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KINETICS OF THE REACTION BETWEEN SULFUROUS ACID AND CALCIUM HYDROXIDE

A kinetic study of the chemical reaction between sulfurous acid and calcium hydroxide in aqueous solution to give solid calcium sulfite has been performed to clear the basic steps involved in wet desulfurization processes with lime slurries.

Results achieved below the concentrations of 2.80×10^{-3}M of sulfurous acid and 4.05×10^{-2}M of calcium hydroxide show relatively slow reaction rates, which can be fitted by crystal growth models or nucleation-growth models depending on the concentration level.

These results show the dramatic influence of the reagent concentrations on the rate of the wet desulfurization processes in which lime slurries are used, which should be taken into account in order to design and optimize the process.

LIST OF SYMBOLS

A, B — reactants in the liquid phase,
C — concentration (mol l^{-1}),
C_0 — initial concentration (mol l^{-1}),
C_P — concentration referred to the solid product (mol l^{-1}),
C_S — saturation concentration (mol l^{-1}),
D — diffusivity (cm^2 s^{-1}),
K — kinetic constant used in mass transfer modelling (mol^{-1} l s^{-1}),
K_c — kinetic constant for chemical reaction control (mol^{-1} l s^{-1}),
K_g — mass transfer parameter in the gas phase (m s^{-1}),
K_G — kinetic constant of a solid growth controlled reaction (m s^{-1} mol$^{(1-G)}$ l$^{(G-1)}$),
K_L — mass transfer parameter in the liquid phase (m s^{-1}),
K_S — solubility constant (mol^2 l^{-2}),
K_{app} — apparent kinetic constant (min^{-1}),
γ — rate of solid precipitation (mol l^{-1} min^{-1}),

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s — supersaturation $(-)$,
X — conversion referred to sulfurous acid $(-)$,
x_e — value of conversion at equilibrium $(-)$,
x — dimensionless thickness of the boundary layer $(-)$,
y — molar fraction $(-)$,
z — thickness of the boundary layer (m),
α — dimensionless variable $\left(\dfrac{C_0 - C}{C_0 - C_S}\right)$,
λ — thickness of the reaction plane (m).

1. INTRODUCTION

Sulfur is a reliatively abundant element and is present in the atmosphere as a result of emissions from both natural and anthropogenic sources. The most important anthropogenic source of sulfur dioxide is the combustion of fossil fuels, coal and petroleum derivatives are the dominant energy sources of anthropogenic emissions of sulfur dioxide [1].

The emission of sulfur dioxide from stack gases of fossil fuel power plants is one of the most important factors of the increase in the concentration of sulfur in the atmosphere leading to complex effects, such as acid rains [2], on man and environment. Increasing importance of removal of SO_2 from combustion plants is reflected in the regulation directed to the control of sulfur dioxide emissions.

Recent development of the European activities for the control of SO_2 emissions is centered in the Federal Republic of Germany [3], where stringent control regulations have been adopted, tab. 1.

Table 1

Federal SO_2 control requirements for West German coal-fired boilers

Size MW(e)	SO_2 emission limit mg/Nm³	% removal	Compliance deadline	Approx. No. boilers
over 110	400	85	7/1/88	160
35 to 110	2000	60	4/1/93	370
18 to 35	2000	—	4/1/93	300

An absolute limit on the rate of SO_2 emission and a minimum amount of removal is specified for 35 MW(e) boilers and larger, thus preventing the use of fuel switching to achieve control compliance.

Similar regulations are extended to other European Countries [4]: The Netherlands requires flue gas desulfurization (FGD) with 90% SO_2 removal for coal fired boilers larger than 300 MW(e); in Sweden, limits for SO_2 emission from boilers are 300 mg/Nm³ (108 ppm); in Austria, 300 mg/Nm³ for existing bituminous coal utility

boilers and 400 mg/Nm^3 (144 ppm) for existing lignite fired utility boilers and similar regulations are expected in some other countries.

Stringent regulations increase the use of desulfurization units to reduce SO_2 levels in combustion plants.

