PURIFICATION OF PETROLEUM-REFINERY WASTE
WATERS BY COAGULATION AND REGENERATION
OF THE COAGULANT SLUDGE

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The pollutants of waste waters from petroleum refineries (PR) are petroleum and petroleum products as well as phenols, surfactants, etc., in liquid-drop, emulsified, and colloidally dissolved states [1-3].

At the present time petroleum products are generally removed from the water in a flow scheme including sand traps, oil traps, long-delay tanks, and sand filters [1-5].

The sand traps and oil traps almost completely remove liquid-drop petroleum from the water. Emulsified petroleum is only partially removed by these installations. Up to 50% of the petroleum is also held back by the sand filters [4, 5]. Petroleum in colloidal and true solution is not removed from waste waters by mechanical purification processes. In order to remove emulsified and colloidally dissolved petroleum from PR wastes, it is necessary to use coagulants such as aluminum salts and ferrous and ferric oxides. Aluminum and iron salts are easily hydrolyzed in waste water and form the corresponding hydroxides, which are highly active sorbents with respect to petroleums, petroleum products, and other contaminants.

In addition aluminum or iron salts (soaps) are formed with high-molecular-weight organic acids which then stabilize the petroleum emulsion.

As a result the emulsion is broken up, the petroleum droplets adhere to the porous surface of the iron or aluminum hydroxide, and the latter coagulate to form flocs which fall out as a sludge. The petroleum product content of the water is reduced from 150-250 to 10-15 mg/liter.

It should be noted that hydrolysis of aluminum salts occurs at pH = 3-8. Beginning at pH = 8.4, aluminum hydroxide dissolves owing to the formation of the corresponding aluminate. Ferric salts do not possess this property. Their hydrolysis begins at pH = 3.2 with the formation of a water insoluble ferric hydroxide. The optimum conditions for the hydrolysis of ferric salts lie in the pH range from 6.5 to 7.5.

Regarding the use of ferrous salts as a coagulant, these salts do not hydrolyze below pH = 9.5-10.5. At lower pH values ferrous sulfate is converted to the hydroxide slowly or not at all. For this reason coagulation is incomplete and the water is not efficiently purified. In addition the presence of divalent iron ions gives rise to the growth of iron bacteria in the water, which can lead to choking of the pipelines.

From these considerations it is better to use ferric salts, rather than ferrous, for the purification of PR waste waters: for example, FeCl₃·6H₂O and Fe(SO₄)₃·9H₂O. However, these salts are hygroscopic and highly corrosive. They are little used for water purification. We therefore consider it advisable to prepare ferric salts on site by oxidizing ferrous sulfate with active chlorine.

Ferrous sulfate is weakly hygroscopic and less corrosive. Unlike ferric salts, it can be transported in wooden drums, barrels, and boxes, or in closed freight cars. Provided certain rules are observed, work with ferrous sulfate is not dangerous. Moreover, this material is a by-product (waste) of metallurgical plants. Ferrous sulfate is the principal constituent of valuable wastes from the production of titanium dioxide.

The oxidation of ferrous sulfate with chlorine occurs according to the equation

$$3\text{FeSO}_4 + \frac{1}{2}\text{Cl}_2 = \text{Fe(SO}_4)_3 + \text{FeCl}_3$$

The amount of chlorine consumed is 1/7 the weight of ferrous sulfate.

The mixture of salts obtained is used without further treatment for purification of the waste water. They are easily hydrolyzed in water to form ferric hydroxide, together with sulfuric and hydrochloric acids. In order to ensure that hydrolysis is as complete as possible, the waste water should contain a reserve of alkalinity for neutralization of the acids. If this reserve is insufficient, an amount of an alkaline reagent [Ca(OH)₂, NaCO₃, NaOH, NH₄OH, etc.] is added such that after coagulation the residual alkalinity of the water is 0.5-1.0 meq/liter.

For treating PR waste waters, we prepared samples of mixed ferric salts by adding chlorine water to wastes from the production of titanium dioxide. It was found that in a 10% solution of the wastes (based on hydrated ferrous sulfate) the oxidation of divalent iron to trivalent is almost instantaneous at pH = 3. Under these conditions the salts formed are not subjected to hydrolytic decomposition.

The solution obtained was used for a test coagulation of PR waste waters. Various doses of coagulant were added to beakers containing 500 ml of the water. The mixture was agitated rapidly for 15 sec, then more slowly for 2 min, and finally left for 1.5-2 h without agitation. When necessary, the water was made alkaline with milk of lime. The petroleum-product content was determined colorimetrically [6], using carbon tetrachloride for the extraction.

A test coagulation was carried out on waste water at the Vtoroi Drogobych petroleum refinery. Average samples of water were taken following the oil traps of systems I, II, and III. The effluents contained the following