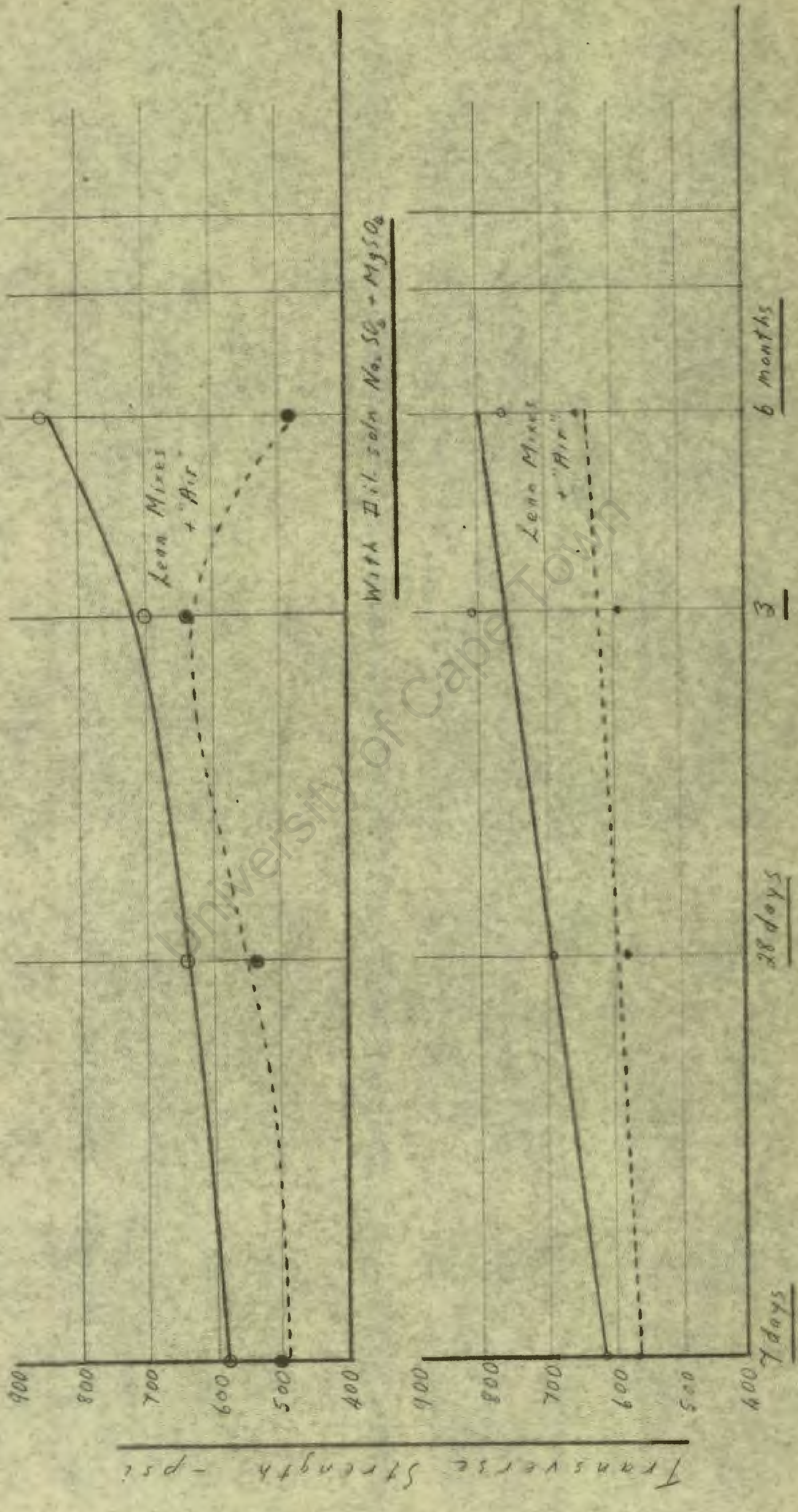


Fig. No. 37

○ SRC/ ● OPC/ Water cured

# CONCRETE PRISMS

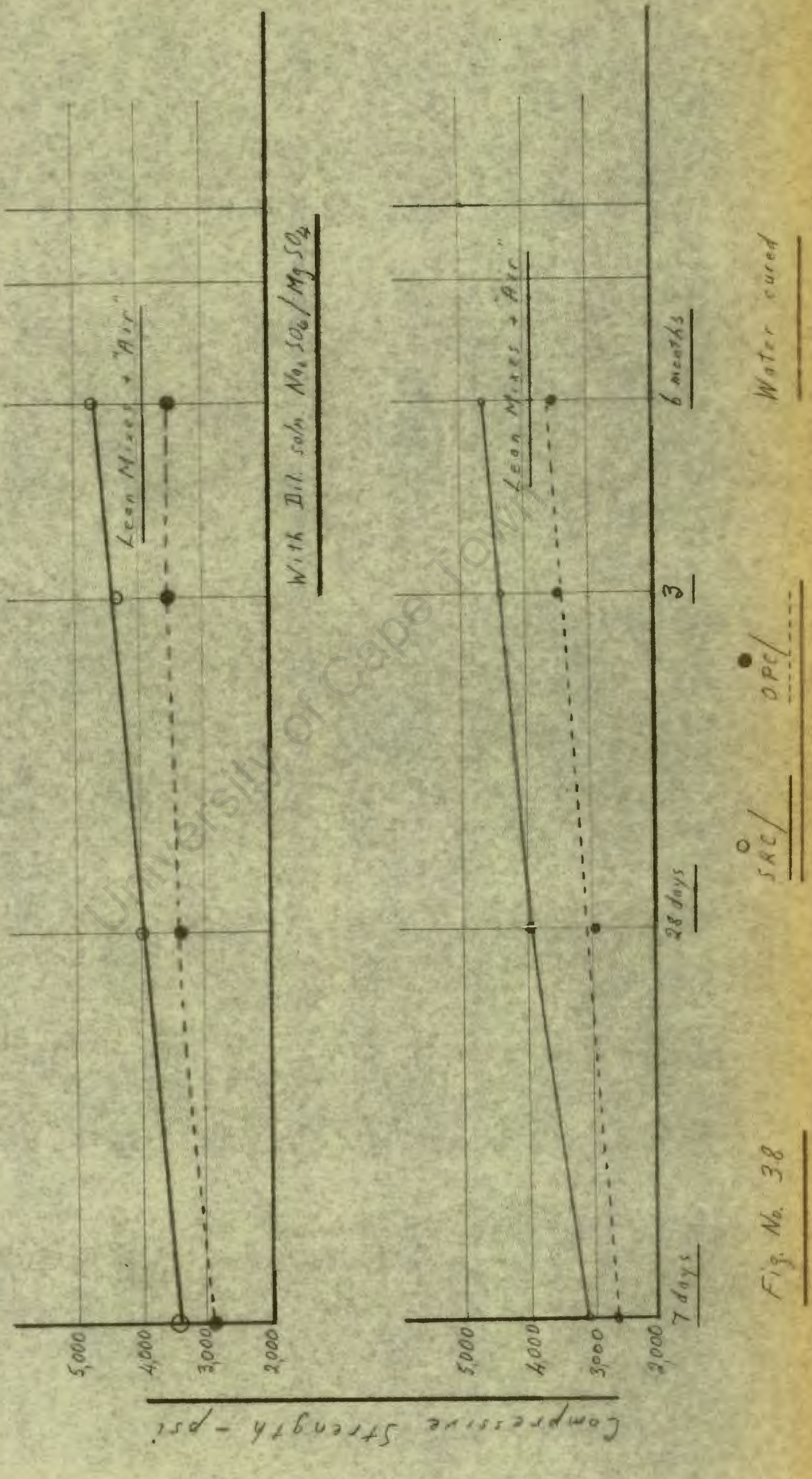


Fig. No. 38

## 9.4. BOND BETWEEN REINFORCING STEEL & CONCRETE

1. The weakest part of concrete is usually the bond between the hydrated cement paste and aggregate (20.49) and the weakest part of reinforced concrete is apt to be the bond between the paste and the steel. It is important, therefore, that this bond should not be affected by any additives, or treatments, used to improve durability.

2. Pozzolanic materials do not appear to affect reinforcing bond strength adversely, and neither does entrained air in reasonable amounts (20.39). However, to be on the safe side, some "pull-out" tests were done on OPC and CM mortar cubes. (1 part cement : 3 parts standard sand, by weight).

3. ½" Steel bars, long enough to project from the specimens, were moulded into the centres of hand-compacted mortar cubes, which were then cured in the usual way for varying lengths of time. A tensile test machine was adapted for pulling the bars out of the cubes and the specimens were tested to failure of bond. Both "bright" and "mild" Steel bars were tested. The mild steel bars were wire-brushed before they were put in the mortar.

4. The first set was made in 2¾" moulds and the machine was unable to pull the mild steel bars out of the moulds at 3 days age. Another test machine was modified in time to test some more specimens at 8 days, and the rest were tested at 28 days. The specimens did not fit into the second machine too well, however, and some cubes split before the bar was pulled out. One specimen of each type was put back into water for a further 28 days, to "re-bond". Some of the re-bonds were as strong as the originals.

5. A second set/................

5. A second set of specimens was made up in 2" cube moulds, and these were rather more successful. All test results are reported in Table No.68.

6. In spite of the "improvements" in the second test series the variation in strength of similar specimens leaves a lot to be desired, but I feel it is safe to infer that there is no significant difference in bond strength between OPC and CM-3 mortars. There is also a definite indication that reducing the water/cement ratio increases the bond strength, and the use of CM-3 in concrete favours lower water/cement ratios.

TABLE NO.68

REINFORCING BOND STRENGTHS OF OPC & CM-3

| TEST AGE ETC. | BRIGHT STEEL BARS |  |  | MILD STEEL BARS |  |  |
|---|---|---|---|---|---|---|
|  | OPC | CM-3 | CM-3/R | OPC | CM-3 | CM-3/R |
|  | psi | psi | psi | psi | psi | psi |
| 1st SERIES : $2\frac{3}{4}$"CUBES |  |  |  |  |  |  |
| At 3 Days | 210 | 220 | - | >280 | >280 | - |
| At 7 Days | 230 | 200 | - | 410 | 420 | - |
| At 28 Days | 250 | 270 | - | 530 | 510 | - |
| "Rebonded"-28 Days (1 specimen only) | 230 | 160 | - | 360 | 510 | - |
| 2nd SERIES: 2"CUBES |  |  |  |  |  |  |
| At 3 Days 1 | 180 | 220 | - | - | - | - |
| 2 | 220 | 190 | - | - | - | - |
| 3 | - | 220 | - | - | - | - |
| Av. | 200 | 210 | - | - | - | - |
| At 7 Days 1 | 340 | 300 | 300 | 360 | 290 | 360 |
| 2 | 250 | 380 | 380 | 380 | 330 | 380 |
| 3 | 380 | 260 | 330 | 380 | 320 | 300 |
| Av. | 320 | 310 | 340 | 370 | 310 | 350 |
| At 28 Days 1 | 350 | 310 | 380 | 410 | 490 | 470 |
| 2 | 350 | 310 | 470 | 420 | 450 | 610 |
| 3 | 310 | 280 | 360 | 360 | 380 | 530 |
| Av. | 340 | 300 | 400 | 400 | 440 | 540 |
| WATER/CEMENT RATIO | 0.50 | 0.50 | 0.45 | 0.50 | 0.50 | 0.45 |

## 9.5. DRYING SHRINKAGE AND MOISTURE MOVEMENT

1. Drying shrinkage, and subsequent expansion on rewetting, is often a source of micro- (and even macro - ) cracking in concrete.

2. Shrinkage is influenced by a number of factors, including aggregate, water/cement ratio, mix design, weather, etc. Pozzolanic materials often increase the drying shrinkage of concrete, and air-entraining agents, by permitting the use of less water, tend to reduce it.

3. The Marine cement produced, therefore, should not be much different from normal cement, but it was deemed advisable to check it.

4. There have been many arguments about this type of test, the factors influencing the "absolute" results obtained, and the interpretation of results. I decided to use standard 10" x 1" x 1" bars, and a mortar mix of 1 cement to 3 standard sand. The idea was simply to check one cement against another under the same conditions.

5. Test conditions used were generally as described in BS.1881 "Methods of Testing Concrete" (18.7).

6. The specimens were de-moulded at 1 day, measured after 7 days, and remeasured after 28 days in water for the initial "wet" measurement. They were then dried to constant length in an oven at 50°C to obtain the "dry" measurement, and the difference between this and the "wet" measurement was taken as "Drying Shrinkage". The specimens were then re-immersed in water for four days, re-measured, and the increase in length taken as "Moisture Movement".

7. All results/.............

7. All results are given in Table No.69. The actual changes in length of the bars are illustrated in Figures 39 and 40.

TABLE NO.69

DRYING SHRINKAGE AND MOISTURE MOVEMENT OF OPC AND CM-2

| "TREATMENT" ETC | OPC | MARINE CEMENT | |
|---|---|---|---|
| W/C Ratio | 0.50 | 0.50 | 0.45 |
| " Length" after demoulding: | 0 | 0 | 0 |
| + 6 days in Humidity Cupboard | -0.019" | -0.018" | -0.018" |
| % Contraction | 0.19 | 0.18 | 0.18 |
| + 28 days in water | +0.002" | -0.003" | -0.004" |
| % Expansion | 0.21 | 0.15 | 0.14 |
| 7 days drying | -0.049" | -0.052" | -0.054" |
| % Drying shrinkage | 0.51 | 0.49 | 0.50 |
| + 4 days in water | -0.008" | -0.024" | -0.020" |
| % Moisture movement | 0.41 | 0.28 | 0.34 |
| "Length" after demoulding | 0 | 0 | 0 |
| + 6 days in water | +0.007" | +0.004" | +0.003" |
| % Expansion | 0.07 | 0.04 | 0.03 |
| + 28 days in water | +0.040" | +0.010 | +0.006 |
| % Expansion (7 to 35 days) | 0.33 | 0.06 | 0.03 |
| % Expansion (total) | 0.40 | 0.10 | 0.06 |
| + 7 days drying | -0.036" | -0.056" | -0.054" |
| % Drying Shrinkage | 0.76 | 0.66 | 0.60 |
| + 4 days in water | +0.017 | -0.025" | -0.021" |
| % Moisture movement | 0.53 | 0.31 | 0.33 |

Figures 39 and 40

pages 250 and 251

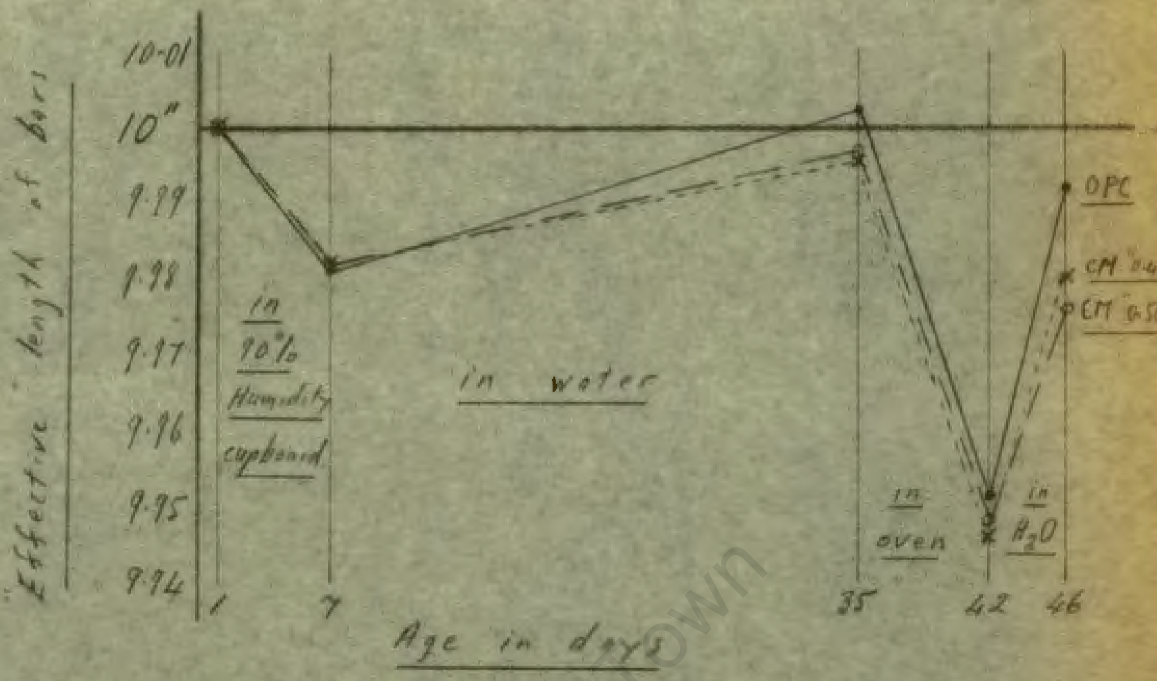


Fig No. 39 Shrinkage/Expansion of mortar bars

Legend:
O.P.C. with 0.50 w/c ratio : ————
C.M. with 0.45 w/c ratio : ············
C.M. with 0.50 w/c ratio : – – – –

