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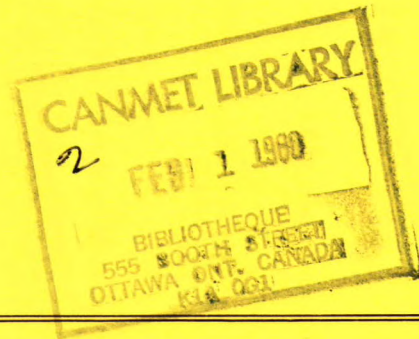
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REPORT 79-28

SULPHUR CONCRETE AND SULPHUR INFILTRATED CONCRETE: PROPERTIES, APPLICATIONS AND LIMITATIONS

V.M. MALHOTRA



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SULPHUR CONCRETE AND SULPHUR INFILTRATED CONCRETE:
PROPERTIES, APPLICATIONS AND LIMITATIONS

by

V.M. Malhotra*

ABSTRACT

Sulphur is one of the most important and useful industrial materials. In recent years there has been a considerable oversupply of this element resulting in investigations to find new uses for it. This paper in two parts, describes sulphur and sulphur-infiltrated concretes.

Sulphur concrete consists of elemental sulphur, stone and fine aggregates and contains no water or cement. Its high compressive strength at early age - of the order of 35 MPa at eight hours - makes it ideal for small precast units for outdoor use; its good chemical durability makes it suitable in industrial plants. However, its low melting point at 119°C, its vulnerability to combustion and the production of toxic gases, its corrosive effect on reinforcing steel under wet or humid conditions and its brittleness make it unfit for most structural uses.

The available published data suggest that concrete made with unmodified sulphur is unsuitable under thermal cycling, including freeze-thaw, because the thermal coefficient of expansion of sulphur is much higher than that of aggregates; concretes made with modified sulphur perform only marginally better.

Sulphur-infiltrated concrete is produced by infiltrating conventional portland cement concrete having water to cement ratios of the order of 0.70, with or without pressure. The infiltrated composite has increased mechanical properties, its compressive and flexural strengths being of the order of 100 and 10 MPa respectively. Its performance under freeze-thaw cycling is generally satisfactory although there are exceptions. This concrete is more durable than conventional concretes in acidic environments but is unstable in alkaline solutions and when left submerged in water over long periods.

Both sulphur concrete and sulphur infiltrated concrete are specialized products. They are not intended as substitutes for conventional concrete but are useful alternatives where conventional concrete has a limited life expectancy and the use of the above concretes can increase it by a factor of 2 or 3.

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BETON DE SOUFRE ET BETON IMPREGNE DE SOUFRE:
PROPRIETES, APPLICATIONS ET LIMITES

par

V.M. Malhotra*

RESUME

Le soufre est l'un des matériaux industriels les plus importants et utiles. L'abondance de cet élément au cours des dernières années a incité la création de projets d'étude pour trouver des nouveaux usages. Le présent rapport est divisé en deux parties et décrit les bétons de soufre et les bétons imprégnés de soufre.

Le béton de soufre est composé de soufre élémentaire, de pierres et d'agrégats fins et ne contient ni eau ni ciment. Dès le début on peut mesurer une résistance à la compression de l'ordre de 35 MPa après huit heures lui donnant des propriétés idéales à la fabrication de petits articles d'extérieur coulés d'avance. Sa durabilité du point de vue chimique en fait un matériau convenable pour les industries. Par contre, il ne peut convenir à la plupart des usages en construction d'immeubles à cause de son bas point de fusion (119°C), sa vulnérabilité à la combustion, la production de gaz toxiques, son effet sur l'acier de renforcement dans des conditions humides ou imbibées d'eau et sa fragilité.

Les données disponibles démontrent que le béton fabriqué à partir de soufre non-modifié ne convient pas aux usages soumis au cycle thermique complet, y compris le gel-dégel, car le coefficient thermique de dilatation du soufre est beaucoup plus élevé que celui des agrégats. Les bétons fabriqués à partir de soufre modifié ont un rendement quelque peu meilleur.

Le béton imprégné de soufre est fabriqué en imprégnant sous pression ou non le béton de ciment portland classique ayant un rapport eau à ciment de l'ordre de 0,70. Le composé imprégné est doué de propriétés mécaniques meilleures, notamment une résistance à la compression et à l'extension de l'ordre de 100 et 10 MPa respectivement. Son rendement durant le cycle de gel-dégel est habituellement satisfaisant quoique il y ait des exceptions. Ce béton est plus résistant que les bétons classiques dans des milieux acides mais est instable en solution alcaline et lorsque submergé dans l'eau durant de longues périodes de temps.

Le béton de soufre et le béton infiltré de soufre sont des produits spécialisés. Ils ne sont pas destinés à remplacer le béton classique mais plutôt comme alternative utile dans les cas où le béton classique serait de faible durée et que l'usage des bétons mentionnés ci-dessus pourrait allonger la vie deux ou trois fois.

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INTRODUCTION

Sulphur is an important element with many industrial uses. In spite of this it has been in considerable oversupply in recent years, especially in Canada. The year-end inventory in Canada in 1970 was 3.17 million tonnes which built up to 18.2 million tonnes in 1977 (1). However, world production in all forms was 47.6 million tonnes in 1977 with consumption at 45.8 million tonnes indicating a slowdown in the build-up of inventories. As inventories increased in the early 1970's, the price fell from about \$38/t in 1968 to about \$6 in 1972 but has since climbed back to about \$27 (1).

During the low-price period there was considerable interest to find other uses for sulphur, especially as a construction material, and in 1978 an international Symposium was held in Canada with the theme "Sulphur in Construction" (2).

This paper is divided into two parts: the first discusses the development of sulphur concrete, gives its mechanical properties, advantages and limitations, and the second describes sulphur-infiltrated concrete and discusses its mechanical properties, durability, applications and limitations. Both types are potentially useful construction materials but have serious limitations which must be recognized.

SOME FUNDAMENTAL PROPERTIES OF SULPHUR

Pure solid sulphur is yellow in appearance and weighs between 2000 and 2100 kg/m³. At normal temperatures, it has an orthorhombic crystalline structure; upon heating, it inverts slowly at 96°C to a monoclinic less dense allotrope which melts at about 119°C. The liquid ranges in colour from transparent straw yellow to dark reddish brown depending on its temperature, and its viscosity changes markedly, particularly above 159°C. Some of the properties are summarized below (3,4,5).

Viscosity

at 120°C	11.8 x 10 ⁻³ Pa.s*
at 159°C	6.6 x 10 ⁻³ Pa.s
at 188°C	100 Pa.s

Specific gravity

of solid	1.96 - 2.07
of liquid at 120°C	1.80

Compressive strength

on 75 x 150-mm cylinders = 28 MPa

**Thermal coefficient of expansion

at 25°C	74 x 10 ⁻⁶ /°C
---------	---------------------------

*The viscosity of water is 10⁻³ Pa.s at 20.3°C.

**Thermal coefficient of expansion of concrete made with limestone aggregate is of the order of 7 x 10⁻⁶/°C.

PART I - SULPHUR CONCRETE

HISTORICAL BACKGROUND

The earliest known use of sulphur in construction was in the 17th century in Latin America where it was employed to anchor metal to stone, examples of which still exist (6). In 1859 Wright referred to the cementing property of sulphur in a U.S.A. patent (7). For the next 60 years there was little reported on the possible uses of sulphur in construction. At the end of World War I, sulphur was in oversupply in North America and this gave impetus to research for new uses. Bacon and Davis in 1921 reported the development of acid-resistant mortars containing 40% sulphur and 60% sand for use in the chemical industry (8). Payne and Duecker, and Duecker in early 1930's reported the development and use of additives to overcome the instability of sulphur-sand mortars in thermal cycling (9,10). The reasons for this instability are that molten sulphur on cooling below 95.5°C transforms from the monoclinic $S\beta$, form to orthorhombic, $S\alpha$, crystalline form, the latter being denser, occupying less volume and being subject to disintegration on thermal cycling. The use of an olefin polysulphide, commercially known as Thiokol, in sulphur sand mortars improved their resistance to thermal cycling and it did lead to somewhat wider use of sulphur in chemical plants, particularly for acid tanks and pickling baths.

Following the work of Payne and Duecker, considerable effort was devoted over the next 30 years to develop plasticizers/modifiers for sulphur (9,11). Almost all of the materials used as modifiers for sulphur are either polymeric polysulphides or chemicals which react with elemental sulphur to form polymeric polysulphides in situ (12). For the reaction to take place the sulphur must be molten, and on cooling, the modified sulphur contains polysulphides and elemental sulphur in a variety of forms, mostly $S\beta$, $S\mu$ and S_8 (liquid). These forms have been found to be stable and there does not appear to be crystallization to $S\alpha$. In modifying sulphur it is important to take into account the reaction

time and temperature. One of the modifiers which is relatively cheap and has been investigated with success is dicyclopentadiene (13).

