THE FORM-OF-OCCURRENCE OF CHLORINE IN U.S. COALS: AN XAFS INVESTIGATION

Frank E. Huggins[1], *Gerald P. Huffman*[1], *Farrel W. Lytle*[2], *and Robert B. Greegor*[2]

[1]University of Kentucky, Lexington, KY 40506
[2]The Boeing Company, Seattle, WA 98124

ABSTRACT

X-ray absorption fine structure (XAFS) spectroscopy determinations have been made at the chlorine K absorption edge on a number of U.S. coals in order to investigate the form-of-occurrence of chlorine in the coals. The coals vary in chlorine content from 0.04 to 0.84 wt% and in rank from lignite to hvA bituminous. For the most part, the chlorine K-edge XAFS spectra of the coals are very similar and no significant variation is noted among spectra of leached samples of the same coal. The coal XANES spectra differ significantly from spectra of all organo-chlorine compounds and inorganic chlorides examined. However, spectra of hydrated chloride species, including NaCl solutions and $CaCl_2.6H_2O$, and of organic hydro-chlorides, are quite similar to the coal spectra. Analysis of the EXAFS region for the coals suggests the presence of a relatively long bond (~3.0 - 3.1Å) to water molecules in the nearest neighbor shell around the chlorine. These data and results are compatible with hydrated chloride anions in the moisture associated with coals as the major form-of-occurrence of chlorine in U.S. coals.

INTRODUCTION

Coals with appreciable chlorine contents (>0.3 wt%) can be troublesome during utilization due to the corrosive effect of chlorine on both metallic and ceramic materials. In the U.S., such problems related to chlorine content are relatively uncommon except for certain deep-mined coals from the Illinois basin in which the chlorine contents can be as high as 1 wt% (1). Although much of the chlorine in Illinois coals can be removed by aqueous leaching treatments (2,3), the form-of-occurrence in these and other U.S. coals is still not known with any certainty. Float-sink tests for "organic affinity" as developed by Zubovic (4) do not appear to have been applied to chlorine in U.S. coals. Compositional correlations have been used to suggest that chlorine has both inorganic (NaCl) and organic forms in Illinois coals (1,5). Conversely, the lack of the association of chlorine with other elements in a microprobe study of Upper Freeport coal has been interpreted as indicating organic chlorine forms (6). However, other investigators, based largely on microscopic examinations, list only inorganic chlorides, such as NaCl, KCl, $MgCl_2.6H_2O$, etc., as the primary occurrences of chlorine in coal (7,8). Chakrabarti (9), working principally with Gondwana coals, has described detailed analytical procedures for determining both organic and inorganic forms of chlorine in coal. British researchers working with their native high chlorine coals for the most part have proposed that most, if not all, of the chlorine in coal is inorganic and derived from NaCl-rich ground waters penetrating the coal seam (10,11). Recent pyrolysis/mass spectroscopic work (12) on British coals has rather convincingly confirmed this occurrence.

X-ray absorption fine-structure (XAFS) spectroscopy is perhaps the best method currently available for elucidating the local structure and bonding of a specific element in a complex, heterogeneous, noncrystalline matrix such as coal. Not only can the element be investigated directly in coal at quite dilute levels (~100 ppm), but, in principle, information about the immediate coordinating ligands can also be derived from an analysis of the XAFS spectrum. In this work, XAFS spectroscopy

was used to examine the occurrence of chlorine in a number of U.S. coals. From these measurements it can be concluded that much, if not all, of the chlorine in these coals is present as chloride anions in the moisture associated with the pores and microcracks of the coal matrix.