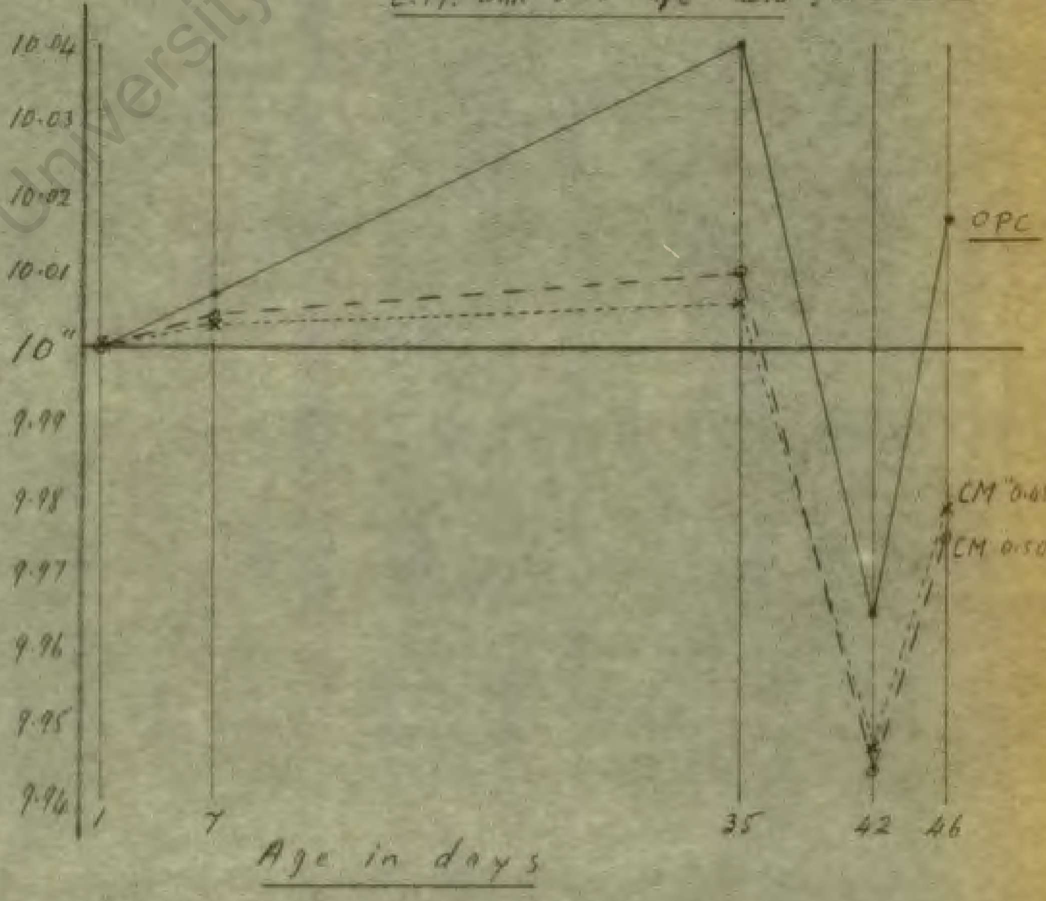


Fig. No. 40 Expansion/Shrinkage of mortar bars

8. The results obtained were:

| PROPERTY ETC. | OPC | CM-2 | CM-2 |
|---|---|---|---|
| Water/Cement ratio | 0.50 | 0.50 | 0.45 |
| <u>1st 7 days in Humidity Cupboard</u>: | | | |
| Drying shrinkage | 0.51% | 0.49% | 0.50% |
| Moisture movement | 0.41% | 0.28% | 0.34% |
| <u>1st day in Humidity cupboard, followed by water curing</u>. | | | |
| Drying shrinkage | 0.76% | 0.66% | 0.60% |
| Moisture movement | 0.53% | 0.31% | 0.33% |

9. Differences in drying shrinkage are probably not significant, but the CM-2 sample does appear to have a lower moisture movement than the O.P.C.

10. Reference: 18.7

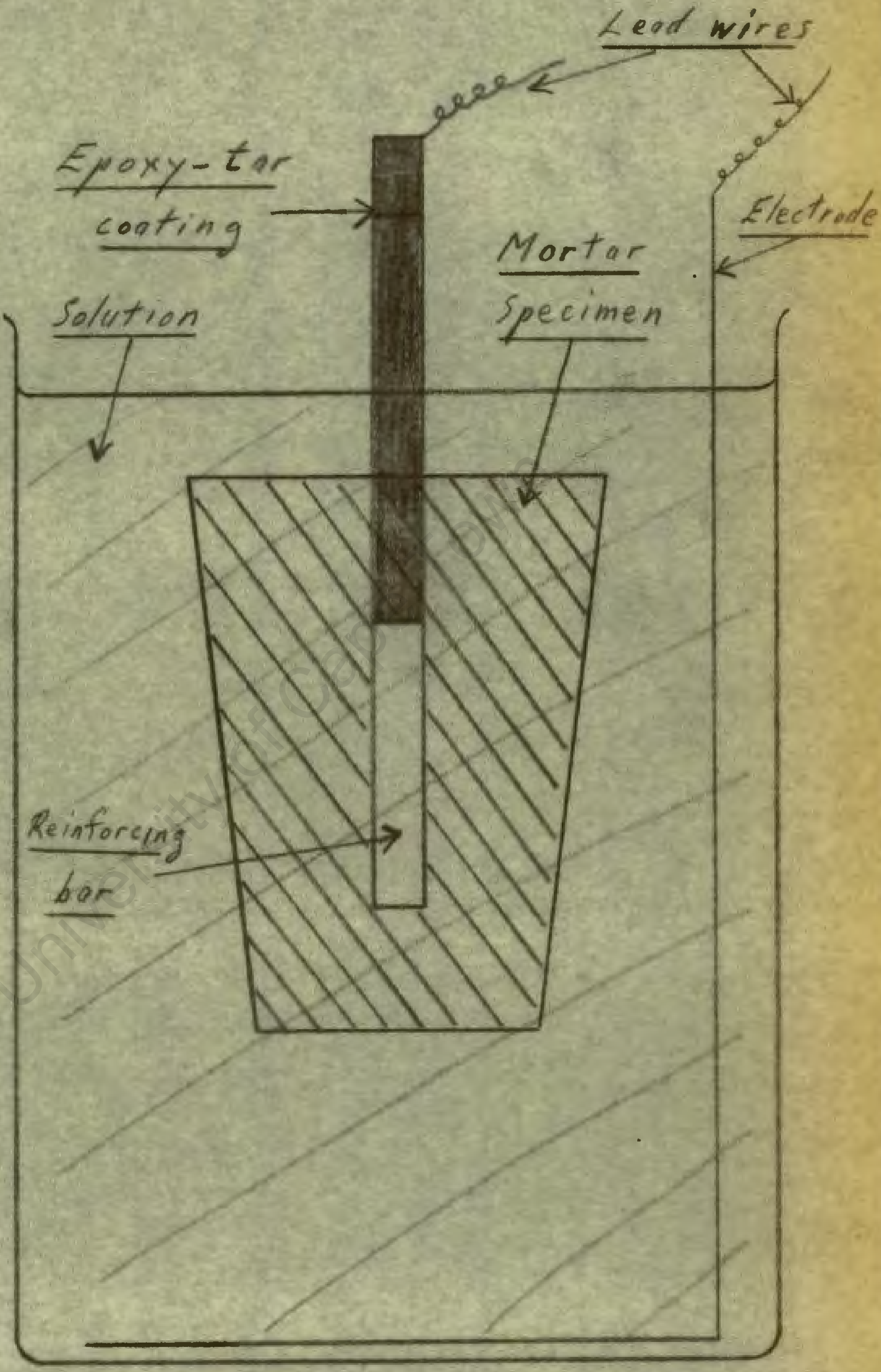
## 9.6. "PERMEABILITY" TEST

1. Some initial "exploratory" tests have been carried out with a view to checking, indirectly, the permeability of mortar specimens by electrical means.

2. Specimens were made up in plastic or paper "cups" (so as not to contaminate the specimens with oil from steel moulds), and a short length of reinforcing rod inserted in the centre. These rods were coated at the top with epoxy tar paint so that only the portion actually inside the mortar was "unprotected" - see Figure No.41 Before coating it with paint a lead wire was soldered to the top of the bar.

Figure No.41/........

# Sketch of Specimen for "Permeability" Tests.



Scale : = "life-size"

Fig. No. 41.

3. The following general tests have been carried out on these specimens:

3.1. Some were partially immersed in sodium chloride solution and connected to a battery through copper coulometers. The electrodes were weighed periodically to determine the amount of current which had passed through the specimens, from which their electrical resistances were calculated. There was an indication that Marine Cement mortar had higher resistance than OPC mortar, but a number of "snags" were encountered, and the test is to be repeated with silver coulometers.

3.2. Another set of specimens were immersed in a solution of sodium chloride and magnesium sulphate and their potential emf's determined relative to a glass electrode. Here, too, the CM-3 seemed to be giving better protection to the steel, but improved techniques are obviously needed and all tests are to be repeated under better conditions.

3.3. Hausmann has reported on some similar work in a recent issue of the American Concrete Institute Journal (20.50)

## 9.7. TESTS IN "MARINE ENVIRONMENTS"

1. A number of specimens similar to those described in the previous section were made up. Through the kind offices of Commander Copenhagen, of the C.S.I.R.Corrosion Unit, arrangements were made to expose these to "marine environments" at the Sea Point Aquarium. Some of the specimens have been partially immersed in running sea water, and the others have been hung above the tanks in the "salty atmosphere".

2. After three months some of the O.P.C.specimens showed signs of iron "staining", but all the Marine Cement specimens were "clean". The test is continuing.

# CHAPTER 10

## CONCLUSION

10.1 The averred aim of this project was to produce "sulphate-resisting and marine cements from local raw materials". That is, to produce cements which will assist South African engineers, builders and contractors to make concrete more durable under the aggressive conditions of sulphatic and marine environments.

10.2 A thorough study was made of the literature of similar cements produced elsewhere, raw materials were investigated, experiments carried out, and, finally, two "new" types of cement were produced. These cements were then subjected to intensive testing to reveal their strengths and weaknesses, so that proper recommendations can be made as to their use.

10.3 Some of the test methods, particularly those used for checking "Pozzolanic Activity", may seem somewhat "crude" to the pure analyst, but cement seldom lends itself to "exact" treatment.

10.4 The emphasis throughout has been on "comparing" the properties of the special cements with those of "ordinary" Portland cement. I feel that the test results have indicated conclusively that, properly used for their designed purposes, these two special cements will help to make structures which will "survive" longer than concrete made with ordinary cement would have done, because they will be "fitter". There seems to be no valid reason why these cements, "Sulfacem" and "Cemarine", should not be able to compete with similar cements made anywhere in the world, and, in fact, they may even have a slight "edge" on the others.

3rd October, 1964

# APPENDIX 1

## "A SULPHATE SUSCEPTIBILITY TEST FOR PORTLAND CEMENT"

BY TAYLOR AND BOGUE

REFERENCE : 2.7

PARAGRAPH : 4.3 - 1

METHOD:

"The $SO_3$ content of the cement to be tested is first determined by any acceptable procedure.

About 30g of Ottawa sand, or some similar sand, is placed in a dry 100-ml. graduated cylinder, so designed that it can be fitted with a stopper. (A blank determination should be made with each lot of sand employed). A sample of cement is weighed out equal in grams to 5.4 divided by the percentage of $SO_3$ in the cement. This sample is placed in the cylinder containing the sand. One hundred millilitres of saturated limewater is measured in a 100-ml. pipette and added rapidly to the cylinder by inverting the pipette. A clean rubber stopper is inserted and the mixture at once shaken vigorously by hand. The cylinder is fastened to a rotary shaker that is operated at a rate of 60 r.p.m. for 6 hours from the time of the addition of the limewater. (The rack should be so designed that no cylinder is more than 6 ins. from the hub). In order to obtain consistent results within a laboratory or between different laboratories, it is essential that the test be performed at a constant temperature.

Just before the end of the 6-hour reaction period, a 9-cm No.42 filter paper (or a comparable paper) is inserted in a Buchner funnel and moistened with distilled water. Suction is applied, and the contents of the cylinder are poured into the funnel. The cylinder is washed with 50 to 60 ml. of distilled water and the washings poured onto the funnel. This step is repeated once.

The filtrate is transferred to a 600-ml beaker. The filter

flask/..................

flask is twice washed with 50 to 60 ml. of distilled water and the washings added to the filtrate. The volume is then made up to about 350 ml, 5 ml. of concentrated HCl added, and the weight of $SO_3$ determined by precipitation with $BaCl_2$ solution in accordance with standard procedure.

After the amount of $SO_3$ remaining in the solution is determined, that value is subtracted from the amount of $SO_3$ that was present in the sample of the cement taken. This difference is assumed to be the quantity of $SO_3$ that has reacted to form calcium sulfo-aluminate during the period of the test. This is calculated as percentage of the $SO_3$ originally present in the cement and is designated as the 'sulfate reaction value'. The values are reported to the nearest whole number."

# APPENDIX 2

## "A SULPHATE SUSCEPTIBILITY TEST FOR PORTLAND CEMENT" MODIFIED TAYLOR AND BOGUE METHOD

PARAGRAPH : 4.3 - 1

METHOD:

1. Determine the sulphate content of the cement or ground clinker.

2. Place 30 grams of standard sand in a stoppered 100 ml. measuring cylinder. Add weights of cement or clinker sample and of A.R. quality $CaSO_4.2H_2O$ in accordance with the table below.

3. Pipette 100 ml. of saturated limewater into the measuring cylinder, insert its stopper, and shake vigorously for 30 seconds.

4. Mix the contents of the cylinder for a further 6 hours on the rotary shaker.

5. Then filter through a Whatman No.42 paper, using vacuum. Wash the cylinder twice, using 50 - 60 ml. distilled water per washing.

6. Transfer the filtrate to a 600 ml. beaker, and wash the filter flask twice with 50 - 60 ml. distilled water, adding the washings to the beaker. Add sufficient distilled water to bring the volume to about 350 ml.

7. Add 5 ml. of concentrated hydrochloric acid, and determine the $SO_3$ content gravimetrically, using barium chloride.

8. Calculate the Sulphate Reaction Value (SRV) as follows:-

$$\underline{SRV = 100 - 1850 \times S}$$

Where S = grams of $SO_3$ which remained in solution.

9. A blank/.................

9. A blank test must be performed on the sand, and the blank value subtracted if necessary.

## 10. WEIGHTS OF CEMENT (OR CLINKER) SAMPLE AND $CaSO_4.2H_2O$ TO BE USED

| % $SO_3$ in Cement | Wt. of Cement | Wt. of $CaSO_4.2H_2O$ | % $SO_3$ in Cement | Wt. of Cement | Wt. of $CaSO_4.2H_2O$ |
|---|---|---|---|---|---|
| | grams | grams | | grams | grams |
| 0.0 | 1.684 | 0.116 | 1.5 | 1.740 | 0.060 |
| 0.1 | 1.687 | 0.113 | 1.6 | 1.744 | 0.056 |
| 0.2 | 1.691 | 0.109 | 1.7 | 1.748 | 0.052 |
| 0.3 | 1.695 | 0.105 | 1.8 | 1.752 | 0.048 |
| 0.4 | 1.698 | 0.102 | 1.9 | 1.756 | 0.044 |
| 0.5 | 1.702 | 0.098 | 2.0 | 1.760 | 0.040 |
| 0.6 | 1.706 | 0.094 | 2.1 | 1.764 | 0.036 |
| 0.7 | 1.710 | 0.090 | 2.2 | 1.768 | 0.032 |
| 0.8 | 1.713 | 0.087 | 2.3 | 1.772 | 0.028 |
| 0.9 | 1.717 | 0.083 | 2.4 | 1.776 | 0.024 |
| 1.0 | 1.721 | 0.079 | 2.5 | 1.780 | 0.020 |
| 1.1 | 1.725 | 0.075 | 2.6 | 1.784 | 0.016 |
| 1.2 | 1.728 | 0.072 | 2.7 | 1.788 | 0.012 |
| 1.3 | 1.732 | 0.068 | 2.8 | 1.792 | 0.008 |
| 1.4 | 1.736 | 0.064 | 2.9 | 1.796 | 0.004 |
| 1.5 | 1.740 | 0.060 | 3.0 | 1.800 | 0.000 |

## APPENDIX 3

## RELATIONSHIP BETWEEN, AND CORRELATION OF, SULPHATE REACTION VALUES OBTAINED BY THE BOGUE AND THE MODIFIED TEST METHODS.

It is assumed that a given weight of tri-calcium aluminate, in a particular cement, will react with a definite weight of $SO_3$ in both test methods.

### 1. Calculations by the Bogue Method:

Let : S1 = % $SO_3$ in the cement.

