Sodium and Cl in Illinois coals hinder the marketability of at least half of the State's economically minable coal reserves, much of which is also high in S. A successful solution to the problem depends on a fundamental understanding of the distribution and forms of Na, Cl, and S in coal, their removability through coal cleaning, and their behavior during coal combustion in boilers. Experiments were conducted for the purpose of finding a solution to the Na and Cl problem, and major findings can be summarized as follows:

(1) The results on the distribution of Na and Cl in coal lithotypes showed that Cl is concentrated in the organic matter, while Na is largely associated with the mineral matter. We, thus, proposed that most of the Cl is adsorbed on organic matter in micropores of coal. A small portion of Cl occurs as dissolved NaCl in pore water, primarily in megapores.

(2) Chlorine can be effectively removed from finely-ground (-325 mesh) coal samples by water leaching at 93°C or by soaking and subsequently leaching with water at room temperature. Leaching of coal with NaOH, NH4OAc, and NH4OH solutions was tested, and the results indicated that NH4OH is the most effective among these three reagents for removing Cl from coal.

(3) Zeta potential determinations of coal particles showed that surface charges of coal and mineral matter can be altered significantly by adding surfactants to the coal-water mixtures. Thus, some surfactants may not only enhance the flotability of coal, but may also affect the leachability of adsorbed forms of Cl and Na from coal during physical cleaning.

(4) Formation of minerals in slags and ashes was found to be related to variable temperatures at different locations within a boiler. Sodium and K are enriched in slags and ashes during the formation of complex metal sulfates. Chlorine is highly depleted in slags and ashes due to its high volatility.
EXECUTIVE SUMMARY

At least half of the economically minable coal reserves in Illinois have a Cl content above 0.3%. The Na content of the Illinois Basin coals varies widely but can be as high as 0.4%. At these levels, Cl and Na hinder the marketability of coal because they cause corrosion and fouling of coal-fired steam boilers and of fractionation columns in coal-conversion plants. The primary purpose of this project is to solve the Na and Cl problem of the Illinois coal. Much of high-Cl coal in the Illinois Basin is also high in S, and some of high-Cl coals being actively mined are medium-S coals (about 1% total S). This project also generated data on the distribution and removability of S and ash in coal while searching for a solution to the Na and Cl problem.

The objectives of this project during the past year were:

(1) to provide a clear understanding of the distribution and chemical forms of Na, Cl, and S in coal.

(2) to determine the physical and chemical factors that control the leachability of Na and Cl from coal.

(3) to test the effect of physical cleaning techniques under controlled laboratory conditions on the removal of Na, Cl, S, and ash from Illinois coals.

(4) to study surface charges of coal and mineral matter in relation to coal cleaning.

(5) to study mineralogical and chemical compositions of boiler slags and ashes in relation to the behavior of Na, Cl, and S during coal combustion.

1. Distribution and chemical forms of Na, Cl, and S in coal lithotypes and channel samples.

A good understanding of the distribution and chemical forms of Na, Cl, and S in coal is necessary in order to develop efficient cleaning techniques for the removal of these elements from coal. We hand-picked lithotypes from coal samples and analyzed them for ash, Na, Cl, S, and other elements. Our previous results on lithotypes of Herrin (No. 6) Coal and recent result on those of Springfield (No. 5) Coal showed that the Cl, Na, and ash contents vary systematically among lithotypes. The Cl content is the highest in vitrain and decreases from vitrain, through bright banded coal, subbright banded coal, and dull coal to shale parting, whereas the ash content increases in this order. These data indicate that Cl occurs mainly in the organic portion of coal and diluted by the ash. In contrast, there is a positive correlation between the Na and ash contents. Apparently, there are two components of Na in coal; one component is adsorbed by clay minerals in coal and the other component is associated with a small fraction of Cl occurring as dissolved NaCl in pore water. Volatility experiments on six
lithotypes indicated that all the Cl in lithotypes was volatilized during low-temperature ashing whereas all or at least 90% of Na, and K remained in the ash. This again suggests that the main mode of occurrence of Cl in coal is not in the form of alkali chlorides.

2. Leaching studies

Our leaching studies involved the determination of various factors that control the leachability of Na and Cl from coal. The factors tested include coal particle size, temperature, soaking, water-to-coal ratio, multiple leaching, coal lithotypes, coal rank, and chemical agents (NH₄OH, NaOH, NH₄OAc).

Our previous results on the water leaching of Cl from three different size fractions (14-28 mesh, 100-200 mesh, -325 mesh) of a Herrin Coal sample at two different temperatures (27°C, 93°C) showed that percentages of Na and Cl removed from coal increase with decreasing particle size and increasing temperature. Multiple leaching (three times) of -325 mesh coal samples at 93°C, for example, caused the dissolution of all the Cl in the leaching solution. Soaking one of the -325 mesh sample for 96 hours and subsequently leaching it with water three times at 27°C gave almost similar results; that is, almost all of the Cl entered the leaching solution. Also, we have previously shown that the water leachability of Cl varies from one lithotype to another. The lithotypes (vitrain, bright banded coal, subbright banded coal, dull coal, and fusain) were characterized on the basis of their low-temperature ash contents and maceral compositions. The low-temperature ash and inertinite contents increase slightly from vitrains, through bright banded and subbright banded coal, to dull coal and then increase appreciably from dull coal to fusains. The opposite trend was observed for the vitrinite content. The Cl leachability increases with decreasing vitrinite content among the lithotypes. This is likely related to pore structures of the lithotype samples; vitrain, which predominantly consists of vitrinite, has more micropores than other lithotypes, and thus it is more difficult to remove Cl from vitrain. The Na leachability is higher than Cl for the lithotypes; apparently water can penetrate the pores of the mineral fraction (where most of the Na is located) more easily than it can penetrate the micropores of organic matter (where most of the Cl is located). The leachability of Cl, as well as that of Na, from the lithotype samples also increase with increasing temperature. Adding NH₄OH to water also increased the leachability of Cl significantly.

