Coal Extraction and Utilization Research Center

Southern Illinois University at Carbondale

SIU

Mechanistic Study of Chlorine Removal from Coal by High-Temperature Leaching

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ABSTRACT

The objectives of this research were to: (1) continue the experimental investigation of removal of chlorine from coal using high-temperature leaching techniques, (2) understand the mechanisms involved in the leaching of chlorine from coal, and (3) develop a mathematical model which can be used to correlate the data and to describe the performance of the process. Efforts involved developing procedures for estimation of effective pore volumes of coal samples and measurement of surface areas of coal samples by use of carbon dioxide rather than nitrogen. Different mesh sizes of Illinois No. 6 seam and Illinois No. 5 seam coals were evaluated. Based on the pore volume and CO₂ surface areas obtained, average pore diameters were calculated for the samples examined. This information was compared to the chlorine removal of the coal samples that occurred during hot water leaching. A second aspect of this research involved study of chloride evolution rates from coal and model chlorine compounds heated in a tube furnace under continuous nitrogen flow. Kinetic parameters were determined.

INTRODUCTION

The objectives of this research were to: (1) continue the experimental investigation of removal of chlorine from coal using high-temperature leaching techniques, (2) understand the mechanisms involved in the leaching of chlorine from coal, and (3) develop a mathematical model which can be used to correlate the data and to describe the performance of the process.

Previously, we postulated the following kinetic model for the removal of chlorine from coal (Chen and Viswanath 1989):

$$\ln\left(1 - \frac{C_s}{C_o}\right) = -K t^{\frac{1}{3}} + p_R \quad (1)$$

where: $(1 - C_s/C_o)$ = the fraction of chlorine remaining in coal,

$-K t^{1/3}$ = the diffusion part, and

p_R = the relaxation part.

Our previously published work (Chen and Pagano 1986, Chen and Viswanath 1989) has investigated the effects of temperature, leaching time, and coal particle size on the hot water leaching process.

The agreement between the experimental data and model prediction was excellent. At short leaching times, the experimental data also fitted the theoretical diffusion model as shown elsewhere (Chen and Viswanath 1989). Furthermore the kinetic parameters, K and p_R , for different temperatures and coal particle sizes fitted the Arrhenius type relation:

$$K = A \exp\left(\frac{-B}{T}\right) \quad (2)$$

where A and B could be represented as a function of the coal particle size. The values of A and B fitted the equations:

$$A = \exp(-1.42 - 0.343 \ln d) \quad (3)$$

$$B = \exp(7.14 + 0.0397 \ln d) \quad (4)$$

where: d = particle diameter in cm.

Equations 1 through 4 represent the kinetic model which has been used to describe the leaching process. The correlations gave excellent fit for -60 mesh, -100 mesh, and -200 mesh coal particle sizes. For -20 mesh and -325 mesh sizes, the maximum deviation was about 25%. This shows that the validity of the proposed mathematical model for the leaching process is good.

Our previous studies employing hot water leaching of five coal samples having similar initial chlorine contents (0.4 to 0.46%) have indicated significant differences in chlorine removal under identical experimental conditions, indicating possible differences in effective pore volume and/or differences in the nature of the chemical bonds and their distribution in the coal structure. An experimental procedure was developed to permit assessment of the effective pore volume of a given coal sample. This data, together with surface area determinations using carbon dioxide rather than nitrogen, allowed calculation of mean pore diameters for the coal samples. This information was then compared to the chlorine removal obtained during hot water leaching of the coal samples.

To gain insight with respect to the type of bonding of chlorine in coal, studies were performed in a tube furnace to permit comparison of the chlorine evolution rates observed for coal, evaluated in terms of kinetic parameters, with those observed for selected model compounds.

EXPERIMENTAL

Coal Preparation

The coal samples used were an Illinois No. 6 seam coal (8601) having 0.42% CI obtained from a mine in Jefferson County, Illinois; an Illinois No. 5 seam coal (8602) having 0.40% CI obtained from a mine in Saline County, Illinois; and an Illinois No. 6 seam coal (IBCSP No. 9) having 0.42% CI obtained from the Illinois Coal Development Board sample bank. Analyses of these coals are presented in Appendix A.

