

SULPHATE RESISTANCE OF SLAG CEMENTS



By

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2

ABSTRACT

The vulnerability of concrete to sulphate attack has been recognized and studied for at least two centuries. The basic needs that prompted the study were: (a) there are no available Canadian Standards on the sulphate resistance of slag cements; and (b) slag cements in general are not well known in Canada. There were three main phases in the study: Phase One - involved 76.2 by 152.4 mm (3 by 6 inch) concrete cylinders made from actual field mixes and subjected to various sulphate solutions representative of field conditions; Phase Two - involved an accelerated test program employing 25.4 by 25.4 by 285.75 mm (1 by 1 by 11½ inch) mortar prisms and 50.8 mm (2 inch) mortar cubes stored in more concentrated sulphate solutions; and Phase Three - followed along the same lines as Phase Two, but encompassed a wider range of samples, solutions and tests. The slag cement studied in detail was cementitious hydraulic slag meeting CSA A363.

Experimental results show that: the sulphate attack is generally intensified with higher sulphate concentrations but the degree of attack is not proportional to concentration; Na_2SO_4 and K_2SO_4 solutions produced more rapid deterioration than MgSO_4 solutions; sulphate attack increases in rate and

magnitude as the C_3A content of the portland cement increases and as the alumina (Al_2O_3) content of the slag cement (i.e. pelletized blastfurnace slag) increases; the higher the slag cement content of the blended cement, the greater its resistance; and a 50 per cent slag cement (cementitious hydraulic slag)/50 per cent Type 10 portland cement blend appears to be equivalent in sulphate resistance to a Type 50 portland cement. No abnormal, or significant, amount of ettringite was found in any of the specimens examined, which tends to substantiate one hypothesis that ettringite formation has little to do with sulphate expansion. The 76.2 by 152.4 mm concrete cylinder program did not yield any significant results. The accelerated mortar test procedure was found to be the most reliable test for evaluating a cement's sulphate resistance performance in a relatively short time, and it is recommended that this test be adopted as a standard.

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TABLE OF CONTENTS

	<u>PAGE</u>
SCOPE AND CONTENTS	ii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF TABLES	viii
LIST OF FIGURES	ix
Chapter	
1. INTRODUCTION	1
2. SLAG CEMENTS	9
2.1 Blastfurnace Slags	9
2.2 Composition and Cementitious Behaviour of Glassy Slags	14
2.3 Portland Blastfurnace Slag Cements	21
3. MECHANISM OF SULPHATE ATTACK	27
4. EXPERIMENTAL	38
4.1 Background	38
4.2 Phase One	38
4.3 Phase Two	44
4.4 Phase Three	47
4.4.1 Mortar Bars Subjected to Immersion Cycles (Wetting and Drying) in a Severe Sulphate Environment	52
4.4.2 The Lok-Test	55
4.4.3 Porosity Measurements	62
4.5 Criteria of Failure	63
5. EXPERIMENTAL FINDINGS AND DISCUSSIONS	65
5.1 Phase One	65
5.2 Phase Two and Phase Three Results	69

TABLE OF CONTENTS (Cont'd)

Chapter	<u>PAGE</u>
5.2.1 Effect of Type of Sulphate Salt	69
5.2.2 Effect of Salt Concentration	75
5.2.3 Effect of C_3A in Portland Cement	80
5.2.4 Comments on C_3A Influences	83
5.2.5 Effect of Variation of Slag Cement Content in Blended Cements	88
5.2.6 Alumina Content of Slag (Slag Type)	94
5.2.7 Slag Cement Addition Level	96
5.3 Scanning Electron Microscope Study	98
5.4 Effect of Wetting and Drying on Partially Submerged Specimens	112
5.5 Lok-Test	117
5.6 Alkali Silica Test Program	120
6. CONCLUSIONS	123
REFERENCES	128
APPENDIX	
A. The Lok-Test Procedure	133
B. Determination of Capillary Porosity	144
C. Compressive Strength, Ultrasonic Pulse Velocity and Expansion Data for Phase One	147
D. Compressive Strength and Expansion Data for Phase Two	170
E. Compressive Strength and Expansion Data for Phase Three	175
F. Porosity Measurements	184
G. Mix Specifications and Length Changes of Partially Submerged Specimens Subjected to Alternate Wetting and Drying Cycles	186
H. Alkali-Silica Test Program	189

LIST OF TABLES

<u>TABLE</u>	<u>PAGE</u>
2-1 Principal Uses of Blastfurnace Slag	12
2-2 Chemical Composition of Iron Blastfurnace Slags and Portland Cement	16
4-1 Mix Specifications for Phase One	39
4-2 Chemical Compositions of the Test Cements (Phase 1)	41
4-3 Mix Specifications for Phase Three	49
4-4 Chemical Compositions of the Test Cements of Phase Three	51
4-5 Lok-Test Mix-Specifications	61
5-1 Length Changes of Partially Submerged Specimens Subjected to Alternate Wetting and Drying Cycles	113
5-2 Lok Test Results	119
C-1 Compressive Strength of Concrete Cylinders in Phase One	148
C-2 Ultrasonic Pulse Velocities of Concrete Cylinders	151
C-3 Longitudinal Expansions (%) of Batches 1,3,4,5, to 6,7,8, and 9 (Phase 1)	154
C-10	
C-11 Lateral Expansions (%) of Batches 1,3,4,5,6, to 7,8, and 9 (Phase 1)	162
C-18	
D-1 Compressive Strengths of 50 mm Mortar Cubes of Phase Two	171
D-2 Longitudinal Expansions (%) of Phase Two	173
E-1 Compressive Strengths of Phase Three	176
E-2 Longitudinal Expansions (%) of Phase Three	179

LIST OF TABLES (Cont'd)

<u>TABLE</u>	<u>PAGE</u>
F-1 Porosity Measurements	185
G-1 Mix Specifications (Alternate Wetting and Drying Cycles)	187
G-2 Length Changes (Alternate Wetting and Drying Cycles)	188
H-1 Mix Specifications for Alkali-Silica Test Program	190
H-2 Chemical Composition of Cementitious Hydraulic Slag and Portland Cements (Alkali-Silica Test Program)	191
H-3 Chemical Composition of Ordinary Waste Glass and Pyrex Glass (Alkali-Silica Test Program)	191
H-4 Longitudinal Expansions (Alkali-Silica Test Program)	192

LIST OF FIGURES

<u>FIGURE</u>	<u>PAGE</u>
4-1 Apparatus for Measuring Length Changes of Concrete Cylinders and Mortar Bars	43
4-2 Typical Storage of Prisms and Cubes in Sulphate Solutions in Air-Tight Plastic Containers	43
4-3 Test Equipment Simulating Immersion Cycles (Wetting and Drying) in a Severe Sulphate Environment.	54
4-4 Lok-Test Instrument	56
4-5 The Lok-Test Method	57
4-6 Plywood Formwork Containing Lok-Test Bolts and 4-7	58
5-1 Top View of Concrete Cylinders Showing Signs of Sulphate Attack After 24 Months in Sulphate Solutions	68
5-2 Effect of Sulphate Type on Expansion of 100% Type 10 PC (11.8% C ₃ A) Mortar Prisms	70
5-3 Miniature Mortar Prisms and Cubes After About 320 Days of Immersion 5-4	73
5-5 Effect of Salt Concentration	76
5-6 Progress of Corrosion by Na ₂ SO ₄	78
5-7 Influence of C ₃ A	82
5-8 Effect of Blends	90
5-9 Effect of Cement Mortars in 50,000 ppm SO ₃ as Na ₂ SO ₄ (Phase 2).	91
5-10 Effect of Slag Variation	95
5-11 SEM Micrograph of Specimen 7A-90° to the Surface, Polished and Etched	103

LIST OF FIGURES (Cont'd)

<u>FIGURE</u>		<u>PAGE</u>
5-12	SEM Micrograph of the Surface of Specimen 7D	103
5-13	SEM Micrograph of Specimen 7D-90° to the Surface	104
5-14	SEM Micrograph of an Ettringite Spherulite	104
5-15	SEM Micrograph of Specimen 7D-90° to the Surface	105
5-16	SEM Micrograph of Specimen 7D-90° to the Surface	105
5-17	SEM Micrograph of Specimen 7D-90° to the Surface	106
5-18	SEM Micrograph of the Surface of Specimen 7E	106
5-19	SEM Micrograph of the Clusters of Figure 5-18	107
5-20	SEM Micrograph of Specimen 7E-90° to the Surface	107
5-21	SEM Micrograph of a Pore of Specimen 7E-90° to the Surface	109
5-22	SEM Micrograph of Specimen 7E-90° to the Surface	109
5-23	SEM Micrograph of Figure 5-22 at a Higher Magnification	110
5-24	SEM Micrograph of Specimen 7E-90° to the Surface	110
5-25	Two Specimens After 128 Days of Partial Submergence in a 50,000 ppm SO ₃ as Na ₂ SO ₄ Solution and Subjected to Wetting and Drying Cycles	115

CHAPTER 1

INTRODUCTION

Concrete is vulnerable to attack in sulphate environments and this susceptibility to attack was recognized at least two centuries ago. It was not uncommon to ascribe the deterioration to bad workmanship or poor concrete as little was then known about the design of concrete mixes. However, when important and well designed structures became affected, engineers became very concerned and started to seriously study this problem.

Even before the invention of portland cement the sulphate attack of cementitious materials was being studied. One of the early investigators was John Smeaton, who in 1756 experimented in improving pozzolanic mortars when he was commissioned to erect a lighthouse on the Eddystone Rock in Great Britain. Another of the early investigators was Vicat of France, who in 1812 worked on limes and natural cements (1).

Owing to the failure of concrete work on the P.L.M. Railway in the South of France around 1890, the sulphate attack problem became of increased importance in Europe. In 1898 Bied investigated some of these failures and came

to the conclusion that they were due to: the attack of the concrete by gypsum (calcium sulphate) in the soil and ground waters; the disintegration caused by the formation of calcium sulphotoaluminate; and the crystallization of gypsum in the pores of the concrete. In 1900 and 1902 further problems due to gypsum were experienced in tunnels at Alicum, Rimont and La Plagnotte and also, due to magnesium sulphate and sodium sulphate, in structures on the Sou-Saada line in Southern Algeria (2). The destructive action of alkali ground waters on concrete structures in Western Canada was generally recognized to be a problem of major importance by 1918. T. Thorvaldson was one of the first Canadians to study the sulphate attack problem, and contributed much to our understanding of the subject (3). Within the last seventy years, there have been numerous investigations worldwide into the mechanism and prevention of sulphate attack.

There are three major ways in which sulphates are formed: sulphates in nature; sulphates due to biological action; and, sulphates due to industrial pollution.

(a) Sulphates in Nature

Soluble sulphates are found in most soils and groundwaters, and particularly in sea water. In most soils the SO_4 contents are low and harmless to concrete, typically

between 0.01 to 0.05 per cent*. However, considerable quantities of sulphates are sometimes present in the soils of specific areas. For instance, clays containing 5 per cent or more gypsum and sometimes appreciable quantities of other sulphates are found in Great Britain. Soils with high gypsum contents are also found in North Africa, France and other parts of Europe. Groundwaters high in sulphates are common in Hungary. In the northern Great Plains states (the Dakotas and Montana) of the USA, and extending into the Prairie provinces of Canada, there occur the so called "alkali soils", containing high concentrations of sulphates in the soils and groundwater. Concentrations of sulphates in many areas of Southern Ontario also require the consideration of potential concrete attack and the selection of a suitable portland cement type.

The distribution of sulphate salts in a clay is often very irregular. In the Canadian Prairies the concentrations are usually very variable both in the vertical and horizontal directions. This is largely the result of the factors causing moisture movement in the soils. In the extensive glacial-lacustrine and glacial-fluvial deposits of Western Canada, poor subdrainage of the near surface silts and clays greatly restricts leaching (4). In arid regions where the rates of evaporation are high, the zone of accumulation of sulphate salts generally occurs within

*Sulphate concentrations in soils are usually expressed in per cent by weight or in grams per litre of SO_4 or SO_3 ; and in groundwater as parts per million (ppm) of SO_4 or SO_3 . To convert from SO_4 to SO_3 multiply by 0.83.

4

a few feet of the surface. Also associated with a dry climate is its action in "wicking up" the soluble sulphates from the lower salt bearing layers.

The sulphate salts most commonly found in groundwaters and soils are sodium, potassium, magnesium and calcium. Sodium, potassium and magnesium sulphates have high solubilities, whereas calcium sulphates' solubility is relatively low at only about 0.2 per cent; limiting its concentration to approximately 1200 ppm SO_3 .

The Canadian Standards Association Standard A23.1 (Concrete Materials and Methods of Concrete Construction) gives guidelines as to the degree of attack one can expect for various ranges of concentrations as follows:

"negligible" attack up to 150 ppm sulphate (SO_4) in groundwaters or up to 0.10 per cent sulphate (SO_4) in soils;

"mild but positive" attack where the corresponding values are 150 to 1000 ppm and 0.10 to 0.20 per cent;

"considerable" attack where the corresponding values are 1000 to 2000 ppm and 0.20 to 0.50 per cent;

"severe" attack where the corresponding values are over 2000 ppm and over 0.50 per cent.

These levels should be used with caution as many influencing factors, such as seasonal variations of rainfall and water table fluctuations varying the sulphate concentration, should be taken into account. Also, under certain conditions the sulphate concentration may be considerably


reduced; for instance, insufficient ventilation of the soil or the presence of certain organic substances (coal particles, etc.). The high variability of concentrations makes sampling, mapping and prediction of sulphate occurrence a difficult task.

(b) Sulphates Produced by Biological Action

The decomposition of organic substances containing sulphur by biological action can produce sulphates in soils. This process is rather slow, and may give rise to an increase in the soils' acidity. Sewage can cause the sulphate concentration to increase in both soil and groundwater. Manure and fertilizers also raise the sulphate content of the soil, which also increases with the degree of cultivation. On ploughing, the soil becomes loose and hence ventilation is increased promoting the oxidation of sulphur. It has been found that the sulphate content in a cultivated soil is twice as much as in an uncultivated one. Biczók(5) has provided considerable detail in his book on this subject.

(c) Sulphates Produced by Industrial Pollution (5)

Many industries have large coal or slag piles in their proximity. The soil and groundwater under these piles may have very high sulphate concentrations due to



leaching of the coal or some slags. The pyrite and sulphur in coal and some slags oxidize to form sulphates. Dumpsites formed from industrial or domestic wastes may also have high sulphate contents. Acid sludges or acid waste dumps may increase the sulphate concentration of groundwater as high as 7000 ppm SO_4 . Waste waters from coal mines rich in pyrites sometimes also carry considerable amounts of sulphates. Where coal burning or metallurgical smelting is carried out, the smoke may cause sulphate pollution of the surrounding area (i.e. acid rain).

Coupled with materials conservation through aspects such as increased durability, there is increasing emphasis being placed on energy conservation, recycling and residuals (wastes, byproducts, coproducts) utilization in construction. One building material that contributes to both the durability, energy and coproduct utilization aspects of conservation is iron blastfurnace slag cement (termed slag cement throughout). It has been utilized in Europe and other parts of the world for centuries and is now gaining popularity in North America. As Emery et al (6) put it:

Although the United States and Canada (until very recently) have lagged behind other countries (many Cembureau members for instance) in utilizing glassy blastfurnace slags for their cementitious properties, there is little doubt that the escalating cost of cementing agents such as asphalts and portland cements (primarily due to world

energy distribution problems) will focus more attention on slag cements. As our energy needs continue to develop in a time of potential shortage, it is critical that structural materials that have an "energy content" are fully utilized for cementitious purposes.

This study deals specifically with the sulphate resistance of slag cements which has been identified as a potential utilization advantage over conventional portland cements. There appears to be a vital need for such a study since:

- (1) There are no available Canadian standards (i.e. Canadian Standards Association) on the sulphate resistance of slag cements; and
- (2) slag cements are not well known in Canada.

Research has been carried out on the sulphate resistance of slag cements in many countries, and although it has generally been found that slag cements are more resistant to sulphate attack than ordinary portland cement, there are many discrepancies and questions still unresolved. One of the contributing factors to these conflicting findings is that blastfurnace slags differ in their composition and properties depending on the source. For this reason, attention is focused on the only Canadian slag cement produced at the time - cementitious hydraulic slag - produced by Standard Slag Cement from Dofasco pelletized slag.

Since little research has been done in Canada on the sulphate resistance of slag cements, the following main objectives were adopted for the study:

1. to develop and refine a sulphate resistance test procedure(s) (i.e., no realistic standard test exists);
2. to study the suitability of various durability monitoring techniques;
3. to study the influence of various slag cement/portland cement blends on sulphate resistance (main aspect of study);
4. to study the influence of some common sulphate salts on sulphate attack;
5. to study the influence of the sulphate concentration on sulphate attack; and
6. to study the influence of the portland cement type and source (Tricalcium Aluminate, C_3A , influence) on sulphate resistance.

This study is unique in that both a vitrified . pelletized slag based slag cement and a fairly representative range of actual concrete mixes are involved. It should be noted that while the research reported herein began in early 1977, much of the work is continuing as long term durability tests at typical sulphate levels are time consuming.

CHAPTER 2

SLAG CEMENTS

2.1 Blastfurnace Slags

The American Society for Testing Materials (ASTM C125) defines blastfurnace slag as "the nonmetallic product consisting essentially of silicates and aluminosilicates of lime, and other bases, which is developed simultaneously with iron in a blastfurnace."

There are two prime functions of an iron blast-furnace. Primarily, the oxygen combined with the iron in the ore has to be removed. Iron ore is a mixture of oxides of iron, silica and alumina. The oxygen is removed by chemical reactions between the iron oxides and carbon in the form of coke to produce carbon monoxide, carbon dioxide and metallic iron (at this stage called pig iron). Secondly, the process must separate the resulting metal from the remaining non-metallic or gangue content of the ore and from the ash residue of the coke. This is brought about by melting the charge and allowing differences in density to cause a separation into a layer of slag containing most of the unwanted non-metallic components which floats on top of the liquid metal, and that can be freely tapped from the furnace (7,8).

The amount of raw materials used per ton* of iron produced is about 1.7 tons of ore and other iron-bearing materials (for example, sinter and pellets), 0.50 to 0.65 ton of coke or other fuel, about 0.25 ton of limestone or dolomite, and 1.8 to 2.0 tons of air. The limestone and/or dolomite act as fluxes and their functions are:

(a) to form a fluid slag with the coke ash, ore gangue, and any other charged impurities; and (b) to form a slag with a chemical composition so that it will provide a degree of control on the sulphur content of the iron. The blastfurnace products are typically 1.0 ton of iron, 0.2 to 0.4 ton of slag, 0.05 ton or less of flue dust and 2.5 to 3.5 tons of blastfurnace gas (9). The quality and quantity of slag produced is essentially a function of the iron content of the ore (10, 11). In North America, where the iron contents of burden are high, the slag content may be as low as 200 to 250 kg/ton of iron (8). The annual world production of blastfurnace slags is approximately 115 million metric tons based on an average generation of 23 per cent of iron production (11).

The use of iron blastfurnace slag depends upon its chemical composition and the physical form in which

*1 tonne or metric ton = 1000 kg = 0.9842 ton .

it is allowed to solidify. Blastfurnace slag is produced in four main forms: air-cooled, expanded or foamed, granulated and pelletized.

Air-cooled slag is produced by pouring the molten slag on to a slag bank or into a pit. It is permitted to solidify by slow cooling under atmospheric conditions; cooling may then be accelerated by water sprays on the solidified mass. The slag develops a crystalline structure similar to that of an igneous rock. This slag following processing has many conventional aggregate application uses as outlined in Table 2-1.

Expanded or foamed (also called lightweight) blastfurnace slag is the product obtained when the molten slag is expanded by applying a limited quantity of water or with a controlled quantity of water and air or steam. The water is controlled to properly expand the slag and to prevent granulation. Expanded blastfurnace slag has a relatively high structural strength, good insulating and acoustical properties and is used as lightweight aggregate in concrete (9,12, Table 2-1).

Granulated blastfurnace slag is made by sudden quenching of the molten slag. With sudden cooling the crystals have no time to form and it solidifies as a glassy or vitrified material. Granulated slag has hydraulic properties when ground to cement fineness and mixed with

TABLE 2-1

PRINCIPAL USES OF BLASTFURNACE SLAG (9)

Air Cooled Crushed and Screened Slag	Ballast, Railroad Concrete, Portland cement	Cushion Course for Brick or Block Pavement	Traffic Bound Roads; Berms, Shoulders Stabilized Roads and Bases
	Concrete Units; Masonry, Hollow Binder Course, Sheet Asphalt Pavement	Sand or Sheet Asphalt or Bituminous Concrete	Porous Back-fill and Underdrains Lightweight Aggregate (Expanded Slag)
	Bituminous Concrete Base or Surface Course	Waterbound Base or Wearing Course Sewage Trickling Filter Media	Embankments, Roadway Fills (Bank Slag)
	Bituminous Surface Treatment	Roofing Granules (Bituminous Built- up Roofing)	Glass Sand, Ceramic Ware
	Bituminous Macadam Base or Surface Course	Mineral Wool Sub-bases and Special Subgrade (Insulations)	
Expanded Slag	Concrete Masonry Units	Precast Products Floor Joists and Slabs	Acousticle Tile Curtain Walls
	Structural Concrete Fireproofing Floor Tile	Building Blocks Brick	Back-Up, Insulation, Fire Resistive
Granulated and Pelletized Slag	Portland Cement Slag Cements	Roadway Insulation Courses	Roadway Fills and Embankments
	Soil Corrective, Agricultural Slag	Special Subgrade and Sub-bases Ceramic Ware, Glass Sand	Concrete Units Building Blocks

an alkaline activator such as lime or portland cement. It is used in the manufacture of many cements, mainly portland blastfurnace cement and super-sulphated cement (Table 2-1).

Pelletized slag can be categorized between expanded and granulated slag because of the physical and mineralogical properties related to its lightweight pellet shape and potential vitrified nature, respectively. The slag pelletizing process is relatively new and was developed by National Slag Limited in Hamilton, Canada. Many countries are adopting this process and it is now in use in Canada, Great Britain, U.S.A., Finland, Sweden, Luxembourg, France and Australia. In this process the molten slag is expanded under water sprays and the resulting pyroplastic material is passed over a rotating drum where the fins on the drum break it up and throw it into the air for sufficient time for pellets to form by surface tension. This provides a quick cooling method which produces a slag product that can be immediately handled (molten slag usually takes several days to cool). The pelletizer also provides a means of controlling the high gas emissions (primarily hydrogen sulphide and sulphur dioxide), typical of many foaming and granulating processes, since the slag is cooled in the air so quickly that the gas does not have time to escape before the hardening surface of the pellet effectively seals it

in (6). Pelletized slag has many advantages as a product over conventional vesicular expanded slags, including a significantly lower water absorption and excellent workability in masonry and structural concrete mixes. By varying the pelletizing process either glassy pellets having cementitious properties, or crystalline pellets for concrete mixes, can be produced which provide a full range of marketing possibilities. The main current applications for pelletized slag are as a lightweight aggregate in masonry and structural concrete mixes and in separately ground slag cement manufacture.

In this study, the slag cements tested (primarily cementitious hydraulic slag) were produced from suitably pelletized vitrified slag. As already mentioned, both granulated and suitably pelletized slags have latent cementitious properties. These slags have been vitrified by sudden cooling, and are the only slags considered herein as vitrified or glassy slags.

2.2 Composition and Cementitious Behaviour of Glassy Slags

The glass formed on rapid cooling of the molten slag is really a supercooled liquid. The transformation from the molten to the solid crystalline form is carried out by a rearrangement of the ions which take up definite

orientation of the crystals, and the viscosity of the molten silicates near the freezing point is so large that this rearrangement only takes place slowly. Sudden cooling prevents the ions from organizing themselves into crystals and they retain most of their irregular arrangement. In this case the slag is transformed from the liquid state to that of a glass without developing a crystalline structure. Glasses have no definite melting point, they soften and gradually pass into a liquid state on heating. Below the freezing point of the crystallized mix the stable condition is that of a completely crystalline solid, and the glasses are unstable and tend to pass into the crystalline state; but glasses have very high internal viscosity which restrains this tendency and reduces the mobility of the constituent ions (7,13).

The main components of blastfurnace slag are the same oxides as are present in portland cement, but differing in proportions. The essential constituents are CaO , MgO , SiO_2 and Al_2O_3 with small amounts of MnO , S and FeO or Fe_2O_3 . Other oxides such as TiO_2 , V_2O_5 , Cr_2O_3 can also be found depending on the type of ore used. The amount of gangue material in the ore and the degree of gaseous reduction in the furnace also affect its composition. Table 2-2 gives typical ranges of composition of slags gathered from many sources and a typical composition of

TABLE 2-2

CHEMICAL COMPOSITION OF IRON BLASTFURNACE SLAGS AND PORTLAND CEMENT

Composition	Iron Blastfurnace Slag		Portland Cement
	Usual	Range* Typical	
Silicon dioxide	SiO ₂	32-40%	37.9%
Aluminium dioxide	Al ₂ O ₃	9-17	8.4
Lime	CaO	34-44	38.2
Magnesium oxide	MgO	5-15	11.5
Sulphur	S	1-3	2.0
Iron oxide	FeO	0.3-1.5	Fe=1.5
Manganese oxide	MnO	0.2-1.5	Mn=0.63
			SO ₃ =3.7
			Fe ₂ O ₃ =2.2
			-

* Williams (14).

a slag used in this study; for comparative purposes the corresponding amount of oxides found in a portland cement is presented.

Glassy blastfurnace slags generally have little or no cementitious properties alone, but in the presence of a suitable activator they exhibit significant cementitious properties. (It should be noted that the Hamilton slag cement is particularly active). Lime, portland cement, alkalies (for example, caustic soda), or the sulphates of the alkalies, lime or magnesia may be used as activators. There is an impermeable acidic gel coating on the slag grains preventing hydration, and the role of the activator is to either react with the coating themselves or to release enough calcium hydroxide to do so, in order that hydration can take place. When portland cement is used, the real activator is the calcium hydroxide released on setting. Some of the products of hydration identified by researchers are a tobermorite-like phase, ettringite, calcium aluminate hydrate and tetracalcium aluminate monosulphate hydrate. Le Chatelier (15) in 1894 stated that the hydraulic properties of granulated slag are due to the presence of a silica-alumina ferrite of calcium corresponding to the formula $3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. This compound appears also in portland cements, but in them it is inert owing to the slow cooling it has undergone. However, when it is cooled suddenly - as in the case of glassy slags - it becomes an important hydraulic agent. The cementitious

behaviour of glassy slags is a complex subject and is the topic of much current research.

To assess the cementitious properties of glassy slags various chemical formulae have been suggested in order to calculate a hydraulic index. Some authors have suggested the following two formulae:

$$(a) \quad 1.30 < \frac{\text{CaO}}{\text{SiO}_2} < 1.40$$

Note: - slag with a low $\frac{\text{CaO}}{\text{SiO}_2}$ ratio is sometimes called acid (below 1.20)
 - slag with a high $\frac{\text{CaO}}{\text{SiO}_2}$ ratio is sometimes called basic (above 1.30)

$$(b) \quad 0.45 < \frac{\text{Al}_2\text{O}_3}{\text{SiO}_2} < 0.55$$

In general, a high $\frac{\text{CaO}}{\text{SiO}_2}$ ratio means a high furnace temperature and therefore a better chance of obtaining good vitrification. A slag of low basicity but with a high alumina content may be of excellent quality; alumina is an important factor in the mechanical strength of slag. The current trend is towards the production of less and less basic slag (10). One of the most popular formulae was proposed by Roquejoffre:*

$$\frac{\text{CaO} + \text{MgO} + 1/3 \text{Al}_2\text{O}_3}{\text{SiO}_2 + 2/3 \text{Al}_2\text{O}_3} \geq 1$$

*The CSA has recently adopted a similar oxides ratio:

$$\frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2} \geq 1 \quad (\text{CSA A363-M1977}).$$

Another is Keil's German formula:

$$F = \frac{\text{CaO} + \text{CaS} + 1/2 \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{MnO}}$$

for $F < 1.5$: low-grade slag

$1.5 < F < 1.9$: slag of acceptable quality

$F > 1.9$: high-grade slag .

A French formula by C. de Langavant is also often used:

$$i = 20 + \text{CaO} + \text{Al}_2\text{O}_3 + \frac{\text{MgO}}{2} - 2 \text{SiO}_2$$

for $12 < i < 15$: low grade slag

$15 < i < 20$: slag of acceptable quality

$i > 20$: high grade slag .

All the above formulae are based on experience and have been used to indicate the hydraulic value of a slag. Chemical formulae in themselves do not really enable the evaluation of the true quality of a slag and such assessments of hydraulicity have not proven suitable. No clear strength development-hydraulic moduli relationship was found by Gupta (16). Coale et al (17) have reported that the hydration of a slag cement is a highly complex process depending on a great number of factors, and it is therefore unrealistic to expect such a reaction to be governed by relatively simple relationships. They found that certain trends can be seen in hydraulic behaviour and composition, but no definite relationships can be formulated for the entire range of slags suitable for cement.

The glass content of a vitrified slag is a prime factor in determining its cementitious properties and can be used as an indicator of the slags' hydraulicity. A rapid method for visually assessing glassy slags often used in Germany is the fluorescence test. In this test the slag sample is examined under ultra-violet light where the different types of grains emit different luminescent colours, separating the various types of glasses which possess varying degrees of hydraulicity. Particles emitting red and pink colours are claimed to be vitreous, developing high strengths; yellow, blue and violet colours are highly crystalline with lower strengths. Work done with slags from Great Britain seems to indicate that the fluorescence test is useful only for slags produced by one particular process or even by a single furnace. There are several other glass count methods available. For example, the South African method which uses cross-polarized light and an orange filter, and the McMaster Method in which microscope counts are done under plane and cross-polarized light. Lea (13) states that neither a composition modulus nor a glass content alone are sufficient to characterize the hydraulic properties of a slag and that some product of the two is required.

Recalescence tests (latent heat of crystallization) to correlate the activity of a glassy slag have not proven successful. Studies by differential thermal analysis have

not been very successful either. Chemical methods and various other means have been proposed. One of the most recent proposals was that of Fierens using thermoluminescence and electron exoemission techniques, which have proven successful in work done on artificial, but not industrial, glassy slags. These methods presently require sophisticated equipment and highly trained technicians, and are really only suited for research purposes. It appears that the most reliable method at this time is the measurement of its mechanical strength development (i.e. performance testing). The samples can be made from crushed slag and its hydration accelerated by grinding, heating or by using a strong base like sodium hydroxide.

2-3 Portland Blastfurnace Slag Cements

The use of blastfurnace slag in cement manufacture was probably foreseen by Vicat when he recognized that its chemical composition was similar to that of portland cement. In 1862 Langens found that a cementitious material could be produced from water granulated slag mixed with lime. A portland blastfurnace slag cement was first produced in Germany in 1892 by intergrinding portland cement and granulated slag.

There are three main types of cements containing vitrified blastfurnace slag:

supersulphated cement - composed essentially of
vitrified blastfurnace
slag, calcium sulphate, and
a small percentage of
portland cement or lime;

portland blastfurnace slag cement - produced either
by intergrinding various
portions of glassy slag
with portland cement clinker,
or by adding the ground
glassy slag directly at
the batching plant or mixer
on site;

low heat portland blastfurnace slag cement - similar
to portland blastfurnace
slag cement but with a higher
slag content.

Only portland blastfurnace slag cement was used in this
study, and is discussed further in this section. The term
slag cement is used throughout to refer to portland blast-
furnace slag cements, and in particular cementitious hydrau-
lic slag cement.

In Great Britain slag cement is known as portland
blastfurnace cement with not more than 65 percent slag
(BS 146); in the U.S.A. it is called Type IS cement with

a slag content of 25 to 65 per cent (ASTM C595); in Germany it is called Eisenportland for up to 35 per cent slag and Hochofen cement for 36 to 85 per cent slag (DIN 1164); in France, Ciment de Fer contains 25 to 35 per cent slag, Ciment Métallurgique Mixte contains 45 to 55 per cent slag, Ciment de Haut Fourneau contains 65 to 75 per cent slag and Ciment de Laitier au Clinker contains at least 80 per cent slag and finally, in Canada a CSA preliminary standard exists - CSA A 363-M1977 - for cementitious hydraulic slag.

