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Leaching of Sodium and Chlorine from Coals

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Abstract

The presence of sodium and chlorine in coals often causes fouling and corrosion of boiler tubes and downstream equipment in power plants. These elements are also suspected of augmenting materials problems in fluidized-bed combustors and coal-burning gas turbines. Battelle Columbus Laboratories has developed a process to remove the sodium and chlorine from coal. Experiments carried out with Illinois No. 6 coal suggest that substantial reductions in sodium and chlorine levels can be achieved by extracting the coal with water in the presence of calcium oxide under appropriate conditions. The degree of removal is a function of temperature, extraction time, and coal particle size, and is independent of the water-to-coal ratio. The effects of these process variables on removal are discussed. The data are also interpreted to postulate the mode of sodium and chlorine occurrence in coal.

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INTRODUCTION

Interest in minor elements in coal, especially chlorine and alkali metals, has increased considerably due to difficulties encountered in coal-fired steam boilers. Alkali-bonded deposits can be formed on boiler tube surfaces while combusting coals with high sodium and chlorine contents. These deposits eventually cause loss of boiler availability (*1*–*4*).

The chlorine content in Illinois No. 6 coal ranges from zero near the outcrop to values in excess of 0.6% in the deeper part of the Illinois Basin (*5*, *6*). In some core samples, the average alkali content is 0.4–0.5% and the average chlorine content about 0.5%. Serious slagging problems may be encountered when burning this coal. Clearly, the sodium and chlorine contents must be reduced prior to using the coal as boiler fuel. This prompted Battelle to conduct a detailed investigation into the methods for removing sodium and chlorine from coal, based on their mode of occurrence in the coal. This paper presents the results of experiments conducted with Illinois No. 6 coal. Before discussing the details of the Battelle study, it is appropriate to review briefly the work done in the past by other investigators.

REVIEW OF PAST WORK

Edgecomb determined that all chlorine present as soluble chlorides could be extracted with water, provided the coal was ground sufficiently fine. He conducted experiments to prove the presence of ion-exchangeable chlorine in coals (*7*). Ter Muelen also found that not all the chlorine in coal could be extracted with water alone, and suggested the existence of organic chlorine (*8*). On the other hand, Sexton and Davidson (*9*) and Crossley (*10*) concluded that all the chlorine was associated with the sodium and potassium present in coal. Daybell and Pringle found that the chlorine in coal was in excess of the stoichiometric free alkalies present and that the excess was ion-exchangeable (*11*). Daybell and Gillham first quantified the relationship between particle size and chlorine extractability (*12*). Bettelheim conducted water leaching studies with British coals. He postulated that the rate of leaching of chlorine from coal particles is controlled by a combination of dissolution and diffusion mechanisms, and that the relative importance of these two mechanisms could differ widely from coal to coal (*13*).

Paulson and Fowkes investigated the feasibility of removing sodium from North Dakota lignites by ion exchange with a variety of inorganic reagents. They observed that an ion with a higher valency removed sodium preferentially at equivalent concentrations (*14*). Neaval et al. performed laboratory experiments on the removal of sodium from Illinois coal by water extraction. They found that the extraction rate conformed to Fick's law of diffusion (*15*).

Battelle's involvement with sodium removal from coal stemmed from its original intent to remove sulfur from coals chemically using the Battelle hydrothermal coal process (*16, 17*). While achieving substantial reduction in sulfur, the process infused additional sodium which had to be removed from the coal. Calcium was found to have a dual beneficial effect in achieving this goal. While displacing significant amounts of chlorine and sodium, the excess calcium was found to retain the sulfur not removed by the hydrothermal process during combustion. These findings led to more detailed calcium oxide treatment studies at elevated temperatures and pressures for the removal of sodium and chlorine from coals and lignites. Over 70% of the sodium and chlorine could be extracted with calcium oxide under appropriate conditions (*18*).

APPARATUS

The apparatus used is shown in Fig. 1. It consists of an externally heated, stirred 1-gal batch autoclave with attachments for sample charging and withdrawal, temperature and pressure measurements, and overpressurizing and purging. Sample charging and withdrawal were done using high-pressure cylinders.

COAL SAMPLING AND ANALYSIS

Representative core samples of coal were obtained by drilling into the Illinois No. 6 seam at different locations. The samples were divided into various segments. Each segment was analyzed for total sodium and chlorine by the standard ASTM procedure. The distribution of sodium and chlorine was fairly uniform. The sodium content varied from 0.25% along the length of the core, the average being about 0.25%. The chlorine content varied from 0.47 to 0.63%, the average being about 0.52%. To obtain samples for bench-scale experiments, the core samples were broken into smaller pieces. A representative sample was taken by quartering and coning. This sample was then crushed and sized into different fractions. Representative samples of each size fraction were obtained by riffling. The samples were stored in a nitrogen atmosphere