Sample preparation involved grinding riffled samples to provide four different particle size ranges: -20, -60, -100, and -200 mesh (only -60 and -200 mesh samples were available for sample 8602).

Determination of Effective Pore Volume

The effective pore volume determination was performed by weighing a 1 g sample of the coal to be tested in a 50 mL beaker. Twenty-five milliliters of distilled water was added gradually, with stirring, to the coal sample. The coal/water mixture was then heated to 100° C, and maintained at the boiling point for a period of 3 hr. Warm make-up water was added at half-hour intervals, if necessary, to replace any evaporative losses. The mixture was then allowed to cool to room temperature and transferred to a tared centrifuge tube. Additional distilled water was used to rinse all coal particles from the beaker. Vacuum was applied to remove excess moisture from the sample. When no additional water was observed leaving the centrifuge tube, it was removed from the vacuum filter, capped, and weighed. The centrifuge tube was then placed in a specifically constructed centrifuge container and placed inside the centrifuge. Four tests were performed concurrently to permit balancing of the centrifuge. The timer on the centrifuge was set for the desired duration, and the weight of each centrifuge tube recorded at 1 hr intervals over an 8 hr period to

determine approach of steady-state conditions, which was defined as a weight loss of less than 0.01 g since the previous weighing. The centrifuge tubes were then dried in a 104° C oven to constant weight, and the effective pore volume calculated based on the mass of water retained per unit mass of dry coal. Since the density of water is 1.0 g/cm³, the value obtained also represents the effective pore volume of the sample, in units of cm³/g of dry coal.

The weight losses that occurred during centrifugation of the four different mesh sizes of the 8601 coal sample are presented in Appendix B. Note that following an initial large drop in weight, the weight loss became quite small. As might be expected, the effective pore volume of the coal increases slightly as the particle size decreases. The smaller particles provide greater accessibility for water to penetrate the coal structure.

It was found that the centrifuge rpm and sample size used did have an effect on the result obtained. Thus, standard conditions of a centrifuge speed of 2600 rpm and a nominal sample size of 1 g were established. The results of this procedure provide a useful tool for comparison of relative values of effective pore volume of different samples, rather than providing absolute values of that parameter.

Determination of Surface Area Using CO₂ as Adsorbate

We have found, consistent with the work of others (Thomas et al. 1976), that CO₂ used as the adsorbate for surface area determination of coals generally gives values an order of magnitude greater than those resulting when nitrogen is used as the adsorbate.

The surface area was determined by use of a Quantasorb™ surface area instrument utilizing CO₂ as the adsorbate. Approximately 0.35 g of sample was added to a preweighed U-tube sample cell, and outgassed at 105° C under a helium flow rate of 25 cm³/min for approximately 38 hr. The sample was then cooled, weighed, and

placed in the instrument for analysis. A mixture of helium and CO₂ gas at flow rates of 14 and 6 cm³/min, respectively, was passed through the sample cell, which was immersed in a Dewar flask filled with dry ice. The time required for the adsorption step varied; the IBCSP No. 9 coal usually required about 30 min. Following the adsorption step, the Dewar flask containing the dry ice was replaced with one containing water at room temperature. When the desorption signal became stable, the integrator values were recorded, and a calibration performed. The adsorption, desorption, and calibration procedures were repeated several times, and an average of the values obtained was used for the surface area calculations. Typical data obtained with the Quantasorb™ surface analyzer, using CO₂ as the adsorbate, is given in Appendix C.

Calculation of Effective Mean Pore Diameter

Values of effective mean pore diameter were calculated by assuming that all pores are right cylinders. Accordingly:

pore volume $V = (\pi d^2/4) \times L$, and

pore area $A \approx \pi \times d \times L$.

The pore diameter is determined by dividing the pore volume by the pore area, giving

pore diameter $d \approx 4V/A$.

