

Sulfate reduction with carbon is strongly influenced by bed surface temperature

ABSTRACT

Sulfate reduction with carbon was followed through the evolution of carbon dioxide and carbon monoxide from a sodium carbonate melt. Sulfate reduction was found to be an autocatalytic reaction, to vary from zero to first order in sulfate, and to be proportional to the square root of the carbon surface area. These results are explained through the existence of a carbon dioxide-carbon monoxide cycle. Sulfate reduction, an endothermic reaction, was found to have a high activation energy. This combination of a high reactant energy and endothermic reaction means that reduction is heat-transfer limited and the most important variable influencing reduction is bed temperature.

KEYWORDS

Sulfates
Reduction
Carbon
Carbon dioxide
Carbon monoxide
Chemical reactions

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One of the key reactions in kraft chemical recovery is the reduction of sodium sulfate to sodium sulfide. Although this reaction is industrially important, little information is available concerning its mechanism or controlling parameters. In a kraft recovery furnace, reduction occurs in a melt consisting principally of sodium carbonate, sodium sulfate, sodium sulfide, and carbon at temperatures in excess of 1400° F (760°C). Here molten sulfate reacts with carbon to form sulfide, carbon monoxide, and carbon dioxide. The lack of information about this reaction results from the difficulty of studying a reaction involving three phases (solid, liquid, and gas), the high temperature required for the reactions, and the corrosive nature of the reaction system.

The basic objectives of this work were to obtain fundamental kinetic data on sulfate reduction with carbon, to define the rate-controlling process in reduction, and to develop insights as to how macroscopic process variables can be controlled to improve reduction in a kraft recovery furnace.

Results

Carbon surface area effect

Since carbon is the reducing agent, the reduction rate should be highly dependent on the amount of carbon surface area available and the type of carbon used. The effect of carbon surface area on reduction rate is shown in Fig. 1. Carbon rods were used as the carbon source, and the carbon surface area was

calculated assuming that the shrinkage of the carbon rods during reaction was uniform. Each reduction experiment shown in Fig. 1 initially had 1.0 mole of sulfate present, and the reaction rate was measured with 0.2 mole of sulfate converted to sulfide. This ensured that the reaction rates shown in Fig. 1 were measured with the same amount of sulfate and sulfide present.

Since Fig. 1 is a plot of log (reaction rate) vs. log (carbon surface area), the slope of this curve gives the reaction order with respect to carbon surface area. A least-squares fit of this curve yields a slope of 0.50 ± 0.06 . Therefore, the sulfate reduction is proportional to the square root of the carbon surface area.

Sulfate effect

Figure 2 illustrates the effect of sulfate on the rate of sulfate reduction. The reaction rates shown in Fig. 2 were determined with 0.1 mole of sulfate converted to sulfide. This ensured that each rate was determined with the same level of sulfide and carbon surface area present. As seen in Fig. 2, sulfate reduction with carbon varies from first order in sulfate at low sulfate concentrations to zero order in sulfate at high sulfate concentrations.

Sulfide effect

With hydrogen as the reducing agent, Birk *et al.*¹ reported that the autocata-

¹Birk, J.R., Larsen, C.M., Vaux, W.G., and Oldenkamp, R.D., *Ind. & Eng. Chem.* 10(1):7 (1971).

lytic nature of sulfate reduction resulted from the increase in sulfide as the reaction proceeded. To determine if sulfide could account for the autocatalytic nature of sulfate reduction with carbon, several reduction experiments were conducted with initial amounts of sulfide added. Two of these experiments with initial levels of sulfide are Runs 87 and 90 in Fig. 2.

Sulfate reduction with initial sulfide present indicates that sulfide has no effect on the sulfate reduction rate. Although Runs 87 and 90 have initial amounts of sulfide present, their reduction rates fall on the same curve in Fig. 2 as the runs with no initial sulfide present.

