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Fundamental studies on a new concept of flue gas desulphurization

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A new process for removal of sulphur dioxide from waste gases is proposed consisting of both electrochemical and catalytic sulphur dioxide oxidation. In the catalytic step a part of the sulphur dioxide is oxidized by oxygen on copper producing sulphuric acid and copper sulphate. The other part is oxidized electrochemically on graphite. The cathodic reaction of this electrolysis is used for recovering the copper dissolved in the catalytic step. The basic reactions of this process have been studied experimentally in detail. It has been shown that sulphur dioxide can be electrochemically oxidized on carbon electrodes to sulphuric acid with high current efficiency. The reaction rate of the electrochemical copper deposition is increased by dissolved sulphur dioxide in the electrolyte. The catalytic oxidation of sulphur dioxide on copper has been investigated for different sulphur dioxide concentrations and temperatures. The ratio of the reaction products, sulphuric acid and copper sulphate, varies over a wide range depending on the experimental conditions.

Nomenclature

$c^{g}_{SO_2}$	SO_2 concentration (gas phase) (vol % SO_2)
$c^{l}_{SO_2}$	SO_2 concentration (electrolyte) ($g\,l^{-1}$)
E	potential vs saturated calomel electrode (V)
E_s	specific energy consumption ($W\,g^{-1}\,SO_2$)
F	Faraday constant ($A\,s^{-1}\,mol^{-1}$)
i	current density ($mA\,cm^{-2}$)
M_{SO_2}	molecular weight ($g\,mol^{-1}$)
T	temperature (° C)
U_c	cell voltage (V)
ν_e	number of electrons being transferred
ϱ_{SO_2}	space–time yield of SO_2-oxidation ($g\,SO_2\,h^{-1}\,dm^{-3}$)
ϱ_{Cu}	space–time yield of Cu-corrosion ($g\,Cu\,h^{-1}\,dm^{-3}$)
γ	ratio $\varrho_{SO_2}:\varrho_{Cu}$
X_{SO_2}	fractional conversion of SO_2
$\phi^{e}_{SO_2}$	current efficiency for SO_2 oxidation

1. Introduction

The electrochemical oxidation of sulphur dioxide has been investigated by many authors with respect to hybrid processes for hydrogen production by water-splitting at low cell voltage levels. The rate of this reaction is relatively slow and two possible ways of overcoming this problem exist. The first is the direct electrochemical oxidation of sulphur dioxide using noble metal electrocatalysts as electrode materials. This is realized by the Westinghouse Process for hydrogen production [1, 2]. A second possibility is by the indirect electrochemical sulphur dioxide oxidation using suitable redox mediators. For this purpose the bromine–bromide system is used in the Mark-13 process [3, 4]. Another version using iodine–iodide as redox mediator has also been suggested [5, 7]. Stimulated by the increasing importance of sulphur dioxide pollution control many attempts have been made to develop electrochemical processes for removal of sulphur dioxide from flue gas. Thermal/electrochemical hybrid cycles such as the Mark-

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Table 1. Compilation of various electrochemical sulphur dioxide removal processes

Direct processes	*Indirect processes*
Adsorption and regeneration of the adsorbant by electrochemical SO_2 oxidation [12, 13]	Homogeneous redox mediators – outer cell processes [21, 22] – inner cell processes
Absorption with separate electrochemical SO_2 conversion [14, 15]	Heterogeneous redox mediators [23]
Absorption within the electrolysis cell [8–11, 16–18]	Catalytic oxidation with oxygen and electrochemical regeneration of the catalyst [24–26]
Electrochemical reaction at a gas diffusion electrode [19, 20]	

13 and the iodine sulphuric acid cycle can be opened in principle to sulphur dioxide consuming processes producing sulphuric acid.