Heat Treatment Runs

The heat treatment unit consisted of a nitrogen tank, a flowmeter, a furnace, a temperature controller, an absorber (a 400 mL beaker containing distilled and de-ionized water), a chloride electrode (Model 94-17B), a reference electrode (Model 90-02), an Orion PH/ISE meter (Model 720), and an IBM PC. The original ceramic furnace tube was replaced by one constructed of quartz, to minimize adsorption of

the HCl released from the sample, a problem encountered with earlier studies with this system. The nitrogen flow was controlled at 2.5 ± 0.3 mL/sec. Prior to starting a run, the heating tube was first purged with nitrogen at 2.5 mL/sec for 10 min. A predetermined amount of coal (about 5.0 g) was weighed accurately into a tared quartz boat which was then placed in the heating tube. The temperature controller was used to control the rate of temperature increase from ambient to reaction temperature in 1 hr, and to hold the temperature constant for the desired reaction period. The computer was used to record the chloride concentration (ppm) in the absorber over the test period. After the heat treatment was complete, the furnace was allowed to cool to room temperature, the coal sample was removed for analysis, and the tubing rinsed with approximately 600 mL of warm water. The rinse water was also analyzed for chloride content, for use in calculation of the chlorine mass balance.

In some runs, the model chlorine compounds used in the heating experiments were mixed with -200 mesh IBCSP No. 6 coal, which has only 0.02% chlorine, in proportions to provide chlorine contents similar to those of the coals studied (about 0.42% Cl). The coal was preheated in the furnace to 300° C for 1 hr to remove moisture. The coal was then allowed to cool to room temperature before the model compound was added to the coal. The three model compounds studied were treated at 250°, 300°, and 350° C as pure compounds, and at 250° and 300° C, when mixed with the low chlorine content coal. The compounds studied were 9-chloromethyl-anthracene (MD1), which has chlorine covalently bonded to a CH₂ group; neocuproine hydrochloride trihydrate (MD2), which has HCl present as a hydrate; and 10-chloro-9-anthracene-methanol (MD3), which has chlorine covalently bonded directly to an aromatic ring.

To model the chlorine evolution rate observed during heat treatment, a first order rate equation employing a time lag term was used to fit the absorber data.

$$\% \text{ removal of chlorine} = R(1 - \text{EXP}(-k(t - t^0)))$$

where: R = the % ultimate chlorine removal under the reaction conditions;
 k = the first order rate constant, hr^{-1} ;
 t = the reaction time measured from the beginning of the heating period, hr ; and
 t^0 = the time lag prior to the onset of significant chlorine evolution, hr .

The calculation procedure employed a least squares fit of the data to obtain the value of the rate constant k . The ultimate % removal values (R) were assigned equal to that attained on the 24 hr samples, based on titration of the absorbing liquid. The lag constant, t^0 , was the actual lag time observed, which was defined as the time immediately preceding the reading where chloride concentration in the absorber exceeded 10% of the 24 hr value.

RESULTS AND DISCUSSION

Average Pore Diameter Determinations

The results of effective pore volume determinations, surface areas as determined by CO_2 adsorption, and calculated average pore diameters, together with the maximum chlorine removal attained by hot water leaching of coals 8601 and 8602 are given in Table 1.

There is a general trend of increasing effective pore volume (mass ratio) with a decrease in particle size of a given coal. Presumably this reflects a greater exposure of the water to the porous structure of the coal, as particle size is reduced. A similar trend is noted for the surface areas determined for different mesh sizes of a given coal.

Table 1

Effective Pore Volume, Surface Area, Average Pore Diameter,
and Maximum Chlorine Removal by Hot Water Leaching of the Coals Studied

Coal Sample Mesh Size	Mass Ratio (g H ₂ O/g coal)	Surface Area (m ² /g)	Average Pore Diameter (Å)	Maximum Chlorine Removal by Leaching (%)
Coal 8601				
-20	0.2728	106.61	102.35	60%
-60	0.3257	139.43	93.43	
-100	0.3655	143.25	102.05	
-200	0.3578	157.94	90.61	
Average			97.11	
Coal 8602				
-60	0.2194	130.72	67.13	30%
-200	0.2714	148.96	72.87	
Average			70.00	

There is no apparent trend of average pore diameter with different particle sizes for a given coal. This is not an unexpected finding; grinding coal to different particle sizes would not be expected to affect the average pore diameter of the coal.