In the late 1960's Dale and Ludwig pioneered the work on sulphur/aggregate systems (14,15). This was followed up by the investigations of Crow and Bates on the development of high strength sulphur-basalt concretes (16). In 1973-74 Malhotra investigated the stability of sulphur concretes in freeze-thaw cycling and the effect of specimen size on mechanical properties of sulphur concrete (4,17). Since then, a number of investigators including Vroom, Loov, Loov et al. Gregor and Hack, Diehl, McBee and Sullivan and others have published papers and reports dealing with various aspects of sulphur and sulphur concrete (13,18-36). A small plant in Calgary is producing precast sulphur concrete bumpers for parking lots and sidewalk slabs (36).

PROCESS TECHNOLOGY

Sulphur concrete is a composite material consisting of sulphur, coarse aggregate and fine aggregate. It contains no water or cement. The process technology for producing it is simple. The powder sulphur and aggregates can be mixed in a conventional mixer equipped with a heater so that the temperature of the sulphur/aggregate mix is raised to 140°C in a matter of minutes and this temperature is maintained long enough for the ingredients to form a flowable homogeneous mixture which can be cast in test moulds. Heating the mixer drum can pose difficulties. To overcome this problem Ludwig and Malhotra have suggested preheating of the aggregates to about 180°C (15,4). The procedure as described by Malhotra is as follows (4):

"The aggregates for each mix are placed in tin pails and heated overnight in standard laboratory heating cabinets to about 180°C. The following morning, the coarse aggregates are placed in a tilting mixer which is then started. Immediately afterwards, a sufficient amount of sulphur is added so as to finely

coat the aggregates. This is followed in order by the addition of the sand, the remaining sulphur and the silica flour. (The silica flour is used as a workability agent.) Mixing is continued for one more minute by which time the sulphur and aggregates have combined to form a flowable mixture".

Following mixing, test specimens are cast immediately. To overcome shrinkage of sulphur on cooling, extra sulphur concrete is placed on top of test specimens. On cooling, the extra concrete is removed by sawing.

MIX PROPORTIONS

As sulphur concrete contains no water or cement, the mix proportions are primarily concerned with achieving the highest strength properties with a minimum amount of sulphur, and with the provision that the resulting mixture is workable. Published data indicate a sulphur content of the order of 20 wt % of total mix for concrete made with 19-mm maximum size aggregate. The percentage of sulphur may be further reduced by selecting aggregate gradings which result in minimum void content (21,29). A comparison of the mix proportions of sulphur concrete and conventional portland cement concrete is given in Fig. 1.

STRENGTH DEVELOPMENT

Compared with normal portland cement concrete, sulphur concrete gains strength very rapidly and reaches about 90% of its ultimate strength in 6 to 8 h under ambient temperature and humidity conditions (Fig. 2). There appears to be no loss of strength with time. A summary of physical and mechanical properties of sulphur concrete is given in Table 1. A comparison of strength properties of modified and un-modified sulphur mortars and conventional cement mortars is given in Table 2.

EFFECT OF AGGREGATE TEXTURE AND TYPE ON STRENGTH

As with normal portland cement concrete, strength properties of sulphur concrete are affected by the type of aggregate used. Gregor

and Hack have shown that compressive and flexural strengths for sulphur concrete made with crushed basaltic aggregate were 80 MPa and 11 MPa respectively; the corresponding values made with natural gravel aggregate were 49 MPa and 9 MPa. The strengths were obtained on 70- and 100-mm cubes (21).

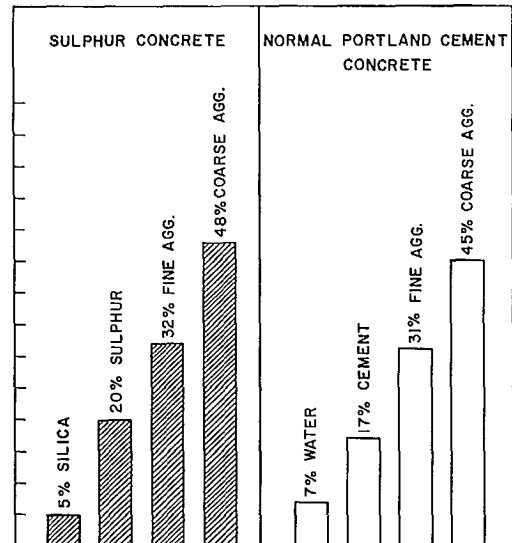


Fig. 1 - A comparison of mix proportions (by weight) for sulphur concrete and normal portland cement concrete

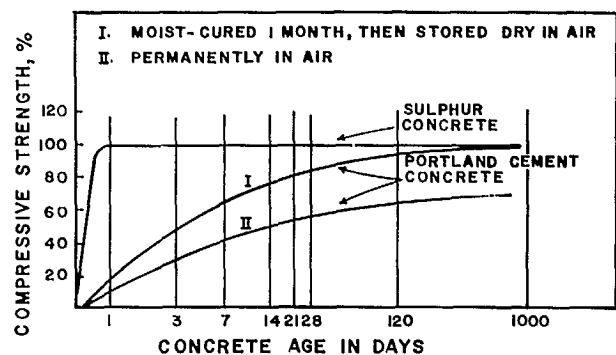


Fig. 2 - Age versus strength development for sulphur concrete and normal portland cement concrete; from reference 21

Table 1 - Physical and mechanical properties
of sulphur concretes*

Physical and mechanical properties	Range
Compressive strength, MPa	
28 - 70	
Modulus of rupture, MPa	
3 - 10	
Ratio, modulus of rupture to compressive strength, %	
12 - 20	
Tensile strength, MPa	
3 - 8	
Ratio, tensile strength to compressive strength, %	
10 - 20	
Modulus of elasticity, GPa	
20 - 45	
Coefficient of thermal expansion per °C(x 10 ⁻⁶)	
8 - 35	
Thermal conductivity, W/m.°C	0.4 - 2.0
Water absorption, %	0 - 1.5

* From reference 11

COMPARISON OF THE RATIOS BETWEEN FLEXURAL
AND COMPRESSIVE STRENGTHS

For the normal portland cement concrete with compressive strength of about 40 MPa, the ratio of flexural to compressive strength is of the order of 13%. The corresponding ratio for sulphur concrete varies between 12 and 16% (4). This higher ratio can be a decided advantage in certain design applications (4,21).

EFFECT OF SPECIMEN SIZE ON COMPRESSIVE STRENGTH

Malhotra has investigated the effect of specimen size on compressive strength of sulphur concrete (17). The compressive strength of 100 x 200-mm concrete cylinders was considerably higher than those of 150 x 300-mm cylinders. For a typical sulphur concrete mix containing about 20% sulphur, the 28-day compressive strengths of 100 x 200-mm cylinders ranged from 32.8 to 46.2 MPa, whereas the corresponding strengths of 150 x 300-mm cylinders ranged from 26.1 to 34.4 MPa (Fig. 3). However density of the smaller cylinders was only slightly higher than of the larger cylinders. For 28-day test results the densities

Table 2 - Strength of unmodified and modified sulphur
and cement mortars*

	1	2	3
Binder	DCPD-modified sulphur	Sulphur	Cement and H ₂ O
Composition (% weight)	Standard sand 78.0 Sulphur 20.9 DCPD 1.1	Standard sand 64.0 Sulphur 36.0	Standard sand 65.2 Cement 21.7 H ₂ O 13.1
Compressive strength (kgf/cm ²)	680	450	550
Tensile strength in flexure (kgf/cm ²)	140	75	70
Days stored until strength tested	2	1	28

*From reference (13).

of 100 x 200-mm cylinders ranged from 2388 to 2428 kg/m³, the corresponding values for 150 x 300-mm cylinders ranged from 2375 to 2411 kg/m³ (Fig. 4).

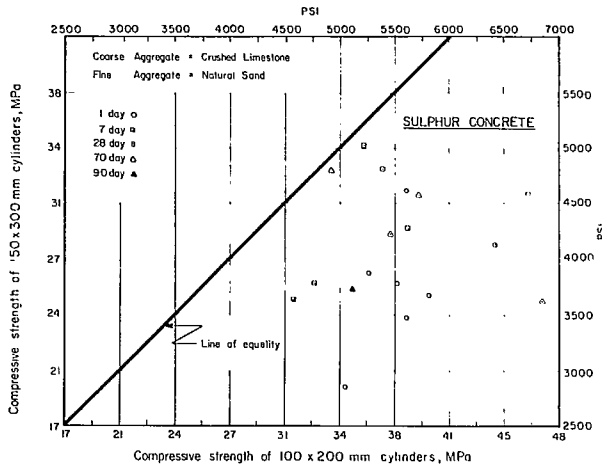


Fig. 3 - Relationship between compressive strength of 100 x 200-mm and 150 x 300-mm cylinders; from reference 17

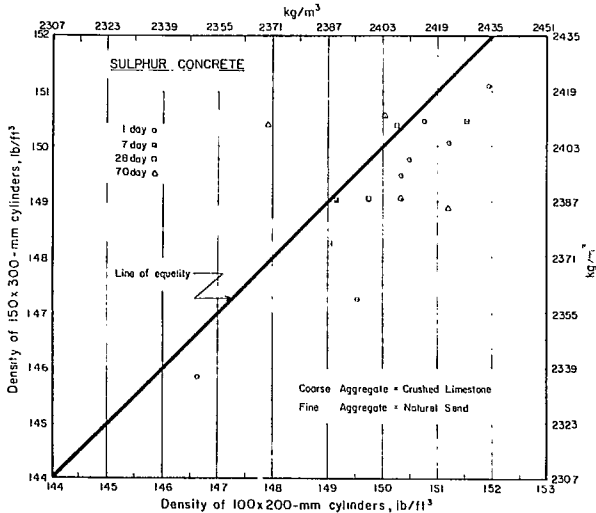


Fig. 4 - Relationship between density of 100 x 200-mm and 150 x 300-mm cylinders; from reference 17

The decrease in strength of large specimens is probably due to the combined effect of specimen size and slower rate of cooling while

they are still in the moulds. This aspect of sulphur concrete could pose serious problems in its use for structural members - problems which would have to be overcome by either controlling cooling or by redesigning members such that thickness is kept to a minimum and a large surface area is provided.

