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ORIGINAL ARTICLE

Sulfur based hazardous waste solidification

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Abstract Existing uses for sulfur are relatively advanced and offer limited opportunities to consume significant new supplies. Currently, sulfur is in net surplus on a global basis, and with environmental regulations, greater sulfur recovery from petroleum and gas processing is mandated. The outlook is clear: there will be substantial and growing surpluses in global sulfur supply in the foreseeable future. Sulfur prices are likely to be under pressure, and producers could face substantial and growing disposal fees. Therefore, new markets must be found for sulfur to avoid disposal crises. One potential new market is the production of sulfur-solidified concrete. This is a thermoplastic composite of mineral aggregates bound together with chemically modified sulfur. The product is more durable than Portland cement. There may be monetizeable benefits in reducing greenhouse gas emissions that would enhance the attraction of sulfur solidified cement applications. The main objective of this study is to evaluate experimentally the potential use of sulfur as a solidifying agent for hazardous waste. To achieve this objective, the study reviewed the sulfur concrete literature, analyzed locally produced sulfur, evaluated a number of sulfur polymer modifiers and physical stabilizing agents, designed a set of experiments and evaluated the produced product for its hydro-mechanical-chemical properties. The results indicated that the manufactured sulfur polymer cement is an excellent candidate for: waste management practices such as solidification/stabilization of hazardous waste; barrier systems for landfilling of hazardous waste; and waste water treatment plants.

Keywords Fly ash · Sand · Molten sulfur · Modified sulfur · Orthorhombic · Monoclinic · Compressive strength · Temperature · Structure · Voids · Density · Mineral formation

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Introduction

In the last decades, the availability of sulfur has considerably grown in many countries. This is mainly due to the current environmental restrictions regarding petroleum and gas refining processes, which limit the maximum quantity of sulfur present in the combustibles. Extremely large quantities of sulfur are thus obtained as a by-product of these processes, for example, in the United Arab Emirates (UAE), which is ranked as the world's fourth largest producer, natural gas reserves are of roughly 212.0 trillion cubic feet. The Abu Dhabi National Oil Company (ADNOC) has placed increasing emphasis on the development and uses of its natural gas resources to meet the growing demand for power generation, water desalination, petrochemical plants and enhanced oil recovery. Concurrently, an environmental priority has been given to recovering and processing the associated gas.

The development of new applications for sulfur becomes fundamental. Sulfur concrete has a relatively simple composition and manufacture, and very interesting characteristics and properties. Sulfur concrete

construction materials are used in many specialized applications in industry and transportation. They are currently used primarily in areas where conventional materials like Portland cement concrete (PCC) failed, such as in acidic and saline chemical environments.

Sulfur concrete research

There is evidence of even earlier uses of sulfur, and both archeological sites and classic literature offer proofs of the knowledge and utilization of sulfur as a binder. Study on the use of surplus sulfur in the manufacture of construction materials was reported by Bacon and Davis (1921); they found that a mixture of 60% sand and 40% sulfur produced an acid-resistant material with excellent strength. This product was further studied by Duecker (1934), who found an increase in volume on thermal cycling with loss in flexural strength. He was also able to retard both the tendency for volume increase and the resulting loss of strength on thermal cycling by modifying the sulfur with an olefin polysulfide. The testing methods for sulfur materials outlined by McKinney (1940) have been adopted and are documented in ASTM specifications for chemical-resistant sulfur mortar. The acid-resistant properties of materials prepared from sulfur and coke were reported by Kobbe (1924). The work on sulfur aggregate systems was pioneered by Dale and Ludwig (1966, 1968).

This work was followed by Crow and Bates (1970) for the development of high strength sulfur basalt concrete. Construction materials such as sulfur concrete and sulfur asphalt continue to receive more attention since they are environmentally friendly and cost effective. Since the beginning of the 1970s, successful projects in which sulfur concrete has been used as a construction material have been carried out at different levels. The United States Department of the Interior's Bureau of Mines and The Sulfur Institute (Washington, DC) launched a cooperative program in 1971 to investigate and develop new uses of sulfur. At the same time, the Canada Center for Mineral and Energy Technology (CANMET) and the National Research Council (NRC) of Canada initiated a research program for the development of sulfur concrete (Malhotra 1973, 1974 ; Beaudoin and Sereda 1973). A number of investigators (Sullivan et al. 1975; Vroom 1977, 1981; Sullivan and McBee 1976; McBee and Sullivan 1979a, b, 1982a, b; Funke and McBee 1982; McBee et al. 1981a, b, 1983a, b, 1986; Sullivan 1986) and other published papers and reports investigated various aspects of sulfur and sulfur concrete. All of these activities have led to an increased awareness of the potential use of sulfur as a construction material.

While sulfur concrete materials could be prepared by hot mixing unmodified sulfur and aggregate, the durability of the resulting product was a problem. Unmodified sulfur concretes failed when exposed to repeated cycles of freezing and thawing, humid conditions or immersion in water. Studies were aimed at establishing the reasons for the failure of these sulfur concrete materials and determining the means of preventing the failures. 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°C with a volume decrease of 7%. On further cooling to below 96°C, the S_β begins to transform to orthorhombic sulfur (S_α), which is the stable form of sulfur at ambient temperatures (Lin et al. 1995). This transformation is rapid, generally occurring in less than 24 h. Since S_α form is denser than S_β, high stress is induced in the material by solid sulfur shrinkage. Thus, the sulfur binder can become highly stressed and fail prematurely.

It was further necessary to develop an economical means of modifying sulfur, so that the sulfur concrete product would have good durability, and reducing the expansion/contraction of sulfur concrete during thermal cycling. Since 1984, the American Concrete Institute (ACI), through its Committee 548, polymers in concrete, and subcommittee (ACI Committee 548D 1993), sulfur concrete, has been active in developing guidelines for the use of sulfur polymer concrete (SPC). There are two main methods for modifying sulfur; both of them try to control sulfur crystallization chemically or physically. The first one tries to combine chemical substances to inhibit the transformation of sulfur to the orthorhombic structure; as a result of the chemical reaction with the substance, sulfur remains in the monoclinic state after cooling. Several substances have been tried for this methodology, the most common are dicyclopentadiene or a combination of dicyclopentadiene (DCPD), cyclopentadiene and dipentene (Currell 1976; Bordoloi and Pierce 1978; Beaudoin and Feldmant 1984; Lin et al. 1995). Modification of sulfur by reaction with DCPD has been investigated by many researchers, but its practical use in commercial applications has been limited because the reaction between sulfur and DCPD is exothermic, requiring close control, and unstable when exposed to high temperatures (greater than 140°C), especially when mixing with hot aggregates. It may react further to form an unstable sulfur product. McBee and Sullivan (1982a, b) solved this problem by developing a process for preparing modified sulfur cement that is stable and not temperature sensitive in the mixing temperature range for the production of sulfur concrete. This process utilizes the control reaction of cyclopentadiene.

The second method utilizes modified sulfur concrete by combining sulfur with olefin hydrocarbon polymers (such as RP220 or RP020 by Exxon Chemical, or Escopol) and a physical stabilizer such as fly ash or other fine substances (Vroom 1981, 1992; Nnabuife 1987). In both methods, the issue involves controlling sulfur crystallization, either chemically or physically. Depending on the ultimate use of the produced sulfur concrete, one chooses the method of treatment.

Methods of treating sulfur for use in sulfur concretes have been reported by many researchers. They include: Leutner and Diehl (1977) by using DCPD; Gillott et al. (1980) by using crude oil and glycol; Vroom (1981) by using olefinic hydrocarbon polymer such as Escopol to prepare modified sulfur cement; Woo (1983) by using phosphoric acid to improve freeze-thaw resistance; Nimer and Campbell (1983) by using organosilane to improve water stability; Beaudoin and Feldmant (1984) by using DCPD to improve porous durability of the porous system; and Pickard (1985) by using modified sulfur cement to control expansion/contraction during thermal cycles.

The main advantage of sulfur concrete is its use as a highly durable replacement for construction materials, especially PCC. Sulfur concrete has properties, which for certain applications are superior to PCC as indicated in Table 1. The other advantages of sulfur concrete are its fast setting time and rapid gain of high strength. Since it achieves most of its mechanical strength in less than 1 day, forms can be removed and the sulfur concrete placed in service without a long curing period.

Because of the abundance of physical stabilizers (fly ash, sand dunes and cement kiln dust) in the UAE, this study has utilized sulfur, polymer modifier, fly ash and sand dunes for producing SPC.

Table 1 Comparison between the composition properties of SPC and PCC (McBee and Weber 1990)

	Sulfur concrete[a]	Portland cement concrete[b]
Strength (psi)		
Compressive	7,000–10,0000	3,500–5,000
Splitting tensile	1,000–1,500	500
Flexural	1,350–2,000	535
Coefficient of thermal expansion (μ in./in.)/°C	14.0–14.7	12
Moisture absorption,	0.0–0.10	0.30–3.0
Air void content (%)	3.0–6.0	4.0
Elastic modulus 10^6psi	4.0	4.0
Specific gravity	2.4–2.5	2.5
Linear shrinkage (%)	0.08–0.12	0.06–0.10
Impact strength, ft-1b		
Compressive	100–119	81
Flexural	0.3–0.5	0.2
Mix proportions (wt%)		
Sulfur polymer cement	14–18	0
Water	0	6–9
Mineral filler	6–9	0
Portland cement	0	12–18
Sand	38–42	30
Coarse aggregate	33–37	45

[a] Properties obtained at the age of 1 day

[b] Properties obtained at the age of 28 days

Materials and methods

Details of the materials used, specimen grain size and procedures for the preparation of modified sulfur, elemental sulfur concrete (ESC) and SPC, are described below.