Temperature and melt composition effects

To determine the effect of temperature, sulfate reduction was studied over a temperature range of 1500 to 1800° F (815 to 982°C). Due to freezing of the melt, 1650° F (899°C) was the lowest temperature at which sulfate reduction in a melt consisting primarily of Na_2CO_3 was studied. To study reduction below this temperature, Li_2CO_3 and K_2CO_3 were added to the Na_2CO_3 melt. In addition to producing lower melting point systems, the addition of Li_2CO_3 and K_2CO_3 enabled the effect of different melt compositions to be studied.

The melt compositions studied and the calculated activation energies for reduction in these melts are shown in Table I.

The activation energies were calcu-

LOG (SULFATE REDUCTION RATE, moles/min)

1. Effect

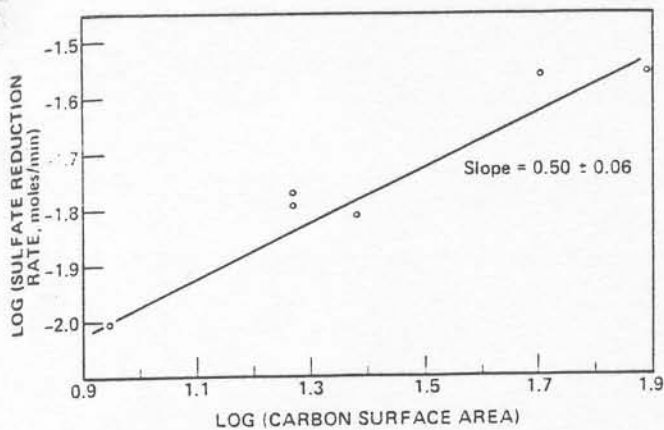
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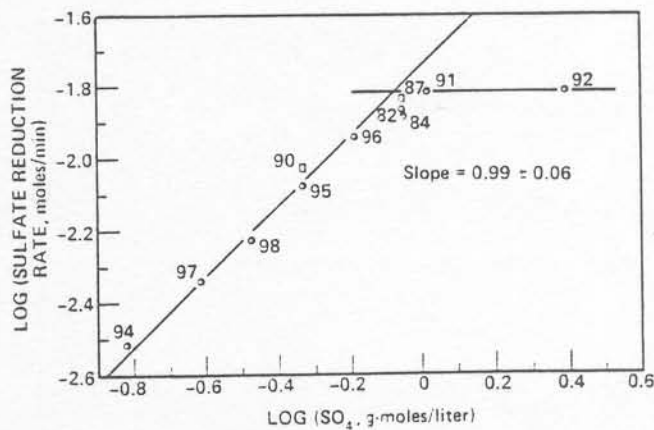
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1. Effect of carbon surface area on sulfate reduction with carbon.



2. Effect of sulfate on sulfate reduction with carbon.

I. Effect of composition on activation energy

Melt composition, g/mol					Activation energy, kcal
Na ₂ CO ₃	K ₂ CO ₃	Li ₂ CO ₃	Na ₂ SO ₄	Carbon	
25.0	0.0	0.0	1.0	4.0	49
15.0	10.0	0.0	1.0	4.0	53
3.61	7.48	13.92	1.0	4.0	71

lated assuming that the temperature dependency can be represented by Arrhenius' Law:

$$\text{Rate} = K_0 e^{-\Delta E/RT} f(\text{composition}) \quad (1)$$

where

- K_0 = frequency factor.
- ΔE = activation energy.
- R = ideal gas constant.
- T = absolute temperature.
- f = (composition) represents the composition dependent terms.

Proposed mechanism

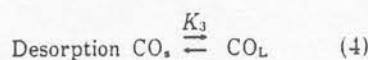
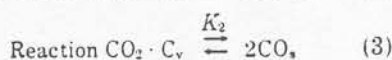
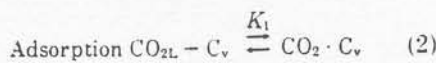
Based on the experimental results described in the previous section, the following mechanism is proposed for sodium sulfate reduction with carbon. The reduction reaction is initiated by the adsorption of carbon dioxide in the melt onto the surface of the carbon. The adsorbed carbon dioxide then reacts with the carbon to form two molecules of carbon monoxide. These carbon monoxide molecules then desorb from the carbon and react with sulfate in the melt to produce sulfide and additional carbon dioxide. The carbon dioxide and carbon monoxide are desorbed from the melt into the nitrogen purge stream. In this mechanism, the autocatalytic behavior is due to the increase in carbon dioxide and carbon monoxide during the reaction.

