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Hydro-mechanical behavior of a newly developed sulfur polymer concrete

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ABSTRACT

This study has focused on evaluating the durability of the newly manufactured sulfur polymer concrete (SPC) from recycled waste materials such as sulfur (by-product from oil industry), fly ash (recovered from the gases of burning coal during the production of electricity) and desert sand from abundant sand dunes quarries. The first step in such manufacturing process is the sulfur modification using polymeric additives to control sulfur crystallization and to prevent macro-crystals growth. In a controlled temperature surroundings, modified sulfur was mixed with elemental sulfur, fly ash and desert sand to form the newly SPC. The durability of the SPC was evaluated in: de-ionized water, acidic solutions of 20, 40, 70, and 98 wt% H₂SO₄ solutions, and saline solutions of 0.5, 1, 2, 3, 4, and 5 wt% NaCl, at different temperatures for different periods of time. To compare the SPC results with known material, normal Portland cement concrete (PCC) mortars were also studied. The results indicated that the manufactured SPC material has high compressive strength, low hydraulic conductivity, and high resistance to permeation of water, and particularly resistant to corrosion in acid and salt environments.

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1. Introduction

In our day-to-day engineering practice, hydraulic cement based concrete materials are used for transporting and handling of troublesome fluids, such as acidic sewer wastes, industrial leach solutions, salt solutions, and acidic mine wastes. Hydraulic cement is a term used here since the water is the hydrating medium. Previous studies have indicated that concrete materials are subject to corrosion and disintegration, due to the reaction of the transporting fluids with the hydraulic cement binder material. Therefore, service life (i.e., durability) of concrete materials must be evaluated. Durability is an extremely complex subject and still going under extensive investigation by the scientific community.

Interest in sulfur cement, as an alternative to hydraulic cement, dates back to the early 20th century. Sulfur treated structural materials have been utilized for forming tanks or vents for holding leach or pickling solutions, for pipes or tiles for handling acidic sewer waters, flooring material for industrial plants and as patch material for concrete floors or walls. Its corrosion resistant properties made it a candidate for potential use as a construction material in the chemical industry.

Failures of sulfur cement products were encountered due to internal stresses set up by changes in the crystalline structure upon cooling. When unmodified sulfur and aggregate are hot-mixed, cast, and cooled to prepare sulfur concrete products, the sulfur binder, on cooling, from the liquid state, first crystallizes as

monoclinic sulfur (S_β) at $114\,^\circ C$ with a volume decrease of 7%. On further cooling to below 96 $^\circ C$, the S_β starts to transform to orthorhombic sulfur (S_α) , which is the stable form of sulfur at ambient temperatures [1–4]. This transformation is rapid, generally occurring in less than 24 h. Since S_α is more dense than S_β high stresses are induced in the material. Hence, the sulfur binder can highly stressed and fail prematurely due to formation of microcracks.

Attempts were made by various investigators [5–12] to improve sulfur cement concrete products by using chemical additives for sulfur modification. Hence the term modified sulfur concrete (MSC) was introduced in the literature. Several substances have been tried, in order to inhibit the transformation of sulfur from monoclinic to orthorhombic states. The most common ones are: (1) dicyclopentadiene, or a combination of dicyclopentadiene, cyclopentadiene and dipentene [5–8], and (2) olefinic polysulfide additives [9–12]. The practical use of the former in commercial application has been limited because the reaction between sulfur and dicyclopentadiene is exothermic and requires close control; also the dicyclopentadiene-modified sulfur cement is unstable when exposed to high temperature. While the later had shown promise in these applications, their costs were deemed prohibitive for use in preparing sulfur concrete for large scale construction uses

The preceding highlights the importance of the use of sulfur modifying agents in MSC manufacturing process. Therefore, this study is a continuation to previous studies, which reported by Mohamed and El Gamal [2] and Mohamed et al. [5], to produce an inexpensive MSC from waste recycled materials such as sulfur

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(by-product from oil industry), fly ash (by-product of burning coal), and desert sand from abundant sand dunes quarries. In the previous studies [2,5], olefin hydrocarbon polymeric material was used to modify sulfur, which upon solidification, remains in the monoclinic form and does not go through phase transformation to the orthorhombic form; hence the term sulfur polymer concrete was utilized (SPC). In this study, the durability of SPC is evaluated in terms of SPC ability to absorb water, and resist salt and acid penetration as a function of temperature and time.

2. Experimental

2.1. Materials

2.1.1. Sulfur

Elemental sulfur as a granular shape with purity of 99.9% was obtained from petroleum and natural gas, Al Ruwais refinery, United Arab Emirates (UAE).

Polymeric material, which is black oily, viscous, with specific gravity of 1.0289 g/C m³, Kinematics viscosity at 135 °C of 431 cSt, and softening point of 48.8 °C, naturally-occurring as by-product of decomposed organic materials, achieved from the distillation of crude oil, and was obtained from Geo-Chem Middle East, Dubai UAE. From elemental analysis of the polymer, it contains 79% carbon, 10% hydrogen, 3.3% sulfur, and 0.7% nitrogen.

