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OXIDATION OF SULFITES IN WET FGD PROCESSES: MECHANISM OF OXIDATION INVOLVING ATMOSPHERIC OXYGEN AND Fe(III) CATALYST

On the basis of literature data, as well as making use of the results obtained from our own investigations, we proposed a mechanism for the oxidation of sulfites in the presence of Fe(III) ions. The kinetic equations describing the course of the reaction were derived and their agreement with experimental data was verified. The stages of the oxidation process were identified, and the order of the reaction for each stage was determined.

1. INTRODUCTION

Self-oxidation of sulfites in flue gas desulfurization (FGD) processes is an important part of many industrial treatment technologies. The rate of self-oxidation varies with each change in the reaction conditions, depending on the presence of such substances that may accelerate or inhibit the process [1]. According to HUSS and co-workers [2], self-oxidation is a catalytic process, as there are always a number of external factors that might affect it. Thus, not only can the oxidation reaction be initiated by the presence of metals displaying catalytic properties (transition metals), but it may also be thermally or photolytically induced [3]. Hence, the reaction rate depends on the method of initiating the reaction.

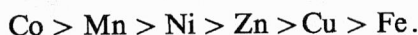
The mechanism governing the oxidation of sulfites is still far from being well understood. But there are two major factors affecting the course of the oxidation process – the pH of the solution (which contributes to the formation of HSO_3^- or HSO_3^{\cdot} and SO_3^- or SO_3^{\cdot} radicals, the intermediate products of the reaction) and the type of the initiating factor involved.

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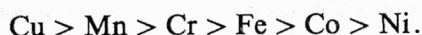
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Some major results obtained with a homogeneous and a heterogeneous system of sulfite oxidation were reported by LINEK and VACEK [4]. As the reaction conditions (SO_3^{2-} and O_2 concentrations, catalyst, apparatus) vary from one process to another, the values of the kinetic constants are also variable. The reaction order ranges between 0 and 2, irrespective of the component considered. The oxidation proceeds most frequently in the presence of CuSO_4 , CoSO_4 or MnSO_4 catalysts, but a mixed catalyst, Mn, $\text{Fe}(\text{SO}_4)$ of synergistic activity of the two metals, may also be of utility [5], [6]. There has been a difference of opinion on the catalytic activity of transition metals. But the Fe(III) catalyst has raised the most serious objections.

On investigating the oxidation of sulfites in the citrate method of FGD, KARLSSON and co-workers provided the following (ascendent) order of activity for the catalysts in question [7]:

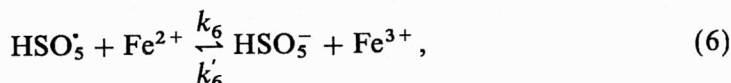
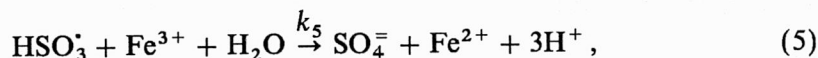
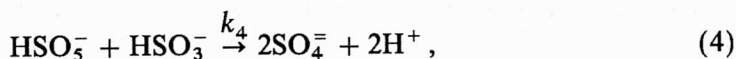
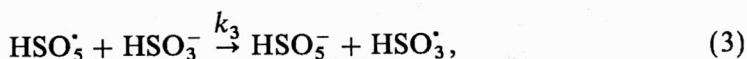
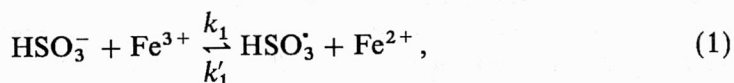


According to those investigators the Fe(III) exerted an inhibiting effect, particularly at high oxygen concentrations. But PRADO [5] found that in an acidic solution (pH ~ 5) at a molar concentration from 10^{-4} to 10^{-3} the catalytic activity of iron was higher than that of Mn, Co, or Ni, so he established a different order:



2. THEORETICAL COMMENTS

On the basis of literature data the following assumption can be put forward: The oxidation of sulfites to sulfates in the presence of both atmospheric oxygen and Fe(III) ions, which act as a catalyst, is a multi-stage process which proceeds as follows:





Many other concomitant reactions have no contribution to the course of the entire process [3].