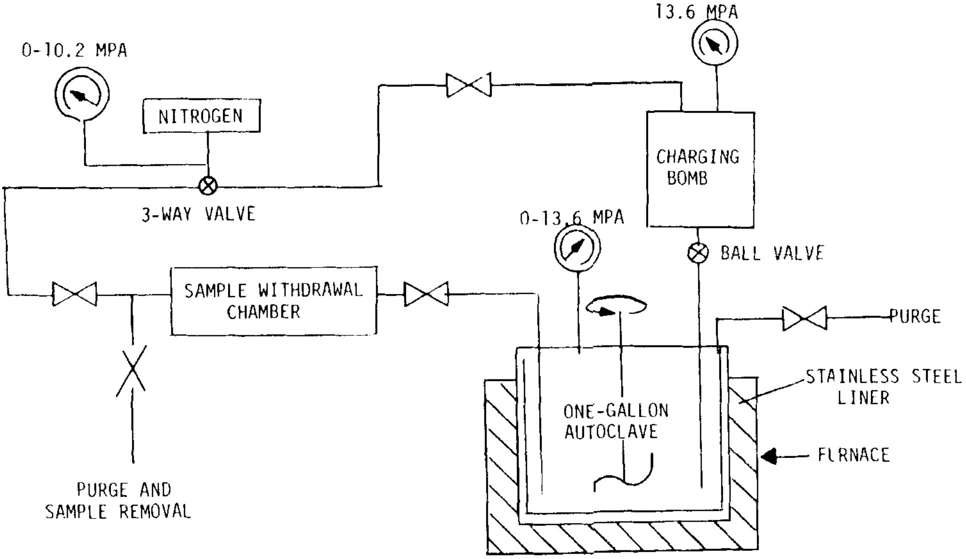

FIG. 1. Schematic diagram of the 1-gal autoclave system.

for later use. Table 1 shows the ultimate analysis of the raw coal. Table 2 shows the total sodium and chlorine in various size fractions of the raw coal.

Experimental Procedure

Experiments were conducted to evaluate the effect of the following process variables on sodium and chlorine removal:

Temperature
Time
Particle size
Water/coal ratio

Coal (100 g) of a given size fraction and 300 mL of chlorine-free distilled water were mixed well in a stirred tank to obtain a homogeneous slurry. In some experiments, 1% powdered CaO was also added. The slurry was then transferred to the autoclave (Fig. 1). The autoclave was heated to the desired temperature and pressure, and the extraction of coal

TABLE 1
Ultimate Analysis of Raw Coal

Component	Percent (dry coal basis)
Carbon	69.71
Hydrogen	4.70
Nitrogen	1.22
Chlorine	0.52
Sulfur	4.07
Ash	13.28
Oxygen	6.50

was carried out in the presence of nitrogen. After holding the slurry for a given time, it was cooled and filtered. The coal was washed with chlorine-free distilled water till all the chloride was extracted from the coal. The coal was further dried at 105°C and preserved for analysis.

The procedure was somewhat different for investigating the effect of time. In this case the autoclave was heated to a temperature slightly above the desired temperature and purged with nitrogen. The well-mixed slurry was then charged into the autoclave under nitrogen pressure. The cold slurry attained the desired temperature quickly (usually within 5–8 min of charging). Samples were then withdrawn at desired time intervals. Since the autoclave was under pressure, this consisted of simply connecting a sampling cylinder and opening the sampling valve. For experiments performed with coarser sizes (190 mm × 4 mesh and 4 × 12 mesh), the sampling line was too small for the coal particles. Therefore, samples of the water extract were collected and the amount of sodium and chlorine retained on the coal was calculated by difference.

TABLE 2
Total Sodium and Chlorine in the Various Size Fractions of Raw Coal

Size of fraction	Sodium (wt%)	Chlorine (wt%)
190 mm × 4 Mesh	0.23	0.71
4 × 12 Mesh	0.20	0.50
12 × 100 Mesh	0.22	0.50
50 × 100 Mesh	0.22	0.51
100 × 0 Mesh	0.22	0.57

