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FINAL REPORT

DETERMINATION OF VALUABLE METALS IN LIQUEFACTION PROCESS RESIDUES

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Illinois State Geological Survey
Urbana, IL 61801

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Prepared For

THE DEPARTMENT OF ENERGY
Oak Ridge, TN 37830

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DETERMINATION OF VALUABLE METALS IN LIQUEFACTION PROCESS RESIDUES

PART A, CHEMICAL ANALYSES
PART B, MINERALOGICAL AND PETROGRAPHIC ANALYSES
PART C, MINERALS—ECONOMIC EVALUATION

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ABSTRACT

Feed coals, corresponding solid residues, and 18 sample sets representing the SRC, H-Coal, Synthoil, Lignite, Clean Coke, and COED liquefaction processes were investigated chemically, mineralogically, and petrographically. The data were evaluated from an economic viewpoint. Most of the 71 elements determined chemically, with the exception of Hg, As, B, S, Ti, Mg, and N, are generally retained in the residues. X-ray diffraction and electron microscopy analyses indicated that most mineral species remain unchanged during the liquefaction process. Mineralogical changes observed included the conversion of pyrite to pyrrhotite, the probable formation of metakaolinite from kaolinite, and the collapse of some expandable clay minerals to a 10 Å basal spacing. Microscopy of selected samples indicated that small amounts of solid organic particles, mostly vitroplast, are left in the residues. The chemical and mineralogical data, in conjunction with certain economic criteria, were utilized in a hypothetical economic evaluation of the minerals present in the residues as possible secondary sources for some metals. On the basis of 50 million tons of coal conversion the value of 17 economically and strategically important metals was calculated, of which Al, V, and Ge were the most important.

SUMMARY

The mineral resources in the United States for the economical supply of some metals are rapidly being depleted. Our projections to the year 2000 indicate a severe shortage of many metals. The nation could become almost solely dependent upon foreign sources—a situation analogous to that now existing for crude oil. Other sources of minerals—perhaps uneconomical at present—must be investigated for future use.

One possible low-grade source of many important metals is the waste residue from coal liquefaction plants. Although coal liquefaction is now in the research stage, commercial production in the future will create large amounts of residues that contain significant amounts of some metals. If these residue materials, available without the cost of mining, are found to contain recoverable valuable metals, a secondary domestic mineral resource would then be available.

The primary objective of this project was to determine if the residues from several coal liquefaction processes contain recoverable amounts of valuable metals and can be reliably classified as potential resources for those metals. The data generated from this study can also aid in assessing the role of elements in the liquefaction process from an engineering standpoint and could also have implications for environmental control.

Eighteen sample sets of feed coal and residue from the SRC (both Washington and Alabama plants), Synthoil, H-Coal, Lignite, and Clean Coke processes, and a residue from the COED process were obtained and analyzed chemically for some 71 major, minor, and trace elements. Complete mineralogical analysis included X-ray diffraction and scanning electron microscopy on these samples. Petrographic analyses were done on selected samples. Finally, the chemical, mineralogic, and petrographic data and data on the current resources, supply, imports, and demand for each metal were evaluated to determine the economic feasibility of using liquefaction residues as a source of metals. The final report is in three parts: Part A describes the samples and gives the experimental details, results, and conclusions of the chemical analyses; Part B describes the mineralogical and petrographical analyses; and Part C contains the minerals-economic evaluation. The appendices provide detailed procedures and data. The principal conclusions for the project follow.

The range of concentrations in the liquefaction residues indicates the amounts available for beneficiation. Most of the 71 elements determined in the coals were retained in the residues, completely or with insignificant loss. Highly mobile elements are S, N, As, Mg, Ti, B and Hg; moderately mobile elements are Ca, Zn, Na, Eu, Dy, F, Yb, Ta, Sc, and Br. The composition of a residue usually reflects the mineral composition of the coal from which it is produced.

During the liquefaction process, most of the identified elements remained in the mineral species in which they occurred in coal. Liquefaction residues are similar in composition and morphology of mineral particles from process to process. Major changes in mineral composition from coal to residue after liquefaction include conversion of pyrite to pyrrhotite, formation of metakaolinite from kaolinite, and collapse of some expandable clay mineral structures to approximately 10 Å. The transformation of pyrite can account for the mobility of such elements as As and S. Microscopy of certain feed coals and their residues indicates that the vitrinite and exinite maceral components in the coals were largely converted to liquid products during liquefaction; a notable fraction of vitroplast and traces (in part) of semi-coke types of organic particles were present in the residues. In addition small amounts of unreacted, inertinite macerals remain in the residues.

Elements were classified according to demand, growth of demand, and critical reserves ratios. Twenty-three elements were identified as having significant long-term economic and strategic importance. They are Al, I, F, W, Ta, Cd, Zn, Au, V, Sb, Ni, Hg, Cr, Sn, Bi, Co, Ag, In, Mn, Ge, Mg, U, and S. The mineralogical occurrence of elements in the liquefaction residue is entirely different than in presently mined ores. Commercially practicable processes for the recovery of metals from minerals in the liquefaction residue are presently not available. A hypothetical economic evaluation was therefore made and projected to the year 2000. The value of 17 metals in liquefaction residues was calculated on the basis of 50 million tons of coal converted annually. These values ranged up to $807 million depending upon the process and the coal. They represented a credit value of up to $16.10 per ton of coal used. Al, V, and Ge share the greatest contribution to the credit value. This evaluation indicates the limits to which new commercial processes may cost and yet contribute financially and/or strategically to the nation's economy. The ranges in weights of elements in the residue from 50 million tons of coal are given.

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Clean Coke Process; Dr. C. A. Johnson, Mr. A. Comolli, Mr. N. Feinberg, and Mr. C. Battista, Hydrocarbon Research, Inc., *H-Coal Process*; Dr. R. Tracy Eddinger and Mr. L. Friedman, COGAS Development Co., *COED Process*; Mr. E. Huffman and Mr. G. Styles, Southern Company Services, Inc., *SRC Process* (Wilsonville, AL); Mr. R. Perrussel and Mr. D. Marsh, Pittsburgh and Midway Coal Co., *SRC Process* (Ft. Lewis, WA); Dr. H. Schultz and Dr. G. Gibbon, Pittsburgh Energy Technology Center, *Synthoil Process*; and Mr. A. M. Souby and Professor D. E. Severson, University of North Dakota, *Project Lignite*.

CHEMICAL ANALYSES

CHEMICAL CHARACTERIZATION

Samples were acquired only through complete cooperation of personnel at the liquefaction process plants. An "equilibrium" set of samples for a process run was requested such that the sample of liquefaction residue would be produced from the designated feed coal within a reasonable time during "steady-state" running conditions.

A review of the literature on chemical analysis of liquefaction residues (Appendix A) showed only limited studies yielding semiquantitative data on certain processes. Hence, our objective was to determine quantitatively as many elements as practical on as many process sample sets as could be obtained conveniently. The existence of several kinds of methods of analysis at Illinois State Geological Survey permitted the quantitative determination of up to 71 elements in these various materials, generally with good accuracy and precision.

The chemical data are presented in tables and graphs, including graphs of concentrations of elements in the residues compared to concentrations in the corresponding feed coals, i.e., the retention of the elements. The data show the amounts of metals available for extraction in the waste residues; they also point out potential losses of elements that are volatile or that occur in other effluent streams.

Liquefaction Processes

Coal liquefaction, a general term describing the conversion of coal to various liquid or solid products, can be accomplished by many differing hydrogenation and pyrolysis processes. In general, these refined products are depleted in sulfur and mineral matter, relative to the raw coal. Samples from seven liquefaction processes were studied. The processes, which have been described in various DOE and EPA reports (Seamans and White, 1976; Koralek and Patel, 1978) are:

1. Clean Coke, United States Steel Corporation, Monroeville, PA
2. H-Coal, Hydrocarbon Research, Inc., Trenton, NJ
3. Project Lignite, University of North Dakota, Grand Forks, ND
4. Solvent Refined Coal, Southern Company Services, Wilsonville, AL
5. Solvent Refined Coal, Pittsburgh and Midway Coal Mining Co., Ft. Lewis, WA
6. Synthoil, Pittsburgh Energy Technology Center, Bruceton, PA
7. COED, FMC Corporation, Princeton, NJ

The Clean Coke process is a hydrogenation and carbonization process. In the hydrogenation stream, ground coal is slurried in medium-weight recycle oil. The slurry is reacted with hydrogen recovered from the gas treatment section. The process is conducted at approximately 455°C and 270 atm. The hydrogenated slurry is sent to a vapor stripper where the vaporization of the lighter components leaves a heavy residue. The liquid stream is further treated in the liquid processing section. One set of samples of feed coal and vapor stripper bottoms were received and analyzed.

In the H-Coal process, dried coal, ground to -60 mesh, is slurried with recycle oil from the process and is pumped to a pressure of 200 atm. Hydrogen is added, and the mixture is pumped through a fired preheater, then into an ebullient bed reactor at 455°C. The solid-liquid product mixture from the reactor is let down to atmospheric pressure in a flash separator. The vapor is passed to an atmospheric pressure still, and the heavy oil/solid portion is passed through a hydroclone for further separation. The hydroclone overhead stream is recycled for coal slurrying. The hydroclone bottom product is further separated in a liquid-solid separator, then in a vacuum still. Samples of primary interest were the feed coal and vacuum still bottoms. Four sample sets of feed coal and vacuum still bottoms were analyzed.

The Solvent Refined Coal process is being developed by Pittsburgh and Midway Coal Mining Co. at Ft. Lewis, WA., and by Southern Company Services at Wilsonville, AL. This process converts high-ash, high-sulfur coal to low-ash, low-sulfur fuel. Ground coal is fed into a slurrying tank where it is mixed with recycle solvent. The slurry is mixed with hydrogen and passed into a preheater, then into a dissolver. In the dissolver about 90 percent of the coal is dissolved, depolymerization and hydrogenation take place, the solvent is cracked to lower molecular weight hydrocarbons in the light oil to methane range, and organic sulfur is removed as hydrogen sulfide. The mixture is passed to a separator, and gas is drawn off to a hydrogen recovery and gas desulfurization unit. The slurry from the separator is filtered, and the coal solution is sent to a solvent recovery unit where the final product is recovered. The solids from the filter unit are processed with coal, steam, and oxygen to produce hydrogen for the process and ash. Six sample sets of feed coal and residue, representing both Mode 1 (solid product) and Mode 2 (liquid product) runs, were analyzed from the Ft. Lewis plant. Five sample sets representing different sources of feed coal were analyzed from the Wilsonville facility. With the exception of the Mode 2 operation at Ft. Lewis, all the runs included a filtering procedure in which a mat of diatomaceous earth and asbestos filter material was used and subsequently was detected in the residues by scanning electron microscopy.

The Lignite Liquefaction Process is operated at the Engineering Experiment Station of the University of North Dakota. The process is similar in principle to the Solvent Refined coal process but uses lignite rather than coal. One sample set of lignite, solvent-refined lignite, and residue was analyzed. The residue is separated by a counter-current flow gravity-settling tower.

In the Synthoil process ground coal is slurried with recycle oil. The slurry, with added recycle hydrogen, is fed into the fired preheater containing ceramic pellets for more efficient heat transfer. The slurry is pumped to a fixed bed catalytic reactor, which contains cobalt molybdate ceramic prill catalyst, operating at 200 atm and 450°C. The hydrogen flow propels the slurry through the reactor in turbulent flow to prevent the column from clogging as the coal passes through the plastic phase before becoming liquid. After cooling, the mixture passes into a separator in which the liquid and unreacted solids are separated from product gases. The liquid/unreacted solids mixture is centrifuged. A portion of the oil from centrifugation is recycled for coal slurrying, and the remainder is product oil. Gases are separated into hydrogen, water, ammonia, and hydrocarbon gases. The hydrocarbon gases are to be further processed in a gasifier. The two resulting hydrogen streams are to be combined and recycled. The unreacted solids from the centrifuge are to be pyrolyzed to yield more product oil and ash, and the ash is then to be processed in the gasifier and shift converter. One set of samples of ground feed coal, solids from the centrifuge, and centrifuge liquid product was analyzed. Because of radial and axial inhomogeneity of the centrifuge solids, the entire centrifuge load was withdrawn and slurried in methyl isobutyl ketone at the plant. An aliquot of the slurry was withdrawn and the solvent was evaporated before shipment to the Illinois State Geological Survey.

The COED process, a four-stage pyrolysis system, converts coal to low-sulfur synthetic crude oil, clean fuel gas, and a char. Because this plant had ceased operation it was possible to obtain only an undocumented char sample prepared from a western lignite.

Table 1 lists for each set of samples the process, source of feed coal, sample type, process identification number, and ISGS sample number. Multiple sample sets obtained for a process from the H-Coal and the SRC-Washington and SRC-Alabama plants have been designated as H-Coal-1, H-Coal-2, SRC-WASH-1, SRC-ALA-1, etc.

Table 2 lists the operating parameters and other documentary information that were made available from the process plants. The only documentation for the COED char sample was that it was derived from a North Dakota lignite.

Table 1. Identifications of feed coal, residue and product samples

Process (Run # or Date)	Coal Source	Sample Type	Supplier Sample Number	ISGS Sample Number
Clean Coke 3/77	Illinois No. 6 seam Old Ben Mine #24	coal	USS 77.03-2006	C-19660
		residue	USS 77.03-2007	C-19661
		concentrated residue	USS 9760-27-1	C-19876
COED undocumented	Scranton seam (ND) Glen Harold Mine	residue	C-8493-128	C-19963
H-Coal run 130-72-13 (H-Coal-1)	Illinois No. 6 seam Burning Star Mine #2	coal	LO-79	C-18903
		residue	LO-83	C-18941
run 130-77-10A (H-Coal-2)	Illinois No. 6 seam Burning Star Mine #2	coal	LO-275	C-19194
		residue	LO-277	C-19196
run 130-82-5A (H-Coal-3)	Illinois No. 6 seam Burning Star Mine #2	coal	LO-843-1,2	C-19916
		residue	LO-845	C-19917
run 130-83-23A (H-Coal-4)	Wyodak seam Wyodak Mine Gillette, WY	coal	LO-1096	C-20021
		residue	LO-1095	C-20022
Project Lignite run M-11A	Beulah-Zap seam (ND) Indian Head Mine	lignite	lignite	C-19590
		residue	V-8 bottoms	C-19591
		product	F-1 bottoms	C-19592
Solvent Refined Coal (Alabama) run #52 (SRC-Ala-1)	Illinois No. 6 seam Monterey Mine	coal	24772	C-19702
		residue	24771	C-19703
		solvent refined coal	16575	C-19704
run #25 (SRC-Ala-2)	Illinois No. 6 seam Burning Star Mine #2	coal	24765	C-19705
		residue	24764	C-19706
		solvent refined coal	16573	C-19707
run #72 (SRC-Ala-3)	W. Kentucky Nos. 9 & 14 seam Colonial Mine	coal	24663	C-19708
		residue	24768	C-19709
		solvent refined coal	16577	C-19710
run #57 (SRC-Ala-4)	Wyodak seam (ND) Belle Ayr Mine	coal	24770	C-19711
		residue	24769	C-19712
		solvent refined coal	16576	C-19713
run #37 (SRC-Ala-5)	Pittsburgh seam (WV) Loveridge Mine	coal	24767	C-19714
		residue	24766	C-19715
		solvent refined coal	16574	C-19716

Table 1. Identifications of feed coal, residue and product samples (continued)

	Process (Run # or Date)	Coal Source	Sample Type	Supplier Sample Number	ISGS Sample Number
	Solvent Refined Coal (Washington)	W. Kentucky Nos. 9 & 14 seam Colonial Mine	coal	366	C-19141
			residue	368	C-19142
MODE 1	3/76 (SRC-Wash-1)		solvent refined coal	369	C-19143
MODE 1	9/76 (SRC-Wash-2)	W. Kentucky Nos. 9 & 14 seam Colonial Mine	coal	547	C-19488
			residue	548	C-19487
			solvent refined coal	549	C-19486
MODE 2	8/77 (SRC-Wash-3)	W. Kentucky Nos. 9 & 14 seam Colonial Mine	coal	812	C-19899
			residue	819	C-19902
			solvent refined coal	830	C-19915
MODE 2	10/77 (SRC-Wash-4)	Illinois No. 6 seam River King Mine	coal	917	C-20014
			residue	922	C-20015
MODE 2	11/77 (SRC-Wash-5)	Pittsburgh seam (WV) Blacksville #2 Mine	coal	982	C-20016
			residue	983	C-20017
MODE 2	12/77 (SRC-Wash-6)	Pittsburgh seam (WV) Blacksville #2 Mine	coal	1040	C-20019
			residue	1042	C-20020
	Synthoil 5/76	W. Kentucky Nos. 9,11,12, and 13 seam Homestead Mine	coal	run FB-55	C-19276
			residue	batch 67	C-19349
			product		C-19512

Appendix B (Sample Pretreatment Log) lists the samples received and analyzed Besides the feed coals and residues, some intermediate residues and products from some processes were also analyzed.

The liquefaction residues received from each process were not the ultimate waste products. Most contained appreciable amounts of organic matter. The percentage of residue produced from dry coal for each sample set is shown in Table 2. It would be anticipated that in a commercial scale operation these residues would be further processed in order to recover the carbon content.

Laboratory Procedure

Pretreatment of samples. Figure 1 outlines the preparation and analyses for the liquefaction residues and coal samples. Separate portions of the coal samples were ashed in a conventional furnace at 500°C or in an oxygen plasma environment at ∿150°C (Gluskoter, 1965). The procedure for preparation of the 500°C ash is described in Appendix C. Whether an as-received sample or an ash was analyzed depended upon the method of analysis. A previous study on the analysis of coal (Gluskoter et al., 1977) indicated that the 500°C ash retains many elements that can be determined readily by the following methods: atomic absorption spectrometry (AA), photographic optical emission spectroscopy (OEP), direct-reading optical emission spectrometry (OED), wavelength-dispersive X-ray fluorescence (XRF), energy-dispersive X-ray fluorescence (XES), and neutron activation analysis with radiochemical separation (NAA-RC).

The low-temperature ash (∿150°C) of whole coal was prepared specifically for scanning electron microscopy (SEM), X-ray diffraction (XRD) and selected analyses

Table 2. Operating parameters and documentary information for samples received

Process	Clean Coke	Project Lignite	Synthoil
Sampling Date	3/77	6/22-6/23/76	5/17/76
Coal size	-100 mesh	90% -200 mesh	70% -200 mesh
Coal slurry ratio	1 part coal(wt)/2.5 parts oil		40# coal/60# oil
Reactor temperature	455°C	455°C	450°C
Reactor pressure	3000 psi	2500 psig	4000 psi
Contact time	Approx. 1 hour		
Coal feed rate		23.33 #/hr	25# coal slry/hr
Conversion (residue/dry coal)	84% (estimated from ash concentrations)	25.03%	11-12%

Process	H-Coal			
Sample Set	H-Coal-1	H-Coal-2	H-Coal-3	H-Coal-4
Sampling Date	9/24/75	4/7/76	9/8/77	12/11/77
Coal size	-100 mesh	-100 mesh	-100 mesh	-100 mesh
Reactor temperature	455°C	455°C	455°C	449°C
Reactor pressure	2700 psig	2700 psig	2700 psig	2800 psig
Catalyst	Co-Mo on Al_2O_3	Co-Mo on Al_2O_3	Co-Mo on Al_2O_3	Co-Mo on Al_2O_3
Space rate			30#/(hr-ft^3 reactor vol)	32#/(hr-ft^3 reactor vol)
Conversion (residue/dry coal)	64.45%	70.05%	40.15%	42.55%

Process	Solvent Refined Coal - Alabama				
Sample set	SRC-Ala-1	SRC-Ala-2	SRC-Ala-3	SRC-Ala-4	SRC-Ala-5
Sampling date	10/13-10/14/75	4/1/73	4/19/76	11/22/75	7/21/75
Coal concentration in feed slurry	25% by weight	33% by weight	38.5% by weight	20% by weight	33% by weight
Reactor temperature	457°C	447°C	454°C	457°C	457°C
Reactor pressure	2400 psig	1700 psig	1650 psig	2400 psig	1700 psig
Coal feed rate	500#/hr	530#/hr	540#/hr	400#/hr	55#/hr
Space rate	25#/(hr-ft^3)	26#/(hr-ft^3)	30#/(hr-ft^3)	16#/(hr-ft^3)	41#/(hr-ft^3)
Feed gas rate	10,000 scfh	6,400 scfh	5,300 scfh	10,000 scfh	5,000 scfh
hydrogen concentration	86% by volume	88% by volume	85% by volume	85% by volume	86% by volume
Hydrogen consumption	2.9% MAF coal	1.9% MAF coal	2.2% MAF coal	3.3% MAF coal	2.7% MAF coal
Conversion (residue/dry coal)	∿16*	∿25*	∿18*	∿22*	∿15*

*Based on % conversion of MAF feed coal and ash values.

	Solvent Refined Coal - Washington					
Process	MODE 1		MODE 2			
Sample set	SRC-Wash-1	SRC-Wash-2	SRC-Wash-3	SRC-Wash-4	SRC-Wash-5	SRC-Wash-6
Sampling date	3/2/76	9/20/76	8/26/77	10/31/77	11/15/77	12/5/77
Reactor temperature	449°C	449°C	460°C	456°C	461°C	447°C
Reactor pressure	1545 psig	1500 psig	1920 psig	1883 psig	2012 psig	2007 psig
Coal feed rate	3525 #/hr	2150 #/hr	1979 #/hr	2619 #/hr	1675 #/hr	1675 #/hr
Conversion (residue/dry coal)	18.00%	19.3%	14.1%	9.3%	20.8%	21.4%

by AA. The procedure for preparation of the low-temperature ash is also described in Appendix C.

Whole coal samples from the process plants were analyzed directly by instrumental neutron activation analysis (INAA), ion-selective electrode (ISE), NAA-RC, ASTM methods of coal analysis, and XES. In general, the coal samples received were very finely divided (-100 mesh).

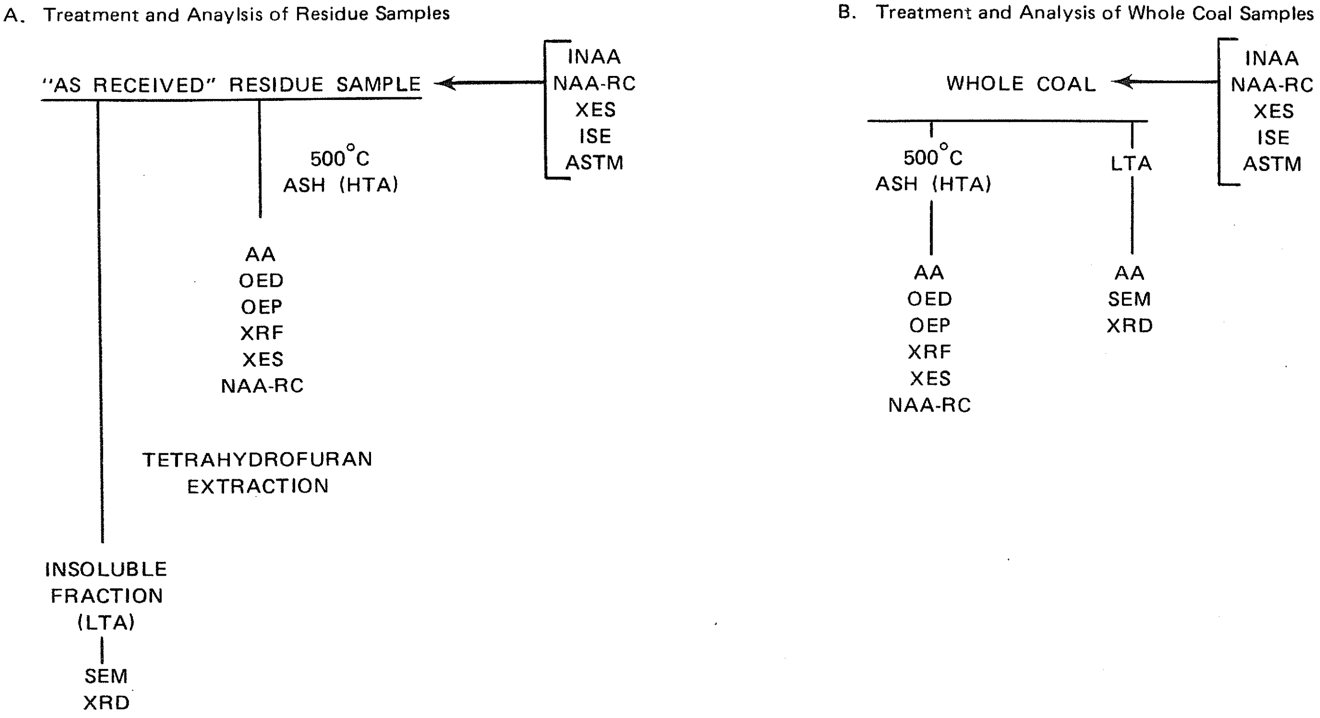


Figure 1. Flow sheets of treatments of samples and their analyses.

The liquefaction residue samples were either ashed conventionally at 500°C, extracted with tetrahydrofuran (THF), or analyzed as received; the preparation of the sample depended upon the analytical method (see Appendix C for details). The high-temperature ash from residue samples, like that from the coal samples, was suitable for AA, OED, OEP, XRF, XES, and NAA-RC. To prepare the low-temperature ash samples for SEM and XRF analysis, the "as received" residues were first extracted with THF. The insoluble residue was then subjected to the low-temperature plasma ashing as for whole coal; this method was deemed necessary because the residue samples were often intractible and possibly inhomogeneous mixtures of product oil, unreacted and partially reacted coal, and mineral matter. To remove most of the volatile components from the mineral matter portion of the residue so that low-temperature ashing could be completed more readily, the product oil portion of the residue sample was removed from the solid portion by slurrying the sample in THF as described in Appendix C.

Initial studies analyzing both the THF insoluble and THF soluble fractions of the residue indicated that most elements (except Br, Dy, Ge, Sc, U, and Yb and possibly some other elements) were quantitatively retained in the insoluble fraction. Because it was more convenient to analyze the unextracted residue sample and not be concerned with possible losses due to extraction, the THF extracted residue samples were thereafter not analyzed.

The "as received" residues were suitable for analysis by INAA, NAA-RC, ISE, ASTM, and XES procedures. In most cases the sample was not finely divided and a large amount (>1 gram) was taken for each determination.

Chemical procedures. The chemical procedures developed and used in this project are detailed in Appendix C. They include atomic absorption spectrometry (AA), instrumental neutron activation analysis (INAA), direct-reading optical emission spectrometry (OED), photographic optical emission spectroscopy (OEP), energy-dispersive X-ray fluorescence (XES), wavelength-dispersive X-ray fluorescence

Table 3. Methods used to determine various elements in coal liquefaction feed coals and residues.

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

*Strontium results by INAA are satisfactory for concentrations above 10 ppm.

(XRF), procedures for coal analysis by the American Society for Testing and Materials (ASTM), ion-selective electrode analysis (ISE), and neutron activation analysis with radiochemical separation (NAA-RC). The 71 elements determined and the best method or methods for the determination of each are listed in table 3. Whenever possible, results for an element were checked by using two or more methods of analysis. The best method for the determination of a particular element was chosen on the basis of the known applicability of a method for the particular element, results obtained for known standards, and comparison of results from three or more methods. Generally, when two or more methods were used for determining an element, the values were averaged.

Treatment of data. The analytical results for major, minor, and trace elements for feed coals, liquefaction residues, and products were calculated to the moisture-free, unashed basis and are reported and defined as "as received" data. The results for C, H, N, and S are reported without correction for moisture; however, the moisture contents are given. The data for the feed coals and residues are listed in Appendix D. The "as received" data were also calculated to the "500°C ash-basis" using the determined ash values and are reported in Appendix E. These data on the 500° ash basis were used to compare concentrations of elements in the residue with their concentrations in the corresponding feed coal to measure retention during liquefaction. Such a comparison assumes that the ash from the feed coal is comparable to the corresponding ash from the liquefaction residue and that the feed coal sample is representative of the coal used to generate the liquefaction residue sample. These assumptions were tested and verified by using the Hotelling's T^2 test on 13 elements. These results are presented and discussed in Appendix F.

An estimate of the retention of an element during the liquefaction process was calculated by taking into account the mean sampling error and the analytical error for a particular method. The mean sampling error was estimated from the relative standard deviations of determinations made on replicated samples of ashed (500°C) feed coals and residues. Comparison of replicated ash determinations were used as a rough measure of the homogeneity of samples. This is an estimate of laboratory sampling reproducibility for feed coals and residues. The estimate may be low for any particular element. The results of replicate 500°C ash determinations for feed coals and residues are given in Appendix G.

For 18 feed coals, each of which had been ashed from 2 to 10 times, the mean relative sampling error was 0.64 percent. The mean relative sampling error for residues for 12 samples, each of which had been ashed from 2 to 5 times, was 0.85 percent. The overall relative sampling error (RSE) of $\sim$0.75 percent indicated only minor inhomogeneity in sampling both coal and residue and is not considered to be significant.

The relative analytical error (RAE) of a method was estimated for each element from replicate determinations on samples with concentrations over the range observed for that element. These values varied from 3 percent to over 40 percent depending upon the method, the element, and its concentration.

The overall relative standard deviation (RSD) was then derived from the RSE and RAE as follows:

$$\mathrm{RSD} = \sqrt{\mathrm{RSE}^2 + \mathrm{RAE}^2}$$

In most cases the RAE>>RSE.

When an element was determined by more than one method, the overall RAE was calculated as the square root of the sums of the squares of the individual RAEs, divided by the number of methods.

The term "retention range" for an element is arbitrarily defined as *twice the overall relative standard deviation*, (2 x RSD). To compare the concentration of an element in the liquefaction residue to the concentration in the feed coal the term "percentage change" is defined as

$$100 \times \frac{\text{Concentration in residue (ash basis) - Concentration in feed coal (ash basis)}}{\text{Concentration in feed coal (ash basis)}}$$

When the percentage change is less than 2 x RSD for an element it is *retained* (i.e., it is neither depleted nor enriched in the residue relative to the concentration in the feed coal). If the "percentage change" is *greater* than the upper limit of the "retention range" for an element, a depletion (loss) or enrichment (gain) has occurred owing to the liquefaction process. Table 4 lists for each element the "retention range" limit, rounded off to the nearest 5 percent. This method of determining the retention of an element during liquefaction is only an estimate, subject to the assumptions and errors discussed. The data are from a small number of sample sets of feed coal and residues and may not be completely representative of the process at a plant. Also, some elements (I, Pd, Ag, and W) could not be accurately determined, usually because of their low concentrations in the coals and liquefaction residues.

RESULTS AND DISCUSSION

The results of chemical analyses for 71 elements in 19 sets of feed coals and liquefaction residues are listed in Appendix D. These data are reported on the "as received" basis and have been corrected for moisture content.

Concentration units are in ppm, unless otherwise noted. For those elements that were determined by more than one method, all data are reported.

The "as received" values vary from set to set because of the different sources of coal, the different organic matter contents of the residues, and the particular liquefaction process involved. Because the "as received" data are difficult to compare when going from feed coal to corresponding liquefaction residue, concentrations were normalized for carbon content by calculating them to 500°C ash (based upon % ash value of the "as received" samples). These data are presented in Appendix E.

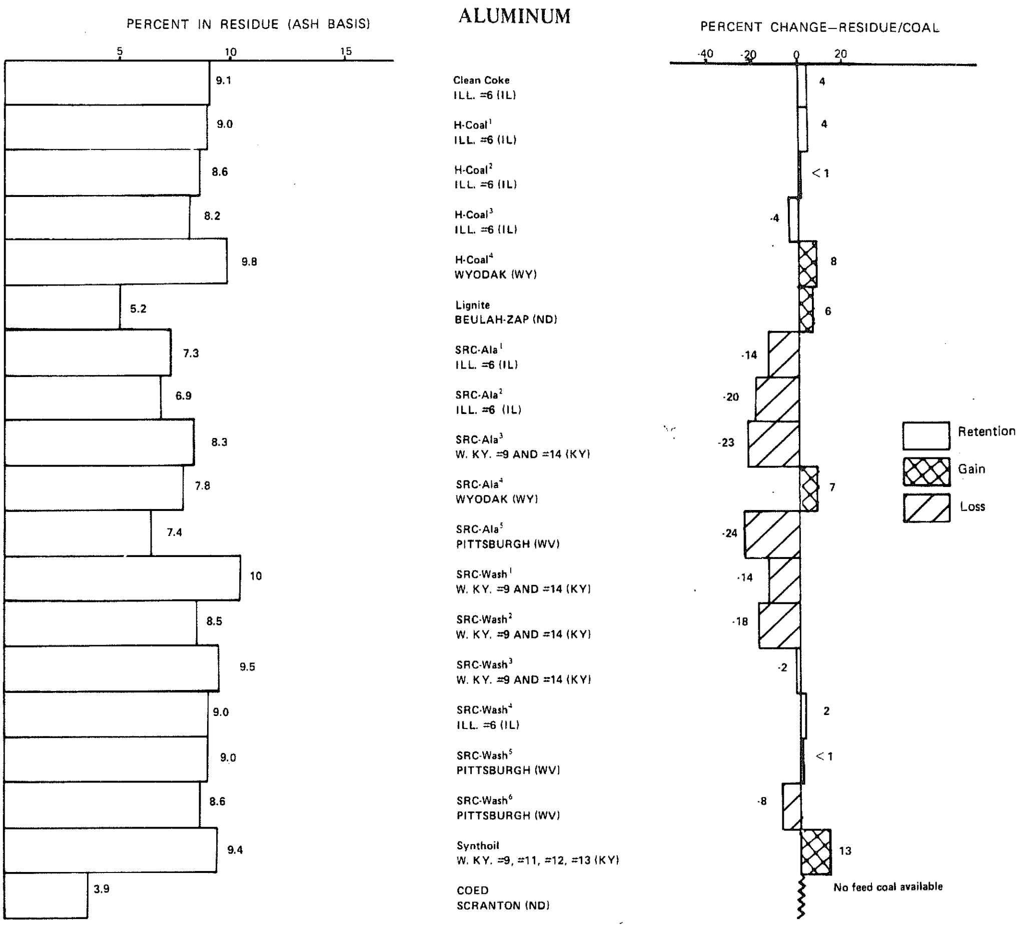
Data for each element on the 500° ash-basis (except for Ag, Bi, Cd, In, and Pt which were predominantly "less than" values) are given in graphic form in Figures 2.1 to 2.32. Concentrations in the residues (ash basis) and percentage change (loss or retention) of an element in the residue as compared to the corresponding feed coal are both illustrated.

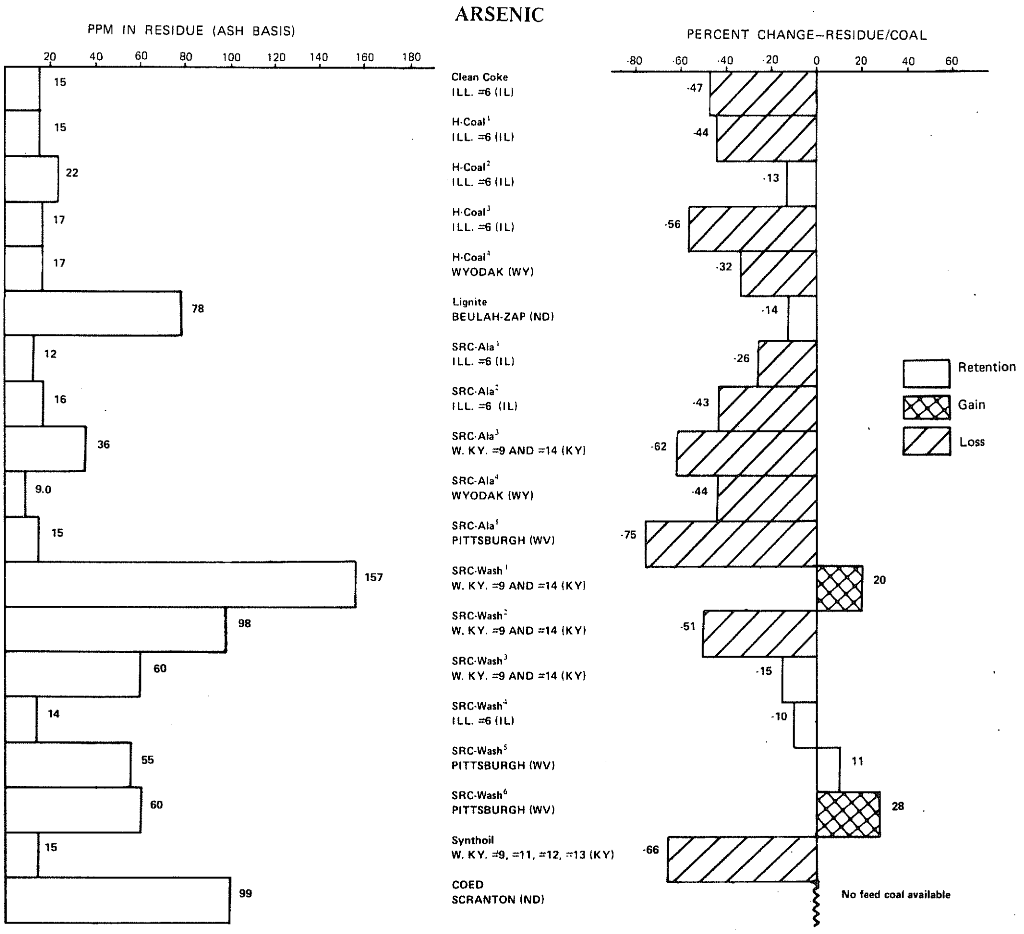
Table 4. Retention ranges or limits of change in elemental concentration (on ash basis) from feed coal to residue defining retention in the coal liquefaction processes

Element	Retention Range (%)	Element	Retention Range (%)	Element	Retention Range (%)
Al	±5	Ge	±40	S	±5
Ag	±40	Hf	±30	Sb	±20
As	±20	Hg	±30	Sc	±10
Au	±80	Ho	±15	Se	±30
B	±20	I	±100	Si	±5
Ba	±20	In	±60	Sm	±10
Be	±20	K	±15	Sn	±30
Br	±30	La	±15	Sr	±20
Ca	±5	Li	±25	Ta	±20
Ce	±25	Lu	±25	Tb	±20
Cl	±30	Mg	±10	Te	±50
Co	±20	Mn	±20	Th	±20
Cr	±20	Mo	±20	Ti	±5
Cs	±30	Na	±10	Tl	±30
Cu	±20	Nd	±10	Tm	±50
Dy	±20	Ni	±35	U	±40
Er	±40	P	±50	V	±25
Eu	±10	Pb	±30	W	±60
F	±10	Pd	±100	Y	±50
Fe	±10	Pr	±20	Yb	±20
Ga	±30	Pt	±40	Zn	±10
Gd	±50	Rb	±40	Zr	±40

Concentrations for each element in the residues (Figures 2.1 to 2.32) from the 7 different liquefaction processes, show the potential amounts available for extraction and beneficiation. These data form the basis for the minerals-economic evaluation later in this paper. Concentrations of elements in the residues generally reflect their concentrations in the feed coals, except for extremely mobile elements. For example, in figure 2.14, the concentrations of K in residues that were derived from Illinois No. 6 seam coal (a bituminous coal) are similar. Also, the K concentrations in those residues are somewhat higher than the K concentrations in residues derived from the Wyodak seam (a subbituminous coal) or the lignite seams.

Of geochemical interest is the complete set of data that was generated in this study on the rare-earth elements (REE) in coal and their respective liquefaction residues. The REE are generally retained in the residues and reflect the REE concentrations of the feed coals. There is a similarity of the REE abundance pattern for coal compared to the REE abundance pattern for shale (Appendix L, Figures L1 and L2). The results for all samples are given in tables in Appendices D and E, and they are shown in Figures 2.1 to 2.32. Analytical methods and a discussion of results are presented in Appendices C and L respectively.



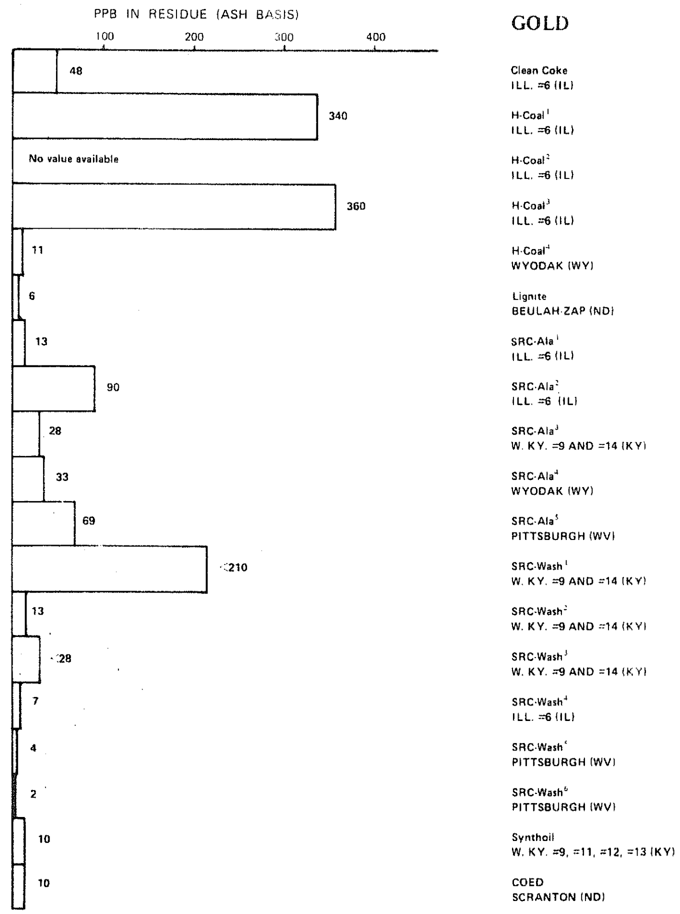


Figures 2.1 to 2.32

Concentrations of elements in residues and percentage change in concentration (ash basis) of elements from coal to residue.

