ELECTROCHEMICAL REGENERATION OF USED CAUSTIC SOLUTIONS

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Straight-run naphtha cuts are alkalized with 8 - 12% solutions of caustic soda to neutralize the acid and organosulfur compounds in them.

The used caustic solutions (UCS) formed contain: 1) 3.5% free and 2-5.7% bound alkali (overall alkalinity: 3 - 7%); 1.5 - 4% sulfides and thiosulfates (the latter are formed by oxidation of sulfides by atmospheric oxygen during storage between operations); 35 - 100 g/dm³ (total) sodium.

In addition, they also contain different amounts of naphthenates, phenolates, carbonates, emulsified petroleum products, and suspended products of corrosion of steels (oxides and sulfides). The specific conductivity of UCS is 0.1 - 0.5 S·cm.

The problem of utilizing and deactivating UCS is pressing for all petroleum refineries. According to the data in [1], the volume of these solutions in 45 European refineries is approximately 138,000 tons/year for a total amount of refined petroleum of 252 million tons/year, i.e., 550 tons per million tons of crude oil. Approximately 750 tons of UCS per million tons of crude oil is formed at Angarsk Refinery, and this is characteristic of all domestic refineries.

Methods of direct oxidation with air, carbonization with stack gases, neutralization with stripping and aerobic biological treatment are used for processing such solutions [1 - 3]. Use of UCS for alaklization of crude oil is spreading is domestic practice, and this is resulting in a number of negative factors:

* the high sodium content in atmospheric resid, which causes deposition of coke in furnaces and caustic embrittlement of towers and furnace pipes;
* additional entry of corrosive compounds in the crude oil – naphthenic acids, phenols, organic and inorganic sulfides, thiosulfates, etc.;
* contamination of oil refining products with colloidal products of corrosion of metals and thus decreased efficiency of catalytic processes (cracking, hydrotreating).

Two regimes for electrochemical treatment of sulfide - alkaline wastewaters are described in the literature [2, 3]. However, in our opinion, the possibilities of the electrochemical scheme in these cases are not fully implemented. Judging by the chemical composition, UCS can be considered acceptable feedstock for manufacture of caustic soda. The characteristics of the chemistry and technology of electrolysis indicate the expediency of using this method for regeneration of UCS: up to 90% of the alkali is recycled.

We investigated the mechanism and kinetics of anodic oxidation of the components of UCS to develop an electrochemical method of regeneration and corrosive deactivation of UCS. The experiments were conducted in an electrochemical cell with separated electrode spaces using different electrode materials (platinum, graphite, Ti/Pl, Pb/PbO₂, Ti/PbO₂, Ti/MnO₂) and a PI-50-1 potentiostat.

The somewhat complicated process of electrochemical anodic oxidation is characterized by the following reactions:

\[
2\text{H}_2\text{O} + 4e^- \rightarrow 2\text{OH}^- + \text{H}_2 \uparrow \tag{1}
\]
on the anode

\[
2\text{H}_2\text{O} - 4\text{e} \rightarrow 4\text{H}^+ + \text{O}_2 \uparrow \quad (2)
\]

\[
2\text{OH}^- - 4\text{e} \rightarrow 2\text{H}^+ + \text{O}_2 \uparrow \quad (3)
\]

\[
\text{S}^{2-} - 2\text{e} \rightarrow \text{S}^0 \quad (4)
\]

\[
\text{S}^{2-} + 4\text{H}_2\text{O} + 8\text{e} \rightarrow \text{SO}_4^{2-} + 8\text{H}^+ \quad (5)
\]

in the anolyte

\[
\text{S}^{2-} + \text{O}_2 + \text{OH}^- \rightarrow \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \quad (6)
\]

\[
2\text{S}_2\text{O}_3^{2-} + 6\text{H}^+ \rightarrow \text{SO}_4^{2-} + 3\text{S}^0 \downarrow + 3\text{H}_2\text{O} \quad (7)
\]

\[
\text{S}^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} \quad (8)
\]

Organosulfur compounds - mercaptans, thiophenes, phenols, naphthenes, etc., are simultaneously oxidized.

Thermodynamically, reactions (2) - (5) are almost equally probable. However, in anodic oxidation, the anode material plays a large role as it has an electrocatalytic effect on the kinetics of the reaction, causing primarily anodic production of crystalline sulfur or sulfates, which was confirmed during the studies.

The corrosion resistance of the anode materials is also important. Graphite is subject to significant deterioration due to oxidation of carbon with liberation of atomic and molecular oxygen and formation of carbon dioxide, and also due to the low chemical stability of the impregnation material in basic media.

In basic (pH > 7) anolyte, intense deterioration of Pb/PbO₂ and Ti/PbO₂ lead electrodes with formation of plumbates is observed. Corrosive wear of the lead anodes can be reduced to 0.0015 g/(m²·h) by preliminary treatment of the electrodes and optimization of the conditions of the anode process. Platinum-containing electrodes are characterized by elevated corrosion resistance at pH 2 - 12.

With an increase in the anode current density \( i_a \), the degree of conversion of sulfides increased, attaining -100\% at \( i_a > 400 \text{ A/m}^2 \) due to bulk oxidation reactions. Bulk dismutation of thiosulfates according to reaction (7), formed in bulk oxidation of sulfides according to reaction (6) by anodic oxygen, takes place in neutral medium (pH 6 - 7.5) with the formation of colloidal sulfur. At pH < 5, the anolyte is degassed - liberation of hydrogen sulfide according to reaction (8).

As a result of anodic and bulk reactions with the oxygen liberated, active oxidation of organic compounds takes place in electrolysis. The degree of conversion of phenols for a current density above 400 A/m² attains 87 - 95\%, the chemical oxygen demand (COD) decreases by 98 - 99\%, and the specific power consumption is 40 A·h/dm³.

We developed and fabricated a laboratory setup for determining the optimum process parameters and technical and economic electrolysis indexes; it consists of an electrolyzer with a flow-through asbestos membrane and steel wiregauze cathode for a current load of 5 - 40 A. The conditions and different variants of organizing the electrolysis process were worked out during the studies.

In laboratory conditions, after 1000 h of continuous operation, the membrane electrolyzers had the following technical indexes: alkali current efficiency greater than 90\%; specific power requirement no greater than 4000 kW·h/ton NaOH; voltage on electrolysis unit 4.5 - 5.5 V; free alkalinity of regenerated solution 6 - 12\% NaOH; degree of conversion of sulfides greater than 98\%; 98\% decrease in COD.

Different industrial problems can be solved by varying the conditions of electrolysis (anode current density, pH of anolyte, temperature, load for used alkali) and electrolyzer circuit. The following variants of the process regime and design of the electrolysis scheme were developed based on the results of the studies:

* at pH < 4: removal of hydrogen sulfide and carbon dioxide from the electrolyte;
* at pH \( \geq 6 \): active separation of elemental sulfur from the anolyte; the sulfur is floated off with the electrolysis gases and goes out with the spent anolyte;
* complete filtration of the electrolyte through the electrolyzer;
* partial filtration of the electrolyte through the electrolyzer.

The technical and economic calculations based on the data obtained showed that the cost of producing