

# POSSIBILITIES OF SO<sub>2</sub> STORAGE IN GEOLOGICAL STRATA OF PERMAFROST TERRAIN

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**Abstract:** This report considers the possibility of SO<sub>2</sub> recovery using liquid sulphur dioxide generation and the disposal of excessive liquid SO<sub>2</sub> in geological structures within permafrost areas. Analysis demonstrates this option allows the use of exhaust sulphur dioxide in the required volumes in order to achieve an ecologically safe level. Geological analysis shows a section of the northwestern limb of the Vologochanskaya syncline seems to be the most favorable area for disposal of excessive liquid SO<sub>2</sub>. It is located between the South-Pyasinskaya and Bolgokhtokhsкая brachyanticlines, 30km west of Norilsk.

**Key words:** geological structures; liquid sulphur dioxide; metallurgical gases; permafrost areas; sulphur dioxide disposal.

## 1. INTRODUCTION

The problem of sulphur dioxide disposal at the plants of the Norilsk Nickel Company represents an extremely serious environmental problem. Up to 2Mtpa of SO<sub>2</sub> are produced by the company's plants, of which only 10% is disposed. As a result the sulphur dioxide emissions greatly exceed the maximum permissible values.

At metallurgical plants worldwide the problem of SO<sub>2</sub> disposal is typically solved using a well-developed process of commercial sulphuric acid production, with up to 99.5% of the sulphur dioxide being caught. As

this option is unacceptable for Norilsk due to the geographical isolation and required sulphuric acid transportation, it was decided to apply the technology of enriched sulphurous gas disposal (20-50% SO<sub>2</sub>), and the recovery of elemental sulphur via the technology of the Outokumpu Company, Finland (Abramov et al., 1987). Originally it planned to utilize coal dust as a reducing agent, but the process was later converted to natural gas. The technology includes the high-temperature (approx. 1250°C) natural gas reduction of sulphur dioxide to elemental sulphur with the subsequent recovery of sulphur from off-gases during the Klaus' catalytic stages, with sulphur condensation after each step. The technology was first applied for flash smelter gases, and later with a modification it was used for liquid bath smelter gases, subsequently named Vanyukov smelting (VS) (Mechev et al., 1989). Sulphur production from flash smelter gases is currently down (for over 10 years - Platonov et al., 2004), and only 14% of the SO<sub>2</sub> produced from VS off-gases is disposed of (Ladin et al., 2003a).

The objective of the present work was to assess the possibility of using an alternative option of effluent sulphurous gas disposal in order to attain the maximum permissible emission level. This procedure involves straight condensation with the recovery of liquid sulphur dioxide and disposal of excessive liquid sulphur dioxide in geological structures within permafrost areas.

## **2. ASSESSMENT OF DISPOSAL OPTIONS FOR ENRICHED AND IMPOVERISHED GASES TO REACH MAXIMUM PERMISSIBLE EMISSION LEVELS**

According to the General Production Development Strategy adopted by the Norilsk Nickel Company (Geoinfo, 2003), the proportion of enriched sulphurous gases in the total volume of generating gases is expected to increase up to 80% by 2007. It is planned to dispose of these gases, and recover sulphur, using the methane technology once it is updated. According to calculations, after system updating sulphur recovery will be around 90-92%, and the off-gases generated in sulphur production will contain 1-3 vol.% SO<sub>2</sub> (Ladin et al., 2003a, b).

It should be noted, however, that despite a number of improvements over the last 20 years during which methane technology has been used for sulphurous gas disposal and sulphur recovery, sulphur recovery from both flash smelter gases and liquid bath smelter gases has not exceeded 60% (Burukhin et al., 2000).

The principal factors that limit sulphur recovery efficiency are (Ladin et al., 2003b, Commission Report, 1985): i) significant fluctuations in the composition and volume of smelter off-gases, which considerably hampers process optimisation; ii) high water vapour content in the gases after reduction; iii) air inflow; iv) difficulties in providing complete condensation of sulphur generated at all process stages; and v) limited equipment availability. The presence of water vapour reduces sulphur recovery at both the high-temperature reduction stage and the catalytic stages. The presence of oxygen in the gases leads to SO<sub>3</sub> generation, which aggravates the problem of equipment corrosion, and to deactivation of the catalyst used. Due to low technology efficiency the tail gases (after the burning furnaces) in the currently-operating sulphur production system contain up to 3-5% SO<sub>2</sub>.

