CHARACTERISATION OF SOLID SULFUR IN THE TENGIZCHEVROIL

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ABSTRACT

The present paper treats some issues referring to processing of high-sulfur oil in Tengiz RK. Those connected with the environmental aspects of open storage of sulfur on sulfur maps close to the oil refinery factory are focused on as the amounts of open storage sulfur increase in parallel with the increase of oil production. It is pointed out as well that the method of underground sulfur storage is not acceptable for Kazakhstan due to the presence of water in the upper layers of the rocks in the areas of sulfur storage.

Sulfur storage as sulfur cards is the cheapest and easily realized method. According to a number of research institutes in Kazakhstan and the Canadian Institute of Alberta, which is recognized as the world's leader in sulfur storage, sulfur cards do not affect the environment. But coating of the sulfur maps surface is required to avoid negative atmospheric effects.

Experimental data referring to certain physico-chemical characteristics of sulfur in absence and presence of a surfactant/polymer coating is presented.

Keywords: sulfur maps, environmental protection, surfactants, polymer complexes, process of Claus.

INTRODUCTION

Tengiz oil and the gas there contain about 14 % of hydrogen sulfide [1]. Environmentally more hazardous substances - sulfur anhydride, hydrogen sulfide and mercaptans should be converted to less dangerous forms of sulfur [2] to reduce the presence of sulfur compounds in petroleum products. Therefore, oil has to be purified from sulfur. At the factory, the oil and the accompanying gas are separated. This step is followed by transformation of hydrogen sulfide into water and sulfur. After that, the liquid sulfur obtained is sent for granulation, or poured into cisterns or sulfur cards. Currently, TCO produces 4 types of sulfur: granular, scaly - by the standards of China, liquid and lump. The latter is stored on cards in the form of blocks [1].

The environmental issues of open sulfur storage on sulfur maps have always drawn public's attention. There are numerous investigations on the storage of sulfur produced in the course of oil refining. [3 - 5]. The effect of open storage sulfur of Tengiz RK on the environment is investigated by Kazakhstan scientific research institutes together with the Canadian Institute of Sulfur located in Calgary. Based on the results, it is concluded that the effect of sulfur maps on the environment is limited to the production site where the technological operations on sulfur treatment are carried out. Thus, it is concluded that it is harmless to humans.

The method of sulfur storage on open sulfur maps is the cheapest and easily realized one. It determines the sulfur producing companies. The sulfur maps of TCO refer to a specific site for the placement and storage of technical sulfur in blocks. The latter comprise of solid sulfur obtained by layer wise pouring of liquid sulfur into specified forms for long-term storage. Blocks have a size of the order of 300 m x 400 m and a height of 12

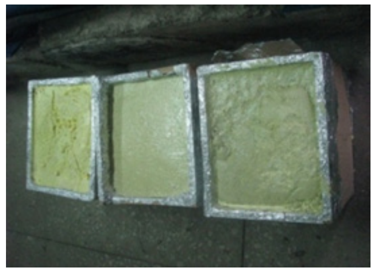


Fig. 1. Sulfur of TCO.

m (Fig. 1a). The blocks sulfur is characterized by hardness and an weak cement ability between the layers of filling (Fig. 1b).

However, open long-term storage of sulfur can be potentially environmentally hazardous due to factors such as generation of H_2SO_4 by sulfur bacteria, self-destruction of blocks, distribution of elemental sulfur in the form of dust and aerosols, evaporation of H_2S, possible ignition of sulfur with the release of sulfur dioxide. Therefore, it is necessary to protect the surface of the open sulfur card from the atmospheric effect.

EXPERIMENTAL

Materials and methods

The anionic surfactant sodium dodecyl sulphate (SDS) and the cationic surfactant cetyltrimethylammonium chloride (CPCL) (99 mass % purity) were purchased from Sigma-Aldrich Co. and were used as received. Polyacrylic acid (PAA) of a molecular weight of 100 KDa was purchased from Waco Pure Chemical Industries, Ltd. (Osaka, Japan), while polyvinylpyrrolidone (PVP) powder of a molecular mass of 360 KDa was purchased from Aldrich chemistry (USA).

Dynamic laser light scattering (DLS) «Malvern Zeta sizer Nano ZS90 (UK) » was developed as a technique to measure the size of solid nanoparticles in aqueous sulfur suspensions.

Spectraturbid metric titration of solutions of the sulfur - surfactant complex was carried out at $\lambda = 400$ nm using «UV-210 plus BU» (Germany) spectrophotometer.