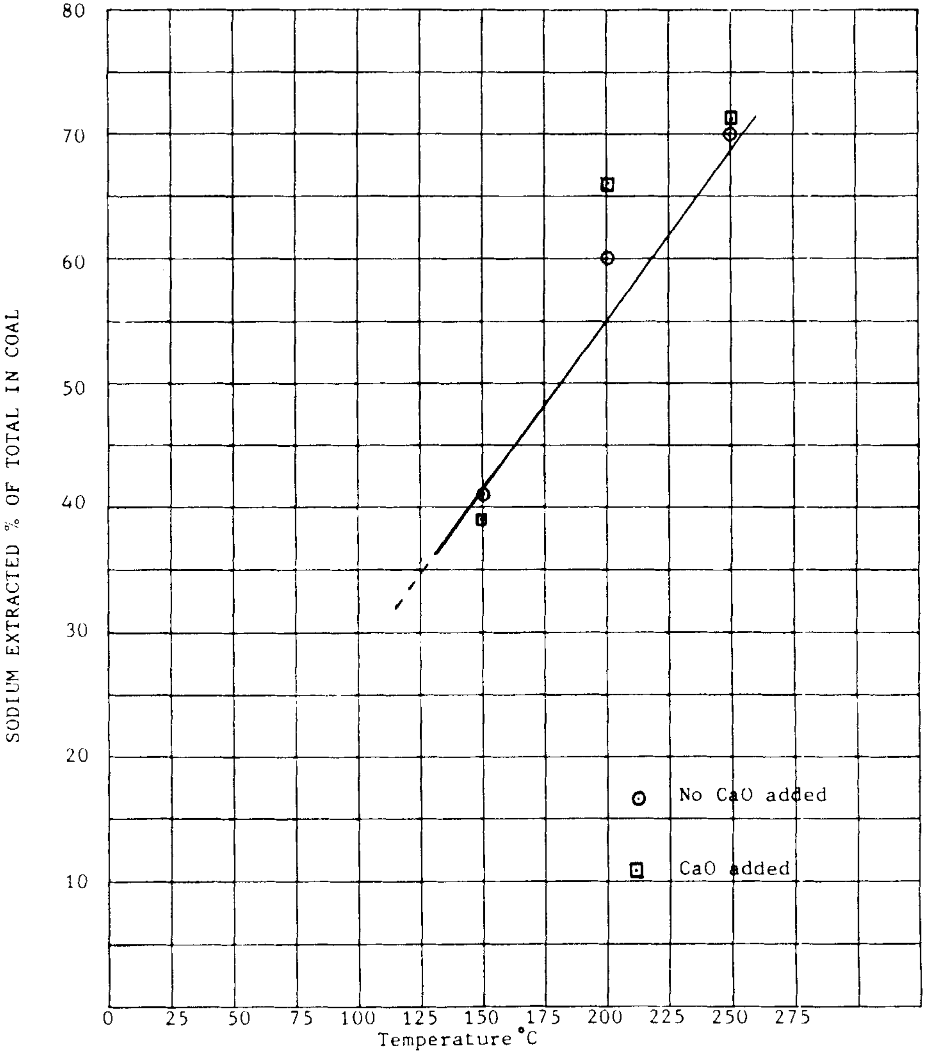

FIG. 2. Sodium extracted after 1 h for 4 × 12 mesh coal particles.

RESULTS AND DISCUSSION

The results from the tests carried out with Illinois #6 coal are explained below by the individual parameters tested.

Effect of Temperature

Figure 2 shows the effect of temperature on sodium removal from 4 × 12 mesh coal particles after treatment for 1 h at various temperatures. Figure 3 shows the effect of temperature on chlorine removal under identical conditions. In both cases an increase in temperature increases sodium and chlorine removal. Note that addition of CaO improves

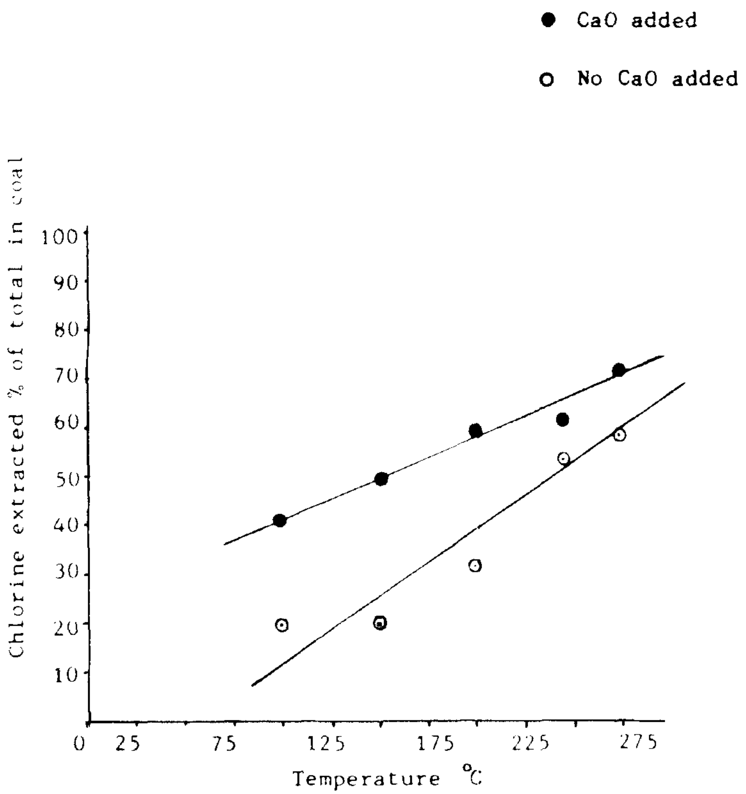

FIG. 3. Chlorine extracted after 1 h for 4 × 12 mesh coal particles.

chlorine removal. However, the effect of CaO addition on sodium removal is not as significant, and indicates that the amount of ion-exchangeable sodium present in the coal is very small. The addition of CaO appears to remove some of the ion-exchangeable chlorine associated with the coal. Figures 2 and 3 show the effect of temperature for only 4 × 12 mesh particles. Experiments with 12 × 100 mesh and 100 × 0 mesh coal particles produced similar results.

