Pilot tests of low-temperature catalytic reduction of sulfur dioxide in realistic conditions of sulfur recovery unit at copper plant of Polar Division of PSC “Norilsk Nickel”

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Abstract. Pilot tests of low-temperature catalytic reduction of sulfur dioxide in realistic conditions (technological gases of Vanyukov furnace) of sulfur recovery unit at Copper Plant of Polar Division of JSC “Norilsk Nickel” have been carried out. It has been demonstrated that the developed CuCr catalyst provides sulfur recovery not less than 90% at GHSV - 2000 h⁻¹ in a temperature range 200-260°C.

1. Introduction
Sulfur dioxide, one of the most toxic "large-tonnage" air pollutants and the main factor in the formation of acid rain, the fallout of which has catastrophic consequences for the environment, and living in areas with a constant excess of SO₂ concentration above the MPC (Norilsk) leads to significant health problems population [1-3].

The natural sources of sulfur dioxide entering the atmosphere are mainly volcanoes and forest fires. The natural background concentration of SO₂ in the atmosphere is quite stable and is included in the biochemical cycle [4]. The total amount of sulfur dioxide of anthropogenic origin in the atmosphere now significantly exceeds its natural intake and is over 100 million tons/year [5-6].

The main source of atmospheric air pollution with sulfur dioxide from stationary sources in the Russian Federation is the metallurgical complex, and the undisputed "leader" of the Polar Division of OJSC MMC Norilsk Nickel, whose emissions account for up to 45% of the total SO₂ emissions of all industrial enterprises of the Russian Federation (thermal power, oil and gas complex, pulp and paper industry).

2. Results and discussion
Desulphurization processes of metallurgical waste gases can be conditionally divided into three groups (Figure 1):
- sorption;
- catalytic oxidation to sulfur trioxide with further production of sulfuric acid;
- catalytic reduction to elemental sulfur.
Catalytic reduction processes with the production of elemental sulfur have undoubted advantages, since their use leads to the utilization of sulfur dioxide with the formation of a non-toxic product that does not require special measures during storage and transportation.

**Selective reduction of sulfur dioxide (classification and summary analysis).**

Currently, three main processes can be distinguished based on the direct catalytic reduction of sulfur dioxide to elemental sulfur, differing in the type of reducing agent:

1. Reduction of sulfur dioxide with hydrogen sulfide (Claus process);
2. Recovery of sulfur dioxide with methane (natural gas);
3. Reduction of sulfur dioxide with hydrogen, carbon monoxide or their mixture with synthesis gas.

Comparative characteristics of the processes used are shown in Table 1.

**Table 1. Comparative characteristics of the desulphurization processes**

| Process                                      | Temperature, °C | Yield of sulfur, % | Number of stages |
|----------------------------------------------|-----------------|--------------------|------------------|
| Claus process: H₂S generator                 |                 |                    |                  |
| Catalytic steps 250-400°C                    |                 | > 90               | 3-4              |
| Reduction of sulfur dioxide with methane     |                 |                    |                  |
| (natural gas): Homogeneous                   | 1250°C          | 60                 | 1                |
| Catalytic                                    | 700-900°C       | 70                 | 1                |
| Reduction of sulfur dioxide with synthesis   |                 |                    |                  |
| gas                                          | 300-400°C       | > 90               | 1                |

The Claus process, despite more than a century of operating experience, is used mainly at oil and natural gas processing plants (refineries and gas processing plants) and primarily as a method for utilizing hydrogen sulfide, and its use at metallurgical enterprises is limited due to the fact that the need arises creation of a hydrogen sulfide generator.

In this regard, the reduction of sulfur dioxide with natural gas (high temperature modification of the process) or synthesis gas (low temperature reduction) are the most applicable.

The main benefits of the SO₂ synthesis gas reduction process are:

- low reaction temperature (operating temperature range 350-550°C);
• high, thermodynamically allowed yield of the target product - elemental sulfur (up to 90% at 350°C).

An additional motivation is the fact that this process can be integrated into the existing technological chain of the actual sulfur production.

To conduct pilot-industrial tests of the low-temperature catalytic reduction process on real gases, a pilot plant was manufactured and installed on the 1st technological line of sulfur production of Copper Plant.

The block diagram of the pilot plant and picture are shown in Figure 2.

The results of the pilot tests are presented in Table 2.

![Figure 2. The block diagram and photo of the pilot plant.](image)

| Parameters                      | Value  |
|--------------------------------|--------|
| Catalyst load, kg              | 10 (9.22) |
| Gas supply, nm³/h              | 20     |
| GHSV, h⁻¹                       | 2000   |
| Temperature in reactor, °C:     |        |
| Upper part                      | 280    |
| Lower part                      | 200    |
| Sulfur recovery,%               | 92.5   |

As can be seen from the presented results, the developed low-temperature reduction process on the in the temperature range from 200 to 280°C, the space velocity of 2000 h⁻¹ provides a decrease in the content of sulfur-containing components. The recovery of elemental sulfur in the second stage of catalysis attains - 92.5%.

3. Conclusion

As a result of pilot tests of low-temperature reduction of sulfur dioxide on real gases from Vanyukov furnaces, it was shown that the copper-chromium catalyst in the temperature range 200-260°C, space velocity 2000 h⁻¹, provides a decrease in the content of sulfur-containing components in the process gas after the catalytic Claus stage of sulfur recovery unit at Copper plant, extraction into elemental sulfur in a catalytic pilot reactor was up to 92.5%.

The results obtained once again confirm the high prospects of the low-temperature process for the reduction of sulfur dioxide with synthesis gas and its undoubtedly advantages over the high-temperature version.

The use of the developed catalyst in the existing production of at the second (third) stage of catalysis will reduce the risk of soot formation in the thermal reactor, increase the total sulfur recovery (in the presence of three catalytic stages) to 96%, and increase the line controllability level when changing
volumetric flow rate and composition of the process gas at the reactor inlet, which is associated with the ability of the catalyst to simultaneously carry out the Claus reaction and the reduction of sulfur dioxide with hydrogen and carbon monoxide to obtain elemental sulfur.

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4. References
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