When slag and cement clinker are interground the softer material, which tends to be the clinker, is preferentially ground. Lea (13) noted that with slag contents up to about 50 to 60 per cent the early strength of interground slag cements is mainly determined by the fineness of the clinker fraction and later strengths by that of the slag fraction. For cements with greater slag contents the fineness of the slag is of major importance at all ages. If both have the same fineness there appears to be little difference in strength development between intergrinding and separate grinding. While there are still some differences in opinion as to which method is actually more effective, separate grinding is generally preferred as it has significant advantages such as avoidance of preferential grinding and ease in varying slag cement/portland cement blends.

The Trief process developed in Belgium is another method of producing slag cement, particularly from granulated slags. After granulation the slag is ground wet and stored as a wet slurry. When the concrete is ready for mixing, the slurry is fed into the concrete mixer together with portland cement and aggregate.

In South Africa a slag cement known as Slagment is produced by dry grinding granulated slag to the same fineness as portland cement for addition at the mixer as a partial replacement for portland cement (18). A similar process is used in Britain under the name of Cemsave. In Canada, ground glassy pelletized blastfurnace slag is utilized in a similar fashion and is termed Cementitious Hydraulic Slag (CHS) by the producer, Standard Slag Cement Company.

The workability of concrete mixes incorporating these cements is higher than ordinary portland cement containing mixes of the same aggregate content, thereby allowing a lower water to cement ratio that is used to advantage during mix design. The rate of hardening of slag cements is slower than ordinary portland cement, but at later ages equal or even superior strengths are reached. By careful control of workability, strength equivalency at early stages (3 to 7 days) can be achieved for slag cement replacement of portland cement at up to about 40 per cent. Lea (13) reports that it is slower than portland cement during the

first 28 days but then increases so that at 12 months equal or greater strengths are attained; Venuat (10) states that often after only 7 days at 20°C (later at a lower temperature, and earlier at higher temperatures) the strengths become the same. The writer has produced results similar to Venuat's using slag cement mortar cubes incorporating up to 70 per cent slag cement replacement of portland cement at 23 degrees celcius. Less heat is given off during hydration of slag cement/portland cement blend than for ordinary portland cement, which is more noticeable in the early stages. This property is successfully applied in the building of mass concrete structures such as dams, or foundations, where there is danger of excessive heat buildup that can result in cracking of the concrete. It is a disadvantage in cold weather and care must be exercised to prevent frost damage due to the coupling of the low heat of hydration of the slag cement and its relatively low rate of strength development.

In portland cement clinker, periclase (crystalline MgO) is known to be deleterious to cements. The MgO content expands in volume when it slowly hydrates to form brucite (a mineral having the composition $Mg(OH)_2$, and a specific crystal structure), and may continue to expand long after the cement has set causing the hardened cement matrix to disrupt. A safe limit is prescribed in various specifications

generally limiting the periclase to less than 5 per cent (for example in DIN 1164). This specification is sometimes applied to slag cements even though it has been shown that the MgO present in a glassy state is harmless (17,18). Other potentially deleterious materials are sulphides and CaO present in slag cements. The sulphides oxidize to sulphates accompanied by damaging expansions if present in excess. British Standard BS 146 requires that the sulphur present as sulphide shall not exceed 1.5 per cent; ASTM (C595-68) specifies no limit on MgO, and limits SO_3 to 3 per cent and the sulphide to 2 per cent. Coale et al (17) note that the lime unsoundness results from the phase change of beta to gamma dicalcium silicate ($2 \text{ CaO} \cdot \text{SiO}_2$), accompanied by a volume increase of the slag.* However, rapid quenching during the granulating or pelletizing process prevents the crystallization of dicalcium silicate precluding the possibility of the phase change. Various formulae and moduli have been proposed for the assessment of slags for slag cements manufacture; the main ones have been given in the last section.

Other favourable properties of slag cements are low shrinkage, low absorption and high chemical resistance. The potential sulphate resistance properties of slag cements have been recognized for some time and were the prime motivation for this study.

*It should be noted that X-ray diffraction studies on a wide range of Ontario blastfurnace slags show an evidence of dicalcium silicate.

CHAPTER 3

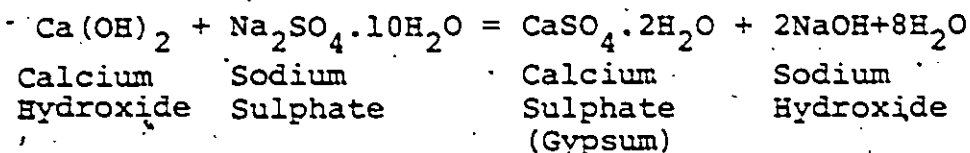
MECHANISM OF SULPHATE ATTACK

When concrete is placed in aggressive or potentially aggressive environments, its resistance to corrosion must be a major consideration during design. The durability of concrete is largely dependent on the physical and chemical nature of its components. Corrosion processes can be classified into two main types: physical caused by abrasion, mechanical wear, frost action and the like; and chemical caused by aggressive liquids or gases infiltrating into the hardened concrete. Only concrete deterioration by chemical or physico-chemical means is considered here. Cement gel (colloidal material which makes up the major portion of the porous mass of which mature hydrated cement is composed) is basic and is attacked by water, certain salts, acids and bases; though in most cases the rate of deterioration is so slow that they are unimportant. Under certain conditions the deterioration process results in severe corrosion and in some cases complete failure of concrete structures has been experienced. In the majority of cases involving concrete deterioration due to salts, sulphates have been found to be the aggressive agent.

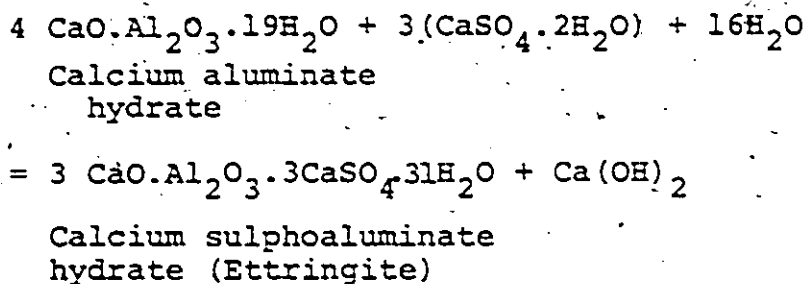
Sulphate attack has received the greatest attention of all in concrete corrosion studies, and as a result chemical attack and sulphate attack have frequently been regarded as synonymous in the literature (5).

Potassium, sodium, calcium, magnesium, ammonium and various other sulphates in aqueous form, react with the hydrated calcium aluminate and/or the free calcium hydroxide in the set cement paste. The resulting products are gypsum and calcium sulphotoaluminate hydrate, accompanied by an increase in volume and deterioration. This is known as "sulphate attack". The chemical reactions involved in the attack of cements by sodium and magnesium sulphates are (13,19):

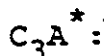
(a) The sodium sulphate reacts with calcium hydroxide:



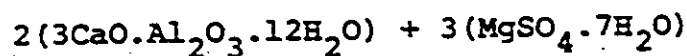
(b) The gypsum reacts with calcium aluminate:



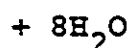
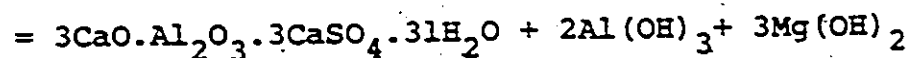
(c) The magnesium sulphate reacts with hydrated



*Cement chemistry nomenclature used: C = CaO,
A = Al_2O_3 , S = SiO_2 , F = Fe_2O_3 , M = MgO, K = K_2O , N = Na_2O ,
H = H_2O .

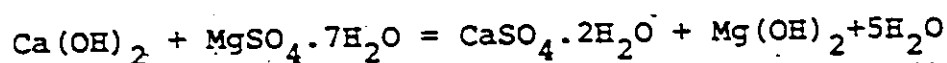


Magnesium Sulphate

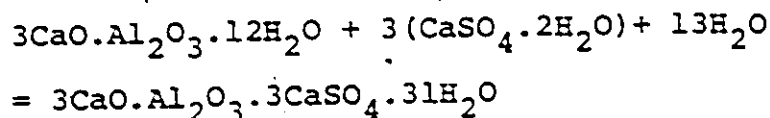


Aluminium Magnesium
Hydroxide Hydroxide

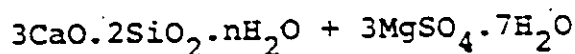
- (d) The magnesium sulphate also reacts with calcium hydroxide:



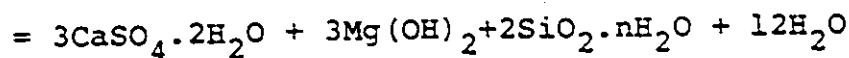
- (e) The gypsum formed in (d) or (f) also reacts with hydrated C_3A :



- (f) The magnesium sulphate also reacts with calcium silicate hydrate:

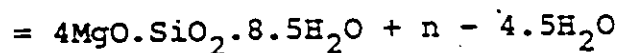


Calcium Silicate
Hydrate



Silica Gel

- (g) The magnesium hydroxide formed in (c) or (d) reacts with silica gel formed in (f):



Magnesium Silicate Hydrate

Calcium hydroxide is liberated immediately as the portland cement comes in contact with water. A saturated or supersaturated solution is soon formed filling the capillaries and gel pores. This solution is highly basic - not less than pH 12 - mainly because the calcium hydroxide and other alkali hydroxides (for example, that of sodium or potassium) in the cement contribute to higher values and will dissolve gypsum. But in blended slag cements the calcium hydroxide from the portland cement acts as the activator to the finely ground glassy slag and therefore the calcium hydroxide in solution is comparatively very low. Aluminates play a significant role in the corrosion process. They are in the form of calcium aluminates in the portland cement. Hydrated aluminous compounds such as crystalline hydrogranite and gehlenite hydrates are known to be sulphate resistant, whereas tricalcium aluminate produces compounds highly susceptible to sulphate attack.

Lea (13) discusses the conditions controlling the extent to which reactions (a) and (b) take place. In flowing waters, with a constant supply of sodium sulphate and removal of the sodium hydroxide, reaction (a) will eventually proceed to completion. If the sodium hydroxide accumulates an equilibrium is reached depending on the sulphate concentration; with a 5 per cent sodium

hydroxide solution only about one-third of the sulphur trioxide is deposited as calcium sulphate when equilibrium is reached, and with 2 per cent sodium sulphate only about one-fifth. Reaction (b) can occur only if calcium sulphate is present. Lea also notes that alkali sulphates do not attack the hydrated calcium silicates to any appreciable extent because they are more insoluble than the calcium sulphate and alkali silicates which would result. Calcium hydroxide liberated in the setting of tri - and dicalcium silicates reacts according to equation (a). In sodium sulphate solution crystals of gypsum are soon formed from tricalcium silicate, but with dicalcium silicate the reaction proceeds much more slowly, corresponding with the very slow rate at which this compound splits off calcium hydroxide in water.

The action of magnesium sulphate on hardened cement paste is different to that of other sulphates. Magnesium sulphate not only reacts with the calcium aluminates and calcium hydroxide but also attacks the hydrated silicate phases. As shown in equation (f) its reaction with calcium silicate hydrate results in gypsum, nearly insoluble magnesium hydroxide and silica gel. This behaviour may be attributed to the low solubility of magnesium hydroxide and the reduction in pH of its saturated solution in the presence of magnesium sulphate. The resulting pH is about

10.5 and at this low pH the hydrated calcium silicate is very unstable. Lea explains "the silicate liberates lime to the solution to establish its equilibrium pH, but when magnesium sulphate is present the lime reacts with it, forming magnesium hydroxide and calcium sulphate. The former at once separates from solution, reducing the pH value to 10.5 again; more lime passes into solution by decomposition of a further part of the hydrated calcium silicate to re-establish the pH and so the action proceeds. The calcium sulphate accumulates in solution until it becomes saturated and crystals of gypsum then separate out." The silica gel formed can react with magnesium hydroxide slowly to form magnesium silicate hydrate as presented in equation (g). Magnesium silicate hydrate has no cementing properties and represents the final stage in the magnesium sulphate attack.

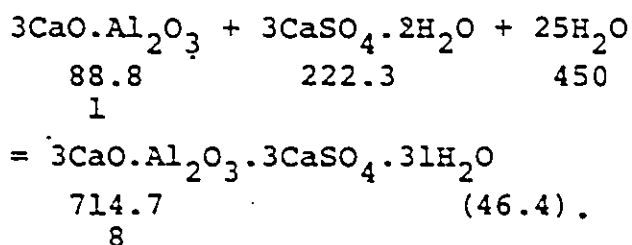
Equations (c), (d) and (e) show other possible reactions with magnesium sulphate. It may react with hydrated tricalcium aluminate forming calcium sulphoaluminate, aluminium hydroxide and magnesium hydroxide. Magnesium sulphate may also react with calcium hydroxide forming gypsum and magnesium hydroxide (Equation (d)). Because of the low solubility of magnesium hydroxide, it precipitates as very fine or colloidal particles. Hansen (20) points out that water in the gel pores is in equilibrium with the surface forces of the colloidal

reaction products, but precipitation of colloidal magnesium hydroxide in the gel pore introduces new surface forces upsetting this equilibrium. To re-establish equilibrium between the surface forces and water, additional water will be drawn into the gel pores and this can only be accomplished by enlargement of the pores by osmotic pressure. Equation (e) shows how the gypsum formed in (d) and (f) can react with the hydrated tricalcium aluminate to form calcium sulphoaluminate hydrate.

In sulphate attack there is a marked increase in the solid volume which can result in the disruption of the cement. When calcium hydroxide is converted to gypsum the solid volume more than doubles, the molecular volumes of $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are 33.2 and 74.2 cc respectively (13). The solid volume also more than doubles when calcium aluminate and gypsum combine to form calcium sulphoaluminate hydrate. The relative contribution of the conversion from calcium hydroxide to gypsum to the total volume change is not clear (21). It is generally believed in most theories that the main cause of expansion is the formation of calcium sulphoaluminates from the alumina-bearing compounds in cements.

Two types of calcium sulphoaluminates are known to exist: a low sulphate compound with the composition $3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ called monosulphate, and a high sulphate compound with the composition $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$ commonly called ettringite (also known as cement bacillus,

trisulphate or Candlot's salt). One of the early expansion theories was put forward by Lafuma and is still accepted by many researchers. He suggested that the volume expansion is due to the formation of ettringite by two mechanisms. If the liquid phase containing sulphate ions is saturated with calcium hydroxide, ettringite is formed through a solid state reaction between the tricalcium aluminate and SO_4^{2-} and Ca^{2+} ions. However when the liquid phase is unsaturated with calcium hydroxide, the reaction proceeds by going through the liquid phase and ettringite is crystallized in the gel pores without causing any expansion. Hansen and Offutt (22) showed that solid state conversion of tricalcium aluminate to ettringite could result in an eightfold increase in volume as follows:



The numbers in the first line below the equation are the volumes, and as can be seen there is a net reduction in volume of the reactants by 46.4 cc. The next line compares the relative volumes of anhydrous tricalcium aluminate to that of ettringite. Lea (13) notes that there are difficulties in ascribing expansion in sulphate solutions directly to the increased volume of solids produced because there

is little correlation between the amount of gypsum or ettringite formed and the degree of expansion observed. This difficulty is also noted by Metha (23) when he studied ettringite formation in three types of expansive cements. He found, on the basis of stoichiometric equations, that there was a 7 to 8 percent reduction in volume on completion of ettringite forming reactions instead of volumetric increase. Metha proposed an alternative hypothesis for the expansion associated with ettringite formation:

- (i) only colloidal ettringite is capable of developing large expansions. In the presence of lime, the nature of ettringite formed is colloidal, and not long lathe-like crystals;
- (ii) for colloidal ettringite to form large expansions, it must be in contact with an outside source of water. The high specific surface of colloidal ettringite, and its peculiar crystal structure with a negative net charge, as proposed by Moore and Taylor, are probably responsible for attracting a large number of water molecules which surround the ettringite crystals and cause interparticle (perhaps double-layer type) repulsion. This causes an overall expansion of the system, without any change in the crystal lattice of ettringite.

Thorvaldson (24) suggested that volume changes are controlled by osmotic forces concerned with the shrinkage and swelling of the gel system. Chemical reactions condition the cement gel and attack the cementing substances. Lea states that the formation of new crystalline substances as a result of these reactions is incidental to them and

not the prime cause of expansion. He also states that it still remains to be seen if such a theory can account for the gross expansion that can occur in sulphate solutions and whether direct crystal thrust by anisotropic growth (a proposed mechanism for the expansion of plaster of Paris on setting) can be ignored.

Another mechanism of sulphate attack was proposed by Chatterji and Jeffery (25,26) which does not involve ettringite formation as the cause of attack. The expansion mechanism is attributed to the solid state conversion of pre-existing $4 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ to calcium aluminate monosulphate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$) by reaction with SO_4^{2-} ions in the liquid phase. The experimental basis for this mechanism was an observation that in a $\text{C}_3\text{A} + \text{Ca}(\text{OH})_2 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ paste, expansion had occurred when ettringite was disappearing and monosulphate was forming. The volume expansion due to the formation of monosulphate from C_4AH_{13} may or may not be accommodated in the structure depending on the calcium hydroxide concentration in the liquid phase. If the concentration of calcium hydroxide is high the solubility of C_4AH_{13} will be depressed, making the accommodative process inoperative, and as a result there will be disruptive expansion. There is evidence developing that throws doubt on this hypothesis, for instance the $13\text{H}_2\text{O}$ in the tetracalcium aluminate hydrate is questionable and $19\text{H}_2\text{O}$

has been suggested.

As is evident from the above summary of the various hypotheses for the mechanism of sulphate attack, there is still much controversy involved. To fully comprehend the mechanism or mechanisms involved, further research must be completed in the field of cement chemistry.

CHAPTER 4

EXPERIMENTAL

4-1 Background

The sulphate resistance test program, supported by a grant-in-aid from the Standard Slag Cement Company, was initiated in 1977. The first test program involved 76.2 by 152.4 mm (3 by 6 inch) concrete cylinders made from actual field mixes and subjected to various sulphate solutions representative of field conditions. Due to the slow rate of apparent deterioration, an accelerated test program using 25.4 by 25.4 by 285.75 mm (1 by 1 by 11½ inch) mortar prisms and 50.8 mm (2 inch) cubes stored in sulphate solutions of high concentrations was also initiated. In 1978 this study was further augmented by the writer's graduate research program. The concrete cylinder program, the accelerated test program, and graduate research program will be referred to as Phases One, Two and Three respectively. These three phases combine to form a comprehensive study on the sulphate resistance of slag cements.

4-2 Phase One

Eight concrete mixes, involving Types 10, 20 and 50 portland cements and slag cement as detailed in Table 4-1,

TABLE 4-1

MIX SPECIFICATIONS FOR PHASE ONE

Batch No.	1	2	9	3	4	5	6	7	8
Date Cast - April '77	21	21	27	25	25	26	26	27	27
Portland cement type	10	10	10	10	10	50	50	20	10
% Slag in binder	72	72	72	45	65	0	0	0	0
% C ₃ A equivalent*	3.4	3.4	3.4	6.4	4.3	3.5	3.5	7.1	12.1
W/C ratio	.45	.50	.50	.50	.45	.45	.50	.50	.50
Slump, mm	101.6	88.9	101.6	88.9	88.9	88.9	88.9	92.25	88.9
inches	4.0	3.5	4.0	3.5	3.5	3.5	3.5	3.75	3.5
% Air content	6.2	6.8	6.5	6.5	6.3	6.9	5.5	5.4	5.2
Placed In Solution									
Age (days)	46	-	58	14	29	8	8	12	8
f'c, MPa**	28.3	-	23.4	32.4	31.0	29.7	33.1	31.7	30.3
psi	4100	-	3400	4700	4500	4300	4800	4600	4400

* C₃A equivalent calculated using C₃A values given in Table 4-2.

** Interpolated from strength curves.

were cast at the Red-D-Mix concrete plant in Brantford, Ontario. All of the blended cements used in this study were made by replacing portland cement with slag cement (cementitious hydraulic slag) in varying proportions, directly at the mixer. Full, 6.12 cubic metre (8 cubic yard) batches were cast into a mix truck. The first 0.76 cubic metre (1 cubic yard) of concrete discharged from each mix was discarded to ensure uniform mixing and workability. Slump and air contents were measured and then approximately 600, 76.2 by 152.4 mm (3 by 6 inch) concrete cylinders were cast. Compaction was done by means of a vibrating table. After two days moist curing, the cylinders were transported to the Construction Materials Laboratory at McMaster University where they were then stripped of their molds and cured under water at 23 degrees celcius. When they had achieved compressive strengths of 27.6 ± 5.5 MPa (4000 ± 800 psi) they were placed in their designated aggressive sulphate solutions. Some of the cylinders from batch 2 were damaged in transit, therefore this batch was discarded and recast as batch 9. Some 152.4 by 304.8 mm (6x12 inch) cylinders were also cast from each mix, and were moist cured and tested for strength development at the Red-D-Mix laboratory in Hamilton. The chemistries of the cements used are given in Table 4-2.

7

TABLE 4-2

CHEMICAL COMPOSITIONS* OF THE TEST CEMENTS (PHASE 1)

	Type 10 Portland	Type 20 Portland	Type 50 Portland Cementitious Hydraulic Slag	
% CaO	62.96	63.57	62.39	39.72
% SiO ₂	20.39	21.77	21.98	37.58
% Al ₂ O ₃	5.85	4.18	4.06	8.52
% MgO	2.65	2.78	3.67	9.72
% Fe ₂ O ₃	1.91	2.33	4.32	Fe= 0.36
% SO ₃	3.25	3.29	2.46	2.02
% CaO Free	0.61	0.87	0.27	N.A.**
% Na ₂ O Equiv.	N.A.	N.A.	0.78	K ₂ O=0.39
% Mn	N.A.	N.A.	N.A.	0.69
% Insoluble	N.A.	0.13	<0.7	N.A.
% L.O.I.	1.64	0.99	0.60	N.A.
% C ₃ S	50.0	49.9	45.0	--
% C ₂ S	20.9	24.5	29.2	--
% C ₃ A	12.3 (Bogue)	7.1 (Bogue)	3.46 (2.0) (Bogue)	0.00
% C ₄ AF	5.8	7.1	13.15	--
Blaine (cm ² /g)	3270	3420	3280	4430
% Autoclave Exp.	0.15	N.A.	0.11	N.A.

Note: N.A. = Not Available.

*Chemistries are the plant production average for one month.

**Three samples of pelletized blastfurnace slag were tested for free CaO using the ethylene glycol method (at St. Lawrence Cement Ltd. Laboratory) and no trace was found.

***By X-ray diffraction (at Canada Cement Lafarge Ltd.)

The cylinders from each batch were divided into five sets (with 16 cylinders per set) and each set was then stored in one of five separate solutions:

- A. water
 - B. 1000 ppm SO_3
 - C. 2000 ppm SO_3
 - D. 3000 ppm SO_3
 - E. 3000 ppm SO_3
-] as Na_2SO_4
-] as MgSO_4

The remaining cylinders from each batch were stored under water to establish strength development. Three cylinders in each solution were fitted with stainless steel measuring points for monitoring longitudinal expansion. A 6.35 mm (1/4 inch) diameter hole was drilled 6.35 mm deep in the centre of both ends of these cylinders and then the measuring points or gauge studs were epoxied on, producing a 139.70 mm (5.5 inches) effective gauge length (i.e. length between the innermost ends of the stainless steel gauge studs). On each of these cylinders one gauge stud was rounded and the other pointed at a bevel of 45 degrees, to be compatible with the measuring apparatus. Lateral expansion was monitored across two diameters at the mid-height on each of two cylinders. Longitudinal expansion was measured by means of a dial gauge graduated to read in 0.0001 inch units, and mounted vertically on an adjustable stand as shown in Figure 4-1. A stainless steel bar was used as a reference. Lateral expansion was measured by a micrometer reading to 0.0001 inch. The solutions



FIGURE 4-1: Apparatus for measuring length changes of concrete cylinders and mortar bars.

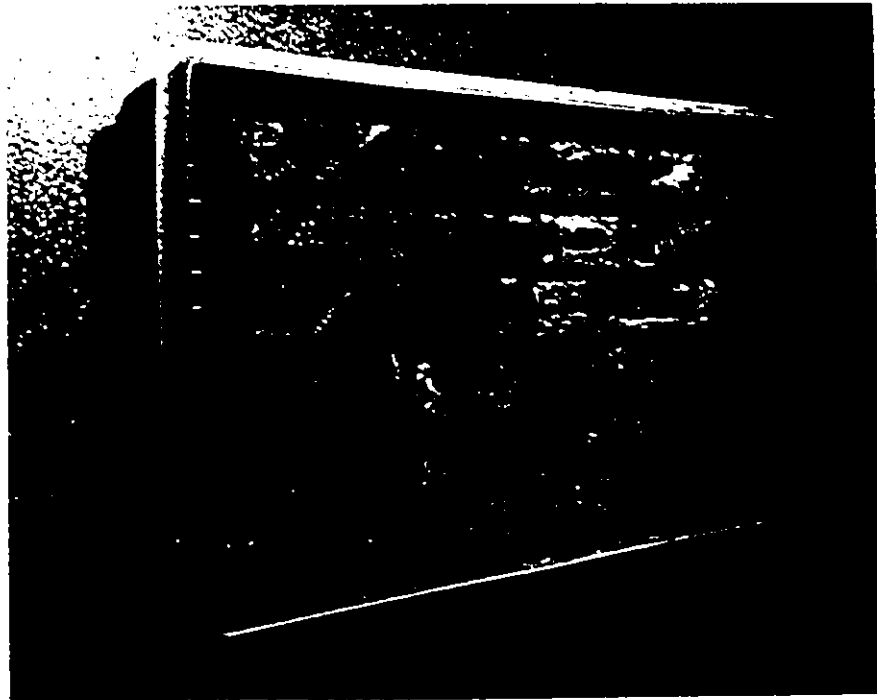


FIGURE 4-2: Typical storage of prisms and cubes in sulphate solutions in air-tight plastic containers (lid not shown).

were changed almost every time measurements were made, at 7,28,60,90,210 days and so on. Three cylinders from each of the 40 solution tanks (8 concrete mixes each stored in 5 solutions) were tested for strength periodically. Before testing, a measure of each cylinder's elastic modulus was determined by ultrasonic pulse velocity and the cylinders visually examined for signs of deterioration. Some fractured samples from the broken concrete surfaces were examined under the Scanning Electron Microscope (SEM) and also with the energy dispersive X-ray analyzer on the SEM.

4.3 Phase Two

To obtain more rapid results an accelerated test method using mortar cubes and prisms was initiated. The test method was roughly in accordance with K. Mather's proposed ASTM procedure (26,27) for evaluation of the sulphate resistance of various cements. Mortars of constant flow or workability (110 ± 5) as described in ASTM C109 were made, and molded into 50.8 mm (2 inch) cubes and 25.4 by 25.4 by 285.75 mm (1 by 1 by $11\frac{1}{4}$ inch) prisms. ASTM C109 silica sand was used throughout the mortar prism and cube testing. Mechanical mixing was carried out as prescribed in ASTM C305. The molds for making the prisms are described in ASTM C490. These molds are designed to allow for two stainless steel gauge studs to extend into the specimen 1.59 ± 0.64 mm (0.0625 ± 0.025 inch), on either end, providing a 254 mm

(10 inch) effective gauge length. The cubes and prisms were stored under deionized water until they had reached 24.1 ± 5.2 MPa (3500 ± 750 psi) and then placed in sodium sulphate solutions. In many similar types of experiments carried out by various researchers, a specified number of days is used as the criteria for placing the samples in sulphate solutions. This approach is not applicable when comparing various cements because their rates of hydration are different. K. Mather (27) notes that attempts to use ASTM C452 (test method for potential expansion of portland cement mortars exposed to sulphate) for slag cements and other blended cements have not been successful, since the reaction of the pozzolan or hydration of the slag in slag cements takes some time to achieve equal impermeability to otherwise comparable portland cement mortars. Thus it seems reasonable to start all the sulphate tests at equivalent strength and presumably equivalent impermeability, permitting comparisons to portland cement performance.

Six sets of cement mortars were evaluated for strength and expansion. A set consisted of 6 prisms and about 25 cubes. Each set was subdivided and stored in:

- A. de-ionized water
 - B. 3000 ppm SO_3
 - C. 50,000 ppm SO_3
- } as Na_2SO_4

The six cements were:

1. 100% Type 10 PC*
2. 100% Type 20 PC
3. 100% Type 50 PC
4. 50% SC/50% Type 10 PC
5. 70% SC/30% Type 10 PC
6. 50% SC/50% Type 20 PC.

The cements used were the same as those used in Phase One.

The containers in which the prisms and cubes were immersed were plastic tanks, with a plastic mesh approximately 12.70 mm (0.5 inch) thick placed at the bottom to allow free access of the solutions to all sides of the specimens. The tanks were covered to minimize evaporation, and additional solution was put in when required to maintain the solution level at about 12.70 mm above the surface of the mortar specimens. A constant temperature of 23 degrees celcius was maintained. In all of the tests, the sulphate solutions were made with reagent grade anhydrous sulphate salts in granular form dissolved in distilled or deionized water.

The solutions were changed almost everytime expansion readings were taken at approximately 3, 7, 28, 60 days and so on. Before expansion readings were made the prisms were surface dried, weighed and visually examined for any signs of deterioration.

*SC = Slag Cement, PC = Portland Cement.

4-4 Phase Three

Phase Three consists of a representative range of cement mortars subjected to various sulphate salts at different concentrations, along the lines of Phase Two. Three 25.4 by 25.4 by 254.0 mm (1 by 1 by 10 inch) gauge length mortar bars were made for each particular test to monitor length changes. They were compacted by hand tamping the mortar at two stages during the filling of the molds. Miniature mortar cubes were prepared in the same way and using the same molds. One day after casting demoulding was carried out and the prisms stored in deionized water. After about two days when they had gained enough strength to be handled, the prisms to be made into miniature cubes were cut into 25.4 mm (1 inch) cubes by a high speed saw with a diamond-edged blade. The miniature cubes were then used to monitor strength development.

The time required for the development of a given degree of corrosion varies exponentially with the size of the test specimens. The small size of the specimens used in these experiments permitted easier handling, less storage area requirements and quicker sulphate permeation into the interior. The concrete cylinders of Phase One have a low surface area to volume ratio of 0.07 mm^{-1} (1.67 inch^{-1}), on the other hand the 25.4 by 25.4 by 254.0 mm (1 by 1 by 10 inch) gauge length mortar bars have a higher surface area

to volume ratio of 0.16 mm^{-1} (4.18 inch^{-1}), allowing a more accelerated rate of attack. The miniature cubes have an even higher surface to volume ratio of 0.24 mm^{-1} (6.0 inch^{-1}) and an additional accelerating effect is produced by the increased rate of attack at the edges and corners. In two of the batches, 50.8 mm (2 inch) mortar cubes were also prepared in order to correlate the strengths of the 25.4 and 50.8 mm cubes.

