Preparation of Sulfur Mortar from Modified Sulfur

Bahrami Adeh, Narmin*+; Mohtadi Haghighi, Mitra; Mohammad Hosseini, Nahid

Inorganic Chemical Industries Research Group, Iranian Research and Development Center for Chemical Industries (IRDCI), P.O. Box 13145-1494 Tehran, I.R. IRAN

ABSTRACT: *Mixtures of mineral aggregate and modified sulfur, wherein the modified sulfur functions as a binder, are termed sulfur concretes or sulfur mortars depending on the form of the mineral aggregate. Molten sulfur reacted with olefinic additive, at 130-140 ºC, and then mixed with preheated filler and aggregates. Sulfur mortar samples were prepared by mixing 32 % molten sulfur, 10 % filler and 58 % aggregates. The effects of reaction temperature, and heating time, were tested on mechanical properties of sulfur mortar. Sulfur mortars were prepared by silica flour, mica and carbon as filler in which silica flour can reduce odor problems. Sulfur mortar specimens have compressive strength (200-424 kg/cm^2), tensile strength (more than 80 kg/cm^2), and flexural strength (110-120 kg/cm^2).*

KEY WORDS: *Modified sulfur mortar, Sulfur concrete (SC), Mechanical properties, Filler.*

INTRODUCTION

The early study on the use of surplus sulfur in manufacture of construction material was reported by *Bacon* and *Davis* (1921) that produce a mixture of, 60 % sulfur as an acid-resistant material with excellent strength [1]. Various substances are used as additives to modify elemental sulfur, nearly, all of which fall under the heading of polymeric polysulfides or, alternatively olefinic hydrocarbons.

In 1934, *Duecker* showed that mortar proposed by *Bacon* and *Davis* suffered an important volume fluctuation and cracking under thermal cycles, with loss in flexural strength. This unstability comes from a phase transformation at 95.4 ºC between two crystalline structures, monoclinic (S_β), stable over that temperature and orthorhombic sulfur (S_α) stable below 95.4 ºC and at room temperatures .

Duecker was able to retard the volume change tendency by modifying the sulfur with an olefin poly-sulfide, known commercially as Thiokol [2]. Remarkable research in development of sulfur cement and concrete materials has been carried out by *Alan H. Vroom* in 1977 and 1981. A process was developed, involved modifying sulfur by reacting it with olefinic hydrocarbon polymers [3,4].

In 1974, *McBee* and *Sullivan* investigated on modification of sulfur by reaction with dicyclopentadiene (DCPD) [5]. In 1977, *Currell et al.* studied the modification of Sulfur with different amounts of

* To whom correspondence should be addressed.
+ E-mail: n_bahrami@irdci.ac.ir
1021-9986/08/1/123 5/$/2.50

dicyclopentadiene and styrene at 140 ºC with varying heating times. The percentages of unreacted free sulfur were identified by Gel Permeation Chromatography [6].

Elemental sulfur first crystallizes as monoclinic sulfur (S) at 114 ºC with a volume decrease of about 7 %. On further cooling to below 96 ºC, sulfur undergoes a transformation to (S), the stable orthorhombic polymorph at ambient temperatures [7]. This transformation is rapid, generally occurring in less than 24 hours. Since (S) is denser than (S), high stress is induced in the material by solid sulfur shrinkage. Thus, the sulfur binder can become highly stressed and can fail prematurely [8].

In present paper sulfur was modified with a native additive in different reaction times and temperatures. Sulfur mortars were prepared by optimized modified sulfur with different fillers and mechanical properties were tested.

EXPERIMENTAL

Modified Sulfur

To optimize modification of sulfur, three conditions were tested. In first condition, sulfur was melted in oil bath then olefinic additive was added in 130-140 ºC, the temperature being maintained at about 130-140 ºC during the mixing process, which lasted about 3 hours [6]. In second condition, additive was added in 150-160 ºC and the mixture was heated in same temperature for about 3 hours. In third condition, after addition of olefinic additive to sulfur in 130-140 ºC, the mixture was heated for 0.5, 1, 2 and 3 hours to produce modified sulfur (tables 1 and 2).