To overcome the problem with slow cooling, Malhotra and Winer investigated the incorporation of asbestos fibres (26). Also investigated was quenching of test specimens immediately after casting. They concluded as follows:

1. The 100 x 200-mm cylinders showed no significant difference whether cured or quenched and whether asbestos were added or not.
2. Quenching of 150 x 300-mm cylinders without asbestos fibres increased the compressive strength of cylinders.
3. When the 150 x 300-mm test cylinders were cast from concrete incorporating asbestos fibres, the compressive strength was of the same order whether curing was done normally or by quenching. This would imply that this costly and not very practical procedure of quenching would not be necessary in large structural elements made from sulphur concrete incorporating asbestos fibres.

The SEM photomicrographs of quenched and unquenched cylinders are shown in Fig. 5.

FATIGUE BEHAVIOUR

Lee et al. have investigated the fatigue behaviour of sulphur concrete for its possible use in highway paving (31). Their study indicated that sulphur concrete with fly ash as an additive had higher fatigue life and that with dicyclopentadiene it had lower fatigue life than without additives. It was also shown that all concretes exhibited significantly better engineering properties in terms of fatigue resistance than normal portland cement concrete (Fig. 6).

STRESS-STRAIN RELATIONSHIP

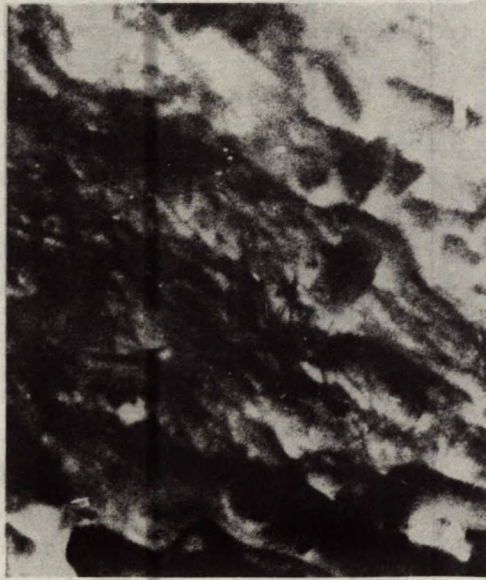
Sulphur concrete is a relatively brittle material. This is quite evident during the testing of specimens in compression. Loov has pub-



(a) Unquenched incorporating 2% fibre; mag. x 112



(b) Quenched incorporating 2% fibre; mag. x 164



(c) Quenched, incorporating 2% fibre; mag. x 1645

Fig. 5 - SEM photomicrographs of quenched and unquenched 150 x 300-mm cylinders of sulphur concrete incorporating 2% asbestos fibres.

(a) Unquenched incorporating 2% fibre; mag. x 112

(b) Quenched, incorporating 2% fibre; mag. x 164

(c) Quenched, incorporating 2% fibre; mag. x 1645;

from reference 26

lished stress-strain relationship for sulphur concrete and has shown that in the testing of sulphur concrete specimens there is no gradual reduction in stiffness as the ultimate load is approached and the failure coincides with the ultimate or lower stress at a strain of approximately 0.0014 (Fig. 7) (19). The brittleness of the material is a disadvantage but it may be overcome by using fibrous materials.

The modulus of elasticity of sulphur concrete is comparable with that of normal portland cement concrete and is of the order of 3×10^4 MPa.

CREEP

Limited published data indicate that sulphur concrete exhibits considerably more creep than portland cement concrete (Fig. 8) which can be a serious disadvantage for structural concrete members.

DURABILITY

Resistance to Freeze-thaw Cycling

As sulphur concrete contains no water or cement, its performance in freeze-thaw cycling is principally a problem of resistance to thermal cycling. This is further compounded by the fact that sulphur has a very high thermal coefficient of expansion. Malhotra has shown that sulphur concrete produced with crushed gravel aggregate is not durable under freeze-thaw cycling (ASTM C666, Procedure B: Freezing in air and thawing in water) (4). This investigation indicated that the prisms had been extensively damaged after exposure to less than 75 cycles (Fig. 9); the relative dynamic modulus of elasticity was between 19.4 and 40% but was generally less than 30% (4).

Studies by Beaudoin and Sereda have shown that the freeze-thaw resistance of mortars may be improved by the addition of pyrites (23). The best freeze-thaw performance was obtained with mortars containing 20% or more of pyrite by weight (Fig. 10).

McBee and Sullivan modified sulphur with

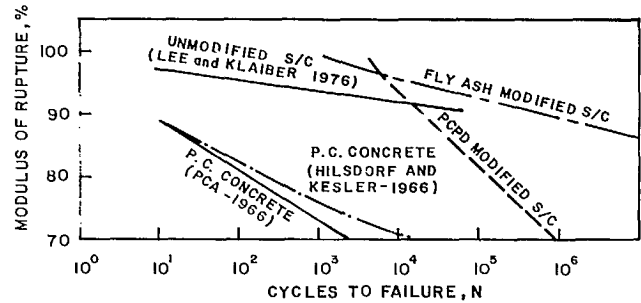


Fig. 6 - Fatigue curves for different series of sulphur concrete and portland cement concrete; from reference 31

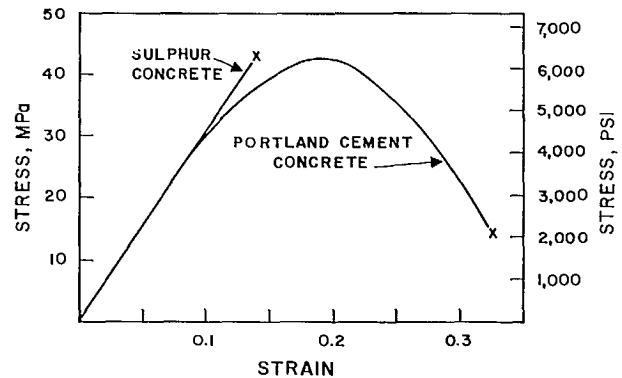


Fig. 7 - Stress strain curves for sulphur and normal portland cement concretes; from reference 19

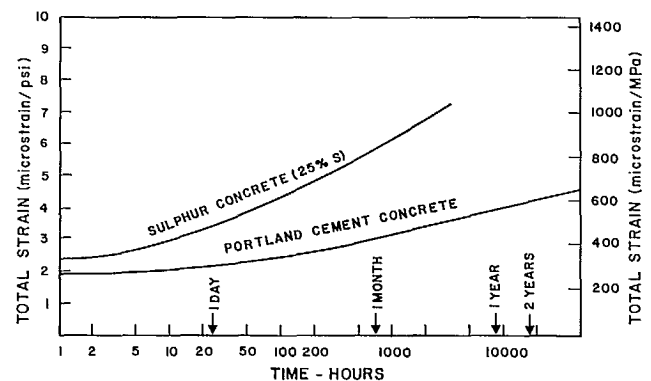


Fig. 8 - Creep behaviour of sulphur concrete at 21°C; from reference 19

5% dicyclopentadiene to improve the freeze-thaw resistance of sulphur concrete (22). Two types of concretes were investigated: for one type the coarse and fine aggregate were crushed quartz and for the other type coarse aggregate was crushed limestone and fine aggregate was manufactured limestone sand.

The relative dynamic values and residual

flexural strengths of test specimens after freeze-thaw cycling are shown in Fig. 11 and Table 3. The test data do indicate marginal improvement in the freeze-thaw resistance of sulphur concrete. Increased freeze-thaw durability of sulphur concrete by the use of a proprietary stabilizer has been claimed but no published data are available (20).

