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MIECZYSŁAW GOSTOMCZYK*, JOANNA MINKIEWICZ*

ON THE TREATMENT OF SOME INDUSTRIAL GASES

Methods for the treatment of flue gases generated by glass industry and by the manufacture of sulphuric acid are discussed. There are analyzed the following problems: the efficiency of SiF_4, HF and dust particulate removal from flue gases produced during manufacture of clouded glass (consideration is also given to the utilization of the products obtained); the efficiency of HF and SiF_4 removal from flue gases generated during sulphuric acid production (by the mixed-acid process and contact method), and the utilization of nitrogen oxides and sulphur dioxide.

The results discussed in this report have been obtained from many years' studies on full-scale installations designed and patented by the research staff affiliated with the Institute of Environmental Protection Engineering, Technical University of Wrocław.

1. METHOD OF REMOVING SILICON FLUORIDE, HYDROGEN FLUORIDE AND DUST PARTICLES FROM OUTLET GASES PRODUCED IN THE MANUFACTURE OF GLASS: UTILIZATION OF PRODUCTS

1.1. PRINCIPLES OF THE TREATMENT PROCESS

The gas stream passes through the dryer (in which slime containing calcium fluoride (CaF_2) and some other substances recovered from the charge applied are dried) to undergo two-stage absorption. Stage I consists of dust separation, cooling and removal of the main portions of silicon fluoride and hydrogen fluoride. At stage II the remaining amounts of hydrogen fluoride and silicon fluoride are removed. The spraying solution sodium hydroxide circulates in the following way: stage I – pumps, scrubber nozzles, settling tank, fan cooling tower, pump, nozzles; II – nozzles of the packed column, tank, pump.

*Institute of Environment Protection Engineering, Technical University of Wrocław, pl. Grunwaldzki 9, 50-370 Wrocław, Poland.

The absorption process involves the following reactions

$$SiF_4 + 2H_2O = 4HF + SiO_2,$$
$$HF + NaOH = NaF + H_2O,$$
$$SiF_4 + 2HF = H_2SiF_6 \text{ (at decreased pH)},$$
$$H_2SiF_6 + 2NaOH = Na_2SiF_6 + 2H_2O.$$

The spraying solution circulates in a closed cycle until its sorbing capacity is exhausted. Then, it enters the reactor for calcium hydroxide regeneration according to the following equations:

$$2NaF + Ca(OH)_2 = CaF_2 + 2NaOH \text{ (principal reaction)},$$
$$Na_2SiF_6 + Ca(OH)_2 = CaSiF_6 + 2NaOH \text{ (side reaction)}.$$

Rinsed sediments from the reaction and settling tank are sent to the dryer and recirculated to the manufacture unit. The regenerated solution passes to the absorbers.

The system described here has been working in one of Poland's glass works since 1977. It is operated to treat outlet gases from the manufacture of French-licence mosaic. The treatment efficiency meets the requirements adopted: G = 7000 m^3/h, T = 573–603 K; C_{SiF_4} = 100–400 mg/m^3; C_{HF} = 30–200 mg/m^3; C_{dust} = 1–3 g/m^3; F = 96–99.5^o/o; F_{dust} = 99–99.8^o/o.

The liquid circulates in a closed cycle. No wastewater is produced. The dry products of the treatment procedure calcium fluoride and dust particles are reused. The user intends to increase the output volume and calls for a larger treatment installation.

Technology and principal scruber are patented in Polish patents 101910 (1977) and 103217 (1979), respectively.

2. METHOD OF REMOVING HYDROGEN FLUORIDE AND SILICON FLUORIDE FROM OUTLET GASES GENERATED DURING CHEMICAL POLISHING OF CRYSTAL GLASS

2.1. PRINCIPLES OF THE TREATMENT PROCESS

Chemical polishing of crystal glass involves a hot bath containing sulphuric acid and hydrogen fluoride. This yields considerable amounts of silicon fluoride and hydrogen fluoride coming from the polishing machines, leakage, loading and unloading. The treatment process is carried out in two separate units for concentrated gases polishing machines and diluted gases air flux from the ventilation of the polishing room, respectively. The principle of the treatment process is the following: the gases to be treated flow in the countercurrent through a packed absorber which is sprayed with sodium hydroxide solution. The processes occurring in the absorber yield high removal of silicon fluoride, hydrogen fluoride and entrained sulphuric acid droplets:

$$SiF_4 + 2H_2O = 4HF + SiO_2,$$
$$HF + NaOH = NaF + H_2O,$$
$$SiF_4 + 2HF = H_2SiF_6,$$
$$H_2SiF_6 + 2NaOH = Na_2SiF_6 + 2H_2O.$$

