A semi-quantitative method for integrating Occupational Safety and Accident Hazard risk has been developed and tested at the plant of propane deasphalting sludge of «Naftan» JSC. The model can be applied at processing plants characterized by different units featuring different risk types.

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TECHNOLOGY OF RECEIVING ELEMENTAL SULFUR FROM HYDROGEN SULPHIDE ACID GASES AT OJSC «NAFTAN»: ENVIRONMENTAL ASPECTS AND FEATURES OF THE TECHNOLOGY

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Sulfur-bearing compounds are very detrimental to the environment and to industrial process equipment. They are formed during the purification of hydrocarbon gases from acidic components and usually convert into sulfuric acid or elemental sulfur. Currently industrial production of sulfur is mainly performed by using the Claus process. Utilization of sulfur, obtained during the process of oil refining, is a problem of great environmental significance.

Currently OJSC «Naftan» is at the stage of «reconstruction and modernization program of OJSC «Naftan» for 2010 – 2015», which is based on the latest achievements in the field of oil refining and takes into account the rapidly changing market demands in order to improve efficiency of enterprise performance. Project of delayed coking unit construction is underway, the purpose of which is to increase the depth of oil refining up to 92 – 94 % and the output of additional volumes of light petroleum products.

Due to implementation of technology of environmentally clean diesel fuel production, with sulfur content of 10 ppm (0.001 wt.%) at the hydrotreating units L-24/7 and LCH-24/7 with «Merox» unit, and also due to the introduction of value-added oil refining process (construction a delayed coking unit) the amount of generated hydrogen sulfide increases and it should be utilized.

With an increase of oil refining (up to 12 million tons) and implementation of all the tasks specified by «Development Programme», the production of hydrogen sulfide will become approximately 8800 nm^3/h by 2015[1].

Today hydrogen sulfide, produced at facilities of OJSC «Naftan», is utilized at:

– «unit of sulfuric acid production» I and II stages;

– «unit of sulfuric acid regeneration».

The total designed capacity of the plant is 4800 nm^3/h.

Existing units of hydrogen sulfide utilization work practically with full designed load. Their capacity currently can't be increased above the designed.

In this respect, problem of sulfur-containing gases utilization at the enterprise has become crucial.

Novopolotsk industrial complex has a significant impact on the environment of the city, primarily due to the emission of pollutants into the air and discharges into surface water and groundwater. Powerful industrial development of Novopolotsk not only increases the anthropogenic load on the environment, but also has a negative impact on the living conditions of the population. Table 1 presents data of pollutants emissions into the air in Novopolotsk over the past 13 years [2].

Table 1 – Dynamics of pollutants emissions into the atmosphere in Novopolotsk, thous. tons/year

	2000	2005	2006	2007	2008	2009	2010	2011	2012	2013
From stationary sources	51,5	54,2	64,0	80,0	58,6	63,9	50,3	51,2	67,8	53,5
Per capita, kg	481	519	599	750	548	614	480	485	636	498

These table data show the total amount of emissions and amount of emissions per capita. Of course, the real impact of emissions on population cannot be submitted to simple arithmetic. In reality, it is necessary to take into account the remoteness of the industrial area from the residential one (at least 4 – 5 km), and a wind rose, which allows to dissipate most of the emissions opposite in direction to residential areas. However, emissions of pollutants are large enough to have their negative impact on ecosystems and human health.

Gaseous and liquid substances dominate in the structure of pollutant emissions into the atmosphere of Novopolotsk (99,5 %), the share of solid accounts only for 0,5 %. The main share among them are volatile organic compounds (VOCs – 52,4 %), hydrocarbons without VOCs – 7,5 %. Other substances are distributed as follows: sulfur dioxide – 25,5 %, carbon oxide – 5,0 %, nitrogen dioxide – 8,5 %, other liquid and gaseous substances – 0,6 % (Table 2).

Table 2 – Average annual concentrations of pollutants in ambient air, mg/m^3

Controlled substance	2005	2009	2010	2011	2012	2013
Solid particles	30	<15	<15	<15	<15	<15
Sulfur dioxide	2	1	2	1	1	3
Carbon monoxide	902	1633	1509	835	330	577
Nitrogen dioxide	38	45	40	42	47	54
Formaldehyde	8	7	7	6	3	3
Phenol	0,7	0,6	0,6	0,9	1,0	1,0
Ammonia	2	9	5	8	10	8
Hydrogen sulfide	1,5	1,4	1,2	1,0	1,0	1,2

In this way, the above information shows that Novopolotsk refers to the type of cities with the highest density of harmful substances emissions in the Republic of Belarus. The main sources of air pollution are the enterprises of oil refining, chemical industry, power engineering, and motor vehicles. The largest volume of pollutant emissions from stationary sources in Novopolotsk falls on OJSC «Naftan». A significant contribution to air pollution in the city is also made by the following companies: Plant «Polymir» OJSC «Naftan», Novopolotsk CHP.

