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# SULFUR REMOVAL FROM FLUE GASES

## PART I. MODIFIED DOUBLE-ALKALI METHOD

A new technology is proposed for sulfur removal from stack flue gas emitted by a thermal-electric power station. The system has been designed for treating a flue-gas volume of 420,000 $m^3/h$ by the modified double-alkali method. The technology brings about an over 90% abatement of $SO_2$ emission for $SO_2 \leqslant 10$ $g/m^3$ concentration in the flue gas stream. Making use of the modified technology, the treatment system is economic, relatively modest in space demand, and easy to operate. This treatment method is best suited for industrial objects where fly ash and bottom ash disposal involves sluicing to ponds.

## 1. INTRODUCTION

Continuing population growth, as well as the ever increasing rate of industrial production throughout the world have made pollution control a problem of global significance. Of the problems dealt with in pollution control, atmospheric pollution deserves particular attention. The main class of primary air pollutants includes sulfur oxide, as well as the products of its oxidation. Needless to say that the greatest portion of $SO_2$ released into the atmosphere comes from power generation. The process of sulfur removal is not as difficult as the utilization of the by- or end-products. Among various methods of sulfur removal from gases, wet techniques have become dominant [1]–[3]. Although wet processes are economic and easy to conduct, they have the disadvantage of producing large amounts of sludge and effluents from sorption, which call for adequate management. The choice of an appropriate method for the separation of $SO_2$ depends primarily on the local possibilities of storage and/or reuse. The solutions used for the absorption of $SO_2$ in industrial systems require regeneration [4], [5] as otherwise they would become a waste products which would take the form of nuisant wastewaters. Following regeneration, the solution is sent to the absorption system for reuse because of the high cost of fresh sorbent.

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Taking into account the ever increasing shortage of water resources and damping sites in Poland, preference is given to such technologies which enable utilization of the by-product or end-product as a building material or facilitate recovery of sulfuric acid [6], [7], [9], [10].

At laboratories of the Institute of Environment Protection Engineering, Technical University of Wrocław, a sulfur removal technology has been developed. The technology involves the double alkali method and regeneration of the effluent from sorption, and enables utilization of the by-product, i.e., $CaSO_4 \cdot 2H_2O$ [10].

If the technology is to work under industrial conditions, then space demand becomes a vital problem. A complete technological system installed for the needs of a medium-size thermal-electric power station covers an area which is several times as large as that for the power station itself. In Poland, many of the existing industrial plants were designed and constructed decades ago, when no consideration was given to environmental problems. As these plants are often obsolete, the necessity of designing industrial-scale sulfur-removal systems with moderate space requirements has become urgent. Keeping this in mind, is was possible to develop a modified double-alkali technology (with no utilization of the by- and end-products). The technology applies well to those obsolete objects suffering from constriction for space because it reduces the area requirement by almost two-thirds. Both technologies were tested under laboratory- and pilot-scale conditions (BOBREK Metallurgical Works and Świecie Papermaking Plant).

Basing on the two technologies (modified and non-modified), two-scale systems for sulfur removal from stack flue gases have been designed [11]. The systems are to be installed in the thermal-electric power station operated by the chemical plant CHEMITEX-CELWISKOZA of Jelenia Góra. The station produces power and heat not only for the chemical plant, but also for some part of the city. Five steam boilers are in operation, and two water heaters are under construction. As the object has been located in a recreational and touristic area, the abatement of sulfur compound emission is a problem of vital significance.

## 2. GENERAL CHARACTERIZATION OF THE METHOD

The system is designed for sulfur removal from flue gas streams leaving three steam boilers of ·OKR-50 type at the rate of 420,000 $m^3$/h. The temperature of the flue gas approaches 438 K. The concentrations of $SO_2$ and particulates average 1.3 $g/m^3$ and 0.6 $g/m^3$, respectively. The flue gas stream also contains small amounts of $SO_3$ and nitrogen oxides.

