Absorption with photochemical oxidation of sulfur dioxide in sulfuric acid

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1 Introduction

Removal of sulfur dioxide from industrial gases is still an important environmental challenge. Stringent emission limits and limited landfill area demand search for new or alternative processes to state of the art precipitation.

Absorption of sulfur dioxide in aqueous hydrogen peroxide is a state of the art desulfurization process [1] which avoids the production of solid waste and produces salable sulphuric acid.

The hydrogen peroxide process uses hydrogen peroxide of less than 60 weight percent. The aqueous absorbent and the oxidation of sulphurous acid to sulphuric acid contribute to the final water content of the product. Process performance of this absorption process is limited to a maximum concentration of sulfuric acid of less than 70 % by weight, which is not sufficient for many industrial applications.

As a consequence improvement of the process performance was discussed and investigated. Investigation was based on the experience in advanced photochemical wastewater treatment. These wastewater treatment processes base on the generation of strong oxidising species such as ozone or hydroxyl radicals which can accelerate oxidation of sulfur dioxide in the aqueous phase and, as a consequence enhance SO_2 absorption in sulfuric acid even at elevated concentration.

Subject of this project was investigation and modelling of sulfur dioxide absorption in H_2O_2 as well as absorption of SO_2 with photochemical oxidation in sulfuric acid with the aim to enhance the absorption capacity and to rise the sufuric acid concentration to concentration of more than 80%wt.

2 Experimental

2.1 Experimental setup

The experiments were carried out in a film absorption column, as shown in Figure 1, which was equipped with a 700 W medium pressure Hg-lamp. The column can also be operated in the bubble column mode, and without rinsing it can be operated in the tubular gap gas phase reactor mode.

The experiments were carried out with ambient air. Analytical grade SO_2 was admixed to the carrier gas. Sulfuric acid of selected concentration was prepared with technical grade sulfuric acid 96%wt and RO-grade water. For experiments with H_2O_2 technical grade H_2O_2 of 60%wt concentration was fed to the absorbent liquor.

The setup was equipped with an online National Instruments LabView data recorder.