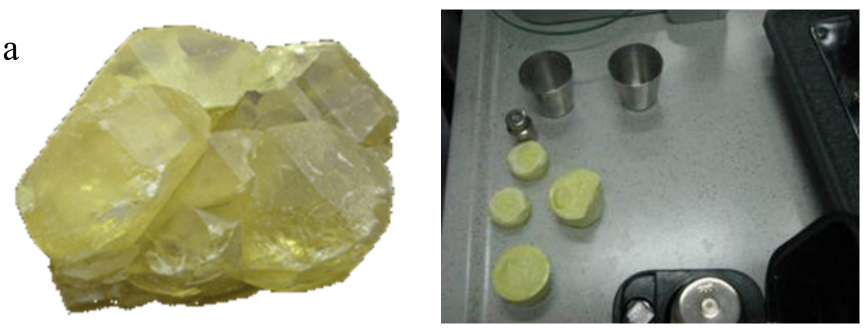
Atomic Force Microscopy (AFM) was carried out on AFM XE-70 Park system at 25^0C in no contact mode using samples with aluminum.

The pH of the solution was measured with Mettler-Toledo pH meter (Switzerland). The conductometric titration of polymers solutions was carried out with ES-215 conductivity meter. The structural analysis of the sulfur block samples was carried out with the metallographic microscope METAM LI-31 in reflected light.

RESULTS AND DISCUSSION

A cylindrical or conical stamp with a flat base is pressed using a special Mechanical installation with a hydraulic press unit aiming to determine the sulfur hardness on the ground surface of a rock sample of plane-parallel faces. The most convenient geometric form of the indenter (stamp) is that of a cylindrical die with a flat base. In this case, there is no contact area increase during indentation, which is in fact observed during the pressing of a cone, a wedge or a sphere. These samples,

a



b

Fig. 2. Natural sulfur (a) and solid, obtained from liquid sulfur (b).

Table 1. Hardness values of block sulfur samples.

Sample number Block sulfur	Capacity, N		
	Indenter 1 F=7,0 x $10^{-6}$$m^2$	Indenter 2 F = 12,56 x 10^{-6} m^2	Indenter 3 F=19,62 x 10^{-6} m^2
Sample 1	18,4	32,7	50,0
Sample 2	18,0	32,9	51,0
Sample 3	18,2	32,8	52,0
Average value	18,2	32,8	51,0

30 mm - 50 mm high and 40 mm - 60 mm in diameter, should have two plane-parallel surfaces, which are obtained by grinding with an abrasive powder (Fig. 2).

The recording of the graphs in the coordinates "the depth of the insertion of the stamp - the load" is automatically carried out at a special mechanical installation with a hydraulic press. The principle operation of the plant is based on a method developed under the guidance of Prof. L.A. Schreiner. The installation is designed for a load of 0 - 1000, 0 - 2500, 0 - 5000 and 0 - 10000 with a maximum penetration value of 750 microns and provides to obtain, working on a single tape, several load schedules on the ground of the value of the injection carried out at different points. This provides to follow the homogeneity of the sample and the corresponding scatter of values. The latter determines the necessary number of experiments referring to a single sample. The experimental data on the hardness of block sulfur samples is given in Table1.

The hardness of such bodies is described as:

$$P_h = P_p / F \quad (1)$$

where P_h is the hardness stamp (N/м^2), P_p is the load at the time of the general destruction (N), while F is the area of the stamp (m^2).

The hardness values of a sulfur block sample are:

$$P_h^1 = \frac{18.2}{7x10^{-6}} = 2.6x10^6\ N/m^2 = 2.6MPa$$

$$P_h^2 = \frac{32.8}{12.56x10^{-6}} = 2.61x10^6\ N/m^2 = 2.61MPa$$

$$P_h^3 = \frac{51}{19.62x10^{-6}} = 2.599x10^6\ N/m^2 = 2.599MPa$$

Thus, the average hardness value is 2.6 x 107 Pa, which corresponds to the 2nd Mohs strength group, and the 2 group according to L.A Schreiner's scale.

Since sulfur is stored in the open, periodic precipitation in the form of rain, as well as the direct sunlight can lead to the occurrence of chemical processes.

For research of the oxidation of elemental sulfur under the influence of moisture and UV radiation, the sulfur particles are washed several times with bidistilled water and the aqueous sulfur suspension resulted is placed in a quartz cuvette of the spectrophotometer. The cuvette is frozen several times and thawed to remove the air (oxygen) from the solution. The system is purged with nitrogen and irradiated at wavelengths of 253.7 nm and 366 nm for more than one day. The dependence of the solution pH on the time of irradiation is followed (Fig. 3).

