

EFFECTS OF MULTIVALENT CATIONS FOUND IN COAL
ON ALKALI- AND BIOSOLUBILITIES

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ABSTRACT

Extraction of low-rank coals with dilute hydrochloric acid resulted in the removal of a small percentage of total ash present. Calcium, and to a lesser extent, aluminum, magnesium and iron were present in acid extracts. Resulting coals were significantly more soluble in dilute alkali and more readily biosolubilized than water treated controls. These data suggest that some of the multivalent cations are present in coals as alkali insoluble complexes and contribute to the structural integrity of the coal.

INTRODUCTION

Since the observations of microbial coal solubilization in the early 1980's (1,2), there has been considerable interest in those mechanisms involved. Two mechanisms have been reported to be involved in coal biosolubilization: direct enzyme attack and production of alkaline materials. Enzymes implicated in the biosolubilization process include lacasses (3), ligninases (4), and peroxidases (4). Unfortunately, the degree of involvement of any of these enzymes in coal biosolubilization has yet to be rigorously demonstrated. Microbial production of alkaline materials which are able to solubilize coals has been clearly demonstrated (5-8). These alkaline materials appear to be nitrogenous in nature and increase medium pH sufficiently to cause coal solubilization. This mechanism does not appear to alter coal molecular structure.

There is now suggestive evidence that a third mechanism is involved in coal biosolubilization. This mechanism involves the removal of multivalent metal ions resulting in coal becoming more soluble in dilute alkali. In this paper, we report how the removal of small amounts of ash present in coals dramatically increases coal alkali- and biosolubilization.

EXPERIMENTAL

Texas lignite was obtained from Northwestern Resources, Jewett, TX. Wyodak and Beulah Zap coals were from the Argonne Premium coal sample program, Argonne IL. Mississippi Wilcox lignite was obtained from a

weathered outcrop as previously described (9). Texas and Wilcox lignites were ground to -100 mesh and stored under a nitrogen atmosphere. Wyodak and Beulah Zap coals were received preground to -100 mesh and packaged under an inert atmosphere. While under a nitrogen atmosphere, coals were dried (50°C for 48 hours) and aliquots (1g) were extracted with either water or 6N HCl (50ml). Extractions were performed by shaking (140RPM) at ambient temperature (22±2°C). Coals were recovered by centrifugation (10,000xg for 10 min) and washed using deionized water until the pH of the wash water exceeded 3.0. Solubilities of coals in dilute alkali were determined by placing coal aliquots (1g) in 50mM Tris buffer (pH 8.0, 100ml), shaking (140RPM) for 72 hours and measuring the absorbance of the filtered fluid (Gelman GA-8 SUPOR, 0.2µm pore dia.) at indicated wavelengths.

Fungal strains RWL-40 (unidentified Basidiomycete) and YML-1 (*Cunninghamella* sp.) (9) were grown and maintained on yeast-malt agar slants at room temperature. Biosolubilization was tested by placing coal aliquots (0.5g) in late log cultures of each organism growing in yeast malt broth and monitoring the amounts of coal going into solution as a function of time. The amount of coal solubilized was estimated by measuring the absorbance of filtered culture fluids at indicated wavelengths.

Ultimate and proximate analyses were performed at the Fuel Characterization Laboratory, University of Utah, Salt Lake City, UT. Element analyses were performed on an ARL Model 3520 Atomic Absorption Spectrophotometer using the ICP mode.

RESULTS AND DISCUSSION

Preliminary drying at 50°C under nitrogen did not appear to oxidize coal samples, but did reduce coal moisture content to a consistent 3-6% (data not shown). Extractions of coals with 6N hydrochloric acid likewise did not result in significant increases in coal oxygen content as compared to water extracted controls (Table 1). These data indicate that no significant amounts of either acid catalyzed hydrolysis (e.g., ethers, esters, etc.) or oxidation occurred. Acid extraction of coals reduced total ash content by a consistent 2-5% and appeared to be independent of original ash content. It is unlikely that any of the ash reduction is due to decreasing pyrite content because sulfur contents remain essentially unchanged.