This year, we tested the effect of leaching coal with NH₄OH, NaOH, and NH₄OAc of various strengths on the removal of Cl. A 0.1 M NH₄OH solution removed more Cl than deionized H₂O from the 60-200 mesh fraction of a sample of Springfield Coal; soaking the coal with the NH₄OH solution for 67 days resulted in the leaching of 95% of the Cl.

Results on the leaching of Cl from a Herrin Coal sample, ground to -60 mesh, with the same three reagent solutions with concentrations ranging from 0.05 M to 1 M are compared in Figures 1a and 1b. The
figures indicate that NH$_4$OH is more effective than NH$_4$OAc and NaOH in leaching Cl from coal, and, on the average, NaOH is slightly more effective than NH$_4$OAc. These observations suggest that: (1) Cl in coal is replaced by OH$^-$ or OAc$^-$ during leaching; (2) OH$^-$ is more effective than OAc$^-$ in replacing Cl; and (3) NH$_4^+$ apparently tends to open up the pore structure of coal making it more penetrable by the leaching solution and thus increasing the Cl leachability.

3. Physical Coal Cleaning

The 14-20 mesh fraction of a sample of the Springfield Coal was cleaned by a laboratory-scale jig to test the effectiveness of this technique on the removability of Cl, as well as S and ash, from coal. The jiggling process reduced Cl, pyritic S, and ash contents in the clean coal fraction by 14-18%, 34-47%, and 32-35%, respectively, relative to the feed coal. This indicates that conventional jiggling technique is reasonably effective for reducing pyritic S and ash contents, but not Cl content, in coal.

4. Studies of Surface Properties

Zeta potential measurements were carried out for the purpose of understanding the effect of surfactants on the surface charge of coal and mineral matter. This, in turn, may have important implications for the flotability of coal and for the removal of Na and Cl from coal during surface-dependent coal cleaning processes. It was found that fresh coal samples and their low-temperature ashes in contact with H$_2$O tend to have positive surface charge at low pH values and negative surface charge at high pH values. Adding one particular surfactant (e.g. 1008-11-39) to the suspensions made the surfaces of coal and low-temperature ash more negative. However, its effect on the surface charge of coal was significantly greater than its effect on that of low-temperature ash. Increasing the difference between the surface charges of coal and mineral matter may improve the separation of these two components during surface-dependent coal-cleaning processes.

5. Boiler Slags and Ashes

In order to understand the behavior of mineral impurities during coal combustion in relation to boiler fouling and corrosion, we studied the mineralogical and chemical compositions of boiler ashes, slags, and feed coal. We found that mineralogical compositions of slags and ashes vary with temperature which is different at different locations of a boiler. Furnace wall and bottom cyclone slags consist predominantly of high temperature mineral phases such as Al$_2$O$_3$ and cristobalite. Bottom cyclone slags are also enriched in chromite. Deposits from the lower temperature areas of the boilers (superheater, re heater, economizer) contain much hematite, glass, and sulfate minerals. Sulfates cause corrosion and assist in the binding and deposition of fly ash particles on heat exchange tube surfaces, which reduces the efficiency of the boilers. Sodium and K are enriched in slags and ashes during the formation of complex metal sulfates. Chlorine is highly depleted in slags and ashes because of its high volatility. It is likely that Cl first reacts with metal surfaces and then volatilizes.
Fig. 1. Ranges of Cl leachability from a sample of Herrin Coal at room temperature with solutions of NH₄OH, NaOH, and NH₄OAc. Particle size is -60 mesh. Raw coal contains 0.50% Cl on a dry basis.
OBJECTIVES

The objectives of this project are: (1) to provide a clear understanding of the distribution and chemical forms of Na, Cl, and S in coal; (2) to determine the physical and chemical factors that control the efficiencies of physical coal cleaning processes; (3) to develop cleaning techniques for the efficient removal of Na and Cl from Illinois coals; and (4) to study the behavior of Na, Cl, and S in coal during combustion in utility boilers and its relation to corrosion and fouling of boilers.

Our approach to the problem includes: (1) determination of ash, Na, Cl, S, and trace element contents of fresh channel samples and hand-picked lithotypes; (2) studying the kinetics of Na and Cl removal from coal by conducting leaching experiments on well-characterized lithotype separates and whole-coal samples; (3) studying the behavior and removability of Na, Cl, and S at industrial preparation plants; (4) testing the effect of conventional coal cleaning methods on the removal of Na, Cl, S, and ash under controlled laboratory conditions; (5) studying the surface properties of coal by measuring zeta potentials of coal and low-temperature ash particles suspended in water in the presence and absence of surfactants; and (6) determining the mineralogical and chemical compositions of feed coal, ashes, and slags collected at power plants.

