

NEW PEROXIDE-BASED TECHNOLOGY OF HEAT EXCHANGERS CLEANING

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ABSTRACT

In spite of variety of known cleaning methods of heat exchangers, yet there is a high demand for new cleaning technologies, which are effective, safe and timesaving. The core principle of our AlfaPEROX cleaning technology is a combination of chemical action of the cleaning solution and physico-chemical action of hydrogen peroxide catalytic decomposition. The cleaning solution contains the catalysts of peroxide decomposition and inhibitors blend to solve the corrosion problem. Peroxide decomposition takes place in pores of deposits which results in mechanical destruction of even nonreactive fouling like coke. The technology is the most effective for particulate deposits, sludge, deposits of refineries and petrochemical plants formed under 400 °C.

The plate heat exchanger AlfaLaval CPK75-V-150Pls at CDU, with tar at hot side and crude oil at cold side, was successfully cleaned. The cleaning process was monitored by pressure gradient and free volume. The wastes after the cleaning were discarded into industrial sewage because the solutions are environmentally friendly. After 8 hours of the cleaning the temperature difference changed from 9 °C to 65 °C at hot side and from 42 °C to 70 °C at cold side.

INTRODUCTION

Fouling is a huge problem for heat exchange processes. Even little fouling in heat exchange zones can dramatically (up to 50 % and even more) decrease efficiency of this process. To compensate this decrease in efficiency, oil refineries traditionally choose the way of extra fuel consumption. Maintaining heat exchange processes efficiency is highly important problem in the context of ecological impact reduction.

At the moment two methods of heat exchange equipment cleaning from fouling are widely used. These are mechanical and chemical methods. Both have substantial limitations which don't allow to treat equipment effectively. Mechanical method is labor-consuming, demands much time for disassembling-assembling of heat exchange equipment and its setting up. Such method cannot be applied for nondemountable heat exchange apparatus. Chemical method supposes using of ecologically hazardous acids, bases or organic solvents needed subsequent expensive disposal.

This method is useless against nonreactive deposits (such as coke deposits) which constitute significant fraction of fouling in oil industry.

AlfaPEROX technology combines advantages of both chemical and mechanical cleaning methods. It is safe for equipment, it doesn't need equipment dismantling and reagents disposal after cleaning, it is effective against nonreactive deposits (see Table 1). The cost of cleaning is comparable to the cost of chemical cleaning and depends on many factors like quantity and type of deposits, type of equipment, equipment material, logistics, etc.

Table 1.

Characteristics	Mechanical methods	AlfaPEROX technology	Chemical methods
Cleans hard-to-reach areas and non-demountable equipment	—	+	+
Removes most types of fouling (including non-reactive deposits)	+	+	—
Cleaning time	several days	12-36 hours	12-36 hours
Safe for equipment	±	+	±
Easy waste-processing	+	+	—
Green and environment-friendly	+	+	—

ALFAPEROX TECHNOLOGY

AlfaPEROX technology is based on chemical reaction of hydrogen peroxide catalytic decomposition which produces water and oxygen. The key point of our process is that this decomposition reaction occurs in fouling pores resulting in the formation of local zones of high pressure at micro scale providing bursting disjoining effect, leading to mechanical crushing of depositions (see Figure 1).



Fig. 1. Decomposition of hydrogen peroxide and mechanical destruction of deposits

This leads to increase of contact surface between deposits and solution. Together with exothermic effect of decomposition reaction this leads to few times increasing rate of oxidative destruction of organic deposits, such as resins and asphaltenes [4], and some inorganic scales [5]. Hydrogen peroxide provides also soft oxidation of pyrophoric fouling.

This combination of chemical and mechanical actions allows to destroy and remove even non-reactive fouling such as coke formed in processes at temperature up to 400 °C.

The principal scheme of the cleaning unit in connection with heat exchanger is presented in the Figure 2. Hydrogen peroxide is added to the flow via separate inlet.

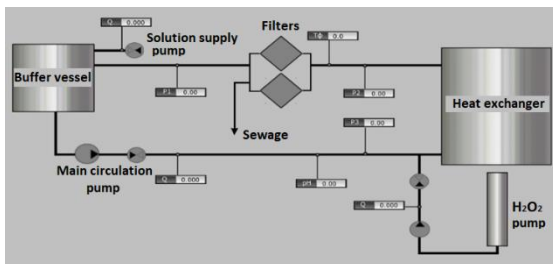


Fig. 2. Principal scheme of the working cleaning unit.