The development of fluidized bed combustors (FBC) for the reduction of SO_2 amount in flue gases [5]–[12] is only useful for new plants. At present, the lime and limestone FGD processes, by either wet or dry scrubbing, are the most advanced of the throw-away FGD systems. In the dry scrubbing method, solid particles react with the hot flue gas stream, after an appropiate retention time. Some works have been given in the literature reporting the gas–solid heterogeneous reaction [13]–[35] under different conditions.

In the wet scrubbing process, sulfur dioxide is absorbed in a solution or slurry using an alkali; lime, limestone and dolomite have the advantage of being easy and cheap raw materials but other similar products, such as sodium carbonate, sodium hydroxide, etc., have been used. Some works have been given reporting the gas–liquid–solid heterogeneous reaction under different conditions [36]–[50].

In these systems SO_2 is removed from flue-gases after chemical reaction to calcium sulfite or/and calcium sulfate sludge depending on the natural or forced oxidation.

Selection of dry or wet processes depends basically on the system; dry-processes require usually forced conditions of temperature or pressure and wet-processes are able to work under milder conditions.

When dealing with the wet process, the chemical reaction kinetics producing the solids as well as the kinetics of physical phenomena involved in the process such as diffusion of the gaseous reagent through the gas and liquid films are specially important in designing and operating FGD systems.

The rate of solid precipitation is important in controlling scaling on scrubber surfaces and in designing reaction tanks [9]. On the other hand, precipitation rates determine the particle size distribution of the sulfur sludge, which has been shown to be a major factor affecting the settling and dewatering properties of sludges.

Since the first work of BJERLE et al. [40] many papers have been reported dealing with the modelling of SO_2 absorption in a slurry with different dissolved solids. Many of them refer to the modelling of SO_2 absorption in calcium carbonate slurries in a laminar jet absorber [40], or in a stirred tank reactor with a plane gas–liquid interface [41]–[46], or calcium hydroxide slurries in similar geometries [36]–[39]. Different slurries have been reported for SO_2 absorption such as sodium hydroxide [47], magnesium hydroxide [49] or different mixtures [48].

These works have been focused mainly to the kinetic analysis and modelling of mass-transfer phenomena involved in the whole process assuming instantaneous or very fast chemical reactions.

However emission limits for SO_2 in fossil-fuel combustion plants are usually less than the corresponding to the reported range of concentrations, indicating that a

proper study of the chemical kinetics in the range of low concentrations is necessary to understand the basic steps involved in the process.

In the present work, the chemical kinetics of the reaction between absorbed SO_2 in an aqueous solution of calcium hydroxide has been investigated in the following range of concentrations: $6.76 \times 10^{-3}M \leqslant [Ca(OH)_2] \leqslant 4.05 \times 10^{-2}M$ and $1.7 \times 10^{-3}M \leqslant [H_2SO_3] \leqslant 2.8 \times 10^{-3}M$ at $T = 20\,°C$, covering the range of variables corresponding to the stringent regulations.

2. EXPERIMENTAL

Experiments at different initial concentrations of aqueous sulfur dioxide and calcium hydroxide were performed isothermally at $20\,°C \pm 1\,°C$ under batch conditions in a stirred tank reactor. Calcium hydroxide powder was stored in a 25 kg tank under a carbon dioxide free atmosphere. Initially all the inlets to the stirred reactor were closed and vacuum was applied. After distilled water was added to the filtration unit and allowed to flow into the reactor, calcium hydroxide powder was added to the reactor by pneumatic transport under nitrogen. The vacuum was then released to the atmosphere. Absorbed sulfur dioxide was stored into a 25 l bottle and controlled amounts of calcium hydroxide and sulfurous acid were used for each experiment.

The sulfite ion concentration was determined by iodometric titration after filtration of the samples and separation of the residual solid.

3. RESULTS AND INTERPRETATION

Two different sets of experiments were performed at variable concentrations of sulfurous acid: $1.70 \times 10^{-3}M$, $2.15 \times 10^{-3}M$ and $2.80 \times 10^{-3}M$ and constant initial concentration of calcium hydroxide, $1.0 \times 10^{-2}M$ (fig. 1), and at constant initial concentration of sulfurous acid, $2.00 \times 10^{-3}M$ and variable concentrations of calcium hydroxide, $6.76 \times 10^{-3}M$, $1.35 \times 10^{-2}M$, $2.70 \times 10^{-2}M$ and $4.05 \times 10^{-2}M$ (fig. 2), in order to study the influence of both variables on the reaction rate.