S2 = weight of cement used

$= \frac{5.4}{S1}$

S3 = weight of $SO_3$ in sample

= 0.054 grams (both methods)

S4 = wt.of $SO_3$ remaining in soln. after shaking.

S5 = wt.of $SO_3$ used up by aluminate

= S3 - S4

$$\text{S.R.V.} = \frac{S3 - S4}{S3} \times 100$$

$$= \frac{S5}{S3} \times 100$$

$$= \frac{S5}{0.054} \times 100$$

$$= \underline{1853 \times S5}$$

Call this "Old" S.R.V.

### 2. Calculations for the Modified Method:

S6 = weight of Cement + $CaSO_4 \cdot 2H_2O$

= 1,800 grams.

S7 = % $SO_3$ in $CaSO_4 \cdot 2H_2O$

= 46.5%

S8 /......................

## 2. Calculations for the Modified Method: Continued

$$S8 = \% \ SO_3 \text{ in mixture of Cement} + CaSO_4.2H_2O$$

$$= \underline{3.0} \ \%$$

S9 = weight of cement used in modified method.

$$= \frac{S7 - S8}{S7 - S1} \times 1.800$$

$$= \frac{43.5}{46.5 - S1} \times 1.800$$

$$= \frac{78.3}{46.5 - S1}$$

S10 = weight of $SO_3$ used up in modified method.

$$\text{"New" SRV} = \underline{1853 \times S10}$$

## 3. Correlations:

S2 g cement reacted with S5 g $SO_3$ (para. 1)

therefore S9 g cement will react with $\frac{S5 \times S9}{S2}$ g $SO_3$

$$\text{i.e. } S10 = \frac{S5 \times S9}{S2}$$

$$\text{but } S2 = \frac{5.4}{S1} \quad \text{(paragraph 1)}$$

$$\text{and } S9 = \frac{78.3}{46.5 - S1} \quad \text{(paragraph 2)}$$

$$\text{therefore } S10 = S5 \times \frac{78.3}{46.5 - S1} \times \frac{S1}{5.4}$$

$$= S5 \times \frac{14.5 \times S1}{46.5 - S1}$$

$$\text{"New" SRV} = 1853 \times S10 \quad \text{(paragraph 2)}$$

$$= 1853 \times S5 \times \frac{14.5 \times S1}{46.5 - S1}$$

but 1853 x S5 = "Old" SRV (paragraph 1 )

therefore:

$$\text{"New" SRV} = \text{"Old" SRV} \times \frac{14.5 \times S1}{46.5 - S1}$$

(where S1 = % $SO_3$ in Cement )

4. Tabulation/..........

## 4. Tabulation:

| S1 = | 1.0 | 1.5 | 1.8 | 1.9 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|---|---|
| a = 14.5 x S1 = | 14.5 | 21.75 | 26.1 | 27.55 | 29.0 | 36.25 | 43.5 |
| b = 46.5 - S1 = | 45.5 | 45.0 | 44.7 | 44.6 | 44.5 | 44.0 | 43.5 |
| a/b = | 0.319 | 0.483 | 0.584 | 0.618 | 0.652 | 0.824 | 1.000 |
| "Old" SRV : | "New" Sulphate Reaction Values | | | | | | |
| 20 | 6 | 10 | 12 | 12 | 13 | 16 | 20 |
| 30 | 10 | 14 | 17 | 18 | 20 | 25 | 30 |
| 40 | 13 | 19 | 23 | 25 | 26 | 33 | 40 |
| 50 | 16 | 24 | 29 | 31 | 33 | 41 | 50 |
| 60 | 19 | 29 | 35 | 37 | 39 | 49 | 60 |
| 65 | 21 | 31 | 38 | 40 | 42 | 54 | 65 |
| 70 | 22 | 34 | 41 | 43 | 46 | 58 | 70 |
| 80 | 25 | 39 | 47 | 49 | 52 | 66 | 80 |
| % $SO_3$ | 1.0 | 1.5 | 1.8 | 1.9 | 2.0 | 2.5 | 3.0 |

## 5. Justification:

Davis (23.5) checked the "Bogue" method on a clinker with varying amounts of $CaSO_4.2H_2O$ and obtained the following results:

| | | | | | | |
|---|---|---|---|---|---|---|
| $CaSO_4.2H_2O$ | : | 3% | 4% | 5% | 6% | 7% |
| SRV | : | 64 | 45 | 37 | 30 | 24 |
| % $SO_3$ (by calculation) | : | 1.40 | 1.86 | 2.33 | 2.79 | 3.26 |

Putting the/ ....................

Putting the equations of paragraphs 2 & 3 above into a "general" form, we get:

$$\text{New SRV} = \text{Old SRV} \times \frac{SC}{SM} \times \frac{46.5 - SM}{46.5 - SC}$$

where : $SC = \%\ SO_3$ in "cement"

& $SM = \%\ SO_3$ in "mixture"

If we take the 4% mix (1.86% $SO_3$) as the "cement", and the other mixes as the "mixtures", we can calculate the SRV for each, thus:

$$\underline{\text{New}}\ \text{SRV} = \text{Old SRV} \times \frac{1.86}{SM} \times \frac{46.5 - SM}{44.64}$$

$$= 45 \times \frac{1.86}{44.64} \times \frac{46.5 - SM}{SM}$$

$$= 1.875 \times \frac{46.5 - SM}{SM}$$

---

**For 3% $CaSO_4.2H_2O$**

$$\text{New SRV} = 1.875 \times \frac{46.5 - 1.40}{1.40}$$

$$\underline{= 60}$$

**For 5% $CaSO_4.2H_2O$**

$$\text{New SRV} = 1.875 \times \frac{46.5 - 2.33}{2.33}$$

$$\underline{= 36}$$

**For 6% $CaSO_4.2H_2O$.**

$$\text{New SRV} = 1.875 \times \frac{46.5 - 2.79}{2.79}$$

$$\underline{= 29}$$

**For 7% $CaSO_4.2H_2O$**

$$\text{New SRV} = 1.875 \times \frac{46.5 - 3.26}{3.26}$$

$$\underline{= 25}$$

Summary/..................

## Summary of Results:

| % $CaSO_4.2H_2O$ in mix. | Sulphate Reaction Value Found | Sulphate Reaction Value Calculated |
|---|---|---|
| 3% | 64 | 60 |
| 4% ("Standard") | (45) | (45) |
| 5% | 37 | 36 |
| 6% | 30 | 29 |
| 7% | 24 | 25 |

## Conclusion:

The close agreement between the calculated values and the SRV's found by experiment indicates that correlating the "Bogue" and "Modified" results by calculation, as in paragraphs 2 & 3, is justified.

# APPENDIX 4.

## EXAMPLES OF METHODS USED FOR CALCULATING PROPORTIONS OF RAW MATERIALS REQUIRED FOR MIXES

### 4.1. FOR FIRST BATCH OF S.R.CEMENT.

1. Requirements: $C_3S$ = 50% (maximum)
$C_3A$ = 1.5% (0 - 5% )

2. Partial Analysis of Materials Available.

| OXIDES, ETC. | | LIMESTONE | SAND | SPENT-OXIDE | COAL ASH |
|---|---|---|---|---|---|
| $SiO_2$ | % | 6.7 | 93.5 | 10 | 43 |
| $Al_2O_3$ | " | 1.7 | 3.5 | 10 | 29 |
| $Fe_2O_3$ | " | 0.3 | 1.0 | 75 | 6 |
| CaO | " | 48.7 | 0.5 | - | 13 |
| $SO_3$ | " | - | - | 2 | 7 |
| Loss on Ign. | " | 41.0 | 1.0 | 2 | - |
| | | 98.4 | 99.5 | 99 | 98 |

3. Proportions:

Limestone = a = 100 x a%
Sand = b = 100 x b%
Spent-oxide = c = 100 x c%
Coal Ash = 0.015 = 1.5 %

TOTALS 1,000 100%

4. Composition of mix and clinker:

| CONSTITUENTS | | LIMESTONE | SAND | SPENT-OXIDE | ASH | TOTAL | CLINKER |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | % | 6.7a | 93.5b | 10c | 0.65 | M.S. | S |
| $Al_2O_3$ | % | 1.7a | 3.5b | 10c | 0.44 | M.A. | A |
| $Fe_2O_3$ | % | 0.3a | 1.0b | 75c | 0.09 | M.F. | F |
| CaO | % | 48.7a | 0.5b | - | 0.19 | M.C. | C |
| $SO_3$ | % | - | - | 2c | 0.10 | M.su | su |
| Loss | % | 41.0a | 1.0b | 2c | - | L | 0 (nil) |
| Totals | | 98.4a | 99.5b | 99c | 1.47 | M.T. | T |

For any clinker/............

## 4. Composition of mix and clinker: Continued.

For any clinker constituent, e.g. "S" :

$$S = \text{Total } SiO_2 \text{ in mix} \times \frac{100}{(100 - \text{Loss})}$$

$$\text{Let } M = \frac{100 - L}{100} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$\text{Then : } S = \frac{\text{Total } SiO_2 \text{ in mix}}{M}$$

Whence : Total $SiO_2$ in mix $= M \times S$

Total $Al_2O_3$ " " $= M \times A$

Total $Fe_2O_3$ " " $= M \times F$

Total $CaO$ " " $= M \times C$

Total $SO_3$ " " $= M \times su$

## 5. Equations.

$$a + b + c + 0.015 = 1.000 \quad \text{(from "proportions")}$$

$$\therefore a + b + c = 0.985 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$C_3A = 2.65\ A - 1.69\ F = 1.5 \quad \text{(postulated)}$$

$$\therefore M \times C_3A = 2.65\ MA - 1.69\ MF = 1.5 \times M$$

$$2.65\ MA = 4.51a + 9.27b + 26.50c + 1.166$$

$$1.69\ MF = 0.51a + 1.69b + 126.72c + 0.152$$

{MA and MF from Table in para. 4.}

$$\text{Subtract : } 4.00a + 7.58b - 100.22c + 1.014 = 1.5M$$

$$\therefore 2.67a + 5.05b - 66.82c + 0.676 = M \quad (3)$$

$$C_3S = 4.07\ C - (7.6S + 6.72A + 1.43F + 2.85\ su) = 50 \quad \text{(postulated)}$$

$$\therefore M \times C_3S = 4.07\ MC - (7.6\ MS + 6.72\ MA + 1.43\ MF + 2.85\ Msu) = 50 \times M$$

$$= 4.07\ MC - t = 50\ M \quad \ldots\ldots\ldots\ldots\ldots\ldots (3a)$$

$$7.60\ MS = 50.92a + 710.65b + 76.00c + 4.94$$

$$6.72\ MA = 11.42a + 23.52b + 67.20c + 2.95$$

$$1.43\ MF = 0.43a + 1.43b + 107.25c + 0.13$$

$$2.85\ Msu = - \quad - \quad 5.70c + 0.28$$

$$\text{Add : } 62.77a + 735.60b + 256.15c + 8.30 = t \ldots\ldots (3b)$$

4.07 MC/..........

$$4.07\ MC = 198.20a + 2.03b + 0.00c + 0.77$$

(3b) $$t = 62.77a + 735.60b + 256.15c + 8.30$$

Subtract : $135.43a - 733.57b - 256.15c - 7.53 = 50\ M$ (from 3a)

$$\therefore \quad 2.71a - 14.67b - 5.12c - 0.151 = M \quad (4)$$

$L = 41.0a + 1.0b + 2.0c$ (from para.4 above).

(1) : $$M = \frac{100 - L}{100}$$

$$\therefore \quad 100M = 100 - L$$

$$= 100 - 41.0a - 1.0b - 2.0c$$

$$\therefore \quad -0.41a - 0.01b - 0.02c + 1.000 = M \quad (5)$$

(3) : $2.67a + 5.05b - 66.82c + 0.676 = M$

(5) : $-0.41a - 0.01b - 0.02c + 1.000 = M$

Subtract : $3.08a + 5.06b - 66.80c - 0.324 = 0$

$$\therefore \quad 3.08a + 5.06b - 66.80c = 0.324 \quad (6)$$

(4) : $2.71a - 14.67b - 5.12c - 0.151 = M$

(5) : $-0.41a - 0.01b - 0.02c + 1.000 = M$

Subtract : $3.12a - 14.66b - 5.10c - 1.151 = 0$

$$\therefore \quad 3.12a - 14.66b - 5.10c = 1.151 \quad (7)$$

## 6. Solution of Equations:

We now have three equations:

(2) $a + b + c = 0.985$

(6) $3.08a + 5.06b - 66.80c = 0.324$

and (7) $3.12a + 14.66b - 5.10c = 1.151$

for the three unknowns, a, b & c.

(6) : $3.08a + 5.06b - 66.80c = 0.324$

(2) x 3.08 : $3.08a + 3.08b + 3.08c = 3.034$

Subtract: $1.98b - 69.88c = -2.710 \quad (8)$

(7) : 3.12a /.................

$$\begin{array}{lll} (7) & : & 3.12a - 14.66b - 5.10c = 1.151 \\ (2) \times 3.12 & : & \underline{3.12a + 3.12b + 3.12c = 3.073} \\ \text{Subtract:} & & \underline{-17.78b - 8.22c = -1.922} \quad (9) \end{array}$$

$$\begin{array}{lll} (8) & : & 1.98b - 69.88c = -2.710 \\ (9) \div 8.98 & : & \underline{-1.98b - 0.92c = -0.214} \\ \text{Add} & : & -70.80c = -2.924 \end{array}$$

$$\therefore \quad \underline{c} = \frac{2.924}{70.80} = \underline{0.0413}$$

and $\underline{\underline{100.c = 4.1}}$

Substitute $c = 0.0413$ in (8)

Then : $1.98b - 2.886 = 2.710$

$\therefore \quad 1.98b = 0.176$

$$\therefore \quad \underline{b} = \frac{0.176}{1.98} = \underline{0.0889}$$

and: $\underline{\underline{100\ b = 8.9}}$

Substitute $c = 0.0413$ and $b = 0.0889$ in (2),

Then : $a + 0.0889 + 0.0413 = 0.985$

$\therefore \quad \underline{a} = 0.9850 - 0.1302 = \underline{0.8448}$

and : $\underline{\underline{100\ a = 84.5}}$

7. **Mix Proportions Used:**

| | | | |
|---|---|---|---|
| Limestone | : | $84\frac{1}{2}$ % | (calculated value = 84.5) |
| Sand | : | 9 % | ( " " = 8.9) |
| Spent-Oxide | : | 4 % | ( " " = 4.1) |
| Ash pick-up | : | $1\frac{1}{2}$ % | |
| | | 100 % | |

Using these values to calculate the theoretical clinker composition gave:

| | | | | | |
|---|---|---|---|---|---|
| Potential | $C_3S$ | : | 49.7% | (Reqd : | 50% ) |
| Potential | $C_3A$ | : | 1.6% | ( " : | $1\frac{1}{2}$% ) |

See Table No.7/..............

See Table No.7, on page 82, for details of the calculation and of the other mix constituents.

## 4.2. FOR THE HIGH-LIME S.R. CEMENT.

1. Requirements:

$C_3S$ = Maximum obtainable

$C_3A$ = 1% ( 0 - 5% )

To obtain the maximum $C_3S$ the CaO content must be as high as possible but there is no point in adding much more CaO than can be combined with the other constituents. There are two possible methods of calculating mix proportions for maximum $C_3S$ :

1.1. Postulate $C_2S$ = 0%

This gave proportions of:

| | | |
|---|---|---|
| Limestone | : | 84.8 % |
| Sand | : | 11.1 % |
| Iron Ore | : | 2.6 % |
| Ash | : | 1.5 % |
| | | 100.0 % |

Calculations for the above are given in paragraphs 5 and 6 below.

1.2. An L.S.F. of 1.00 gives the maximum CaO which can be combined with the other constituents , but an L.S.F. of 1.02 is permitted by B.S.12 and S.A.B.S.471.
A small surplus of CaO in the mix should according to the "Law of Mass Re-action" (28.6), assist in obtaining full combination of the other materials.
A free-lime content of 1% is quite tolerable in clinker, and for this an L.S.F. of 1.015 is required - see paragraph 7.6 below.
Using this method the proportions came out at:

Limestone :85.0%/.............

| | | | |
|---|---|---|---|
| Limestone | : | 85.0 | % |
| Sand | : | 10.9 | % |
| Iron Ore | : | 2.6 | % |
| Ash | : | 1.5 | % |
| | | 100.0 | |

Details of the calculations are given in paragraphs 5 and 7 below.

