Unusual Behavior of a Pollution Abatement System: SO_2 Capture by Red Ochre

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Red ochre is a naturally occurring ore containing iron along with inerts like oxides of Si, Al, and Ti. The ore can be calcined easily to change the goethite type structure (FeOOH) to the Fe_2O_3 form by removal of water, and subsequent oxidation. Experiments were carried out using cylindrical pellets prepared from crushed powders of the ore, to see whether this ore can be used for SO_2 removal. Preliminary runs on SO_2 capture with these pellets indicated two unusual patterns of behavior: the reaction at 560°C was lower than at 428°C, and conversion-time data showed S-shaped behavior after a certain conversion. These features suggest that the behavior of red ochre upon calcination is quite complex, making the study of this system interesting from a mechanistic point of view.

The experimental observations stated above are somewhat peculiar for this kind of system, involving an increase in molar volume of the product ($Z_v = 4.14$). The theoretical maximum sulfation before pore plugging for pure Fe_2O_3 pellet (0.44 porosity), as reported earlier (Ramachandran and Smith, 1977), is 32%. The presence of inerts improves the conversion of calcined red ochre to a value of 60% in 120 min at 470°C (Prasannan et al., 1985). It is the aim of the present investigation to probe into the details of SO_2 capture by iron oxide in red ochre, and to propose a reaction mechanism.

Experimental

The red ochre stones were crushed and sieved through a 200 mesh sieve for use in the experiments. The chemical composition of the red ochre sample used, is given in Table 1. All the experimental runs were carried out using a thermo-gravimetric analyser, described earlier (Dhupe et al., 1987). The experimental program involved:

i. Study of the reaction kinetics by reacting flat plates of the material at different temperatures

ii. Measurement of the Fe/S profiles in partially reacted infinite cylinders using electron probe micro analysis (EPMA)

iii. Determination of the two different oxygen states present

Kinetic runs

Flat plates of 19 mm dia., 5.7 mm thickness, and 0.44 porosity, were prepared from fine (−200 mesh) red ochre powder. The pellet was kept at 650°C for 15 min in the reactor, where an air flow of 21 mL/s was maintained, to attain steady weight. The furnace was subsequently cooled to the reaction temperature and the pellet was allowed to remain at the reaction temperature for five minutes before SO_2 was introduced into the reactor at 7.2 mL/s. These flow rates of air and SO_2 were found to be sufficient to overcome any external mass-transfer limitations. The conversion-time data were obtained at three temperatures (400, 440, and 470°C) by monitoring the weight increase during reaction (up to 180 min).

Fe/S ratio by EPMA analysis

A cylinder of 5 mm dia. and $L/D = 4$, was placed vertically in a perforated quartz basket and the reaction carried out at 470°C, according to the above procedure. Several pellets (of 0.44 porosity), reacted for different time intervals, were collected (the reaction in each case being quenched after the desired time interval by cutting off SO_2 supply and by fast cooling of the partially reacted pellet) and stored for EPMA studies. Each of the pellets was then sliced into a disc of 2 mm thickness,

Table 1. Chemical Composition of Calcined Red Ochre

Component	Wt., %
Fe_2O_3	14.35
SiO_2	49.64
Al_2O_3	22.12
TiO_2	4.41
Na_2O	0.17

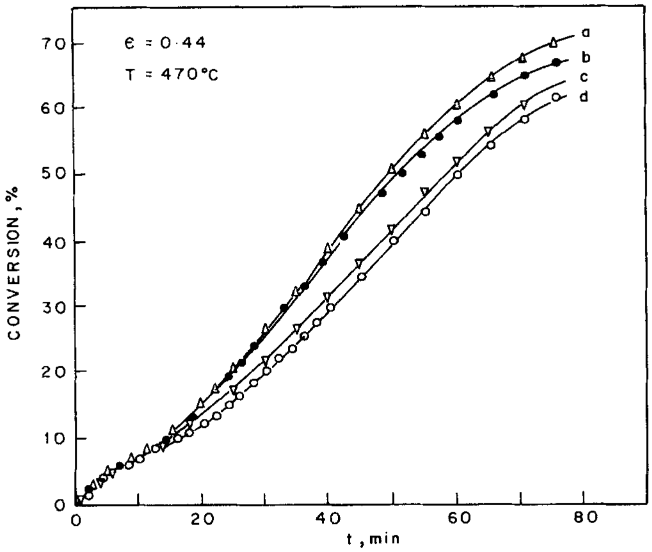

Figure 1. Right circular cylindrical pellets of red ochre, first calcinated, then:
a (△) = 10 min. reaction, 3 hr air flow at 400°C, 1 hr reaction; b (●) = 1 hr reaction; c (▽) = 3 hr N_2 flow at 400°C, 1 hr reaction; d (○) = 10 min reaction, 3 hr N_2 flow at 400°C, 1 hr reaction

and the surface to be analyzed was smoothed by gentle rubbing. The concentrations of Fe and S were then determined across the pellet diameter from one end to the other, using EPMA.