EXPERIMENTAL

Samples: Pulverized samples of as-collected Illinois basin coals and the same coals subjected to an aqueous leaching treatment were provided by Professor H. L. Chen, Southern Illinois University. These samples were originally collected by the Illinois State Geological Survey. Other coal samples used in this study were selected from the Pennsylvania State University coal bank on the basis of their high chlorine contents. Chlorine contents and apparent rank data for the coals are listed in Table I. A large number of standard organochlorine compounds and inorganic chlorides were also assembled for XAFS spectral measurements, including:

Aryl chlorides: 1,2,4,5-tetrachlorobenzene, 9,10-dichloroanthracene, 2,6-dichlorophenol;

Acyl chlorides: diphenylacetyl chloride, 2-naphthoyl chloride;

Alkyl chlorides: polyvinylchloride, 1,2-bis(chloromethyl)benzene, 1,4-bis(chloromethyl)benzene;

Org. hydrochlorides: semicarbazide hydrochloride, tetracycline hydrochloride;

Gases and vapors: Cl_2, CCl_4, $C_2H_4Cl_2$;

Alkali chlorides: NaCl, KCl, RbCl, CsCl, saturated NaCl solution;

Alk. earth chlorides: $CaCl_2$, $SrCl_2$, $CaCl_2.2H_2O$, $CaCl_2.6H_2O$;

Misc. Cl compounds: $KClO_3$, $H_2PtCl_6.6H_2O$, Hg_2Cl_2, $HgCl_2$, $CuCl_2$, CuOCl.

XAFS Experiments: XAFS experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) under dedicated running conditions. Electron energies were held at 3.0 Gev while the beam current decayed from 80 to 40 mA between beam fills, which were typically eight hours or more apart. A pure helium path to the sample was employed to minimize attenuation of the X-ray intensity at the low energies in the vicinity of the chlorine K absorption edge (2820-2835 eV). XAFS spectra were recorded in fluorescent geometry in a Stern-Heald type detector (13) for all coals and standards from approximately 100 eV below the edge to about 400 eV above the edge using a rotating double crystal Si(111) monochromator. At the high-energy end of the scan, the K absorption edge for argon (from air contamination in the beam path) was encountered at 3205 eV. This edge served effectively as an internal energy calibration point. The X-ray near-edge structure (XANES) data and spectra shown in the paper are given relative to the zero point defined as the maximum in the differential of the XAFS spectrum of sodium chloride, which occurs at 2826 eV. It was found that the variation in position of the argon edge relative to the NaCl zero point was less than 0.1 ev for the different spectra measured. Spectra were obtained from the coal samples and from solid standards as pressed pellets in pressed boric acid (HBO_3) supports; liquid samples were contained in mylar bags or on filter papers; gaseous and vaporous species were introduced to the sample chamber at dilute (<1%) levels in helium (14). Analysis of the spectral data was performed on a MicroVAX II computer using conventional methods (15,16) for the XANES and extended fine-structure (EXAFS) regions of the spectra.

TABLE I: COALS EXAMINED BY CHLORINE XAFS

Coal Seam & State	Rank	Wt% Chlorine	Source
#6 seam, Illinois*	hvAb	0.82	C-20154 (ISGS)
#6 Seam, Illinois*	hvAb	0.42	C-8601 (ISGS)
-- after 1st. leaching		0.24	
-- after 2nd. leaching		0.12	
#6 Seam, Illinois*	hvAb	0.42	C-22175 (ISGS)
-- after 1st. leaching		0.18	
-- after 2nd. leaching		0.13	
Pittsburgh, PA	hvAb	0.22	USS Mining
Elkhorn #3, KY	hvAb	0.33	PSOC - 1475
Mineral seam, KS	hvAb	0.27	PSOC - 251
Mineral seam, OK	hvAb	0.24	PSOC - 768
Wildcat sbb, TX	sbbC	0.06	PSOC - 639
Beulah lignite, ND	lig	0.04	PSOC - 1483

*supplied by Prof. H. L. Chen, Southern Illinois University

RESULTS

XANES Spectra: Figure 1 shows the XANES spectra of an Illinois #6 coal that contains 0.42 wt% chlorine and two samples obtained from the coal after aqueous leaching treatments (2,3) that first reduced the chlorine content to 0.24 wt% and then to 0.12 wt%. It is obvious from this sequence that the chlorine K-edge absorption spectrum is not significantly changed by the leaching treatments and therefore it can be concluded that chlorine has only one significant form-of-occurrence in this coal. Furthermore, the reason that chlorine becomes progressively more difficult to remove from the coal is not because of the response of different forms of chlorine to the leaching treatment but because the one form-of-occurrence of chlorine becomes less accessible or more strongly bound to the coal as its abundance decreases.

