Activation of Sulfur and Opal-Cristobalite-Tridymite Phase in Sulfur Concrete Technology

Vladimir Erofeev 1, Alsu Yusupova 2 and Alexander Bobrishev 2

1 Ogarev Mordovia State University, Saransk, ul. Bolshevistskaya, 68, Saransk, Russia
2 Kazan National Research Technological University, Russia
3 Kazan Federal University, Naberezhnye Chelny Institute, 68/19, Prospekt Mira, Naberezhnye Chelny, Russia

E-mail: misharin_82@mail.ru

Abstract. The paper investigates the influence of the metal chlorides (Al, Zn, Ti, Fe) on the properties of sulfur binder. The addition of Lewis acids stimulated the synthesis process for inorganic sulfides and sulfur concrete based on them. The resulting sulfur concrete has high performance characteristics. It was found that aluminum, titanium and iron chlorides acted as activators for sulfur ring opening, reduced the activation energy in the process and simultaneously encouraged the chemical interaction between sulfur and surface silicon of silica-containing compounds. It was revealed that the reactivity of sulfur modifiers decreased in a series of Zn>Al>Ti>Fe. Chemical modification of the silicate surface with chlorides of Zn, Al, Ti, Fe results in intended change of its chemical properties. The paper shows that modification increases a number of active reaction sites on the silicate surface. The designed technology is environmentally sound and economically feasible: it ensures the efficient use of sulfur waste from the oil and gas industry, and provides durable and corrosion resistant composite materials that have lower production cost than the known analogues. The designed materials can be used in road construction for roadbeds, paving slabs, curbstones, pavestones, gutters.

1. Introduction

The usage of sulfur in the building materials technology resulted in a new trend – sulfur binders. Usually, they are based on thermal activation of raw materials. Most of sulfur materials technologies are based on physical/mechanical interaction between sulfur and filler [1 - 5]. High activation energy and inability of processes to run at acceptable temperatures make a chemical interaction with inorganic and organic compounds difficult. That’s why, today’s widely used thermal activation of raw materials cannot provide the desired result by itself – a material with high physical mechanical properties and low manufacturing cost. This is especially the case in the processes with silicon dioxide: its high bond energy and chemical inertness are well known [6].

In light of this, it is critically important to find new methods for activation of raw components, especially, in the processes involving a thermodynamically stable silica component.

The objective of the paper is to develop an activation process for raw components during sulfur concrete production using various Lewis acids.

2. Theoretical
The motivation behind using sulfur in sulfur concrete technology lies in its chemical properties and electronic structure. During reactions at a temperature range from 160 to 200 °C, as well as pyrolysis of some sulfur compounds, sulfur reacts already as biradicals $S_n$, and that's why it initiates radical transformation. The electronic structure of sulfur ($3s^2\ 3p^4\ 3d^0$) defines its activating ability under the influence of Lewis acids [7].

The resulting polysulfide chains have much higher reactivity than relatively stable cyclic $S_8$ molecules. For this reason, reagents of the above-mentioned types can act as catalysts for reactions of elemental sulfur [8-11].

Opal-cristobalite-tridymite phase with its high specific surface area and reactivity is used as a filler. It encourages a chemical interaction between sulfur and filler in order to produce materials with high physical mechanical properties [12-15].

Study of interaction in the sulfur-opal-cristobalite-tridymite phase-metal chlorides (Al, Fe, Ti, Zn) system is of significant practical interest in the context of development of a resource saving technology, sulfur waste recovery and production of a high-quality building material that meets applicable regulatory requirements.

The quantum chemical methods used in this paper were helpful in clarifying the mechanisms and energy efficiency of running processes under study during synthesis [16-17].

3. Experimental
The sulfur concrete was made from the following raw components: sulfur (S), which was the waste from the Nizhnekamsk oil refinery and contained 99.98% wt. of base material (GOST 127-93); aluminum chloride AlCl₃ (GOST 3759-75); titanium chloride TiCl₄ (TU 6-09-2118-77); iron chloride hexahydrate FeCl₃·6H₂O (GOST 4147-74), zinc chloride ZnCl₂ (GOST 4529-78); silica gel of KSGM type (GOST 3956-76); opal-cristobalite-tridymite rock from the Dobrinskoe field, Saratov oblast (mineral composition, % wt.: 78±7 of opal-cristobalite, 7±2 of zeolite, 5 of montmorillonite).