Determination of the oxygen states

A right circular cylinder of 0.44 porosity and 12 mm dia. was used at a temperature of 470°C and the following experiments were carried out to determine the state of oxygen during reaction.

a. Here the reaction with SO_2 was stopped after 10 min. The pellet was kept in air flow for three hours at 400°C and then again reacted for one hour at 470°C.

b. The run was carried out according to normal procedure as described under i of experimental.

c. The pellet, ready for reaction, was first kept in N_2 flow for three hours at 400°C, and was then reacted at 470°C for one hour.

d. In this case the procedure was the same as in a, but the pellet was in N_2 flow rather than air, for three hours.

Results and Discussion

Determination of the oxygen states

Figure 1 shows the conversion-time data for all the four sets of runs carried out for the determination of oxygen states in calcined red ochre. It was assumed that the thermally decomposed red ochre contains two kinds of adsorbed oxygen: irreversibly

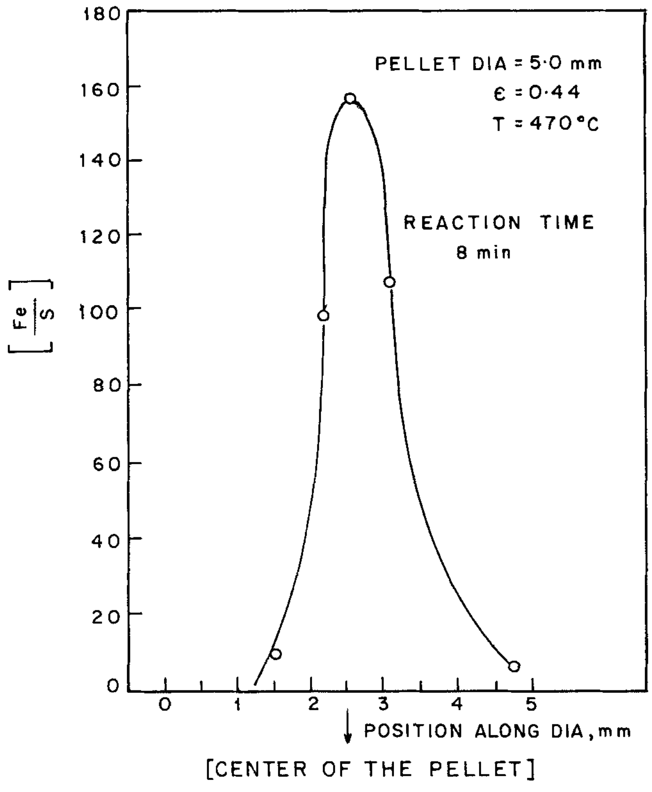

Figure 2. [Fe/S] ratio: EPMA analysis of red ochre reacted at 8 min.
Across dia. of an infinite cylindrical pellet.

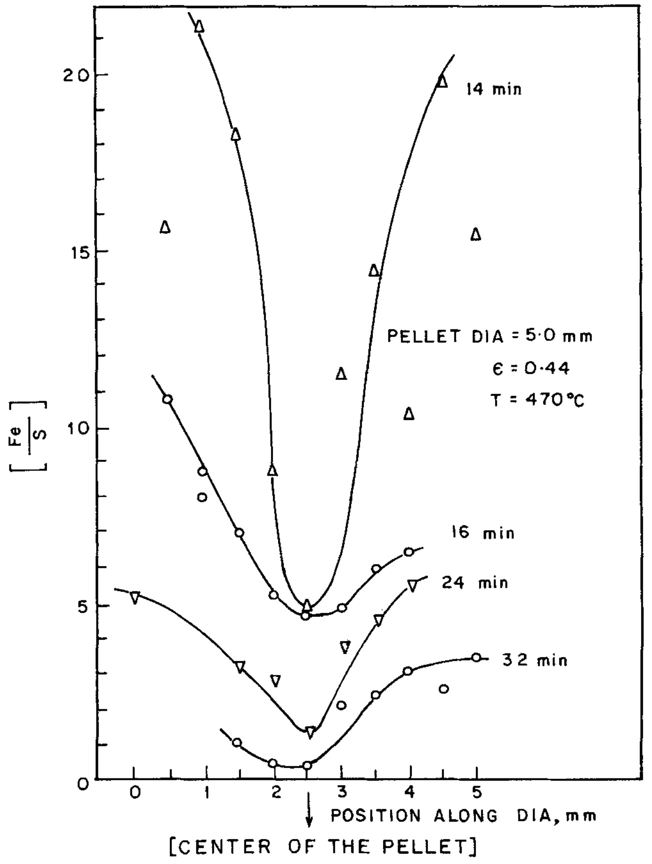

Figure 3. [Fe/S] ratio: EPMA analysis of red ochre reacted at various time intervals.
Across dia. of an infinite cylindrical pellet.