2. Partial Analysis of Materials Available.

| OXIDE | LIMESTONE | SAND | IRON-ORE | COAL ASH |
|---|---|---|---|---|
| $SiO_2$ % | 3.3 | 93.5 | 14 | 43 |
| $Al_2O_3$ % | 0.8 | 3.5 | 9 | 29 |
| $Fe_2O_3$ % | 0.3 | 1.0 | 73 | 6 |
| CaO % | 51.0 | 0.5 | - | 13 |
| $SO_3$ % | - | .. | - | 7 |
| Loss on Ign. % | 43.3 | 1.0 | 3 | - |
| TOTALS | 98.7 | 99.5 | 99 | 98 |

3. Proportions:

| | | | | |
|---|---|---|---|---|
| Limestone | = | a | = | 100 x a % |
| Sand | = | b | = | 100 x b % |
| Iron Ore | = | c | = | 100 x c % |
| Coal Ash | = | 0.015 | = | 1.5 % |
| TOTALS | = | 1.000 | = | 100% |

4. Composition of mix and clinker:

| CONSTITUENTS | LIMESTONE | SAND | IRON ORE | ASH | TOTAL | CLINKER |
|---|---|---|---|---|---|---|
| $SiO_2$ | 3.3a | 93.5b | 14c | 0.65 | M.S | S |
| $Al_2O_3$ | 0.8a | 3.5b | 9c | 0.44 | M.A. | A |
| $Fe_2O_3$ | 0.3a | 1.0b | 73c | 0.09 | M.F. | F |
| CaO | 51.0a | 0.5b | - | 0.19 | M.C. | C |
| $SO_3$ | - | - | - | 0.10 | M.su | su |
| Loss | 43.3a | 1.0b | 3c | - | L | - |
| TOTALS | 98.7a | 99.5b | 99c | 1.47 | M.T. | T |

5. Equations common to both calculations.

Once again:

$$M = \frac{100 - L}{100} \qquad (1)$$

(see paragraph 4.1 - 4 )

and: $a + b + c = 0.985 \qquad (2)$

(see paragraphs 4.1 - 5 and 4.2 - 3 )

$C_3A = 2.65\ A - 1.69\ F = 1.0$ (postulated).

$\therefore\ M \times C_3A = 2.65\ MA - 1.69\ MF = 1.0 \times M = M$

$$\begin{aligned} 2.65\ MA &= 2.12a + 9.27b + 23.85c + 1.166 \\ 1.69\ MF &= 0.51a + 1.69b + 123.37c + 0.152 \end{aligned}$$

Subtract : $1.61a + 7.58b - 99.52c + 1.014 = M \qquad (3)$

$$(1) \qquad M = \frac{100 - L}{100}$$

$$\begin{aligned} \therefore\ 100\ M &= 100 - L \\ &= 100 - 43.3a - 1.0b - 3.0c \end{aligned}$$

$\therefore\ M = 1 - 0.43a - 0.01b - 0.03c.$

or $-0.43a - 0.01b - 0.03c + 1.000 = M \qquad (4)$

$$\begin{aligned} (3) &:\ 1.61a + 7.58b - 99.52c + 1.014 = M \\ (4) &:\ -0.43a - 0.01b - 0.03c + 1.000 = M \end{aligned}$$

Subtract : $2.04a + 7.59b - 99.49c + 0.014 = 0$

$$\begin{aligned} \therefore\ 2.04a + 7.59b - 99.49c &= -0.014 \\ (2) \times 2.04:\ 2.04a + 2.04b + 2.04c &= 2.009 \end{aligned}$$

Subtract: $5.55b - 101.53c = -2.023 \qquad (5)$

6. Calculations for 1st method (paragraph 1.1 above)

$C_2S = 8.6\ S + 5.07\ A + 1.08F + 2.15\ su - 3.07C = 0$ (postulated)

$\therefore\ M \times C_2S = 8.6MS + 5.07\ MA + 1.08MF + 2.15\ Msu - 3.07MC = 0$

$$\begin{aligned} 8.60MS &= 28.38a + 804.00b + 120.40c + 5.590 \\ 5.07MA &= 4.06a + 17.75b + 45.63c + 2.231 \\ 1.08MF &= 0.32a + 1.08b + 78.84c + 0.097 \\ 2.15Msu &= - \quad - \quad - \quad 0.215 \end{aligned}$$

Add : 32.76a/..........

$$\begin{array}{lrcrcrcrcl}
\text{Add :} & 32.76a & + & 822.83b & + & 244.87c & + & 8.133 & & \\
3.07MC: & 156.58a & + & 1.53b & & - & + & 0.583 & & \\
\hline
\text{Subtract:} & -123.82a & + & 821.30b & + & 244.87c & + & 7.550 & = & 0 \\
\therefore & -123.82a & + & 821.30b & + & 244.87c & = & -7.550 & & \\
(2) \times 123.82: & 123.82a & + & 123.82b & + & 123.82c & = & 121.980 & & \\
\hline
\text{Add :} & & & 945.12b & + & 368.69c & = & 114.43 & & (6)
\end{array}$$

$$\begin{array}{lrcl}
(5)\ : & 5.55b - 101.53c & = & -2.023 \\
(6) \div 170.3: & 5.55b + 2.17c & = & 0.672 \\
\hline
\text{Subtract :} & -103.70c & = & -2.695
\end{array}$$

$$\therefore \quad \underline{c} = \frac{2.695}{103.7} = \underline{0.0260}$$

$$\text{and :} \quad \underline{\underline{100\,c = 2.6}}$$

Substitute $c = 0.0260$ in (5)

$$\begin{array}{lrcl}
\text{Then :} & 5.55b - 2.639 & = & -2.023 \\
\therefore & 5.55b & = & 0.616
\end{array}$$

$$\therefore \quad \underline{b} = \frac{0.616}{5.55} = \underline{0.1110}$$

$$\text{and :} \quad \underline{\underline{100b = 11.1}}$$

Substitute $b = 0.111$ and $c = 0.026$ in (2),

$$\text{Then} \quad a + 0.111 + 0.026 = 0.985$$

$$\therefore \quad \underline{a} = 0.985 - 0.137 = \underline{0.848}$$

$$\text{and :} \quad \underline{\underline{100a = 84.8}}$$

That is, by this method, the materials should be used in the proportions:

| | | |
|---|---|---|
| Limestone | : | 84.8% |
| Sand | : | 11.1% |
| Iron Ore | : | 2.6% |
| Ash | : | 1.5% |
| | | 100.0% |

7. Calculations for 2nd method (paragraph 1.2 above)

7.1. $$\text{L.S.F.} = \frac{C - 0.7\,su}{2.8S + 1.2A + 0.65F}$$

7.2 For an L.S.F. of /............

7.2. For an L.S.F. of 1.00 the combination of CaO with other constituents should be complete. Call this value of CaO "$C_1$"

7.3. An L.S.F. greater than 1.00 means that there will be uncombined, or "free" CaO present. Call the amount of free CaO "$C_f$".

7.4. The postulated value for $C_f$ is 1% (see paragraph 1.2 above). The equivalent L.S.F. must now be calculated. Call this L.S.F. "m" and the requisite value for CaO "$C_m$".

7.5. Assumptions:

Approximate values for $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ are:

| | |
|---|---|
| $SiO_2$ : | 22% |
| $Al_2O_3$ : | 3% |
| $Fe_2O_3$ : | 4% |

Then 2.8S = 61.6%
1.2A = 3.6%
0.65F = 2.6%
Add : 67.8%

i.e. $2.8S + 1.2A + 0.65F = 67.8\%$

7.6. Calculation of L.S.F.

$$C_m = C_1 + C_f$$

$$\frac{C_1 - 0.7su}{2.8S + 1.2A + 0.65F} = 1$$

$$\therefore C_1 - 0.7su = 2.8S + 1.2A + 0.65F$$
$$= 67.8\% \text{ (para. 7.5)}$$

$$\therefore C_1 = 67.8 + 0.7su$$

$$\frac{Cm - 0.7\ su}{2.8S + 1.2A + 0.65F} = M$$ /........

$$\frac{C_m - 0.7su}{2.8S + 1.2A + 0.65F} = m$$

$$\therefore \quad C_m - 0.7su = m\,(2.8S + 1.2A + 0.65F)$$
$$= 67.8m$$

$$\therefore \quad C_m = 67.8\,m + 0.7su$$
$$C_1 = 67.8 + 0.7su$$

Subtract: $C_m - C_1 = 67.8\,(m - 1)$

but $C_m = C_1 + C_f$

$$\therefore \quad C_1 + C_f - C_1 = 67.8\,(m - 1)$$

i.e. $C_f = 67.8\,(m - 1)$

It was postulated (para 7.4) that:

$$C_f = 1$$

$$\therefore \quad 67.8\,(m - 1) = 1$$
$$\therefore \quad 67.8m - 67.8 = 1$$
$$\therefore \quad 67.8m = 68.8$$
$$\therefore \quad m = \frac{68.8}{67.8}$$
$$= 1.015$$

i.e. For a free-CaO of 1% in the clinker, the L.S.F must be 1.015

## 7.7. Equations for calculating a, b & c.

From paragraph 5 above:

(2) $a + b + c = 0.985$

(5) $5.55b - 101.53c = -2.203$

Additional:

$$\text{L.S.F.} = \frac{C - 0.7su}{2.8S + 1.2A + 0.65F} = 1.015 \text{ (para. 7.6}$$

$$= \frac{M\,(C - 0.7su\ )}{M\,(2.8S + 1.2A + 0.65F)}$$

$$= \frac{MC - 0.7Msu}{2.8MS + 1.2MA + 0.65MF} = \frac{r}{t}$$

$MC = 51.0a + 0.5b + 0.19$

$0.7\ Msu = 0.07$

Subtract: $51.0a + 0.5b + 0.12 = r$

$2.8\ MS = 9.24a + 261.80b$/..........

$$\begin{array}{lcrcrcrcrcl}
2.8MS & = & 9.24a & + & 261.80b & + & 39.20c & + & 1.82 & & \\
1.2MA & = & 0.96a & + & 4.20b & + & 10.80c & + & 0.53 & & \\
0.65MF & = & 0.20a & + & 0.65b & + & 47.45c & + & 0.06 & & \\
\hline
\text{Add:} & & 10.40a & + & 266.65b & + & 97.45c & + & 2.41 & = & t
\end{array}$$

$$\text{L.S.F.} = \frac{r}{t} = 1.015$$

$$\therefore \quad r = 1.015\ t$$

$$\therefore \quad r - 1.015\ t = 0$$

$$\begin{array}{lcrcrcrcrcl}
r & = & 51.00a & + & 0.50b & & & + & 0.12 & & \\
1.015t & = & 10.56a & + & 270.60b & + & 98.90c & + & 2.45 & & \\
\hline
\text{Subtract:} & : & 40.44a & - & 270.10b & - & 98.90c & - & 2.31 & = & 0
\end{array}$$

$$\therefore \quad 40.44a - 270.10b - 98.90 = 2.31 \text{.......(7)}$$

### 7.8 Solution of equations;

$$\begin{array}{lcrcrcrcl}
(7) & : & 40.44a & - & 270.10b & - & 98.90c & = & 2.31 \\
(2) \times 40.44 & : & 40.44a & + & 40.44b & + & 40.44c & = & 39.83 \\
\hline
\text{Subtract} & : & & - & 310.54b & - & 139.34c & = & -37.52\text{..(8)}
\end{array}$$

$$\begin{array}{lcrcrcl}
(5) & : & 5.55b & - & 101.53c & = & -2.023 \\
(8) \div 55.94 & : & -5.55b & - & 2.49c & = & -0.671 \\
\hline
\text{Add} & : & & - & 104.02c & = & -2.694
\end{array}$$

$$\therefore \quad c = \frac{2.694}{104.02} = 0.0259$$

$$\text{and} : \quad 100\ c = 2.6$$

Substitute $c = 0.0259$ in (5),

Then : $5.55b - 2.629 = -2.023$

$\therefore \quad 5.55b = 0.606$

$$\therefore \quad b = \frac{0.606}{5.55} = 0.1092$$

$$\text{and} : \quad 100b = 10.9$$

Substitute $b = 0.1092$ and $c = 0.0259$ in (2),

Then : $a + 0.1092 + 0.0259 = 0.9850$

$\therefore \quad a = 0.9850 - 0.1351 = 0.8499$

$$\text{and} : \quad 100\ a = 85.0$$

That is,/.................

That is, according to this method, the materials should be used in the proportions:

| | | |
|---|---|---|
| Limestone | : | 85.0% |
| Sand | : | 10.9% |
| Iron Ore | : | 2.6% |
| Ash | | 1.5% |
| | | 100.0% |

The mix design was based on these figures and the calculated ratios and constituents for the clinker (Table No.13, page 94) were:

L.S.F. = 1.014

Free CaO = 1.0%

$C_3A$ = 0.9%

$C_3S$ = 84.1%

$C_2S$ = 0.5%

# APPENDIX 5

# NOTES ON THE CONSTITUTION AND CALCINATION OF CLAYS AND SHALES

## 5.1. NOTES ON SHALES, CLAYS AND CLAY MINERALS.

1. Geologically, clays are composed of various minerals of primary and secondary origin, all of which are of a comparatively "fine" or small grain size. Clays may be found in a variety of forms. They may occur as a soft paste (mud), or as a soft solid (mudstone), or as a laminated rock (shale). There are certain minerals or classes of minerals which occur in all clays and have been termed "clay minerals". Deposits of clays of all kinds are described as "argillaceous" to distinguish them from sandy ("arenaceous") formations.

2. The earliest rocks to be formed were similar to the granites diorites and other igneous formations which have crystallised from volcanic masses. These rocks, which are termed "primary" are rich in felspathic, micaceous and quartzizitic components. In the course of geological time such agglomerations have been subjected to the action of air, water and other external agencies, which have broken down the hard, crystalline formation to a finely-grained mass of "secondary" and some unchanged primary minerals. These mixtures may remain in situ or be transported and deposited elsewhere - in the first case the clay is termed "residual", whilst in the second case it is known as "sedimentary". Sedimentary clays are by far the most common.

3. The three most important primary minerals in clays derived from igneous rocks are quartz, felspars and micas. Secondary minerals are of much more common occurrence in clays and they include the clay minerals of the kaolin and

montmorillonite group/...............

and <u>montmorillonite</u> group, <u>chlorites</u>, <u>vermiculites</u> and <u>hydrous micas</u> (<u>illites</u>)

4. <u>Quartz</u> is one of the three crystalline forms in which silica ($SiO_2$) can exist, the other two being Tridymite and Cristobalite and all three polymorphic forms can exist in more than one modification with different crystal structures. The <u>con</u>version of one form to another is <u>slow</u>, as big structural rearrangements are involved. Beta-quartz changes to beta-tridymite at 870°C and to beta-cristobalite at 1470°C. In most cases cristobalite is the first crystallisation product of amorphous silica at high temperatures; tridymite may re-form from the cristobalite provided conditions are favourable. The <u>in</u>versions involve only slight structural rearrangements and the changes are instantaneously reversible. Beta-quartz changes to alpha-quartz on cooling at 573°C; beta-cristobalite to alpha-cristobalite at 220°C; $beta_2$-tridymite to $alpha_2$-tridymite at 163°C; and $beta_1$-tridymite to $alpha_1$-tridymite at 117°C. The beta modifications of all these minerals are stable at the higher temperatures and have the most symmetrical structures.

5. <u>Felspar</u> is the name given to a group alumino-silicates containing one or more of the following metals as bases: potassium, sodium, calcium and barium. The felspars form isomorphous mixtures, and, consequently, may vary greatly in composition, especially as regards the metals present. The structure of all felspars is based on a framework of silica($SiO_2$) but one which is more open than that of the silica minerals. There is a replacement of Si by Al <u>ions</u>, which results in charge deficiencies and these are balanced by cations of K, Na, Ca or Ba entering the crystal lattice, thus:

$4SiO_2 = Si_4O_8$/................

$$4SiO_2 = Si_4O_8 = Si.Si_3O_8 = Si_2.Si_2O_8$$

$$K + Al + Si.Si_3O_8 = K.Al.Si_3O_8 + Si$$

$$Ca + {}_2Al + Si_2.Si_2O_8 = Ca.Al_2.Si_2O_8 + 2\ Si.$$

(for the sake of simplicity the ionic charges have not been shown above).

6. Felspars can change to <u>kaolinite</u> ($Al_2O_3.2SiO_2.2H_2O$) under suitable weathering conditions, but the mechanism of the alteration remains something of a mystery.

7. <u>Mica</u> is a term used to designate a group of minerals crystallising in the mono-clinic system in characteristic plate-like masses or particles, and consisting of alumino-silicates of potassium, sodium, lithium, iron and magnesium. <u>Muscovite</u> ($K_2O.3Al_2O_3.6SiO_2.2H_2O$) is one of the principal micas. It usually occurs in thin flat plates or scales and, being fairly stable, is often found in clays. Hydrous micas are an alteration product of true micas from which some of the alkali ions have been leached away and more water has entered the crystal lattice; they are often known as <u>Illites</u>.

8. <u>Biotite</u> ($K\,(Mg,Fe)_3Al\,Si_3\,O_{10}\,(OH)_2$), or iron-magnesium mica, occurs either as scales or in large massive crystals of a black or dark green colour. It is the "parent" of a well-defined series in the ferro-magnesian mineral group.

9. <u>Chlorites</u>, which are degradation products of biotite, are a group of hydrous alumino-silicates with iron (either ferrous or ferric) and magnesium as essential ingredients. They are the most usual alteration products in recent clays derived from minerals rich in magnesium and iron, and they are common constituents in many sedimentary clays. The crystals are greenish flakes resembling mica in appearance, but they are

softer. The interdonvertibility of muscovite or biotite micas, montmorillonite and chlorite, under suitable conditions, is well established but no change to kaolin has been fully proved. Chlorites are double-layer minerals.

