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M. Vorbach[a]; R. Marr[a]; M. Siebenhofer[b]; W. Zapfel[b]
[a] Institute of Chemical Engineering and Environmental Technology, Graz, Austria [b] VTU Engineering GmbH Grottenhofstrasse 3, Graz, Austria

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REDOX-ABSORPTION OF SULFUR DIOXIDE

M. Vorbach,[1] R. Marr,[1] M. Siebenhofer,[2] and W. Zapfel[2]

[1]Institute of Chemical Engineering and Environmental
Technology Inffeldgasse 25, A-8010 Graz, Austria
[2]VTU Engineering GmbH Grottenhofstrasse 3, A-8010
Graz, Austria

ABSTRACT

The absorptive precipitation of sulfur dioxide from dilute gaseous mixtures with an aqueous solution of chromate was tested. The objective of the project was to combine detoxication of aqueous chromate with absorptive desulfurization of off-gas. The absorption process is based on the overall reaction

$$Cr_2O_7^{2-} + 3\ SO_2 + 2\ H^+ \Leftrightarrow 2\ Cr^{3+} + 3\ SO_4^{2-} + H_2O$$

The mechanism of absorption was investigated in tests where the feed concentration of chromate was varied. The feed concentration of sulfur dioxide was held within the range of representative off-gas concentration levels (≈3000 mg/m^3).

The literature has reported rate control of the process when pH values exceed 2. Detailed information about the influence of the concentration of chromate was not available. Therefore, the process was investigated relative to the influence of chromate on the rate of absorption for pH values below 2. The tests of mass transfer and rate control were based on experiments in a film absorption column.

INTRODUCTION

Sulfur dioxide can be separated from off-gas by different absorption methods. The standard method is absorption with neutralization by adding lime to the absorption liquor and by oxidizing the dissolved and neutralized sulfur dioxide with oxygen. The final product, gypsum, usually has to be disposed of.

Aqueous chromate, on the other hand, is a strong oxidizer. Wastewater containing chromate is detoxicated by reducing chromate to chromium(III), which can then be precipitated as chromium hydroxide. Under acidic conditions, the predominating species dichromate is reduced according to Eq. (1):

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \Leftrightarrow 2\,Cr^{3+} + 7\,H_2O \tag{1}$$

The standard redox potential of this reaction is $E = +1.33$ V; thus, several reducing agents such as sulfur compounds (sulfur dioxide, sodium pyrosulfite, sodium sulfite, sodium dithionite) or iron(II) compounds can be applied (1). Most commonly, the detoxication of chromate-containing wastewater is carried out with sulfur dioxide under acidic conditions as described by Serota (2) and Channon (3). Therefore, sulfur dioxide is dissolved in the wastewater effluent by forming sulfurous acid in a first step:

$$SO_2 + H_2O \Leftrightarrow H_2SO_3 \Leftrightarrow H^+ + HSO_3^- \tag{2}$$

Combining Eqs. (1) and (2) results in the overall reaction, Eq. (3):

$$Cr_2O_7^{2-} + 3\,SO_2 + 2\,H^+ \Leftrightarrow 2\,Cr^{3+} + 3\,SO_4^{2-} + H_2O \tag{3}$$

The objective of the present investigation was to combine off-gas purification and wastewater detoxication. For that purpose, experiments on the absorption of sulfur dioxide with acidic aqueous solution of chromate were conducted. In particular, mass transfer and mass transfer-determining boundaries were considered.

EXPERIMENTAL PROCEDURE

The experiments were performed in a falling-film absorption column. The column and its calibration have been described in detail elsewhere (4). Falling-film reactors have proven applicable in testing gas-liquid mass transfer, as already published by Roberts and Danckwerts (5) and Sherwood et al. (6) and also in recent literature (7, 8).

