

One-Step SO₂ Removal From The Simulated Flue Gas On Platinum Anode In Acidic Solution

UMRAN TEZCAN UN, A. SAVAS KOPARAL, ULKER BAKIR OGUTVEREN
 Department of Environmental Engineering
 Anadolu University,
 Iki Eylul Campus, 26470 Eskisehir
 TURKEY

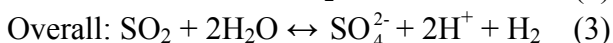
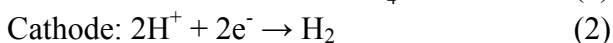
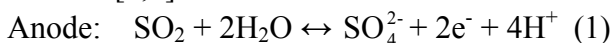
Abstract: In this study, removal of SO₂ absorbed into sulfuric acid solution from simulated flue gases was studied on Pt expanded mesh anode as three dimensional packed bed electrode in a batch mode. The conversion of the gaseous impurity can be considered as the main performance criterion. The effects of the parameters such as current density, gas flow rate, and initial SO₂ concentration were determined. The energy consumptions of the system were also evaluated.

An increase in current density yields an increase in the removal of SO₂. The removal efficiency of SO₂ was decreased with increasing gas flow rate and initial SO₂ concentration. High removal efficiency of 100% which meets the regulations requirement was achieved. The results of this investigation have shown that the absorption of the SO₂ into the electrolyte and electrochemical oxidation of the SO₂ on expanded mesh Pt anode in sulfuric acid can be performed in one step.

Keywords: SO₂, Desulfurization, Air pollution, Electrochemical oxidation, Flue gases

1. Introduction

In the second half of the 20th century, technologies for desulfurization of flue gases in power stations and heating plants were developed. Electrochemical processes, which do not require the continuous use of chemical reagents, can bring a helpful contribution in the proposal or development of depollution processes, as demonstrated by the various investigations published [1]. The electrochemical oxidation of sulfur dioxide can be achieved either through a direct process at an anode surface or using a redox mediator through a chemical process, which has to be regenerated at the electrode [1]. In the electrolysis of the sulfur dioxide absorbed in aqueous sulfuric acid solution, SO₂ is oxidized at the anode while hydrogen is produced at the cathode [2,3].



The electrochemical methods have successfully been used for the treatment of flue gases [4, 5, 6, 7]. A general problem in removal of

gases is the more or less low solubility of the gas in the aqueous electrolyte. This difficulty can be overcome shifting the gas-liquid equilibrium towards the liquid phase by permanent electrochemical conversion of the primarily dissolved species in the aqueous phase [8]. When making use of an absorption column with conducting material operating as a packed bed electrode, a definite improvement of absorptivity can be expected even at relatively short residence times of the gas phase.

2. Experimental Details

In this study two steps were applied simultaneously. SO₂ was converted to sulfate by electrochemical oxidation while it has been absorbing in the sulfuric acid solution. The reactor used in this study was a cylindrical electrochemical reactor having a height of 50 cm and an internal diameter of 7.5 cm. The reactor combines the function of gas absorption and electrochemical reaction in one unit. Titanium rod cathode (Bağ-San Tic. San. A.Ş.) and platinum expanded mesh anode (Magneto Chemie) separated by a cation exchange membrane were

used as electrodes. The platinum expanded mesh sheet having a height of 50 cm and a length of 170 cm was so wrapped as cylindrically that the packed bed anode was formed. The cathode was located in the center of the reactor. Cell voltage was supplied by a power supply (Statron, Type 2257).

Model gas mixture was prepared using SO₂ and N₂ by means of multi channel flow controller (MKS Inst. 647B Multi Channel Flow/pressure Controller and Mass Flow Meter Type 1179A). SO₂ concentration was determined by infrared SO₂ analyzer (Teledyne Analytical Inst., Type IR 7000) at the inlet and outlet of the reactor. The analyzer was calibrated at 0 ppm SO₂ with nitrogen and at 2000 ppm SO₂ with standard calibration gas before each experiment. Experimental set up was shown in Figure 1.