10. References: 28.1 to 28.8

## 5.2. EXTRACTS FROM: "SYMPOSIUM ON USE OF POZZOLANIC MATERIALS IN MORTARS AND CONCRETES", SPECIAL TECHNICAL PUBLICATION NO.99 - ASTM, 1949.

1. "Effect of Calcination on Natural Pozzolans" by Mielenz, Witte and Glantz, p.43.

Activity type : 3c. Essential active constituent: Illite type clay.

Sample No.70 : Shale from near Trident, Monterey. Gray to buff hard, fissile. Composed of illite with muscovite (30%), quartz and felspars (60%), iron-oxides, biotite, and other minerals (10%)

2. Effect of calcination on composition: The illite-type clays, or hydromicas are a poorly defined group of minerals apparently intermediate in composition, crystallographic structure, and properties between beidellite and muscovite. Illite-type clay minerals are common constituents of clays, shales and soils.

With heating, illite-type clays lose free water between about 30°C and 100°C; absorbed water is lost between about 100°C and 300°C; complete dehydration is accomplished at about 700°C. The details of dehydration and lattice change with calcination vary with the composition, alteration, and exchangeable cations of the illite.

The dimensions of the crystallographic lattice respond less

to calcination/..................

to calcination than do those of the montmorillonite clays. Calcination from 100°C to 870°C produces little change in the X-ray diffraction patterns of two specimens analysed, other than slight changes in position and intensity of line 001. After calcination from 870°C to 980°C the lattice has disintegrated with production in one specimen of spinel, quartz, and other unidentified compounds.

3. Effect of Calcination on Physical Properties and "Pozzolanic Activity":

Pozzolans of activity type 3c are affected significantly by calcination in the range from 430°C to 980°C. Water requirement is decreased moderately, especially after destruction of the clay by calcination at 980°C. For pozzolans of this activity type producing set of lime-pozzolan paste, time of set is reduced to a minimum by calcination of the pozzolan at 760°C. Compressive strength of lime-pozzolan mortar is improved slightly or moderately by calcination, maximum strength occurring after destruction of the clay component by heating to 980°C.

4. Effect of Calcination on Alkali Reactivity of Pozzolans:

None of the type 3c pozzolans tested proved capable of controlling alkali-aggregate reaction in high-alkali cement-pyrex glass mortars.

5. Conclusions: Calcination will improve the quality of some pozzolans, reduce the quality of others, and induce pozzolanic properties in some otherwise essentially nonreactive materials. Natural pozzolans or natural materials in which pozzolanic properties can be induced by calcination at temperatures less than 1100°C can be classified by the essential active ingredient into eight groups ......

Pozzolans of/...............

Pozzolans of activity types 3c and 3d resist changes in properties because illite-type clays and vermiculite show little change in position and structure with heating below 760 - 870°C .....

6. Reference: 13.3

# APPENDIX 6

## THE HYDRATION OF SULPHATE RESISTING PORTLAND CEMENTS

6.1 Hydration of a typical , low $C_3A$, Sulphate-Resisting ("Type V") Portland cement, with weights of reacting materials and products, can be represented thus:

**Composition of Cement :**

| | | |
|---|---|---|
| $C_3S$ | : | 50 |
| $C_2S$ | : | 29 |
| $C_3A$ | : | 2 |
| $C_4AF$ | : | 16 |
| $C\bar{S}H_2$ | : | 3 |
| Total | : | 100 |

**Hydration Reactions (simplified)**

1. $2C_3S + 6H = C_3S_2H_3 + 3CH$
   $50.0 + 11.85 = 37.5 + 24.35$

2. $2C_2S + 4H = C_3S_2H_3 + CH$
   $29.0 + 6.05 = 28.8 + 6.25$

3a. $C_3A + 3C\bar{S}H_2 + 26H = C_3A.3C\bar{S}.H_{32}$
   $1.6 + 3.0 + 2.7 = 7.3$

3b. $C_3A + 6H = C_3A\ H_6$
   $0.4 + 0.15 = 0.55$

4. $C_4AF + 2CH + 10H = C_3A\ H_6 + C_3F\ H_6$
   $16.0 + 4.9 + 5.95 = 12.45 + 14.4$

---

Adding (changing + 2CH on L.H.S.of equation 4 to -2CH on R.H.S):

---

**L.H.S.**: $2C_3S + 2C_2S + 2C_3A + C_4AF + 3C\bar{S}\ H_2 + 52H =$
$50.0 + 29.0 + 2.0 + 16.0 + 3.0 + 26.7 =$

**R.H.S.**: $= 2C_3S_2H_3 + C_3A.C\bar{S}.H_{32} + 2C_3AH_6 + C_3FH_6 + 2\ CH$
$= 66.3 + 7.3 + 13.0 + 14.4 + 25.7$

| Left Hand Side | | | | Right Hand Side | | | |
|---|---|---|---|---|---|---|---|
| | | grams. | % | | | grams | % |
| $C_3S$ | : | 50.0 | 39.5 | $C_3S_2H_3$ | : | 66.3 | 52.3 |
| $C_2S$ | : | 29.0 | 22.9 | $C_3A.3C\bar{S}.H_{32}$ | : | 7.3 | 5.8 |
| $C_3A$ | : | 2.0 | 1.55 | $C_3A.H_6$ | : | 13.0 | 10.2 |
| $C_4AF$ | : | 16.0 | 12.6 | $C_3F.H_6$ | : | 14.4 | 11.4 |
| $C\bar{S}H_2$ | : | 3.0 | 2.35 | CH | : | 25.7 | 20.3 |
| H | : | 26.7 | 21.1 | – | : | – | – |
| Totals ... | | 126.7 | 100.0 | Totals ... | | 126.7 | 100.0 |

Notes: (1) The hydrated product still contains about 20% $Ca(OH)_2$.

(2) The $C_3A\ H_6$ has only been reduced from 15.7% (para.2.3.6.) to 10.2%, but most of it comes from $C_4AF$ (instead of from $C_3A$ and so it probably takes much longer before it is in a form which can be attacked by sulphates.

6.2. For a "Ferrari-type" Sulphate-Resisting Portland Cement, the hydration will be rather more complicated. It can, perhaps, be represented thus:

| Composition of Cement: | | | |
|---|---|---|---|
| | $C_3S$ | : | 50 |
| | $C_2S$ | : | 29 |
| | $C_3A$ | : | nil |
| in solid solution | $C_4AF$ | : | 16 |
| | $C_2F$ | : | 2 |
| | $C\bar{S}H_2$ | : | 3 |
| | Total | : | 100 |

Hydration Reactions (simplified).

1. $2C_3S + 6H = C_3S_2H_3 + 3CH$
   $50.0 + 11.85 = 37.5 + 24.35$

2. $2C_2S + 4H = C_3S_2H_3 + CH$
   $29.0 + 6.05 = 28.8 + 6.25$

3. $C_3A =$ nil

4a. $C_4AF + 2CH + 10H = C_3A.H_6 + C_3F.H_6$
   $16.0 + 4.9 + 5.95 = 12.45 + 14.4$

4b. $C_3AH_6 + 3C\bar{S}H_2 + 20H = C_3A.3C\bar{S}.H_{32}$
   $2.2 + 3.0 + 2.1 = 7.3$

5. $C_2F + CH + 5H = C_3FH_6$
   $2.0 + 0.55 + 0.65 = 3.2$

---

Add, after transferring:

1. + 2 CH on L.H.S. of equation 4a to −2 CH on R.H.S.;
2. + $C_3AH_6$ on L.H.S. of equation 4b to $-C_3AH_6$ on R.H.S.;
3. + CH on L.H.S. of equation 5 to − CH on R.H.S.

---

L.H.S.: $2C_3S + 2C_2S + C_4AF + C_2F + 3C\bar{S}H_2 + 45H =$
$50.0 + 29.0 + 16.0 + 2.0 + 3.0 + 26.6 =$

R.H.S.: $= 2C_3S_2H_3 + (o)C_3AH_6 + 2C_3FH_6 + C_3A.C\bar{S}.H_{32} + CH$
$= 66.3 + 10.25 + 17.6 + 7.3 + 25.15$

| Left Hand Side | | grams | % | Right Hand Side | | grams | % |
|---|---|---|---|---|---|---|---|
| $C_3S$ | : | 50.0 | 39.5 | $C_3S_2H_3$ | : | 66.3 | 52.3 |
| $C_2S$ | : | 29.0 | 22.9 | $C_3A.3C\bar{S}.H_{32}$ | : | 7.3 | 5.8 |
| $C_4AF$ | : | 16.0 | 12.6 | $C_3AH_6$ | : | 10.25 | 8.1 |
| $C_2F$ | : | 2.0 | 1.6 | $C_3FH_6$ | : | 17.6 | 13.9 |
| $C\bar{S}H_2$ | : | 3.0 | 2.4 | CH | : | 25.15 | 19.9 |
| H | : | 26.6 | 21.0 | – | | – | – |
| Totals | : | 126.6 | 100.0 | Totals | : | 126.6 | 100.0 |

Notes: (1) The $Ca(OH)_2$ in the hydrated product is not significantly less than for other cements.

(2) The $C_3AH_6$ has now been reduced to 8.1% (15.7% in OPC and 10.8 in "ordinary" sulphate resisting – see previous paragraph. The reactions are, possibly, even slower than in the previous case.

# APPENDIX 7

## CHEMICAL TEST FOR POZZOLANIC ACTIVITY

7.1. The object of the test was to check the relative affinity of a particular shale for $Ca(OH)_2$

1. When calcined at different temperatures and
2. When calcined at a particular temperature and ground to different degrees of fineness.

7.2. To develop the test I used the first sample of shale calcined (in the laboratory) with coal (A/EF) and ground very finely (Specific surface was 13,500 $cm^2/g$).

7.3. Solubility of $Ca(OH)_2$ in water:

At 0°C : 1.85g per 1,000 ml = 185 mgm per 100 ml.
At ± 20°C : 1.6 g per 1,000 ml = 160 mgm per 100 ml.
At 100°C : 0.77g per 1,000 ml = 77 mgm per 100 ml.

(From "Handbook of Chemistry & Physics").

7.4. Standard solution of $Ca(OH)_2$

Molecular weight : 74.08g.
Equivalent weight : 37.04g.

1 N solution would contain 37.04g per 1,000 ml.

$\therefore$ N/50 solution contains $\frac{37.04}{50}$g per 1,000 ml.

= 0.74g per 1,000 ml.

= 74 mgm.per 100 ml.

(A saturated solution at 100°C has 77 mgm.per 100 ml- para.3 above)

7.5. First method (only attempt)

1. Solutions prepared.

1.1. 0.1 N Hydrochloric acid soln.
1ml = 3.7mgm $Ca(OH)_2$

1.2. 0.2 N Sodium Hydroxide soln.
1ml = 2 ml of 0.1 HCl soln.

1.3. 0.02 N Calcium Hydroxide soln.
1ml = 0.74mgm $Ca(OH)_2$

1.4. 0.1 N/.........

1.4. 0.1 N EDTA solution
1ml = 3.7mgm. $Ca(OH)_2$

1.5. 2 N Potassium Hydroxide solution.

2. **Apparatus.**

Pipettes, flasks, condenser, beakers, piston-burette, mechanical-magnetic stirrer.

3. **Method.**

Pipette 200 ml of 0.02 N $Ca(OH)_2$ solution into a flask, heat to near boiling, add 1.00g of calcined shale sample, then boil under reflux for 1½ hours. Filter rapidly, while still hot, into a flask. Stopper the flask, and cool to room temperature.

3.1. Pipette out 25 ml of filtrate, dilute to about 200 ml, add 15 ml of 2 N KOH and a "pinch" of murexide indicator. Titrate with 0.1 N EDTA solution.

3.2. Pipette out 20 ml of filtrate, add 20 ml of 0.1 N HCl, and back-titrate with 0.2 N NaOH, using phenolphthalein indicator.

4. **Results:**

4.1. **EDTA Titration:** quadruplicate titrations agreed within 0.1 ml, and the average was 3.1 ml. Titration of EDTA vs 25 ml 0.02 N $Ca(OH)_2$ was 5.1 ml. "Blank" titration was 0.1 ml EDTA, so titration of filtrate was taken as 3.0 ml.

25 ml aliquot requires 3 ml EDTA

$\therefore$ 200 " aliquot required $3 \times \frac{200}{25}$

$= 24$ ml EDTA.

1ml EDTA = 3.7 mgm $Ca(OH)_2$

$\therefore$ 24 ml EDTA = $3.7 \times 24$

= 88.6 mgm $Ca(OH)_2$

1 ml of 0.02N $Ca(OH)_2$/...........

1 ml of 0.02N $Ca(OH)_2$ soln. = 0.74 mgm $Ca(OH)_2$
∴ 200 " of 0.02N $Ca(OH)_2$ soln. = 0.74 x 200
= 148 mgm $Ca(OH)_2$

∴ $Ca(OH)_2$ used up by 1 g shale:

= 148 - 89 mgm
= 59 mgm

4.2. Acid/Alkali Titrations: Triplicate titrations agreed within 0.1 ml, and the average back-titration was 8.7 ml NaOH.

1 ml 0.2N NaOH = 2 ml 0.1 N HCl
∴ 8.7" 0.2N NaOH = 2 x 8.7
= 17.4 ml 0.1 N HCl.

∴ HCl neutralised by $Ca(OH)_2$ remaining in solution in 20 ml filtrate

= 20.0 - 17.4 = 2.6 ml.

20 ml filtrate neutralise 2.6 ml HCl
∴ 200 ml filtrate neutralise 26 ml HCl

1 ml HCl = 3.7 mgm $Ca(OH)_2$
∴ 26 ml HCl = 3.7 x 26
= 96.1 mgm $Ca(OH)_2$

∴ $Ca(OH)_2$ used up by 1 g shale:

= 148 - 96
= 52 mgm

## 5. Conclusions:

5.1 The EDTA and the acidimetry methods give results of the same order of magnitude. The difference of 7 mgm $Ca(OH)_2$ is not too large considering the small titrations - it is equivalent to an error of 0.25 ml in the EDTA titration.

5.2. The results indicate that the method "works", i.e. a measurable quantity of $Ca(OH)_2$ is "used up" by the shale.

## 7.6. Second Method.

1. I felt that it might be better to use the cement, with which the shale was to be interground, as a source of $Ca(OH)_2$, rather than the solution of $Ca(OH)_2$.

2. Instead of boiling under reflux, I marked beakers with rings to indicate 500 ml liquid, and maintained this level, during boiling, by adding hot distilled water. Boiling time was increased to 2 hours.

3. 100 ml Aliquots of filtrate were titrated with EDTA solution to determine the $Ca(OH)_2$ in solution.

4. All titrations were done with a piston burette and with the aid of a magnetic **stirrer**.

## 7.7. Second method - 1st Attempt

1. Method:

Measure 500 ml distilled $H_2O$ into a "ringed" beaker, and heat to boiling. Add 1 g of S.R.Cement and 1 g of Shale sample. Do a duplicate with 1 g of cement and 1 g of washed "standard" sand. Continue to boil for 2 hours, adding distilled water as necessary to maintain volume at 500 ml. Filter rapidly (Whatman No.541) while still hot, into an erlenmeyer flask. Stopper the flask, and cool filtrate to room temperature. Pipette out 100 ml, add 100 ml $CO_2$-free distilled water, 15 ml of 2 N KOH, and murexide indicator. Titrate with 0.1 N EDTA solution.

2. Results/...........

2. Results of duplicate titrations:

Cement + Sand : 6.6 ml EDTA

Cement + Shale : 4.0 ml EDTA

3. Calculations:

3.1. Cement + Sand.

100 ml Filtrate requires 6.6 ml EDTA

∴ 500 ml Filtrate requires 6.6 x 5

= 33 ml EDTA

1 ml EDTA = 3.7 mgm $Ca(OH)_2$

∴ 33 ml EDTA = 3.7 x 33

= $\underline{122 \text{ mgm } Ca(OH)_2}$

i.e. 1 g Cement liberates 122 mgm $Ca(OH)_2$

∴ 100g Cement liberates $\frac{122 \times 100\text{g}}{1,000}$ $Ca(OH)_2$

= $\underline{12.2\text{g } Ca(OH)_2}$

i.e. Under these conditions (2 hours boiling in excess $H_2O$ ) the cement liberates 12.2% $Ca(OH)_2$. (See, however, paragraph 7.9-6)

3.2. Cement + Shale

100 ml Filtrate requires 4.0 ml EDTA

∴ 500 ml Filtrate requires 4 x 5

= 20 ml EDTA

1 ml EDTA = 3.7 mgm $Ca(OH)_2$

∴ 20 ml EDTA = 3.7 x 20

= $\underline{74 \text{ mgm } Ca(OH)_2}$

3.3. Shale activity.

$Ca(OH)_2$ used up by 1g shale:

= 122 - 74 mgm

= 48 mgm

3.4 Formula/................

3.4. Formula for future calculations:

$Ca(OH)_2$ used up = $(T_1 - T_2) \times 5 \times 3.7$ mgm

i.e. "Activity" = $\underline{(T_1 - T_2) \times 18.5}$ mgm $Ca(OH)_2$

Where : $T_1$ = ml EDTA reqd. for "cement" titration.

