

# AN EMPIRICAL KINETIC MODEL AND SIMULATION FOR ANODIC OXIDATION OF COAL SLURRY

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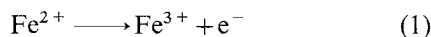
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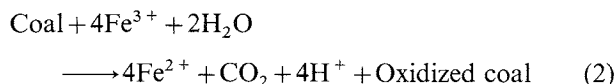
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**Key Words:** Electrolysis, Chemical Reaction, Coal Slurry, Anodic Oxidation, Iron Redox Couple, Anodic Depolarization, Oxidation Current

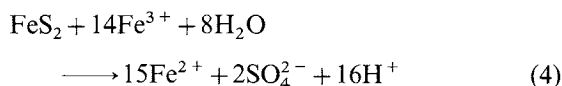
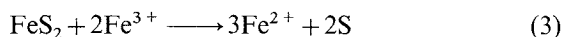
Recent studies on the electrolysis of coal slurries<sup>1-6,8-10)</sup> have revealed that dissolved iron ion in acidic media plays an important role in the anodic depolarization process. The reaction mechanism of coal slurry in the anodic chamber may be represented as shown in Fig. 1. The anodic current is predominantly controlled by the electrochemical oxidation of Fe(II) which is leached into the acid solution from the coal.<sup>2,9)</sup>



The Fe(III) ions formed at the anode oxidize the organic matrix of coal,<sup>1,3,4,10)</sup>



as well as pyrite naturally present in the coal,<sup>6)</sup>



and Fe(III) itself is reduced to Fe(II). Thus the iron redox couple, Fe(II)/Fe(III), acts as an electron shuttle between the anode and coal particles, and the anodic current is maintained to some extent for a much longer period. Therefore, it is expected that an addition of ionic iron to the coal slurry leads to an increase in the current density<sup>1,5)</sup> as well as an increase in the desulfurization rate of coal.<sup>5-7)</sup>

In this study, the time-dependence of the rate of anodic oxidation was measured at various concentrations of Fe(III) ion and coal loadings. An attempt was also made to interpret the observed current density in terms of a postulated reaction model.

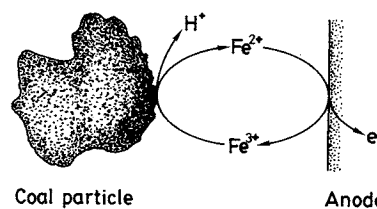


Fig. 1. Schematic reaction pathways for anodic oxidation of coal slurry.

## Experimental

Illinois No. 6 coal pulverized under 200  $\mu\text{m}$  was used in the experiments. The ultimate analysis of this coal sample is given in the previous paper.<sup>5)</sup>

The electrolysis cell consisted of two compartments joined by a cation exchange membrane with a circular geometric area of 15.9  $\text{cm}^2$ . The anode compartment containing 460  $\text{cm}^3$  of coal slurry was agitated by two-stage impellers with four flat paddles made of ruthenium-plated titanium. The impellers also worked as an anode of 38.7  $\text{cm}^2$  area. The cathode compartment containing 265  $\text{cm}^3$  of electrolyte (4  $\text{kmol} \cdot \text{m}^{-3}$  sulfuric acid) was stirred with a magnet bar. The cathode was a 3-cm  $\times$  6.5-cm platinum plate. The anolyte composition was 10–100  $\text{kg} \cdot \text{m}^{-3}$  coal particles and 0.1–1  $\text{kmol} \cdot \text{m}^{-3}$  ferric sulfate in a 4  $\text{kmol} \cdot \text{m}^{-3}$  sulfuric acid solution. The temperature was maintained at 40°C, and the speed of rotation of the anode impellers was 800 rpm.

During the first two hours of the experiment, the anolyte mixture was allowed to form Fe(II) by the reaction between Fe(III) added and coal under the non-electrolysis condition. After that, the anodic potential was applied at a constant 1.3 V vs. NHE, and the change in current density was monitored. The concentration of Fe(II) was determined by the 1,10-phenanthroline method.

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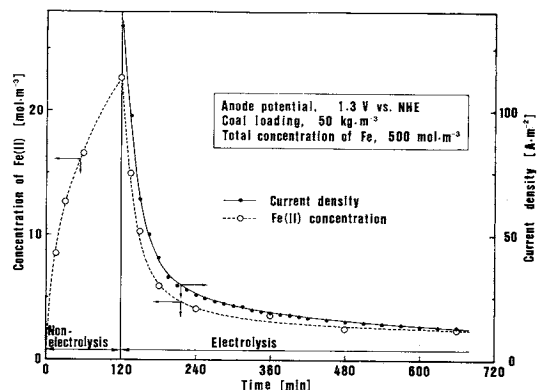


Fig. 2. Typical example of time-dependence of Fe(II) concentration and current density.