Direct electrochemical oxidation using electrocatalytically active electrodes is very difficult due to catalyst poisoning by flue gas impurities. Therefore a direct electrochemical gas purification process has been developed using an absorption packed bed column with particles working as a three-dimensional electrode [8–11]. The packed bed absorption column provides a high specific electrode area which is necessary to compensate the low microkinetic current density of sulphur dioxide oxidation. A literature survey of various proposals for electrochemical flue gas desulphurization is given in Table 1. Both direct and indirect electrochemical processes are possible. Some further processes have been suggested which are in principal chemical absorption processes using alkaline and acid solutions which are produced electrochemically [27–29]. At the present only one of these processes (adsorption of sulphur dioxide on carbon particles with electrochemical regeneration of the carbon) has been realized on a technical scale for flue gas purification at a 500 MW power station [12].

A serious problem with all electrochemical routes for sulphur dioxide removal is the energy consumption. Therefore it has been proposed that sulphur dioxide oxidation might be achieved in an electrochemical fuel cell with the reduction of oxygen at the cathode [20]. Another way of decreasing the energy consumption is offered by a combination of electrochemical and catalytical sulphur dioxide oxidation [26]. The aim of the present paper is to report investigations into such a process.

2. Description of the new electrochemical-catalytical flue gas desulphurization

Processes for direct electrochemical oxidation of sulphur dioxide usually produce hydrogen at the cathode. The specific energy consumption is given as

$$E_S = \frac{U_c \nu_e F}{M_{SO_2} \phi^e_{SO_2}} \qquad (1)$$

The basic idea of the new process is directed to a decrease of energy consumption by two means:

1. Reducing the cell voltage by using another cathodic reaction with a more noble electrode potential than hydrogen evolution.
2. Decreasing the charge consumption for sulphur dioxide oxidation by parallel chemical oxidation with oxygen (air).

It is known that sulphur dioxide can be oxidized by oxygen in the presence of water and copper particles. This reaction produces sulphuric acid and copper sulphate by copper corrosion. In the new electrochemical–catalytic process a partial stream of sulphur dioxide corresponding to the amount of copper sulphate produced in the catalytic step can be oxidized electrochemically with copper deposition as the cathodic reaction. By this means the cell voltage of the electrolysis is decreased compared to use of a hydrogen evolving cathode. Furthermore, the corroding copper particles of the catalytic step are regenerated by the cathodic reaction of the electrochemical sulphur dioxide oxidation. A three-compartment reactor as shown schematically in Fig. 1 can be used. The central compartment works as an electrochemical absorption column and is filled with graphite particles. The anolyte and the sulphur dioxide-containing flue gas flow in a co-current mode. In this compartment the

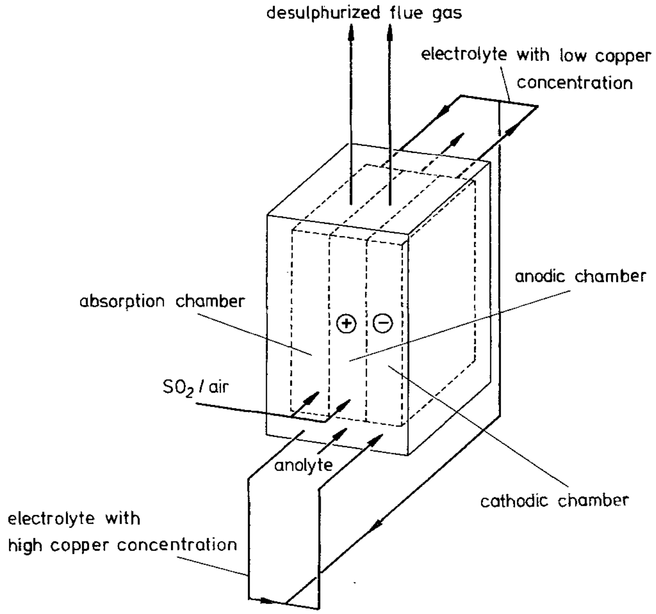

Fig. 1. Scheme of the electrochemical–catalytic process for flue gas desulphurization.

electrochemical oxidation of sulphur dioxide always occurs. Separated by a diaphragm or an ion-exchange membrane on both sides of the central compartment are further compartments which are filled with copper particles. Both of these contain copper metal sheets which act as feeder electrodes. One of these copper compartments works as the cathode and copper is deposited from a copper sulphate-containing electrolyte. The other copper containing compartment works as an absorption column for the catalytic oxidation. The copper dissolved in the catalytic reactor is deposited in the cathodic bed electrode. This means that copper metal is moved from the absorption chamber to the cathodic bed. After a certain operation time the function of both copper compartments is changed.