The composition and properties of modified sulfur were evaluated in terms of chemical analysis (table 3) and FT-IR spectra (Figs. 1 and 2). XRD diagrams for pure sulfure, sulfur modified with 10 % by weight of olefinic additive and Chempruf [9] sample is shown in Figs. 3,4 and 5. The determination of C, H and S was carried out with CHN - 600 Leco and S was measured using gravimetric procedures. The IR spectrum was recorded by using Shimadzu FT-IR. The IR spectrum of modified sulfur was taken as powder mixed with a small amount of KBr powder to make the IR pellet.

Sulfur Mortar

Sulfur mortars were prepared by mixing molten modified sulfur and heated mineral aggregates. The

Table 1: Compressive strength of sulfur mortar prepared at (0.5,1,2,3) heating time and 140 ºC.

Sample	Reaction time (hr)	Compressive strength (kg/cm^2)
1	0. 5	73
2	1	180
3	2	138
4	3	207

Table 2: Compressive strength of sulfur mortar prepared at 140 ºC and 160 ºC and 3 hr.

Sample	Reaction Temp. (ºC)	Compressive strength (Kg/cm^2)
1	160	104
2	160	112
3	160	82
4	160	126
5	140	203
6	140	208
7	140	246
8	140	372
9	140	320

Table 3: Chemical analysis of modified sulfur.

Property	Modified Sulfur
Sulfur, % by weight	65.3
Carbon, % by weight	12
Hydrogen, % by weight	1.4
Specific gravity at 25 ºC	1.75

mineral aggregates in the compositions of the sulfur mortar include fine aggregate and fines. Fine aggregate includes sand and other material of mineral composition having a particle size of about 150 μm to about 4.75 mm. Fines include silica flour, stone powder and other material of mineral composition having a particle size less than about 150 μm [10].

Mineral aggregates proportion of sulfur mortar in this paper include, 58 % fine aggregate (sand) and 10 %

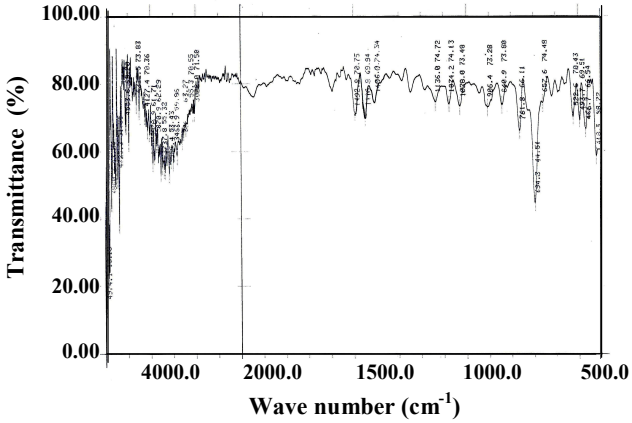

Fig. 1: FTIR spectra of modified sulfur.

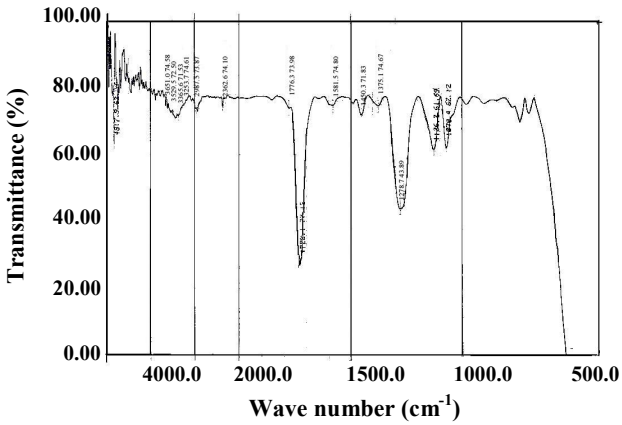

Fig. 2: FTIR spectra of olefinic additive.