In all reduction experiments, a small level of carbon dioxide from the decomposition of Na₂CO₃ was detected before the addition of the carbon. Therefore, carbon dioxide was present in the melt to initialize the proposed sulfate

reduction mechanism.

Reaction of carbon dioxide with carbon

Sulfate reduction begins with the adsorption of carbon dioxide on a vacant reactive site on carbon. The adsorbed carbon dioxide molecule reacts with the carbon to form two adsorbed carbon monoxide molecules which desorb from the carbon into the melt. These steps are illustrated by Eqs. 2-4:



where

CO_{2L} = carbon dioxide dissolved in the melt

C_v = a vacant site on the carbon

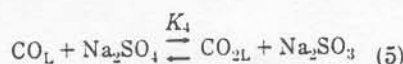
CO₂ · C_v = adsorbed carbon dioxide on the carbon

CO_s = adsorbed carbon monoxide on the carbon

CO_L = carbon monoxide dissolved in the melt

Sulfate reduction with carbon monoxide

Once the carbon monoxide desorbs from the carbon, it reacts with sulfate in the melt, forming sulfite and additional carbon dioxide:



In analyzing the experimental data in this study, this reaction was considered to be irreversible. The rate of sulfate reduction with carbon monoxide

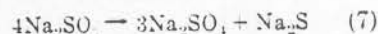
is given by:

$$\frac{d[\text{Na}_2\text{SO}_4]}{dt} = -K_4 [\text{CO}_L] [\text{Na}_2\text{SO}_4] \quad (6)$$

Here sulfate reduction is first order in terms of both carbon monoxide and sulfate.

Decomposition of sulfite

Since sulfite is unstable above 150°C and no sulfite was found in any melt sample, it is assumed that little sulfite exists in the melt and the rate of sulfite decomposition is greater than that of sulfate reduction.



Equation 7 is not a mechanism but represents a summary of rapid sequential events in sulfite decomposition.

Desorption of carbon monoxide and carbon dioxide from the melt

As reduction proceeds, the concentration of carbon monoxide and carbon dioxide in the melt exceeds the concentration which would be in equilibrium with the purge stream or gas above the melt. The carbon dioxide and carbon monoxide in the melt are desorbed from the melt into the nitrogen purge stream.

Application to recovery furnace

The kinetic equations can be simplified to apply to the conditions inside the recovery furnace by assuming carbon is present in excess, reduction approaches completion (sulfate concentrations are small), and the induction period is negligible.

Under these conditions, the kinetic equation for the reduction of sulfate by carbon can be simplified to:

$$\frac{-d[\text{Na}_2\text{SO}_4]}{dt} = K_1 e^{-\Delta E/RT} [\text{Na}_2\text{SO}_4] \quad (8)$$

where

[Na₂SO₄] = sulfate concentration, mole/mole of melt

k₁ = constant

- ΔE = activation energy
- R = gas constant
- T = absolute temperature

It can be shown that, under many conditions, the thermal effects completely dominate the kinetics. Under these conditions, the two parameters that control the reaction kinetics are the activation energy, ΔE , and the heat of reaction, ΔH_R . (The latter is dependent on the CO_2/CO ratio in the product gas.)

Activation energy

For all practical purposes the activation energy can be taken to be 50 kcal/mole, which gives the reaction rate doubling for about a 70°F (21°C) rise (at 1700°F, or 927°C). The rate would drop by about an order of magnitude for a 200°F (93°C) drop from 1700°F to 1500°F (927°C to 815°C).

Heat transfer effects

In an adiabatic system, the heat balance becomes:

$$\Delta H_R \frac{d}{dt} [\text{Na}_2\text{SO}_4] = M C_p \frac{dT}{dt} \quad (9)$$

where M is the mass of the reaction system, and C_p is the system's specific heat.