The spraying solution circulates in a closed cycle until its sorbing capacity becomes exhausted. The solution is then pumped to the reactor for calcium hydroxide regeneration:

$$2NaF + Ca(OH)_2 = CaF_2 + 2NaOH \text{ (principal reaction)},$$
$$Na_2SiF_6 + Ca(OH)_2 = CaSiF_6 + 2NaOH \text{ (side reaction)}.$$

Rinsed sediments containing calcium fluoride and silica (which have settled in the reactor) along with unreacted calcium and calcium fluosilicate constitute a waste product which acts as artificial fluorite and may be reused for hadrogen fluoride production (or in other industries). The regenerated solution is recirculated to the production unit.

A large-scale system of that type has been working in one of Poland's largest glass works (which also belong to the largest glass works of the world) since July, 1984. The treatment efficiencies achieved so far average higher than it has been anticipated. Two separate systems are operated:

1. For condensed gases – $G = 150{,}000\ m^3/h$, $T = 293$-297 K, $C_F = 10$-$30\ mg/m^3$, $F_F = 90$-$95^o/o$.

2. For ventilation gases – $G = 7500\ m^3/h$, $T = 298$–305 K, $C_F = 1500$–$3000\ mg/m^3$, $F_F = 98$-$99.5^o/o$, $C_{H_2SO_4} = 10.40\ mg/m^3$, $F_{H_2SO_4} = 95$-$99.5^o/o$.

Advantages: high efficiency, low losses of calcium hydroxide during regeneration, recirculation in a closed cycle, small quantity of solid wastes of artificial fluorite which are easy to utilize. The system is also easy to operate.

Another system of that type has been installed lately in one more glass works.

3. DESULPHURIZATION OF FLUE GASES FROM THE MANUFACTURE OF SULPHURIC ACID

Based on many years' experience with a prototype system, two technological variants are proposed.

3.1. VARIANT 1

Absorption of sulphur dioxide in sodium sulphite and pyrolysis of sodium bisulphite. Utilization of sulphuric acid dioxide for the manufacture of sulphuric acid with sodium sulphate as by-product.

Applications: for ppower generation in 200 MW or larger plants fired with coal containing two and more percent of sulphur. The flow diagram is given in fig. 1.

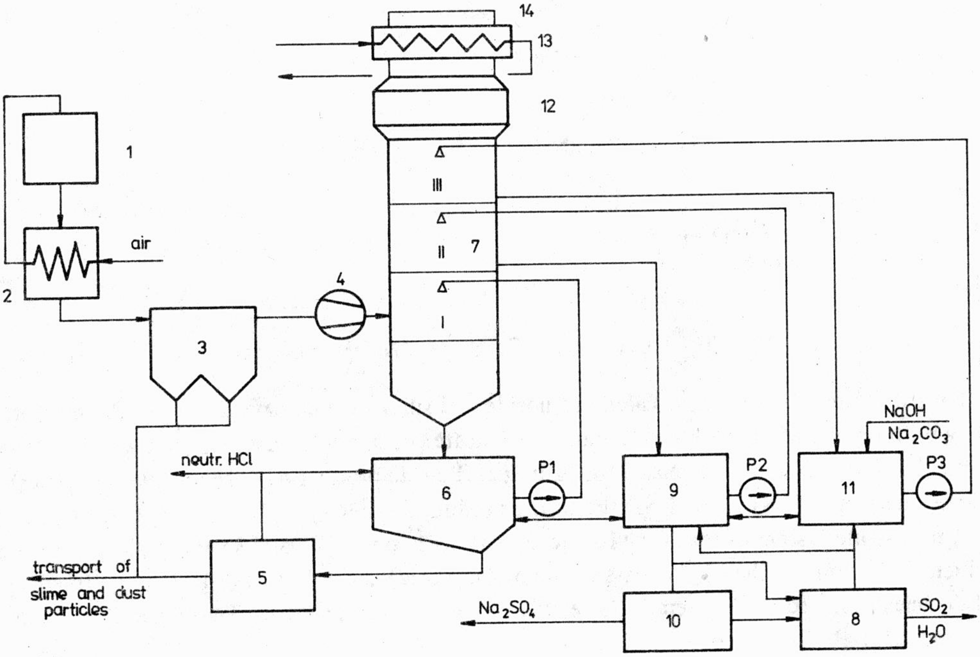

Fig. 1. Flow diagram for sorption and desorption of sulphur dioxide
Rys. 1. Schemat instalacji do sorpcji i desorpcji tlenku siarki

