Recycling of waste to secondary raw materials as a way to increase environmental safety of production

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Abstract. Complex influence of the ground of waste of the oil refinery including three sections of a pond store, a pond evaporator, a pond - the store of synthetic fatty acids, a dump of solid industrial wastes, the card of viscous waste of production of additives on the environment is investigated. It is revealed that the main pollutant are oil products (oil hydrocarbons), the steady trend of their accumulation in the environment is noted.

It is established that extent of utilization of the petrowaste which is valuable secondary raw materials is small that leads to their accumulation on the grounds and sludge collectors which are sources of environmental pollution. Extent of recycling of production of additives is especially low that is explained by their complex structure causing the low productivity and high cost of technological process of their processing.

The scheme of the organization of monitoring of a condition of the environment around placement of the ground of waste including control of a condition of the atmosphere, underground waters and soils is offered.

Reduction of environmental pollution by waste of oil processing due to their greatest possible secondary use and consequently, and economy of scarce and expensive natural raw materials, it is possible only in the presence at the enterprise of the comprehensive program of waste management.

The theoretical and pilot researches directed to decrease in negative impact of the ground of waste of oil refineries on the environment are conducted, the method of liquidation of the map of viscous production wastes of additives with use of production wastes of the additive DF-11 (KEK) is developed.

Landfills of oil refineries occupy significant areas, and are constant sources of environmental pollution due to evaporation of oil products and their entering into groundwater. Consequently, a comprehensive assessment of negative environmental impact by the refinery waste landfill and the development of measures to reduce this impact by increasing the usage of oil waste in construction and other industries are very relevant tasks [28-31].

The main objective of the research is to study composition and properties of additive production waste produced by the Volgograd refinery on the basis of “Lukoil” LLC. The composition and properties of additives production wastes were studied, it was found that the additives production DF-11 KEK is a polyampholyte with a high static exchange capacity both for HCL and NaOH, and the processes occurring during the chemical interaction contents of the viscous waste card with KEK can be characterized as a physical and chemical sorption with the ion exchange reactions, complexation,
oxidation-reduction reactions, also, was studied the influence of the main factors on the interaction of KEK with oil waste.

It is known [4,5–10] that, based on the petroleum products waste, high-performance powdered and granular ionites have been obtained.

Ionites are insoluble solids that can exchange ions in them. They have ion exchange properties as natural compounds (aluminosilicates, zeolites), in which alkali or alkaline earth metals ions, located in the crystal lattice, can be exchanged for ions of a liquid or gaseous phase, as well as synthetic resins. Known ionites with complexing, oxidation-reduction and electron-exchange properties.

Based on a previous analysis of the composition of the waste additives, it can be assumed that the waste additive DF-11 (KEK) is a polyampholyte.

One of the main sorbents properties is static exchange capacity (SOE). The value of SOE was determined according to the procedure [1,12,27]. Obtained data shown in table 2. An analysis of the data presented shows that KEK has a fairly high SOE in both HCL and NaOH, significant normal humidity, and a high degree of swelling.

Swelling is an important property of ionite, which provides high speed and significant efficiency of ion exchange. Water in petroleum products can be in solutions, in a free state, and also in the form of emulsions. Very stable emulsions are formed in cases where the density of oil products and water differ slightly from each other. The stability of emulsions increases in the presence of resinous compounds, macromolecular substances, as well as sulfur, nitrogen and oxygen compounds. Free water causes the complete saturation of petroleum products and is a source for the formation of water-fuel emulsions.

The presence of KEK ion-exchange properties can be explained by its composition and chemical structure.

As mentioned earlier, OPP DF-11 includes oxygen-containing substances - alcohols having an active basic group R-OH, which allows to conclude that the OPP DF-11 has an anion exchange properties.

For KEK is typical to have high content of inorganic substances, with up to 50% of them being Al2O3.