Figure 2.1 Al and As

GOLD



BORON

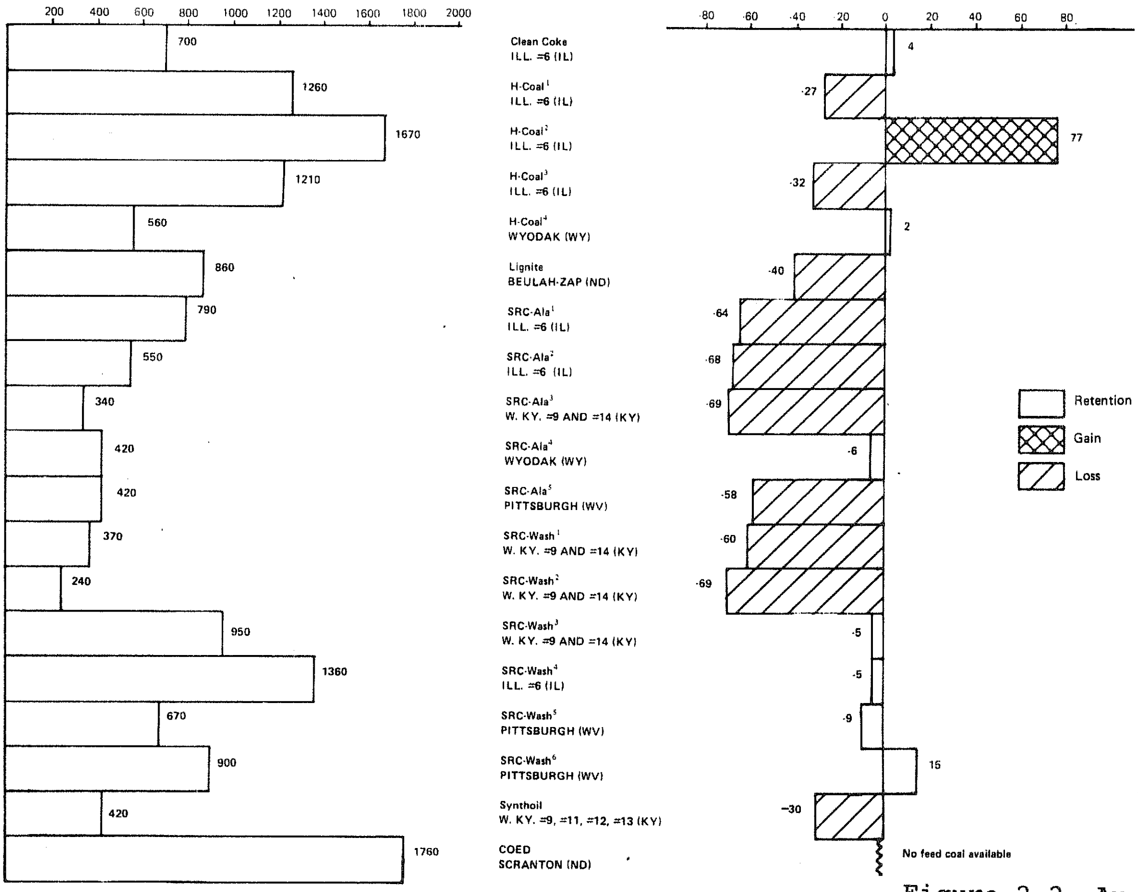
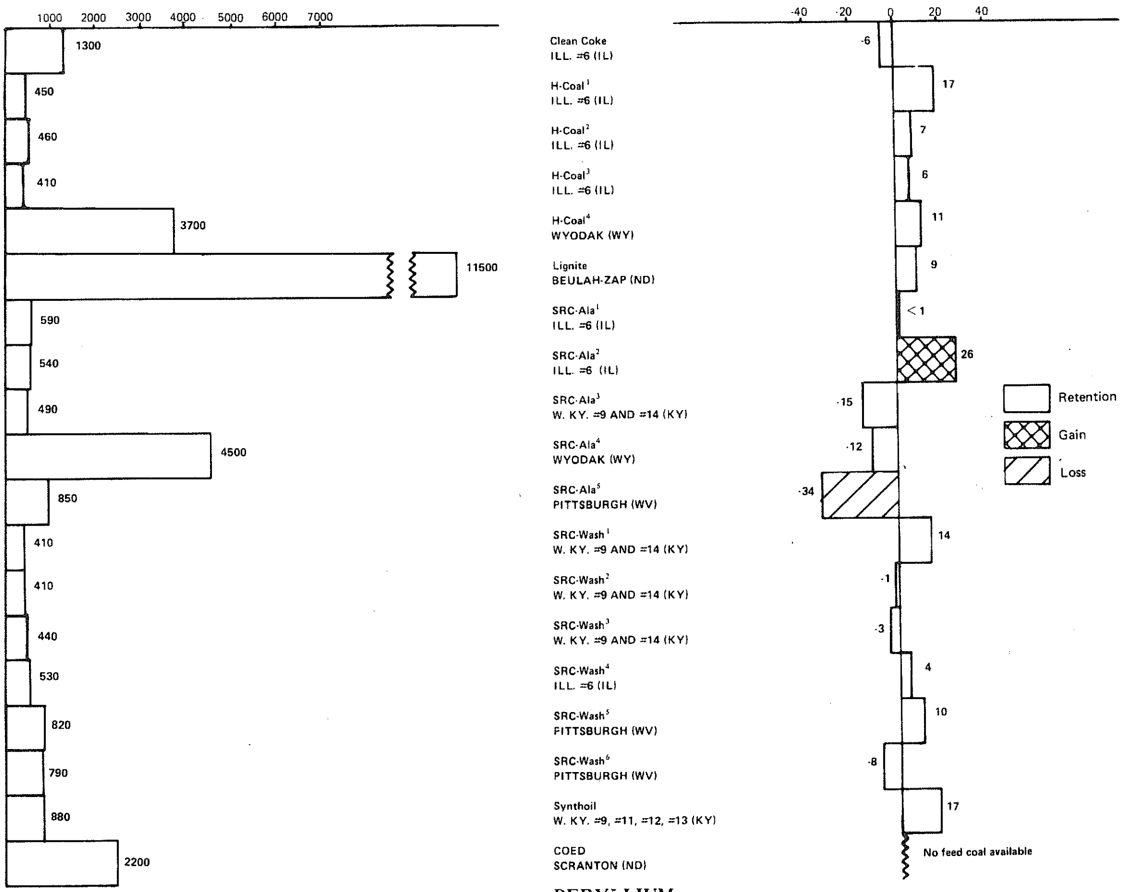


Figure 2.2 Au and B

BARIUM



BERYLLIUM

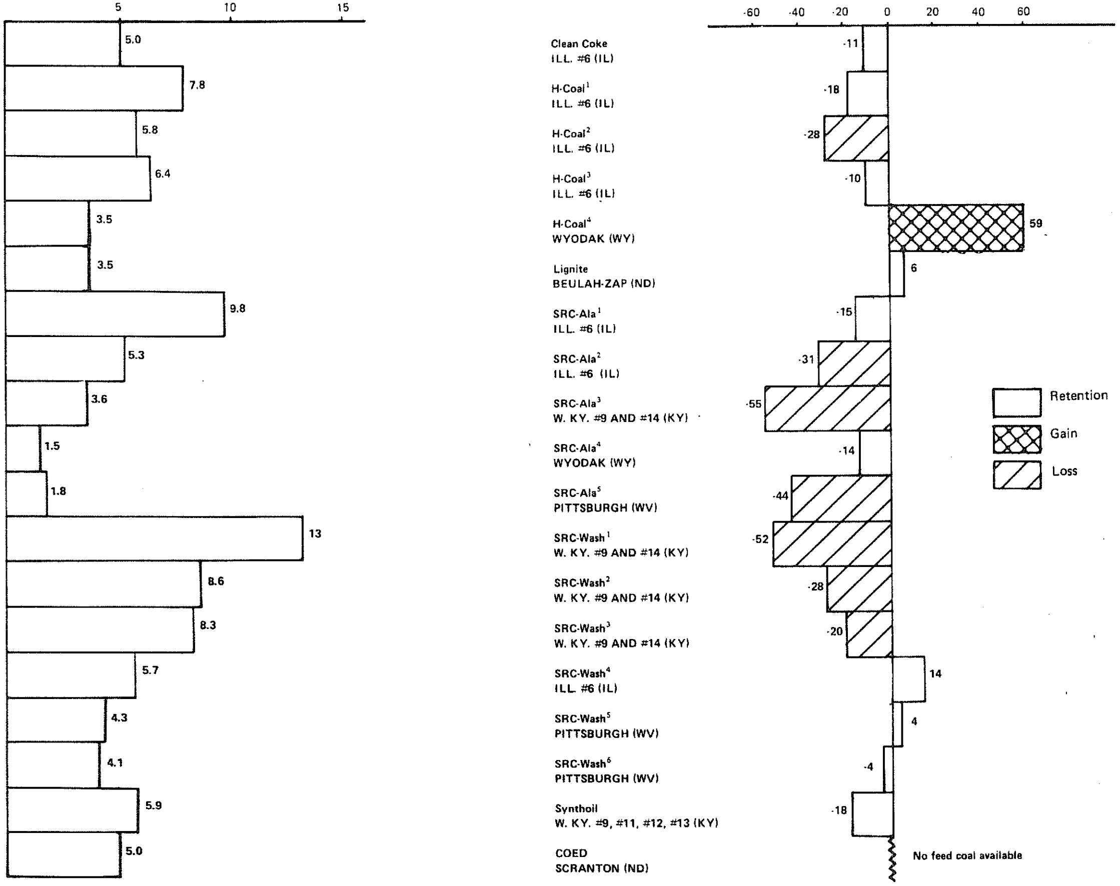


Figure 2.3 Ba and Be

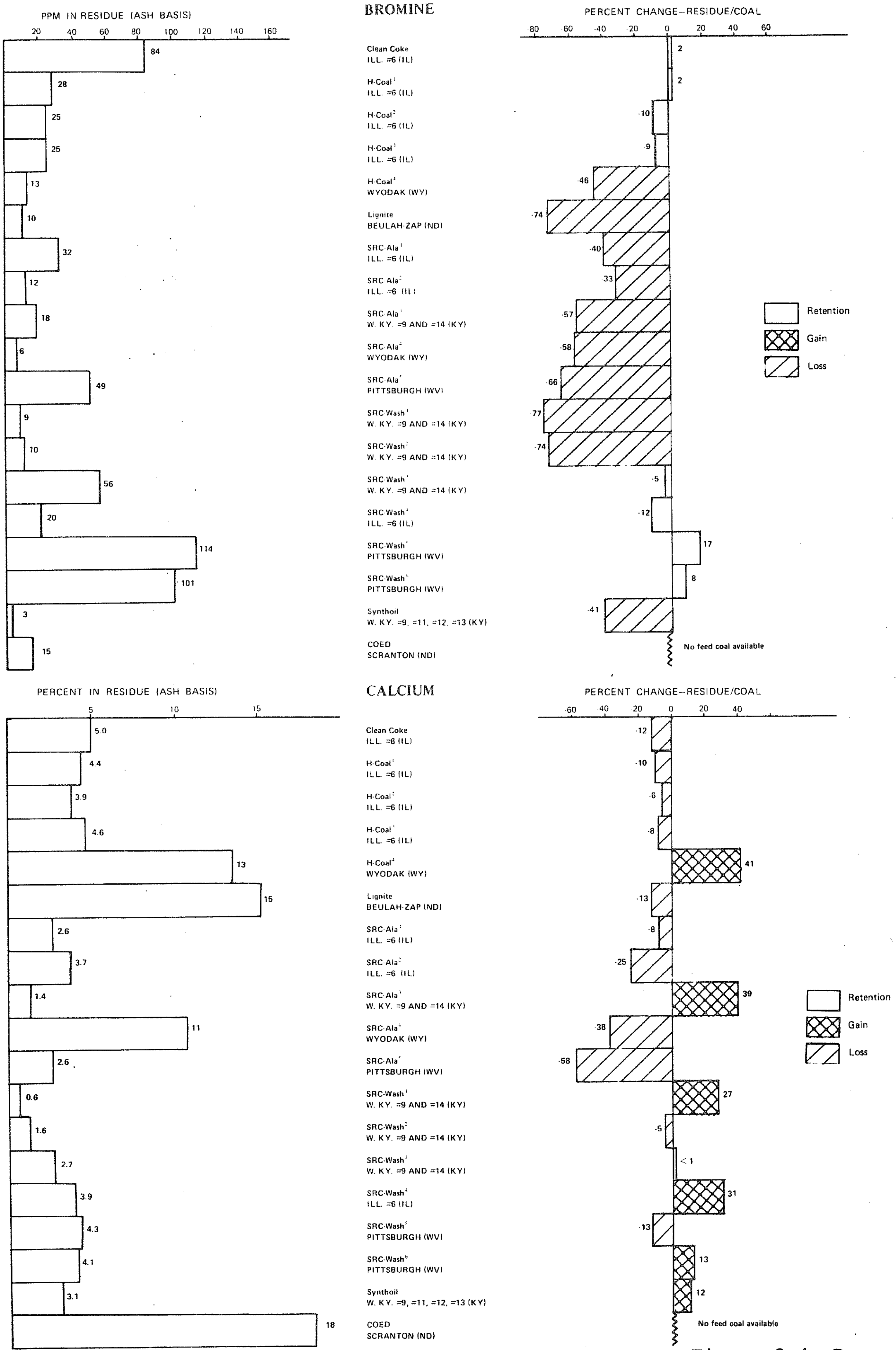


Figure 2.4 Br and Ca

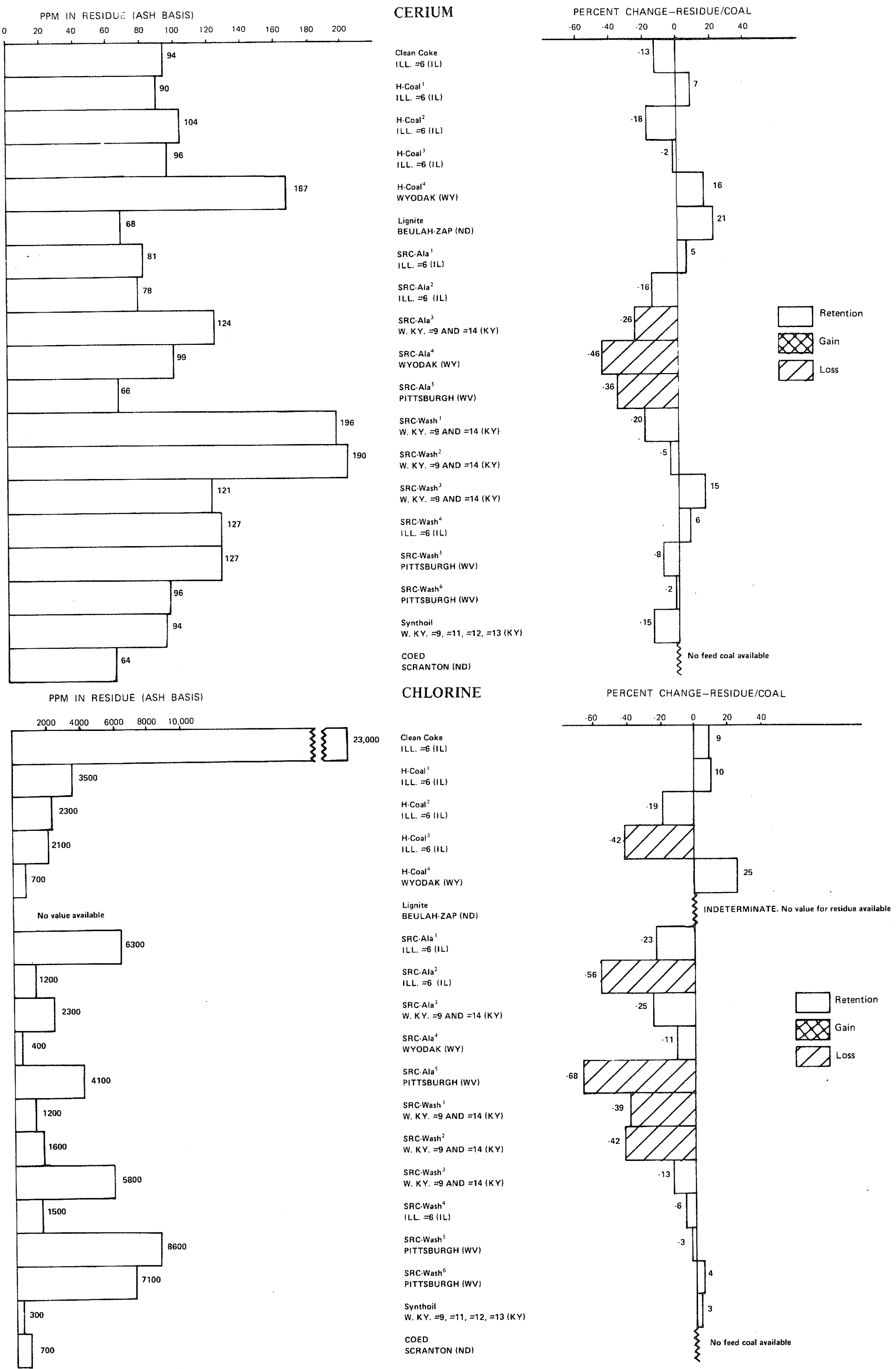
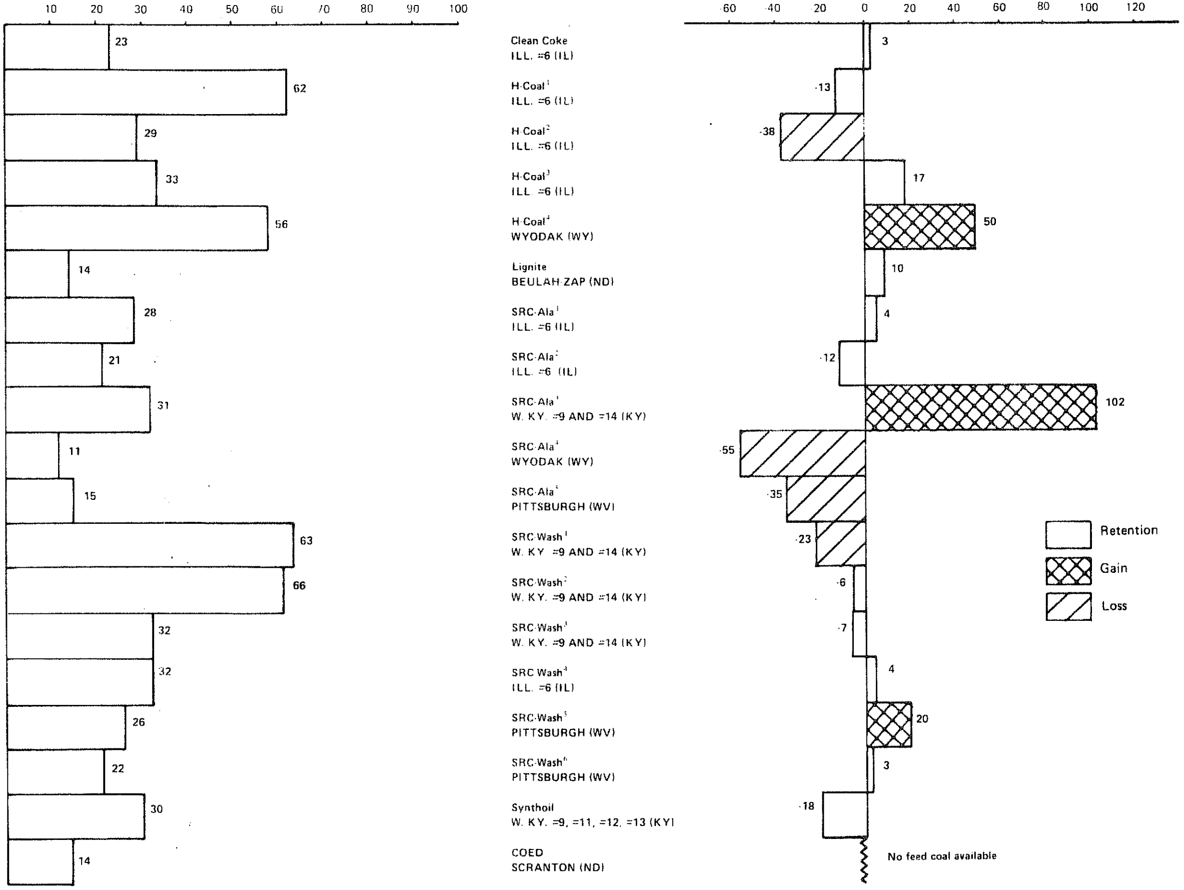


Figure 2.5 Ce and Cl

COBALT



CHROMIUM

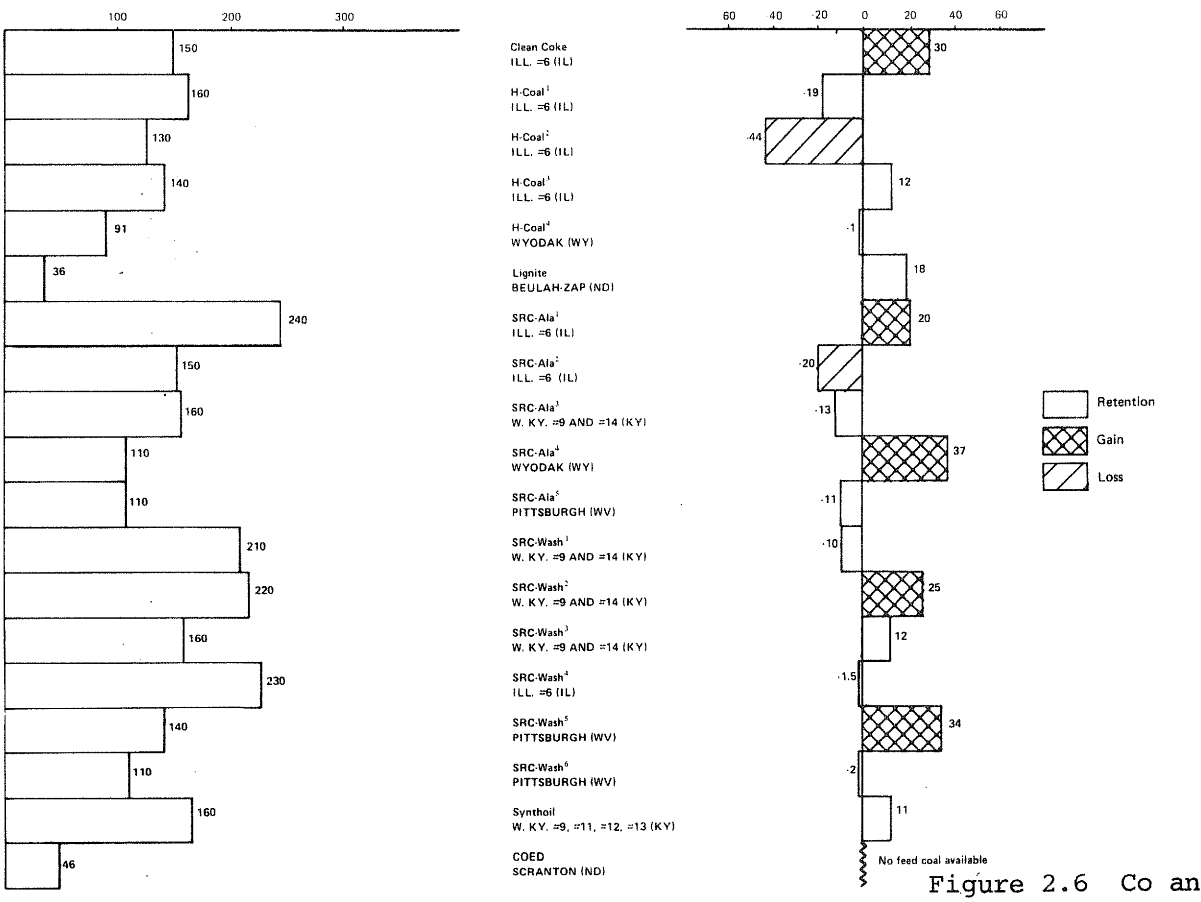


Figure 2.6 Co and Cr

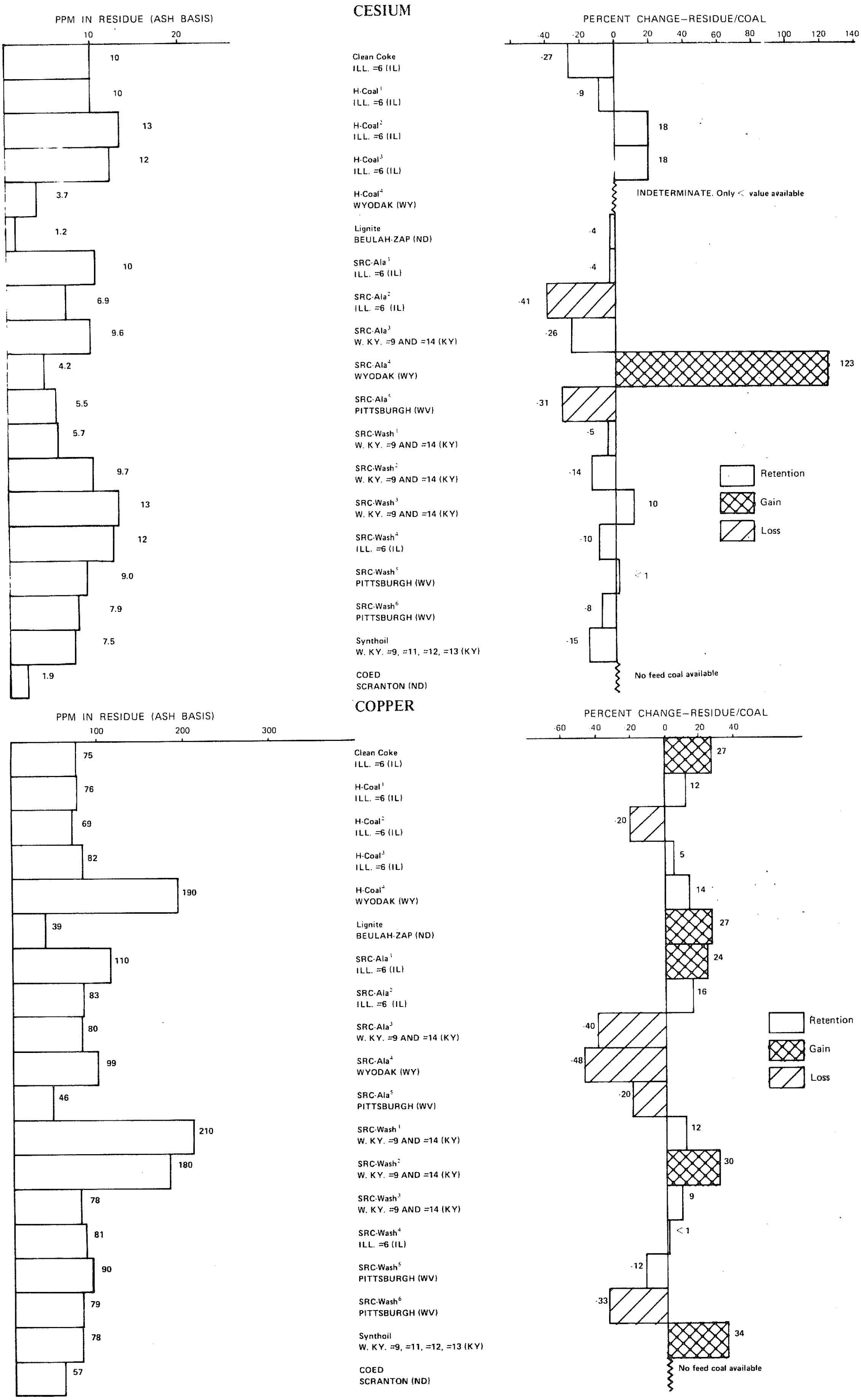


Figure 2.7 Cs and Cu

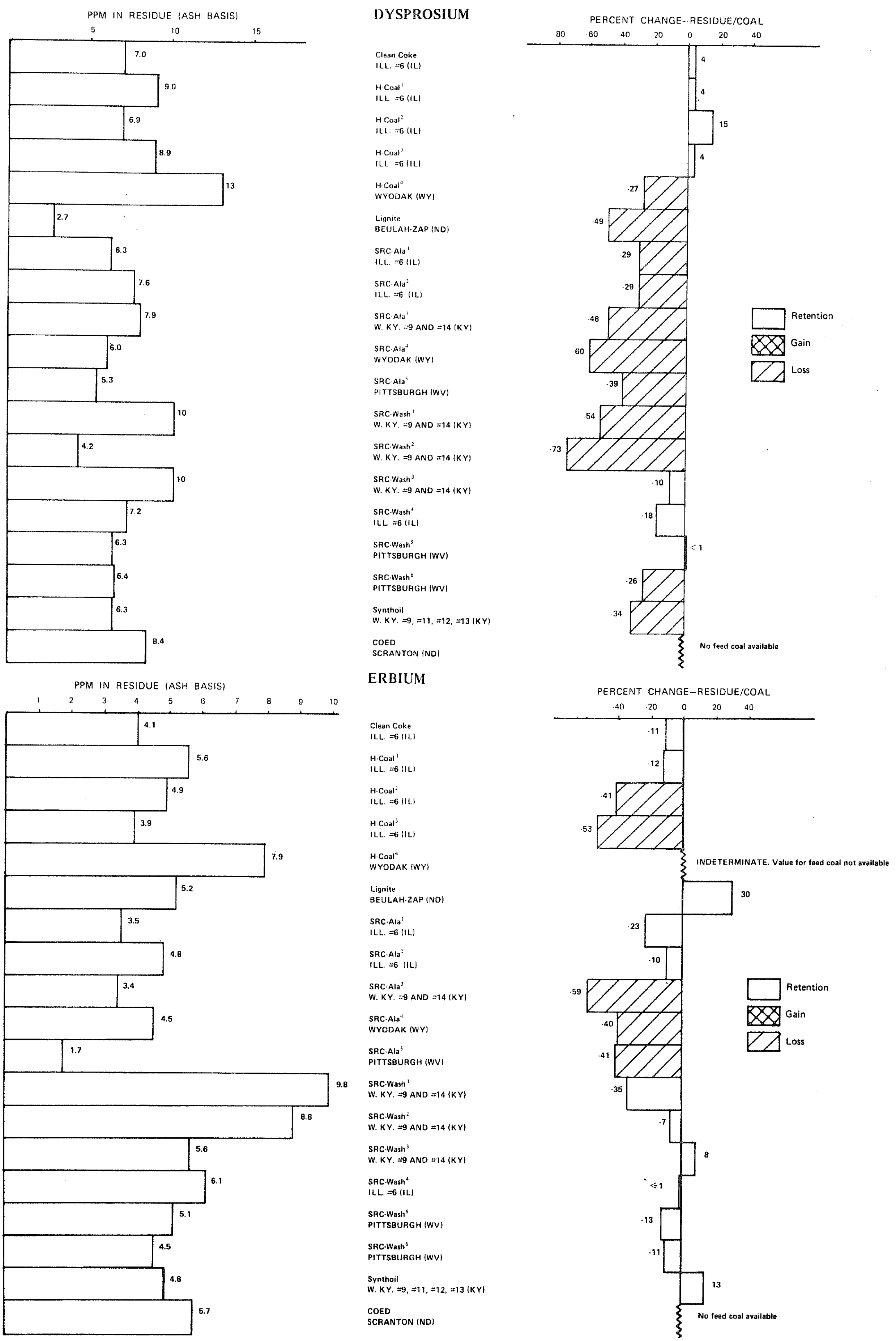
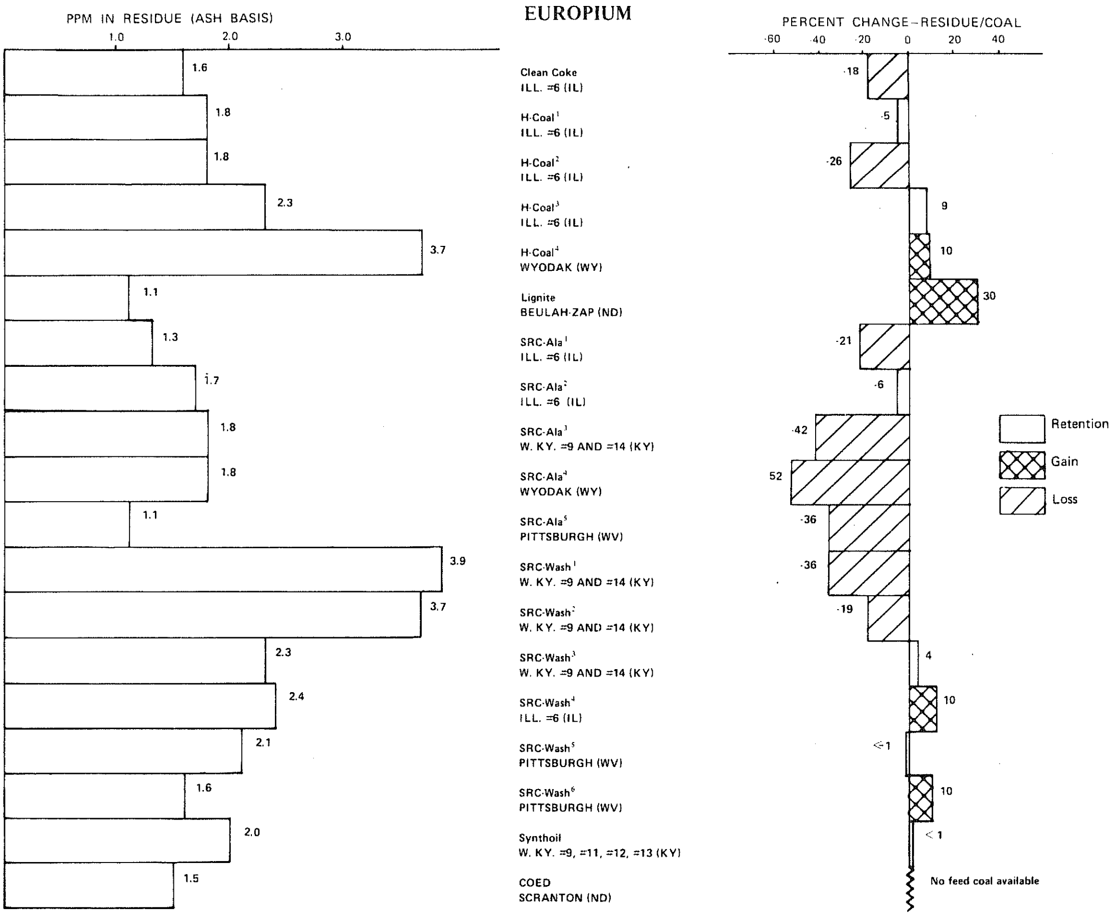


Figure 2.8 Dy and Er



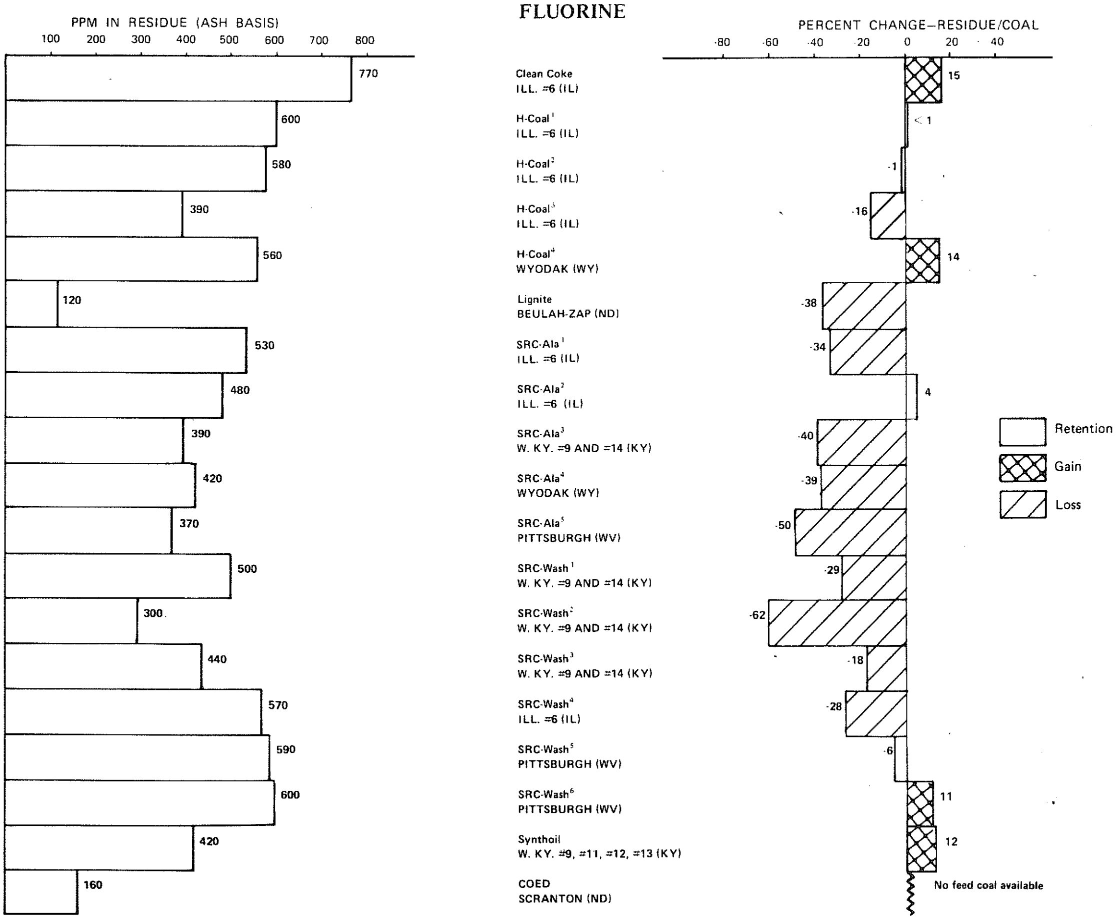


Figure 2.9 Eu and F

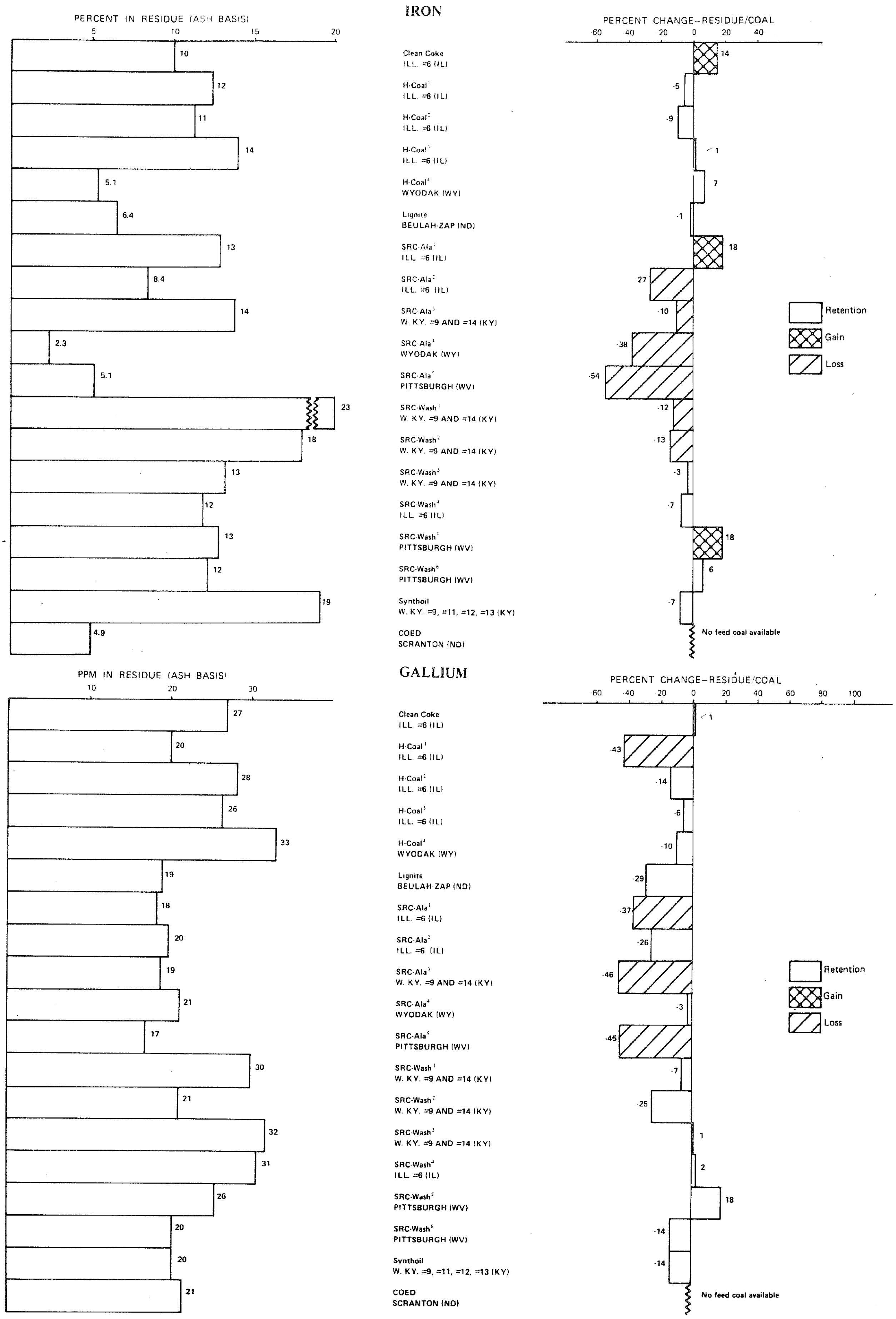
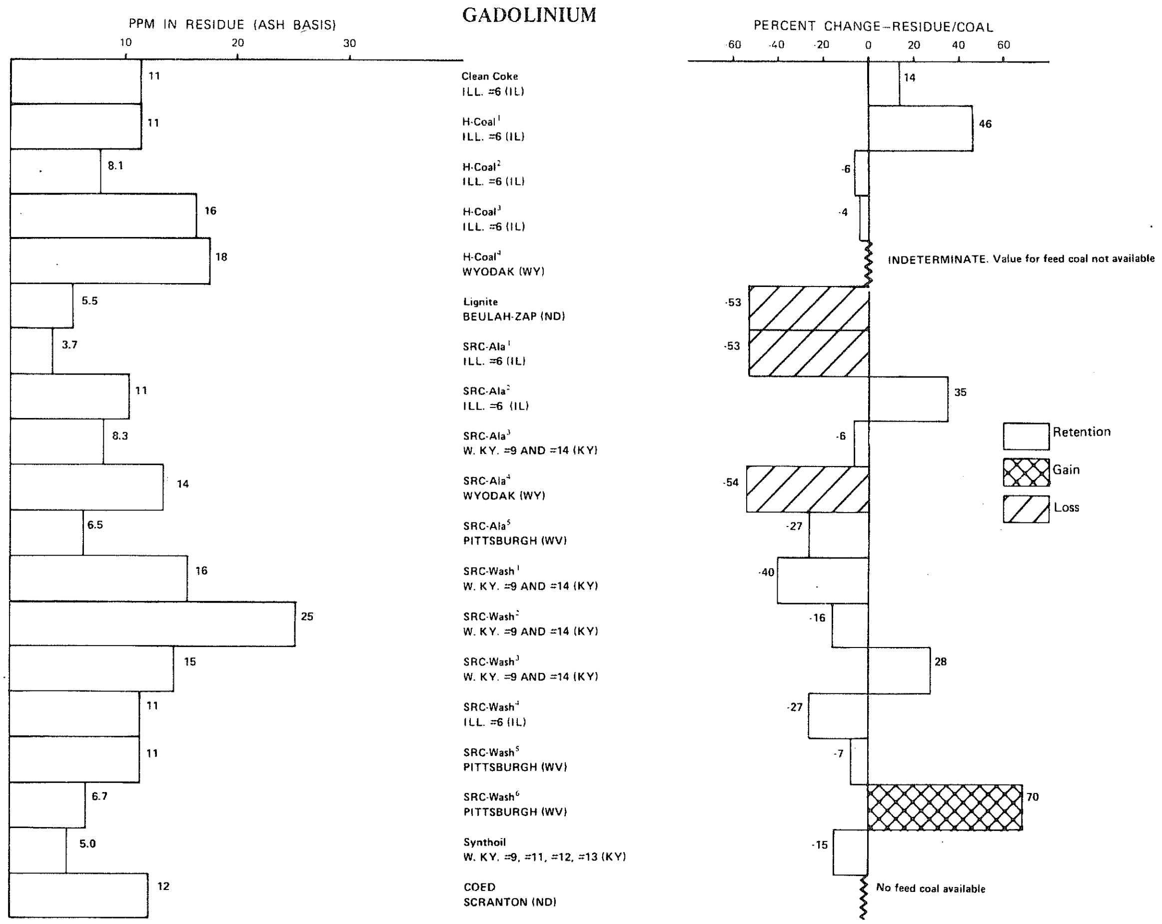


