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EFFECT OF TEMPERATURE ON THE KINETICS OF THE OXIDATION OF SULFITES IN WET FGD PROCESSES

The contribution of temperature to the kinetics of the sulfite oxidation in solution was investigated in the range typical of FGD processes (295–319 K). Kinetic constants (reaction order and rate constant) were determined for each temperature tested. The Arrhenius equation and activation energy were established. It was found that the oxidation reaction proceeded in the region intermediate between kinetic and diffusional.

1. INTRODUCTION

The mechanisms of sulfite oxidation in solutions have been reported in professional literature a number of times [1]–[4]. Each of them indicates that both SO_3^{2-} and HSO_3^- ions are oxidized via formation of the $HSO_3^{\cdot}$ radical, which means that the oxidation reaction proceeds in several stages. This finding is of particular importance to the oxidation of $CaSO_3$ in the solid–liquid system (heterogeneous catalysis). In its principal stage, the oxidation reaction in solution proceeds with the participation of the HSO_3^- ion and $HSO_3^{\cdot}$ radical. Thus, the oxidation is limited by the solubility of $CaSO_3$ in the solution [5]. According to TSENG and ROCHELLE [6] the dissolution of $CaSO_3 \cdot \frac{1}{2}H_2O$ is mass-transport-controlled.

Solubility is a function of the following factors: temperature, pH, concentration and diffusivity of the components involved, so they should also be regarded as responsible for the rate at which sulfites are oxidized in a two-phase system. The course of the oxidation is influenced by the presence of transition metals (Mn, Co, Cu, Fe), which may catalyze the process, as well as by the hydrodynamics of the system (method of gas/liquid contact, time of contact) [7], [8]. In order to determine the rate of the chemical reaction, it is convenient to make the process takes place in the kinetic region.

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2. EXPERIMENTAL

The oxidation reaction was conducted in the temperature range from 295 to 319 K which is typical of sorption effluents produced in the wet FGD methods. The temperature desired was kept constant by thermostating. Sulfite concentration (c_s), linear air flow velocity (v_p), pH of the solution and catalyst concentration (c_k) amounted to 3.76 kg/m^3, $2 \cdot 10^{-3}$ m/s, 7.1 and 0.1 wt.%, respectively.

3. DISCUSSION OF RESULTS

The investigated temperature range provided an increase in the efficiency of oxidation and a loss in SO_2 due to desorption (figure 1). The shortest time required for a complete oxidation corresponded with the temperature of 319 K at which the rate of SO_2 desorption was also the highest (17.2% loss).

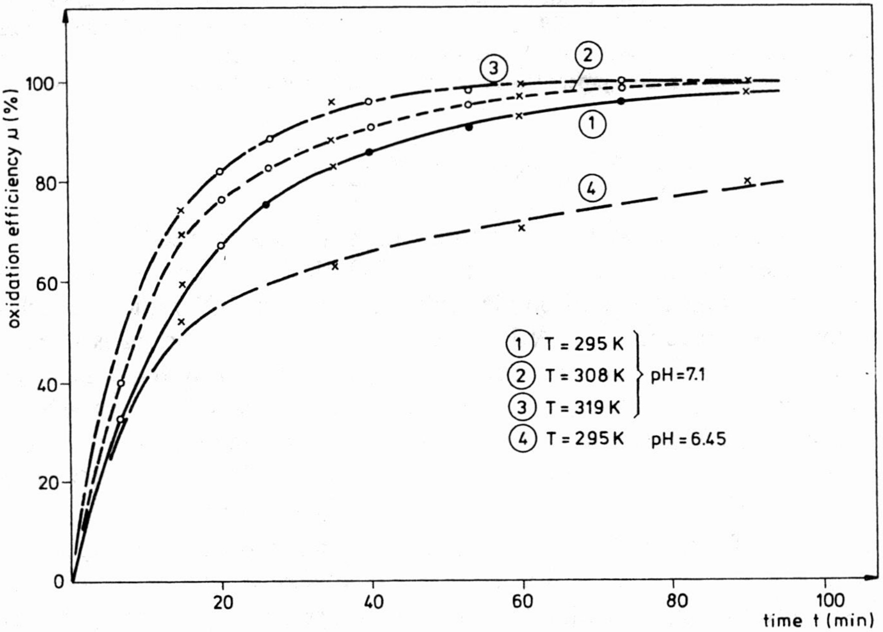

Fig. 1. Time-dependent oxidation efficiency versus temperature at $c_{0s} = 3.76$ kg/m^3, $c_k = 0.1\%$ wt., $v_p = 2 \cdot 10^{-3}$ m/s

The increase in the oxidation rate with temperature should be attributed to the effect of the latter on the equilibrium of the reaction

$$SO_3^{-2} + H^+ \rightharpoonup HSO_3^- . \quad (1)$$

At acid solution, the rise in temperature resulted in the shift of the reaction equilibrium toward the bisulfite formation. This finding was supported by the pH difference, $\Delta\mathrm{pH} = 4.65$ (which was higher than the ones obtained at other temperatures), and by the very low pH at the end of the aeration process. There was also a contribution of the iron salt present in the solution, which made the reaction rate vary with each change in temperature [9].