The studies were performed using electron paramagnetic resonance and the radio spectrometer RE-1306 (at a frequency of 9100 and 9370 MHz) at 77 and 300 K, respectively. Single-crystal ruby with Cr³⁺ was used as an internal standard. The spectra were recorded in three scanning ranges of the external magnetic field.

The quantum chemical calculations mentioned in the paper were made with Gaussian 98 (B3LYP, PM3) and Priroda (DFT) application software. Often, the unrestricted Hartree-Fock method was used to estimate radical decomposition reactions and study the structure of biradical transition states. It involved mixing of the highest occupied and lowest unoccupied molecular orbitals at the start of calculations.

4. Activating effect of metal chlorides (Al, Zn, Ti, Fe) on sulfur and silicate components
The activating effect of Lewis acids on sulfur was addressed first. Viscosity of sulfur melt was used as an estimation criterion. The viscosity of sulfur melt changes over a wide range depending on the temperature, and the properties of sulfur depend directly on viscosity [7]. Lower viscosity of sulfur melt is caused by chemically reactive short sulfur radicals, and higher viscosity – by their polymerization. At a temperature of up to 150 °C sulfur melt is a thin fluid that contains radicals with a different number of atoms in the chain. At a temperature of above 150 °C the melt contains polymeric sulfur (7.3%), sulfur rings (5.4%) and cyclo-octasulfur (87.3%). At a temperature of above 157 °C the melt becomes viscous due to polymerization: cross-linking of radicals and formation of long sulfur chains containing up to a million atoms of sulfur.

The experiment was made to define the effect the added activating agent (metal chloride) would have on sulfur melt. For purposes of comparison, a pure sulfur melt and melt modified with 5% ZnCl₂ AlCl₃ TiCl₄, FeCl₃ were taken.

The studies demonstrated that with added zinc and aluminum chlorides the viscosity of sulfur melt always remained low through the whole range of operating temperatures (130-170 °C). Therefore, zinc
chloride encourages the formation and stabilization of a vast number (S2, S4, S6, S8) of chemically reactive radicals and hence increases the reactivity of a sulfur component.

The studies found that with added titanium chloride the viscosity of sulfur melt always remained low in the range of operating temperatures (130–160 °C). Therefore, titanium chloride encourages the formation and stabilization of a vast number (S2, S4, S6, S8) of chemically reactive radicals and hence increases the reactivity of a sulfur component.

With added iron chloride (III), sulfur becomes polymerized at a temperature as low as 145°C, S8 rings start to break and form open chains, as for pure sulfur this temperature is 159°C. Therefore, the effect of iron chloride (III) is manifested by a lower temperature at which polymeric chains start to form due to opening of stable sulfur rings. The formation of some “plastic” or polymeric sulfur (which has better stress-strain properties, higher tensile strength, greater adhesion to fillers and lower internal stress during transition from viscous liquid state to solid one (by 60%) than crystalline modifications of sulfur) will have a positive effect on the physical mechanical properties of resulting sulfur materials. It appears that iron chloride (or products of its decomposition) interacts with sulfur by joining the ends of a polymeric chain, saturates available valence bonds, disrupts the polymerization process and transforms a material into cross-linked polymer. It leads to a rapid decrease in depolymerization rate.

Therefore, aluminum, zinc, titanium and iron chlorides act as activators for sulfur ring opening and encourage the formation of active radicals and plastic sulfur which in case of iron chloride is cross-linked to deformation-resistant polymer.

The theoretical quantum chemical studies were performed to evaluate thermodynamics of activation of cyclic sulfur molecules with Lewis acids and formation of active radicals.

Table 1 shows the comparative analysis of thermodynamics of sulfur ring S8 opening with the activators present – chlorides of Zn, Al, Ti, Fe.

