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COMPOSITION AND PROPERTIES OF PETROLEUM SLUDGE PRODUCED AT THE REFINERIES

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Abstract. Petroleum sludge composition and physico-chemical characteristic and thermal stability of its organic matter have been investigated. The regularities of sludge layers distribution in the storage ponds have been established.

Keywords: petroleum sludge, lubricating fluid, oil basis.

1. Introduction

A great amount of petroleum sludge is formed during oil processing at the refineries. It is stored in special storage ponds of the open type. Sludge is formed as a result of waste water treatment, during repair works, reservoirs cleanup, *etc.* [1]. Petroleum sludge is capable to penetrate into ground and to pollute water and air [2]. Moreover, hydrocarbons present in sludge are irreversible losses at the refineries. The amount of sludge constantly increases. Therefore the problem of its utilization is an urgent question [2].

The existing methods of sludge utilization do not allow to treat it completely. In most cases only organic matter of sludge is under processing but a considerable amount of solid wastes and contaminated water remains untreated [3]. While burning – the most common utilization method – a great amount of ash is formed and contaminates the environment [4]. The main method of sludge primary treatment is separation of organic matter from water and mechanical impurities [5]. Sludge organic matter may be added to the crude oil supplied for the refineries [6] but sometimes it is impossible due to the peculiarities of oil and sludge composition. One of the ways of sludge utilization is its usage for the production of bitumen [7, 8], building [9] and lubricating materials [10]. The promising methods of sludge treatment are pyrolysis and coking [11-13] as a result of which hydrocarbon gases and distillates are formed. Nevertheless all the mentioned methods were studied insufficiently; therefore the problem of sludge treatment is still unsolved. Our approach to the problem solving includes two stages: the first one is studying physico-chemical properties and group composition of petroleum sludge in detail and the second one – investigation of possibility of sludge qualified treatment.

2. Experimental

For the experiments we used sludge recently formed at Turkmenbashi Refinery (Turkmenistan). To study the sludge composition and properties as well as to determine phase separation we withdrew samples at different heights and different places of the core pool; then averaged samples were prepared.

To separate the organic matter the multistage process was used consisting of settling at elevated temperature, washing by water, drying and filtrating at elevated temperature.

Physico-chemical properties of the sludge organic matter were determined using the known methods [14]. The content of asphaltene-tar substances in the sludge organic matter was determined using Marcusson method [14]. The content of separate groups was determined by means of chromatographic method using silicagel of ASK type. Petroleum ether, benzene and alcohol-benzene mixture were used for washing [14].

Thermal stability of the sludge organic matter was studied using Q-1500 D derivatograph of Paulic-Paulic-Erdey system with computer recording of analytical signals of weight loss and thermal effects. The samples were analyzed under dynamic regime with the heating rate of 5 K in argon medium. The samples weight was 0.2 g. Aluminum oxide was used as a reference substance.

3. Results and Discussion

Petroleum sludge consists of organic phase (hydrocarbons, heteroatom compounds and asphaltene-tar substances), water phase and mechanical impurities (sand, clay, *etc*.). In most cases these phases form complex emulsion-suspension system which is hardly separated. Moreover, the composition and properties of sludge vary along the depth of the storage pond. Therefore we studied samples picked near the surface and different depths of the storage pond.

The analysis of investigated samples shows (Table 1) that the content of water, mechanical impurities and organic (hydrocarbon) matter varies within wide range. The appearance of the samples varies as well.

The upper layer (PS1) is an oil-residue mixture consisted of organic (hydrocarbon) matter and small amount of water and mechanical impurities. It is the layer of trapped petroleum product.

The medium layer formed in the storage pond is water layer. It mainly consists of water polluted by petroleum products and mechanical impurities. In this intermediate layer the suspension-hydrocarbon aggregates are settled and emulsive and dropping hydrocarbons are floated.

Under the water layer the petroleum sludge layers are situated, namely:

– fresh sludge (PS2) – very mobile layer of saturated black color caused by the great amount of tar components entrapped by mechanical impurities during their settling;

– emulsive sludge (PS3) – layer of dark-grey color with high viscosity typical of concentrated emulsion. It contains hydrocarbons in the complex suspension-emulsion aggregative state together with small mechanical impurities;

– suspension sludge (PS4) – layer of light-grey color with pronounced plastic-viscous properties typical of pastes or mastics. It contains medium-sized mechanical impurities and hydrocarbons, the main part of which is adsorbed over the surface;

– bitumen sludge (PS5) – stiff layer of grey-black color. It is not mobile at low temperatures and consists of pressed hydrocarbons plus mechanical impurities.

To establish the possibility of further treatment of sludge hydrocarbon matter we studied its physico-chemical properties. The results are represented in Table 2.

The nature of changes in sludge properties reproduces the previously made hypothesis about the distribution of sludge layers along the depth of the storage pond. The physico-chemical properties of PS1 are similar to those of oil heavy fractions. The content of light fractions in this sample is 30 wt % at low values of specific viscosity, coking capacity and freezing point. Therefore in the future this product can be added to the crude oil but it is necessary to determine the peculiarities of their mixing.

Table 1

Petroleum sludge composition

Content in petroleum sludge	Sample number				
	PS1	PS2	PS3	PS4	PS5
Water, wt %	2.5	38.7	26.9	12.6	6.1
Mechanical impurities, wt %	0.3	5.3	12.2	24.9	28.7
Organic matter, wt %	97.2	56.0	60.9	62.5	65.2

Note: The samples were taken along the depth of the storage pond so that sample PS1 was taken at the surface and sample PS5 – at the bottom, respectively.