Provided that this assumption is true, the rate of HSO_3^- ion decay can be described as

$$\begin{aligned} -\frac{d[\text{HSO}_3^-]}{dt} &= k_1[\text{HSO}_3^-][\text{Fe}^{3+}] - k'_1[\text{HSO}_3^*] \\ &\quad \times ([\text{Fe}^{3+}]_0 - [\text{Fe}^{3+}]) + k_3[\text{HSO}_3^-][\text{HSO}_5^*] \\ &\quad + k_4[\text{HSO}_3^-][\text{HSO}_5^-] + k_7[\text{HSO}_3^-][\text{O}_2]. \end{aligned} \quad (8)$$

It can further be assumed that within a short time following the initiation of the reaction, a stationary state will be established, and the rate of the intermediate products (HSO_3^* , HSO_5^- , HSO_5^* and Fe(II) ions) formation will be balanced with the rate of their decay. The stationary state should persist until the substrate has been exhausted almost entirely. Furthermore, under experimental conditions dissolved oxygen concentration in the solution should be constant throughout. If this is true and if the process proceeds in the kinetic, and not in the diffusional region, the term describing the concentration of the intermediate products in equation (8) can be replaced by relevant functions describing the concentrations of the substrates and the catalyst, by virtue of the approximation of the stationary state.

Thus, we can anticipate that the general form of the kinetic equation (8) becomes

$$-\frac{d[\text{HSO}_3^-]}{dt} = -\frac{dc_s}{dt} = \sum_i \frac{a_i \cdot c_s^{n_i} \cdot c_{0k}^{m_i}}{1 + b_i \cdot c_s^{p_i} \cdot c_{0k}^{q_i}} \quad (9)$$

where

$c_s = [\text{HSO}_3^-]$ - sulfite concentration,

$c_{0k} = [\text{Fe(III)}]_0$ - initial concentration of catalyst,

a_i, b_i - constants, k_1-k_7 functions,

n_i, m_i, p_i, q_i - exponents (partial orders) taking integers, fractions, positive and negative values or zero.

Some of the a_i, b_i constants may also be equal to zero.

Considering the general form of equation (9), we can anticipate that, in the absence of the catalyst, the order of the reaction ranges between zero and unity, and the contribution of the reaction to the entire process is insignificant. A catalytic reaction should be of a higher order; but the order of the reaction depends on the concentration of both substrate and catalyst. With decreasing quantity of the substrate the order of the reaction may increase.

3. EXPERIMENTAL

In order to determine the effect of Fe(III) on the oxidation of sulfites, the experiments with a solution which provided the best oxidation efficiencies were carried out. The experimental conditions were as follows: sulfite concentration, 7.5 kg/m^3 , catalyst concentrations, 0.0 – 0.5% wt. of SO_3^{2-} content; $\text{pH} = 7.1$, $T = 295 \text{ K}$, and linear velocity, $2 \cdot 10^{-3} \text{ m/s}$. The reaction proceeded until the efficiency of sulfite oxidation had reached 80%. Concentration of sulfites in solution and pH value were measured throughout.

4. DISCUSSION OF RESULTS

Figure 1 shows the $(c_{0s} - c_s) = f(t)$ relation for the reaction tested. Initial sulfite concentration was identical in each experiment. Catalyst content with respect to sulfite totalled 0% (curve 1), 0.05% (curve 2), 0.1% (curve 3) and 0.5% (curve 4). In figure 1 there are also presented the $\text{pH} = f(t)$ relations associated with the reactions.

