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# Properties and Application of Polymer Modified and Sulphur Repair Mortars in Aggressive Environments

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## ABSTRACT

One of the most aggressive environments for reinforced concrete is a marine environment such as that in the Persian Gulf region. The high cost involved in repairing of deteriorated concrete structures in this region makes it essential that the repair materials are compatible with parent concrete. This paper presents the engineering and compatibility related properties of ordinary and polymer modified repair concretes containing silica fume and styrene butadiene rubber latex under simulated Gulf condition. An optimum formulated modified sulphur concrete has also been tested to demonstrate the feasibility of its utilization. Mechanical properties and dimensional stability of repair concretes were assessed. The results show that the silica fume and the polymer modified concretes are appropriate materials for repair in the Persian Gulf region. The study of properties of sulphur concrete as a repair material in simulated condition of Persian Gulf assured its appropriate characteristic to be used in this region.

## INTRODUCTION

A marine environment is any place where concrete becomes wet with seawater. This could happen to concrete submerged under water, in a tidal zone, in a splash zone, or at any place inland where wind could carry the salt water spray [Rasheeduzzafar and Bader, 1986]. The marine environment in the Persian Gulf area is characterized by high concentration of sulphate and chloride ions coupled with elevated ambient temperatures with wide daily and seasonal fluctuations of heat and humidity, which accelerates the deterioration of concrete and corrosion of reinforcing steel [Pigeon and Saucier, 1994].

Deteriorated concrete is usually repaired using polymer modified concrete. The method of application of repair materials depends on the extent of the deterioration and size of the concrete repair areas [El-Hawary et al., 2000]. Epoxy resins may be also introduced for repair and injection of cracks. Repaired structures are usually subjected to the same environmental conditions that initiated the deterioration, which necessitates the study of the performance of repair materials.

Good bonding between repair materials and in situ concrete substrate is of vital importance in the concrete repairs [El-Hawary et al., 2000, Geymayr, 1980, Jadkowski et al, 1985]. It was reported that many applications of concrete repairs were not reliable though the necessary measures were taken to obtain as perfect adherence as possible (such as roughing the in situ concrete, application of a bond coat, etc.)

Sulphur concretes can be also considered as an alternative to Portland cement concrete for structural purposes and repair of deteriorated concrete structures. Sulphur concretes are materials in which coarse and fine aggregate are bound together by elemental sulphur; the concretes are cast in the molten state and bonding occurs on cooling when the sulphur crystallizes. The physical properties of elemental sulphur affect the properties of sulphur concretes which in some respects are superior to those of Portland cement concrete. These properties include rapid strength development, high strength, low permeability, and superior resistance to strong acids and salts. The high strength and corrosion resistance of sulphur concrete make it a very attractive material for pipes and floors in hostile environments, such as marine environment, chemical and battery plants, sugar refineries etc. In structural applications its high strength has the potential to reduce the design thickness of walls, slabs and beams. As it melts at a relatively low temperature (~119ºC) sulphur is not suitable as a construction material where there is a risk of fire, but it could be an excellent replacement for Portland cement concrete in marine structures and other applications which require resistance to saline solutions and impermeability [Czarnecki , 1989].

Sulphur concrete is a very brittle material however and in certain applications this property may cause problems. Two approaches have been used to modify the properties of sulphur concrete: the use of admixtures which modify the binder, and the addition of admixtures which alter the sulphur-to-aggregate bond. Admixtures, such as olefins and thiocols, tend to stabilize the sulphur as long chain molecules and inhibit the formation of orthorhombic sulphur, hence the sulphur concrete is more ductile [Lee & Klaiber 1981]. The effect of this type of admixture on strength and ductility is time-dependent, however, and the ductility disappears after a relatively short period. This is due to the inversion of the mix of polysulphides, non-crystalline sulphur and monoclinic sulphur to the brittle orthorhombic form [Currel, Williams, Mooney & Nash 1975]. The aging of the system in terms of changes of mechanical properties with time follows a similar pattern regardless of the type of modifier used [Blight, Currel, Merral, Scott & Stillo 1978].

The second group of admixtures capable of improving the ductility of sulphur concretes does not modify the sulphur binder. These admixtures are believed to alter the bond characteristic between the sulphur matrix and the aggregate and between the sulphur crystals within the matrix [Gillott, Jordaan, Loov & Shrive 1980]. Petroleum additives and some polyols improve the strain capacity of sulphur concrete and the properties of such concretes remain stable over extended periods of time [Jordaan, Gillott, Loov and Shrive 1978].