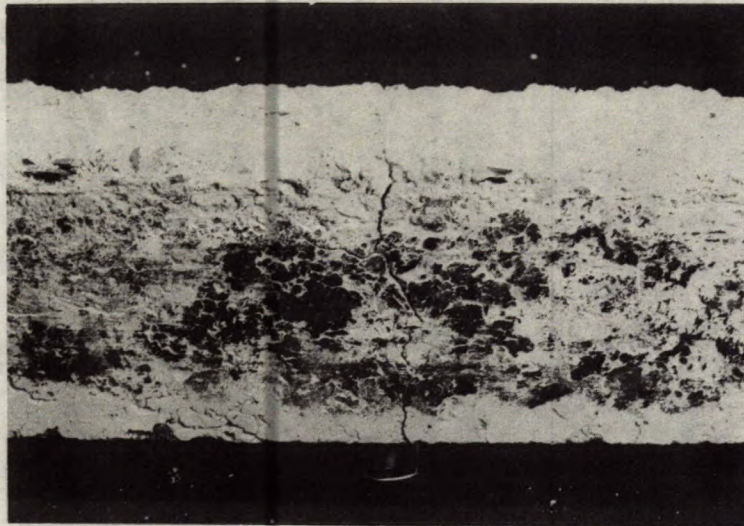


Fig. 9 - Sulphur concrete prisms after exposure to freeze-thaw cycling; from reference 4

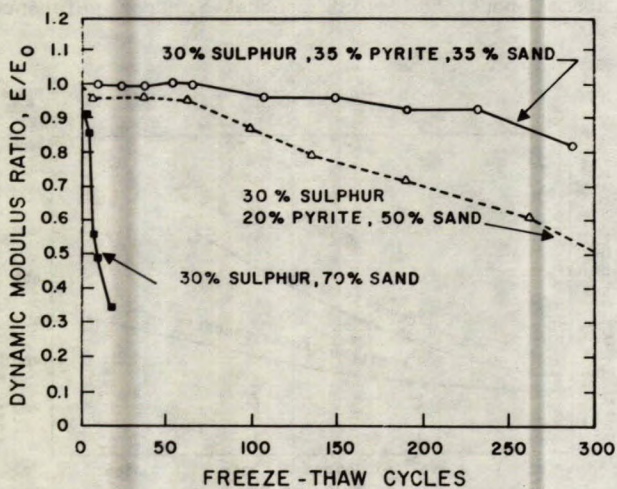


Fig. 10 - Effect of freeze-thaw cycling on dynamic modulus of elasticity of sulphur mortars; from reference 23

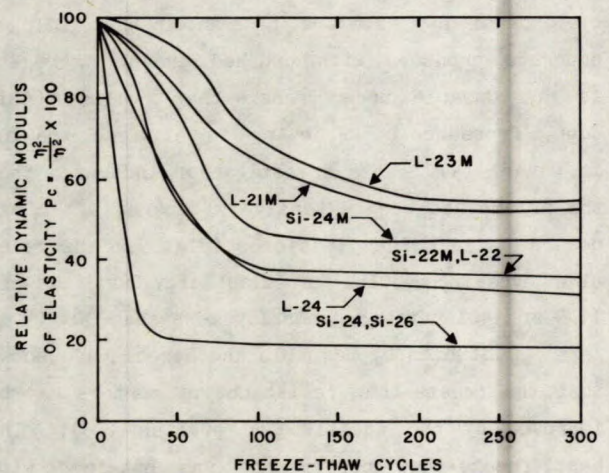


Fig. 11 - Effect of freeze-thaw cycling on relative dynamic modulus of elasticity of sulphur concrete; from reference 23

Table 3 - Residual flexural strengths of sulphur concrete after 300 freeze-thaw cycles*

Aggregate	Sulphur, %	Modulus of rupture, psi		Residual strength %
		Original	Final	
Silica	24	845	125	14.8
Silica	26	905	140	15.5
Silica	22M**	1,220	285	23.4
Silica	24M**	1,335	310	23.2
Limestone	22	700	235	33.6
Limestone	24	810	285	35.1
Limestone	21M**	1,235	470	38.0
Limestone	23M**	1,330	400	30.1

*From reference (22).

**M=Modified with 5% DCPD

Resistance to Aggressive Chemicals

Limited data are available on the long-term performance of sulphur concrete in acid and alkali solutions. Data by McBee and Sullivan show that concretes prepared with the silica aggregate and modified sulphur binder were superior to those made with unmodified sulphur binder (22). The effects on the mechanical properties of modified sulphur test specimens immersed in water, and in 1.0, 5.0 and 10.0 wt % H_2SO_4 for up to one year are shown in Fig. 12. There are no changes in the compressive and tensile strengths during exposure to the solutions though there was some loss in flexural strength which may be explained by a loss in plasticity of the modified sulphur with time. There was no appreciable gain in weight during the period of immersion indicating very low water absorption.

Investigations by McBee and Sullivan also show that sulphur concrete prepared from silica or limestone aggregates and modified sulphur were not affected by exposure to 5% NaCl, 5% $CaCl_2$ or 5% Na_2SO_4 salt solutions (22). The test specimens did not show any loss in weight and there was only negligible gain in weight ranging from zero to 0.30%.

Notwithstanding the above, unmodified sulphur is attacked or dissolved by strong oxidizing agents - concentrated sulphur, nitric, and chromic acids, sodium hypochlorite; strong alkalis at pH 10; polysulphide solutions and certain or-

ganic chemicals - carbon disulphide, phenols and others. Sulphur also reacts with a number of metals in solutions - copper and beryllium - to form insoluble sulphides (25).

Some data by Diehl on the performance of sulphur mortars and DCPD-modified sulphur mortars exposed to aggressive chemicals are shown in Table 4 (13).

Resistance to Biological Attack

It has been demonstrated that sulphur mortars are susceptible to attack by bacteria,

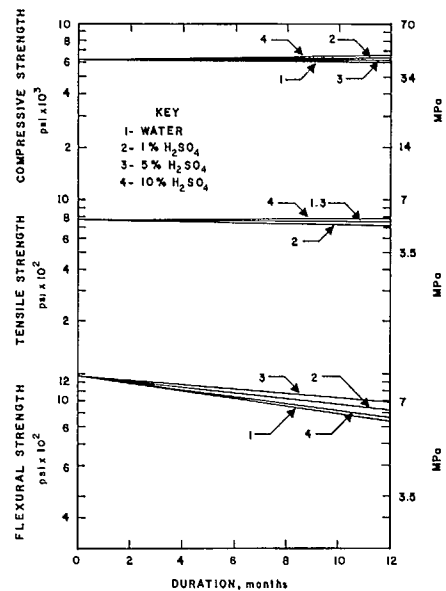


Fig. 12 - Mechanical properties of sulphur concrete corrosion test specimens; from reference 22

Table 4 - Data on behaviour of sulphur mortars
exposed to aggressive chemicals*

	1	2
Binder	DCPD-modified sulphur	Sulphur
Erosion caused by organic solvents (mm/year)		
Methanol	0.03	0.02
Acetone	0.09	0.06
Mineral spirit	0.54	0.85
Methylene chloride	1.80	2.72
Toluene	2.38	4.32
Cyclohexane	2.58	4.90
Erosion caused by salts (mm/year)		
NaCl 0.1 mol/l	0.0	0.02
1.0 mol/l	-	-
5.4 mol/l	-	-
Erosion caused by acids (mm/year)		
H ₂ SO ₄ 0.1 mol/l	0.02	0.02
1.0 mol/l	0.03	0.06
6.6 mol/l	0.02	-

*From reference (13).

primarily thiobacillus thiooxidans, which results in the production of sulphurous and sulphuric acids. Investigations have been reported on the use of bactericides to counter this attack (34,35). However, no quantitative data are available on the degree of biological attack on sulphur concrete and in many instances the amounts of bactericides needed for effective protection resulted in undesirable chemical or mechanical effects on the products and were costly.

Resistance to Fire and Ultra Violet Rays

Elemental sulphur melts at about 119°C and sulphur concrete when subject to this or higher temperature will melt and lose all its structural strength. Because of the low melting point of sulphur, the use of sulphur concrete is limited to applications where temperature does not exceed about 80°C. In spite of the develop-

ment of fire retardants, sulphur concrete cannot be considered stable in fire. In addition, sulphur combustion is self-sustaining and, thus once ignited, will continue to burn until extinguished; in the presence of oxygen, sulphur will burn to sulphur dioxide, a toxic gas.

No data are available on the effects of ultraviolet rays of sunlight on sulphur concrete. However sulphur does oxidize in the presence of moisture and Kemp et al. have shown that action is accelerated by ultraviolet light (24). It may be speculated that large surfaces of sulphur concrete when exposed to the above environment may result in the formation of sulphuric acid. Research is needed in this direction.

SULPHUR CONCRETE AND STEEL REINFORCEMENT

Limited available data indicate that under moist and humid conditions, steel reinforced

sulphur concrete disintegrates rapidly, failure occurring along the reinforcement due to the corrosion of steel; however, under dry conditions, the performance is satisfactory (11,19). Thus, in general, the use of steel reinforcement in sulphur concrete is not desirable and this is one of the several serious disadvantages of sulphur concrete. Data on the use of other reinforcing materials such as fibres in sulphur concrete are sketchy.

RECYCLING

One attractive feature of sulphur concrete is that, if needed, sulphur concrete can be melted to recover sulphur and aggregates and the recycled materials can be used again for concrete. Limited data by Lee et al. show that strength properties of concrete made with recycled sulphur are comparable to the original strength values (Table 5) (31).