Mass balance analysis of the methane technology demonstrated that disposal of the entire volume of enriched gases, even at the calculated maximum possible efficiency (which is not likely achievable, as practice shows), does not ensure reducing rates to the maximum permissible emission levels. It is therefore necessary to further treat either the high volume tail gases generated during sulphur production at an efficiency of more than 0.98, or impoverished gas streams generated by other production sections of the plant with an efficiency of more than 0.70. As is well known, the cost efficiency of impoverished gas disposal is nearly proportional to the gas volume. It should also be noted that the utilization of natural gas as the sulfur dioxide reducing agent and as the gas flux heating agent (up to 1250°C after water treatment) will produce significant amounts of carbon dioxide, the emissions of which must also be regulated, as Russia has signed the Kyoto Protocol. How the situation would change when using high-performance processes for sulphurous gas disposal is discussed below.

Analysis shows that the use of high-performance processes for enriched gas disposal, with sulphur dioxide recovery of 98-99% and sulphur dioxide content in the off-gases of 0.5-0.6 vol.%, will make it possible to reach the maximum permissible emissions.

A high-performance process of straight condensation with liquid sulphur dioxide recovery was selected for consideration as the most promising option for enriched gas disposal. The process allows for an easy attainment of the preset sulphur dioxide concentrations in the off-gases. It is suggested that impoverished gases (until main production and enriched/impoverished gas ratios are stable) should be concentrated and liquefied along with enriched gases. A number of methods are applied in the industry for impoverished gas concentration with the recovery of concentrated or liquid sulphur dioxide.

### 3. SCHEME FOR GENERATING LIQUID SO<sub>2</sub> USING LOW TEMPERATURES

The following scheme was considered for generating liquid sulphur dioxide from gases having an SO<sub>2</sub> concentration of 20-50% (Figs.1, 2). The gas is compressed to 10 atmospheres, cooled to -30°C and passed through the turbo-expander where it is cooled to -78°C. Liquefied sulphur dioxide is separated after each stage. The effluent gas contains 0.6% SO<sub>2</sub>, and sulphur dioxide recovery at the last stage is 97.6% and 99.4% for gas streams containing 20% and 50% SO<sub>2</sub>, respectively.

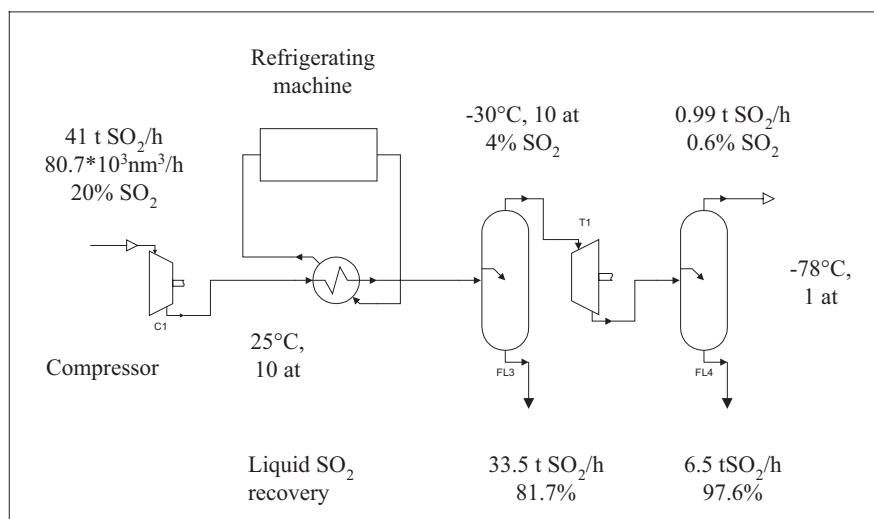


Figure 1. Schematic diagram of low temperature production of liquid sulphur dioxide, 20% SO<sub>2</sub> in gas.

Power inputs to generate liquid SO<sub>2</sub> (calculated per ton) using gas streams with 20% and 50% SO<sub>2</sub> at the compression and cooling stages are 205 and 78.5kW/t and 133 and 94.9kW/t, respectively. Figure 3 shows the change in the total power inputs (compression and cooling) needed to generate liquid sulphur dioxide using the proposed scheme, with liquid sulphur dioxide concentrations increasing in the considered gases. It is evident that power inputs reduce considerably as sulphur dioxide concentrations increase in the original gas stream.