The primary goals of the project are to develop practical coal cleaning techniques for the removal of Na, Cl, and S from Illinois coals and to assess the effects of inorganic impurities in coal on boiler fouling and corrosion.

INTRODUCTION AND BACKGROUND

Sodium, Cl, and S are detrimental elements in the utilization of coal. At least half of the economically minable coal reserves in Illinois have a Cl content above 0.3%. The Na content of the Illinois Basin coals generally varies between 0.01 and 0.4%. Like S, Na and Cl at high concentration levels hinder the marketability of coal because they are associated with corrosion and fouling of boilers at power plants. This project was initiated primarily to solve the Na and Cl problem of the Illinois coal.

During this past year, we conducted experiments in the following areas:

(1) Leaching of Na, Cl, and K from coal

We have previously studied leachabilities of Cl, Na, and other elements from coal using water. The results indicated that Cl can be effectively removed from -325 mesh coal samples by water leaching at 93°C or by soaking with water prior to water leaching at room temperature (Demir et al., 1986). Addition of a small amount of NH₄OH to the leaching water remarkably increased the leachability of Cl from coal samples, reflecting the exchange of OH⁻ for Cl⁻. During this past year, we conducted leaching experiments on samples
of Springfield (No. 5) and Herrin (No. 6) Coals and on an Argonne
Premium coal sample using H2O and solutions of NH4OH, NaOH, and
NH4OAc.

(2) Coal Cleaning with a Jig

Jigging is one of the most commonly used coal cleaning techniques at
industrial coal-preparation plants. Conducting jigging experiments
under controlled laboratory conditions should help to understand and
improve conventional cleaning techniques for the efficient removal
of Na and Cl, as well as S and ash, from coal. We cleaned the 14-20
mesh fraction of a Springfield Coal sample using a laboratory-scale
jig, and the results are discussed in this report.

(3) Volatility of Cl, Na, and K during low-temperature ashing

Volatile experiments at low temperature yield data related to
chemical forms of Cl, Na, and K in coal and these data have a
bearing on the behavior of these elements during coal preparation
and coal combustion. Results of low-temperature ashing experiments
on a raw coal (C22652) and a coal-chlorides mixture showed that
almost all the Cl in coal was lost by volatilization and Na and K
were retained in the ash (Chou et al., 1986b). In this report, we
discuss similar experiments conducted on six lithotype separates
(vitrain, bright banded coal, subbright banded coal, dull coal,
fusain, and shale parting).

(4) Surface charges of coal and mineral matter

The mineral matter of Illinois coal consists mainly of clays (on the
average about 50% of total mineral matter), pyrite, calcite, and
quartz. These minerals can largely be liberated from coal particles
by fine grinding. The finely-ground coal and the mineral particles
can then be separated through fine-coal cleaning processes such as
froth flotation and aggregate flotation. The success of such
cleaning processes depends on a thorough understanding of the
surface properties of coal and mineral matter. We discussed the
surface charge (zeta potential) data on some coal samples in our
previous reports. In this report, we discuss the measurement of
zeta potentials of two additional coal samples, clay minerals, and
low-temperature ashes.

(5) Mineralogical and chemical compositions of boiler slags and
ashes

Research on mineralogical and chemical compositions of slags and
ashes from utility boilers was conducted for the investigation of
the behavior of Na, Cl, and S during combustion of Illinois coal in
relation to boiler fouling and corrosion. We discuss, in this
report, the mineralogical compositions of boiler slags and ashes
collected from the power plants A (Coffeen Units 1 and 2), B (Newton
Unit 1), and C (Lakeside).
EXPERIMENTAL PROCEDURE

Analytical Methods

Chlorine concentration in coal samples was determined by potentiometric titration after digesting the samples in an oxygen bomb. The titration method was also used to determine Cl⁻ in coal leachates.

A Dionex 2000i Ion chromatograph was used to determine other anions (F⁻, Br⁻, NO₃⁻, SO₄²⁻, PO₄³⁻) along with Cl⁻ in coal leachates as well as in coal. Preparation of coal samples for ion chromatography was similar to that for potentiometric titration, except the potentiometric titration technique included an extra step (acidification with HNO₃). Leachates were analyzed as they were, with the exception of occasional dilution step when the concentrations were too high. For coal samples, the values for Cl⁻, F⁻, and Br⁻ reflect their true concentrations in coal. However, the values for NO₃⁻, SO₄²⁻, and PO₄³⁻ do not reflect their true concentrations in coal because these anions can form through the oxidation of N, S, and P in coal during the combustion and leaching processes. The ion chromatography technique was also tested for determination of cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) in leachates.

A Cl⁻ combination electrode, in conjunction with an Orion EA-940 Ion Analyzer, was also used for quick determination of Cl⁻ in leachates during leaching experiments.

Sodium and trace elements in coal were determined by neutron activation analysis technique. Proximate and ultimate compositions, forms of S, and calorific values for coal samples were determined by ASTM methods.

Leaching Experiments

Batch samples of Illinois coal (120 grams each) were mixed with 600-ml of distilled water or aqueous solutions of NH₄OH, NaOH, and NH₄OAc in a leaching apparatus, and the mixtures were stirred at a constant temperature for a given amount of time. During stirring the mixtures were sampled periodically, and the samples were filtered to obtain clear leachates which were then analyzed for Cl⁻. The last samples of the mixtures were centrifuged at 2800 RPM for 30 minutes to dewater the leached coal efficiently. The dewatered samples of the leached coal were analyzed for Na, Cl, and other elements.