Very similar XANES spectra to those in Figure 1 are exhibited by all the coals listed in Table I with two exceptions: the Illinois coal with the highest chlorine content (0.84 wt%) and the Beulah lignite with the lowest chlorine content (0.04 wt%). Figure 2 documents the similarity of the chlorine K edge XANES spectra of three coals from different coal basins. Figure 3 shows the XANES spectrum of chlorine in the two Illinois coal with highest chlorine contents. The differences between these spectra can be explained readily by the presence of a minor component (<25%) of crystalline NaCl in the Illinois #6 coal with 0.84 wt% chlorine. The extra peaks in the spectra of this coal match exactly with prominent peaks in the spectrum of NaCl, which is also shown in Figure 3. The XANES spectrum of the Beulah lignite, although very weak, differs significantly from those of the other coals and the position of its main peaks are well outside the ranges for the two peaks present in the spectra of the coals of higher rank. Based on XANES peak position

TABLE II: CHLORINE XANES DATA SYSTEMATICS*

Compound	Zero Point (ev)	1st. Peak (ev)	2nd. Peak (ev)
Mercury chlorides	-3.62 - -3.60	-3.0 - -2.6	13.4 - 13.6
Alky' chlorides	-3.35 - -2.80	-2.5 - -1.2	11.0 - 20.8
Acyl chlorides	-2.60 - -2.50	-1.3 - -1.0	15.3 - 20.9
Aryl chlorides	-2.40 - -2.00	-0.8 - -0.4	16.1 - 19.2
Beulah lignite	-1.80	-0.7	18.5
All other coals	-1.75 - -1.20	0.9 - 1.3	19.0 - 21.2
Sat. NaCl solution	-1.55	0.2, 3.1	20.9
Organohydrochlorides	-1.10 - -1.00	1.1 - 2.1	19.2 - 20.7
Alkali chlorides	-0.90 - 0.00	0.4 - 2.2	16.9 - 20.6
Hydrated Ca chlorides	-0.75 - -0.60	2.3 - 2.5	21.6
Alk. earth chlorides	-0.60 - -0.45	1.7 - 2.1	19.0 - 19.6
Copper chlorides	-0.60 - -0.30	1.4 - 3.0	19.8 - 27:3
Chloroplatinic acid	-0.20	4.2	18.7
Potassium chlorate	4.20	5.8	18.5

Energies of zero point and peaks relative to zero point for NaCl.
*For most standard chlorine compounds, data are given only for the two peaks that most closely match the peaks in the coal spectra.

systematics (Table II), the XANES spectrum from chlorine in the lignite is most similar to that from chlorine bound to aromatic rings. However, given the low abundance of chlorine in this coal and the poor quality spectrum, it is perhaps premature to conclude that this coal has a significantly different form-of-occurrence for chlorine.

With the possible exception of the lignite, the data in Table II and the general appearance of the XANES spectra from chlorine in the coals, compared to those of the numerous standard chlorine compounds examined, indicate that the form-of-occurrence of chlorine is clearly neither an organochlorine compound nor one of the traditional crystalline inorganic chlorides. The substances that most closely resemble the XANES spectral data from chlorine in coal are (i) $CaCl_2.6H_2O$, (ii) saturated NaCl solution, and (iii) organohydrochlorides. A comparison of the XANES spectra of these substances to that of the Illinois #6 coal is shown in Figure 4. The XANES spectra of all three substances exhibit an overall general similarity to the coal spectra, but minor dif-ferences are apparent upon close inspection so that it can not be concluded that one or other of these substances is the preferred match. However, all three substances do have some structural and bonding features in common that are, no doubt, reflected in similar XANES spectra: (i) chlorine is present in these substances as chloride anions, (ii) the bonding is relatively weak and largely ionic in character, and (iii) the chlorine-oxygen or chlorine-nitrogen distances are quite long: between 3.0 and 3.2Å (17,18). The chlorine in coals can be expected to be similar.

