

## REMOVAL OF TRACE ELEMENTS DURING CHEMICAL CLEANING OF COAL

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### ABSTRACT

Different samples of Illinois No. 6 coal, which had been treated with aqueous  $\text{Na}_2\text{CO}_3$  solutions at elevated temperatures and pressures and with molten  $\text{NaOH/KOH}$  mixtures at atmospheric pressure in order to remove sulfur and ash, were analyzed for trace elements before and after treatment. Although removal of sulfur and ash were the primary objectives of those treatments, the removal of trace elements by these chemical cleaning methods was investigated in this work. X-ray fluorescence, atomic absorption, and inductively coupled plasma-atomic emission spectroscopy were the instrumental methods used to determine levels of numerous trace elements in the raw and treated coals. In general, the aqueous  $\text{Na}_2\text{CO}_3$  treatments reduced levels of Mn, Pb, and Zn by 75% or more, while levels of Cd and Ni were reduced by lesser amounts. In one run, significant reductions in the levels of Ba, Cr, Rb, Se, and Sr were also observed. The coals treated by the molten caustic showed substantial reductions in concentrations of As, Cd, Hg, Pb, Rb, Se, Sr, and Zn. However, levels of Cr and Ni were elevated in the treated coals, probably due to corrosion of the reactor components.

### INTRODUCTION

Coal contains virtually every element, most of which are present in trace quantities of 100 ppm or less. Many of these trace elements are toxic to plant and animal life, even at low concentrations. Because power plants consume on the order of 600 million tons of coal annually for the production of electricity (1), coal combustion can mobilize thousands of tons of potentially hazardous trace elements into the environment each year. Because of the large quantities of coal combusted, even trace amounts of toxic elements can accumulate to hazardous levels. Also, potentially deleterious effects of particulate stack emissions from coal combustion may be enhanced since many trace elements are surface enriched (2) and concentrate preferentially in the smaller, more respirable particle sizes (3).

Aside from the detrimental environmental aspects of trace elements in coal, there are also adverse technological aspects of trace elements in coal, such as catalyst poisoning in catalytic hydrogenation and gasification reactions (4,5,6).

Physical methods can effectively remove some trace elements from coal, especially if deep cleaning methods are employed (7). However, such methods do not adequately remove finely disseminated minerals or organically bound elements, thereby necessitating chemical treatments for removing many of the deleterious elements in coal.

A literature survey was conducted to acquire information pertinent to the removal of trace elements from U.S. coals by chemical means. This survey included trace element associations with minerals and the affinities of trace elements for organic or inorganic components. Previous studies on chemical cleaning methods were also reviewed in order to ascertain any reductions in trace element contents. A thorough literature survey of all chemical cleaning methods revealed that caustic or alkaline treatments, especially when followed by an acid wash, are very effective in removing ash-forming minerals.

\*Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

In this study, the effectiveness of trace element removal by two chemical coal cleaning methods was examined. One method involved treatment with aqueous  $\text{Na}_2\text{CO}_3$  solutions, and the other involved treatment with molten  $\text{NaOH/KOH}$  mixtures. In each case, acid washes were used as subsequent cleaning steps to decrease the ash content, followed by water washes in the final step.

#### BACKGROUND

Based on the reviewed literature, it is evident that modes of occurrence in U.S. coals vary considerably, although several generalizations can be made. Many elements of environmental concern, including As, Cd, Hg, Pb, and Zn, generally associate with the mineral portion of the coal and tend to associate with pyrite or accessory sulfide minerals. The element As has been found to occur in solid solution in pyrite (8), while Cd has been found in solid solution in sphalerite (9,10). The predominant mineral species containing a particular element can vary. In one example, Pb seems to be present mostly as  $\text{PbSe}$  in Appalachian Basin coals, but it tends to exist in the form of  $\text{PbS}$  in coals from other regions (8,11). Minerals in coal often occur, at least partially, as finely disseminated grains. Although most trace elements appear to be largely inorganically associated, several of them have a strong affinity for the organic portion of the coal and are believed to be present as metal chelates. Among the elements in the latter category are B, Be, and Ge. Many elements, such as Cr, Cu, Ni, and Se, appear to have a mixed or highly variable organic/inorganic affinity in some coals. Again, these are only generalizations, since organic/inorganic associations of trace elements can vary widely from coal to coal and can show both extremes in their affinities.

