As we know, coke-oven gas contains ammonia and hydrogen sulfide, which must be removed (to residual contents of $\leq 0.03$ and $\leq 0.5$ g/m$^3$ according to European standards). Therefore, the removal of hydrogen sulfide from coke-oven gas by the ammonia method is in increasing use [1]. This method includes the capture of hydrogen sulfide by an aqueous solution of ammonia and subsequent treatment of the acidic gas by the Claus process, to obtain elementary sulfur, which is a commercial product.

After this method was introduced at enterprises in North America [2], two lines for sulfur production from coke-oven gas went into operation in Poland, in 1997 and 1999 [3, 4]. There is also information on the design, construction, and startup of similar units for removing sulfur from coke-oven gas in the Czech Republic (Nova Huta, Ostrava), in France (Dunkirk), China (five units), South Korea, and elsewhere [5].

Factors encouraging the wide use of the ammonia method of hydrogen-sulfide removal from coke-oven gas include the absence of toxic emissions and the generation of a product (elementary sulfur) capable of withstanding transportation and prolonged storage. This is especially important in view of the global overproduction of sulfur and sulfuric acid and the geographic separation of regions that produce and consume sulfur. Accordingly, there are good prospects for wider use of the ammonia method. In this context, experience in introducing this method in the coke plant at OAO Magnitogorski Metallurgicheskii Kombinat (MMK) may be of interest for Russian coke specialists.

In the present work, we analyze experience at MMK in introducing the least-developed part of the technology: the processing of gas that contains hydrogen sulfide so as to obtain commercial sulfur.

Profound sulfur extraction in classical Claus equipment involves four or more catalytic-conversion stages, with corresponding capital expenditures [2, 7]. Both the capital expenditures and the losses of sulfur are reduced in a design employed by Krupp–Koppers (now Thyssen–Krupp EnCoke, Germany) [8].

In this design, after sulfur extraction in a condenser and trapping in a separator, the tail gas from the sulfur-removal unit (SRU) is cooled to $\sim 60^\circ$C in a contact cooling unit by excess water from the gas collector, according to patent [8]. This gas is then returned to the incoming coke-oven gas, thereby boosting the reserves of hydrogen sulfide. To reduce the sulfur losses with SO$_2$ in the coolant and simplify the regulation of the process, treatment of the acidic gas by the Claus method is characterized by high Claus ratio (HCR technology) [9]. The air supply to the Claus furnace is regulated so that the Claus ratio at the SRU output is $CR \equiv [H_2S]/[SO_2] = 10$.

The first SRU of Krupp–Koppers type in the former Soviet countries went into operation in September 2000 in purification shop 2 for coke-oven gas at OAO MMK. Operational experience in this shop indicates that the desulfurization technology is highly efficient [10]. The existing system with a closed hydrogen-sulfide cycle differs somewhat from a classical SRU. This must be taken into account in the design of future equipment (shops) for the purification of coke-oven gas, with sulfur production.

In the existing system for sulfur removal from acidic gas in purification shop 2 at MMK, the hydrogen-sulfide concentration is low, while the ammonia concentration is high. According to measurements throughout shop operation, the H$_2$S concentration is 5–8 vol % and the NH$_3$ concentration is 12–17 vol %. This may be attributed to inadequate initial data on the design (the H$_2$S reserves in the coke-oven gas are overestimated by a factor of 2–3) and to the design of the section for trapping hydrogen sulfide [11]. As a result, Superclaus processing of concentrated (24 vol %) hydrogen sulfide cannot be fully implemented in MMK purification shop 2.

In the Combiclaus processing system for acidic gas at Ostrava, the gas supplied to the SRU in 2000 contained 3.5–9.3 vol % H$_2$S and 16.3–34.6 vol % NH$_3$. 

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**Desulfurization of Coke-Oven Gas**

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Similar \( \text{H}_2\text{S} \) and \( \text{NH}_3 \) concentrations in the acidic gas are typical for equipment purifying coke-oven gas at Moscow coke plant. Thus, existing (admittedly limited) experience does not provide examples of the successful implementation of ammonia technology for selective trapping of hydrogen sulfide in the coke industry. In all cases, the ratio of components in the acidic vapor \([\text{NH}_3]/[\text{H}_2\text{S}] \approx 3\) is determined by their proportions in saturated water, which means that existing reducing agents are inefficient and the technology differs significantly from classical Claus processing of acidic gas.