Table 4-3 gives the cement blends and solutions in which the various mortar specimens were stored. The mortar specimens were kept under deionized water at 23 degrees celcius until compressive strengths of $24.1 \pm 4.1 \text{ MPa}$ ($3500 \pm 600 \text{ psi}$) had been attained. Magnesium and sodium sulphate solutions are most frequently used for testing the sulphate resistance of cements and concretes. Calcium sulphate has a relatively low solubility, only about 2 g/l can be dissolved in water and therefore the effects of highly concentrated solutions cannot be studied. Ammonium sulphate solution attacks so rapidly that satisfactory observations of the varying resistance of different cements are prevented. In Phase Three the aggressive solutions used were sodium, magnesium and potassium sulphates. The chemical compositions of the test cements are given in Table 4-4. Note that the chemistries of the Type 10 portland cements are those of the various plants' production average for one

TABLE 4-3 MIX SPECIFICATIONS FOR PHASE 3

Batch No.	Mix (Blends) *	Cast (1978)	Placed in Solns.		Type & Conc. of Solutions	Specimens		
			Age (days)	f'c (MPa) **		25.4 x 25.4 mm x 254.0 mm prisms	25.4 mm (1") Cubes	Misc. Cubes
1MA	100% Type 10PC (12.2% C ₃ A) ***	June 28	7	25.3	deionized H ₂ O	x	x	50.8mm
1MB	100% Type 10PC (12.2% C ₃ A) ***	June 28	7	25.3	50,000 ppm Na ₂ SO ₄ ***	x	x	50.8mm
1MB ₂	100% Type 10PC (12.2% C ₃ A)	Sept. 1	9	26.8	28,184 ppm Na ₂ SO ₄	x	x	—
1MC	100% Type 10PC (12.2% C ₃ A)	July 25	7	22.3	50,000 ppm K ₂ SO ₄	x	x	—
1MD	100% Type 10PC (12.2% C ₃ A)	July 25	7	22.3	50,000 ppm MgSO ₄	x	x	—
2MA	50% SC/50% Type 10PC (12.2% C ₃ A)	July 2	10	21.2	deionized H ₂ O	x	x	—
2MB ₁	50% SC/50% Type 10PC (12.2% C ₃ A)	July 24	10	23.0	28,184 ppm Na ₂ SO ₄	x	x	—
2MB ₂	50% SC/50% Type 10PC (12.2% C ₃ A)	July 24	10	23.0	35,000 ppm Na ₂ SO ₄	x	x	—
2MB ₃	50% SC/50% Type 10PC (12.2% C ₃ A)	July 2	10	21.2	50,000 ppm Na ₂ SO ₄	x	x	—
2MB ₄	50% SC/50% Type 10PC (12.2% C ₃ A)	Aug. 30	11	24.3	10,000 ppm Na ₂ SO ₄	x	x	—
2MC	50% SC/50% Type 10PC (12.2% C ₃ A)	Aug. 31	11	25.4	50,000 ppm K ₂ SO ₄	x	x	—
2MD	50% SC/50% Type 10PC (12.2% C ₃ A)	Aug. 31	11	25.4	50,000 ppm MgSO ₄	x	x	—
3MB	60% SC/40% Type 10PC (12.2% C ₃ A)	July 31	17	27.5	50,000 ppm Na ₂ SO ₄	x	x	—

..... cont'd

TABLE 4-3 (Cont'd)

Batch No.	Mix (Blends) *	Cast (1978)	Placed in Solns.		Type & Conc. of Solutions	Specimens		
			Age (days)	f'c(MPa)		25.4 x 25.4 x 254.0 mm	25.4 mm (1")	Misc.
						Prisms	Cubes	Cubes
4MB	65% SC/35% Type 10PC (12.2% C ₃ A)	July 31	20	25.6	50,000 ppm Na ₂ SO ₄	x	x	—
5MB	70% SC/30% Type 10PC (12.2% C ₃ A)	July 31	20	25.2	50,000 ppm Na ₂ SO ₄	x	x	—
6MB	40% SC/60% Type 10PC (12.2% C ₃ A)	Aug. 30	9	25.3	50,000 ppm Na ₂ SO ₄	x	x	—
7MB	100% Type 10PC (6.6% C ₃ A)	Aug. 28	13	24.6	50,000 ppm Na ₂ SO ₄	x	x	—
8MB	50% SC/50% Type 10PC (6.6% C ₃ A)	Sept. 1	11	24.1	50,000 ppm Na ₂ SO ₄	x	x	—
9MA	100% Type 10PC (8.9% C ₃ A)	Aug. 28	9	22.6	deionized H ₂ O	—	x	—
9MB	100% Type 10PC (8.9% C ₃ A)	Aug. 28	9	22.6	50,000 ppm Na ₂ SO ₄	x	x	—
10MA	50% SC/50% Type 10PC (8.9% C ₃ A)	Sept. 4	15	28.3	deionized H ₂ O	—	x	—
10MB	50% SC/50% Type 10PC (8.9% C ₃ A)	Sept. 4	15	28.3	50,000 ppm Na ₂ SO ₄	x	x	—
11MB	50% No. 1762 SC/50% Type 10PC (12.2% C ₃ A)	(1979) Jan. 7	15	26.2	50,000 ppm Na ₂ SO ₄	x	—	—
12MB	50% French SC/50% Type 10PC (12.2% C ₃ A)	Jan. 7	12	25.9	50,000 ppm Na ₂ SO ₄	x	—	—
13MB	100% Type 10PC (12.2% C ₃ A)	Jan. 9	10	26.3	50,000 ppm Na ₂ SO ₄	x	—	—
14MB	50% SC/50% Type 10PC (12.2% C ₃ A)	Jan. 9	10	25.2	50,000 ppm Na ₂ SO ₄	x	—	—

* Mortars made in accordance with ASTM C109 and C305. ** Average compressive strength obtained from

*** Sulphate concentration calculated as SO₃ 25.4 mm cubes; 145 psi = 1 MPa.

**** Obtained from chemistries of plant production for the average of one month (Bogue Calculations).

TABLE 4-4

CHEMICAL COMPOSITIONS OF THE TEST CEMENTS OF PHASE 3

Composition	Slag Cements				
	Type 10 Portland Cement*	Cementitious** Hydraulic Slag	No. 1762	French	
% CaO	62.96	63.88	63.71	38.19	38.58
% SiO ₂	20.39	21.76	22.14	37.93	36.14
% Al ₂ O ₃	5.85	4.72	4.14	8.42	9.06
% MgO	2.65	2.51	2.36	11.45	12.35
% Fe ₂ O ₃	1.91	2.16	2.60	Fe _{Total} =1.53	Fe _{Total} =0.48
% SO ₃	3.25	3.69	2.93	S = 2.00	S = 2.00
% CaO Free	0.61	0.42	0.59	N.A.	N.A.
% K ₂ O	N.A.	N.A.	N.A.	0.47	0.40
% Na ₂ O	N.A.	N.A.	N.A.	N.A.	N.A.
% TiO ₂	N.A.	N.A.	N.A.	N.A.	N.A.
% Mn	N.A.	N.A.	N.A.	0.63	0.46
% LOI	1.64	0.54	1.21	N.A.	N.A.
% C ₂ S	20.9	25.4	25.8	-	-
% C ₄ AF	5.8	6.5	7.8	-	-
% C ₃ A***	12.2	8.9	6.6	-	-
% C ₃ A***	11.8	8.3	6.1	-	-
Blaine (CM ² /g)	3270	3380	3570	3960	3881
					3873

N.A.= Not Available

* Chemistries are the plant production average for one month.

** Used in all samples containing slag in Phase 3, except specimens 11MB and 12MB containing No. 1762 and French slag cements, respectively.

*** Bogue calculation. **** by x-ray diffraction on actual batch samples used.

month. X-ray diffraction was also carried out on samples from the actual portland cements used in Phase Three, at the Canada Cement Lafarge Ltd. Research Laboratory, Belleville, Ontario, to determine a more precise estimate of the tricalcium aluminate contents. The chemistries of the slag cements are those of the actual batch used and were analyzed by X-ray fluorescence at the Dofasco Research Department.

The prisms and cubes were kept fully immersed in the various solutions in plastic containers as shown in Figure 4-2. The containers have air tight lids preventing evaporation of the solutions. A plastic mesh, approximately 12.7 mm (0.5 inch) thick, lined the container providing a means for supporting the specimens so that no end or side rests against the container and allowing the solutions free access to all sides of the specimens.

4.4.1 Mortar Bars Subjected to Immersion Cycles (Wetting and Drying) in a Severe Sulphate Environment

It has been found that where concrete structures are only partially submerged in an aggressive solution, or where only one side of the concrete structure is in direct contact with aggressive water or soil, a continuous capillary action is set up through evaporation on the air side. The capillary action creates a driving force which may cause a much higher concentration of sulphates in the concrete

than would normally occur, resulting in more extensive damage. Thus, damage occurring in the zone of fluctuation of the groundwater table is often the severest and of greatest interest. To simulate this condition where evaporation of the aggressive solution takes place causing solution level fluctuations, immersion equipment involving mortar prisms was developed. The sulphate solution was placed in a polythene tank approximately 304.8 by 355.6 by 203.2 mm (12 by 14 by 8 inches), on top of which rests a 9.5 mm ($3/8$ inch) thick plexiglass lid. The lid contained several holes, 38.1 mm (1.5 inches) in diameter, so that 25.4 by 25.4 by 285.75 mm (1 by 1 by $11\frac{1}{4}$ inch) prisms can pass through and stand with their long axes upright. The prisms were held by adjustable plexiglass clamps in order that their depths of immersion could be controlled. A view of this equipment is shown in Figure 4-3. The prisms were prepared and cured the same way as those previously described and when they had reached the required strength (24.1 ± 4.1 MPa) they were immersed 101.6 mm (4 inches) in 50,000 ppm SO_3 as Na_2SO_4 . After 7 days they were raised so that only 50.8 mm (2 inches) of the prisms were immersed; when another 7 days had elapsed the cycle was repeated. There was thus a 14 day cycle of wetting and drying of an effective length of 50.8 mm (2 inches) of a prism. Two batches, each containing three prisms, were subjected to this test. One was a 100% Type 10 portland cement (11.8% C_3A)

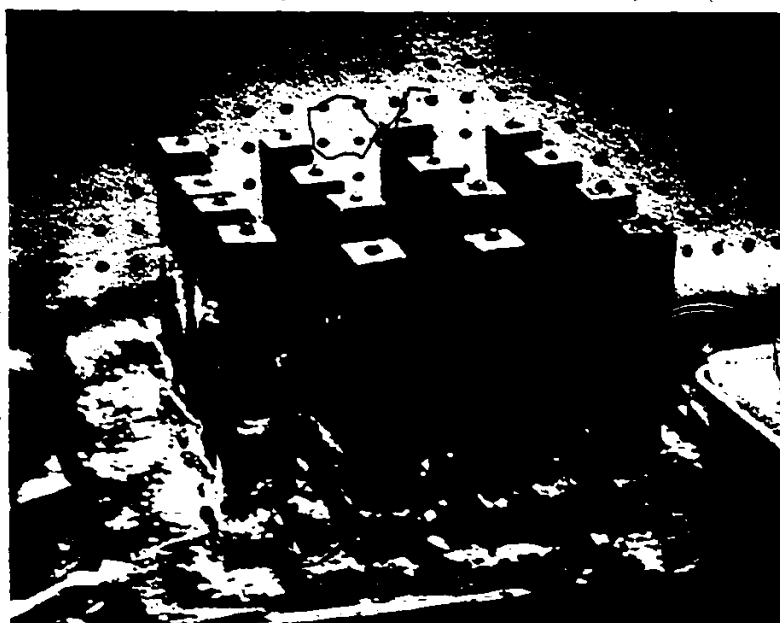


FIGURE 4-3: Test equipment simulating immersion cycles (wetting and drying) in a severe sulphate environment.

blend and the other 50% SC/50% Type 10 PC (11.8% C_3A), designated as 13MB and 14MB respectively.

Two batches were cast to study the effects of variations in pelletized blastfurnace slag chemistries on the sulphate resistance of blended cements. The chemistries of the two slag cements are given in Table 4-4, referred to as No. 1762 slag and "French" slag. Both of these blastfurnace slags were received in the form of pellets and were ground to cement fineness in a ball-mill in the laboratory. The Blaines were 3881 and 3872 cm^2/g for the No. 1762 and French slags respectively, which are very close to that of the slag cement used for the rest of the samples of Phase Three (3960 cm^2/g). (The fineness of these slag cements was made as close as possible to one another to eliminate fineness as a variable, since it influences strength development and resistance to corrosion).

4.4.2 The Lok-Test

The "Lok-Test" pullout method was employed for monitoring the strength influence of sulphates on some actual concrete mixes in Phase Three to supplement the Phase One work (Figures 4-4 to 4-7). This is an indirect method for determining the compressive strength of the concrete in the structure itself. The force required to pull out special test bolts embedded in the concrete is measured and then

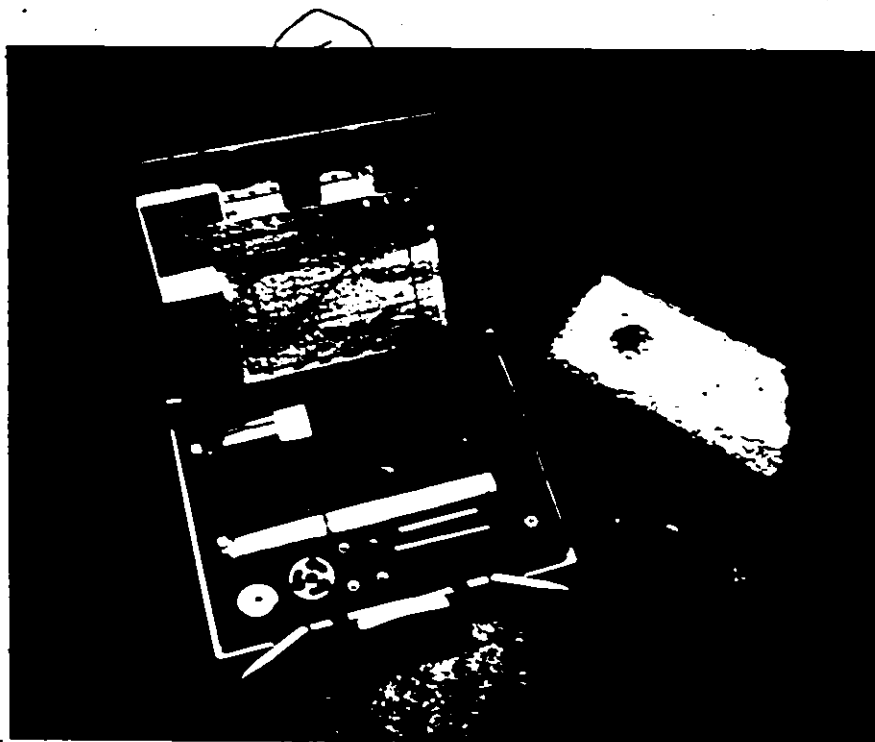
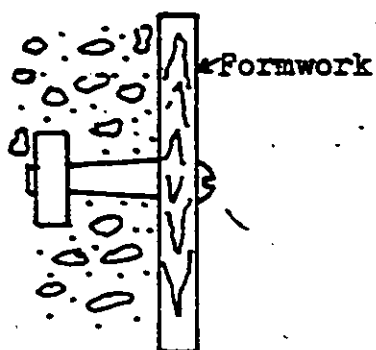
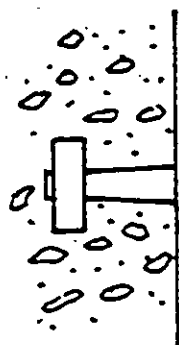


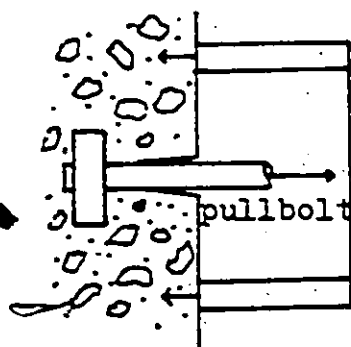
FIGURE 4-4: Lok-Test instrument. The photograph shows the Lok-Test machine and its accessories in a briefcase. A tested concrete specimen is also shown.



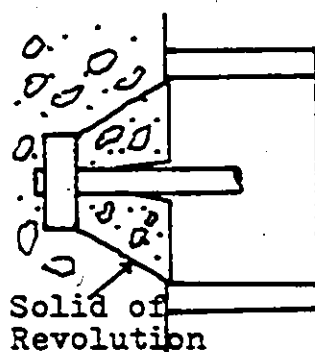
The test bolt (incl. disc and stem) is mounted on the inside of the form prior to placing concrete.



The formwork (or part of the formwork) and the stem of the test bolt are removed.

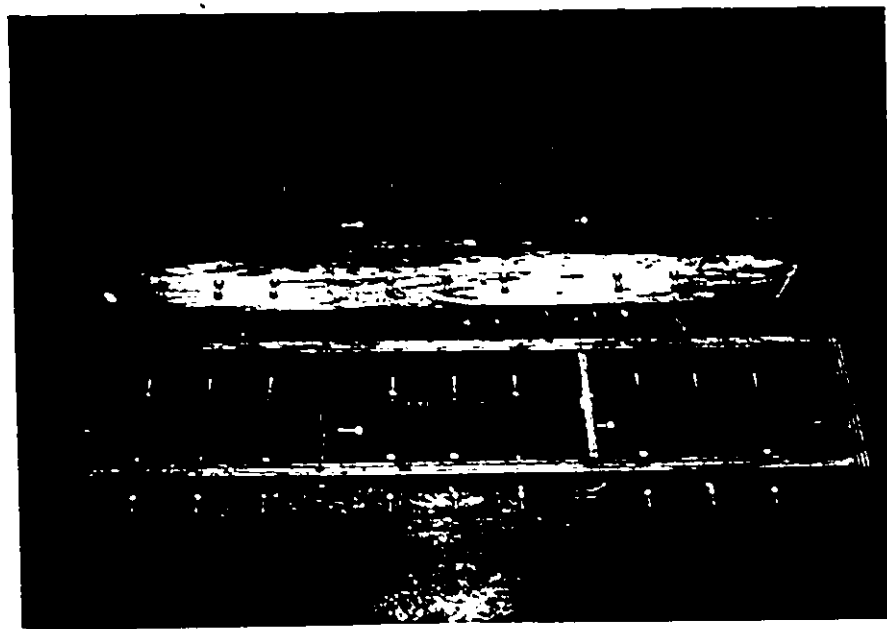


A pull bolt is screwed into the disc, and the instrument is mounted on the surface of the concrete.



By applying a force with the instrument a small piece of concrete is dislodged. The force required to extract the disc through the cylindrical counter-pressure device is called the lok-strength.

Fig. 4-5: THE LOK-TEST METHOD



FIGURES 4-6 and 4-7: Two views of the plywood formwork containing Lok-Test bolts, used for making 152.4 by 152.4 by 325.1 mm concrete prisms.

an empirically established linear relationship is used to convert the measurement to the conventional cylinder compressive strengths of the concrete. Since a failure plane near the surface is involved, concrete deterioration should be more evident than in conventional compression tests.

The Lok-Test was developed and patented by Kierkegaard-Hansen in Denmark about 1962 (28). A Model 4 Lok-Test instrument was used which is capable of measuring within a compressive strength range of 6 MPa (900 psi) to 55 MPa (8000 psi). The Lok-Test instrument consists of a hydraulic jack with gauge, pull bolt, centering plate, and coupling which fits into a briefcase as shown in Figure 4-4. The hydraulic jack and gauge weigh about 4300 g (9.5 lb). The jack has a circular bearing surface with an inside diameter of 55 ± 0.1 mm ($2.2 \pm 3.9 \times 10^{-3}$ inches), and an outside diameter of at least 70 mm (2.8 inches). The instrument may be used to a total load of 65 kN, and for this load range the force can be determined within ± 3 per cent (29). The instrument ensures perpendicular loading on the concrete surface and can be continually loaded at a speed of 30 ± 10 kN per minute. A test bolt consists of a screw with a long shank, a steel disc and a stem. The disc has a diameter of 25 ± 0.05 mm ($0.98 \pm 2 \times 10^{-3}$ inch) and is 8 mm (0.31 inch) thick. The length of the stem is such that the distance between the disc and concrete surface is 25 mm. To prevent the bolt from bonding

to the concrete a special coating is factory applied to the bolt. This coating does not influence the strength of the adjacent concrete. The Lok-Test method can be used for destructive and non-destructive testing. For non-destructive testing the load is relieved when the Lok strength is reached just before a full breakage of the concrete, and only a hair-line circular crack results. For destructive testing the loading is applied until the concrete breaks. Only in some cases will a small concrete cone be pulled out, leaving a hole in the specimen about 25.4 mm (1 inch) deep and 50.8 (2 inches) in diameter. The rest of the specimen remains undamaged.

Figure 4-5 gives a brief outline of the Lok-Test method and the detailed procedure is given in Appendix A. Concrete prisms, 152.4 by 152.4 by 325.1 mm (6 by 6 by 12.8 inches), each containing seven or eight Lok-Test bolts were made. The forms were made out of 9.53 mm (3/8 inch) plywood and divided up into three sections with 6.35 mm (1/4 inch) holes drilled perpendicular to the formwork and the test bolts attached as shown in Figures 4-6 and 4-7. Mixing of the concrete was done by means of an Eirich E2 mixer using the mix specifications as presented in Table 4-5. The mix was internally vibrated in two layers in the forms by a poker-vibrator and extra care was taken to compact around the test bolts to try to achieve a homogeneous mix throughout the specimen. Slump

TABLE 4-5

LOK-TEST MIX SPECIFICATIONS

Batch No.	A	B	A ₂	B ₂
Date Cast (1978)	Aug. 10	Aug. 10	Sept. 12	Sept. 12
PC Type (12.2% C ₃ A)*	10	10	10	10
% Slag Cement in Binder	0	0	50	50
W/C ratio	0.40	0.40	0.44	0.44
Slump, mm	63.5	63.5	83.8	83.8
inch	2.5	2.5	3.3	3.3
% Air Content	6.0	6.0	5.8	5.8
Placed in Solution:				
- Age	7	7	10	10
- f'c, MPa	32.4	32.4	27.6	27.6
psi	4700	4700	4000	4000
Solution Stored in	Tap water	50,000 ppm SO ₃ as Na ₂ SO ₄	Tap water	50,000 ppm SO ₃ as Na ₂ SO ₄
Specimen Type/s	Prisms with Lok bolts & 152.4 x 304.8 mm (6x12 inch) cylinders	Prisms with Lok bolts & 152.4 x 304.8 mm (6x12 inch) cylinders	Prisms with Lok bolts & 152.4x304.8 mm (6x12 inch) cylinders	Prisms with Lok bolts & 152.4x304.8 mm (6x12 inch) cylinders

* Bogue calculations.

and air contents were recorded. Demoulding was carried out the following day, and the specimens cured in tap water until compressive strengths of 27.6 ± 4.8 MPa (4000 ± 700 psi) were reached. The specimens were then stored in either a solution of 50,000 ppm SO_3 as Na_2SO_4 or tap water for the control specimens. The tap water used was a moderately hard water with a total hardness* of 140 mg/l, neutral (pH 7), and contained about 30 mg/l chloride, 0.2 mg/l iron, 0.09 mg/l nitrate and 35 mg/l sulphate. Approximately 24 152.4 by 304.8 mm (6 by 12 inch) cylinders were cast with 100% Type 10 portland cement (11.8% C_3A) as the binder and another 24 with 50% slag cement/50% Type 10 portland cement (11.8% C_3A) blend, and stored under tap water in order to check the conventional strength developments of the concrete with that obtained from Lok-Testing. The same slag cement was used as in miniature prisms and cubes of Phase Three. After the Lok-Test pull outs were performed, some of the concrete cones that were completely pulled out were examined under the Scanning Electron Microscope for signs of expansive sulphoaluminate hydrates.

4.4.3 Porosity Measurements

The porosity of two selected mortar mixes (specimens

* A characteristic of water that represents the total concentration of calcium and magnesium ions.

9MA, 9MB, 10MA and 10MB) were periodically measured. Porosity is an important factor in sulphate attack since it dictates the amount and rate of penetration of aggressive ions into the cement mortar or concrete, and the degree of attack. The method used was that of Figg and Bowden (30) in which a thin slice of the specimen was cut and placed in carbon tetrachloride under vacuum and the weight of the carbon tetrachloride absorbed into the specimen was recorded. The volume of the thin slice was measured by a Beckman MDL 930 Air Comparison Psychrometer and knowing the density of the carbon tetrachloride the porosity of the mortar was calculated. The procedure is described in more detail in Appendix B. A modification of this test was later adapted in which methanol replaced the carbon tetrachloride (31). Methanol has many advantages as it is less volatile and less toxic than carbon tetrachloride. One of the main advantages is that the molecules are polar which makes it easier for them to wedge into the tiny pores of the mortar or concrete.

4.5 Criteria of Failure

The indicators of failure due to sulphate attack selected were:

- a. total expansion over 0.10 per cent; or
- b. collapse or fracture of the specimen.

In most cases the tests were continued beyond the

point of failure as defined above to record and observe additional information.

CHAPTER 5

EXPERIMENTAL FINDINGS AND DISCUSSIONS

5.1 Phase One

Out of the eight concrete mixes only one has exhibited signs of sulphate attack after about 26 months of exposure to the aggressive sulphate solutions. Batch number 8 (100% Type 10 Portland cement) is the only one with signs of deterioration. The specimens stored under 3,000 ppm SO_3 as Na_2SO_4 (batch 8D) first showed evidence of attack in the form of slightly bulging surfaces near the edges of the cylinders and cracking at their top edges after approximately 390 days in solution. At 440 days in solution the specimens in 2,000 ppm SO_3 as Na_2SO_4 (batch 8C) showed slight deterioration much like that of batch 8D at 390 days. The concrete cylinders in 3,000 ppm SO_3 as MgSO_4 (batch 8E) have responded similarly. A photograph of typical specimens from batches 8D and 8E, taken after 24 months of exposure, is shown in Figure 5-1. Noticeable concentric cracks can be seen near the top edge of specimen 8D and the edge is beginning to spall off. In 8E very fine, hairline cracks are visible under careful examination. The longitudinal expansions of 8C, 8D and 8E are larger than the control specimens stored under water. The results of the longitudinal length changes were extremely

erratic for all the mixes. Even in a particular batch which represented one cement and one aggressive sulphate solution, longitudinal expansions were found to differ by as much as three times between the highest and lowest readings. In some cases, longitudinal expansions from the same batch would even show expansion in one specimen and shrinkage in another. It was not uncommon for the longitudinal expansions of the control specimens stored in water to show more expansion than those in the sulphate solutions. When the initial lengths of the cylinders were measured they were in a dry state, since the readings were taken soon after the measuring points were epoxied and set. In most cases if these initial readings are used in the calculation of longitudinal expansions, unrealistic expansions are obtained. Therefore, if this was found to be the case, the 7 day expansion reading was taken as the initial reading (only in Phase One). The expansion results are tabulated in Tables C-3 to 10 (Appendix C). The lateral expansions measured across two diameters at the mid-height of the cylinders were even more erratic than the longitudinal expansions. Measurement of the elastic modulus by ultrasonic pulse velocity also produced erratic results. Because of the significant scatter of results the lateral expansions and ultrasonic pulse velocities are not discussed here, but again included in Tables C-11 to C-18 and C-2 respectively in Appendix C.

The compressive strengths measured and summarized in Table C-1 (Appendix C) also do not show any particular trends.

The erratic results of Phase 1 to date are most likely due to the testing program adopted in which actual field mixing conditions were carried out. Also the type and size of the specimen, and the relatively weak sulphate solutions, result in very slow rates of sulphate attack so that there is little happening to observe except for surface attack of batch 8. Monitoring of these specimens is being continued, but at the moment no significant results or conclusions can be drawn from the present data except for the observed attack of batch 8.

Similar types of experiments were carried out by the U.S. Army Corps of Engineers (32,33) using 76.2 by 152.4 mm (3 by 6 inch) concrete cylinders with slag cement/portland cement blends. The cylinders were fitted with inserts and tested for changes in weight and length. Some of the specimens were stored in tap water and others in a 10 percent solution of Na_2SO_4 (56,400 ppm SO_3 as Na_2SO_4). Attempts to measure the fundamental flexural frequency of their specimens were not successful. The results of the tests for length and weight changes were very erratic and yielded no significant results. It would appear that the use of field mixes and representative sulphate environments

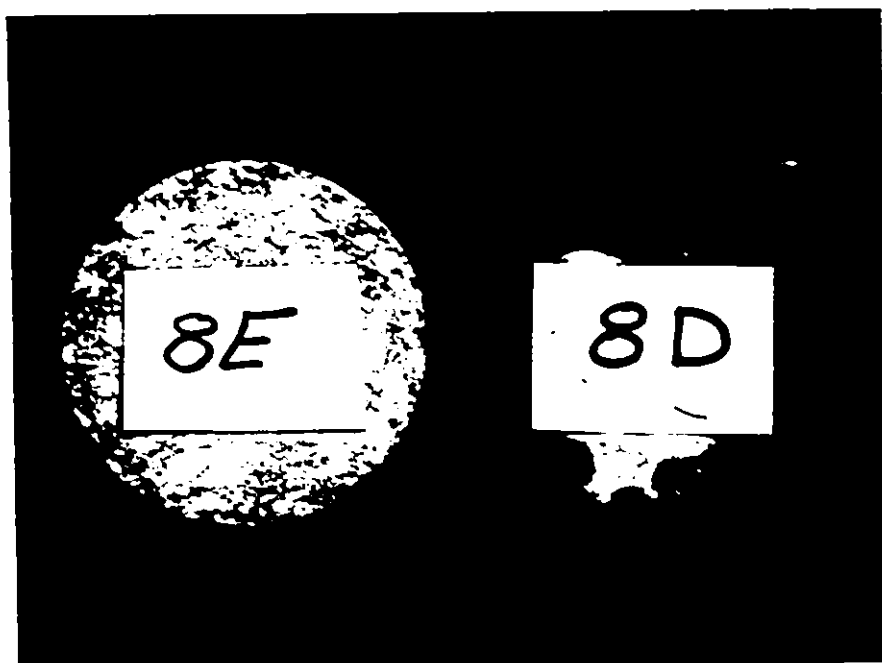


FIGURE 5-1: Top view of concrete cylinders showing signs of sulphate attack after 24 months in sulphate solutions. Specimen 8E was stored in 3,000 ppm SO_3 as MgSO_4 and 8D in 3,000 ppm SO_3 as Na_2SO_4 . These specimens contained no slag cement.

require a long observational period for any trends to develop, and accelerated testing is called for.

5.2 Phase Two and Phase Three Results

As there is considerable overlap in the factors considered in Phases 2 and 3 the results will be integrated under the following topics:

5.2.1 Effect of Type of Sulphate Salt

The mortar specimens stored in 50,000 ppm SO_3 as sodium, potassium and magnesium sulphate solutions in Phase 3 have deteriorated rapidly at early ages. Figure 5-2 illustrates the effect of the type of sulphate salts and their varying degrees of aggressiveness. The per cent expansion versus the time of exposure (in days) in sulphate solutions is plotted for four sets of specimens, all made of 100% Type 10 portland cement (11.8% C_3A) as the binder and 3 of which were subjected to either Na_2SO_4 , K_2SO_4 or MgSO_4 , all of concentration 50,000 ppm calculated in terms of SO_3 . The fourth set of specimens was stored in deionized water and is shown for comparison.

Mortar prisms in the Na_2SO_4 solution (batch LMB) showed signs of attack after only about 80 days exposure, with slightly bulging edges, hairline cracks and spalling corners. Failure (0.10 per cent expansion) occurred at about 95 days of sulphate immersion. Monitoring was

Solution	No.	Symbol
0 (H_2O)	1MA	—•—
50,000 ppm $-Na_2SO_4$	1MB	—△—
50,000 ppm $-K_2SO_4$	1MC	—○—
50,000 ppm $-MgSO_4$	1MD	—+—

* All calculated as SO_3

All specimens 100% Type 10 PC (11.8% C_3A)

Values are the average of 3 readings.

