CHEMICAL ENGINEERING PROTECTION IN PRIMARY CRUDE OIL REFINING UNITS

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Efficient methods of protecting primary crude oil refining units from corrosion are: using demulsifiers in the electric desalting stage, alkalization of the crude oil before vaporization, use of corrosion inhibitors in atmospheric tower distillate lines.

Despite the many years of experience in refining crude oil, the theory and practice of protecting condensation-cooling equipment in primary refining units from corrosion have been insufficiently developed and are abstracted from the real conditions from the point of view of modern ecological and technical-economic requirements. When methods of chemical-engineering protection (CEP) of construction materials are used, a question arises concerning the degree of the effect of process factors (tower load, temperature regime, chemical composition of distillates and crude oil) on the efficiency of these methods and consumption of reagents.

We investigated the corrosion behavior of construction materials for heat-exchange equipment under the combined effect of industrial media and process parameters on the EDU—AVT-6 unit at Angarsk Refinery. The efficiency of the Nalko-Exxon CEP program was investigated and proposals were made [1] for optimizing this program.

It was initially hypothesized that reagents from different manufacturers would have different working properties, reflected in the effectiveness of protecting the equipment and the technical and economic indexes of the CEP programs. We determined the limiting factors and overall characteristics of corrosive disintegration of condensation-cooling equipment using CEP reagents, in particular, Nalko-Exxon reagents.

According to [1], this company’s CEP program in optimum conditions decreases the corrosion rate to 0.01 mm/year and the concentration of dissolved iron in drainage water to less than 1 mg/dm³ for neutralizer and film former consumption of 2 – 8 g per 1 ton of naphtha flow.

Despite the positive results of testing the Nalko reagents, the efficiency of CEP in the operating conditions is primarily determined by the process parameters which affect the stability of operation of the equipment for metering out and adding the reagents and on the corrosiveness of the process medium.

In 1994 – 1997, measures were instituted in the EDU—AVT-6 unit to increase the reliability of the reagent metering and addition systems, the points of addition of the reagents were changed, and the drainage water pH monitoring system was improved, which reduced the number of malfunctions in the CEP system of this unit by four times.

The effective operating time fund of this system increased from 3800 h in 1994 to 5530 h in 1995 and to 6870 h in 1996. For this reason and due to other measures, the average annual corrosion rate decreased by ~40% (Table 1) and the number of routine maintenance interventions on condensation-cooling equipment decreased by 2 times.

A regression equation, obtained by full factorial experiment method using a type 24 design based on statistical data collected over 3 years demonstrates the degree of the effect of CEP factors on corrosive wear of the heat-exchange equipment. The experimental conditions and factor coding are reported in Table 2.

The corrosion rate Y of carbon steel determined in corrosion monitoring on the unit was used as the response function:

\[ Y = 2.2 - 0.3X_1 - 2X_2 - 1.1X_3 - 0.6X_4 \]
As the equation shows, all of the investigated factors significantly affect corrosive disintegration of carbon steel, but factor $X_2$ related to the crude oil alkalization regime, dominates. Equipment malfunction in this regime results in total failure of CEP and an increase in the corrosion rate to 2 mm/year with the upper level of variation of the remaining factors. After two weeks of use without crude oil alkalization, corrosion damage to a depth of up to 6 mm was observed in the tube panel of the air coolers at sites where condensed moisture from the heat-exchange pipes was observed.

Without alkalization of the crude oil, the consumption of 5196 neutralizer for maintaining the standard pH values increases from 3 – 7 to 10 g/ton and higher, and in some cases, the required consumption exceeds the output of the metering pumps. The electric conduction (from 20 – 50 to 250 – 1200 $\mu$S·cm), concentration of chlorides (from 2 – 25 to 70 – 350 mg/dm³), and corrosiveness (by 1.5 – 3 times) of the neutralized drainage water simultaneously increased, which required increasing film former consumption.

The crude oil alkalization and neutralizer feed regimes are rigorously correlated with the process parameters. The alkalization process should be optimized based on the standard values of the basicity of atmospheric resid and the optimum values of electric conduction (150 – 400 $\mu$S·cm) of the drainage water. In the ideal case, a drainage water pH distribution frequency in the range of 5.5 – 7 should obey a normal law with greater than 90% probability.

Factor $X_3$ of the effect of the neutralizer is next in importance. However, neutralizer with no film former does not allow decreasing the corrosion rate to less than 0.15 mm/year. The film former is only highly efficient at the upper level of variation of the other factors, but when it is used, the corrosion rate decreases to 0.05 – 0.01 mm/year.

To decrease the negative effect of the pH of drainage waters, the drainage water was fed into the distillate lines before the air coolers. Incorporation of additional moisture in the distillate decreases the concentration of corrosive compounds (hydrogen chloride, hydrogen sulfide, etc.) at sites of primary moisture condensation and consequently significantly reduces corrosion losses.

Up to 10 g/m³ of sulfur dioxide and up to 30 g/m³ of carbon dioxide were recorded in the gas phase of naphtha distillates. These compounds increase the corrosiveness of the distillates. Their appearance is due to entry of molecular oxygen and active oxygen-containing compounds with the crude oil. We identified two sources of entry of active oxygen: with the washing water in the EDU; with the spent alkaline solutions used for alkalization of the crude oil.

Replacing «fresh» industrial water containing 6 – 10 mg/dm³ of dissolved molecular oxygen by drainage waters with CEP with more than 100 mg/dm³ significantly reduced the corrosiveness of the distillates in the EDU. The savings in industrial water attained 30 – 40 m³/h. In our opinion, the maximum corrosion rate could be reduced in 1996 to 0.36 mm/year due to this engineering solution alone (see Table 1).

Another positive factor was halting use of alkaline solutions depleted in alkalization of naphtha distillates to utilize them for alkalization of crude oils. In our opinion, this prevented a number of associated negative

### TABLE 1

<table>
<thead>
<tr>
<th>Year</th>
<th>Corrosion rate, mm/year</th>
<th>In the stripping tower</th>
<th>In the basic atmospheric tower</th>
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<tbody>
<tr>
<td></td>
<td>average</td>
<td>minimum</td>
<td>maximum</td>
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<td>0.04</td>
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<tr>
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<td>0.04</td>
<td>0.35</td>
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<tr>
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<td>0.05</td>
<td>0.008</td>
<td>0.24</td>
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