All raw materials used for this study were obtained from the UAE. The granular sulfur (99.9% purity) was obtained from the Al Ruwais refinery. Bitumen with a softening point of 48.8°C, specific gravity of 1.0289 Mg/m^3 at 20°C and kinematics viscosity of 431 cSt at 135°C, with a chemical analysis of C:79, H:10, S:3.3 and N:0.7%, was used. Two types of aggregates were used throughout this study. Desert sand was obtained from a sandy dune quarry in the Al Ain area. The most common constituent of sand dunes is silica (silicon dioxide), usually in the form of quartz, which because of its chemical inertness and considerable hardness is quite resistant to weathering. Fly ash, the ashen by-product of burning coal, (India-97/591) was used. It is a very fine, powdery material, predominantly silica, with particles in the form of tiny hollow spheres consisting of oxides of silica, aluminum and iron with lesser amounts of calcium, magnesium and potassium oxides. Since the value of SAF (SiO_2 + Al_2O_3 + Fe_2O_3) is over 50%, it is classified as C type fly ash according to the ASTM C618-01 2002.

Chemical analyses of the used aggregates were performed using Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES) VISTA-MPX CCD simultaneous and the results are listed in Table 2, while the grain size distributions are listed in Table 3. These aggregates should be clean, hard, tough and free of organic and other harmful substances.

Mix design and sample preparation

Preparation of modified sulfur

In an oil bath, 2.5 wt% hot bitumen, 97.5 wt% molten sulfur and an emulsifying agent were mixed and mechanically stirred at 140°C. The temperature was

Table 2 Chemical composition of used aggregates (Mohamed and El Gamal 2006; Mohamed et al. 2006)

Aggregate	Compound (%) (w/w)					
	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	SiO_2
Sand	0.47	16.35	0.676	0.13	1.158	74.4
Fly ash	32.4	0.46	4.34	0.027	0.66	60.9

Table 3 Grain sizes distribution of aggregates (Mohamed and El Gamal 2006; Mohamed et al. 2006)

Sand		Fly ash	
Sieve mesh size (mm)	Mass retained on the sieve (%)	Sieve mesh size (mm)	Mass retained on the sieve (%)
0.425	0.00	0.250	0.40
0.250	8.82	0.150	1.25
0.150	49.90	0.125	2.85
0.106	24.64	0.075	13.35
0.090	8.80	0.063	12.25
0.075	4.85	0.053	46.80
Bottom dish	3.00	0.045	18.35
		Bottom dish	4.75

maintained at about 135–140°C during the mixing process, which lasted about 45–60 min. The progress of the reaction was monitored by the degree of homogeneity of the mixture via careful observation of the temperature and viscosity of the reacting mixture. The development of the reaction was followed from changes in viscosity and homogeneity of the mixture. After mixing, the prepared mixture was allowed to cool at a rate of 8–10°C/min. The final product was a sulfur-containing polymer, which on cooling possessed glass-like properties. The composition and properties of the modified sulfur were evaluated in terms of chemical analysis, FT-IR spectra, X-ray diffraction, scanning electron microscopy and thermal processing including TGA and DSC.

Preparation of elemental sulfur concrete

Elemental sulfur concrete samples were prepared according to the procedure described in (ACI 548.2R-93). The aggregates (sand and fly ash) were heated in an oven to 170–200°C for 2 h. The specified amount of sulfur was melted in a heated mixing bowl, which was placed in an oil bath with the temperature controlled at 132–141°C. The heated aggregates were then transferred to the heated mixing bowl and properly mixed with the molten sulfur until a homogenous viscous mixture was obtained. A cubic steel mold of dimensions $50 \times 50 \times 50$ mm was used. The molds were preheated to approximately 120°C before adding the viscous sulfur concrete, and as the sulfur concrete was added, the material was compacted by tamping with a heated rod and simultaneously vibrated for 10 s on a vibrating table. The surface of each specimen was finished and left in the oven and gradually cooled at a rate of 2°/min. The specimens were de-molded at an age of 24 h after placement in steel molds. Optimization of sulfur ratio in the mixture was studied; if the optimum amount of sulfur were added, the sulfur concrete would be more viscous with a good workable consistency.

Preparation of sulfur polymer concrete

Sulfur polymer concrete samples were prepared in a manner analogous to that of ESC, with the exception that the modified sulfur was not added directly to the molten sulfur, but after the reaction between sulfur and fly ash. Temperature control is very important because SPC melts at 119°C; above 149°C, the viscosity of SPC rapidly increases to an unworkable consistency. Also, the percentage of modified sulfur plays an important role in the workability and mechanical strength of SPC. All the mix designs were analyzed by following up the compressive strength, SEM for homogeneity and porosity studies, and thermal studies including TGA and DSC.

Characterizations of modified sulfur and SPC

The determination of C, H and S was carried out with the Finnigan Flash EA1112 CHN/S elemental analyzer. The reaction between sulfur and bitumen was studied using FTIR spectroscopy. The IR spectrum was recorded by using Nicolet FTIR Magno-IR (Model 560) system. The IR spectra of bitumen were taken after successive treatments with toluene, and the IR spectra of bitumen modified sulfur were taken of the powder mixed with a small amount of KBr powder to make the IR pellet.

X-ray powder diffraction was performed using a Philips PW/1840, with Ni filter, Cu-Kα radiation (λ = 1.542 Å) at 40 KV, 30 mA and scanning speed 0.02°/s. The diffraction peaks between $2\theta = 2°$ and $2\theta = 80°$ were recorded. Measurements were made for samples to examine the interlayer activity in the pure sulfur and sulfur cement.

The internal microstructure of sulfur, modified sulfur, ESC and SPC were examined using SEM; JSM-5600 Joel microscope equipped with an energy Dispersive X-ray detector (EDX) was used for chemical analysis. The microstructure characterization performed for ESC and SPC were carried on the samples fragments, obtained from the mechanical test. The

samples were fastened on a sample rock with carbon glue and coated with a 12 nm gold layer for improved SEM imaging.

Thermo Gravimetric Analyzer Perkin Elmer TGA7 was used to measure weight changes in sample materials as a function of the temperature. A furnace heats the sample, while a sensitive balance monitors loss or gain of sample weight due to chemical changes or decomposition. TGA coupled with mass spectrometry and FT-Infrared spectroscopy provides elemental analysis of decomposition products. Weight, temperature and furnace calibrations were carried out for the usable range of the TGA (100–600°C) at a scan rate of 20°C/min.

Differential scanning calorimeter (Perkin Elmer DSC7) was used for measurements of heat capacity, through phase transitions on heating. 10 mg of the tested sample was heated up to 150°C, with a heating rate of 5°C/min. The sample was allowed to self-cool to room temperature for 24 h and then the sample was reheated up to 150°C. The compressive strength of the samples was determined by the Wykeham Farrance testing machine with a maximum load of (200 KN).

Results and discussion

Modified sulfur

The addition of an amount of 2.5% bitumen on to sulfur initiates chemical reactions of the type that depends on the bitumen content, heating temperature and the time of the reaction. For example, some competing reaction can occur, including those with bitumen incorporation into sulfur molecules or dehydrogenation with the liberation of hydrogen sulfide. It should be pointed that at $T < 95$°C, sulfur exists as a cyclooctasulfane crown with an S–S bond length of 0.206 nm and S–S–S bond angle of 108°; and at $T < 119$°C, sulfur crystallizes. At 119°C (melting point of sulfur), liquid sulfur is thoroughly dispersed in bitumen forming an emulsion (role of emulsifying agent), and cyclooctasulfane turns partly into polymeric zigzag chains (bond length 0.204 nm) (Voronkov et al. 1979). The crystallization features are affected by such factors as the chemical reaction of sulfur with bitumen components and its dissolution or dispersion. On heating to a temperature $T < 140$°C, elementary sulfur forms polysulfide, which initiates the formation of a network. Such structures differ considerably, in chemical and thermal stability, from unmodified sulfur. At 119–159°C, molten sulfur exists essentially as cyclooctasulfane (λ-S). Above 159°C, the eight-member ring rapidly breaks down into biradicals (Voronkov et al. 1979). In turn, the biradicals recombine to form polymeric chains with a maximal length of up to 10^6 sulfur atoms:

$$S_8 \quad \Leftrightarrow \quad S^0 - S_6 - S^0$$

$$S^0 - S_6 - S^0 \quad + \quad S_8 \quad \Leftrightarrow \quad S^0 - S_6 - S^0 - S_8 \quad \text{etc.}$$

However, above 140°C, dehydrogenation of saturated bitumen components can occur; also linear polysulfide can transform into stable cyclic thiophene structures (Syroezhko et al. 2003). It is noted that modified sulfur should be produced within its recommended mixing temperature range of 135–141°C.

Characterization of modified sulfur was performed by different tools: a chemical analyzer was used to determine the chemical composition of modified sulfur, S: 97.4 ± 0.48, C: 1.981 ± 0.074 and H: 0.1 ± 0.067, which indicates that modified sulfur contains organic compounds (related to the presence of C and H). However, the reaction between bitumen and sulfur should be determined by other means. To investigate the nature of the chemical interaction between bitumen and sulfur, the completion of bitumen sulfur reaction was strongly supported by IR measurement of the characteristic double bonds in bitumen, which is the main modifying bitumen constituent. Figure 1 shows the band at 2,975 cm^{-1}, which is consistent with CH stretching. Since C–H is associated with C=C double bonds, the disappearance of C–H bonds in the modified sulfur spectra suggests the consumption of aliphatic C=C bonds, which generally leads to the polymerization of sulfur with bitumen. Negative peak at 2,400 cm^{-1} indicates the removal of NC=O group, showing that they are sites of chemical reaction for polysulfide formation. An increase in the relative intensity in the spectra at 584 cm^{-1}, corresponds to disulfide S–S bond between adjacent thiol groups.

The obtained XRD diagrams for pure sulfur and sulfur modified with a small amount of bitumen (2.5 wt%) are shown in Fig. 2. XRD analysis confirms that the modification of sulfur makes sulfur crystallize with a structure different from the unmodified one. Modified sulfur gives a sharp signal shifted to the lower 2-theta, which in turn indicates that the newly formed structure is fine in its grain size.