The Claus process continues to be the most widely used process for the conversion of H_2S to sulfur. The task of Claus processes is to recover elemental sulfur from hydrogen sulfide and, more generally, from byproduct gases originating from physical and chemical gas and oil treatment units in refineries, natural gas processing, and gasification plants, to quote a few. They consist of a thermal reaction furnace, a waste heat boiler, and a series of catalytic reactors (converters) and condensers (Fig. 1).

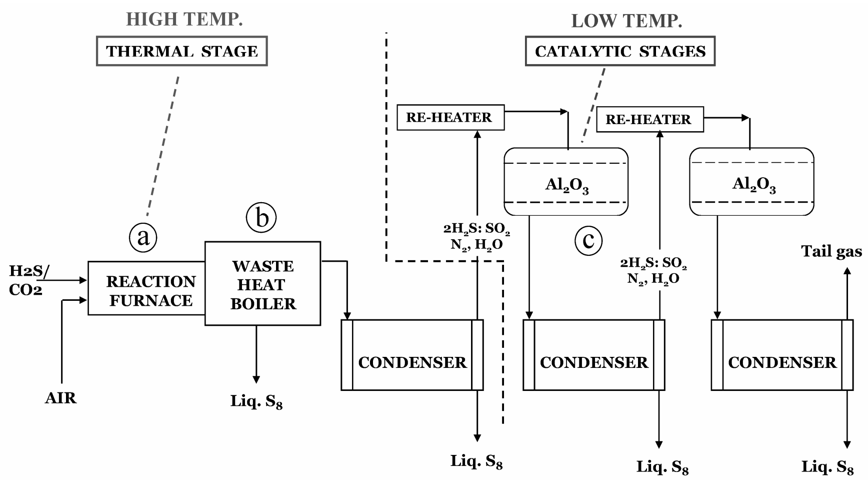

Fig. 1. The schematic structure of a typical Claus unit

The reactions occurring in the furnace are numerous, and several authors have attempted to delineate the important ones. The overall reaction characterizing the process is as follows [3]:

$$2H_2S + O_2 \rightarrow S_2 + 2H_2O. \quad (1)$$

In the first step or thermal stage, one-third of the H_2S is completely oxidized to SO_2 in the reaction furnace, located at the front end of a unit. The production of significant quantities of elemental sulfur (S_2) during the thermal decomposition of H_2S is also beneficial. In fact, the sulfur produced in the furnace makes up 60 – 70 % of the total amount of sulfur condensed at the plant. The main H_2S oxidation reaction is:

$$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O. \quad (2)$$

The reaction furnace is followed by the waste heat boiler (WHB), where heat is recovered by cooling the furnace product gases. In the second step or the catalytic stage, unreacted H_2S is then combined with SO_2, reacting via eq. 2, over an alumina catalyst to form elemental sulfur in fixed bed reactors by the following reaction:

$$2H_2S + SO_2 \leftrightarrow 3/2S_2 + 2H_2O. \quad (3)$$

Since this reaction is exothermic, decreasing the temperature leads the equilibrium reaction toward right hand, i.e. more sulfur yields. On the other hand, low temperatures decrease the reaction rate. Therefore, an appropriate catalyst must be used to increase the reaction rate. However, high sulfur yields still necessitate a multistage process with interstage cooling and sulfur condensation [4].

Sulfur formed in each stage of the Claus unit is condensed and recovered to achieve maximum conversion in the catalytic reactors. The unrecovered sulfur, in elemental or combined form (H_2S, COS, CS_2), is combusted to SO_2 in the tail gas incinerator which is then emitted to the atmosphere. Tail gas clean-up units are added sometimes prior to incineration to increase the sulfur recovery and minimize emissions.

One of the furnace functions is the destruction of any contaminants what may foul downstream equipments. In oil refinery operations, NH_3 is formed as a byproduct and is then directed to the sulfur recovery facility for destruction. Incomplete pyrolysis or combustion of NH_3 in the furnace results in NH_3 and NO carryover into the catalyst beds. Ammonia can form ammonium salts, which can plug or foul the catalyst beds, other equipments, or piping. Although the formation of SO_3 occurs in the catalyst bed regardless of the presence of NO, the presence of NO in the beds acts as a catalyst for the conversion of SO_2 to SO_3, which in turn causes catalyst sulfation. Of the primary causes of catalyst activity loss, catalyst sulfation is regarded as the most significant. It is therefore critical to convert as much NH_3 to N_2, H_2, and H_2O as possible [5].

For ammonia destruction, an empirical rule of thumb in industry is that furnace temperature should be greater than 1200-1250°C. The furnace temperature must be below the temperature limitation of conventional refractories of 1600°C and above the minimum stable furnace temperature of 926°C. The reaction furnace temperature should not exceed 1380 °C in order not to exceed the maximum temperature limitations of the equipment materials [6].