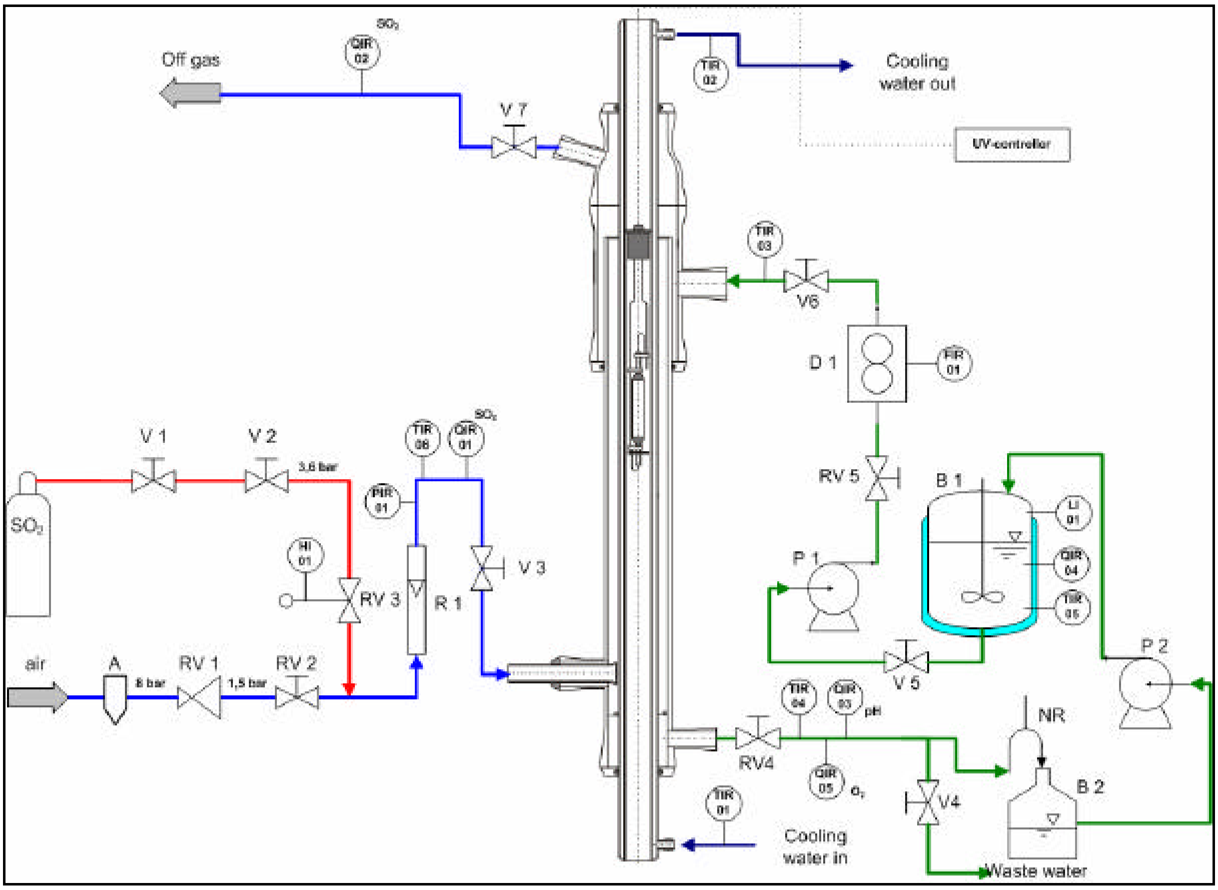

Figure 1: UV film absorption column

2.2 Gas phase reaction – Oxidation kinetics

In a first phase SO_2 oxidation under UV irradiation in humid air in the gaseous phase was investigated The concentration of SO_2 was varied between 300 and 900 mg/m³ and gas flow rate was varied between 0.2 to 1 m³/h. The experiments led to significant aerosol formation with increasing density at low gas flow rate. From the experimental data the rate and rate constant of SO_2-conversion was determined. The results are shown in Figure 2.