Scanning electron microscope reveals how bitumen controls the crystallization of sulfur. Pure sulfur crystallizes and forms dense, large alpha sulfur crystals (S_α) with orthorhombic sulfur morphology as shown in Fig. 3a. With the addition of bitumen, the crystal growth is limited and controlled by the bitumen in such a way

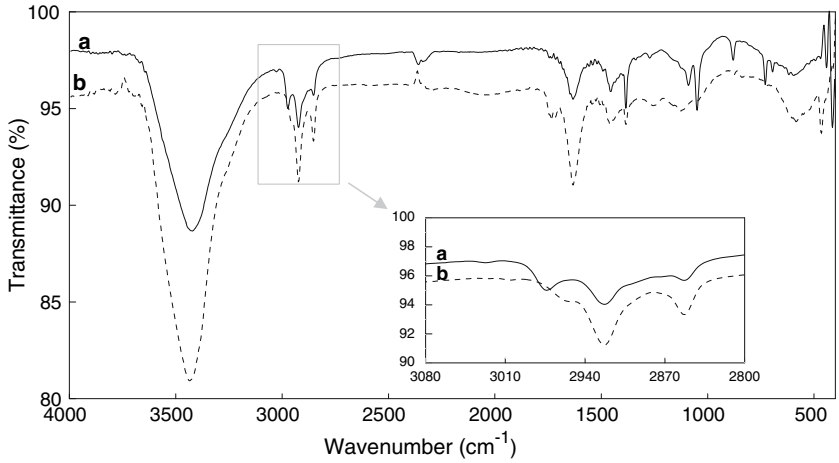


Fig. 1 FTIR spectrum showing the spectra of bitumen (**a**) and sulfur modified with bitumen 2.5 wt% (**b**), viewing the disappearance of CH characteristic double bond of the bitumen after the complete reaction with sulfur

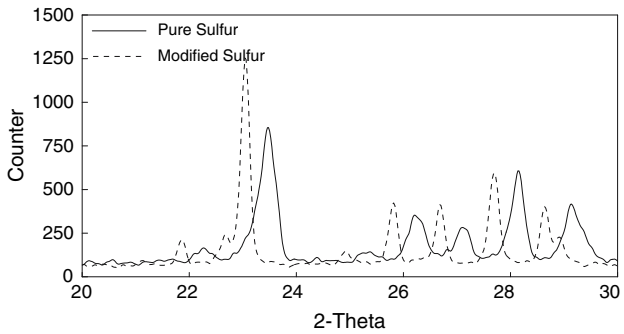


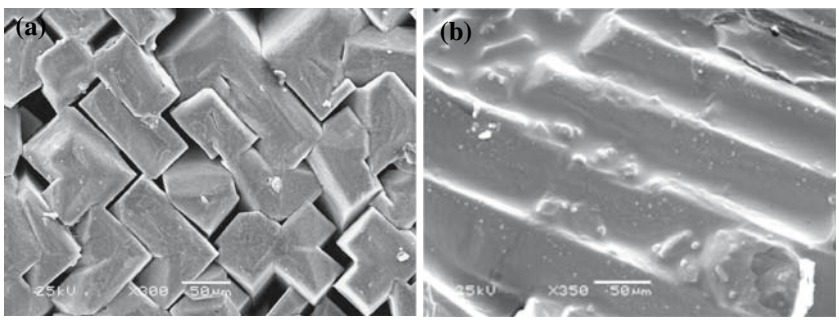
Fig. 2 X-ray diffraction patterns for pure sulfur and modified sulfur

that all the crystals are plate-like, of micron dimension, monoclinic sulfur crystals of beta form ($S_ß$) as shown in Fig. 3b. The microstructure suggested by the scanning electron microscope confirmed the presence of bitumen uniformly dispersed in sulfur, as coverage of sulfur particles and between plates and plate joints. The smallest microstructure, plate like, helps to resist cracking and to tolerate any thermal expansion.

The scanning electron microscope was also used to optimize the bitumen percentage, increasing the bitumen content from 2.5, 3 and 3.5% by weight, causing an additional significant increase in the average dimension of the micron-size microstructure of the interlocked plate-like beta sulfur crystals, as indicated in Table 4.

Thermal analysis techniques such as TGA and DSC have been used effectively for determining the temperature history of sulfur and sulfur cement (Syroezhko et al. 2003). The TGA measures the weight loss of a material from a simple process such as drying, or from more complex chemical reactions that liberate gases and cause structural decomposition. Figure 4a provides comparison of the TGA curves of pure sulfur and bitumen modified sulfur. The maximal thermal effect was observed at 180–450°C for pure sulfur, which was accompanied by the active liberation of hydrogen sulfide, while the maximal thermal effect was observed at 200–540°C for modified sulfur. This effect reflects the increase of thermal stability of modified sulfur.

The DSC results of both sulfur and modified sulfur cement are shown in Fig. 4b. For pure sulfur, melting of alpha and beta was detected in the first run, while only alpha melting was detected in the second run. For modified sulfur, melting of alpha and beta was detected in the first run, while only beta melting was detected in the second run. So, DSC thermographs show that



Orthorhombic (α sulfur crystal)

Monoclinic (ß sulfur crystal)

Fig. 3 SEM image for (**a**) pure crystalline sulfur and (**b**) sulfur modified by 2.5 wt% bitumen

Table 4 Optimization of the percentage of bitumen used for sulfur modification via beta crystal dimensions obtained from SEM

Crystal dimensions (μm)	Bitumen (wt%)		
	2.5	3	3.5
Length	600	1000	1583
Width	147	167	279

modified sulfur remains in the monoclinic modification of beta form and does not undergo a phase transformation to the orthorhombic form (alpha form) upon solidification. The bitumen does, however, prevent the growth of macro sulfur crystals. This is important because sulfur has a relatively high linear coefficient of thermal expansion, 7.4×10^{-5}/C and a low thermal conductivity, 6.1 gcal/cm^2/s (Δt = 1°C), both at 40°C. When a material containing adjacent macro crystals of sulfur is subjected to changing temperatures, there will be constant movement between these macro crystals as each expands or contracts relative to its neighbor. This movement will gradually break the bonds with other cross-laid crystals, causing micro fractures and the eventual formation of cleavage planes (Vroom 1998). Since modified sulfur does not go through allotropic transformation upon solidification, it has less shrinkage and hence develops less residual stress upon cooling (Lin et al. 1995).

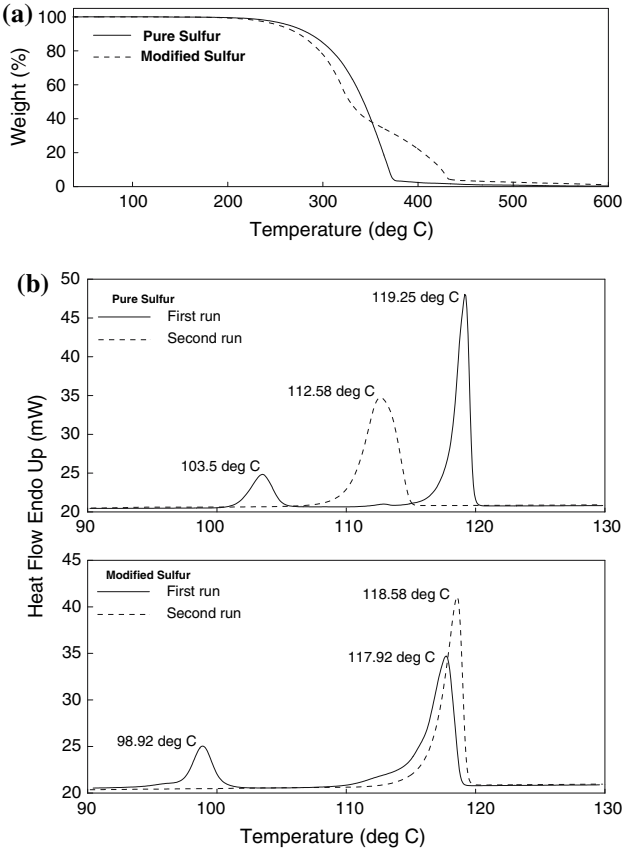


Fig. 4 Thermal properties of pure sulfur and modified sulfur; **a** TGA, with heating rate of 20°C/min, **b** DSC, with heating rate of 5°C/min

ESC and SPC

To utilize the available sulfur for manufacturing ESC, it is necessary to add a finely divided viscosity increasing material such as fly ash, which in turn will increase the consistency and workability of the mixture. Fly ash generated during the combustion of coal for energy production is one of the industrial by-products. Additionally, it is a waste produced by the nuclear industry and is recognized as an environmental pollutant (Kalb et al. 1991). Researches have been attempting to convert this waste into wealth. Fly ash is oxide-rich and can be used as a raw material in building construction. The use of fly ash in the construction of roads and embankments has been successfully demonstrated and accepted. It has been found to impart an extra durability to the final sulfur concrete. Fly ash tends to contribute to concrete strength, when the aluminosilicate components react with calcium oxides to produce additional cementation materials (Mohamed 2002, 2003; Mohamed et al. 2002, 2003, 2007).

The basic mechanical properties were measured for ESC samples to ensure that the developed materials met the properties found in literature. Figure 5 shows the desired optimum amount of sulfur to fly ash ratios according to the mechanical strength of the mortar. The obtained strength tends to increase as the sulfur/fly ash ratio increases up to 0.9, when all the particles are coated with a thin layer of sulfur, which acts as a good binder for aggregate particles and finally leads to increased strength. However, with a large addition of sulfur, the compressive strength decreases, because further increment of sulfur increases the thickness of sulfur layers around the aggregate particles and leads to increased brittleness of the composite material formed.

