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SULPHUR REMOVAL FROM FLUE GASES

PART II. DOUBLE-ALKALI METHOD AND UTILIZATION OF THE BY-PRODUCT ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

The flue gas desulphurization (FGD) technology presented in this paper is designed for a thermal-electric power station. The FGD system receives an hourly volume of flue gases amounting to $530,000 \text{ m}^3$ with an average sulphur dioxide concentration of 1.3 g/m^3 . The FGD process is based on the wet double-alkali method, which ensures: 1) recirculation of the regenerated sorption effluent in the absorption unit, and 2) calcium sulphate sediment as a waste product. In this paper, there is proposed a system for the utilization of the waste product (utilization unit). The processing procedures performed in the utilization unit yield binding materials, commercial gypsum, and building blocks. The FGD process is a no-waste technology which brings about an over 90% abatement of sulphur dioxide and particulate matter emissions.

1. INTRODUCTION

In the first part of this paper [1], we have proposed a modification of the well-known and widely applied double-alkali method. The modified flue gas desulphurization (FGD) system is economic, relatively modest in space demand and easy to operate.

Taking into account the state-of-the-art, as well as the current developmental trends in FGD throughout the world [1], the authors of this paper arrived at the conclusion that in Poland preference should be given to FGD technologies enabling utilization of the by-products. Considering the ever increasing shortage of water resources and dumping (to say nothing of the rapid rise in the demand for building materials), we developed an FGD technology that meets the aforementioned requirements. The technology makes use of the double-alkali method combined with the regeneration of the effluent from the sorption process and with the utilization of the by-product, i.e., $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Of the various advantages of the double-alkali methods [2], the following deserve particular attention: ease of operation, high efficiency

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of SO_2 absorption, lower liquid phase flow rate/gas phase flow rate ratio [3], smaller pressure losses during gas flow through the apparatus, and a smaller size of the absorbers as compared to the suspension methods which are widely used throughout the world [4]. The last, but not the least, advantage of the double-alkali processes is the separation of the precipitation section from the absorption unit [5], which resolves scaling problems.

Basing on the results of laboratory- and pilot-scale investigations, a full-scale industrial FGD system has been designed. The system works for the needs of the thermal-electric power station operated by the synthetic fibre manufacturing plant Chemitex-Celwiskoza of Jelenia Góra, Poland [6].

2. DESCRIPTION OF THE FGD METHOD

The system has been designed for the purification of an hourly volume of $530,000 \text{ m}^3$ of pretreated flue gases emitted from two OKR-50 steam boilers and two WR-46 water heaters. The flue gas stream has a temperature approaching 438 K. Sulphur dioxide concentration and dust particulate concentration average 1.3 g/m^3 and 0.6 g/m^3 , respectively. The flow diagram is shown in fig. 1. Following dust particle separation, the flue gas stream is sent to the spraying

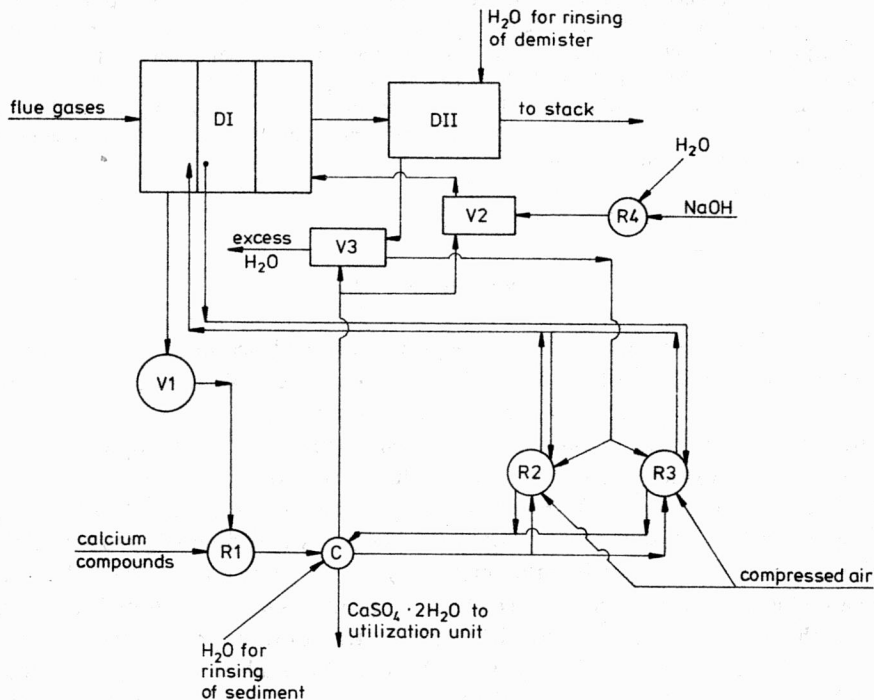
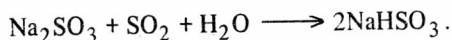