ECONOMICS

Muir has given some data as to the relative costs of sulphur and normal portland cement concretes (Table 6) (28). Due to the large inventories of sulphur, it is likely that the price will remain stable up to year 1985, whereas the increased cost of fuel will doubtless be reflected in higher prices for cement. Thus strictly on a cost basis, sulphur concrete should remain competitive with conventional concretes for the near future (28). However, considerations other than cost must also be taken into account. Figure 13

shows a small plant in Calgary, which produces small precast sulphur concrete units.

CONCLUSIONS

Sulphur concrete is a specialized concrete for applications where normal portland cement concretes have been found wanting. Its very high early strength makes it ideal for use in the Arctic for temporary and emergency structures and in applications in northern Canada where moist curing of normal portland cement concrete may not be possible. However because of the insulating properties of sulphur concrete and specimen size effects, sulphur concrete cannot be used for massive sections and placements but it is ideal for small precast units with large surface to volume ratio. The possible applications are as dead weights for pipelines, parking curbs, highway median barriers and other small precast units for outdoor use. Its good chemical durability makes it suitable in industrial plants.

The available published data suggest that concrete made with unmodified sulphur is unsuitable under thermal cycling including freeze-thaw cycling; the concretes made with modified sulphur perform only marginally better but little is known about their long-term performance under these conditions. The low melting point of sulphur concrete, its vulnerability to combustion and the production of toxic gases, the corrosion of reinforcing steel under humid and wet conditions, and its brittleness make it unfit for structural uses.

Table 5 - Strength of original and recycled sulphur concrete*

Series	Original		Recycled			
	Compressive Strength, Psi	Mod. of Rupture, Psi	Compressive Strength, Psi	Percent Change	Mod. of Rupture, Psi	Percent Change
I	4510	533	4286	- 5.0	466	-12.6
II	4410	497	5506	+24.8	466	- 6.2
III	2610	486	4516	+73.0	479	- 1.4

*From reference (31).

Table 6 - 1978 and projected 1985 cost/m³ of hot poured sulphur and portland cement concretes*

	1978		1985	
	5000 psi (35 MPa)	8000 psi (55 MPa)	5000 psi (35 MPa)	8000 psi (55 MPa)
Portland Cement				
Concrete - Type 10	\$29.50	\$39.00	\$45.00	\$60.00
- Type 50	\$33.50	\$45.00	\$50.00	\$68.00
Sulphur Concretes	\$28.00-\$32.00		\$39.00-\$46.00	

*From reference (28).

Notes:

1. Price assumptions (1978): sulphur = \$60/LT, portland cement, Type 10 = \$57/t, Type 50 = \$68/t, aggregate = \$3.85/t.
2. Includes capital write-off for sulphur handling and transit truck modifications (applicable to in-place operations).

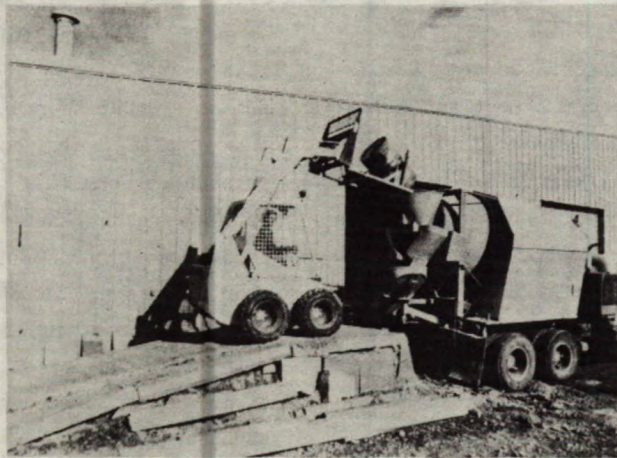


Fig. 13 - Sulfurecrete pilot plant, showing aggregate feeder, conveyors, drier, and 2.25-m³ (3-cu yd) heated transit mix truck, Calgary, Canada; from reference 27

Notwithstanding the advantages and limitations of sulphur concrete and the large inventories of sulphur, it is emphasized that sulphur

is an important and valuable industrial raw material and its indiscriminate use as a binder for concrete cannot be recommended.

PART II - SULPHUR-INFILTRATED CONCRETE

There has been a considerable increase in demand for high strength and durable precast concrete elements in recent years. The development of polymer impregnated concretes (PIC) in the late 1960's was an attempt to meet this growing need (37,38,39). PIC is a composite material which is produced by impregnating conventional concrete with a low viscosity monomer which is then polymerized by radiation or by heat and a catalyst. The impregnated composite has improved mechanical properties (40) and is almost impermeable. However, monomers are expensive and impregnation techniques can be complex because they usually require external pressure. This perhaps explains why, although the development of PIC was first reported in the late 1960's, there have been few industrial applications.

To overcome some of the problems associated with PIC, researches have led to the development of sulphur-infiltrated high-early-strength concrete (41-47). Sulphur is a material which is considerably cheaper than the monomers currently being used in the production of PIC and is widely available in North America.

This part of the report briefly outlines the historical steps in the development of sulphur-infiltrated concrete, describes infiltration procedures and discusses properties, applications and limitations.

HISTORICAL BACKGROUND

A literature study revealed that in 1924, Kobbe had studied the effect of simple immersion in molten sulphur on the tensile strength of mortar briquettes made from 1:5 cement:sand mixes, and reported strength gains of eight times the strength of untreated briquettes (48). In 1973, Rodway observed marked increases in the strength of 150 x 300-mm concrete cylinders which had been immersed in molten sulphur for 7 days (49). In the same year Malhotra observed that conventional concrete specimens when submerged in molten sulphur exhibited considerably increased compressive strengths (42). In 1974, Thaulow reported

an investigation of sulphur-impregnated concrete using exactly the same procedures as those used in the development of PIC (41). Strength gains of 2.4 times were achieved by Thaulow compared with the strength of the control specimens. Although Thaulow did not attempt any simplification of the PIC techniques and did not make full use of the special characteristics of sulphur, he nevertheless did bring to the attention of concrete technologists the use of cheaper materials for impregnating concretes. Malhotra, in a discussion of Thaulow's paper, referred to studies being carried out at CANMET to develop simple and effective procedures for infiltration of lean concrete specimens with molten sulphur (42). Following this, extensive studies were performed at CANMET and elsewhere to investigate the long-term mechanical properties of sulphur-infiltrated concrete and its performance in aqueous solutions and aggressive media (50-65).

PROCESS TECHNOLOGY

Mix Proportioning

According to Malhotra et al. the ideal water to cement ratio for concrete to be infiltrated should be between 0.70 and 0.80 (45). This appears to result in concrete which can be infiltrated without the need for external pressure. Notwithstanding the above, concretes having a water to cement ratio of between 0.50 to 0.70 have been infiltrated with success. There appears to be no special requirement for materials.

Infiltration Procedures

Procedure A consists of moist-curing of concrete test specimens for 24 h, followed by drying at 125°C for 24 h and then immersing in molten sulphur for a period of time. The length of immersion will depend on the type and size of specimen.

Procedure B consists of moist-curing of lean concrete specimens for 24 h, drying at 130°C for 24 h, immersing in molten sulphur under vacuum

for 2 h, releasing the vacuum and soaking for an additional 0.5 h, and then removing from the sulphur to cool. Strength testing is done 1-2 h later.

Procedure C is identical to Procedure B except that following evacuation, external pressure is applied to force sulphur into the concrete. This is especially suitable for low water to cement ratio concretes.

General Comments on Infiltration

The infiltration procedures described seem to produce satisfactory sulphur-infiltrated concrete specimens and may be varied to suit individual job conditions. However, in any procedure the following points should be kept in mind:

- (a) For concretes with a water to cement ratio in the order of 0.70, the 1-d old specimens must be handled with extreme care to avoid damage.
- (b) The drying temperature should be kept as high as possible but not exceeding 150°C as otherwise structure of the young cement paste may be damaged. The duration of drying depends on the size and type of specimens.
- (c) Evacuation time appears to be less critical than soaking time in sulphur after evacuation. For concretes with water to cement ratios of about 0.55, increased soaking time is essential to achieve full infiltration.
- (d) At CANMET, major portions of the investigations have been performed with water to cement ratios of 0.70 ± 0.20 . If water to cement ratios other than these are to be employed, detailed laboratory investigations must first be carried out concerning long-term strength and durability.
- (e) The ideal time to infiltrate test specimens is after 24 h of moist curing but satisfactory infiltration of test specimens has been

achieved after 28 d of moist curing. Prolonged moist curing of test specimens before infiltration may not be desirable (53).

MECHANICAL PROPERTIES

The large increases in the strength of infiltrated specimens probably result mostly from the filling of capillary openings in the hydrated cement paste with sulphur, and partly from filling of the larger voids present at the interface between the aggregate and cement paste. Investigations at CANMET show that under ambient room temperature and 50% relative humidity, the very high strengths achieved at 2 d were maintained for at least up to three years and even exhibited some minor increase (Fig. 14-16). Typical compressive and splitting-tensile strengths of fully infiltrated test specimens at 2 d were of the order of 90 and 7 MPa respectively (50).