Figure 2.10 Fe and Ga



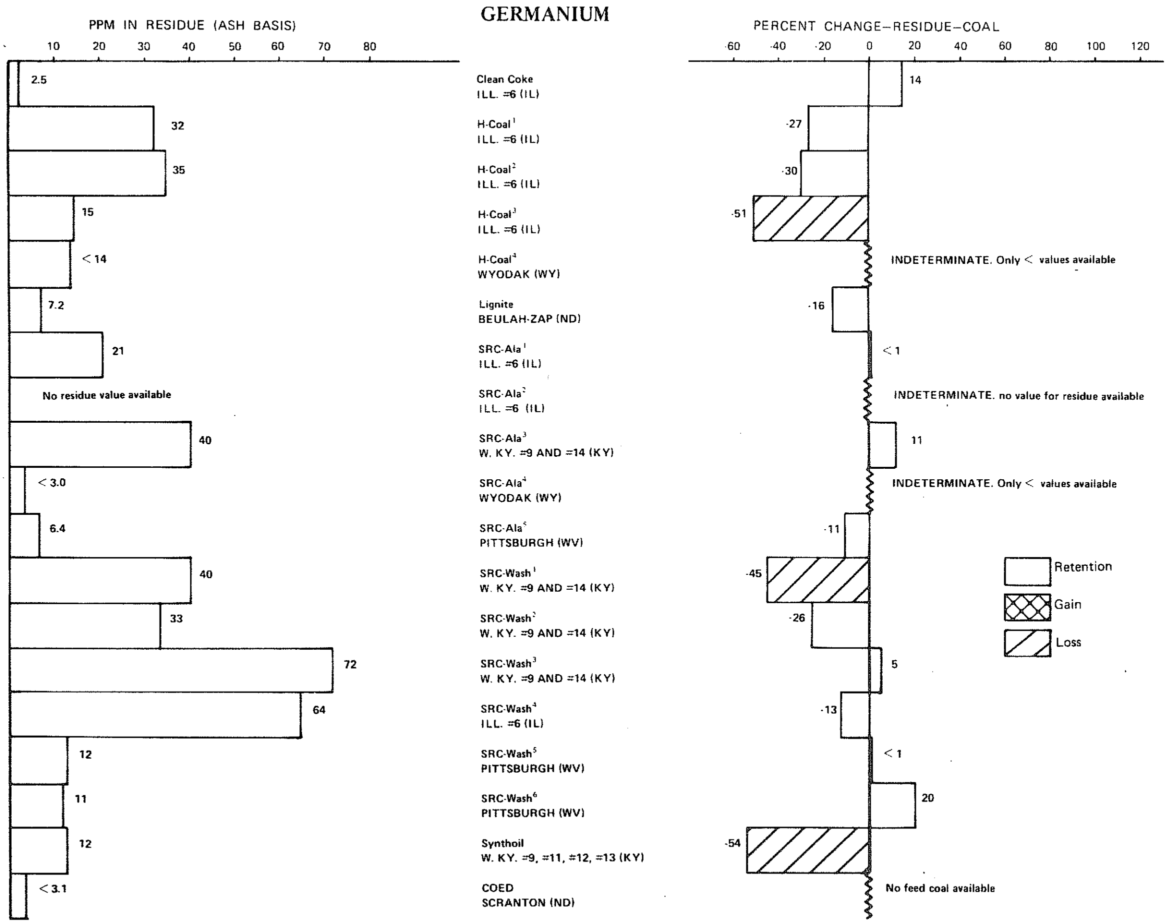


Figure 2.11 Gd and Ge

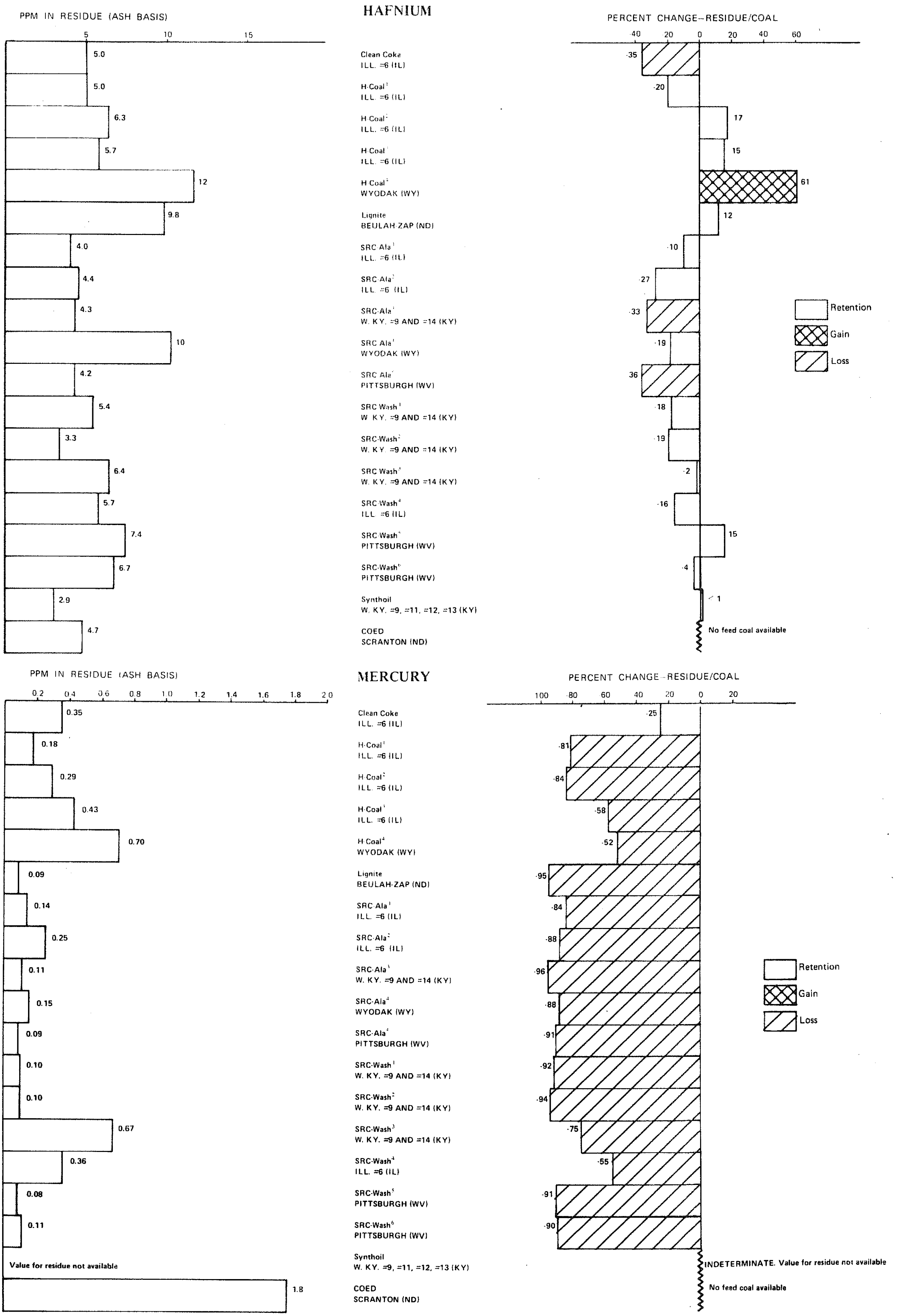


Figure 2.12 Hf and Hg

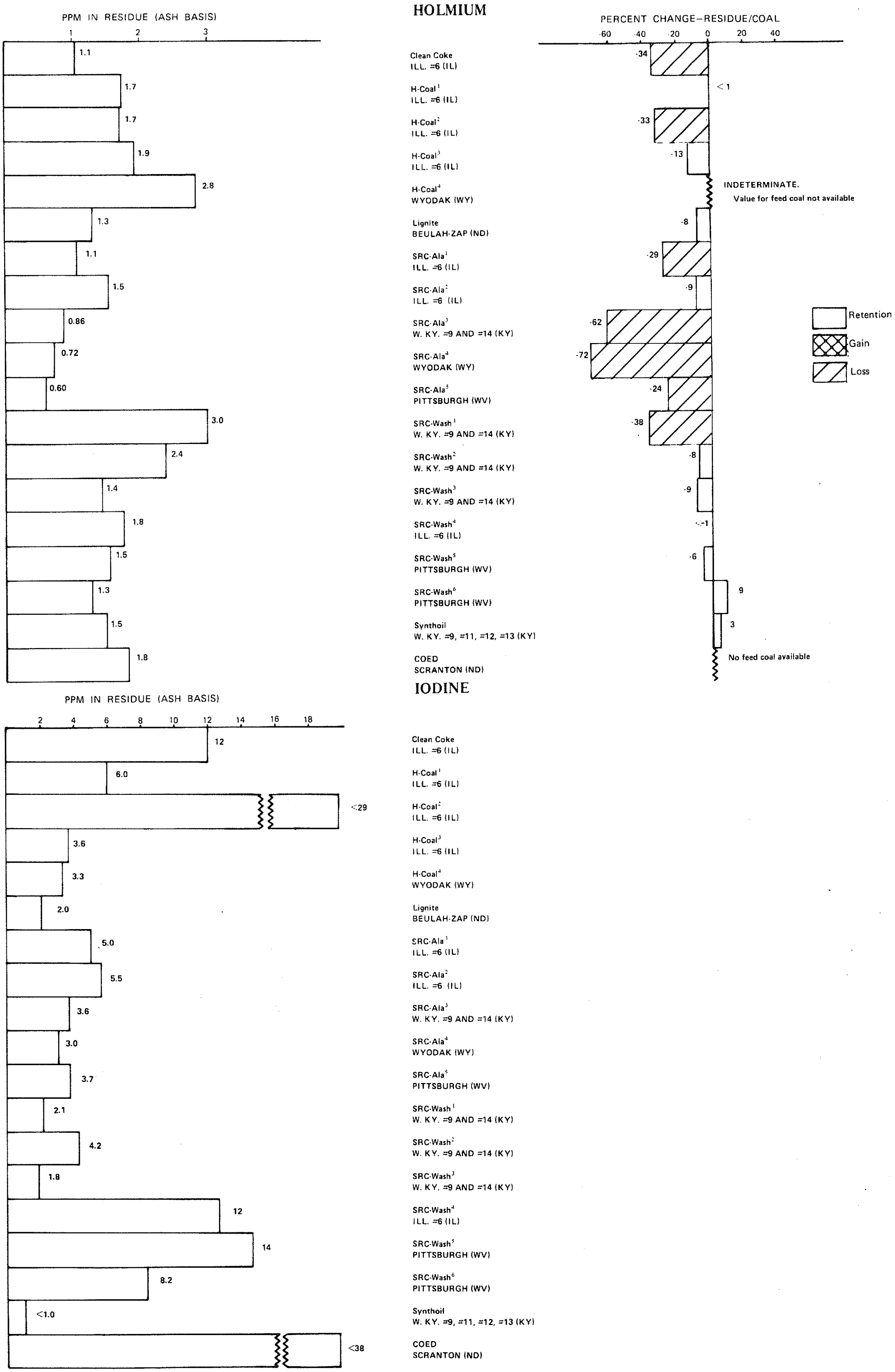
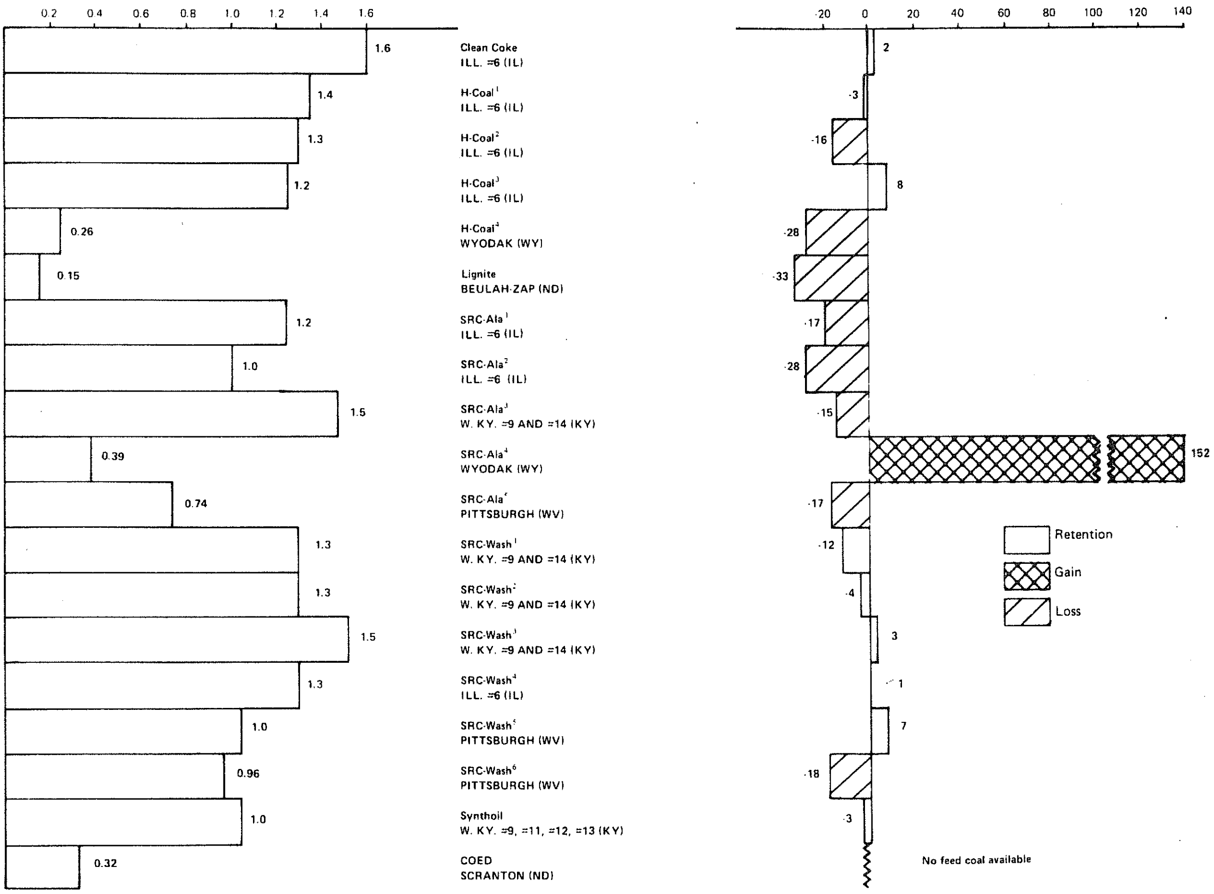
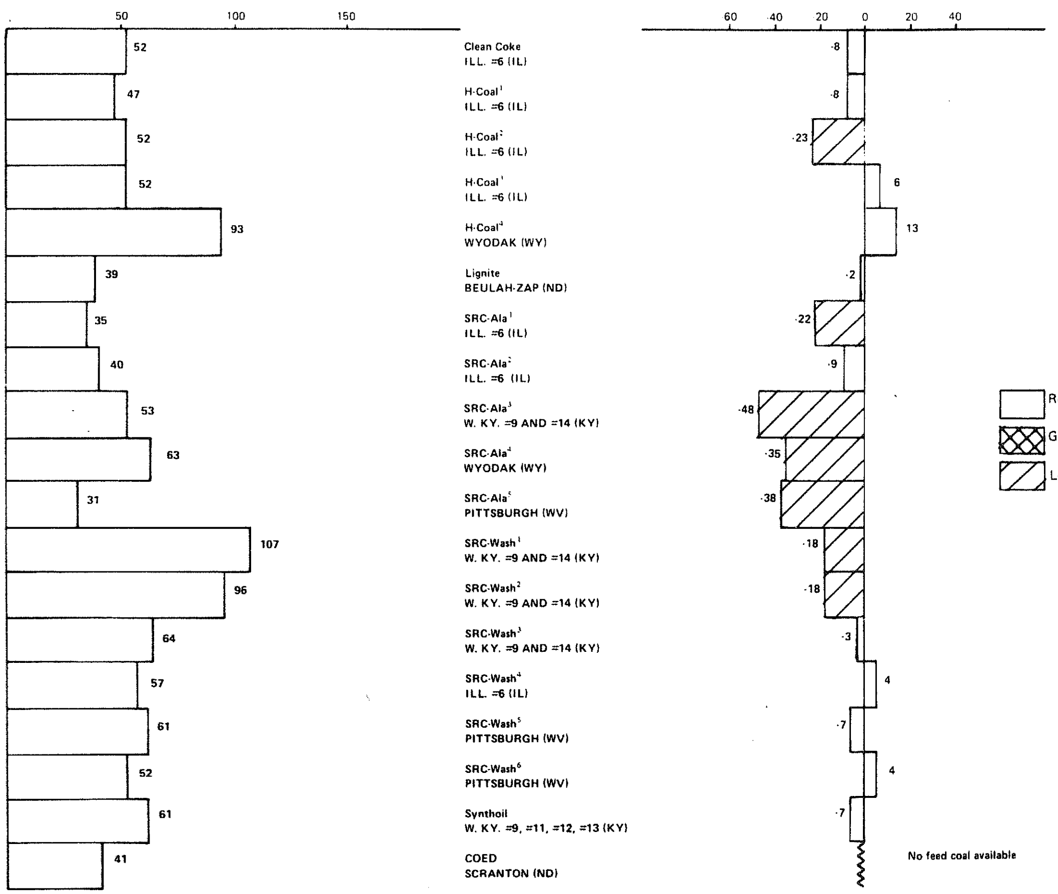


Figure 2.13 Ho and I



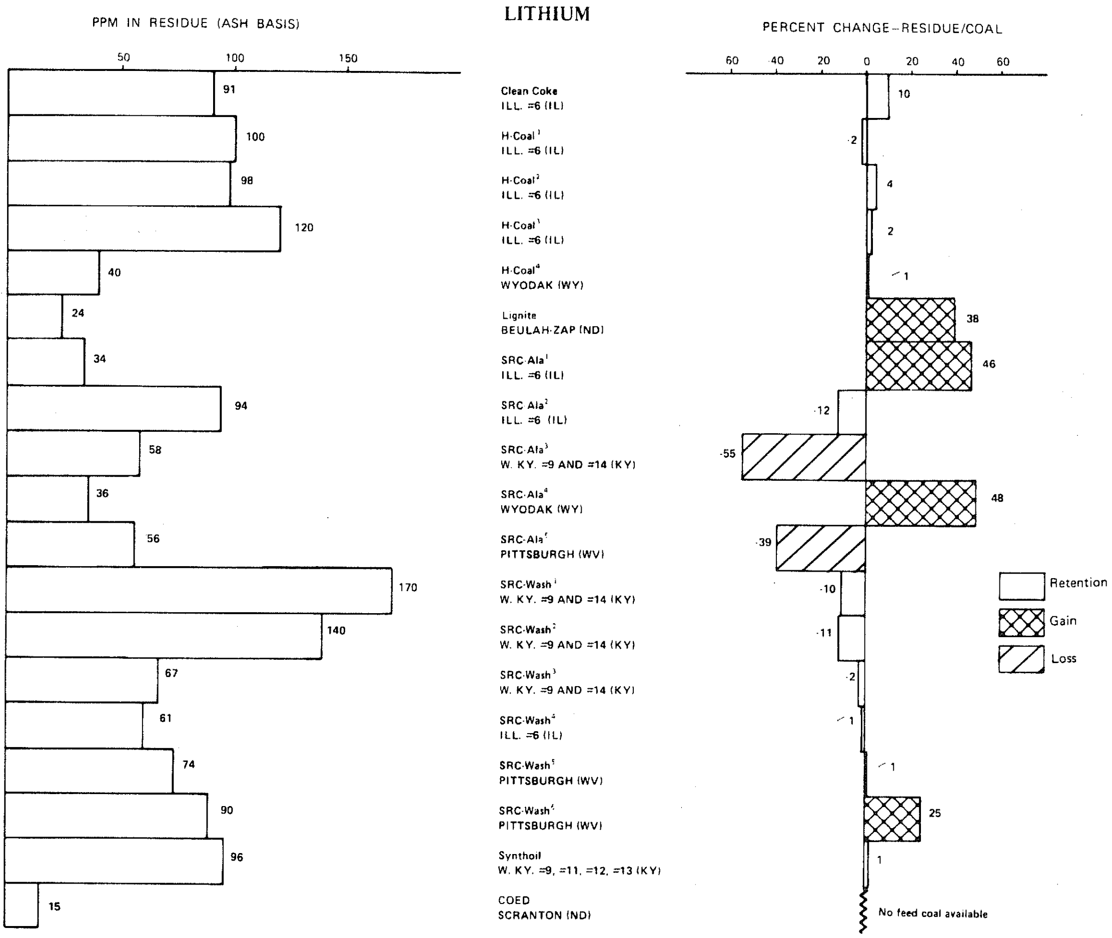
POTASSIUM



LANTHANUM

Figure 2.14 K and La

LITHIUM



LUTETIUM

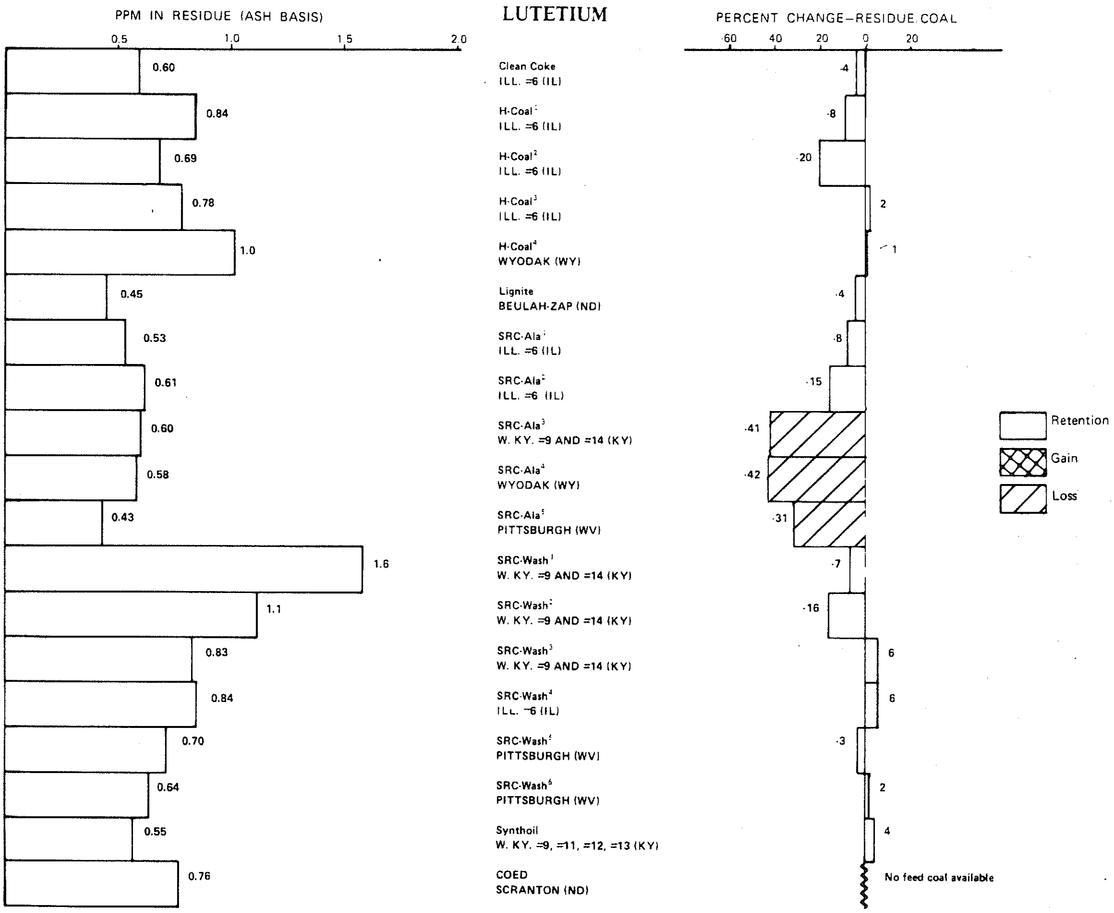
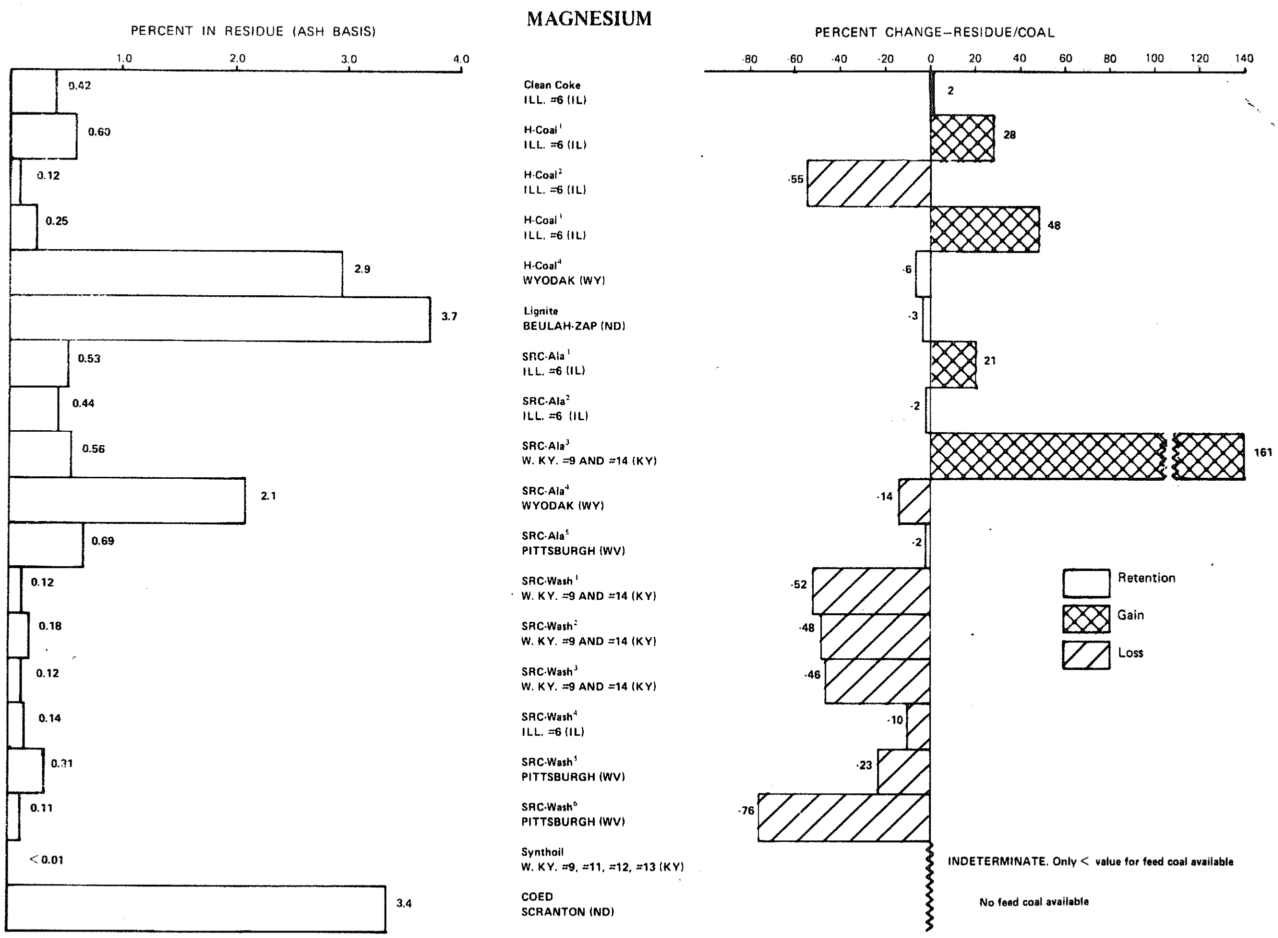


Figure 2.15 Li and Lu



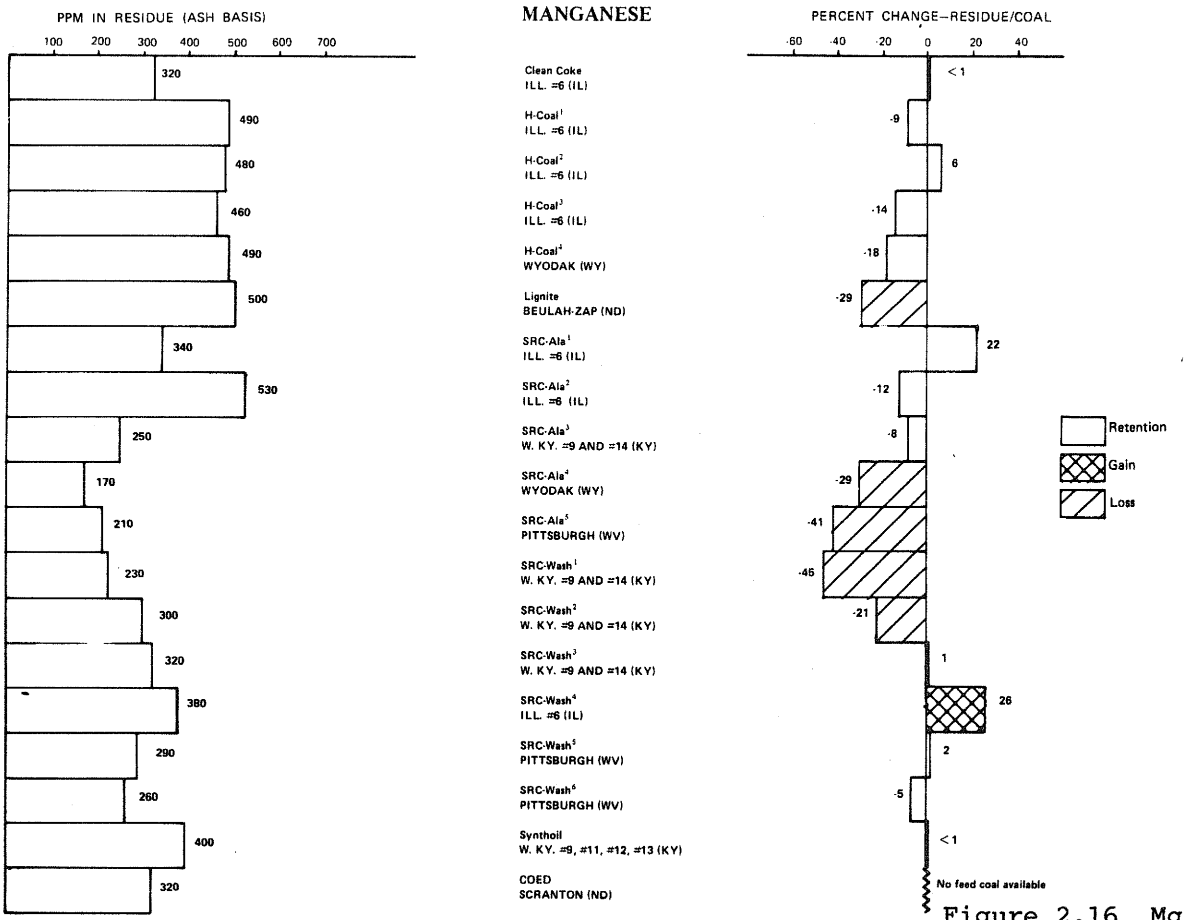


Figure 2.16 Mg and Mn

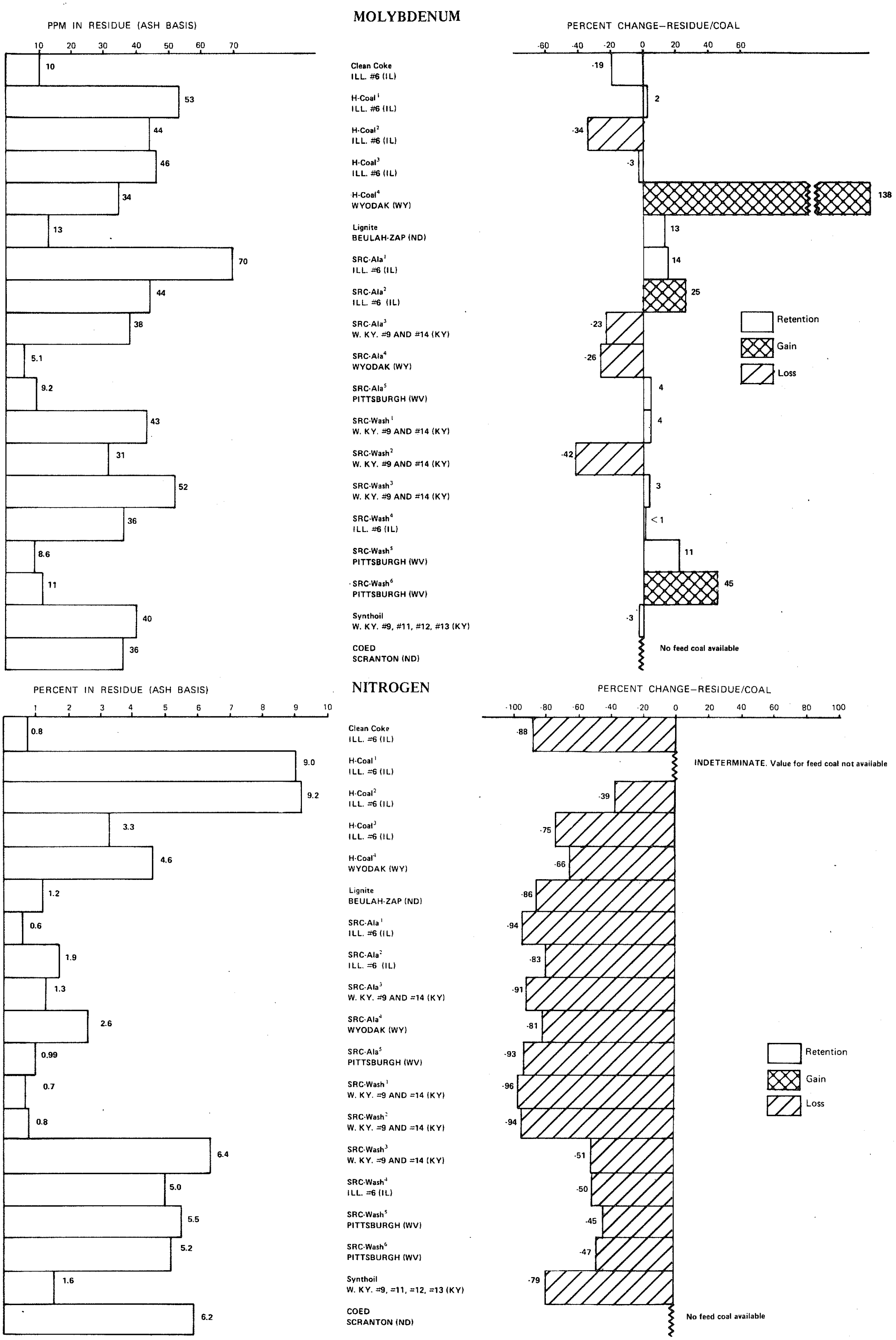


Figure 2.17 Mo and N

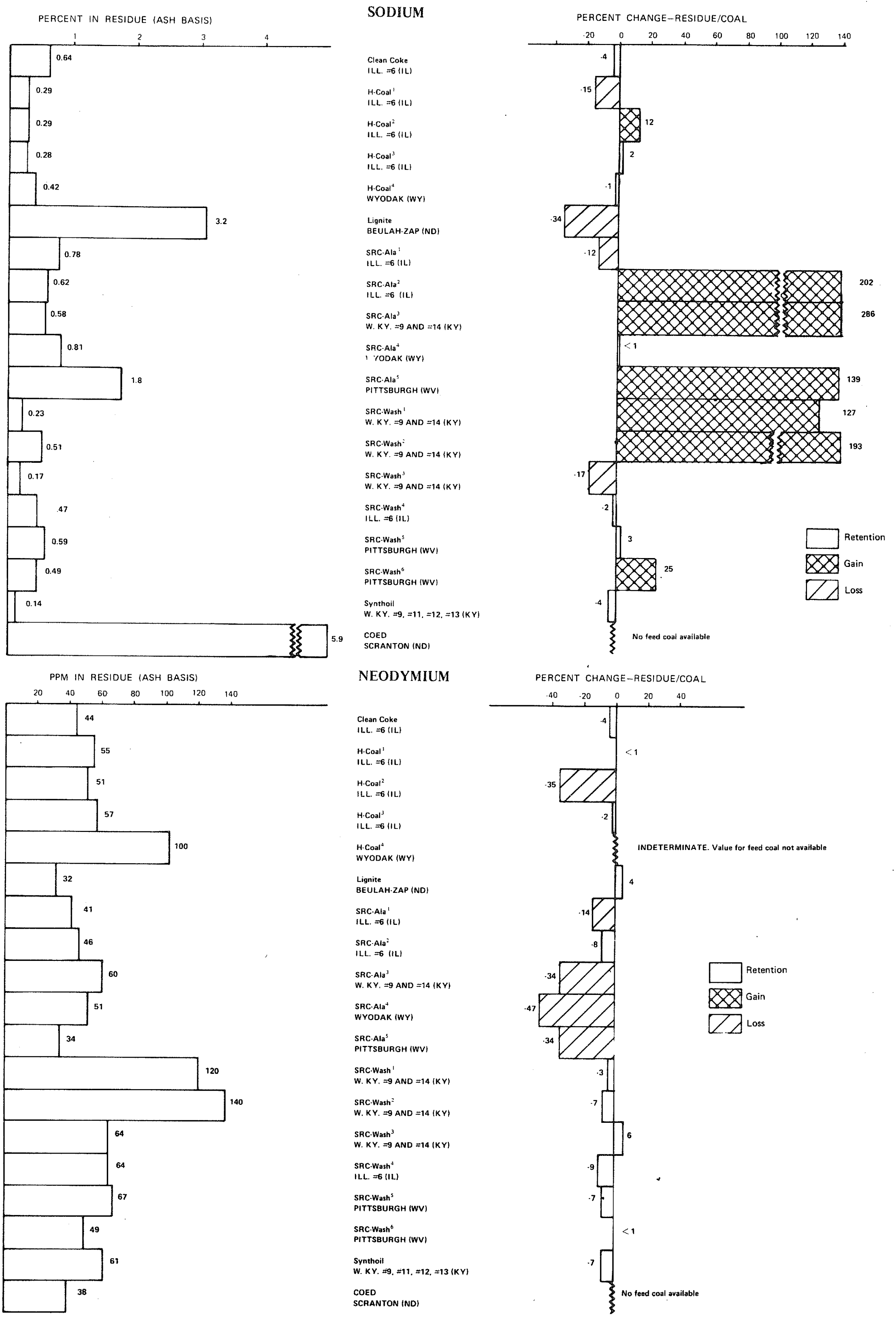


Figure 2.18 Na and Nd

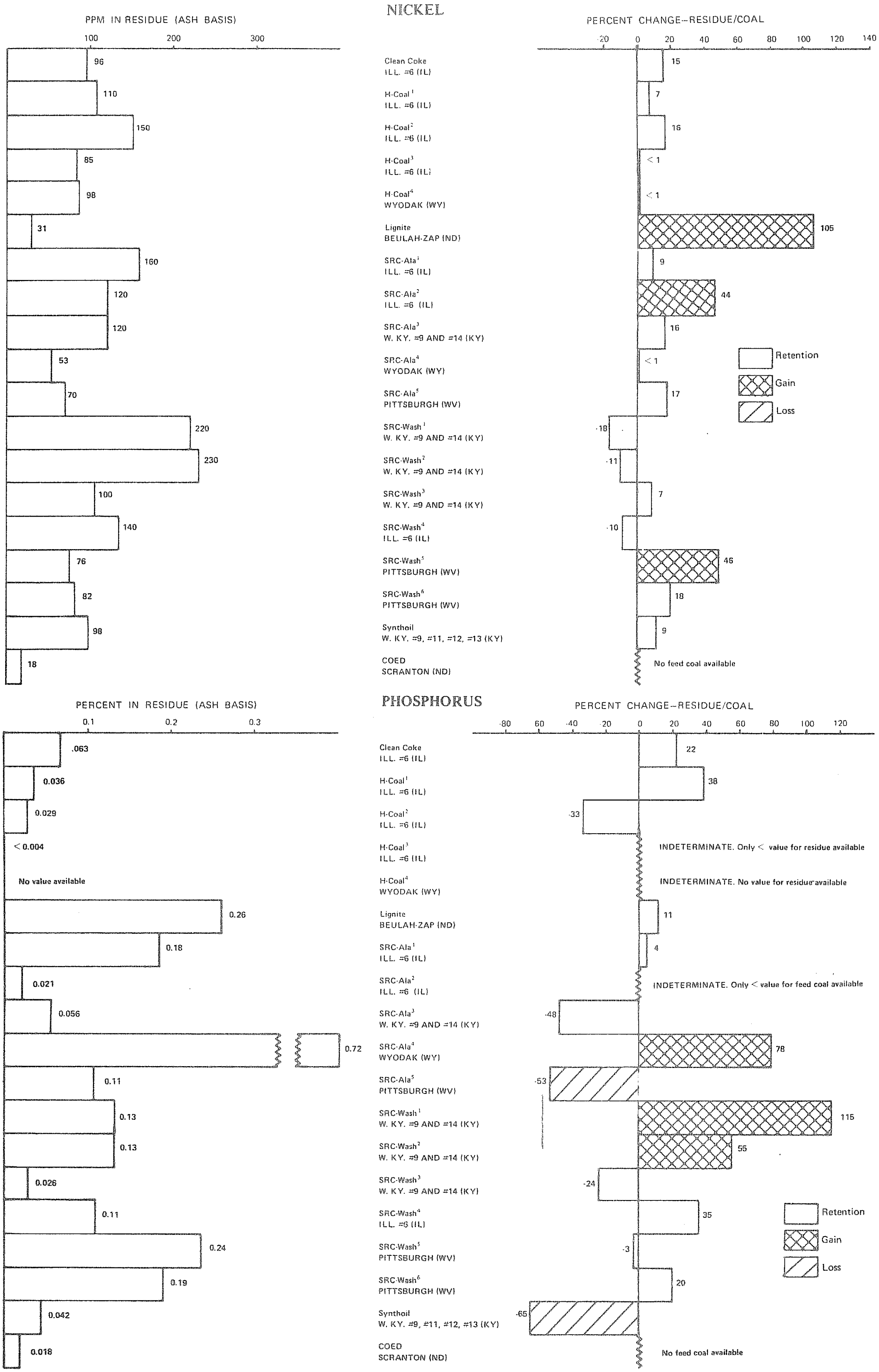


Figure 2.19 Ni and P

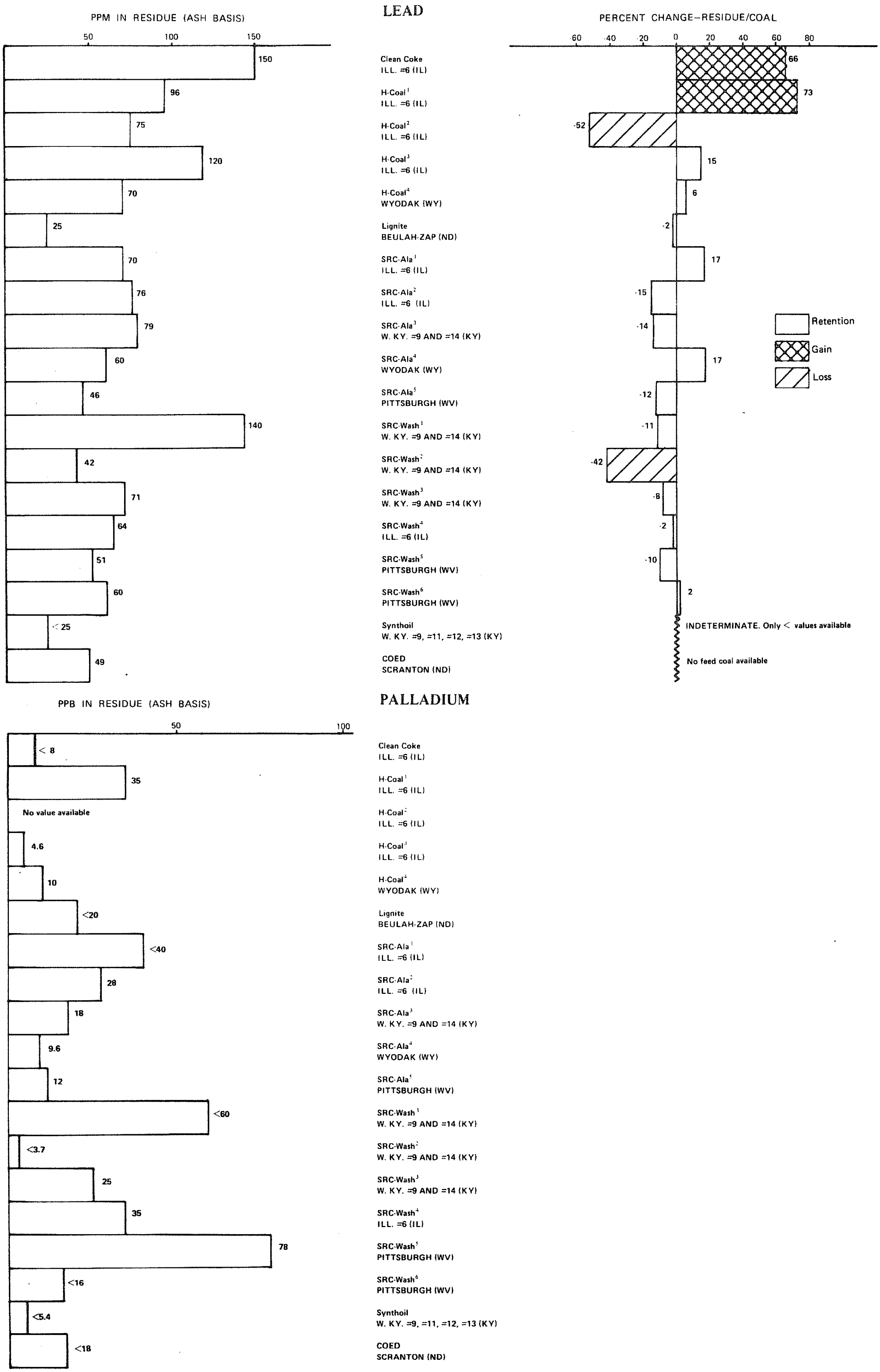


Figure 2.20 Pb and Pd

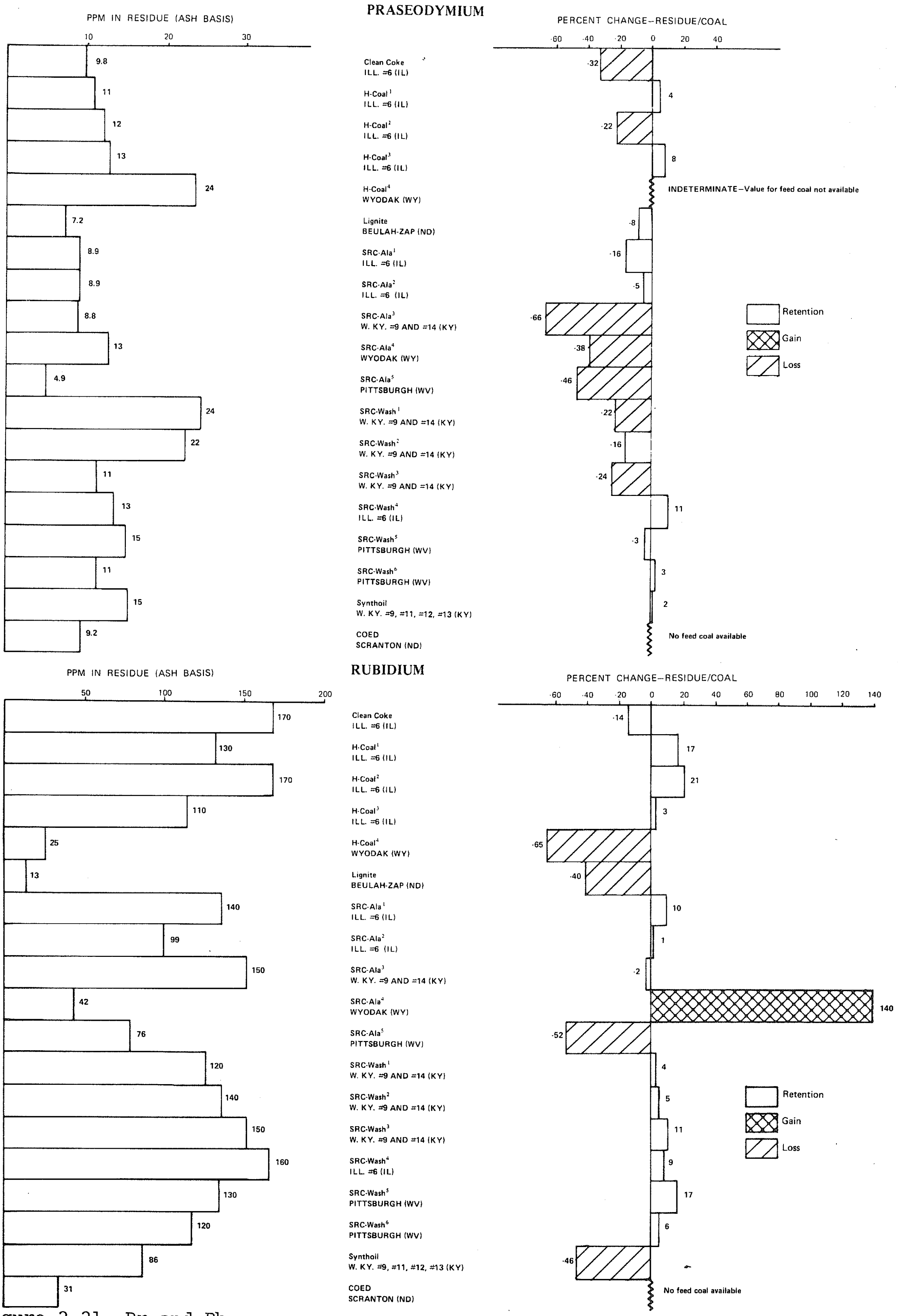


Figure 2.21 Pr and Rb

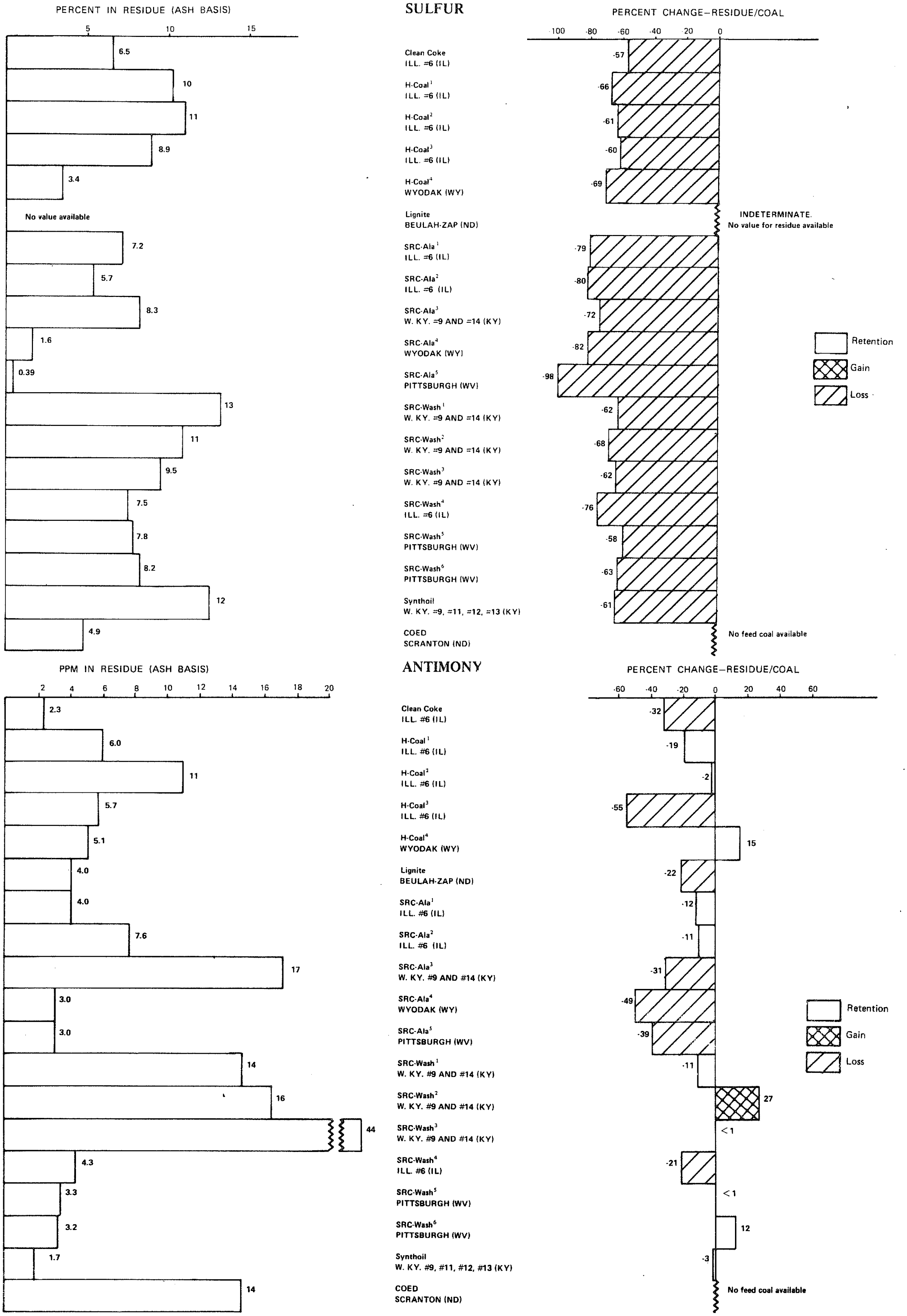
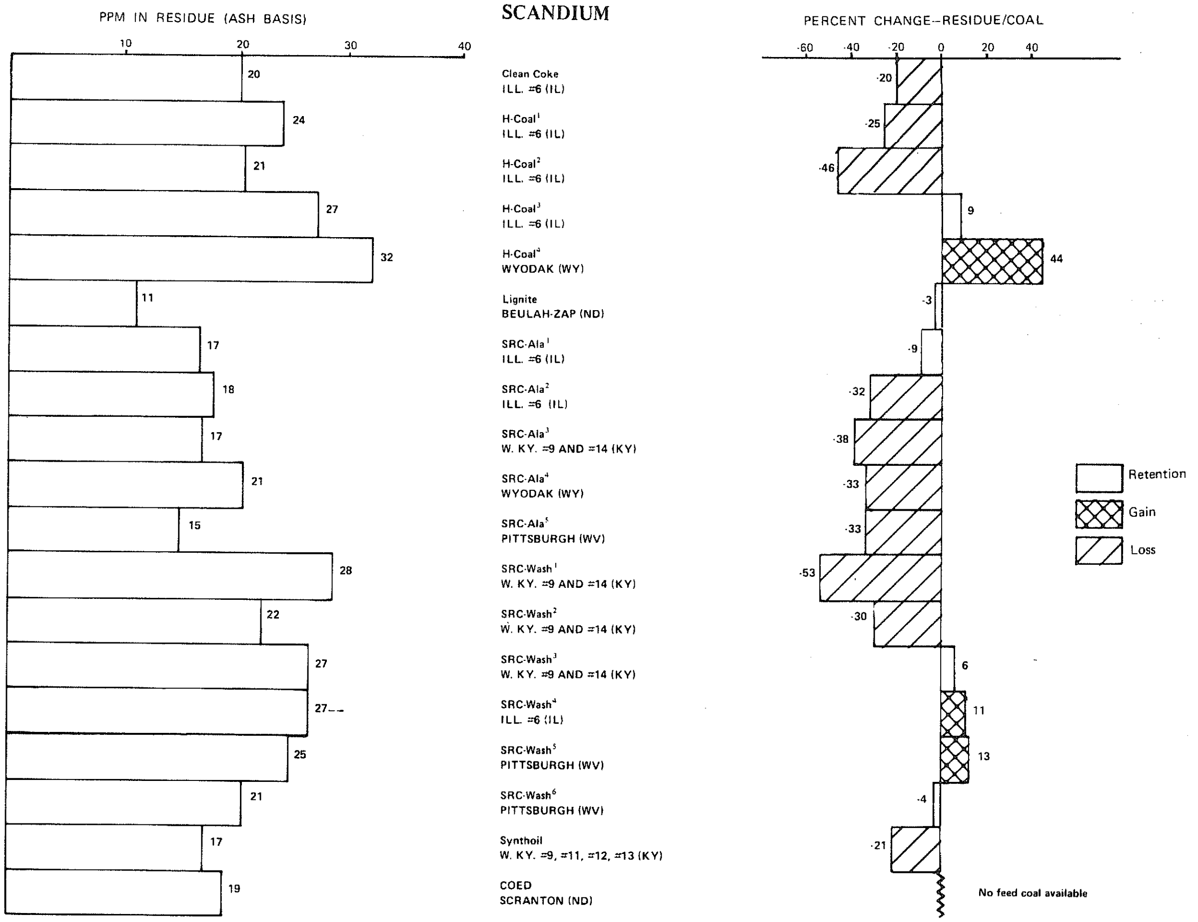