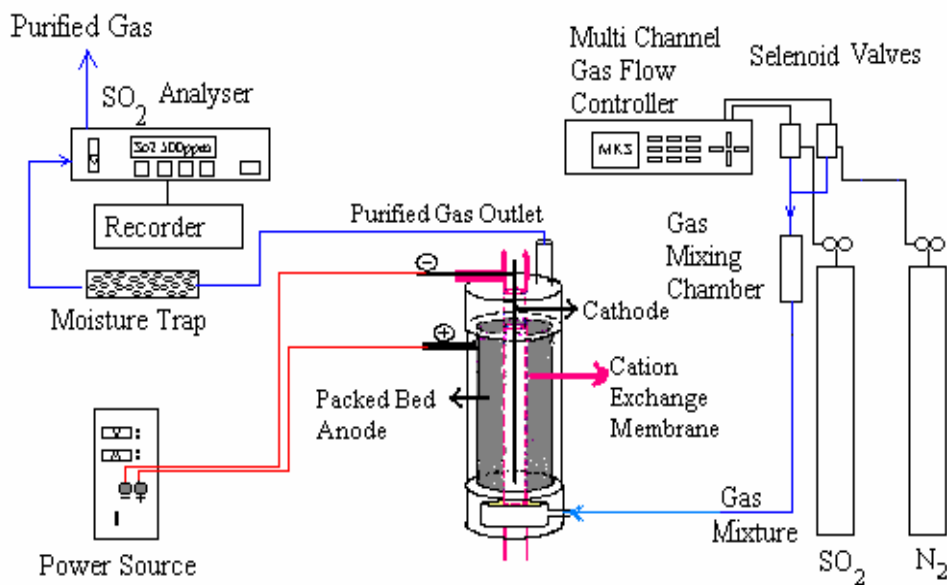


Figure 1: Experimental set up

The cylindrical electrochemical reactor was filled with 1 L of electrolyte (5%wt H₂SO₄), and the gas mixture containing SO₂ was then fed into the reactor continuously from the bottom via stainless steel distributor having 100 μ m pores (Mott Industrial) for distributing the gas uniformly throughout the electrolyte. Thus, the absorption into the electrolyte and electrochemical oxidation of the SO₂ has performed in one step. The electrolyte was slowly enriched with SO₂ and the

gas concentration increased within a couple of hours. After saturation of the electrolyte with SO₂ up to required gas concentration, a given value of current was applied while gas flow was continuing.

3. Results and Discussion

The conversion of the gaseous impurity can be considered as the main performance criterion. The effects of the parameters such as current density, gas flow rate, and initial SO₂ concentration were determined. The initial SO₂ concentration of 2500 ppm was used all experiments (except experiments investigated influence of initial gas concentration).

3.1 Influence of the Parameters

3.1.1 Current Density

Current density has a significant influence on the success of electrochemical SO₂ removal because

it is the driving force in migration of charge. Therefore, the effect of current density on the pollutants removal was investigated. The SO₂ outlet concentration profile up to saturation of the electrolyte (curve I) as well as that after the current was switched on (curve II) was shown in Fig 2. As it can be observed in Figure 2 the rate of electrooxidation increased with increasing current density in the range of 0.1–10 Am⁻² and higher current densities increased the initial reaction rate (dCOD/dt) but it decreased slightly with time. An increase in current density from 0.1 to 10 Am⁻² yields an increase in the efficiency of SO₂ removal from 30.3 to 96.6% which corresponded

1743 and 85 ppm outlet SO₂ concentrations, respectively at gas flow rate of 0.75 Lmin⁻¹ and initial SO₂ concentration of 2500 ppm.