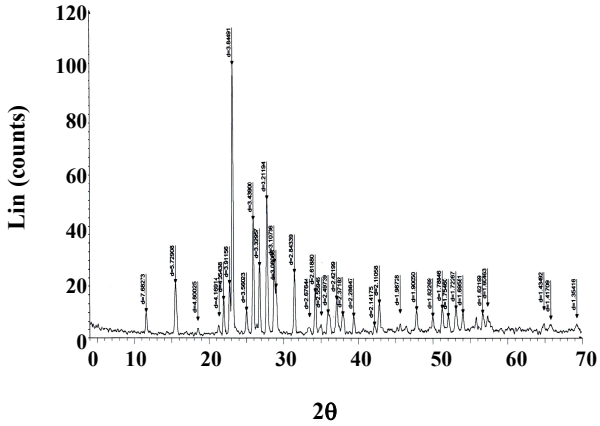

Fig. 3: X-ray Diffraction pattern for pure sulfur.

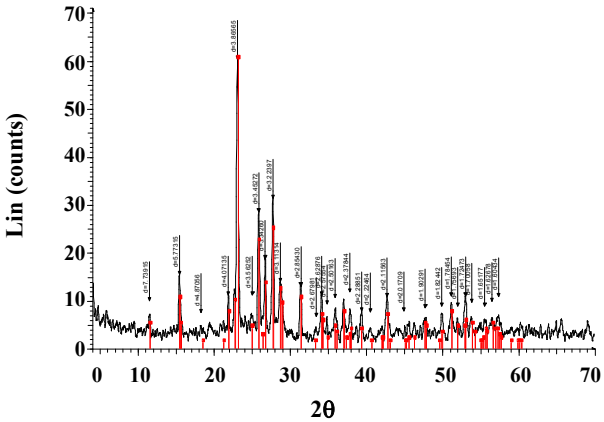

Fig. 4: X-ray Diffraction pattern for modified sulfur.

fines (2 % silica flour, 8 % stone powder)[11]. Aggregate gradings are shown in Fig. 6.

These aggregates were heated in an oven preferably to about 120 ºC and 32 % modified sulfur was melted in a bowl. Pre-heating of the mineral aggregate is desirable to avoid solidification of the molten sulfur by contact with mineral aggregate at a low temperature and to reduce the mixing time.

The heated aggregates were then properly mixed with the molten modified sulfur until a homogenous viscous mixture was obtained. It was casted in preheated cubic mold with dimension 50×50×50 mm. As the sulfur mortar is added the material was compact by tamping with a rod. The surface of each specimen was finished and left in ambient temperature to be self cooled. The samples were de-molded after 24 hours. Mechanical properties measurements are made after 75 hours.

Sulfur mortars were prepared according to above procedure with modified sulfur in three mentioned conditions .The results are given in tables 1 and 2. Tensile and flexural strength are given in table 4.

Mechanical properties of sulfur mortars and their variation with time were studied and the results are shown in Fig. 7. These specimens were made by heating the sulfur with additive for 3hr at 140 ºC.

Other specimens were prepared by same aggregate with different kind of fillers (carbon, mica). Modified sulfur used in these mortars was heated in 130-140 ºC for 3 hours. Sulfur mortars-composition, and mechanical properties are given in table 5.

RESULTS AND DISCUSSION

Figs. 1 and 2 provide modified sulfur and olefinic additive spectra. The bond at 694 cm^{-1} is consistent with c-s stretching and the bond of C=C at 1650 cm^{-1} has disappeared.

Table 4: Tensile and flexural strength of sulfur mortar prepared at 140 ºC and 160 ºC and 3 hr.

Wt % Aggregate	Wt % Modified sulfur	Wt % Filler	Tensile strength (kg/cm^2)	Flexural strength (kg/cm^2)
58 sand	32	10 Silica flour & stone powder	More than 80	115

Table 5: Sulfur mortars - composition and properties.