Figure 2.22 S and Sb


SCANDIUM

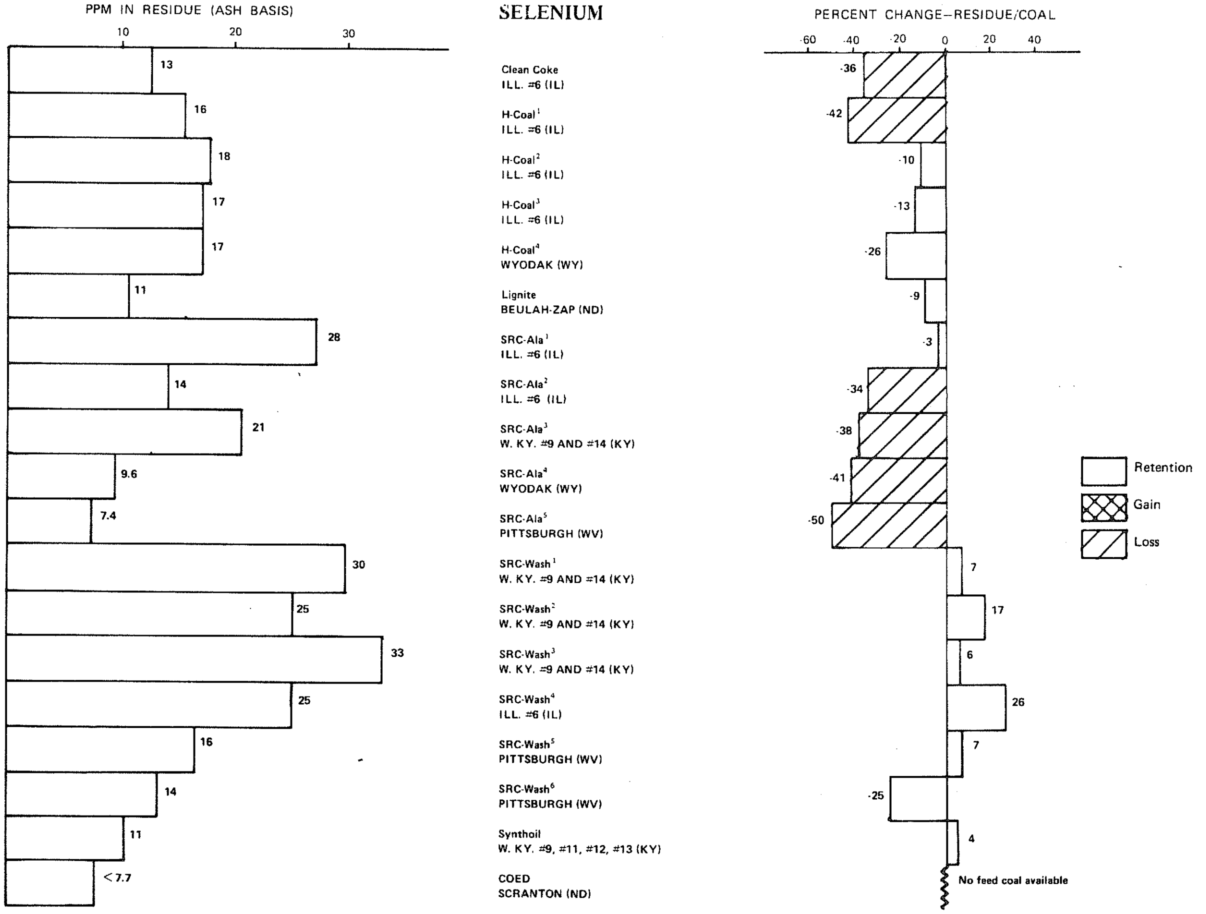

SELENIUM

Figure 2.23 Sc and Se

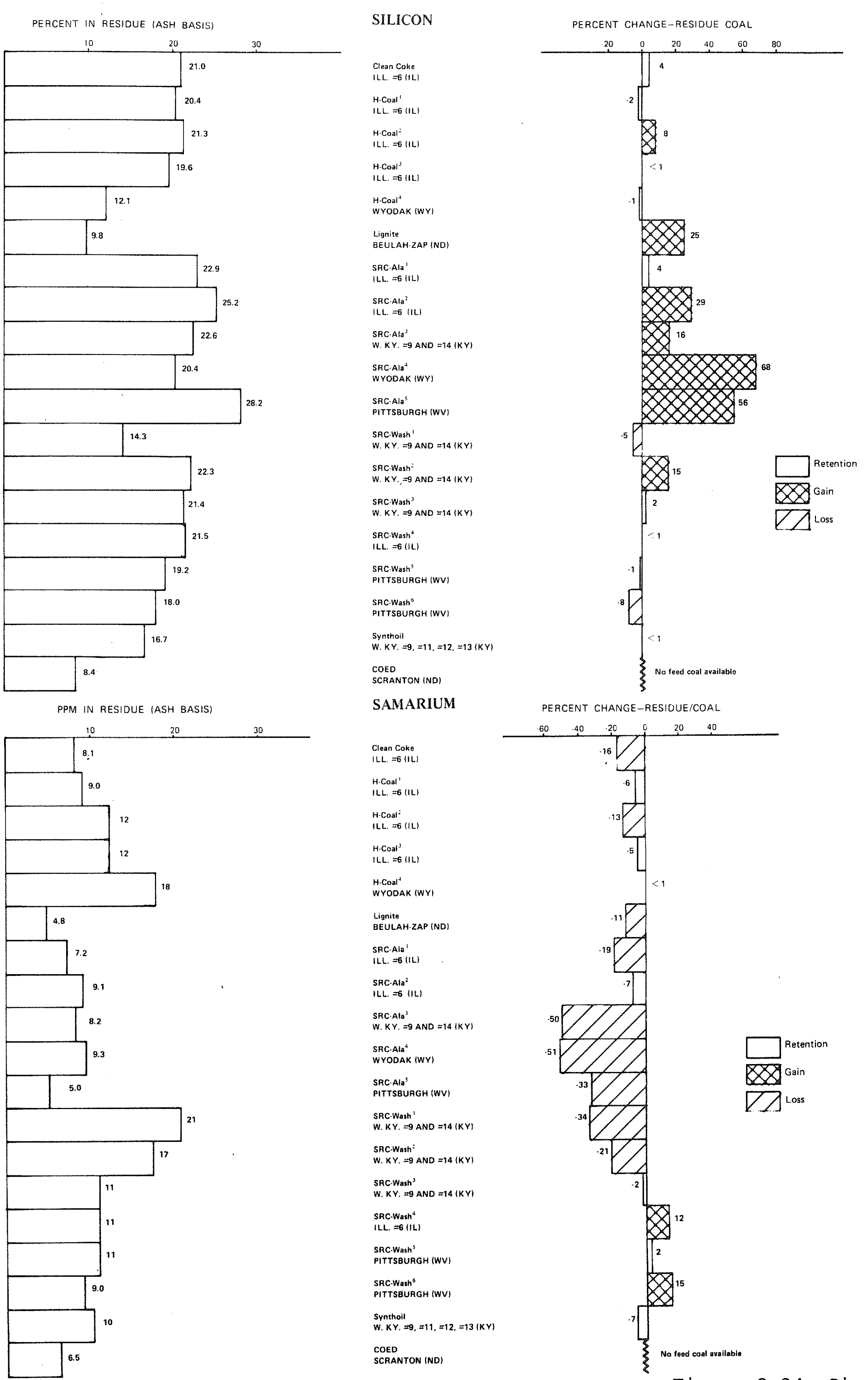


Figure 2.24 Si and Sm

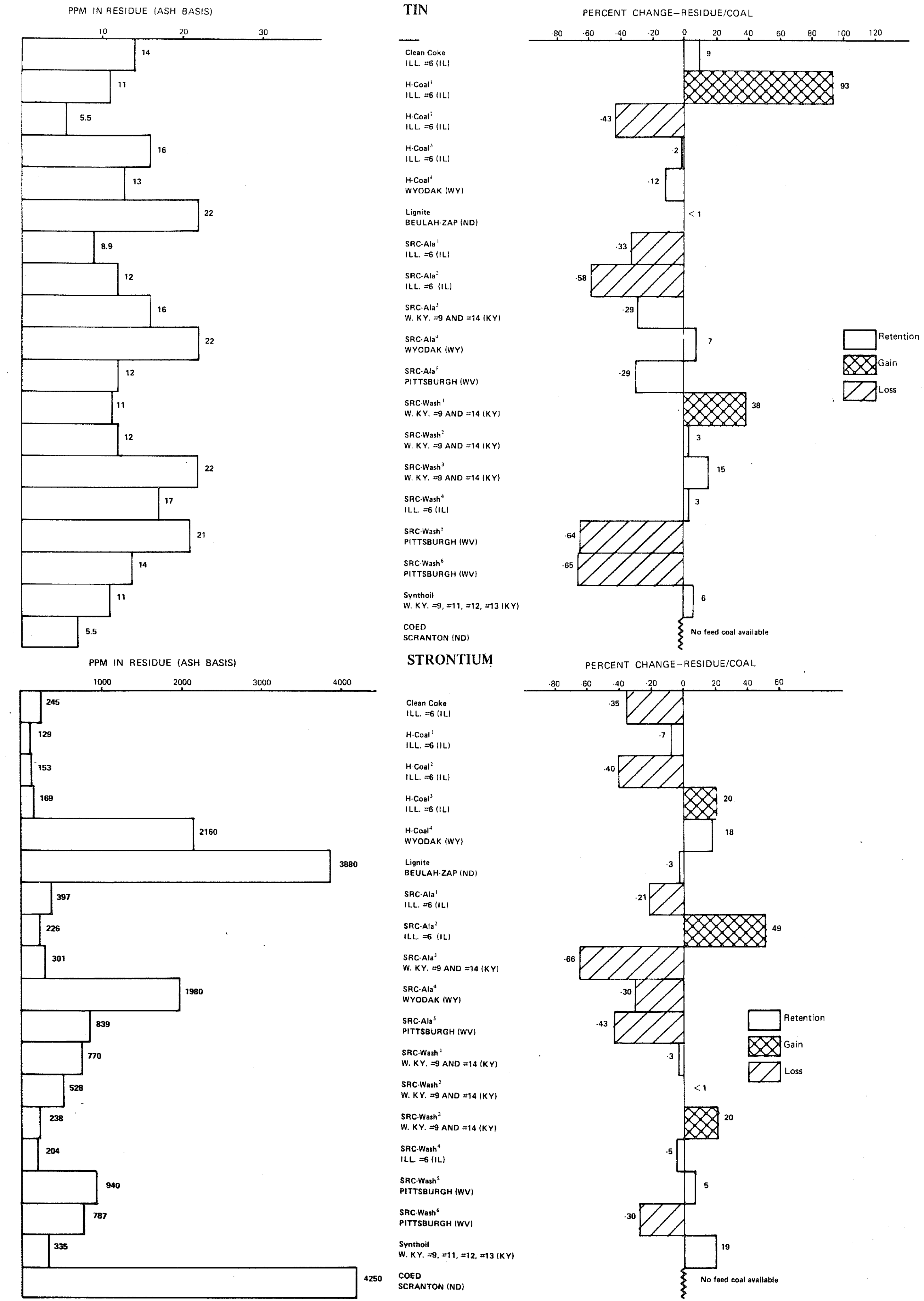


Figure 2.25 Sn and Sr

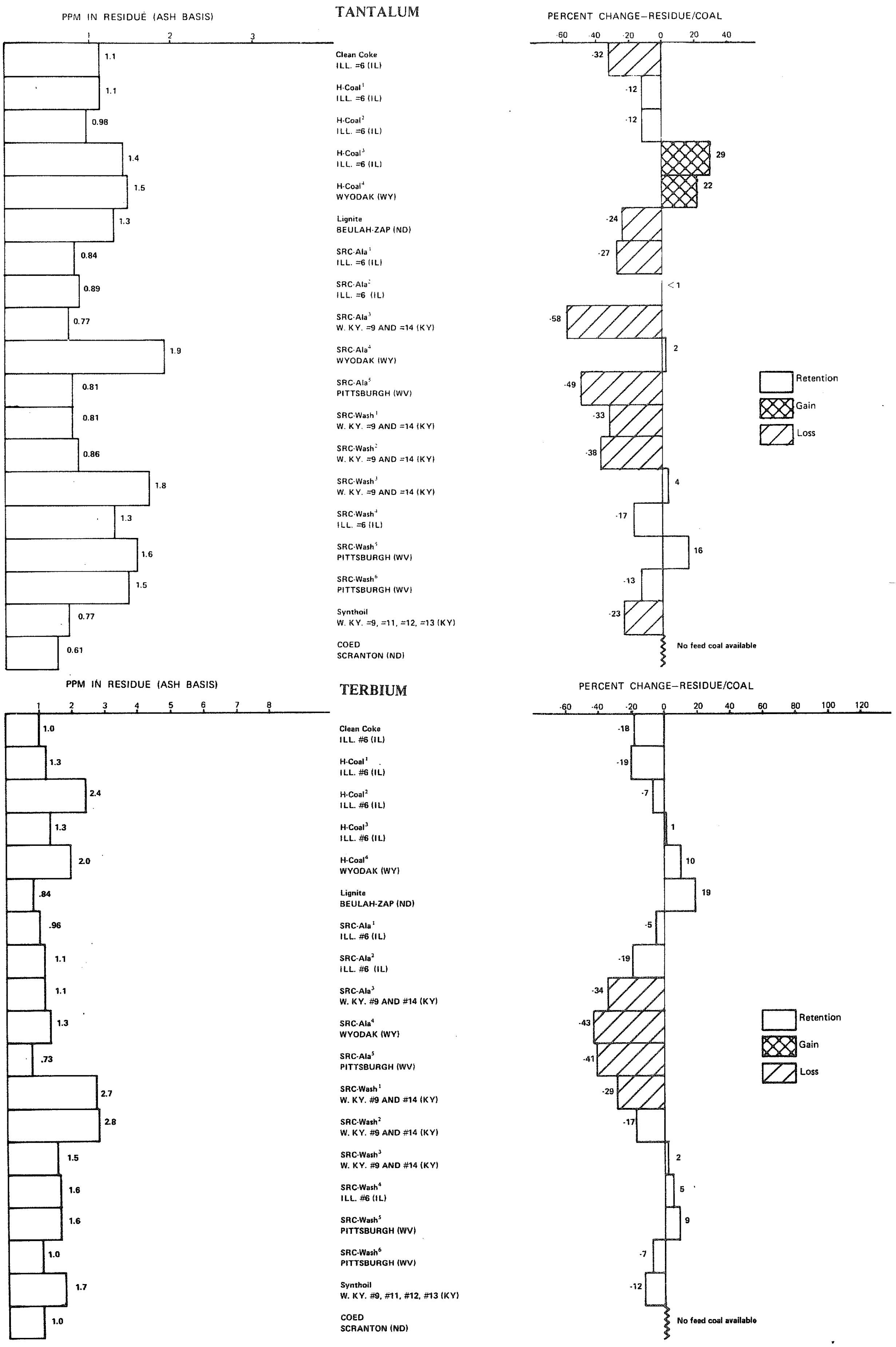


Figure 2.26 Ta and Tb

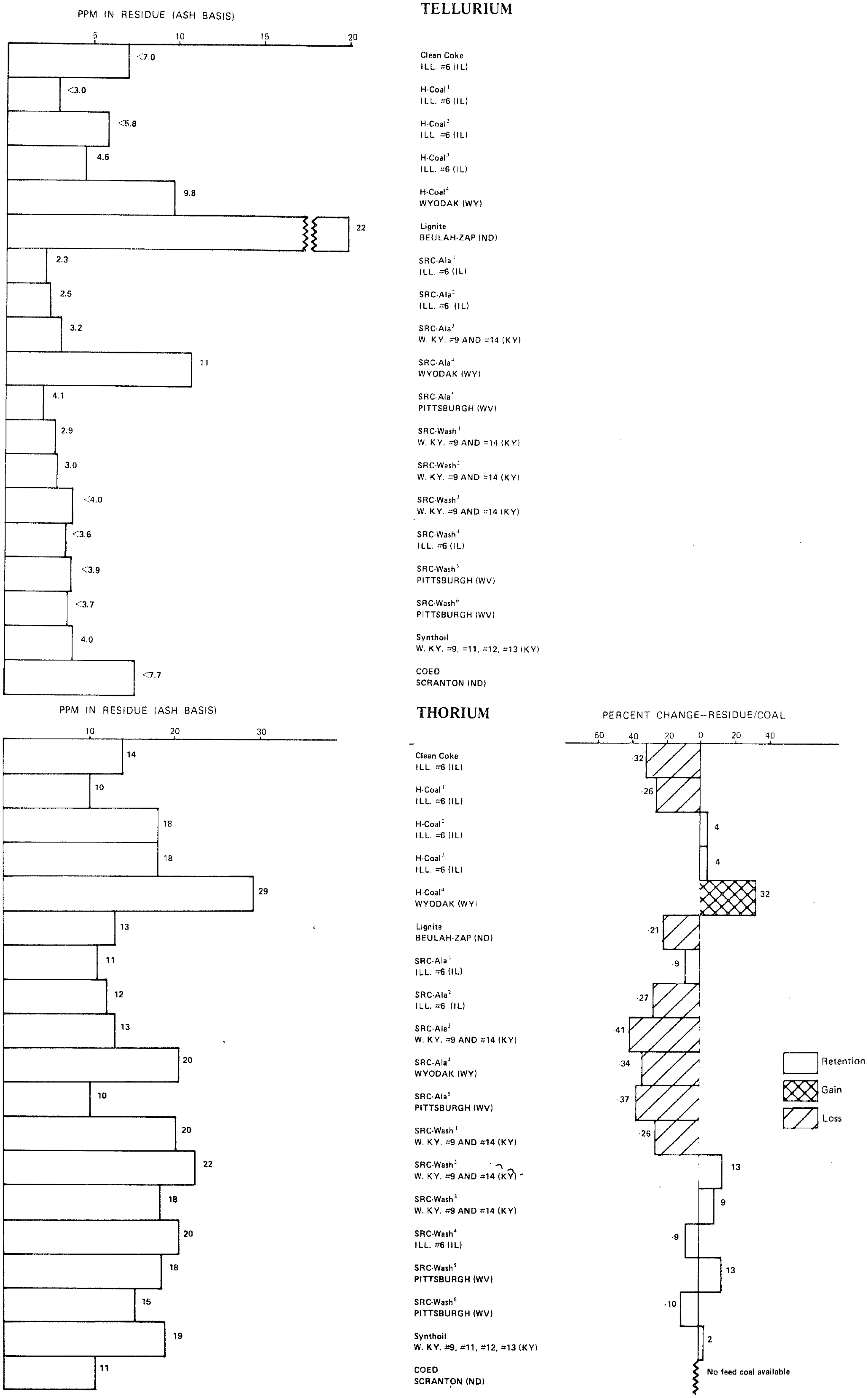


Figure 2.27 Te and Tb

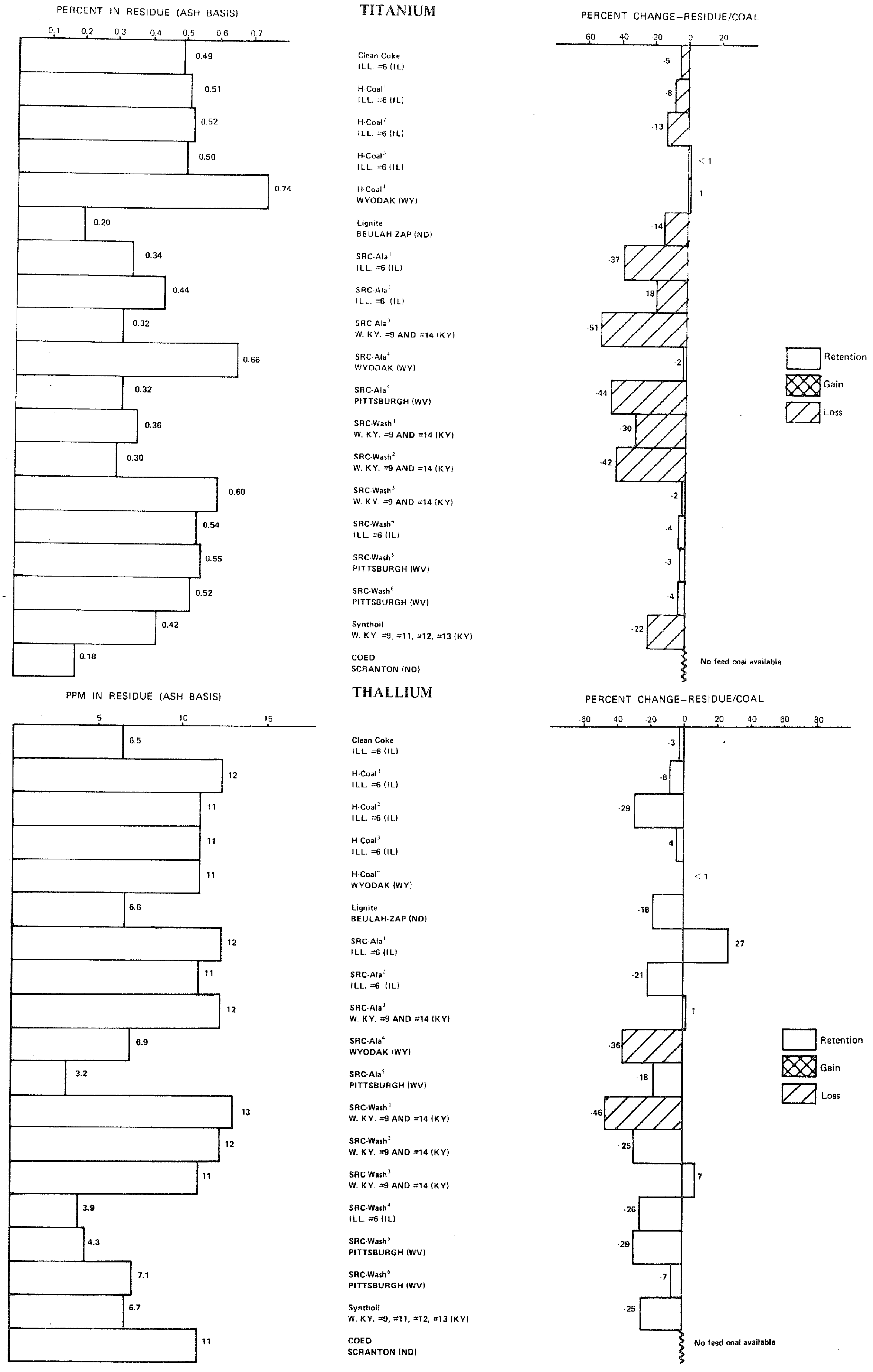


Figure 2.28 Ti and Tl

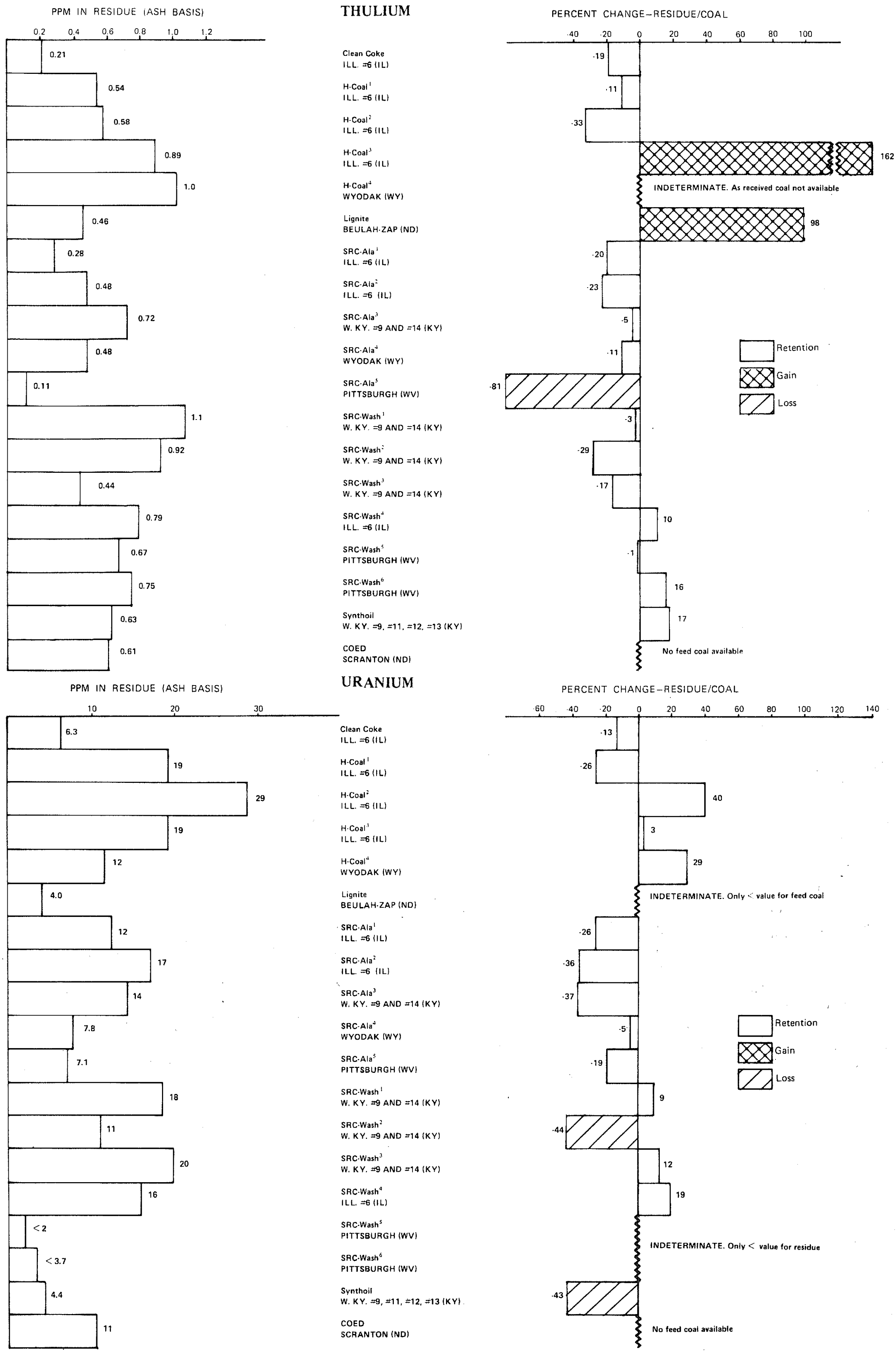


Figure 2.29 Tm and U

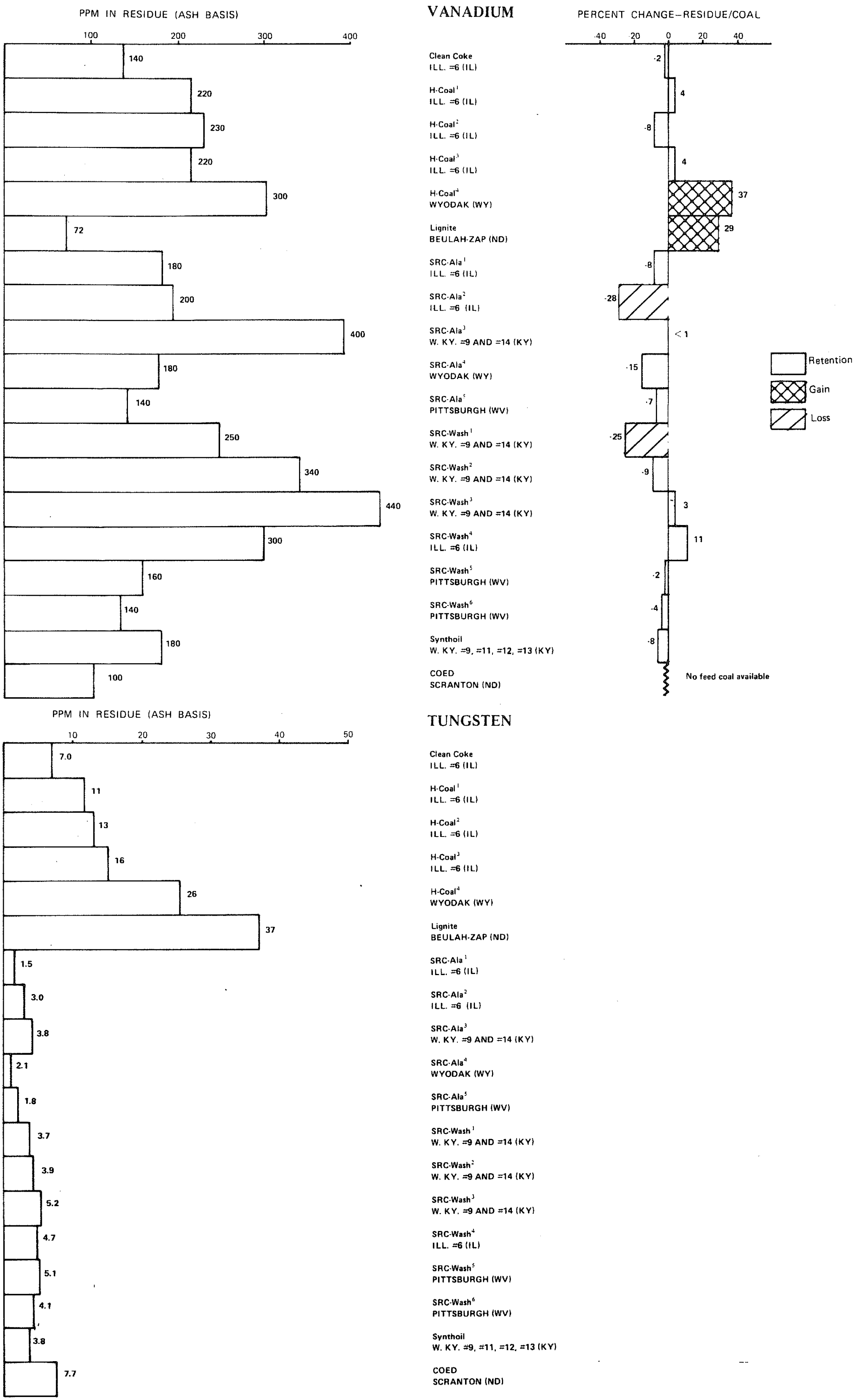
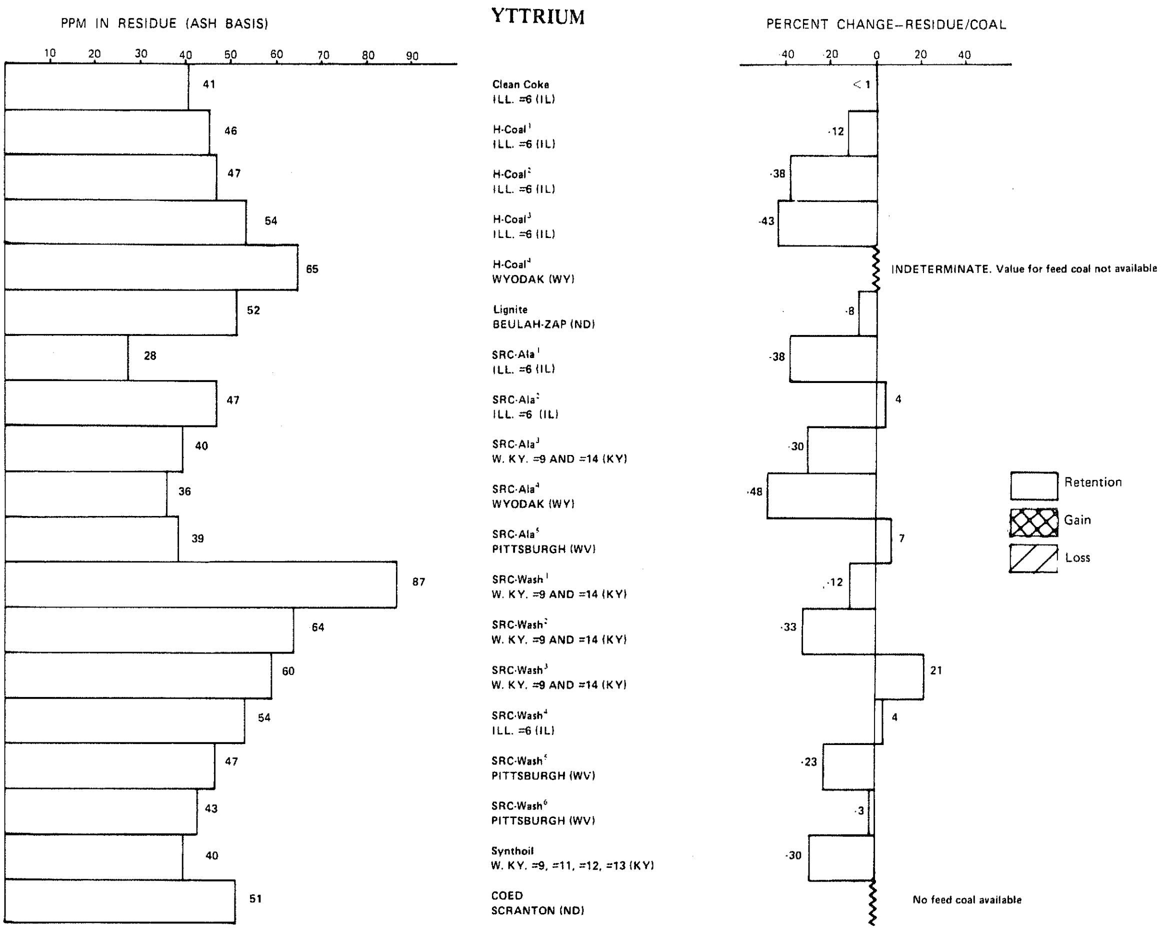


Figure 2.30 V and W



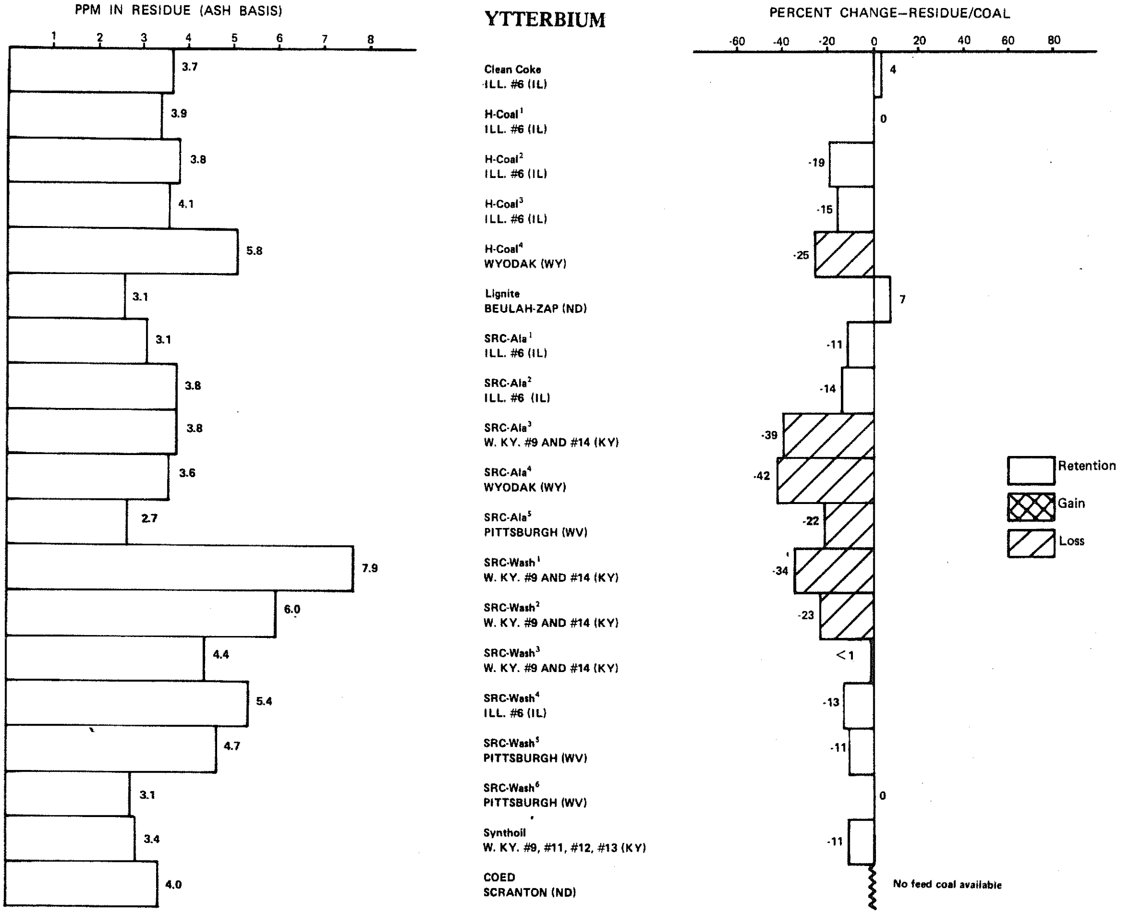
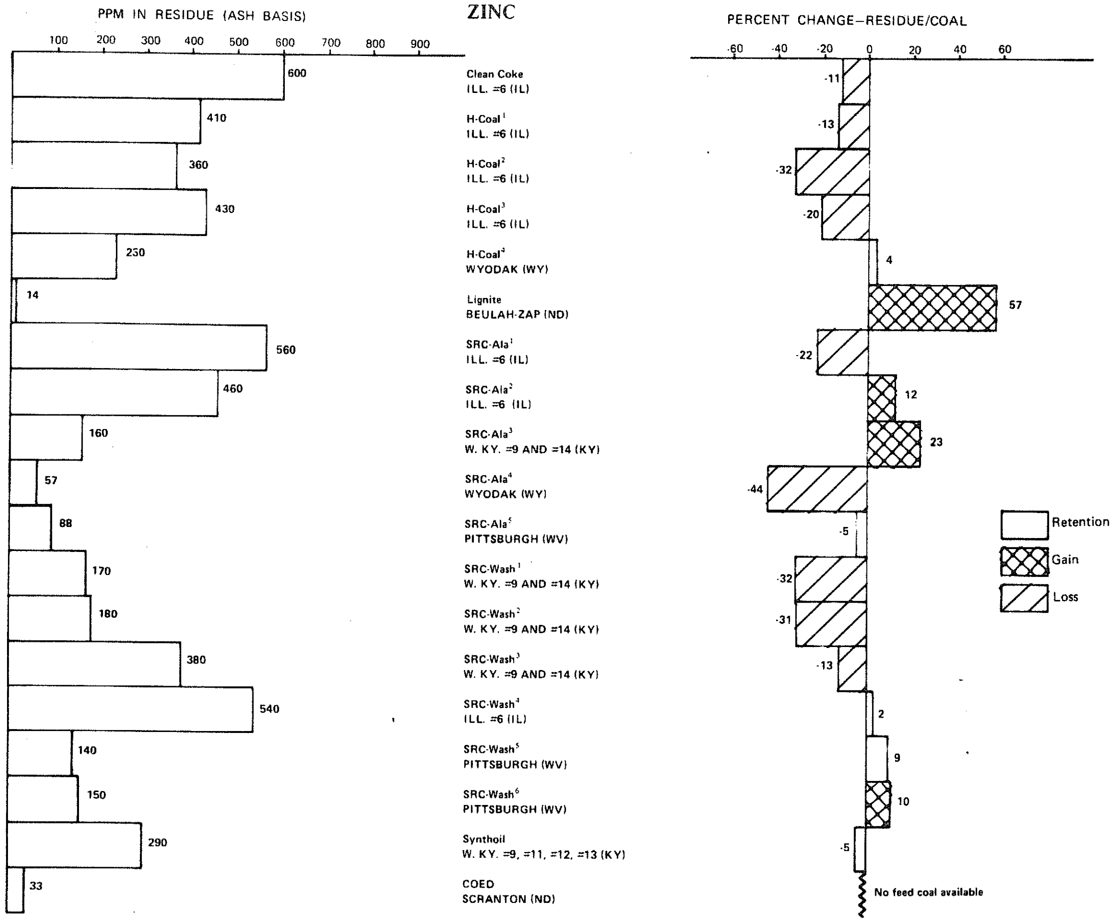


Figure 2.31 Y and Yb

ZINC



ZIRCONIUM

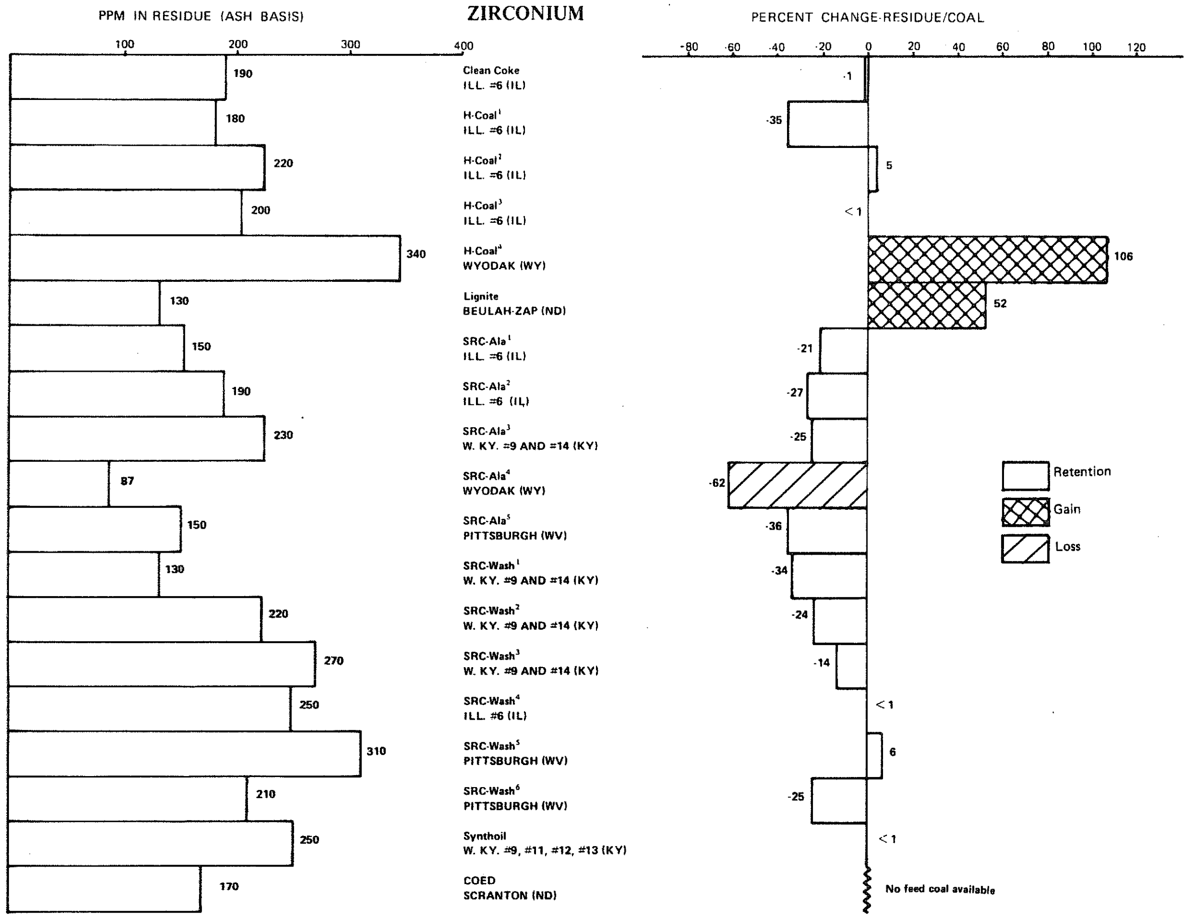


Figure 2.32 Zn and Zr

The "percentage change" calculations (figures 2.1 to 2.32) indicate the mobility of each element during the liquefaction process. (Primarily due to their low concentrations in coal, the elements Ag, Au, I, Pd, Te, and W could not be determined with sufficient accuracy to be evaluated in this manner.) An element mobilized, e.g., S or Hg through volatilization or chemical transformation, will indicate a "loss" or depletion when its concentration in the residue is compared with the concentration in the feed coal. A gain or enrichment of an element in residue relative to feed coal can be due to contamination from degradation of equipment, incorporation of filter-aid material, or catalyst. Inhomogeneous or nonrepresentative samples and large analytical errors could also cause apparent "gain" or "loss" results.