The calcium hydroxide concentration in the solution has been selected to cover the range between saturation and low concentrations of the reagent in the liquid phase.

The sulfurous acid concentration has been selected according to values related to the equilibrium composition of flue-gases containing the SO_2 amounts, which are shown in tab. 2.

A differential method for the kinetic analysis has been developed evaluating the derivatives of the conversion-time curves as follows: experimental results of conversion were fitted to a n-th order polynomial of time by multiple linear regression. An order of four/five has been the exponent used to fit the major part of the curves.
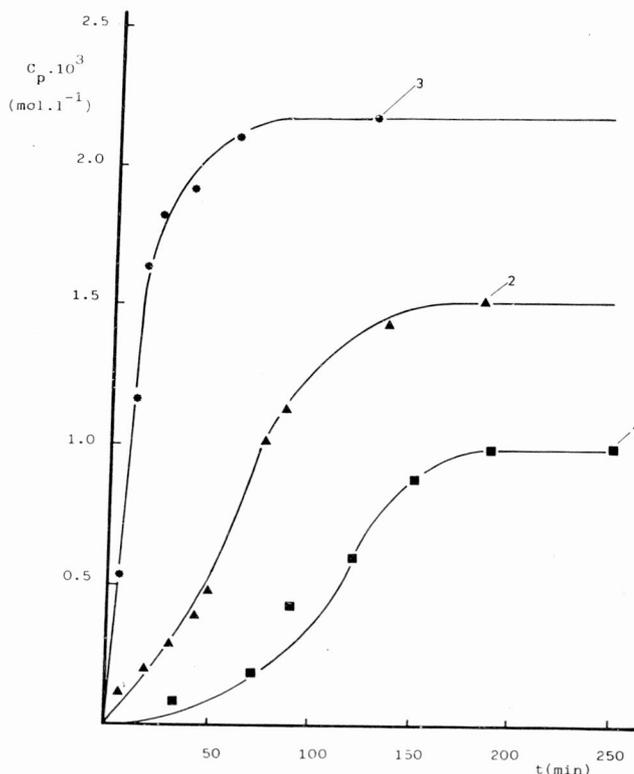
Fig. 1. Experiments at constant concentration of calcium hydroxide 1×10^{-2}M and variable concentration of sulfurous acid: $1 - 1.70 \times 10^{-3}$M, $2 - 2.15 \times 10^{-3}$M, and $3 - 2.80 \times 10^{-3}$M

Results showing a sigmoidal shape have required the use of two different polynomials, depending on the conversion level.

After those fittings reaction rate values were calculated from the derivative of the linear expressions at the experimental points. A graphical picture of reaction rates as a function of conversion is shown in figs. 3 and 4.

Fundamental studies [51] for fluid–solid reactions suggest a nucleation mechanism for reaction rates showing a maximum and growth or chemical mechanism for continuous reaction rates.

Kinetic models have been given for nucleation controlled reactions in the form [51]