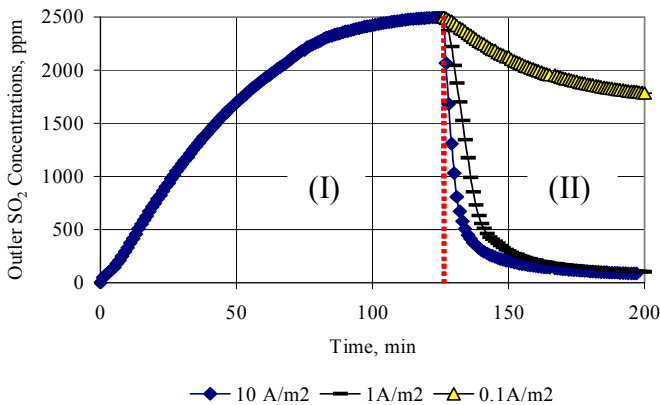


Figure 2: Gas outlet concentration during electrochemical absorption of SO₂ as a function of current density (C₀=2500 ppm, Gas Flow Rate: 0.75Lmin⁻¹).

3.1.2 Gas Flow Rate

Regarding the industrial implementation of an absorption process, the gas flow rate related to the volume of the reactor (space velocity) is a very important economic viability parameter. The abatement of sulfur dioxide is enhanced at lower gas flow rates because of higher residence time in the reactor. Figure 3 represents the SO₂ outlet concentration profiles as a function of gas flow rate. After about 1 hour electrolysis the outlet concentration of SO₂ decreased to 940 ppm (62.4% removal) at 5 Lmin⁻¹, to 95 ppm (96.2% removal) at 1.5 Lmin⁻¹ and to 93 ppm (96.3% removal) at 0.75 Lmin⁻¹ from 2500 ppm at current density of 1 Am⁻².

The removal efficiency of SO₂ in the reactor is very high, due to the continuous regeneration of bubbles along the vertical height of the column. But the removal efficiency decreased with the increase in the gas flow rate, for constant liquid flow rates. This is good agreement with the results of Kreysa and Kùlps [2] with 5% potassium sulfate electrolyte. Especially the decrease in removal efficiency of SO₂, with the increase in gas flow rate was more significant at lower current densities and resulted from overload of SO₂ per unit time. Therefore, higher current density should be applied at higher gas flow rate.

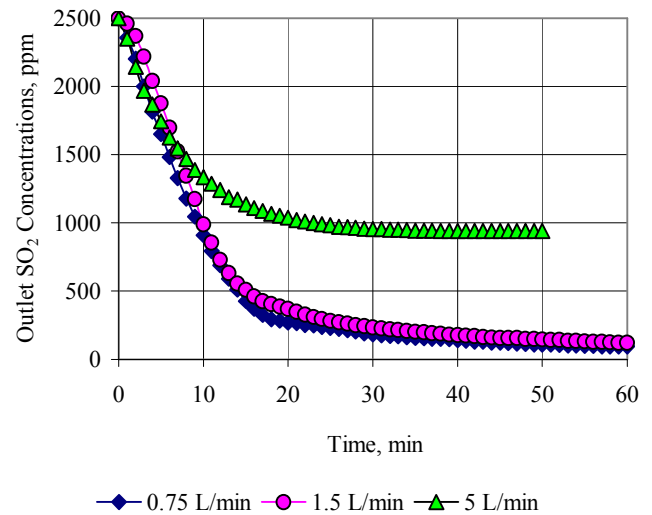


Figure 3: SO₂ outlet concentration profiles as a function of gas flow rate (Current density: 1 Am⁻², Initial SO₂ concentration: 2500 ppm).