Figure gives the schematic diagram of the system which consists of four major parts: a spraying column 1 which acts both as a pre-scrubber and an absorber, two demisters 2, a tank for pH adjustment 3, and a settling tank 4. The absorber is sprayed alternately in co-current and counter-current. The contact of $SO_2$ and dust
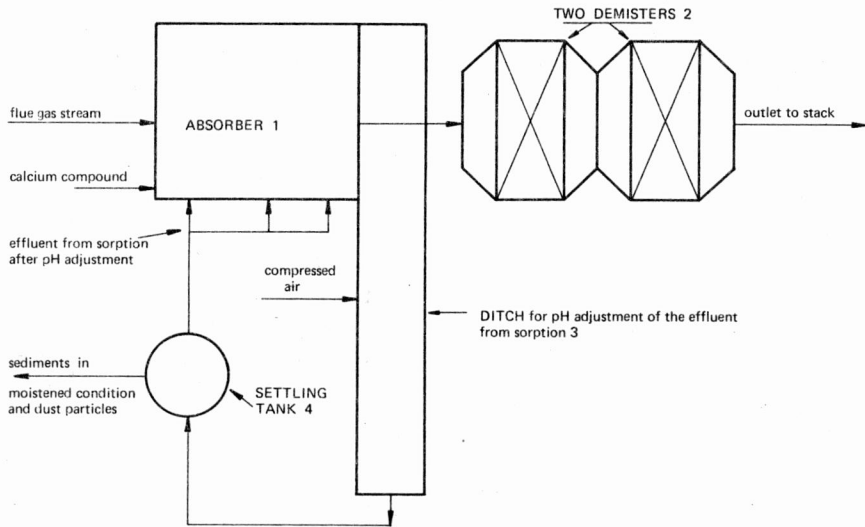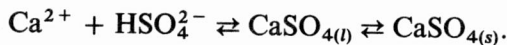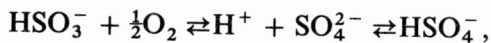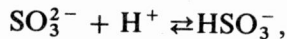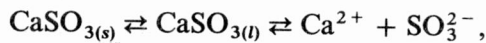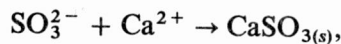
Technological diagram of the treatment system working on principle of the modified double-alkali method

particles with the spraying liquid yields the washout of the two pollutants according to the following reaction:

$$SO_2 + H_2O \rightarrow H_2SO_3.$$
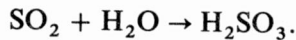
Sulfurous acid produced via the above route reacts with the cations ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$) contained in the sorbing solution to form respective sulfites and bisulfites. $Fe^{3+}$ (coming from the dust particles absorbed in the sorbing solution) and oxygen (carried in the flue gas stream) account for the oxidation of the effluent from sorption, which enters the tank under the column *1* to leave the system through an outflow ditch. The same tank also receives calcium compounds (e.g., pulverized limestone) in order to adjust the pH of the effluent from sorption. The outlet ditch is aerated along the entire lenght to aid further pH adjustment. The reactions in the two tanks run according to the following equations:

$$SO_3^{2-} + Ca^{2+} \rightarrow CaSO_{3(s)},$$

$$CaSO_{3(s)} \rightleftarrows CaSO_{3(l)} \rightleftarrows Ca^{2+} + SO_3^{2-},$$

$$SO_3^{2-} + H^+ \rightleftarrows HSO_3^-,$$

$$HSO_3^- + \tfrac{1}{2}O_2 \rightleftarrows H^+ + SO_4^{2-} \rightleftarrows HSO_4^-,$$

$$Ca^{2+} + HSO_4^{2-} \rightleftarrows CaSO_{4(l)} \rightleftarrows CaSO_{4(s)}.$$

The suspension produced via these reactions has a pH ranging between 7.0 and 7.5 and is pumped to the settling tank for clarification. Following sedimentation, the

effluent is clear enough to be circulated to the absorber nozzles. The bottom sediments (which consist primarily of $CaSO_4 \cdot 2H_2O$ and absorbed dust particles) are sent to the damping site where fly and bottom ashes are stored.

The absorbing solution consists of water and water-soluble high-pH salts (e.g., $Na_2CO_3$, $K_2CO_3$). But absorption may also be conducted with the fluid recovered from hydrotransport, which consists in sluicing the fly and bottom ashes into a pond. Hence, wherever this method of disposal is practiced, the size of the treatment installation may be diminished by eliminating the settling tank and the outlet ditch. The effluent from the sorption process can then be sent directly to the ash hydrotransport system for pH adjustment. The sorbing solution can be made up with the clarified liquid from the pond. But this variation of the treatment system may only be applied after careful analysis of the composition of the fly ash and bottom ash produced. CHEMITEX-CELWISKOZA discharges some portion of the effluent from technological processes to the pond. Thus, the fluid from hydrotransport cannot be made use of in the absorption process. Admixture with technological wastewater has an undesirable effect on the absorption of $SO_2$.