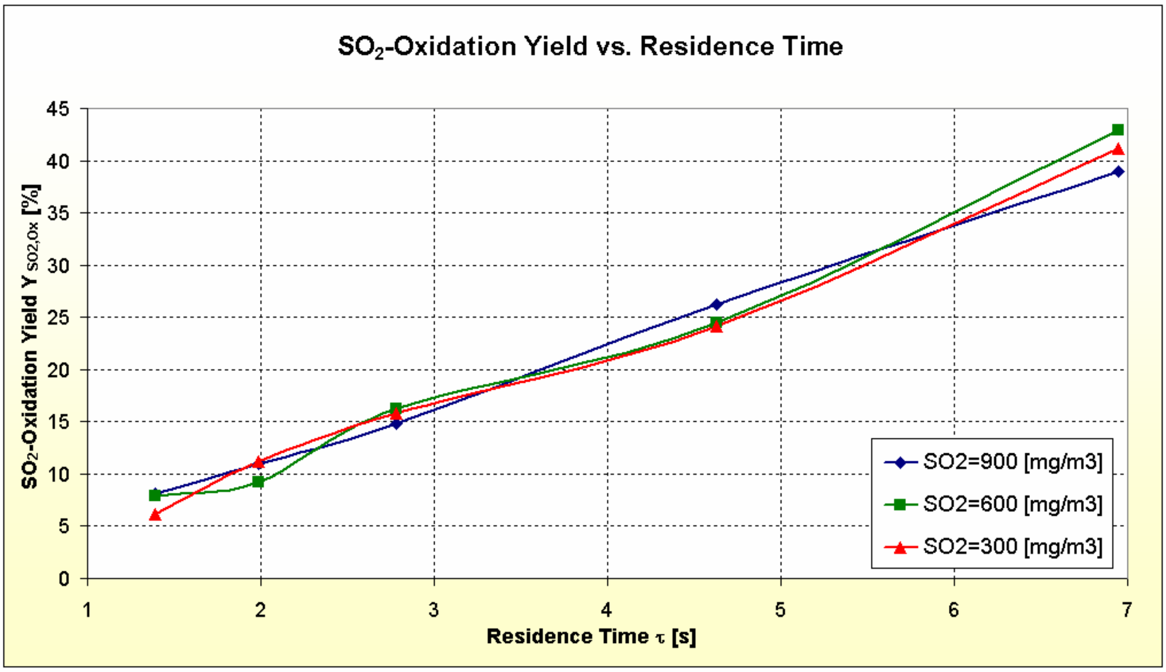

Figure 2: Oxidation yield of SO_2 gas phase oxidation by UV radiation

SO_2 oxidation yield increases with the residence time up to 42 %. The oxidation rate does not depend on the SO_2 feed concentration. This indicates that oxidation is a first order reaction in SO_2 with a rate constant of k=0.07 [1/s].

The mechanism of SO_2 oxidation is based on activation of SO_2 by UV irradiation providing the activation energy for the oxidation reaction. Sulfur dioxide shows strong absorption below 220 nm and strong absorption at about 280 nm which makes application of irradiation sources in the UV-C region necessary. Medium pressure Hg-UV-sources offer distinct emission in the UV-C region.

2.3 Liquid phase reaction

For a technical application the gas phase oxidation of SO_2 is not feasible because of aerosol formation. Oxidation must therefore be followed by precipitation of the aerosol in a wet electrostatic precipitator. To avoid formation of acid aerosols photochemical oxidation can be carried out in the liquid phase after absorption of sulfur dioxide.

These experiments were carried out in the reactor shown in Figure 1, which was operated in the bubble column mode. Sulfuric acid of varying concentration between 0 to 95% wt was used for absorption. Absorption efficiency was compared with the state of the art absorption of SO_2 in hydrogen peroxide.

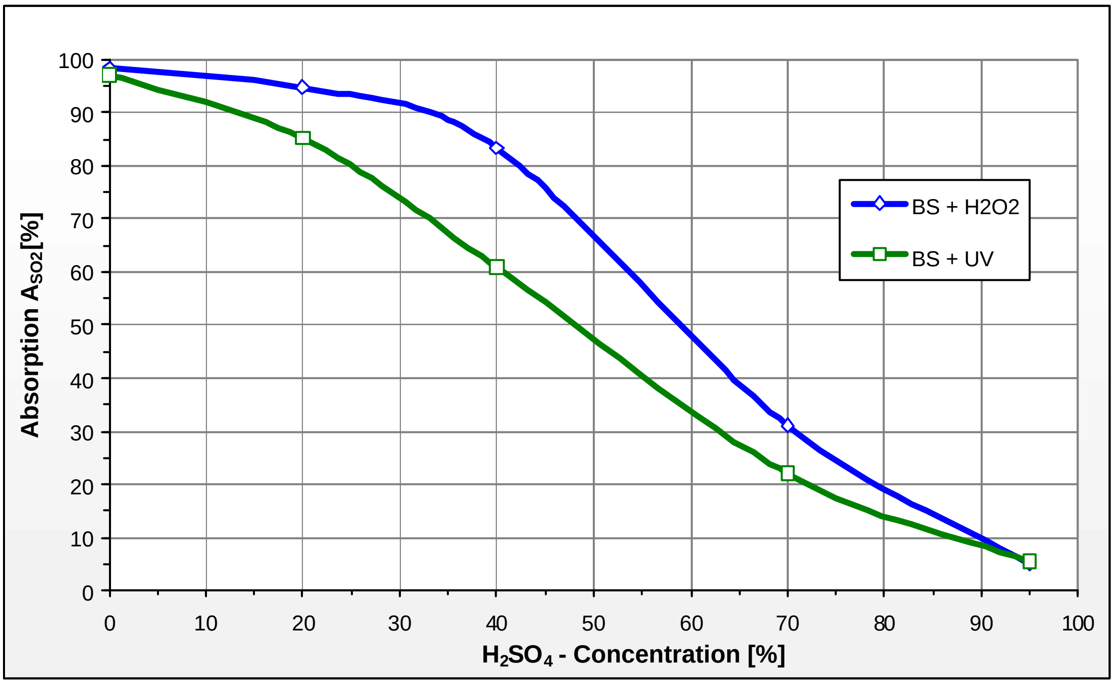

Figure 3: Absorption efficiency of photochemical and chemical SO_2 absorption in sulfuric acid at T = 293 K