**CLAUS PROCESSING OF ACIDIC GAS**

In processing acidic vapor at coke plants, as in the classical treatment technology for acidic gas, one third of the hydrogen sulfide present is first consumed [7]

\[
3\text{H}_2\text{S} + 3/2\text{O}_2 \rightarrow 2\text{H}_2\text{S} + \text{SO}_2 + \text{H}_2\text{O},
\]

and then the partial-oxidation products of \( \text{H}_2\text{S} \) undergo Claus reaction

\[
2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 2\text{H}_2\text{O} + 3/n\text{S}_n,
\]

which occurs most effectively at 230–250°C with aluminum-oxide catalyst.

As in any Claus unit, controlling sulfur production from the acidic gas reduces to regulating the supply of the oxidizing agent (air) to the Claus furnace for combustion of the hydrogen sulfide by Eq. (1). The presence of considerable quantities of ammonia in the acidic gas may create a secondary channel of oxygen consumption, with the formation of water, nitrogen, and nitrogen oxides, which hinders the regulation of hydrogen-sulfide processing to obtain sulfur by Eqs. (1) and (2).

Nevertheless, as shown by prolonged operational experience with the MMK SRU, the use of a catalyst of ammonia decomposition in the Claus furnace permits stable sulfur extraction without excessive of hydrogen sulfide and the formation of \( \text{NO}_x \) and ammonium sulfate, even at low initial \( \text{H}_2\text{S} \) concentrations. To prevent spoiling of the catalyst by the hydrogen sulfide and to increase ammonia decomposition, high temperatures are required (>1100°C) [12]. Consequently, all the existing technologies for low-temperature catalytic oxidation of hydrogen sulfide (and the corresponding catalysts of \( \text{H}_2\text{S} \) oxidation) for processing acidic gas that contains ammonia are inapplicable here.

Accordingly, in the case of joint trapping of hydrogen sulfide and ammonia from coke-oven gas by Aman- sulf technology, the most promising approach is the partial oxidation of \( \text{H}_2\text{S} \) with simultaneous \( \text{NH}_3 \) decomposition on a nickel catalyst at 1100–1200°C; this technology has undergone sufficient industrial development. If the technological oxidation conditions are observed, the guaranteed working life of BASF G1-11 catalyst for ammonia decomposition (2 yr) may be extended severalfold. The actual lifetime of this catalyst in ammonia-decomposition furnaces is ~10 yr [13]; this is acceptable for industrial conditions. However, in view of the fairly high cost of this catalyst (at least 20 euro/kg), it would be expedient to develop a cheaper Russian analog, perhaps on the basis of known low-temperature catalysts of ammonia dissociation [13]. A high-temperature reactor of new design permits significant reduction in the size of the catalyst granules, which makes the main contribution to the gas-dynamic drag of the Claus line [14]. This provides additional reserves of activity and stability for the new Russian catalyst.

The low initial concentration of hydrogen sulfide in the acid coke-oven gas calls for additional fuel consumption in order to reach a temperature of 1150–1200°C in the Claus furnace. When using the natural fuel for coke production—coke-oven gas or natural gas—carbon is introduced in the gas, so as to considerably increase the yield of organic sulfur byproducts (\( \text{COS} \) and \( \text{CS}_2 \)) at the thermal stage. These byproducts may contain up to a quarter of the sulfur. Consequently, their conversion is a priority in the Claus processing of the acidic gas. HCR technology may lead to the formation of secondary \( \text{CS}_2 \) in the catalytic stage of the SRU, as shown by the analysis of data from an industrial experiment [15]; this is unacceptable.

Another problem observed at an early stage in the operation of MMK purification shop 2 is the presence of elementary sulfur (~1 g/m³) in the tail gas of the Claus line [10]. Adhesion of this sulfur causes problems of repeated startup (rotor freezing) of the gas blower. Although elementary sulfur is present in the tail gases of all existing Claus units, it is especially hazardous for those that operate on a closed cycle. According to available information, operation of the SRU in Dunkirk had to be interrupted after a few months on account of sulfur deposition on the walls and clogging of the inverse-gas lines. Purification of the tail gases from Claus units by Shell Claus Off-Gas Treating (SCOT technology) and other methods widely used in the gas industry is too complicated and capital-intensive in the present context [16, 17]. Other methods must be sought.

A considerably simplified SCOT process suitable for the coke industry has been implemented at the SRU in MMK purification shop 2 [18]. It involves the conversion of all the sulfur-containing components of the SRU tail gas to hydrogen sulfide [19]. This hydrogen sulfide is then returned to the incoming coke-oven gas by means of the existing system [8, 10]. To this end, the tail gas in the Claus line is heated to 330–350°C and passes through a catalytic reactor, where the reactions at the catalyst include hydrolysis

\[
\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2,
\]

\[
\text{CS}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{S} + \text{CO}_2
\]

and hydrogenation

\[
2\text{H}_2 + \text{S}_2 \rightarrow 2\text{H}_2\text{S},
\]

\[
3\text{H}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O}.
\]