$$-\ln(1-\alpha) = K_n \cdot t^n \qquad (1)$$

which is the well known (Johanson–Mehl–Avrami–Yerofeev–Kolmogorov)J–M–A–Y–K equation, where K_n is the overall rate constant and n, an exponent, which depends on the type of nucleation.
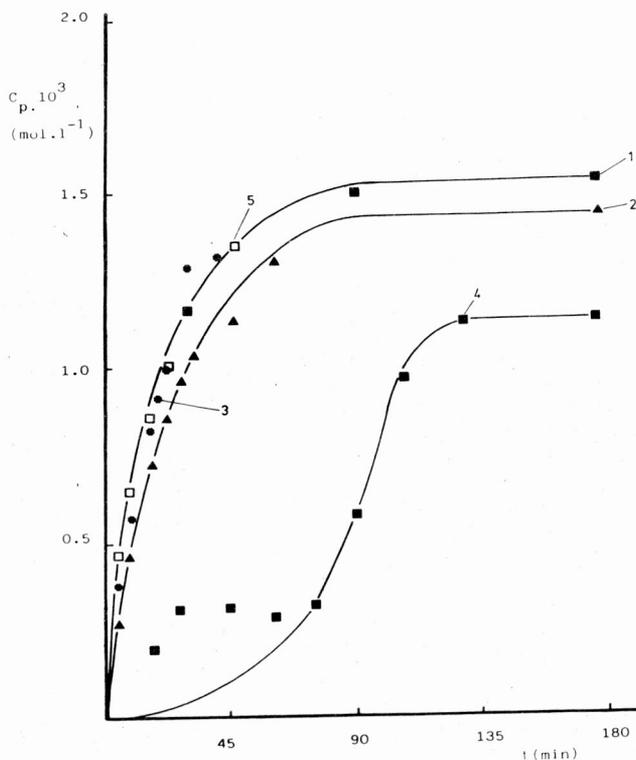
Fig. 2. Experiments at constant concentration of sulfurous acid 2.00×10^{-3}M and variable concentration of calcium hydroxide: 1 — 0.05 g/l, 2 — 1.0 g/l, 3 — 2.0 g/l, and 4 — 3.0 g/l

This model shows the ability to fit experimental curves including a maximum in the reaction rate.

For solid growth controlled reactions, potential laws have been suggested [54]:

$$r = K_G a (C - C_S)^G \qquad (2)$$

where r is the rate of the solid growth; G, the potential order; K_G, the growth rate constant and C_S, the concentration of saturation and a, the surface area of crystals.

Table 2

Relation between sulfurous acid concentration and gas composition

$C_{H_2SO_3}$ (M)	Equilibrium composition of flue gases (ppm)
1.7×10^{-3}	364
2.15×10^{-3}	461
2.8×10^{-3}	601
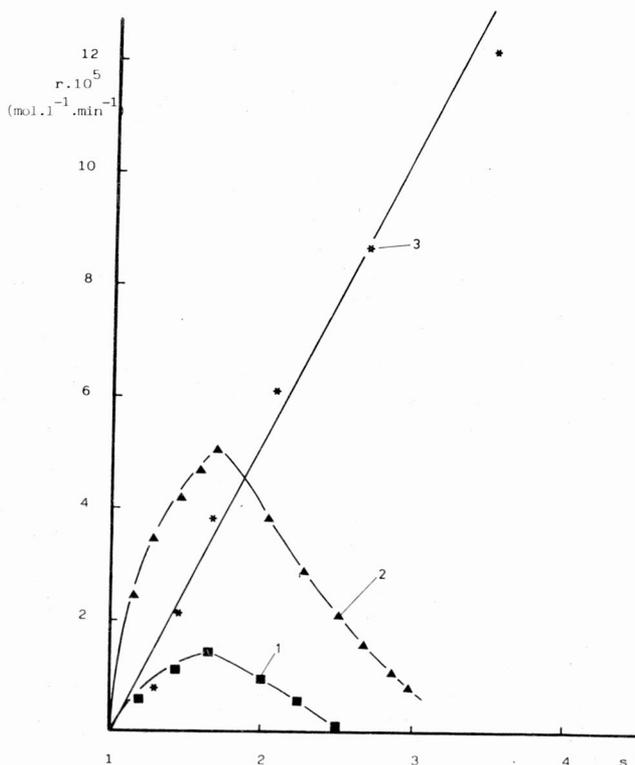
Fig. 3. Reaction rates for the experiments at constant concentration of calcium hydroxide 1×10^{-2}M and variable concentration of sulfurous acid: $1 - 1.70 \times 10^{-3}$M, $2 - 2.15 \times 10^{-3}$M, and $3 - 2.80 \times 10^{-3}$M

Chemical kinetic models have been also given for fluid–solid reactions in the form:

$$r = K_C(C_A C_B - K_S) \tag{3}$$

where r is the chemical reaction rate, K_C is the reaction rate constant, K_S is the solubility constant, and C_A and C_B are the concentrations of both species.