It is seen that the pH value of the unirradiated solution containing suspended sulfur does not exceed 4 pH units despite the careful washing of elemental sulfur. This means that traces of sulfur dioxide are always present in the wet sample. The pH value of the the UV irradiated sample solution decreases exponentially and reaches 2.2 within 28 h of irradiation. It should be noted that UV irradiation of a suspension at a wavelength of 366 nm does not lead to a change in the pH of the medium.The data shows that, depending on the conditions,

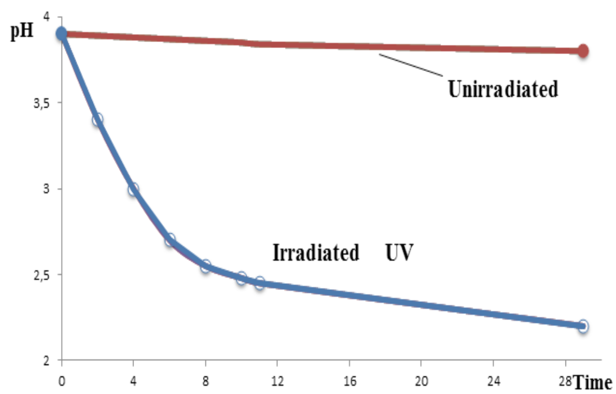
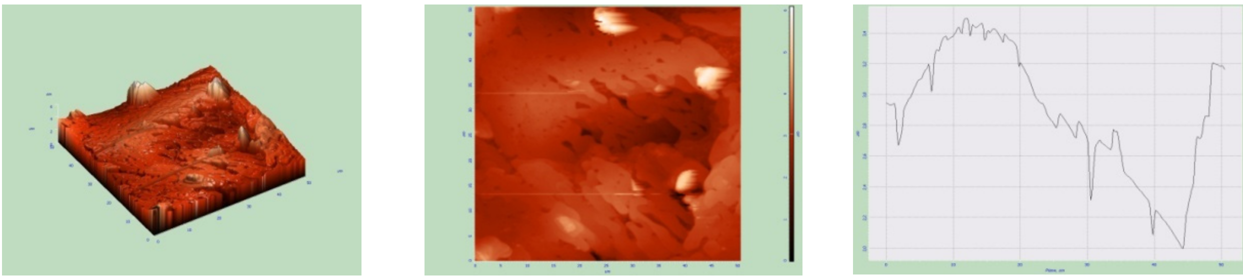
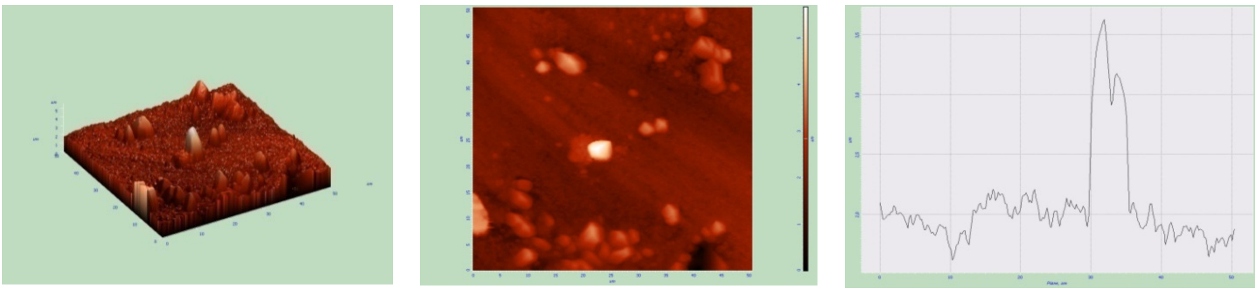


Fig. 3. pH change of an aqueous sulfur suspension prior to and after UV irradiation.



A (3D surface) B(2D surface) C (plot surface cross section)

Fig. 4. AFM micrographs of solid sulfur treated with PVP and SDS. (1:0.5 mol/mol)



A (3D surface) B(2D surface) C (plot surface cross section)

Fig. 5. AFM micrographs of solid sulfur treated with PAA and CPCL (1 : 0.5 mol/mol).

sulfur dust may be released from the sulfur maps surface, which may have negative consequences.

To protect sulfuric cards from atmospheric exposure, Tengizchevroil uses various coatings at its storage facilities, such as limestone, plaster-cement, and koalinic. But their application does not give the desired results.

