THE EFFECT OF LIQUEFACTION CONDITIONS ON THE TRACE ELEMENT CONTENT OF SOLUBLE COAL-DERIVED NON-VOLATILE PRODUCT

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INTRODUCTION

Trace element data on coal-derived products at the pilot plant stage are generally available. Several years ago the feed coal (Kentucky hvBb(1) and West Virginia hvAb(2)) and products from a single batch of a long-term liquefaction run on a 400 lb coal/day process development unit were sampled. Preferential removal of selected elements from the liquid product via centrifugation was observed in each case. Iron-containing minerals were preferentially removed if the West Virginia coal was employed; while, aluminum silicates were removed with Kentucky coal. Numerous elements (V, Cr, Mn, Ni, B, Be, Ti, As) did not show preferential removal upon centrifugation. Other elements were predicted to be associated with organic moieties.

Later multi-element analysis data on wet-ashed Amax feed coal, the chloroform-soluble solvent refined coal (Wilsonville, AL demonstration facility) derived therefrom and several size exclusion chromatographic fractions were obtained.(3) Appreciable metal concentration was found in practically all samples. For several elements, concentrations were higher in SRC than in its parent feed coal. This observation suggested the presence of organometallic species since these materials were soluble in a wide variety of organic solvents and had passed 5.0 μm filters.

Neutron activation analysis has been employed to obtain information on trace elements present in process streams of SRC I and SRC II (Tacoma, WA demonstration facility) products derived from a Western Kentucky coal.(4) In the SRC I process the filtered mineral residue was observed to be the sink for most trace elements with the exception of Ti, Cl, Br and Hg. The SRC I product was found to contain less than 2% of the elemental concentrations in the coal. The SRC II distillate product contained less than 1% of the elemental content of the feed coal. All elements were depleted in SRC I relative to the coal except Br.

A more recent study(5) has been concerned with SRC's which differ (from each other) either in feed coal source, conversion severity or method of residue removal. These materials originated at the Wilsonville facility and were directly analyzed as filtered pyridine solutions via atomic emission spectrometry. Of the metals observed, those which showed any significant concentration (10-1000 μg/g of SRC) were Al, B, Cu, Fe, Si and Ti. West Kentucky SRC from different mines (Lafayette and Fies) exhibited similar metal content with few exceptions. The effect on elemental concentration of mineral matter removal via filtration or critical solvent deashing was varied. The most significant changes were seen with Ca, Fe, Si and Ti. With the exception of Ti, the elemental concentration in the CSD product was two times or greater than the concentration of the filtered product. An increase in hydrogen pressure (2000-2100 psi) and temperature (418°-450°C) had a minimal effect on metal content. Only for Ca, Si and Ti was there greater than 50% reduction in concentration on going to more severe reaction conditions. Those metals which are expected to be most strongly organo-bound (i.e. transition metals) did not significantly change concentration as a function of processing conditions. Mineral-related elements such as Al, Ca, Mg and Si, on the other hand, appeared to fluctuate

in concentration with processing parameters.

As can be seen above, all trace element studies have involved coal-derived process solvents, pilot plant sampling, lengthy and rather severe reaction conditions and mostly bituminous feed coals. In several of these investigations analytical methods were applied to the ashed sample rather than to the unmodified material where less sample-handling and less opportunity for introduction of impurities are possible.

We wish to report soluble trace metal analysis data on an extensive number of "in-house" short-contact time SRC's prepared with various basic nitrogenous and non-basic model process solvents with both bituminous and subbituminous coals. Data are reported as a function of liquefaction time and temperature, method of residue removal and solvent solubility. In addition, size exclusion chromatography (SEC) of selected SRC's with metal-specific inductively coupled plasma atomic emission spectrometric (ICP-AES) "on-line" detection will be utilized to aid in determining the fate of trace metals during liquefaction.

RESULTS AND DISCUSSION

Trace metal analysis of 18 elements in pyridine via ICP-AES has been performed on numerous in-house SRC's in order to determine the effect of various conversion parameters on metal content. Table I list pyridine soluble SRC (Indiana V coal) metal concentrations as a function of process solvent. In order that some point of reference be established in comparing analyses, concentrations are expressed in μg of metal per gram of extracted moisture-free coal not of SRC. The numbers in each case are representative of two independent liquefaction runs and respective metal determinations. Relative standard deviations varied between 1% and 10% depending on the level of metal. Significant metal content is found for 12 of 18 metals monitored. The highest concentrations invariably are observed with Fe, Si and Ti regardless of the process solvent employed. In general, metal content does not appear to be greatly influenced by the various process solvents employed. Initially, one might have argued that the presence of a good ligand donor solvent such as THQ would complex and solubilize more metal than a poor ligand donor solvent. This is not the case with Indiana V SRC. A greater than ten-fold change in metal content with the four solvent systems is observed only with Ca (17.4-319.9) and Mn (3.73-48.4); while, Al (20.3-121.0) and Si (27.1-208.0) also reflect a rather large fluctuation in concentration. Those elements reflecting the greatest fluctuation in concentration are probably mineral related. Differences in both mineral particle size distribution and viscosity of the SRC extract (which would affect the separation achieved by centrifugation) could cause this variation.