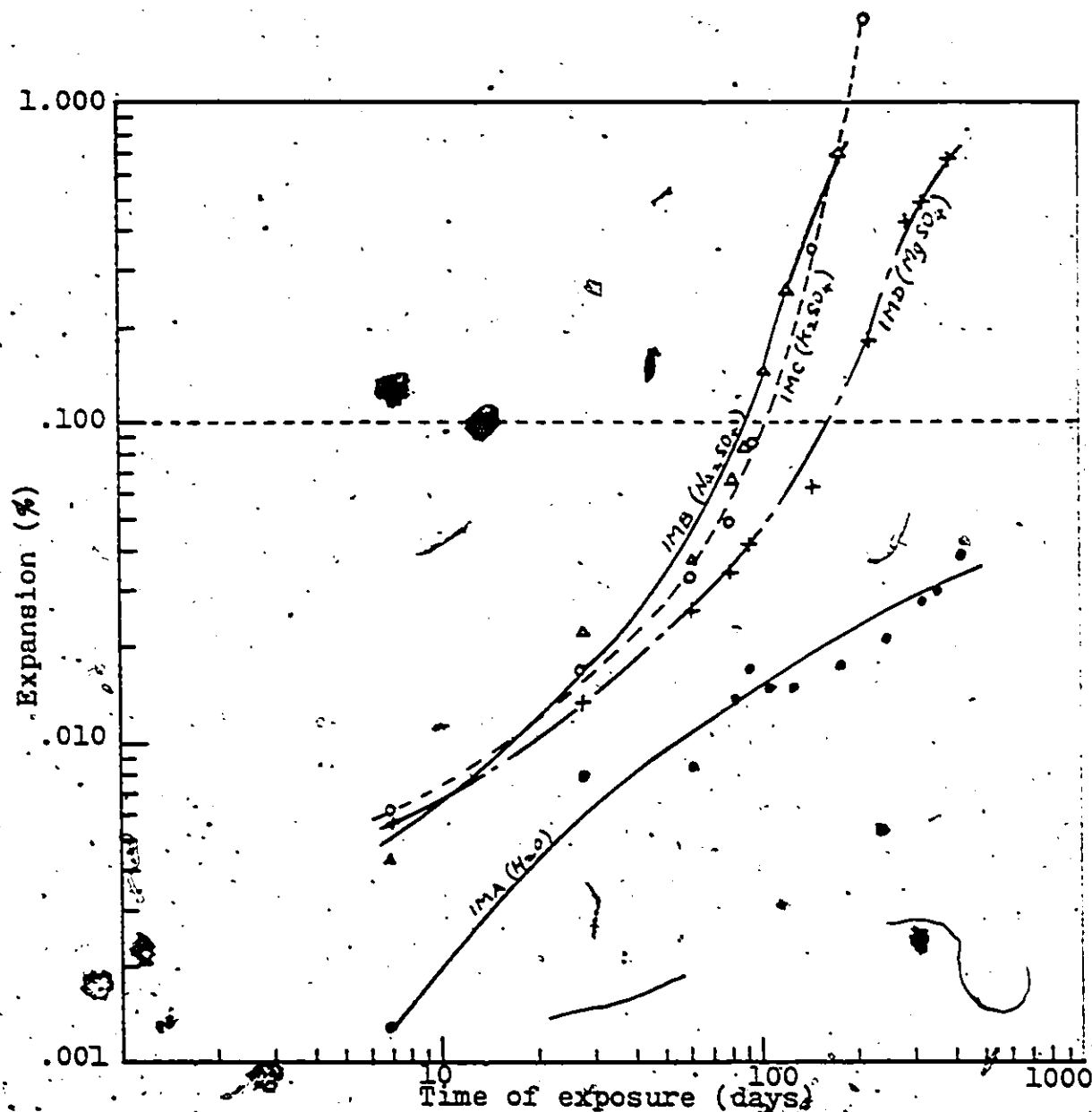


Figure 5-2: EFFECT OF SULPHATE TYPE ON EXPANSION OF 100% TYPE 10PC (11.8% C_3A) MORTAR PRISMS

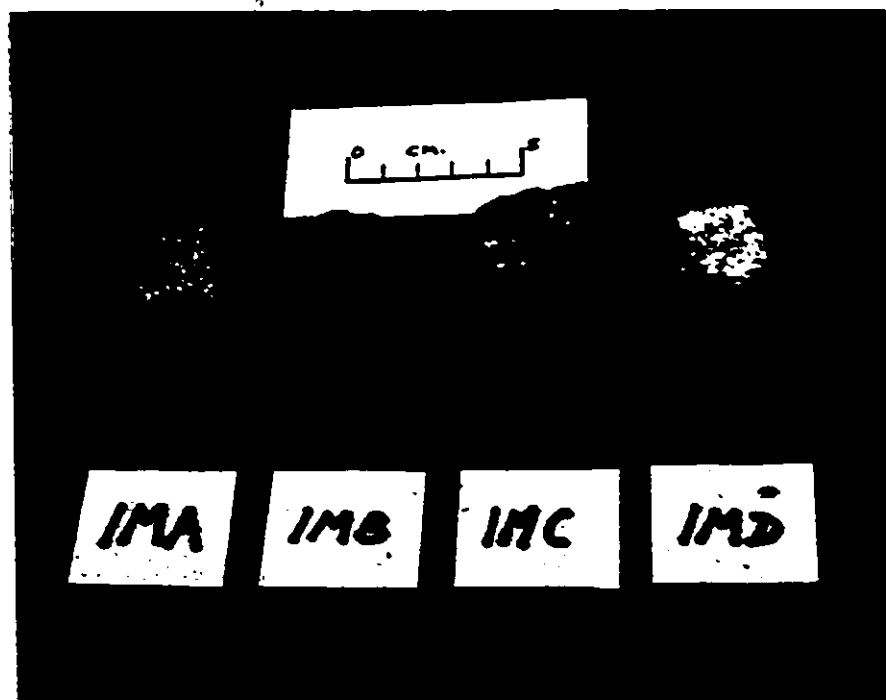
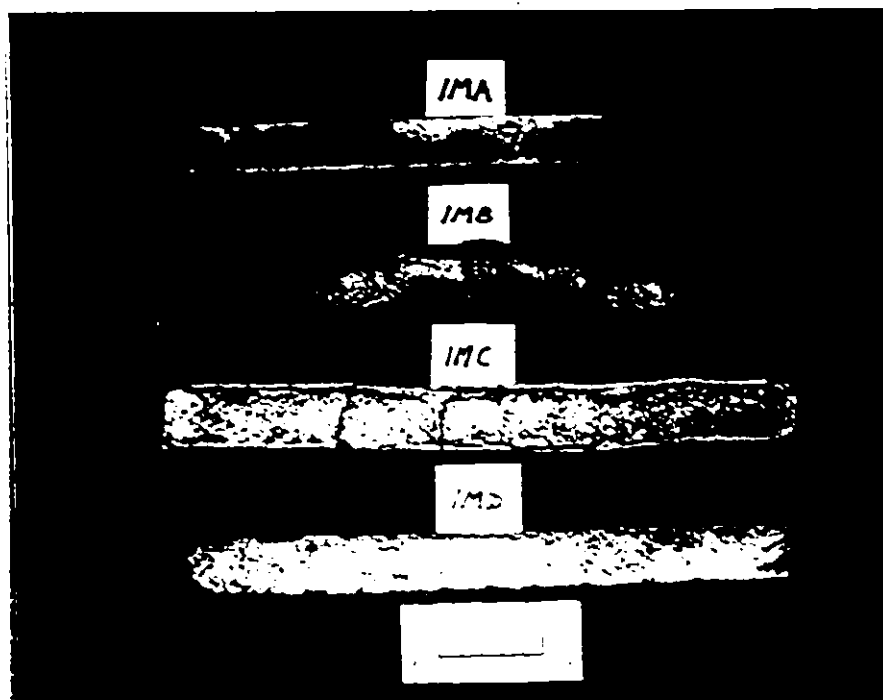
continued until about 200 days when the specimens had physically failed. Cracking and spalling had become quite extensive and the prisms of batch LMB were noticeably bent. This is due to the formation of a rich cement skin on the surface which was finished with a trowel when the prisms were being made in the molds. The rich cement skin is attacked less rapidly than the other surfaces by the sulphate solutions, hence the prism tends to bend during rapid expansion. Before the LMB specimens had completely failed expansions as high as 0.7 percent were recorded. The compressive strengths of the cubes in the sulphate solutions (LMB) did not reflect these trends prior to physical destruction by sulphate attack. The compressive strengths of the 25.4 mm (1 inch) cubes showed a slight decrease with the onset of sulphate attack but the 50.8 mm (2 inch) cubes did not. The compressive strength data for the mortar cubes of Phase Two and Three are summarized in Tables D-1 and E-1 in Appendices D and E respectively.

Within one week of storage in potassium sulphate, a white, slimy, gel-like growth appeared on the surface of the specimens. The white coating was examined by X-ray diffraction analysis and is most likely a potassium salt. After about 17 days the edges and corners began to soften, and the 25.4 mm (1 inch) cubes showed significant strength losses. A similar mode of attack is observed under magnesium

sulphate solution but at a somewhat less rapid rate. The magnesium sulphate forms a hard, slightly slimey, greyish white skin of insoluble $\text{Mg}(\text{OH})_2$ around the specimens. This skin tends to hinder penetration of the solution, retarding corrosion and as a result reducing the degree of attack.

Figures 5-3 and 5-4 vividly show the various degrees of attack on 25.4 by 25.4 by 285.75 mm (1 by 1 by 11½ inch) prisms and 25.4 mm (1 inch) mortar cubes stored under water (1MA), Na_2SO_4 (1MB), K_2SO_4 (1MC) and MgSO_4 (1MD). The mortar specimens are the same as in Figure 5-2. The photographs of Figures 5-3 and 5-4 were taken after 330 days immersion for specimens 1MA and 1MB, and 310 days immersion for specimens 1MC and 1MD.

From Figures 5-3 and 5-4 it can be seen that specimens 1MB, 1MC and 1MD have expanded substantially more than the control specimen 1MA. Specimen 1MC failed (>0.10 per cent expansion) after 100 days immersion and 1MD after about 165 days. 1MB failed by extensive swelling, cracking and spalling. In K_2SO_4 solution, the surface of specimen 1MC was observed to first soften with the mortar losing cohesion, then swelling, cracking and spalling followed. An expansion of 1.8 per cent was recorded before the specimens broke on handling after 214 days in solution. The specimens of 1MC have shown a loss of 35 percent in compressive strength from



FIGURES 5-3 and 5-4: Miniature mortar prisms and cubes after about 330 days immersion in the case of IMA and IMB, and 310 days in the case of IMC and IMD. All are 100% Type 10 PC (11.8% C_3A) subjected to 50,000 ppm CO_2 as Na_2SO_4 (IMB), K_2SO_4 (IMC) and $MgSO_4$ (IMD). IMA is a control batch stored in deionized water.

their 7 day strengths when tested at 90 days. For specimen LMD in MgSO_4 only a few fine hairline cracks were observed under the dense white protective skin of magnesium hydroxide. Its main mode of failure was by surface softening and the hardened cement losing cohesion. On handling, the specimens would disintegrate into a mushy paste of cohesionless cement and sand. LMD expanded at a slower rate and to a lesser degree than LMB and LMC. Failure (>0.1 percent expansion) of specimens LMD occurred after 165 days in the MgSO_4 solution. After 392 days of immersion an expansion of 0.65 percent was recorded. A 12 percent loss of compressive strength at 90 days from its 28 day strength was measured.

The results show the Na_2SO_4 and K_2SO_4 salts to be more rapid in their attack than MgSO_4 , but field experience has shown that the attack by magnesium sulphate is potentially more extensive than that of sodium or potassium sulphates. Na_2SO_4 and K_2SO_4 react with the hydrated calcium aluminate and also the calcium hydroxide of the hardened cement. MgSO_4 not only reacts with the calcium aluminates and calcium hydroxide but also attacks the hydrated silicate phases of the portland cement and thus may have a more far-reaching effect. The high concentrations of these sulphate cations result in slightly acidic solutions of about pH 6.0 to 6.5. In the acid attack the $\text{Ca}(\text{OH})_2$ present in the slag cement/portland cement binder is attacked,

also the calcium silicate hydrate gel (especially in the presence of MgSO_4) is converted to gypsum. These reactions are accompanied by surface softening and strength loss (34). This was found to be the case with K_2SO_4 and MgSO_4 . On the other hand, specimens in Na_2SO_4 were observed to deteriorate by extensive swelling and cracking commonly associated with the formation of ettringite.

5.2.2 Effect of Salt Concentration

The effect of the sulphate salt concentration is presented in Figure 5-5. Four different concentrations of Na_2SO_4 were used in Phase 3 (calculated as SO_3): 10,000 ppm, 28,184 ppm, 35,000 ppm and 50,000 ppm. All the batches consist of a 50 percent slag cement/50 percent Type 10 portland cement (11.8 percent C_3A) blend as the binder. As anticipated, the specimens in 28,184 ppm solution produced greater expansions than the ones under 10,000 ppm. Likewise, the specimens under 35,000 ppm expanded more than those in 28,184 ppm. However, the prisms in the 50,000 ppm solution produced expansions less than those in the 10,000 ppm solution up to 100 days immersion.

Sulphate attack is generally intensified by increasing the concentration of the Na_2SO_4 solution, but the degree of attack is not directly proportional to concentration. Biczók (5) notes that the concentration also affects the type of corrosion. The initially pure sulphate corrosion

Solution	No.	Symbol
0 - (H ₂ O)	2MA	---●---
10,000 ppm - Na ₂ SO ₄ *	2MB ₄	---○---
28,184 ppm - Na ₂ SO ₄	2MB ₁	---△---
35,000 ppm - Na ₂ SO ₄	2MB ₂	---+---
50,000 ppm - Na ₂ SO ₄	2MB ₃	---□---

* All calculated as SO₃

All specimens 50% SC/50% Type 10 PC(11.8% C₃A)

Values are the average of 3 readings.

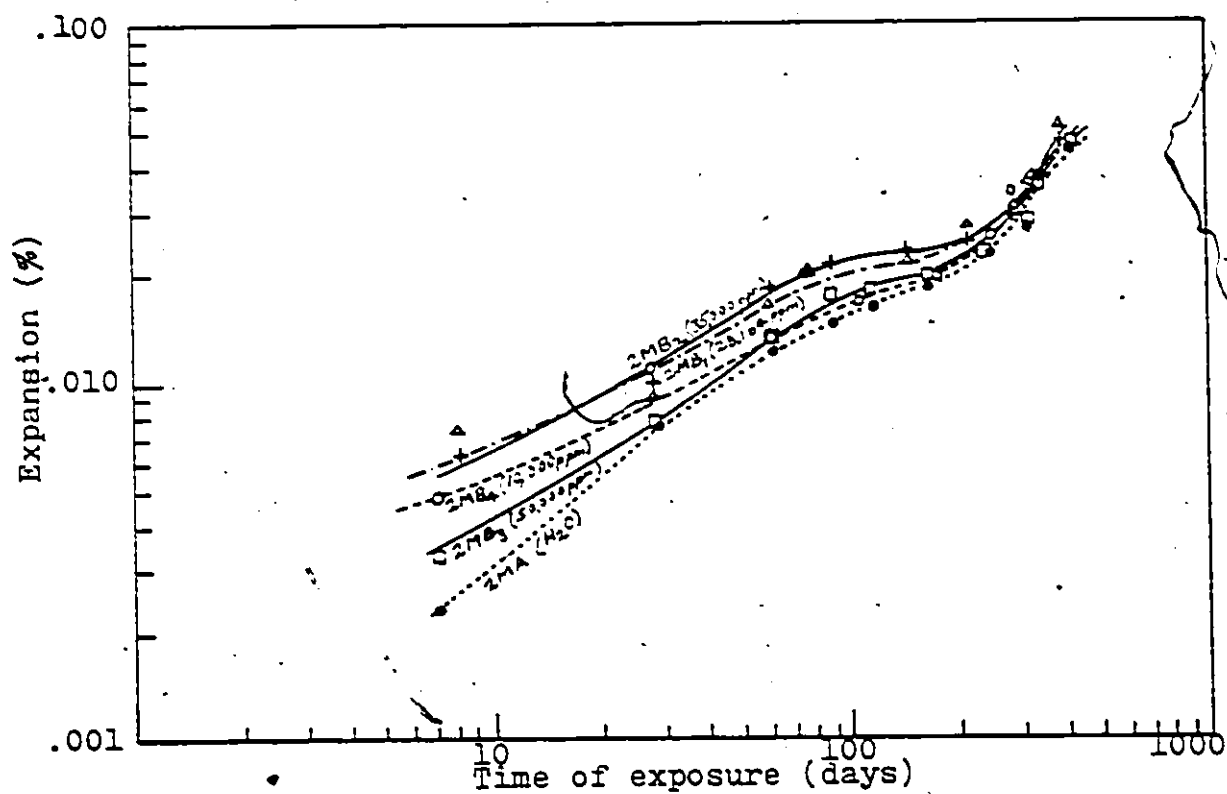


Figure 5-5: EFFECT OF SALT CONCENTRATION

is replaced by a sulphatic gypsum corrosion and then by pure gypsum corrosion as indicated in Figure 5-6. Biczok explains:

As long as the SO_4 content does not exceed 1000 ppm, the corrosion is of an unquestionably sulphatic (sulphoaluminate) character. Increasing concentration initiates simultaneous gypsum corrosion, whose role remains, however, insignificant between fairly wide Na_2SO_4 concentration limits. Pure gypsum corrosion does not gain the upper hand until the concentration becomes very high. The transition between sulphate and gypsum corrosion is of the overlapping rather than of the abrupt kind. The range of transition depends on the mineral composition of portland cement.

Why the specimens in the 50,000 ppm solution expanded less than those of lower concentrations at early stages is not known. It is believed that due to the high salt concentration, the voids and capillaries soon become filled up with time as the chemical reactions proceed. This would limit further migration of the soluble sulphates into the mortar, decreasing further attack at early stages. This phenomenon was explored using porosity measurements. Thin slices of the cube specimens stored in 50,000 ppm Na_2SO_4 solution were cut. Slices from the middle and ends were measured for their porosities. The porosity of the end sample was found to be 12.6 percent and the middle 13.9 percent. This indicates that the porosity may decrease from the centre to the outer surfaces of the specimen as the sulphate attack proceeds. But the difference is only

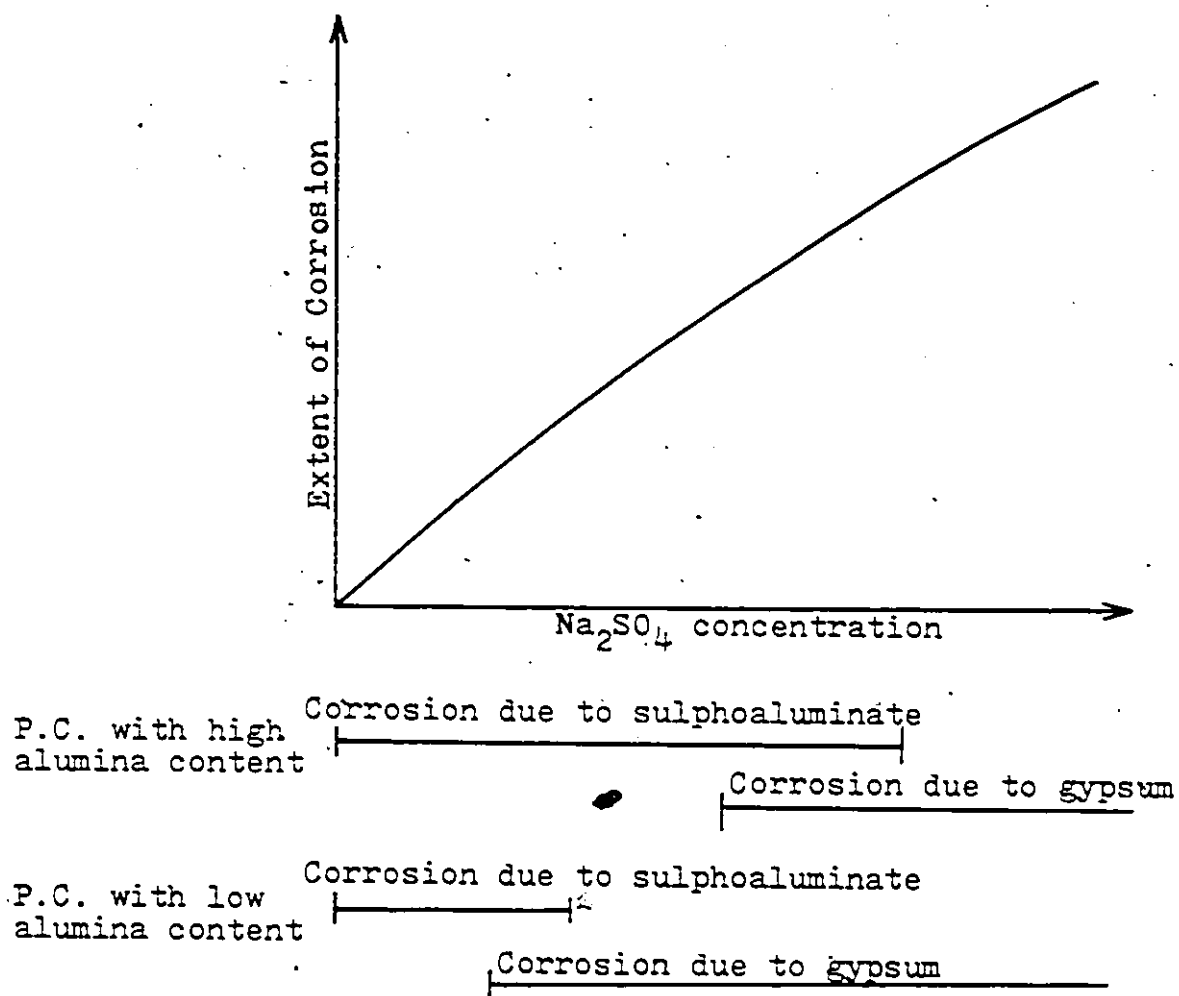


Figure 5-6: PROGRESS OF CORROSION BY Na_2SO_4
(Biczók, 1972)

1.3 percent which is not conclusive evidence to prove the proposed hypothesis.

The compressive strength results (Appendix E) do not show any significant differences between the four batches considered. Figure 5-5 illustrates that all of the specimens are beginning to converge around 0.025 to 0.050 percent expansions after about 300 days of immersion. Specimen 2MA, stored in deionized water, also follows this trend and its expansions are unexpectedly just slightly lower than those in the sulphate solutions. After about 300 days, the expansion curves in Figure 5-5 lie very close together, not exhibiting any significant differences between the various batches.

It is important to remember that the specimens discussed in this section are all of a 50 percent slag cement/50 percent portland cement blend, since the sulphate attack proceeds less rapidly than for a 100 percent portland cement mix. Perhaps if a 100 percent portland cement mix was used instead, more dramatic results would have been obtained at an earlier date allowing more definite trends and conclusions to be drawn. To date no visible signs of attack have been observed in any of the specimens and none has theoretically failed. This should be contrasted with the failure data for 100% portland cement specimens in Figure 5-2.

It must be noted that about March 28, 1979 (which is approximately an average of 300 days in Phase 3) the standard stainless steel bar was inadvertently damaged. A correction is therefore applied to any expansion readings taken after this time. A correction, of -0.002 percent, was determined from recalibration of the stainless steel bar against expansion readings of some water specimens recorded a few days before the stainless steel bar was damaged.

Some of the anomalous behaviour may possibly be partially attributed to the damage of the stainless steel bar and the correction applied may not have fully compensated for this - only when further data is collected will this be evident. Another possibility is that the water solution (batch 2MA) may have been contaminated by sulphate salts, although all solutions were frequently changed and every precaution taken to avoid cross-contamination.

5.2.3 Effect of C_3A in Portland Cement

To study the effect of the C_3A 's influence on the sulphate attack process, three different Type 10 portland cements, a Type 20 portland cement (nominal, actually a low C_3A Type 10 PC) and a Type 50 portland cement were employed (Phases 2 and 3). The C_3A contents varied from 2.0 per cent for the Type 50 portland cement to 11.8 per cent in one of the Type 10 cements. The specimens all incorporated 100 percent portland cements as binder and were subjected

to 50,000 ppm SO_3 as Na_2SO_4 . The results are presented in Figure 5-7.

Examining the results of the Type 10 cements it can be seen that the magnitude and rate of expansion increase with increasing C_3A content. Failure (i.e. $>0.10\%$ expansion) of the cements containing 11.8 and 8.3 percent C_3A was recorded at 90 and 170 days respectively. The Type 10 portland cement containing 6.1 percent C_3A theoretically failed at 250 days. Specimen 1MB containing 11.8 percent C_3A has been severely attacked by the sulphate ions, expanding in an exponential fashion until complete physical failure. Swelling, cracking, spalling and bending of the prisms were observed as shown in Figure 5-3. Complete physical failure has not occurred in the specimens containing 8.3 and 6.1 per cent C_3A after 250 days exposure. Only hairline cracks and slightly spalling edges and corners have been observed in these specimens. The nominal Type 20 portland cement with 7.1 percent C_3A produced the greatest expansions of the five cements examined in this section, for the first 2 months which was not anticipated. Its expansions were then surpassed by the 11.8 percent C_3A (Type 10) cement, after which the Type 20 cement expanded at a decreasing rate. Failure ($>0.10\%$ expansion) occurred after approximately 130 days in solution; at 180 days hairline cracks and spalling edges became visible. Specimen 9MB

PC Type	%C ₃ A	No.	Symbol
10	11.8	1MB	—x—
10	8.3	9MB	—○—
20(nominal)	7.1	2C	—□—
10	6.1	7MB	—●—
50	2.0	3C	—⊕—

All specimens subjected to 50,000 ppm
SO₃(as Na₂SO₄)

Values are the average of 3 readings.

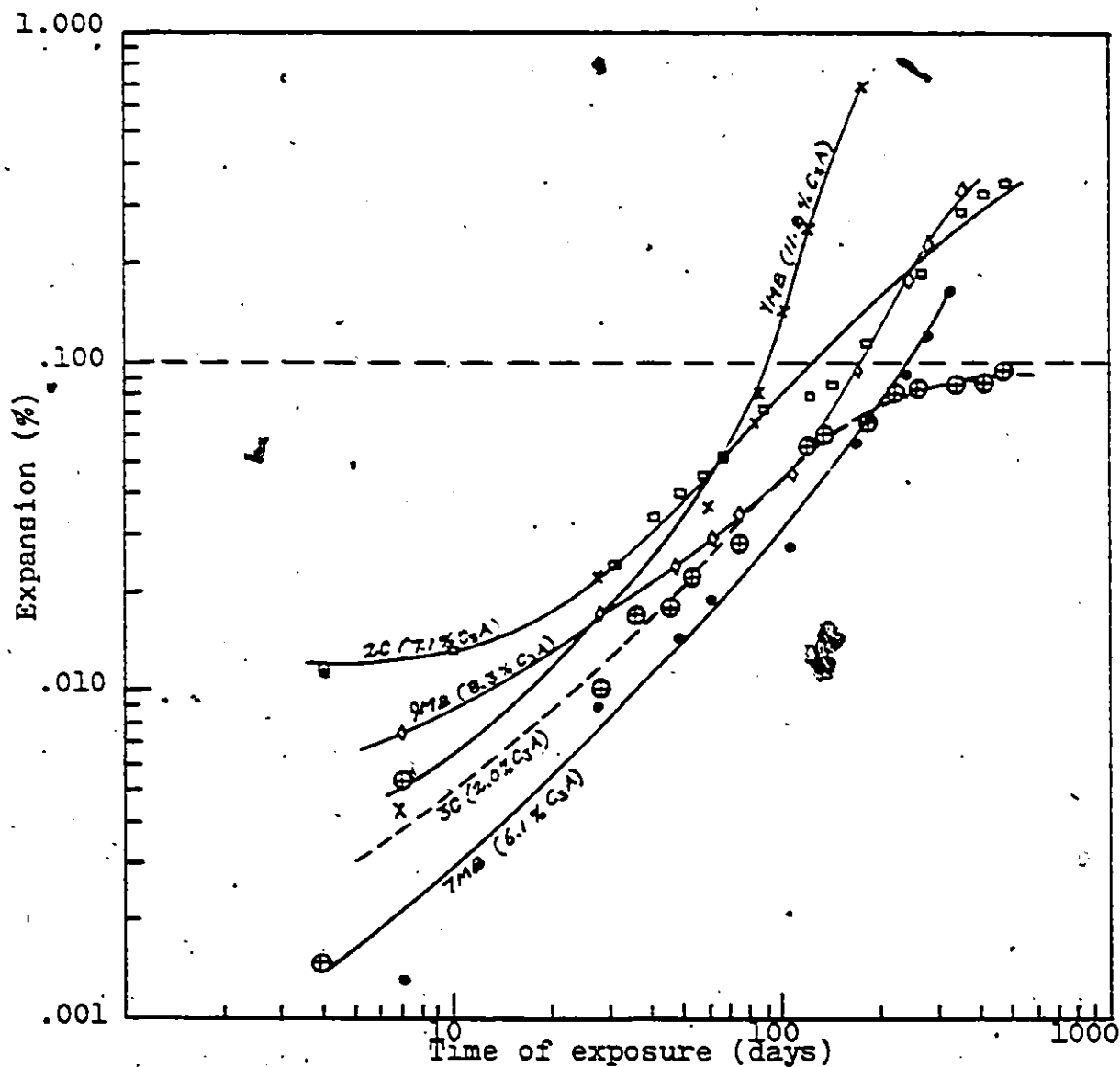


Figure 5-7: INFLUENCE OF C₃A

containing 8.3 percent C_3A began to expand more than the Type 20 cement at 260 days immersion. The Type 50 cement with a C_3A content of 2.0 percent expanded more than the 6.1 percent Type 10 cement for about 200 days. The expansion versus time of exposure curve of the Type 50 cement then began to flatten out. Following its present trend, if its curve was extrapolated, failure ($> 0.1\%$ expansion) would probably occur after 1000 days, demonstrating the well recognized sulphate resistance of the Type 50 portland cement. Although failure in terms of expansion has not been reached, some evidence of attack in the form of slightly spalling edges has been observed.

5.2.4 Comments on C_3A Influences

Due to the research by Bogue and the Portland Cement Association, reported in 1929, the calculation of the main compounds in portland cement clinker - C_3S , C_2S , C_3A , C_4AF - became possible (35). Most of the relationships established between the C_3A content and cement, mortar or concrete properties have to be based on Bogue's calculation of the phase compositions. Yet, everybody agrees today that the figures obtained in this way are misleading to some extent, particularly with regard to C_3A (36). The C_3A content by Bogue's formula is generally higher than that found by X-ray diffraction which gives more accurate results. It should be noted that the "nominal" Type 20 portland cement used

in Phase 2 is actually the 6.1% C_3A Type 10 portland cement given in Table 4-4.

It is generally believed that the destructive action of sulphates on cement and concrete is primarily the result of a chemical reaction involving the C_3A in the portland cement and the sulphate ions in contact with the cement. The resulting crystalline products have a much larger volume than the reactants causing expansion, cracking and eventual disintegration. The precise mechanism is not yet fully understood; a number of hypotheses has been put forward but many discrepancies still exist. Numerous studies have been done investigating the influence of C_3A on sulphate attack and most researchers agree that the vulnerability to sulphate attack increases with increasing C_3A content. Schräml (36) reports that, according to Blaine, Arni and Evans (on the basis of the most recent and most comprehensive multiple regression analysis between characteristics of the cement composition and the results of the potential sulphate expansion test) expansion is a third power function of the C_3A content in the 7 to 15 per cent range of C_3A composition, whereas at lower C_3A contents proportionality seems to apply. However, the correlation between the rate of concrete deterioration in the field and the C_3A content is not a very close one.

In some instances cements with a high C_3A content have proven more resistant to sulphate attack than one with a lower C_3A content. For instance, the nominal Type 20 cement (specimen 2C) with 7.1 per cent C_3A was found to expand more than Type 10 cement (specimen 9MB) containing 8.3 per cent C_3A for the first 260 days of immersion, after which the trend reversed. One of the main reasons why there are so many contradictions in the results reported in the literature by various researchers is because there is no standard sulphate resistance test. Many tests have been proposed, each with different:

- (1) sizes and shapes of specimens;
- (2) mixes and types of specimens (paste, mortar, concrete);
- (3) concentrations and types of aggressive solutions (pure sulphate solution, solution of a blend of sulphate salts; in some tests the sulphate is added directly into the mix and stored in water or a water-saturated environment);
- (4) curing conditions before placing in aggressive solution (in water or lime water for a prescribed number of days or until a desired strength is reached);
- (5) storage or exposure conditions (in situ, specimen partially or fully immersed, stagnant or flowing solutions, wetting and drying cycles, temperature variations);
- (6) monitoring techniques (visual, weight changes, length changes, compressive strength, flexural strength, chemical, etc.); and
- (7) definitions of failure and duration of tests.

If an arbitrary test duration of say 100 days was selected, it could have been wrongfully concluded that the Type 10 cement with 8.3 percent C_3A was more resistant than the nominal Type 20 cement, and similarly the Type 10 cement with 6.1 percent C_3A could have been said to be more sulphate resistant than the Type 50 cement (2.0 percent C_3A) based on the results obtained thus far. Therefore the duration of the test is very important, and monitoring should be continued for a short while after the arbitrarily selected expansion failure point ($>0.1\%$) is reached, since the realistic selection of this point has not been established at this time. The compressive strengths did not produce results which reflected the influence of C_3A in the various cements. Neither did the weight measurements produce any significant results.