EXAFS Spectra: As is usually done (15,16), the EXAFS regions of the spectra were treated mathematically first to isolate the EXAFS periodic structure from the absorption step. Then, by converting this oscillatory structure to a wave vector representation and performing a Fourier transform, a radial structure function (RSF)

is obtained that represents the distribution of shells of atoms or ions around the chlorine atom or ion. Satisfactory radial structure functions were obtained for most of the standard compounds and for some of the coals with the higher chlorine contents. RSFs for the aryl compounds were noticeably more complex than those for the acyl and alkyl organochlorine compounds. This observation reflects the rigid structural relationship of the chlorine to the six carbons of the benzene ring present in the aryl compounds but which is lacking when chlorine is in a peripheral -COCl or $-CH_2Cl$ group that has some rotational freedom. The RSFs for compounds with these latter groups resemble those obtained from the simple molecules, CCl_4, $C_2H_4Cl_2$, etc.

Radial structure functions for chlorine in the inorganic compounds were generally complex and lacking in any strong correlative trends. Given the variety of structures and the range in degree of covalency exhibited by these compounds, this should not be surprising. $CaCl_2.6H_2O$ has a structure (17) in which the Ca and Cl ions are not nearest neighbors but are separated by water molecules. Hence, this compound can act as a model compound for chloride anions surrounded by water molecules. The RSF for this compound is shown in Figure 5a; it is dominated by one major peak representing the coordination shell of six water molecules at a distance of 3.1 - 3.2Å from the central chloride anion. Bond-lengths were extracted from the better RSFs of chlorine in coals (e.g. Figure 5b) using the phase-shift data obtained empirically from $CaCl_2.6H_2O$ for the water molecule shell at ~3.15Å. An excellent correlation of the phase shifts was found at a $Cl-H_2O$ distance of 3.03Å for the coals. The phase-shift data correlated considerably better than that between $CaCl_2.6H_2O$ and the saturated NaCl solution, which implies, perhaps, that the chlorine anions in the saturated NaCl solution have significant contribution from sodium ions in the nearest neighbor shell. The RSFs for the organic hydrochloride compounds consist of one major peak at similar distances (3.1 - 3.3Å) arising from nitrogen atoms in basic amine groups to which the chloride anions are bound (18). However, correlation of the Cl-N phase-shift data with the coal data was not as good as that found between $CaCl_2.6H_2O$ and chlorine in coal. Although such distinctions are not necessarily definitive, the analysis of the EXAFS region does appear to favor water molecules as the most likely environment around chlorine in the coals examined.

CONCLUSIONS

Analysis of chlorine K-edge XAFS data for a number of U.S. coals has shown that in the majority of the coals chlorine is present in a single form as chloride anions in the moisture associated with the microcracks and pores of the coal. In the coal with the highest chlorine content, a second form-of-occurrence was also identified, namely crystalline NaCl, which presumably had precipitated from the chloride-rich solution as the coal dried. The only other exception was a low-chlorine lignite, in which chlorine appeared to be present in organic form. However, given the very low chlorine concentration (0.04 wt%) and the related poor spectral quality, it is premature to attach much significance to this observation at this time.

With chloride anions in moisture as the predominant form-of-occurrence of chlorine in U.S. coals, it is relatively easy to rationalize some of the apparently contradictory conclusions made in previous investigations regarding whether chlorine is inorganically or organically bound in coal. As a result of the association of chlorine with coal moisture, chlorine will have properties similar to a dispersed organically bound element. For example, in microprobe or SEM X-ray mapping techniques, chlorine will be found to be distributed widely in low concentrations in macerals and not strongly correlated with other elements, and in float-sink tests of "organic" affinity, chlorine will favor the maceral-rich float fractions.

Conversely, observations of specific inorganic chlorides in coals can be explained as precipitates that crystallize as the coal moisture evaporates.