For proper criteria to evaluate the difference between the performance of ESC and SPC, SPC samples were prepared using different modified sulfur percentages. The effect of the modified sulfur incorporated into the mortars is shown in Fig. 6. The compressive strength decreased linearly with increasing amounts of modified sulfur due to the partial inhibition of crystallization through the addition of modified sulfur. These results are in agreement with

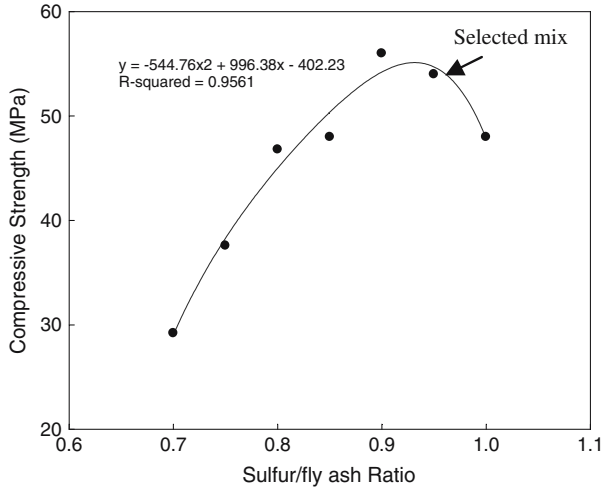


Fig. 5 Effect of sulfur to fly ash ratio on the compressive strength of sulfur concrete

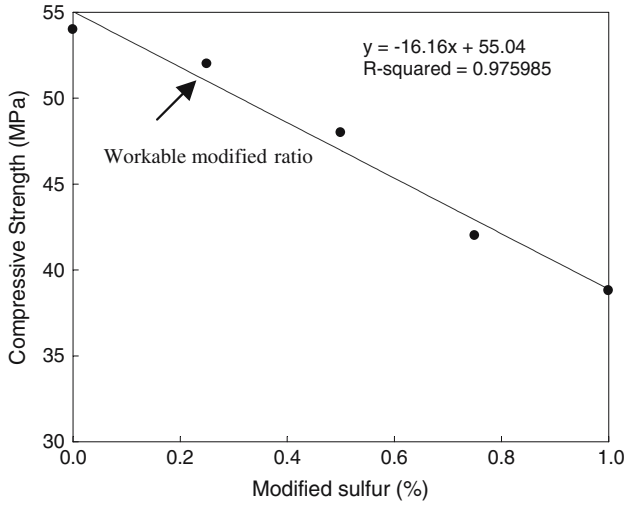


Fig. 6 Effect of modified sulfur percentage on the compressive strength of SPC

that reported by Vroom (1981). Mortars with modified sulfur show higher viscosity than ESC. This fact has an important effect on the crystallization of sulfur. In a more viscous liquid, the growth of crystals will be more difficult and slow, causing partial reduction in compressive strength.

The microstructure characterization, performed by SEM, provides important data on mortar studies. Figure 7a is an image for ESC, in which some common crystallization features were observed. The microstructure shows a considerable degree of packing with some pores, while the SPC microstructure (Fig. 8a) shows sulfur binding the aggregates, filling the inner spaces in such a way that the voids are discrete and discontinuous with good particle homogeneity.

The chemical analyses performed by EDS for ESC and SPC are shown in Fig. 7b, 8b and indicate that the samples are composed mainly of sulfur and silicon containing compounds. For ESC, sharp and intense signals with low atomic sulfur percentage was found, indicating a high crystalline structure; while in the case of SPC, a low crystalline structure was obtained from lower signal intensity, and the increase of atomic sulfur percentage proved lower porosity. It was thought that porous bodies impregnated with modified sulfur might have surface interactive forces different from those of ordinary sulfur (Beaudoin and Feldmant 1984). The cumulative percentage of pore size studied by image analyzer Fig. 9 proved lower porosity in SPC. The presence of modified sulfur has two main effects different from the unmodified one: the homogeneity is higher, which prevents the growth of big crystals, and porosity is lower.

The TGA chart of ESC and SPC (Fig. 10) shows that the decomposition of ESC is faster than that of SPC, indicating that SPC is thermally stable. According to the behavior observed from DSC for ESC and SPC, Fig. 11 shows that the addition of modified sulfur in small percentages to the mix would not directly affect the crystal form of sulfur (making it crystallize in a structure different from the stable one), but would alter the behavior in a hot liquid mix period. Crystallization of sulfur in this case is controlled by the relative percentages and distribution of space between the aggregates and the sulfur binder. The effect of modification seems to be an increase in the degree of polymerization of sulfur. Sulfur itself possesses a high tendency to polymerize; the modified sulfur would thus increase this tendency or maintain it for a longer time. In a more viscous liquid, in which the molecules are more polymerized, the growth of crystals will be more difficult. This fact has an important effect on the crystallization of sulfur. The DSC chart for SPC shows significant reduction in the (α) and (ß) sulfur crystal forms, which is illustrated by the reduction of the areas under melted peaks, confirming that SPC has a low order of crystalline structure compared to ESC.

Compressive strength of SPC

Compressive strength was determined for samples measuring $50 \times 50 \times 50$ mm. SPC samples were prepared at 135°C and cured in the oven with a gradual cooling rate of 5°C/min, then de-molded after 24 h and complete cured of samples in the tested temperature. The raw materials used in these preparations possessed some specific known characteristics. The quartz sand

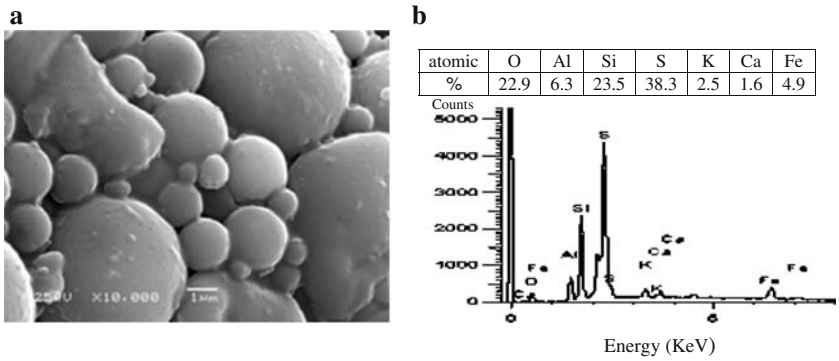


Fig. 7 SEM micrograph showing a variety of particle shapes, sizes and voids for sulfur concrete (**a**), EDX spectrum showing the residue main chemical element for sulfur concrete (**b**)

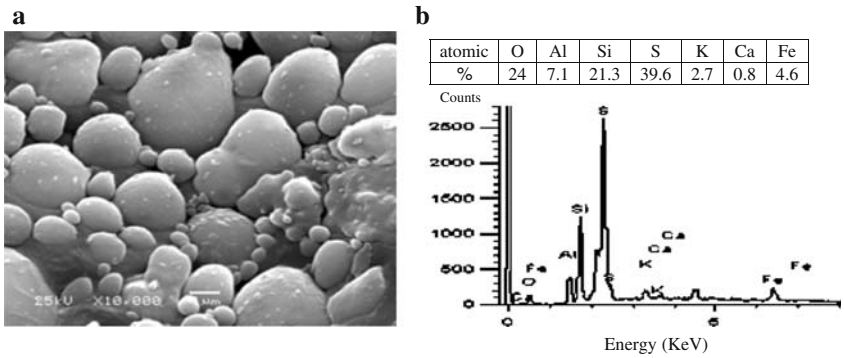


Fig. 8 SEM micrograph showing a variety of particle shapes, sizes and voids for sulfur polymer concrete (SPC) (**a**), EDX spectrum showing the residue main chemical element for SPC (**b**)

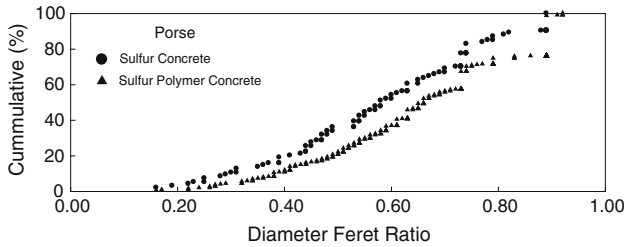


Fig. 9 The cumulative percentage of pore sizes, for SC and SPC, using image analysis program

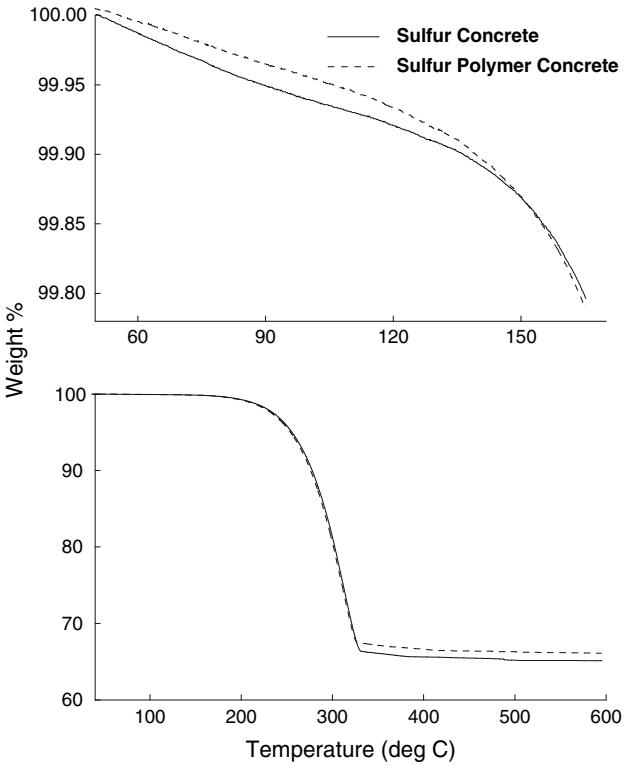


Fig. 10 TGA curves for SC and SPC, the heating rate was 20°C/min

was found to be of good quality, showing a low concentration of impurities and grains with an irregular geometry. This quality of sand grains may reduce the workability of the mortar; in contrast, they enabled the molten sulfur to adhere more easily to the surface of the sand grains (Gemelli et al. 2004). Fly ash was found to be an excellent agent for controlling the viscosity and increasing the durability of the final product. The rapid hardening and early strength gain changed over time, resulting in a very high strength material with an average compression of 54 MPa and modulus of elasticity of 1603 MPa. As a reference, it is worth noting that for mortars made from Portland cement, the strength properties were found to be 22 MPa for