The falling-film absorber used for investigation is designed as a concentric-tube apparatus with an active height of 2.13 m. The diameter of the inner tube is 33.4 mm, and the outside wall diameter is 49.5 mm. The equipment was calibrated with the test system SO_2/air/aqueous sodium hydroxide, as suggested by Danckwerts (9). The results of the calibration tests confirmed the applicability of the correlation in Eq. (4) to describe the gas-phase mass transfer resistance (6, 10):

$$\mathrm{Sh_G} = 0.023 \cdot \mathrm{Re_G^{0.83}} \cdot \mathrm{Sc_G^{0.44}} \tag{4}$$

with

$$\mathrm{Sh_G} = \frac{k_G \cdot d_i}{D_G}, \tag{5}$$

$$\mathrm{Re_G} = \frac{v_G \cdot d_i}{\nu_G}, \text{ and} \tag{6}$$

$$\mathrm{Sc_G} = \frac{\nu_G}{D_G}. \tag{7}$$

The validity of Eq. (4) is limited to $2{,}000 \leq \mathrm{Re_G} \leq 35{,}000$.

The liquid-phase mass transfer resistance was derived (11) from the dimensionless correlation given in Eq. (8).

$$\mathrm{Sh_L} = 0.126 \cdot \mathrm{Re_L^{0.55}} \cdot \mathrm{Sc_L^{0.4}} \tag{8}$$

with

$$\mathrm{Sh_L} = \frac{k_L \cdot f}{D_L}, \tag{9}$$

$$\mathrm{Re_L} = \frac{v_L \cdot f}{\nu_L}, \text{ and} \tag{10}$$

$$\mathrm{Sc_L} = \frac{\nu_L}{D_L}. \tag{11}$$

The validity of Eq. (8) is limited to $70 \leq \mathrm{Re_L} \leq 400$.

The thickness of the falling film was derived (12) from Eq. (12):

$$\dot{L} = d_i \cdot \pi \cdot \frac{g \cdot f^3}{3 \cdot \nu_L}. \tag{12}$$

The aqueous solution was prepared by dissolving analytical-grade CrO_3 (Merck Nr. 100229) in deionized water. The temperature and the pH of the aqueous phase were held constant at 293 K and 1.5, respectively. The process conditions and the results are shown in Table 1.

DISCUSSION

Basically, the absorption process of sulfur dioxide in aqueous dichromate was tested for mass transfer control in either or both phases. Therefore, the results

Table 1. Experimentally Obtained Data of Absorption of Sulfur Dioxide in Aqueous Solutions of CrO_3 (pH = 1.5; T = 293 K; v_G = 2.1 m/ms; $\dot{L}$= 40 L/h)

$C_{Cr(VI)}$ (g/L)	$C_{SO2,in}$ (mg/m^3)	$C_{SO2,out}$ (mg/m^3)
4.49	3045	1680
4.01	3060	1702
3.52	3060	1700
3.10	3030	1695
2.91	3020	1692
2.62	3024	1710
2.40	3014	1710
2.20	3016	1712
2.00	3015	1720
1.20	3020	1725
1.05	3022	1730
0.91	3025	1734
0.85	3077	1765
0.80	3077	1770
0.74	3075	1817
0.60	3075	1839
0.46	3077	1872
0.43	3077	1927
0.38	3077	1956
0.25	3077	1971
0.18	3074	2019
0.07	3074	2097
0.01	3074	2230

shown in Table 1 were interpreted with Eq. (13):

$$k_{OG,SO2} = \frac{\dot{N}_{SO_2}}{A \cdot \dfrac{p_{SO_2,in} - p_{SO_2,out}}{\ln \dfrac{p_{SO_2,in}}{p_{SO_2,out}}}} \cdot \tag{13}$$

According to Eq. (3), the mass transfer of SO_2 is followed by the reaction of the dissolved substance with $Cr_2O_7^{2-}$. Therefore, the possibility of rate control was also investigated. Figure 1 shows a comparison of the k_{OG} values obtained from the data of Table 1 and Eq. (13) and mass transfer control. Both gaseous-phase mass transfer control and mass transfer control for physical absorption were considered.