3.1.3 Initial SO₂ Concentration

The concentrations of sulfur dioxide in the flue gas have been examined at 1 Am⁻² and gas flow rate of 0.75 Lmin⁻¹. The outlet SO₂ concentration profiles for different initial SO₂ concentrations were shown in Figure 4. As shown in Figure 4, the outlet concentration of 0 ppm was obtained within 20 minutes from the inlet SO₂ concentration of 500 ppm. Increasing the concentration of SO₂ in the flue gas from 2500 to 5000 ppm, the outlet SO₂ concentration increased from the 93 ppm to 110 ppm at 80 minutes. The SO₂ concentration of 5000 ppm with a gas flow rate of 0.75 Lmin⁻¹ was treated easily at 1 Am⁻². The high removal efficiency with 5000 ppm can not be obtained if higher gas flow rate or lower current density was applied. On the other hand the amount of gas removed per unit time increased with increasing initial SO₂ concentration.

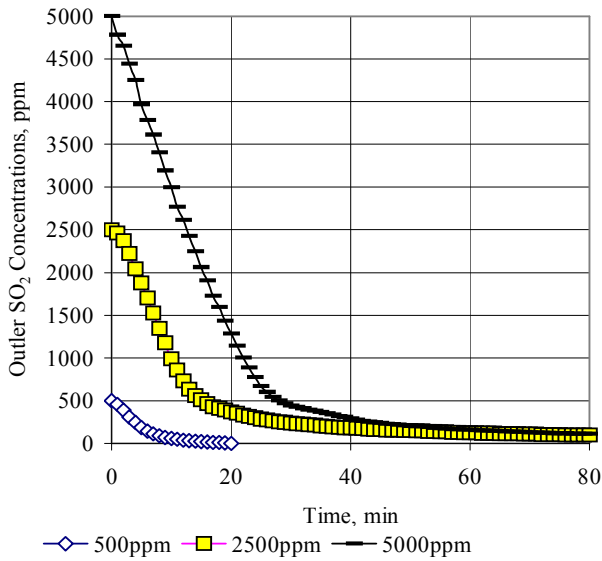


Figure 4: SO₂ outlet concentration profiles as a function of initial SO₂ concentration (Current density: 1 Am⁻², Gas flow rate: 0.75 Lmin⁻¹).

3.2 Energy Consumptions

Electrochemical treatment is undoubtedly an energy-intense process and its efficiency is usually assessed in terms of specific energy consumption (SEC). This is defined as the amount of energy consumed per unit volume of gas treated. Specific energy consumption depends on cell voltage, that is equilibrium potential, the over-potentials at the cathode and the anode and the ohmic voltage losses in the cell [9]. An increase in the current density causes a proportional increase of the specific energy consumption as shown in Figure 5. Increase in energy consumption by increasing current density is attributed to the overpotentials at the electrodes and relatively large gas fractions because of generation of hydrogen and oxygen gases, which significantly reduce the electrolyte conductivity. The specific energy consumptions were decreased with increasing gas flow rate due to lower cell voltage but it was not change significantly with increasing SO₂ concentration.

As a result of the study, treatment efficiency, in terms of both conversion and energy consumption, is affected by the operating conditions employed. The optimal operational parameters can be determined as a function of desired effluent quality besides energy consumption and depends on the geographical as