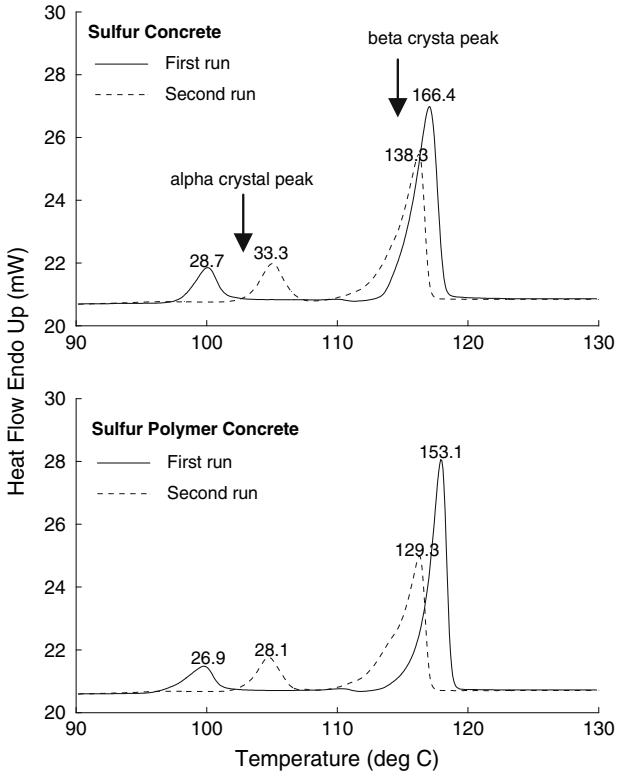


Fig. 11 DSC curves for SC and SPC; indicating the values of area under peak, for alpha and beta sulfur crystals. The heating rate was 5°C/min

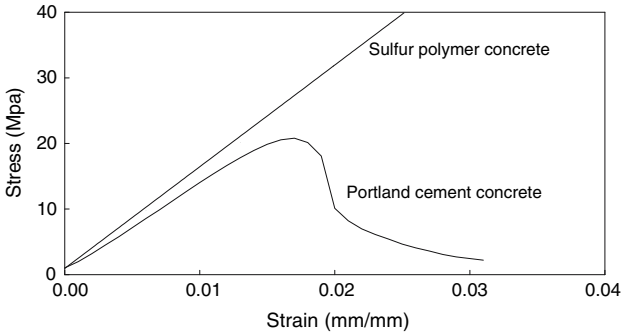


Fig. 12 Stress–strain relationship for SPC and normal PCC

compressive strength and 1461 MPa for modulus of elasticity.

Figure 12 shows typical stress–strain curves for SPC and PCC mortars. The PCC compressive strength increased as the strain increased, up to about 0.017, reaching a maximum value of 20 MPa and then it decreased. However, for SPC, the compressive strength continued to increase with the strain in excess of 0.025, reaching a value of about 40 MPa after which the test was stopped because the stress level reached the maximum capacity of the testing machine. The large mechanical strength for SPC is attributed to the reactive aluminosilicate and calcium aluminosilicate components that are routinely present in their oxide nomenclatures, such as silicon dioxide, aluminum oxide and calcium oxide. Fly ash tends to contribute to concrete strength, when the aluminosilicate components react with calcium oxides to produce additional cementatious materials.

Effect of aging on compressive strength of SPC

Compressive strength was determined for all SPC samples measuring 50 × 50 × 50 mm. Specimens were cured in the oven with a gradual cooling rate of 2°C/min, de-molded after 24 h and stored in incubators at 40°C. The variation of compressive strength with time, for SPC at 40°C, is shown in Fig. 13. It is clear that SPC developed 76% of its ultimate compressive strength within 1 day, and 97% after 3 days. However, at later ages up to 42 days, there was no clear trend in the development of compressive strength, suggesting that the maximum strength was developed during the early days. Similar results were reported by many researchers. For example, Vroom (1981) reported that 80% of the ultimate concrete strength was developed in 1 day, and virtually 100% of the ultimate strength was realized after 4 days. McBee et al. (1983a) showed that the sulfur concrete developed about 70% of its ultimate strength within a few hours after cooling, 75–85% after 24 h at 20°C, and that the ultimate strength was usually obtained after 180 days at 20°C.

Effect of curing temperature on compressive strength of SPC

Compressive strength was measured for SPC samples cured at different temperatures of 26, 40, 60, 80 and 100°C and for different time periods of 1, 2 and 7 days. The variations of compressive strength with temperature and curing time for SPC are shown in Fig. 14. The results indicate that for the same curing time, as temperature increases, the compressive strength decreases. A systematic reduction in compressive strength with temperature was obtained specially at high temperatures (80 and 100°C). For the same temperature, as curing time increases, the compressive strength increases. For temperatures below 60°C, the strength increases with time range between 20 and 30%, while for higher temperatures, the rate of strength increase with time is lower. Similar results were reported by McBee and Sullivan (1979a, b), who found that the strength gain is slower at elevated temperatures and

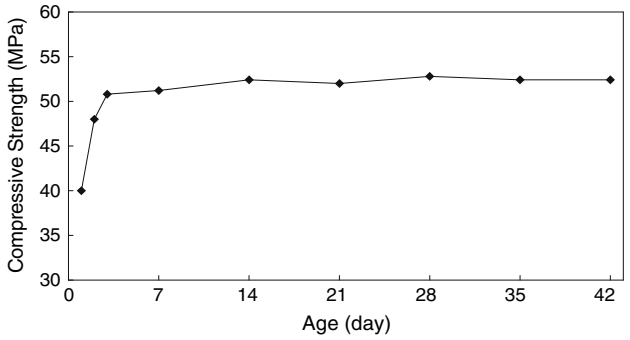


Fig. 13 Variations of compressive strength with time for SPC at 40°C

faster at lower temperatures. The results also indicate that the compressive strength of SPC for temperatures below 60°C is 20–30% more than PCC, and for higher temperatures (60–100°C), the compressive strength remains within the same range of PCC.

Effect of microstructure on compressive strength of SPC

Mechanical strength is directly related to the defects in mortar microstructure, which are generally characterized by SEM. The microscopic studies were determined from a section cut at a distance of 0.5 cm from the surface of SPC samples. Figure 15 shows a comparison between the mortar microstructure of SPC cured after 7 days with different temperatures.

It is obvious that for SPC cured at 40 and 60°C, the voids entrained within the SPC are small and discontinuous. However, while for SPC cured at 80 and 100°C, the voids are large in sizes without any noticeable cracking. The voids in SPC serve as sites for stress relief and for improving the durability of the material (McBee et al. 1983b). Also, the presence of voids in SPC reduces the quantity of sulfur cement required to coat the mineral aggregates, thereby minimizing the cement-related shrinkage.

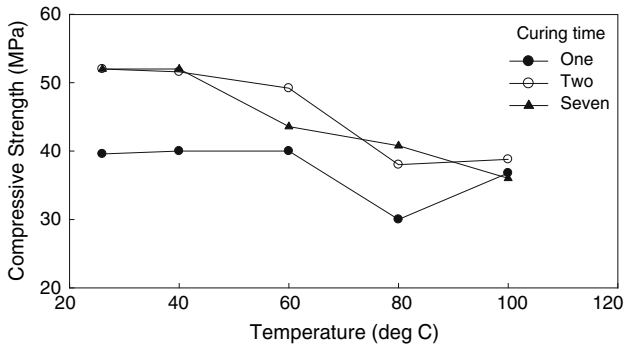


Fig. 14 Variations of compressive strength with temperature and curing time for SPC

The EDX spectrum of SPC at different temperatures is shown in Fig. 16. It can be seen that the sulfur peak intensity decreased with increasing temperatures, which in turn confirms the SEM observations. This lower intensity means lower degree of mineral crystalline form, which in turn led to lower compression strength. To illustrate these sets of results, the data were presented in terms of percentage of atomic sulfur as a function of temperature as shown in Fig. 17. The results indicated that the percentage of atomic sulfur in SPC tended to decrease as the curing temperatures increased, which is compatible with the presence of voids in SPC at elevated temperatures as previously discussed. To further evaluate whether the sulfur was lost due to gas formation or combination with other existing heavy metals to form metal sulfide forms, the loss of sulfur weight as a function of temperature was studied as shown in Fig. 18. The gravimetric changes in elemental sulfur with temperatures show no loss in sulfur weight at 40 and 60°C, and a loss of 0.25% at 80°C and 1% at 100 °C after 7 days indicating that the possible increase in voids at 80 and 100°C could be attributed to sulfur gas formation.

Furthermore, to evaluate the size of the voids from the results of SEM, we have utilized image analysis software. The results are shown in Fig. 19 in terms of the cumulative percentage of voids for SPC at different temperatures. It can be seen that for the same cumulative percent, the diameter Feret ratio increased with increased temperatures, indicating that the size of the voids increased as temperature increased. It is worth noting that when diameter Feret ratio reaches one, the pore sizes are spherical.