With the form-of-occurrence of chlorine now established for U.S. coals, it would appear that it should be possible to remove virtually all of the chlorine from troublesome coals by the combination of fine grinding and aqueous leaching treatments. It is interesting to note that a similar treatment was used by British researchers to remove the supposed "organic" chlorine fraction from an Illinois #6 coal that was left after earlier leaching treatments (12). Alternatively, the fact that the chlorine is now known to be associated with the moisture in coal may lead to new methods for chlorine removal.

ACKNOWLEDGEMENTS

We are grateful to Professor Han Lin Chen of Southern Illinois University for providing us with samples of raw and leached Illinois #6 coals. This work was supported by the U.S. DOE under Contract No. DE-FG22-86 PC90520. We also acknowledge the U.S. DOE for its support of the Stanford Synchrotron Radiation Laboratory, where the XAFS experiments were performed.

LITERATURE CITED

1. H. J. Gluskoter, and R. R. Ruch, Fuel, 50, 65, (1971)
2. H. L. Chen, N. M. Rao, and D. S. Viswanath, Fuel Proc. Technol., 13, 261, (1986)
3. H. L. Chen, and M. Pagano, Fuel Proc. Technol., 13, 271, (1986)
4. P. Zubovic in: Coal Science, (ed. R. F. Gould), Advances in Chemistry Series, Volume 55, 221, American Chemical Society, Washington, D. C., (1966)
5. H. J. Gluskoter, R. R. Ruch, W. G. Miller, R. A. Cahill, G. B. Dreher, and J. K. Kuhn, Illinois State Geological Survey, Circular 499, (1977)
6. J. A. Minkin, E. C. T. Chao, and C. L. Thompson, ACS Division of Fuel Chemistry, Preprints, 24(1), 242, (1979)
7. M. T. Mackowsky, Chapter 2.23 in: Stach's Handbook of Coal Petrology, (eds. E. Stach et al.), 121, Gebrüder Borntraeger, Berlin, W. Germany, (1975)
8. R. B. Finkelman, and R. W. Stanton, Fuel, 57, 763, (1978)
9. J. N. Chakrabarti, Chapter 10 in: Analytical Methods for Coal and Coal Products, (ed. C. Karr, Jr.), Vol. 1, 323, Academic Press, New York, (1978)
10. S. A. Caswell, Fuel, 60, 1164, (1981)
11. N. J. Hodges, W. R. Ladner, and T. G. Martin, J. Inst. Energy, 56, 158, (1983)
12. G. Fynes, A. A. Herod, N. J. Hodges, B. J. Stokes, and W. R. Ladner, Fuel, 67, 822, (1988)
13. E. A. Stern, and S. Heald, Rev. Sci. Instrum., 50, 1579, (1979)
14. F. W. Lytle, R. B. Greegor, E. C. Marques, D. R. Sandstrom, G. P. Huffman, and F. E. Huggins, Stanford Synchrotron Radiation Laboratory Activity Report for 1986, 87/01, 115, (1987)
15. P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid, Rev. Mod. Phys., 53, 769, (1981)
16. G. S. Brown, and S. Doniach in: Synchrotron Radiation Research, (eds. H. Winick and S. Doniach), 353, Plenum Press, New York, (1980)
17. R. W. G. Wyckoff, Crystal Structures, Vol. 3, J. Wiley & Sons, New York, (1963)
18. R. W. G. Wyckoff, Crystal Structures, Vol. 6, J. Wiley & Sons, New York, (1969)

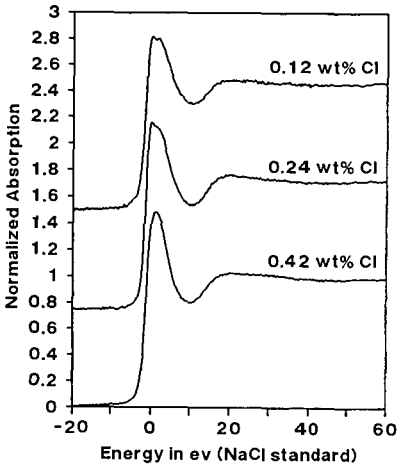

Figure 1. Chlorine K-edge XANES spectra of Illinois #6 coal and two samples of same coal after leaching treatments. Note the similarity of the spectra.