This paper presents the results of experiments on mechanical and repair characteristics of Portland cement-based repair concrete and sulphur concrete made with and without polymer modifiers. To investigate the performance of the sulphur concrete repair system, specimens were placed in a simulated condition of Persian Gulf in a way that they were exposed to wetting and drying cycles in seawater. The main variables in this study are the type of cementitious material and type of primer. The compressive, flexural and tensile strengths of repair concretes together with volume stability and bon strength mixes were investigated for each set of variables.

## EXPERIMENTAL PROGRAMME

The three repair concretes selected and tested in this study are summarized in Table 1. These repair concretes were cured in simulated hot and humid environmental conditions, similar to the Persian Gulf environment, using the mean ambient temperature of this region, 38 $^{o}$C and relative humidity of 50 ± 1 %.

### Table 1. Concrete Mix Designation

| Mix Code | Description |
|---|---|
| **OPC** | Ordinary Portland Cement concrete: (control mix) |
| **SF** | Silica Fume concrete: (consisting of 7% silica fume cement replacement |
| **PMC** | Polymer Modified Silica Fume Concrete: (consisting of 7% silica fume cement replacement and 30% styrene butadiene rubber latex (SBR) ) |
| **SC** | Sulphur Concrete |

### Materials

Chemical analysis of the ASTM type II Portland cement and silica fume is shown in Table 2.

### Table 2. Chemical Analysis of Portland Cement and Silica Fume Used

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | LOI* | Free lime | $SO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Cement | 20.96 | 4.2 | 4.6 | 61.88 | 3.4 | 0.5 | 0.4 | 1.74 | 0.84 | 1.79 |
| Silica Fume | 91.1 | 1.55 | 2.0 | 2.24 | 0.6 | - | - | 2.10 | - | 0.45 |

* Loss On Ignition

Elemental sulphur as a granular shape with purity of 99.9% was obtained from petroleum and natural gas, Bandar Imam refinery, Iran. Polymeric material, dicyclopentadiene (DCPD) with specific gravity of 1.90 g/cm$^3$ and Kinematics viscosity at 135 °C of 100 cSt, was used to enhance the chemical properties of sulphur. From elemental analysis of the polymer, it contains 90.3% carbon, 9.4% hydrogen, and 0.2% nitrogen.

The aggregates used in the mixtures were natural river-bed coarse and fine aggregates. The maximum size of aggregates was 16 mm. The locally obtained stone dust was also used as a filler to modify the grading of aggregates. The physical and chemical characteristics of the aggregates are shown in Table 3. The latex used was a styrene-butadiene co-polymer. The physical properties of the polymer are shown in Table 4.

**Table 3. Physical and Chemical Characteristics of Aggregates**

| Aggregates | Density (SSD)* ($gr/cm^3$) | Water Absorption (%) | Passing Sieve # 200 (%) | Chloride (%) | Sulphate (%) | A.A.R. Expansion** (%) |
|---|---|---|---|---|---|---|
| Coarse Agg. | 2.53 | 2.64 | 2.6 | 0.001 | 0.001 | 0.09 |
| Fine Agg. | 2.56 | 2.71 | 2.46 | 0.001 | 0.002 | 0.09 |
| Stone Dust | 2.57 | 4.0 | 0.7 | 0.002 | - | - |

* Saturated Surface Dry ** using ASTM Prism method

**Table 4. Properties of Styrene-Butadiene Rubber Latex**

| Typical properties | |
|---|---|
| Physical state | Milky white liquid |
| Total solids (by weight of polymer) | 40% |
| Specific gravity | 1.01 |
| pH | 10.5 |
| Mean particle size | 0.17 microns |

Two types of superplasticisers, melamine sulphonated naphthalene based (Melcret TB 101F) and carboxilate based (Glenium), were used enhance the flow properties of concrete mixtures.

**Mix Design**

The mix proportions of repair the concretes used in the investigation are presented in Table 5. These mixes were made using very dense packing of the aggregates and binder particles and also with the lowest possible amount of cement.