Another source of error in the evaluation of gain/loss or percentage of change calculations is caused by the use of filter-aid materials. The presence of filter-aid material in the residue from certain runs (SRC-WASH-1, 2 and SRC-ALA-1 to 5) dilutes the concentration of many elements and causes an apparent loss. (See Appendix G for the data and detailed discussion on these runs.) Based upon the assumption that Si is immobile, calculations were made of the amounts of filter-aid material mixed with the various residues; they ranged from <1 percent for the SRC-WASH-1 run to ~ 50 percent for the SRC-ALA-5 run. The mean value for the seven runs using this predominantly diatomaceous earth material was 21 percent. This figure agrees well with the mean Si gain of 26 percent in those runs using filter-aids (table 5). For the elements Si, Na, Al, Ca, Mg, Cr, Ni, and Ge the incorporation of filter-aid contributes to the concentrations in the residues, as indicated by significant gains.

Table 5 is a summary of the mean gain/loss data for each element for all process runs, for process runs using filter-aids, and for those process runs not using filter-aids in the separation of the residue. Runs without filter-aids indicate only small mean losses for most elements (<15%). Elements showing moderate to high losses (>15%) are S, As, Hg, and N. Those elements indicating moderate gains (>10%) are Mo, Ni, and Tm. The gains for Mo and Tm are due to a single or a few large deviations.

The retention data were evaluated on the basis of frequency as well as on the basis of magnitude; in the case of some elements a large change in concentration in one or a few of the process runs produced a disproportionate effect upon the mean change. Figure 3 summarizes the frequency of observed retention behavior for all 18 runs. Hg, S, and N exhibit a high loss frequency; however, it is impossible to accurately evaluate the behavior of many other elements without considering the effect of filter-aid contribution.

Figures 4 to 6 show the frequencies of observed loss, gain, or retention in runs using and in those runs not using filter-aid material. In the 11 runs without filter-aid (figure 4) Hg, S, and N show consistent loss while Ti, Ca, Mg, As, and Zn show a moderate frequency of loss (>5 out of 11 runs). In those 7 runs with filter-aid there is a large frequency of apparent loss for many elements. The high loss frequency (7 out of 7) observed for N, S, Hg, Br, and Dy is generally similar to that observed from runs without filter-aids (see also Appendix G.) In figure 5, however, Si and Na exhibit a high frequency of apparent gains due to contribution from the filter-aid. Also Cr and P are enriched in several runs. When the data from the filter-aid runs are corrected for Si (see Appendix G) the retention behavior is basically the same as that in runs that did not involve filter-aids. For those runs not using filter-aids no clear-cut gains are exhibited. Figure 6 shows that in those runs without filter-aids, most elements studied are retained (i.e., retained in at least 6 of 11 runs.)

Thus, seven elements—N, Mg, Ti, B, S, Hg, and As—show significant loss or depletion in the residues in most cases. Elements with moderate tendencies for mobility include Ca, Na, Eu, Zn, Dy, F, Yb, Ta, Sc, and Br. The mechanisms

Table 5. Average of % change in concentration of 59 elements from feed coal to residue in 18 liquefaction process runs.

	Average % Gain (Loss)				Average % Gain (Loss)		
	All Process Runs	Runs without Filter Aid Material	Runs with Filter Aid Material		All Process Runs	Runs without Filter Aid Material	Runs with Filter Aid Material
Al	(-5)	2	(-15)	Hg	(-79)	(-71)	(-90)
Ca	(-2)	3	(-10)	Ho	(-20)	(-9)	(-35)
Fe	(-7)	1	(-19)	La	(-12)	(-3)	(-27)
K	(-1)	(-7)	8	Li	2	7	(-5)
Mg	(-5)	(-14)	9	Lu	(-10)	(-2)	(-23)
N	(-73)	(-61)	(-89)	Mn	(-10)	(-4)	(-19)
Na	50	(-3)	130	Mo	6	14	(-6)
P	10	<1	25	Nd	(-12)	(-5)	(-21)
S	(-67)	(-61)	(-76)	Ni	15	19	8
Si	12	3	26	Pb	2	9	(-9)
Ti	(-17)	(-7)	(-32)	Pr	(-16)	(-6)	(-30)
As	(-30)	(-23)	(-40)	Rb	1	(-7)	15
B	(-25)	(-5)	(-56)	Sb	(-14)	(-12)	(-18)
Ba	2	6	(-3)	Sc	(-15)	(-3)	(-33)
Be	(-15)	(-2)	(-34)	Se	(-14)	(-11)	(-20)
Br	(-32)	(-15)	(-58)	Sm	(-14)	(-3)	(-31)
Ce	(-8)	<1	(-21)	Sn	(-9)	(-6)	(-14)
Cl	(-17)	(-3)	(-38)	Sr	(-8)	(-4)	(-16)
Co	<1	3	(-4)	Ta	(-15)	(-6)	(-29)
Cr	4	5	4	Tb	(-11)	(-2)	(-25)
Cs	2	(-3)	<1	Th	(-11)	(-3)	(-23)
Cu	2	6	(-4)	Tl	(-15)	(-13)	(-17)
Dy	(-26)	(-12)	(-47)	Tm	3	22	(-25)
Er	(-18)	(-9)	(-31)	U	(-9)	3	(-23)
Eu	(-10)	2	(-30)	V	(-2)	6	(-13)
F	(-17)	(-5)	(-36)	Y	(-17)	(-13)	(-21)
Ga	(-17)	(-10)	(-27)	Yb	(-21)	(-15)	(-31)
Gd	(-7)	5	(-23)	Zn	(-6)	(-1)	(-14)
Ge	(-15)	(-15)	(-14)	Zr	(-8)	9	(-33)
Hf	(-7)	4	(-23)				

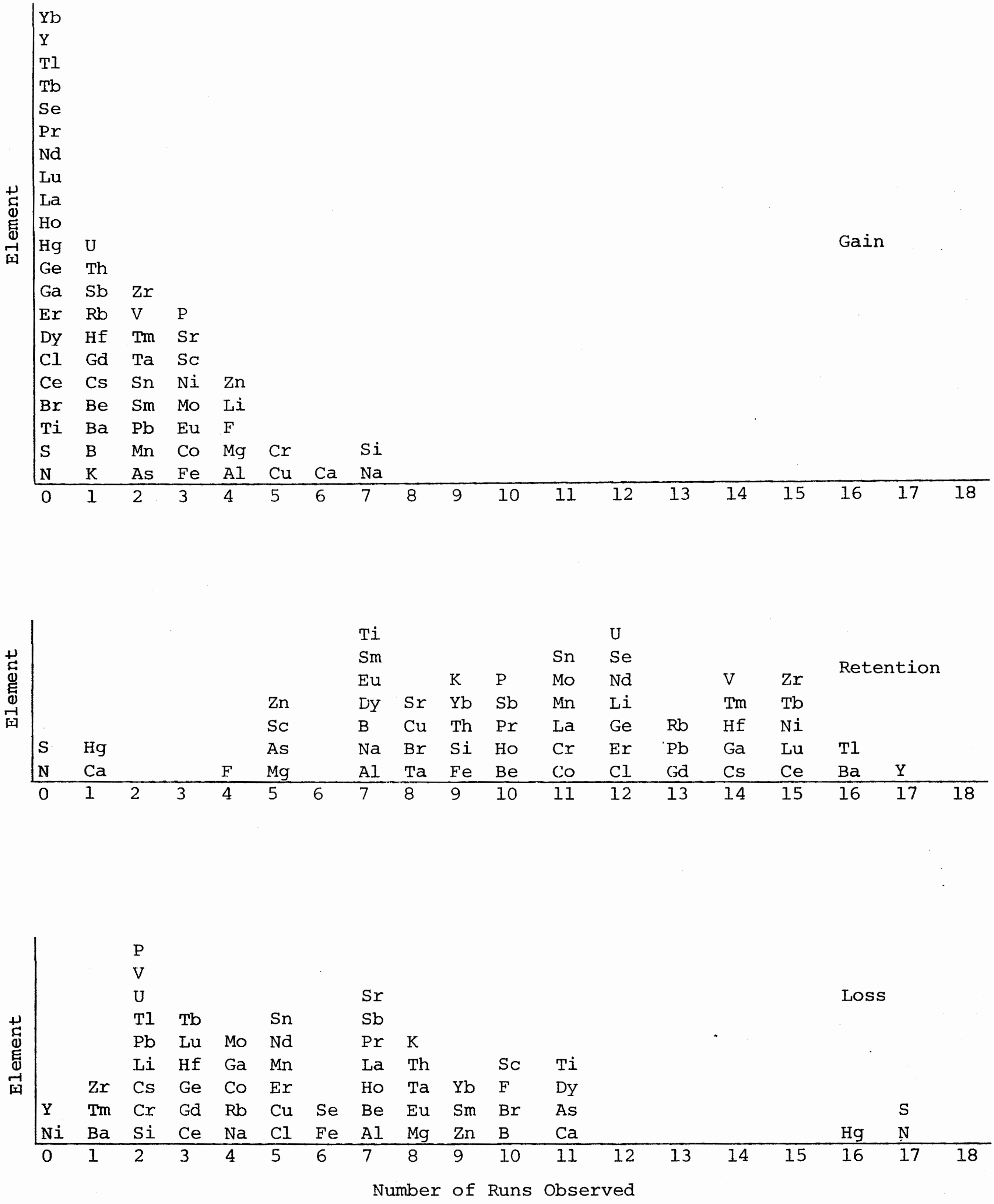


Figure 3. Frequency of observations of gain/loss/retention for the elements in eighteen liquefaction process runs

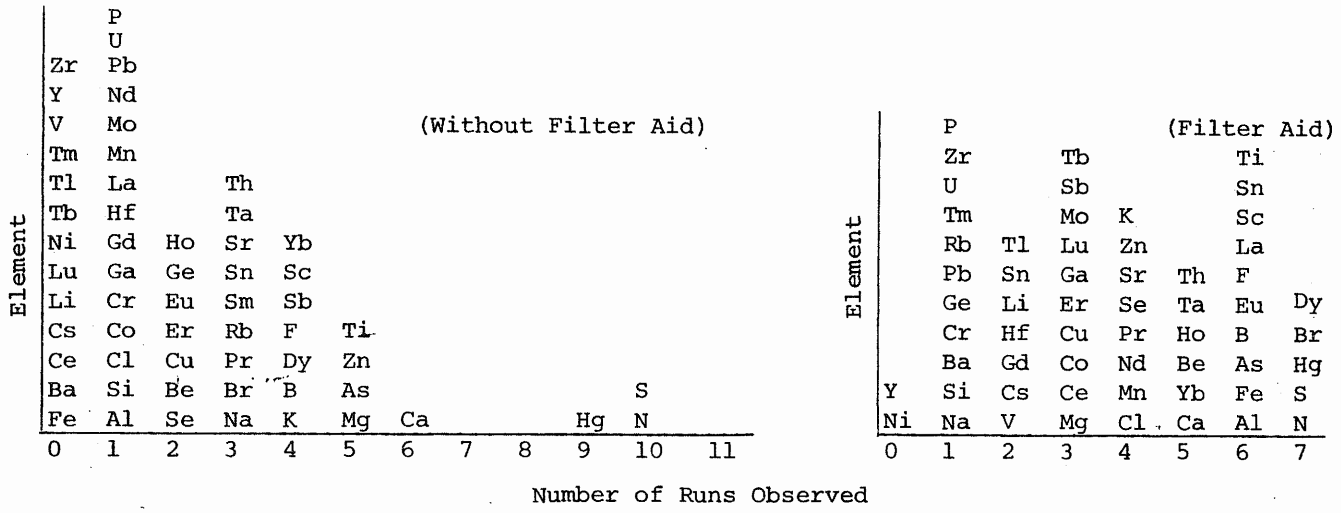


Figure 4. Frequency of observations of loss of elements from feed coal to liquefaction process residue for runs not involving filter aids

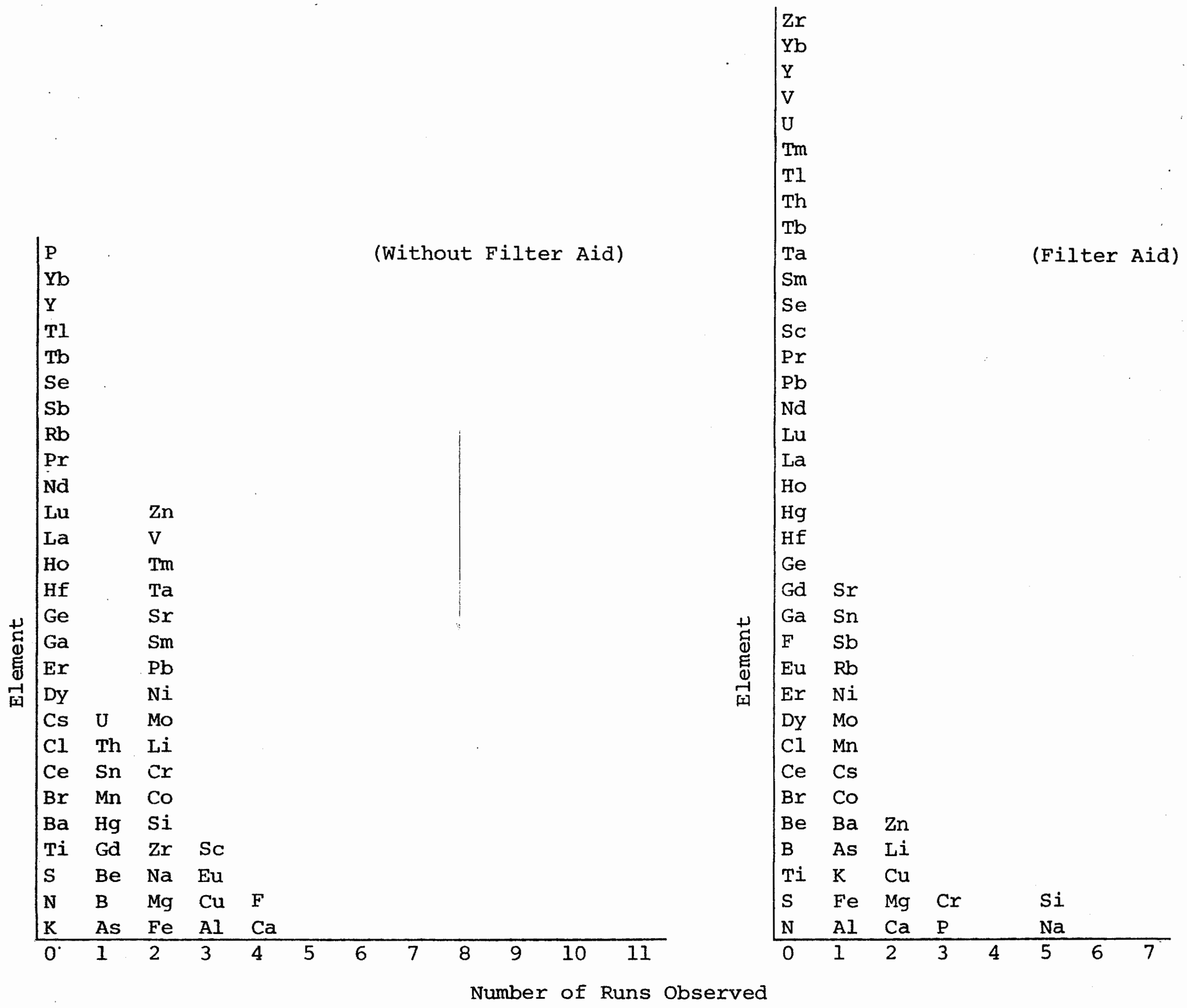


Figure 5. Frequency of observations of gains of elements from feed coal to liquefaction process residue for runs not involving filter aids and for runs involving filter aids

(Without Filter Aid)

Number of Runs Observed	Element
0	S N
1	Hg I Ca
2	
3	F Mg
4	Zn Sc
5	As
6	Ti U Ta Sr Sm Er Cu B Na
7	Yb Th Sn Sb Pr Pb Dy K Al
8	P Tm Rb Mo Ho Ge Gd Er Cr Co Br Be Si
9	Zr V Se Ni Nd Mn Li Hf Cl Fe
10	Y La Ga Cs
11	Tl Tb Lu Ce Ba

(Filter Aid)

Number of Runs Observed	Element
0	Dy Br As Hg S N Fe Ca Al
1	Sm Sc La F Eu B Si Ti Na Zn
2	P K Yb Th Ta Sr Mn Ho Cu Be Mg
3	Se Sb Pr Nd Mo Li Cr Co Cl
4	Tb Sn Lu Ge Ga Er Cs Ce
5	V Tl Rb Hf Gd Ba
6	Zr U Tm Pb Ni
7	Y

Number of Runs Observed

Figure 6. Frequency of observations of retention of elements from feed coal to liquefaction process residue for runs not involving filter aids and for runs involving filter aids.

responsible for these observed mobilities include chemical transformation, volatilization, precipitation within the system, dissolution, sorption onto catalysts, and formation of organic compounds. For the element Ti, Filby et al. (1977) have shown that little Ti is lost going from feed coal to product in the SRC process. Kang and Johanson (1976) also note that Ti is enriched in the catalyst during the H-Coal process. Our data (table 6) on undocumented samples of a used and an unused catalyst (Co-Mo supported on Al_2O_3) from an H-Coal run confirm that Ti is enriched in the catalyst.

The average mobility behavior of all elements, as a function of liquefaction process, is shown in Figure 7, based on the frequency of observed losses. These data are also summarized in Table 7 according to process, type of coal (eastern bituminous coal, western subbituminous coal, or lignite), and whether or not a filter-aid was used. Figures 8.1 to 8.7 illustrate the mobility behavior of individual elements in selected runs from the various processes.

Figure 7 shows that the SRC-WASH-3,-4,-5, and -6 runs (Mode 2 operation) have the smallest frequency of losses; an average of 14 percent of the elements

Table 6. Results of chemical analysis of catalysts from H-coal process.

Sample Number	Sample Description	%						ppm				
		Al	Ca	Fe	K	Si	Ti	Ag	B	Be	Ca	Cd
C18804	H-Coal Fresh Catalyst	37	<.01	.04	.05	.01	<.01	<2.0	<2.0	1.3	<.01	<4.0
C18805	H-Coal Spent Catalyst	35.0	.09	.97	.08	.11	3.6	<2.0	>900	1.4	.09	<4.0

Sample Number	Sample Description	ppm												
		Cr	Cu	Ge	Li	Mn	Ni	Pb	Sn	Sr	Tl	V	Zn	Zr
C18804	H-Coal Fresh Catalyst	<2.0	16	<15	<5.0	22	490	43	63	10	29	22	100	<6.0
C18805	H-Coal Spent Catalyst	190	28	1500	20	100	720	120	130	27	66	420	1000	9.3

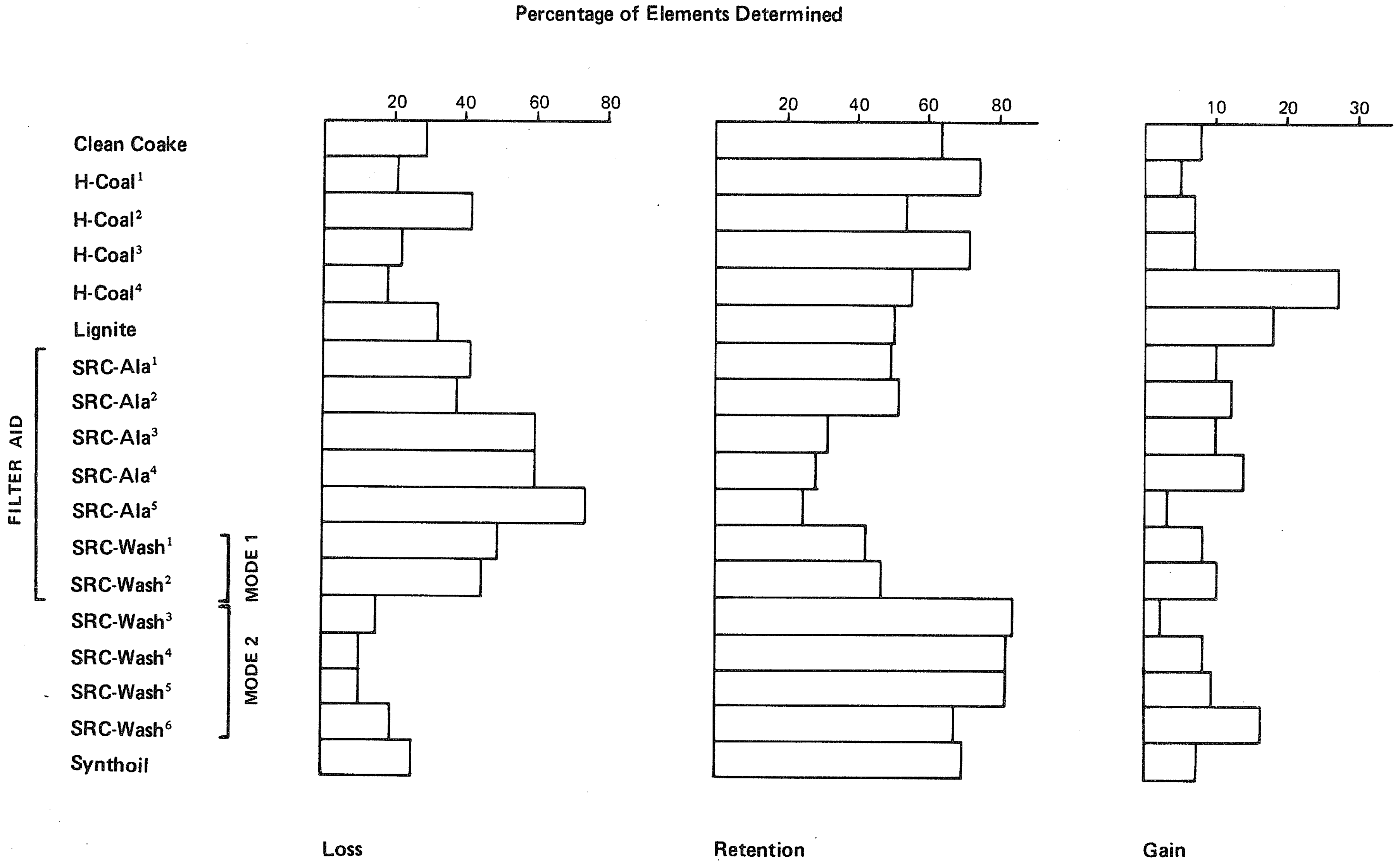
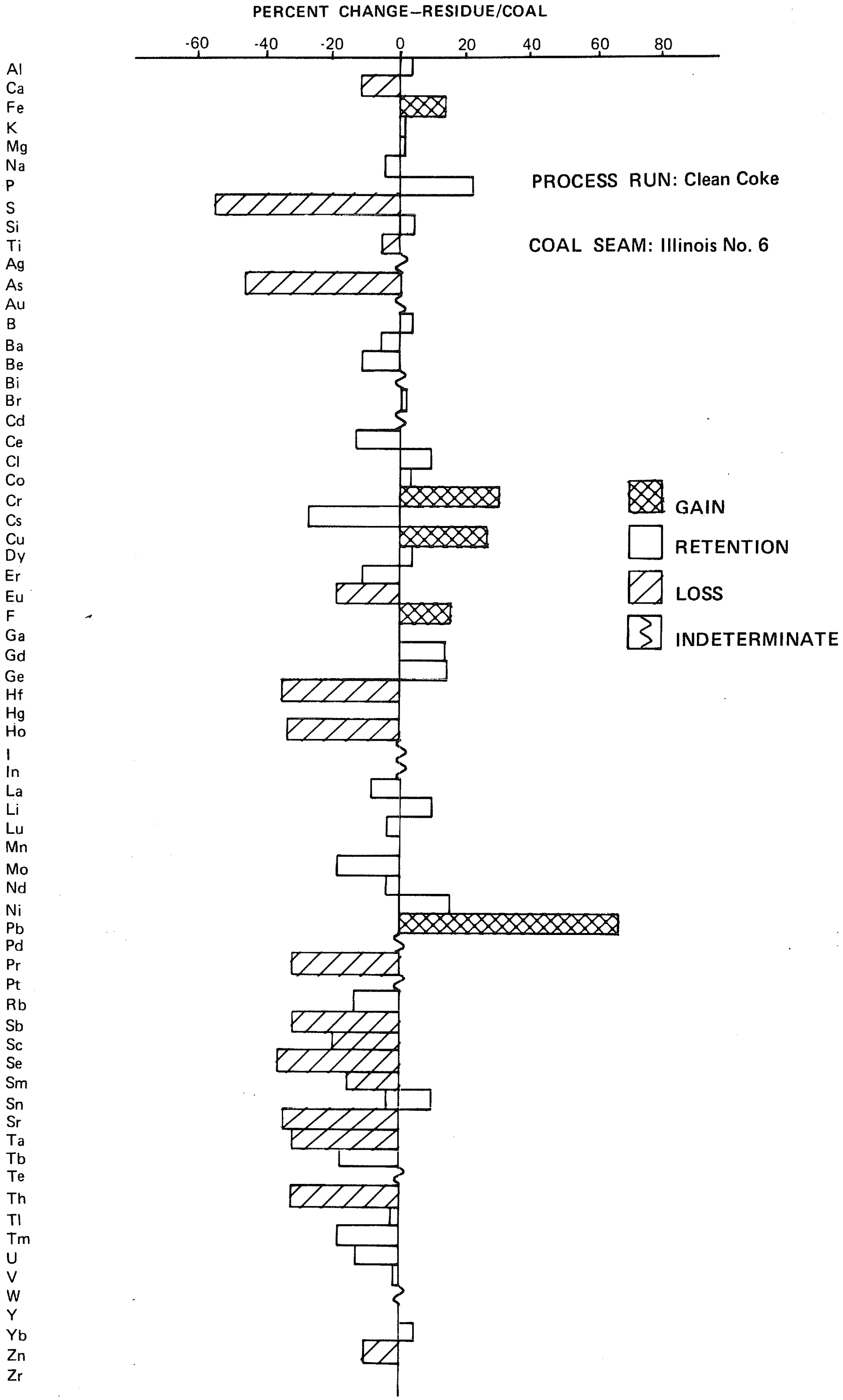
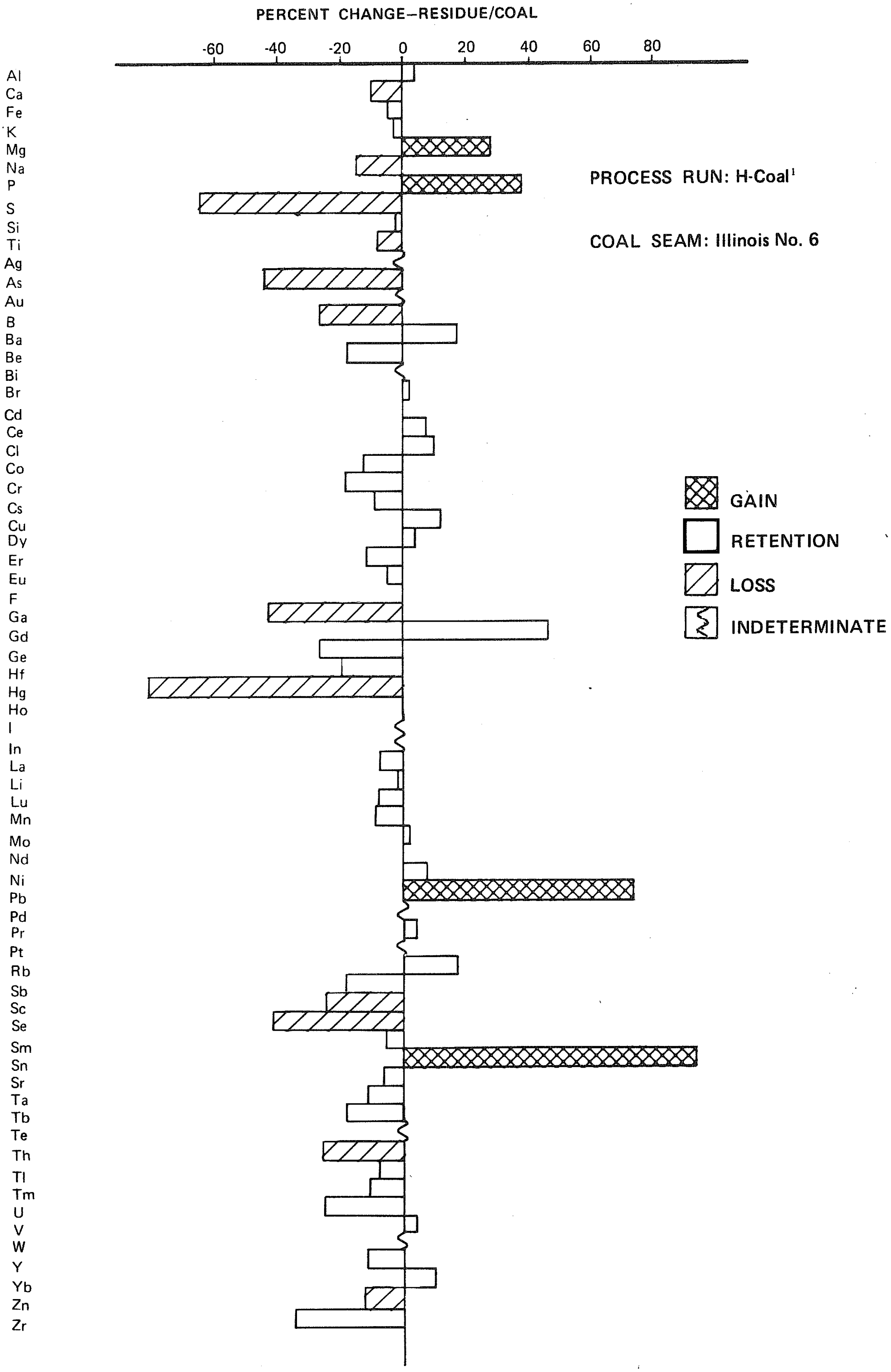


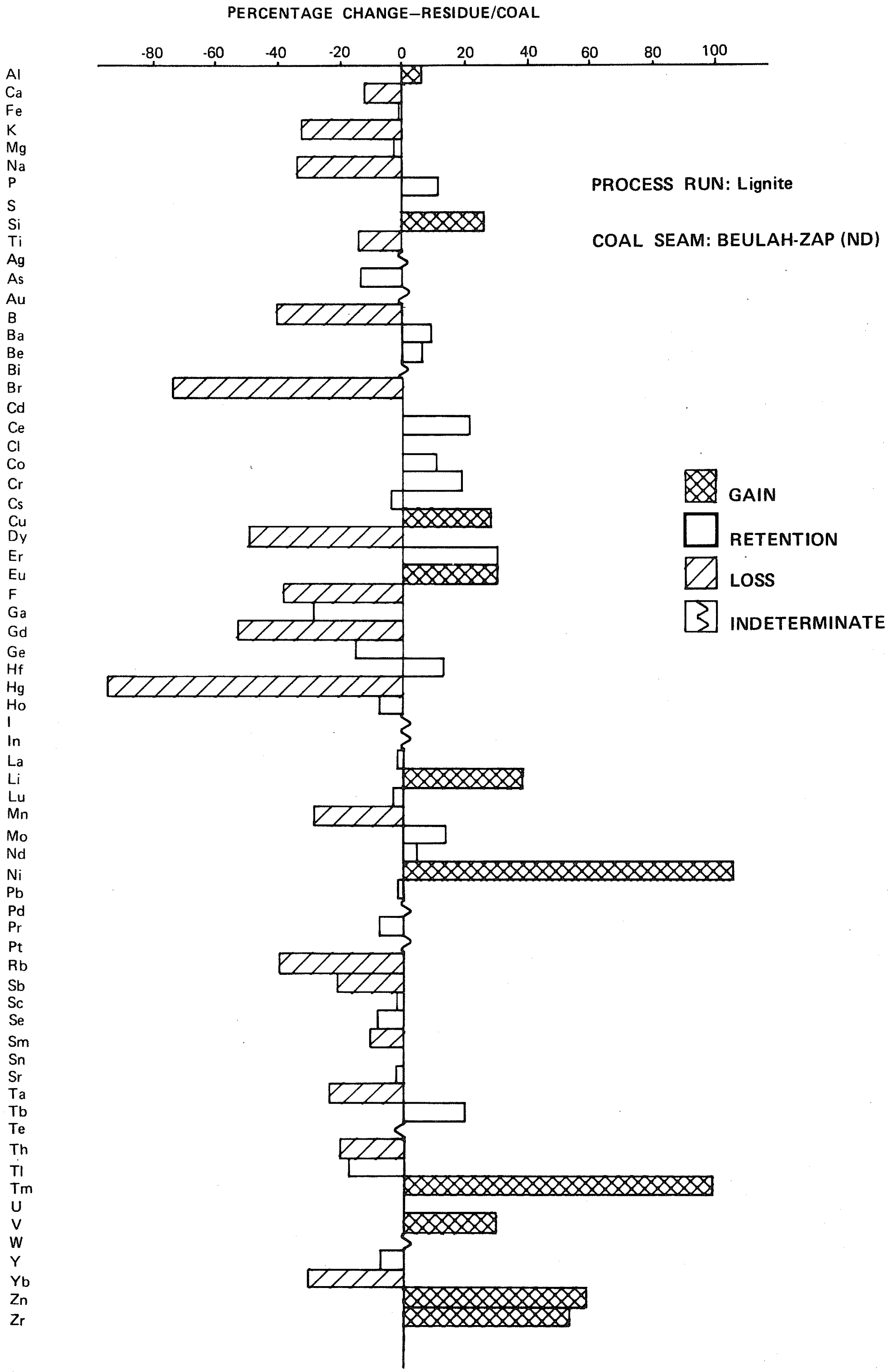
Figure 7. Summary of frequency of mobility behavior of process runs versus percentage of elements determined.



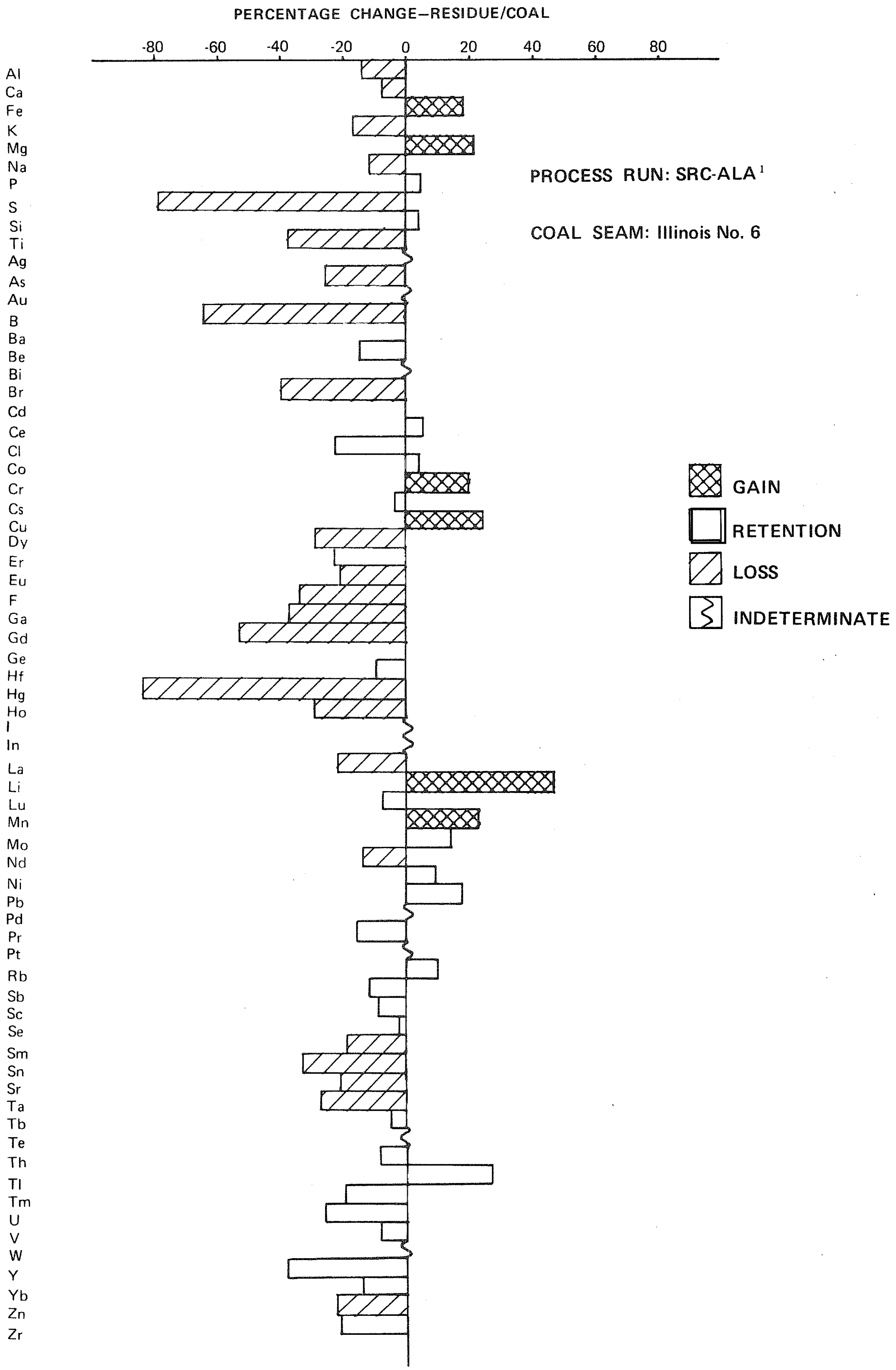
Figures 8.1 to 8.7 Graphs of relative mobility of elements (as measured by change in concentration of elements from feed coal to residue) in 7 liquefaction process runs. Figure 8.1 Clean Coke Process



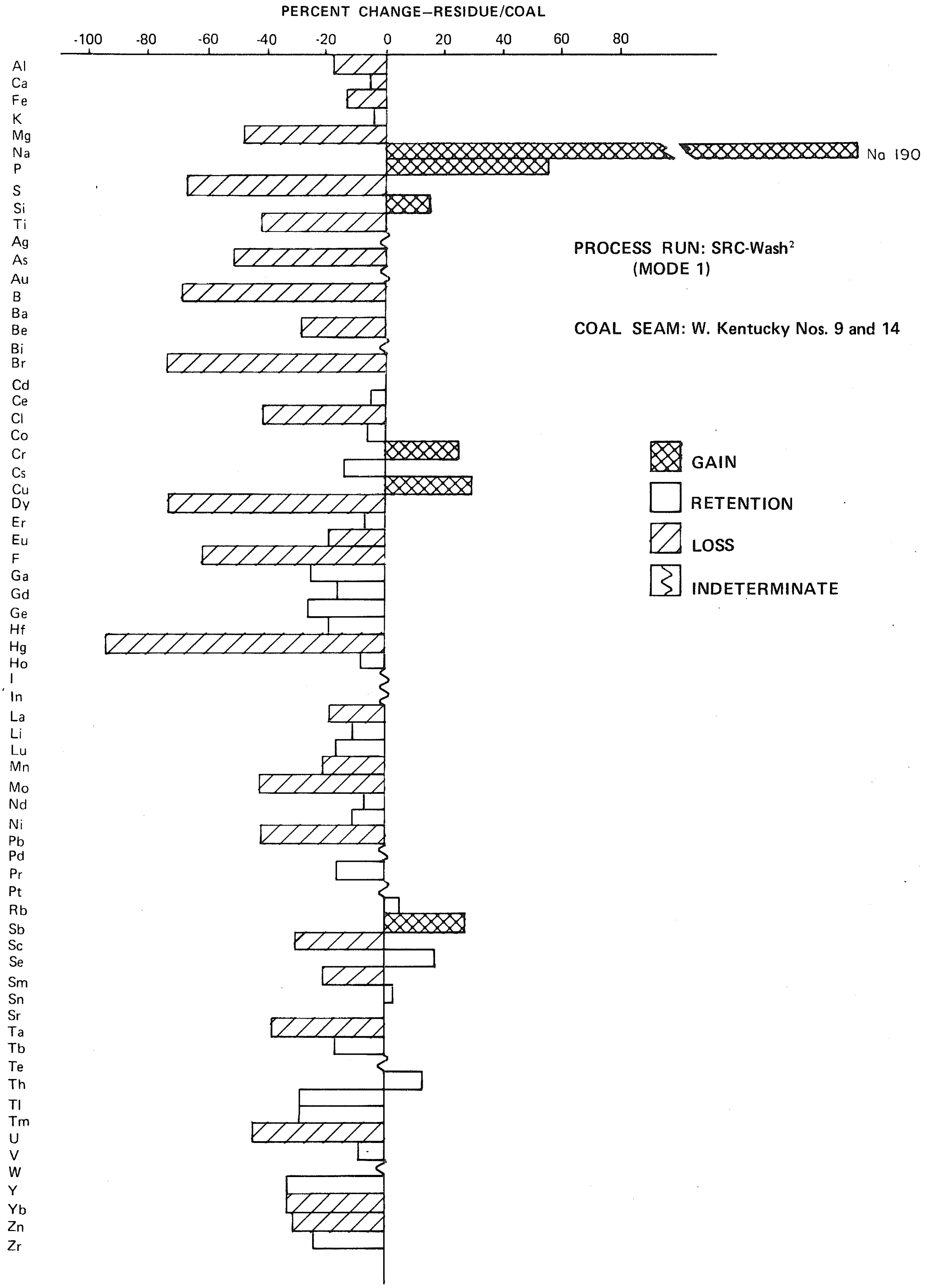
8.2 H-Coal-1 Process



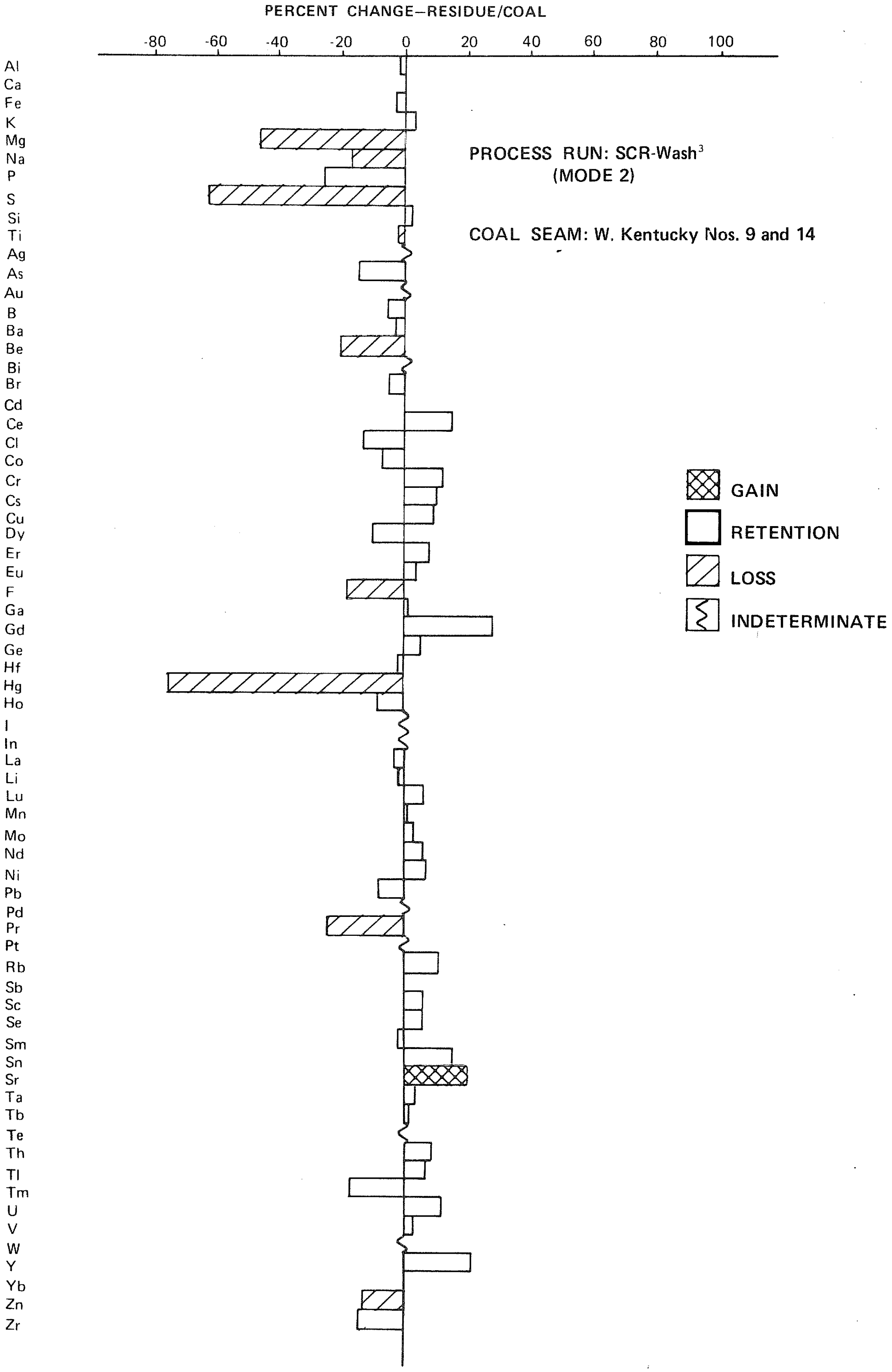
8.3 Lignite Process



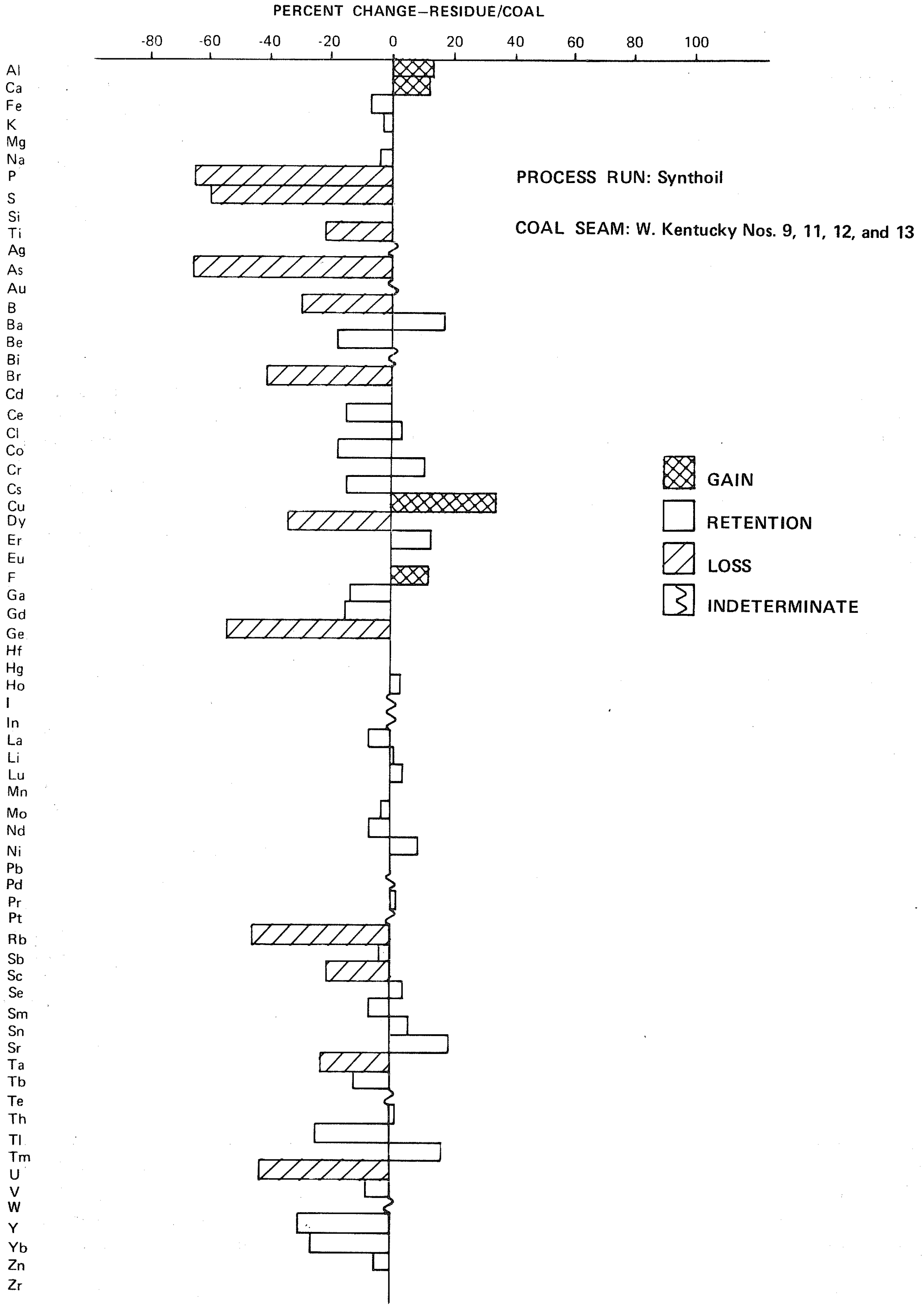
8.4 SRC-ALA-1 Process



8.5 SRC-WASH-2 Process (MODE 1)



8.6 SRC-WASH-3 Process (MODE 2)



8.7 Synthoil Process

Table 7. Summary of mobility behavior by process runs.