Effect of newly formed minerals on compressive strength of SPC

To evaluate the potential formation of minerals during the solidification/stabilization process, SPC samples were tested using X-ray diffraction analysis. The results of the obtained diffractograms are represented in Figs. 20–22. SPC samples were subjected to different temperatures (40°C, 60°C, 80°C° and 100°C) for 1, 2 and 7 days, respectively. Figure 20b shows that the mineralogical components of SPC samples subjected to these temperatures for 1 day are made up of major constituents: sulfur (27.9–35.4%), decreasing percentage of sulfur with increasing temperature, and quartz (44–56.2%), the opposite trend of sulfur. The minor

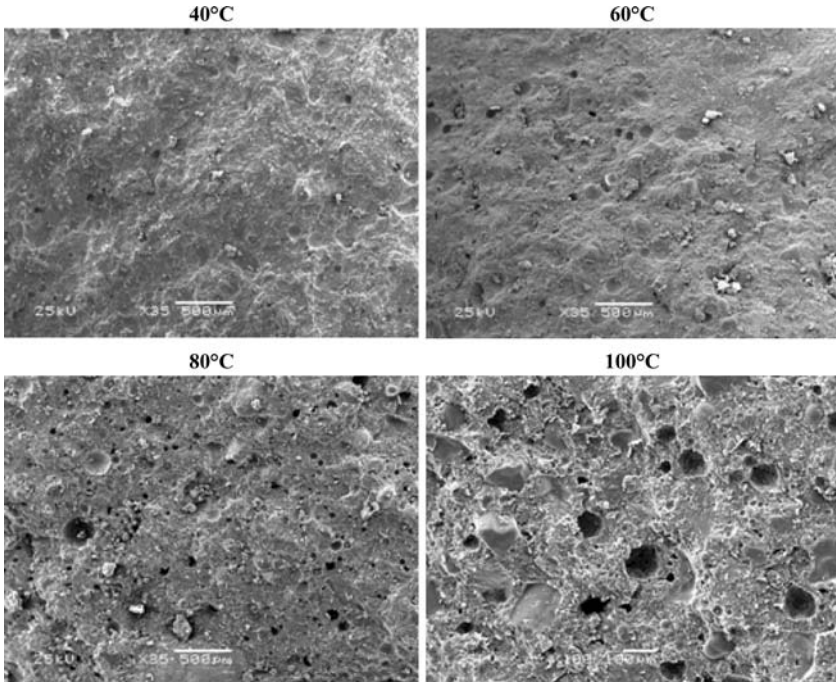


Fig. 15 SEM images for SPC at different temperature

constituents include the following in decreasing order: plagioclase (3.9–7.5%); aluminum oxide hydrate, $5Al_2O_3.H_2O$, (2.9–6.1%); calcium silicate hydrate, $Ca_{1.5}SiO_3{\cdot}5{\cdot}xH_2O$, (2.3–4.4%); calcite, $CaCO_3$, (2.2–2.9%); hematite, Fe_2O_3, (1.1–3.5%); dolomite, $CaMg(CO_3)_2$, (1.0–1.4%) and calcium aluminum oxide hydrate, $Ca_3Al_2O_6{\cdot}H_2O$, (0–1.9%).

The mineral composition of SPC samples, when treated to the same temperatures for 2 days, is shown in Fig. 21b. The major constituents are: sulfur (28–35.2%), characterized by decreasing percentage with increasing temperature, and quartz (42.7–50%) in the opposite trend of sulfur. The minor constituents involved the following constituents: aluminum oxide hydrate (4.4–7.0%), calcite (2.5–5%), calcium silicate hydrate (3.7–4.8%), plagioclase (3.2–3.6%), hematite (1.0–2.5%), dolomite (1%) and calcium aluminum oxide hydrate (1–1.3%).

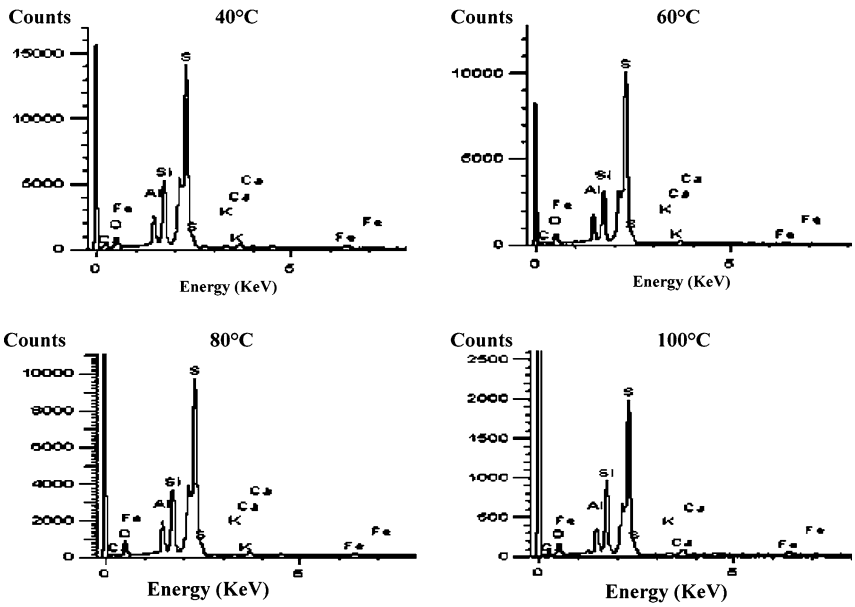


Fig. 16 EDX spectrum of SPC at different temperatures, showing the intensity of the residue main chemical elements

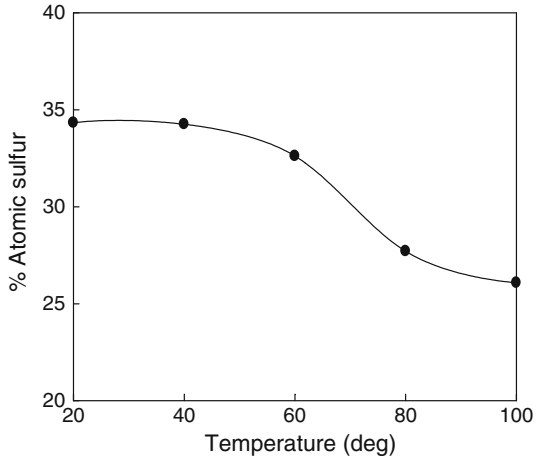


Fig. 17 Change in the sulfur percentage in SPC, with temperature, data obtained from EDX results

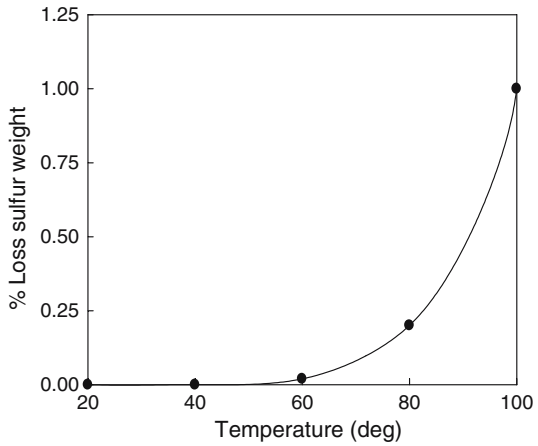


Fig. 18 Percentage loss of weight of sulfur varied with temperature, data obtained from gravimetric analysis

Also, the mineral composition of SPC samples, subjected to the same temperatures for 7 days is shown in Fig. 22b. The mineral composition of SPC samples was made up of major constituents of: sulfur (28.4–31.5%), characterized by decreasing percentage with increasing temperature and quartz, SiO_2, (44.0–50.5), characterized by increasing percentage with increasing temperature, which is approximately the opposite trend of sulfur. The minor constituents involved the following components: aluminum oxide hydrate (1.7–7.9%), calcium silicate hydrate (1.8–5.0%), plagioclase (2.5–4.7%), calcite (2.0–3.8%), hematite (2.2–2.5%), dolomite (1.5–3.9%) and calcium aluminum oxide hydrate (0–1.2%). It is worth noting that the amount of water molecules associated with the formed hydrated compounds is unknown since the process does not utilize water at all. This leads one to pose the following question. Where is the water coming from? Is it from the humidity of the atmosphere or from the bonded water in the recycled aggregates? These issues need further investigation.

Summary and conclusion

In this study, SPC was manufactured with the use of modified sulfur, sulfur and recycled aggregate materials (fly ash and sand dunes). Such a material could be utilized in various public works such as retaining structure, foundations, road construction, base materials for underground piping, etc. Specific conclusions are discussed below.

1. Addition of olefin hydrocarbon polymeric material (bitumen) to the sulfur resulted in:
   (a) sulfur polymerization with bitumen and increasing available sites for chemical reaction that leads to polysulfide formation;
   (b) forming a new structure with fine grain sizes;
   (c) controlling crystallization of sulfur; pure sulfur crystallizes and forms dense and large alpha sulfur crystals with orthorhombic sulfur morphology; with the addition of bitumen, the crystal growth is limited and controlled by the bitumen in such a way that all crystals are plate-like, of micron dimension and as monoclinic sulfur crystals of beta form;
   (d) uniform distribution of bitumen within the sulfur, leading to increased resistance to crack formation and increased thermal stability;
   (e) modification of sulfur mineralogy. Modified sulfur remains in the monoclinic modification of beta form and does not undergo a phase transformation to the orthorhombic form (alpha form) upon solidification. Addition of bitumen does, however, prevent the growth of macro sulfur crystals.
2. The manufactured SPC has resulted in:
   (a) an increase in the compressive strength, as the sulfur/fly ash ratio increases up to 0.9, when all the particles are coated by a thin layer of sulfur; however, with large sulfur addition, the compressive strength decreases, because addition of further sulfur increases the thickness of the sulfur layers around the aggregate particles leading to formation of brittle bonding;
   (b) linear decrease of compressive strength with increasing amounts of modified sulfur, due to the partial inhibition of crystallization;