**Table 5. Mix Proportions of Repair Concretes ($kg/m^3$)**

| Mix | Cem. | SF | Sulphur | Coarse Agg. | Fine Agg. | Stone Dust | Water | Superplast. Melcret (%)* | Superplast. Glenium (%)* | SBR* (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| OPC | 350 | - | - | 1107 | 728 | - | 140 | 0.8 | - | - |
| SF | 325.5 | 24.5 | - | 1107 | 728 | - | 140 | - | 0.54 | - |
| PMC | 325.5 | 24.5 | - | 1107 | 728 | - | 140 | - | 0.12 | 30 |
| SC | - | 47 | 758 | - | 1375 | 190 | - | - | - | - |

* % weight of cement

The basis of mix design of the repair concretes in this investigation was to obtain a concrete with maximum density, minimum binder content and constant workability. The optimum mix proportions were identified using a number of trial mixes. Also in order to obtain a maximum packing density for the binder and the aggregates, ideal particle size distribution curves were used in which fine aggregates, filler and binder particles fill the gaps between coarse aggregates to maximise the density of the concrete. Concrete specimens were cast in 100mm cube and 100 by 100 by 500mm prism moulds. Specimens were demoulded after 24 hours and were fog cured for 7 days, then transferred to the simulated hot and humid Gulf condition.

Sulphur Concrete (SC) consisting of elemental sulphur, silica fume, filler and sand was prepared according to the procedure described by Zamani [1997]. Sand, silica fume and filler were dried in oven at 150 °C for a period of 2 h. The specified amount of sulphur mixed with DCPD was melted in a heated mixing bowl with controlling temperature in the range of 135–141 °C. Sand, silica and filler were then transferred to the heated mixing bowl, and properly mixed with the molten sulphur for about 20 min, to insure a consistent mixture of sulphur and fine particles. Suphur concretes were then cast in 100 mm cube and 100mm by 100 by 500mm prism moulds. In order to reduce the thermal tensions due to temperature difference between mould and molten sulphur concrete mixture, steel moulds were preheated to 120°C using a gas torch. Specimens were compacted in two layers using a vibrator for 5 seconds and surface of each specimen was then trowel finished. After 2 hours specimens were de-moulded and then tested for compressive, tensile and flexural strength after 24 hours.

## TESTING PROGRAM

### Fresh Concrete

The fresh concrete properties that were assessed included concrete density, slump, and percentage of entrained air and also temperature of fresh concrete. The test results for the fresh concretes are summarized in Table 6.

### Table 6. Properties of Fresh Concrete

| Mix Id. | w/c Ratio | Density (kg/m$^3$) | Slump (cm) | Air Entrained in Fresh Concrete (%) | Temperature of Fresh Concrete (° C) |
|---|---|---|---|---|---|
| OPC | 0.4 | 2376 | 8 | 2.1 | 21 |
| SF | 0.4 | 2393 | 7.5 | 2.5 | 20 |
| PMC | 0.4 | 2244 | 9.5 | 6.5 | 17 |
| SC | - | 2370 | Flow | - | 135 |

### Hardened Concrete

The tests performed on the repair concretes in this study included the following:

- Compressive, flexural and tensile strengths, in accordance with BS 1881, Parts 116, 117 and 118 [BSI, 1983].

- Water penetration under pressure according to DIN 1048 standard [ZTV-SIB, 1990].
- Bonding strength: Substrate concrete specimens (50×50×10 $cm^3$ blocks) were made with the necessary surface roughness and repaired with each repair concrete, using three types of primers. The bonding strength was tested after 28 and 45 days by drilling core samples and using the pull-off test method, in accordance with the DIN 1048 Standard [ZTV-SIB, 1990].
- Drying shrinkage: the samples were made using the ASTM C490 Standard [ASTM, 1999] and after de-moulding, transferred to the simulated Persian Gulf condition.

## RESULTS AND DISCUSSION

### Mechanical Properties

The compressive strength of repair material is a basic measure of its ability to carry compressive loads and for most repair operations, compressive strengths of repair materials should approximate the substrate strength. Any substantial difference between repair material and substrate compressive strength may cause incompatible strains and excessive load transfer to the higher strength material. The flexural strength of a repair material is a measure of its resistance to bending, while the tensile strength is an indication of its ability to withstand tensile stress. Modulus of elasticity is a measure of stiffness and repair materials with lower modulus of elasticity reduce the potential for cracking and delamination in repairs [Mangat, 2000].

The compressive, flexural and tensile strengths and also modulus of elasticity test results of the repair concrete mixtures studied in this research are shown in Table 7.