Note that coal sample 8601, which exhibited the higher removal of chlorine by hot water leaching, also has a greater effective pore volume and average pore diameter than the 8602 coal. This is consistent with a leaching mechanism which would permit a more effective transport of the leaching water through the larger pore structure of the coal.

Heat Treatment Runs

The first order rate constants and ultimate removal of chlorine obtained from the three model compounds are given in Table 2. These values for the IBCSP No. 9 are given in Table 3. Figures 1 through 6 illustrate these values; the average values obtained with the IBCSP No. 9 coal (an Illinois No. 6 seam coal) are included in each

Table 2

Kinetic Parameters Obtained from Heat Treatment of Model Compounds

Coal Sample Temp. (°C)	First Order Rate Constant, $k(\text{hr}^{-1})$		Ultimate Chlorine Removal (%)		Time lag term to (hr^{-1})	
	Model Compound	Model Compound + Low Cl Coal	Model Compound	Model Compound + Low Cl Coal	Model Compound	Model Compound + Low Cl Coal
MD1:						
250	2.92	0.59	98.09	63.21	0.67	0.62
300	2.72	0.44	96.33	96.01	0.25	0.58
350	1.33		78.39		0.25	
MD2:						
250	1.26	0.34	56.81	45.18	0.58	0.67
300	1.35	0.51	61.64	74.95	0.58	0.50
350	2.70		80.90		0.42	
MD3:						
250	0.54	0.46	21.34	29.96	1.17	1.17
300	2.45	0.28	47.21	47.28	0.83	1.00
350	2.76		57.17		0.67	

Table 3

Kinetic Parameters Obtained from Heat Treatment of IBCSP No. 9 Coal

Temp. (°C) Run No.	First Order Rate Constant, $k(\text{hr}^{-1})$	Ultimate Chlorine Removal (%)	Time lag term to (hr^{-1})
250:			
R-72	0.11	25.39	1.17
R-73	0.09	25.65	2.00
Average	0.10	25.52	1.59
300:			
R-71	0.23	50.54	0.83
R-74	0.26	60.02	0.83
Average	0.25	55.28	0.83

Figure 1. Comparison of first order rate constant (k) for 9-chloromethyl-anthracene (MD1) and MD1 mixed with low chlorine content coal, with IBCSP No. 9 coal.

Figure 2. Comparison of ultimate chlorine removal (R) for 9-chloromethyl-anthracene (MD1) and MD1 mixed with low chlorine content coal, with IBCSP No. 9 coal.

Figure 3. Comparison of first order rate constant (k) for neocuproine hydrochloride trihydrate (MD2) and MD2 mixed with low chlorine content coal, with IBCSP No. 9 coal.

Figure 4. Comparison of ultimate chlorine removal (R) for neocuproine hydrochloride trihydrate (MD2) and MD2 mixed with low chlorine content coal, with IBCSP No. 9 coal.

Figure 5. Comparison of first order rate constant (k) for 10-chloro-9-anthracene-methanol (MD3) and MD3 mixed with low chlorine content coal, with IBCSP No. 9 coal.

Figure 6. Comparison of ultimate chlorine removal (R) for 10-chloro-9-anthracene-methanol (MD3) and MD3 mixed with low chlorine content coal, with IBCSP No. 9 coal.

figure for comparison. Typical runs showing the % chlorine removal during heating of the IBCSP No. 9 coal are given in Figure 7.

Graphs of the data used to calculate the kinetic parameters for the model compound runs are given in Appendix D. The measured chloride content in the absorber, in terms of percent chlorine removed, is shown over a 24 hr heating period for the 15 model compound runs performed.

Table 4 presents the chlorine mass balance data for the runs given in figures 1 through 7, obtained by analyses of the model compound, model compound/coal mixture, or coal prior to and after heat treatment, and analysis of the rinse water used to clean the tube furnace following the run. With the exception of model compound 3, all of the runs exhibited chlorine mass balances greater than 87%. The high chloride content of the rinse water for MD2 is likely the result of water from that hydrated compound condensing in the system prior to the absorber.