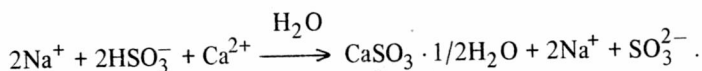
Fig. 1. Flow diagram of the FGD system

DI – absorber, DII – demister, V1 – tank of effluent from sorption, V2 – tank of regenerated absorbent, V3 – tank of washings, R1 – reactor for regeneration of sorption effluent, R2 and R3 – oxidizing reactors, C – centrifuge

column DI which acts both as a prescrubber and an absorber. The spraying liquid is a mixture of following aqueous solutions: Na_2SO_3 , NaHSO_3 and Na_2SO_4 , at a concentration approaching $153 \text{ kg Na}_2\text{SO}_3/\text{m}^3$ and pH of about 6.5. Absorption of sulphur dioxide in the solution proceeds as follows:



Absorber DI consists of three sections (each with an independent circulation of the fluid) and is sprayed alternately in co- and counter-current. Passage through Section I yields cooling of the flue gas stream to the temperature of 323 K, wetting and removal of dust particulates, as well as sorption of such gaseous pollutants, as SO_3 or Cl. Absorption of sulphur dioxide occurs in Sections II and III. Each section has a tank in its bottom part which receives the effluent formed during the sorption process. Since the fluid level differs from one tank to another, the effluent can be passed (by overfall) from Section III to Section II, and from Section II to Section I, after a certain pH value has been achieved. The tank of Section III is fed with fresh absorbent of pH ~ 6.5 coming from the regeneration unit. The effluent, which is received by the tank of Section I and has a pH approaching 4.7, passes to V1 acting as a storage tank for the regeneration unit. From V1 the effluent is sent to reactor R1 for regeneration with calcium compounds (in the form of whitewash or limestone) according to the reaction



The reaction yields a fresh sorbing solution of pH ~ 6.5 (after centrifugation in the centrifugal separator C) and a sediment with calcium sulphite as the main component (the sediment also includes small amounts of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and a portion of dust particulates absorbed in Section I). The fresh absorbing solution is passed to V2 which serves as a storage tank for the absorption unit. The sediment is sent to the oxidation unit consisting of two reactors, R2 and R3. Simultaneously each reactor is supplied with compressed air, the fluid leaving the storage tank for washings (V3), and the flue gas stream from section II of the absorber after separation of dust particulates, but still carrying sulphur compounds for acidification of environment to pH $\sim 4.3-4.5$.

As a results of the oxidation process running via the above route and catalysed by Fe^{3+} ions present in the dust particulates sorbed, a wet sediment is obtained (after centrifugation of suspended matter) which contains about 85% of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The sediment is sent to the utilization unit. The flue gas stream treated in the absorber passes through demister DII to the emitter. Sodium losses (Na^+ ions leave the FGD system along with the wet sediment) are made up with the NaOH solution supplied from reactor R4 where it is prepared.

The sysetm will be modified by the addition of throttles along the feeding pipes to enable by-pass of the flue gas stream.