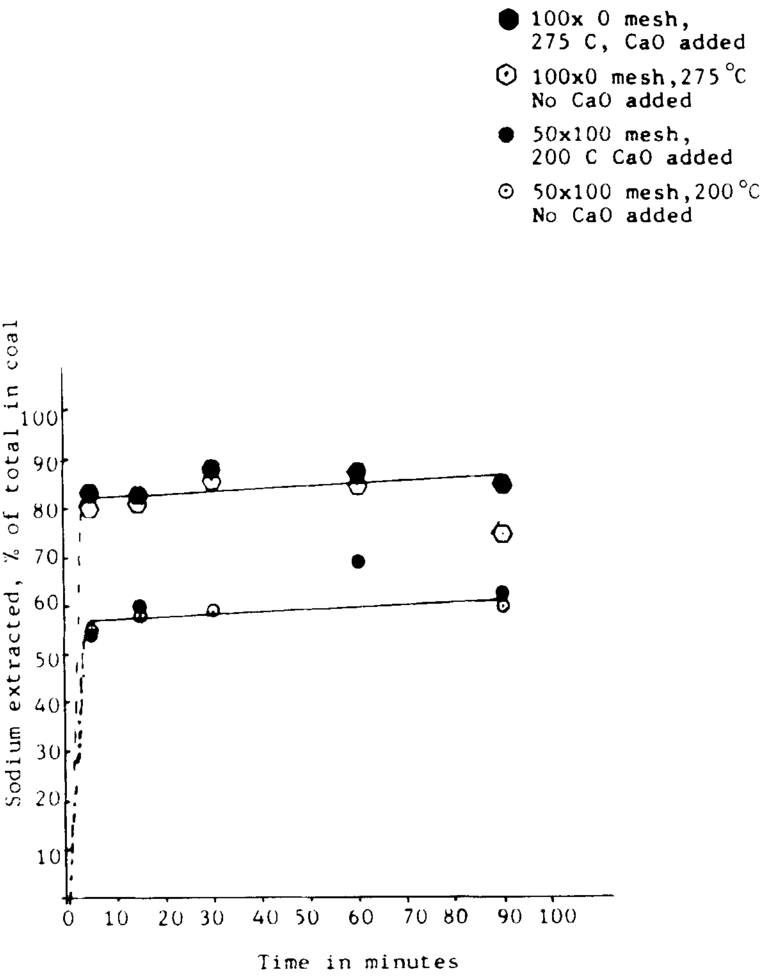

FIG. 4. Sodium extracted as a function of time.

Effect of Time

Figures 4 and 5 show the effect of residence time on sodium and chlorine removal, respectively. The bulk of the extraction occurs within the first 10 min. The amount of sodium and chlorine removed does not increase upon increasing the residence time beyond 10–15 min and remains practically unchanged. Furthermore, the addition of CaO enhances chlorine removal but has only a minimal effect on sodium removal. This confirms earlier results which indicated that the amount of ion-exchangeable sodium in the coal is very small.

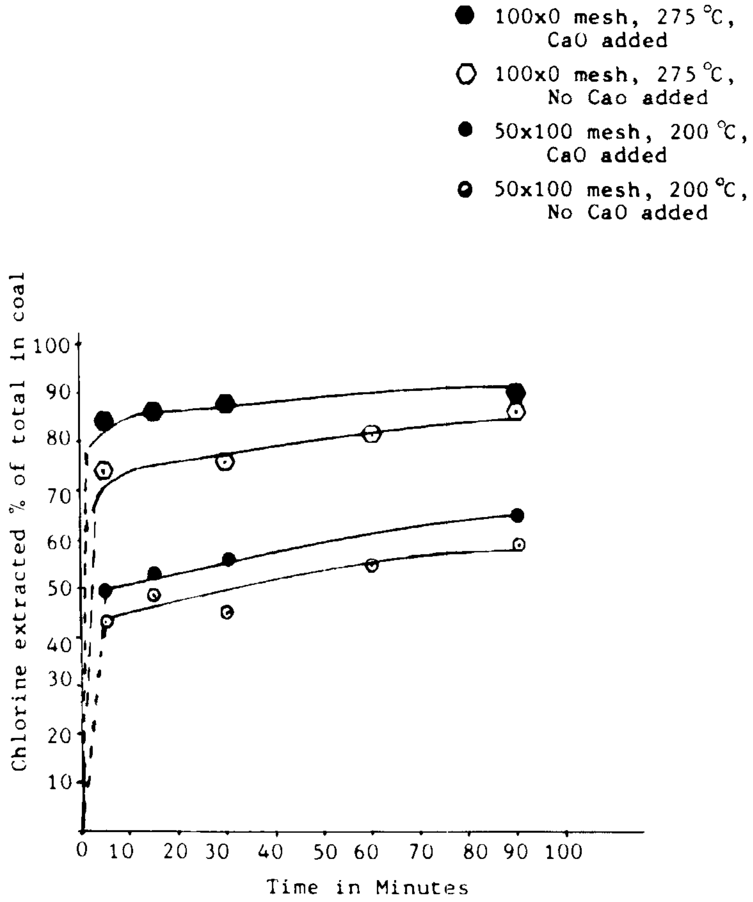

FIG. 5. Chlorine extracted as a function of time.