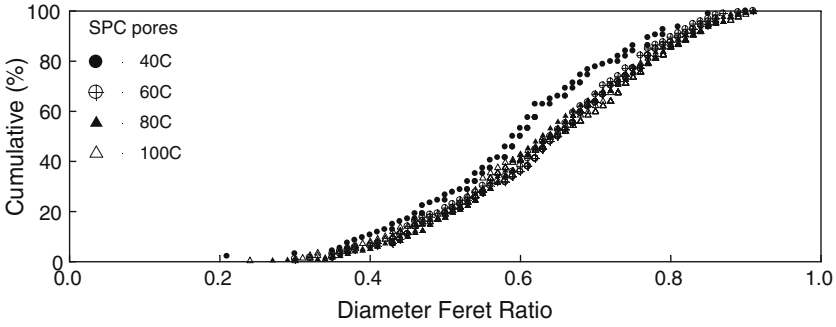


Fig. 19 The cumulative percentage of voids for SPC cured for 7 days at different temperatures, using image analysis program

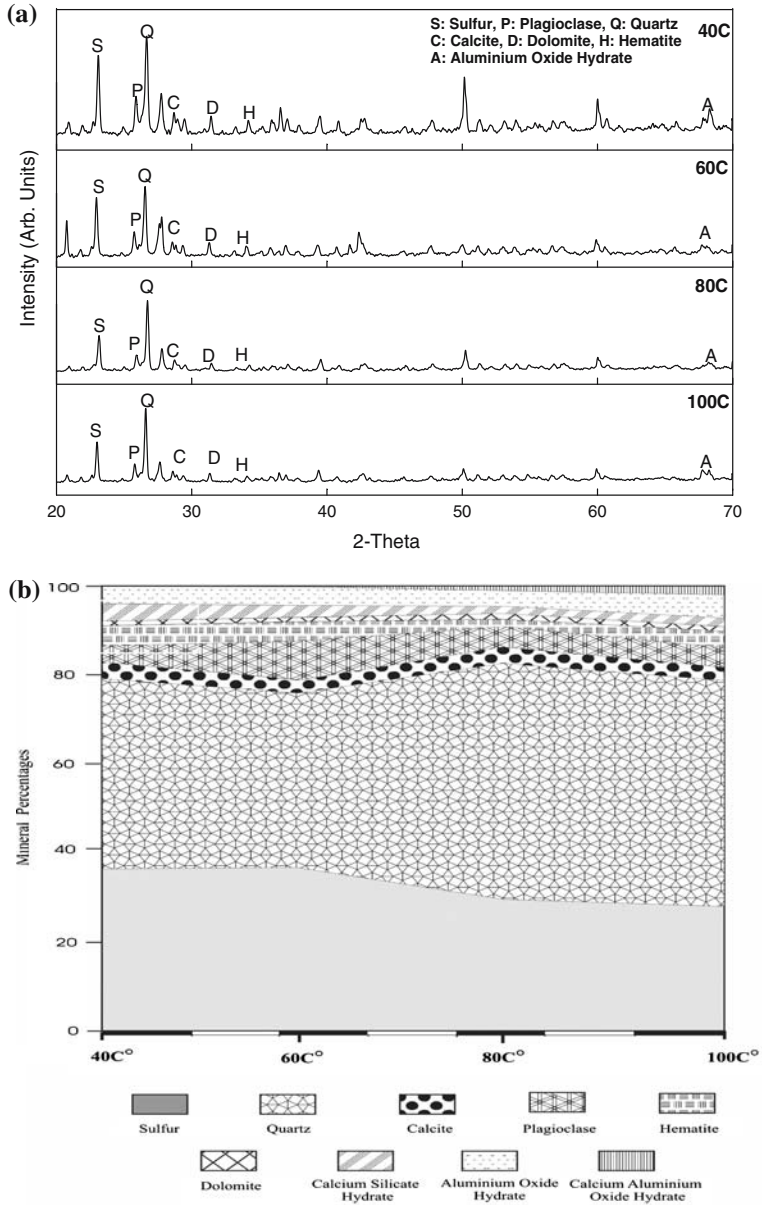


Fig. 20 **a** X-ray diffraction of SPC at different temperatures, **b** the lateral variation in the temperature of mineral composition of SPC sample cured for 1 day at different temperatures

(c) sulfur binding of the aggregates by filling the inner spaces in such a way that the voids are discrete and discontinuous with good particle homogeneity; and

(d) formation of a solid matrix with low porosity.

Additionally, the compressive strength of SPC was evaluated as a function of temperature and curing time.

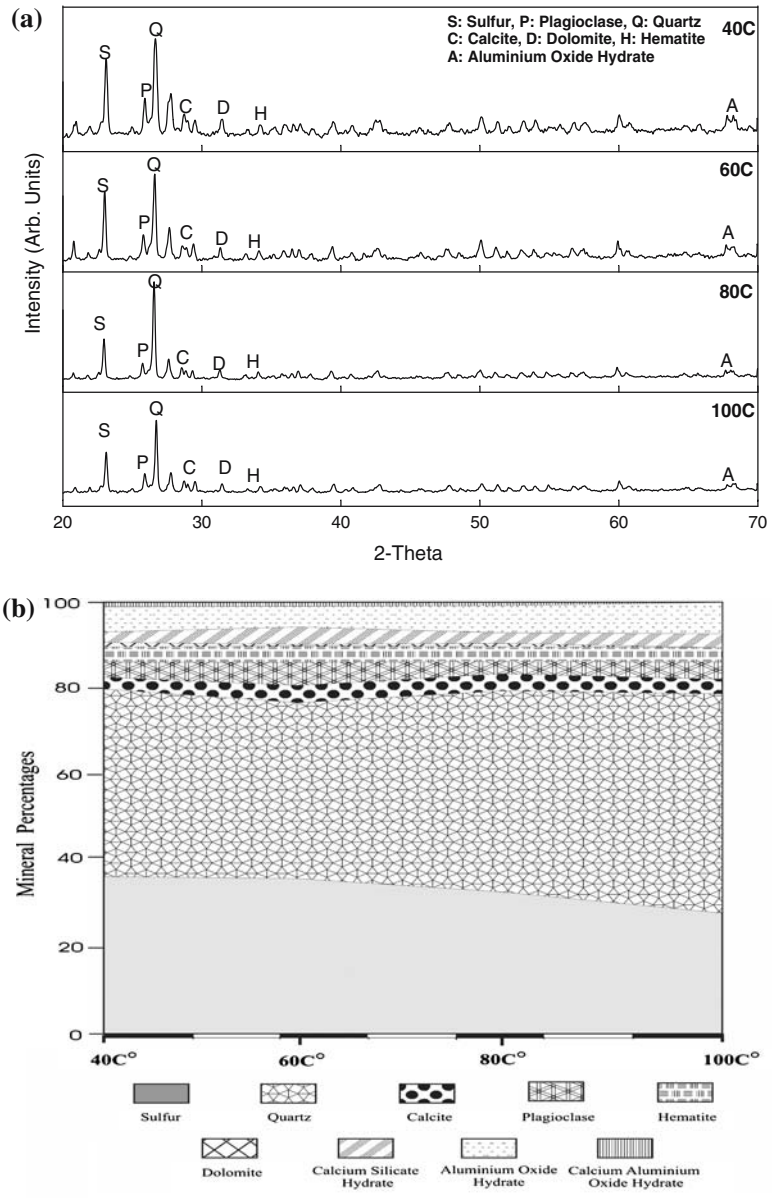


Fig. 21 **a** X-ray diffraction of SPC at different temperatures, **b** the lateral variation in the temperature of mineral composition of SPC sample cured for 2 days at different temperature

SPC samples were prepared and maintained at constant temperatures of 26, 40, 60, 80, and 100°C for different periods of time. The manufactured SPC developed 76% of its ultimate compressive strength after 1 day, and 97% after 3 days. No significant strength gain with time was observed. The compressive strength of SPC was dependent on the temperature at which the material was cured. For temperatures less than 60°C, SPC strength was higher than the PCC by about 20–30%. Whilst for temperatures higher than 60°C and less than 100°C, the compressive strength remained within the range of PCC.

The microstructure analysis of the manufactured SPC revealed that as temperature increased pore sizes increased, which in turn would provide a mechanism for stress release due to thermal stresses, thermal expansion decrease and shrinkage decrease upon cooling. The mineralogical analysis indicated that the increase of compressive strength of SPC was mainly due to the formation of stable minerals such as quartz, calcium aluminum silicate, calcium silicate hydrate, aluminum oxide hydrate, calcium aluminum oxide hydrate, hematite, calcite and dolomite. From the mineralogical viewpoint, it is worth noting that SPC does not allow the formation of ettringite, which constitutes a major problem in PCC due to its ability to absorb large amounts of water, expand and produce cracks in PCC.