Since in the FGD technology proposed calcium sulphate is formed as by-product, the system includes a utilization unit designed for this compound (fig. 2). The utilization unit comprises clarifiers, furnaces, storage tanks for sinters, a ball grinder, a sieve, gypsum storage tanks, dosers, mixers, formers, and stores. In the utilization unit, the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ sediment

is processed to set it into gypsum. According to needs, the product may be either bagged and marketed or may undergo further processing in order to obtain prefabricated slag-gypsum units [7].

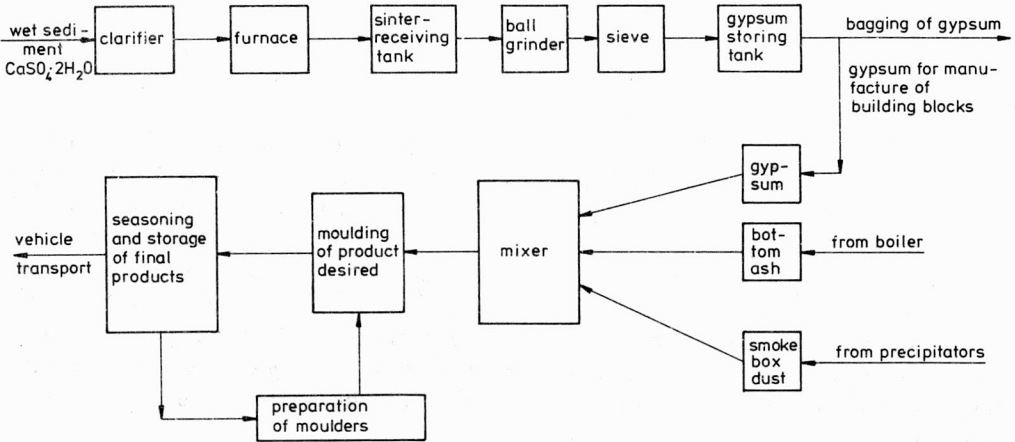


Fig. 2. Gypsum utilization unit

3. OPERATING DATA

The system guarantees 90–98% efficiency (η) of SO_2 and particulate removal, irrespective of the variations in flue gas loading or composition. To regenerate the effluent from the sorption process, it is necessary to apply hourly doses of approximately 1025 kg of CaCO_3 (calculated in terms of pure limestone). Oxidation of the $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$ sediment (a product of the regeneration process) requires an air of about 8000 m^3/h and a flue gas volume of about 20,000 m^3/h , i.e., $\sim 6250 \text{ m}^3/(\text{h} \cdot 1000 \text{ kg of } \text{CaSO}_3 \cdot 1/2\text{H}_2\text{O})$; the flue gas carries sulphur compounds, dust particles have been separated. To make up the hourly sodium loss, about 47 kg of NaOH are needed. Of these, $\sim 4.5 \text{ kg of NaOH/h}$ are spent for the make-up of Na^+ ions (which pass together with the sediment to the utilization unit), and $\sim 42.5 \text{ kg of NaOH/h}$ are utilized for the make-up of Na^+ ion losses resulting from their reaction with H_2SO_3 , which oxidizes to H_2SO_4 in the absorber. Pressure losses in the gaseous part of the FGD system approach 2000 Pa, whereas the total energy demand amounts to 1.3 MW (about 0.16 MW being used in the utilization unit).

During operation, the system produces wet sediments at a rate of about 3440 kg/h. The sediment has a moisture content approaching 40 wt.% and a pH falling between 5 and 6. As far as its composition is concerned, content of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ accounts for approximately 85%, the remainder consisting of dust particulates which have been sorbed in the course of the

treatment process. Further processing in the utilization unit yields about 1.5 t of commercial gypsum per hour as the final product, and about 0.8 m³ of material for building prefabricates per hour.

It is necessary to remove from the FGD system the water volume of about 101 m³/h. The water of a pH varying between 6.5 and 7.0 contains small amounts of sodium (between 0.7 and 1.0 kg Na⁺/m³). It can be reused in the unit for the manufacture of building materials or in the hydrotransport of fly ash and bottom ash.