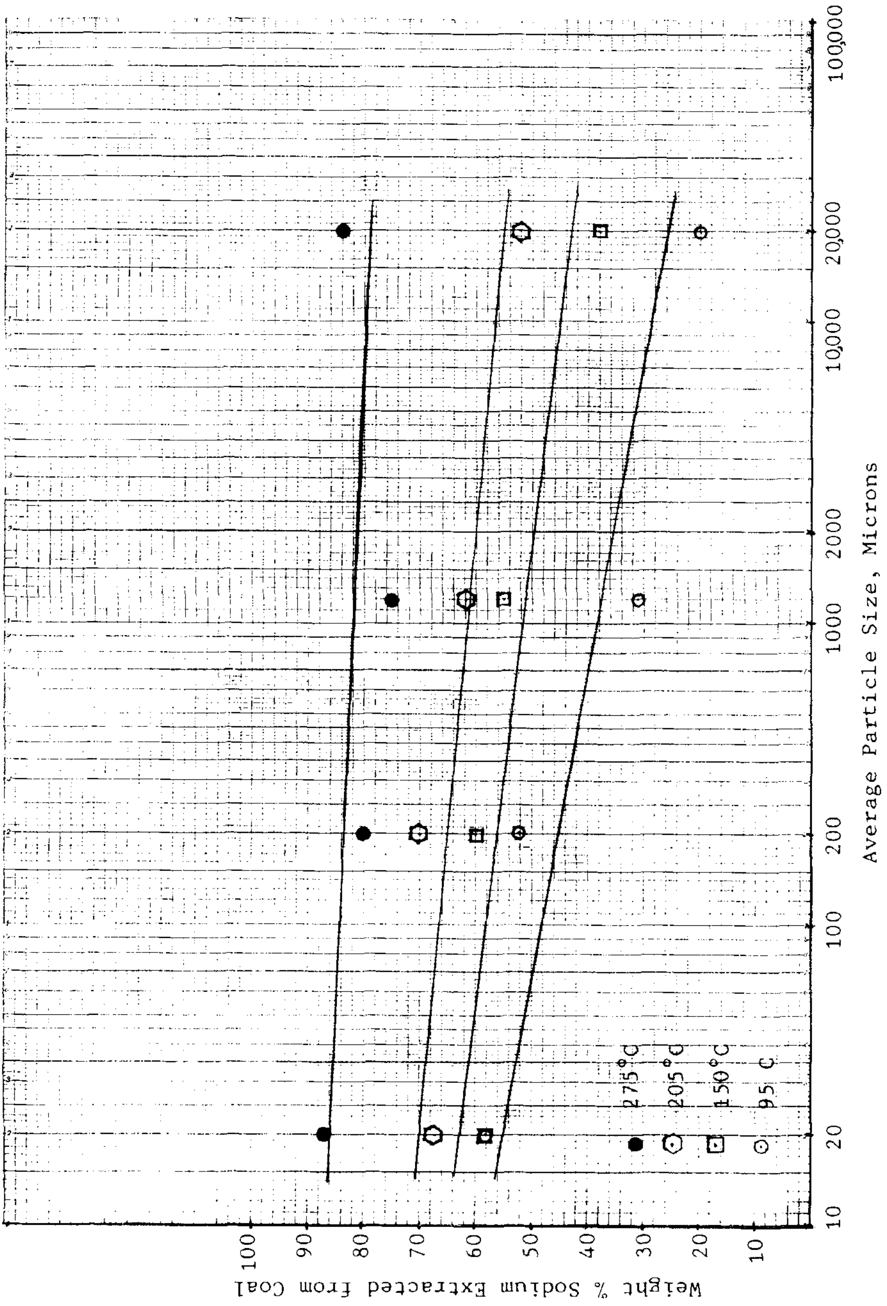

FIG. 6. Sodium extracted after 1 h as a function of particle size and temperature in the presence of CaO.

Effect of Particle Size

Figures 6 and 7 show the effect of coal particle size on sodium and chlorine removed, respectively. Although the effect on sodium removal is not quite dramatic, the results show that the degree of removal increases with finer sizes. The effect of particle size on chlorine removal is more pronounced, presumably because of the addition of CaO which facilitates the removal of ion-exchangeable chlorine.

Effect of Water/Coal Ratio

Figures 8 and 9 illustrate the effect of the water-to-coal ratio. In most cases the sodium or chlorine extracted is insensitive to the water/coal ratio. We are not certain as to why the results of the chlorine extracted for the 4 × 12 mesh fraction are different from the rest. Since the water/coal ratio does not affect the degree of removal, the only important criterion for selecting a suitable ratio for large-scale operations is the pumping characteristics required for the slurry.

INTERPRETATION OF DATA BY THEORETICAL PRINCIPLES

The data obtained from bench-scale experiments may be interpreted by considering the basic processes influencing the extraction rate of sodium and chlorine. The extraction of solute from a porous medium may occur as follows:

The solvent penetrates the particle interior. This process may be controlled by the rate of solvent diffusion or by capillary flow mechanism.

The solute dissolves in the solvent at a rate proportionate to the interphase surface area as long as the solvent is in sufficient excess.

The dissolved solute is carried from the interior to the particle periphery by diffusion.

The solute is transferred from the particle surface to the bulk of the leaching solvent.

