

## ECOLOGY

### EXHAUSTIVE LOCAL TREATMENT OF REFINERY EFFLUENTS TO REMOVE HYDROGEN SULFIDE AND AMMONIA

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UDC 665.68:628.544

Due to stiffening of environmental requirements for emissions from process units, the problem of treating water vapor condensates sent to treatment plants to remove hydrogen sulfide and ammonia is becoming critical in oil refineries.

Condensate from the G-43-107 cat cracker (free-standing and part of the KT-1/1 complex for exhaustive refining of atmospheric resid) can contain up to 10,000 mg/liter of both sulfide sulfur and ammonium nitrogen as a function of the quality of the refined feedstock, features of the cracking technology, process implementation, and the unit's feedstock load. The amount of condensate formed can vary from 20 to 50 m<sup>3</sup>/h.

Single-tower schemes are usually used in existing process units for local treatment. The use of such schemes in primary oil refining units is justified since the condensates from these units are primarily contaminated with hydrogen sulfide. However, in secondary oil-refining units (catalytic cracking, hydrocracking, hydrotreating of heavy distillates), treatment with the one-tower scheme becomes problematic due to the appearance of a large amount of ammonia nitrogen in the condensates.

Local treatment with the single-tower scheme is basically conducted with two methods: for hydrogen sulfide and ammonia – by desorption with hydrocarbon gas or water vapor; for sulfide sulfur – by a heterogenic catalytic method.

The essence of treating condensate by desorption with hydrocarbon gases consists of the following. The hydrogen sulfide and ammonia are stripped with a dry gas or propane stream in a desorber tower at a pressure of 0.12-0.13 MPa and temperature of 95-98°C. Hydrogen gas consumption is approximately 100 m<sup>3</sup> per 1 m<sup>3</sup> of condensate. The hydrocarbon gas with the desorbed components – hydrogen sulfide, ammonia, and water vapors – goes to amine treatment. After treatment, the gas is used in the process and the absorbed hydrogen sulfide enters the sulfur production unit after separation of amine from the solution.

The drawbacks of the method primarily include the low degree of removal of sulfide sulfur from the condensate (in treated condensate, 10-50 mg/liter in terms of H<sub>2</sub>S) and ammonia nitrogen (in treated condensate, 200-250 mg/liter in terms of NH<sub>3</sub>). In addition, the high water and ammonia content in the blowing gas undesirably dilutes the amine solution and saturates it with ammonia, which negatively affects both the absorption capacity of the amines and their regeneration.

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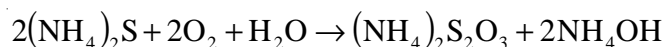
Elistek Engineering LLC. I. M. Gubkin Russian State University of Oil and Gas. Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No. 2, pp. 52 – 54, March – April, 2006.

Instead of hydrocarbon gas, water vapor was used for desorption of hydrogen sulfide and ammonia. The degree of removal of hydrogen sulfide from the condensate increases slightly, but as previously, the ammonia content remains high.

In addition, in joint removal of hydrogen sulfide and ammonia, ammonium hydrosulfide salts are deposited in the gas lines of the single-tower units at temperatures below 100°C, which clogs the pipelines. When high temperatures are maintained in the unit, the problem of deposition of ammonium hydrosulfide salts is shifted to the amine desorption unit.

In some cases, the hydrogen sulfide and ammonia desorbed by the water vapor are delivered to process unit furnaces, which increases the amount of atmospheric emissions of harmful substances, primarily sulfur oxides. In the case of discharge of the gas stream into a flare line, ammonium salts accumulate in flare-system separators and pipelines. In combined removal in a condensate treatment block, hydrogen sulfide and ammonia in the form of ammonium salts totally enter the refinery treatment plants in washing and stripping of equipment and pipelines. As a result, the real load on the refinery's biological treatment unit does not decrease.

Heterogeneous-catalytic treatment of condensate to remove sulfide sulfur (removal of ammonia is not hypothesized) consists of oxidation of toxic sulfides with atmospheric oxygen in the presence of a catalyst into less toxic thiosulfates [1], in particular, according to the reaction:



Oxidation is conducted in a packed-column unit in the presence of a catalyst, cobalt phthalocyanine on a polymer base, for example. The process is conducted in the 90-93°C operating temperature range at atmospheric pressure. This process is not selective and is very sensitive to the temperature. At a temperature below the indicated temperatures, sulfides (hydrogen sulfide) are incompletely oxidized, and at a higher temperature, ammonium hydrosulfide is intensively hydrolyzed with liberation of gaseous ammonia and hydrogen sulfide.