The flue gas of boiler *1* passes through the air heater *2* and dust separator *3* to be pumped by a fay *4* to the first stage of the sorber *7*. The contact with an alkaline spraying solution (predominant sodium sulphite) brings about a cooling down of the flue gas to approximately 333 K, as well as the separation of dust particles and removal of hydrogen chloride. The spraying solution circulates in a closed cycle: settling tank *6*, pump P_1 and nozzles of the first stage of the absorber *7*. The bottom sediments (slime) of the settling tank *6* are passed through a filter *5* to be disposed off (together with the dust particles from the separator *3*)at a dumping ground. The filtrate is recirculated to the first stage of the absorber. Some part of it is sent to the neutralizing unit, depending on the persistent chloride concentration. The second stage of the absorber *7* is predominantly fed with acid sodium sulphite through pump P_2, nozzles of the second stage and tank *9*. Some part of the solution passes through the desorber *8* to be subject to pyrolysis:

$$2NaHSO_3 \longrightarrow Na_2SO_3 + SO_3 + SO_2 + H_2O.$$

Sulphur dioxide (after drying) is sent to the manufacture of sulphuric acid. The third stage of the absorber *7* is a safety measure to provide adequate operation. The alkaline spraying solution circulates in a closed system: tank *11*, pump P_3 and nozzles of absorber *7*. The purified flue gas flows through the demister *12* and heater *13* to enter stack *14*. Sodium sulphate (which forms in the course of the absorption process) crystallizes from the effluent solution (crystallizer *10*).

Major advantages: high degree of sulphur removal (90-95%); easy operation, high economy, possibility of application in regions with no dumping facilities.

3. 2. VARIANT 2

Absorption of sulphur dioxide as in variant 1. Regeneration of the sorption effluent with calcium hydroxide according to the following equation:

$$NaHSO_3 + Ca(OH)_2 = CaSO_3 + NaOH + H_2O.$$

Separation and rinsing of the $CaSO_3 \cdot 1/2\,H_2O$ evolved and oxidation to $CaSO_4 \cdot 2H_2O$. Application of gypsum in a mixture with slag and cement to the manufacture of building materials.

Major advantages: the method is well suited both for incorporation in the design of new boiler rooms and for retrofit to an operating unit and yields high efficiencies of sulphur removal (90-95%); the system is easy to operate both in small and large objects.

The flow diagram is shown in fig. 2. The difference between variant 1 and variant 2 consists in the regeneration unit; depending on the size of the industrial object, some of the devices (e.g. dust separator) or some of the absorption stages (stage II or stage III) may be eliminated. The sorption effluent passes from tank *9* to reactor *8* for regeneration with calcium hydroxide or calcium carbonate according to the following reactions:

$$NaHSO_3 + Ca(OH)_2 = CaSO_3 + NaOH + H_2O, \quad (1)$$

$$Na_2SO_4 + Ca(OH)_2 = CaSO_4 \cdot 2H_2O + 2NaOH. \quad (2)$$

The yield of reaction (1) varies from 50 to 70%, whereas that of reaction (2) falls between 5 and 20%. Thus, the absorption process should be conducted so as not to oxidize sulphites. The slime produced in reactor *8* is separated by centrifiguration *10* and oxidized to $CaSO_4 \cdot 2H_2O$ in the oxidizing reactor *15* and from there, it may either be sold to a building materials manufacturing plant or disposed off on a dumping ground. The effluent solutions from reactor *8* and from the centrifugal separator *10* are pumped to the settling tank *6* through tank *16*.

