Oxidation of aqueous sulphur dioxide in suspensions of magnesium oxide: Removal of $\text{SO}_2$ from flue gases

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The kinetics of oxidation of aqueous $\text{SO}_2$ in acetate buffered suspensions of $\text{MgO}$ obeys rate law (i)

$$R_{\text{obs}} = k[\text{MgO}][\text{S(IV)}][H^+]^{-1} \quad \ldots (i)$$

and the main oxidation product is sulphate. The suggested mechanism involves the formation of surficial complexes between hydroxylated magnesium and $\text{S(IV)}$. There exists a close parallelism between $R_{\text{obs}}$ and $p\text{H}$ of zero point charge, $p\text{H}_{\text{ZPC}}$, for $\text{CdO}$, $\text{MgO}$ and $\text{SiO}_2$. The results suggest that in wet-scrubbers, which utilize the slurries of $\text{MgO}$ for removal of $\text{SO}_2$ from the flue gases, the sulphite formed as a result of $\text{SO}_2$ absorption will be oxidized by atmospheric oxygen to sulphate, the extent of which will increase with increase in $p\text{H}$, temperature, slurry density and absorbed $\text{SO}_2$.

The use of lime, limestone, magnesium oxide, dolomite etc. is widely recommended in the desulphurization of flue gases, FGD, for controlling air pollution. In the pre-combustion dry method, the incipient $\text{SO}_2$ is removed by its reaction with limestone and lime and in the furnace of coal fired power station $\text{SO}_2$ reacts to form $\text{CaSO}_3/\text{CaSO}_4$ (ref. 1). For the post combustion FGD, wet and dry scrubbers are used. In the wet process, the slurries of alkaline materials such as lime, limestone, dolomite and $\text{Mg(OH)}_2$ are used. The absorption of $\text{SO}_2$ from flue gases by slurries leads to the formation of metal sulphites. In the presence of oxygen and catalysts, oxidation to sulphate takes place. For the removal of $\text{NO}_x$ from pollutant gases in boiler and process industries too, the aqueous solutions of magnesium hydroxide, magnesium carbonate, calcium hydroxide and ammonia or their combinations are used$^{9-11}$.

Judeikis et al.$^{12}$ have studied the rate of removal of gaseous $\text{SO}_2$ over $\text{MgO}$. The rate of removal was enhanced from 12 mg $\text{SO}_2$/g of $\text{MgO}$ at 50% relative humidity to 400 mg $\text{SO}_2$/g of $\text{MgO}$ at 95% relative humidity, and the quantitative conversion of adsorbed $\text{SO}_2$ into adsorbed sulphate was shown. The surface $p\text{H}$ was considered to be a dominant factor.

In continuation of our earlier studies on the oxidation of sulphur(IV) using glass$^{13}$ and ceramic$^{14}$ powders as catalysts, we report herein the kinetics of $\text{SO}_2$ oxidation in aqueous $\text{MgO}$ suspensions and compare the results with those obtained with other similar systems.

Experimental
Magnesium oxide (single point B.E.T. surface area $\dagger$ 28.03 $\text{m}^2\text{g}^{-1}$) and all other chemicals were of reagent grade. The kinetic procedure has already been described$^{15}$. The reactions were conducted in 0.15 dm$^3$ Erlenmeyer flasks and the reaction mixtures were continuously stirred magnetically at $150 \pm 100$ rpm based on the observation that the reaction rate is independent of stirring rate $>1200$ rpm. Thus the reaction is not oxygen mass transfer controlled at $1500 \pm 100$ rpm. The reactions were initiated by adding $\text{MgO}$ to buffered $\text{S(IV)}$ solution. The progress of reaction was followed by estimating unreacted $\text{S(IV)}$ by adding the aliquot samples to a predetermined quantity of iodine and back-titrating the unconsumed $\text{I}_2$ against standard sodium thiosulphate solution using starch as indicator. For maintaining desired $p\text{H}$, the overall concentration of $\text{CH}_3\text{COONa}$ was maintained at 0.16 mol dm$^{-3}$ and $[\text{CH}_3\text{COOH}]$ was varied. The initial rates were reproducible within $\pm 10\%$.