The crystallographic form of the C_3A is thought to be very important in relation to its sulphate resistance. Taylor (37) notes that rapid cooling of the clinker as it leaves the kiln improves the sulphate resistance, either because it causes less C_3A to be formed, or because it affects the size or perfection of the crystals. Schrämli (36) more or less sums up the present state of knowledge:

It appears that little is known about the factors which govern the generation of each individual polymorphic form of aluminate. The question arises whether it is relevant from a practical point of view, with regards

to the performance of the cement, to investigate all these different forms in which the aluminate can appear. There are some indications that it really is. As an example, reference is made to Regourd, *et al** about the sea water attack on hardened cement paste made with cements containing different amounts of aluminate polymorphs. It could reveal that a cement paste, containing 14 percent tetragonal and 2 percent of the cubic polymorph did not deteriorate more in sea water than one containing only 7 percent of the cubic form.

It is obvious that it would foster such investigations very much if more reliable and - this is more important - less time-consuming techniques would be available for the quantitative determination of these different forms of aluminate.

.... the crystallographic form of the C_3A ... may be the explanation for the puzzling findings of many researchers; although they observed the outlined relationship between C_3A content and the rate of sulphate attack, they recorded some cases where the cement was highly sulphate-resistant in spite of a high C_3A content.

If the C_3A content of the portland cement is reduced, it appears that the sulphate resistance would increase. In practice this is achieved by lowering the alumina content or changing the iron content of the raw mix. Changing the C_3A content alters the characteristics of the cement composition. C_3A is believed to be related to the burnability of the cement raw mix, the formation of coatings in the rotary kiln, formation of lumps during cement storage, setting

*Regourd, M., H. Hornain and B. Mortureux, "Influence Du Mode de Cristallisation de L'aluminate Tricalcique. Sur La Resistance Des Ciments à L'eau de Mer", Rev. Mat. Constr., No. 687, 69, 1974.

performance, strength development, heat of hydration; shrinkage and durability. It is therefore not a simple matter to alter the C_3A content. Of course, a simple alternative is to use slag cement, made by intergrinding cement clinker and glassy slag or by replacing some of the portland cement by ground glassy slag directly in the mixer as described in Chapter 2.

5.2.5 Effect of Variation of Slag Cement Content in Blended Cements

In Phase 2, three blends of slag cement/portland cement were used:

50%SC/50% Type 10 PC (12.3% C_3A)

70%SC/30% Type 10 PC (12.3% C_3A)

50%SC/50% Type 20 PC (7.1% C_3A).

The C_3A contents given are from Bogue's calculations. If they were analyzed by X-ray diffraction, the Type 10's would probably have been found to be close to 11.8 percent, since they were from the same plant as the Type 10 cement (11.8 percent C_3A by X-ray diffraction, and 12.2 percent by Bogue's formula) of Phase 3. In Phase 3, five different blends of slag cement with one Type 10 portland cement (11.8 percent C_3A) were made:

70% SC/30% Type 10 PC

65% SC/35% Type 10 PC

60% SC/40% Type 10 PC

50% SC/50% Type 10 PC

40% SC/60% Type 10 PC

All of the batches were stored in 50,000 ppm SO_3 as Na_2SO_4 solutions. Control specimens incorporating 100 per cent of the Type 10 portland cement as binder were stored under deionized water. The expansion results are plotted in Figures 5-8 and 5-9 for Phases 3 and 2 respectively.

It is difficult to explain the upturn in expansion readings in Figure 5-8 after about 200 days, as possible contributing factors such as correction to the stainless steel measuring bar, readings by different individuals and possible cross-contamination, do not seem to be involved. While further data will help to clarify the observed behaviour, it is considered likely that the upturn could be due to the initiations of some cracking at about 200 days, or simply the type of plot selected -log-log- which may in retrospect not be the most suitable for showing expansion trends.

The 100 per cent Type 10 portland cement mortar specimens have expanded substantially more than those containing slag cement in Phases 2 and 3. In Phase 2 the per cent expansion versus the time of exposure curve of specimen 1C (Figure 5-9) reached a peak at 1.4 per cent expansion. The expansions then began to decrease due to the excessive warping of the

% Slag Cement	% Type 10 PC (11.8% C_3A)	No.	Symbol
70	30	5MB	—□—
65	35	4MB	—△—
60	40	3MB	—+—
50	50	2MB ₃	—●—
40	60	6MB	—○—
0	100	1MB	—x—

All specimens subjected to 50,000 ppm
 SO_3 (as Na_2SO_4)

Values are the average of 3 readings

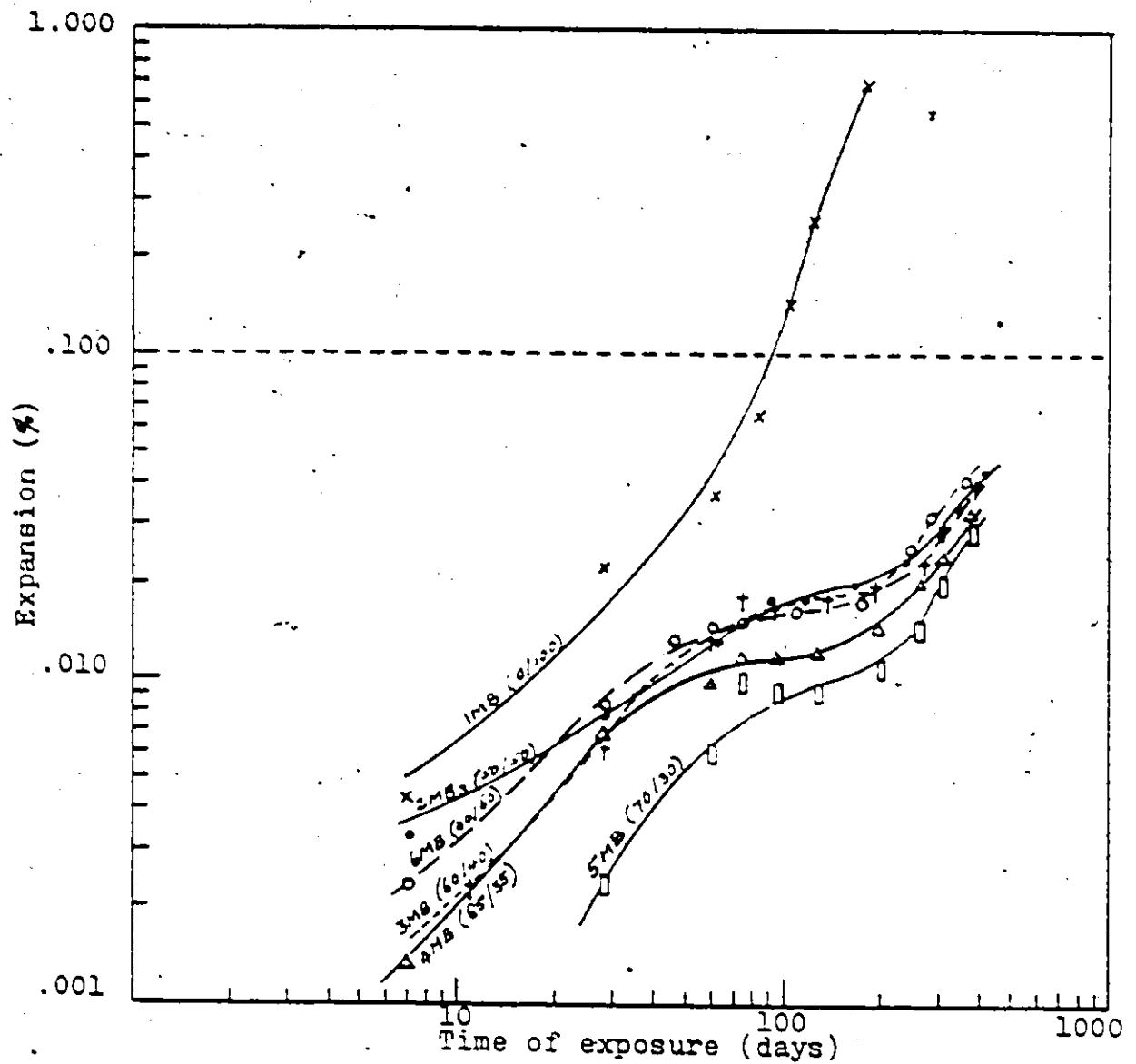


Figure 5-8: EFFECT OF BLENDS

Mix	No.	Symbol
100% Type 10 PC (12.2% C_3A)	1C	—○—
100% Type 20 PC (7.1% C_3A)	2C	—×—
100% Type 50 PC (2.0% C_3A)	3C	—●—
50% SC/50% Type 10 PC (12.2% C_3A)	4C	—•—
70% SC/30% Type 10 PC (12.2% C_3A)	5C	—□—
50% SC/50% Type 20 PC (7.1% C_3A)	6C	—△—

All specimens subjected to 50,000 ppm SO_3 as Na_2SO_4

Values are the average of 2 readings.

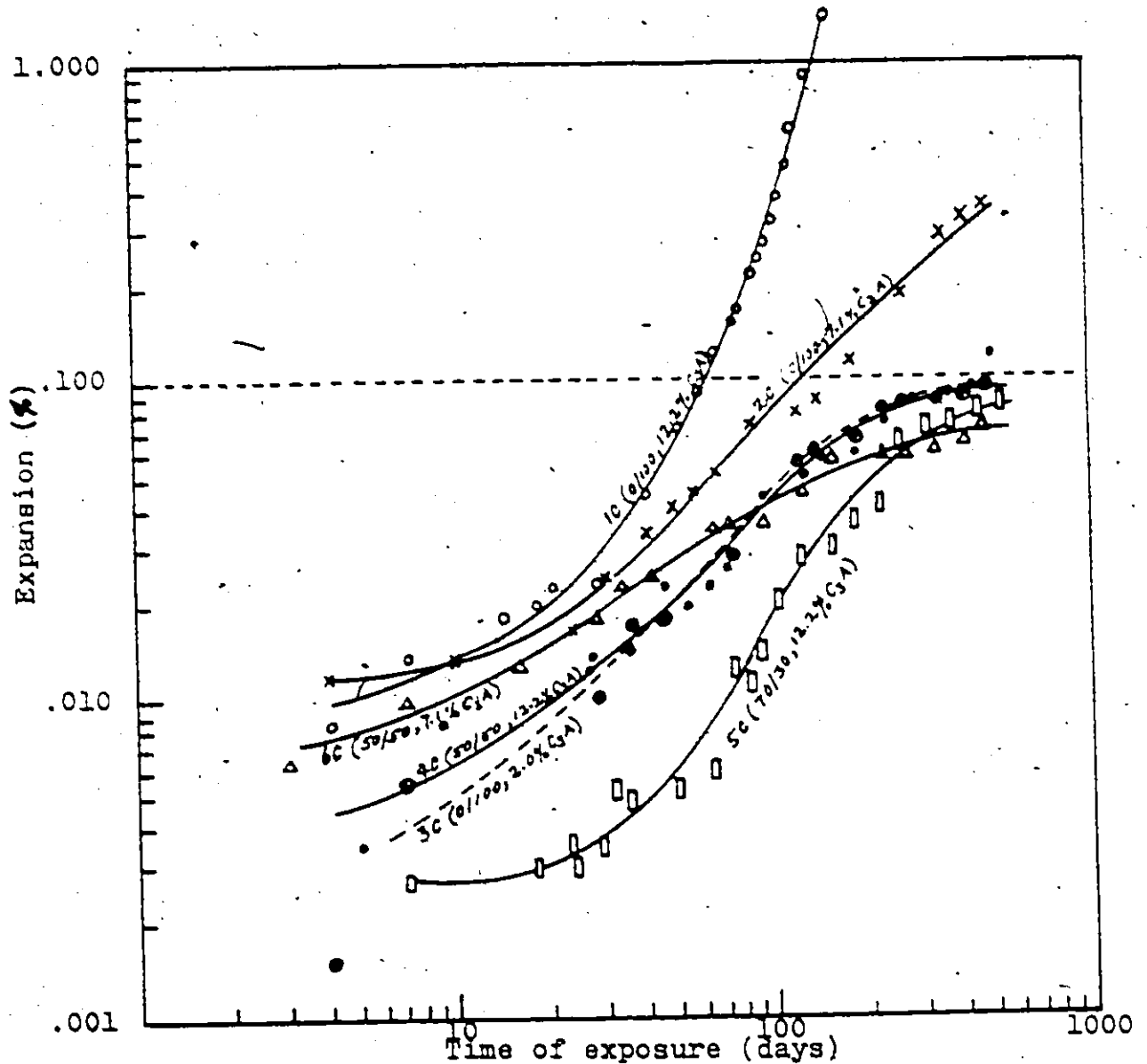


Figure 5-9: EFFECT OF CEMENT MORTARS IN 50,000 ppm SO_3 (as Na_2SO_4)

prisms. The results indicate that the greater the slag cement content the more sulphate resistant the cement. Figure 5-8 shows that the 40% SC/60% Type 10 PC blend expands slightly more than the 50% SC/50% Type 10 PC blend, but the difference is not very significant. From a close examination of the curves of Figure 5-8, the trend seems to be that the expansions of all the specimens except IMB become progressively closer as if to converge at some point. This implies that no significant gain in sulphate resistance is attained by increasing the slag content from 50 percent to 65 percent in the long term, i.e., the degree of sulphate resistance is not very sensitive to the slag cement content in this range. No final conclusion can yet be drawn on this point, since none of these specimens has failed as yet. The 70% SC/30% Type 10 PC blend is the most sulphate resistant of the blends in Phase 3 to date, but strength development of concrete mixes for such high slag cement additions would preclude its practical use.

Figure 5-9 clearly shows that the slag cement/portland cement blends are more resistant to sulphate attack than the nominal Type 20 portland cement. The 50% SC/50% Type 10 PC blend appears to offer approximate sulphate resistance equivalence to the Type 50 portland cement up to about 600 days in the accelerated tests. Longer exposure may or may not show the need for a higher slag content to maintain this equivalency.

in the accelerated tests. However, this equivalency up to 600 days is probably the key point for practical mixes. The 70% SC/30% Type 10 PC blend produced the smallest expansions up to 300 days of exposure, when the 50% SC/50% Type 20 PC blend started to yield slightly smaller expansions (Figure 5-9). The specimens stored in 3000 ppm SO_3 as Na_2SO_4 of Phase 2 generally behave in a similar fashion to those of identical types in stronger solutions, reinforcing those findings, but since they react at a much slower rate their present results are not very dramatic or illustrative, except to support conclusions for field application (Appendix D). All of the specimens of Phase 2 stored in 50,000 ppm SO_3 as Na_2SO_4 solutions, except for the 50% SC/50% Type 20 PC blend, have shown some signs of deterioration. Hairline cracks and spalling corners have been observed although in some cases theoretical failure ($>0.1\%$ expansion) has not yet been reached. It should be made clear that in Phase 2 the values given for expansions are the average of 2 specimen readings (in order to investigate as wide a range of samples as possible under limited time, materials and budget). In general, the two readings of identical specimens subjected to similar conditions showed very good agreement, but in a few instances they were found to differ by as much as 30 percent. In the latter case if in a set of readings, one expansion reading was "correct" and the other lower because of an error in

recording or a bad specimen (for example due to insufficient compaction) or something of that nature, the average of the readings could be somewhat lower than its true value. The results are much more sensitive to testing problems than if three or more specimens were made.

5.2.6 Alumina Content of Slag (Slag Type)

Blended slag cement/portland cements are accepted as being more sulphate resistant than ordinary portland cement. It is generally agreed that the higher the slag content the greater the resistance. The alumina (Al_2O_3) content of the blastfurnace slag is probably the most significant of the slag components to sulphate resistance; the lower the alumina content the higher the resistance. Figure 5-10 shows the behaviour of 3 different ground pelletized blastfurnace slags used in 50% SC/50% Type 10 PC blends subjected to 50,000 ppm SO_3 as Na_2SO_4 . The chemistries of the slags are given in Table 4-4. Specimen 12MB containing 11.4 percent Al_2O_3 in its slag expanded the greatest. Specimen 2MB₃ (8.4 percent Al_2O_3 in its slag) initially expanded more than specimen 11MB (9.1 percent Al_2O_3); after about 110 days of immersion this trend reversed. The alumina content varies in different slags depending on their source and manufacture, therefore the performance of the slag cements used in this study must not be considered representative of all slag cements.

Major Slag Chemistries(%)				% Slag	% Type 10 PC (11.8% C ₃ A)	No.	Symbol
C ₂ O	SiO ₂	Al ₂ O ₃	MgO				
38.6	36.1	9.1	12.4	50 (No. 1762)	50	11MB	—●—
42.4	34.9	11.4	7.8	50 (French slag)	50	12MB	—○—
38.2	37.9	8.4	11.5	50	50	2MB ₃	—○—

* Dofasco Furnace No. 4, Hamilton, May 3/76

All specimens subjected to 50,000 ppm SO₃ as Na₂SO₄

Values are the average of 3 readings.

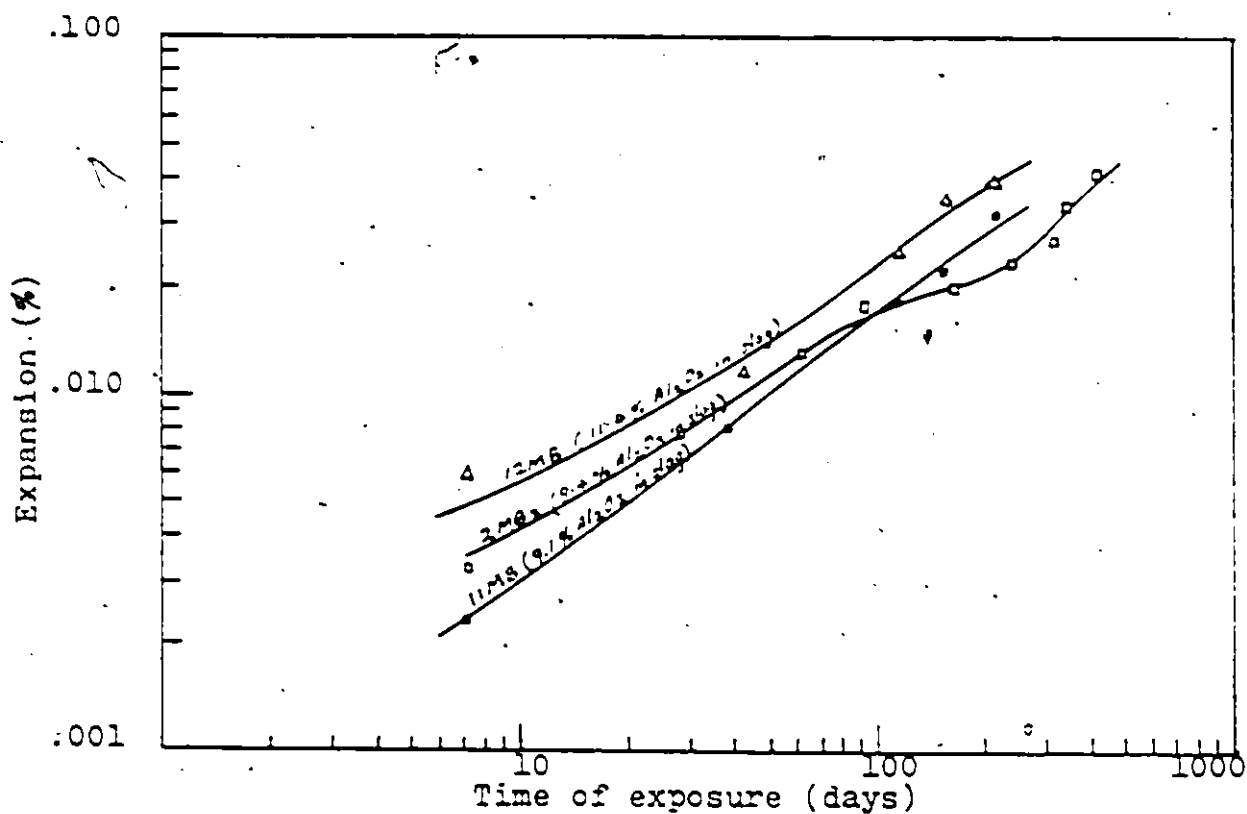


Figure 5-10: EFFECT OF SLAG VARIATION

5.2.7 Slag Cement Addition Level

In the literature it is commonly reported that slag cement/portland cement blends are sulphate resistant provided their slag content is higher than 65 per cent. Blended cements are accepted as being highly sulphate resistant in Germany if the proportion of slag (or slag cement) is over 70 per cent in general, or over 41 per cent if the maximum content of Al_2O_3 in the slag is less than 13 per cent, and the maximum C_3A content in the ordinary portland cement is less than 3 per cent (38). Van Aardt and Visser (39) have found that a substantial addition, say 30 per cent, of slag cement with a high alumina content renders even a sulphate-resisting portland cement vulnerable to sulphate attack. The results obtained so far indicate that the 40 per cent blend of slag cement, with an alumina content of 8.4 per cent in the slag (low by international standards) and 11.8 per cent C_3A in the ordinary portland cement, is sulphate resistant.

Free calcium hydroxide liberated during the hydration of portland cement acts as a basic stimulator of the slag, promoting the hydration of the slag components. Biczók (5) states that since the alkalinity of these compounds is low, calcium hydrosilicates and calcium hydroaluminates of low basicity are formed as a result of hydration. The corrosion resistance of slag cements is due to the considerable stability of the hydrosilicates and aluminates of low lime content

incorporated in them. Taneja (40) asserts that the function of slag cement in sulphate resisting blended cements is to reduce the quantity of free lime liberated on hydration to less than 1.08 g/litre, so that calcium sulphotoaluminate hydrate can form through solution only and thus does not cause expansion. Metha (41) relates that Satarin attributes the high durability to the characteristic microstructure, which consists of denser formations of silicate hydrate gel and smaller amounts of crystalline CH than are found in a hydrated portland cement paste. While Locher (42) claims that slag cements, which are resistant to sulphate attack owe this property not to the nature of the hydration products, but the ability of the hardened cement paste to prevent the formation of trisulphate. He proposes that the reason for this behaviour must be in some way connected with the composition of the hardened cement paste, and presumably it is either that the pore space is such that no trisulphate nuclei are able to form there, or that the diffusion resistance of the hardened cement paste is so great that no sulphate ions can penetrate into it. Four batches are being monitored for their porosities. They are 9MA, 9MB, 10MA and 10MB. The measured porosities are given in Appendix F. In all cases the porosities were found to decrease with time, but no particular trends have been found yet.

5.3 Scanning Electron Microscope Study

Fractured samples were examined under a Cambridge Stereoscan scanning electron microscope (SEM) which was connected to a Revere energy dispersive X-ray analyzer (EDXRA), by which the elemental compositions of the specimens could be determined. The main advantages of the SEM over optical and conventional electron-optical techniques are (43,44):

- (a) large depth of field;
- (b) moderately high resolution ($\approx 200\text{\AA}$);
- (c) the availability to switch over a wide range of magnifications, so as to zoom down to fine detail on some part identified in position on the whole specimen;
- (d) direct observation of the external or internal form of real objects, such as complex fracture surfaces, at high magnifications - thus avoiding the necessity to make thin replicas for use in direct transmission electron microscopy; and
- (e) ease of sample preparation and relatively large sample sizes.

Caution must be exercised when interpreting information from the SEM, as Gattan-Bellew, Quinn and Sereda (45) state:

The reliability of information obtained with the scanning electron microscope is influenced

by human and instrumental factors. The human factor enters, for example, when a microstructure is described as being typical of the material when in fact it is only a minor component. Some instrumental factors include charging of the specimen, problems differentiating between positive and negative relief and distortion of the shape of the sample in micrographs. The determination of the amount of a phase present in a composite is a complex problem involving both preparation of representative surfaces and appropriate methods of evaluation.

Diamond, Young and Lawrence Jr. (46) further point out:

Application of SEM-EDXRA to rough fracture surface specimens of cement systems should be carried out with due regard to certain inherent problems. Data indicate that the effective lateral spread of the X-ray source may be as much as 1.5mm. Theoretical calculations and experimental evidence indicate that variations in take-off and incidence angles can cause significant variations in ratios of peak heights obtained for a given composition ...

In this study identification of the components was based on examination of the micrographs and EDXRA results. There are many geometrically-related difficulties which arise when attempting to determine chemical composition of specimens in regions exposed on rough surfaces by EDXRA that can produce spurious results (46). Thus identification was based on purely qualitative results.

A total of seven specimens from Phase I was studied under the SEM-EDXRA instrumentation. The samples incorporated 100 percent Type 20 portland cement, batch number 7. They

were examined after 90 days of immersion in one of three separate solutions:

A. de-ionized water

D. 3,000 ppm SO_3 as Na_2SO_4

E. 3,000 ppm SO_3 as MgSO_4

Fractured samples from broken concrete surfaces were taken from cylinders 7A, 7D and 7E. Three of the seven specimens were polished on their examined surfaces and etched by hot water. Five specimens were scrutinized at a surface 90 degrees to the original cylindrical surface, and the other two at the original cylinder surface.

Figure 5-11 shows the scanning electron micrograph of specimen 7A, 90 degrees to the surface which was polished and etched with hot water. It shows the structure lining a pore 260 μm in diameter. The internal structure is seen to consist of needle like crystals growing out from the pore wall and bunched at their ends into nodular like structures. The EDXRA results indicate several phases present. An analysis of the nodular formations indicates calcium aluminate hydrates (CAH). The needle like structures are most likely calcium silicate hydrates (CHS) and/or calcium aluminate hydrates, including ettringite. A few other pores were found to contain similar crystals lining their walls in a sparse manner occupying only a small insignificant portion of the pores.

Specimen 7D-90 degrees to the surface, polished and etched, showed no pores containing crystals. EDXRA showed high Ca and Si counts and low S, Al, Mg and Fe. Mostly CSH gel was found. The surface of specimen 7D is shown in Figure 5-12, the tablet shaped crystals and rhomboids are hydrated lime and calcite (CaCO_3). They are dispersed between CSH gel. The calcite is a product of carbonation due to exposure to the atmosphere.

Figures 5-13 and 5-14 are micrographs of specimen 7D-90 degrees to the surface. Figure 5-13 gives the location of the pore in relation to the surface. Its diameter is 75 μm and is located 20 μm from the surface. The arrow indicates a spherulite formation growing out of the pore wall. A closer view of the ettringite spherulite structure is shown in Figure 5-14. The micrograph shows typical needles of ettringite, which can also be described as acicular or hexagonal prisms, occurring as relatively long narrow rods with parallel sides and no branching. The crystals are well formed and are about 12 μm long and 0.4 μm thick. Another location on specimen 7D-90 degrees to the surface is displayed in Figure 5-15. Well-formed, short, slender, prismatic needles of ettringite can be seen forming around and out of CSH plates. The needles are roughly 8 μm long and 0.4 μm thick. The crystals can be seen to be growing in rather cramped quarters. From an examination of these and other

pores containing ettringite it was generally found that slender needles and spherulites are formed only if sufficient space is available, alternatively ettringite occurs as relatively short prismatic crystals. This was also concluded by Metha (47) while studying ettringite formation.

Hexagonal cross sections of the prismatic gypsum crystals can be seen in Figure 5-16. The crystals are uniform and grow out from the base. Unfortunately, due to the projection of the micrograph, the length of the crystals could not be measured. Their thicknesses are in the order of 0.3 to 0.5 μm . The gypsum crystals are densely packed in the pore and almost fill it up. Another micrograph of specimen 7D-90 degrees to the surface is shown in Figure 5-17. Sparsely deposited ettringite crystals of very small sizes are shown to grow out and away from the CAH plates. The crystals are not well formed, lacking the slender acicular shape.

The surface of specimen 7E is displayed in Figure 5-18, showing spherical clusters or "balls" of fibers closely packed together. The average diameter of the spherical clusters are about 20 μm . Figure 5-19 gives a magnified view. The clusters are made up of thin, petal-like magnesium sulphate plates. This specimen was stored in 3,000 ppm SO_3 as magnesium sulphate solution, which explains their presence.

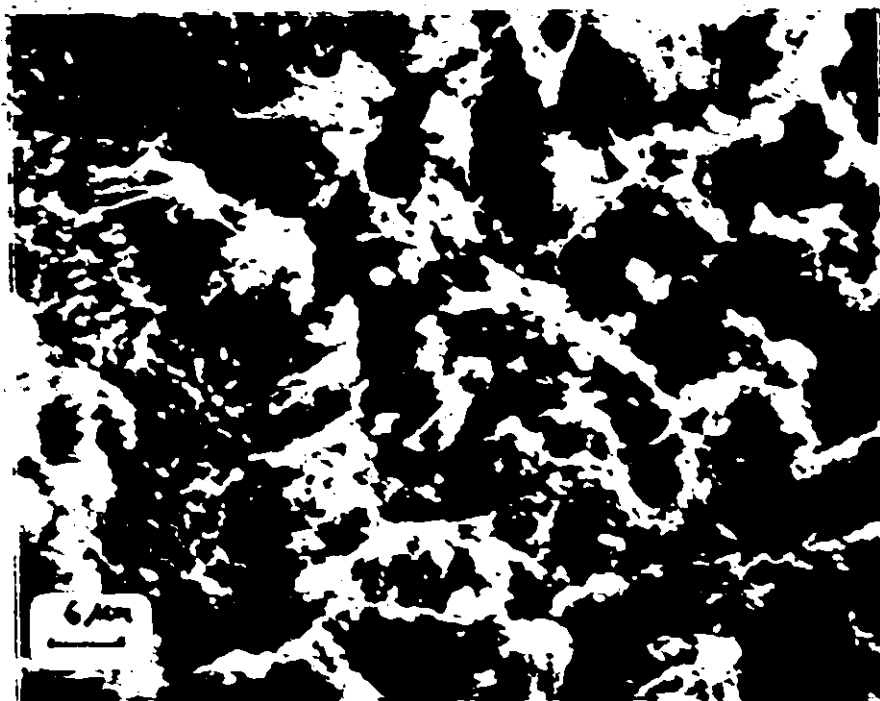


FIGURE 5-11: SEM micrograph of specimen 7A-90° to the surface, polished and etched. It illustrates the micro-structure of a pore containing CSH and CAH.



FIGURE 5-12: SEM micrograph of the surface of specimen 7D with $\text{Ca}(\text{OH})_2$ and CaCO_3 dispersed between CSH gel.



FIGURE 5-13: SEM micrograph of specimen 7D-90° to the surface, showing the pore in relation to the surface. The arrow indicates the spherulite structure of Figure 5-14.



FIGURE 5-14: SEM micrograph of an ettringite spherulite.



FIGURE 5-15: SEM micrograph of specimen 7D-90° to the surface, illustrating short, slender, prismatic needles of ettringite growing sparsely out of the CSH plates. Ettringite is formed in cramped quarters.

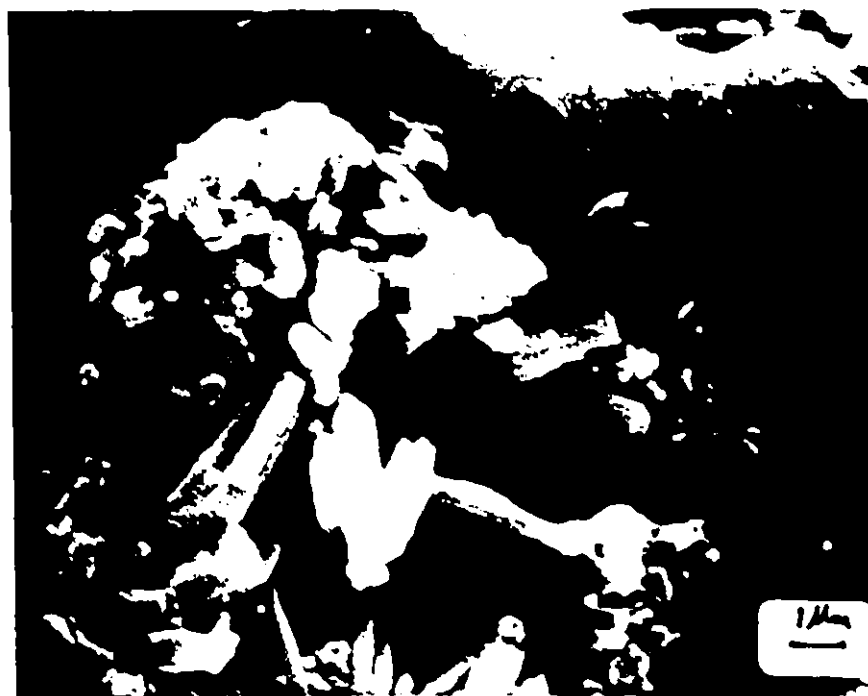


FIGURE 5-16: SEM micrograph of specimen 7D-90° to the surface, illustrating a pore almost full of elongated, prismatic gypsum crystals.