The relative rates of the solvent penetrating the pores and the solute coming out of them may be compared by using mathematical models. The model developed by Crank is generally applicable for the case of coal particles submerged in liquid. Crank's model (*19*) assumes that the extraction rate conforms to Fick's law of diffusion. According to Fick's

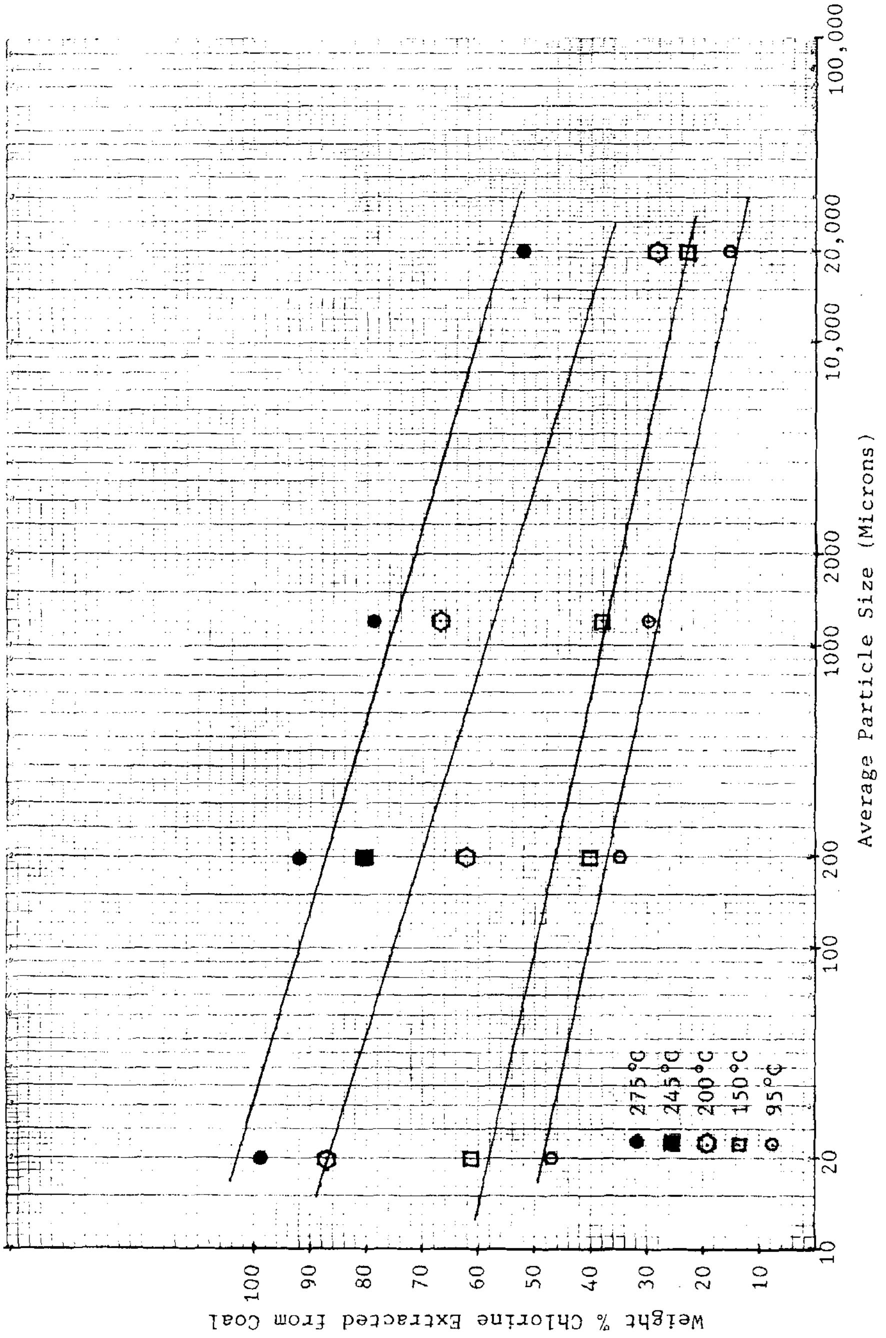

FIG. 7. Chlorine extracted after 1 h as a function of particle size and temperature in the presence of CaO.