2.1.2. Fly ash

Fly ash is the ashy by-product of burning coal, in this work fly ash Class C was used, which was imported from India under trade No. 97/591 by Unibton ready-mix company UAE. Chemical analysis of fly ash was performed using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) VISTA-MPX CCD simultaneous. The fly ash mainly consists of oxides of silica (59.31%), calcium (22.4%), aluminium (11.33%), iron (5.26%), magnesium (0.7%) potassium (0.5%), and sodium (0.31%). The cumulative grain size distribution is represented in Fig. 1.

2.1.3. Sand

The desert sand used in this production was obtained from a sandy dunes quarry in Al Ain area, UAE. The most common constituent of sand is silica (silicon dioxide), with specific gravity of 2.58 g/cm3, usually in the form of quartz, which because of its chemical inertness and considerable hardness, is quite resistant to weathering. Chemical analysis using ICP-AES indicate that the sand mainly consists of oxides of silica (74.4%), calcium (16.35%), magnesium (1.158%), iron (0.676%), aluminum (0.47%), and potassium (0.13%). The sand was screened to obtain grain sizes ranging

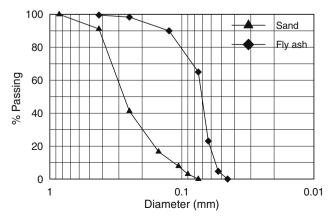


Fig. 1. Grain size distribution of the used fly ash and sand.

from 0.08 to 0.43 mm. The cumulative grain size distribution is represented in Fig. 1.

2.2. Preparation of modified sulfur cement

In an oil bath, 2.5 wt% of olefin hydrocarbon polymeric material and 97.5 wt% of molten sulfur were mechanically mixed at a controlled temperature of 140 °C for a period of about 45–60 min. The reaction progress was monitored by recording the temperature and viscosity variations during the mixing process. Then samples were allowed to cool at a controlled rate of 8–10 °C/min. The product is a sulfur containing polymer, which on cooling exhibits glass like properties. This product is commonly called modified sulfur cement (MSC). Distribution of the olefin hydrocarbon polymer in sulfur and free sulfur crystal type (orthorhombic or monoclinic) was evaluated using scanning electron microscopy, JSM-5600 Joel microscope, equipped with an energy dispersive X-ray detector (EDX). The specimen was sputter coated with 12 nm gold to render them conductive.

2.3. Preparation of sulfur polymer concrete

Sulfur polymer concrete (SPC) consisting of elemental sulfur, modified sulfur, fly ash, and sand was prepared according to the procedure described in [13]. The physical additives or aggregates (sand and fly ash) were dried in an oven from 170-200 °C for a period of 2 h. The specified amount of sulfur was melted in a heated mixing bowl that placed in oil bath with controlling temperature in the range of 132-141 °C. Fly ash was then transferred to the heated mixing bowl, and properly mixed with the molten sulfur for about 20 min, to insure complete reaction between sulfur and fly ash. Modified sulfur was then added and mixing continues for additional 5 min. Finally, desert sand was added, mixed and continued for about 20 min. In this process, we have used the proportions of 0.25 by wt% of modified sulfur cement, a ratio of 0.9 for sulfur to fly ash, and a ratio of one for sulfur to sand as recommended by [2,5]. At this stage of preparation, sulfur concrete mixture will be more viscous with a good workable consistency and can be easily bored into specified moulds for casting.

For specimen preparations, cubical steel moulds with dimensions of $50 \times 50 \times 50$ mm, and cylindrical with dimensions of 85×38 mm were used. The moulds were preheated to approximately $120\,^{\circ}\text{C}$ before addition of the mixture. During the boring of SPC into the specified moulds the mixture was compacted using vibrator for $10\,\text{s}$. The surface of each specimen was then finished and the moulds were placed in an oven with a controlled cooling rate of five degrees per minute. After $24\,\text{h}$, specimens were demoulded and then cured in the tested solutions such as; de-ionized water, sulfuric acid solutions of; 20, 40, 70, and 98 wt% and sodium chloride solutions of 0.5, 1, 2, 3, 4, and 5 Wt% intended for different period. With respect to the reference samples, normal Portland cement concrete (PCC) mortars were prepared from sand and Portland cement with water to cement ratio of $0.5\,\text{Wt/Wt}$.

Specimens were then qualified by evaluating the changes in weight after immersion, ability to resist water flow, microstructure arrangements, mineralogical composition, and the ability to desorb ionic species via leaching tests.

2.4. Durability testing techniques

2.4.1. Moisture absorption

For SPC and PCC moisture absorption was determined by using the method described in [14]. Concrete samples were weighed, immersed in de-ionized water, and saline solution of 3% NaCl concentration at 24 °C for 24 h, surface dried, and reweighed.

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