Inspection of figures 1 through 6 indicates that all three of the model compounds tested gave rate constants nearly an order of magnitude greater than that observed for the Illinois No. 6 seam coal, when the pure compounds were used. However, when the model compounds were mixed with the coal of very low chlorine content to give a mixture of approximately the same chlorine content as the Illinois No. 6 seam coal (0.42%), the observed rate constants were reduced to values in the same range as that obtained for the coal.

CONCLUSIONS

The centrifuge technique for determination of effective pore volume of coal samples, together with surface area determinations on the same samples employing CO₂, rather than nitrogen, permitted estimation of mean pore diameter of the coal samples studied. This information was consistent with the chlorine removal attained by hot water leaching of the samples. The coal that was more readily reduced in

Figure 7. Chlorine removal observed during heat treatment of IBCSP No. 9 coal in a tube furnace under nitrogen flow at 250 and 300°C.

Table 4
Mass Balance on Chlorine*

Temp. (°C)	Run No. (Sample)	Percent of Chlorine in Coal Processed			
		Heated Product	Absorber	Rinse Water	Total
250	R57 (MD1)	/	98.09	0.84	98.93
	R63 (MD2)	/	56.81	42.79	99.60
	R75 (MD3)	/	21.34	0.38	21.72
	R62 (MD1 + coal)	21.65	63.21	10.75	95.61
	R70 (MD2 + coal)	37.22	45.18	14.59	96.99
	R68 (MD3 + coal)	52.69	29.96	2.35	85.00
	R72 (No. 9 coal)	61.44	25.39	0.85	87.68
	R73 (No. 9 coal)	60.20	25.65	2.11	87.96
300	R47 (MD1)	/	96.33	1.58	97.91
	R51 (MD2)	/	61.64	37.08	98.72
	R76 (MD3)	/	47.21	2.21	49.42
	R60 (MD1 + coal)	1.58	96.01	0.65	98.24
	R61 (MD2 + coal)	14.92	74.95	6.17	96.04
	R67 (MD3 + coal)	33.38	47.28	2.77	83.43
	R71 (No. 9 coal)	35.67	50.54	1.14	87.35
	R74 (No. 9 coal)	27.76	60.02	2.32	90.10
350	R58 (MD1)	/	78.39	17.56	95.95
	R64 (MD2)	/	80.90	18.76	99.66
	R77 (MD3)	/	57.17	1.99	59.16

*Samples as indicated.

Conditions: nitrogen flow rate 2.5 ± 0.3 mL/sec; temperature as indicated.

chlorine content by hot water leaching (8601) exhibited the greater values of effective pore volume and average pore diameter.

Results of the furnace studies indicate that when chlorine is released from the model compounds as HCl, its transport to the flowing nitrogen stream is hindered by the presence of the coal, resulting in significant lowering of the value of the first order rate constant. Since the HCl generated by the model compounds in the presence of the coal was not initially present in the pore structure of the coal, it is unlikely that diffusion would totally explain the observed effect. The reduction in

values of the rate constants describing the release of the chlorine for both the model compounds in the presence of the low chlorine coal, and for chlorine released from heated coal samples, is most likely the result of recombination of the HCl released from the model compound with reactive functional groups on the coal structure, by chemical bonding or adsorptive forces.

REFERENCES

- Chen, H. L., and M. Pagano. 1986. Removal of chlorine from Illinois coal by high temperature leaching. Fuel Processing Technology 13:261-269.
- Chen, H. L., and D. S. Viswanath. 1989. A generalized model for leaching of chlorine from Illinois coal and the effect of particle size. Fuel 68:1184-1188.
- Thomas, J., Jr., and H. H. Damberger. 1976. Internal surface area, moisture content and porosity of Illinois coals: Variations with coal rank. Circular No. 493. Urbana: Illinois State Geological Survey.

APPENDIX A

Proximate Analysis, Calorific Value, and Chlorine Content of Coal Samples 8601, 8602, IBCSP No. 9, and IBCSP No. 6

Sample	Mesh Size	Fixed Carbon wt %	Volatile Matter wt %	Ash wt %	Cal. Value Btu/lb	Chlorine Content wt %
8601	-100	NA	34.53	NA	12,725	0.42
8602	-100	NA	33.01	NA	12,869	0.40
IBCSP No. 9	-20	57.10	34.19	8.71	13,046	0.41
	-60	57.56	34.16	8.28	13,388	0.42
	100	57.46	34.14	8.40	13,021	0.42
	200	57.52	34.00	8.48	13,206	0.42
	-100	51.40	39.60	9.00	13,231	0.02

APPENDIX B

Moisture reduction during centrifugation of water saturated coal samples. Coal 8601, 2600 rpm.