To leach an Argonne Premium coal, the samples of the coal were mixed with distilled water in a glass beaker, and the mixtures were stirred with a magnetic stirrer at a constant temperature for a given amount of time. Each run was repeated three times with fresh water. At the end of the third wash the coal-water slurry was centrifuged to separate leachates from coals. The leachates and leached coals were analyzed for Na, Cl, and other elements.
Physical coal cleaning

A laboratory-scale CT (coal test) jig, purchased from Coal Processing Associates Ltd. in England, was used to test the effectiveness of jigging for reducing ash, S, Na, and Cl contents in Illinois coals under controlled laboratory conditions. The jig was operated at a speed of 25 upstrokes/minute, and 1500 ml of glass beads were used as ragging material during the operation. Two cleaning products, clean coal (light fraction) and mineral-rich residue (heavy fraction), were obtained at the end of each run. The recovery rate of the clean coal was 77%. The clean coal and mineral-rich residue were analyzed for ash, Na, Cl, and other elements.

Zeta-potential measurements

Coal samples were ground to -325 mesh and suspended in distilled H$_2$O (the H$_2$O/coal ratio = 10$^4$) with and without surfactants added to the suspensions. The suspensions were placed in an ultrasonic bath for 5 minutes to ensure complete dispersion of the particles in the liquid. Suspensions of pure clays and low-T ashes of coal were prepared the same way, except the grinding step was omitted for pure clays which already had very small particle sizes (<2 μm).

The pH of the suspensions was adjusted to desired values using 0.1 M HCl and/or 0.01 M NaOH solutions. Subsequently, the zeta potential of the solid particles in the suspensions was measured with a ZM3-83 Zeta meter.

Volatile of Na, Cl, and K in coal during low-T ashing

Six coal lithotypes were hand-picked from a channel sample. A split of each lithotype was ashed at a low temperature (125°C-140°C) under oxygen plasma using low-temperature asher. The lithotypes and their low-temperature ashes were analyzed for Na, Cl, and K to determine the volatile loss of these elements during the ashing process.

Boiler Ashes and Slags

Samples of boiler ashes, slags, and feed coal from power plants were dried and pulverized in a Spex steel mill. Pulverized samples were then split into separate portions for XRD and chemical analysis.

Mineralogical compositions of the samples were determined by XRD using Cu K-alpha radiation. Thin sections were prepared from some of the more indurated boiler tube deposits for petrographic characterization. Samples were also analyzed for Na, Cl, K, and other elements using neutron activation analysis, XRF, and other techniques.
RESULTS AND DISCUSSION

1. Leachability of Na, Cl, and K from Coal

Springfield Coal. Two leaching experiments, one with distilled $H_2O$ and another with a 0.1 M NH$_4$OH solution, were run to study the kinetics of Cl removal from the 60-200 mesh fraction of a channel sample of Springfield Coal. The highest rate of Cl removal occurred within the first 5 minutes, and the rate was higher for the NH$_4$OH solution than for $H_2O$ although the temperature of the experiment with the former was lower than that with the latter (Fig. 3 in Chou et al., 1986b). This indicates that increasing the supply of OH$^-$ (in the form of NH$_4^+$ in solution), which replaces Cl$^-$, and/or swelling effect of NH$_4^+$ were more important in enhancing the leachability of Cl than raising the temperature of distilled $H_2O$ from 27°C to 50°C.

It is likely that primarily the Cl around the external surfaces of coal particles and in large pores was leached out during the first 5 minutes of leaching with the NH$_4$OH solution. The leaching of Cl located within micropores is a very slow process because of the difficulty the leaching solution encounters in penetrating the micropores. Then, the leaching of Cl from the micropores probably accounted for most of the Cl removal after the first 5 minutes as indicated by a very small slope of the leaching curve between 5- and 60-minute time intervals in Fig. 3 of Chou et al. (1986b). A 60-minute stirring with the NH$_4$OH solution resulted in the leaching of 38% of the Cl from the coal. After the 60-minute stirring period, the mixture of coal and NH$_4$OH solution was equilibrated for 67 days. The soluble Cl increased with increasing duration of the equilibration, and after 67 days almost all of the Cl (96% of the total Cl) became soluble in the leachate.

Leaching with distilled $H_2O$ probably resulted mainly in the removal of dissolved Cl in large pores within the first 5 minutes of leaching. After that, some of the exchangeable Cl around the external surfaces of coal particles and large pores was leached out at a gradually reduced rate. Because distilled $H_2O$ has a much lower OH$^-$ content and lower ability for penetrating pores of coal than NH$_4$OH solutions, it leached out a smaller amount of Cl than the NH$_4$OH solution.

Argonne premium coal. Two samples of an Argonne premium coal were leached with distilled $H_2O$ at 27°C and 93°C (Chou et al., 1987a). At 27°C, the leachabilities of Cl, S, K, and Ca were very low (0.1-3.2% of the original amount in coal), but that of Na was moderate (21.4%). This again suggests that most of the Na and Cl are not associated with each other in this coal, which was also the case for other coals we have studied. Sodium is present in dissolved form and exchangeable ionic form adsorbed on clays and thus removed relatively easily whereas most of the Cl likely occurs in micropores and thus is difficult to be removed. The leachabilities of S, K, and Ca were very small because these elements are primarily located in the molecular structure of minerals or adsorbed on ion exchange sites more strongly than Na.
Results on the leaching of the -20 mesh sample at 93°C showed that leachabilities for all elements increased only slightly as compared to those for the same sample at 27°C. These results differ considerably from those obtained earlier for Illinois coals. The water (single wash) leachability of Cl for the 14-28 mesh fraction of a Herrin Coal sample, for example, increased from 11% at room temperature to 26% at 93°C (Chou et al., 1986c).