Aluminum compounds are characterized by an ionic bond. Ion Al3+, having a small radius and a large charge, is prone to complexation. As for all ions of p- and s- elements, Al3+ is also characterized by the complexes formation with water, OH. The tendency toward complex formation is manifested in the presence of a large number of crystalline hydrates and crystalline solvates of aluminum compounds [24,25]. In water-rich crystalline hydrates and aqueous solutions of aluminum salts are contained octahedral complexes. With hydrogen ions, Al3+ forms a tetrahedral complex [2,3,6,7,18-22].

It is most likely, that during the interaction of aluminum-oxygen KEK component with oil waste occurs isomorphic substitution in the tetrahedral layer Al3+ on a doubly charged ion of barium, calcium or magnesium. In reaching a certain degree of KEK crystals saturation with ions, a “collapse” can be observed, i.e. sharp compression of the crystalline packet, in which it "closes", forming another aluminum-containing crystal [3,17-19,21].

Table 1 shows the physic-chemical properties of aluminum oxide contained in KEK (sample 1) compared with finely dispersed aluminum oxide (sample 2), aluminum oxide mixed with other inorganic residues of oil waste (sample 3) and aluminum oxide in KEK after calcination at temperature 300 °C (sample 4). For the study, samples were taken containing the same mass of Al2O3, taking into account its concentration.

Hygroscopic humidity was determined by a standard method with a temperature of 20°C and a relative humidity of 65%. The specific surface area was found from the isotherms of sorption-desorption of caprylic acid, sedimentation in water and industrial oil. Porosity was determined according to the procedure [4,15-17].
An analysis of the obtained data shows that $\text{Al}_2\text{O}_3$ has a high porosity, a significant specific surface, smaller than that of the initial aluminum oxide, which is explained by the influence of organic substances contained in KEK.

Aluminum oxide in KEK contains a significant amount of adsorption-bound water (9.6%), and this moisture is not only on the surface, but also probably fills the pore space. Noted circumstance contributes to an increase in the overall moisture content of KEK, and increases the degree of swelling and increases the ion-exchange ability.

### Table 1. Physico-chemical properties of aluminum

| Indicator                                           | Sample |       |       |       |       |
|-----------------------------------------------------|--------|-------|-------|-------|-------|
| Porosity, %                                         | 1      | 2     | 3     | 4     | 5     |
| Hygroscopic humidity                                | 1.38   | 1.36  | 0.99  | 0.98  |       |
| The amount of adsorption bounded water, %           | 9.6    | 13.52 | 7.58  | 5.9   |       |
| Specific surface area, cm$^2$/g, determined by the method of sedimentation in water industrial oil sorption-desorption of capric acid | 2524   | 3476  | 3398  | 3208  |       |
|                                                     | 3079   | 5005  | 3398  | 4096  |       |
|                                                     | 28930  | 31500 | 29420 | 24040 |       |

KEK contains about 8.1% SiO$_2$. Given the technological process for producing the DF-11 additive, it can be assumed that silicon dioxide is present in the form of silica gel $\text{SiO}_2\cdot\text{H}_2\text{O}$, which is one of the most widely used sorbents. It has high porosity and has a huge specific surface area.

Aluminum, silicon dioxide, magnesium and calcium can also be included in the KEK composition in the form of aluminosilicates, for example, in the following composition $\text{M}^{n+}/(\text{Al}_2\text{O}_3)_k(\text{SiO}_2)_i\cdot m\text{H}_2\text{O}$, where M is an alkaline-earth metal ion. These are the so-called zeolites, which are widely used in sorption processes. As indicated above, alkaline earth metal ions in the crystal lattice can be exchanged for ions of liquid or gaseous phase of the sorbate [26].

In addition to silica gel, KEK contains sulfur and phosphorus, which can be part of various functional groups, including $-\text{SH}$, $-\text{SO}_3\text{H}$, and $-\text{PO(OH)}_2$, which makes it possible to characterize KEK as cation exchanger. It should be noted that phosphate cation exchangers are highly selective for ions of chromium, copper, zinc, cadmium, nickel and some others, due to the complexes formation.

Thus, the processes occurring during the interaction of KEK with oil waste can be characterized as physico-chemical sorption with the ion exchange reactions, complexation, and oxidation-reduction reactions.