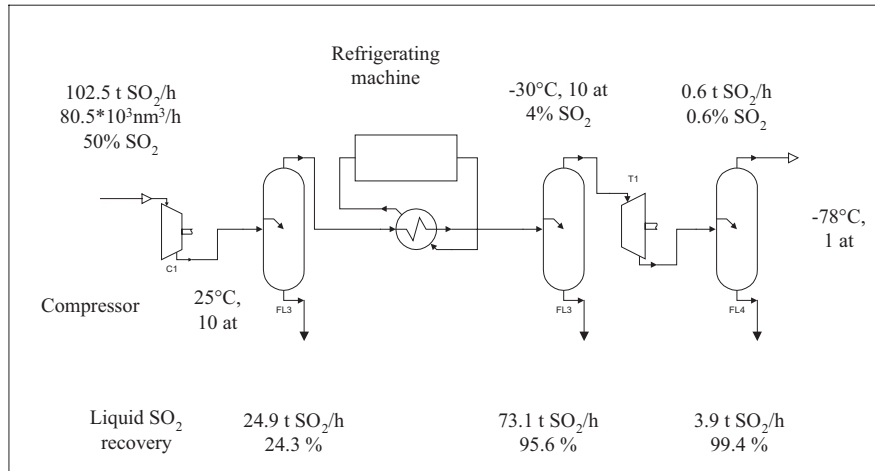


Figure 2. Schematic diagram of low temperature production of liquid sulphur dioxide, 50% SO<sub>2</sub> in gas.

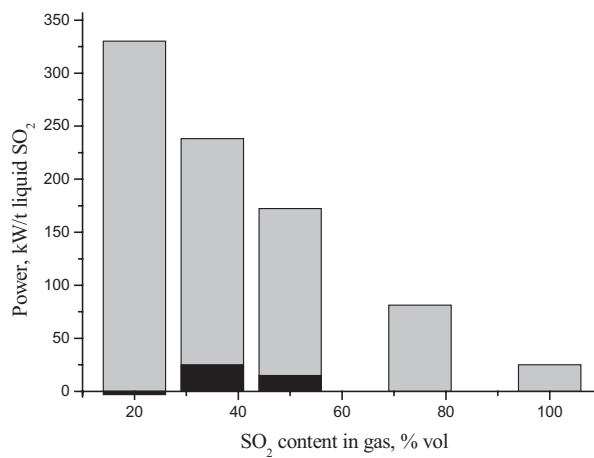


Figure 3. Power inputs for low temperature production of liquid SO<sub>2</sub>: ■ - with heat recuperation, □ - without heat recuperation.

Power inputs can be reduced at the cooling stage by using cold recovery. The calculations based on using cold recovery for 20% SO<sub>2</sub> streams under the scheme shown in Figure 4 demonstrate that power inputs reduce by nearly 2.5 times at the cooling stage. Another way to conserve energy can be

the use of power generated by hot gases emerging from the smelters. Power-input data based on the use of energy recovered from cooling gases when generating liquid sulphur dioxide from gas streams containing 20, 50 and 75% SO<sub>2</sub> is shown in Figure 3. It is evident that power inputs for compression and cooling are almost compensated with the energy generated via gas cooling.