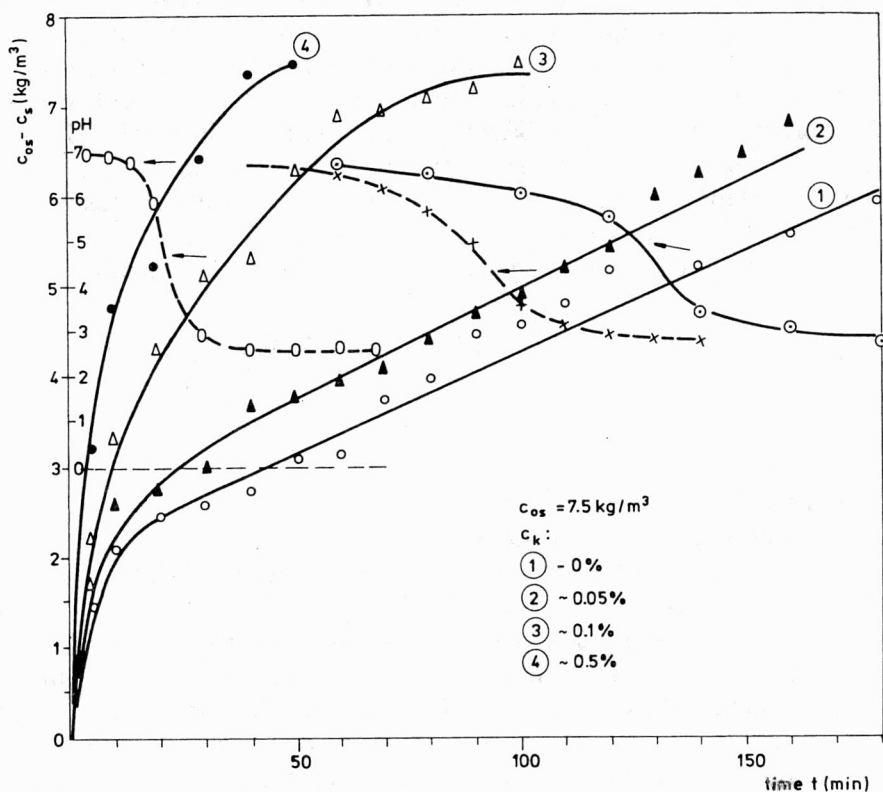


Fig. 1. Functions $c_{0s} - c_s = f(t)$ and $\text{pH} = f(t)$ for $c_{0s} = 7.5 \text{ kg/m}^3$ and c_k range from 0 to 0.5% wt., the plots being necessary for determination of reaction rate

As shown by these plots, the process involved at least two stages. One of these was likely responsible for the stationary state, whereas during the other one the reaction proceeds of itself. This pattern is particularly distinct in the case of the curves 1 and 2. At the first stage of the reaction (even in the absence of the catalyst), the conversion of the substrate approached 20%. And this is an indication that the reaction did not proceed at a fast rate. As soon as the efficiency of conversion reached 60 – 70%, there was a rapid decrease in pH, which might be due to the exceeded buffering capacity of the $\text{HSO}_3^-/\text{SO}_3^{2-}$ system. The linear increase in the concentration of the product (curves 1 and 2) enables two generalizations to be made: (1) reaction with no catalyst added was a zeroth-order reaction, (2) the addition of a 0.05% catalyst portion did not noticeably affect either the principal reaction rate or the reaction order.

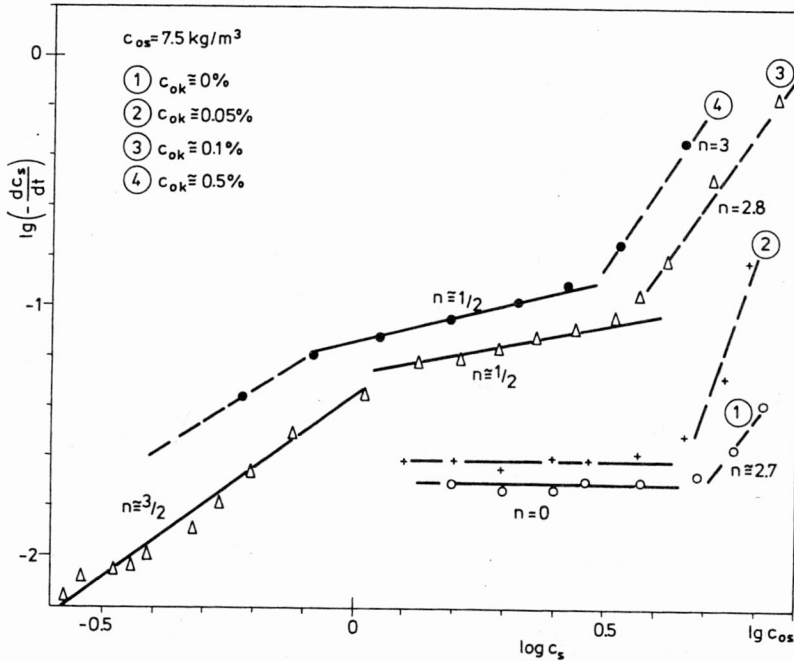


Fig. 2. Functions $\log v = \log k + n \log c_s$, necessary for determination of reaction order

Curves 3 and 4 follow a different pattern. They show no linear relationship between the concentration of the product and the time of the reaction. By determining the direction factors which are tangential to those curves at arbitrary points, we can find the relationship between the reaction rate and the HSO_3^- ion concentration. The order of the reaction may then be established by plotting the calculated results in the bilogarithm scale. Such plots are presented in figure 2. As shown by these data, we can distinguish in the process three distinct stages – initial, principal and final. At the initial stage there was a rapid decrease of the reaction rate. In the principal stage, the reaction order takes the value about 1/2.