Processes Exhibiting Loss of Most Elements	Processes Exhibiting Retention of Most Elements	Processes Exhibiting Gain of Most Elements
SRC-ALA 1,2,3,5 (Eastern bituminous Filter Aid)	Clean Coke (Eastern bituminous)	H-Coal 4 (Western subbituminous)
SRC-ALA 4 (Western subbituminous Filter Aid)	H-Coal 1 and 3 (Eastern bituminous)	Lignite (Western lignite)
SRC-WASH 1,2 (Eastern bituminous Filter Aid Mode 1)	SRC-WASH 3,4,5,6 (Eastern bituminous Mode 2)	
H-Coal 2 (Eastern bituminous)	Synthoil (Eastern bituminous)	

indicate a loss. The Clean Coke, H-Coal, Lignite, and Synthoil process runs show losses for an average of 25 to 32 percent of the elements. The SRC-ALA 1-5 runs and SRC-WASH-1 and -2 (Mode 1 operation) runs show higher percentage losses, $\sim$54 percent and $\sim$46 percent respectively, but many of these are apparent losses caused by dilution of the residue with the filter-aids. From these data it is difficult to deduce any direct dependence of mobility upon the pressure used ($\sim$1500 to 4000 psi) by the various processes. Also the use of catalysts probably is not a major factor on mobility.

The process runs indicating retention of the greatest number of elements were those using eastern bituminous coal (table 7). The runs indicating gains for the greatest number of elements were those that used western subbituminous coal or lignite. An exception was noted in the case of the SRC-ALA-4 run, which showed losses for many of the elements from a western subbituminous coal, but which used a filter-aid. One possible explanation for the difference in behavior of eastern and western coals during liquefaction is that western coals generally have lower trace element concentrations than eastern coals. A minor to moderate change in concentrations, whether because of mobility of an element or because of contamination, would cause larger relative changes in the retention behavior than would an equivalent change in concentration of an element in eastern coal.

Table 8 gives the results of analyses of some of the liquefaction products (and their respective feed coals) from various runs. These data, on the "as received" basis, show that the products are significantly depleted in mineral matter compared to the feed coal. Table 9 lists, for the four processes from which products were analyzed, the mean ratio for an element's concentration in the feed coal to its concentration in the product. The ratios range from 1.6 to 820 and average 51 for 37 elements, demonstrating a generally refined product relative to the feed coal.

CONCLUSIONS

The following conclusions are made from the chemical analysis of samples from a limited number of liquefaction runs and are based primarily upon data derived from runs in which filter-aids were not used and from runs in which the residue was corrected for the presence of filter-aids. These conclusions are based upon means and frequencies of observations on only a limited number of samples.

1. The range of concentrations for the 71 elements in the residues studied indicate the amounts available for beneficiation. The data include results from samples derived from different ranks of coal and different types of liquefaction processes. The processes studied included Clean Coke, H-Coal,

Table 8. Analyses of product and feed coal (as received)

		Concentration																	
		%			ppm														
Process	"Sample Number"	Fe	K	Na	As	Br	Ce	Cl	Co	Cr	Cs	Dy	Eu	F	Ga	Hf	Hg	In	La
LIGNITE	C19590 (Lignite)	0.64	0.018	0.41	7.7	3.4	6.1	29	0.99	3.0	0.11	0.46	0.07	16	2.3	0.75	0.16	<0.14	3.0
	C19592 (Product)	0.006	<0.001	0.014	0.75	0.26	0.04	11	0.30	0.58	0.015	0.014	0.004	4.0	0.13	0.03	0.14	0.01	0.06
SRC-ALA-1	C19702 (Coal)	1.0	0.16	0.10	1.9	6.1	7.9	920	3.0	21	1.2	1.0	0.19	91	3.3	0.50	0.10	0.01	4.8
	C19704 (Product)	0.04	0.0037	0.0029	0.68	0.91	0.3	--	0.52	4.6	0.05	0.02	0.006	8.0	0.91	0.04	0.43	0.002	0.12
SRC-ALA-2	C19705 (Coal)	1.4	0.18	0.023	3.2	2.0	9.9	310	2.7	23	1.3	1.2	0.20	52	3.0	0.67	0.24	0.01	4.8
	C19707 (Product)	0.082	<0.001	0.0005	0.57	1.8	<1	--	0.32	4.8	<0.1	0.02	0.004	8.0	0.95	<0.05	0.04	--	0.04
SRC-ALA-3	C19708 (Coal)	1.4	0.16	0.014	8.7	3.9	16	280	1.6	17	1.2	1.4	0.31	61	3.2	0.60	0.26	0.014	9.2
	C19710 (Product)	0.001	0.0024	0.0004	2.1	4.2	0.43	55	0.63	1.5	1.5	0.16	0.014	9.0	0.93	0.12	0.02	<0.01	0.13
SRC-ALA-4	C19711 (Coal)	0.28	0.011	0.06	1.2	1.1	14	35	1.9	6.0	0.14	1.1	0.28	51	1.6	0.93	0.09	0.024	7.2
	C19713 (Product)	0.02	0.004	0.0038	0.33	<0.20	0.41	<2.0	1.5	1.4	--	0.07	0.011	6.0	0.55	<0.05	0.06	--	0.40
SRC-ALA-5	C19714 (Coal)	0.94	0.078	0.065	5.3	13	10	1100	2.3	12	0.7	0.76	0.17	65	2.7	0.58	0.09	0.015	5.4
	C19716 (Product)	0.03	0.0011	0.0016	2.2	6.6	0.17	30	0.87	2.3	0.044	0.03	0.008	9.0	0.96	0.04	0.02	<0.01	0.08
SRC-WASH-1	C19141 (Coal)	3.4	0.16	0.01	13	3.7	29	190	9.5	24	0.6	2.2	0.7	70	3.2	0.66	0.13	0.1	14
	C19143 (Product)	0.034	0.0003	<0.0005	2.1	6.3	0.55	110	0.28	1.6	<0.05	0.41	0.06	13	1.1	0.11	0.01	--	0.15
SRC-WASH-2	C19488 (Coal)	2.2	0.16	0.020	23	4.7	19	330	6.4	18	1.3	1.8	0.54	90	3.2	0.47	0.21	0.02	13
	C19486 (Product)	0.036	0.0008	0.0009	3.3	7.2	0.50	--	0.44	6.6	0.12	0.37	0.12	9.6	1.0	0.2	0.02	--	0.29
SRC-WASH-3	C19899 (Coal)	1.2	0.12	0.02	6.7	5.6	9.1	640	2.9	15	1.1	1.1	0.23	51	3.0	0.62	0.26	--	6.4
	C19915 (Product)	0.0021	<0.0001	0.0001	0.045	1.4	<0.1	220	<0.4	0.6	0.02	--	0.001	6.0	<0.5	--	0.02	--	1.1
SYNTHOIL	C19276 (Coal)	3.7	0.18	0.024	7.5	0.9	19	48	5.6	22	1.5	1.6	0.34	63	4.0	0.49	0.21	--	11
	C19512 (Product)	0.40	0.022	0.0060	1.4	0.45	5.4	--	2.2	9.0	0.51	0.47	0.13	34	1.4	0.36	0.02	0.008	2.6

Table 8. Analyses of product and feed coal (as received) continued

Process	"Sample Number"	Concentration																		
		ppm																		
		Lu	Mn	Ni	Rb	Sb	Sc	Se	Sr	Ta	Tb	Th	U	W	Yb	Sm	Ba	I	Sn	Te
LIGNITE	C19590 (Lignite)	0.04	95	<4	1.9	0.44	0.99	1.0	420	0.15	0.07	1.4	<0.4	2.9	0.33	0.41	860	7.9	2.0	5.1
	C19592 (Product)	<0.01	1.7	0.96	<2.0	0.06	0.009	0.07	2.8	--	<0.03	0.013	<0.5	--	0.02	0.003	19	1.1	<1.0	1.0
SRC-ALA-1	C19702 (Coal)	0.07	36	18	14	0.51	2.1	3.2	73	0.13	0.10	1.4	1.9	0.26	0.40	1.0	67	--	--	--
	C19704 (Product)	<0.01	3.5	3.9	<1.0	0.27	0.08	0.34	<20	0.03	<0.01	0.04	<1	0.05	0.01	0.03	6.2	1.2	<1.0	<1.0
SRC-ALA-2	C19705 (Coal)	0.08	90	--	11	0.95	2.9	2.4	16	0.10	0.16	1.8	3.0	0.23	0.41	1.2	50	--	--	--
	C19707 (Product)	<0.05	16	--	<1.0	7.2	0.06	0.09	<10	<0.05	<0.1	0.03	0.22	<0.1	0.02	0.02	2.7	<1.0	<1.0	<1.0
SRC-ALA-3	C19708 (Coal)	0.10	28	14	14	2.3	2.6	3.1	94	0.17	0.16	2.0	2.1	0.83	0.64	1.5	62	--	--	--
	C19710 (Product)	0.02	4.3	2.3	<1.0	0.43	0.44	0.30	<10	0.05	0.02	0.30	0.79	0.075	0.10	0.13	3.8	1.7	<1	<1
SRC-ALA-4	C19711 (Coal)	0.08	20	9.9	1.3	0.44	2.3	1.2	270	0.14	0.15	2.3	0.61	0.39	0.47	1.5	400	--	--	--
	C19713 (Product)	0.004	2.6	3.3	--	0.21	0.17	<0.5	4.0	<0.05	<0.1	0.17	0.11	--	0.02	0.06	12	<1.0	<1	<1
SRC-ALA-5	C19714 (Coal)	0.06	38	7.9	14	0.43	2.0	1.3	150	0.14	0.12	1.4	0.77	0.29	0.30	0.82	120	--	--	--
	C19716 (Product)	0.005	5.3	4.9	<1.0	2.1	0.10	0.30	<20	<0.05	0.01	0.03	--	--	0.02	0.02	<1.0	<1.0	<1	<1
SRC-WASH-1	C19141 (Coal)	0.18	44	29	12	1.6	6.0	2.8	68	0.12	0.76	2.7	1.7	0.5	1.3	3.1	34	2.1	1.2	<1.0
	C19143 (Product)	0.03	24	<5	<1.0	0.04	0.9	0.21	6.0	0.03	0.17	0.36	0.39	<1	0.23	0.30	<1.0	1.3	<1	<1
SRC-WASH-2	C19488 (Coal)	0.15	44	29	15	1.5	3.7	2.5	66	0.16	0.43	2.3	2.3	0.55	0.83	2.5	48	1.5	<1.0	<1.0
	C19486 (Product)	0.02	18	--	<5.0	0.2	1.2	0.18	--	0.10	0.10	0.45	0.95	0.12	0.27	0.30	<1.0	<1.0	<1	<1
SRC-WASH-3	C19899 (Coal)	0.09	34	12	13	4.2	2.4	3.0	--	0.16	0.14	1.6	1.7	0.50	0.44	1.2	44	2.0	<1.0	1.9
	C19915 (Product)	<0.004	0.23	--	--	<0.01	0.0003	<0.3	1	<0.01	<0.05	<0.2	--	<0.2	0.02	--	--	--	--	--
SYNTHOIL	C19276 (Coal)	0.09	70	<11	27	0.29	3.7	1.7	49	0.17	0.43	3.1	1.3	1.0	0.67	1.9	130	2.1	2.0	1.8
	C19512 (Product)	0.06	12	8.1	5.9	0.20	1.8	0.70	10	0.11	0.18	1.0	0.56	0.20	0.40	0.57	--	--	--	--

Table 9. Ratio of concentration in feed coal to concentration in product

	Fe	K	Na	As	Br	Ce	Cl	Co	Cr	Cs	Dy	Eu	F	Ga	Hf	Hg	In	La	Lu
LIGNITE (One Run)	110	18	29	10	13	150	2.6	3.3	5.2	7.3	33	18	4.0	18	25	1.1	--	50	4.0
SRC-(ALA) (All 5 Runs)	300	73	34	3.0	3.2	33	20	4.1	6.0	13	32	30	8.1	3.2	13	5.0	2.6	63	9.1
SRC-(WASH) (All 3 Runs)	240	640	81	54	1.7	61	2.3	19	14	26	5.1	82	7.8	4.0	4.2	12	--	48	12
SYNTHOIL (One Run)	9.3	8.2	4.0	5.4	2.0	3.5	--	2.5	2.4	2.9									
AVERAGE ALL SETS	230	230	45	20	3.7	50	11	8.2	8.1	16	23	42	6.9	4.9	11	7.3	2.6	51	8.7

	Mn	Ni	Rb	Sb	Sc	Se	Sr	Ta	Tb	Th	U	W	Yb	Sm	Ba	I	Sn	Te
LIGNITE (One Run)	56	--	--	13	110	14	150	--	2.3	110	--	--	17	140	45	7.2	2.0	5.1
SRC-(ALA) (All 5 Runs)	7.5	3.8	13	1.9	23	9.8	18	3.1	6.6	32	5.9	6.2	21	34	40	--	--	--
SRC-(WASH) (All 3 Runs)	50	5.8	7.5	160	2700	12	11	7.2	3.9	6.9	3.4	3.5	10	9.3	41	1.6	1.2	--
SYNTHOIL (One Run)						2.4	4.9	1.5	2.4	3.1	2.3	5.0	1.7	3.3	--	--	--	--
AVERAGE ALL SETS	25	4.2	10	49	820	11	32	4.3	4.9	2.9	4.7	5.1	15	37	41	3.4	1.6	5.1

Project Lignite, Solvent Refined Coal (both Alabama and Washington plants), Synthoil, and COED. The various coals used included Illinois No. 6; West Kentucky Nos. 9, 11, 12, 13, 14; Pittsburgh; Wyodak; Scranton; and Beulah-Zap seams.

2. Most of the elements studied are retained in the residues; only minor (<10%) losses occurred in going from feed coal to residue. The concentrations of some elements (Ag, Au, I, Pd, Te, and W) were too low to draw any conclusions concerning their behavior.

3. The elements that were significantly mobilized and therefore were depleted in the residues when compared to the feed coals were S, N, As, Mg, Ti, B, and Hg. An element was considered to be depleted if the mean decrease in its concentration from coal to residue was greater than 15 percent and/or if it was lost in most of the sample sets studied. The elements that have moderate mobility are Zn, Ca, Na, Eu, Dy, F, Yb, Ta, Sc, and Br.

4. No element was consistently enriched in the residue. Nickel was moderately enriched (gained) in several runs. Probably this was due to erosion of equipment.

5. Data from four sample sets from the SRC (Ft. Lewis, Washington) Mode 2 operation showed that the residue from that process had the best retention statistics. Only ∿14 percent of the elements studied displayed significant losses while the other processes showed losses for 25 to 32 percent of the elements studied.

6. The mobility of most elements does not depend to any significant extent on the pressures or catalysts used. Nor do the source and type of coal appear to be major factors in the retention behavior of an element.

7. The presence of filter-aid materials in some of the residues studied masked the mobility behavior of many elements. Semi-quantitative estimates of the dilution produced by the filter-aids were calculated, and the elemental concentrations in the residues were then corrected for the dilution. The results for most elements were then comparable to those obtained for residues from runs not involving filter-aids. In the runs employing filter-aids, the elements generally mobile were S, N, As, Hg, Mg, Na, Ti, B, Br, and to a lesser extent Eu, Sc, and Ta.

MINERALOGICAL AND PETROGRAPHIC ANALYSES

INTRODUCTION

The mineralogical study is a complement to the major objective of this project. After determination of the amounts of valuable metals in coal liquefaction solid residues, it becomes important to know the location of the metals to determine if their removal is economically feasible. A study of the inorganic residue, the mineral matter, will aid in characterizing the sites of some of the valuable metals and in ascertaining the difficulties in beneficiation of the metals.

Both the mineral matter in the coal and that in the residue were characterized to determine the changes that occur in the minerals with liquefaction. The low temperature ash (LTA) of the coal and the LTA of the residue extracted by tetrahydrofuran (THF) were used for mineralogical analysis. The coal LTA and residue LTA were analyzed by X-ray diffraction for mineral composition and by scanning electron microscopy for mineral morphology and interrelationships of particles. Selected samples were examined by optical microscopy and the organic and inorganic fractions were described using coal petrographic methods.

MINERALOGICAL CHARACTERIZATION

X-Ray Diffraction Characterization

Qualitative determination of mineral composition was performed for all coals and residues. A quantitative determination of the major minerals quartz, calcite, and pyrite for coal and quartz, calcite, and pyrrhotite for liquefaction residues was run. Standard curves were constructed for quartz, calcite, pyrite, and pyrrhotite using Al_2O_3 as an internal standard.

Clay minerals were separated from the other components of the LTA of coals and residues by a procedure from Jackson (1975). The less than 2 µm fraction was removed from suspension and sedimented on a ceramic tile according to the method of Kinter and Diamond (1956). Relative percentages of the minerals illite, kaolinite, and expandable (expand with ethylene glycol solvation) clays were calculated by the method of Griffin (1971) as modified by Ward (1977). The detailed procedures for X-ray diffraction analysis are described in Appendix J.

SEM Characterization

SEM examination of the coals and liquefaction residues was conducted on the low temperature ash. Several forms of preparation were used. Samples for study of the morphology of the mineral matter were prepared by sprinkling the LTA onto an SEM specimen stub. Interrelationships of particles were studied by embedding LTA particles in epoxy, making a chip that was polished until sections through the particles were exposed. Heavy and light fractions of the LTA of both coal and liquefaction residue were separated with bromoform and observed. Inspection of the heavy minerals was made easier by bromoform separation, which eliminated most of the light fraction that would adhere to and obscure the heavier particles. The light mineral fraction, composed predominantly of clay minerals and quartz, was sedimented onto an SEM stub from an aqueous solution to which a deflocculant had been added. Details of the techniques for preparation of SEM specimens appear in Appendix K.

Coal Petrography

Polished specimens of selected coal samples and their corresponding residues were prepared and examined by reflected light microscopy. Macerals, minerals, and organic residue components were characterized and quantified on a volume percent basis. Comparisons were made of the composition of organic particles in the feed coals and in the solid residues to evaluate the types of reactive and unreactive particles in terms of the various processes and feed coals.

Other Analyses

Size analysis of residue samples was attempted, but meaningful results were not obtained.

Emphasis on interpretation of mineralogical data is on differences in mineral and elemental composition between the feed coals and their corresponding residues.

Large differences in mineralogical composition of the feed coals are noted, but a careful evaluation of these differences was not made. The method used to sample the feed coals was not adequate to insure a representative sample of each seam for comparison of mineral composition among seams.

Results and Discussion of X-ray Diffraction

Qualitative mineral composition of coals and residues. Table 10 presents the qualitative mineral composition of the feed coals and their corresponding residues from the six liquefaction processes studied. The samples are grouped by process, the first sample in each pair being the feed coal and the second sample, the THF-insoluble residues (the "A" fraction). Uncertainty concerning the presence of a mineral may be caused by, among other possibilities, superposition of peaks or the presence of only one characteristic peak of a mineral. Each sample in Table 10 also contains expandable clay minerals that for this study are not individually differentiated.

The major change in mineral composition from the coal to the residue is the transformation of the pyrite and/or marcasite (FeS_2) in the coal to pyrrhotite ($Fe_{1-x}S$ where X=0 to 0.2) during liquefaction. In most cases the transformation is probably complete with no pyrite detectable in the residue. The exceptions are samples C-19709A SRC-ALA and C-19349A Synthoil in which pyrite was detected along with pyrrhotite.

The absence of pyrite and calcite in some coals samples is due to the oxidation of pyrite in the presence of atmospheric moisture. Iron sulfates are formed from the oxidation of the pyrite. Both the iron sulfides and sulfates are water soluble and react with water to form sulfuric acid (H_2SO_4). The acid reacts with calcite producing gypsum ($CaSO_4 \cdot 2H_2O$) (Rao and Gluskoter, 1973). Some of the samples, both coals and residues, listed in Table 10 have undergone partial oxidation of pyrite and pyrrhotite and contain pyrite, pyrrhotite, iron sulfate—coquimbite ($Fe_2 [SO_4]_3 \cdot 9H_2O$) and/or jarosite ($KFe_3 [SO_4]_2 [OH]_6$)—and calcite and calcium sulfates—anhydrite ($CaSO_4$) and bassanite ($2CaSO_4 \cdot H_2O$). Coquimbite and jarosite are direct oxidation products of pyrite and pyrrhotite while anhydrite and bassanite are products of the dehydration of gypsum in bituminous coals which occurs during low temperature ashing. (In subbituminous coals and lignites, calcium sulfates can form during low temperature ashing from exchangeable calcium present in organic combination. This reaction is discussed in detail below.) The gypsum present in samples

Table 10. Mineral matter detected in LTA of liquefaction samples by X-ray diffraction.

Lab #	Sample Set	Anhydrite	Bassanite	Calcite	Coquimbite	Feldspar	Ferroan-Dolomite	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
C-18903	H-Coal 1	X		X	X	X[1]			X		X		X		X
C-18941A		X		X		?			X	?	X			X	X
C-19194	H-Coal 2	X		X	X	X[1]			X		X		X		X
C-19196A		?		X		X[1]			X	?	X			X	X
C-19916	H-Coal 3			X	X				X		X		X		X
C-19917A		X		X					X	?	X			X	X
C-20021	H-Coal 4		X	X		?			X		X		X		X
C-20022A			X	X		X			X		X			X	X
C-19590	Lignite		X	X					X		X		X		X
C-19591A			?	X		X[1]	X		X		X			X	X
C-19702	SRC-Ala 1			X					X		X		X		X
C-19703A				X		?		X	X	?	X			X	X
C-19705	SRC-Ala 2	X			X	?			X	X	X				X
C-19706A		?		X					X	?	X			X	X
C-19708	SRC-Ala 3				X				X		X		X		X
C-19709A		X							X	?	X		X	X	X
C-19711	SRC-Ala 4		X						X		X		X		X
C-19712A				X				X	X		X				X
C-19714	SRC-Ala 5		X	X		X			X		X		X		X
C-19715A				X		X[1]		X	X		X			X	X
C-19141	SRC-Wash 1				X				X		X	X	X		X
C-19142A		X							X	X	X			X	X
C-19488	SRC-Wash 2			X		?			X	?	X	X	X		X
C-19487A		X				X[2]			X	?	X			X	X
C-19899	SRC-Wash 3	X	X	X	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	X	X		X
C-20015A				X		?			X		X			X	X
C-20016	SRC-Wash 5	X	X	X		X			X		X		X		X
C-20017A		X		X		X			X		X			X	X
C-20019	SRC-Wash 6	X		X		X[1]		X	X	X	X		X		X
C-20020A		?		X		X[1]			X	?	X			X	X
C-19276	Synthoil	X		X	X	X[2]			X		X		X		X
C-19349A		X		X		X[2]			X		X		X	X	X

X denotes that the mineral is present
? denotes that the mineral is probably present

[1] Plagioclase feldspar

[2] Alkali feldspar

C-19703A, C-19712A, C-19715A, and C-20019 probably originated from the hydration of bassanite after low temperature ashing during storage of the sample. Sulfate minerals may form in the residue and not in its corresponding coal sample and conversely, depending upon the conditions each sample is exposed to.

Table 11. X-ray diffraction data for ferroan-dolomite found in sample C-19591A

2θ	dÅ	I/I_1
23.9°	3.72	4
30.7°	2.91	10
33.3°	2.69	4
40.8°	2.21	4
50.7°	1.80	2

The major minerals, calcite, illite, kaolinite, pyrite, quartz, and expandable clay minerals are present in all the coals represented by the samples in Table 10. The difference in LTA composition from coal to coal lies in the amount of each mineral in the ash. Differences in minor minerals include the presence of marcasite in three western Kentucky coal samples (C-19141, C-19488, and C-19899) and one Illinois coal (C-20014); and the presence of ferroan-dolomite in C-19591, the residue of a North Dakota lignite. The ferroan-dolomite is thought to have formed in the reactor vessel of the lignite process. Walker et al. (1977) and Stone et al. (1979) reported the formation of calcite and vaterite (a $CaCO_3$ polymorph) in the reactor vessel of the SRC-Alabama liquefaction process and the occurrence of excess calcite in the residue of the process. This phenomenon appeared when feed from the Wyodak seam, a low rank coal, was used. Walker et al. suggested that the source of calcium was exchangeable calcium present in the organic fraction of low rank coals. A study of lignites (Miller and Given, 1978) showed that the elements Ba, Ca, Mg, Mn, Na, and Sr are available for exchange from carboxyl groups in lignite. It is probable that ferroan-dolomite formed from the Ca and Mg from the above mentioned source, Fe from the dissociation of pyrite, and C and O from the coal in the reactor vessel. Table 11 gives the X-ray diffraction data for the ferroan-dolomite found in sample C-19591A.

Quantitative analysis of nonclay minerals. The principal nonclay minerals present in the coal samples are quartz, calcite, and pyrite and in the residues, quartz, calcite, and pyrrhotite. The percentages of these minerals present in liquefaction samples appear in Table 12. The absence of pyrite and/or calcite in a sample is most likely due to the oxidation of pyrite, the formation of sulfuric acid, and the dissolution of calcite. Calcite is not quantified in samples C-20021 and C-19711 because of the interference of a large (200) peak of bassanite with the (104) peak of calcite. The same bassanite peak also interferes with the (200) peak of pyrrhotite in C-20022A. Pyrrhotite also cannot be quantified in C-19591A because the (104) peak of calcite completely obscures the (200) peak of pyrrhotite. The large amount of calcite in C-19591A (an increase from C-19590) is attributed to the formation of some calcite in the reactor vessel as explained earlier.

In all samples but two, C-19709A and C-19349A, all detectable pyrite has been converted to pyrrhotite. The reason for lack of total conversion in these two samples is not known. The ratio of pyrrhotite to pyrite has been calculated for each sample pair and is reported in Table 12. The molecular weight ratio of FeS/FeS_2 is 0.73. If all the iron from pyrite remained to form pyrrhotite and one sulfur atom per molecule of pyrite were lost, then the ratio of pyrrhotite to pyrite in each sample pair should be 0.73. The average

Table 12. Average percentage of principal minerals by X-ray diffraction in LTA of liquefaction samples. Average mineral percentages, by weight, ± 7.5% absolute.

Lab #	Sample Set	Coal	Quartz	Calcite	Pyrite	Pyrrhotite	Clays and Others	%Pyrrhotite / %Pyrite
C-19660	Clean Coke	Ill. No. 6	21	11	19	—	49	.84
C-19661A			15	3	N.D.[1]	16	66	
C-18903	H-Coal 1	Ill. No. 6	22	13	22	—	43	.68
C-18941A			17	8	N.D.	15	60	
C-19194	H-Coal 2	Ill. No. 6	22	9	25	—	44	.72
C-19196A			16	4	N.D.	18	62	
C-19916	H-Coal 3	Ill. No. 6	15	4	22	—	59	.91
C-19917A			14	5	N.D.	20	61	
C-20021	H-Coal 4	Wyodak	11	*	9	—	80	-
C-20022A			10	12	N.D.	*	78	
C-19590	Lignite	N. Dakota lignite	7	<21[2]	10	—	>62	-
C-19591A			12	28	N.D.	*	60	
C-19702	SRC-Ala 1	Ill. No. 6	22	3	21	—	54	.62
C-19703A			15	<1	N.D.	13	72	
C-19705	SRC-Ala 2	Ill. No. 6	18	N.D.	N.D.	—	82	-
C-19706A			12	5	N.D.	12	71	
C-19708	SRC-Ala 3	W. Kentucky Nos. 9 & 14	13	N.D.	23	—	64	.30
C-19709A			13	N.D.	7	7	73	
C-19711	SRC-Ala 4	Wyodak	16	*	6	—	78	-
C-19712A			16	12	N.D.	N.D.	72	
C-19714	SRC-Ala 5	Pittsburgh	12	6	16	—	66	.63
C-19715A			9	1	N.D.	10	80	
C-19141	SRC-Wash 1	W. Kentucky	8	N.D.	40	—	52	.68
C-19142A		Nos. 9 & 14	7	N.D.	N.D.	27	66	
C-19488	SRC-Wash 2	W. Kentucky	9	<1	37	--	54	.46
C-19487A		Nos. 9 & 14	7	N.D.	N.D.	17	76	
C-19899	SRC-Wash 3	W. Kentucky	18	2	29	—	51	.69
C-19902A		Nos. 9 & 14	16	1	N.D.	20	63	
C-20014	SRC-Wash 4	Ill. No. 6	18	4	26	—	52	.65
C-20015A			15	3	N.D.	17	65	
C-20016	SRC-Wash 5	Pittsburgh	16	5	21	—	58	.90
C-20017A			14	3	N.D.	19	64	
C-20019	SRC-Wash 6	Pittsburgh	15	N.D.	22	—	63	.64
C-20020A			11	3	N.D.	14	72	
C-19276	Synthoil	W. Kentucky	15	7	27	—	51	.81
C-19349A		Nos. 9,11,12&13	13	6	<1	22	59	

[1] N.D. means not detected

[2] Upper limit of amount present. Calcite cannot be accurately quantified here due to interference from a small amount of bassanite in the sample.

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

pyrrhotite/pyrite value for the samples in Table 12 is 0.68 although the range of values for the ratio is broad (0.3 to 0.91). It appears from the ratios that nearly all, if not all, of the iron in pyrite goes to form pyrrhotite in the residues. Chemical data (Appendix E) support the conclusion that iron is retained in the residues. Sample pair C-19708 - C-19709A has a low ratio, which is due to pyrite left in the residue. The set C-19488 - C-19487A also has a low pyrrhotite to pyrite ratio. There may be undetected pyrite still present in C-19487A, or one of the samples in the set may not have been representative of the whole. The iron concentrations, on the 500°C ash basis, of C-19488 and C-19487A indicate no loss of iron. In several sample pairs the pyrrhotite to pyrite ratio is greater than 0.73. For two such pairs, C-19276 - C-19349A (Synthoil) and C-19916 - C-19917A (H-Coal), the pyrite percentage reported in Table 12 is lower than the percentage that would be reported for the fresh coal as indicated by the presence of the mineral coquimbite, a product of pyrite oxidation. The lower value for pyrite would increase the pyrrhotite/pyrite ratio. The sample pair C-19660 - C-19661A also has a high pyrrhotite/pyrite ratio; for this pair, the high ratio is probably due to an incorrect, high determination of pyrrhotite, which was caused by superposition of the (200) peak (3.00Å) of bassanite (intensity 100) with the (200) peak (2.98Å) of pyrrhotite, which is the peak used in the quantitative analysis (where the 6.01Å [intensity 95] bassanite peak was small as in this case, the quantitative determinations of pyrrhotite and calcite were made on the assumption that interference of the 3.00Å peak of bassanite with the 2.98Å peak of pyrrhotite would be small). The high ratio of pyrrhotite to pyrite for C-20016 - C-20017A may be due to the oxidation of some pyrite in C-20016 reducing its original concentration in the coal; however, Fe sulfates have not been detected in this sample by X-ray diffraction.

Seven samples of the SRC-Alabama and SRC-Washington residues had been contaminated by a filter-aid material used in separating the final liquid from the solid residue. An extensive discussion of the chemical effects of this contamination is the subject of Appendix H. The effect of contamination by the filter-aid on the mineral matter is to dilute its reported concentration by the percentage of filter-aid present. Appendix H gives calculations of the amount of the contamination in each residue. These figures are used to estimate the percentages of nonclay minerals the residues would have if the contamination by filter-aids was not present (Table 13) (sample pair C-19141 - C-19142A was not included in table 13 because the calculated amount of filter-aid in C-19142A is less than 1%). The calculations produce an increase in the percentage of quartz from coal to residue for three of the samples (C-19709A, C-19712A, and C-19715A) and a percent pyrrhotite/percent pyrite ratio greater than 1 for C-19715A. True increases are unlikely (unless they represent reactor solids material accumulated from previous liquefaction runs that have contaminated the residues) and the excess quartz and pyrrhotite may be due to an overestimation of the amount of filter-aid in the sample splits analyzed by X-ray diffraction. Probably the values for quartz, calcite, and pyrrhotite for the seven contaminated samples lie somewhere between those reported in Table 12 and those reported in Table 13.

The (102) peak of pyrrhotite is used to differentiate monoclinic from hexagonal pyrrhotite by the presence of a doublet in monoclinic pyrrhotite (Scott, 1974). Slow X-ray diffraction scans 1/4 - 1/2° 2θ/min. over this position show a single peak that in some residues is broad. The position of this peak can, in conjunction with standards, also be used to determine the percent iron in pyrrhotite (Scott, 1974). The presence of a broad (102) peak may indicate pyrrhotite with varying iron concentrations.

Table 12 shows an apparent decrease in the percentages of quartz and calcite for all sample pairs except C-19590 - C-19591A (lignite set) and some of

Table 13. Percentage of principal minerals in liquefaction samples adjusted for contamination by filter-aid.

Lab #	Sample set	Coal	Quartz	Calcite	Pyrite	Pyrrhotite	Clays & others	%Pyrrhotite / %Pyrite
C-19702	SRC-Ala 1	Ill. No. 6	22	3	21	--	54	.67
C-19703A			16	<1	N.D.	14	70	
C-19705	SRC-Ala 2	Ill. No. 6	18	N.D.	N.D.	--	82	--
C-19706A			17	7	N.D.	17	59	
C-19708	SRC-Ala 3	W. Kentucky	13	N.D.	23	--	64	.39
C-19709A		Nos. 9 & 14	16	N.D.	9	9	66	
C-19711	SRC-Ala 4	Wyodak	16	*	6	--	78	--
C-19712A			23	17	N.D.	N.D.	60	
C-19714	SRC-Ala 5	Pittsburgh	12	6	16	--	66	1.25
C-19715A			18	2	N.D.	20	60	
C-19488	SRC-Wash 2	W. Kentucky	9	<1	37	--	54	.54
C-19487A		Nos. 9 & 14	8	N.D.	N.D.	20	72	

N.D. Not detected.

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

the sample pairs contaminated by filter-aid. From coal to residue in set C-19590 - C-19591A, quartz and calcite increase. The increase in quartz may be due to inhomogeneity in the original residue sample. The increase in calcite, in sample C-19591A may also be due to inhomogeneity of the original sample; however, since C-19590 is a low rank coal, the increase probably results from formation of calcite in the reactor of the liquefaction process as discussed above. For other sample pairs, the decrease in quartz and calcite could be caused by the formation in the residues of pyrrhotite aggregates that incorporate other mineral particles such as quartz, calcite, and clay minerals. These aggregates, which are common in the residues, are discussed extensively in the following section. Many of these aggregates are smaller than 74 µm (200 mesh), which is the maximum size of particles in samples used for X-ray diffraction analysis. Quartz and calcite particles within pyrrhotite aggregates smaller than 74 µm would not be detected by X-ray diffraction. Particles present within larger aggregates presumably would be freed by grinding.

An apparent increase in the components of the category "clays and others" occurs from the coals to the residues. This increase is an artifact of calculation caused by two factors: (1) A net loss in weight of mineral matter occurs during liquefaction in the form of sulfur lost from pyrite in its transformation to pyrrhotite, a lighter molecular weight mineral. (2) There is an apparent decrease in the percentages of quartz and calcite from the coals to the residues as discussed above. In calculating to 100 percent, because of these losses, the "clays and others" appear to increase. In cases where the "clays and others" decrease from the coal to the residue, either calcite in the coal could not be quantified (as in C-20021 and C-19711), sulfates had formed from the breakdown of pyrite and calcite (as in C-19705), or a mineral was

Table 14. Relative percentages of clay minerals in LTA of liquefaction samples by X-ray diffraction.

Lab #	Sample Set	Coal	%Kaolinite	%Illite	%Expandable	%Meta-kaolinite	%I/%Ex
C-19660	Clean Coke	Ill. #6	26	34	40	—	0.85
C-19661A			11	36	38	15	0.95
C-18903	H-Coal 1	Ill. #6	47	31	22	—	1.41
C-18941A			27	24	29	20	0.83
C-19194	H-Coal 2	Ill. #6	27	32	41	—	0.78
C-19196A			20	34	39	7	0.87
C-19916	H-Coal 3	Ill. #6	33	29	38	—	0.76
C-19917A			26	38	29	7	1.31
C-20021	H-Coal 4	Wyodak	70	15	15	—	1.00
C-20022A			62	16	14	8	1.14
C-19590	Lignite	N.Dakota Lignite	14	8	78	—	0.10
C-19591A			6	17	69	8	0.25
C-19702	SRC-Ala 1	Ill. #6	23	38	39	—	0.97
C-19703A			13	43	34	10	1.26
C-19705	SRC-Ala 2	Ill. #6	39	25	36	—	0.69
C-19706A			36	37	24	3	1.54
C-19708	SRC-Ala 3	W. Kentucky #9 and 14	42	48	10	—	4.8
C-19709A			35	39	19	7	2.05
C-19711	SRC-Ala 4	Wyodak	69	13	18	—	0.72
C-19712A			44	17	14	25	1.21
C-19714	SRC-Ala 5	Pittsburgh	44	27	29	—	0.93
C-19715A			42	35	21	2	1.67
C-19141	SRC-Wash 1	W. Kentucky #9 and 14	34	29	37	—	0.78
C-19142A			47	40	13	0	3.08
C-19488	SRC-Wash 2	W. Kentucky #9 and 14	35	33	32	—	1.03
C-19487A			37	54	9	0	6.0
C-19899	SRC-Wash 3	W. Kentucky #9 and 14	30	42	28	—	1.5
C-19902A			18	43	26	13	1.65
C-20014	SRC-Wash 4	Ill. #6	26	47	27	—	1.74
C-20015A			28	32	40	0	0.80
C-20016	SRC-Wash 5	Pittsburgh	38	48	14	—	3.43
C-20017A			39	47	14	0	3.36
C-20019	SRC-Wash 6	Pittsburgh	34	32	34	—	0.94
C-20020A			23	54	11	12	4.91
C-19276	Synthoil	W. Kentucky #9,11,12,&14	27	39	34	—	1.15
C-19349A			23	38	34	5	1.12

formed in quantity during liquefaction (C-19591A).

Quantitative analysis of clay minerals. The relative percentages of the clay minerals kaolinite, illite, and expandables are reported in Table 14. The filter-aid contamination in the seven samples apparently has no effect upon the quantitative determination of clay minerals owing to the techniques involved in the preparation of the samples for clay mineral analysis. The <2 μm particle size is used for clay analysis, and very little filter-aid material is found at this size. Most of the expandables in the coals and residues are heterogeneous swelling material and are not subdivided further. The expandables of sample C-19590 are smectites, however, and this material is partially collapsed by the process of liquefaction.

Because the calculation of illite is dependent on the amount of kaolinite (see Appendix J) and the calculation of expandables is determined by difference, the ratio of illite to expandables seems to be a better measure of the behavior of illite and expandable clays during liquefaction than their percentages.

From the data in Table 14, two trends in the clay mineral composition of the samples are discernible. The first trend is a decrease in the percentage of kaolinite from the coals to their corresponding residues. Kaolinite is affected by heat and at 550°C breaks down to form metakaolinite, an alumino silicate that tends to show little crystallinity in X-ray diffraction patterns. X-ray diffraction patterns of the residue clays show no clay mineral peaks other than those of kaolinite, illite, and expandable clays, suggesting that the decrease in kaolinite may reflect the formation of metakaolinite. (Calculation of the clay mineral percentages of the liquefaction residues was modified from the calculation of the clay minerals in the coal owing to the probable addition of a new component, metakaolinite. Because the crystallinity of metakaolinite is so poor that it cannot be detected in X-ray diffraction patterns, it was assumed that the percentage difference between kaolinite calculated in the coal and kaolinite calculated in the residue was the percentage metakaolinite formed. The percentage of illite plus expandables for the residues was calculated to be 100 - [%kaolinite + %metakaolinite] and the remaining calculations proceeded as shown in Appendix J.)

The percentage decrease in kaolinite does not seem to be related to the type of feed coal used or to the liquefaction process. Three sample pairs, C-19488 - C-19487A, C-20014 - C-20015A, and C-20016 - C-20017A, show a slight increase in kaolinite, which should be regarded as basically no change in the kaolinite percentage from the coal to the residue. The sample pair C-19141 - C-19142A shows a marked increase in kaolinite percentage in C-19142A which may be due to sample inhomogeneity.

The second trend is the increase of illite/expandables in most sample sets from the coals to the residues. The increase in this ratio shows that some expandables are being permanently collapsed to 10Å during liquefaction. There are three sample sets in which the illite/expandables decreases from the coal to the residue and two sets in which the ratio is unchanged. The reason for these discrepancies is not known.

The clay mineral compositions of the low rank coals are distinctly different from that of the higher rank coals. Subbituminous Wyodak coal (C-20021 and C-19711) has a much larger percentage of kaolinite than the higher rank coals. The North Dakota lignite (C-19590) has the highest percentage by far of expandable clays. The coals C-20021 (Wyodak), C-19590 (N. Dakota lignite), and C-19711 (Wyodak) show relatively low percentages of illite (Table 14) relative to the other coals. The percentage of K in these coals is also low (Appendix E). This suggests that most of the K in the residues is present in illite.

Results and Discussion of Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray Analysis

The morphology of most minerals characterized in this study has not changed during liquefaction from the coal to its corresponding residue. Identification of the minerals in the low temperature ash of coals and residues is based upon particle morphology and elemental composition determined by energy-dispersive X-ray analysis. Clay minerals appear typically as anhedral to euhedral flakes (Fig. 9, 10) in both the coal and the residue LTA. Kaolinite, illite, and expandable clays can be differentiated by their elemental composition. Although some kaolinite is lost by the liquefaction process, other kaolinite is present in the residue in well crystallized plates stacked in "books" (Fig. 11). This kaolinite apparently survives liquefaction unchanged. Other minerals which exhibit no change during liquefaction are quartz, feldspar, barite, and sphalerite. Barite ($BaSO_4$) and sphalerite (ZnS) are present in amounts lower than the detection limits of X-ray diffraction, but have been found by SEM in the coal and liquefaction residues. Most calcite is unaffected by liquefaction. Figure 12 shows a typical calcite particle, with characteristic rhombohedral cleavage, in a liquefaction residue.

Two minerals that have been formed during liquefaction are pyrrhotite (from pyrite) and wollastonite, $CaSiO_3$ (from quartz and calcite) (Russell, 1977). The presence of pyrrhotite is readily detectable by X-ray diffraction; however, wollastonite has been found by SEM examination in only H-Coal residue in minute quantities. When H-Coal residue is treated with HCl, the wollastonite is etched and assumes a fibrous appearance as in Figure 13 (wollastonite is soluble in HCl). Experimental studies of quartz and calcite show that they may react to form the calcium silicate wollastonite under the timperature and pressure conditions present in the liquefaction processes. Four temperature-pressure curves for the wollastonite reaction, taken from Correns (1969), are shown in Figure 14. Wollastonite and CO_2 form in the fields to the right of the curves, and quartz and calcite form to the left. Curves 1 to 3 are experimentally and theoretically determined for closed systems. Curve 4 was calculated by Barth (1962) for an open system in which all CO_2 can escape. The fourth curve would be applicable

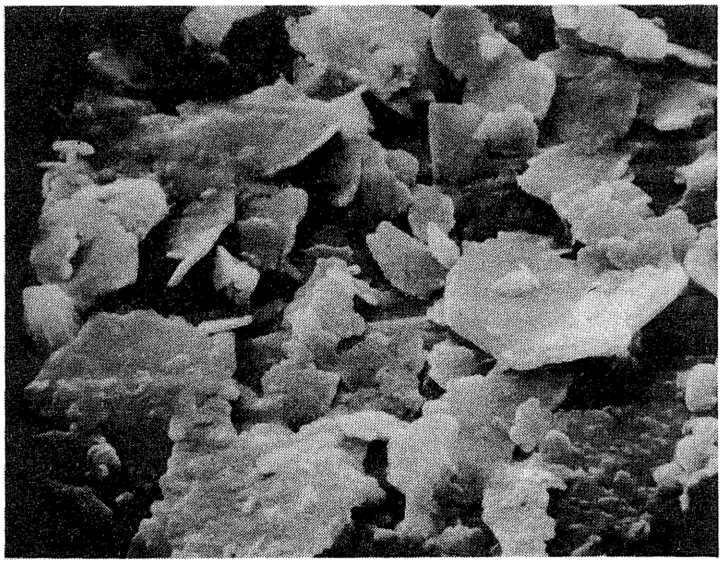


Figure 9. Kaolinite and other clay minerals from liquefaction residue. 5253X

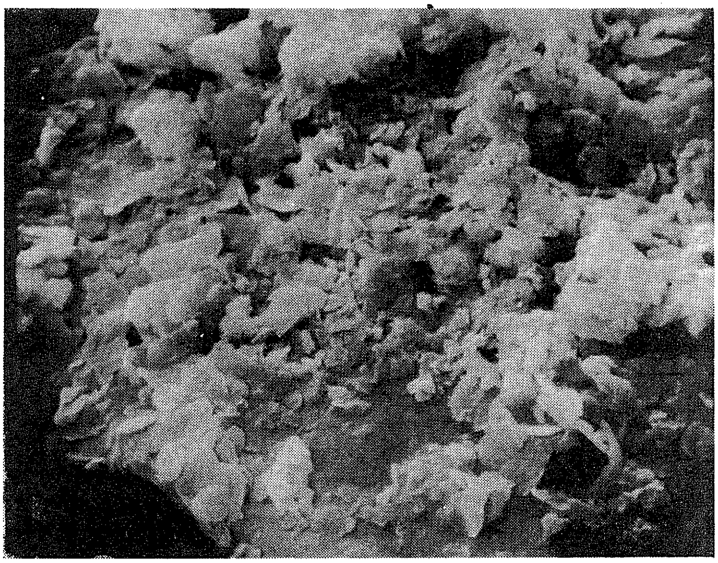


Figure 10. Illite from liquefaction residue. 10,413X

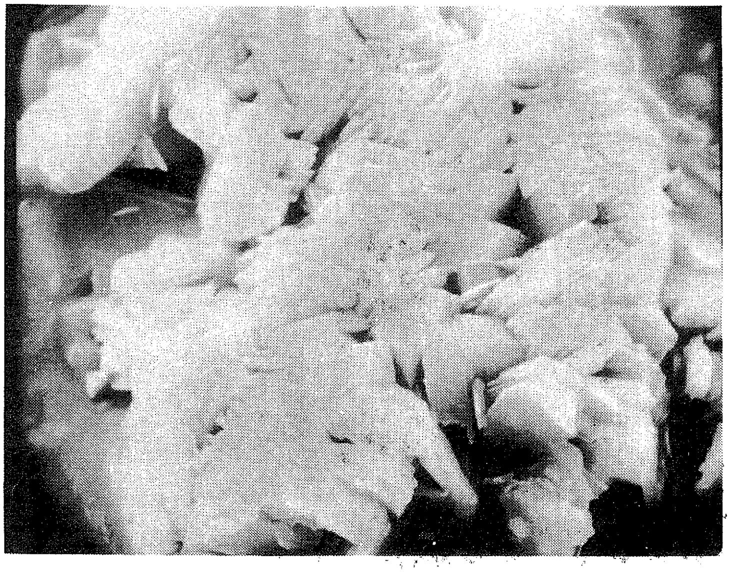


Figure 11. Euhedral kaolinite from liquefaction residue. 2491X

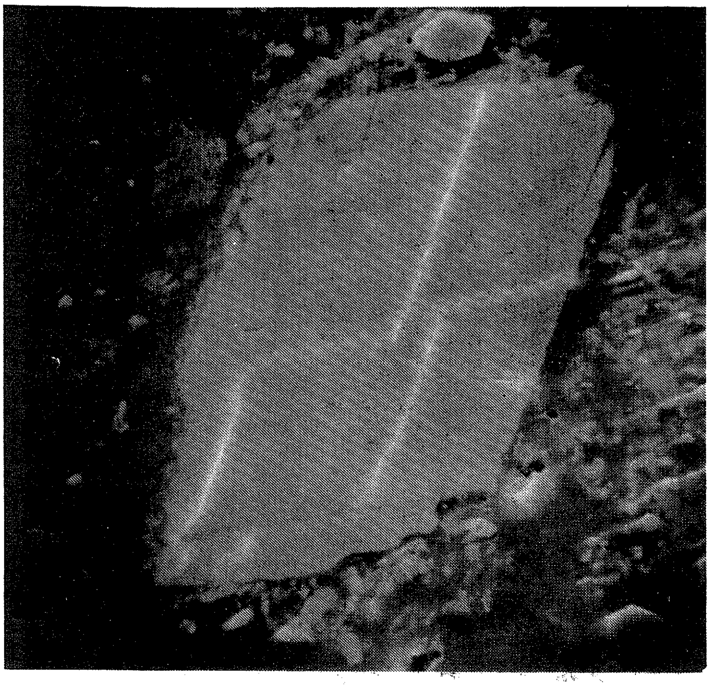


Figure 12. Calcite particle from liquefaction residue. 1156X

to the liquefaction system in which the partial pressure of CO_2 would be very low in comparison to the total pressure of the system. At the pressures (2000 to 4000 psig) and temperatures (about 450°C) of liquefaction for this curve, wollastonite is expected to form. The three phases, wollastonite, calcite, and quartz are stable on either side of the curve if the partial pressure of CO_2 is very low. In fact, all three phases are seen in the samples of H-Coal residue. To react with quartz to form wollastonite, calcite would have to break down to CaO and CO_2. Evidence for this reaction exists in some particles (Figure 15) that exhibit a spongy texture similar to that seen in calcined carbonates. The CaO would then combine with SiO_2 to form $CaSiO_3$.

Pyrrhotite typically occurs in the liquefaction residues as fine-grained aggregates of rounded particles 1 to 2 µm and less in size (Fig. 16). It can also occur, although less commonly, in a network structure such as in Figure 17, which is thought to be derived from a pyrite framboid aggregate. Parts of the interior of this network have very well crystallized material that may still be pyrite. Generally, the pyrite totally dissociates prior to forming pyrrhotite. Evidence for this exists in the fine-grained nature of the pyrrhotite, in the coatings of pyrrhotite over grains of minerals in the residue, and in the widespread incorporation of other mineral particles into the fine-grained pyrrhotite aggregates. Examples of pyrrhotite coatings are seen in Figure 18, which shows the development of at least 2 layers of pyrrhotite over a pyrrhotite particle, and in Figures 19 and 20, (optical micrographs) which display a thin coating of pyrrhotite over calcite and quartz particles. Figures 21 and 25 are polished samples of liquefaction residue LTA. In Figure 21, quartz particles (in high relief) are seen embedded in a matrix of clay minerals and pyrrhotite which aggregated during the liquefaction. Figures 22, 23, and 24 show in succession the X-ray maps for Si, Fe, and S for the area in Figure 21. From Figure 22, the quartz grains can easily be located and it is apparent that the silicon is distributed throughout the matrix (in clay minerals). The iron and sulfur X-ray maps together reveal the presence of pyrrhotite concentrated

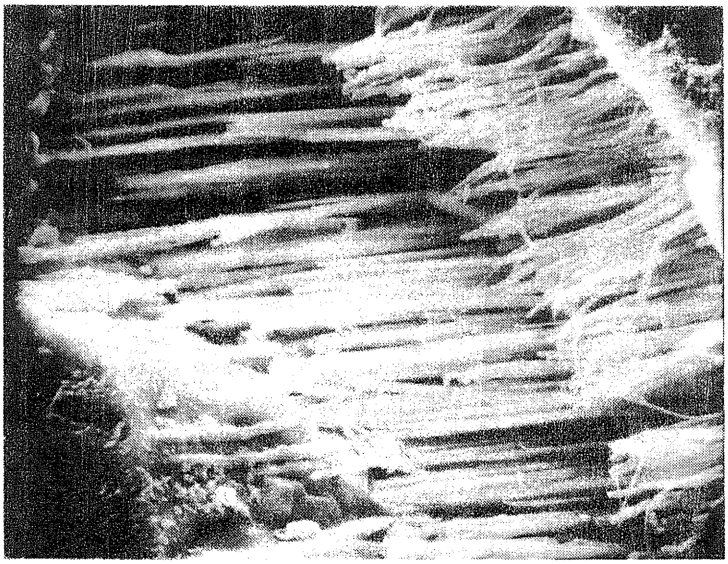


Figure 13

Wollastonite from H-Coal residue. 1122X

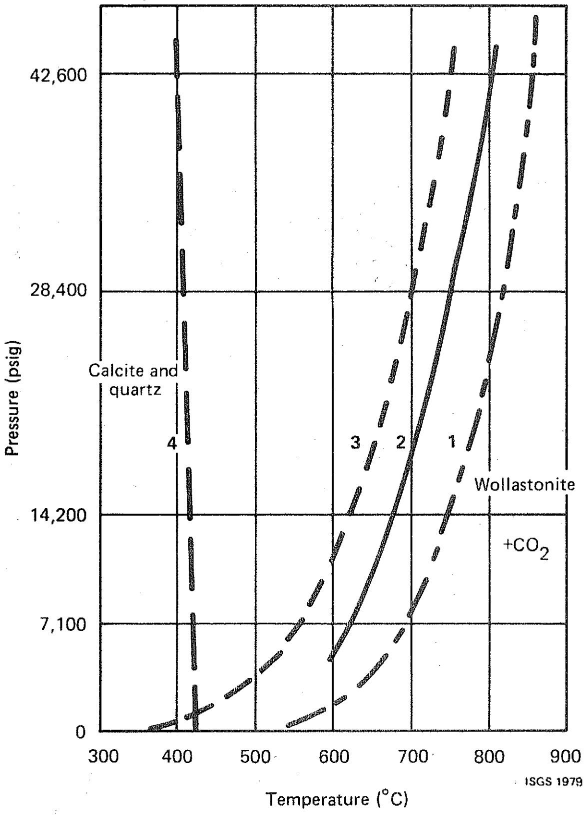


Figure 14

Temperature-pressure curves for the wollastonite reaction.

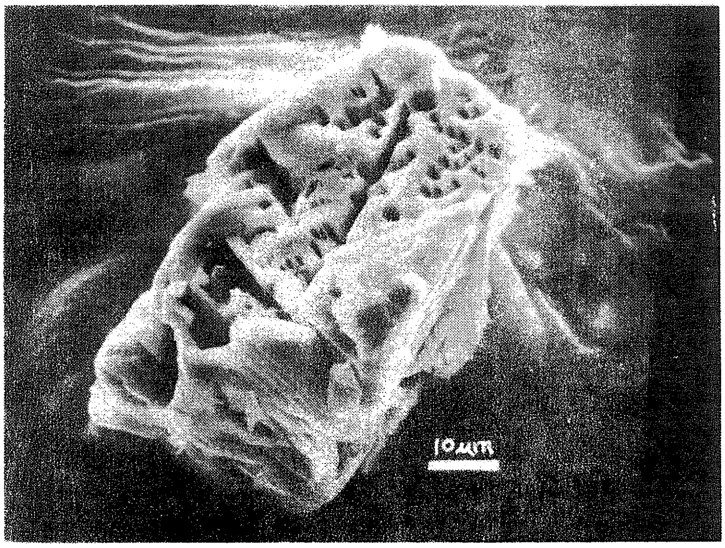


Figure 15

Calcite with "spongy" texture from liquefaction residue. 935X

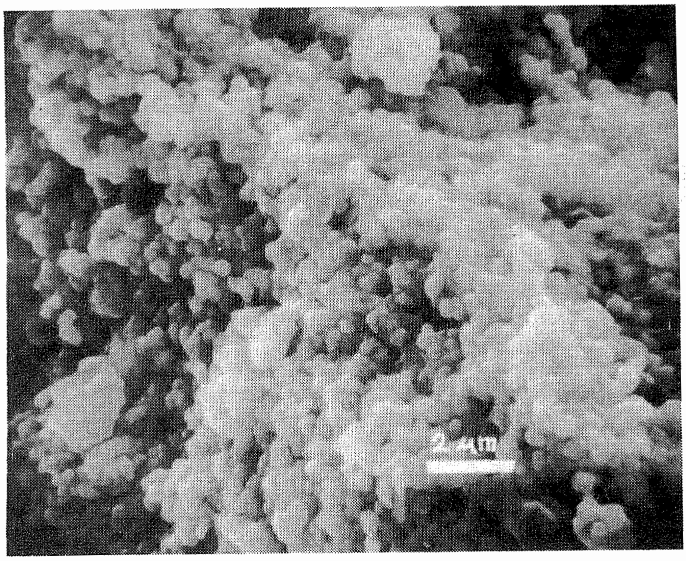


Figure 16

Typical pyrrhotite from liquefaction residue. 2550X

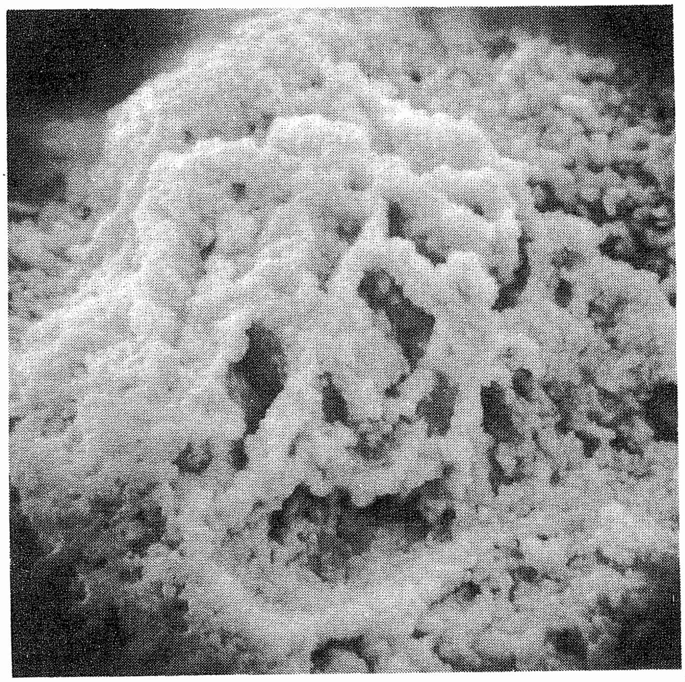


Figure 17

Pyrrhotite network. 2321X

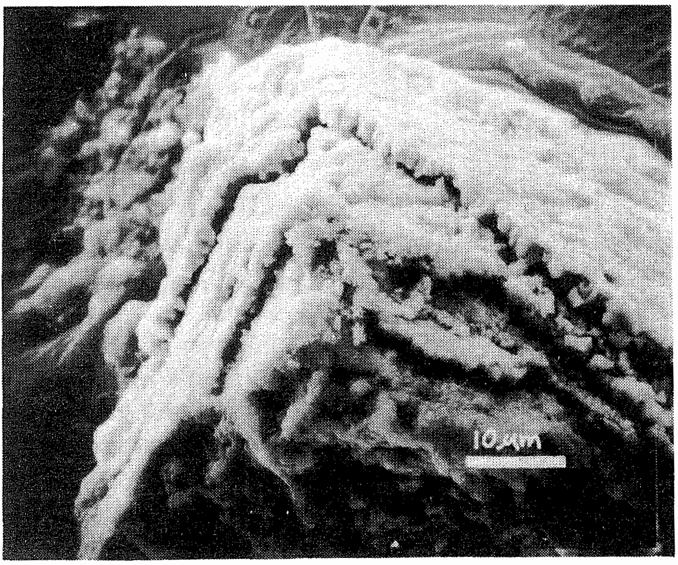


Figure 18

Pyrrhotite layers on a pyrrhotite particle. 1267X

Figure 19

Calcite particle with a thin coating of pyrrhotite. 120X

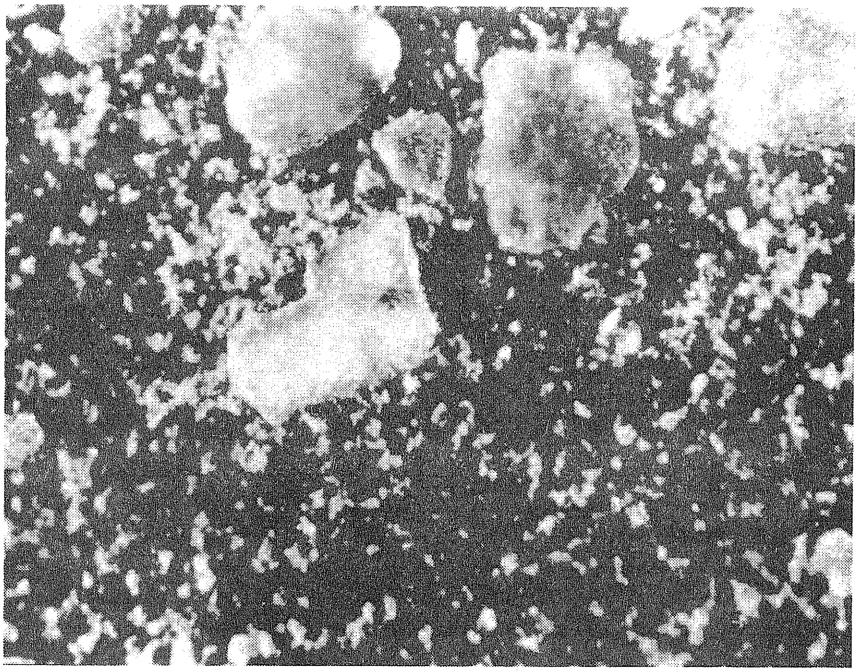
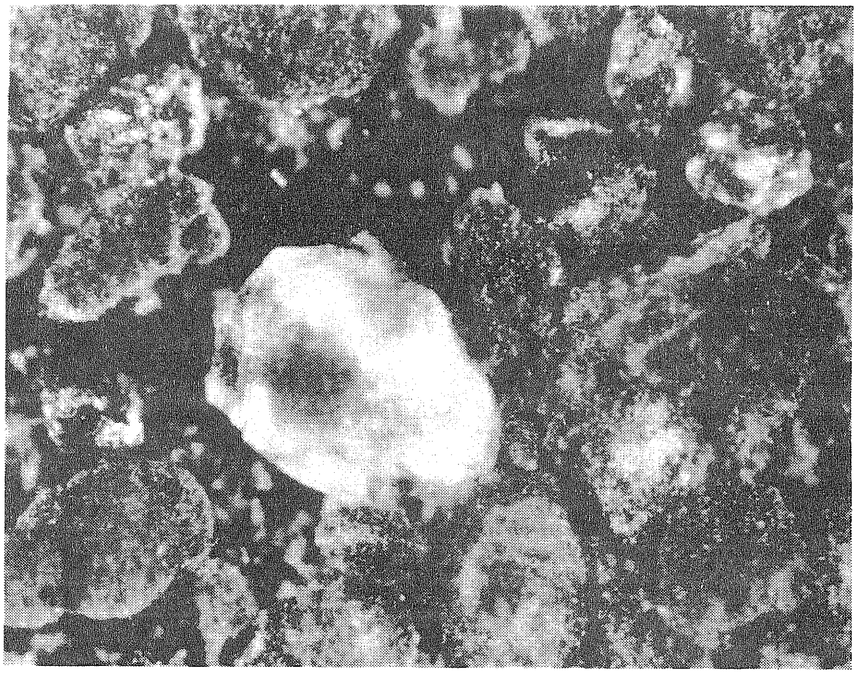


Figure 20

Quartz particle with a thin coating of pyrrhotite. 120X



in areas and also distributed throughout the matrix. Figure 25 shows a unique particle in that the matrix contains very little pyrrhotite; it is mostly clays. The large inclusion in the upper right of the particle is barite; the remaining inclusions are quartz. A close-up of the pyrrhotite and clay association is pictured in Figure 26. The pyrrhotite is smooth; the clay minerals are the rough-surfaced material. The pyrrhotite forms around and incorporates the clays. Pyrrhotite may begin nucleating as a coating on mineral particles; the fine granules stick together to form small aggregates that coalesce with other small aggregates to develop a large aggregate that includes particles of other mineral matter. This interpretation is evidenced in Figure 27 by a pyrrhotite

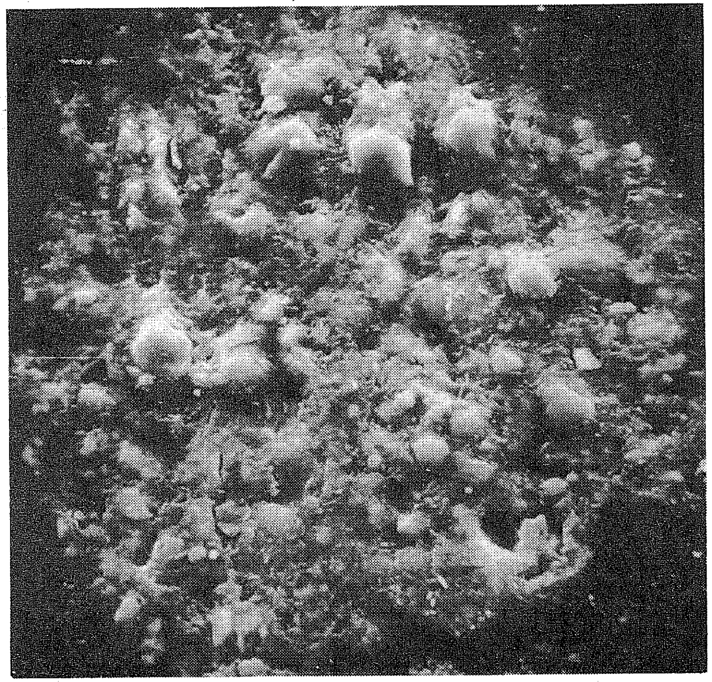


Figure 21

Quartz particles in a matrix of pyrrhotite and clay minerals. 1105X

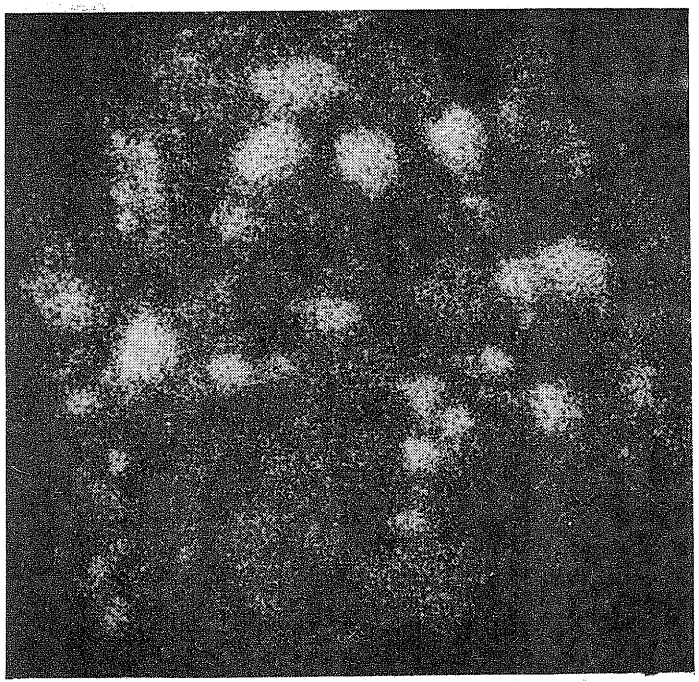


Figure 22

X-ray map of silicon for Figure 21. 1105X

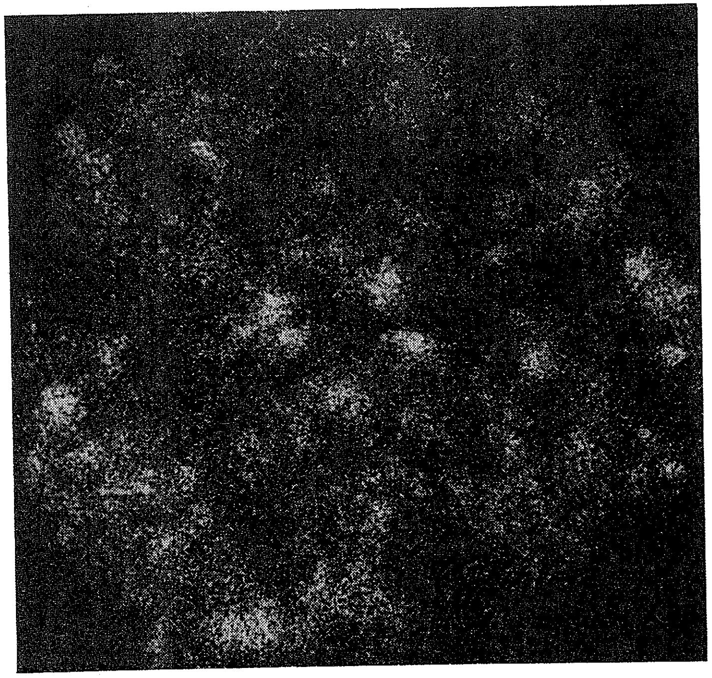


Figure 23

X-ray map of iron for Figure 21. 1105X

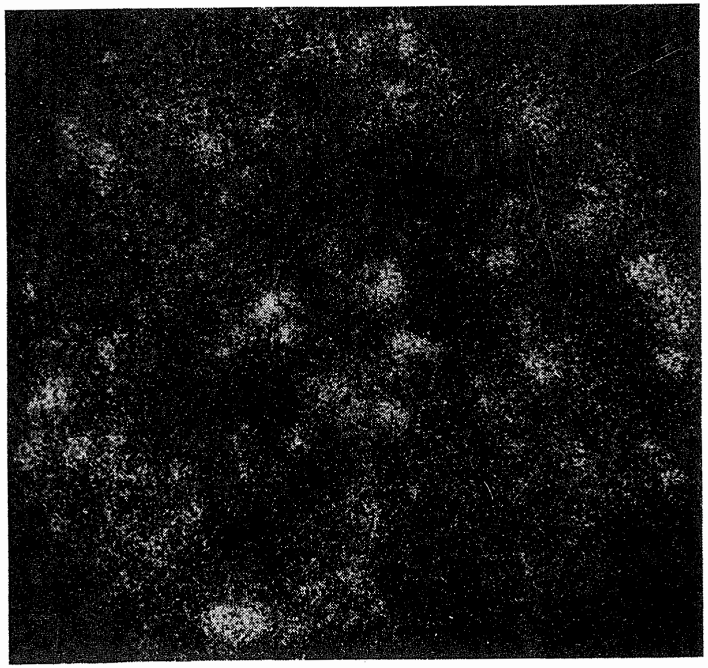


Figure 24

X-ray map of sulfur for
Figure 21. 1105X

Figure 25

Particle with clay matrix and
quartz and barite inclusions.
2130X

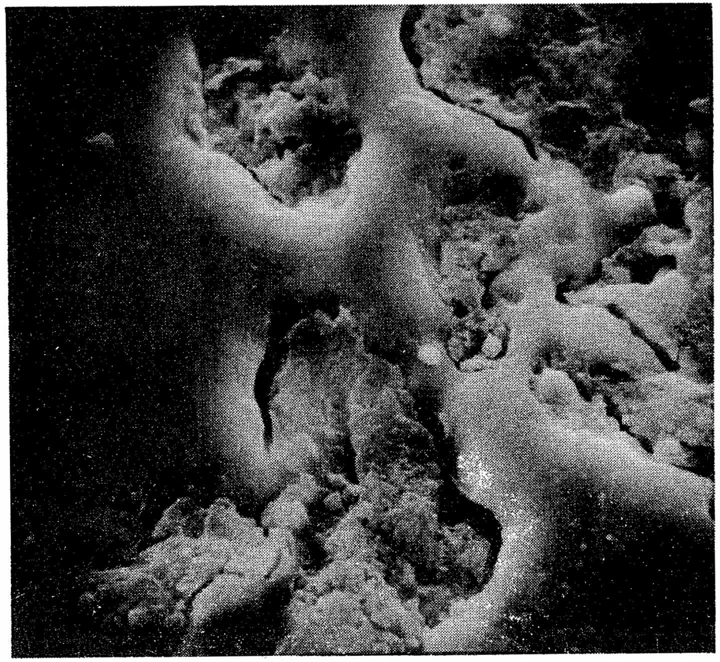


Figure 26

Pyrrhotite-clay association in
liquefaction residue. 2091X

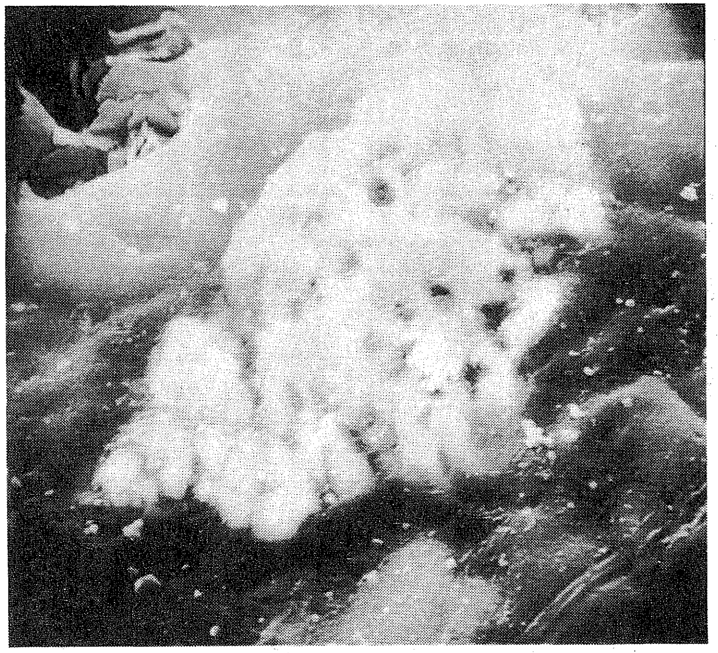


Figure 27

Coalescence of smaller pyrrhotite particles to form larger aggregate. 4118X

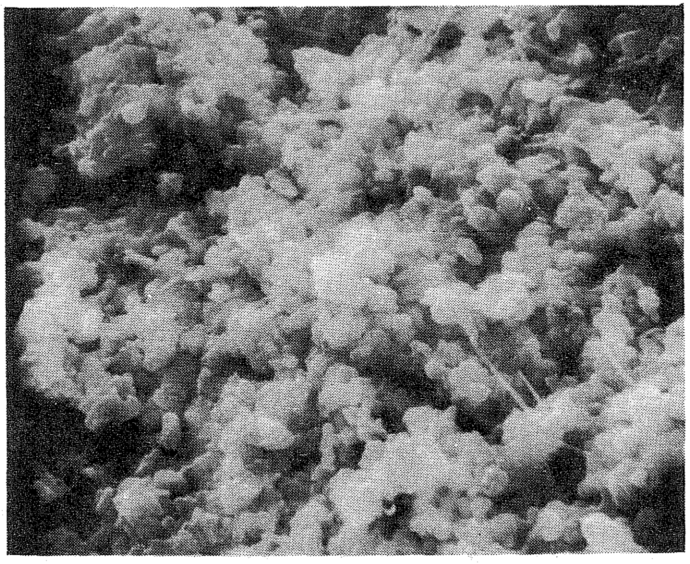


Figure 28

Asbestos fibers from filter aid and pyrrhotite in liquefaction residue. 5525X

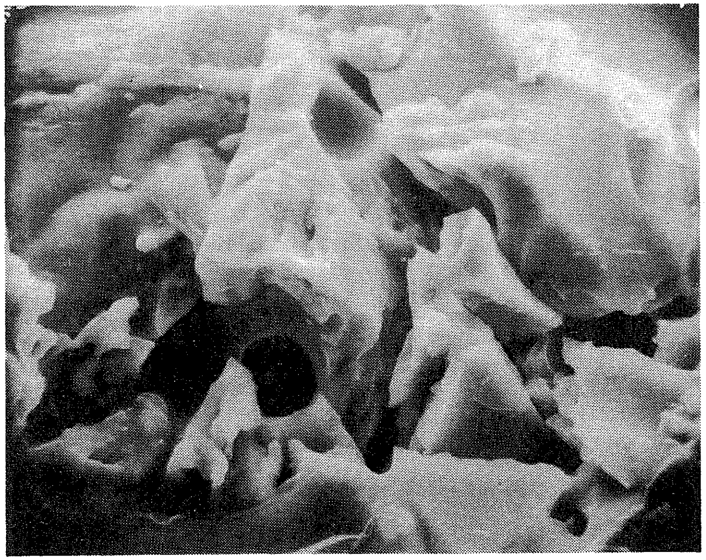


Figure 29

Sintered diatoms from filter aid found in liquefaction residue. 1037X aggregate that appears to have formed from smaller individual pyrrhotite aggregates that have coalesced.

Several liquefaction residue samples (SRC-Alabama and SRC-Washington) exhibited contamination from the filter-aid used in the separation process. Scanning electron microscopy revealed three components of the filter-aid in the residue: diatoms, sintered diatoms, and asbestos fibers. Figure 28 shows asbestos fibers with pyrrhotite in the residue, and in Figure 29 the angular siliceous particles are products of sintered diatoms. In the manufacture of the filter-aids, the diatoms are flux calcined which causes some of them to sinter.

PETROGRAPHIC ANALYSES OF FEED COALS AND SOLID RESIDUES

Optical microscopic studies were made of some samples of feed coals and of their solid residues taken from conversion processing at the following liquefaction facilities: SRC plants in Alabama and in Washington, an H-Coal plant, and a Synthoil plant. Such studies could prove useful in evaluating the nature of the chemical and physical changes that occur to the coal as it passes through the various stages of liquefaction. These considerations sometimes enable optimization of the operating variables of the conversion process. To complete such tasks, however, requires a sample collection program closely coordinated with varied operating conditions of the plant. This was not possible in this study, and therefore, the results here are of more limited value—they provide a comparison of the composition of the organic particles in the various feed coals at the various plants, and they show variability in the resulting residues generated at the plants.

Standard methods of petrographic analyses (ASTM, D2798, D2799, and applicable documents, 1977), were used to characterize the feed coals, except that the samples had been previously crushed finer (<0.15 mm) than that size called

Table 15. Petrographic analyses of feed coals

			Petrographic Composition (vol. %)										
			Macerals (whole sample - mineral free bases)						Minerals				
Process	Seam State	Seam Name	Sample No.	Vitrinite	Exinite[2]	Semifusinite and macrinite	Micrinite	Fusinite	Pyrite	Others	Reflectance[1] of Vitrinite (%, mean-max, oil)	Range of possible organic reactants (mineral free)	
SRC (ALA)	WV	Pitt #8	C19714	77-81	3-3	8-9	4-5	2-2	1	5	0.71	84	93
	KY	#9 + 14	C19708	76-81	3-3	6-7	7-8	1-1	1	5	0.63	84	94
	IL	#6	C19705	73-79	3-3	7-8	7-7	4-4	1	6	0.57	82	91
	IL	#6	C19702	71-77	3-3	6-6	11-12	2-2	1	6	0.48	80	95
	WY	Wyodak	C19711	79-8[3]	4-4	6-6	6-6	1-1	tr	4	0.38	86	95
SRC (WASH)	KY	#9 + 14	C19141	79-85	4-5	4-5	5-5	tr-tr	2	5	0.62	90	97
H-Coal	IL	#6	C18903	73-79	3-4	6-7	9-10	2-2	1	6	0.58	83	96
			C19194	80-86	3-4	4-4	4-5	1-1	1	7	0.60	90	97
Synthoil	KY	# 5, 4 and others[4]	C19276	73-82	2-3	4-5	7-8	2-2	3	9	0.58	85	95

1. Reflectance of vitrinite (and huminite) increases with increasing rank of the coal.
2. Sporinite, cutinite, and resinite.
3. Huminite which, in lignites, is a precursor to vitrinite that is in coals of higher rank.
4. Kentucky seams No. 5, No. 9, No. 11, No. 12, and No. 13 were blended at the mine.

for in the standard procedure (<0.85 mm). The methods involve reflected light microscopy of polished specimens prepared from representative crushed coal particles mixed with a cold-setting epoxy.

The results of analyses of the feed coals are listed in Table 15. The coals are high volatile bituminous in rank except the subbituminous coal from Wyoming. The relative rank of the samples is given by the reflectance of vitrinite (Table 15). Increasing rank is indicated by higher reflectance. The highest ranking sample is the one from a mine in West Virginia that produces from the Pittsburgh No. 8 seam (sample C-19714).

The maceral composition of the coals studied are moderately consistent, all composed of at least 77 percent or more (volume %, mineral free) of vitrinite. Exinite values range between 3 and 5 percent. Vitrinite and exinite macerals are considered reactants in the liquefaction process. Semifusinite and macrinite macerals are grouped together in Table 15 because they are both partly reactive in these processes (Mitchell, Davis and Spackman, 1977). These macerals range from 5 to 9 percent in the samples. Micrinite is a questionable reactant in liquefaction. This maceral varies from 5 to 12 percent in the samples. Two of the samples (C-19702, C-18903, both from the Illinois No. 6 seam) contain essentially twice the amount of micrinite as the other samples. Because of its very small particle size (<1 μm) and its occurrence as inclusions within reactant macerals (vitrinite and exinite), micrinite may also be partly reactive in liquefaction of the types of coals studied here. Fusinite, the only maceral that is known to be entirely unreactive (Mitchell et al., 1977) varies in amount in the samples from a trace to as much as 4 percent.

The minerals were observed in the samples microscopically, but we counted only pyrite and other minerals undifferentiated (Table 15). The pyrite content of the samples varies from a trace amount (the subbituminous coal from Wyoming) to 3 volume percent (the Kentucky coal tested in the Synthoil Process). The other minerals (mainly clay, quartz, and calcite) in the samples totaled from 4 to 9 volume percent of the samples.

The results of our studies of four samples of the solid residues obtained from three different processes are given in Table 16. For these studies, we used the criteria developed and described by Mitchell et al. (1977) for identification and classification of the various solid organic particles. This

Table 16. Petrographic analyses of solid residues in volume percent

Process	Source of feed coal (sample no.)	Residue sample no.	Minerals		Mixed:	Organic Particles (whole sample-mineral and granular residue free basis)				
			Pyrrhotite	others	Granular residue	Unreacted vitrinite	Fusinite and other inertinite	Angular vitroplast	Spherical vitroplast	Semi-coke
SRC (ALA)	IL#6 (C19702)	C19703	17	4	58	tr-1	4-19	15-72	1-6	1-2
(Mineral residues)	WV Pitt.#8 (C19714)	C19715	7	1	61	tr-1	4-13	23-74	tr-1	4-11
H-Coal (unfiltered vacuum bottoms)	IL#6 (C19194)	C19917	17	3	64	0-0	3-20	12-74	1-6	0-0
Synthoil (centrifuge residue)	KY#5 and others (C19276)	C19349	37	2	34	0-0	7-26	20-73	tr-1	0-0

Table 17. Behavior of coal organic constituents during liquefaction*

Maceral Precursor	Mechanisms of Reaction		Organic Residue Components
Vitrinite	Slightly altered vitrinite (contracted and/or swollen)	semi-coke	Unreacted vitrinite
	Granular residue		Granular residue
	Vitroplast (high molecular weight) → cenosphere		Cenosphere
	Vitroplast (intermediate molecular weight) → vitroplast		Vitroplast
	Hydrogenated product (repolymerized) → liquid-crystal mesophase → semi-coke		Semi-coke (anisotropic)
Exinite	Fractional contribution to submicron granular material		Granular residue
Semifusinite	Possible fractional contribution to liquid product, mechanism similar to vitroplast		Semifusinite, semi-coke, or vitroplast
Fusinite	No observable mechanism		Fusinite
Macrinite	Possible fractional contribution to liquid product, mechanism unknown		Unknown
Micrinite	Mechanism unknown		Unknown

* From Mitchell, Davis, and Spackman, 1977, table 2, p. 260.

classification is also described in Walker et al. (1977). These authors have shown by laboratory hydrogenation tests of high volatile bituminous and subbituminous coals that certain macerals in feed coals convert to certain types of organic particles. They summarized these conversions in a table which is reproduced here in Table 17. Each of the macerals that were either unreactive or partly unreactive were observed in our samples: fusinite, semifusinite, and traces of unreacted vitrinite; other types of components derived from the liquefaction reactions that were observed in our samples are vitroplasts and semi-coke.

In our samples, all of the vitroplast particles (derived mainly from vitrinite in feed coal) have reflectances notably higher than that of the original vitrinite, although a significant portion had retained their original angular morphology and isotropic character as they passed through the liquefaction process. Other vitroplast type particles were spherical in shape; these had even higher reflectances, but still were optically isotropic. We depart slightly from the classification of Mitchell et al. (1977) by listing these two types separately in Table 16, angular vitroplasts and spherical vitroplasts. Apparently, spherical ones had undergone higher temperatures or longer residence times in the reactor than those with shapes like the unreacted vitrinite. In addition, we depart somewhat from Mitchell et al. concerning cenospheres, which are small spherical (or complexly reticulate) particles with relatively large central cavity(ies) and high reflecting walls. We counted these types as spherical vitroplasts if they were isotropic, and as semi-coke if they were anisotropic. We judge isotropy, or anisotropy, to be an important optical property in this study because it gives a direct indication of the relative intensity of the physical-chemical environment experienced by the particles as they passed through the liquefaction process. Abundant semi-coke particles, it is thought, indicate the most intense process environment. All mesophase (Mitchell et al., 1977; see reaction mechanism in Table 17) particles observed were anisotropic and they were counted as semi-coke, but this type of particle was quite rare in all the samples studied. Granular residue particles are very fine-grained (<8 μm) mixtures of variously altered minerals and small amounts of amorphous organic matter—a tarlike matter of very low reflectance that is a cementaceous component in these particles. Some of the high-reflecting specks that occur in these aggregated particles may also be a carbonrich residue product, but most of these specular grains are pyrrhotite. We estimate from our microscopic observations that less than about 10 percent by volume of the granular residue is organic matter, but this estimate is subject to considerable error because of the very fine grain size and amorphous character of the material. Much additional work would be required to obtain a reliable value. According to Mitchell et al. (1977) the organic fraction of the granular residue is derived from liquid production from vitrinite and exinite macerals.

Comparison of the results in tables 15 and 16 indicate pyrrhotite mineral and the granular residue components are two of the three main components in each of the residue samples. These components are enriched in the residue for the reason that they contain the residues of the mineral matter from the feed coal, which do not contribute to the liquid product.

The other main component is the angular vitroplast. This type of vitroplast represents 12 to 23 volume percent of the samples studied (72 to 74 mineral free) (Table 16).

A small fraction of the angular vitroplast particles in the residue from the Synthoil process are strikingly porous (Fig. 30). The pores are oval and cylindrical in shape, oriented somewhat radially, and diameters range up to 1.2 μm, averaging about 0.5 μm; these pores occur throughout the cross sectional surfaces of the particles. We interpret these structures to have formed during the early stages of the liquefaction; they represent passageways for reaction products to be expelled from the particles. More important, these structures show that reaction occurs in the main simultaneously throughout whole vitrinite particles rather than being restricted to the outer surfaces. It is possible, however, that only certain types of vitrinite particles undergo this type of reaction mechanism; we observed these types of particles in residues from only the Synthoil process. We observed only traces of unreacted vitrinite in residue from the SRC plant in Alabama and none in the other residues indicating the processes were carried essentially to completion with respect to this coal maceral. Unreacted inertinite particles constitute 4 to 7 volume percent of the residues (13 to 26 mineral free).

The residues differ most distinctly from one another in the relative proportion of granular residue, it being particularly low in abundance in the Synthoil sample. They also differ in the relative abundance of semi-coke. This component is most abundant in the SRC residue derived from the highest ranking coal sample, the West Virginia coal. The residue from this coal is also enriched somewhat in

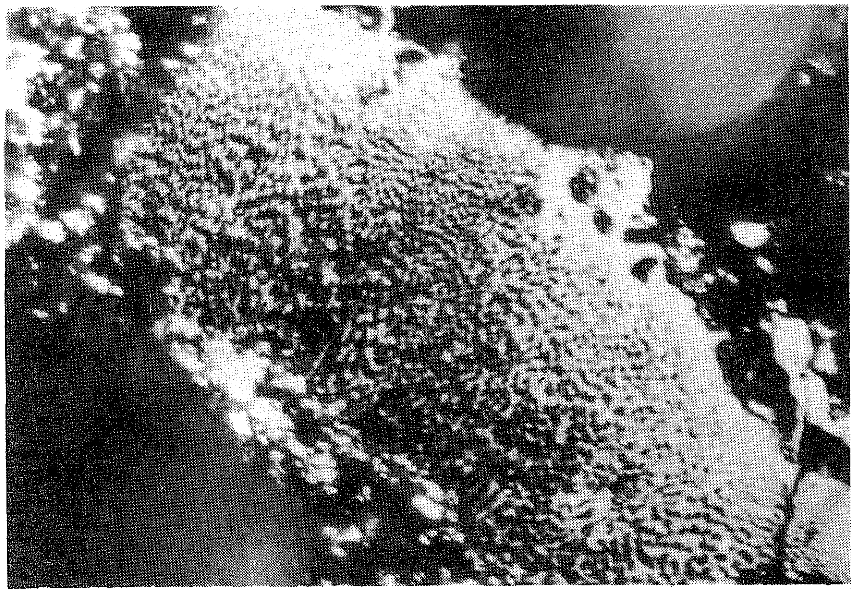


Figure 30

A porous vitroplast particle preserved in the early stage of conversion to liquid products during the Synthoil process (Sample C-19349, in reflected light, 870X).

the angular vitroplast component. Lastly, consideration of the inertinite fractions in the residues and their respective feed coals can give an indication of the relative conversion of these macerals. The ratio of these components in the residue to that in the feed coal, on a mineral and granular residue free basis, yields 1.2 and 1.5 for the SRC, 2.6 for the Synthoil, and 3.3 for the H-Coal samples. The higher values indicate higher fractions are left unconverted. Thus, these data suggest inertinites were somewhat less reactive in the H-Coal than in the other processes.

Further work on the behavior of the macerals during hydrogenation processes is needed to fully interpret these observations concerning the organic residue components.

SIZE ANALYSIS OF LIQUEFACTION RESIDUES

An attempt was made to perform size analysis by pipette on the low temperature ash of liquefaction residue samples, but meaningful results could not be obtained. The usefulness of size analysis results is questionable because the low temperature ash is not a good representation of the residue, which is a solid mass of organic and inorganic components (previous to low temperature ashing, other organics, the THF-solubles, are removed). During low temperature ashing, the organic portions of the granular residue would be oxidized causing the size of at least some of these particles to change.

BEHAVIOR AND INORGANIC ASSOCIATIONS OF SOME ELEMENTS IN COAL AND RESIDUE SAMPLES

The proceeding sections characterized the minerals present in the coals studied and their corresponding liquefaction residues. Behavior of elements during liquefaction and associations of elements with particular mineral species are the subjects of this section. Mineral associations are determined through integration of the mineralogical and chemical data from this study and incorporation of experimentally established associations from other studies. In addition to the discussion of inorganic elemental associations, this section will center on elemental and mineralogical variations in samples caused by differences in the chemical composition of the feed coals and differences in composition between feed coals and their corresponding residues due to the liquefaction process.

Mineralogical interpretations in this section were based on chemical data reported on the 500°C ash basis. As stated in the chemical portion of this report, the concentration of elements in the "A" fraction of the residues is equivalent to the concentration of elements in the "as received" residue samples. Therefore, data from the "as received" samples could be used in mineralogical interpretations.

A number of elements—Ca, Mg, Sr, Ba, Mn, and Na in lignite (C-19590) and Ca, Mg, Ba, and Sr in the Wyodak subbituminous coal (C-19711, C-20021)—are concentrated in the low rank coals and their corresponding residues. These elements occur in sulfate and carbonate minerals in the LTA of coals and residues. The elements are thought to be originally present in the organic fraction of the coal associated with carboxyl groups as exchangeable cations (Miller and Given, 1978). During the process of low temperature ashing, Ca from the organic fraction combines with organic sulfur to form calcium sulfates such as bassanite ($2CaSO_4 \cdot H_2O$) (Miller and Given, 1978). According to Miller and Given (1978) the other exchangeable elements Mg, Sr, Ba, Mn, and Na may also form sulfates or substitute for Ca in sulfate lattices, but only bassanite has been detected by X-ray diffraction in samples from this study. Miller and Given (1978) found sodium sulfates and calcium sulfates in low temperature ash of low rank coals. The sulfate compounds (thought to be formed as described above), in the low temperature ash of samples from this study, account for the high concentration of Ca, Mg, Sr, Mn, and Na reported in the 500°C ash of the low rank feed coals. The liquefaction residues of the low rank feed coals also show high concentration of the same elements. However, in the residues these elements occur in carbonate compounds identified by X-ray diffraction. Walker et al. (1977) and Stone et al. (1979) found that calcium carbonate was formed in reactor vessels during the liquefaction of low rank coals. Calcium, and probably also Mg, Sr, Ba, Mn, and Na which are bound to the carboxyl and sometimes to the phenolic groups (Stone et al., 1979) in the coal, form carbonates of which some remain in the reactor vessel as deposits and others lodge with the rest of the mineral matter in the residue. Stone et al. (1979) found a Na-Mg carbonate, eitelite, in reactor vessel mineral matter after the liquefaction of North Dakota lignite. The only carbonates detectable by X-ray diffraction in the residues of low rank coals studied here are calcite and ferroan-dolomite which account for a portion of the Ca, Mg, Fe, Sr, Ba, and Mn in the residues.