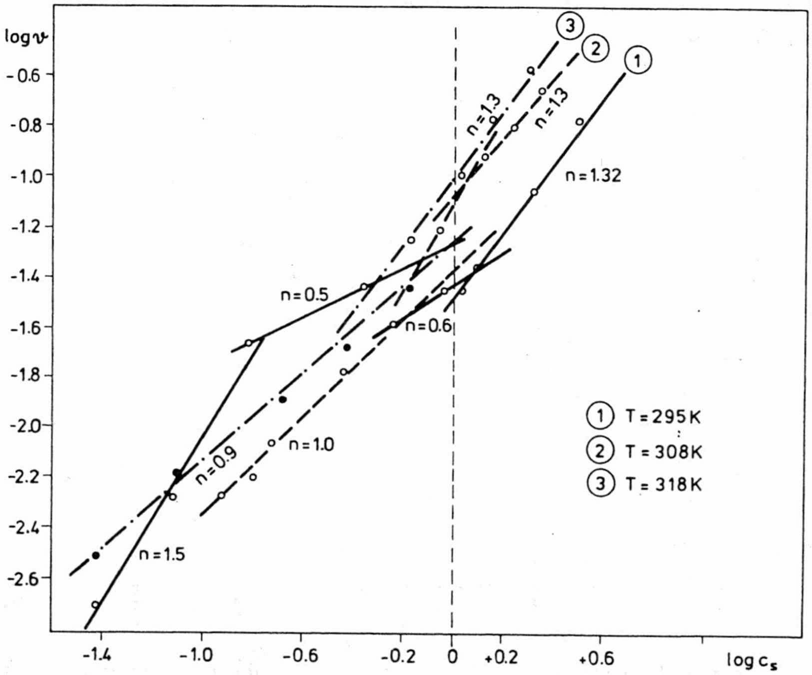

Fig. 2. Dependence $\log v = \log k + n \log c_s$ for different temperatures at $c_{0s} = 3.76$ kg/m^3, $c_k = 0.1\%$ wt., pH ~ 7.1, $v_p = 2 \cdot 10^{-3}$ m/s

Making use of the $c_0 - c_s = f(t)$ curves it was possible to present graphically the reaction rate ($v = -dc_s/dt$) and to determine the functions

$$\log v = \log k + n \log c_s \tag{2}$$

for each of the temperatures investigated. It was found that the variation in the reaction rate with time involved three oxidation stages (figure 2). The order of the reaction was determined from the slopes of respective sections of the lines, and was found to range from 1.3 (initial stage), through 0.5–0.6 (principal stage) to 0.9–1.6 (final stage). The final stage corresponded with HSO_3^- ion oxidation and was characterized by the slowest oxidation rate. Because of the presence of SO_3^{2-} it seemed advisable to adopt the average order of reaction at the final stage as being approximately 1 for the entire range of the temperatures investigated. Accepting this assumption, we arrive at the relation between reaction rate constant and concentration:

$$k = \frac{2.303 \cdot A \cdot R}{t} \log \frac{c_{0s}}{c_s}. \tag{3}$$

By virtue of (3) we determined and plotted the $\log c_s = f(t)$ relation (figure 3), which appeared to be a straight line for all the cases considered here, and justified the reaction order adopted.

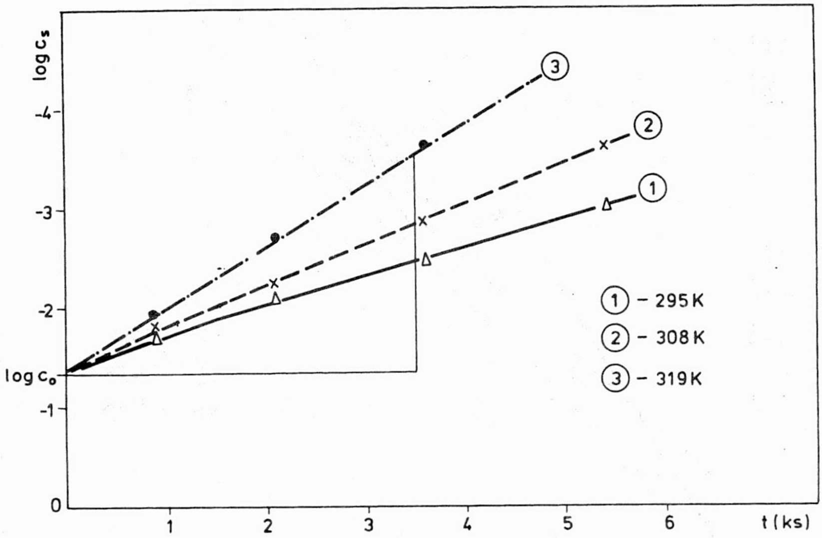

Fig. 3. Dependence $k = 2.303/t \cdot \log(c_{0s}/c_s)$ for different temperatures

Making use of the plots, the rate constant for particular temperatures and the Arrhenius diagram were determined (figure 4). Activation energy was calculated in terms of the Arrhenius equation

$$\log k = B - \frac{A}{T} \tag{4}$$

and took the form of

$$E = 2.303 \cdot A \cdot R \tag{5}$$

where A, B denoted numerical coefficients (characteristic of the reaction in question), and R was gas constant.