Young's modulus of elasticity and Poisson's ratio for the sulphur infiltrated concrete specimens are considerably greater than for the control moist-cured specimens (44,45). Generally the increase in Young's modulus of elasticity of the infiltrated specimens is more than 100%. The stress-strain relationships are linear and the strain at failure is not substantially increased because of the brittleness of the sulphur component (Fig. 17).

FINAL POROSITY

Hope and Nashid have shown that final porosity is the only factor affecting the mechanical properties of SIC regardless of the mix proportion (55). This is in agreement with the behaviour of polymer impregnated concrete. Figures 18 and 19 shown the relationships between final porosity and the mechanical properties of concrete.

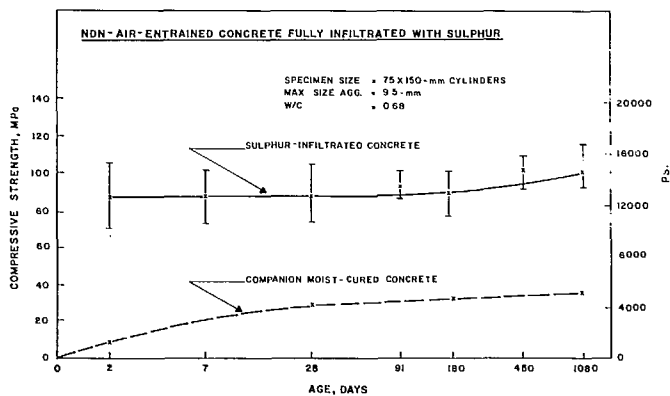


Fig. 14 - Relationship between age and compressive strength of non-air-entrained concrete; from reference 50

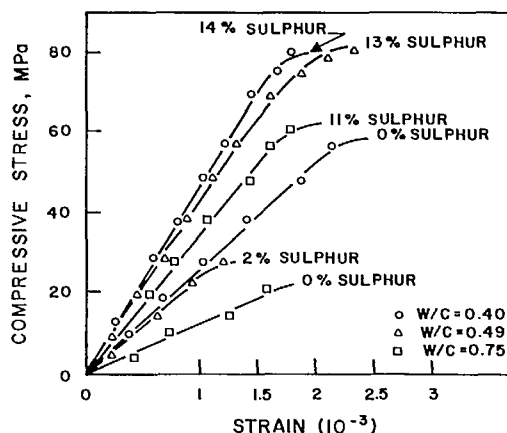


Fig. 17 - Selected stress-strain relationships for concrete moist cured for 60 days; from reference 55

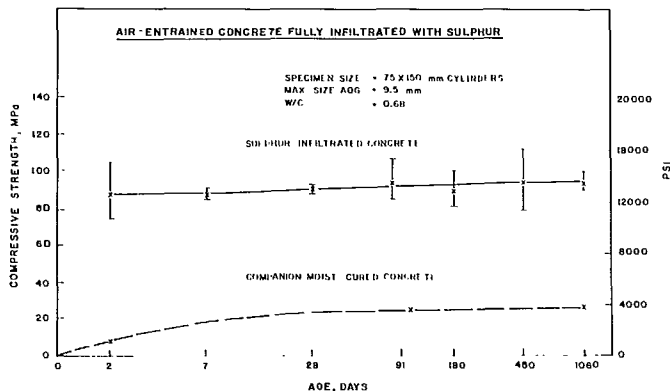


Fig. 15 - Relationship between age and compressive strength for air-entrained concrete; from reference 50

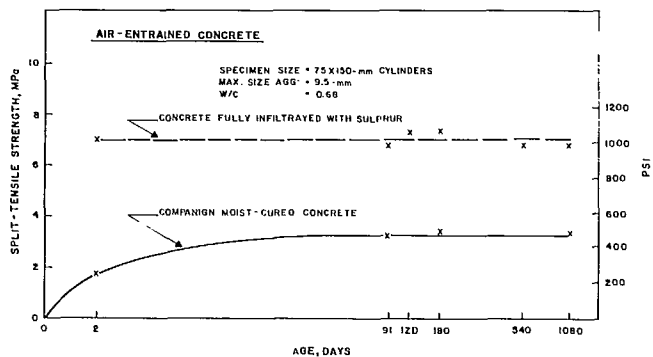


Fig. 16 - Relationship between age and splitting-tensile strength for air-entrained concrete; from reference 50

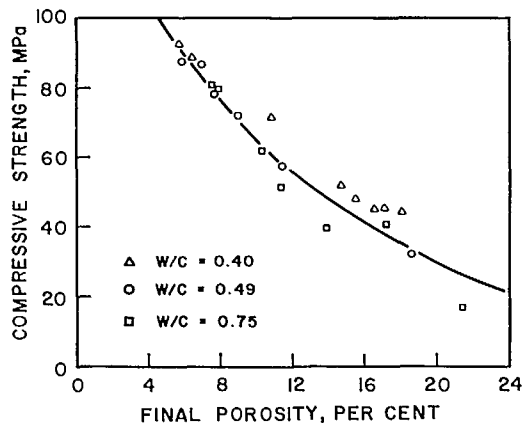


Fig. 18 - Compressive strength versus porosity of cylinders; from reference 55

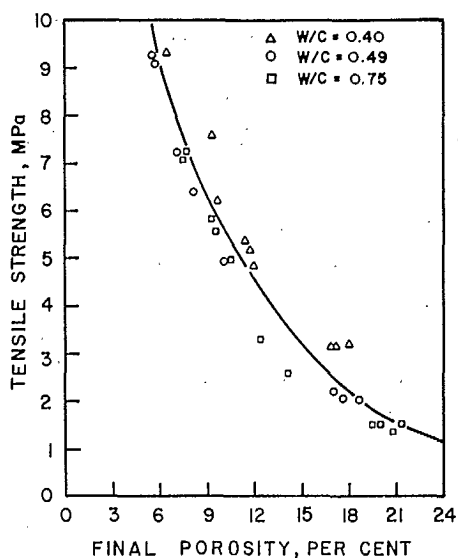


Fig. 19 - Tensile strength versus porosity of cylinders; from reference 55

DURABILITY

Resistance to Freeze-thaw Cycling

Carette et al. have reported voluminous data on the long-term freeze-thaw durability of sulphur infiltrated concrete. The freeze-thaw equipment was capable of performing 8 accelerated cycles in one 24-h period and the test procedure was in accordance with ASTM Standard C666, Procedure B, "Freezing in Air and Thawing in Water" (50). In general, the test data showed no significant loss of mechanical strength after 1000 cycles of freezing and thawing and most specimens were in excellent condition after 1800 cycles (Fig. 20). Occasionally some specimens did show distress after about 600 cycles particularly for concrete made with 0.80 water to cement ratio (Tables 7 and 8).

In addition to the laboratory studies, Caréte et al. have reported the installation of sulphur-infiltrated silo staves and 100 x 200-mm cylinders at an outdoor exposure station at Treat Island, Maine, a facility operated by the U.S.A. Corps of Engineers (Fig. 21) (50). At this station, the test specimens are exposed to extreme

conditions which involve seawater attack, freezing and thawing (130 cycles a year), and wetting and drying. After a two-year exposure, the test specimens are in satisfactory condition.

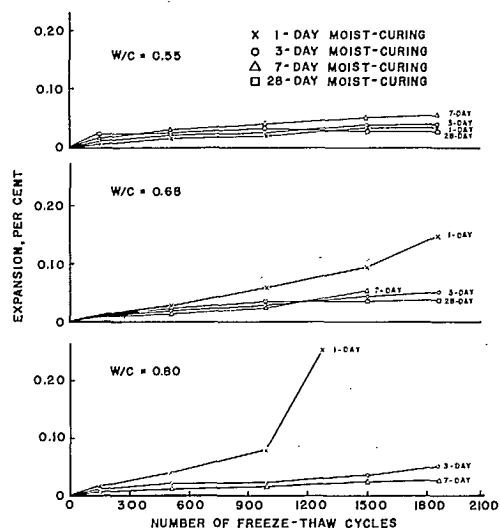


Fig. 20 - Percentage expansion during freeze-thaw cycling of sulphur-infiltrated test specimens for different water/cement ratios and pre-infiltration moist curing times; from reference 50

Stability in Aggressive Media

The stability of sulphur-infiltrated concrete in an aggressive environment has been discussed in detail elsewhere (47). Experience at CANMET has indicated that (50):

- It is more durable than conventional concrete in higher concentrations of H_2SO_4 and HCl (Fig. 22).
- It appears to be mechanically stable when left submerged in stagnant water for periods up to 18 months although some slight leaching of the sulphur has taken place. However, when left submerged in water over extended periods of time, the concrete eventually shows undesirable expansion followed by some cracking
- Performance of specimens in laboratory experiments and in the extreme environments of a sodium sulphate plant was superior to the

- reference uninfiltreated specimens for periods of up to one year.
- (d) It was found to be unstable in 5% sodium hydroxide solution (Fig. 23).
- (e) Infiltration with sulphur greatly reduces destructive acid attack in active silage environments, but extended submersion in neutralized juice should be avoided as leaching of sulphur will occur (52).
- (f) Instability in aqueous media is apparently related to the presence of polysulphide anions formed during infiltration and found to be highly soluble in the alkaline pore

solutions of wet concrete. Under leaching conditions in the absence of air, polysulphide and calcium ions are dissolved from concrete to form the concentrated yellow orange leachate. Under moist aerated conditions the calcium polysulphide is leached but reacts with oxygen to form the sulphur efflorescence observed on the surface of the specimens.