It was observed that the used activators decreased the energy required for activation of sulfur ring opening for ZnCl2 – by 27.05 kJ/mol, AlCl3 – 20.85 kJ/mol, TiCl4 – 10.75 kJ/mol. Strong bonds are formed between metal and sulfur in the system with a bond energy from 218.3 to 290.0 kJ/mol. Interaction with chlorides of these metals results in bond alternation and distortion of dihedral angles of a sulfur ring. The sulfur rings do not weaken with iron chloride present. Besides, chemical bonding of sulfur decreases the toxic levels for production.

| Activator | $E_{\text{bond in } \text{S}_8}^\circ$, [kJ/mol] | $E_{\text{bond Me-S}}^\circ$, [kJ/mol] | Decrease in bond energy in ring, [kJ/mol] | $E_{\text{act}}$, [kJ/mol] | $\Delta H_{\text{reaction}}$, [kJ/mol] | Note |
|-----------|-----------------|-------------------------------|---------------------------------|-----------------|-----------------|------|
| ZnCl$_2$  | 250.5           | 209.7                         | 35.8                            | 123.9           | 81.60           | Bond alternation in rings, distortion of dihedral angles |
| AlCl$_3$  | 231.4           |                               | 27.7                            | 130.1           | 97.50           |                  |
| TiCl$_4$  | 227.8           |                               | 20.2                            | 140.2           | 120.30          |                  |
| FeCl$_3$  | 220.7           |                               | 1.7                             | 146.1           | 135.80          |                  |
| No activator |                  |                               |                                 | 150.9           | 160.31          |                  |

Therefore, chlorides of Al, Ti, Zn contribute to the destabilization of sulfur rings and, as a result, their opening. They encourage the formation of sulfur radicals by increasing the reactivity of a sulfur component. The reactivity of sulfur modifiers was found to decrease in a series of Zn>Al>Ti>Fe.
Next, the paper discusses the effect metal chlorides (Al, Zn, Ti, Fe) have on a silicate component. A series of advanced physico-chemical and theoretical analysis methods was used to evaluate the activation of the surface of opal-cristobalite-tridymite phase under the influence of zinc, aluminum, titanium and iron chlorides and during chemical interaction between the activator and amorphous silica.

In the simulation experiment zinc, aluminum, titanium and iron chlorides were used for activation of surface silanol groups.

The samples of silica gel modified with metal chlorides (Al, Zn, Ti, Fe) were studied using electron paramagnetic resonance (EPR). Electron-hole centers were recorded with EPR method, and represent defects of the crystalline structure of the studied objects. In general, electron-hole centers can be described as special electronic structures of atom clusters, which are associated with defective areas in the atomic structure that have taken over an electron or electron hole.

The EPR spectrum for paramagnetic centers (in this case, for electron-hole centers) is represented with a single line with g-factor ≈ 2.00, as well as g-factor ≈ 4.2. The shape, width and position of the line in a magnetic field scale (H=3300 Gs, g ≈ 2.036) correspond to those for paramagnetic centers (free radicals) formed due to broken chemical bonds.

Table 2 shows a number of electron-hole centers (in conditional units) in the samples of initial and modified silica gels.

| No | Sample                      | number of electron-hole centers (cond. un.) |
|----|-----------------------------|--------------------------------------------|
| 1  | Dried silica gel            | 24                                         |
| 2  | Modified silica gel (AlCl₃~5%) | 96                                         |
| 3  | Modified silica gel (ZnCl₂~5%) | 115                                        |
| 4  | Modified silica gel (TiCl₄~5%) | 77                                         |
| 5  | Modified silica gel (FeCl₃~5%) | 31.5                                       |

The maximum number of electron-hole centers (115 cond. un.) was recorded in sample 2. The chemical modification with aluminum chloride results in intended change in chemical properties of the silica gel surface. The vacant d-orbitals in the resulting silica gel – aluminum chloride system are electron-hole centers of the surface. Table 2 shows that modification with aluminum chloride (AlCl₃~5%) leads to a higher number of electron-hole centers (up to 96 cond. un.). Modification with zinc and titanium chloride also gives a significant increase in a number of electron-hole centers, the lowest increase is observed for iron chloride: 31.5.

Therefore, we get the material with active centers on the surface. Chemical modification of a silicate surface with chlorides of Zn, Al, Ti, Fe results in intended change of its chemical properties. It shows that modification increases a number of electron-hole centers by 4.8 times for zinc chloride, by 4.0 times for aluminum chloride, by 3.2 times for titanium chloride and by 3.15 times for iron chloride.

Conclusion
The quantum chemical and physical mechanical studies showed that the resulting polysulfides of metal silicates had high energy of Me-S bond and were thermodynamically stable compounds. The formed polysulfides of metal silicate make sulfur concrete homogeneous and durable, and give it high strength, corrosion resistance, frost resistance and low water absorption [18-20].