A preliminary insight into the chemistry of this process is given by the thermodynamic scheme in Fig. 2. Above the potential axes the higher oxidation states of the redox systems are arranged. The arrows denote the direction of the reaction. The reaction between two systems occurs spontaneously if the connecting line between the arrow tips falls. Combination of the systems I and II yields the cell reaction for electrochemical sulphur dioxide oxidation with copper deposition as the cathodic reaction,

$$CuSO_4 + SO_2 + 2H_2O \xrightarrow{e} Cu + 2H_2SO_4 \qquad (2)$$

With a reversible cell voltage of -0.116 V this reaction should be spontaneous; however, an electrical energy input is required due to the

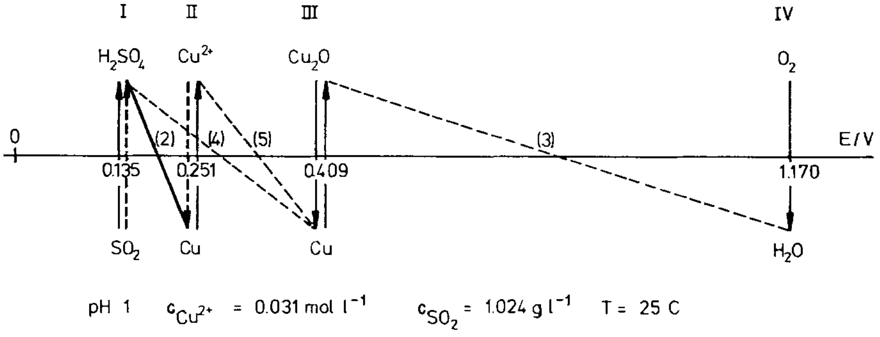

Fig. 2. Thermodynamics of the SO_2 oxidation.

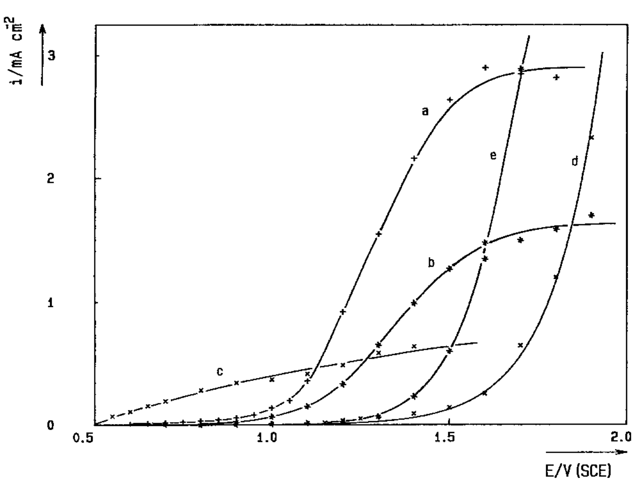

Fig. 3. Polarization curves of SO_2 oxidation and oxygen evolution at the rotating glassy carbon disc electrode. 1000 r.p.m., $c_{H_2SO_4}$ = 30 wt %. (a–$c^g_{SO_2}$ = 1.05 vol %, T = 50° C; b–$c^g_{SO_2}$ = 0.53 vol %, T = 50° C; c–$c^g_{SO_2}$ = 1.05 vol %, T = 90° C; d–$c^g_{SO_2}$ = 0 vol %, T = 50° C; e–$c^g_{SO_2}$ = 0 vol %, T = 90° C.)