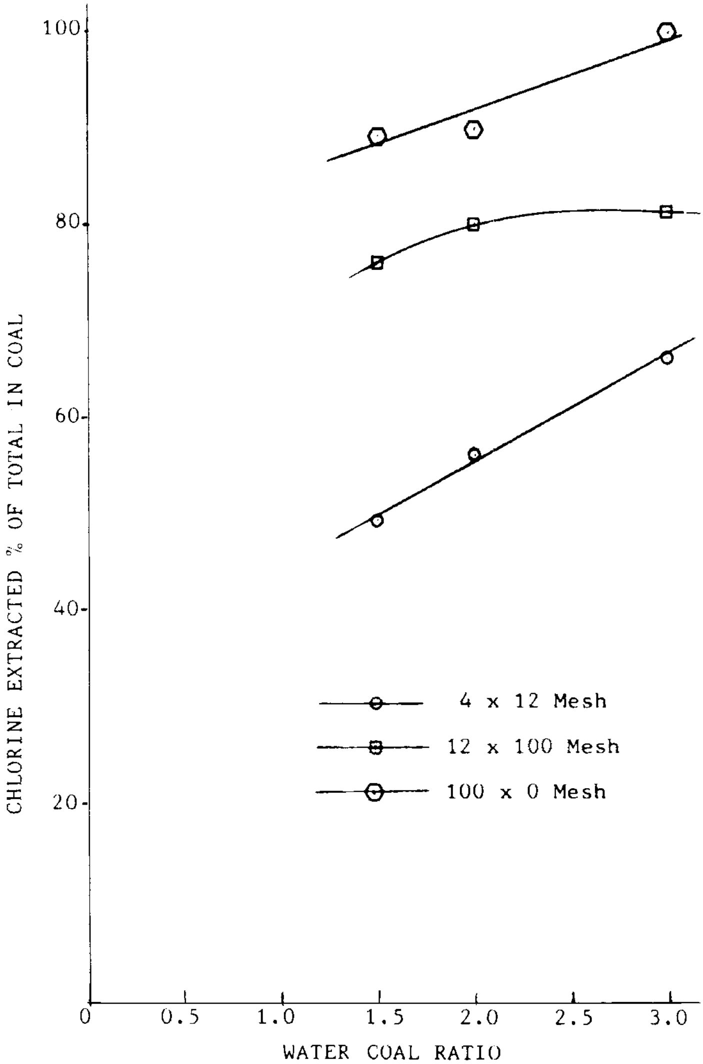

FIG. 8. Chlorine extracted in the presence of CaO after 1 h as a function of coal/water ratio and particle size at 275°C.

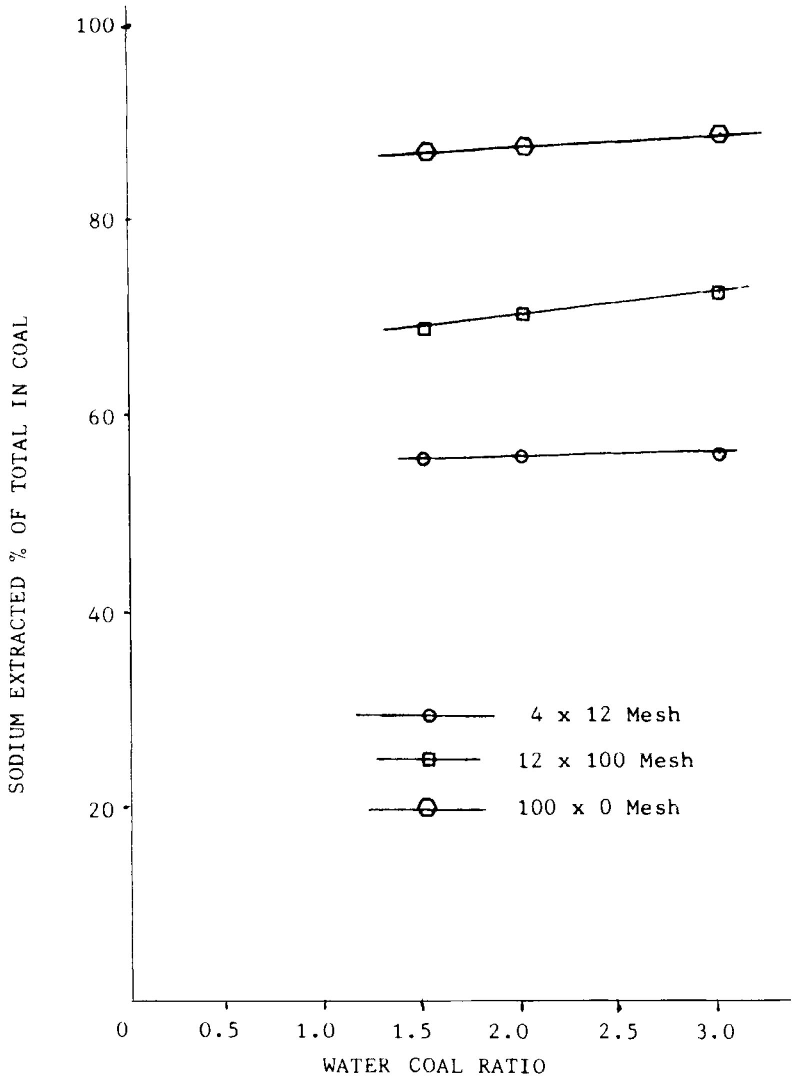

FIG. 9. Sodium extracted in the presence of CaO after 1 h as a function of coal/water ratio and particle size at 275°C.

law, the diffusion of solute from a spherical particle (in which the initial concentration is uniform) into a well-stirred solution initially free of solute is given by

$$\frac{\delta C}{\delta T} = D\left[\frac{\delta^2 C}{\delta r^2} + \frac{2\delta C}{r\delta r}\right]$$

where C = the concentration at radius r
T = time
D = diffusivity of the solute, assumed constant

It is also assumed that the density of the medium remains constant and that there are no chemical reactions occurring. Crank obtained a graphical solution for this equation (Fig. 10). The data from bench-scale experiments were examined to determine how well they conform to Fick's law. The diffusivity of sodium chloride at 25°C were obtained from the literature (*20*). The diffusivity at other temperatures was calculated by the Wilke-Chang estimation method (*21*).