Sample	Wt % Aggregate	Wt % Modified sulfur	Wt % Filler	Density (kg/m^3)	Compressive strength (kg/cm^2)
1	58 sand	32	10 silica flour & stone powder	2262	214
2	58 sand	32	10 silica flour & stone powder & mica	1152	461
3	58 sand	32	10 stone powder & mica	1146	351
4	58 sand	32	10 silica flour & stone powder & carbon	2309	226

XRD analysis of modified sulfur (before seperation of polysulfide) does not show any significant shift compared with pure sulfur (Figs. 3 and 4). Unreacted sulfur presumably covers modified one. It also appeares in chempruf sample in spite of the fact that it should be mixed with additional elemental sulfur (1:4) (Fig. 5). Compressive strengths of sulfur mortar prepared at 140 ºC are more than the sample prepared at 160 ºC. It should be pointed that, at 119-157 ºC , molten sulfur exists essentially as cyclooctasulfane.

Sulfur reacts with olefins at 90 to 160 ºC in the liquid phase to form several types of polysulfide products [12]. By increasing temperature from 90 ºC, the S_8 rings progressively break up into reactive biradicals. If there is no olefin, these reach sufficient concentration at around 160 ºC to polymerize spontaneously into μ-sulfur chains [13]. Polymeric chains have low affinities than other compounds thus reactivity of sulfur with additive reduces at 160 ºC as compared with sulfur at 140 ºC.

No literature data is available in previous works as this subject, although the nearest data to our work are the results from *Diehl* who has also investigated the compressive strength of concrete prepared by using sulfur modified with different additive (Dicyclopentadiene). His results show that the compressive strength of the concrete is very dependent on the reaction time and temperature [6].

The test result in table 5 shows that there is a considerable increase in the compressive strength of specimens prepared in 3 hours. Fig. 7 shows that sulfur mortars have constant compressive strength till 30 days which increase rapidly after approximately 46 days which is consistent with the results obtained by Currell et al by using different additives [6] and this is presumably due to formation of crystalline sulfur.

Addition of filler increases viscosity because of sufficient matrix relative to the amount of sulfur to obtain a workable mixture and decreases void space in mortar. The function of the filler is to stabilize the sulfur mortar and reduce the amount of modified sulfur needed. To prepare sulfur mortar, silica flour, carbon, mica and etc can be used as fillers.

Silica flour fillers produce a stiffer mix, which is useful in placing sulfur mortar on a slope. Tensile and flexural strength of sulfur mortars prepared by mixing 58 % sand, 2 % silica flour, 8 % stone powder 32 % modified sulfur, are > 80 and 115 kg/cm^2, respectively.

CONCLUSIONS

In this study, manufactured sulfur polymer mortar led to the following conclusions:

1- Iinitially, there is linear relation between time and compressive strength.

2- Reaction temperature and heating time are effective factors to modify sulfur .In this paper optimized temperature and heating time are, 140 ºC and 3 hours, respectively.

3- Sulfur mortars have high flexural and tensile strength because of their thermoplastic properties.

4- The high compressive strength of sulfur mortars can be obtained by changing mixture proportion and using favorable grain distribution with little void space.

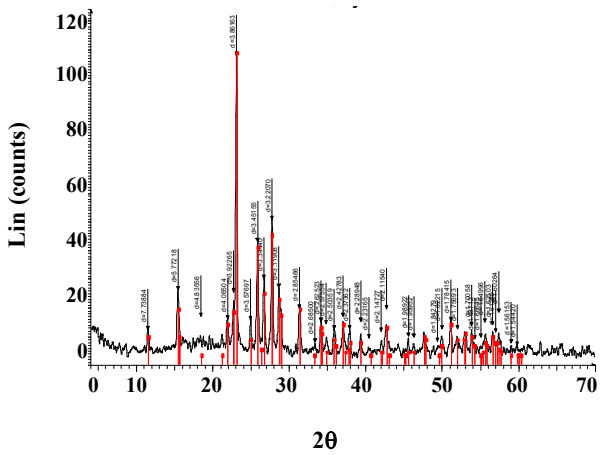

Fig. 5: X-ray Diffraction pattern for chempruf sample.