A literature review on trace element removal by chemical cleaning methods indicated that leaching coals with various acids to study trace element removal was common. In one study, various coals from eastern, central, and western coal regions were cleaned by a combination of physical and chemical means, and extraction efficiencies for numerous elements were ascertained by analyzing the raw and treated coals (12). Cleaning was performed by floating the coals at a specific gravity of 1.40, grinding the float fraction to -325 mesh, and then successively leaching with 10%  $\text{HNO}_3$ , 49%  $\text{HF}$ , and 25%  $\text{HCl}$ . Results of the analyses on the raw and cleaned coals showed that levels of Be were reduced by 90% or more, while levels of As, B, Cr, Cu, Mo, Ni, Se, and V were reduced by at least 70%. However, these are only average values, and standard deviations were sometimes larger than the averages. In that study, physical separation by flotation followed by acid leachings was found to be much more efficient at removing trace elements than flotation alone.

Results on trace element removal during desulfurization and demineralization by a chemical treatment are sparse. Only a few of the chemical cleaning processes studied in the past or currently being developed present trace element data in addition to the conventional sulfur, ash, and heating values.

One of these exceptions is the Jet Propulsion Laboratory Chlorinolysis Process, in which cleaning was generally accomplished by bubbling chlorine through a mixture containing 100 grams of finely ground coal, 200 grams of solvent (either methylchloroform, carbon tetrachloride, or tetrachloroethylene), and 20-70 grams of water (13). The chlorination step was conducted at 50-100°C at atmospheric pressure for 10-20 minutes. The coal was then hydrolyzed by washing with water for 60-120 minutes at 60-100°C and subsequently dechlorinated at 350-550°C in a steam atmosphere. For some coals treated under these conditions, levels of As, Be, Pb, and V were reduced by 50-90% (13,14).

In another one, the Battelle Hydrothermal Process (15,16), an aqueous slurry of finely ground coal,  $\text{NaOH}$ , and  $\text{Ca(OH)}_2$  was heated for 10-30 minutes at 250-350°C at pressures of 600-2500 psig. Based on averages from several Ohio coals, this process reduced levels of As, B, Be, Pb, and V by 70-90% (16).

In yet another chemical cleaning process, the Meyers Process, crushed coal was leached with an acidic solution of ferric sulfate at 100-130°C for several hours (17). If the leaching time was long enough, almost all of the pyritic sulfur was extracted. At the same time the content of many trace elements, such as As, Cd, Cr, Mn, Ni, Pb, V, and Zn was significantly reduced (18). Still, the data discussed above represent only a small fraction of the chemical processes that have been studied.

#### EXPERIMENTAL

Because caustic or alkaline treatments are relatively effective at removing ash-forming minerals from coal, particularly when followed by an acid wash, the extraction efficiency of trace elements was assessed for several of these treatments in this study. Two samples of an Illinois No. 6 run-of-mine coal were obtained which had been treated for one hour with 1.0 M  $\text{Na}_2\text{CO}_3$  at 250°C in an inert atmosphere (19). One of the samples was then washed with 2.0 M HCl to obtain the final product. The other sample was first pretreated with 0.2 M  $\text{Na}_2\text{CO}_3$  at 150°C for one hour under 13.6 atm. oxygen, then treated as the above sample in an inert atmosphere, and subsequently washed with 1.8 M  $\text{H}_2\text{SO}_4$ . All the  $\text{Na}_2\text{CO}_3$  treatments were performed under pressure in an autoclave.