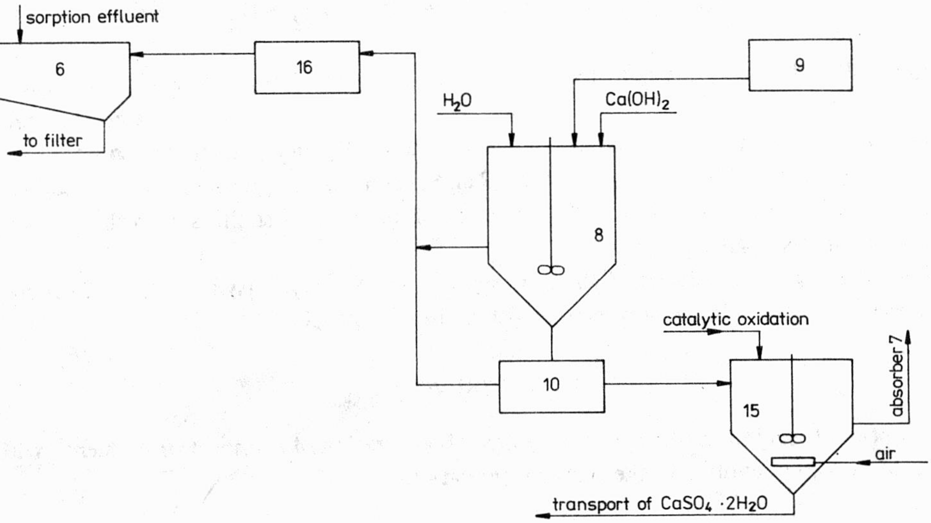

Fig. 2. System for desulphurization of flue gases. Variant 2 with gypsum production
Rys. 2. Schemat instalacji do odsiarczania spalin. Wariant 2 z produkcją gipsu

5. REMOVAL AND UTILIZATION OF NITROGEN OXIDES FROM THE MANUFACTURE OF SULPHURIC ACID BY THE MIXED ACID METHOD

5.1. PRINCIPLE OF THE PROCESS

The outlet gases flow through a demister of a special design for the removal of sulphuric acid mist. The effluent sulphuric acid mist concentration is below 100 mg/m^3. From the demister, the gases (concurrently with the spraying solution) through the absorber packed with I-15M polyethylene rings. The spraying solution sodium hydroxide circulates in a closed system: tank, pump, nozzles of the absorber until its sorbing capacity is exhausted (at controlled pH).

The absorber involves the following reactions:

$$2NO_2 + 2NaOH = NaNO_3 + NaNO_2 + H_2O,$$

$$N_2O_3 + 2NaOH = 2NaNO_2 + H_2O,$$

$$NO + {}^1/2O_2 = NO_2$$

$$NO + NO_2 + 2NaOH = 2NaNO_2 + H_2O,$$

$$H_2SO_4 + 2NaOH = Na_2SO_4.$$

The sorption effluent contains: sodium nitrite (88-90%), sodium nitrate (5-10%), Na_2SO_4 (2-6%), and other substances (1-3% dry wt). Its utilization consists in the chemical degradation of excess sulphuric acid:

$$2NaNO_2 + H_2SO_4 = Na_2SO_4 + N_2O_3 + H_2O.$$

The process is conducted in reactors, and concentrated nitric oxides are passed to the Glover tower or production power (manufacture of sulphuric acid). Excess sulphuric acid (together with Na_2SO_4 and $NaNO_3$ salts dissolved in it) is to the manufacture of superphosphate.

Such a system has been operated in Poland since January, 1981. The system works with the anticipated efficiency: G = 25,000 m^3/h, T = 303-310 K, $C_{H_2SO_4}$ = 40-100 mg/m^3, C_{NO_2} = 2-5 g/m^3, C_{NO} = 0.5-3.0 g/m^3, $F_{H_2SO_4}$ = 95-98%, F_{NO_2} = 85-90%, and F_{NO} = 60-80%. Prior to the installation of the system, nitric acid demand for the manufacture of sulphuric acid by the mixed acid method amounted to 20-22 kg of nitric acid per 1000 kg of sulphuric acid. During 4.5 years of operation, the demand for nitric acid has averaged to 9.2 kg of nitric acid per 1000 kg of sulphuric acid. No wastewaters or solid wastes are produced in this method. Diluted sulphuric acid from the sodium nitrite degrading reactors combines with 75% sulphuric acid from the production process to degrade phosphorites. Na_2SO_4 and sodium nitrate act as microelements in superphosphate, thus improving its agricultural uses.