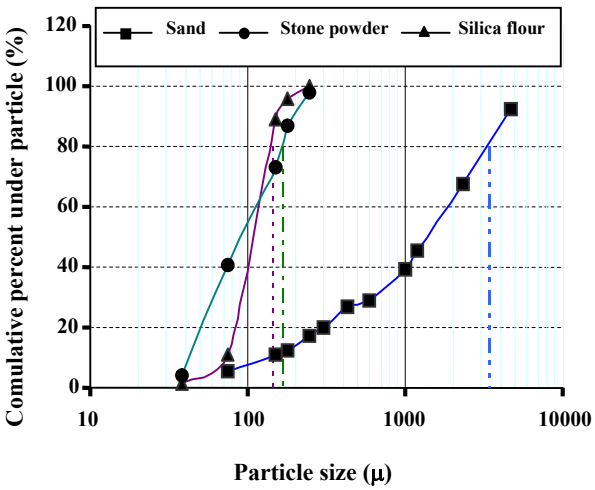

Fig. 6: Grading curve of aggregates for sulfur mortars.

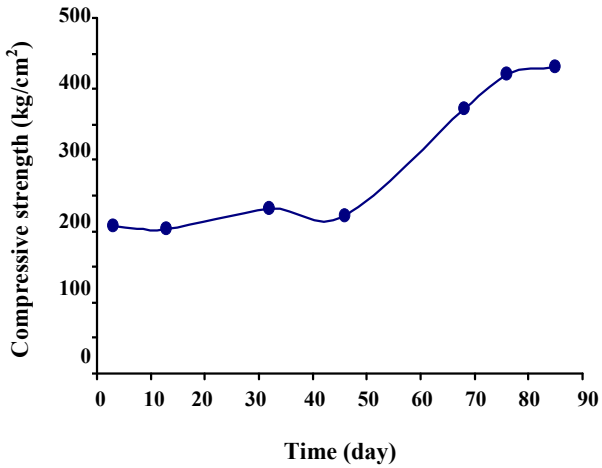

Fig. 7: Compressive strength vs. time plots of sulfur mortars.

Received : 5th November 2006 ; Accepted : 18th November 2007

REFERENCES

[1] Bacon, R.F., Davis H.S., Recent Advances in the American Sulfur Industry, *Chem. Metallurgical Eng.*, **24**(2), 65 (1921).

[2] Duecker, W.W., Admixtures Improve Properties of Sulfur Cements, *Chem. Metallurgical Eng.*, **41**(11), 583 (1934).

[3] Vroom, A.H., Sulfur Cements, Process for Making Same and Sulfur Concretes Made There From, U.S. Patent NO. 4,058,500, Nov.15, (1977).

[4] Vroom, A.H., Sulfur Cements, Process for Making Same and Sulfur Concretes Made There From, U.S. Patent NO. 4,293,463, Oct.6, (1981).

[5] McBee., W.C., Sulliven, T.A. and Jong, B.W., Modified Sulfur Concrete Technology, Proceedings, SUFUR-81 International Conference on Sulfur, Calgary, pp. 367-388,(1984).

[6] Blight, L., Currell, B.R., Nash, B.J., Scott, R.A.M. and Stillo, C., "Preparation and Properties of Modified Sulfur Systems", New Use of Sulfur-II, Advances in Chemistry Series 165 (American Chemical Society) 13-30 (1977).

[7] Lin, S.L., Lai, J.S. and Chian, E.S.K., *Waste Management*, **15** (5/9), 441 (1995).

[8] Mohamad, A.M.O., El Gamal M.M., Compositional Control on Sulfur Polymer Concrete Production for Public Work, *Dev Arid Region*, **3**, 15 (2006).

[9] www.Chemprufconcrete.com

[10] Gillott, J.E., Jordaan, I. j., Loov, R.E., Shriye N.G., Sulfur Concretes, Mortars and the Like, U.S. Patent NO. 4,188,230, Feb.12, (1980).

[11] Bahrami, N., Mohtadi, M., Improvement of Sulfur Properties to Produce Sulfur Cement, *Nashrieh Shimi va Mohandesi Shimi Iran*, **22** (2), p. 65 (2003).

[12] Pryor, William A., "Mechanisms of Sulfur Reactions", McGraw-Hill, New York, (1962).

[13] Sander, U.H.F., Fisher, H., Rothe, U., Kola, R., "Sulfurs Sulfur Dioxide and Sulfuric Acid", the British Sulfur Corporation, London, (1984).