Let's take into account the mechanism of the reaction:

$$SO_3^= + Ca^{2+} \overset{1}{\rightleftharpoons} CaSO_3 \overset{2}{\rightleftharpoons} CaSO_3 \, (solid). \tag{4}$$

Reaction (1) should be instantaneous due to the fast rates of ionic reactions and reaction (2) should be the slow step. In the course of precipitation new particles are born by nucleation processes and once crystals have been produced by nucleation they will grow. Many problems related to precipitation are rooted in the crystal growth process.
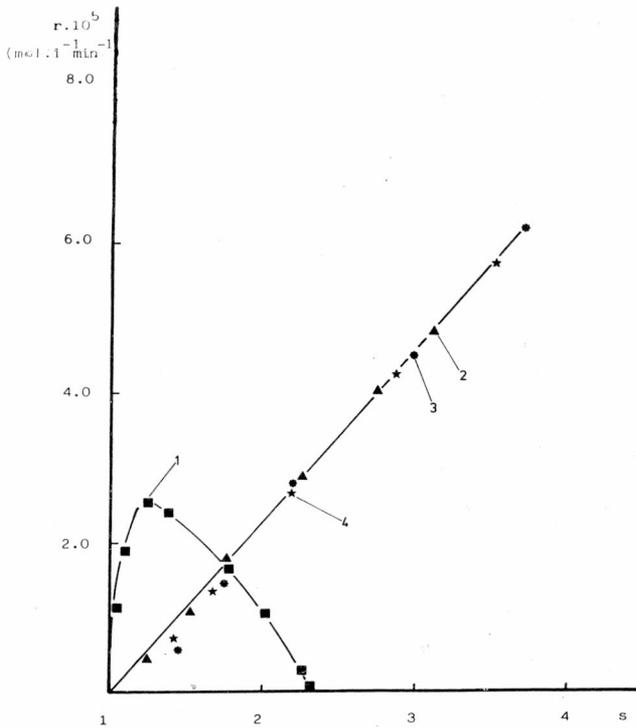
Fig. 4. Reaction rates for the experiments at constant concentration of sulfurous acid 2.00×10^{-3}M and variable concentration of calcium hydroxide: *1* — 0.5 g/l, *2* — 1.0 g/l, *3* — 2.0 g/l, and *4* — 3.0 g/l

Figures 3 and 4 indicate that a nucleation process is the slow step at low concentrations of calcium hydroxide, $[Ca(OH)_2]_0 \leqslant 6.76 \times 10^{-3}$M and sulfurous acid, $[H_2SO_3]_0 \leqslant 2.15 \times 10^{-3}$M, leading to sigmoidal conversion-time curves if unseeded solutions are used.

Considering the J–M–A–Y–K model for nucleation processes, where $\alpha = (C - C_S)/(C_0 - C_S)$, a graphical plot of $\ln[-\ln(1-\alpha)]$ vs. $\ln t$ is shown in fig. 5.

After linear regression fitting, parameters are shown in tab. 3.

A nucleation order between 1.5 and 2.0 is shown by the experimental results; considering the different types of nucleation, which are shown in tab. 4, further experimental studies should be necessary to determine the nucleation mechanism but these results allow an evaluation of reaction rates for design purposes.

On the other hand, growth processes seem to be the slow step at near saturation concentrations of calcium hydroxide, $[Ca(OH)_2]_0 \geqslant 1.35 \times 10^{-2}$M and sulfurous acid, $[H_2SO_3]_0 \geqslant 2.8 \times 10^{-3}$M, where first order kinetics can be used to fit the experimental results, as it is shown in fig. 5.