Due to the constant flow rate of both phases, the gas-phase resistance and the overall resistance for physical transport remained constant. Figure 1 points out a shift of the mass transfer resistance from gaseous-phase mass transfer control to mass transfer control for physical absorption with decreasing concentrations of chromate. The distance to both boundaries of mass transfer control indicates enhancement of absorption of sulfur dioxide by chemical reaction in the liquid film.

The overall resistance increases with decreasing concentrations of chromate to finally give the conditions for physical absorption at $c_{Cr(VI)} = 0.01$ g/L.

For further discussion of the experimentally obtained data, enhancement by pseudo-first-order reaction and fast second-order reaction in the liquid film was considered. According to Levenspiel (13), enhancement of the rate of absorption by pseudo-first-order reaction can be described by Eq. (14):

$$-r''''_{SO_2} = \frac{1}{\dfrac{1}{k_{G,SO_2} \cdot a} + \dfrac{H_{SO_2}}{a \cdot \sqrt{D_{SO_2} \cdot k \cdot c_{Cr(VI)}}}} \cdot p_{SO_2}. \qquad (14)$$

With $k_{G,SO2}$ derived from Eq. (4), $k_{L,SO2}$ derived from Eq. (8), Henry's constant $H_{SO2} = 34.9$ bar (14), and the diffusion coefficient of sulfur dioxide in aqueous solution $D_{SO2} = 1.6 \cdot 10^{-9}$ m^2/s (15), the rate constant, k, can be calculated.

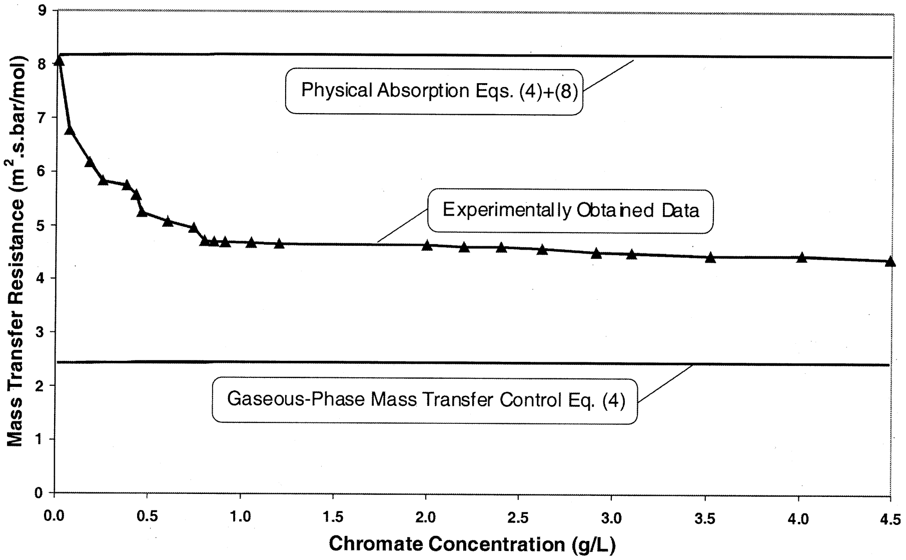

Figure 1. Overall mass transfer resistance of sulfur dioxide absorption in aqueous solutions of chromate derived from the experimentally obtained data of Table 1. Comparison of the experimentally obtained data with gaseous-phase mass transfer control and physical absorption.