EVALUATION OF RISKS

For industrial application of AlfaPEROX technology we must consider and minimize any possible risks.

Corrosion

Corrosion tests were performed in conditions similar to those during real cases. Static gravimetric tests were conducted according to Russian state standard GOST 9.502-82.

Samples of carbon steel 1.0038, stainless steel 1.4541, brass 2.0360 (DIN), titanium, as the most used materials, were tested with our different compositions containing inhibitor blends.

The lowest corrosion rates were found to be 0.01 mm/year for both steels and titanium, and 0.05 mm/year – for brass.

Oxygen pressure

During hydrogen peroxide decomposition large amount of oxygen is released, therefore we estimated risks of high pressure during the cleaning procedure.

Normally we use vent valves on heat exchanger to release extra amount of oxygen. Here in further calculation we do not assume the release of oxygen through these valves, so pressures and quantities evaluated here are never reached in real process. They only show the order of upper limit in the “worst case”.

This evaluation was done by comparing the flows of oxygen concentration in our system during cleaning: formation flow due to peroxide decomposition, release flow from buffer vessel into atmosphere, flow with circulating solution.

Calculation showed that release flow is an order higher than circulating flow, therefore it has no much significance for further calculation. By combination of two flows (formation and circulation) we get the following equation for overall rate of oxygen concentration change:

$$\frac{dC_{Ox}}{dt} = \frac{1}{2}kC(H_2O_2) - \frac{f}{V_{HE}}C_{Ox} \quad (1)$$

where k is kinetic constant of peroxide decomposition reaction (s^{-1}); f – flow rate (m^3/s), V_{HE} – heat exchanger volume (m^3).

Assuming the rate of H_2O_2 supply being $\frac{dC_{supply}(H_2O_2)}{dt} = je^{-\varphi t}$, where t is time, j and φ are constant parameters, we can solve the equation (1):

$$C_{Ox}(t) = \frac{1}{2} \left(\frac{j}{\alpha - k} e^{-kt} - \frac{j}{\alpha - \varphi} e^{-\varphi t} + \left(\frac{j}{\alpha - \varphi} - \frac{j}{\alpha - k} \right) e^{-\alpha t} \right) \quad (2)$$

According to this equation (2) with certain parameters of peroxide supply j and φ , maximum pressure in the system does not exceed 2 bars with

concentration of peroxide 0,5 – 2 %, even with closed air valves.

CASE STUDIES

Cleaning of plate heat exchanger at VDU of "TANECO" refinery

AlfaPEROX technology was successfully used to clean plate heat exchanger Alfa Laval CPK75-V-150PLS at VDU of "TANECO" refinery.

Medium is tar at hot side and crude oil at cold side. Volume is 0.6 m³ each side. Deposits at both sides are products of thermal destruction of crude oil and tar, crude oil coke and pyrocoke. Deposit thickness is 2 mm.

According to our tests solubility of deposits in toluene is 70 %, in HCl solution — 25 %.

Cleaning procedure started with filling the heat exchanger with cleaning solution AlfaPEROX (700 l) and its circulation. After 30 min. hydrogen peroxide solution was added to the cleaning solution periodically by small portions. Due to peroxide decomposition the temperature raised up to 60 °C. During all the cleaning process we monitored pressure and free volume. To measure directly the quantity of remaining deposit is difficult during and right after the cleaning process. However, the cleaning efficiency can be controlled by pressure / volume monitoring. After restart of industrial process the final quality of cleaning can be evaluated via videoscope and by temperature gradient.

Pressure monitoring

Pressure gradient monitoring is one of criterion of cleaning efficiency which helps to evaluate cleaning rate. In this well-known method, the pressure at the inlet and at the outlet of the heat exchanger is measured. In case of constant decrease of the pressure gradient during the cleaning, the procedure is effective and must be continued. Otherwise, if the pressure gradient does not change — the solution must be renewed.