## 3. TECHNOLOGICAL AND OPERATING PARAMETERS

The absorber is a fundamental part of the system. It consists of a cubicoidal steel column divided into three two-compartment sections which differ in rate and method of spraying. Each compartment has a $2 \times 10$ m cross-section. One of the three sections acts as a pre-scrubber which is responsible for the removal of dust particles, chlorine compounds, $SO_3$, etc., for the cooling of the passing gases, and for their complete humidification. The remaining two sections are designed for the absorption of sulfur dioxide. The bottom part of the absorber comprises a special tank which receives the effluent from each of the three sections.

The system gives the efficiency of sulfur and particulate removal $\eta$ ranging between 90 and 98%, which depends on the quantity and on the composition of the incoming flue gas stream. pH adjustment in the effluent from the absorber requires an hourly limestone portion of about 0.8 t, and an hourly air portion of about 10,000 $m^3$. During one-hour operation the system produces about 5.5 t of waste sediments in moistened condition (containing some 1.6 t of dry settled matter, primarily $CaSO_4 \cdot 2H_2O$). Resistance of flow in the gaseous section of the system approaches 2000 Pa, and the predicted total energy demand amounts to 0.6 MW/h. The entire system covers the area of about 1600 $m^2$.

## 4. SUMMARY

Taking into account the urgent need of constructing a prototype system for sulfur removal from industrial gases, it seems advisable to recommend the treatment system

described in this paper. The system is economic, easy to handle, and moderate in space demand.

A major advantage of the system is the possibility to control the quantity of the absorbing solution which enters the nozzles of the absorber, and the quantity of limestone for pH adjustment. Removal efficiency is greater than 90% despite considerable variations in the gas flow rate and $SO_2$ concentration.

The size of the treatment system (making use of the technology proposed) can be increased or decreased, whenever necessary. The system applies to sulfur removal from waste gases of an $SO_2$ concentration equal to or lower than 10 $g/m^3$. When the quantity of the waste gases to be treated exceeds 1,000,000 $m^3/h$, it is advisable to design two absorbers arranged in parallel.

To perform its duty a system designed for treating an hourly flue-gas volume of 1000 $m^3$ needs 2.0 kg of limestone or 1.5 kg of lime, 0.25 $m^3$ of technological water for the rinsing of the demisters, 24.8 $m^3$ of compressed air for pH adjustment and for the oxidation of $CaSO_3 \cdot \frac{1}{2}H_2O$ and 1.4 kW of electric energy.

During 1 hour of operation the following substances are to be removed from the system: 13.3 kg ($\sim 0\,0.01\ m^3$) of sediments in moistened conditions (containing 3.98 kg of dry matter which consists of $\sim$ 86% of $CaSO_4 \cdot 2H_2O$ and 14% of dust particulates absorbed) and 9.3 kg ($\sim$ 9.3 $m^3$) of water; additionally, 0.22 $m^3$ of water leaving the demisters and displaying a pH of approximately 7.0.

Water balance includes the water amount evaporating in the absorber, which is anticipated to approach 0.015 $m^3/h$.

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## ODSIARCZANIE GAZÓW SPALINOWYCH
## CZĘŚĆ I. SKRÓCONA METODA DWUALKALICZA

Na przykładzie instalacji oczyszczającej 420000 m³ spalin/h przedstwiono technologię odsiarczania gazów odlotowych elektrociepłowni. W procesie odsiarczania zastosowano zmodyfikowaną metodę dwualkaliczną. Opisana technologia umożliwia ponad 90% ograniczenie emisji dwutlenku siarki w gazach o stężeniu $SO_2 \leqslant 10 \ g/m^3$. Instalacja jest korzystna ekonomicznie, nie wymaga dużej powierzchni i jest prosta w obsłudze. Nadaje się do wdrożenia głównie w objektach, w których stosuje się mokry transport żużla i popiołu.

## ОБЕССЕРИВАНИЕ ГАЗОВ СГОРАНИЯ
## ЧАСТЬ 1. СОКРАЩЁННЫЙ ДВУХЩЕЛОЧНЫЙ МЕТОД

На примере установки, очищающей 420000 м³ газов сгорания/час представлена технология обессеривания отходящих газов из теплоэлектростанции. В процессе обессеривания применён модифицированный двухщелочный метод. Описанная технология даёт возможность свыше 90% ограничения эмиссии двуокиси серы в газах концентрации $SO_2 \leqslant 10 \ г/м^3$. Установка полезна экономически, не требует большой поверхности и проста в обслуживании. Она подходит для внедрения главным образом в объектах, в которых применяют мокрый транспорт шлака и пепела.