The rate of absorption enhanced by fast second-order reaction is described by Eq. (15):

$$-r_{SO_2}^{''''} = \frac{1}{\frac{1}{k_{G,SO_2}} \cdot a + \frac{H_{SO_2}}{k_{L,SO_2} \cdot a \cdot E}} \cdot p_{SO_2}. \qquad (15)$$

According to Westerterp et al. (16) and Danckwerts (9), the rate of reaction relative to physical mass transfer in the liquid phase was estimated by means of the Hatta number [Eq. (16)],

$$Ha = \frac{\sqrt{D_{SO_2} \cdot k \cdot c_{Cr(VI)}}}{k_{L,SO_2}}, \qquad (16)$$

and the enhancement factor, E_i, for infinitely fast reaction [Eq. (17)]:

$$E_i = 1 + \frac{D_{Cr} \cdot c_{Cr(VI)}}{\frac{1}{3} \cdot D_{SO_2} \cdot c_{SO_2,1}}. \qquad (17)$$

The diffusion coefficient of chromate in aqueous solution is $D_{Cr(VI)} = 1.132 \cdot 10^{-9}$ m^2/s (for infinite dilution) (14).

For

$$E_i > 5 \cdot Ha\,, \qquad (18)$$

enhancement of mass transfer is based on pseudo-first-order reaction in the liquid film (13).

For

$$5 \cdot E_i > Ha > \frac{E_i}{5}, \qquad (19)$$

enhancement of mass transfer is based on fast second-order reaction (13).

Based on Eqs. (18) and (19), interpretation of the results shown in Table 1 points out enhancement of mass transfer by pseudo-first-order reaction for $c_{Cr(VI)} > 0.4$ g/L. The comparison of the results with Eqs. (18) and (19) is shown in Fig. 2 and Table 2.

Contrary to the recommended limits for enhancement by pseudo-first-order reaction in the liquid film [Eq. (18)], Fig. 3 points out that actually the enhancement of sulfur dioxide absorption in aqueous chromate by pseudo-first-order reaction is limited to a concentration of chromate of $c_{Cr(VI)} > 0.8$ g/L.

Based on the recommendation of Westerterp et al. (16), the shift from enhancement by pseudo-first-order reaction to fast second-order reaction is well described for $E_i > 10$ Ha. Consequently, the validity of Eq. (14) is limited to a chromate concentration of $c_{Cr(VI)} > 0.8$ g/L. As shown in Fig. 4, the trend of the enhancement factor, E, derived from Eq. (15), confirms the experimentally deter-

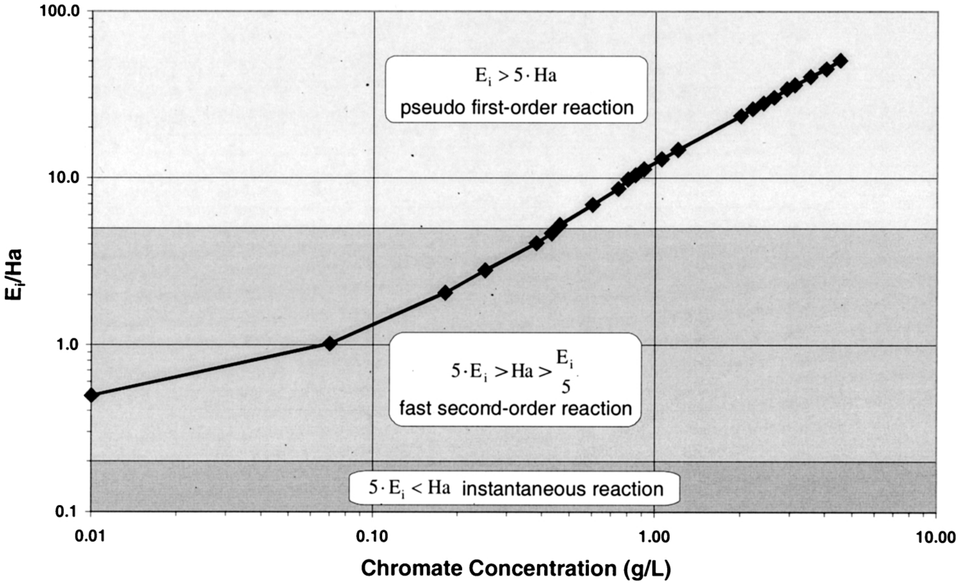

Figure 2. Boundaries of enhancement of sulfur dioxide absorption in aqueous chromate by pseudo-first-order reaction and fast second-order reaction.