Data at 93°C for the -100 mesh sample of the Argonne premium coal showed a slight increase in the leachability of Cl (4.2%) and a slight decrease in that of Na (27.4%) as compared to those (3.1% for Cl, 29.8% for Na) for the -20 mesh sample at the same temperature. This observation on the Upper Freeport Coal (the Argonne premium coal) is also different from what we observed for Illinois coals. For example, the Cl leachability at 93°C for the 100-200 mesh fraction of a Herrin Coal sample, was 40% compared to 25% for the 14-28 mesh fraction of the same sample at the same temperature (Chou et al., 1986c). Based on these limited data, it appears that water leaching of Cl from medium-volatile coal may be more difficult than that from high-volatile coal.

Herrin (No. 6) Coal Identical splits of a sample of Herrin Coal (ground >60 mesh) were leached with solutions of NaOH, NH₄OAc, and NH₄OH to remove Cl. The Cl leachabilities were determined at various intervals between 5 minutes and 120 minutes. The results are listed in Table 1. The Cl leachability generally increased with time for all solutions.

Four different concentrations (0.05 M, 0.1 M, 0.5 M, and 1 M) of NaOH were used to leach Cl from coal. The Cl leachability was higher for more concentrated NaOH solutions (0.5 M and 1 M) than for less concentrated NaOH solutions (0.05 M and 0.1 M) used. Leaching with 1 M NaOH removed 30.8% of the Cl in 1 hour.

The results of Cl leachabilities with two concentrations of NH₄OAc (0.05 M and 0.1 M) are slightly different from the values we reported earlier (Chou et al., 1986b; Table 4). The previous data were based on values obtained by Cl⁻ ion selective electrode method, which had interference from OAc⁻ ions in solution. A correction was made when the solutions were reanalyzed for Cl using potentiometric titration. These data along with data on leaching of coal with two more solutions of NH₄OAc are tabulated in Table 1. The highest Cl leachability was obtained with 1.0 M NH₄OAc; it is 29.3% for 1 hour, and 33.4% for 2 hours leaching.

For NH₄OH solutions (0.05 M, 0.1 M, 0.5 M, and 1 M), the lowest Cl leachability was obtained when the sample was leached with 0.05 M NH₄OH solution. Higher Cl leachabilities were obtained when more concentrated NH₄OH solutions were used. Leaching with 1 M NH₄OH removed 38% of the Cl in one hour and 40.9% of the Cl in two hours.

Comparison among the solutions. The Cl leachabilities for the three reagent solutions with concentrations ranging from 0.05 M to 1 M were compared. Figure 1a in the Executive Summary section compares
the Cl leachabilities for NH₄OH and NaOH solutions, and Figure 1b compares those for NH₄OH and NH₄OAc solutions. Ammonium hydroxide is more effective than NH₄OAc and NaOH for leaching Cl from coal, and, on the average, NaOH is slightly more effective than NH₄OAc. These results suggest that: (1) the leaching of Cl from coal was an ion exchange reaction involving the replacement of Cl⁻ by OH⁻ or OAc⁻; (2) OH⁻ is more effective than OAc⁻ for replacing Cl⁻; and (3) NH₄⁺ apparently has a swelling effect which opens up the pore structure of coal making it more penetrable by leaching solutions and thus increases the Cl leachability.

2. Coal Cleaning with a Jig

Jigging is one of the most commonly used techniques at coal preparation plants for reducing ash and pyritic S contents in coal. But its effect on the removal of Na and Cl from coal has not been investigated adequately. Three jigging experiments were completed. The first experiment was conducted on the 14-28 mesh fraction of a Herrin Coal sample, and the results were reported in Chou et al. (1985) and Demir et al. (1987). The second and third jigging experiments were conducted in the current project year on the 14-20 mesh fraction of a sample of Springfield Coal, and the results were reported in an earlier quarterly report (Chou et al., 1986b).

The process of jigging reduced the ash and pyritic S contents in the clean coal (light) fraction by 32-35% and 34-47%, respectively, relative to feed coal (Table 4 in Chou et al., 1986b). The heavy fraction was significantly enriched in ash and pyritic S relative to feed coal. The reduction of total S was lower than that of pyritic S because organic S content in the light fraction was only slightly reduced or even increased because of the removal of ash which dilutes organic S in coal.

The Cl content was reduced by 14-18% in the light fraction and by 25-26% in the heavy fraction relative to feed coal. A lower Cl content in the heavy fraction, relative to that in the light fraction, is caused by higher ash content in the heavy fraction; ash dilutes Cl which is concentrated in the organic matter. The removal of Cl from coal is controlled by the dissolution of this element in the leaching solution. For the relatively coarse particle size of coal (14-20 mesh) used in the jigging experiments, only a small amount of Cl (14-18% of the total) was removed.