overvoltages caused by a finite current. With regard to the catalytic oxidation, the thermodynamic scheme suggests that copper is primarily oxidized by oxygen to cuprous oxide.

$$4Cu + O_2 \longrightarrow 2Cu_2O \qquad (3)$$

This can either be reduced by sulphur dioxide according to

$$Cu_2O + SO_2 + H_2O \longrightarrow 2Cu + H_2SO_4 \qquad (4)$$

or disproportionate to copper metal and copper sulphate

$$Cu_2O + H_2SO_4 \longrightarrow Cu + CuSO_4 + H_2O \qquad (5)$$

Assuming that all cuprous oxide produced by Reaction 3 is consumed by Reactions 4 and 5 a combination of these equations yields the overall reaction

$$SO_2 + \frac{n+1}{2} O_2 + n\,Cu \longrightarrow n\,CuSO_4 + (1-n)\,H_2SO_4 + (n-1)\,H_2O \qquad (6)$$

The reasons which cause a variation of the ratio of copper sulphate to sulphuric acid will be discussed later.

For a possible technical realization of this process the following points are of interest:

1. The kinetics and current efficiency of electrochemical sulphur dioxide oxidation.
2. The possible influence of sulphur dioxide reduction products on the copper deposition rate.
3. The rate of formation of sulphuric acid and copper sulphate in the catalytic step.

These problems have been investigated in detail and are discussed in the following.

3. Electrochemical SO_2 oxidation

The kinetics using various electrocatalysts [30–33], and the mechanism [34–41] of electrochemical sulphur dioxide oxidation has been investigated by several authors. Data for simple graphite electrodes and low sulphur dioxide concentrations are relatively poor. Therefore the sulphur dioxide oxidation has been studied on rotating glassy carbon disc electrodes. With respect to technical application it is advantageous to produce the sulphuric acid at a concentration level as high as possible. Therefore an electrolyte of 30 wt % sulphuric acid was chosen. The electrolyte was saturated with sulphur dioxide containing air. Experiments were conducted at 50 and 90° C. The sulphur dioxide concentrations in the gas phase were 0.5 and 1.0 vol %.

Potentiostatic polarization curves for sulphur dioxide oxidation and oxygen evolution are shown in Fig. 3. Curves d and e are taken for oxygen evolution in the SO_2 free electrolyte. The oxygen overvoltage is decreased with increasing temperature. Curves a and b correspond to the partial current density of sulphur dioxide oxida-

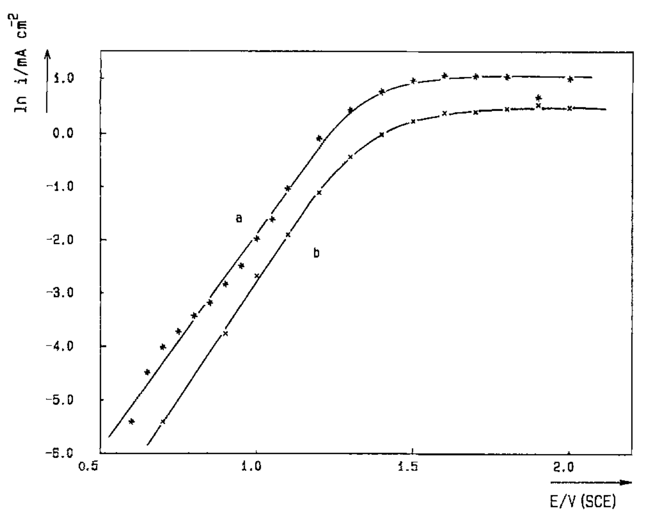

Fig. 4. Tafel plots for SO_2 oxidation at 50° C (for parameters, see Fig. 3).