Two additional samples were obtained from a different Illinois No. 6 coal used for molten caustic treatments at Ames Laboratory under conditions simulating the TRW Gravimelt Process. In that process, coal was treated with a molten 4:1 NaOH/KOH mixture for one hour at 370°C. After separating and washing the coal with water, the coal was treated with 10%  $\text{H}_2\text{SO}_4$  and then with a final water wash. Two runs were made, one being made in the normal manner and the other with powdered reagent-grade iron included in the coal/caustic mixture. The iron was added in hopes that it would act as a sulfur scavenger and improve coal desulfurization.

In addition to these samples, several coal samples were provided by TRW Systems, Inc. (Redondo Beach, CA). The samples represented Illinois No. 6 and Pittsburgh No. 8 coals before and after treatment by the Gravimelt Process.

#### ANALYTICAL METHODOLOGY

All coals were analyzed at Ames Laboratory using energy-dispersive x-ray fluorescence (ED-XRF), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and atomic absorption spectrophotometry (AA).

For the determinations of Cd and Pb by AA, the coal samples were ashed at 500°C and the ashes were subsequently dissolved in accordance with procedures described in ASTM Method D-3683 (20). Basically, the ash was dissolved in a mixture of  $\text{HNO}_3$ , HCl, and HF in a tightly capped plastic bottle in a steam bath. Saturated  $\text{H}_3\text{BO}_3$  solution was then added to the mixture to complex the excess fluoride and to improve flame properties during AA measurements. For the AA determinations of As, Sb, and Se, sample solutions were prepared by first treating the coal with hot  $\text{HNO}_3$  and then with fuming  $\text{H}_2\text{SO}_4$ . For these dissolutions, an Erlenmeyer flask-reflux cap apparatus was used (21). Conventional flame AA was used for the Cd and Pb determinations, while hydride generation AA was used for the As, Sb, and Se. For the Hg determination, a portion of the coal was placed in a Parr bomb containing 10%  $\text{HNO}_3$ . After ignition, the contents of the bomb were washed into an Erlenmeyer flask, and  $\text{SnCl}_2$  solution was added to the mixture to reduce the Hg for conventional cold vapor AA measurements. Corrections were made for reagent blanks in all analyses by AA.

For the coals analyzed by XRF, samples that were +60 mesh were first ground to -60 mesh with a boron carbide mortar and pestle. The samples were then prepared by mixing two grams of sample with 0.2 grams of Somar Mix, a granulated plastic binding

agent. If less than two grams of sample were available, the amount of binding agent was scaled down proportionally. The powder was then pressed into disks at a pressure of about 5000 psi. The XRF analyses were performed using a Mo-target x-ray tube.

Analyses by ICP were performed on the same dissolutions used for the AA analyses for Cd and Pb. The solutions were diluted as necessary and were then nebulized and introduced into the plasma. Line spectra were collected with a multi-channel analyzer and corrections were made for reagent blanks and background shifts. For all analyses, NBS Standard Reference Material 1632, a bituminous coal, was used for instrument calibration.

## RESULTS AND DISCUSSION

Results of the analyses on coals before and after treatment with aqueous  $\text{Na}_2\text{CO}_3$  solutions and molten  $\text{NaOH/KOH}$  mixtures at Ames Laboratory are shown in Table 1. Levels of Cd, Pb and Zn were relatively high in the raw Illinois No. 6 run-of-mine coal used for the  $\text{Na}_2\text{CO}_3$  treatments. The elevated Cd levels correlate well with the high Zn levels, since Cd in coal is commonly associated with sphalerite ( $\text{ZnS}$ ). The Pb was probably present largely as galena ( $\text{PbS}$ ). For the alkali-treated coal washed subsequently with  $\text{HCl}$ , levels of Mn, Pb, Rb, Sr, and Zn were reduced by 75% or more, while levels of Ba, Cd, Cr, Ni, and Se, were reduced by 30-60%. The coal that had been pretreated showed reductions of 75% or more for Mn, Pb, and Zn, while Cd and Ni were reduced by 60% or more. It is interesting to note that every alkali and alkaline earth metal determined was enriched in the pretreated coal relative to the coal that was leached with no pretreatment. Some of these, such as Ba and Ca, were more concentrated in the pretreated coal than in the raw coal. The reason for the elevated levels of Ba, Cu, Se, and Sr in the pretreated coal is uncertain at this time.