FIGURE 5-17: SEM micrograph of specimen 7D-90° to the surface showing sparsely deposited ettringite crystals growing out and away from CAH plates.

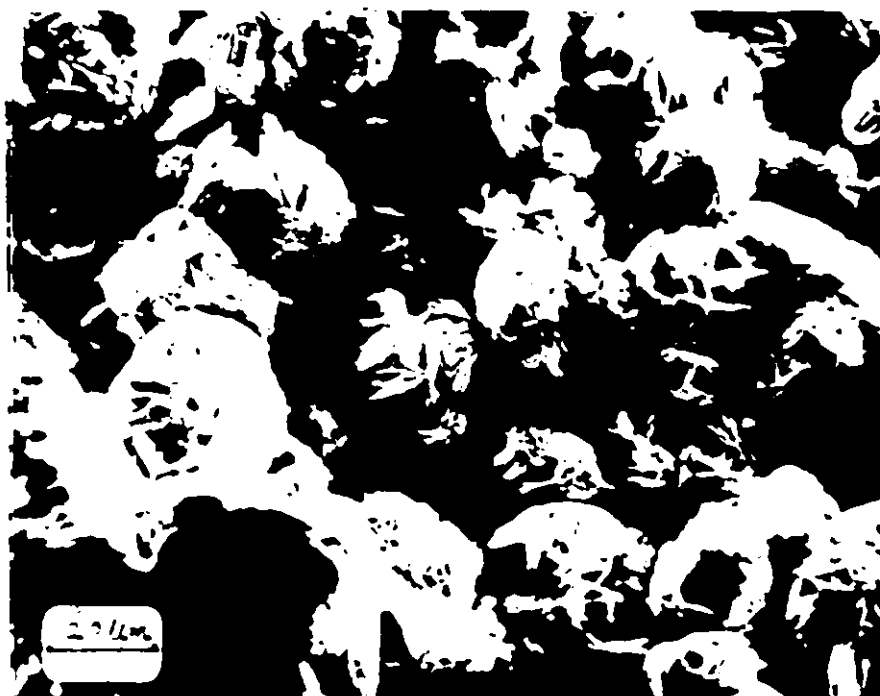


FIGURE 5-18: SEM micrograph of the surface of specimen 7E illustrating spherical clusters, or "balls" of fibres of magnesium sulphate.

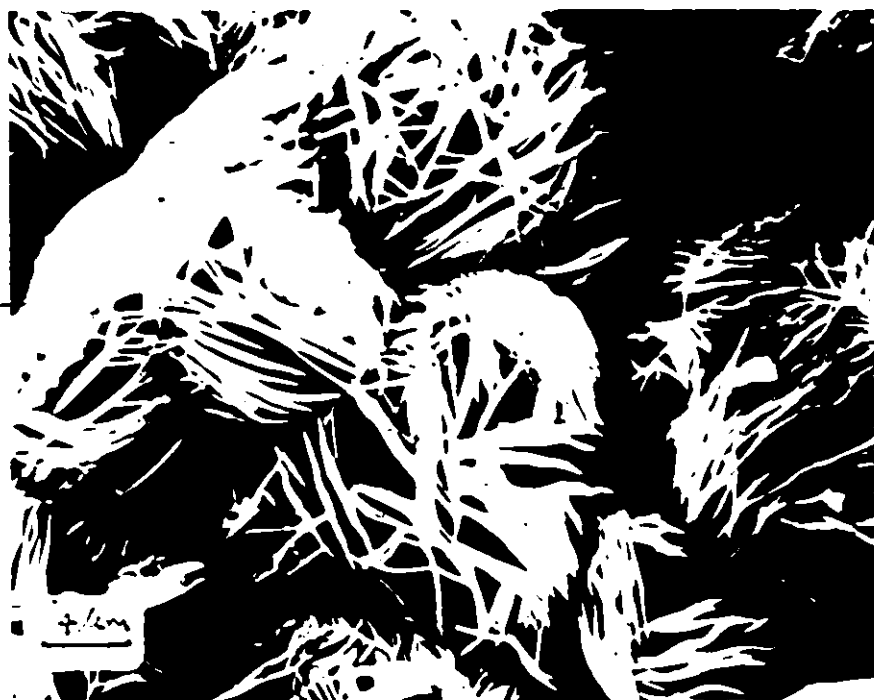


FIGURE 5-19: SEM micrograph of the clusters in Figure 5-18 illustrating the thin magnesium sulphate plates.



FIGURE 5-20: SEM micrograph of specimen 7E-90° to the surface, displaying a large columnar crystalline gypsum growth in the pore.

Figure 5-20 shows a large well-formed columnar crystal protruding out of a void of specimen 7E-90 degrees to the surface. The penetration distance is 135 μm and the diameter of the pore is about 365 μm . The columnar crystal, occupying over a quarter of the pore, is a large gypsum crystal. On its tip is an orange peel like texture where it was in contact with the other end of the pore when the concrete was intact. Small amounts of ettringite were detected in various areas of the specimen.

Specimen 7E-90 degrees to the surface, polished and etched, is presented in micrograph photos Figures 5-21 to 5-24 inclusive. The void of Figure 5-21 has a diameter of 65 μm . Typical thin hexagonal plates of calcium hydroxide can be seen lining the walls of the void. Figure 5-22 shows a pore completely filled with elongated chips of gypsum. The rounded edges are due to polishing. The arrow points to a cluster of acicular ettringite crystals growing out of the gypsum crystals. Figure 5-23 gives a closer view. Slender needles of ettringite can also be seen to grow around the perimeter of the void. With time the gypsum crystals will transform into ettringite, fill up the pore completely and eventually result in disruption of the concrete matrix. Another pore of the same sample is shown in Figure 5-24. It is full of gypsum crystals but no ettringite was detected. The rounded shape of the gypsum crystals is due to polishing.

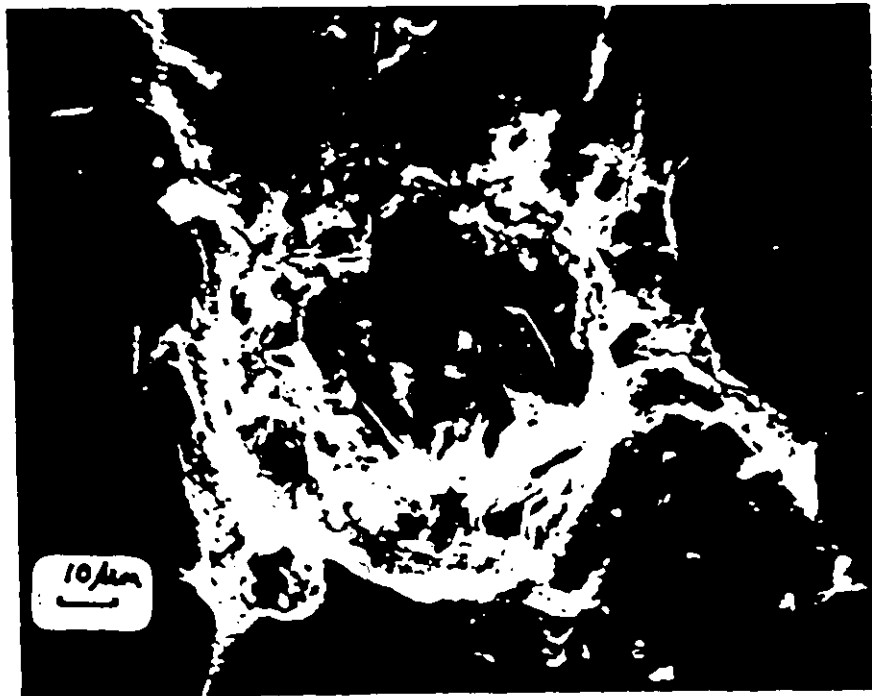


FIGURE 5-21: SEM micrograph of a pore of specimen 7E-90° to the surface, polished and etched, containing thin hexagonal plates of calcium hydroxide.

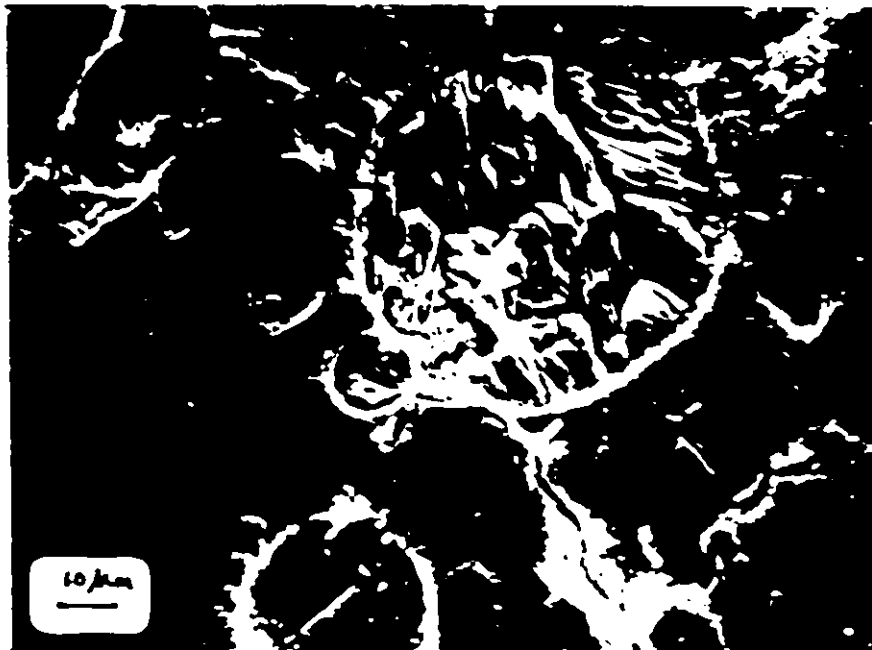


FIGURE 5-22: SEM micrograph of specimen 7E-90° to the surface, polished and etched, displaying a pore full of elongated gypsum chips. The arrow indicates ettringite growth.



FIGURE 5-23: SEM micrograph of Figure 5-22 at a higher magnification illustrating a spherulite of ettringite growing out of the tip of a gypsum crystal.

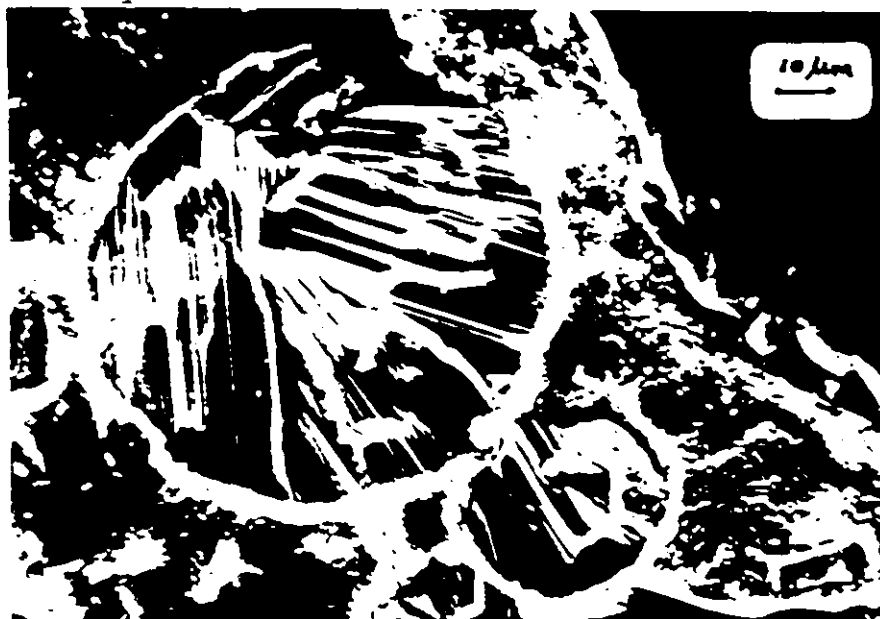


FIGURE 5-24: SEM micrograph of specimen 7E-90° to the surface. Three pores can be seen full of gypsum crystals, flattened and smooth by polishing and etching.

In all the samples of Phase 1 examined after 90 days immersion, calcium aluminate hydrates and ettringite were found in minor quantities. Well-formed, distinct acicular and spherulite ettringite, and prismatic gypsum crystals were seen to grow in the pores of specimens 7D and 7E. In specimen 7E spherulites of ettringite could be seen growing out of the tip of gypsum crystals, indicating the initiation of sulphate attack. The minor quantities of ettringite found in the other samples are most likely due to hydration and not to sulphate attack. No external evidence of deterioration was visible in the concrete cylinders. Samples from the same batches were later examined after 720 days of immersion. The morphologies were found to be almost identical to those observed at 90 days. Greater amounts of ettringite were detected but still in minor quantities. Extensive deposits of calcium hydroxide were found in specimen 7E; they were recognized by parallel planes and smooth featureless surfaces except where fractured. This is typical of calcium hydroxide in mature cements when they grow massive and lose their hexagonal outlines. Some pores were packed with crystals, but none was full enough to cause disruptive stresses in the concrete.

The D's and E's of batches 3, 6 and 8 of Phase 1; 1MB, 2MB₃, 1MC, 2MC, 1MD and 2MD of Phase 3 and samples from the Lok-Test were also examined by the SEM-EDXRA system.

The morphologies observed were quite similar to those seen in batch 7. Ettringite, CAH, CSH, gypsum and lime were detected. Pores full of gypsum were found in specimen 8E of Phase 1 (examined after 720 days in $MgSO_4$ solution), which had visible external cracks in their cylinders as shown in Figure 5-1. No distinction in the internal structures between the specimens containing slag cement and those without was noticeable. In the examined specimens which showed obvious external evidence of sulphate attack - such as cracking observed in specimen 8E - no abnormal or significant increase of ettringite was detected. These findings tend to substantiate Chatterji's hypothesis that ettringite formation has little to do with sulphate expansion.

5.4 Effect of Wetting and Drying on Partially Submerged Specimens

The resulting length changes of the two batches partially exposed to air and partially immersed in a sulphate solution, and in which 5.08 cm (2 inches) of the specimens were subjected to alternate wetting and drying in 14 day cycles, are shown in Table 5-1. In both batches the specimens first shrank and later expanded. The specimens were initially stored under water until they gained the required strength to be partially immersed in the sulphate solution, since a portion of each specimen was then exposed to the

TABLE 5-1

LENGTH CHANGES OF PARTIALLY SUBMERGED SPECIMENS
SUBJECTED TO ALTERNATE WETTING AND DRYING CYCLES

Days in Solution	Number of Cycles	% Length Changes	
		Specimen No.	
		13 MB *	14 MB **
7	0.5	- 0.034	- 0.022
14	1.0	- 0.061	- 0.047
21	1.5	- 0.060	- 0.048
28	2.0	- 0.063	- 0.063
35	2.5	- 0.061	- 0.053
42	3.0	- 0.055	- 0.060
84	6.0	+ 0.076	- 0.057
112	8.0	+ 0.364	- 0.026
126	9.0	+ 0.572	- 0.033
133	9.5	+ 0.700	- 0.002
140	10.0	+ 0.832	+ 0.009
147	10.5	+ 1.116	+ 0.085
154	11.0	+ 1.253	+ 0.070
161	11.5	+ 1.316	+ 0.042

* 100% Type 10 PC (11.8% C_3A) subjected to 50,000 ppm SO_3 as Na_2SO_4

** 50% SC/50% Type 10 PC (11.8% C_3A) subjected to 50,000 ppm SO_3 as Na_2SO_4

air, shrinkage occurred due to moisture loss in the mortars. The maximum recorded shrinkage in both batches was 0.063 per cent after 2 cycles. At the same time cracks and bulging edges were first observed in all the specimens in their portions immersed in the sulphate solution. These were much more pronounced in the 100 per cent Type 10 portland cement specimens (13MB) than the 50% SC/50% Type 10 PC specimens (14MB). After about 4 cycles, expansion due to sulphate attack became greater than the shrinkage due to moisture loss of the mortar in batch 13MB; in batch 14MB this occurred after 9.5 cycles. Batch 13MB continued to expand in an exponential manner, reaching failure (>0.1 per cent expansion) at about 6.5 cycles. Figure 5-25 is a photograph of two typical specimens after 128 days (9.5 cycles). Cracking and spalling at the edges and progressive scaling in the fluctuation zone is clearly visible in specimen 13MB1. In 14MB1 there are a few hairline cracks along the edges but they are not visible in the photograph, some scaling and white salt precipitation can be seen in the fluctuation zone.

The capillary rise was found to be higher in specimens 14MB than in 13MB for the first cycle only, afterwards the capillary rise was identical in the two batches. These experimental results do not indicate, as some researchers claim, that slag cement requires more protection than ordinary portland cement in environments of fluctuating sulphate levels

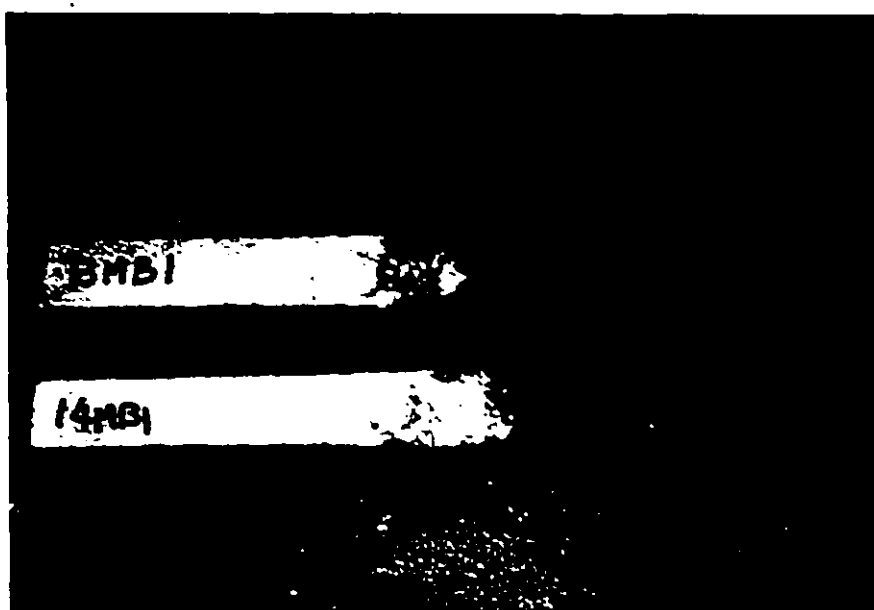


FIGURE 5-25: Two specimens after 128 days of partial submergence in a 50,000 ppm SO_3 as Na_2SO_4 solution and subjected to wetting and drying cycles.

because the capillary rise tends to be greater. In the range of sulphate level fluctuation neither batch was fully resistant to corrosion, however the specimens containing slag cement deteriorated at a much slower rate. In general, the batch containing slag cement showed only slight attack and was essentially sound.

A similar parallel study involving various blends of slag cements, two concentrations of sodium sulphate solution and control specimens in water, was carried out as part of an undergraduate laboratory at McMaster University under the supervision of J.J. Emery and the writer. Sulphate attack was monitored by means of visual observations and length changes. The mix specifications and length changes are given in Appendix G. The study also produced evidence that the specimens containing slag cement were more resistant than ordinary portland cement. Initially 7 day cycles were used, and later 14 day cycles were adopted. All of the 100 percent portland cement specimens have failed while none of the slag cement/portland cement binder specimens have failed. The results also indicated that in general the greater the percentage of slag cement, the greater the specimens' sulphate attack resistance. In the fluctuation zone of all specimens progressive scaling was observed. Cracking, spalling and bulging edges appeared in the 100 percent portland cement specimens in the zones

immersed in the sulphate solutions. In one batch, number 6, the prisms were rotated end for end instead of being adjusted in a vertical direction. This accelerates the capillary rise to the centre or axis of rotation of the prisms. As expected, this produced the most accelerated rate of deterioration especially at the centre of the specimens where the sulphate salt precipitated and began to eat away at the mortar until the cross-sections of the specimens became so slender that they broke on handling.

The mechanism of progressive scaling was studied by Hansen (48). He states that as water evaporates from the surface exposed to air, the salt solution in the concrete becomes concentrated near the surface sufficiently to cause crystals to form in the larger capillary pockets. Such a crystal, being in contact with solution in smaller pores in which crystals will not nucleate at that concentration, grows because salt molecules from this solution attach themselves to the base of the crystal. As the crystal grows, it exerts sufficient pressure to spall off a thin layer of mortar that covers the pocket.

5.5 Lok-Test

Conventional 15.2 by 30.5 cm (6 by 12 inch) concrete cylinders were cast in batches A and A2 in order to check the Lok Test results. The results are presented in Table

5-2. Using the recommended conversion equation* to convert the Lok strength to the compressive strength, compressive strengths very close to the conventional cylinder compressive strengths were obtained. The conventional cylinder strengths were found to be an average of 3.4 percent higher and this could be due to the calibration of the testing machine. The results indicate that the Lok-Test method is an accurate and alternative method for determining the strength of concrete. Many researchers in Europe have reached the same conclusion (49) and the Lok-Test method has been accepted as a Danish standard.

No evidence of sulphate attack has yet been indicated physically or observationally in any of the 4 batches. Nothing unusual was observed when examining fractured samples under the SEM. The Lok-Test is ideal for long-term tests studying the sulphate resistance of concrete, since many tests can be performed on one specimen containing a number of Lok-bolts, each Lok-bolt taking the place of a conventional cylinder, and thus avoiding test and mix related experimental scatter. Hence an enormous space and economic savings can be made. It is also well suited for in situ studies. The Lok-Test specimens are being constantly monitored, as it is hoped that these long-term tests will help to form part

* Recommended conversion equation by Lok-Test Ltd:

$$L(KN) = 5 + 0.8f'c \text{ (MPa)}$$

where L = Lok strength, $f'c$ = compressive strength.

TABLE 5-2

LOK-TEST RESULTS

Specimen No.	% Slag in Binder	Solution Stored in	Age	Compressive Strength (f'c)			
				Lok Test		Conventional Cylinder	
				psi	MPa	psi	MPa
A	0	Tap water	7	4539	31.3	4715	32.5
			28	6163	42.5	6260	43.2
			101	7192	49.6	7584	52.3
			285	8193	56.5	8294	57.2
B	0	50,000 ppm SO ₃ as Na ₂ SO ₄	7	4539	31.3		
			28	6221	42.9		
			101	7134	49.2		
			285	8164	56.3		
A2	50	Tap water	8	3712	25.6	3901	26.9
			34	5554	38.3	5742*	39.6
			252	6714	46.3	7033	48.5
B2	50	50,000 ppm SO ₃ as Na ₂ SO ₄	8	3712	25.6		
			34	5539	38.2		
			252	6946	47.9		

* Tested at the Trow Group (Hamilton) Ltd.

of the still missing link between accelerated tests and the actual performance of field mixes completed in Phase 1.

5.6 Alkali-Silica Test Program

The alkali-silica (or alkali-aggregate) reaction is a chemical reaction which can occur between reactive silicates such as chert, flint, chalcedony and opal, and the hydroxyl ions (of the sodium and potassium alkalies), in the pore solution of the mortar or concrete. The reaction leads to the formation of a gelatinous alkali silicate which may produce expansive forces capable of causing cracking of the mortar or concrete. The expansion mechanism is not yet fully understood but many proposals have been put forward (for instance see Hobbs (50)).

A test program employing basically the same procedure as the accelerated sulphate resistance test program previously discussed was initiated as part of an undergraduate laboratory at McMaster University under the guidance of J.J. Emery and the writer. 15 different batches were made using a high and a low alkali portland cement and also blended portland cements. Slag cements were blended with a normal Type 10 portland cement (i.e. high alkali). Two synthetic glasses, ordinary waste glass and "Pyrex" brand glass, were used as the reactive aggregates while a natural silica sand from Ottawa, Illinois, was used as a standard. The synthetic glasses were obtained

by separately crushing clean glass rods and pyrex ovenware and grading them in accordance with ASTM C109 as follows:

<u>Sieve</u>	<u>Percent Retained</u>
No. 100 (150 μ m)	98 \pm 2
No. 50 (300 μ m)	75 \pm 5
No. 40 (425 μ m)	30 \pm 5
No. 30 (600 μ m)	2 \pm 2
No. 16 (1.18 mm)	none.

The mortar bars, 25.4 by 25.4 by 285.75 mm (1 by 1 by 11.25 inches), were made as prescribed in ASTM C109 and C305. They were stored under tap water or a saturated lime solution (after initial curing for 28 days in water) in sealed containers at 23°C. The various batches and their mix specifications are given in Table H-1 (Appendix H). The chemical compositions of the cements and the synthetic glasses are presented in Appendix H, in Tables H-2 and H-3 respectively. Also, the percent expansions are given in Table H-4.

The main findings of the alkali-silica program are:

1. as anticipated, the specimens containing low alkali portland cement were more resistant to alkali-silica reactivity than those made with a normal Type 10 portland cement (high alkali);
2. greater longitudinal expansions were recorded in the ordinary waste glass specimens than the

pyrex samples when stored in tap water, but in a saturated lime solution the reverse was found to be the case;

3. in general, when slag cement is blended with normal portland cement the expansions were lower than those containing no slag cement. This is best illustrated by the pyrex specimens stored in a lime solution; the various blended batches stored in water do not show any significant differences in expansions at present;
4. to date no visible signs of cracking have been observed;
5. the results indicate that the test method used has positive potential as a standard means for determining the potential alkali-silica reactivity in cements. Slight modifications such as raising the storage temperature and providing humid storage conditions should be further investigated to enhance the potential alkali-silica reaction, thus reducing the required testing period.

CHAPTER 6

CONCLUSIONS

This broad study which embodies both long (representative of field conditions) and short (accelerated) term tests on the sulphate resistance of slag cement/portland cement blends is still in progress. The short term, or accelerated, tests have furnished most of the experimental evidence on which the following conclusions are made:

1. sulphate attack is generally intensified by increasing the concentration of the sulphate solution. The degree of attack is not proportional to concentration. An anomaly was found in which specimens in a 50,000 ppm solution expanded less than those in a 10,000 ppm solution, but this trend reverses at later ages;
2. Na_2SO_4 and K_2SO_4 solutions proved more rapid in their attack than MgSO_4 solution. Deterioration in the form of cracking, swelling and spalling was observed in Na_2SO_4 solutions; whereas the failure process of the mortar samples in MgSO_4 and K_2SO_4 solutions commences with surface softening and the hardened cement soon loses cohesion, disintegrating into a mushy paste;

3. sulphate attack increases in rate and magnitude as the C_3A content of the portland cement increases. A Type 50 portland cement containing 2.0 percent C_3A was found to be highly resistant to sulphate attack as anticipated from CSA standards;
4. the higher the slag cement content in the slag cement/Type 10 portland cement blend, the greater its sulphate resistance. Even a 40 percent slag cement replacement for Type 10 portland cement has exhibited good resistance. A 50 percent slag cement/50 percent Type 10 portland cement blend appears to be equivalent to a Type 50 portland cement in sulphate resistance for the accelerated testing and time involved;
5. the lower the alumina (Al_2O_3) content in the pelletized blastfurnace slag used during manufacture, the higher the sulphate resistance of the slag cement;
6. the SEM-EDXRA study indicates that slender needles and spherulites of ettringite form only if sufficient space is available, alternatively ettringite occurs as short prismatic crystals. In none of the specimens examined,

even those which had failed by sulphate attack, was abnormal or significant amounts of ettringite found. These findings tend to substantiate Chatterji's hypothesis, contrary to popular belief, that ettringite formation has little to do with sulphate expansions;*

7. the 7.62 by 15.24 cm (3 by 6 inch) concrete cylinder test program produced very erratic results. Only the batch of a 100 percent Type 10 portland cement blend showed visual signs of deterioration. This test program has produced no significant results to date;
8. the test in which specimens were partially submerged in a sulphate solution and subjected to alternate wetting and drying cycles produced the most accelerated results of all the tests. After only 28 days signs of sulphate attack were visible. The batch containing a 50 percent blend of slag cement with portland cement was more resistant than the batch without any slag. In both batches, progressive scaling was observed. This test is too severe for the evaluation of various cements' performance, and is not suited as a standard test for sulphate resistance;

*The lack of ettringite may also be a function of techniques adopted to study this aspect. Further research is required on this topic.

9. monitoring sulphate attack by weight changes, compressive strength or elastic moduli by ultrasonic methods have not proven successful;
10. the Lok-Test method produced strengths comparable to conventional cylinder compressive strengths. The Lok-Test procedure is well suited for long term or in situ testing, providing accurate results with an enormous storage and economic savings;
11. the accelerated mortar test method was found to be the most reliable test which can give an indication of a cement's performance in a relatively short time. The testing duration can be further shortened by decreasing the required strength before the samples are immersed in the sulphate solutions. It is recommended that this test method be adopted as a standard test for the evaluation of various cements;
12. it is recommended that the tests in progress be continued in order to develop a correlation between the accelerated and field conditions.

The most significant finding from a practical viewpoint is, of course, Number 4, in which a 50% SC/50% Type 10 PC (11.8% C_3A , about highest anticipated) has shown

equivalent sulphate resistance to a 100% Type 50 portland cement (sulphate resistant cement) in the test program. This is now being followed on a design and field basis with 50% cementitious hydraulic slag/50% Type 10 PC blend being used by many organizations as a sulphate resistant blended cement. This must be carried out in conjunction with good concrete practice which is oriented to field performance. Since each slag cement has specific characteristics, the above findings are limited to cementitious hydraulic slag cement produced in Hamilton with some favourable indications for the French slag.

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APPENDIX A

THE LOK-TEST PROCEDURE *

* Reference: "Guide For The Use of Lok-Test Instrument Model 4", Lok-Test Ltd. January 1977.

A. Procedure for Testing

A.1.1. Placement of Lok-Test Bolts

The Lok-Test Bolts may be fastened to the formwork or they may be placed floating in the surface of the plastic concrete.

A.1.2. Fastening to Formwork

The supplied standard screw, 50 mm (2"), is based on a maximum thickness of formwork of 42 mm (1 5/8").

In the case of formwork in excess of 38 mm (1 1/2"), the nut will not be used. In all cases, however, the washer shall be used as shown in Fig. A-1 and A-2. Fig. A-3 shows the use of the special placing plate.

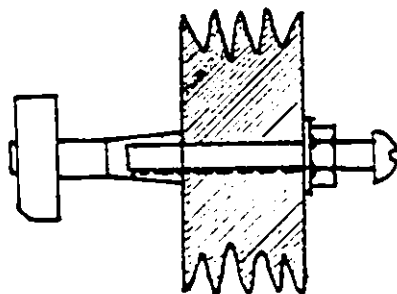


Fig. A-1

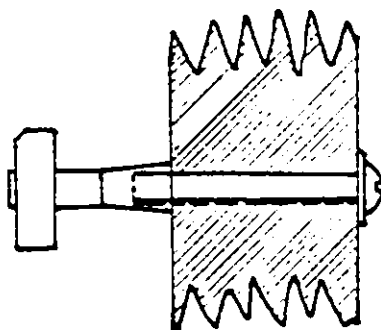


Fig. A-2

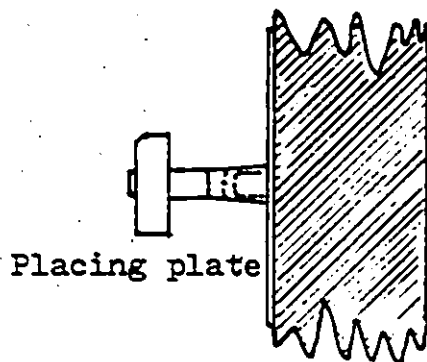


Fig. A-3

Please note the following items as part of the placing of the bolts.

1. The bolts shall be coated and fully threaded prior to placing.
2. The placing hole of 6.2 mm (1/4") diameter shall be drilled perpendicular to the formwork at least 10 cm (4") from edges or corners and such that the bolt is free of any reinforcing bars. The special Lok-Test drill which ensures perpendicular drilling is recommended for drilling the hole.
3. The formwork surface shall be plane for a distance of 4 cm. (1 5/8") from the drilled hole. If this is not the case then the casting plates shown in Fig. A-3 must be used.
4. If the formwork is porous or water absorbent, the bolts shall be used with the fastening plate shown in Fig. A-3.
5. It is important that the test bolt is not fastened so tightly that the ends of the stems cut into the formwork. If there is any risk that this may happen, use the fastening plate as in Fig. A-3.