well as economical situation where the electrochemical treatment is applied

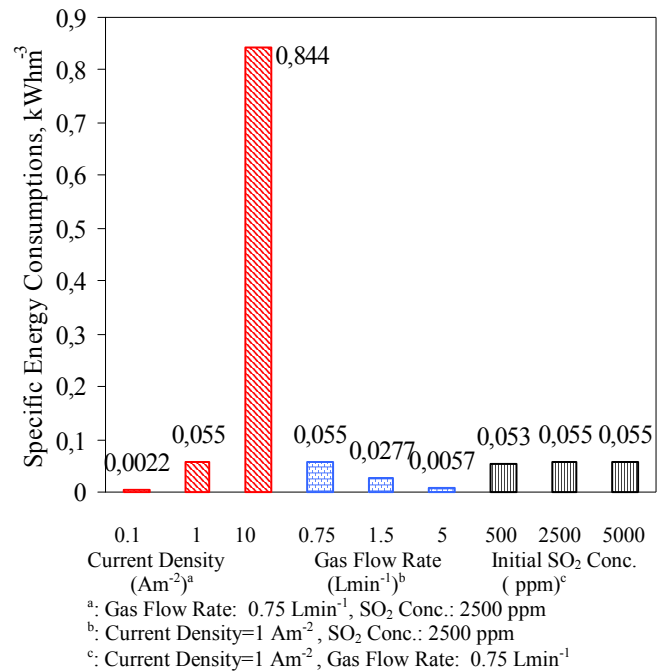


Figure 5: Specific energy consumptions dependence of current density, gas flow rate and initial SO₂ concentration.

4. Conclusion

The results of this investigation have shown that absorption and electrochemical removal of SO₂ can be performed on an expanded mesh Pt anode in one step. Removal efficiency of 100% which meets the regulations requirement was achieved.

The energy consumption per unit volume is of main interest for the operating cost of electrochemical system. Considering the current density of 1 Am⁻² and gas flow rate of 0.75 Lmin⁻¹ shown in Fig. 5, the energy consumption per unit volume was 5.5x10⁻² kWhm⁻³ at a removal efficiency of 96.3% for a waste gas containing 2500 ppm SO₂. According to this value, purification of 1 m³ of gas requires about 0.000257 Euro (industrial electricity price at 2006 in Turkey is 0.0467Euro/kWh [10]) in estimated energy costs. However, before applying to industry, a detailed cost analysis must be carried out using a pilot scale.

For a far-reaching economic comparison of electrochemical absorption with conventional methods, several more aspects have to be considered. Since there is no need for a desorption

step, the investment and energy costs can be kept lower in electrochemical absorption. Furthermore, no chemicals are required instead a re-usable solution such as sulfuric acid is produced for which an equivalent credit is obtained. It may be additionally of interest to find a profitable use for the produced hydrogen. Finally, electrochemical oxidation of SO₂ can be considered as a process in which no waste is produced.

10. Turkey Energy Market Regulation Foundation web page, <http://www.epdk.org.tr/>, (accessed March, 2007)

References

1. Arousseau M., Hunger T., Storck A., Lapicque F., Electrochemical scrubbing Of SO₂-containing gas: coupling absorption to electrochemical reaction. *Chem. Eng. Sci.*, 48 (3), 1993, 541–549.
2. Kreysa G., Külps H.J., A new electrochemical gas purification process. *Ger. Chem. Eng.*, 6, 1983. 325–336.
3. Scott, K., Taama W.M., Electrolysis Of Simulated Flue Gas Solutions In An Undivided Cell. *J. Chem. Tech. Biotechnol.*, 70, 1997, 51-56.
4. Tezcan Ün Ü., Koparal A. S. and Bakır Ögütveren Ü., Electrochemical Desulfurization of Waste Gases in a Batch Reactor. *J. Environmental Engineering (ASCE)*, 133(1), 2007, 13-19.
5. Tezcan Ün Ü., Koparal A. S. and Bakır Ögütveren Ü., Sulfur dioxide removal from flue gases by electrochemical absorption. *Separation and Purification Technology*, 53 (1), 2007, 57-63.
6. Scott K., Taama W., Cheng H., Towards an electrochemical process for recovering sulphur dioxide. *Chem. Eng. J.*, 73, 1999, 101–111.
7. Colle S., Vanderschuren J., Thomas D., Pilot-scale validation of the kinetics of SO₂ absorption into sulphuric acid solutions containing hydrogen peroxide. *Chem. Eng. Process*, 43, 2004, 1397–1402.
8. Kreysa G., Storck A., New Concepts for Electrochemical Gas Purification. *Dechema-Monographs*, VCH, Verlagsgesellschaft, vol. 123, 1991, 225–243.
9. Scott, K., *Electrochemical Processes for Clean Technology*, The Royal Society of Chemistry, Cambridge, UK., 17-20, 1995.