Analysis of the XRF data on coals treated with molten caustic at Ames Laboratory (Table 1) showed that levels of Fe, which is predominantly associated with pyrite in coal, was reduced by about 90% for each of the two runs. Reductions in concentrations of other elements which form abundant minerals in coal, including Al, K, and Si, were also substantial. Because roughly 90% of the ash was removed, substantial concentration reductions in the major mineral-forming elements are expected. Of the trace elements, levels of Ba, Rb, Sr, and Zn were reduced by 70% or more and Se was reduced by 30% or more in the coal treated in the normal fashion (Run 1). In the coal from the test containing the iron additive (Run 2), levels of Rb, Sr, and Zn were also reduced by 70% or more. Pb levels remained essentially constant for each of the treated coals. The elevated Cr and Ni levels are believed to be corrosion byproducts from the reactor.

In the coal treated by molten caustic in Run 2, the Cr and Ni levels are significantly higher than in Run 1, suggesting a more severe attack in the second test. If the attack were more severe, then levels of Fe, Al, Si, and ash would be anticipated to be somewhat lower than in Run 1. As can be seen from these data, this is indeed the case. However, despite the apparently more severe attack in Run 2, overall trace element reductions did not seem to be significantly improved.

In the coals treated by the Gravimelt Process at TRW (Table 2), the ash content was decreased to 1% or less, and levels of As, Be, Cd, Hg, Pb, Se, Sr, and Zn were reduced by 75-95%. It is interesting to note that most of these elements are commonly associated with pyrite. Thus, substantial reductions in levels of these elements can be anticipated when most of the pyrite is removed (as indicated for both coal samples). In addition, the levels of Ba, Ge, Mn, and Rb were also reduced; however, the reduction levels are not as prominent nor as clear-cut.

Table 1. XRF Data on Coals Before and After Treatment.<sup>a</sup>

	Molten NaOH/KOH Treatment			Aqueous Na <sub>2</sub> CO <sub>3</sub> Treatment		
	Raw Ill. No. 6	Run 1	Run 2 <sup>b</sup>	Raw Ill. No. 6	Run 1	Run 2 <sup>c</sup>
Ash (%)	14.17	1.24	1.02	13.24	2.61	2.97
Ag	<2	<20	<2	<20	<20	<20
Al (%)	1.9	0.72	0.29	2.0	0.70	0.79
As	3.4	1.0	3.8	<5	2.1	<1.0
Ba	49	<10	36	27	17	59
Br	1.7	<1.0	<1	2.7	6.3	5.7
Ca	5650	<284	<247	4560	264	7180
Cd	<2	<20	<2	49	<20	20
Cl (%)	<1100	<0.1	<0.5	<0.1	0.86	<0.1
Cr	27	58	144	26	18	98
Cu	12	<61	<113	38	53	2100
Fe (%)	1.19	0.189	0.142	1.50	0.87	0.12
Ga	2.9	5.4	1.4	<12	4.5	<4.5
Ge	<2	<1.0	<2	<17	5.1	5.3
K	1960	810	804	1775	65	1260
Mn	51	<18	22	62	14	9.5
Ni	20	241	344	24	14	<10
Pb	14	17	10	210	10	24
Rb	10	<1.0	<1	9.6	<1.0	7.5
S <sup>d</sup> (%)	4.52	0.96	0.84	3.71	2.40	1.84
Sb	<2	<20	<5	<20	<20	<20
Se	1.8	<1.0	<2	3.0	1.2	9.1
Si (%)	3.1	0.64	0.18	2.6	0.68	1.5
Sr	24	1.0	<2	11	<1.0	42
Ti	640	240	165	700	610	450
V	<150	<25	<19	<78	<61	<58
Zn	49	11	8.2	1100	36	<240

<sup>a</sup> Values are in ppm unless otherwise noted and are corrected to a dry basis.