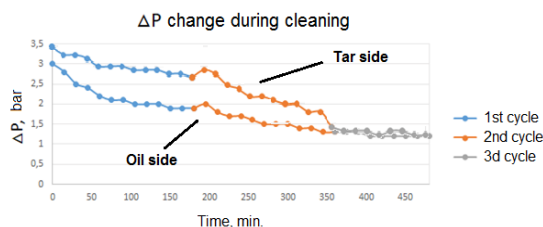


Fig. 3. ΔP change during cleaning

In this particular case pressure gradient was measured every 15 minutes. Data presented in the Figure 3 show that at both sides most deposits were removed during two first cycles of circulation. At the oil side the most productive was the first cycle ($\Delta P = 1.1$ bar), and at the tar side this was the second one ($\Delta P = 1.3$ bar). It is probably because deposits

at the tar side were harder and it took them some time to become softer.

Free volume monitoring.

Free volume is direct criterion of cleaning efficiency because certain quantity of deposits decrease the volume which can be filled with a liquid.

In the Table 2 free volume is presented after each cycle as well as initial volume in the clean heat exchanger according to documents.

Table 2. Change of free volume of the fouled heat exchanger during three cycles of cleaning.

Free volume, m ³	Circuit	
	Crude oil	Tar
1 st cycle	0.52	0.46
2 nd cycle	0.57	0.51
3 ^d cycle	0.6	0.59
Initial (clean)	0.6	0.6

According to these data the heat exchanger was fouled 13 % and 23 % of the whole volume at the oil and tar sides correspondingly.

The volume data also confirm that most part of the deposits was removed during two first cycles.

The results of the cleaning of the tar side are presented in Figure 4 and Table 3.



Fig. 4. Tar side before and after cleaning

Table 3. Parameters of the tar side before and after cleaning.

Measured parameter	Before cleaning	After cleaning
Pressure gradient, bar	3.5	1.2
Temperature gradient, °C	9	65
Free volume, m ³	0.46	0.59

The results of the cleaning of the crude oil side are presented in Figure 5 and Table 4.



Fig. 5. Crude oil side before and after cleaning

Table 4. Parameters of the crude oil side before and after cleaning.

Measured parameter	Before cleaning	After cleaning
Pressure gradient, bar	3.1	1.2
Temperature gradient, °C	42	70
Free volume, m ³	0.52	0.6

According to calculation based on heat exchanger throughput of 400 m³/h and market price of refined products, 21,1 GJ/h is needed to compensate inefficiency of fouled heat exchanger which is converted to 17,5 MT of additionally burned fuel per one fouled heat exchanger, and to **\$180k** of additional revenue that could be realized during the first 20 days after the heat exchanger cleaning with **AlfaPEROX**.

Cleaning of Hydrofluoric Acid Alkylation Unit at LUKOIL-NNOS

Heat exchangers 52-E3003/1.2, 52-E3004, total tube volume – 15,56 m³, total shell side volume – 2,88 m³.

Shell side

At the beginning of cleaning free volume was 2.1 m³. Each of the three cycles of circulation took 10 hours. Temperature raised to 53 °C. Totally 1500 kg of FeF₂ was removed according to analysis of the Fe concentration in waste solutions.

Tube side (two contours)

Total volume of two tube contours was 15,6 m³. 24800 kg of FeF₂ was removed.

As a result, pressure in the acid settler was reduced from 1.6 MPa to 1.25 MPa (-22 %).

CONCLUSION

AlfaPEROX is a new solution-based cleaning technology with its key feature catalytic decomposition of hydrogen peroxide. This technology widens the range of usual chemical cleaning and makes it applicable for deposits formed in processes at temperatures up to 400 °C. On the other hand, AlfaPEROX reduces cleaning time and therefore costs in comparison to mechanical

cleaning. It is applicable for wide range of equipment geometry: shell and tube, plate, spiral heat exchangers. According to laboratory tests it is safe for equipment and has no harmful residues after cleaning.

Efficiency and safety of AlfaPEROX technology was demonstrated in cleaning operations at TANECO refinery, LUKOIL NNOS, Gazpromneft MNPZ and ONPZ.

NOMENCLATURE

C concentration, mol/m³

k kinetic constant, s⁻¹

f flow rate, m³/s

V_{HE} heat exchanger volume, m³

t time, s

j, ϕ dimensionless parameters

ΔP pressure gradient, Pa

Subscript

Ox Oxygen

HE Heat Exchanger

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