Table 2

Physico-chemical properties of sludge organic matter

Index	Index values				
	PS1	PS2	PS3	PS4	PS5
Density at 293 K, g/cm^3	912	924	932	946	958
Specific viscosity at 353 K	3.3	6.5	8.9	12.4	14.9
Specific viscosity at 373 K	1.2	2.5	3.1	3.5	3.8
Content of mechanical impurities, wt %	traces	traces	traces	traces	traces
Water content, wt %	0.2	0.3	0.3	0.5	0.6
Sulfur content, wt %	0.91	1.06	1.09	1.15	1.34
Freezing point, K	266	272	281	287	294
Flash point, K	352	364	387	410	468
Coking capacity, wt %	2.3	4.1	5.7	7.3	8.9
Ash content, wt %	0.18	0.21	0.24	0.26	0.38
Fractional content:					
boiled till 473 K, wt %	4.2	2.3	1.8	1.2	0.3
boiled till 623 K, wt %	25.7	18.7	16.4	13.1	8.2

Table 3

Carbon group composition of the sludge organic matter

Index	Index values				
	PS1	PS2	PS3	PS4	PS5
Content of paraffin-naphthene hydrocarbons	18.2	17.4	17.8	19.2	22.3
Content of monocyclic aromatic hydrocarbons	22.8	20.5	21.7	18.4	15.2
Content of bicyclic aromatic hydrocarbons	27.8	27.8	21.5	19.2	14.4
Content of polycyclic aromatic hydrocarbons	26.3	28.2	30.2	31.7	34.9
Content of asphaltene-tar substances	4.9	6.1	8.8	11.5	13.2

Table 4

The results of sludge samples thermal analysis

Sample	Stage	Temperature range, K	Weight loss, %	Effect
PS2	I	293–608	19.4	Endothermal (293–553 K) Exothermal (553–608 K)
	II	608–753	56.6	Endothermal
	III	753–1073	15.92	Exothermal
PS4	I	293–618	14.4	Endothermal (293–544 K) Exothermal (544–618 K)
	II	618–755	56.4	Endothermal
	III	755–1073	19.7	Exothermal
PS5	I	293–644	9.8	Endothermal (293–573 K) Exothermal (573–658 K)
	II	644–758	54.7	Endothermal
	III	758–1073	26.25	Exothermal

While deepening into the storage pond (the sample number increases from PS2 to PS5) the amount of light fractions decreases in sludge and its density increases. Moreover, the specific viscosity, freezing point and flash point increases as well. All these facts testify to the weighting of fractional content with deepening into the storage pond.

To characterize the change of sludge components chemical structure we studied their carbon group composition. One can see from Table 3 that sludge bottom layers are characterized by 2-3-fold increase in the content of asphaltene-tar substances and slight increase in polycyclic aromatic hydrocarbons compared with upper layers. The deeper the position of the sludge layer, the higher the values of coking capacity and ash content, which is in full agreement with carbon group composition.

The important property of the sludge organic matter is its thermal stability. To determine the temperature range of the components thermal decomposition and study their behavior while heating we conducted derivatographic investigations. Derivatogram of the organic matter of the upper layer (PS2) is represented in Fig. 1 and derivatogram of the bitumen sludge (PS5) – in Fig. 2. Table 4 represents the results of TG, DTG and DTA analyses. The comparison of TG and DTA curves is represented in Figs. 3–4.

Within the range of 293–758 K the mass loss is observed at TG curves, which is accompanied by the appearance of clear endothermal effect on DTA curves and corresponds to the release of sludge volatile components. The process becomes complicated by polycondensation of the most high-molecular unstable components. The appearance of exothermal effect on DTA curves at the temperature above 544 K indicates this fact.

The intensive mass loss within the temperature range of 608–758 K corresponds to the proceeding of sludge components thermal destruction. The appearance of clear endothermal effect on DTA curves indicates this fact. The destruction is completed by consolidation of sludge heavy residue accompanied by heat absorption jump. The appearance of exothermal effect on DTA curves at the temperatures above 523 K and simultaneous decrease of mass loss rate confirm this.

At the temperatures above 753 K the intensity of mass loss sharply decreases. The reason is that consolidation processes predominate over the destruction ones. The clear exothermal effect typical of condensation and coke forming appears on DTA curves.

On the basis of thermal analysis results we conclude that the sample PS2 has the greatest amount of volatile components released in the area of relatively low temperature (Fig. 3). In this sample thermal destruction proceeds more intensively. The confirmation is an appearance of deeper endothermal effect on DTA curve at the temperatures above 753 K accompanied by the greatest mass loss (Table 4, Figs. 3–4) compared with other samples. The sample PS5 contains the least amount of volatile hydrocarbons. In this sample the consolidation processes predominate over the destruction processes in the area of high temperatures. The confirmation is an appearance of intensive exothermal effect at the temperatures above 753 K.

4. Conclusions

On the basis of investigation results concerning petroleum sludge composition and physico-chemical properties of its organic matter we propose layering structure of the petroleum sludge in the storage pond. By means of derivatographic investigations we determined the main stages of organic matter thermal conversions of the sludge picked at different levels of the storage pond. The investigation results may be used for the development of technological bases of sludge treatment.

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СКЛАД І ВЛАСТИВОСТІ НАФТОВИХ ШЛАМІВ, УТВОРЕНИХ НА НАФТОПЕРЕРОБНИХ ЗАВОДАХ

Анотація. *Наведено результати досліджень складу нафтошламів та фізико-хімічних характеристик їх органічної частини. Вивчено термічну стабільність органічної частини нафтошламів. Встановлено закономірності розподілу шарів нафтошламів у ставках-накопичувачах.*

Ключові слова: *нафтошлам, мастильна рідина, оливна основа.*