After linear regression fitting, parameters are shown in tab. 5. Growth order g can
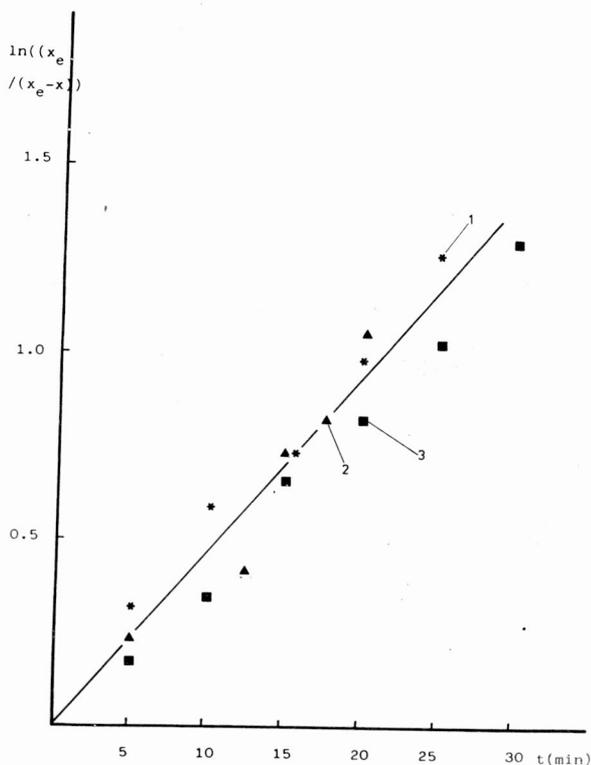
Fig. 5. Linear fitting to a first order integral equation for some experiments at constant concentration of sulfurous acid 2.0×10^{-3}M and variable concentration of calcium hydroxide: $1 - 1.0$ g/l, $2 - 2.0$ g/l, and $3 - 3.0$ g/l

be taken as one for all the experiments but the overall kinetic constant depends on the initial concentration of sulfurous acid.

This result could mean a different surface area of crystals depending on the initial concentration of sulfurous acid, but an interpretation of this phenomenon requires further experimental study, specially related to the species surface of the final solid obtained under different initial conditions.

Table 3

Kinetic parameters for nucleation controlled reactions

$C_{A_0} 10^{-3}$ (M)	C_{B_0} (g/l)	T (°C)	k (m$^{-1/r}$)	n
2.0	0.50	20 ± 1	1.11×10^{-4}	1.97
2.15	0.74	20 ± 1	6.09×10^{-4}	1.71
1.70	0.74	20 ± 1	7.46×10^{-7}	2.92

Table 4

Characteristic parameters of the J–M–A–Y–K nucleation growth equation

Type of nucleation N	Geometry of nuclei and of their subsequent growth	Chemical reaction G (linear law)		Diffusion D (parabolic law)	
		n	E	n	E
Instantaneous nucleation (saturation of the sites capable of nucleation prior to the process)	Bulk mechanism				
	one-dimensional growth	1	E_G	0.5	$E_D/2$
	two-dimensional growth	2	$2E_G$	1	E_D
	three-dimensional growth	3	$3E_G$	1.5	$3E_D/2$
	Surface mechanism				
	two-dimensional growth	2	$2E_G$	1	E_D
Constant rate of homogeneous nucleation during the process	Bulk mechanism				
	one-dimensional growth	2	E_G+E_N	1.5	$E_D/2+E_N$
	two-dimensional growth	3	$2E_G+E_N$	2	E_D+E_N
	three-dimensional growth	4	$3E_G+E_N$	2.5	$3E_D/2+E_N$
	Surface mechanism				
	two-dimensional growth	3	$(2E_G+E_N)$	2	(E_D+E_N)
Decreasing rate of nucleation (n_{dec})		$(n-1) < n_{dec} < n$			
Heterogeneous nucleation (n_{het})		$(n-1) < n_{het} < n$			
Increasing rate of nucleation (n_{inc})		$n < n_{inc} < (n-1)$			