At the final stage (curve 3) the order of the reaction increased to $3/2$. The curve 1 and curve 2 show that there is a clear distinction between the initial and the principal stages, but it was at the principal stage that the zeroth order of the reaction established itself.

Making use of the results obtained, we may anticipate that the kinetic equation describing the course of the reaction in the presence of a 0.1% and 0.5% contents of the catalyst will take the form of

$$v = -\frac{dc_s}{dt} = v_0 + \frac{a + \sqrt{c_s^3}}{1 + b \cdot c_s} \quad (10)$$

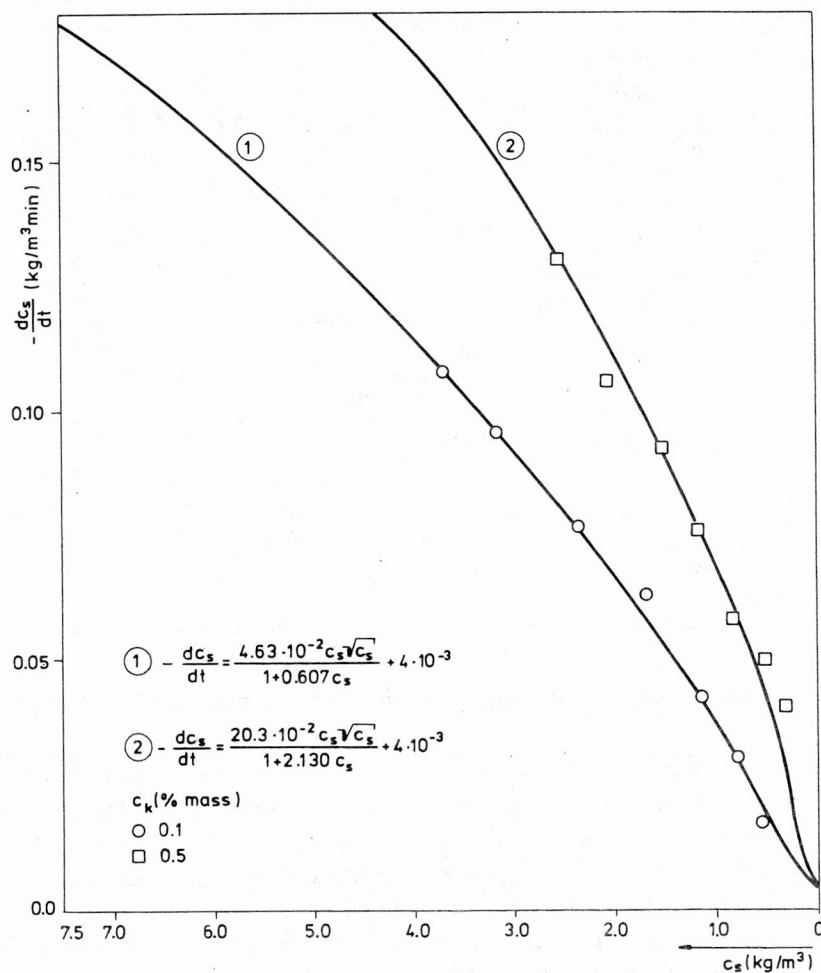


Fig. 3. Function (10) determined by means of parameters from table, the experimental points being indicated

Table

Constants of the kinetic equation (10) for the curve in figure 1

Curve	c_{0s} $\text{kg}\cdot\text{m}^{-3}$	c_{0k} %	ϑ_0 $\text{kg}\cdot\text{m}^{-3}\cdot\text{min}^{-1}$	a $\text{kg}^{3/2}\cdot\text{m}^{9/2}\cdot\text{min}^{-1}$	b $\text{kg}^{-1}\cdot\text{m}^3$	D min
3	7.5	0.1	0.004	0.0463	0.607	40
4	7.5	0.5	0.004	0.2030	2.130	43

The constants a , b and v_0 were fitted so as to achieve the best agreement between the calculated and experimental results. The values of the kinetic equation constants which satisfy the criterion of (10) are gathered in the table for curves 3 and 4. Making use of the parameters determined via this route, the functions of (10) were plotted in figure 3, and the experimental points were incorporated.