tion at 50° C. Both curves are corrected by subtraction of the base current density for oxygen evolution taken from curve d. The polarization curves indicate that sulphur dioxide oxidation at this temperature is determined by a combined activation and diffusion control. The limiting current density is nearly proportional to the gas phase concentration of sulphur dioxide. Curve c corresponds to sulphur dioxide oxidation at 90° C. Due to the decreased solubility a lower limiting current density results and the shape of the polarization curve is mainly determined by diffusion control. At 90° C there is a wide range of potential without parallel oxygen evolution. In this range sulphur dioxide oxidation is possible with a current efficiency of 100%; however, the microkinetic current densities are very low. At 50° C sulphur dioxide can be oxidized under activation control with high current efficiency and relatively high current densities within a potential region of about 400 mV. This means that the dimensions of a technical cell are strongly influenced by the operation temperature.

Tafel plots of the polarization curves for sulphur dioxide oxidation at 50° C are given in Fig. 4. These give a Tafel slope of 275 $\pm$ 12 mV. This value is different from the Tafel slopes of 60–80 mV found for noble metal electrodes [2], but is in close agreement with the results of Voroshilov [35] for a graphite anode. From polarization curves published in Voroshilov's paper a Tafel slope of 288 mV can be inferred.

4. Copper deposition in the presence of SO_2

Electrochemical reduction of sulphur dioxide and deposition of copper have been investigated at a rotating copper disc electrode. In these experiments the electrolyte containing 0.1 M sulphuric acid and 0.05 M Cu^{2+} was made free of oxygen by flushing with nitrogen. Various sulphur dioxide concentrations in the electrolyte were achieved by adding a solution presaturated with sulphur dioxide. To ensure that no remarkable concentration changes occurred during the experiments the potentiostatic measurements were taken under differential reactor conditions. During the measurements the electrolyte was pumped from a reservoir through the electrolytic cell. The electrolyte flow rate was chosen in such a way that, in all cases, the degree of conversion of SO_2 was less than 1%. Potentiostatic polarization curves for sulphur dioxide reduction and copper deposition at a temperature of 50° C are given in Fig. 5. Curves a and b were taken in a copper-free electrolyte and reflect the reduction of sulphur dioxide. Curve c corresponds to the copper deposition from a sulphur dioxide-free electrolyte. The polarization curves show that within a potential range of more than 200 mV, copper deposition is possible without any electrochemical reduction of sulphur dioxide. Similar polarization curves taken at 85° C are shown in Fig. 6. At a sulphur dioxide concentration of 5.08 g l^{-1} a wide potential range is available for copper deposition with a current efficiency of 100%.

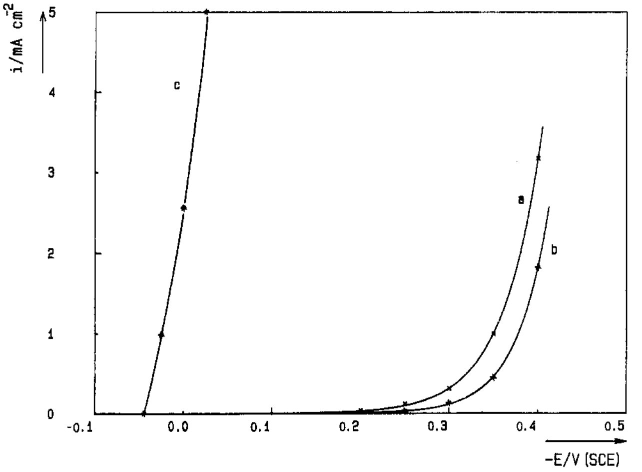

Fig. 5. Potentiostatic polarization curves for copper deposition and SO_2 reduction at the rotating copper disc electrode. 1000 r.p.m., T = 50° C, $c_{H_2SO_4}$ = 0.1 M. (a–$c^1_{SO_2}$ = 1.06 g l^{-1}; b–$c^1_{SO_2}$ = 0.29 g l^{-1}; c–$c^1_{SO_2}$ = 0 g l^{-1}, $c_{Cu^{2+}}$ = 0.05 M.)