As shown in Figure 3 separation efficiency of SO_2 absorption rapidly decreases with increasing concentration of sulfuric acid for both processes. Efficiency of photochemical absorption plus oxidation in comparison with chemical absorption and oxidation with hydrogen peroxide is competitive. Absorption with photochemical oxidation does not need additional oxidising additives. Manufacture of sulfuric acid with concentration above 70 % wt is possible. Major economic disadvantage of the process is the enormous specific energy consumption.

3 Dual step process

Based on the knowledge from the gas phase oxidation process and bubble column experiments a dual step process for absorption of SO_2 with chemical and photochemical oxidation may serve as an applicable compromise.

The process is based on absorption of SO_2 from highly concentrated off-gas in medium concentrated sulfuric acid and photochemical oxidation in the liquid phase in a first step, followed by absorption of the residual sulfur dioxide from the tail gas with H_2O_2 in a second step according to state of the art processes. The laden absorption liquor of the second absorption step with a sulfuric acid concentration of less than 70 % by weight is fed to the first desulfurization step. The process schematic is shown in Figure 4.

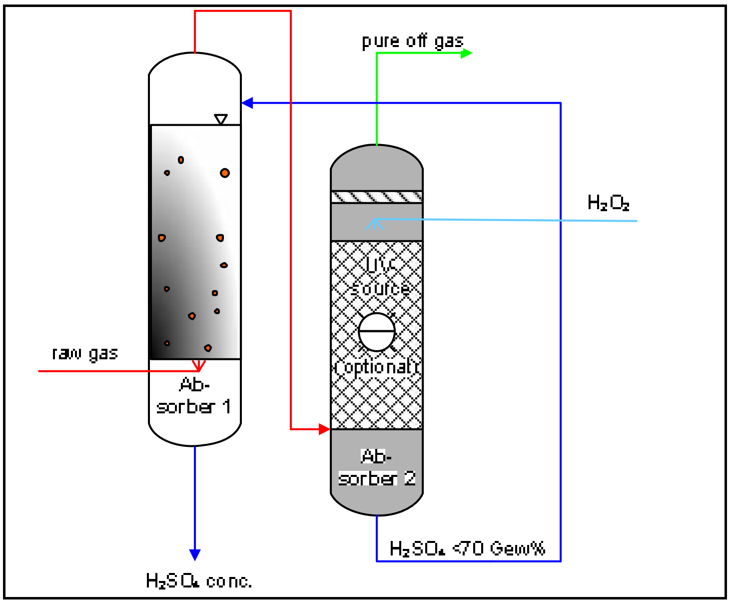

Figure 4: Dual step process for flue gas desulfurization

This process may possibly offer an extended version of the hydrogen peroxide process.

4 Summary

The aim of this project was the production of concentrated sulfuric acid by photochemical oxidation of sulfur dioxide. Technological base of the project was the hydrogen peroxide process for flue gas desulfurization. Absorption of SO_2 and oxidation in the liquid phase was investigated and quantified. The maximum concentration of sulfuric acid obtained by this dual step process is 95 % wt, but must necessarily not be obtained in technical application. From the technical point of view applicability of this dual step process has been confirmed in lab scale.

[1] Colle, S., Thomas, D. Vanderschuren, J., Process simulations of sulfur dioxide abatement with hydrogen peroxide solutions in a packed column, Chemical Engineering Research and Design, 83 (1A), 81-87, 2005