Data were also obtained as a function of reaction time (10 and 30 minutes) for pyridine soluble SRC derived from Wyodak #3 coal. Increased reaction time lowers the content of most metals. Again, many of those elements decreasing in soluble metal concentration with an increase in reaction time could be mineral related (Ca, Mg, Si and Ti). A possible explanation for this observation is that a longer reaction time may more extensively de-complex these elements thereby removing them from the pyridine soluble SRC into the residue. This finding is somewhat surprising in that one might have reasoned that a longer reaction time would lead to more extensive metal solubilization (i.e. mineral matter converting to organometallics). This may very well be the case with Ag, Al, Cu and Fe which show an increase in concentration with reaction time.

The most dramatic change in SRC metal content is found with the extraction solvent employed. Table II compares the analysis of 9 elements obtained on toluene and pyridine soluble fractions (Wyodak #3 SRC). The

TABLE I

METAL ANALYSIS DATA OF SRC'S PREPARED WITH VARIOUS PROCESS SOLVENTS[a,b]

Element	TETRALIN/PYRENE (50:50) 86.4%[c]	THQ (100) 93.7%[c]	TETRALIN/MN (50:50) 91.9%[c]	TETRALIN/THQ/PYRENE (25:50:25) 92.8%[c]
Al	50.9	107.0	20.3	121.0
B	95.4	97.9	104.0	105.1
Ca	319.9	65.7	17.4	90.4
Cu	10.2	6.87	9.01	5.35
Fe	240.3	165.4	277.4	219.8
Mg	17.9	19.2	6.93	5.35
Mn	21.5	3.73	48.4	13.4
Ni	21.9	19.9	12.4	30.1
Si	132.9	201.4	27.1	208.0
Ti	133.4	113.7	116.2	199.9
V	6.17	5.06	4.82	9.04
Zn	40.8	19.2	15.4	27.3

[a]Indiana V Coal; S:C, 2:1, 400°C; 30 minutes; 7.5 MPa H_2

[b]<1 μg/g MF Coal measured for Ag, Ba, Cd, Cr, Mo, Sn. Units are μg/gMF coal.

[c]Pyridine Conversion (MAF)

TABLE II

METAL ANALYSIS DATA OF PYRIDINE AND TOLUENE SOLUBLE SRC'S[a]

	WYODAK #3[b]		INDIANA V[b]	
Element	Toluene Conversion[c] 77.85%	Pyridine Conversion[c] 82.59%	Toluene Conversion[c] 84.2%	Pyridine Conversion[c] 93.9%
Al	21.5	436.6	6.44	170.1
B	4.56	6.82	40.9	93.7
Ca	18.4	135.2	3.01	90.0
Fe	25.6	207.5	9.58	141.3
Mg	0.81	68.8	0.63	19.7
Ni	1.72	5.63	0.74	6.57
Si	17.9	775.6	16.9	314.5
Ti	15.9	130.0	7.48	43.9
Zn	3.71	8.83	6.74	15.1

[a]THQ; S:C, 2:1; 418°C; 7.5 MPa H_2; 30 minutes

[b]<1 μg/g MF Coal: Ag, Ba, Cd, Cr, Mn, Mo, Sn, V (Toluene)
<1 μg/g MF Coal: Cd, Mo, Sn (Pyridine)

[c]MAF basis

differences in concentration are large. In many cases metal concentrations are approximately one to two orders of magnitude higher in pyridine soluble SRC relative to toluene soluble SRC. Also, the number of elements appearing at concentrations less than 1 μg/g MF coal are 3 times more numerous for toluene soluble SRC relative to pyridine soluble SRC (9 versus 3) given nearly the same percent conversion. This observation is especially important in that it indicates that the metals concentrate themselves in the toluene insoluble-pyridine soluble products. Again similar findings (Table II) are observed with SRC derived from Indiana V. This finding has an implication regarding metal speciation. The greater concentration of metals in the pyridine soluble fraction suggests that the nature of many of these soluble coal-derived metals is more like a coordination complex rather than a true organometallic metal to carbon bonded species.

Trace metal analysis data are also available for SRC material derived from four different Wyodak coals, Table III. Identical liquefaction conditions were employed. Conversions are based on pyridine solubility which accounts for the relatively high metal contents found. A relatively wide variation (>200%) exists between high and low specific metal content for the four SRC's even though they are all derived from Wyodak coals. The highest metal content appears to be almost uniformly associated with SRC from Wyodak #4 coal (e.g. 13 out of 18 elements). Our Wyodak coals differ considerably from each other in ash content, fixed carbon, %C, %O and %S. Table IV lists ultimate and proximate analyses for these four coal samples. On a moisture free basis the ash content of Wyodak #3 is approximately double the ash content of the other Wyodak coals; yet, its SRC has the lowest metal content for half of the elements monitored. SRC from Wyodak #4 which contains the highest concentration of soluble metals has a feed coal of intermediate ash content and percent sulfur and the lowest percent oxygen. This lack of correlation between ash content and soluble SRC metal content supports the idea of organo-bound metals in coal-derived products. In fact SRC soluble metal content appears to not correlate with either ash, moisture, volatiles nor fixed carbon content. A general trend of metal content versus percent conversion is also not apparent.

Information regarding the number of groups of species for a particular metal and the effective molecular size of each group have been obtained via SEC-ICP-AES on both pyridine and toluene soluble Wyodak #3 SRC (Table II). In both cases the SRC was generated under identical liquefaction conditions. Seven common elements (Ca, Cu, Fe, Mg, Si, Ti, B) were chromatographically detectable in both SRC's employing pyridine elution (e.g. toluene soluble material was re-dissolved in pyridine and eluted from the column with pyridine) and a μ-styragel column. As might have been expected a greater overall concentration of metal is detected in the separation of pyridine soluble SRC than toluene soluble SRC. A greater concentration of larger "sized" material is also observed in pyridine soluble SRC (VR-85) relative to toluene soluble SRC (VR-39) as evidenced by the greater emission intensity of the earlier eluting metal-containing species in the respective metallograms. Totally size-excluded material (retention volume ≅ 3.5 mL) as well as selectively permeated metal species are apparent. This implies that there exists a group of organo-metallics of rather large size and another (usually broader) distribution of organometallics of considerably smaller size. This bimodal behavior is especially pronounced in the pyridine soluble fractions.

Metallographic comparison data are available on SRC's prepared at different reaction times. Pyridine extraction was employed; therefore, a greater number of chromatographically detectable metals was realized. Changes in reaction time do not appear to cause as extensive alterations in metal size distribution as changes in reaction temperature. The minor changes which are observed are not consistent from one metal to another. More specifically, B and Ca appear to have a greater concentration of large

TABLE III

METAL ANALYSIS DATA OF SRC'S PREPARED WITH DIFFERENT WYODAK COALS[a,c]

Element	Wyodak #1 72.3%[b]	Wyodak #2 84.7%[b]	Wyodak #3 85.4%[b]	Wyodak #4 83.3%[b]
Ag	1.57	-	0.97	5.75
Al	397.0	312.0	194.0	483.0
B	31.8	28.5	14.9	28.6
Ba	3.76	3.27	0.97	15.9
Ca	1567	1228	540.6	4069
Cd	-	-	-	2.02
Cr	1.17	2.35	1.70	4.28
Cu	5.64	4.07	6.92	13.1
Fe	125.0	171.0	157.9	180.0
Mg	391.0	258.0	90.5	320.0
Mn	19.6	21.9	7.12	17.0
Mo	-	-	-	4.35
Ni	13.8	17.6	20.6	53.0
Si	113.0	170.0	104.5	169.0
Sn	-	-	-	-
Ti	49.0	44.2	39.5	66.9
V	4.28	4.34	5.28	7.10
Zn	11.6	22.1	9.43	52.7

[a]50% tetralin/50% methyl naphthalene; S:C, 2:1; 400°C; 7.5 MPa H_2; 30 minutes.

[b]Pyridine conversion (MAF)

[c]Units are μg/g of MF coal

TABLE IV

ULTIMATE AND PROXIMATE ANALYSES

	Wyodak[a] #1	Wyodak[a] #2	Wyodak[a] #3	Wyodak[a] #4	Ind V[c]
%C	65.81	64.00	48.27	64.80	65.8
%H	5.15	5.34	4.47	5.59	5.0
%N	0.86	0.85	0.71	0.88	1.4
%O	21.19	20.97	24.32	17.52	7.6
%S	0.41	1.07	6.60	1.96	3.7
Ash	5.1	5.9	20.3	0.1	10.3
Moisture	9.9	8.1	7.0	7.6	5.1
Volatiles	36.1 (54.8)	37.7 (52.6)	35.0 (37.0)	39.4 (48.6)	37.4
Fixed Carbon	49.3 (40.1)	48.3 (41.0)	37.7 (41.4)	44.9 (42.6)	47.2

[a]Samples prepared by drying for 5 days, 133 Pa, 20°C to remove storage water.

[b]Numbers in parenthesis are proximate analyses on moisture free basis obtained in our laboratory.

[c]Data obtained from Kerr McGee Corp., Cresent, OK.

size species at the longer reaction time (30 minutes) than the shorter one (10 minutes). The reverse situation operates with Cu, Fe, Ti and Zn. An interpretation of these results suggest that B and Ca may incorporate with initial regressive reaction products; whereas Cu, Fe, Ti and Zn are tied-up more with the progressive reaction products. A longer reaction time should be conducive to both primary-secondary product progressive reactions as well as to regressive reaction behavior.

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