6. At the time of placing the screw or the nut it should be tightened by hand but sufficiently tight that the end of the stem is tight against the formwork. (If a nut is not used as in Fig. A-4 it is sufficient to tighten the screw with a penny). The plate shall also be completely screwed on to the end of the stem.
7. A day or two after the casting, or as soon as the concrete has hardened, the screw, nut and washer are removed.

A.1.3 Floating Lok-Test Bolts

The test bolt can be delivered mounted on a special plate in a buoyancy container.

The Lok-Test bolt plus plate and container is pressed 1 to 2 cm (1/2" to 1") into the concrete following casting. Thereafter the concrete is normally consolidated. When it is time to test the concrete, the buoyancy container, cover plate, screw and nut can be removed.

The testing takes place as given in clause A.2 but with the use of a distance piece for surface testing and lengthened pull bolt as illustrated in Fig. A-4.

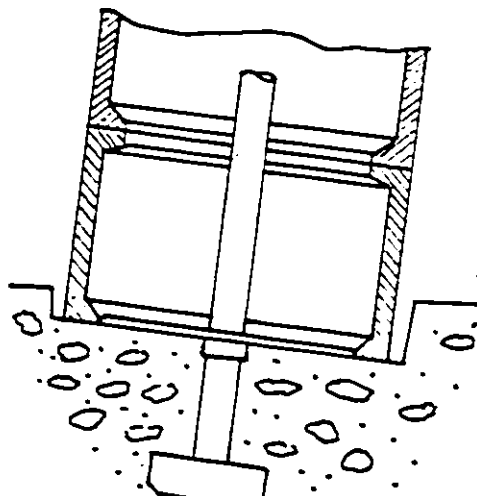


Fig. A-4

If the coupling will not turn on its axis, screw the pull bolt back very slightly (clockwise) such that the coupling can turn on its axis.

A.2.3 Placement of the Instrument

The handle on the instrument shall be screwed out completely so that the telescope is fully extended.

Hold the right hand under the large cylinder of the pull apparatus and guide the apparatus over the coupling while the left hand turns the coupling. With the thumb and index finger of the left hand in each of the two finger holes in the plate in the large cylinder turn the coupling clockwise until the coupling is completely engaged in the three screw-heads. If the coupling will not engage, it may be due to the fact that the handle is not screwed completely back, or there may be dust or dirt between the coupling parts, or the coupling may be fastened too rigidly, or the stem may not be mounted perpendicular to the formwork. If the coupling cannot turn around its axis, disassemble the instrument and turn the pull bolt clockwise bringing it back such that the coupling is a little looser. If the stem is not placed perpendicular to the formwork testing cannot be carried out.

A.2.4 Testing

The inner or outer handle is turned clockwise until the gauge starts to show a reading and the handle is heavy to turn.

After this, turn the outer handle with an easy pressure such that the speed becomes 1 KN per second. The instrument is then pulled to the specified value (according to calibration) or until the concrete breaks.

It is important that the handle is used with a constant easy pressure such that the speed of loading is kept reasonably even.

If the pressure is too strong, the handle will slip. The instrument does not suffer from this but it is exposed to unnecessary wear.

The gauge is read as it goes up. When the concrete breaks, a small sharp noise can be heard caused by the concrete breaking and the needle on the gauge will be stationary for a moment (2 to 10 seconds depending on the quality of the concrete), after which it will move back.

A.2.5 Demounting the Instrument

If the concrete breaks, the handle can be turned to the bottom after which it can be judged whether the concrete cone can be taken out with the instrument coupled in. Note: Do not twist and turn the instrument. If the concrete cone will come out, then demount the coupling by turning it until the screw heads hit the three small nuts. At this stage the plate, the pull bolt, the concrete cone, the centering plate and the coupling are pulled out of the apparatus. The pull bolt is screwed off the plate using the wrench, (remember left hand thread).

All parts are then cleaned of dust and gravel.

If non-destructive testing is carried out or if the concrete cone is not removable from the concrete, turn the instrument's handle quickly back to the initial position (with the telescope fully extended) and the coupling is then turned clockwise until the three screwheads in the pull apparatus reach the three stop nuts of the coupling. The instrument can then be pulled out from the coupling in a movement perpendicular to the concrete surface.

A.2.6 Dismounting of Centering Plate, Coupling and Pull Bolt

The centering plate, coupling and pull bolt can be dismounted by turning the pull bolt clockwise with the wrench. Dust and gravel is removed from all parts.

A.3 Maintenance

A.3.1 Check List Prior to Testing

A.3.1.1 All the parts of the coupling shall be lightly oiled and free of gravel or dust.

A.3.1.2 The pull bolts shall be lightly oiled and the threads shall be free of dust or dirt and they shall not be worn.

A.3.1.3 Check with a gauge that the permanent part of the coupling of the pull apparatus has a movement of at least 4.5 mm ($1/5''$) when the handle is wound completely out. If this is not the case the instrument has to receive more oil.

During the addition of oil, the apparatus is held with the gauge in the thick pull cylinder down and the thin cylinder with the oil screw up. Turn the handle all the way out.

Unscrew the oil screw and add oil from the oil bottle. Only use oil supplied by Lok-Test. The oil screw must be tightly fastened after adding oil.


Following this, the movement of the cylinder is checked again.

A.3.1.4 Check whether the telescope is moving freely by moving the handle back and forth.

A.3.1.5 The needle on the gauge must be resting against the zero stop at the start of a test.

A.3.1.6 The pull bolt should fall into place and the coupling part easily, and the centering plate shall be equally easy to attach to the pull-bolt.

A.3.1.7 Check whether the following parts are present in the carrying case:



1. Instrument
2. Extra pull bolts
3. Stem tool
4. Pliers to screw stem off the stem tool
5. Wrench
6. Coupling
7. Centering plate
8. Flask with extra Lok-oil.

A.3.2 Check List Following Testing

4.3.2.1 Check the apparatus for damage or oil leakage.

A.3.2.2 Clean the carrying case inside and out of any concrete dust.

A.3.2.3 Clean the instrument with a dry cloth, (especially the coupling part) and give each part a light oiling.

A.3.2.3 Check that the pull bolts fall into place easily in the coupling.

A.3.2.5 Check that the coupling can easily be fed into the instrument.

A.3.2.6 Check that the surface of the centering plate is in line with the instruments bearing surface when the centering plate coupling and pull bolts are installed in the instrument and its handle is screwed all the way back (the telescope fully extended).

APPENDIX B


DETERMINATION OF CAPILLARY POROSITY

Determination of Capillary Porosity (30,31)

A thin slice of miniature mortar prism or cube (also applicable for concrete) is cut. Dry it in an oven at 110 degrees celcius (or at a lower temperature with reduced pressure known to produce similar results) until the weight is constant within $\pm 0.01g$.

Place the specimen (thin slice) in a beaker, put the beaker in a glass desiccator. Reduce the pressure as far as possible by means of a good vacuum pump capable of handling fairly large quantities of vapour. Methanol (or carbon tetrachloride) is added to the beaker under vacuum, via a petcock and tube passing through the top of the desiccator. Add enough to completely cber the specimen. To reduce contamination of the pump-oil a vapor-trap of liquid nitrogen should be placed between the desiccator and vacuum pump. Care must be taken to ensure that the vapor-path is clear at all times. If carbon tetrachloride is used, avoid grease-sealed joints since the carbon tetrachloride dissolves most greases making dismantling difficult. Use sleeves on standard ground joints, seal the flange of the desiccator by an O-ring of resistant synthetic material.

Continue pumping until no more bubbles of air emerge from the specimen even when the dessicator is given a sharp tap (with caution). Release the vacuum and allow the



specimen to remain under the methanol (or carbon tetrachloride) at atmospheric pressure for 5 minutes.

Using forceps or wearing plastic gloves, remove the specimen and rapidly blot off surplus liquid with paper tissues. Place the specimen in a weighed polythene bag and quickly close its neck with a wire or plastic closure to prevent evaporation. Weigh the specimen saturated with methanol (or carbon tetrachloride). Remove from the polythene bag and drive off the absorbed liquid by heating in an oven at 110 degrees celcius. Cool and re-weigh to obtain the dry weight. Determine the density of the methanol (or carbon tetrachloride) used and calculate the porosity as follows:

$$\text{Porosity} = \frac{V_p}{(V_{sv} + V_p)} \times 100\%$$

where

$$V_p = \text{Volume of pores} = \frac{(\text{surface saturated weight} - \text{dry weight})}{\text{density of methanol}}$$

V_{sv} = Solid volume obtained by Pycnometer.

APPENDIX C

COMPRESSIVE STRENGTH, ULTRASONIC PULSE
VELOCITY AND EXPANSION DATA FOR PHASE ONE

TABLE C-1: COMPRESSIVE STRENGTH OF CONCRETE CYLINDERS IN PHASE ONE (Contd.)

Batch No: 6			7			8		
Age (Days)	Type	f'c MPa Psi	Age (Days)	Type	MPa Psi	f'c MPa Psi	Type	f'c MPa Psi
3	Ext.	-	3	Ext.	-	-	Ext.	-
7	Ext.	31.5	7	Ext.	26.6	3850	Ext.	29.4
8*	Curve	33.1	12*	Curve	31.7	(4600)	Curve	30.3
13	Ext.	36.0	28	Ext.	34.0	4935	Ext.	31.3
28	Ext.	41.7	42	A	39.5	5725	Ext.	32.9
36	A	43.3		B	28.3	4105	A	38.8
	B	44.6		C	36.5	5290	B	37.7
	C	40.7		D	33.5	4855	C	37.7
	D	40.4		E	37.9	5490	D	38.8
	E	44.3	72	Ext.	40.9	5925	E	37.4
69	Ext.	44.2	91	Ext.	38.4	5570	Ext.	40.1
90	Ext.	43.2	103	A	42.4	6115	Ext.	39.3
98	A	48.1		B	38.3	5560	A	38.5
	B	40.7		C	37.0	5370	B	37.7
	C	40.5		D	33.2	4820	C	39.6
	D	37.7		E	39.9	5780	D	41.0
	E	44.9	177	Ext.	44.6	6460	E	31.6
178	Ext.	49.5	273	Ext.	35.8	5190	Ext.	37.5
274	Ext.	45.3	615	A	49.3	7149	Ext.	37.7
616	A	34.4		B	52.8	7654	A	47.8
	B	56.9		C	54.0	7828	B	54.4
	C	59.8		D	55.5	8050	C	43.4
	D	62.0		E	57.5	8339	D	51.5
	E	59.3					E	49.1
								4270
								4400
								4540
								4765
								5625
								5460
								5460
								5620
								5425
								5815
								5695
								5588
								5460
								5740
								5950
								4580
								5440
								5460
								6927
								7889
								6295
								7470
								7116

* = Age placed in solution

Ext. = Extra cylinders stored in water

() = f'c interpolated values from strength curves

Note: Strengths given are the average of 3 readings.

in water.

151

TABLE C-2; ULTRASONIC PULSE VELOCITIES OF CONCRETE CYLINDERS (PHASE 1)(Contd.)

Batch No: 3			4			5		
Age (days)	Type	Pulse vel. (m/sec.)	Age (days)	Type	Pulse vel. (m/sec.)	Age (days)	Type	Pulse vel. (m/sec.)
3	Ext.	3387	3	Ext.	3110	7	Ext.	4236
7	Ext.	4240	7	Ext.	4127	8	Ext.	4236
8	Ext.	4121	9	Ext.	4233	13	Ext.	4618
9	Ext.	4294	11	Ext.	4247	28	Ext.	4763
11	Ext.	4354	14	Ext.	4240	36	A	4396
16	Ext.	4618	15	Ext.	4240		B	4439
29	Ext.	4690	16	Ext.	4354		C	4439
30	Ext.	4763	21	Ext.	4618		D	4439
42	A	4233	29	Ext.	4690		E	4354
	B	4527	30	Ext.	4618	69	Ext.	4527
	C	4482	57	A	4813	90	Ext.	4713
	D	4572		B	4763	98	A	4763
	E	4482		C	4618		B	4713
74	Ext.	5316		D	4916		C	4763
91	Ext.	4439		E	4618		D	4763
105	A	4618	91	Ext.	4439		E	4572
	B	4665	119	A	4713	616	A	4273
	C	4618		B	5024		B	4253
	D	4665		C	4916		C	4194
	E	4618		D	4970		D	4273
617	A	4396	617	E	5024		E	4194
	B	4482		A	4396			
	C	4396		B	4375			
	D	4375		C	4439			
	E	4396		D	4527			
				E	5048			

Ext. = Extra cylinders stored in water.

TABLE C-2: ULTRASONIC PULSE VELOCITIES OF CONCRETE CYLINDERS (PHASE 1)(Contd.)

6			7			8		
Batch No.	Age (days)	Type	Pulse vel. (m/sec.)	Age (days)	Type	Pulse vel. (m/sec.)	Age (days)	Type
7	8	Ext.	4440	6	Ext.	4276	6	Ext.
		Ext.	4482		Ext.	4176		Ext.
		Ext.	4763		Ext.	4418		Ext.
		Ext.	4763		Ext.	4714		Ext.
		Ext.	4916		Ext.	4354		Ext.
10	13	A	4572	28	A	4354	13	A
		B	4482		B	4354		B
		C	4572		C	4396		C
		D	4527		D	4273		D
		E	4665		E	4354		E
36	69	Ext.	4482	72	Ext.	5255	69	Ext.
		Ext.	4970		Ext.	4439		Ext.
		A	4763		A	4572		A
		B	4916		B	4763		B
		C	4763		C	4482		C
90	98	D	4864	90	D	4527	90	D
		E	4763		E	4618		E
		A	4334		A	4439		A
		B	4354		B	4343		B
		C	4334		C	4253		C
616	615	D	4273	615	D	4273	615	D
		E	4233		E	4293		E

Ext. = Extra cylinders stored in water.

TABLE C-3: LONGITUDINAL EXPANSIONS (%) OF BATCH NO. 1 (PHASE 1)

Type	Days in Solution								
	27	61	95	218	253	393	441	574	714
A	.015 .016 .025	.020 .018 .016	.029 .027 .035	.049 .044 .047	.033 .020 .029	.038 .029 -.007	.042 .022 .033	.045 .024 .035	.065 .035 .038
B	.007 .011 .027	.011 .013 .013	.016 .016 .016	.016 .038 .035	.016 .027 .025	.033 .036 .040	.035 .036 .049	.038 .035 .053	.047 .044 .065
C	.042 .016 .018	.062 .024 .020	.049 .018 .036	.067 .020 .029	.062 .035 .049	.089 .055 .051	.091 .058 .069	.089 .067 .073	.093 .076 .076
D	.029 .024 .029	.031 .022 .025	.040 .015 .033	.047 .024 .053	.053 .020 .042	.007 .029 .047	.075 .024 .049	.111 .020 .045	.113 .020 .044
E	.002 .015 .005	-.004 .016 .009	.002 .038 .015	.004 .035 .024	.002 .024 .011	- .058 .025	.011 .049 .036	.013 .040 .075	.016 .065 .058

7 day expansions are used as the initial readings, except in set E in which 0 day readings are used.

The expansion readings of each of the 3 cylinders placed in a particular solution are presented.

TABLE C-4: LONGITUDINAL EXPANSIONS (%) OF BATCH No. 3 (PHASE 1)

Type	Days in Solution								
	28	60	91	212	277	393	441	556	739
A	.064 .009 -.002	.011 .020 .016	.004 .009 -.002	.005 .020 .025	.009 .025 .009	.002 .035 .025	.020 .049 .035	.016 .065 .029	.035 .087 .047
B	.011 .022 .042	.004 .020 .051	.009 .038 .144	.024 .035 .093	.016 .098 .053	.045 .067 .067	.065 .073 .082	.056 .091 .113	.080 .120 .135
C	.018 .007 -.005	-.002 .015 -.002	.011 .022 .020	.031 .029 .025	.045 .022 .022	.064 .025 .033	.065 .031 .053	.067 .038 .051	.115 .038 .064
D	.040 -.005 -	.055 .002 .013	.040 .002 .015	.055 .011 .016	.078 .015 .022	.109 .024 .033	.138 .031 .042	.133 .036 .040	.171 .051 .042
E	-.005 -.011 -.005	.009 -.002 .007	.015 -.020 .004	.016 - .015	.016 .009 .024	.031 .013 .033	.040 .022 .044	.025 .015 .047	.055 .027 .051

7 day expansions are used as the initial readings.

TABLE C-5: LONGITUDINAL EXPANSIONS (%) OF BATCH No. 4 (PHASE 1)

type	Days in Solution								
	28	62	90	211	279	392	440	584	723
A	.020	.111	.155	.165	.115	.087	.115	-.055	-
	.000	.002	-.002	.011	.002	.015	.018	.009	.033
	.020	.051	.062	.067	.062	.080	.075	.080	.135
B	.009	.029	.033	.042	.024	.055	.049	.038	.042
	.033	.075	.049	.055	.093	.124	.098	.111	.105
	.013	.035	.018	.038	.029	.033	.038	.011	.015
C	.000	.024	.005	.018	.040	.067	.073	.067	.129
	.015	.042	.024	.047	.027	.044	.042	.036	.051
	.027	.095	.055	.060	.093	.111	.113	.113	.125
D	.002	.009	.007	.022	.038	.055	.058	.051	.058
	.015	.016	.009	.020	.038	.038	.042	.029	.024
	.013	.015	.013	.022	.051	.100	.104	.113	.105
E	.015	.011	.027	.051	.067	.078	.084	.095	.098
	.031	.044	.053	.055	.075	.078	.100	.115	.129
	.009	.013	.024	.036	.047	.042	.049	.015	.007

7 day expansions are taken as the initial readings.

TABLE C-6: LONGITUDINAL EXPANSIONS (%) OF BATCH No. 5 (PHASE 1)

Type	Days in Solution								
	28	62	90	211	273	392	440	557	742
A	.038 .013 .029	.051 .024 .144	.055 .020 .035	.064 .033 .031	.069 .031 .069	.073 .021 .075	.080 .042 .089	.078 .036 .091	.144 .080 .113
B	.018 .009 .064	.031 .000 .075	.011 .009 .062	.047 .015 .089	.038 .031 .082	.056 .071 .104	.051 .065 .102	.089 .078 .107	.125 .138 .165
C	.044 .035 .038	.062 .051 .065	.051 .053 .056	.069 .056 .058	.065 .056 .075	.075 .073 .080	.075 .087 .091	.067 .115 .093	.125 .131 .107
D	.031 -.036 .035	.055 .016 .069	.035 .013 .055	.049 .020 .078	.060 .025 .073	.085 .040 .065	.087 .031 .075	.076 .035 .075	.102 .036 .085
E	.031 .031 .044	.064 .045 .076	.055 .044 .082	.062 .051 .084	.073 .071 .122	.075 .076 .131	.082 .084 .158	.084 .089 .159	.087 .093 .184

7 day expansions are taken as the initial readings, except in set B in which 2 day expansions are used.

TABLE C-7: LONGITUDINAL EXPANSIONS (%) OF BATCH No. 6 (PHASE 1)

Type	Days in Solution								
	28	61	90	211	273	392	440	537	742
A	.035	.058	.045	.071	.089	.082	.095	.082	.138
	.071	.082	.073	.085	.087	.111	.118	.107	.155
	.018	.031	.027	.027	.042	.049	.053	.025	.080
B	.025	.042	.007	.040	.058	.065	.051	.055	.087
	.045	.051	.045	.095	.113	.182	.147	.160	.213
	.027	.038	.002	.035	.056	.058	.075	.051	.087
C	.015	.018	.013	.062	.095	.118	.111	.113	.151
	.035	.040	.029	.047	.085	.084	.069	.091	.100
	.036	.025	.051	.075	.078	.069	.071	.071	.078
D	.033	.042	.035	.040	.044	.051	.055	.055	.071
	.031	.042	.033	.049	.069	.056	.056	.078	.107
	.027	.027	.031	.040	.053	.065	.075	.062	.084
E	.035	.031	.025	.044	.056	.062	.075	.080	.089
	.027	.027	.029	.040	.047	.051	.055	.055	.067
	.038	.044	.045	.045	.065	.073	-	.085	.085

7 day expansions are taken as the initial readings, except in set A in which 2 day expansion readings are used.

TABLE C-8: LONGITUDINAL EXPANSIONS (%) OF BATCH No. 7 (PHASE 1)

Type	Days in Solution								
	28	60	90	212	276	392	440	559	738
A	.025 .022 .036	.031 .013 .044	.029 .005 .051	.029 .009 .044	.040 .013 .060	.049 .024 .067	.056 .024 .069	.062 .029 .080	.085 .036 .098
B	.025 .022 .042	.035 .029 .067	.038 .024 .065	.033 .033 .042	.025 .035 .098	.047 .047 .107	.044 .062 .118	.047 .078 .107	.060 .080 .131
C	.005 .038 .015	.007 .042 .016	.031 .069 .031	.005 .051 .044	.040 .071 .035	.049 .078 .047	.055 .085 .075	.078 .098 .100	.082 .118 .084
D	.018 .044 .031	.045 .071 .053	.018 .087 .060	.035 .078 .045	.029 .095 .075	.040 .113 .089	.049 .118 .105	.060 .122 .111	.065 .127 .118
E	.027 .095 .040	.044 .095 .060	.045 .107 .053	.035 .109 .044	.051 .175 .076	.069 .031 .085	.062 .047 .093	.084 .055 .096	.091 .080 .096

7 day expansions are taken as the initial readings.

TABLE C-9: LONGITUDINAL EXPANSIONS (%) OF BATCH No. 8 (PHASE 1)

Type	Days in Solution								
	28	61	90	210	274	391	440	558	742
A	.007 .005 .075	-.002 .005 .129	.011 .024 .149	.020 .013 .155	.044 .011 -	.044 .027 -	.071 .038 -	.075 .058 -	.089 .069 -
B	.047 .038 .029	.038 .024 .015	.033 .027 .009	.073 .038 .024	.109 .049 .089	.118 .045 .104	.131 .062 .048	.193 .069 .105	.235 .075 .185
C	.042 .062 .042	.035 .069 .025	.058 .095 .042	.049 .062 .063	.091 .133 .062	.102 .189 .069	.107 .180 .073	.107 .155 .068	.171 .242 .073
D	.040 .031 .056	.025 .009 .044	.040 .027 .060	.056 .042 .071	.073 .058 .071	.091 .078 .087	.107 .084 .100	.102 .089 .102	.124 .109 .118
E	.053 .058 .067	.031 .058 .095	.044 .067 .098	.078 .109 .113	.087 .124 .131	.113 .160 .173	.125 .140 .155	.129 .205 .145	.144 .205 .215

7 day expansions are taken as the initial readings.

TABLE C-10: LONGITUDINAL EXPANSIONS (%) OF BATCH No. 9 (PHASE 1)

Type	Days in Solution								
	28	61	93	210	270	292	440	554	694
A	.020	.022	.020	.049	.051	.058	.055	.067	.075
	-.005	.000	-.002	.002	.015	.009	.011	.027	.038
	.011	.040	.027	.015	.042	.051	.040	.036	.084
B	.013	.015	.011	.013	.035	.011	.020	.011	.044
	.000	-.011	.005	-.015	.007	.004	.007	.025	.038
	.024	.013	.029	-.005	.022	.035	.038	.051	.075
C	.013	.016	.024	.002	.015	.035	.011	.025	.084
	.013	.020	.013	.015	.031	.035	.055	.044	.065
	.031	.038	.042	.053	.080	.095	.111	.115	.144
D	.036	.060	.064	.038	.095	.102	.102	.115	.142
	.025	.025	-.045	.033	.051	.047	.082	.071	.089
	.011	.005	.009	.018	.038	.044	.067	.055	.078
E	.044	.055	.065	.064	.064	.082	.073	.091	.118
	.004	-.065	.015	.022	.067	.047	.065	.048	.124
	.055	.084	.080	.093	.087	.096	.095	.109	.122

7 day expansions are taken as the initial readings.

TABLE C-11: LATERAL EXPANSIONS (%) OF BATCH NO. 1 (PHASE 1)

Type	Days in Solution									
	7	27	61	95	218	253	393	441	546	685
A	.0002	.0001	.0301	.0001	.0000	.0003	.0005	-.0005	-.0005	-.0004
	.0015	-.0003	-.0103	-.0007	-.0011	-.0011	-.0010	-.0009	-.0014	-.0011
B	.0000	.0006	.0984	-.0011	-.0006	-.0004	-.0004	-.0005	-.0009	-.0009
	-.0002	-.0003	.0077	-.0009	-.0007	-.0009	-.0011	-.0015	-.0022	-.0018
C	-.0002	-.0003	.0724	-.0004	-.0004	-.0006	-.0004	-.0009	-.0012	-.0010
	.0002	-.0011	.0209	-.0007	-.0007	-.0005	-.0017	-.0017	-.0020	-.0016
D	.0000	.0006	.0575	.0005	.0001	.0005	.0014	-.0005	-.0008	-.0006
	.0004	.0000	-.0157	-.0004	.0017	-.0006	-.0008	-.0016	-.0021	-.0017
E	-.0002	.0004	.0860	-.0006	-.0010	-.0006	.0002	-.0007	-.0010	-.0004
	.0004	-.0002	-.0008	-.0005	-.0002	-.0007	-.0009	-.0012	-.0012	-.0010

The expansions of each concrete cylinder (average of 2 readings) are presented.

TABLE C-12: LATERAL EXPANSIONS (%) OF BATCH No. 3 (PHASE 1)

Type	Days in Solution									
	7	28	61	91	212	277	393	441	559	737
A	.0008	.0014	.0014	.0011	.0010	.0005	.0008	.0011	.0008	.0010
	.0000	.0008	.0010	.0011	.0011	.0009	.0009	.0005	.0002	.0003
B	.0301	.0021	.0024	.0030	.0027	.0024	.0023	.0019	.0016	.0020
	-.0156	-.0008	-.0013	-.0014	.0023	-.0014	-.0022	-.0020	.0011	-.0017
C	.0009	.0009	.0006	.0003	.0003	.0007	.0002	.0002	.0002	.0000
	.0018	.0021	.0019	.0018	.0016	.0017	.0011	.0013	.0011	.0010
D	.0004	.0010	.0010	.0010	.0007	.0005	.0003	.0005	.0005	.0005
	.0007	.0008	.0005	.0004	.0006	.0003	.0003	.0002	-.0001	-.0001
E	.0005	.0006	.0004	.0006	.0003	.0000	.0000	.0001	.0000	.0006
	.0005	.0006	.0006	.0009	.0005	.0006	.0004	.0004	.0004	.0003

The expansions of each concrete cylinder (average of 2 readings) are presented.

TABLE C-13: LATERAL EXPANSIONS (%) OF BATCH No. 4 (PHASE 1)

Type	Days in Solution									
	7	28	62	90	211	279	392	436	580	719
A	.0011	.0013	.0011	.0013	.0012	.0015	.0001	.0009	.0009	.0017
	.0007	.0016	.0013	.0014	.0009	.0014	-.0005	.0007	.0008	.0007
B	.0006	.0004	.0005	.0009	.0003	.0007	-.0007	-.0004	.0003	.0004
	.0007	.0012	.0014	.0013	.0011	.0008	-.0123	.0007	.0002	-.0001
C	.0014	.0014	.0015	.0014	.0010	.0015	-.0003	.0010	.0011	.0014
	.0007	.0012	.0003	.0005	.0001	.0028	-.0008	-.0003	-.0007	-.0006
D	.0009	.0013	.0014	.0014	.0010	.0012	.0004	.0010	.0009	.0009
	.0005	.0005	.0007	.0012	.0011	.0011	.0003	.0007	.0005	.0005
E	.0505	.0510	.0516	.0511	.0513	.0517	.0517	.0519	.0506	.0511
	.0010	.0013	.0014	.0019	.0014	.0015	.0002	.0010	.0004	.0006

The expansions of each concrete cylinder (average of 2 readings) are presented.

TABLE C-14: LATERAL EXPANSIONS (%) OF BATCH No. 5 (PHASE 1)

Type	Days in Solution									
	7	28	61	90	211	273	392	440	557	742
A	.0024	.0030	.0027	-.0097	.0027	.0023	.0022	.0020	.0016	.0018
	.0053	.0062	.0068	.0054	.0062	.0061	.0059	.0058	.0050	.0053
B	.0014	.0024	.0021	.0018	.0014	.0021	.0023	.0019	.0016	.0019
	.0039	.0042	.0045	.0044	.0042	.0041	.0034	.0035	.0029	.0031
C	.0023	.0031	.0031	.0016	.0028	.0026	.0031	.0029	.0027	.0028
	-.0088	.0043	.0052	.0048	.0051	.0044	.0042	.0039	.0028	.0029
D	.0019	.0025	.0028	.0022	.0016	.0019	.0019	.0023	.0016	.0017
	.0031	.0047	.0047	.0045	-	.0047	.0029	.0031	.0020	.0022
E	.0015	.0212	.0032	.0027	.0022	.0019	.0021	.0018	.0016	.0014
	.0160	.0168	.0169	.0168	.0171	.0174	.0177	.0166	.0163	.0162

The expansions of each concrete cylinder (average of 2 readings) are presented.

TABLE C-15: LATERAL EXPANSIONS (%) OF BATCH No. 6 (PHASE 1)

Type	Days in Solution									
	7	28	61	90	211	273	392	440	557	742.
A	.0034	.0039	.0037	.0038	.0037	.0035	.0034	.0033	.0031	.0025
	.0039	.0049	.0042	.0041	.0045	.0038	.0036	.0036	.0033	.0005
B	.0152	.0041	.0164	.0161	.0162	.0161	.0154	.0159	.0155	.0154
	.0038	.0039	.0042	.0039	.0040	.0041	.0040	.0040	.0034	.0036
C	.0024	.0027	.0019	.0020	.0016	.0018	.0014	.0018	.0012	.0004
	.0033	.0039	.0045	.0035	.0039	.0037	.0038	.0035	.0033	.0033
D	.0025	.0028	.0031	.0028	.0029	.0028	.0019	.0022	.0019	.0016
	.0033	.0042	.0045	.0041	.0040	.0046	.0039	.0045	.0036	.0038
E	.0021	.0024	.0024	.0021	.0018	.0019	.0017	.0021	.0015	.0013
	.0022	.0022	.0033	.0025	.0027	.0025	.0023	.0023	.0019	.0015

The expansions of each concrete cylinder (average of 2 readings) are presented.

TABLE C-16: LATERAL EXPANSIONS (%) OF BATCH NO. 7 (PHASE 1)

Type	Days in Solution									
	7	28	61	91	212	276	393	440	558	737
A	.0006	.0007	.0013	.0011	.0013	.0007	.0021	.0009	.0010	.0010
	.0008	.0006	.0008	.0010	.0010	.0008	.0004	.0004	.0003	.0006
B	.0001	.0002	.0005	.0009	.0003	.0004	.0001	.0003	.0002	.0002
	.0008	.0009	.0013	.0014	.0010	.0008	.0008	.0009	.0009	.0008
C	.0006	.0014	.0010	.0012	.0011	.0010	.0006	.0007	.0006	.0007
	.0042	.0040	.0047	.0019	.0047	.0051	.0044	.0041	.0042	.0038
D	.0006	.0011	.0015	.0021	.0025	.0023	.0015	.0014	.0009	.0006
	.0012	.0013	.0107	.0018	.0016	.0114	.0010	.0019	.0004	.0012
E	.0009	.0012	.0017	.0019	.0016	.0017	.0011	.0014	.0014	.0013
	.0001	.0009	.0013	.0010	.0010	.0015	.0011	.0014	.0008	.0015

The expansions of each concrete cylinder (average of 2 readings) are presented.

TABLE C-17: LATERAL EXPANSIONS (%) OF BATCH NO. 8 (PHASE 1)

Type	Days in Solution									
	28	62	91	211	275	392	441	558	742	
A	.0022	.0035	-.0519	.0026	.0035	.0026	.0029	.0027	.0019	
	.0020	.0026	.0017	.0012	.0022	.0013	.0016	.0017	.0021	
B	.0035	.0035	-.0948	.0034	.0031	.0029	.0030	.0025	.0029	
	.0032	.0032	-.0049	.0025	.0023	.0009	.0011	.0012	.0010	
C	.0030	.0037	-.0744	.0027	.0031	.0024	.0022	.0015	.0011	
	.0039	.0044	-.0180	.0040	.0036	.0028	.0031	.0032	.0031	
D	.0023	.0033	-.0544	.0027	.0030	.0030	.0029	.0024	.0025	
	.0036	.0041	.0062	.0041	.0038	.0035	.0023	.0024	.0020	
E	.0026	.0031	-.0834	-.0092	.0032	.0030	.0031	.0034	.0035	
	.0034	.0030	.0035	.0031	.0027	.0030	.0034	.0037	.0039	

The expansions of each concrete cylinder (average of 2 readings) are presented.