The value of $\sqrt{Dt/a^2}$ was calculated for each given time interval and particle size. For each of these values, the corresponding value of the fraction extracted was plotted. The values of $\sqrt{Dt/a^2}$ were too large and did not correlate well. Therefore, the surface area of the particles was measured by BET for each site fraction. The values of $\sqrt{Dt/a^2}$ from measured surface area were too low and did not correlate well with Crank's diffusion model. Finally, the surface area values were adjusted to force-fit Crank's model (Fig. 9). The surface area needed to achieve this was 1/5000 of the actual surface area. Data analysis suggests that the extractable material in the test coal occurs mostly in macropores or crevices. This has been verified experimentally (*22*).

The following conclusions are drawn from the Battelle study:

Addition of small amounts of calcium oxide enhances chlorine removal.
Increase in temperature increases removal of sodium and chlorine.
About 80% of the removal is accomplished within the first 15 min of extraction.
The removal of sodium and chlorine increases with a decrease in particle size.
The water/coal ratio does not have a significant effect on sodium or chlorine removal. This indicates that the amount of water required for large-scale operations will depend primarily on the pumping characteristics of the slurry.

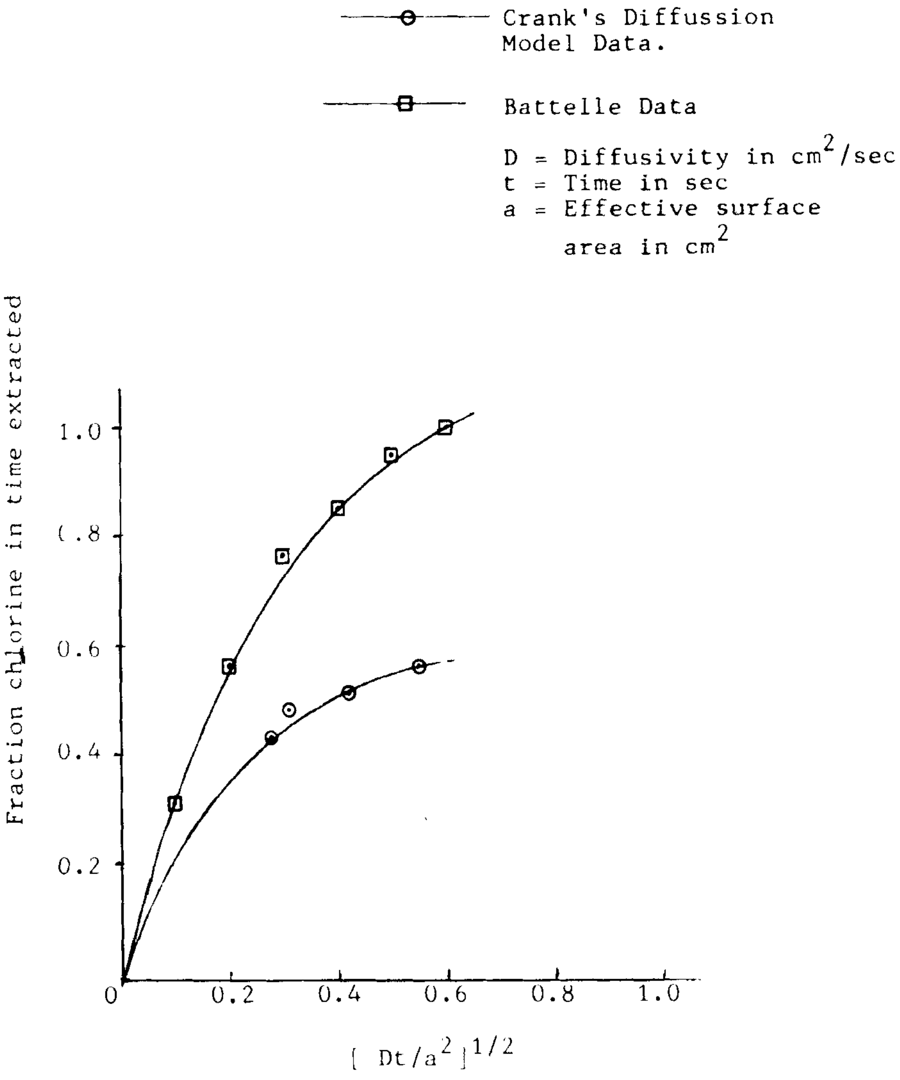

FIG. 10. Diffusion from spherical particle in stirred solution.

The amount of chlorine removed in the presence of CaO is always greater than that removed by water leach alone under identical conditions. This suggests that not all of the chlorine in the coal is in the form of water-soluble chloride. Some of the chlorine is perhaps also associated with the coal in ion-exchangeable form.

The majority of sodium and chlorine in the samples of coal used in the study occurs in the macropore region.

The test coal contained very little ion-exchangeable sodium. However, simultaneous removal of sodium and chlorine from Illinois No. 6 coal is technically feasible by treatment with calcium oxide under appropriate conditions.

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