The contribution of the activation energy term to the declining rate for two initial temperatures is shown in Table II, for $\Delta E = 50,000$ cal/mole.

The temperature drops in the tabulation may be compared with estimates of the adiabatic temperature drop for complete reduction ($T_o - T_F$). These can vary from 300°F (149°C) to over 1500°F (815°C), depending on the sulfate load and the heat of reduction. The importance of accurate knowledge of the heat of reduction under the conditions that prevail in the furnace is clearly evident. The uncertainty that exists with regard to the heat of reduction makes it impossible to accurately interpret temperature-drop data.

It is seen that the activation energy term will tend to dominate thermal effects. It is also evident that it is advantageous to start at a higher initial temperature. Not only will the initial rate be higher, but the rate will drop less sharply for the same temperature change. The preceding results are for the adiabatic case and show that the temperature drop associated with the endothermic heat of reduction will cause the reaction rate to decline by as much as two orders of magnitude. Unless the initial temperature is high enough that the reduction rate is extremely rapid, the declining reduction rate will essentially become self-limiting in any reasonable time. However, if heat can be transferred into the reaction mass at reasonable rates, the reaction endotherm can be supplied without a great (or any) temperature

drop, and the reaction will proceed at reasonable rates.

Thus, reduction can occur in a recovery furnace in two distinct ways:

1. The initial temperature of the smelt-char reacting mass is high enough so that reduction can proceed rapidly toward completion even though the temperature drops significantly as the reaction proceeds.

2. The temperatures at which the reaction occurs are moderate, and reduction will approach completion only if external heat is supplied. In the limit, the rate of the reduction reaction will be completely controlled by the rate of heat transfer.

Conclusions

1. Sulfate reduction with carbon occurs through a carbon dioxide-carbon monoxide cycle. The cycle is initiated by the adsorption of carbon dioxide on the surface of carbon. This adsorbed carbon dioxide reacts with the carbon to form two molecules of adsorbed carbon monoxide. The carbon monoxide desorbs from the carbon and reacts with sulfate in the melt to form sulfite and carbon dioxide. This sulfite undergoes a fast decomposition reaction to form sulfide and sulfate. The autocatalytic nature of sulfate reduction with carbon results from the increase in carbon dioxide and carbon monoxide in the melt.

2. The reduction of sulfate in the char bed of a recovery furnace is governed by thermal effects. The combination of an endothermic reaction and strongly temperature-sensitive kinetics (high activation energy) causes the reaction to become self-limiting unless heat is added. The extent of reaction is determined by the initial amount of sensible heat available in the reacting mass and the rate of heat transfer into the material.

3. The most important single parameter influencing reduction in the kraft furnace is the bed surface temperature. This sets the initial rate of reaction, determines the amount of sensible heat available for the endothermic reaction to draw on, and influences the apparent thermal conductivity of the bed. High bed surface temperatures are favorable for reduction.

Analysis of data

More complete analyses of the carbon dioxide-carbon reaction and effect of heat transfer on sulfate reduction are presented in this section.

Reaction of carbon dioxide and carbon

To obtain a reduction rate dependent on the square root of the carbon surface area, desorption of carbon monoxide from the surface of carbon was chosen

as the rate-limiting step. Considering carbon monoxide desorption to be an irreversible reaction, the carbon monoxide desorption rate is given by

$$\text{Rate of carbon monoxide desorption} = \frac{K_3 [\text{CO}_s]}{K_3 [\text{CO}_s]} \quad (10)$$

For Eq. 10 to be meaningful, the concentration of adsorbed carbon monoxide $[\text{CO}_s]$ must be written in terms of measurable quantities such as carbon dioxide in the melt $[\text{CO}_{2L}]$ and total active sites on the carbon surface $[\text{CT}]$.