MOISTURE CONTENT OF COAL BY CENTRIFUGE

C-8601, (-20,-60,-100,-200; 2600 rpm)

APPENDIX C

Typical Data for Surface Area Determination Using Carbon Dioxide as the Adsorbate

Date: 7-6-90

- Acal = Area of calibration
Acs = Cross sectional area of adsorbate molecule = $22.1\text{E}-20$ (CO_2)
As = Area of signal for adsorption
Fa = Adsorbate flow rate
Fc = Carrier flow rate
N = Avogadro's $6.02\text{E} + 23$ molecules/mole
P = Partial pressure of adsorbate = $Fa \times Pa / (Fa + Fc)$
Pa = Ambient pressure, atm
Po = Saturated vapor pressure of adsorbate = $(Pa + 30)$ mm Hg for CO_2
R = Gas constant $82.1 \text{ cm}^3 \text{ atm} / (\text{K mole})$
S = Specific area = $St / \text{Wt. sample}$
St = Sample total surface area, m^2
T = Room temperature in degree K
Vcal = Volume of calibration

Equation for surface area:

$$St = \frac{\left(1 - \frac{P}{Po}\right) \times \left(\frac{As}{Acal}\right) \times Vcal \times N \times Acs \times Pa}{R \times T} \text{ m}^2$$

Outgassing condition: Heating time (hr) = $14.4\text{E}4 \times T \times \exp(-1.77)$

Surface Area Measurement by CO₂ as Adsorbate

Date 7-6-90

Sample ID: U30-20

Coal Sample: C-8601, (-20 mesh)

Adsorbate: CO₂

Ambient Pressure, Pa: 753 mm Hg = 0.99078151 atm

Po = 783 mm Hg

Sample Weight (Pre run): 0.3242 g

Sample Weight (Post run): 0.3242 g

Room temperature = 24° C = 297.16K

Fa, CO₂ = 6 cm³/min

Fc, He = 14 cm³/min

Outgassing Condition: 38 hr, 105° C, Helium purge

P = 225.9 atm

(1-P/Po) = 0.711494

Acs, CO₂ = 2.21E-19 m²

N x Acs x Pa/(RT) = 5.405669 m²/cm³

Adsorption		Desorption		Total St (m ²)	Specific Surface Area(S) (m ² /g)	Attenuation
Time (min)	As	Vcal (cm ³)	Acal			
59	674	10.00	650	39.88	123.01	256
50	590	8.90	577	35.00	107.96	256
50	585	8.90	574	34.89	107.61	256
50	565	8.90	580	33.35	102.85	256
50	576	8.90	563	35.02	108.02	256

Average of S: 106.61 m²/g

Stand. Dev.: 2.18

Std of N-1: 2.51

APPENDIX D

Tube furnace runs using model compounds and model compounds + low chlorine content coal.

HEAT TREATMENT

PURE MD1 AT 250C

HEAT TREATMENT

MD1+COAL AT 250C

HEAT TREATMENT

PURE MD1 AT 300C

HEAT TREATMENT

MD1+COAL AT 300C

HEAT TREATMENT PURE MD2 AT 250C

HEAT TREATMENT MD2+COAL AT 250C

HEAT TREATMENT PURE MD2 AT 300C

HEAT TREATMENT MD2+COAL AT 300C

HEAT TREATMENT

PURE MD3 AT 250C

HEAT TREATMENT

MD3+COAL AT 250C

HEAT TREATMENT PURE MD3 AT 300C

HEAT TREATMENT MD3+COAL AT 300C

HEAT TREATMENT PURE MD1 AT 350C

HEAT TREATMENT PURE MD2 AT 350C

HEAT TREATMENT PURE MD3 AT 350C

END

DATE FILMED

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