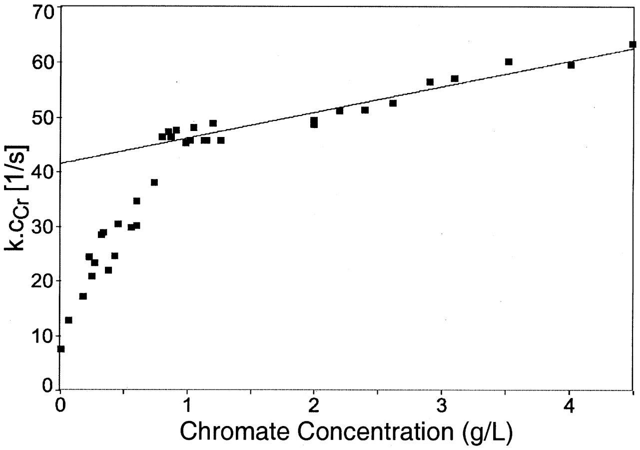

Figure 3. Determination of the rate constant k ($k = 0.49\ m^3/mol \cdot s$) for enhancement of sulfur absorption by pseudo-first-order reaction and determination of the concentration limit, based on Eq. (14).

Table 2. Results of Data Interpretation According to the Data of Table 1 ($v_G = 2.1$ m/s; $\dot{L} = 40$ l/h; $k_G = 9.88\cdot10^{-3}$ m/s; $k_L = 1.08\cdot10^{-4}$ m/s)

CCr(VI) (g/L)	$k_{OG}\cdot 10^3$ (m/s)	$k.c._{Cr(VI)}$ (1/s)	k (m^3/mol.s)	E	E_i	Ha
4.49	5.5	63.4	0.49	2.9	148.9	2.9
4.01	5.4	59.6	0.49	2.9	129.5	2.9
3.52	5.4	60.1	0.49	2.9	114.2	2.8
3.10	5.4	57.1	0.49	2.8	99.9	2.8
2.91	5.4	56.4	0.49	2.8	93.8	2.8
2.62	5.3	52.6	0.49	2.7	82.5	2.7
2.40	5.3	51.3	0.49	2.7	75.3	2.7
2.20	5.2	51.1	0.49	2.6	69.0	2.7
2.00	5.2	49.4	0.49	2.6	62.1	2.6
1.20	5.2	48.8	0.49	2.6	37.5	2.5
1.05	5.2	48.0	0.49	2.6	32.7	2.5
0.91	5.2	47.6	0.49	2.6	28.4	2.5
0.85	5.2	47.4	0.49	2.5	26.1	2.5
0.80	5.1	46.4	0.49	2.5	24.5	2.5
0.74	4.9	38.0		2.3	21.4	2.5
0.60	4.8	34.7		2.2	17.1	2.5
0.46	4.6	30.5		2.0	12.9	2.4
0.43	4.3	24.5		1.8	11.4	2.4
0.38	4.2	22.0		1.7	9.9	2.4
0.25	4.1	20.8		1.7	6.8	2.4
0.18	3.9	17.2		1.5	5.0	2.4
0.07	3.6	12.7		1.3	2.4	2.4
0.01	3.0	7.6		1.0	1.2	2.4

mined ratio, E_i/Ha, of enhancement by pseudo-first-order reaction and fast second-order reaction. Additionally, Fig. 4 shows that the enhancement of sulfur dioxide absorption by fast second-order reaction is further limited by a minimum chromate concentration of chromate of $c_{Cr(VI)} < 0.01$ g/L. Below this minimum concentration, the absorption of sulfur dioxide is controlled by physical absorption.

SUMMARY

The absorption of sulfur dioxide in aqueous solutions of caustic soda is controlled by the mass transfer resistance in the gaseous film.