The total number of active sites on the carbon surface is equal to the sum of the vacant sites and the sites containing adsorbed molecules:

$$\text{CT} = C_v + \text{CO}_2 \cdot C_v + \text{CO}_s \quad (11)$$

Substituting for C_v and $\text{CO}_2 \cdot C_v$ from Eqs. 2 and 3, Eq. 11 becomes:

$$\text{CT} = \frac{[\text{CO}_s]^2}{K_2} + \frac{[\text{CO}_s]^2}{K_1 K_2 [\text{CO}_{2L}]} + [\text{CO}_s] \quad (12)$$

Solving Eq. 12 for adsorbed carbon monoxide yields:

$$[\text{CO}_s] = \left[-1 + \left(1 - 4\text{CT} \frac{K_1 [\text{CO}_{2L}] + 1}{K_1 K_2 [\text{CO}_{2L}]} \right)^{1/2} \right] \times \frac{K_1 K_2 [\text{CO}_{2L}]}{2(K_1 [\text{CO}_{2L}] + 1)} \quad (13)$$

Equation 13 predicts that the concentration of adsorbed carbon monoxide will initially increase as the concentration of carbon dioxide in the melt increases. However, at high carbon dioxide concentrations the adsorbed carbon monoxide becomes independent of the carbon dioxide concentrations in the melt.

Heat of reaction

The heat of reduction for sulfate can be expressed in terms of percent CO in the product gas as follows:

$$\Delta H \left[\frac{\text{Btu}}{\text{lb Na}_2\text{SO}_4} \right] = 1550 - 2050 \frac{(100 - \% \text{CO})}{(200 - \% \text{CO})} \quad (14)$$

There is little information available on the proportions of CO and CO_2 in the char bed of a recovery furnace. In one very limited experiment, about equal amounts of CO and CO_2 were found. This would give a heat of reaction of 867 Btu/lb Na_2SO_4 .

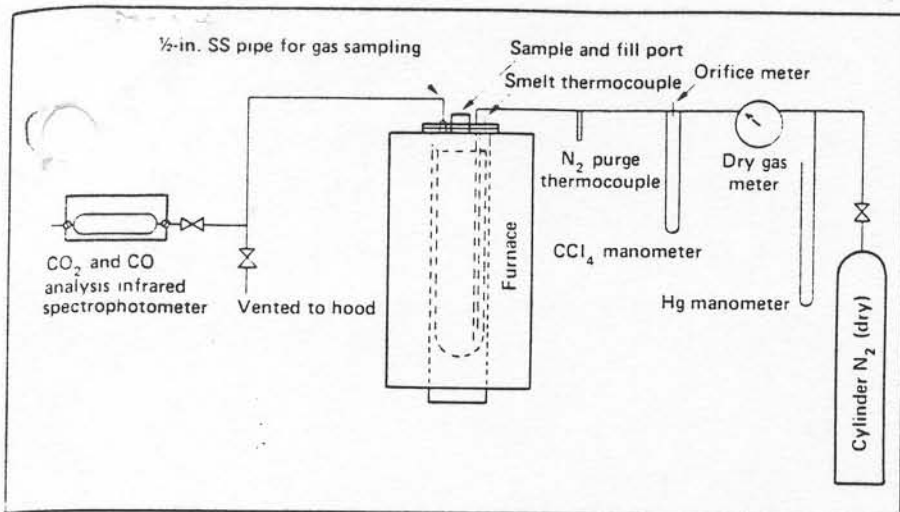
Heat transfer effects

There is a one-to-one correspondence between the temperature and the sulfate concentration. Thus, the kinetic expression Eq. 9 can be written as

$$\frac{dT}{dt} = -k_1 (T - T_F) e^{-\Delta E/RT} \quad (15)$$

where T_F is defined by

$$(T_o - T_F) = \frac{\Delta H_R [\text{Na}_2\text{SO}_4]_o}{M C_p} \quad (16)$$



3. Experimental system.

and T_0 is the initial temperature.

It is of interest to look at how the rate at time t compares with the initial rate.

$$\frac{(dT/dt)}{(dT/dt)_0} = \frac{(T-T_F)}{(T_0-T_F)} e^{-\Delta E(T_0-T)/RT_0T} \quad (17)$$

Through this analysis, the relative reduction rates in Table II were obtained.