Mehta and Chen have reported data on improving moisture resistance of sulphur-infiltrated mortars (54). In one series of tests it was attempted to inhibit the reaction between sulphur and Ca(OH)_2

Table 7 - Freeze-thaw data on 50 x 50 x 150-mm sulphur-infiltrated prisms*

Water-Cement Ratio	Moist-Curing Time Before Infiltration, Days	Sulphur Loading, %	Freeze-Thaw Data after 1800 Cycles		
			Weight Change, %	Length Change, %	Visual Examination
0.55	1	11.8	+0.1	+0.04	No significant visual deterioration**
	3	9.1	+0.2	+0.04	No significant visual deterioration
	7	5.6	+1.7	+0.05	No significant visual deterioration
	28	3.1	+1.5	+0.03	No significant visual deterioration
0.68	1	13.1	+0.3	+0.15	Some surface cracking
	3	11.2	+0.3	+0.05	No significant visual deterioration***
	7	8.5	+0.1	+0.06	No significant visual deterioration
	28	7.0	+0.2	+0.04	No significant visual deterioration
0.80	1	13.1	+0.6	+0.46	Failed****
	3	10.0	+0.3	+0.05	No significant visual deterioration
	7	7.6	+0.1	+0.03	No significant visual deterioration
	28	5.7	+0.4	—	No significant visual deterioration

* From reference (50).

** Except for the odd pop-out

*** One accidentally damaged specimen failed upon cycling at early stages

**** Severe cracking after 1000 cycles

Note: Each result is average of tests on 2 to 4 specimens.

Table 8 - Freeze-thaw data on 75 x 150-mm sulphur-infiltrated cylinders*

Water-Cement Ratio	Moist Curing Time Before Infiltration Days	Sulphur Loading %	Freeze-Thaw Data after 1800 Cycles			
			Weight Change, %	Pulse Velocity Change %	Residual Compressive Strength %	Visual Examination
0.55	1	11.1	+0.2	-4.6	99	No significant visual deterioration**
	3	7.3	+0.3	-3.5	103	No significant visual deterioration
	7	4.6	+0.3	-3.0	100	No significant visual deterioration
	28	1.7	+0.2	-1.0	119	No significant visual deterioration
0.68	1	13.2	+0.2	-9.3	85	Slight surface cracking
	3	10.6	+0.3	-5.2	101	No significant visual deterioration
	7	8.4	+0.5	-3.5	103	No significant visual deterioration
	28	5.2	+0.5	-1.8	102	No significant visual deterioration
0.80	1	14.0	+0.4	-22.0	55	Failed or severely cracked
	3	11.2	+0.1	-4.6	102	No significant visual deterioration
	7	6.9	+0.1	-3.5	--	No significant visual deterioration
	28	5.1	+0.1	-2.8	--	No significant visual deterioration

*From reference (50).

**Except for the odd pop-out

Note: Each result is average tests on 2 to 4 specimens.



Fig. 21 - Test specimens at Treat Island exposure station; from reference 50

by coating the $\text{Ca}(\text{OH})_2$ with a film of insoluble calcium salts. In the second series, cements which did not contain $\text{Ca}(\text{OH})_2$ in hydration products were investigated for sulphur infiltration. They reported that both approaches gave encouraging results in improving moisture resistance (Fig. 24).

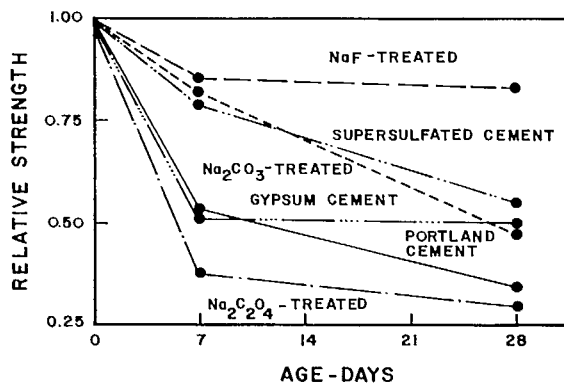


Fig. 24 - Strengths of sulphur-infiltrated mortars after water immersion; from reference 54

Recent work by Feldman shows that sulphur infiltrated matrices with a surface area less than $20 \text{ m}^2/\text{g}$ scarcely expanded after 400 days of exposure to 100% RH (53). The same samples have experienced 800 cycles of freezing and thawing without any observable deterioration whereas the samples with surface areas higher than $20 \text{ m}^2/\text{g}$ disintegrated in less than 100 cycles. To achieve surface areas of $20 \text{ m}^2/\text{g}$ the mortars should be infiltrated at an early age of hydration i.e., after about 24 h of moist curing. However, the surface area values of $20 \text{ m}^2/\text{g}$ quoted above are for mortars. Data by Carette et al. shows satisfactory freeze-thaw performance of concrete prisms which had been infiltrated after moist curing period which varied from 1 to 28 days (Fig. 20). The apparent discrepancy between the mortar data by Feldman and concrete data by Carette et al. may be explained in terms of different compositions of the test specimens (53,50). Further research is indicated.

PIPES

Concrete sewer pipes are prone to corrosion due to attacks by sulphuric acid. Figure 25 shows the mechanism of such corrosion (58). Briefly, the sewage gases, principally H_2S , are oxidized by thiobacillus bacteria present in the sewer to sulphuric acid which in turn attacks normal portland cement concrete. The problem may be further compounded by the presence of sulphate

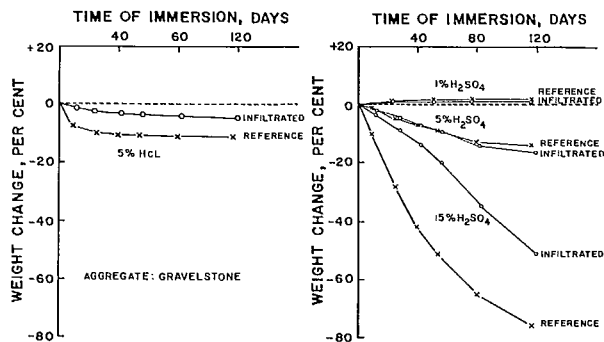


Fig. 22 - Changes in weight of test specimens after immersion in HCl and H_2SO_4 solutions; from reference 50

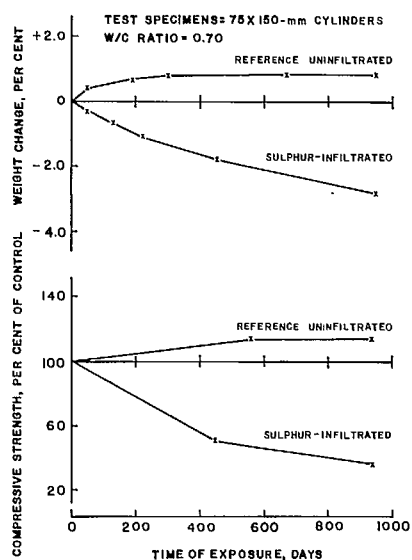


Fig. 23 - Changes in weight and strength of test specimens after immersion in 5% NaOH; from reference 50

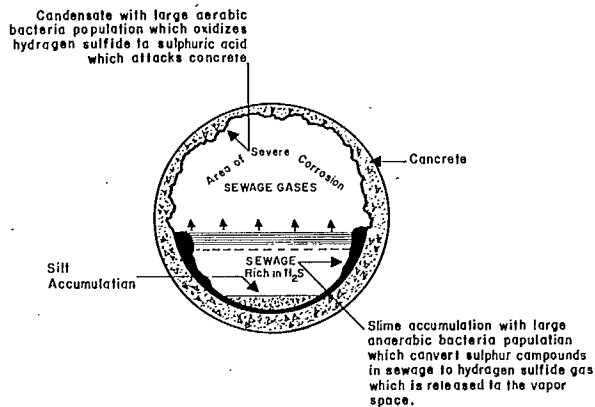


Fig. 25 - Cross section of concrete sewer pipe under typical corrosive conditions; from reference 58

in water which penetrates concrete pores causing it to swell and disintegrate. Investigations by South West Research Institute, by Hawkins and by Yuan and Chen have shown that SIC pipes are from 2 to 10 times more resistant to sulphuric acid attack than uninfiltreated control pipes (59,60,63). Malhotra et al. have also shown that 75 x 150-mm cylinder SIC test specimens were about 4 times as resistant as control cylinders in 15% H_2SO_4 solution (45). The increased durability of SIC pipes is due to the extremely low permeability of the infiltrated product. Hawkins has studied the cost of infiltrating large diameter concrete pipes of 900 mm with sulphur to resist attack by H_2SO_4 (60). His investigations show that the life-span of 900-mm diam SIC pipes could be doubled at a cost of only 19% higher than for uninfiltreated concrete pipes. This increase in cost compares favourably with coatings or linings which have been variously estimated at 35 to 80% of the pipe cost. Similar cost figures have been suggested by S.W.R.I. (59). Over 300 m of SIC pipe has been placed in four Texas cities on an experimental basis as part of an Environmental Protection Agency/Texas Waters Quality Board Study (61).