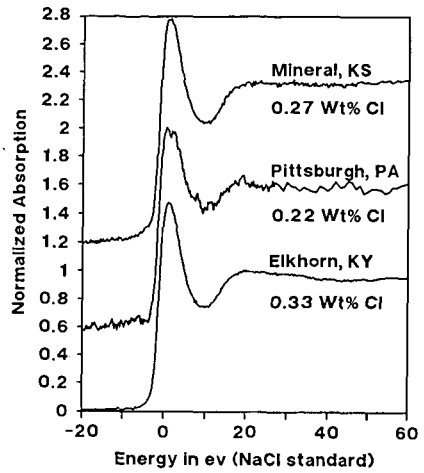

Figure 2. Chlorine K-edge XANES spectra of three coals from different states and geological provenances. Note the similarity of the spectra.

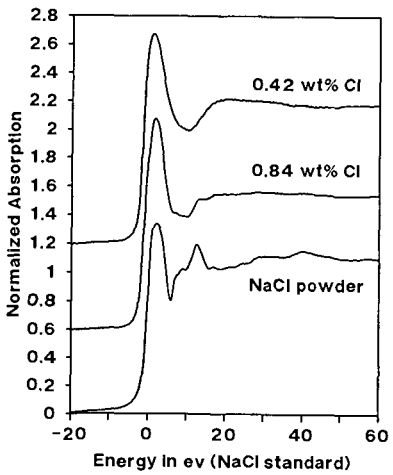

Figure 3. Chlorine K-edge XANES spectra of two high-chlorine Illinois #6 coals and of NaCl.

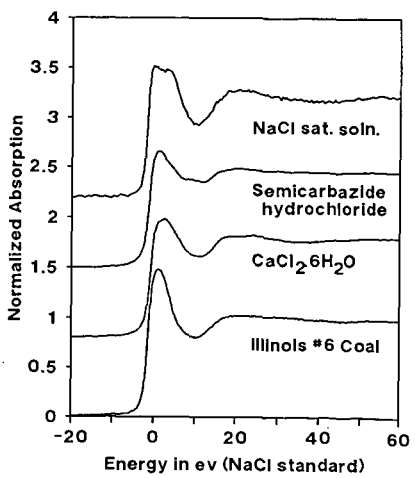

Figure 4. Chlorine K-edge XANES spectra of Illinois #6 coal and various standard Cl compounds with similar spectra.

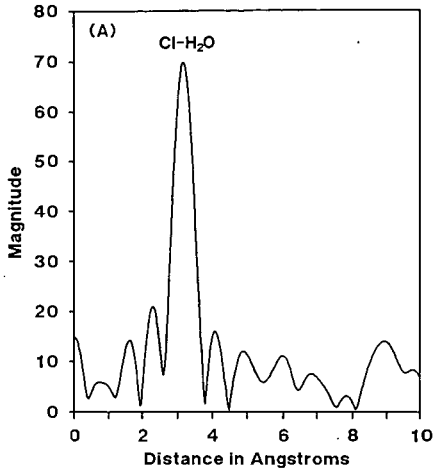

Figure 5(a). Phase-shift corrected radial structure function for the compound, $CaCl_2.6H_2O$.

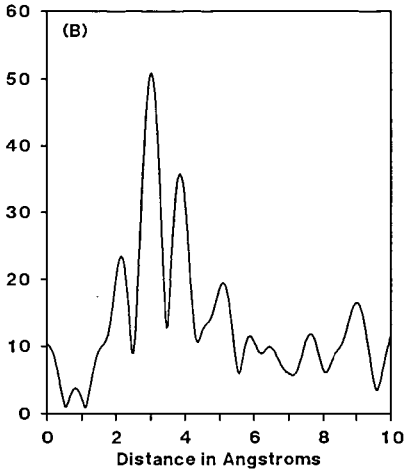

Figure 5(b). Phase-shift corrected radial structure function for chlorine in an Illinois #6 coal.