3. Volatility of Cl, Na, and K in Coal Lithotypes during Low-T Ashing

Volatility experiments at low temperatures yield data about chemical forms of Cl, Na, and K in coal, and such data are useful for understanding the behavior of these elements during coal preparation and coal combustion. During this year volatility experiments on six lithotypes (hand-picked from a channel sample of Springfield Coal) were completed (Table 3 in Chou et al., 1987b). The Cl content of lithotypes decreases from vitrain (0.55%), through bright banded coal (0.54%), subbright banded coal (0.49%), and dull coal (0.43%),
to shale parting (0.30%), whereas the Na, K, and low-temperature ash contents increase in this order. This is consistent with our previous results, suggesting that Cl is concentrated in the organic matter whereas Na is enriched in the mineral matter. As we discussed earlier, fusain is different from those of other lithotypes.

The volatile losses of Cl, Na, and K during low-temperature ashing were calculated from their concentrations in the ash residues and in raw coals. The results indicated that all the Cl in the lithotypes was volatilized during low-temperature ashing. The volatile loss of Na for these samples varied between 0.1% and 8.1%. Because the analytical uncertainty for low-temperature ashing and Na determinations is about 5-10%, it appears that all the Na in coal was retained in the low-temperature ashes. Similarly, all the K in coal was also retained in the low-temperature ashes. These results again suggest that the main mode of occurrence of Cl in coal is not in the form of alkali chlorides.

4. Surface Charge Studies

Electrostatic charge on coal particles in solutions affects flotation recovery of coal during aggregate flotation and froth flotation processes as well as adsorption of ionic species by coal. It is therefore important to monitor surface charge on coal particles and alter it, if necessary, using surfactants to increase the efficiency of these surface-dependent coal cleaning processes.

Zeta-potential is a direct measure of surface charge of colloids suspended in liquids. In earlier experiments, we determined zeta potentials of lithotype samples (vitrain, bright banded coal, subbright banded coal, dull coal, and fusain) at pH values ranging from 3 to 7 (Chou et al., 1986a). With the exception of fusain, zeta potentials were positive at pH 3 and 4 and became negative at pH 5-7. Fusain was positively charged at pH values between 3 and 7.

During this year, we determined the zeta potential for three coal samples suspended in water, with and without surfactants added to the suspensions. We also determined the zeta potential for pure clays and for low-temperature ashes of coal.

Zeta potential of a table-cleaning product of a composite sample of Springfield (No. 5) Coal. Figure 2 shows the variation of zeta potential of coal particles with pH and with types of surfactants. The zeta potential decreased with increasing pH for all four sets of measurements. Surfactants 1008-11-31 and 1008-11-26 made the coal particles more positively charged, whereas the surfactant 1008-11-39 made them more negatively charged, relative to using distilled H₂O, suggesting that these surfactants are adsorbed and consequently change the surface charge on coal particles.

Zeta potential of a run-of-mine sample of the Colchester (No. 2) Coal. Figure 3 shows the variation of zeta potential of coal particles as a function of pH, with and without the surfactant No. 1008-11-39 added. When coal particles were dispersed in water
without the surfactant added, the zeta potential decreased rapidly from +41.5 mV at pH 3 to -35.5 mV at pH 9. When the surfactant No. 1008-11-39 was added to the coal-water mixture zeta potential became negative for the entire pH range (3-9). Furthermore, with surfactant 1008-11-39, the zeta potential of this coal increased slightly from pH 3 to pH 7 and then decreased slightly from pH 7 to pH 9.

Zeta potential of an Argonne Premium Coal (No. 1) Sample. Two separate bottles (-20 mesh and -100 mesh) of Argonne Premium Coal No. 1 were also used for surface charge studies (Chou et al., 1987a). Zeta potentials for these samples were rather similar for pH values between 4.25 and 8.5, but at pH 3 the zeta potential for the -100 mesh sample was less positive than the -20 mesh sample. We are not certain about the cause of a large difference in the zeta potentials at pH 3 for these two samples.

We also reported previously that the pH of fresh coal-water mixtures is acidic, generally less than pH 4.0. All three coal samples suspended in distilled H2O yielded positive surface charge at very acidic pH values. This again confirms our earlier suggestions that Cl is likely adsorbed as an exchangeable ion on or around the positively charged coal surface and leaching coal with a highly basic solution would result in the exchange of OH- for Cl in coal.

Zeta potential of clays and low-temperature ashes. Figure 4 shows that the zeta potentials of clay samples suspended in water were negative. The zeta potentials of illite were between -15.5 mV and -17.2 mV for pH 3-9, being more or less constant within the analytical error. The zeta potentials of kaolinite and montmorillonite were more negative and showed greater variation with pH than that of illite.

The zeta potentials of kaolinite and montmorillonite were nearly identical at pH 3 and 5. But at pH 7 and 9, kaolinite became more negatively charged than montmorillonite. This may be explained as follows: the so-called pH-dependent charge accounts for most of the charge of kaolinite, but less than 25% of total charge on montmorillonite. At high pH values, hydrogen from exposed O-H groups at crystal edges of kaolinite dissociates, causing an increase in its negative charge. However, other factors, such as the presence of soluble and insoluble impurities in the clays, may also influence their surface charges.