The latter causes continued oxidation of hydrogen sulfide in the gas phase and consequently, formation of the most varied oxygen-containing sulfur compounds and elemental sulfur, which is deposited in pipelines and

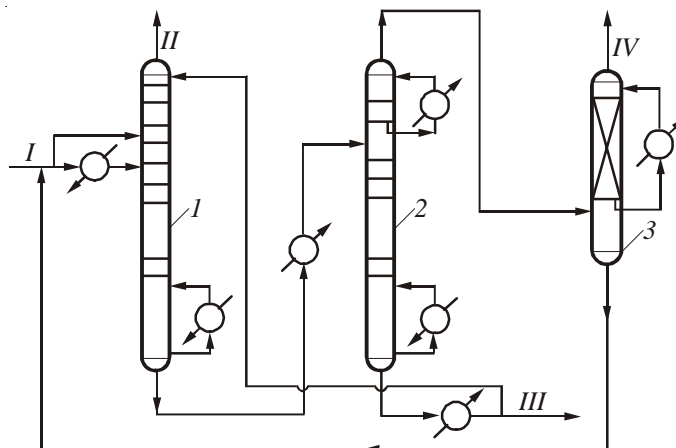


Fig. 1. Process diagram of treatment of condensate: 1, 2) towers for separation of hydrogen sulfide and ammonia; 3) packed scrubber; I, III) untreated and treated process condensate; II) hydrogen sulfide; IV) ammonia.

Table 1

Unit	Pressure (excess), MPa	Temperature, °C	
		at top	at bottom
Separation tower			
hydrogen sulfide	0.5 – 0.7	50 – 90	160 – 168
ammonia	0.05 – 0.2	90 – 125	110 – 138
Scrubber	0.03 – 0.15	40 – 80	–

clogs them. In addition, pyrophoric compounds are formed during oxidation and can ignite when the units are opened for maintenance.

Used air with a high hydrogen sulfide content according to the design must go to the sulfur production unit [2]. However, in practice, it is usually burned (which is probably only possible for weak environmental requirements for sulfur oxide emissions into the atmosphere).

The drawbacks of the method also include the low degree of removal of sulfide sulfur from the condensate (20-50 mg/liter at outlet), high ammonia content (1000 mg/liter and higher), and formation of other sulfur compounds, sulfates, for example, instead of the expected thiosulfates as a result of oxidation and reciprocal transformation.

Not only biological pretreatment but removal of sulfates are required for using the treated condensate in a refinery's closed water supply system. This situation significantly complicates the process scheme for the treatment unit for large volumes of treated condensate, so that use of the method of catalytic oxidation becomes unfeasible. This method is recommended for use in refineries that discharge treated wastewaters into ponds [3].

Nevertheless, the described method is the basis for the standard design of the condensate treatment block on G-43-107 cat crackers and KT-1/1 units for exhaustive refining of atmospheric resid. Experience in operating such blocks unambiguously indicates the low efficiency of the method, important operating problems, and impossibility of attaining even the rated values for the residual sulfide sulfur and ammonia nitrogen content.

As domestic and foreign experience shows, fractionation is the most effective method of treating process condensate [3]. In fractionation with the two- or three-tower scheme, a lower content of sulfide sulfur and ammonium nitrogen is obtained in the treated condensate. In contrast to other methods, it allows directly separating hydrogen sulfide and ammonia by separate highly concentrated gas streams. Fractionation is recommended for treatment of large (greater than 30 m<sup>3</sup>/h) volumes of sulfide- and ammonia-containing condensates alone, since the method involves relatively high capital investments and operating costs.

Elistek Engineering Co. has developed and is successfully introducing its own method for exhaustive treatment of process wastewaters to remove sulfide sulfur and ammonia nitrogen [4]. A flow chart of the process is shown in Fig. 1.

Treatment takes place as follows. The initial condensate is fed to the absorption-stripping tower for separation of hydrogen sulfide into two streams: upper cold and lower, heated to the initial boiling point. For posttreatment of the hydrogen sulfide stream to remove ammonia, cold treated condensate is fed into the upper section of the tower and heat is delivered to the lower section. The following are obtained as products: almost pure hydrogen sulfide at the top of the tower, condensate with hydrogen sulfide removed at the bottom, delivered to the ammonia tower after cooling.