$T_2$ = ml EDTA reqd. for "cement + shale" titration.

## 4. Conclusions.

4.1. The second method gives results of the same order of magnitude as the first, i.e. 48 mgm $Ca(OH)_2$, as compared with 59 mgm $Ca(OH)_2$.

4.2. One likely reason for the lower result is the lower concentration of $Ca(OH)_2$ in the second case : 122 mgm in 500 ml compared with 148 mgm in 200 ml. (See also para. 7.9 - 3)

4.3. The percentage $Ca(OH)_2$ liberated by the cement was reasonably in accord with expectation. (With complete hydration the cement should liberate about 25% $Ca(OH)_2$ - see Appendix 6 ).

## 7.8. Second Method - 2nd Attempt

1. The test was repeated, using duplicate portions of cement and cement + shale. This time the "cements" were done without sand. A complete "blank" was included - i.e. with reagents only.

2. Results of titration:

| | | |
|---|---|---|
| 1st Cement only | : | 6.7 ml. |
| 2nd Cement only | : | 6.9 ml. |
| 1st Cement + Shale | : | 4.3 ml. |
| 2nd Cement + Shale | : | 4.3 ml. |
| Blank | : | 0.1 ml. |

3. Results/............

3. Results of calculations:

Ca$(OH)_2$ liberated by 1g shale:

| | | |
|---|---|---|
| Using 1st Cement titration | : | 44 mgm |
| Using 2nd Cement titration | : | 48 mgm |
| Previous result (1st attempt) | : | 48 mgm. |

4. Conclusions: The method appears to be reasonably reproducible, but determinations should be done in duplicate (when possible).

### 7.9. Second method - further investigation:

1. As the titrations were so small I felt that accuracy could, perhaps, be improved by using larger weights of cement and shale. Theoretically, the weight of cement should only be limited by the solubility of Ca$(OH)_2$ in boiling water - i.e. 77 mgm/100 ml - and increased concentration should result in more Ca$(OH)_2$ being used up per 1g shale - see para.7.4.2.above. (See also Appendix 9, paragraph 9.1-2 on solubility of Ca$(OH)_2$.)

2. Materials.

The main series of tests were done on a sample of the shale calcined by the University of Stellenbosch (U.S.shale), because there was insufficient of the A/EF' sample left, but one test with it was included as a check.

3. Results (1)

| Wt. Cement | Shale | Vol.EDTA | Ca$(OH)_2$ used per 1g shale |
|---|---|---|---|
| 1g | 1g (A/EF ) | 4.4 ml | 48 mgm |
| 1g | 0 | 7.0 ml | - |
| 1" | 1g (U.S.) | 4.9 " | 39 mgm |
| 2g | 0 | 11.9 ml | - |
| 2" | 1g (U.S.) | 8.9 " | 55 mgm |
| 2" | 2" ( " ) | 7.9 " | 37 " |
| 3g | 0 | 15.9 ml | - |
| 3" | 3g (U.S.) | 11.1 " | 30 mgm |
| 4.5g | 0 | 22.9 ml | - |
| 6.0g | 0 | 24.4 ml | - |
| 100 ml 0.02 N Ca$(OH)_2$ | | 20.7 ml | - |

4. Conclusions (1)/............

## 4. Conclusions (1)

4.1. Increasing the weights of both the cement and the shale increases the total weight of $Ca(OH)_2$ used up, but reduces the amount used up per 1g of shale. (For 1,2 and 3 grams of cement and shale, the amounts of $Ca(OH)_2$ used per 1 gram of shale were, respectively : 39, 37 and 30 mgm).

4.2. Using 2g of cement and 1g of shale did increase the amount of $Ca(OH)_2$ used per 1 gram of shale by a significant amount - from 39 to 55 mgm.

## 5. Results (2)

5.1. In this instance, as a matter of interest, I also titrated 25 ml aliquots of the "cement only" filtrates with 0.0533N HCl, using methyl orange indicator. (1 ml HCl = 1.97 mgm $Ca(OH)_2$ )

5.2. The EDTA titration against standard 0.02 N $Ca(OH)_2$ indicated a slight change in the EDTA, the strength being:

1 ml EDTA = 3.6 mgm $Ca(OH)_2$

Using this to calculate the concentration of $Ca(OH)_2$ in the "cement" filtrates, the results became:

| Wt. of Cement | EDTA used | $Ca(OH)_2$ per 100 ml filtrate | $Ca(OH)_2$ liberated per 100g. cement |
|---|---|---|---|
| 1g | 7.0 ml | 25.2 mgm | 12.6g |
| 2g | 11.9 ml | 42.7 mgm | 10.7g |
| 3g | 15.9 ml | 57.2 mgm | 9.5g |
| 4.5g | 22.9 ml | 82.4 mgm | 9.1g |
| 6 g | 24.4 ml | 87.8 mgm | 7.3g |

5.3. Results of the HCl titrations were:

| Wt.of Cement | HCl/ 25 ml filtrate | $Ca(OH)_2$ per 100ml filtrate | $Ca(OH)_2$ liberated per 100g.cement |
|---|---|---|---|
| 1g | 2.9 ml | 22.9 mgm | 11.4 g |
| 2" | 4.5 " | 35.5 " | 8.9 " |
| 3" | 6.0 " | 47.3 " | 7.9 " |
| 4.5g | 8.3 " | 65.3 " | 7.3 " |
| 6 | 9.5 " * | 75.0 " | 6.2 " |

* Total alkalinity of solution = 20.3 millimols per litre, therefore all $Ca(OH)_2$ will be soluble (See Appendix 8)

5.4. The differences between the "$Ca(OH)_2$ per 100 ml" found by the two methods is probably due to the $CaSO_4$ in the cement. Ca from $CaSO_4$ will be included in the EDTA determination, but not, of course, in the HCl titration.

$SO_3$ = 2.0%

i.e. 1 g Cement contains 0.02 g $SO_3$

$\therefore$ 1 g Cement contains 0.02 x 1.7 $CaSO_4$

= 0.034 g $CaSO_4$

136g $CaSO_4$ is equivalent to 74 g $Ca(OH)_2$

$\therefore$ 0.034 $CaSO_4$ is equivalent to $\frac{74 \times 0.034}{136}$

= 0.0185 g $Ca(OH)_2$

= 18.5 mgm "

5.5. To "correct" the EDTA results to HCl results, therefore, the following weights of $Ca(OH)_2$ should be subtracted from the EDTA results:

| Wt.of Cement | Wt.of $Ca(OH)_2$ | Wt. of $Ca(OH)_2$ per 100 ml filtrate |
|---|---|---|
| 1 | 18.5 mgm | 3.7 mgm |
| 2 | 37.0 " | 7.4 " |
| 3 | 55.5 " | 11.1 " |
| 4.5 | 83.2 " | 16.6 " |
| 6 | 111.0 " | 22.2 " |

5.6 Applying/.........

5.6. Applying the "correction", we have:

| Wt. of Cement | Weight of $Ca(OH)_2$ per 100 ml filtrate | | |
|---|---|---|---|
| | EDTA | Corrected EDTA | HCl |
| 1g | 25.2 mgm | 21.5 mgm | 22.9 mgm |
| 2" | 42.7 " | 35.3 " | 35.5 " |
| 3" | 57.2 " | 46.1 " | 47.3 " |
| 4.5g | 82.4 " | 65.8 " | 65.3 " |
| 6g | 87.8 " | 65.6 " | 75.0 " |

5.7. The corrected EDTA results agree well with the HCl results for 1,2,3 and 4.5 grams of cement, but not so well for 6 grams. This is, no doubt, because with 6 g cement the solution will be saturated with $Ca(OH)_2$, and, indeed, the HCl figure for 6 grams (75 mgm $Ca(OH)_2$ per 100 ml) agrees well with the 77 mgm given in the tables (paragraph 7.3 above)

5.8. It is noteworthy that these results confirm that the cement used had zero $C_3A$, otherwise some of the $CaSO_4$ would have been precipitated as ettringite.

## 6. Further observations.

6.1. Plotting the weights of $Ca(OH)_2$ given in paragraph 5.6 against the weights of cement (1 to 4.5g) gives straight lines passing through the point at 10 mgm $Ca(OH)_2$ for 0 grams cement - see Fig. No. 42 on page 295 This indicates some sort of "blank" in the cement - equal to 1.4 ml of EDTA or 1.3 ml of HCl solution. Blanks on the reagents give 0.1 ml, so this is something else to follow up when time is available. It should not affect the activity test on shale, as that is a "difference" figure, and the same weight of cement is

used with/.................

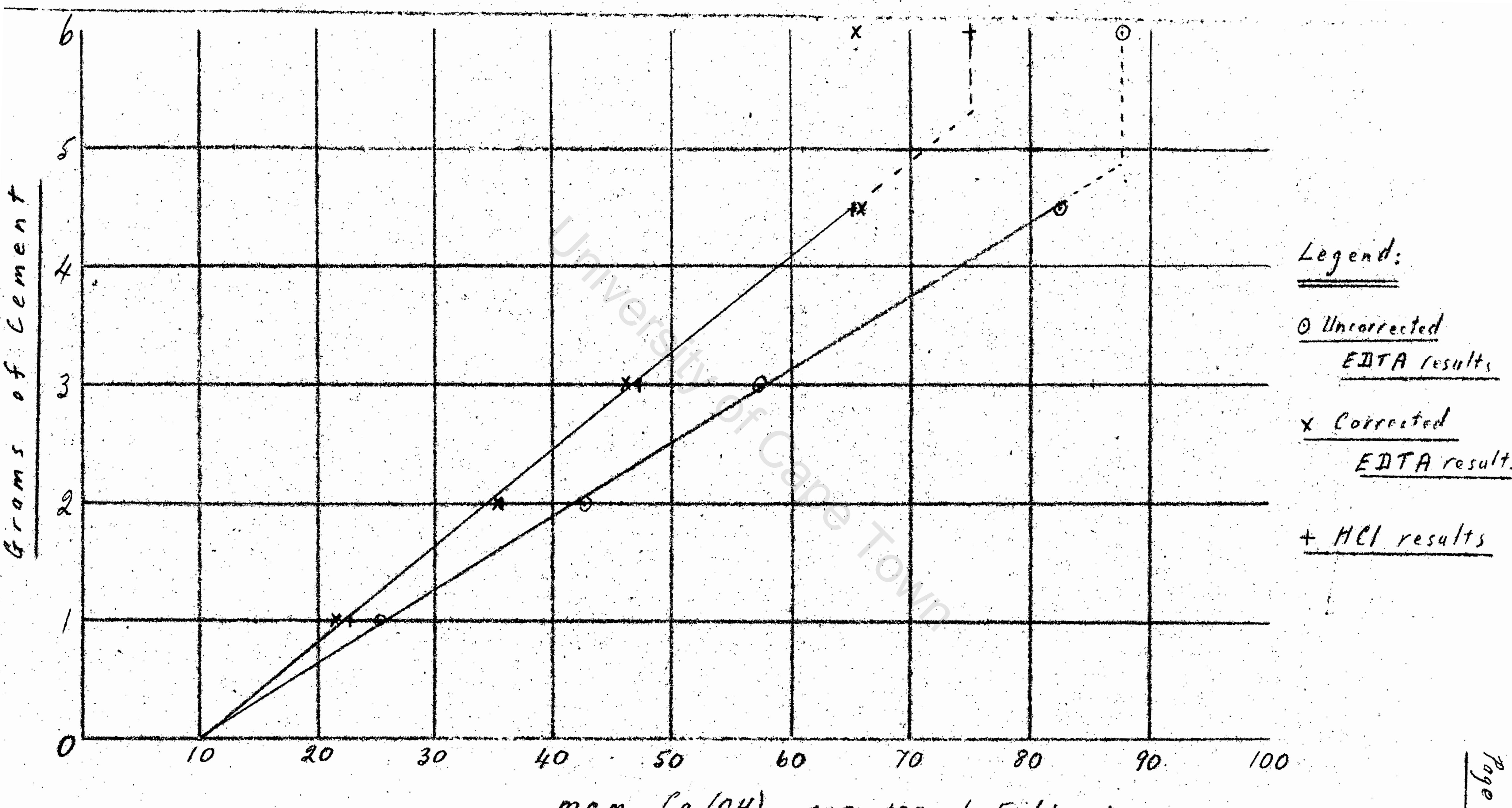

6
5
4
3
2
1
0
Grams of Cement
10
20
30
40
50
60
70
80
90
100
mgm. $Ca(OH)_2$ per 100 ml Filtrate
Legend:
⊙ Uncorrected EDTA results
x Corrected EDTA results
+ HCl results

Fig. No. 42

used with and without shale.

6.2. Subtracting this 10 mgm "blank" from the $Ca(OH)_2$ per 100 ml filtrate gives the following results for the percentage $Ca(OH)_2$ liberated by the cement during the boiling:

| Weight of Cement | Corrected $Ca(OH)_2$ per 100 ml filtrate | | | $Ca(OH)_2$ liberated per 100g. cement | | |
|---|---|---|---|---|---|---|
| | EDTA | Corr.EDTA | HCl | EDTA | Corr.EDTA | HCl |
| | mgm | mgm | mgm | g | g | g |
| 1 | 15.2 | 11.5 | 12.0 | 7.6 | 5.8 | 6.4 |
| 2 | 32.7 | 25.3 | 25.5 | 8.2 | 6.3 | 6.4 |
| 3 | 47.2 | 36.1 | 37.3 | 7.9 | 6.0 | 6.2 |
| 4.5 | 72.4 | 55.8 | 55.3 | 8.0 | 6.2 | 6.1 |
| 6 | 77.8 | 55.6 | 65.0 | 6.5 | 4.6 | 5.4 |

Except for the 6 gram sample, which liberated more $Ca(OH)_2$ than is required for a saturated solution, the percentage $Ca(OH)_2$ released by the different weights of cement is now reasonably constant, as would be expected in such dilute solutions. The problem looks interesting but must, unfortunately, await the time and opportunity for further investigation.

7.10. Method as used for subsequent tests.

1. Referring back to paragraph 7.8 – 3, it is seen that slightly larger titrations can be obtained by using 2 grams of cement and 1 gram of shale, also that a higher "reactivity" figure is obtained. Using 4 grams of cement and 2 grams of shale would probably improve matters still further, but using 1 gram of each gave me successive results of : 48, 44, 48, and 48 mgm $Ca(OH)_2$ per 1 gram shale (paragraphs 7.7-3.3,

7.8-3/.................

7.8-3, and 7.9-3), which I felt indicated sufficient reproducibility for the intended use of the test.

## 2. "Activity" Test for Calcined Shale.

2.1. Mark 2 x 800 ml beakers with "rings" at the 500 ml level.

2.2. Fill them to this level with distilled water and bring to boil.

2.3. Remove from hot-plate, "scratch" bottom of beaker with glass stirring rod to get rid of any super-heated liquid.

2.4. Add as follows:

Beaker No.1 - 1.000 gm Sulphate Resisting Cement.

Beaker No.2 - 1.000 gm Sulphate Resisting Cement +
1.000 gm Shale.

Stir well, break up any lumps, cover with clock glass and boil for a further two hours.

2.5. During the boiling period, at 15 to 20 minute intervals, add boiling (or nearly boiling) distilled water to maintain volume at 500 ml. Make the last addition just before removing from hot plate.

2.6. Filter rapidly (while still nearly boiling) through a No.541 Whatman Filter Paper (or similar) into a suitable flask. (500 ml conical flask). Do NOT wash, stopper flask immediately and cool in running water. Release stopper once or twice, if necessary, to prevent "implosion".

2.7. Pipette 100 ml of the cooled filtrate into a suitable conical flask. Add 100 ml of distilled water which has been boiled and cooled in a stoppered flask, and 15 ml of Carbonate-free 2N KOH. Titrate to 0.1 ml with $N/_{10}$ EDTA solution using murexide indicator.

2.8. This titration is most conveniently done with a piston burette and with the aid of a magnetic stirrer.

2.9 Calculation/............

2.9. Calculation.

For 0.1 N EDTA.

"Activity" = $(T_1 - T_2) \times 18.5$ mgm $Ca(OH)_2$

For any other normality of EDTA:

Activity = $(T_1 - T_2) \times 185 \times$ (normality of EDTA) mgm $Ca(OH)_2$

Where: $T_1$ = ml EDTA soln. reqd. for "cement only" titration.

and $T_2$ = ml EDTA soln. reqd. for "cement + shale" titration.

3. I feel I must stress, once more, that this test is intended for use only with the particular type of pozzolan with which it was developed and it is purely "relative" - i.e. suitable only for comparing one sample with another. It must also not be forgotten that the "activity" value obtained will depend on the fineness of the shale sample.

The test does not work with pulverised fuel ash.