<sup>b</sup> Powdered iron included in coal/caustic mixture.

<sup>c</sup> Pretreated with 0.2 M Na<sub>2</sub>CO<sub>3</sub> and oxygen.

<sup>d</sup> Determined by a high-temperature combustion instrumental method.

Table 2. XRF, AA, and ICP Data on Raw and Chemically Cleaned Coals Received from TRW Systems, Inc.<sup>a</sup>

	Illinois No. 6		Pittsburgh No. 8		
	Raw	Cleaned	Raw	Cleaned	
Ash (%)	9.23	0.53	9.88	1.00	
Pyr. S (%)	1.04	0.02	1.78	0.01	
Hg	0.28	0.04	0.15	0.10	A A D A T A
Pb	5.8	1.4	5.6	1.4	
Cd	0.70	0.16	0.44	0.024	
As	0.33	0.14	3.9	0.18	
Sb	0.09	0.08	0.06	0.06	
Se	1.5	0.6	1.6	0.19	
Ag	<20	<20	<20	<20	
Al (%)	1.6	<0.7	1.2	<0.7	
As	<5	<10	<10	<5	
Ba	40	<40	~30	<40	
Ba*	<25	<0.4	13	<3.1	
Be*	0.77	<0.10	0.6	<0.06	
Br	9.9	16	7.9	3.4	
Ca (%)	0.16	0.015	0.18	0.027	
Ca*	978	63	545	72	
Cd	<20	<20	<20	<20	
Cl (%)	0.10	0.041	<0.02	0.053	
Cr	23	62	23	152	
Cr*	10	54	<6	110	
Cu	16	I(Ni)	20	I(Ni)	
Cu*	16	28	12	16	
Fe (%)	0.968	0.078	1.54	0.107	
Fe* (%)	1.1	0.051	~1.3	0.033	
Ga	<1	<1	~2.3	<1	
Ge	5.0	3.6	4.5	3.1	
K	1500	360	1100	620	
Mn	49	9.9	51	21	
Mn*	42	1.7	23	4.4	
Ni	17	100	15	132	
Ni*	4.8	47	4.3	58	
Pb	<10	<10	<10	<10	
Rb	10	<5	7.4	<5	
S (%)	2.6	0.47	2.4	0.78	
Sb	<20	<20	<20	<20	
Se	<3	<3	<3	<3	
Si (%)	2.2	<0.2	2.0	0.23	
Sn	<20	<20	<20	<20	
Sr	17	<5	41	<5	
Ti	630	370	770	350	
Ti*	489	290	480	190	
V*	<2.5	<0.9	~14	1.5	
Zn	31	~3.9	23	~4	
Zn*	39	2.1	20	<0.6	

<sup>a</sup> Values are in ppm unless % is noted and are corrected to a dry basis. An "I" indicates an unsatisfactory determination due to an interference from another element (shown in parentheses).

• ICP data.

## CONCLUSIONS AND RECOMMENDATIONS

The aqueous  $\text{Na}_2\text{CO}_3$  and molten  $\text{NaOH/KOH}$  treatments, followed by acid washes, effectively remove many trace elements from the coals studied. However, due to corrosion of reactor components in the molten caustic system, levels of some elements, predominantly Ni and Cr, are substantially elevated in the treated coals. Similar tests should be conducted on a greater variety of coals in order to ascertain the general efficiency of trace element removal by these processes. In addition, reproducibility should be examined by making a number of runs using the same reaction conditions on different portions of the same raw coal.

## ACKNOWLEDGEMENTS

This work was supported by the Assistant Secretary for Fossil Energy, Division of Coal Utilization, through the Pittsburgh Energy Technology Center, Coal Preparation Branch.

The authors gratefully acknowledge Dr. T.D. Wheelock and Dr. C-W. Fan at Iowa State University and Dr. Robert Meyers and Dr. Walter Hart at TRW Systems, Inc., for supplying samples of raw and chemically desulfurized coal on which our analyses were performed. Coals chemically cleaned at Ames Laboratory were provided by Mr. David Mroch.

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