Table 2

Indexes	Before treatment	After treatment
Output of block, m <sup>3</sup> /h	25 – 40	25 – 40
Content in condensate, mg/liter		
hydrogen sulfide	4000 – 10000	1 – 10
ammonia	4000 – 10000	≤20
Content in exit gases, wt. %		
hydrogen sulfide in ammonia	–	≤0.1
ammonia in hydrogen sulfide	–	≤0.1
pH	8.5 – 9.5	9 – 10

Ammonia and residual hydrogen sulfide are removed from the aqueous condensate in the ammonia tower. Ammonia vapors with hydrogen sulfide and water vapors are taken off at the top of the tower, and treated process condensate is taken off from the tower's still. To remove heat, a circulating reflux stream is organized in the upper part of the tower. Heat is delivered to the lower part of the tower.

The head product from the ammonia tower – ammonia with hydrogen sulfide and water for production of pure ammonia – is cooled by the cold circulating reflux stream in a packed scrubber. As a result, the water vapors are condensed, ammonia is dissolved in water, and the residual hydrogen sulfide totally reacts with the ammonia at low temperature with formation of ammonium hydrosulfide. The ammonium hydrosulfide solution obtained is returned to the absorption-stripping tower for distillation of hydrogen sulfide, and the pure ammonia vapors at the top of the scrubber enter the utilization unit.

The basic treatment process parameters are reported in Table 1.

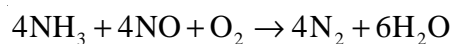
When the condensate treatment block heat flows are connected to a cat cracker or another unit with excess heat, the block's towers are heated by the heat of the circulating reflux streams from the unit's basic towers, for example, the basic catalytic fractionation tower. The heat of the exit streams can be used for heating the initial condensate. By eliminating use of steam for heating in the block, it is possible to significantly reduce operating costs.

The characteristics of the feedstock and products from the standard process condensate treatment block in the G-43-107 cat cracker with out of 2 million tons/year in feedstock are reported in Table 2.

The treated condensate can be sent to the common refinery sewage treatment plant or used as feed water in EDU blocks. In the last case, the phenols contained in the condensate are partially extracted by the crude oil, which decreases the overall phenol load in sewage treatment plants and the total amount of fresh water required.

The hydrogen sulfide and ammonia separated in the unit can be delivered for further processing: the hydrogen sulfide to the elemental sulfur production unit, and the ammonia for production of saltpeter and ammonia water or for liquefaction. These relatively attractive methods of further processing ammonia require additional investments for constructing the corresponding utilization units, which is not always economically feasible.

Against this background, the use of gaseous ammonia (or ammonia water) as a reducing gas in high-temperature noncatalytic reduction of nitrogen oxides [5] seems least expensive and most effective. Feed of ammonia for burning to a furnace significantly reduces the nitrogen oxide content in stack gases from process furnaces according to the reaction:



In addition to the fundamental problem – treating catalytic effluents to remove hydrogen sulfide and ammonia, the process also allows indirectly making two other environmental problems less acute: reducing nitrogen oxide emissions into the atmosphere and decreasing the phenol load on refinery sewage treatment plants.

The proposed treatment technology allows flexibly varying the quality indexes of the unit's products as a function of the quality of the initial condensates, the requirements for the block's products, and the ways of utilizing them. Not only effluents from cat crackers, but also condensates from hydrotreating, hydrocracking, primary crude oil refining, and other units can also be treated.

The process condensate treatment blocks utilizing Elistek technology in cat crackers were started up in 1999 at Mazheiko Nafta JSC and in 2003 at LikNOS LLC.

As a result of revamping the blocks, the quality of the treated condensate improved (the sulfide sulfur, ammonia nitrogen, and phenol content decreased), emissions of nitrogen oxides and sulfur dioxide into the atmosphere decreased, consumption of clean water for EDU blocks and circulating water systems was reduced, and clogging of equipment and pipelines by ammonium hydrosulfide salts was eliminated.

The process condensate treatment blocks can be revamped by stages, during scheduled maintenance of the units.

The process condensate treatment block in the cat cracker at Nizhnekamsk Oil Refiner at TAIF Co. is being prepared for start up, and plans are being drawn up for treatment units for Sibneft'–Omsk Oil Refinery and Lukoil Neftokhim Burgas.

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