In the Claus process, other sulfur compounds will be formed, such as carbon disulfide (CS_2) and carbon oxysulfide (COS), and these compounds can often contribute from 20 to 50 % of the pollutants in the tail-gas. Furthermore, presence of O_2 traces in the CS_2-H_2O mixture caused a decrease in the activity of alumina and titania catalysts due to sulfate formation. Therefore, COS and CS_2 should be hydrolyzed in the catalytic converter, as shown below:

$$COS + H_2O \leftrightarrow H_2S + CO_2, \quad (4)$$

$$CS_2 + 2H_2O \rightarrow 2H_2S + CO_2. \quad (5)$$

The temperature of the first catalytic reactor is maintained at about 350°C to hydrolyze COS and CS_2, while that of the subsequent reactors is just above the sulfur vapor dew point. Transition metal oxides can be used to modify gamma-alumina to form a catalyst that is effective at temperatures higher than the dew point of sulfur. However, thermodynamics provide a strong incentive to operate the catalytic converters at low temperature as a lower temperature should increase the exothermic reaction efficiency. Therefore, the temperature of the process gas at the inlet of the catalytic converters should be such that the effluent gas temperature is about 14 – 17°C higher than the expected outlet sulfur dew point and high enough for hydrolysis of COS and CS_2 for the first catalytic converter only (about 350°C) [7].

Figure 2 shows the theoretical conversion of H_2S to elemental sulfur by the Claus reaction as a function of temperature.

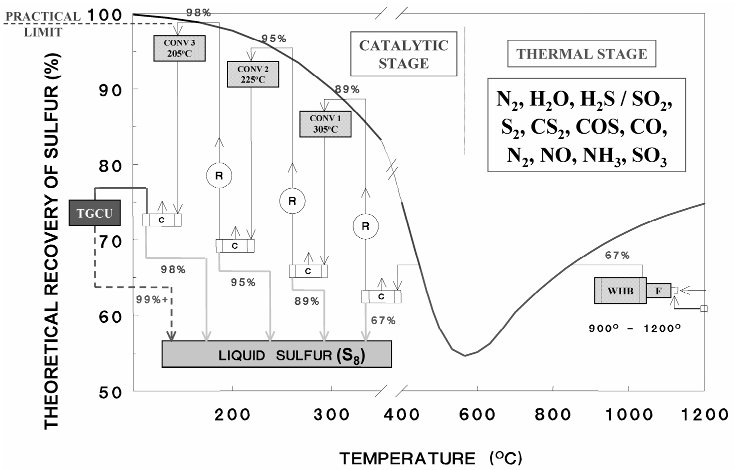

Fig. 2. Theoretical Conversion of H_2S to Sulfur by the Claus Reaction

The temperature of reaction furnace of a typical Clause Sulfur Recovery Unit is adjusted to ensure suitable NH_3 destruction. Moreover, the inlet temperatures of SRU converters are determined in order to achieve proper conversion without any processing problems. The process temperatures are important in designing the Claus sulfur recovery units.

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PRODUCTION OF SULFONATE ADDITIVES FOR LUBRICATING OILS FROM PETROLEUM AND SYNTHETIC FEEDSTOCKS

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This article gives a brief overview of the stages of production and mechanism of action of sulfonate additives (detergents). The prospect of switching to synthetic raw materials in the production of high-alkali sulfonate additives at the enterprise JV «LLK-Naftan» is considered.

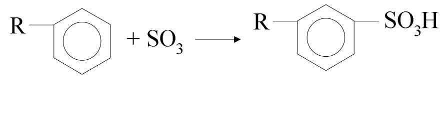
JV «LLK-Naftan» has the largest and most complex facilities for production of lubricant additives in the CIS area. The assortment of manufactured additives and additive packages for lubricating oils includes products of different functional groups capable of providing a wide range of operating properties of modern and prospective lubricants. A special place among the additives, according to their universality of application, efficiency, production volumes, occupy sulfonate additives that have detergent, dispersant, neutralizing and anti-corrosion properties.

The main purpose of detergent and dispersant additives is to prevent the deposition of oxidation products and their consolidation on metal surfaces, reducing the amount of residue, and carbon deposits on the details.

The synthesis of additives depends on the choice of raw materials and a sulfonating agent. As a raw material for petroleum sulfonates (C-150, C-300) highly purified oil distillates are used. Sulfonate additives CCK-300, CCK-300D, CCK-400, and CCK-400D NSSK-30 are produced on the basis of synthetic materials, for example, sulfonate additive CCK-300 is synthesized on a synthetic alkyl benzene sulphonic acid.

The production process of sulfonate additives consists of the following steps:

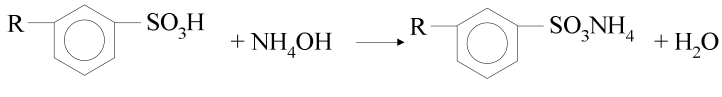
1) Oil-sulfonation with gaseous sulfur trioxide:



Adverse reactions:
$SO_2 + H_2O \rightarrow H_2SO_3$;
$SO_3 + H_2O \rightarrow H_2SO_4$.

2) Separation of the acid tar from oil.

3) Neutralization of the sulfonated oil and extraction of ammonium sulfonate:



4) Stage of exchange reaction (exchange decomposition reaction) and partial receiving of calcium sulfonate salt as a result of «thermal stabilization»: