

## Chemical and Mineralogical Characterization of Coal Liquefaction Residues

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The Illinois State Geological Survey, with support from the U.S. Department of Energy, is characterizing the residues from several advanced-stage coal liquefaction processes. Coal liquefaction in plants of commercial size, if developed on a large scale, will eventually result in the production of large tonnages of waste materials. It is desirable to know the compositions of these residues for possible evaluation as sources of valuable metals and also to know whether they are potential environmental hazards. A major objective of this project is to determine whether the residues from several coal liquefaction processes consistently contain recoverable amounts of valuable elements and can, therefore, be reliably classified as potential secondary source reserves for these elements. In this study the concentration levels of some 70 major, minor, and trace constituents have been determined and, where possible, the mineralogy for certain elements has been ascertained. An economic evaluation of the data will be made. The chemical and mineralogical data will aid in predicting the behavior of various elements during certain liquefaction processes.

Sampling and pretreatment. The processes from which samples were obtained are Clean Coke at United States Steel Research, Monroeville, PA; H-Coal, Hydrocarbon Research, Inc., Trenton, NJ; Lignite Project, University of North Dakota, Grand Forks, ND; Solvent Refined Coal, Southern Company Services, Wilsonville, AL (SRC-Ala); Solvent Refined Coal, Pittsburgh and Midway Coal Company, Ft. Lewis, Wash. (SRC-Wash); and Synthoil, Pittsburgh Energy Research Center, Bruceton, PA. In addition, one residue sample from the COED process has been obtained and analyzed. Each of these processes has been described elsewhere (1). Seventy constituents have been determined in 18 sample sets consisting of feed coal, corresponding residue, and where available, product material. The residues as we have received them are not envisioned to be the ultimate waste products; further processing of the materials beyond that which was being conducted when the samples were taken is anticipated for most processes.

The following coals have been used in the sample sets studied: feed coals from the Herrin (No. 6) coal of Illinois; composite samples of No. 9 and No. 14 coal beds and No. 9, No. 11, No. 12, and No. 13 coal beds of western Kentucky; the Pittsburgh No. 8 coal; Wyodak seam from Wyoming; and a lignite from North Dakota.

Residue samples from the liquefaction processes are often intractable mixtures of product oil, partially reacted coal, and unreacted coal. To produce samples that are more easily handled, more homogeneous, and convenient to use in low-temperature ashing procedures, the product oil portion was separated from the mineral matter portion by extraction with tetrahydrofuran (THF). The unextracted residues, however, have been found to be generally homogeneous, and the extracted residues have primarily been used in producing low-temperature (150°C) ashes for mineralogical analyses. The high temperature ash contents of the unextracted ash samples compare favorably with those recovered from the THF soluble and insoluble portions for most samples, indicating that the samples are fairly homogeneous with respect to ash content.

Methods of analysis. The analytical techniques used (shown in Table 1) are atomic absorption spectrometry (AA), instrumental neutron activation analysis (INAA), direct-reading optical emission spectrometry (OED), photographic optical emission spectrography (OEP), energy dispersive X-ray fluorescence spectrometry (XES), wavelength dispersive X-ray fluorescence spectrometry (XRF), radio-chemical separation followed by neutron activation analysis (RC), ion selective electrode (ISE), and standard ASTM methods (ASTM). Mineralogical studies were made by X-ray diffraction analysis and scanning electron microscopy using low-temperature ash samples prepared in an activated oxygen plasma asher. These methods have been described elsewhere (2). Sample pretreatment is summarized in Figure 1.

Results and discussion. All results on "as received" feed coal and residue samples were corrected for moisture and calculated to the 500°C ash basis. It was assumed that (a) the oxidized inorganic material (the 500°C ash) from a feed coal is comparable to that from the corresponding residue, and (b) that the feed coal sample is representative of the coal used to generate a particular residue. When the ash-basis data for a residue is compared to that for the feed coal, an indication is given as to whether an element is lost, retained, or possibly increased during the liquefaction processes. The "ash-basis" data are used to calculate the percentage of change of each element for which data are available.

Ranges for estimating whether an element was retained were calculated by taking into account an average sampling error and the random error of the particular analytical method used for that element. The "retention range" for an element is arbitrarily defined as twice the overall standard deviation of possible errors in analysis of the feed coal and residue. An element is indicated as having undergone a gain if results for that element exhibit a percentage of change (residue, concentration relative to feed coal concentration on the ash-basis in a given process) which is greater than the upper limit of the retention range. Elements undergoing losses exhibit the opposite tendency. All other elements are said to have been "retained" during the liquefaction process. Figures 2 and 3 are bar graphs showing representative gain-loss data for mercury and manganese in the 18 sample sets, and Figure 4 summarizes the gain-loss data obtained for most elements detected in a SRC(Wash) set.

Some general conclusions can be drawn about the mobilities of various elements in the liquefaction processes studied. In many cases only limited conclusions are possible because of a combination of low elemental concentrations coupled with a moderate-to-high analytical uncertainty of measurement. In addition it should be emphasized that these sample sets, in most cases, represent one-time, short-interval sampling under equilibrium conditions, where possible, and may not be fully representative of long-term continuous operation.

1. Ca, S, Ti, As, B, F, Hg, La, Sc, and Zn are generally ( $\geq 51\%$  of the sample sets in which the element was determined) lost during the liquefaction process. Dy, Eu, Tb, and Yb are lost or retained in the liquefaction processes in approximately equal numbers.
2. Most of the elements determined show general retention during the liquefaction processes. These are: Fe, K, Si, Ba, Be, Br, Ce, Cl, Co, Cr, Cs, Cu, Ga, Ge, Hf, Li, Lu, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sm, Sn, Sr, Ta, Th, Tl, U, V, W, and Zr.
3. Four elements, Al, Mg, Na, and P behave randomly, exhibiting no clear pattern.
4. Observed gains, where present, most probably reflect contamination or degradation of equipment.
5. Some elements generally occur at concentrations too low to be accurately measured by the methods used and, thus are too low to be considered in the gain-loss data evaluation. These include Ag, Bi, Cd, In, Nd, Pt, Te, Au, and Pd.

In particular, three sample sets from the SRC-Ala process and two sets from the SRC-Wash process exhibit the greatest apparent losses. Elements which exhibit apparent losses in three or more of these sample sets are Al, Fe, Mg, S, Ti, As, B, Be, Br, Co, Dy, Eu, F, Hg, La, Lu, Mn, Mo, Sc, Se, Sm, Ta, Tb, Th, Yb, and Zn. Elements which exhibit increases in concentration in two or more of these five liquefaction processes are Na, P, Si, Cr, and Cs. Filtering aid materials were used in conjunction with all five SRC-Ala sample sets (Johns-Manville 7A, consisting of 92.5 percent diatomaceous earth and 7.5 percent asbestos) and the first two SRC-Wash sample sets. It is probable that at least Na, P, Si, and Cr increases are due to the filtering aids. Diatomaceous earth consists primarily of silicon dioxide and

asbestos minerals which contain the elements Na and Si among others. These materials have been detected by scanning electron microscope analysis of the SRC-Ala residues.

Mineralogical analysis. In addition to the chemical analyses, mineralogical analyses have comprised a major portion of this study. They have yielded information about the modes of occurrence of some elements and may shed some light on the behavior of certain chemical elements during the liquefaction processes.

The major mineralogical change which takes place in the liquefaction processes is the transformation of pyrite ( $\text{FeS}_2$ ) in the feed coal to pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ , where  $x = 0. \text{ to } 0.2$ ) in the residue by the reaction  $2\text{FeS}_2 \rightarrow 2\text{Fe}_{1-x}\text{S} + 2\text{S}$ . Sulfur probably is evolved as  $\text{H}_2\text{S}$ . Pyrrhotite occurs in the residues primarily as fine-grained (crystal size about  $1 \mu\text{m}$ ) aggregates sometimes incorporating other mineral matter. It also occurs as a fine granular layer on mineral particles.

A small amount of wollastonite,  $\text{CaSiO}_3$ , formed by the reaction  $\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2$ , was detected by scanning electron microscopy in one residue from an H-Coal set. Some calcite particles found in the residue have a spongy texture similar to that seen in calcined carbonates (3). It appears that some dissociation of the calcite occurred, enabling a small amount of  $\text{CaO}$  to combine with  $\text{SiO}_2$ . In a closed system, calcite, quartz, and wollastonite are stable together under the pressures and temperatures present in liquefaction process preheaters and reactors, if the  $\text{CO}_2$  partial pressure is not appreciable (4).

A qualitative summary of mineral matter detected by X-ray diffraction analysis in feed coals and residues is presented in Table 2. An "X" indicates the presence of a mineral in a sample. A question mark indicates uncertainty in the presence of a mineral as determined from the diffraction patterns. Marcasite, a dimorph of pyrite, has been observed in only one feed coal sample. It is also transformed to pyrrhotite during liquefaction. Other minerals may be present in the samples in quantities below the detection limits.

Semi-quantitative X-ray diffraction data for quartz, calcite, pyrite, and pyrrhotite in the low temperature ash samples of several feed coals and their corresponding residues are shown in Table 3. Inclusion of quartz and calcite in pyrrhotite aggregates contributes to an apparent decrease in quartz and calcite from the feed coals to the residues. A decrease in the pyrrhotite concentration in the residue with respect to the pyrite concentration in the feed coals is due to the loss of sulfur from pyrite in the transformation to pyrrhotite. In samples which show the presence of calcite in the residues but not in the corresponding coal, calcite and some pyrite have broken down to form sulfate minerals during storage of the coal. This is a common reaction in coals exposed to moisture (5).

Conclusions. Data from the limited number of sample sets covering several liquefaction processes indicate that relatively few elements (e.g. Hg, S, As, Br, and B) are consistently lost to any significant degree from the resultant residues. Only a few mineralogical changes occur during the processes in which the transformation of pyrite to pyrrhotite most consistently occurs. These experimental observations, including the general range of elemental concentrations found in the residues, along with extensive trace element distribution data now available (2,6) from analyses of many coals from the various U.S. coal fields, will be used for an economic evaluation for many metals. Trace element concentrations for such economically significant metals such as Au, Ag, Pt, Pd, Ta, etc. in most cases will probably be too low for consideration as resources. In some cases, however, such as Zn, there are areas (7) where concentrations are high enough for serious consideration. The more abundant metals in coal--such as Al, Fe, Si, and possibly Ti--although perhaps currently not economical to extract may require attention in the future.

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References.

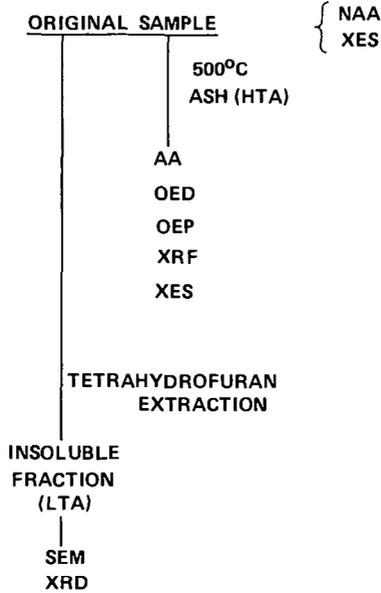
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Table 1  
 Selection of Methods for Determining Various Elements  
 In Coal Liquefaction Feed Coals and Residues

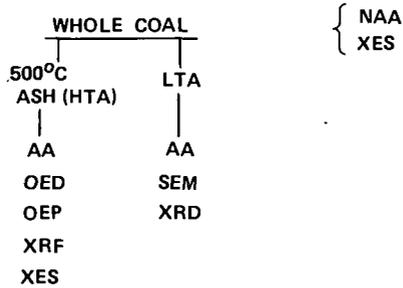
Element	AA	INAA	OED	OEP	XES	XRF	ASTM	ISE	RC	Element	AA	INAA	OED	OEP	XES	XRF	ASTM	ISE	RC
Al					X					Hf		X							
C						X				Hg									X
Ca					X					Ho									X
Fe	X	X			X					I					X				
H						X				In		X							
K		X			X					La		X							
Mg					X					Li		X							
N						X				Lu		X							
Na		X								Mn		X		X					
O					X					Mo			X						
P					X					Nd		X							
S						X				Ni	X	X	X	X	X				
Si					X					Pb		X							
Ti					X					Pd									X
Ag		X		X						Pt									X
As		X								Rb			X						
Au		X						X		Sb		X							
B			X							Sc		X							
Ba					X					Se		X							
Be				X						Sm		X							
Bi				X						Sn			X		X				
Br		X								Sr		X*	X						
Cd		X								Ta		X							
Ce		X								Tb		X							
Cl		X								Te					X				
Co		X	X	X						Th		X							
Cr		X	X							Tl			X						
Cs		X								Tm									X
Cu		X	X	X						U		X							
Dy			X							V			X	X					
Er								X		W		X							
Eu		X								Y					X				
F								X		Yb		X							
Ga		X								Zn		X							
Ge			X							Zr						X			

\*Strontium results by INAA are satisfactory above 10 ppm.

A. FLOW SHEET OF RESIDUE SAMPLE PRETREATMENT



B. FLOW SHEET OF WHOLE COAL SAMPLE PRETREATMENT



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Figure 1 - Flow sheets of sample pretreatments.

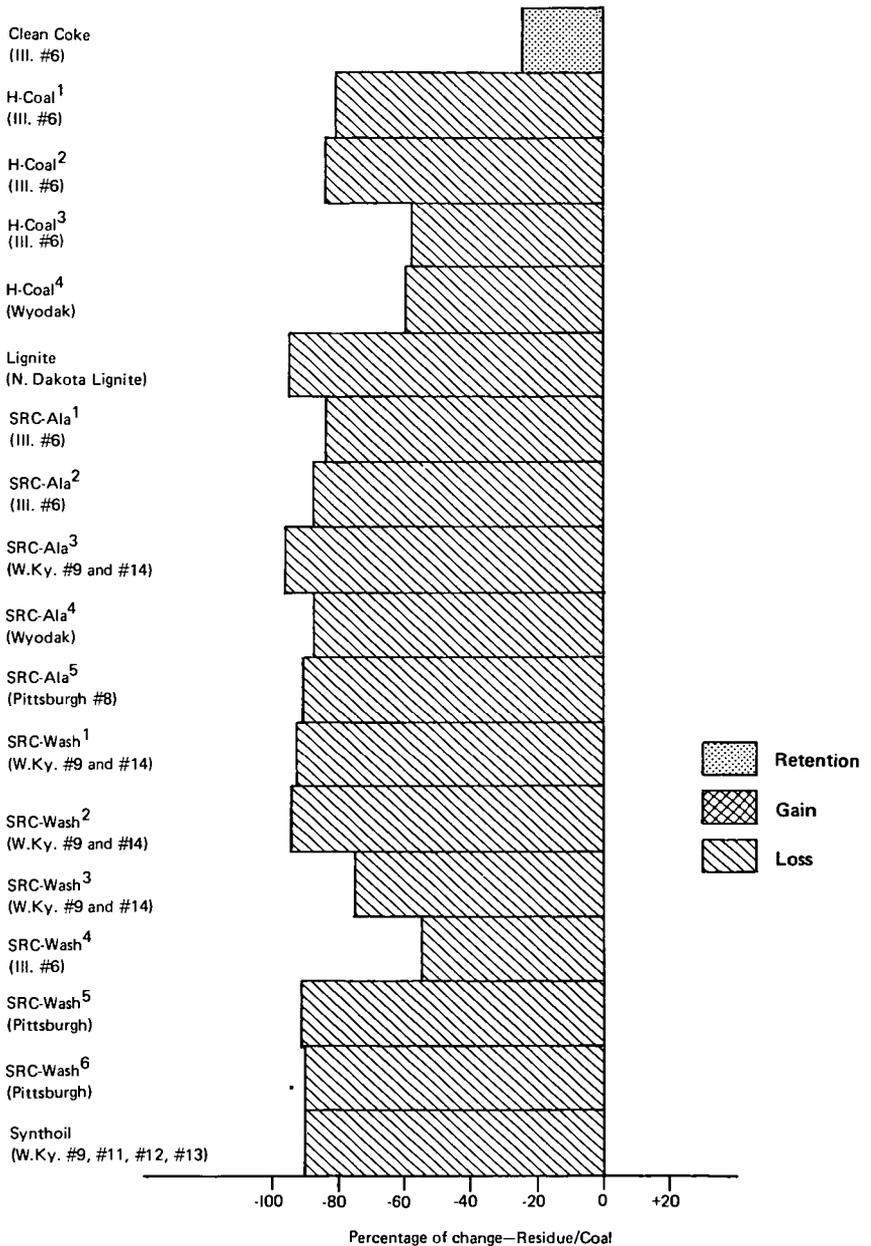


Figure 2 - Summary of percentage of change in elemental composition (500°C ash basis) for Hg in several liquefaction processes from feed coal to residue.

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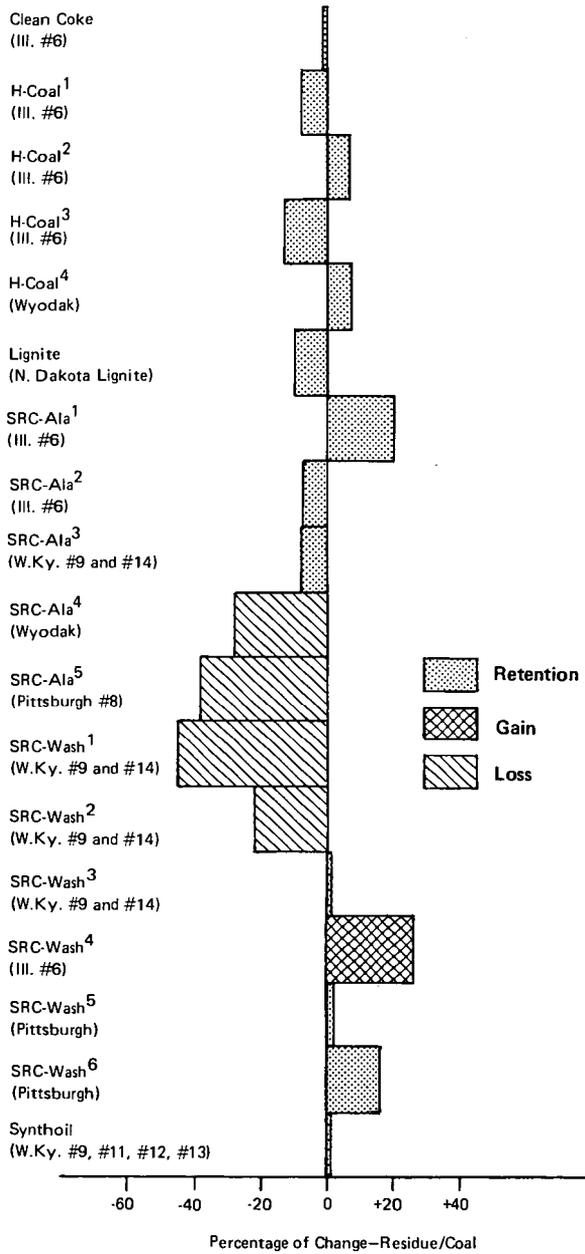
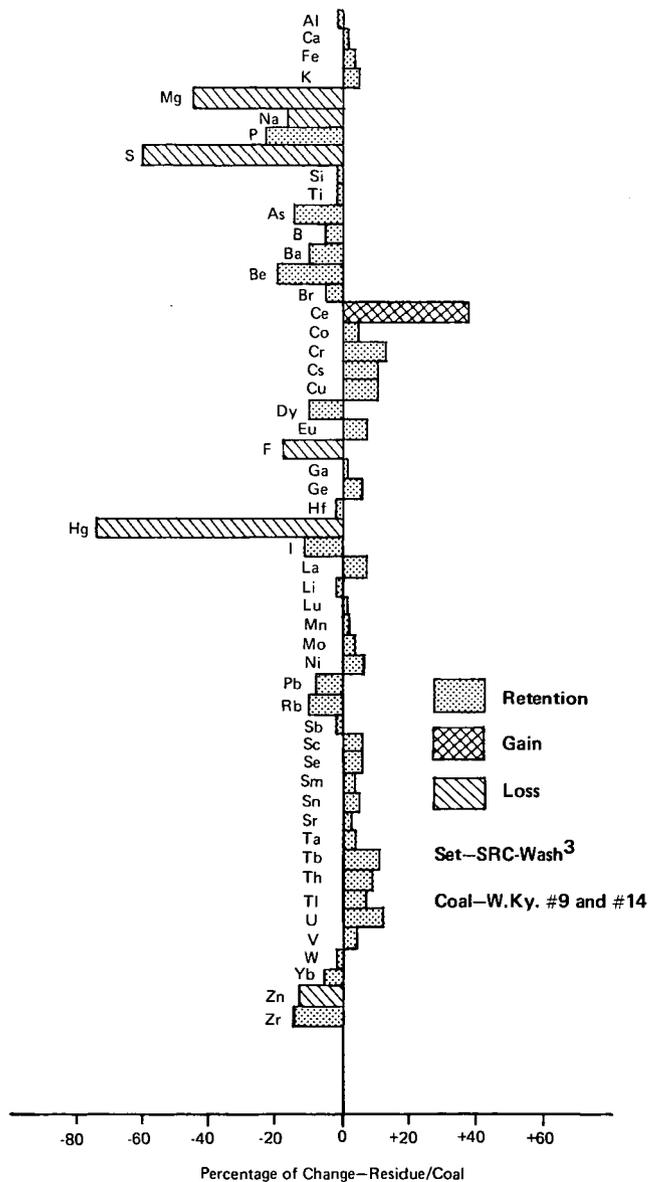


Figure 3 - Summary of percentage of change in elemental composition (500°C ash basis) for Mn in several liquefaction processes from feed coal to residue.

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Figure 4 - Summary of percentage of change in elemental composition (500°C ash basis) from feed coal to residue.

Table 2

Mineral Matter Detected in Low Temperature Ash  
of Liquefaction Samples by X-ray Diffraction Analysis

Lab No.	Sample Set	Anhydrite	Bassanite	Calcite	Coquimbite	Feldspar	Gypsum	Illite	Jarosite	Kaolinite	Marcasite	Pyrite	Pyrrhotite	Quartz
C-19660	Clean Coke			X				X		X		X		X
C-19661A		X	X	X		X		X		X			X	X
C-18903	H-Coal 1	X		X	X			X		X		X		X
C-18941A		X		X				X		X			X	X
C-19194	H-Coal 2	?		X	X			X		X		X		X
C-19196A		?		X		X		X		X			X	X
C-19916	H-Coal 3			X	?					X		X		X
C-19917A		X		X				X	?	X			X	X
C-20021	H-Coal 4		X	X						X		X		X
C-20022A			X	X		X		X		X			X	X
C-19590	Lignite		X	X								X		X
C-19591			?	X		X							?	X
C-19702	SRC-Ala 1			X				X		X		X		X
C-19703				X			X	X		X		?	X	X
C-19705	SRC-Ala 2	X			X	?		X	X	X				X
C-19706		?		X						X		X	X	X
C-19708	SRC-Ala 3				X					X		X		X
C-19709						X		X	X	X		X	X	X
C-19711	SRC-Ala 4	X	X							X		X		X
C-19712				X			X			X				X
C-19714	SRC-Ala 5		X	X		X		X		X		X		X
C-19715						X	X			X			X	X
C-19141	SRC-Wash 1				X					X	X	X		X
C-19142A								X		X			X	X
C-19488	SRC-Wash 2			?				X	X	X		X		X
C-19487		X						X	?	X			X	X
C-19899	SRC-Wash 3	X		X	X			X		X		X		X
C-19902A		X		X		X		X	X	X			X	X
C-20014	SRC-Wash 4			X				X		X		X		X
C-20015A				X				X		X			X	X
C-20016	SRC-Wash 5	X	X	X		X		X	X	X		X		X
C-20017A				X		X		X		X			X	X
C-20019	SRC-Wash 6	?					?	X	X	X		X		X
C-20020A				X				X	?	X			X	X
C-19276	Synthoil			X	X			X		X		X		X
C-19349A				X		X		X		X		X	X	X

Table 3

Average Percentage of Principal Minerals by X-Ray Diffraction  
in Low Temperature Ash of Liquefaction Samples

Lab No.	Sample Set	Sample Type	Average Mineral Percentages, by weight, ± 7.5%, absolute			
			Quartz	Calcite	Pyrite	Pyrrhotite
C-19660	Clean Coke	Coal	21	11	19	N.D.
C-19661A		Residue	15	3	N.D.	16
C-18903	H-Coal 1	Coal	22	13	22	N.D.
C-18941A		Residue	17	8	N.D.	15
C-19194	H-Coal 2	Coal	22	9	25	N.D.
C-19196A		Residue	16	4	N.D.	18
C-19916	H-Coal 3	Coal	15	4	22	N.D.
C-19917A		Residue	14	5	N.D.	20
C-20021	H-Coal 4	Coal	11	*	9	N.D.
C-20022A		Residue	10	12	N.D.	*
C-19590	Lignite	Coal	7	*	10	N.D.
C-19591		Residue	12	28	N.D.	*
C-19702	SRC-Ala 1	Coal	22	3	21	N.D.
C-19703		Residue	15	<1	N.D.	13
C-19705	SRC-Ala 2	Coal	18	N.D.	N.D.	N.D.
C-19706		Residue	12	5	N.D.	12
C-19708	SRC-Ala 3	Coal	13	N.D.	23	N.D.
C-19709		Residue	13	N.D.	7	7
C-19711	SRC-Ala 4	Coal	16	*	6	N.D.
C-19712		Residue	16	12	N.D.	N.D.
C-19714	SRC-Ala 5	Coal	12	6	16	N.D.
C-19715		Residue	9	1	N.D.	10
C-19141	SRC-Wash 1	Coal	8	N.D.	39	N.D.
C-19142A		Residue	7	N.D.	N.D.	27
C-19488	SRC-Wash 2	Coal	9	N.D.	37	N.D.
C-19487		Residue	7	N.D.	N.D.	17
C-19899	SRC-Wash 3	Coal	18	2	29	N.D.
C-19902A		Residue	16	1	N.D.	20
C-20014	SRC-Wash 4	Coal	18	4	26	N.D.
C-20015A		Residue	15	3	N.D.	17
C-20016	SRC-Wash 5	Coal	16	5	21	N.D.
C-20017A		Residue	14	3	N.D.	19
C-20019	SRC-Wash 6	Coal	15	N.D.	22	N.D.
C-20020A		Residue	11	3	N.D.	14
C-19276	Synthoil	Coal	15	7	27	N.D.
C-19349A		Residue	13	6	N.D.	22

\*Mineral present, but cannot be quantified due to the interference of other mineral peaks.

N.D. = Not Detected