### Table 7. Compressive, Flexural and Tensile Strength

| | OPC | SF | PMC | SC |
|---|---|---|---|---|
| Compressive strength $f_c$ (MPa) | | | | |
| 7 days | 42.7 | 45.1 | 34.2 | (24 hours) 32 |
| 28 days | 57.2 | 64.9 | 39.9 | - |
| 90 days | 50.1 | 66.9 | 40.5 | - |
| Flexural strength $f_f$ (MPa) | | | | |
| 7 days | 3.95 | 5.02 | 3.39 | (24 hours) 7.1 |
| 28 days | 5.64 | 6.03 | 3.86 | - |
| 90 days | 5.99 | 6.41 | - | - |
| Tensile strength $f_t$ (MPa) | | | | |
| 7 days | 3.09 | 4.34 | 2.55 | (24 hours) 3.8 |
| 28 days | 3.81 | 4.49 | 2.78 | - |
| 90 days | 4.02 | 4.34 | - | - |

The SF repair concrete had the highest (at 90 days, a 33.5% increase compared to control) and the PMC samples had the lowest compressive strengths, in comparison with the OPC samples.

From Table 7 it can be also seen that the compressive strength of sulphur concrete at 24 hours was comparable with strength of polymer modified concrete at 7 days.

The flexural and tensile strength results were similar to the compressive strength results, at 90 days the SF mix had a 7% increase in flexural strength and an 8% increase in tensile strength compared to the control mix. It can be seen that sulphur concrete achieved the highest flexural strength compared to all mixes. The tensile strength of sulphur concrete was also similar to tensile strength of normal concrete at 28 days.

**Water Permeability Under Pressure**

The permeability of the repair concrete is one of the most important durability parameters of concrete. This property can indicate the rate at which aggressive ions can penetrate the protective cover over reinforcement and cause corrosion. The test results for the repair concretes are shown in Table 8. As seen in this table, and according to the classification in the DIN standard, both SF, PMC and SC repair concretes are in the low permeability range and the SC mix has the lowest permeability. The polymer modified concrete also showed an approximately 75% decrease in permeability compared to control mix at 90 days.

**Table 8. Water Permeability Results for Repair Concrete Mixtures**

| Mix | Water penetration depth (mm) | |
|---|---|---|
| | 28 days | 90 days |
| OPC | 2.7 | 3.5 |
| SF | 1.5 | 2.2 |
| PMC | 1.9 | 2.0 |
| SC | 0.1 | 0.2 |

**Bond Strength**

The adequate bonding between repair and existing concrete substrate is essential for a successful repair. In this aspect, surface preparation of the concrete and the use of suitable bonding agents (primers) play an important role in the bond between the repair material and the parent concrete.

The primers used for ordinary, silica fume and polymer modified repair concretes were as follows:

- Cement paste: (mixture of cement and water, w/c: 0.45
- Cement and silica fume: (mixture of 93% cement and 7% silica fume, w/c: 0.45
- Polymer modified cement paste: (mixture cement and polymer, 1 kg SBR polymer per 2.5 kg cement

The repair concretes and three primers used are summarised in Table 9.

**Table 9. Repair Concretes and Primers Used in Testing Bonding Strength**

| Repair Concretes | Primer | Id. |
|---|---|---|
| OPC | cement paste | RCC |
| | cement and silica fume | RCM |
| SF | cement paste | RMM |
| | cement and polymer | RMS |
| PMC | cement and polymer | RSS |
| SC | - | SC |

For sulphur concrete the application of ordinary and polymer modified cement paste as a primer resulted in poor bond and therefore only drying the surface was considered as the best surface preparation. The bond strength results obtained from the pull-off test for all repair concretes are shown in Table 10.

**Table 10. Bond Strength of Repair Systems**

| Repair System | 28 days Bond strength (MPa) | 45 days Bond strength (MPa) |
|---|---|---|
| RCC | 2.0 | 2.5 |
| RCM | 2.25 | 2.75 |
| RMM | 3.0 | 3.75 |
| RMS | 3.25 | 3.5 |
| RSS | 2.25 | 3.5 |
| SC | 2 | 2 |

The bond strength test results indicate that silica fume replacement in repair concrete increases the strength considerably. These results also show that polymer modification of the repair concrete enhances bond strength of the repair. The RMM silica fume modified repair system had the highest bond strength and showed a 50% increase in strength at 45 days compared to the RCC control. The RSS repair system modified with SBR also had significant bonding strength improvement compared to the RCC control; the increase in bond strength at 45 days was 40%. The breaking point of core samples of the repair concretes was generally from inside the concrete substrate, which shows that the adhesion between the two materials was adequate (see Figure 1). The bonding strength of sulphur concrete was comparable with bonding of polymer modified repair system. It can be seen from the results that the bonding strength of sulphur concrete was not affected by time and therefore it can be an ideal repair material for locations where rapid striking of shutters is needed.