Experimental system

The experimental system employed to study sulfate reduction with carbon is illustrated in Fig. 3. The reaction vessel consisted of an alumina crucible con-

tained in an electric furnace. The reduction reaction was followed by measuring the evolution of carbon monoxide and carbon dioxide, which were removed from the reactor with a nitrogen purge stream. Knowing the nitrogen purge rate to the reactor and the percentages of carbon monoxide and carbon dioxide in the purge stream from the reactor allowed the rate of sulfate reduction to be determined.

The nitrogen purge stream plus any carbon dioxide and carbon monoxide generated by the reaction were conveyed from the reactor in a 1/2-in. (1.3-

II. Effect of temperature on reduction rate^a

$(T_0 - T), ^\circ F$	Relative rate	
	$T_0 = 1800^\circ F$	$T_0 = 2000^\circ F$
0	1.00	1.00
100	0.395	0.458
200	0.1426	0.196
300	0.0465	0.0774
400	0.0134	0.0279
500	0.0033	0.0091

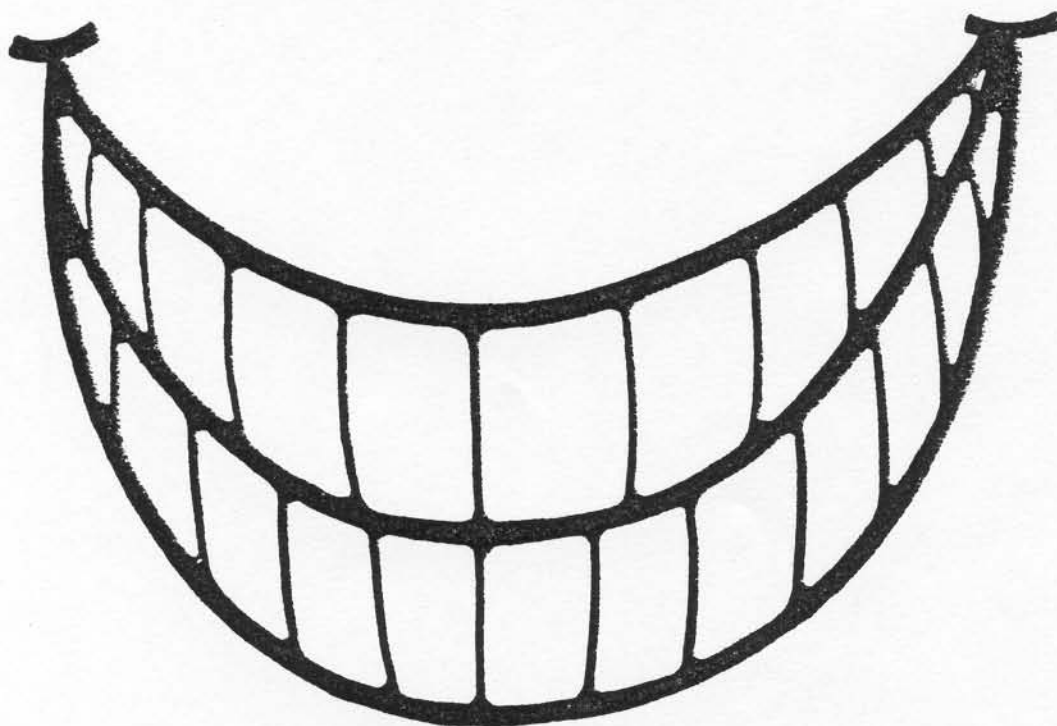
^a Conversion: $^\circ C = \frac{1}{2} (^\circ F - 32)$.

cm) steel tube. This gas stream then passed through a filter to remove any particles and to a carbon monoxide-carbon dioxide infrared gas analyzer. The infrared analyzer was capable of simultaneously measuring both carbon monoxide and carbon dioxide over a 0-30% range. Before each experimental run, the infrared analyzer was calibrated using a standard carbon dioxide, carbon monoxide, and nitrogen mixture. Checking the calibration after each run indicated that the infrared system was very stable during the reduction runs.

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