The stoichiometric measurement showed sulphate to be the only oxidation product and sulphate recovery as $\text{BaSO}_4$ was $97 \pm 1\%$ of the theoretical value in accordance with Eq. (1).

$$\text{Sulphur(IV)} + \frac{1}{2} \text{O}_2 \xrightarrow{\text{MgO}} \text{Sulphate} \quad \ldots (1)$$

Results and discussion
The suspension on stirring turned milky due to dispersion of fine particles. The slow dissolution of $\text{MgO}$ in the buffered suspension was noticed. Experiments in the presence of $\text{MgCl}_2$ ruled out its catalytic effect on the rate of oxidation.

In the absence of $\text{O}_2$, and in nitrogen atmosphere, the oxidation did not take place. This

$\dagger$Courtesy: Advanced Centre for Material Science, I.I.T. Kanpur, India.
MgO and S(IV) dependences were in agreement with the experimental rate law (3).

$$R_{obs} = k_3 [\text{MgO}] [\text{S(IV)}]^2$$ ...

(3)

The results of pH variation at two different [S(IV)], but at a fixed [MgO], showed an inverse first order in $H^+$ as in Eq. (4).

$$R_{obs} = k [\text{MgO}] [\text{S(IV)}]^2 [H^+]^{-1}$$ ...

(4)

A plot of $(R_{obs}/[\text{MgO}] [\text{S(IV)}]^2)$ versus $[H^+]^{-1}$ is shown in Fig. 2 which yielded a best fit value of $1.96 \times 10^{-6} \text{ dm}^3 \text{ g}^{-1} \text{ S}^{-1}$ for $k$ at $30^\circ$. $R_{obs}$ values of $4.0 \times 10^{-7}$, $5.0 \times 10^{-7}$ and $9.0 \times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$ at $25^\circ$, $30^\circ$, and $35^\circ$ respectively for $[S(IV)] = 2 \times 10^{-3}$ mol dm$^{-3}$, $[\text{MgO}] = 0.2$ g dm$^{-3}$ and $pH = 5.06$ yielded an energy of activation of 65 kJ mol$^{-1}$.

In some experiments no buffer additive was used and the initial pH was adjusted with dilute perchloric acid. The reaction profiles shown in Fig. 3, display the reaction to occur in two stages. In the first stage, there is an initial rapid fall in $[\text{S(IV)}]$ followed by its much slower disappearance in the second stage. Although the reaction is accompanied by a rapid decrease in pH, the second stage cannot be ascribed to the effect of falling pH, as the reaction profiles at two different pH values viz. 6.10 and 3.5 ($[\text{MgO}] = 0.2$ g dm$^{-3}$, $[S(IV)] = 2 \times 10^{-3}$ mol dm$^{-3}$) have almost same initial average rapid rate i.e. $\Delta [S(IV)]/\Delta t$. As the $\Delta [S(IV)]/\Delta t$ values at two widely different pH values are the same, the reaction in unbuffered suspensions appears to be independent of $[H^+]$. It should be mentioned here that an exactly similar kinetic behaviour was ob-

Fig. 1—Variation of $\text{MgO}$ at various $[\text{S(IV)}]$ at $pH = 5.34$ and temp = $30^\circ$.

$\bigcirc$, $[\text{S(IV)}] = 2.5 \times 10^{-3}$ mol dm$^{-3}$; $\triangle$, $[\text{S(IV)}] = 5 \times 10^{-3}$ mol dm$^{-3}$; $\otimes$, $[\text{S(IV)}] = 7.5 \times 10^{-3}$ mol dm$^{-3}$.

Fig. 2—A plot of $R_{obs}/[\text{S(IV)}][\text{MgO}]$ versus $[H^+]^{-1}$ at temp = $30^\circ$. 

$10^5 [S(IV)] = 2 \times 10^{-3}$ mol dm$^{-3}$; $\Delta$, $[S(IV)] = 5 \times 10^{-3}$ mol dm$^{-3}$; $\otimes$, $[S(IV)] = 7.5 \times 10^{-3}$ mol dm$^{-3}$.
Fig. 3—Rate profiles for [S(IV)] autoxidation at different pH in unbuffered solutions and [S(IV)] = 2 × 10⁻³ mol dm⁻³; [MgO] = 0.2 g dm⁻³ and temp = 30°.