Figure 26 shows a suggested layout for the sulphur in infiltration of concrete pipes (60).

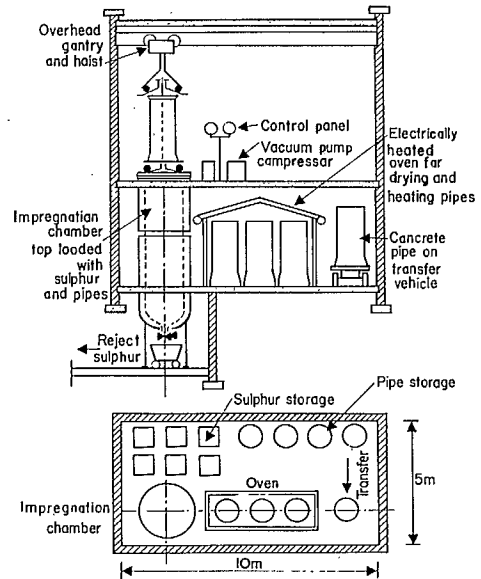


Fig. 26 - Layout for the infiltration of concrete pipes; from reference 60

STABILITY OF AUTOCLAVED TEST SPECIMENS

Studies associated with the sulphur infiltration of autoclaved specimens have indicated that specimens should be autoclaved without the use of silica flour or fly ash (51). The incorporation of silica or fly ash makes the autoclaved sulphur-infiltrated specimens susceptible to undesirable expansion when exposed to water.

STABILITY AT ELEVATED TEMPERATURES

Brown and Baluch have published data for short-term compressive strength tests at elevated temperatures (56). Test specimens consisting of 50-mm cubes, made with aggregate:cement ratios of 3:1 and 5:1 were heated for one hour prior to being tested at 50, 70 and 100°C. From the test results, the authors concluded that strength was not significantly affected when SIC was exposed to short-term temperatures up to 100°C. An examination of recorded plots of load against deformation for 100°C showed that specimens had exhibited a certain amount of ductile behaviour before failure, something noticeably absent at low temperatures.

RESISTANCE TO ABRASION

Data by Yuan and Chen show that SIC bricks had increased abrasion resistance compared with control specimens (63). The magnitude of increase was a function of the sulphur loading of the test specimens.

THERMAL CONDUCTIVITY

Mirkovich has published limited data on thermal conductivity of fully infiltrated concrete test specimens using a modified, guarded hot plate apparatus (62). The measurements were carried out on discs, 25 mm in thickness and 100 mm in diameter, cut from 100 x 200-mm cylinders. The concrete had a water to cement ratio of 0.70 with crushed limestone and natural sand as coarse and fine aggregates. The results indicated that thermal conductivity of the infiltrated specimens was higher than that of normal, dry concrete and increased up to a point with increasing quantity of infiltrated sulphur (Fig. 27). The increased values of thermal conductivity are due to the sulphur filling the pores in concrete and thus providing an uninterrupted path for heat flow.

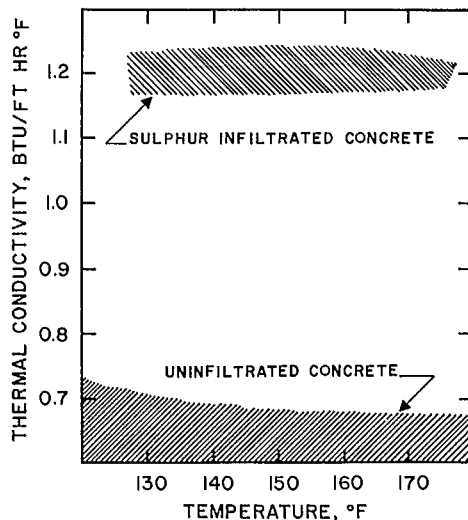


Fig. 27 - Thermal conductivity of sulphur-infiltrated concrete specimens; from reference 62

BEHAVIOUR OF REINFORCED CONCRETE BEAMS

Supariwayok and Fowler have studied the behaviour of reinforced sulphur-infiltrated concrete beams for flexure components (57). Their experimental program consisted of testing ten inverted-T beams each with a 1375-mm simple span. The flange and the rib widths were 100 and 70 mm respectively. The variables considered were percentage of tensile reinforcement, compressive reinforcement and depth of sulphur infiltration. The steel ratio varied from 0.03 to 0.13. All beams were reinforced against diagonal tension failure by vertical No. 2 smooth stirrups. From their investigation the authors concluded:

- i The strength of SIC beams was found to be higher than conventional beams with the same amount of reinforcement. The load-deflection responses for infiltrated beams were more linear and were accompanied by greater stiffness than conventional concrete beams.
- ii The beams with sulphur in the compression zone only behaved approximately the same as fully infiltrated beams.
- iii The stress-strain relationship obtained from the regression of experimental data were approximately linear.

STEEL FIBRES

Shah, Naaman and Smith have shown that the incorporation of steel fibres can significantly increase the ductility of sand/cement mortars infiltrated with sulphur (64). Typical load deflection curves for fibre-reinforced sulphur-impregnated and plain mortar specimens are plotted in Fig. 28. The curves for unreinforced sulphur-impregnated and plain mortar specimens are also shown for comparison. It can be seen from Fig. 28 that the addition of fibres increased both the ultimate flexural strength and the peak deflection for both sulphur-infiltrated and plain mortar specimens. For sulphur infiltrated specimens, the addition of fibres increased the peak deflection by as much as six times.

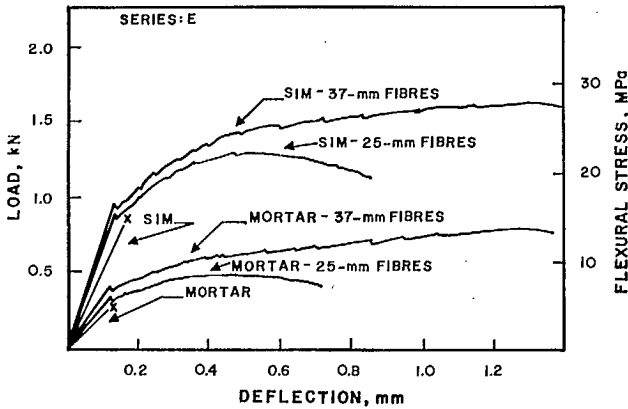


Fig. 28 - Typical load-deflection curves for plain and fibre-reinforced sulphur infiltrated mortars; from reference 64

APPLICATIONS

The applications for sulphur-infiltrated concrete are in the precast industry. This new type of concrete is ideally suited for precast units such as patio slabs, sidewalks, curbs, sewer pipes, and precast units for tunnel linings. Because of its excellent durability characteristics which are due to its impermeability, sulphur-infiltrated concrete should find considerable use in industrial applications where high corrosion resistance concretes are required. An idealized line diagram for the production of sulphur-infiltrated precast concrete units in a plant is shown in Fig. 29.

Sulphur-infiltrated concrete offers job-site applications such as in the repair of deteriorated structures and bridge decks. However, it is doubtful if cast-in-place concrete can be economically sulphur-infiltrated. Furthermore, because of the low melting point of sulphur, applications of sulphur-infiltrated concretes would have to be limited to structures in which concrete is not expected to reach temperatures exceeding 100°C.

Preliminary cost estimates indicate that the sulphur-infiltrated precast concrete units should be competitive with, if not cheaper than, conventional concrete. The added cost of the sulphur and equipment for infiltration should offset considerable savings in cement.

CONCLUDING REMARKS

The sulphur-infiltrated concrete, like polymer impregnated concrete, is a specialized product. The process technology is simple and commercially viable. The elements can be easily produced in precast concrete plants and obvious applications seem to be small precast units for curbs, patio slabs, concrete pipes and for use in rural areas.

In applications where good chemical resistance, high mechanical properties and high impermeability are of paramount importance, this form of concrete can play a useful role.

It is not intended to be a substitute for conventional concrete but may be a valuable alternative where conventional concrete has a limited life expectancy which can thereby be increased by a factor of 2 or 3.

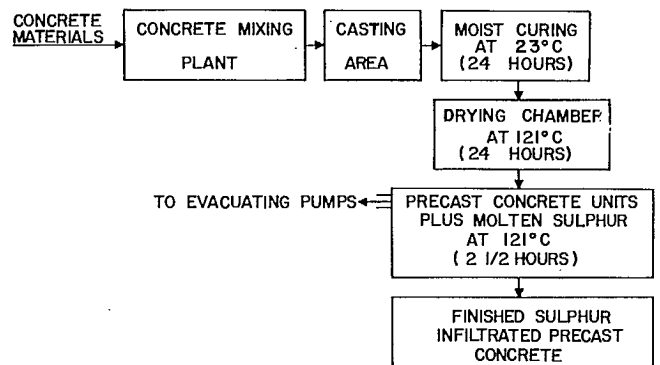


Fig. 29 - Idealized line diagram for the production of sulphur-infiltrated precast units in a plant; from reference 44

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