Acid extracts of coals were a deep yellow or yellow-green color and contained a relatively large amount of calcium and lesser amounts of magnesium, aluminum, iron (Table 2). Sodium and potassium were also present. Very low concentrations of metals were observed in controls (water extracts). The total amount of metals observed in each acid extract was between 60% and 180% of the decrease in ash content caused by acid extraction.

Extraction of coals with hydrochloric acid significantly enhanced the amount of coals soluble in pH 8 buffer (Table 3). Initial amounts of coal solubilized were 145% to 675% greater for acid extracted coals than for water washed controls. In all cases, except for Wilcox, increased solubilities of acid extracted coals continued to be observed in all

subsequent extractions. That is, it did not appear to be the case that each acid and water extracted coal had the same total alkali solubility and that the former was initially more readily solubilized.

Treatment of coals with microbial cultures yielded mixed results. Both organisms used produced a yellow pigment with an absorbance maximum at 400nm and little absorbance at 500nm in controls that did not contain coal (data not shown). Because of this, biosolubility experiments were monitored by following absorbances at 500nm. As control cultures aged, however, the pigment present began to change and absorb more at 500nm.

Mississippi Wilcox lignite was more readily biosolubilized than those other coals tested and did not behave as did other coals. As observed with alkali solubilization, acid treated Wilcox was more readily biosolubilized than water treated controls (Figure 1). It is not likely that the increased biosolubility of acid treated Wilcox was due to an increase in the amount of alkali produced because pH values of cultures containing water extracted Wilcox were consistently one half pH unit greater than those observed for the acid extracted coal (data not shown).

Cultures containing Texas lignite, Wyodak or Beulah Zap became lightly colored after several days of incubation and then lost color as the experiment proceeded (data not shown). The initial colored material in solution appeared to be solubilized coal. It is unknown if the decolorization of these culture media in the latter stages of incubation represents soluble coal being metabolized and suppression of pigment formation or if solubilized coal and extracellular pigments were being removed from solution (e.g., coprecipitated, absorbed...). Since the pH of all cultures were increased and maintained at values greater than 7.5 (data not shown), it is unlikely that coals became insoluble due to pH effects. The net result was that absorptions at 500nm increased initially and then decreased sharply (data not shown). Initial increases in absorbances were small (less than 0.1 absorption unit) but were consistently greater in cultures containing acid treated Texas lignite, Wyodak or Beulah Zap than those observed in controls.

From these data, it appears that the removal of multivalent metal ions significantly enhances both the alkali- and biosolubility of coals without causing measurable oxidation. It appears that low-rank coals have two types of ash present: peripheral and intergral. Peripheral ash would be that ash present as inclusions (e.g., pyrite, clays, etc.) while integral ash would be that which is incorporated into the molecular structure of the coal as metal complexed with organic components of the coal (e.g., carboxylic acids, phenols, alcohols or their sulfur analogs). The presence of multivalent cations present in coal structure as metal complexes is consistent with the suggested structure for other low-rank coals (10). These metal complexes would be less soluble in dilute alkali and, because multivalent cations are involved, they may act as crosslinks between organic molecules in coal. If this working hypothesis is correct, then removal of integral ash by any method will result in lower molecular weights of coal organics and larger populations of free carboxylic acids, phenols and alcohols which will result in increased coal solubilities and greater opportunity for enzyme attack (bioconversion).

While alkali solubility has been shown to be a mechanism in coal biosolubilization, pyrolysis-mass spectral data has suggests that there may be another mechanism involved (11). This other mechanism may involve direct enzyme attack or it may involve the removal of metal ions by microbes. The illucidation of this other mechanism will be the subject of a subsequent manuscript.

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Table 1. Analyses of Treated Coals.