From the relation of (4) it follows that the rate constants and, consequently, the reaction rate increase with temperature. And this increase shows high values with the increasing activation energy. Table includes calculated and graphically deter-

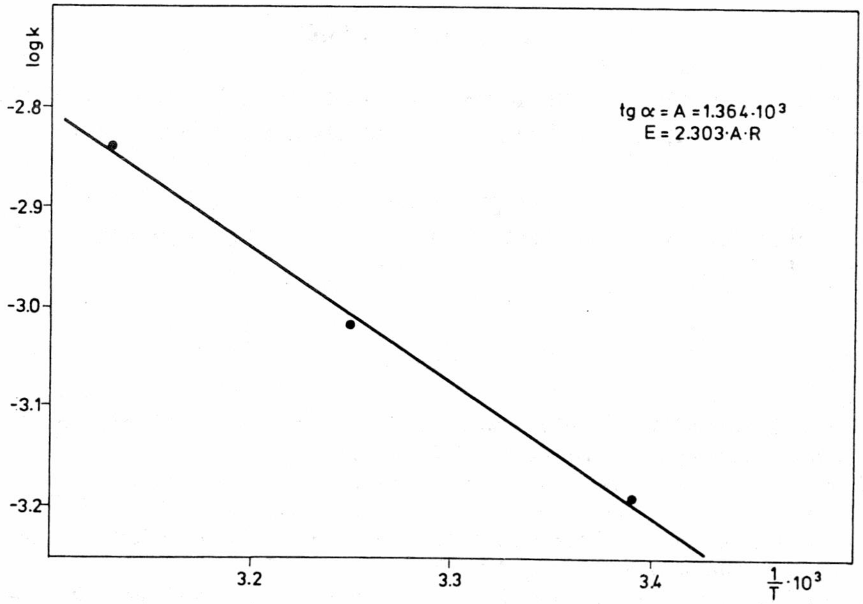

Fig. 4. Dependence $\log k = B - A/T$ (Arrhenius diagram)

mined data for the temperatures investigated. Thus the Arrhenius equation representing the reaction occurring under the conditions considered here will take form

$$\log k = 1.43 - \frac{1364}{T}. \tag{6}$$

Table

Data for the determination of activation energy

T K	$k \cdot 10^4$ s^{-1}	$\log k$	$A \cdot 10^{-3}$	B	E kJ/mol
295	6.44	–3.19			
308	9.65	–3.015	1.364	1.43	26.126
319	14.34	–2.84			

The plot of the relation between reaction rate and temperature depends on type of the reaction involved. According to POHORECKI [10], this relationship may be useful when determining the region in which the reactions proceed. In the case considered here, the region in question is likely to be intermediate between the kinetic and the diffusional ones, as indicated by the activation energy value. To sum up: the oxidation rate in the present study was influenced not only by the rate of the chemical reaction, but by the rate of oxygen diffusion as well.

4. CONCLUSIONS

1. In the temperature range investigated (295–319 K), oxidation efficiency and SO_2 loss due to physical and chemical desorption were found to be temperature-dependent.

2. The value of activation energy (calculated on the basis of experimental data) indicated that the oxidation reaction proceeded in a region intermediate between kinetic and diffusional.

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WPŁYW TEMPERATURY NA KINETYKĘ REAKCJI UTLENIANIA SIARCZYNÓW PODCZAS ODSIARCZANIA SPALIN

Zbadano wpływ temperatury na kinetykę reakcji utleniania siarczynów w roztworze w zakresie temperatur (295–319 K) typowym dla procesów odsiarczania spalin. Określono stałe kinetyczne (rzędowość i stałe szybkości) w założonych temperaturach. Wyznaczono diagram Arrheniusa i na jego podstawie energię aktywacji. Stwierdzono, że reakcja utleniania w badanych warunkach przebiega w obszarze pośrednim między kinetycznym a dyfuzyjnym.

ВЛИЯНИЕ ТЕМПЕРАТУРЫ НА КИНЕТИКУ РЕАКЦИИ ОКИСЛЕНИЯ СУЛЬФИТОВ ВО ВРЕМЯ ОБЕССЕРЕНИЯ ДЫМОВЫХ ГАЗОВ

Исследовано влияние температуры на кинетику реакции окисления сульфитов в растворе в пределах температур (295–319 K), типичных для процессов обессерения дымовых газов. Определены кинетические постоянные (порядок и постоянные скорости) в заданных температурах. Определили диаграмму Аргениуса и на ее основе – энергию активации. Установили, что реакция окисления в исследуемых условиях протекает в промежуточной области между кинетической и диффузионной.