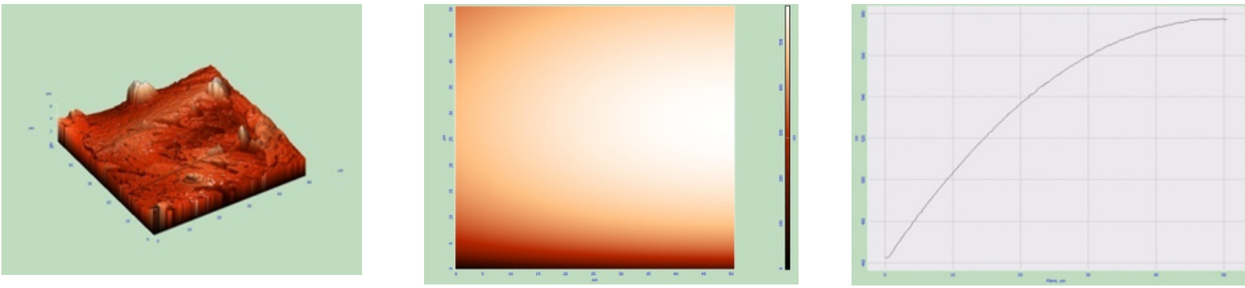
Recently Skarakho et al. [6] suggested a new method of sulfur surface protection from solar radiation heating. However, it is ineffective for sulfur maps.

It is considered expedient to use organic coatings based on polymers of structure-forming properties [7]. However, the hydrophobic surfaces of the sulfur blocks usually interact weakly with polymeric macromolecules. However, it is known that ionic surfactants interact with water-soluble polymers of various types [8, 9]. So it was customary to use a solution of surfactants and polymers [10] to impart hydrophilicity to sulfur blocks.

Three model samples of solid sulfur are prepared for their surface hydrophilization. Two of them are treated with a surfactant solution using a 0.05 mol/l pulverizer. After drying of the surface, 0.01 mol/l polymer solution in ethyl alcohol is additionally appllied. The first sample treated with a cationic surfactant, cetyltrimethylammonium chloride, is coated with a film of polyacrylic acid, while the second one, treated with the anionic surfactant dodecyl sulfate sodium, is coated with polyvinylpyrrolidone. The third sample is used for a comparison. The film formation on the prototypes can be followed in the photographs of the sulfur block surface.

Integra Prima atomic force microscope is used to study the properties of the polymer coating applied. The metallographic microscope allows performing structural analysis in reflected light with a digital video camera with a magnification from 50x to 1000x, performing high-precision measurements of microobjects, surface layers, coatings, films, composites, etc. The atomic force microscope is a high-resolution scanning probe microscope used to determine the surface relief with a resolution of tens of angstroms up to atomic resolution. The size of the scanning area ranges in the experiments carriued out from 5 μm to 50 μm. The surface relief of each sample is obtained as a 3D pattern. The topography of the surface (2D figure) of each sample is also obtained.

Fig. 4a shows the surface of the first sample of sulfur treated with polymer PVP ($C = 1 \times 10^{-2}$ mol/l) and SDS surfactant ($C = 5 \times 10^{-2}$ mol/l). The scan size of the test sample is 50 μm x50 μm/256 lines. The image processing shows an uneven rough surface. Figs. 4b and 4c illustrate



A (3D surface) B(2D surface) C (plot surface cross section)

Fig. 6. AFM micrographs of solid sulfur (control sample).

the topography and the cross section of the surface of the first sample. It is seen that the thickness of the sprayed film varies from 2 nm to 4 nm.

Fig. 5a shows the surface of the second sample treated with PAA polymer (C = 1 × 10^{-2} mol/l) and CPCL surfactant (C = 5 × 10^{-2} mol/l). The scan size of the sample is also 50 μm x 50 μm/256 lines. The results show that this sample has also an uneven surface after application of the polymer complex. Figs. 5b and 5c present the 2D surface and the cross section of the second sample. In this case, the film thickness about 2 nm - 2.5 nm is evident from the cross section of the sample.

Fig. 6a shows the surface of the third sample which is used for a comparison. It is seen that it is smooth with no roughness, breaks, small protrusions or depressions. The scan size of the sample is also 50 μm x 50 μm/256 lines. Figs. 6b and 6c present the topography and the cross section of the third sample, respectively.

The data shows that stable polymeric films are formed in case of hydrophilic surfactants application.

CONCLUSIONS

The article considers the current state of open storage on sulfur maps of sulfur from Tengiz RK. The hardness of the sulfur surface found equal to 2.6 x 10^7 Pa corresponds to the second strength group on the Mohs scale, and the 2 group on the Schreiner scale LA. The results referring to the oxidation of elemental sulfur under the influence of moisture and UV radiation of the sulfur particles show that trace amounts of sulfur dioxide can exist in the moist sample, which contributes to a change of the solution pH. To protect the cards sulfur from the atmospheric effect the surface is hydrophobized by surfactants and further treated by a polymer solution for the formation of a surface film. It is experimentally verified that the surface of the polymer film obtained is resistant to external weathering.

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