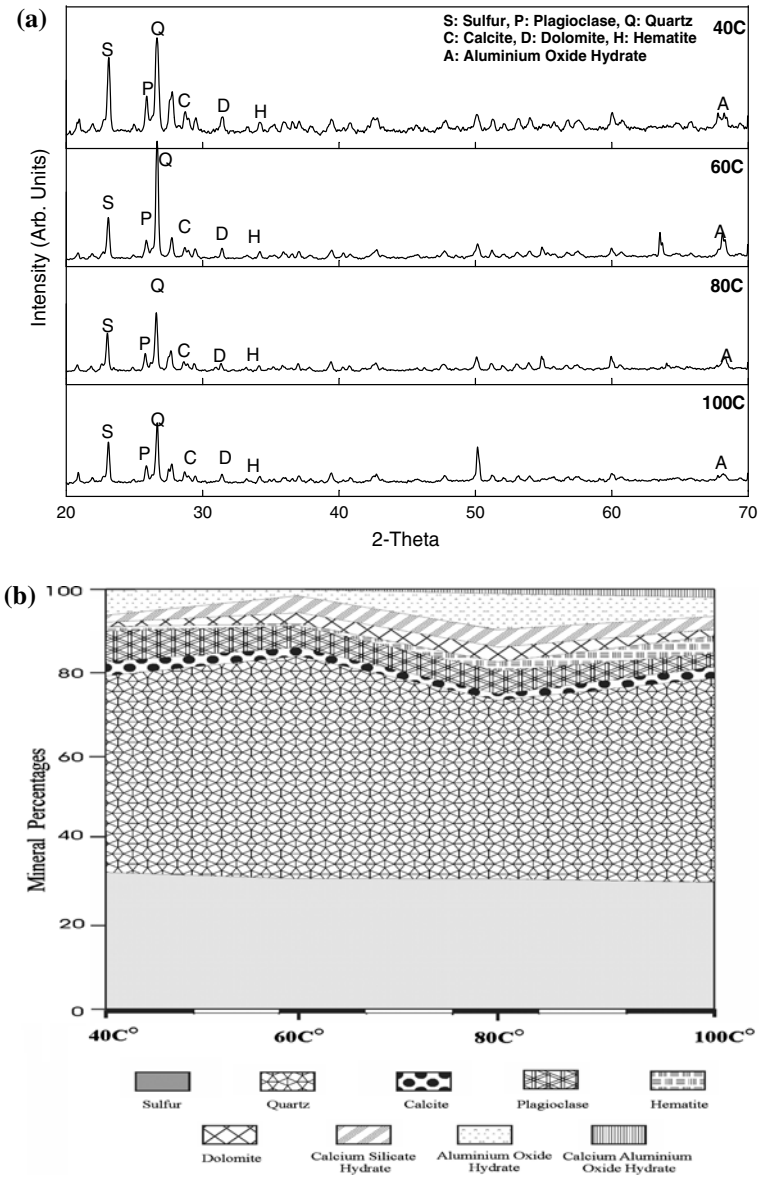


Fig. 22 **a** X-ray diffraction of SPC at different temperatures, **b** the lateral variation in the temperature of mineral composition of SPC sample cured for 7 days at different temperature

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References

ACI Committee 548 (1993) Guide for mixing and placing sulfur concrete in construction (ACI 548.2R-93), American Concrete Institute, Farmington Hills, Mich

ASTM C618-01 (2002) Standard specification for coal fly ash and raw or calcined natural pozzolan for use as a mineral admixture in concrete. Annual Book of ASTM Standards 04.02 West Conshohocken, PA, vol 14, p 381

Bacon RF, Davis HS (1921) Recent advances in the American sulfur industry. Chem Metallurgical Eng 24(2):65–72

Beaudoin JJ, Sereda PJ (1973) The freeze-thaw durability of sulfur concrete. Building Research Note, Division of Building Research, National Research Council, Ottawa, p 53

Beaudoin JJ, Feldmant RF (1984) Durability of porous systems impregnated with dicyclopentadiene-modified sulfur. Int J Cement Compos Lightweight Concrete 6(1):113–117

Bordoloi BK, Pierce EM (1978) Plastic sulfur stabilization by copolymerization of sulfur with dicyclopentadiene. Advances in Chemistry Series No. 165, American Chemical Society, Washington DC, pp 31–53

Crow LJ, Bates RC (1970) Strength of sulfur-basalt concretes. Bureau of Mines Report no. RI 7349, US Bureau of Mines, Washington, DC, p 21

Currell BR (1976) The importance of using additives in the development of new applications for sulfur. In: Symposium on new users for sulfur and pyrites, Madrid, pp 105–103

Dale JM, Ludwig AC (1966) Feasibility study for using sulfur-aggregate mixtures as a structural material. Technical report no. AFWL-TR-66–57, Southwest Research Institute, San Antonio, p 40

Dale JM, Ludwig AC (1968) Advanced studies of sulfur aggregate mixtures as a structural material. Technical report no. AFWL-TR-68–21, Southwest Research Institute, San Antonio, p 68

Duecker WW (1934) Admixtures improve properties of sulfur cements. Chem Metallurgical Eng 41(11):583–586

Funke RH Jr, McBee WC (1982) An Industrial application of sulfur concretes. ASC Symposium Series No. 183, American Chemical Society, Washington, DC, pp 195–208

Gemelli E, Cruz AAF, Camargo NHA (2004) A study of the application of residue from burned biomass in mortars. Materials Res 7(4):545–556

Gillott JE, Jordaan IJ, Loov RE, Shrive NG (1980) Sulfur concretes, mortars and the like, US patent no 4,188,230

Kalb PD, Heiser JH, Colombo P (1991) Modified sulfur cement encapsulation of mixed waste contaminated incinerator fly ash, vol 11, no. 3. Waste Manage J, Pergamon Press, New York

Kobbe WH (1924) New uses for sulfur in industry. Ind Eng Chem 16(10):26–1028

Leutner B, Diehl L (1977) Manufacture of sulfur concrete, US patent no. 4,025, 352

Lin SL, Lai JS, Chian ESK (1995) Modification of sulfur polymer cement (SPC) stabilization and solidification (S/S) process. Waste Manage 15(5/6):441–447

Malhotra VM (1973) Mechanical properties and freeze-thaw resistance of sulfur concrete. Division report no. IR 73–18, Energy, Mines and Resources Canada, Ottawa, p 30

Malhotra VM (1974) Effect of specimen size on compressive strength of sulfur concrete. Division report no. IR 74–25, Energy, Mines and Resources Canada, Ottawa

McBee WC, Sullivan TA (1979a) Development of specialized sulfur concretes. US Bureau of mines report no. RI 8346, US Bureau of Mines, Washington, DC, p 21

McBee WC, Sullivan TA (1979b) Development of specialized sulfur concretes. US Bureau of mines, report no. RI 8346, Washington, DC, p 21

McBee WC, Sullivan TA (1982a) Concrete formulations comprising polymeric reaction products of sulfur/cyclopentadien oligmer/dicyclopenetadiene. US patent no. 4,348,313

McBee WC, Sullivan TA (1982b) Modified sulfur cement. US patent no. 4,311,826

McBee WC, Sullivan TA, Jong BW (1981a) Modified sulfur concrete for use in concretes, flexible paving, coatings, and grouts. US Bureau of mines report no. RI 8545, US Bureau of Mines, Washington, DC, p 24

McBee WC, Sullivan TA, Jong BW (1981b) Modified sulfur concrete technology. In: Proceedings, SULPHUR-81 international conference on sulfur, Calgary, pp 367–388

McBee WC, Sullivan TA, Fike HF (1986) Corrosion-resistant sulfur concretes. Corrosion and Chemical Resistant Masonry Materials Handbook, Noyes Publications, Park Ridge, pp 392–417

McBee WC, Sullivan TA, Jong BW (1983a) Corrosion-resistant sulfur concretes. US Bureau of Mines, report no. 8758, Washington, DC, p 28

McBee WC, Sullivan TA, Jong BW (1983b) Industrial evaluation of sulfur concrete in corrosive environments. US Bureau of Mines, report no. RI 8786, Washington, DC, p 15

McBee WC, Weber HH (1990) Sulfur Polymer Cement Concrete. In proceedings of the Twelfth Annual Department of Energy Low-Level Waste Management Conference, CONF-9008119, National Low-Level Waste Management Program, Idaho Natl. Engineering Lab., Idaho Falls, Idaho

McKinney PV (1940) Provisional methods for testing sulfur cements. ASTM Bulletin 96–107, pp 27–30

Mohamed AMO (2002) Hydro-mechanical evaluation of soil stabilized with cement-kiln dust in arid lands. Environ Geol 42(8):910–921

Mohamed AMO (2003) Geoenvironmental aspects of chemically based ground improvement techniques for pyretic mine tailings. Ground Improvement 7(2):73–85

Mohamed AMO, El Gamal MM (2006) Compositional control on sulfur polymer concrete production for public works. Dev Arid Region Res 3:15–26

Mohamed AMO, Hossein M, Hassani FP (2002) Hydro-mechanical evaluation of stabilized mine tailings. Environ Geol 41:749–759

Mohamed AMO, Hossein M, Hassani FP (2003) Role of fly ash addition on ettringite formation in lime-remediated mine tailings. J Cement Concrete Aggregates ASTM 25(2):49–58

Mohamed AMO, El Gamal M, El Saiy AK (2006) Thermo-mechanical behavior of newly developed sulfur polymer concrete. Dev Arid Region Res 3:27–38

Mohamed AMO, Hossein M, Hassani FP (2007) Leachability potential of the newly developed ALFA technology for solidification/stabilization of mine tailings. J Materials Civil Eng Spec Ed Adv Physico-chem Stabil Geomaterials (in press)

Nimer EL, Campbell RW (1983) Sulfur cement-aggregate—organosilane composition and methods for preparing, US patent no. 4,376, 830

Nnabuife EC (1987) Study of some variables affecting the properties of sulfur-reinforced sugarcane residue based boards. Indian J Technol 25:363–367

Pickard SS (1985) Sulfur concrete for acid resistance. Chem Eng 92(15):77–78

Sullivan TA (1986) Corrosion-resistant sulfur concretes—design manuals. The Sulfur Institute, Washington DC, p 44

Sullivan TA, McBee WC (1976) Development and testing of superior sulfur concretes. US Bureau of Mines report no. RI 8160, US Bureau of Mines, Washington, DC, p 30

Sullivan TA, McBee WC, Blue DD (1975) Sulfur in coatings and structural materials. Advances in chemistry series no. 140, American Chemical Society, Washington, DC, pp 55–74

Syroezhko AM, Begak OY, Fedorov VV, Gusarova EN (2003) Modification of paving asphalts with sulfur. Russian J Appl Chem 76(3):491–496

Voronkov MG, Vyazankin NS, Deryagina EN (1979) Reaction of sulfur with organic compounds. Nauka, Novosibirsk

Vroom AH (1977) Sulfur cements, process for making same and sulfur concretes made there from. US patent no. 4,058,500

Vroom AH (1981) Sulfur cements, process for making same and sulfur concretes made there from. US patent no. 4,293,463

Vroom AH (1992) Sulfur polymer concrete and its application. In: Proceedings of 7th international congress on polymers in concrete, Moscow, pp 606–621

Vroom AH (1998) Sulfur concrete goes global. Concrete Int 20(1):68–71

Woo GL (1983) Phosphoric acid treated sulfur cement-aggregate compositions, US patent no. 4,376,831