Some authors have reported that copper deposition is electrocatalysed in the presence of sulphur dioxide [38, 39]. Curve a (Fig. 7) shows the i–E curve for copper deposition in a SO_2-free solution of 0.1 M sulphuric acid. In the presence of 1 g l^{-1} sulphur dioxide (curve b) at potentials higher than 100 mV the deposition rate is electrocatalytically increased. Also in this case the current efficiency for copper deposition is higher than 95%. At potentials lower than 100 mV the copper deposition seems to be inhibited by SO_2. Curves c and d are measured at 90° C. Curve c reflects the copper deposition from a SO_2-free solution whereas curve d also shows a catalytical increase of the copper deposition due to the presence of SO_2. In the literature [38] a catalytic mechanism via S or S^{2-} formed from sulphurous acid is postulated. Whereas it is possible to reduce sulphur dioxide-containing solutions to colloidal sulphur, no formation of sulphur can be observed during copper deposition. Because the reaction

$$Cu^{2+} + e^- \longrightarrow Cu^+ \qquad (7)$$

is the rate determining step for copper deposition, the formation of Cu^+ seems to be catalysed by the presence of sulphur dioxide. Since the reversible potential of sulphur dioxide reduction to dithionite,

$$2SO_2 + H^+ + 2e^- \longrightarrow HS_2O_4^- \qquad (8)$$

is 0.08 V this reaction may occur parallel to copper deposition. Dithionite is able to reduce Cu^{2+} ions in aqueous acid solution; however, a detailed understanding of this mechanism needs further investigation.

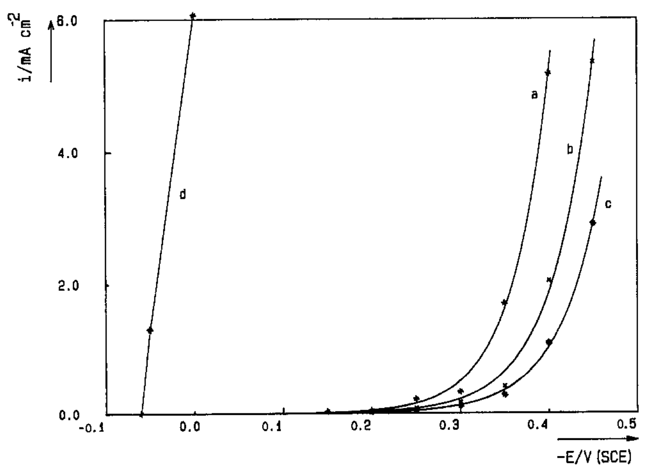

Fig. 6. Potentiostatic polarization curves for copper deposition and SO_2 reduction at the rotating copper disc electrode. 1000 r.p.m., T = 85° C, $c_{H_2SO_4}$ = 0.1 M. (a–$c^1_{SO_2}$ = 5.08 g l^{-1}; b–$c^1_{SO_2}$ = 1.06 g l^{-1}; c–$c^1_{SO_2}$ = 0.29 g l^{-1}; d–$c^1_{SO_2}$ = 0 g l^{-1}, $c_{Cu^{2+}}$ = 0.05 M.)