# APPENDIX 8

## MODIFIED "FRANTINI" TEST FOR POZZOLANS

1. Weigh out 20 grams of "Pozzolan plus Cement" into a stoppered measuring cylinder.

2. Add 100 ml of distilled water, shake vigorously for 1-2 minutes, then mix on a rotary shaker for 6 hours.

3. Place the tightly stoppered cylinders in a water bath, maintained at 40°C, for 8 days.

4. Filter the solution, and determine the alkalinity of the filtrate by titrating 25 ml with 0.1N HCl, using methyl orange as indicator. Use another 25 ml aliquot, dilute to 200 ml, add 15 ml of 2 N KOH and murexide indicator, and titrate with 0.1N EDTA to determine the $Ca(OH)_2$ concentration in the filtrate.

5. Calculations.

   5.1 Concentration of Alkali = $4 \times t_1$ millimols/Litre

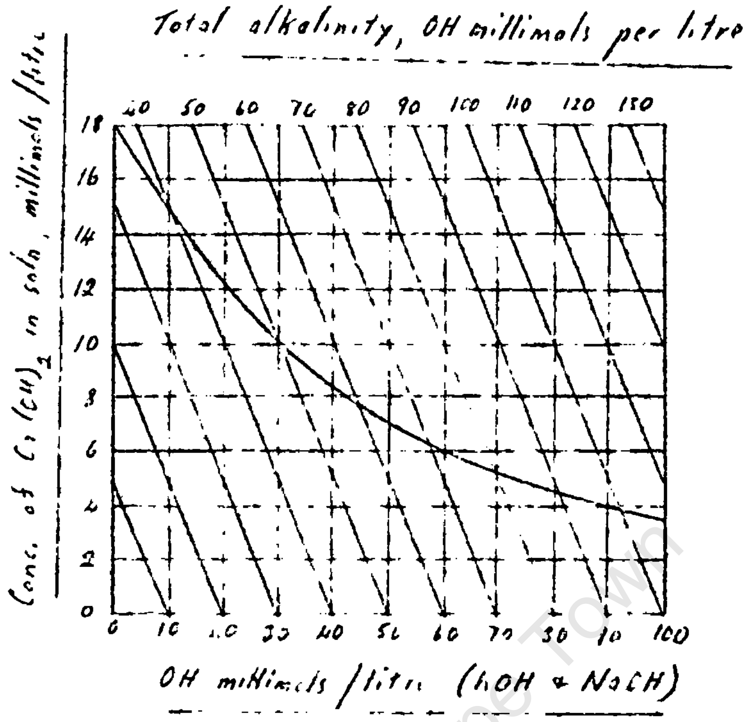
   where $t_1$ = ml of 0.1 N HCl used to neutralise 25 ml of filtrate.

   5.2. Concentration of $Ca(OH)_2$ = $2 \times t_2$ millimols/Litre

   where $t_2$ = ml of 0.1 N EDTA solution used to titrate $Ca(OH)_2$ in 25 ml of filtrate.

6. Compare the results with Figure No. 43 on page 300 to see whether or not the filtrate was saturated with $Ca(OH)_2$ at 40°C.

7. An unsaturated filtrate indicates satisfactory pozzolanicity, and the more unsaturated the better.



Solubility isotherm (15° C) for $Ca(OH)_2$ in the presence of alkalies.

After Milquori - ref 7.14 p 145.

Figure No. 43.

# APPENDIX 9

## METHOD DEVELOPED TO DETERMINE WATER-SOLUBLE $Ca(OH)_2$ IN HARDENED CEMENT PASTE, MORTAR, AND CONCRETE SPECIMENS

### 9.1. SOLUBILITY OF $Ca(OH)_2$ IN WATER.

1. At 0°C : 185 mgm per 100 ml.
At 30°C : ± 150 mgm per 100 ml.
At 100°C : 77 mgm per 100 ml.
(from tables - Appendix 7 - and interpolation).

2. According to the graph in Appendix 8, at 40° about 15 millimols of $Ca(OH)_2$ are soluble per litre, in a total alkalinity concentration of 40 millimols per litre, i.e. 1110 mgm/litre, or 111 mgm per 100 ml. At an alkalinity concentration of 50 millimols per litre, 74 mgm of $Ca(OH)_2$ are soluble per 100 ml at 40°C.

### 9.2. % $Ca(OH)_2$ in hardened cement paste.

At "complete" hydration the % $Ca(OH)_2$ in hardened cement paste is about 20% (Appendix 6).

### 9.3. Weight of Sample per 100 ml $H_2O$

1. Taking into consideration the figures given in para.9.1 above, and experience obtained to date, I assumed that 100 mgm of $Ca(OH)_2$ would be soluble in 100 ml $H_2O$ at 20 - 25°C.

2. If the cement paste should be fully hydrated, then:

20 mgm $Ca(OH)_2$ are contained in 100 mgm paste

$$\therefore 100 \text{ mgm } Ca(OH)_2 \text{ are contained in } \frac{100 \times 100}{20}$$

$$= 500 \text{ mgm paste.}$$

3. I accordingly decided to use 0.5 g sample per 100 ml water.

9.4./..................

## 9.4. Some test results.

1. Using 0.1 N EDTA to determine the total Ca¨ in solution, and reporting it as $Ca(OH)_2$, the following results were obtained on a sample of S.R.cement mortar which had been water cured for 12 months.

| Wt. of sample | 0.5g | 0.5g | 0.5g | 1.0g |
|---|---|---|---|---|
| Water added | 100 ml | 100 ml | 100 ml | 100 ml |
| Time of Stirring | 15 mins | 30 mins | 60 mins | 30 mins |
| $Ca(OH)_2$ found | 4.5% | 4.8% | 5.0% | 4.5% |

2. Duplicate tests indicated that results appear to be reproducible within about 0.5% (i.e ± 0.25%) $Ca(OH)_2$.

## 9.5. Description of method now used.

1. Grind a representative sample of the specimen or specimens to - 100 mesh size.

2. Determine moisture at 105°C and loss on ignition at 900°C.

3. Weigh 0.5 g of dried (105°C) sample into an erlenmeyer flask; add 100 ml of $CO_2$-free distilled water and a "slave" magnet; stopper tightly and stir on magnetic stirrer for 30 minutes ( ± 2½ minutes).

4. Filter rapidly (Whatman No.541), wash 3 times with $CO_2$-free water, and make volume up to 200 ml. Add 15 ml of 2 N KOH (also $CO_2$-free) and murexide indicator. Titrate with standard 0.1 N EDTA solution, using a piston burette and magnetic stirrer.

5. Calculations:

$$\% \ Ca(OH)_2 = 0.74 \times t$$ in dried sample and

$$\% \ Ca(OH)_2 = \frac{0.74 \times t \times 100}{100 - \text{loss}}$$ on "loss-free" basis

where: t = ml of 0.1 N EDTA used for titration.

## APPENDIX 10

### STRENGTH TEST ("LEA") METHOD OF CHECKING POZZOLANIC ACTIVITY

10.1. Any of the following strength testing methods may be used:

1. Tensile test as per B.S.12 (Tensile strength tests are generally in "disfavour" and are seldom used nowadays.)

2. Flexural test as per S.A.B.S.471 of 1959. This may be followed by a compressive strength test on the broken ends of the specimens, as per the Cembureau test method (23.7)

3. Vibrated Mortar Cube compressive strength test, as per B.S.12 : 1948 or S.A.B.S.471 : 1949.

4. 4" Concrete Cube compressive strength test as per B.S.12 :1948.

10.2. Make up 4 sets of strength test specimens, as follows:

A and B : Using Portland cement only,

C and D : Using half the normal weight of Portland cement (from the same sample as used for A & B above) and an equal weight of the ground pozzolanic material to be tested. (i.e. a 50 : 50 mixture of pozzolan and cement is used instead of cement).

10.3. All sets are to be cured, as usual, in the 90% humidity cupboard for 24 hours, and then, after demoulding, under water for a further 6 days.

1. Sets A & C must be cured at the normal temperature, specified for the test, for the whole period.

2. Sets B & D to be cured as above up to 5 days age. They must then be cured, still under water, at 50°C for 46 hours, and then allowed to cool, for 2 hours, under water at standard test temperature.

3. Break all specimens at 7 days.

10.4 Calculations/...........

## 10.4. Calculations.

1. The strengths of the specimens cured at 50°C should be higher than the strengths of the specimens cured at ordinary temperature, and the difference indicates the degree of pozzolanicity. This is conveniently reported as a percentage of the "normal" strength.

2. $$\text{"Activity Index"} = 100 \times \frac{\text{Strength}(50) - \text{Strength}(N)}{\text{Strength } (N)} \ \%$$

where:

Strength(50) = Average strength of set B or D,

and

Strength (N) = Average strength of set A or C, respectively.

## 10.5. Significance.

1. The "Activity Index" should not exceed 15% for Portland cement - it is generally less than 10%.

2. An "Activity Index" above 30% generally indicates a satisfactory pozzolan, and the higher the better.

# APPENDIX 11

## METHOD OF DETERMINING THE REGRESSION LINE FOR SQUARE-ROOT OF SPECIFIC SURFACE VERSUS CHEMICAL ACTIVITY INDEX OF CALCINED SHALE

11.1 The experimental data were:

| Specific Surface | Square-root of Specific Surface | Chemical Activity Index |
|---|---|---|
| 2750 $cm^2/g$ | 52.4 | 25.9 |
| 4500 " | 67.1 | 29.6 |
| 6450 " | 80.3 | 35.1 |
| 7700 " | 87.7 | 37.9 |
| 8500 " | 92.2 | 42.5 |
| 10200 " | 101.0 | 43.4 |
| 11650 " | 107.9 | 44.4 |
| 13500 " | 116.2 | 48.0 |

11.2 Let $s$ = square root of specific surface and
$i$ = chemical activity index.

11.3 Equation required in the form:

$$i = a.s + b$$

11.4 <u>Tabulation</u>

| $s$ | $\bar{s}$ | $(s - \bar{s})$ | $i$ | $\bar{i}$ | $(i - \bar{i})$ |
|---|---|---|---|---|---|
| 52.4 | 88.1 | - 35.7 | 25.9 | 38.35 | - 12.45 |
| 67.1 | 88.1 | - 21.0 | 29.6 | 38.35 | - 8.75 |
| 80.3 | 88.1 | - 7.8 | 35.1 | 38.35 | - 3.25 |
| 87.7 | 88.1 | - 0.4 | 37.9 | 38.35 | - 0.45 |
| 92.2 | 88.1 | 4.1 | 42.5 | 38.35 | 4.15 |
| 101.0 | 88.1 | 12.9 | 43.4 | 38.35 | 5.05 |
| 107.9 | 88.1 | 19.8 | 44.4 | 38.35 | 6.05 |
| 116.2 | 88.1 | 28.1 | 48.0 | 38.35 | 9.65 |

| $(s - \bar{s})^2$ | $(i - \bar{i})^2$ | $(s - \bar{s})(i - \bar{i})$ |
|---|---|---|
| 1274 | 155 | 444 |
| 441 | 77 | 184 |
| 61 | 11 | 25 |
| 0 | 0 | 0 |
| 17 | 17 | 17 |
| 166 | 26 | 65 |
| 392 | 37 | 120 |
| 790 | 93 | 271 |
| Sum: 3141 | Sum: 416 | Sum 1126 |

## 11.5 Test for linear correlation co-efficient

$$r = \frac{\text{Sum} \quad (s - \bar{s})(i - \bar{i})}{\text{sq.root } (S(s - \bar{s})^2 . S\,(i - \bar{i})^2\,)}$$

$$= \frac{1{,}126}{\text{sq.root } (3{,}141 \times 416\,)} = \frac{1{,}126}{1{,}143}$$

$$= \underline{0.985}$$

For 8 pairs of observations, there are 6 degrees of freedom. For 6 degrees of freedom $\underline{r = 0.925}$ at the 0.1% level of significance.

The calculated value of $r = 0.985$; therefore there is a better than 999 to 1 chance that there is a correlation between the pairs.

## 11.6 The Regression Line Equations

$$i = p \pm q\,(s - \bar{s}\,)$$
$$s = p^1 \pm q^1\,(i - \bar{i}\,)$$

$$p = \frac{S\,(i)}{n} = \bar{i} \qquad p^1 = \frac{S\,(s)}{n} = \bar{s}$$

$$q = \frac{S\,(s - \bar{s})(i - \bar{i})}{S\,(s - \bar{s})^2} \qquad q^1 = \frac{S\,(s - \bar{s})(i - \bar{i})}{S\,(i - \bar{i})^2}$$

$$\underline{\bar{i} = 38.35} \qquad \underline{\bar{s} = 88.1}$$

$$\underline{(s - \bar{s})^2 = 3141} \qquad \underline{(i - \bar{i})^2 = 416}$$

$$\underline{(s - \bar{s})(i - \bar{i}) = 1126}$$

$$\underline{p = 38.35} \qquad \underline{p^1 = 88.1}$$

$$q = \frac{1126}{3141} \qquad q^1 = \frac{1126}{416}$$

$$= \underline{0.358} \qquad = \underline{2.71}$$

$$i = p + q\,(s - \bar{s}) \qquad s = p^1 + q^1\,(i - \bar{i})$$

$$= 38.35 + 0.358(s - 88.1) \qquad = 88.1 + 2.71(i - 38.35)$$

$$= 38.35 + 0.358\,s - 31.55 \qquad = 88.1 + 2.71\,i - 103.9$$

i.e. $\underline{i = 0.358\,s + 6.80}$ and $\underline{s = 2.71\,i - 15.8}$

$$\therefore \quad 2.71\,i = s + 15.8$$

$$\therefore \quad \underline{i = 0.369s + 5.83}$$

11.7 Equation used for line:

$$i = 0.36\,s + 6.3$$

(This is statistically indefensible, but aesthetically satisfying).

11.8 Note that this relationship will hold only for this type of shale, calcined in this particular kiln under the specific conditions of time and temperature ( 1150°C) used.

11.9 The line drawn from the above equation - see Figure No. 2A on page 152 - "fits"the plotted experimental points well.

## APPENDIX 12

## DERIVATION OF FORMULA FOR MEAN PARTICLE DIAMETER FROM SPECIFIC SURFACE

### 12.1 Assuming particles are cubes:

1. Let:

$S$ = specific surface in sq.cm/g.

$d$ = mean diameter in microns.

$D$ = mean diameter in centimeters.

$p$ = density of material in g/cu.cm.

$n$ = number of particles in 1 gram.

2. Then:

$$\text{Weight of 1 particle} = \frac{1}{n} \text{ grams}$$

$$p \text{ grams have volume } 1 \text{ cu.cm.}$$

$$\therefore \frac{1}{n} \text{ grams have volume } 1 \times \frac{1}{n} \times \frac{1}{p}$$

$$= \frac{1}{n.p} \text{ cu.cm.}$$

$$\text{But Volume of 1 particle} = D^3 \text{ cu.cm.}$$

$$\therefore D^3 = \frac{1}{n.p.} \text{ cu.cm} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\text{Surface area of 1 particle} = 6\ D^2$$

$$\therefore \text{Surface area of n particles} = 6.n.D^2$$

$$= S$$

$$\text{i.e.} \quad 6.n.D^2 = S$$

$$\therefore D^2 = \frac{S}{6.n}$$

$$(1) \ldots\ldots D^3 = \frac{1}{n.p.}$$

$$\frac{D^3}{D^2} = D = \frac{1}{n.p.} \times \frac{6.n}{S}$$

$$\therefore D = \frac{6}{p.S} \text{ cms}$$

$$\therefore d = \frac{60,000}{p.S} \text{ microns.}$$

3. This agrees with the formula given in the ASTM (18.1-8)

12.2. Assuming/.................

## 12.2 Assuming particles are spheres:

1. Let:

$S$ = Specific surface in sq.cm/g.

$d$ = mean diameter in microns

$D$ = mean diameter in centimeters.

$R$ = mean radius in centimeters.

$p$ = density of material in g/cu.cm.

$n$ = number of particles in 1 gram.

2. $D = 2\,R$

Surface Area of sphere $= 4\,\text{pi}\,R^2$

Volume of sphere $= \frac{4}{3}\,\text{pi}\,R^3$

3. Then:

Weight of 1 particle $= \frac{1}{n}$ grams.

$p$ grams have volume 1 cu.cm.