The entire space demand for the FGD system amounts to about 10,000 m³; of these, approximately 4800 m³ are required for the gypsum utilization unit. After passage through the FGD system, the flue gases entering the stack have a temperature of 323 K, a sulphur dioxide concentration of 0.079 g/m³, and a dust particulate content of 0.05 g/m³.

4. SUMMARY

The FGD system involves a modern no-waste technology and gives an efficiency of sulphur removal (η) equal to 90% or higher.

The dust particulates retained in the absorbent can be sent to the regeneration unit together with the effluent formed during sorption. The investigations have revealed that the presence of particulates has no adverse effect on the mechanical or setting properties of commercial gypsum, which is the end-product of the utilization procedure.

Gypsum and slag gypsum prefabricates, the by-products of the FGD process, may be used for building purposes.

The FGD system ensures smooth operation, irrespective of the $\pm 10\%$ variations in the flow rate or sulphur dioxide concentration of the flue stream.

The characteristics of the FGD system (in terms of 1000 m³ hourly flue gas volume) can be presented as follows:

I. Demand and requirements

- 1) dry, pulverized CaCO₃ (grain size ≤ 0.003 m) for the regeneration unit, 2.0 kg/h;
- 2) compressed air for the oxidation unit, 15 m³/h;
- 3) flue gases with no particulate content (passing from Section II of the absorber to the oxidation unit), 38 m³/h;
- 4) NaOH for the make-up of sodium losses in the FGD system, 0.09 kg/h;
- 5) technological water (for rinsing of demisters, preparation of NaOH solutions, and washing of the sediments in the utilization unit), 0.21 m³/h;
- 6) electric power, 2.45 kW.

II. Products obtained

- 1) commercial gypsum, 2.8 kg/h;
- 2) building materials in the form of slag gypsum blocks, 1.5 dm³/h;
- 3) wastewater (pH ~ 6.5 – 7.0 ; Na⁺ concentration, ~ 0.7 – 1.0 kg/m³), 0.2 m³/h.

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ODSIARCZANIE GAZÓW SPALINOWYCH
CZĘŚĆ II. METODA DWUALKALICZNA Z UTYLIZACJĄ PRODUKTU
UBOCZNEGO (CaSO₄ · 2H₂O)

Opisano technologię odsiarczania gazów odlotowych z elektrociepłowni na przykładzie instalacji oczyszczającej 530 000 m³/h spalin o średnim stężeniu 1,3 g SO₂/m³. Podstawą procesu odsiarczania jest mokra metoda dwualkaliczna, dzięki której powstaje zregenerowany roztwór sorpcyjny cyrkulujący w węzle absorpcji oraz odpadowy osad siarczanu wapniowego. Przedstawiono także projekt instalacji do utylizacji odpadowego siarczanu wapniowego. W wyniku pracy węzła utylizacji otrzymuje się materiał wiążący, gips handlowy oraz prefabrykaty budowlane. Zaprezentowana technologia pozwala na ponad 90% ograniczenie emisji SO₂ i pyłów i jest całkowicie bezodpadowa.

ОБЕСЕРЕНИЕ ГАЗОВ СГОРАНИЯ.
ЧАСТЬ II. ДВУЩЕЛОЧНЫЙ МЕТОД С УТИЛИЗАЦИЕЙ
ПОБОЧНОГО ПРОДУКТА (CaSO₄ · 2H₂O)

Описана технология обесерения отходящих газов из теплоэлектростанций на примере очищающей установки 530 000 м³/ч газов сгорания средней концентрации 1,3 г SO₂/м³. Основой процесса обесерения является мокрый двухщелочной метод, благодаря которому образуется регенерированный сорбционный раствор, циркулирующий в узле абсорбции, а также отходный осадок сульфата кальция. Представлен также проект установки для утилизации отходящего сульфата кальция. В результате работы узла утилизации получают вяжущий материал, торговый гипс, а также строительные бетониты. Представленная технология позволяет ограничить на свыше 90% эмиссию SO₂ и пылей и она является вполне безотходной.