TABLE C-18: LATERAL EXPANSIONS (%) OF BATCH No. 9 (PHASE 1)

Type	Days in Solution									
	7	28	61	91	209	270	392	440	544	684
A	.0001	.0007	.0009	.0007	.0008	.0002	.0002	-.0003	-.0005	-.0004
	.0037	.0046	.0046	.0040	.0045	.0045	.0036	.0030	.0029	.0023
B	.0010	.0023	.0025	.0022	.0006	.0018	.0005	.0004	.0004	.0008
	.0032	.0032	.0025	.0026	.0023	.0027	.0025	.0019	.0017	.0014
C	.0035	.0047	.0045	.0040	.0043	.0042	.0006	.0046	.0034	.0029
	.0005	.0007	.0004	.0000	-.0005	-.0005	.0327	.0325	-.0002	.0000
D	.0005	.0001	-.0014	.0006	-.0013	-.0009	-.0026	-.0028	-.0016	-.0017
	.0017	.0034	.0009	.0011	-.0001	.0002	.0162	.0162	-.0006	-.0006
E	.0008	.0013	-.0001	.0014	.0016	.0017	.0010	.0004	.0004	.0004
	.0009	.0013	.0017	.0012	.0013	.0018	.0010	.0003	.0008	.0004

The expansions of each concrete cylinder (average of 2 readings) are presented.

APPENDIX D

COMPRESSIVE STRENGTH AND EXPANSION DATA
FOR PHASE TWO

TABLE D-1: COMPRESSIVE STRENGTHS OF 50 mm MORTAR CUBES OF PHASE 2

1			2			3		
Batch No.	Age (days)	Solns. Weight (g)	f'c MPa	f'c Psi	Age (days)	Solns. Weight (g)	f'c MPa	f'c Psi
3	A	291.8	29.3	4250 (3)+	2	A	290.5	25.1 3633 (3)
7	A	296.3	31.5	4570 (3)	7	A	294.3	28.8 4179 (3)
28	A	298.3	39.2	5683 (3)	28	A	294.0	35.5 5141 (3)
31	A	301.3	39.5	5725 (2)	30	A	300.0	38.4 5575 (2)
	B	302.9	34.6	5012 (2)		B	295.2	39.9 5787 (2)
	C	297.9	39.2	5687 (2)		C	298.2	37.4 5425 (2)
91	A	298.9	39.3	5700 (2)	182	A	298.2	38.8 5619 (4)
	B	296.7	44.2	6412 (2)		B	299.0	37.3 5408 (3)
	C	303.4	35.3	5112 (2)		C	298.4	35.3 5117 (3)
184	A	298.4	43.1	6250 (2)				
	B	295.6	42.3	6138 (2)				
	C	314.3	29.8	4325 (2)				
					182	A	301.3	49.0 7100 (2)
						B	300.6	39.7 5750 (2)
						C	304.1	25.5 3700 (2)
					91	A	297.8	38.9 5640 (2)
						B	300.7	42.8 6200 (2)
						C	302.2	41.5 6012 (1)
					182	A	301.3	49.0 7100 (2)
						B	300.6	39.7 5750 (2)
						C	304.1	25.5 3700 (2)

* solns. : solutions stored in, where A = deionized water

B = 3000 ppm SO₃ as Na₂SO₄

C = 50,000 ppm SO₃ as Na₂SO₄

+ Strength values are the average of the number of cubes indicated in parentheses.

TABLE D-1. COMPRESSIVE STRENGTHS OF 50 mm MORTAR CUBES OF PHASE 2(Contd.)

Batch No. 4				5				6			
Age (days)	Solns. Weight (g)	f'c MPa	f'c Psi	Age (days)	Solns. Weight (g)	f'c MPa	f'c Psi	Age (days)	Solns. Weight (g)	f'c MPa	f'c Psi
5	A	298.5	26.0 3775 (3)+	7	A	-	18.3 2650 (2)	3	A	294.3	18.9 2742 (2)
28	A	298.4	35.2 5100 (2)	10	A	-	21.0 3038 (2)	4	A	297.9	21.1 3056 (2)
33	A	295.7	39.5 5731 (2)	28	A	294.7	31.6 4575 (3)	7	A	296.6	25.9 3762 (2)
	B	297.1	41.4 6006 (2)	38	A	292.0	28.5 4138 (2)	28	A	299.7	35.6 5162 (2)
	C	299.5	41.4 5956 (2)		B	293.0	31.3 4538 (2)	32	A	298.7	36.6 5300 (2)
91	A	302.8	43.8 6358 (3)		C	293.3	34.1 4950 (2)		B	295.9	35.7 5175 (2)
	B	301.8	40.0 5794 (2)	102	A	295.6	36.4 5283 (3)		C	297.7	38.1 5525 (2)
	C	297.0	38.8 5631 (2)		B	295.6	37.6 5450 (2)	182	A	298.3	38.6 5595 (2)
182	A	300.9	34.8 5050 (4)		C	296.4	40.3 5838 (2)		B	299.1	35.6 5155 (2)
	B	302.1	25.4 3688 (2)	192	A	296.1	29.0 4200 (2)		C	299.9	35.5 5145 (2)
	C	299.7	25.1 3640 (1)		B	272.6	30.9 4475 (2)				
					C	297.5	37.3 5413 (2)				

* solns. : solutions stored in, where A = deionized water

B = 3000 ppm SO₃ as Na₂SO₄

C = 50,000 ppm SO₃ as Na₂SO₄

+ Strength values are the average of the number of cubes indicated in parentheses.

TABLE D-2: LONGITUDINAL EXPANSIONS (%) OF PHASE 2

Specimen No.				Specimen No.				Specimen No.						
Days in Soln.		1A	1B	1C	Days in Soln.		2A	2B	2C	Days in Soln.		3A	3B	3C
4		.001	.002	.009	4		.006	.007	.012	4		-	.000	.000
7		.002	.005	.014	8		.004	.007	-	7		.004	.004	.005
10		.002	.006	.013	10		.002	.075	.014	28		.003	.005	.010
14		.003	.007	.019	24		.004	.013	.016	36		.010	.015	.017
18		.003	-	.020	31		.006	.016	.024	45		.007	.010	.018
20		.004	.002	.023	40		.011	.021	.034	53		.007	.015	.022
28		.005	.004	.022	49		.011	.018	.041	63		.012	.018	.029
40		.002	.007	.044	57		.013	.022	.045	84		.020	.030	.036
50		.004	.016	.071	67		.019	.027	.052	91		.018	.027	.036
59		.004	.015	.093	88		.026	.035	.072	118		.016	.033	.056
67		.006	.022	.122	122		.029	.039	.080	137		.021	.037	.061
75		.005	.021	.152	141		.024	.037	.085	182		.024	.038	.066
77		.009	.023	.166	182		.028	.039	.115	227		.030	.053	.080
88		.009	.023	.219	228		.033	-	-	262		.031	.061	.084
91		.014	.024	.238	266		.040	.051	.187	349		.033	.062	.085
98		.015	.041	.279	353		.042	.056	.281	413		.033	.066	.088
101		.017	.042	.324	417		.043	.064	.328	472		.043	.075	.095
105		.016	.040	.380	491		.052	.075	.346					
111		.016	.041	.478										
119		.017	.042	.623										
132		.015	.043	.912										
151		.017	.047	1.401										
184		.019	.051	.288										
226		.022	.061	-										
277		.028	.080	-										
363		.031	.111	-										
427		.032	.141	-										
501		.036	.171	-										

Values are the average of 2 readings.

TABLE D-2: LONGITUDINAL EXPANSIONS (%) OF PHASE 2 (Contd.)

Days in Soln.	Specimen No.			Days in Soln.	Specimen No.			Days in Soln.	Specimen No.		
	4A	4B	4C		5A	5B	5C		6A	6B	6C
2	.000	.001	.001	.004	.001	-	15	.003	.005	.007	
5	.000	.002	.004	.003	.001	.003	18	.006	.007	.010	
9	.004	.002	.009	-	.003	.003	24	.005	.006	.013	
21	.001	.002	-	.006	-	.004	29	.009	.009	.018	
26	.003	.002	.013	.003	.004	.006	32	.013	.009	.023	
36	.005	.004	.014	-	.005	.005	35	.017	.014	.025	
45	.013	.013	.023	-	-	.006	65	.014	.015	.025	
54	.012	.011	.020	.005	.008	.013	75	.024	.025	.035	
62	.011	.012	.023	.005	.006	.012	84	.027	.026	.037	
72	.015	.016	.027	.002	.006	.015	92	.025	.033	.037	
84	.015	.017	.035	.007	.011	.021	102	.033	.032	.045	
93	.024	.026	.043	-	.022	.030	123	.036	.038	.053	
127	.022	.029	.049	.013	.020	.031	157	.034	.038	.057	
146	.025	.031	.057	.014	.022	.034	176	.036	.042	.059	
184	.025	.031	.060	.014	.022	.036	182	.040	.043	.060	
225	.026	.033	.076	.018	.026	.041	227	.041	.046	.065	
271	.028	.037	.087	.018	.028	.064	251	.048	.053	.073	
358	.037	.037	.091	.019	.032	.074	301				
422	.038	.038	.095	.018	.030	.075	388				
496	.043	.045	.125	.018	.031	.080	452				
				.025	.037	.087	526				

Values are the average of 2 readings.

APPENDIX E

COMPRESSIVE STRENGTH AND EXPANSION DATA
FOR PHASE 3

TABLE E-1: COMPRESSIVE STRENGTHS OF PHASE 3

Batch No.: LMA			LMA*			LMB			LMB*		
Age (days)	f'c		Age (days)	f'c		Age (days)	f'c		Age (days)	f'c	
	MPa	Psi		MPa	Psi		MPa	Psi		MPa	Psi
3	20.7	2998	3	24.2	3508	3	20.7	2998	3	24.2	3508
7	25.5	3700	7	28.1	4075	7	25.5	3700	7	28.1	4075
14	22.7	3285	14	34.2	4965	14	22.8	3313	14	25.9	3750
33	26.4	3825	33	31.9	4630	33	28.3	4110	33	29.9	4330
90	35.3	5125	90	38.6	5600	90	22.6	3270	90	33.4	4845
116	39.1	5665	116	41.6	6030	116	20.9	3025	116	33.8	4900
			334	42.1	6100						

Batch No.: LMB2			LMC			LMD			2MA		
Age (days)	f'c		Age (days)	f'c		Age (days)	f'c		Age (days)	f'c	
	MPa	Psi		MPa	Psi		MPa	Psi		MPa	Psi
7	18.8	2730	7	22.3	3235	7	22.3	3235	3	10.0	1450
9	26.8	3890	14	28.2	4090	14	26.6	3850	8	20.6	2980
52	34.0	4930	28	24.6	3570	28	27.9	4040	10	21.2	3080
			65	18.3	2650	90	24.6	3560	17	24.3	3520
			90	14.5	2100				28	27.7	4020
									90	41.8	6055
									113	39.0	5650
									330	40.5	5878

* Compressive strength of 50.8 mm cubes; all other compressive strengths are of 25.4 mm mortar cubes.

Values are the average of 3 readings.

TABLE E-1: COMPRESSIVE STRENGTHS OF PHASE 3 (Contd.)

Batch No.: 2MB ₁			2MB ₂			2MB ₃			2MB ₄		
Age (days)	f'c		Age (days)	f'c		Age (days)	f'c		Age (days)	f'c	
	MPa	Psi		MPa	Psi		MPa	Psi		MPa	Psi
10	23.0	3340	10	23.0	3340	10	21.2	3080	11	24.3	3520
17	32.7	4735	17	29.5	4280	17	25.3	3675	28	29.0	4205
28	29.8	4315	28	29.4	4270	28	32.2	4675	271	38.3	5547.
91	32.2	4665	91	31.9	4620	90	32.3	4690			
308	40.0	5798	308	35.5	5143	111	29.5	4273			
						330	38.7	5610			

Batch No: 2MC			2MD			3MB			4MB		
Age (days)	f'c		Age (days)	f'c		Age (days)	f'c		Age (days)	f'c	
	MPa	Psi		MPa	Psi		MPa	Psi		MPa	Psi
11	25.4	3680	11	25.4	3680	14	20.6	2990	17	19.6	2845
28	30.4	4415	28	27.0	3912	17	27.5	3990	20	25.6	3715
53	24.1	3500	53	33.3	4825	28	27.5	3993	28	28.4	4120
270	25.2	3650				36	30.6	4440	36	30.3	4390
						301	35.2	5110	301	34.7	5033

Values are the average of 3 readings.

TABLE E-1. COMPRESSIVE STRENGTHS OF PHASE 3 (Contd.)

Batch No.: 5MB			6MB			7MB			8MB		
Age (days)	f'c		Age (days)	f'c		Age (days)	f'c		Age (days)	f'c	
	MPa	Psi		MPa	Psi		MPa	Psi		MPa	Psi
20	25.2	3660	9	25.3	3665	9	19.3	2800	11	24.1	3495
28	28.5	4130	28	31.4	4550	13	24.6	3560	28	30.1	4370
36	30.3	4390	271	37.5	5440	28	29.0	4205	269	34.9	5064
301	35.1	5094				56	30.1	4370			
						273	25.2	3656			

Batch No.: 9MA			9MB			10MA			10MB		
Age (days)	f'c		Age (days)	f'c		Age (days)	f'c		Age (days)	f'c	
	MPa	Psi		MPa	Psi		MPa	Psi		MPa	Psi
9	22.6	3270	9	22.6	3270	10	18.3	2655	10	18.3	2655
28	36.5	5290	28	37.0	5370	13	15.0	2170	13	15.0	2170
56	37.2	5400	56	35.4	5140	266	33.6	4077	15	28.3	4105
273	38.1	5524	273	31.9	4624				49	33.8	4900
									266	24.7	3580

Values are the average of 3 readings.

TABLE E-2: LONGITUDINAL EXPANSIONS (%) OF PHASE 3

Batch No.: IMA		IMB		IMB ₂		IMC		IMD	
Days in Soln.	% Exp. (g)	Days in Soln.	% Exp. (g)	Days in Soln.	% Exp. (g)	Days in Soln.	% Exp. (g)	Days in Soln.	% Exp. (g)
0	.000 439.7	0	.000 440.5	0	.000 445.2	0	.000 433.8	0	.000 428.9
7	.001 440.7	7	.003 440.7	7	.007 445.4	7	.006 444.8	7	.006 430.2
28	.008 442.7	28	.022 441.7	28	.018 446.4	28	.017 -	28	.013 433.2
61	.008 444.7	61	.036 443.4	50	.029 447.1	60	.033 -	60	.025 -
83	.014 445.1	83	.066 444.6	60	.040 447.6	80	.049 -	80	.033 -
90	.017 445.3	90	.083 444.9	108	.174 448.8	90	.082 -	90	.040 -
106	.015 445.6	106	.149 446.6	173	.689 466.7	148	.350 -	148	.061 -
125	.015 446.0	125	.255 448.1			214	1.837 -	214	.184 -
174	.018 446.4	174	.679 452.0					287	.421 -
239	.021 447.0							325	.496 -
315	.030 447.3							391	.654 -
353	-							392	.654 -
419	.039								

Values are the average of 3 readings.

TABLE E-2: LONGITUDINAL EXPANSIONS (%) OF PHASE 3 (Contd.)

2MB ₁			2MB ₂			2MB ₃			2MB ₄		
Batch No.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)
0	.000	426.3	0	.000	427.5	0	.000	423.0	0	.000	430.3
7	.002	427.0	8	.007	427.8	8	.006	435.2	7	.003	423.1
28	.008	427.6	28	.009	428.0	28	.010	435.6	28	.007	423.3
60	.012	427.8	60	.017	428.4	60	.018	435.9	60	.013	423.7
90	.014	428.1	75	.020	428.5	75	.020	435.9	90	.018	424.2
114	.017	428.3	90	.021	428.5	90	.021	435.9	114	.018	424.2
168	.018	428.4	146	.021	428.7	146	.022	436.3	168	.019	424.2
240	.023	429.3	211	.027	429.0	211	.024	436.6	240	.023	424.7
307	.033	427.8	285	.031	429.4	285	.030	437.0	307	.029	425.1
345	.039	-	323	.038	-	323	.036	-	345	.034	-
412	.042	-	389	.052	-	389	.046	-	411	.043	-
									414	.043	-

Values are the average of 3 readings.

TABLE E-2: LONGITUDINAL EXPANSIONS (%) OF PHASE 3 (Contd.)

Batch No.: 2MC			2MD			3MB			4MB			5MB		
Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)
0	.000	435.0	0	.000	431.7	0	.000	426.4	0	.000	427.0	0	.000	430.9
7	.008	-	7	.004	432.7	11	.002	426.5	7	.001	426.8	7	.000	430.9
16	.009	-	28	.013	-	28	.006	426.6	28	.007	426.6	28	.002	431.0
28	.014	-	42	.014	-	60	.014	426.4	60	.010	426.9	60	.006	431.2
42	.016	-	60	.019	-	75	.018	426.5	75	.012	427.1	75	.010	431.3
60	.019	-	107	.020	-	97	.017	426.4	94	.011	427.1	94	.009	431.3
107	.021	-	173	.026	-	139	.018	426.6	129	.012	427.2	129	.009	431.4
173	.023	-	246	.036	-	197	.019	426.9	194	.014	427.6	194	.011	431.8
246	.029	-	284	.044	-	271	.022	427.3	268	.020	428.0	268	.014	432.0
284	.031	-	350	.049	-	319	.029	-	306	.024	-	306	.020	-
350	.039	-	351	.047	-	385	.040	-	372	.033	-	372	.031	-

Values are the average of 3 readings.

TABLE E-2: LONGITUDINAL EXPANSIONS (%) OF PHASE 3 (Contd.)

Batch No.: 6MB			7MB			8MB			9MB			10MB		
Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)
0	.000	437.8	0	.000	433.6	0	.000	435.9	0	.000	439.9	0	.000	434.7
7	.002	437.8	7	.001	433.8	7	.004	435.9	7	.007	440.0	7	.005	434.7
28	.008	438.0	28	.009	434.7	28	.010	435.8	28	.017	440.9	28	.010	434.6
45	.013	438.4	50	.015	435.6	60	.014	436.0	48	.024	441.9	46	.011	434.7
60	.014	438.7	60	.019	436.0	113	.014	436.3	62	.028	442.3	64	.014	434.7
75	.015	438.5	108	.028	436.3	171	.015	436.7	75	.034	442.2	99	.013	434.9
110	.016	438.7	173	.057	438.3	245	.024	437.4	111	.045	442.7	164	.015	435.5
175	.017	439.5	247	.090	439.4	349	.042	-	176	.095	444.3	238	.022	435.9
249	.023	440.0	285	.120	-	-	-	-	250	.181	446.0	276	.026	-
287	.031	-	320	.164	-	-	-	-	288	.237	-	342	.039	-
353	.040	-	-	-	-	-	-	-	354	.327	-	-	-	-

Values are the average of 3 readings.

TABLE E-2. LONGITUDINAL EXPANSIONS (%) OF PHASE 3 (Contd.)

11MB			12MB			
Batch No.	Days in Soln.	% Exp.	Weight (g)	Days in Soln.	% Exp.	Weight (g)
	0	.000	-	0	.000	-
	7	.002	-	7	.006	-
	39	.008	-	42	.011	-
	113	.018	-	116	.027	-
	151	.022	-	154	.033	-
	220	.032	-	222	.038	-

Values are the average of 3 readings.

APPENDIX F

POROSITY MEASUREMENTS

TABLE F-1: POROSITY MEASUREMENTS

4 batches of Phase 3 are being monitored for their porosities. The porosity measurements to date are given below.

Specimen No.	Blend	Solution Stored In	Time of Exposure (days)	* % Porosity
9MA	100% Type 10 PC (8.3% C ₃ A)	Deionized water	2	17.9
			58	12.4
			121	15.7
9MB	100% Type 10 PC (8.3% C ₃ A)	50,000 ppm S ₂ O ₃ as Na ₂ SO ₄	2	17.9
			58	16.0
			121	19.6
10MA	50% SC/50% Type 10 PC (8.3% C ₃ A)	Deionized water	0	17.0
			108	12.9
10MB	50% SC /50% Type 10 PC (8.3% C ₃ A)	50,000 ppm S ₂ O ₃ as Na ₂ SO ₄	0	17.0
			108	16.0

* The porosities obtained are lower than normal. The Mercury Porosometer was not available at the time of testing, hence the results could not be verified.

APPENDIX G

MIX SPECIFICATIONS AND LENGTH CHANGES
OF PARTIALLY SUBMERGED SPECIMENS
SUBJECTED TO ALTERNATE WETTING AND
DRYING CYCLES *

* Experimental work initiated as part of an undergraduate laboratory, CE 4G4, at McMaster University, reference: Godo, J.E., D.A.Houston, C.S. Sherwin, "A Study of Slag Cements In Sulphate Environments", Undergraduate Laboratory, in partial fulfilment of the CE 4G4 course, McMaster University, Hamilton, April 1979.

TABLE G-1: MIX SPECIFICATIONS (ALTERNATE WETTING AND DRYING CYCLES)

Batch No.	Blend % SC/% Type 10 PC (11.8% C ₃ A)	Solution Stored in (ppm SO ₃ as Na ₂ SO ₄)	Placed in Solution		
			Age (days)	f'c	
				MPa	Psi
1	0/100	50,000	7	21.3	3087
2	50/50	50,000	7	21.4	3104
3	60/40	50,000	7	20.1	2912
4	0/100	35,000	7	20.5	2977
5	70/30	50,000	7	21.8	3157
6	0/100	50,000	7	21.4	3104
8	50/50	35,000	7	21.4	3100
9	60/40	35,000	7	22.2	3220
10	0/100	0 (tap water)	14	21.4	3100
11	50/50	0 (tap water)	14	21.4	3100
12	70/30	35,000	14	21.4	3100

Mixing was carried out in accordance with
ASTM C109 and C305.

TABLE G-2: LENGTH CHANGES (%) - ALTERNATE WETTING AND DRYING CYCLES

Number of Cycles	Solution: Water		35,000 ppm SO ₃ as Na ₂ SO ₄				50,000 ppm SO ₃ as Na ₂ SO ₄				
	Batch No.	11	4	8	9	12	1	2	3	5	6
0.14**	6/100*	50/50	0/100	50/50	60/40	70/30	0/100	50/50	60/40	70/30	0/100
0.5	-0.003	-0.006	+0.005	-0.007	-0.006	-0.012	-0.012	+0.001	+0.007	-0.007	-0.009
1.0	-0.016	-0.010	-	-0.011	-0.017	-0.012	-0.018	-0.021	-0.013	-0.016	-0.027
1.5	-0.036	-0.025	-0.031	-0.024	-0.027	-0.023	-0.046	-	-	-0.017	-0.025
1.5	-0.045	-0.032	-0.043	-0.029	-0.032	-0.025	-	-0.038	-0.036	-0.020	-0.027
2.0	-0.059	-0.040	-0.041	-0.044	-0.044	-0.047	-0.045	-0.040	-0.032	-0.026	-0.033
2.5	-	-	-0.052	-	-0.034	-	-	-0.043	-0.041	-0.028	-0.029
3.0	-0.057***	-0.041***	-0.042	-0.045***	-0.051	-0.052***	-0.047	-0.032	-0.031	-0.032	-0.033
3.5	-	-	-	-	-0.049	-	-0.053	-0.045	-0.042	-0.044	-0.022
4.0	-	-	-0.051	-	-0.058	-	-0.052	-0.034	-0.036	-0.055	-0.020***
4.5	-	-	-0.050	-	-	-	-0.053	-0.043	-0.042	-	-
5.0	-0.086	-0.076	-0.042	-0.070	-0.046***	-0.090	-0.045	-0.032	-0.031	-0.046***	-
5.5	-0.077	-0.068	-	-0.051	-	-0.068	-0.053	-0.044	-0.038	-	-
6.0	-0.067	-0.058	-0.048***	-0.038	-	-0.055	-0.046	-	-	-	+0.207
6.5	-0.067	-0.059	-	-0.032	-	-0.053	-	-0.033***	-0.022***	-	+0.253
7.0	-0.063	-0.053	-	-0.024	-0.070	-0.058	-0.044***	-	-	-0.067	+0.397
7.5	-0.068	-0.062	-	-0.024	-0.051	-0.054	-	-	-	-0.051	+0.523
8.0	-	-	+0.033	-	-0.048	-	-	-	-	-0.038	+0.605
8.5	-	-	+0.030	-	-0.050	-	-	-0.048	-0.005	-0.024	+0.704
9.0	-	-	+0.091	-	-0.044	-	+0.034	-0.037	-0.033	-0.028	-
9.5	-	-	+0.141	-	-0.045	-	+0.030	-0.020	-0.018	-0.032	-
10.0	-	-	+0.209	-	-	-	+0.089	-0.006	-0.003	-	-
10.5	-	-	+0.413	-	-	-	+0.136	-0.010	+0.007	-	-
11.0	-	-	-	-	-	-	+0.191	+0.027	-	-	-
11.5	-	-	-	-	-	-	+0.257	-	-	-	-

* %SC/% PC

** 7 day cycles; the cycles were later changed to 14 day durations.

*** denotes the beginning of 14 day cycles.

APPENDIX H

ALKALI-SILICA TEST PROGRAM *

* Experimental work initiated as part of an undergraduate laboratory, CE 4G4, at McMaster University, reference: Lau, P.T.S., R.S. Hanmer and W.W.K. Chu, "Alkali-Silica Aggregate Reaction Resistance of Slag Cements", Undergraduate Laboratory, in partial fulfilment of the CE 4G4 course, McMaster University, Hamilton, April 1979.

TABLE H-1: MIX SPECIFICATION FOR ALKALI-SILICA TEST PROGRAM

Batch No.	Binder	Aggregate	Placed in Solution (1979)	Solution Type
B	100% Type 10 PC	glass	Feb. 8	Tap water
C	100% Type 10 PC	Ottawa sand	Feb. 8	Tap water
D	100% Type 10 PC	pyrex	Feb. 8	Tap water
E	50% SC/50% Type 10 PC	pyrex	Feb. 19	Tap water
F	50% SC/50% Type 10 PC	glass	Feb. 8	Tap water
G	100% Type 10 PC	Ottawa sand	Feb. 19	Saturated lime solution
H	100% Low-Alkali PC	Ottawa sand	Feb. 19	Tap water
I	100% Type 10 PC	glass	Feb. 22	Tap water
J	50% SC/50% Type 10 PC	glass	Feb. 27	Saturated lime solution
K	100% Type 10 PC	pyrex	Feb. 27	Saturated lime solution
L	60% SC/40% Type 10 PC	pyrex	Feb. 27	Tap water
M	100% Type 10 PC	glass	Feb. 27	Saturated lime solution
X	100% Low-Alkali PC	glass	March 15	Tap water
Y	100% Low-Alkali PC	pyrex	March 15	Tap water
Z	50% SC/50% Type 10 PC	pyrex	March 15	Saturated lime solution

All specimens made in accordance with ASTM C109 and C305.

TABLE H-2: CHEMICAL COMPOSITION OF CEMENTITIOUS
HYDRAULIC SLAG AND PORTLAND CEMENTS

Composition(%)	Cementitious Hydraulic Slag	Type 10 Portland Cement	Low-Alkali Portland Cement
CaO	38.19	64.1	65.1
SiO ₂	37.93	22.0	22.6
Al ₂ O ₃	8.42	5.5	4.5
MgO	11.45	1.4	1.2
Fe ₂ O ₃	1.53	3.0	3.2
S	2.0	2.1	-
MnO	0.63	-	-
TiO ₂	0.35	-	-
Na ₂ O	0.16	1.10	-
K ₂ O	0.47	-	-

TABLE H-3: CHEMICAL COMPOSITION OF ORDINARY WASTE
GLASS AND PYREX GLASS.

Composition (%)	Ordinary Waste Glass	Pyrex Glass
SiO ₂	71-73	80
Na ₂ O	12-14	4
Al ₂ O ₃	0.5-1.5	3
CaO	10-12	-
B ₂ O ₃	-	12

TABLE H-4: LONGITUDINAL EXPANSIONS

Batch No. B	C		D		E		F		G		H		I	
Days in Soln.	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions
11 .008(2)	11 .001(3)	11 .002(3)	11 .009	17 .007	8 .010(2)	8 .007(2)	8 .009	8 .011(2)	8 .006	8 .007(3)	8 .011	9 .008(2)	9 .004	9 .004
19 .011	19 .005	19 .009	19 .009	17 .007	17 .007	17 .009	17 .009	17 .006	17 .006	17 .011	17 .011	16 .004	16 .004	16 .004
28 .010	28 .013	28 .009	28 .009	24 .004	24 .004	24 .007	24 .007	24 .007	24 .007	24 .002	24 .002	23 .005	23 .005	23 .005
35 .013	35 .002	35 .010	35 .010	31 .015	31 .015	31 .019	31 .019	31 .007	31 .007	31 .006	31 .006	34 .005	34 .005	34 .005
42 .021	42 .015	42 .013	42 .013	42 .017	42 .017	42 .015	42 .015	42 .001	42 .001	42 .008	42 .008	64 .022	64 .022	64 .022
53 .020	53 .014	53 .013	53 .013	67 .028	67 .028	78 .034	78 .034	67 .021	67 .021	79 .014	79 .014	69 .021	69 .021	69 .021
78 .032	90 .021	59 .018	59 .018	72 .019	72 .019	83 .028	83 .028	72 .020	72 .020	86 .016	86 .016	76 .016	76 .016	76 .016
83 .028	97 .022	64 .017	64 .017	79 .023	79 .023	90 .021	90 .021	79 .011	79 .011	93 .018	93 .018	83 .028	83 .028	83 .028
90 .023	104 .024	71 .014	71 .014	86 .024	86 .024	97 .032	97 .032	86 .023	86 .023	100 .017	100 .017	90 .027	90 .027	90 .027
97 .036	111 .024	78 .010	78 .010	93 .024	93 .024	104 .028	104 .028	93 .023	93 .023	107 .021	107 .021	97 .025	97 .025	97 .025
104 .033	118 .026	85 .019	85 .019	100 .030	100 .030	111 .031	111 .031	100 .022	100 .022	121 .024	121 .024	104 .027	104 .027	104 .027
111 .038	132 .035	92 .023	92 .023	107 .032	107 .032	118 .030	118 .030	107 .023	107 .023	188 .025	188 .025	118 .033	118 .033	118 .033
118 .033	199 .043	99 .023	99 .023	121 .037	121 .037	132 .036	132 .036	121 .025	121 .025	-	-	185 .040	185 .040	185 .040
32 .039	-	113 .027	113 .027	188 .046	188 .046	199 .041	199 .041	188 .031	188 .031	-	-	-	-	-
47 .056	-	180 .035	180 .035	-	-	-	-	-	-	-	-	-	-	-
99 .058	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Expansions are the average of the number of readings indicated
in the brackets.

TABLE H-4: LONGITUDINAL EXPANSIONS (Contd.)

Batch No. J		K		L		M		X		Y		Z	
Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions	Days in Soln.	% Expan- sions
9	.002(3)	9	.020(2)	9	.006(2)	9	.003(3)	7	.004(2)	7	.011(2)	7	.006(2)
16	.007	16	.025	16	.002	16	.007	18	.003	18	.008	18	.022
23	.013	23	.033	23	.017	23	.014	43	.021	43	.021	43	.012
34	.012	34	.040	34	.017	42	.012	48	.017	48	.021	48	.031
71	.023	59	.046	59	.026	71	.018	55	.008	55	.014	55	.021
78	.023	64	.046	64	.024	78	.020	62	.019	62	.015	62	.031
85	.026	71	.038	71	.022	85	.026	69	.016	69	.015	69	.032
92	.026	78	.048	78	.025	92	.026	76	.016	76	.019	76	.034
99	.030	85	.048	85	.022	99	.027	83	.016	83	.018	83	.032
113	.036	92	.047	92	.025	113	.039	97	.023	97	.021	97	.039
180	.036	99	.046	99	.025	128	.037	164	.030	164	.027	112	.053
-	-	113	.052	113	.028	180	.034	-	-	-	-	164	.053
-	-	180	.064	180	.035	-	-	-	-	-	-	-	-

Expansions are the average of the number of readings indicated in the brackets.