6. REMOVAL AND UTILIZATION OF SULPHUR DIOXIDE CONTAINED IN OUTLET GASES FROM THE MANUFACTURE OF SULPHURIC ACID BY THE CONTACT METHOD

6.1. PRINCIPLE OF THE PROCESS

The outlet gases flow through a single-stage absorber sprayed with an aqueous solution containing $NaSO_3$, $NaHSO_3$ and Na_2SO_4. The solution circulates in a closed system: nozzles, tank, heat exchanger, evaporator, heat exchanger, nozzles of absorber. Concentrated sulphur dioxide evolved in the evaporators oxidizes to SO_3 and is subject to sorption in the towers of sulphuric acid manufacture.

The system involves the following reactions:

$$\left.\begin{aligned} SO_2 + Na_2SO_3 + H_2O &= 2NaHSO_3, \\ Na_2SO_3 + {}^1/{}_2O_2 &= Na_2SO_4 \end{aligned}\right\} \text{absorber,}$$

$$2NaHSO_3 \xrightarrow{\text{temp}} Na_2SO_3 + SO_2 + H_2O \Big\} \text{ evaporator,}$$

$$Na_2SO_{4(liquid)} \xrightarrow[decrease]{temp} Na_2SO_{4(crystal)} \Big\} \text{crystallizer},$$

$$SO_2 + {}^1/{}_2O_2 = SO_3 \Big\} \text{oxidizer}.$$

A full-scale installation of that type has been designed for a sulphuric acid manufacturing plant in Poland.

OCZYSZCZANIE WYBRANYCH GAZÓW ODLOTOWYCH

Przedstawiono wybrane metody oczyszczania gazów odlotowych powstających podczas produkcji szkła i kwasu siarkowego. Przedmiotem badań były: stopień usuwania fluorku krzemu, fluorowodoru i pyłu z gazów po produkcji szkła mąconego, a także utylizacja otrzymanych produktów; usuwanie fluorowodoru oraz fluorku krzemu z gazów odlotowych po polerowaniu chemicznym kryształów; odsiarczanie i oczyszczanie gazów po produkcji kwasu siarkowego metodą nitrozową i metodą kontaktową, jak również utylizacja tlenków azotu i dwutlenku siarki.

Omawiane wyniki otrzymano na podstawie wieloletnich badań na instalacjach przemysłowych opatentowanych przez pracowników Instytutu Inżynierii Ochrony Środowiska Politechniki Wrocławskiej.

ÜBER DIE REINIGUNG EINER ABGASE

Die in diesem Aufsatz besprochen Abgase werden von der Glasindustrie während der Trübglaserzeugung und des Polierätzens von Kristallglas abgegeben. Diese Abgase belasten die Atmosphäre mit SiF_4, HF und Staubpartikeln.

Andere Abgase, denen auch viel Aufmerksamkeit geschenkt wird, werden während Schwefelsäureherstellung erzeugt. Die damit im Zusammenhang stehende Abgabe von Stickoxyden und Schwefeldioxid verursacht Probleme in der Luft.

Die Mitarbeiter des Instituts für Umweltschutz und Umweltechnik der Technischen Universität zu Wrocław befassen sich schon seit Jahren mit diesen Fragen. Sie haben eigene Reinigungsverfahren und -apparatur entwickelt und patentiert. Die Apparatur arbeitet in den grössten Kristall- und Glasfabriken Polens sowie in den Schwefelsäureherstellungsanlagen.

ОЧИСТКА ВЫБРАННЫХ ОТХОДЯЩИХ ГАЗОВ

Представлены выбранные методы очистки отходящих газов, образующихся при производстве и серной кислоты. Исследовадись не только степень удаления фтористого кремния, фтористого водорода и пыли из газов после производства молочного стекла, но и утилизация полученных продуктов; удаление фтористого водорода и фтористого кремния из отходящих газов после химической полировки кристаллов; обессеривание и очистка газов после производства серной кислоты нитрозным и контактным методами, а также утилизация окислов азота и двуокиси серы.

Обсуждаемые результаты получены на основе многолетних испытаний на промышленных установках, патентованных сотрудниками Института технической охраны среды Вроцлавского политехнического института.