Table 5

Kinetic parameters for crystal growth controlled reaction

$C_{A_0} \times 10^3$ (M)	C_{B_0} (g/l)	K_{ap} (min^{-1})
2.0	1.0	4.50×10^{-2}
2.0	2.0	4.50×10^{-2}
2.0	3.0	4.50×10^{-2}
2.80	0.74	8.60×10^{-2}
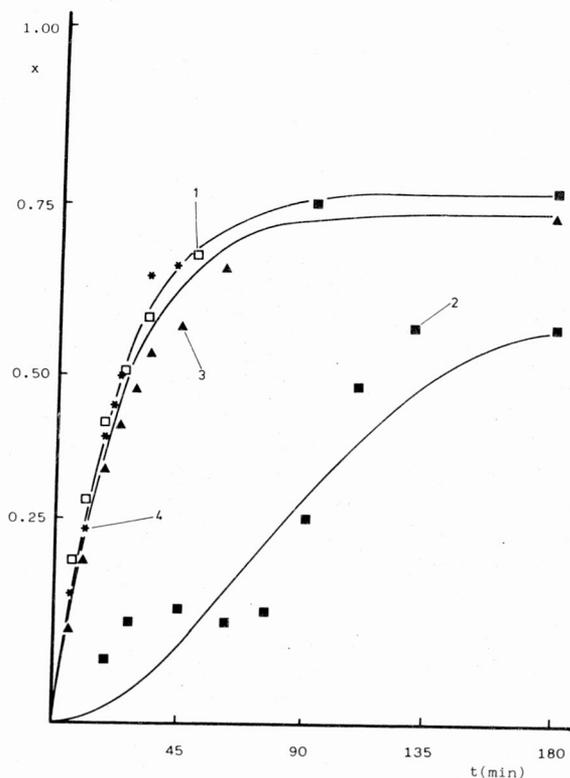
Fig. 6. Simulation (−) and experimental results for the experiments at constant concentration of sulfurous acid 2.00×10^{-3}M and variable concentration of calcium hydroxide: *1* − 0.5 g/l, *2* − 1.0 g/l, *3* − 2.0 g/l, and *4* − 3.0 g/l

4. SIMULATION

A simulation of the kinetics for the precipitation of calcium sulfite has been performed using kinetic parameters obtained above. Results in figs. 5, 6 and 7 show a good agreement between experimental and simulated values, supporting the possibility to use the obtained kinetic model and parameters for design purposes.

5. DISCUSSION

Many authors have reported SO_2 absorption in lime slurries (tab. 6), they have developed different kinetic models taking into account instantaneous or very fast chemical reaction under control of mass transfer kinetics, evaluating the gas side or liquid side mass transfer coefficients.

Table 6

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Kinetic studies of SO_2 absorption in lime slurries

Authors, year	Concentrations SO_2	$Ca(OH)_2$	Contact	Kinetic model	Parameters
SADA et al., 1977	pure	0–20% (solid)	stirred tank with constant G–L area	$D_A \dfrac{d^2 C_A}{dz^2} = K C_A C_B$ (gas) $D_B \dfrac{d^2 C_B}{dz^2} + K_S A_{pd}(C_A)$ $\times (C_{Bs} - C_B) = K C_A C_B$	$K_g = \infty$ $K_{ISO_2} = 1.6 \times 10^{-3}$ cm/s $K \gg K_l$, instantaneous reaction
SADA et al., 1977 simultaneous SO_2–CO_2 absorption	0.02 atm $< P_{SO_2} < 0.048$ atm 0.02 atm $< P_{CO_2} < 0.04$ atm	0–20% solid	idem	idem	$K_{II}^0 = K_{i,N_2O}^0 (D_l/D_{N_2O})^{2/3}$ $K_{ICO_2} = 1.42 \times 10^{-3}$ cm/s $K_{ISO_2} = 1.7 \times 10^{-3}$ cm/s K_g high $K_{(CO_2+OH^-)} = 8400$ l/mol·s $K_{(SO_2+OH^-)} \gg K_l$
SADA et al., 1984	idem	2–40% (solid)	idem	$\dfrac{d^2 Y_A}{dx^2} = 0, \quad 0 < X < \lambda$ $\dfrac{d^2 Y_A}{dx^2} - N Y_A = \dfrac{N}{r-q}, \quad \lambda < X < X_r$	$K_g \gg K_l$ $K \gg K_l$
SADA et al., 1984				$\dfrac{d^2 Y_B}{dx^2} + N(1 - Y_B) = 0, \quad X_r < X < 1$	
LAOHAVICHITRA et al., 1982	10^3–5×10^3 ppm	1.06×10^{-2} M	wet-wall column	Higbie's model for mass transfer	K_g, $N_{Sh} = 0.18 N_{Re}^{0.64} N_{Sc}^{0.33}$ control in the gaseous film
RAM BABU et al., 1984	0.96–2.86% SO_2–N_2	0.025–0.041 gr-ion/l	laminar jet		K_g instantaneous reaction
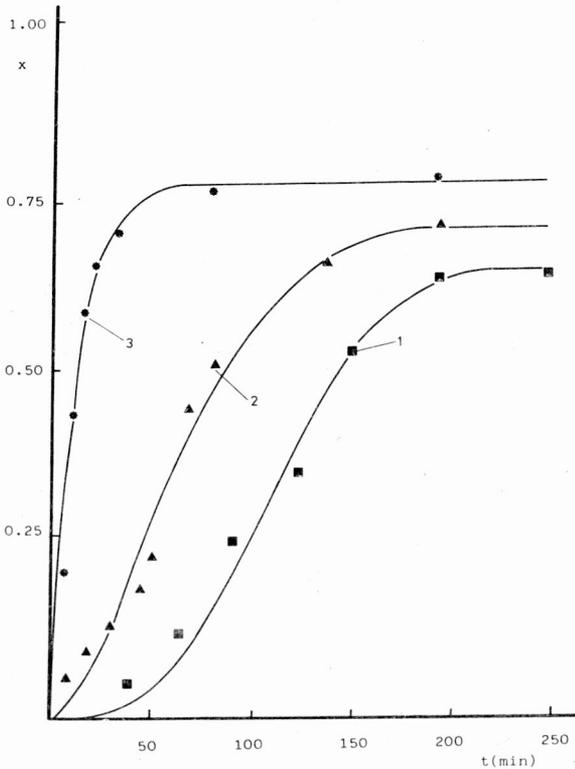
Fig. 7. Simulation $(-)$ and experimental results for the experiments at constant concentration of calcium hydroxide 1.00×10^{-3}M and variable concentration of sulfurous acid: $1 - 1.70 \times 10^{-3}$M, $2 - 2.15 \times 10^{-3}$M, and $3 - 2.80 \times 10^{-3}$M