## Results and Discussion

Figure 2 shows typical patterns of the formation of Fe(II) during the first two hours and the time-dependent Fe(II) concentration and current density in the subsequent electrolysis. Immediately after electrolysis begins, the Fe(II) concentration decreases rapidly due to the anodic oxidation of Fe(II) to Fe(III), and the current density also falls in proportion with the Fe(II) concentration. As Fe(II) is continuously regenerated by reactions (2)–(4), however, the electrolysis current is maintained for a prolonged period. The slow decline in the current density in this period implies a gradual decrease in coal reactivity. The relation between current density and Fe(II) concentration during electrolysis is shown in Fig. 3. The linear relationship suggests that the anodic oxidation of Fe(II) is controlled by the mass transfer of Fe(II) ions to the electrode surface. Figures 4 and 5 show that current density increases with increasing concentration of Fe(III) added and coal loading.

Since coal is a highly heterogeneous organic solid material consisting of macro-molecules of different sizes with varying types and degrees of crosslinking, rigorous modeling of the oxidation of coal by Fe(III) ions seems to be quite difficult. Therefore, we attempted to derive an empirical rate expression for the anodic oxidation of coal slurry on the basis of the following assumptions:

- 1) Fe(II) ions are oxidized at the anode. The rate of oxidation is controlled by the limiting current density, and obeys first-order kinetics.
- 2) Fe(II) and Fe(III) ions are adsorbed competitively at reactive sites on the coal surface, and the reaction rate is proportional to the fraction of reactive sites occupied by Fe(III).
- 3) The oxidation of reactive sites follows the first-order rate law with respect to the unconverted fraction of sites.
- 4) There exists a distribution of the reactivities of

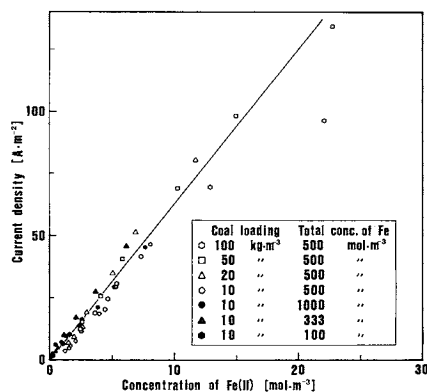


Fig. 3. Relationship between current density and Fe(II) concentration.

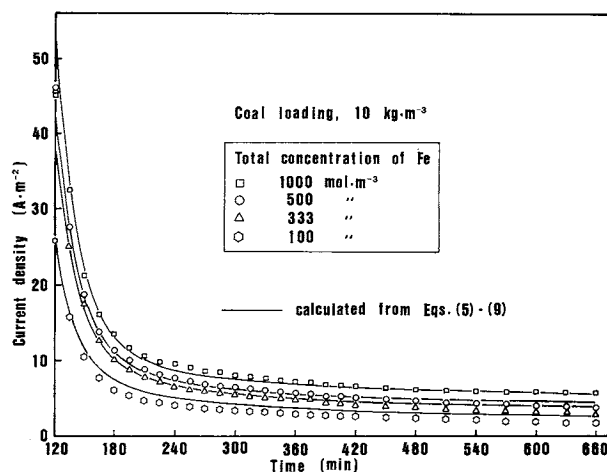


Fig. 4. Effect of concentration of Fe(III) ion initially added on current density.

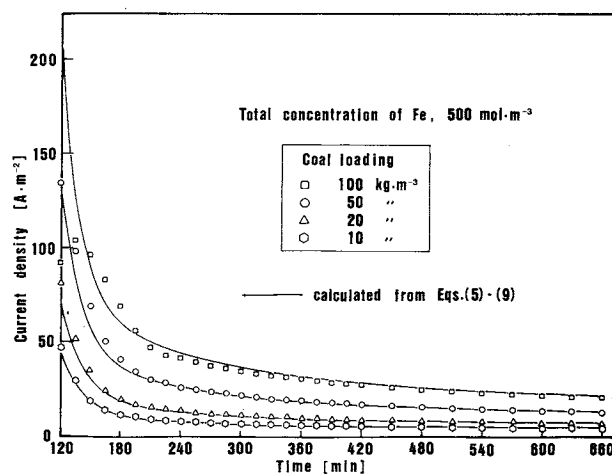


Fig. 5. Effect of coal slurry concentration on current density.

the sites. The different reactive sites disappear at different rates, preferentially from the more rapidly and readily oxidizable sites.