$\therefore\ \frac{1}{n}$ grams have volume $1 \times \frac{1}{n} \times \frac{1}{p}$

$$= \frac{1}{n.p.} \text{ cu.cm.}$$

But volume of particle $= \frac{4}{3}\,\text{pi}\,R^3$

$$\text{i.e.} \quad \frac{4}{3}\,\text{pi}\,R^3 = \frac{1}{n.p.}$$

$$\therefore \quad R^3 = \frac{3}{4\,\text{pi}\,n.p.} \quad \ldots\ldots\ldots(2)$$

Surface area of 1 particle $= 4\,\text{pi}\,R^2$

$\therefore$ Surface area of $n$ particles $= 4.n.\text{pi}.R^2$

$= S$

$$\therefore \quad R^2 = \frac{S}{4.n.\text{pi}}$$

$$\frac{R^3}{R^2} = R = \frac{3}{4.\text{pi}.n.p.} \times \frac{4.n.\text{pi}}{S}$$

$$= \frac{3}{pS}$$

$$D = 2\,R = \frac{6}{pS} \text{ cm.}$$

$$\therefore \quad d = \frac{60{,}000}{pS} \text{ microns.}$$

4. This is the same as the formula obtained assuming the particles were cubical !

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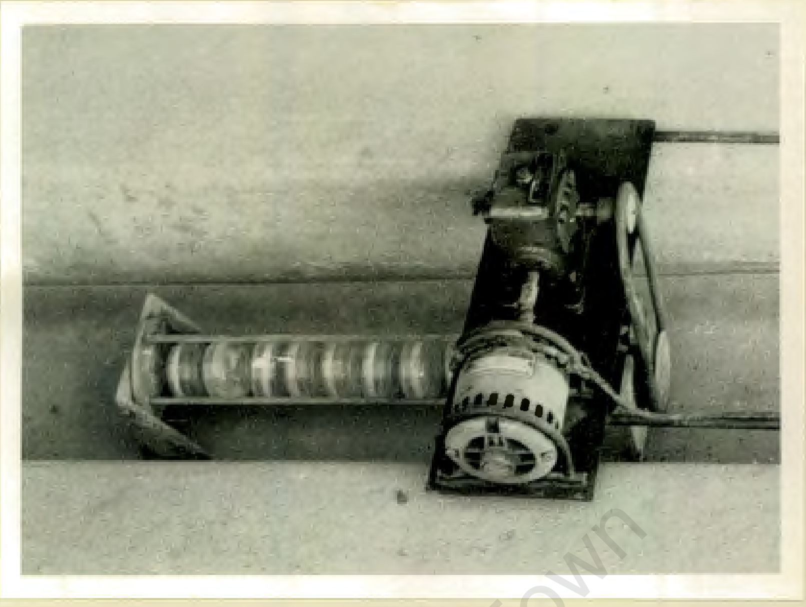
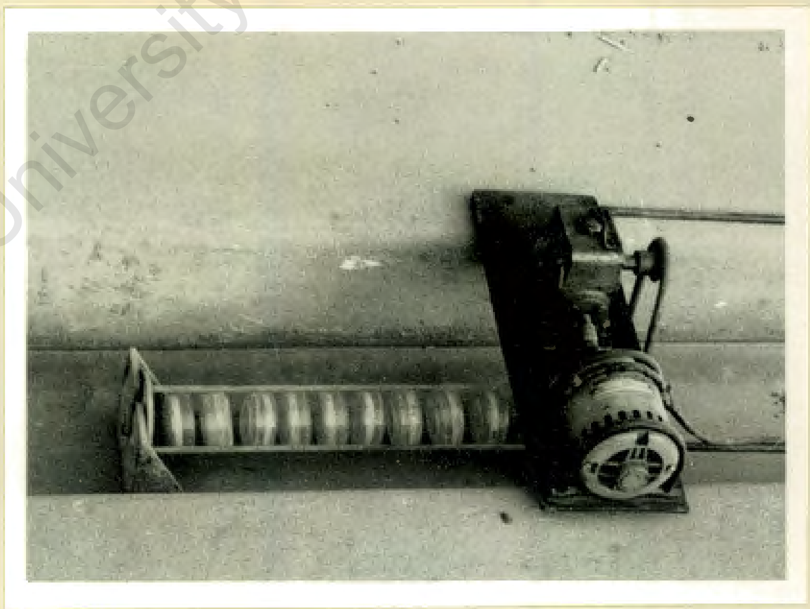
# PHOTOGRAPHIC SUPPLEMENT.

Marine corrosion at Muizenberg.

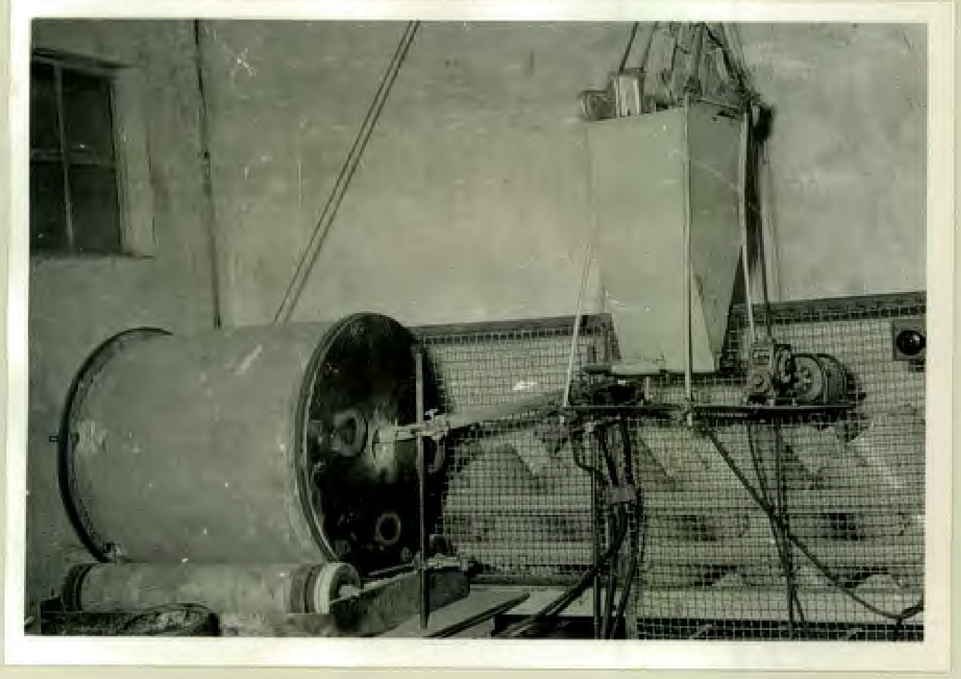
(See page 40.)



Apparatus for comparing the
"activities" of pozzolans.
(See page 132.)



Laboratory kiln,
burner-pipe,
and coal-bin.
(See page 138.)



Cubic-yard blocks of concrete, made for checking temperatures of hydration. (See page 186.)

# SULFACEM

JANUARY 1964

ADDENDUM NO. 1.

## SULPHATE
## RESISTING
## CEMENT

## CEMENT SALES (PTY.) LTD.

Telephone: 2-3766
P.O. Box 2802

Allied Building,
46 St. George's Street,
Cape Town.

# SULFACEM

SULFACEM is a Portland cement intended for use when high sulphate resistance is required and is recommended for use in preference to ordinary Portland cement where sulphate aggression is present.

It is a Portland cement manufactured to comply with the chemical requirements of the American Society for Testing and Materials (A S T M) Type V which is "for use when high sulfate resistance is required". SULFACEM, as well as complying with the chemical requirements of A S T M Type V complies with the physical requirements of ordinary Portland cement specifications.

SULFACEM is freely available for all local requirements.

Information as to price at any station will be supplied by Cement Sales (Pty.) Limited and for large jobs delivery programmes can be arranged in the same way as for ordinary Portland cement.

On the following pages are:—

(1) A typical chemical analysis of SULFACEM compared with A S T M Type V specification limits;

(2) A set of physical test results compared with ordinary Portland cement specification requirements.

# Chemical Analysis

| *Oxides* | | *Typical* **Sulfacem** *Analysis* | A S T M *Type V Limits* |
|---|---|---|---|
| Silica | $SiO_2$ | 22·3% | ... |
| Alumina | $Al_2O_3$ | 3·4% | See (1) & (2) |
| Iron Oxide | $Fe_2O_3$ | 5·3% | See (2) |
| Lime | $CaO$ | 64·0% | ... |
| Magnesia | $MgO$ | 1·5% | Max: 4·0 % |
| Sulphur Trioxide | $SO_3$ | 1·8% | „ : 2·3 % |
| Loss on Ignition | | 1·3% | „ : 3·0 % |
| Insoluble Residue | | 0·5% | „ : 0·75% |
| *Potential Compounds* * | | | |
| Tri-Calcium-Silicate | $C_3S$ | 54% | ... |
| Di-Calcium-Silicate | $C_2S$ | 24% | ... |
| (1) Tri-Calcium-Aluminate | $C_3A$ | *less than* 1% | „ : 5% |
| (2) Tetra-Calcium-Alumino-Ferrite | $C_4AF$ | 16% | (Max for $C_4AF$)<br>($+2C_3A=20\%$) |

*Calculated by the A S T M (i.e. the "Bogue") Formula

# *Physical Test Results*

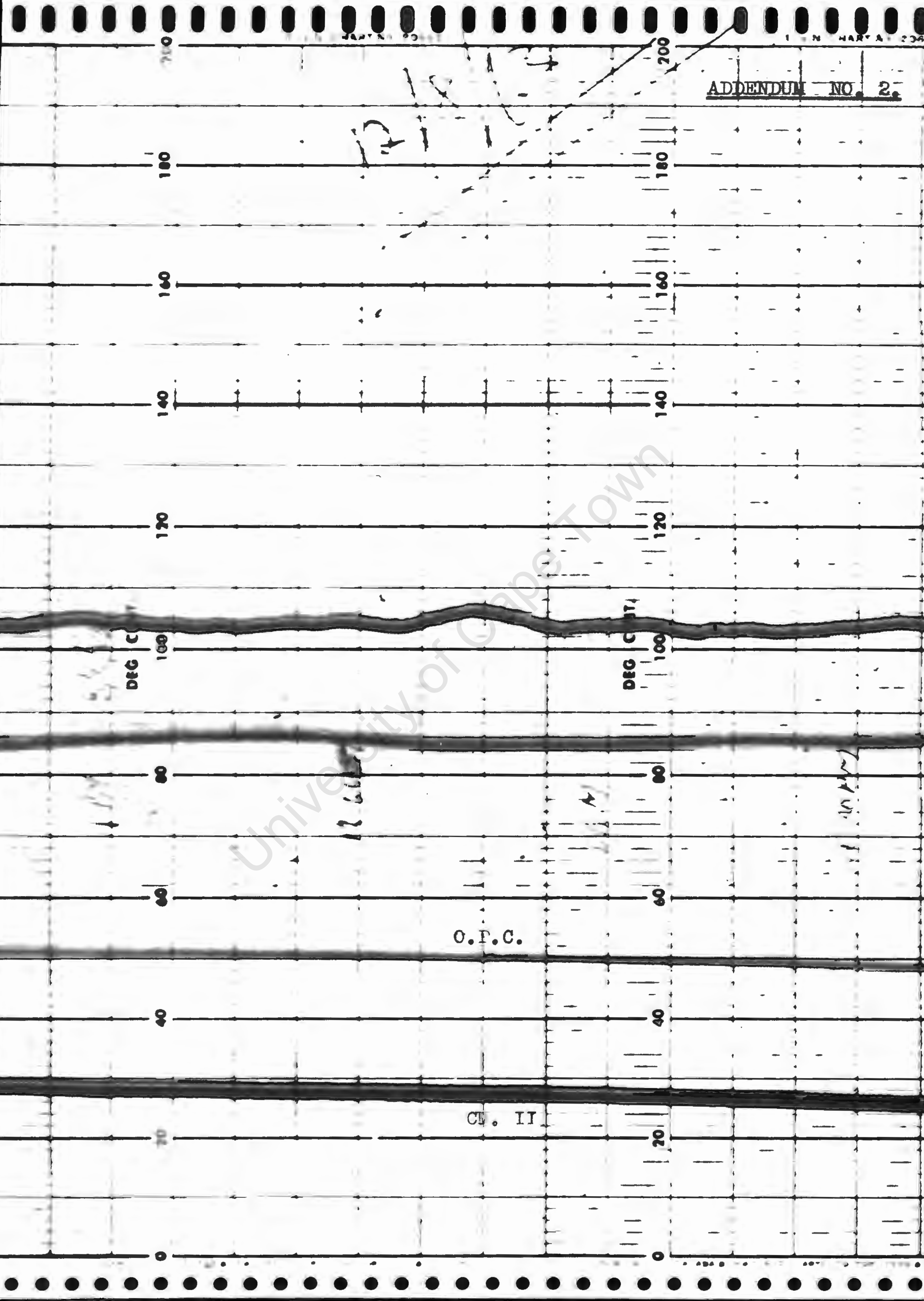
| | *Typical* **Sulfacem** *Results* | *Ordinary Portland Cement Specification Limits* |
|---|---|---|
| *Setting Times* | | |
| Initial | 150 mins. | Min: 45 mins. |
| Final | 4 hours | Max: 10 hours |
| *Fineness* | | |
| Specific Surface | 3,500 cm.$^2$/gm. | Min: 2,250 cm.$^2$/gm. |
| No. 72 Screen Residue | nil | Max: 1·2% |
| *Soundness* | | |
| Le Chatelier Expansion | 1 mm. | Max: 10 mm. |
| *Compressive Strengths* | | |
| Vibrated Mortar Cubes | | |
| (1:3 Cement:Sand, 0·4 w/c ratio) | | |
| at 3 Days | 4,000 lb./in.$^2$ | Min: 2,200 lb./in.$^2$ |
| at 7 Days | 5,000 ,, | ,, : 3,400 ,, |
| at 28 Days | 6,000 ,, | — |
| 4 in. Concrete Cubes | | |
| (approx. 1:6 Cement:Aggregate, 0·6 w/c ratio) | | |
| at 3 Days | 2,000 lb./in.$^2$ | Min: 1,200 lb./in.$^2$ |
| at 7 Days | 2,800 ,, | ,, : 2,000 ,, |
| at 28 Days | 3,600 ,, | — |

**CEMENT SALES (PTY.) LTD.**

**Allied Building ● 46 St. George's Street ● Cape Town**

Pryors, C.T.

ADDENDUM NO. 2.



## ADDENDUM No. 3.

## "CEMARINE" MARINE CEMENT

Cemarine is an entirely new South African cement, recently developed by the Cape Portland Cement Company Limited and now available from Cement Sales (Pty) Limited. Its manufacture was preceded by an intensive search of American, European and other scientific literature, and a comprehensive research programme.

This cement is especially suitable for use in all types of concretes which are to be situated in the sea or exposed to a marine atmosphere.

Cemarine is an interground mixture of a Pozzolan, a low $C_3A$ Portland cement, and an air-entraining agent. The Pozzolan fraction is produced from a special shale which is calcined under carefully controlled conditions to "activitate" it.

Advantages of this entirely new South African product are:-

(1) It has a high resistance to waters containing Sulphate and Magnesium salts in solution.

(2) The temperature rise of Cemarine, during hydration, is substantially lower than that of ordinary Portland cements. This reduces the incidence of incipient cracking and improves the durability of concrete made from it.

(3) Cemarine imparts to freshly mixed concrete the properties of plasticity, cohesion, and a low bleed rate. As a result, better compaction and absence of segregation of the placed concrete may be expected, and these factors, associated with the absence of pores caused by high bleed rates, contribute materially to the prevention of corrosion of reinforcing steel.

(4) The finely divided Pozzolan reacts with Calcium hydroxide liberated during the hydration of Portland cement. The use of Cemarine will, therefore, reduce leaching out of $Ca(OH)_2$ from hardened concrete in contact with soft waters.

/PHYSICAL CHARACTERISTICS ..

## PHYSICAL CHARACTERISTICS:

| | TYPICAL CEMARINE TEST RESULTS | ORDINARY PORTLAND CEMENT SPECIFICATION LIMITS |
|---|---|---|
| **Setting Times:** | | |
| Initial | 150 mins | Min: 45 Mins |
| Final | 4 hours | Max: 10 hours |
| **Fineness:** | | |
| Specific Surface | 5,000 $cm^2/gm$ | Min: 2,250 $cm^2/gm$ |
| No.170 Screen Residue | 1% | Max: 10% |
| No. 72 Screen Residue | Nil | Max: 1.2% |
| **Soundness:** | | |
| Le Chatelier Expansion | 1 m.m. | Max: 10 m.m. |
| **Compressive Strengths:** | | |
| Vibrated Mortar Cube Test: (1:2 Cement : Sand, 0.4 W/C ratio) | | |
| At 3 Days | 3,000 p.s.i. | Min: 2,200 p.s.i. |
| At 7 Days | 4,000 p.s.i. | Min: 3,400 p.s.i. |
| At 28 Days | 5,500 p.s.i. | - |
| 4" Concrete Cube Test: (Approx. 1:6 Cement : aggregate, 0.6 W/C ratio) | | |
| At 3 Days | 1,800 p.s.i. | Min: 1,200 p.s.i. |
| At 7 Days | 2,800 p.s.i. | Min: 2,000 p.s.i. |
| At 28 Days | 4,000 p.s.i. | - |
| **Transverse Strengths:** | | |
| Hand Compacted Mortar Prisms: (1:3 Cement : Sand, 0.5 W/C ratio) | | |
| At 3 Days | 450 p.s.i. | Min: 250 p.s.i. |
| At 7 Days | 550 p.s.i. | Min: 400 p.s.i. |
| At 28 Days | 700 p.s.i. | - |

14/7/64.