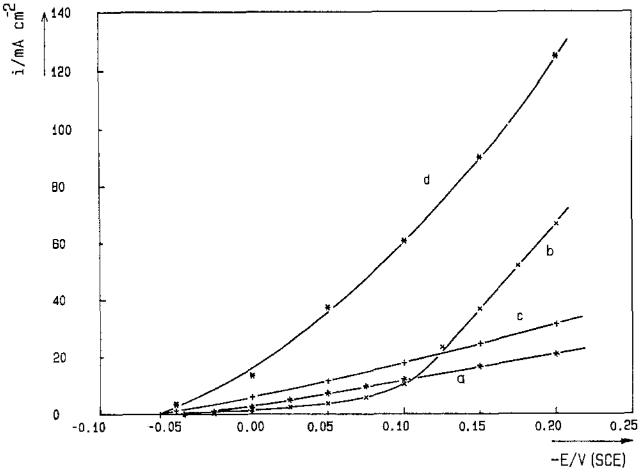

Fig. 7. Electrocatalytical increase of copper deposition rate by SO_2. 1000 r.p.m., $c_{Cu^{2+}}$ = 0.05 M, $c_{H_2SO_4}$ = 0.1 M. (a–$c^l_{SO_2}$ = 0 g l^{-1}, T = 50° C; b–$c^l_{SO_2}$ = 1 g l^{-1}, T = 50° C; c–$c^l_{SO_2}$ = 0 g l^{-1}, T = 90° C; d–$c^l_{SO_2}$ = 1 g l^{-1}, T = 90° C.)

5. Catalytic SO_2 oxidation on copper

The catalytic oxidation of sulphur dioxide absorbed in a copper sulphate solution containing copper powder has been reported previously by Kepinski *et al.* [42]. This reaction has been investigated in a copper particle packed bed reactor shown schematically in Fig. 8. Experiments were conducted both on native copper particles and electrochemically regenerated particles. The complete flow circuit is shown schematically in Fig. 9. Electrolyte and sulphur dioxide containing air flowed in co-current mode through the packed bed electrode which had the following dimensions: cross section, 11 cm^2; height, 5 cm; voidage, 0.4. Copper particles of 1 mm diameter and an electrolyte containing 100 g l^{-1} sodium sulphate and 3 g l^{-1} copper sulphate were used. The sodium sulphate was added as conducting salt for the electrochemical copper regeneration by packed bed electrolysis.

A factorial 2^2-design of experiments was carried out with two levels for temperature and sulphur dioxide concentration in the gas stream. The space–time yields for sulphur dioxide oxida-

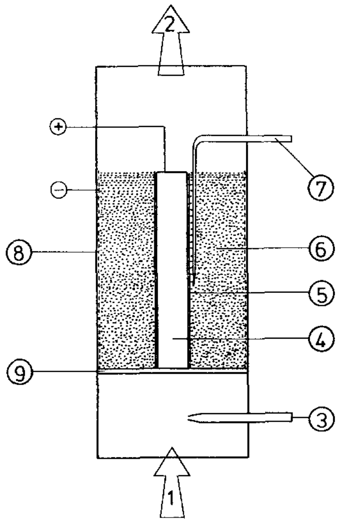

Fig. 8. Packed bed absorber for catalytical SO_2-absorption and electrolytical copper deposition. 1, Electrolyte inlet; 2, electrolyte–gas outlet; 3, gas inlet; 4, anode; 5, diaphragm; 6, packed bed cathode; 7, reference electrode; 8, contact electrode; 9, distributor.

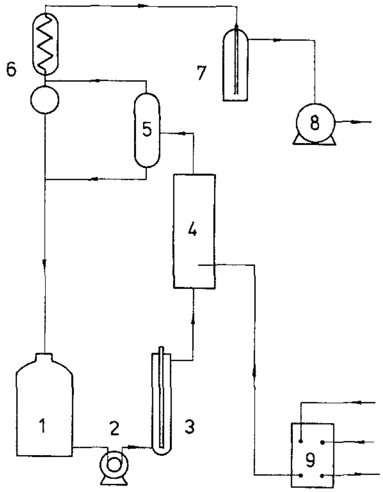

Fig. 9. Schematic flow circuit for catalytical SO_2-oxidation for copper regeneration. 1, Reservoir; 2, peristaltic pump; 3, immersion heater; 4, reactor; 5, gas–electrolyte separator; 6, cooler (with separator for condensed electrolyte); 7, chemical SO_2-absorber (for analysis); 8, flow meter; 9, gas dosing apparatus.