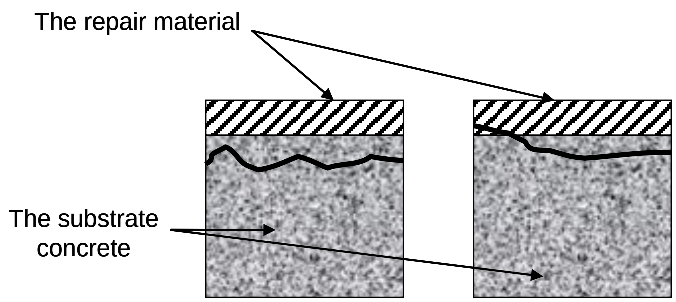


**Fig. 1. Failure Modes of Specimens in Bond Strength Test.**

**Drying Shrinkage**

Volume changes in repair materials, including drying shrinkage can lead to many failures in repair operations, therefore in order to achieve dimensional compatibility with the concrete substrate, the selection of repair material with minimal drying shrinkage is essential for compatible repairs [Decter and Keeley, 1997]. The drying shrinkage test results for the repair concretes considered in this investigation are presented in Fig. 2. These results indicate that the PMC repair concrete modified with SBR and silica fume had lower shrinkage values, specifically at the critical early ages when the repair concrete has not yet achieved adequate tensile strength. This greatly decreases the tendency for cracking in the repair material.

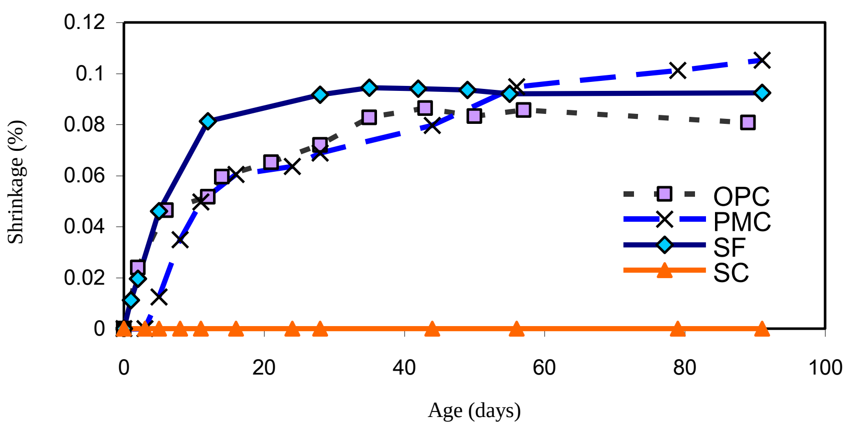


**Fig. 2. Drying Shrinkage Test Results**

## CONCLUSIONS

Based on the test results the following conclusions can be drawn:

- By adding silica fume and styrene butadiene latex to the repair concretes, the mechanical and compatibility properties of the repair material are greatly enhanced compared to control concrete.
- Latex modification in some cases may decrease the strength of concrete but generally, the flexural/compressive strength ratio increases in comparison to conventional concrete. For the modified mixture studied this ratio was 0.15, compared to 0.083 for the control concrete.
- The PMC mixture (modified with SBR and silica fume) showed significant lower drying shrinkage, especially at the early ages (first 5 days) than normal concrete. This reduction can result in stress reduction at the substrate/repair material interface, therefore improving bonding characteristics between the repair material and parent concrete.
- The PMC mixture also showed significantly improved reduction in water permeability. This may be due pore filling characteristics of silica fume and the SBR latex and reduced microcracks.
- The mechanical properties of sulphur concrete were comparable with polymer modified concrete. Sulphur concrete showed zero shrinkage and water permeability. This indicates that sulphur concrete can be a suitable alternative to Portland cement-based repair concretes for use in corrosive condition of Persian Gulf.

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