Two low-temperature ash samples dispersed in distilled H2O had nearly identical zeta potentials (Fig. 5). The zeta potentials were between +14.0 mV and +19.0 mV at pH values of 3, 5, and 7, and they became -19.0 mV and -21.4 mV at pH 9. The zeta potentials of the low-temperature ash samples were quite different from those of the clay samples (compare Figs. 4 and 5). This is expected because, in addition to clays, the low-temperature ashes contain several other minerals, such as pyrite, calcite, and quartz.
The addition of a small amount of the surfactant No. 1008-11-39 to one of the mixtures of low-temperature ash and $\text{H}_2\text{O}$ greatly changed the zeta potential of the ash particles (Fig. 5). At pH 3 and 5, the zeta potentials changed from positive values to -13.5 mV and -18.1 mV, respectively. At pH 7, the surface became neutral, and at pH 9, the surfactant made the surface of the ash particles slightly more negatively charged than at pH 3 and 5. Thus, surfactants apparently can change the surface charges of mineral matter as well as those of coal.

5. Boiler Slags and Ashes

Results on the mineralogical composition of boiler slags and ashes are listed in Table 2. Numbers in the table refer to peak heights measured on the diffractogram in arbitrary units and do not represent quantitative abundances of minerals in each sample. However, broad generalizations with respect to abundances of certain mineral associations in each sample may apply, such as differences in the ratio of hematite to magnetite. Typical XRD patterns are shown in Figures 6 and 7.

In order to understand relationships between mineralogical composition of boiler deposits and their processes of formation, a basic understanding of the temperature regime within the boiler is necessary. Plant A (Coffeen) for example, is cyclone fired with a furnace exit gas temperature of approximately 1180° (2150°F). Temperature at the primary superheater inlet is approximately 650°C (1200°F) and temperature of the flue gas leaving the economizer is 370°C (700°F).

Furnace wall and bottom cyclone slags consist predominantly of high temperature mineral phases and much glass. Many of these phases, such as $\text{Al}_2\text{O}_3$ and cristobalite, form from initial kaolinite only after heating ash beyond 1000°C (Mitchell and Gluskoter, 1976). Chromite also occurs in the bottom cyclone slag where chromium is enriched approximately 65 times relative to feed coal.

Deposits from the lower temperature areas of the boiler (superheater, re heater, economizer) contain much hematite, glass, and sulfate (simple and complex) minerals. Figure 7 compares diffractograms of superheater and re heater deposits of plants A and B, which exhibit the usual types of minerals. The bulk of the deposit consists of glass cenospheres (spherical particles of fly ash) which have been sintered or bonded together in the deposit. Sulfate minerals have been reported from other boiler deposits and are considered by many to be the primary agent in boiler corrosion. Binding fly ash particles assisted by the sulfates causes a consolidated deposit to build-up on heat exchange tube surfaces, reducing the efficiency of the boiler.

Sulfates, due to their bonding and corrosive properties, are of great interest in this project. Problems with sulfates in utility boilers have been discussed in the literature for many years. Sulfate formation begins with the formation of $\text{SO}_2$ by the oxidation of initial pyrite in the furnace. Iron oxide in deposits may aid in
catalyzing oxidation of SO$_2$ to SO$_3$. Alkali-oxides, formed by release of volatile alkalis react with SO$_3$ and condense on lower temperature heat exchange surfaces to form simple alkali sulfates, or they can undergo further reactions to form complex alkali-metal sulfates of the general form (Na,K)$_3$(Fe,Al)(SO$_4$)$_3$. Alkali-iron trisulfates are highly corrosive when molten (593-704°C) and thus expected to react with tube metal. The complex sulfate Na$_3$Fe(SO$_4$)$_3$ was identified in Plant A economizer ash and reheater ash.

The enrichment or depletion of Na, K, and Cl in slags and ashes has been calculated relative to feed coal and normalized to Al$_2$O$_3$ (Table 3). Sodium and K usually show enrichment in fly ash, superheater, and reheater deposits. Potassium, however, is slightly depleted in Plant B reheater deposits. Our data also showed that enrichment or depletion can vary from one plant to the other and may depend on operating temperature and feed coal composition. The mechanism of enrichment is poorly understood, but is probably related to sulfate formation within the tube deposits.

Chlorine is highly depleted in all ash and slag samples. This is related to the high volatility of Cl. Also, no mineral phases with Cl have been identified by XRD. In the boiler, Cl is mostly in the form of HCl (g), which together with SO$_2$ and oxygen can diffuse to the metal surface of heating tubes and form corrosion products of iron sulfide, chloride, and oxide (Raask, 1985, p. 332). However, no significant amount of iron chloride is present in the slags because iron chlorides are volatile at superheater metal temperatures.

**CONCLUSIONS AND RECOMMENDATIONS**

1. Chemical and mineralogical investigations of hand-picked coal lithotypes of Illinois coal and their low-temperature ashes indicated that: (a) most of the Cl is adsorbed on organic matter in micropores of coal; (b) Na is largely associated with the mineral matter in adsorbed (on clays) and dissolved ionic forms; and (c) only a small portion of Cl occurs as dissolved NaCl in pore water, primarily in megapores.