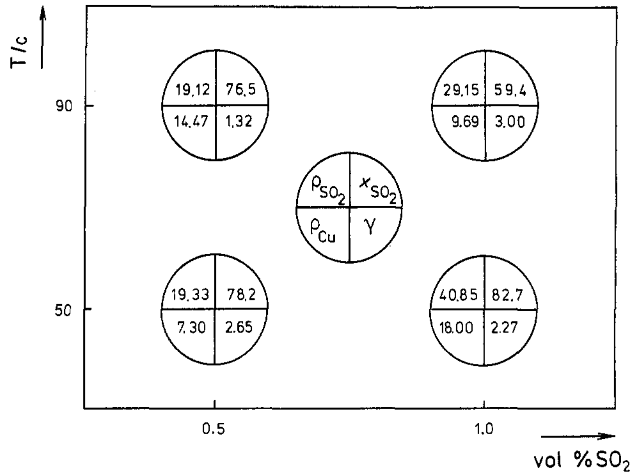

Fig. 10. 2^2-factorial design analysis of SO_2-oxidation as function of temperature and SO_2-concentration.

tion and copper dissolution were determined. The results are shown in Fig. 10. For both space–time yields (ϱ) the following equations can be derived from the results.

$$\varrho_{SO_2} = -16.3 + 0.28\,T + 71.8\,c^{g}_{SO_2} - 0.57\,c^{g}_{SO_2}\,T \tag{9}$$

$$\varrho_{Cu} = -31.7 + 0.57\,T + 60.1\,c^{g}_{SO_2} - 0.77\,c^{g}_{SO_2}\,T \tag{10}$$

The observed fractional conversion (x) for sulphur dioxide is also shown in Fig. 10. In general the space–time yield of sulphur dioxide oxidation increases with increasing concentration of sulphur dioxide. This can be understood with reference to Reactions 3–5. The primary step of this mechanism is the formation of cuprous oxide. This oxide is consumed by the two concurrent reactions of SO_2 oxidation and cuprous oxide disproportionation which leads to copper corrosion. With increasing SO_2 concentration the sulphur dioxide oxidation becomes the preferred reaction. The highest SO_2 space–time yield is observed at the high concentration and the low temperature level. At the same conditions the highest fractional conversion is also observed. The ratio (γ) between sulphur dioxide oxidation and copper corrosion varies between 1.3 and 3.0. This ratio determines the portion of sulphur dioxide which can be oxidized catalytically and is of great technical importance. The higher this reaction rate ratio the less sulphur dioxide must be oxidized electrochemically to compensate the copper losses due to corrosion in the absorber. This means that the energy consumption of the process decreases with increasing ratio of sulphur dioxide oxidation rate to copper corrosion rate. If fresh copper were deposited electrochemically at the surface of the copper particles the results of the factorial design could be reproduced within the experimental accuracy limits. This means that there is no influence of the copper surface state on the catalytical oxidation of sulphur dioxide.

6. Conclusions

A new process for flue gas desulphurization has been proposed. It consists of a parallel electrochemical and catalytical sulphur dioxide oxidation. Compared with a previously published process for direct electrochemical sulphur dioxide oxidation [9, 10], the new process uses the deposition of copper as the cathodic reaction which results in a decreased cell voltage. In this modified process only that part of the SO_2 which corresponds to the dissolved copper in the chemical absorption step has to be oxidized electrochemically. It has been shown that electrochemical SO_2 oxidation is possible at carbon electrodes at very low sulphur dioxide concentration levels with high current efficiency. The current efficiency of the copper deposition is not decreased in the presence of sulphur dioxide, but this reaction is catalysed by sulphur dioxide. The catalytic sulphur dioxide oxidation is accompanied by a copper corrosion. The ratio between the reaction rates of sulphur dioxide energy consumption of the overall process and can be varied over a wide range by control of concentration and temperature.

The present investigation has clearly shown the feasibility of the proposed combined electrochemical–catalytical flue gas desulphurization process. However, further detailed studies are necessary to provide the fuller information required for scale up and optimization.

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