Coal ^a	C ^b	H	N	S	O	Moisture	Ash
Wyodak-W	73.39	5.21	0.98	0.44	19.97	4.00	5.91
Wyodak-A	73.31	5.13	0.91	0.43	20.16	2.00	2.93
Δ				-0.01	+0.19		-2.98
TXL-W	71.61	4.89	0.92	0.68	21.90	5.31	7.95
TXL-A	70.76	4.76	0.97	0.73	22.78	4.41	2.69
Δ				+0.05	+0.88		-5.26
B.Z.-W	72.76	5.6	1.35	1.21	19.08	2.78	13.81
B.Z.-A	71.41	5.49	1.27	1.25	20.58	2.83	9.36
Δ				+0.04	+1.50		-4.45
Wilcox-W	66.58	4.91	1.11	1.29	26.11	4.56	14.21
Wilcox-A	67.52	5.11	1.16	1.25	24.96	4.12	11.48
Δ				-0.04	-1.15		-2.73

a) Abbreviations are as follows: TXL - Texas lignite, B.Z. - Beulah Zap, W - Water extracted, A - Acid extracted.

b) Values are the average of two determinations.

Δ are the difference between the control and experimental values.

Table 2. Metal Concentrations Present in Coal Extracts.

Coal ^a	Al ^b	Ca	Fe	Mg	Na	K
Wyodak-W	0	0.5	0	0.1	3.6	0.3
Wyodak-A	31	243	36	35	17	1.5
TXL-W	0.1	15	0	5	1.6	0.5
TXL-A	36	453	139	66	9	4
B.Z.-W	0.1	0.3	0.1	0.1	12	0.2
B.Z.-A	29	255	34	69	89	3
Wilcox-W	3.6	41	9	5	0.5	0.5
Wilcox-A	95	427	725	23	5	4

a) Abbreviations are as in Table 1.

b) Concentrations are given as mg per liter.

Table 3. Solubilities of Coals in Tris Buffer, pH 8.0

Coal ^a	Treatment	First ^b Extraction	Second Extraction	Third Extraction
Wyodak	Water	0.126	0.164	0.101
Wyodak	Acid	0.532	0.388	0.243
TXL	Water	0.343	0.278	0.198
TXL	Acid	1.45	1.22	0.780
B.Z.	Water	3.78	0.326	0.152
B.Z.	Acid	25.5	1.58	0.800
Wilcox	Water	85.8	26.9	7.3
Wilcox	Acid	124	13.7	4.40

a) Abbreviations are as in Table 1.

b) Values are given as absorbance at 400nm (corrected for any dilution factors).

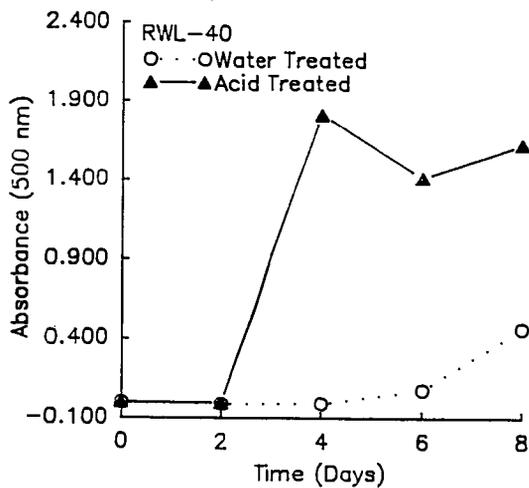
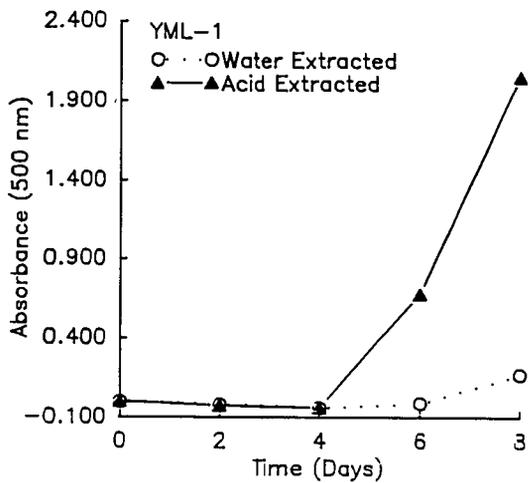


Figure 1. Biosolubilization of acid and water treated Mississippi Wilcox lignite.