O, pH = 6.1; Δ, pH = 5.9; ◇, pH = 5.22; ■, pH = 3.5.

Craved in S(IV) autoxidation in carbon suspensions and the phenomenon of initial rapid fall was shown to be due to the reaction of those carbon particles which had chemisorbed atmospheric oxygen on their surface to form active surficial CₓOₓ₂, prior to their use in making suspensions. In a similar way those magnesium oxide particles which have chemisorbed atmospheric dioxygen on the surface might be responsible for initial rapid reaction. Incidentally in the oxidation of CaSO₃ in its slurries a similar phenomenon has been noted.

A common feature of sulphur(IV)—autoxidation in ZnO, CdO and limestone suspensions is the dissolution of these substances during the reaction. Since the dry and wetted aerosols of these substances aid in atmospheric oxidation of SO₂ leading to acid rain, the study of these systems for understanding the atmospheric chemistry of SO₂ is important.

pKₐ(2) value of 6.3 for equilibrium (5) suggests that

\[ K_{a(2)}^{−} \]
\[ HSO₃^- \rightleftharpoons SO₃^{2−} + H^+ \]  

S(IV) will be present largely as HSO₃⁻ in the range of pH used in this study. The hydroxylation of metal oxides in their aqueous suspensions is well established. In MgO suspensions, the following acid-base equilibria involving its hydroxylated form would be established.

\[ K_{d(1)} \]
\[ Mg(OH)(OH_2)^+ \rightleftharpoons Mg(OH)_2 + H^+ \]  

\[ K_{d(2)} \]
\[ Mg(OH)_2 \rightleftharpoons Mg(OH)^+ + H^+ \]  

The pH of the zero point charge, pH_ZPC, of MgO is reported to be 12.4 (ref. 22) (Eq. 8) which indicates that, in the pH range of this study, MgO

\[ pH_{ZPC} = 1/2(pK_{d(1)} + pK_{d(2)}) \]  

will be largely present as −Mg(OH)(OH₂)⁺ which appears to be the reactive species also. It should be mentioned that in several other oxidation reactions in aqueous suspensions, e.g., α-Fe₂O₃ (ref. 19) and SiO₂ (ref. 23) the hydroxylated oxides interact with aqueous S(IV) and form surficial complexes. Similarly the participation of surface hydroxyl groups present on copper in CuO(aerosol)-SO₂(gas)-water system has also been visualized. A similar mechanism may be operating in the present reaction system also. The number of surface hydroxyl groups in the case of several solid particles such as ZnO, SiO₂, SnO₂, TiO₂ etc. has been determined and this number is reported to vary between 2.8 and 1.5 OH per 100 Å².

Based on above arguments and on the mechanism proposed for α-Fe₂O₃, SiO₂ and glass powder catalyzed reactions, the mechanism in Scheme 1 may be proposed.

The steps would lead to the observed rate law (4).

The measure of caution, it is not out of place to mention that the analysis of [H⁺]-dependence as presented here, is to some extent, not unambiguous as a variation in pH entails a variation in [buffer]. Since the latter affects the rate, the part of [H⁺]-effect may have its origin in [buffer]-dependence.

It is of interest to compare the results of this study with those in CdO and SiO₂ suspensions. The common feature of all these studies is the absence of the involvement of the multiple oxidation states of Mg, Cd and Si. Incidentally, the kinetic rate law (13), at constant pH, for all these oxides is same. The values of k₃, at pH 5.3 and 30° for Si, Cd and Mg oxides are 0.021, 0.30 and 0.50 dm⁶ mol⁻¹ g⁻¹ s⁻¹ respectively whereas the...
respective pH_{ZPC} values for these oxides are 3.0 (ref. 21), 10.4 (ref. 20) and 12.4 (ref. 20). Interestingly a close parallelism is seen in the values of k_3 and pH_{ZPC}, the former increases with increase in the latter. As the pH_{ZPC} values are higher in general, for more basic oxides, it can be inferred that the oxides which have higher surface pH are more effective as a surface catalyst in the oxidation of sulphur(IV).

The present results suggest that the efficiency of MgO in wet scrubbers for desulphurization of flue gases will increase with increase in slurry density, temperature and pH.

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