In case of optimal filling rate, almost all sulfur changes to more homogeneous and finely crystalline state. Under the influence of the electrophilic activator (metal chloride), chemical interaction between sulfur and filler surface contributes to a significant increase in strength.
We developed the sulfur concrete technology based on activation of system components with metal chlorides and formation of sulfides. The paper proposed the process flow design and instrumentation to produce sulfur concrete. It specifies the optimal process conditions.

The designed technologies help to efficiently recover sulfur from the oil and gas industry as there has been its overproduction lately. Production cost of the designed materials is lower than that of the known analogues by 26-40%. The designed materials can be used in road construction for roadbed, paving slabs, curbstones, pavestones, gutters.

References
[1] Review of technologies, methods and practices of sulfur utilization in Russia INFOMINE Moscow, 2015, 100 p.
[2] Y.I. Orlovsky, A.S. Semchenkov, V.I. Kharzhevsky 1995 Concrete and products based on sulfur-containing industrial wastes Concrete and reinforced concrete vol. 3 pp. 21-24.
[3] A.P. Groshin, E.V. Korolev, E.G. Kalinkin 2005 Structure and properties of modified sulfur binder Building materials vol. 7 pp. 6-9.
[4] E.V. Korolev 2003 Building materials based on sulfur Penza-Saransk p. 372.
[5] E.V. Korolev, A.P. Proshin, V.T. Erofeev, 2003 Construction materials based on sulfur PGASA Penza p. 372.
[6] E.V. Korolev, A.P. Proshin, V.T. Erofeev 2003 Construction materials based on sulfur PGASA, Penza p. 372.
[7] V. Voronkov (Ed.) 1979 The reactions of sulfur with organic compounds Nauka Novosibirsk p. 179.
[8] W. A. Pryor 1962 Mechanism of Sulfur Reaction New York – San Francisco – Toronto – London, McGraw-Hill Book Co p. 335.
[9] Zh. T. Suleimanov, M.Sh. Ospanov, A.A. Iglikov 2007 Concretes on the basis of associated sulfur and phosphorus slags Building vol. 2 pp. 113-115.
[10] N.V. Usmanov 2007 Consumer properties of sulfur Building materials, equipment, technologies of the XXI century vol. 3 pp. 41-44.
[11] W. A. Pryor 1962 Mechanism of Sulfur Reaction, New York – San Franciso – Toronto – London, McGraw-Hill Book Co p. 335.
[12] A.F. Wells 1975 Structural Inorganic Chemistry, Oxford University Press, Ely House, London, p. 1127.
[13] V.B. Aleskovskiy 1987 Directed synthesis of solid matters, Moscow p. 255.
[14] G.V. Lisichkina 1986 Modified silica in sorption, catalysis and chromatography Moscow, Chemistry p. 247.
[15] S.I. Koltsov 1967 Study of the interaction of titanium tetrachloride with silica gel Russian Journal of Applied Chemistry vol. 4 pp. 907-950.
[16] V.B. Aleskovsky 2007 Quantum synthesis Russian Journal of Applied Chemistry vol. 11 pp. 1761-1767.
[17] V.G. Rau, K.W. Skvortsov, K.A. Potekhin, A.V. Maleev 2011 Geometric analysis of molecular nanoclusters of sulfur (S8)x in a computer experiment Russian Journal of Structural Chemistry vol. 4 pp. 781-786.
[18] T.G. Akhmetov, R.T. Porfiryeva, L.G. Gaisin, L.T. Akhmetova, A.I. Khatsrinov 2002 Chemical Technology of Inorganic Substances High School, Moscow p. 533.
[19] A.A. Yusupova, A.G. Shamov, R.T. Akhmetova, V.A. Pervushin, A.I. Khatsrinov 2011 Titanium tetrachloride as electrophilic activator in technology of inorganic polysulfides Journal of Quantum Chemistry vol. 11 pp. 2575-2578.
[20] R.T. Akhmetova, A.A. Yusupova, L.R. Baraeva, G.I. Sabahova, V.A. Pervushin, A.I. Khatsrinov, G.A. Medvedeva A.Y. Akhmetova. Patent No. 2555166 Binder / 06/01-2015