Our results show the very sensitive influence of the sulfurous acid and calcium hydroxide concentrations on the reaction rate working in the range of compositions corresponding to the equilibrium with flue gases containing less than 600 ppm, as is shown in tab. 2. This amount of SO_2 in the flue gas leads to precipitation control with kinetic parameters given in tabs. 3 and 4 depending on the slow process. Results allow a suitable fitting of the experimental results useful for design purposes.

Design and optimization of the contact between gas and slurry must be performed considering that low concentration of sulfur dioxide and/or calcium hydroxide leads to very slow reaction rates under control of the precipitation process.

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BADANIA KINETYKI REAKCJI KWASU SIARKAWEGO Z WODOROTLENKIEM WAPNIOWYM

Przeprowadzono badania kinetyki reakcji kwasu siarkawego z wodorotlenkiem wapniowym w procesie mokrego odsiarczania gazów za pomocą mleka wapiennego. Stwierdzono, że przy stężeniu molowym kwasu siarkowego poniżej $2,8 \times 10^{-3}$ i wodorotlenku wapniowego — poniżej $4,05 \times 10^{-2}$, szybkość reakcji jest stosunkowo mała, co można wyjaśnić w oparciu o modele wzrostu kryształów siarczynu wapniowego. Uzyskane wyniki wskazują na istotny wpływ stężeń substratów badanej reakcji na szybkość odsiarczania gazów mlekiem wapiennym, co powinno być uwzględnione przy projektowaniu i optymalizacji procesu.

ИССЛЕДОВАНИЯ КИНЕТИКИ РЕАКЦИИ СЕРНИСТОЙ КИСЛОТЫ С ГИДРООКИСЬЮ КАЛЬЦИЯ

Проведены исследования кинетики реакции сернистой кислоты с гидроокисью кальция в процессе сырого обессеривания газов при помощи известкового молока. Было установлено, что при молярной концентрации сернистой кислоты ниже $2,8 \cdot 10^{-3}$ и гидроокиси кальция ниже $4,05 \cdot 10^{-2}$, быстрота реакции является относительно малой, что можно объяснить, опираясь на модель роста кристаллов сернистого кальция. Полученные результаты указывают на существенное влияние концентраций субстратов исследуемой реакции на быстроту обессеривания газов при помощи известкового молока, что надо учитывать при проектировании и оптимизации процесса.