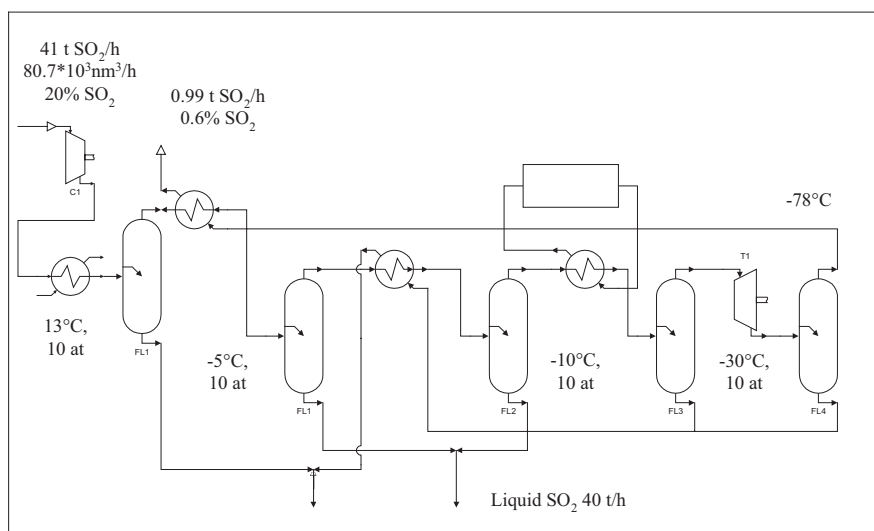


Figure 4. Schematic diagram of low temperature production of liquid SO<sub>2</sub> with cold recuperation; 20% SO<sub>2</sub> in gas.

#### 4. USE OF LIQUID SULPHUR DIOXIDE

When creating a liquid sulphur dioxide buffer there is the desire to generate gases with a constant SO<sub>2</sub> concentration in order to stabilize all operating sections of the plant producing sulphur, sulphuric acid and sodium bisulfite. In the future it would be possible to utilize liquid SO<sub>2</sub> in metallurgical technology, e.g. oxidative leaching of pyrrhotite concentrate (Sobol and Frash, 1974). The laboratory studies of this process demonstrated the increasing recovery efficiency of both base metals and platinum metals etc., and thus liquid sulphur dioxide could become a marketable product if the situation in the market changes.

In the absence of such a market it is suggested to dispose of excessive liquid sulphur dioxide in geological structures within permafrost areas.

## **5. ASSESSMENT OF THE POSSIBILITY TO DISPOSE LIQUID SO<sub>2</sub> IN GEOLOGICAL STRUCTURES**

Methods exist worldwide for the geological disposal of various waste streams, including the injection of CO<sub>2</sub> (Pearce and Rochelle, 1999, Bachu and Gunter, 2004), CO<sub>2</sub>/H<sub>2</sub>S mixtures (Bachu et al., 2003), and liquid toxic and radioactive waste (Stepanov, 2004).

The selection criteria for deep industrial liquid waste storage are relatively well developed (Stepanov, 2004). It is preferable to select water saturated units located within negative platform structures. These should have capacitance properties and be isolated from shallow groundwater and surface water with an overlying impermeable argillaceous mass. The reservoirs should be capable of holding significant volumes of waste and contain it within a limited section of the unit over a long period of time.

The selection of disposal sites for acid gases mainly depends on properties such as phase equilibrium, water content and solubility, and the generation of hydrates causing blockages in both boreholes during pumping and in compressors (Bachu et al., 2003).

Sulphur dioxide is a readily liquefied gas, forming at  $t = -10^{\circ}\text{C}$  at a pressure of 760 millimetres of mercury. The critical parameters for SO<sub>2</sub> are  $T=157.5^{\circ}\text{C}$  and  $P=77.8$  atmospheres. Sulphur dioxide forms gas hydrates relatively easily, even at temperatures of up to  $+12^{\circ}\text{C}$ . Sulphur dioxide gas-hydrate has a low generation pressure equilibrium, for example at  $12.1^{\circ}\text{C}$  the vapor pressure equilibrium is 2.3 atmospheres. Two types of solutions can be formed depending on the sulphur dioxide content in the SO<sub>2</sub>-H<sub>2</sub>O system: sulphur dioxide solution in water and water solution in sulphur dioxide. Depending on the sulphur dioxide concentration, SO<sub>2</sub> gas-hydrate is in equilibrium with one of the solutions or with ice below  $12^{\circ}\text{C}$ . There is a narrow range of water concentration in liquid sulphur dioxide when gas-hydrate is not formed in the solution between temperatures of  $-30$  to  $-40^{\circ}\text{C}$  (at 50 atm). When the water content in the mixture is higher the temperature must be maintained over  $12^{\circ}\text{C}$  to avoid gas-hydrate formation.

## **6. SELECTION OF LIQUID SO<sub>2</sub> DISPOSAL SITE IN THE NORILSK INDUSTRIAL AREA**

A geological analysis of the Norilsk Industrial Area was conducted to select the most appropriate site for liquid sulphur dioxide disposal based on available data.