The waste from the DF-11 additive production is formed by filtering the neutralized product through an inlet filter layer on a strainer. KEK is a gray powder with the following fractional composition (% mass.): Less than 0.1 $\mu$m - 64, (0.1÷0.25) $\mu$m - 21, (0.25÷0.5) $\mu$m - 13, more than 0.5 $\mu$m - 2. Physico-mechanical properties were investigated by standard methods and are shown in table 2. The static exchange capacity was determined by the method of [1,21,27]. The same table shows the properties of the sorbent GP, the processing product of the OPP and KEK components map after calcination at a temperature of (105÷110)$^\circ$C.

The high sorption parameters of GP are explained by the mentioned above structural features of KEK and the processes that occurs during heat treatment.

### Table 2. Physico-mechanical properties of ionites
| Sorbent         | Density, g/m³ | Apparent density, g/m³ | Normal humidity, % | Swelling in water, % | Static exchange capacity, mg-eq/g |
|-----------------|---------------|------------------------|--------------------|----------------------|----------------------------------|
| 1               | 2             | 3                      | 4                  | 5                    | 6                                |
| KEK             | 11            | 0.41                   | 37                 | 40                   | 4.9 on HCL 5.2 on NaOH           |
| GP (after calcination) | 1.76        | 0.56                   | 38                 | 46                   | 2.2 on HCL 2.4 on NaOH           |
| ГП (after drying) | 1.78        | 0.59                   | 42                 | 44                   | 2.1 on HCL 2.6 on NaOH           |

Note: The arithmetic mean sampling error is 12.3%. The coefficient of variation does not exceed 15%.

**Figure 1.** The processed product viscosity dependence on the concentration of KEK:
KEK: 1 – KEK:OP = 1:1; 2 – KEK:OP:GP = 1:4:1; 3 – KEK:OP:GP = 1:1:2

**Figure 2.** The processed product viscosity dependence on temperature:
1 – KEK:OP = 50:50 (%); 2 – KEK:OP:GP = 37.5:50:12.5 (%); 3 – KEK:UP:TP = 25:25:50
An analysis of the data in tables shows that the product of KEK and OPP (GP) interaction can be used as a sorbent in the map of viscous waste PP liquidation, both independently, and in mixture with KEK.

When KEK is mixed with the components of the viscous waste map, a paste-like mass is formed (viscosity according to a standard viscometer is 75-100s). Viscosity was determined with a standard viscometer at a temperature of (10 - 50)°C. The formation time of a homogeneous paste-like mass with the ratio KEK: OPP = 1: 1 at a temperature of 25°C depends on the type of mixer and is equal to: for a vibration mixer - 45 minutes, for a high-speed mixer - 30 minutes, for a blade-type mixer - 20 minutes.

The viscosity of the obtained mixture largely depends on the concentration of KEK and GP in the initial mixture (Figure 1). The maximum viscosity is achieved when the KEK content in the mixture is 50%, with a further increase of KEK, viscosity does not increase. The nature of the dependence is similar when adding GP to the mixture.

The viscosity of the obtained mixture depends on temperature, with increase in temperature the viscosity decreases (Figure 2).

Analysis of the output sorption curves (Figure 3) shows that the maximum amount of oil waste (about 95% of the original oil waste mass) is absorbed after 200-230 hours. The absorption ability of sorbent was researched on a “Finnigan MAT” chromatography-mass spectrometric system.

The obtained dependencies allow to draw next conclusions:
- the most optimal temperature is (25-30) °C and the process time is 200-230 hours.
- under such conditions in the open air, the mixture turns into a powdery mass similar in properties to GP, which can also be used in the process of waste sorption.
- the processes occurring during the interaction of KEK with oil waste can be characterized as physic-chemical sorption with the ion exchange reactions, complexation of oxidation-reduction reactions.
- identified the main areas of additive waste production application of cages, as special additives in the manufacture of concrete and reinforced concrete products and structures with increased requirements for permeability, frost resistance, plasticizers in concrete mixtures.
- additives production wastes were used for the reclamation of lands polluted with oil, as well as for the treatment of oily wastewater.

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