The term v_0 can be interpreted as the rate of the non-catalytic reaction, but its value is approximately one-fifth of the value determined graphically from figure 1 (curve 1).

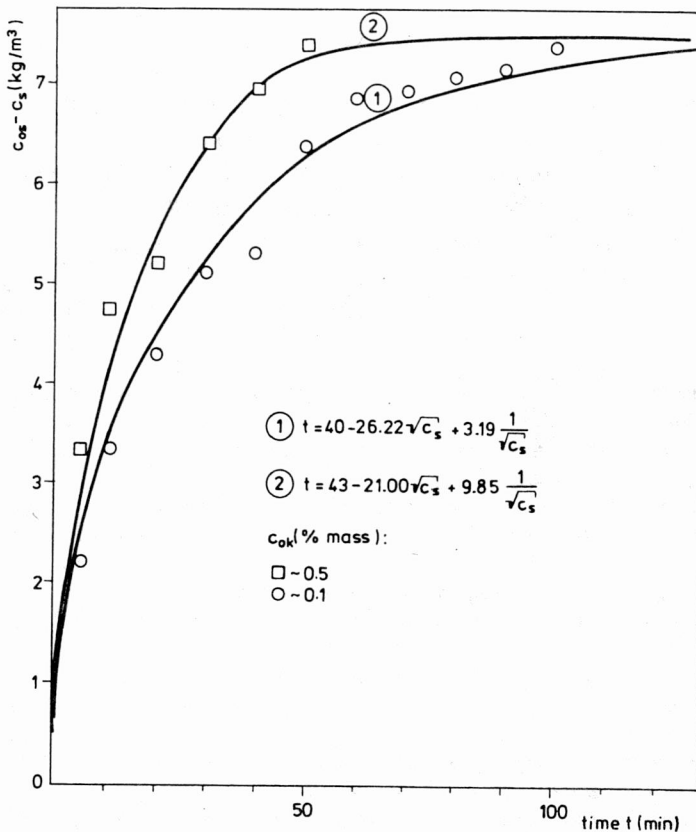


Fig. 4. Function (11), experimental points being indicated

Since the value of v_0 is negligibly small, it can be omitted when solving the reactions of (10). The solution will then become

$$\frac{2}{a\sqrt{c_s}} - \frac{2b\sqrt{c_s}}{a} + D - t = 0, \quad (11)$$

D – an integration constant resulting from the boundary conditions and the application range for equation (11).

The table also comprises the values of D established for the curves 3 and 4. In figure 4, the relations of (11) are plotted in the form of function $c_{0s} - c_s = f(t)$, and the experimental points of figure 1 (curve 3 and curve 4) have also been included. As shown by these data, there is an agreement between experimental points and the kinetic equations within the entire range investigated. The values of a and b are nearly proportional to the concentration of the catalyst added, whereas those of v_0 and D are independent of this concentration.

5. CONCLUSIONS

1. On the basis of literature data the mechanism governing the oxidation of sulfites in the presence of Fe(III) ions was proposed.

2. Making use of the oxidation mechanism, the form of the kinetic equations was suggested. The agreement between the plots and experimental data under optimum oxidation conditions was verified.

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UTLENIANIE SIARCZYŃÓW PODCZAS MOKREGO ODSIARCZANIA SPALIN:
MECHANIZM UTLENIANIA W OBECNOŚCI
TLENU ATMOSFERYCZNEGO I KATALIZATORA Fe(III)

Na podstawie danych literaturowych i badań własnych zaproponowano mechanizm utleniania siarczynów w obecności jonów Fe^{3+} jako katalizatora. Wyznaczono równania kinetyczne i sprawdzono ich zgodność z danymi doświadczalnymi. Zidentyfikowano etapy procesu utleniania i określono rzędowność reakcji.

ОКИСЛЕНИЕ СУЛЬФИТОВ ВО ВРЕМЯ МОКРОГО ОБЕССЕРЕНИЯ ДЫМОВЫХ ГАЗОВ:
МЕХАНИЗМ ОКИСЛЕНИЯ В ПРИСУТСТВИИ АТМОСФЕРНОГО КИСЛОРОДА
И КАТАЛИЗАТОРА Fe(III)

На основе литературных данных и собственных исследований предложен механизм окисления сульфитов в присутствии ионов Fe^{3+} в качестве катализатора. Определены кинетические уравнения и проверено их согласование с экспериментальными данными. Идентифицированы этапы процесса окисления и определен порядок реакции.