Based upon assumptions 2) and 3), the oxidation rate of the reactive sites of coal can be represented by the following equation.

$$\frac{dX}{dt} = k(1-X) \frac{C_{\text{Fe}^{3+}}}{C_{\text{Fe}^{3+}} + KC_{\text{Fe}^{2+}}} \quad (5)$$

Under assumption 4), the lumped rate constant,  $k$ , is presumed to decrease during the reaction in a biexponential form of

$$k = k_1 \exp(-\alpha X) + k_2 \exp(-\beta X) \quad (6)$$

Equation (5) can be related to the rate of Fe(II) formation under the non-electrolysis condition as

$$\frac{dC_{\text{Fe}^{2+}}}{dt} = bw \frac{dX}{dt} \quad \text{for } 0 \leq t < 120 \text{ min} \quad (7)$$

where  $b$  means the molar amount of Fe(III) reducible per unit mass of coal. When Fe(II) ions are oxidized at the anode under the assumption 1), Eq. (7) is modified to become

$$\frac{dC_{\text{Fe}^{2+}}}{dt} = bw \frac{dX}{dt} - k_e \left( \frac{A}{V} \right) C_{\text{Fe}^{2+}} \quad \text{for } t \geq 120 \text{ min} \quad (8)$$

The current density is then expressed by the following equation.

$$J = k_e F C_{\text{Fe}^{2+}} \quad (9)$$

Equations (5)–(8) can be solved numerically with the initial conditions,  $X=0$ ,  $C_{\text{Fe}^{2+}}=0$  and  $C_{\text{Fe}^{3+}}=C_{\text{Fe}^T}$  at  $t=0$ , by the Runge-Kutta-Gill method. Among the seven parameters included in these equations, the value of  $b$  was determined as  $6.0 \text{ mol} \cdot \text{kg}^{-1}$  from the ratio of the Fe(II) concentration to the coal slurry concentration in the reacting mixture, which was stirred for ten days. The mass transfer coefficient of Fe(II) to the anode surface,  $k_e$ , was also calculated to be  $6.48 \times 10^{-5} \text{ m} \cdot \text{s}^{-1}$  from the slope of the straight line shown in Fig. 3. Therefore, the remaining five parameters,  $k_1$ ,  $k_2$ ,  $\alpha$ ,  $\beta$  and  $K$ , were determined so as to fit the observed current density by the non-linear least squares method. The values obtained were  $k_1 = 3.89 \times 10^{-3} \text{ s}^{-1}$ ,  $k_2 = 1.27 \times 10^{-4} \text{ s}^{-1}$ ,  $\alpha = 18.2$ ,  $\beta = 0.054$ , and  $K = 5.80 \times 10^3$ . Figures 4 and 5 show that the calculated curves are in reasonable agreement with the experimental results. Other data were also simulated by the proposed model. The regeneration rate of Fe(II) is affected by the oxidations of both coal (Reaction (2)) and pyrite (Reactions (3) and (4)). An attempt to separate their contributions is now in progress.

## Acknowledgment

This work was supported by Grants-in-Aid for Scientific Research on Energy (Nos. 58040053 and 59040009) from the Ministry of Education, Science and Culture of Japan.

## Nomenclature

$A$	= anode surface area	$[\text{m}^2]$
$b$	= molar amount of Fe(III) ion reducible per unit mass of coal	$[\text{mol} \cdot \text{kg}^{-1}]$
$C_{\text{Fe}^{2+}}$	= concentration of Fe(II) ion	$[\text{mol} \cdot \text{m}^{-3}]$
$C_{\text{Fe}^{3+}}$	= concentration of Fe(III) ion	$[\text{mol} \cdot \text{m}^{-3}]$
$C_{\text{Fe}^T}$	= total concentration of iron ion, concentration of Fe(III) ion initially added	$[\text{mol} \cdot \text{m}^{-3}]$
$F$	= Faraday constant	$[\text{C} \cdot \text{mol}^{-1}]$
$J$	= current density	$[\text{A} \cdot \text{m}^{-2}]$
$K$	= dimensionless adsorption constant	$[-]$
$k$	= lumped rate constant	$[\text{s}^{-1}]$
$k_1$	= rate constant in Eq. (6)	$[\text{s}^{-1}]$
$k_2$	= rate constant in Eq. (6)	$[\text{s}^{-1}]$
$k_e$	= mass transfer coefficient of Fe(II) ion to anode surface	$[\text{m} \cdot \text{s}^{-1}]$
$t$	= time	$[\text{s}]$
$V$	= volume of coal slurry	$[\text{m}^3]$
$w$	= concentration of coal slurry	$[\text{kg} \cdot \text{m}^{-3}]$
$X$	= conversion of reactive sites in coal	$[-]$
$\alpha$	= constant in Eq. (6)	$[-]$
$\beta$	= constant in Eq. (6)	$[-]$

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