adsorbed oxygen in the form of O^- ions, and reversibly adsorbed oxygen in the form of O_2 (molecular oxygen). This reversibly adsorbed oxygen is known to undergo transformations according to

$$O_{2(ads)} \rightarrow O_{2(ads)}^{-} \rightarrow O_{(ads)}^{-} \rightarrow O_{(latt)}^{2-} \qquad (1)$$

and each transformation requires a finite time period. While ionosorbed oxygen $O_{(ads)}^-$ is highly active, molecularly adsorbed oxygen or $O_{2(ads)}$ is comparatively less active. Hence, if a mixture of SO_2 and air is passed through a red ochre pellet, SO_2 is oxidized first by the ionosorbed $O_{(ads)}^-$ to become SO_3. The reversibly adsorbed O_2 can be knocked off by passing N_2 in the pellet before reaction, but ionosorbed oxygen cannot be removed. The highest rate of sulfur capture occurring, in experiment a, followed by a decreasing order of capture in cases b, c and d, indicated that red ochre calcined in oxygen atmosphere contains adsorbed oxygen in two forms:

- Irreversibly adsorbed oxygen in $O_{(ads)}^-$ form, i.e., ionosorbed oxygen, which is very active
- Reversibly adsorbed oxygen $O_{2(ads)}$, i.e., in molecular form. (These finding are in accordance with observations on some other metal oxides: Lalauze and Le Thiesse, 1985; Bielanski and Haber, 1979).

EPMA analysis

Data on the Fe/S profile in the pellet after 8 min of reaction are shown in Figure 2, and for 14 to 32 min, in Figure 3. At 8 min reaction time, the profile shows that the concentration of sulfur decreases from surface to center. The sulfur profiles for higher times, however, show an increase in sulfur concentration from surface to center, see Figure 3. The trend in Figure 3 is completely opposite to that in Figure 2, and clearly shows expanding core behavior. Such an unusual behavior, i.e., expanding core model, has been reported earlier (Gokhale et al., 1975; Revankar et al., 1987) and theoretical explanation has also been attempted (Kulkarni and Doraiswamy, 1980; Erk and Dudukovic, 1983). The concentration profile becomes uniform throughout the pellet at higher values of conversion.

The sulfur profiles just mentioned, throw additional light on the special nature of SO_2 capture by red ochre. Initially, as soon as the calcined red ochre is exposed to SO_2, the reaction involved is the normal sulfation of Fe_2O_3 with SO_2, since the system lacks SO_3 in the beginning. This being a very slow process, SO_2 capture rate is also small and the sulfur concentration shows a decreasing trend from surface to center, Figure 2. This normal reaction is supposed to proceed throughout the pellet all the time, though at a very insignificant rate. Parallel to this reaction, SO_2 gets adsorbed on ionosorbed $O_{(ads)}^-$, which is present in