The objective of the present project was to investigate the mass transfer of sulfur dioxide absorption in an acidic solution of chromate. This process may pos-

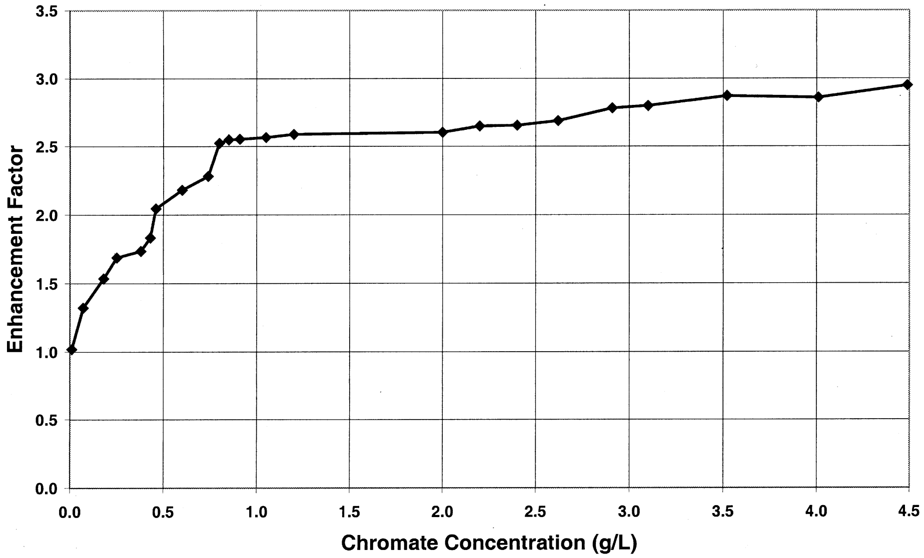

Figure 4. Determination of enhancement of sulfur dioxide absorption in aqueous chromate by fast second-order reaction and enhancement by pseudo-first-order reaction, based on Eq. (15).

sibly be applied in off-gas purification combined with the detoxication of aqueous chromate.

Contrary to the absorption of sulfur dioxide in caustic soda, the latter process is influenced by the rate of the redox reaction of sulfur dioxide and chromate within the liquid film. The results of the project point out that absorption of sulfur dioxide from the dilute gaseous carrier is enhanced by a pseudo-first-order reaction when the concentration of chromate is kept above $c_{Cr(VI)} > 0.8$ g/L. For lower concentrations of chromate, the absorption of sulfur dioxide is enhanced by a fast second-order reaction.

NOMENCLATURE

a	specific mass transfer area (m^2/m^3)
A	mass transfer area (m^2)
c	concentration (mol/L), (g/L)
D	diffusion coefficient (m^2/s)
d_i	diameter of the inner tube (m)
E	enhancement factor (dimensionless)

E_i	enhancement factor for infinitely fast reaction (dimensionless)
f	thickness of the liquid film (m)
g	gravitational constant (m/s^2)
H	Henry's constant ($bar \cdot m^3/mol$)
Ha	Hatta number (dimensionless)
k_G	gas-phase mass transfer coefficient (m/s), ($mol/m^2 \cdot s \cdot bar$)
k_L	liquid-phase mass transfer coefficient (m/s), ($mol/m^2 \cdot s \cdot bar$)
k_{OG}	overall mass transfer coefficient based on driving force in gas (m/s), ($mol/m^2 \cdot s \cdot bar$)
k	reaction rate constant ($m^3/mol \cdot s$)
$\dot{L}$	liquid flow (L/h)
$\dot{N}$	molar flux (mol/s)
p	partial pressure (bar)
r''''	mass transfer rate ($mol/s \cdot m^3$)
Re	Reynolds number (dimensionless)
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
v	velocity (m/s)
ν	kinematic viscosity (m^2/s)

Subscripts:

Cr(VI)	chromate
G	gaseous phase
I	interface
in	entering the absorption column
L	liquid phase
OG	overall gas
out	leaving the absorption column
SO_2	sulfur dioxide

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