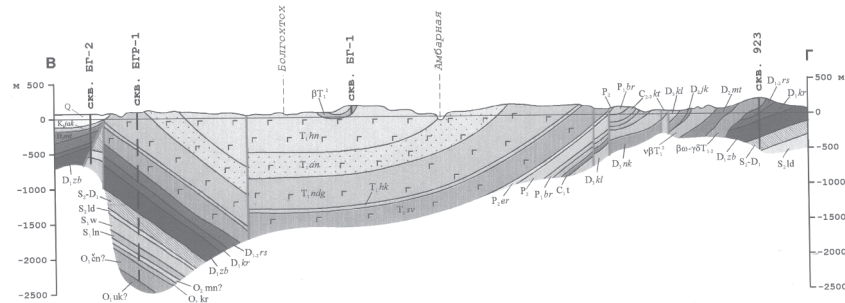


Figure 5. Geological profile of the Vologochanskaya syncline (Mezhvilk et al., 1972):  $T_1hl$  - Lower Triassic, Chachankanskaya Series,  $T_1sv$  - Lower Triassic, Syverminskaya Series,  $D_1zb$  - Lower Devonian, Zubovskaya Suite,  $D_1zb$  - Lower Devonian, Zubovskaya Suite,  $S_2ld_2$  - Upper Silurian, Upper Ludlow Series,  $S_2ld_1$  - Upper Silurian, Lower Ludlow Series,  $S_1w$  - Lower Silurian, Wenlock Series,  $S_1ln$  - Lower Silurian, Llandovery Series,  $O_2mn$  - Middle Ordovician, Mangazeysky Series,  $O_2kr$  - Middle Ordovician, Krivolutsky Series,  $O_1\check{c}n$  - Lower Ordovician, Chunksky Series.

A section of the northwestern limb of the Vologochanskaya syncline seems to be the most favorable area. It is located between the South-Pyasinskaya and Bolgokhtokhsкая brachyanticlines, 30km west of Norilsk (Fig.5). The Vologochanskaya syncline is formed by Lower and Mid-Paleozoic carbonate-terrigenous rocks and Lower Triassic volcanogenic rocks, and is stable tectonically. The size of the syncline provides enough space for a large reservoir suitable for long-term storage, while the negative structure provides a proper isolation from the biosphere. Silurian and Devonian rocks, as well as oil-saturated Lower Triassic tufogenic rocks separated by basalt covers, have good reservoir properties. The prevalence of carbonate rocks in the Paleozoic is a favorable factor for liquid  $SO_2$  disposal. The structure of the syncline and the alternation of reservoir beds with impermeable cover beds create a multilevel target for disposal of liquid sulphur dioxide. The topography of the syncline is a vast, poorly split watershed area with an elevated width of permafrost, which serves as a fluid-resistant cover.

## 7. PRINCIPAL RESULTS AND CONCLUSIONS

- It was demonstrated that in order to reach the maximum permissible emission of sulphur dioxide, straight condensation of sulphur-containing

gases could be used as the basic technology for enriched gas recycling, the sulphur dioxide recovery of which is 98-99% .

- The power inputs of straight condensation depends considerably on SO<sub>2</sub> content. Power inputs at the compression stage are 205 and 79 kW/t SO<sub>2</sub> liq., for input streams of 20 and 50 % SO<sub>2</sub>, respectively. Utilization of naturally cold conditions would allow for a significant reduction in refrigerating machine costs. The use of energy generated by cooling hot gases emerging from the liquid bath smelters (e.g., use of steam turbines) would allow for compensating up to 90-100% of total power inputs.
- It is proposed to dispose excessive liquid SO<sub>2</sub> in the geological structures of the Norilsk Industrial Area, with isolation being accomplished via both stratigraphic traps and the overlying gas-hydrate layer at the lower edge of the permafrost. A geological analysis of the area demonstrates that there is a theoretical possibility of such disposal. The northwestern portion of the Vologochanskaya syncline, between the South-Pyasinskaya and Bolgokhtokhszkaya anticlines, is proposed as a liquid sulphur dioxide disposal site.
- There are two types of geological reservoirs: aluminosilicate volcanogenic and terrigenous rocks and carbonate rocks. The first type ensures sulphur dioxide disposal without reactive interaction, while the latter ensures sulphur dioxide disposal with the formation of calcium salts.

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