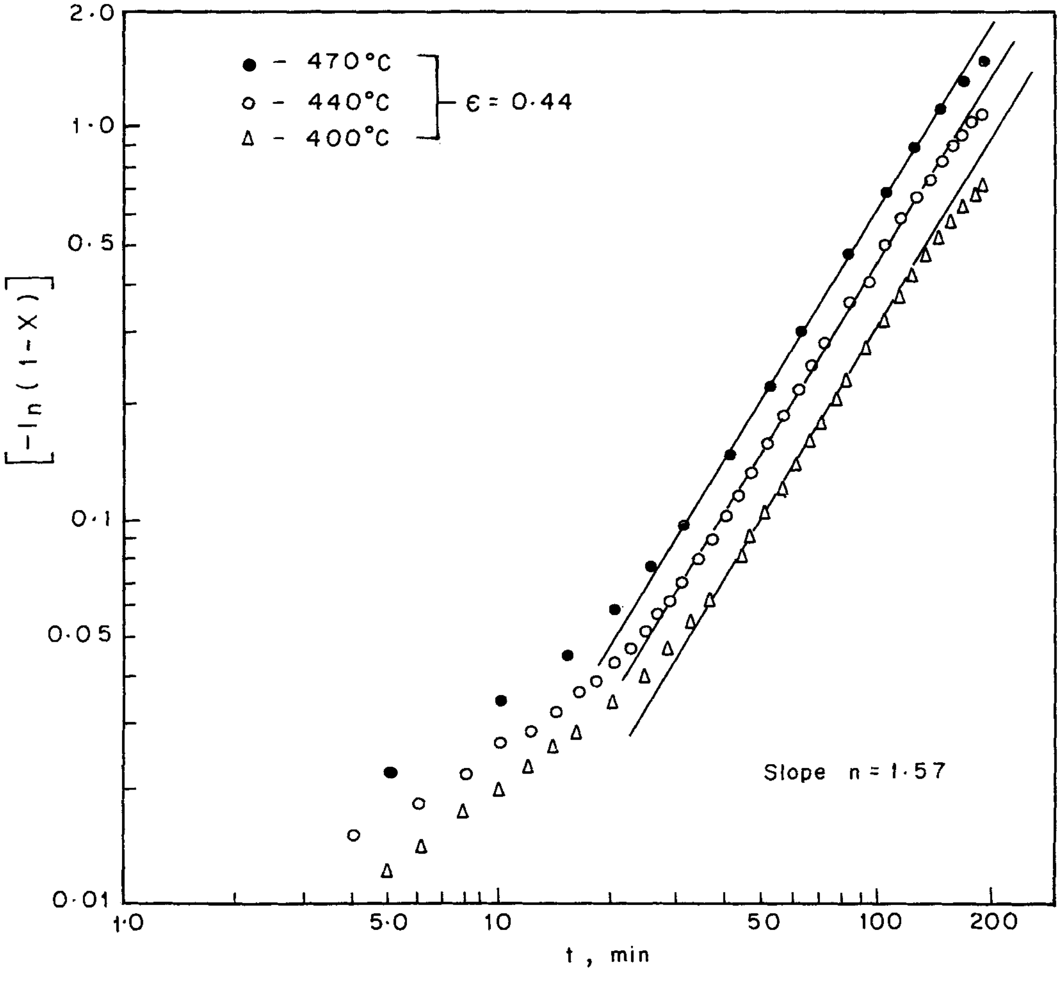

Figure 4. Avrami-Erofee'v model plots for sulfation of red ochre flat plates.

limited quantity on Fe_2O_3, and gets oxidized to SO_3 according to the reaction

$$O_{(ads)}^- + SO_2 \rightarrow SO_3 + e^- \qquad (2)$$

The SO_2 diffusing inside the pellet gets progressively transformed to SO_3 through this reaction, and hence we have the highest concentration with respect to SO_3 at the center, resulting in higher conversion of Fe_2O_3 at the center. This explains why, after some time, the sulfur profiles show a reversal in trend (increasing from pellet surface to center), as shown in Figure 3. Note that the sulfur concentration is now significantly higher, demonstrating the role of SO_3 in this particular case. This expanding core behavior, observed for the first time in the Fe_2O_3-SO_2-O_2 system, lasts for only a short duration, and at higher conversions the profile becomes uniform.

As is known, most of the SO_2 is adsorbed in molecular form on lattice oxygen in Fe_2O_3 (Kim and Chol, 1981), undergoing the following reaction, a slow process:

$$SO_{2(g)} + O_{(latt)}^{2-} \rightarrow SO_{3(ads)}^- + e^- \qquad (3)$$

A time will be reached when, by the two slow processes described above, Eqs. 1 and 3, there will be a gradual buildup of both $O_{(ads)}^-$ and $SO_{3(ads)}^-$, resulting in the formation of SO_3 in large quantity, through the following reactions:

$$O_{(ads)}^- + SO_2 \rightarrow SO_3 + e^- \qquad (2)$$

$$O_{(ads)}^- + SO_{3(ads)}^- \rightarrow SO_3 + O_{(latt)}^{2-} \qquad (4)$$

This large buildup of SO_3 throughout the pellet results in an accelerated sulfation rate of Fe_2O_3, leading to a sigmoidal conversion-time curve. It is to be noted that the bulk of SO_2 capture by Fe_2O_3 in red ochre is probably due mainly to SO_3 formed by the two mechanisms described above.

Kinetic runs

Kinetic runs with flat plates also showed sigmoidal behavior. Hence, the Avrami-Erofee'v model, given by

$$-\ln(1-x) = kt^n \qquad (5)$$

was tried (Figure 4), and found to fit the conversion-time data after an initial short period of 20–30 minutes. The slope was found to be of the order of 1.5, indicating that nucleation is rapid and the growth of nuclei is three-dimensional (diffusion controlled) (Kalandaze, 1985; Hulbert, 1969). The activation energy of 6.1 kJ/mol confirms diffusion control.

Notation

D = diameter of pellet
k = kinetic parameter
L = length of pellet
n = Avrami coefficient
t = time, s
x = fractional conversion
$Z_V = \dfrac{\text{molar volume of product solid}}{\text{molar volume of reactant solid}}$

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