2. Among the various conditions we tested in the past, it appeared that fine-grinding, heating, soaking, and multiple leaching are the most effective means of enhancing the water leachability of Cl and Na from coal. Also, the water leachabilities of Na and Cl at room temperature and at 93°C increase from vitrain, through bright banded, subbright banded, and dull coal, to fusain. This trend may be related to relative abundances of micropores and large pores in the lithotypes. The effect of using NH$_4$OH, NaOH, and NH$_4$OAc solutions of varying strengths on the leachability of Cl from coal was tested during this past year. The results showed that NH$_4$OH is more effective than NaOH and NH$_4$OAc for removing Cl from coal and, on the average, NaOH is slightly more effective than NH$_4$OAc. It can be inferred from these observations that: (a) the removal of Cl from coal is primarily an ion-exchange process involving the replacement of Cl$^-$ for OH$^-$ or OAc$^-$$^-$; (b) OH$^-$ replaces Cl$^-$ more effectively than OAc$^-$$^-$; and (c) NH$_4^+$ tends to open up pore structure
of coal making it more accessible to leaching solutions and thus increases the leachability of Cl.

(3) Jigging is effective for reducing ash and pyritic S contents of coal. For relatively coarse particle size of coal (14-20 M) that we tested, only 14-18% of Cl was removed by using a jig.

(4) Zeta potentials (surface charge) of fresh coal and low-temperature ash particles dispersed in water tend to be positive at low pH values and negative at high pH values. Adding a surfactant (#1008-11-39) to water altered the surface charges of coal and mineral matter with different degrees. This may be important for improving surface-dependent coal cleaning processes which are based on differences between the surface properties of coal and mineral matter.

(5) Mineralogy of boiler deposits is controlled by temperature regime of various boiler components as well as by initial impurities in feed coal. Alkali-sulfates which were identified in boiler deposits in this study have the potential to cause fouling and corrosion of boiler components. The amount of corrosion causing sulfates formed in boiler deposits would be related to initial alkali and sulfur contents of feed coal. Sodium, K, and Ca are often enriched in ashes relative to feed coal during the formation of sulfate phases. Chlorides were not observed in XRD analysis. However, Cl is present as determined by chemical analysis and is greatly depleted due to its high volatility. Significant amounts of Cl compounds have never been observed in superheater deposits because iron chlorides in corrosion products are volatile at superheater metal temperature (Raask, 1985).

REFERENCES


Demir I., Chou C.-L., and Chaven C (1986) Abundances and leachabilities of sodium and chlorine in lithotypes of the


Table 1. Percentages of Cl that were soluble at several time intervals during NaOH, NH₄Ac, and NH₄OH leaching of a < 60 mesh coal sample from the Herrin seam at room temperature (the sample contained 0.50% Cl on dry basis).

<table>
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<tr>
<th>Solution</th>
<th>5 min</th>
<th>10 min</th>
<th>20 min</th>
<th>30 min</th>
<th>40 min</th>
<th>50 min</th>
<th>60 min</th>
<th>120 min</th>
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<td>n.d.</td>
<td>18.9</td>
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<td>24.6</td>
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<td>23.4</td>
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<td>26.3</td>
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<td>25.5</td>
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<td>29.9</td>
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<td>25.4</td>
<td>26.9</td>
<td>28.8</td>
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a Anomalous value, probably due to contamination.
b Solution separated by centrifugation.
c Anomalous value, probably due to evaporation of solution.
d A small correction was made on previously reported values.
### Table 2. Minerals identified in boiler slags and ashes by x-ray diffraction.
The numbers refer to peak heights on the x-ray diffractogram, not quantitative abundances of minerals in the sample.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Quartz</th>
<th>Cristobalite</th>
<th>Al2O3</th>
<th>Cr2O3</th>
<th>Hematite</th>
<th>Magnetite</th>
<th>Plagioclase</th>
<th>Mullite</th>
<th>Anhydrite</th>
<th>KAl(SO4)2·nH2O</th>
<th>Na3Fe(SO4)3</th>
<th>CaO</th>
<th>Glass</th>
<th>Pyrite</th>
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<td>2?</td>
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<td>-</td>
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<td>6</td>
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<td>-</td>
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<td>4</td>
<td>6+</td>
<td>-</td>
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</table>

SH = Superheater; Sec. = Secondary
Fig. 2. Surface charge (zeta potential) of a table-cleaned composite sample of the Springfield Coal (C24598 and C24599) as a function of pH. The surfactant concentrations are 0.042 cm$^3$/l for Nos. 1008-11-31 and 1008-11-26, and 0.042 g/l for No. 1008-11-39.

Fig. 3. Surface charge of a run-of-mine sample (C23955) of the Colchester (No. 2) Coal as a function of pH. Addition of a small amount of surfactant No. 1008-11-39 (0.042 g/l) to the coal-water mixture alters the surface charge more strongly at lower than higher pH values.
Fig. 4. Zeta potentials of three clay minerals as a function of pH.

Fig. 5. Zeta potentials of two low-temperature ashes of a vitrain sample and the effect of a surfactant (#1008-11-39) on the zeta potential of one of the low-temperature ashes as a function of pH.
Fig. 6. Typical X-ray diffractograms of boiler deposits.
1 = Plant A furnace wall slag; 2 = Plant A economizer ash;
3 = Plant A fly ash. (Q, quartz; C, cristobalite; H, hematite;
M, magnetite; Ml, mullite; P, plagioclase; L, lime (CaO);
NFS, Na₃Fe(SO₄)₃)
Fig. 7. Typical X-ray diffractograms of superheater and re heater deposits. 1 = Plant A re heater; 2 = Plant A super heater; 3 = Plant B re heater; 4 = Plant B super heater. (Q, quartz; Cr, cristobalite; H, hematite; M, magnetite; M1, mullite; A, anhydrite; KAS, KAl(SO4)2·12H2O)