Another element whose behavior seems to be related to the formation of reactor solids in liquefaction reactor vessels is Ti. Titanium is seen to decrease by an average of 0.2 percent (Appendix E) from coal to residue in the following sample pairs: C-19702 - C-19703, C-19705 - C-19706, C-19708 - C-19709, C-19714 - C-19715, C-19141 - C-19142, C-19488 - C-19487, and C-19276 - C-19349. Reactor solids formation has been reported for all the coals represented by the above samples in the SRC-Alabama liquefaction plant (Walker et al., 1977, Wakeley et al., 1979) and in the SRC-Washington plant. Except for C-19276 - C-19349, all the above sample pairs are from the SRC process. Wakeley et al. (1979) found titanium oxide in reactor solids from Illinois No. 6 and Western Kentucky Nos. 9 and 14 coals, but not in reactor solids from Wyodak coal. Wyodak coal is the one SRC-Alabama coal-residue pair, C-19711 - C-19712, that shows no change in Ti concentration. The decrease in Ti seen in the sample pairs above probably is caused by the formation of titanium oxide in the reactors, which removes some of the Ti from the mineral matter that will be left as the residue. The Ti concentration in C-19711 - C-19712 is similar to the concentration in the other SRC sample pairs. The failure to lose Ti in this sample pair may be due to a difference in the way Ti is bound in the Wyodak coal. It is not known whether reactor solids form in the Synthoil process (C-19276 - C-19349).

Two elements whose concentrations correlate with the presence of filter-aid in residue samples are Si and Na. The 5 SRC-Alabama runs and the first two SRC-Washington runs used a filter-aid composed of diatomaceous earth and asbestos. X-ray diffraction analysis of the filter-aid material shows it is composed of crystobalite, SiO_2 (composition of the diatoms) and a mineral of the serpentine family, $Mg_3 (Si_2O_5) (OH)_4$ (asbestos). Sample pairs which show an increase in Si in the residue are C-19702 - C-19703, C-19705 - C-19706, C-19708 - C-19709, C-19711 - C-19712, C-19714 - C-19715, and C-19488 - C-19487. The residues of these pairs contain filter-aid. Sample pairs that show in increase in Na in the residue are C-19705 - C-19706, C-19708 - C-19709, C-19714 - C-19715, C-19141-C-19142, and C-19488 - C-19487. The residues of these sample pairs also contain filter-aid. Most of the sample pairs that contain filter-aid show an increase in both the Si and Na concentration in the residue. The increase in Si is undoubtedly due to the two silicate compounds that make up the filter-aid. The increase in Na is probably due to incorporation of Na into the crystobalite lattice. The structure of crystobalite permits the substitution of Si^{4+} by Al^{3+}, providing that alkali or alkali earth ions are incorporated to balance the charge. Sodium enters the crystobalite lattice in this capacity. When half the available voids in the crystobalite structure are filled in a regular manner by

Table 18. Primary minerals found in liquefaction samples and their common ionic substitutions and impurities.

Mineral	Common Substitutions and Impurities
Barite $BaSO_4$	Substitutions: Sr, Pb, Ca for Ba
Calcite $CaCO_3$	Substitutions: Mg, Fe^{2+}, Mn, Sr, Ba, Co, Ni, Zn for Ca
Feldspar $(K, Na)\ [AlSi_3O_8]$ and $Na[AlSi_3O_8]-Ca[Al_2Si_2O_8]$	Substitutions: Ba for K; Fe^{3+}, Ti for Al; Mg, Fe^{2+}, Sr, Mn for Ca. Impurities: Fe^{2+}
Illite $K_{1-1.5}Al_4[Si_{7-6.5}Al_{1-1.5}O_{20}](OH)_4$	Substitutions: octahedral: Fe^{3+}, Fe^{2+}, Mg, Ti, Ca interlayer: Na, Ca
Kaolinite $Al_4[Si_4O_{10}](OH)_8$	Substitutions: Fe, Mg, Ti for Al Impurities: Ca, Na, K
Quartz SiO_2	Substitutions: Al^{3+} for Si Impurities: Li, Na, Ti, Mg
Pyrite FeS_2	Substitutions: Ni, Co, Mn for Fe; Se for S Impurities: Cu, Pb, As, Zn, Ag, Ti, V, Th, Au
Pyrrhotite $Fe_{1-X}S$	Substitutions: Ni, Co, Mn, Cu for Fe
Sphalerite ZnS	Substitutions: Fe, Mn, Cd, Hg Impurities: In, Ga, Tl, Au, Ag

Note: From Palache et al. (1944), Frondel (1962), Deer et al. (1966), and Wedepohl et al. (1969, 1970, 1972, 1974, 1978).

Na and Al is substituted for half the Si atoms, the mineral carnegieite, $NaAlSiO_4$, is formed (Deer, Howie, and Zussman, 1966). The crystobalite in the filter-aid has much less substitution than this, but could account for the increase in Na noticed in the samples mentioned above.

The behavior of S and As is related to the behavior of pyrite during liquefaction. Both of these elements generally decrease in concentration from a coal to its corresponding residue. Chalcophilic elements other than As do not exhibit similar trends. As the pyrite dissociates to form pyrrhotite during liquefaction, some of the S and some As (probably substituting for Fe) (Gluskoter et al., 1977) are released. The sulfur and hydrogen from the reactor atmosphere form H_2S, and As in an undetermined state is carried off with the gases. Most of the iron remains with the mineral matter to form pyrrhotite. Chemical data (Appendix E) for the sample pair C-19714 - C-19715 show an exception to this statement, a significant loss of Fe that is not explainable.

The relatively high Zn concentration seen (Appendix E) in both coals from the Illinois No. 6 seam and their residues (C-19960 - C-19661, C-18903 - C-18941, C-19194 - C-19196, C-19916 - C-19917, C-19702 - C-19703, C-19705 - C-19706, and C-20014 - C-20015) is probably due to the mineral sphalerite present in some

Illinois coals Hatch et al., 1976).

As stated in the first part of this report, the concentrations of most elements in the liquefaction residue reflect the characteristics of the feed coals. Except for the instances mentioned above, generally the elements in the coal mineral matter remain in the residue mineral matter and, in most cases, in the same mineral species.

Table 18 shows the primary minerals found in liquefaction samples and the common ionic substitutions and impurities. The substitutions and impurities represent possible locations of elements in inorganic combination in the feed coals and residues. However, unless each species is isolated and analyzed, we cannot verify which substitutions and impurities are actually present in the minerals of the liquefaction samples. The substitutions and impurities listed are those most likely to occur. Many other elements can occur in each of these minerals in trace amounts. Frondel (1962) states that the following elements have been found in quartz in trace amounts: Mn, Rb, Cs, Ca, Ba, Pb, Ag, Sn, Cu, Zn, V, Cr, Zr, and U. However, the presence of these elements in quartz would not make a significant contribution to the amount reported for them in the entire coal or residue sample. In the same manner, the contribution of Ba from barite (several grains of which have been found by SEM in both coal and residue samples) is probably more important in accounting for the total concentration of Ba than is the concentration of Ba in calcite.

The expandable or mixed-layer clay minerals are not listed in Table 18. These clays "are not pure mineral types, but consist of interstratified units of different chemical composition" (Weaver and Pollard, 1973) and hence, have no one specific chemical formula. The expandable clay minerals are important as inorganic sites for many minor and trace elements. A few of the elements associated with clay minerals as interlayer cations or through adsorption are Na, Ca, Mg, Fe, Al, Ti, K, B, Cs, Ge, Hg, Rb, Sb, Se, and Sr.

Substitution and impurities in the common minerals probably do not account for all of the elements present in the mineral matter. Some elements present in very small concentrations may be present in separate mineral phases such as monazite (Ce, La, Th) PO_4. Monazite was found in coal from the Illinois No. 6 seam by scanning electron microscopy (R. B. Finkelman, personal communication). The broad definition "mineral matter in coal" includes all elements in coal that are considered inorganic (Gluskoter, 1975) and incorporates elements that were organically combined, but remain in the high or low temperature ash. These elements are minor and trace elements and many of them may form oxides when freed from organic combinations.

CONCLUSIONS

The following conclusions are drawn from the study of the mineral matter and petrography of feed coals and their corresponding residues from liquefaction processes.

1. The factors that affect the character of the mineral matter in liquefaction residues are (a) the parent coal, which influences the composition of reactor solids and the formation of inorganics from organically bound, exchangeable cations; (b) accumulation of reactor solids; and (c) use of filter-aid.

Aside from the changes caused by the above factors, liquefaction residues are similar in composition and morphology of mineral particles from process to process.

2. Most of the elements associated with the mineral matter in the coal are retained in the same mineral species in the residue because most of the minerals do not change with liquefaction.

3. The major changes in coal mineral composition that occur during liquefaction are the conversion of pyrite to pyrrhotite, formation of some metakaolinite from kaolinite, and the collapse of some expandable clay minerals.

4. The mobility of two of the most mobile elements, sulfur and arsenic, is related to the transformation of pyrite to pyrrhotite. Sulfur is released and arsenic is thought to be released from the pyrite when it dissociates during liquefaction.

5. The relative contents of the fusinite and other inertinite macerals in the feed coals and in the residues studied petrographically suggest these macerals were somewhat less reactive in the H-Coal than in the other processes.

6. Some vitrinite particles in the feed coal to the Synthoil process undergo conversion to liquid products by means of cylindrical pores, submicrometer in diameter, that form within the central part of the particles during early stages of the conversion.

TECHNOLOGY FOR RECOVERY OF METALS FROM NATURAL ORES

The history of mining and beneficiation technology shows that metals recovery begins with the highest grades of ores available in nature that need a minimum beneficiation effort. As production increases, the reserves of high grade ores are depleted. Utilization of poorer grade ores necessitates technological modifications, higher energy input, and greater costs.

Conventional methods of mineral beneficiation range from manual selection, grinding, sieving, heavy media separation, and floatation to thermal metallurgy. Chemical leaching and electrolytic separation are also used in some instances. Most conventional practices originated at a time when high grade ores were found readily. During the last one hundred years, natural resources have been progressively depleted and conventional beneficiation technology is often inadequate. Grades of some metal ores have already deteriorated to such an extent that in some instances present-day ores are comparable in grade to tailings of a half century ago.

Deteriorating grades of ore necessitate much finer grinding to liberate the minerals of interest; consequently, much higher energy input is required and costs increase. Chemical processes such as solvent extraction and hydrometallurgy are advanced techniques of wet mineral beneficiation involving less input of conventional energy but greater use of chemicals and organic substances such as fuel oil.

Chemical leaching processes can be applied for metal recovery from conventionally mined ores as well as for in-situ metal recovery. In-situ leaching is a step towards avoiding greater mining costs. Most methods, however, are restricted to poor grade "natural" ores. Natural ores in this context can be defined as the ones satisfying two basic conditions:

(a) The ore occurs in the earth's crust as a natural concentration of metal and is mined for the primary purpose of recovering metals.

(b) The metals in the ore appear as independent minerals as sulphides or oxides or other separate forms.

TECHNOLOGY FOR RECOVERY OF METALS FROM LIQUEFACTION RESIDUES

The aggregates analyzed in the course of this investigation can not be considered as natural ores. The analysis contained in the mineralogical section of this investigation suggests a major difference in the character of conventional ores and those of coal liquefaction residues. Only a few elements, such as zinc in sphalerite (Table 10, Mineralogical Section), appear as independent minerals comparable to natural ores. Table 18 (in the Mineralogical Section) shows that most other elements in the coal liquefaction residues do not appear as separate minerals but are present as atoms trapped as isomorphous substitution in other minerals. Mineralogically, therefore, the coal liquefaction residues differ completely from conventional ores. Conventional minerals beneficiation technology cannot, therefore, find application in metals recovery from coal liquefaction residues.

The earth's crust is rich in sources of valuable metals that appear as isomorphous substitutions for other elements in silicate minerals. Any common rock contains large amounts of metal atoms trapped in crystalline structures of silicates; therefore, they resemble the coal liquefaction residues in their basic mineralogical form. In other words, in the mineralogical category in which coal liquefaction residues would be placed, there is no scarcity of metal reserves, but the technology for their recovery is yet to be developed and appears to be a long way from any economic feasibility.

The recovery of metals from residues of coal liquefaction might have some advantages over that from common rock or clays. In processing these residues, the costs of mining bulk materials could be avoided and the problems and costs of disposing of bulk wastes could be minimized.

Considering the foregoing discussion on mineralogy and technology, the authors deem it necessary to state that the following economic analysis is an entirely hypothetical one intended to create current economic background information upon which economic feasibility of future technological developments could be measured.

STRUCTURE AND AIMS OF ECONOMIC ANALYSIS

A number of projections indicate that before the end of the century large quantities of coal will be used in the United States to produce synthetic fuels. The production of synthetic fuel will result in residues that are enriched in metals such as aluminum, zinc, and cobalt. To determine the metals and their concentrations in the liquefaction residue, 18 sets of liquefaction process residues from 6 separate processes were analyzed. The detailed procedures that were applied to determine the concentration and mode of occurrence of various elements in the residue have been discussed in earlier parts of this report. Because of the significant concentrations of various metals in residue, the recovery of these metals from residues could be of both economic and strategic significance. To establish the significance of various elements identified in the residue, with regard to future demand and dollar value, a list of metals that are or soon could attain great economic and strategic value was first prepared. To do this the available data for each metal relating to its demonstrated resources, current supply, imports, and projected demand to year 1985 and year 2000, were collected and analyzed. Increase in demand and availability criteria were considered and the metals were classified into three categories. These categories were later used to group metals into three principal classes of varying significance.

To interpret and evaluate the residue by-product metal concentration data, the "input-output" model approach was adopted and the available input data was calibrated to 1 million tons of coal input. The approach used is outlined in Figure 31.

The material called "residue" in this model contains large quantities of carbon material and cannot be designated as the "final" waste residue of the liquefaction process. However, this material did serve as the basis for analysis and will henceforth be called residue.

In analyzing the residues, carbon and some other elements, such as Hg and F, were left out of consideration because the final waste residue would most probably be depleted in these elements. The interpretation and evaluation of data was therefore limited to the remaining metallic and nonmetallic residue, which was given the name "synthetic ore" and is called ore hereafter.

The overall composition data on ore was used to determine the quantities of various metals that would result at various levels of coal input to the liquefaction process. The dollar values of those metals of economic and strategic importance were calculated on the basis of 1978 market prices. Because the recovery of by-product metals from residue would require a specialized technology, no attempt was made to estimate the costs that will be involved

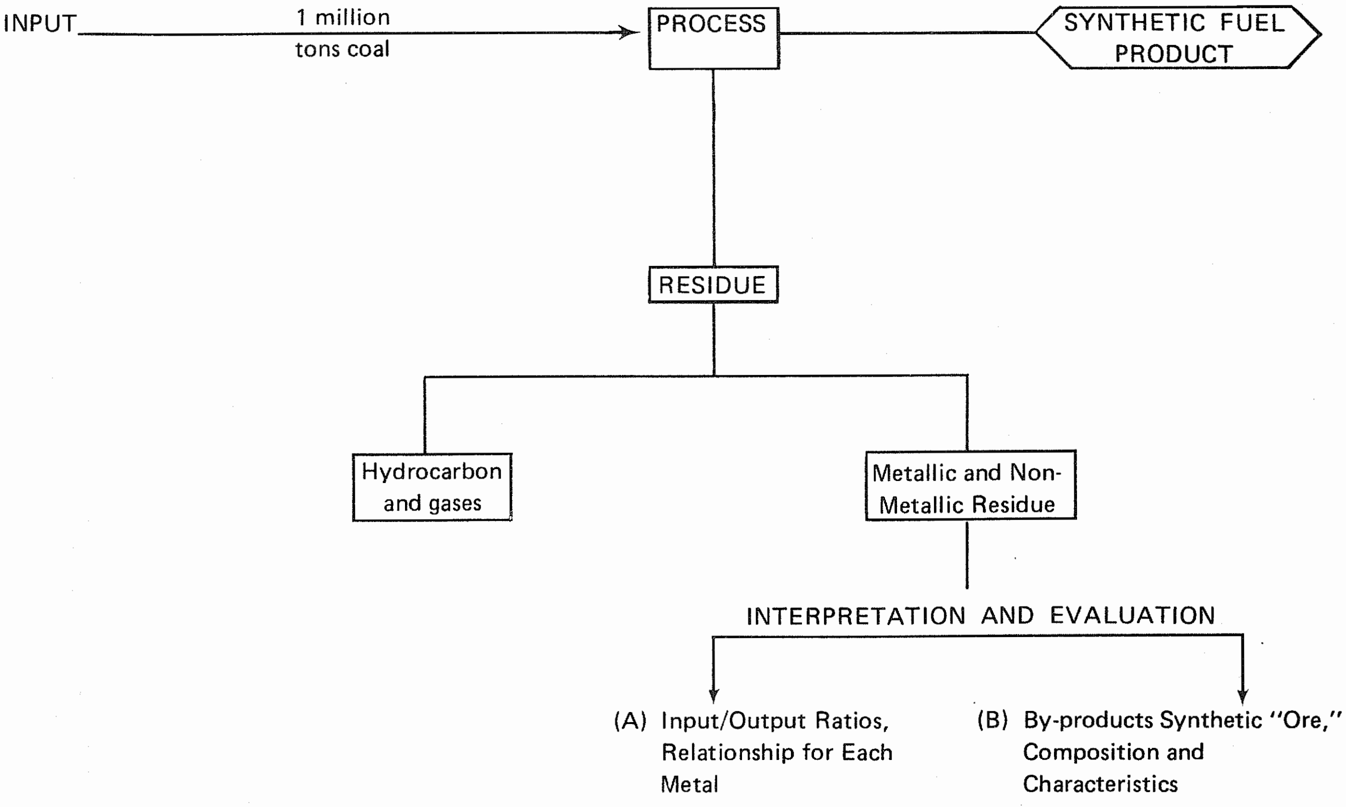


Figure 31 - Input-Output Model

in the recovery of identified metals in the residue. Also no attempt was made to determine the economic impact the recovery of by-product metals will have on the overall economics of a given liquefaction process.

ANALYSIS OF PROJECTED METAL DEMAND AND DETERMINATION OF METALS OF ECONOMIC VALUE

During the next two decades the economic value and strategic significance of many metals within the United States economy are likely to change considerably because of depletion of available sources of supply and/or rapid growth in the demand for metals. To determine the metals that are or will soon become of great economic interest, we collected and grouped available data under three categories.

Category A: Metals of Strategic Nature and Value

Each year the U.S. Bureau of Mines publishes data on amounts of metals that are imported into the United States. An analysis of these data indicates that the United States is dependent upon other countries for many metals. In certain cases the metal is imported from only one or two countries. In other cases, the supply comes from more than five nations, but because of unstable political situations in some governments there is always a possibility of a supply cutoff.

For this study all metals for which more than 25 percent of total 1974 domestic need was met through imports were assumed to be of strategic nature and thus of economic value.

Table 19 presents the data for metals imported by the United States in 1974 (USBM, 1975). More recent data were also examined, but because the change in the import pattern has been very slight, we continued to use 1974 data. Moreover, the data are more significant as they reflect a year of strong metal demand. By arranging the metals in order of decreasing percentages of imports, 41 elements were found to be imported from other nations in 1974; for 33 elements, more than 25 percent of the total United States need was met through imports. For six elements, the quantity of metal/element imported exceeded the total United States demand; in most of these six, stockpiling occurred at the consumer or governmental level. An examination of projected demand for the years 1985 and 2000, as published by the U.S. Bureau of Mines, indicates an increase in imports for some of these elements before the end of this century. In other words, the dependence of the United States on other nations for certain metals will increase further.

Included in the list of imports are those metals for which substantial quantities of reserves within the United States have been identified. In most cases, however, extraction of these metals involves higher costs than import prices, and importing them is currently more economical than mining domestic reserves.

Table 19. U.S. metal imports in 1974

Element	Unit of Measure	Demand 1974	Net imports 1974	Percent imported
Pd	10^3 troy oz.	673	1,108	>100.0
Hf	tons	33	40	>100.0
Sr	tons	17,500	22,000	>100.0
Pt	10^3 troy oz.	848	1,065	>100.0
Ni	10^3 tons	193.6	216.3	>100.0
Sb	tons	20,323	21,278	>100.0
I	10^3 lbs.	7,500	7,323	97.6
Hg	76 lb.flasks	53,539	51,636	96.4
Th	tons	80	72	90.0
Al	10^3 tons	6,222	5,432	87.3
F	10^3 tons	689	598	86.8
Tl	lbs.	1,850	1,346	72.8
Cr	10^3 tons	560	398	71.1
Sn	L. tons	45,845	31,187	68.0
Bi	10^3 lbs.	2,365	1,564	66.1
W	10^3 lbs.	15,548	9,909	63.7
Co	10^3 lbs.	23,183	14,530	62.7
Ta	10^3 lbs.	1,960	1,196	61.0
Ag	10^3 troy oz.	122,900	73,900	60.1
In	10^3 troy oz.	825	493+	59.8
Mn	10^3 tons	1,492	855	57.3
Cd	tons	6,187	3,358	54.3
Zn	10^3 tons	1,464	778	53.1
Te	10^3 lbs.	324	164	50.6
Ge	10^3 lbs.	44	22	50.0
Ti	10^3 tons	588	268	45.6
Au	10^3 troy oz.	3,930	1,752	44.6
Se	10^3 lbs.	1,566	671	42.8
Ba	10^3 tons	931	374	40.2
Sc	Kg	5	2	40.0
As	tons	24,190	9,490	39.2
Fe	10^6 tons	90.8	32	35.2
V	tons	8,453	2,291	27.1
Cu	10^3 tons	1,953	421	21.6
Br	10^6 lbs.	362.77	69.32	19.1
Zr	10^3 tons(1973)	72	11.711	16.3
Si	10^3 tons	686	92	13.4
Pb	10^3 tons	931	56	6.0
Mg	10^3 tons	1,142	25	2.2
N(fixed)	10^3 tons	12,869	106	0.8
Cl	10^3 tons	10,944	57	0.5
H	10^9 std.ft.^{3}	2,570	0-	0
N(elem)	10^3 tons	8,825	0	0
O	10^3 tons	16,127	0	0
Rb	lbs.	1,210	0	0
U	tons	8,000	0	0
S	10^3 L.tons	10,880	-451	0
B	10^3 tons	105	-88	0
Be	tons	209	-11	0
Li	tons	4,530	-950	0
Mo	10^3 lbs.	76,417	-81,647	0

Source: USBM (1975)

The 33 elements for which more than 25 percent of the total United States need was met through imports in 1974 are: Pd, Hf, Pt, Ni, Sb, I, Hg, Th, Al, F, Sr, Tl, Cr, Sn, Bi, W, Co, Ta, Ag, In, Mn, Cd, Zn, Te, Ge, Ti, Au, Se, Ba, Sc, As, Fe, and V. A comparison of this list with elements found in coal liquefaction residues (Appendix E) shows that, except for I, Hg, F, Te and Se, all the elements are present in the coal liquefaction residues in detectable concentrations.

Category B: Metals with Rapidly Growing Demand

In 1974 the U.S. Bureau of Mines published projections for metal demand for the year 2000 (USBM, 1975). These data show that there are 30 elements for which the demand by the year 2000 would more than double (Table 20). The demand for two elements—thorium and cesium—is projected to increase by more than 1000 percent. The demand for four others, uranium, hydrogen, beryllium and gallium, is projected to increase more than 200 percent between 1974 and 2000. The other elements with a projected increase in demand of more than 100 percent include: V, Au, O, Cl, Sc, Al, B, Li, W, Zr, Br, F, Mg, Mo, Sb, Hf, Ti, I, Ta,

Table 20. Projected change in U.S. metal demand to 2000

Element	Demand 1974	Projected demand 2000	Percent change	100% or more
Th	80 tons	1,100	1275.0	X
Cs	15,071 Lb.	200,000	1227.0	X
U	8,000 tons	69,500	768.8	X
H	2,570 billion std. ft.^{3}	14,450	462.3	X
Be	209 tons	1,150	450.2	X
Ga	6,941 Kg.	32,000	361.0	X
V	8,453 tons	33,000	290.4	X
Au	3,930 thous. troy oz.	15,300	289.3	X
O	16,127 thous. tons	62,000	384.4	X
Cl	10,944 thous. tons	39,500	260.9	X
Sc	5 Kg	17	240.0	X
Al	6,222 thous. tons	29,960	236.9	X
B	105 thous. tons	340	223.8	X
Li	4,530 tons	14,400	217.9	X
W	15,548 thous. Lb.	49,400	217.7	X
Zr	72,000 tons (1973)	222,000	208.3	X
Br	363 million Lb.	1,110	205.8	X
F	689 thous. tons	1,940	181.6	X
Mg	1,142 thous. tons	2,915	155.3	X
Mo	76,417 thous. Lb	193,000	152.6	X
Sb	20,323 tons	49,500	143.6	X
Hf	33 tons	80	142.4	X
Ti	588 thous. tons	1,425	142.3	X
I	7,500 thous. Lb	18,000	140.0	X
Ta	1,960 thous. Lb	4,600	134.7	X
N(fixed)	12,869 thous. tons	29,000	125.3	X
Cu	1,953 thous. tons	4,200	115.0	X
S	10,880 thous. L. tons	23,000	111.4	X
Zn	1,464 thous. tons	3,050	108.3	X
Cd	6,187 tons	12,700	105.3	X
N(elem)	8,825 thous. tons	18,000	104.0	X
Pd	673 thous. troy oz.	1,340	99.1	
Ni	193.6 thous. tons	385	98.9	
Sr	17,500 tons	34,700	98.3	
Cr	560 thous. tons	1,100	96.4	
Se	1,566 thous. Lb.	3,020	92.8	
Bi	2,365 thous. Lb	4,500	90.3	
Ag	122,900 thous. troy oz.	230,000	87.1	
Co	23,183 thous. Lb	43,000	85.5	
In	825 thous. troy oz.	1,520	84.2	
Ge	44 thous. Lb	81	84.1	
Si	686 thous. tons	1,200	74.9	
Ba	931 thous. tons	1,585	70.2	
Pb	931 thous. tons	1,530	64.3	
Te	324 thous. Lb	510	57.4	
Rb	1,210 Lb	3,000	47.9	
Pt	848 thous. troy oz.	1,225	44.4	
Mn	1,492 thous. tons	2,130	42.8	
Fe	90.8 million tons	129	42.1	
Sn	45,845 L. tons	64,000	39.6	
As	24,190 tons	26,200	8.3	
Hg	53.539 thous. fl.	47	-12.2	
Tl	1,850 Lb	1,400	-24.3	

Source: USBM (1975)

Table 21. Ratio of reserves to demand*

Element	Demand 1974	Demand 1985	Demand 2000
Co	0	0	0
Mn	0	0	0
Rb	0	0	0
Sn	0	0	0
Sr	0	0	0
Ta	0	0	0
Ni	1	0	0
Al	2	0	0
F	4	2	2
Cr	4	3	2
Sb	5	3	2
Mg	9	6	3
U	33	7	4
W	15	9	5
Bi	11	6	6
V	23	13	6
Ag	12	8	7
In	12	10	7
Au	31	13	8
Hg	8	8	10
S	21	16	10
Ge	20	15	11
Cd	29	21	14
Zn	62	24	16
Cu	46	33	21
Ba	38	25	22
Ti	54	35	22
Li	72	47	23
Be	134	43	24
Se	49	46	25
Zr	83 (1973)	50	27
I	71	50	29
As	33	32	31
Fe	44	37	31
Mo	79	59	31
Ga	144	105	31
Te	56	49	35
Pb	63	49	39
B	190	108	59
Tl	81	107	107
Th	1,750	933	127
Sc	45,600	17,538	13,412

*Ratio of reserves to demand is based on recoverable reserves and demand for the metal concerned in the year of consideration. This ratio is expressed in years.

N, Cu, S, Zn, and Cd. If supply is to meet demand, development of available domestic resources is necessary. The United States must keep its imports to a minimum.

Category C: Metals Lacking Sufficient Domestic Reserves to Meet Projected Demand

The U.S. Bureau of Mines published reports listing for each metal the quantity of reserves that could be considered economically minable using available technology (USBM, 1975). Because development of any major mineral deposit requires a minimum of 20 years of supply, the demonstrated reserves to demand ratio below 20:1 should be viewed as an indication of possible supply shortages.

An examination of 1974 demand data (Table 21) shows that for 13 elements—cobalt, manganese, rubidium, tin, strontium, tantalum, nickel, aluminum, iron, chromium, antimony, magnesium, and mercury—the economically minable reserves would not last more than 10 years at current demand (USBM, 1975). By 1985 uranium, tungsten, bismuth, silver, and indium will join the list. Our analysis shows that if the projected demand for the year 2000 materializes and the reserves added to the economic base are depleted between now and the year 2000, the list of elements with less than 10 years reserves to demand ratio would be extended to 20 by the addition of vanadium and gold.

By applying the reserves to demand ratio criterion of 20:1, four more elements—germanium, cadmium, zinc, and sulfur—are added to the list of scarce elements in the year 2000. In 2000, 20 out of 24 scarce elements would have reserves for less than 10 more years. Domestic reserves of 6 elements were already completely depleted in 1974. On the other hand, alternate sources of sulfur will most likely be developed by the year 2000, e.g. from flue gas desulfurization in electricity generation plants.

Because each of the categories described above has an economic significance of its own, and there are certain elements that are common to two or more categories, the elements were ranked in order of economic priority by further subdividing the identified elements into three classes:

Class I includes elements which fall under all three categories and thus constitutes elements of most economic and strategic value.

Class II includes elements which are common to the Category A and Category C, i.e. metals of strategic nature having more than 25 percent of 1974 demand met through imports and metals for which the United States lacks sufficient reserves to meet demand. These elements basically represent metals of greatest strategic significance.

Class III includes elements which are common to Category B (metals with rapidly growing demand) and to the Category C (metals for which the United States lacks sufficient reserves to meet demand). This class basically represents metals of economic significance but could soon become a strategic value.

Class I—Elements with both economic and strategic significance

Nine elements, Al, Zn, Cd, F, Sb, Ta, W, Au, and V, fall under the three categories described above and are thus classified as elements of most economic and strategic value (Table 22). Because fluorine was found to be significantly depleted in the final residues, it was excluded from further economic analysis.

An examination of projected demand for the other eight elements shows that for Al, W, V, and Au, the demand may increase by more than 200 percent over the next two decades. More than 60 percent of the total aluminum and tungsten currently used in the United States is obtained from other nations: the projected reserves to demand ratio for year 2000 shows that sufficient reserves will not be available in the United States to meet projected needs of aluminum. Also, reserves of tungsten will only be enough to meet demand for 5 years. To meet its future needs for these two metals, the United States will either have to increase its dependence on other nations or will have to look for other domestic sources of supplies.

Table 22. Classification of elements under 3 classes of strategic and economic values.

Elements/Class	Category I Imports > 25 %	Category II Rapid Demand Growth %△1974-2000	Category III Insufficient Reserves
Class I			
Al	87.2	236.9	0
F	86.8	181.6	2
W	62.7	217.7	5
Ta	61.0	134.7	0
Cd	54.3	105.3	14
Zn	53.1	108.3	16
Au	44.6	289.3	8
V	27.1	290.4	6
Sb	>100.0	143.6	2
Class II			
Ni	>100.0	98.9	0
Hg	96.4	-12.2	10
Cr	71.1	96.4	2
Sn	68.0	39.6	0
Bi	66.1	90.3	6
Co	62.7	85.5	0
Ag	60.1	87.1	7
In	59.8	84.2	7
Mn	57.3	42.8	0
Ge	50.0	84.1	11
Class III			
Mg	2.2	155.3	3
U	0	768.8	4
S	0	111.4	10

For vanadium and gold, 27.1 percent and 44.6 percent of the total 1974 demand was met through imports. The demonstrated reserves data show that by 2000 the nation's available reserves of vanadium and gold will be considerably depleted. It is very likely that, for these two metals, dependence of the United States on other nations may further increase,

For Sb, Ta, Zn, and Cd, the demand to the year 2000 is projected to increase by 143, 134, 108 and 105 percent, respectively. Reserves of tantalum were completely depleted in 1974 and will remain so to the year 2000. The available reserves of antimony will not be sufficient to meet the projected demand in the year 2000 for more than 2 years. Currently more than 50 percent of the total amount used for each of these elements is imported. The nation may have to depend upon other sources of supplies to meet its needs.

Class II—Elements of strategic significance

Ten elements, Ni, Hg, Cr, Sn, Bi, Co, Ag, In, Mn, and Ge, are common to Category A and Category C and are therefore of strategic significance (Table 22). Reserves of Ni, Sn, Co, and Mn would be completely depleted by the year 2000. For the other six metals the available reserves would not in general last more than a decade.

An examination of metals included in Class I and Class II show that one of the reasons why we are so dependent upon other nations for these materials is the limited availability of economically minable resources in the United States. For Cd, Zn, Hg, and Ge, we will have minable reserves lasting a decade or more but in most cases it is far more economical to buy the metal than to produce it.

For these 10 metals, the demand is projected to increase less than 100 percent over the next two decades. Environmental restrictions and efforts to substitute other materials for mercury might actually cause a decrease in its demand. We could expect the nation's dependence on imports of Class II metals to grow somewhat slower than that for elements listed under Class I. However, if there is a rapid growth in demand for any of these metals, the metal would fall under Class I and thus could be viewed as both economic and of strategic value.

Class III—Elements of economic value and significance

Included in Class III are three elements, Mg, U, and S, which are of economic significance, i.e. the demand is projected to more than double over the next two decades, and reserves may not last more than 20 years. It is likely the nation will have to depend upon other countries to meet its needs unless additional reserves are found. Because the reserves for all the three elements identified under Class III could be obtained from secondary sources, we do not anticipate any major problems in the supply of these elements.

In summary an analysis of available data suggests there are 19 elements that should be considered of economic and strategic value—Al, F, W, Ta, Cd, Zn, Au, V, Sb, Ni, Hg, Cr, Sn, Bi, Co, Ag, In, Mn, and Ge.

INTERPRETATION OF DATA ON METAL CONCENTRATIONS IN RESIDUE BY-PRODUCTS

The residue samples obtained from 18 sets of liquefaction process runs were quantitatively analyzed for the presence of 71 elements. The data were normalized to 1 million tons of coal input. The difference between the sum of 71 elements and the 1 million tons coal input was accounted for by the oxygen in coal.

Table 23. Process details

				"Intermediate" Residue Characteristics				Input-Output Relationships		
Process Run	Coal Type	Pressure PSI	Temp	Input (thousand tons)	Hydrocarbon and gases (thousand tons)	Metallic (thousand tons)	Total (Oxygen-Free) (thousand tons)	Residue % total input	Metallic % total residue	Residue conversion factor
Clean coke	Ill #6	3,000	455°	1,000	720	58	770	77.0	7.5	0.84
H-coal^{1}	Ill #6	2,700	455°	1,000	530	53	580	58.0	9.1	0.64
H-coal^{2}	Ill #6	2,700	455°	1,000	570	56	620	62.0	9.0	0.70
H-coal^{3}	Ill #6	2,700	455°	1,000	290	55	350	35.0	15.7	0.40
H-coal^{4}	Wyodak	2,800	449°	1,000	300	42	340	34.0	12.3	0.43
Lignite	N. Dakota	2,500	455°	1,000	170	40	210	21.0	19.0	0.25
SRC-Ala^{1}	Ill #6	2,400	457°	1,000	60	51	110	11.0	46.4	0.16
SRC-Ala^{2}	Ill #6	1,700	440°	1,000	140	51	190	19.0	26.9	0.25
SRC-Ala^{3}	W. Ky 9&14	1,650	454°	1,000	88	47	140	14.0	33.6	0.18
SRC-Ala^{4}	Wyodak	2,400	457°	1,000	140	34	170	17.0	20.0	0.22
SRC-Ala^{5}	Pittsburgh #8	1,700	457°	1,000	64	40	100	10.0	40.0	0.15
SRC-Wash^{1}	W. Ky 9&14	1,545	449°	1,000	71	63	130	13.0	48.5	0.18
SRC-Wash^{2}	W. Ky 9&14	1,500	449°	1,000	72	70	140	14.0	50.0	0.19
SRC-Wash^{3}	W. Ky 9&14	1,920	460°	1,000	110	17	120	12.0	14.2	0.14
SRC-Wash^{4}	Ill #6	1,883	456°	1,000	65	12	77	7.7	15.6	0.09
SRC-Wash^{5}	Pittsburgh	2,012	447°	1,000	160	26	180	18.0	14.4	0.21
SRC-Wash^{6}	Pittsburgh	2,007	447°	1,000	160	25	180	18.0	13.9	0.21
Synthoil	W. Ky 9&14	4,000	450°	1,000	68	29	97	9.7	29.9	0.12

As shown in Table 23, the 71 elements formed an *intermediate residue* (hereafter called *residue*) of between 77,000 and 770,000 tons depending upon the type of process or coal used. The residue contained large amounts of carbon, hydrogen, nitrogen, sulfur, and other volatile elements such as Br, Cl, F, Hg, I, Se, and Te.

The *metallic residue*, which is the subject of this economic analysis, was calculated by subtracting the above 11 elements from the residue. The metallic residue served as the *hypothetical ore* and ranged in quantities from about 12,000 tons for the SRC-Wash^{4} run to about 63,000 tons for the SRC-Wash^{1} run. Between 7.5 and 50 percent of the residue, or between 1.2 and 7 percent of the coal input, thus ended up in the hypothetical ore.

Table 24 lists the elements that constitute essentially the *metallic* portion of the residual material (excluding O, S, H, C, etc.). Also given in Table 24 is the tonnage of total metallic residue. Eight elements, Si, Fe, Al, Ca, K, Na, Mg, and Ti, account for 94 to 99 percent of the total metallic material. Aluminum as a percentage of the total metallic material ranges from as low as 11 percent for the lignite run to as high as 22 percent for the H-Coal^{4} run. Similarly the titanium concentration ranges from 0.43 to 1.6 percent of the total metallic material. This variation in metallic concentration is dependent on the coal type and the process used to produce the synthetic fuel.

Table 24. List of elements constituting the metallic material in the residue* and their respective concentrations.

Symbol of Element							PROCESS RUN	
	Clean Coke	H-Coal^1	H-Coal^2	H-Coal^3	H-Coal^4	Lignite	SRC-Ala^1	SRC-Ala^2	SRC-Ala^3
Al	19	18	18	17	22	11	15	15	17
Ca	10	8.9	8.4	9.4	29	33	5.3	7.9	2.7
Fe	21	25	23	29	11	14	26	18	27
K	3.3	2.8	2.9	2.3	.58	.33	2.6	2.2	2.9
Mg	.86	1.2	.27	.51	6.5	8.1	1.1	.94	1.1
Na	1.3	.57	.62	.54	.94	7.1	.16	1.3	1.1
Si	43	42	45	40	26	21	47	53	46
Ti	1.0	1.0	1.1	1.0	1.6	.43	.69	.94	.63
Subtotal	99.46	99.47	99.29	99.75	97.62	94.96	97.85	99.28	98.43
P	.13	.07	.062	.008	--	.58	.35	.002	.11
Ag	.00019	.000072	.00018	.00020	.0011	.00020	.00020	.0002	.0001
As	.003	.003	.0048	.0034	.0039	.017	.0026	.0033	.0072
Au	.0000093	.000068	--	.000072	.0000024	.0000013	.000028	.000019	.000059
B	.14	.27	.37	.23	.13	.19	.16	.12	.069
Ba	.26	.09	.10	.083	.81	2.4	.12	.12	.099
Be	.001	.0016	.0013	.0013	.00077	.00075	.0020	.011	.00071
Bi	.00023	.00097	.0011	.00072	.0010	.00025	.00026	.00098	.0011
Cd	.00038	.0007	.00051	.00038	.001	.00040	.00063	.00039	.00036
Ce	.018	.018	.021	.020	.039	.015	.017	.016	.023
Co	.005	.013	.0062	.0067	.013	.003	.0057	.0045	.0063
Cr	.03	.032	.029	.029	.020	.0078	.050	.031	.032
Cs	.002	.0019	.0029	.0023	.00081	.0025	.0020	.0014	.0019
Cu	.015	.015	.015	.016	.043	.0086	.024	.018	.016
Dy	.0014	.0018	.0015	.0018	.0029	.00058	.0013	.0016	.0016
Zr	.039	.036	.048	.040	.075	.028	.031	.041	.046
Total** 1000 tons	58.3	52.8	56.0	55.3	41.6	39.6	50.9	50.9	47.5

Symbol of Element	SRC-Ala^4	SRC-Ala^5	SRC-Wash^1	SRC-Wash^2	SRC-Wash^3	SRC-Wash^4	SRC-Wash^5	SRC-Wash^6	Synthoil
Al	17	16	20	16	20	19	19	19	19
Ca	23	5.4	1.1	2.8	5.5	7.9	8.9	9.1	6.2
Fe	4.9	11	45	36	26	24	27	26	38
K	0.81	1.6	2.5	2.4	3.1	2.7	2.1	2.1	2.0
Mg	4.4	1.4	.23	.33	.24	.28	.66	.24	.012
Na	1.7	3.7	.45	.93	.35	.97	1.2	1.1	.27
Si	44	60	28	40	43	43	39	39	34
Ti	1.4	.67	.70	.54	1.2	1.1	1.1	1.1	.82
Subtotal	97.21	99.77	97.98	99.00	99.39	98.95	98.96	97.64	99.30
P	1.5	.23	.25	.24	.05	.22	.50	.43	.082
Ag	.0002	.0002	.000075	.00014	.00019	.0011	.0011	.0011	.00013
As	.0019	.0032	.031	.019	.012	.0028	.011	.013	.0030
Au	.000069	.000015	.00004	.000024	.0000057	.0000015	.00000014	.00000047	.000019
B	.090	.089	.070	.044	.20	.28	.14	.20	.082
Ba	.96	.18	.081	.075	.092	.10	.17	.17	.17
Be	.00032	.00038	.0025	.0016	.0016	.0011	.00089	.00090	.0011
Bi	.0012	.0011	.0011	.00082	.00080	.00073	.00081	.00083	.00082
Cd	.00037	.00037	.00067	.00044	.00039	.00089	.00089	.00099	.00045
Ce	.021	.014	.039	.034	.024	.026	.027	.021	.019
Co	.002	.0032	.012	.012	.0063	.0064	.0054	.0047	.0058
Cr	.023	.023	.040	.040	.032	.047	.029	.024	.033
Cs	.0009	.0012	.0011	.0017	.0026	.0024	.0019	.0017	.0014
Cu	.021	.0097	.041	.033	.016	.016	.019	.017	.015
Dy	.0012	.0011	.002	.00078	.0021	.0014	.0013	.0014	.0012
Zr	.019	.032	.025	.048	.055	.051	.066	.047	.048
Total** 1000 tons	34.4	40.1	63.9	69.7	17.4	12.4	25.8	25.3	29.1

* Residue is calculated on an oxygen-free basis after deducting carbon, hydrogen, nitrogen, etc. from the analyzed intermediate products of liquefaction processes.

** This now gives the tonnage (1000 tons) of "Ore" obtained from 1 million tons coal input (see also Table 23)

Table 25. Expected demand for class I metals in A.D. 2000, ratio of reserves to demand and hypothetical reserves from coal liquefaction residues (scenarios).

Metal	Demand in 2000	Ratio Reserves to Demand in 2000	Range of Hypothetical Reserves from Coal Liquefaction Residues Depending upon System and Coal Used. and Amount of Coal Input for Liquefaction per year (million tons per year)				
			1	3	10	30	50
Al	29,960,000 (ton)	0	2,280-12,600	6,840-37,800	-Tons- 22,800-126,000	68,400-336,000	114,000-630,000
Zn	3,050,000 (ton)	16	1.20-69.60	3.60-208.8	12.00-696.00	36.00-2,088.00	60.00-3,480.00
Cd	12,700 (ton)	14	0.07-0.42	0.12-1.27	0.66-4.22	1.99-12.66	3.32-21.11
Sb	49,500 (ton)	2	0.10-1.96	0.30-5.88	1.00-19.60	2.96-58.80	4.93-98.00
Ta	2,300 (ton)	0	0.03-0.16	0.10-0.48	0.32-1.60	0.97-4.79	1.62-7.98
W	24,700 (ton)	5	0.12-3.24	0.35-9.72	1.16-32.4	3.49-97.20	5.82-162.00
V	33,000 (ton)	6	6.40-43.40	19.20-130.20	64.00-434.00	192.00-1,302.00	320.00-2,170.00
Au	15,300,000 (oz.)	8	0-1,280 (oz)	0-3,840 (oz)	0-12,800 (oz)	0-38,400 (oz)	0-64,000 (oz)

To determine the quantity of each element produced or to determine the hypothetical reserves base for each element under a given process for a given level of output, a simple computer program was developed. With the help of this program, the quantity of each element that would result under the 18 different process runs at 8 different levels of inputs was determined and is listed in Table 25. As an example, the data show that for an input of 50 million tons of coal the available aluminum resources base could vary from 114,000 tons to 630,000 tons.

ESTIMATE OF ECONOMIC VALUE OF BY-PRODUCT METALS IN THE LIQUEFACTION RESIDUE OF COAL

On the basis of projected future demand, the supply, and the development of reserves, metals were classified according to their strategic and economic significance.

Under Class I, nine elements, Al, Zn, Cd, Sb, Ta, W, V, Au, and F, satisfied the criteria of strategic and economic importance. Of these, the F determined in these intermediate residues was considered to be not available in final waste residues and was excluded from the economic evaluation. The data in Table 25 suggest that even at 50 million tons of coal input, the amount of metal that could possibly be obtained from liquefaction residues will not be sufficient to fulfill projected demand. However, the amounts of metals could be large enough for recovery to be economically attractive and strategically important.

The maximum and minimum amounts of metals in the residue from an input of 50 million tons of coal as percentages of demand in year 2000 are presented in Table 26. As shown in the first two columns of the table, the available amounts of metals could satisfy about 7 percent of the demand for vanadium. On the other hand, gold may not be available at all. The availability of aluminum would be between 0.4 and 2.1 percent of demand in year 2000.

Table 26 also presents the total value of each metal at 1978 and 1974 prices. In dollar value aluminum and vanadium are the most valuable metals

Table 26. Minimum and maximum hypothetical reserves and total value in 1978 and 1974 for class I metals.

Metal	Reserves as percent of demand in 2000 at 50 million tons/year coal input		Total value in 1978 dollars at 1978 prices		Total value in 1974 dollars at 1974 prices	
	Minimum Hypothetical	Maximum Hypothetical	Minimum	Maximum	Minimum	Maximum
Al	0.38	2.10	120,840,000	667,800,000	77,520,000	428,400,000
Zn	0.002	0.10	41,268	2,393,544	43,140	2,502,120
Cd	0.03	0.17	16,268	103,439	27,158	172,680
Sb	0.01	0.20	17,452	346,920	17,922	354,290
Ta	0.07	0.35	89,100	438,900	45,781	225,515
W	0.02	0.66	113,723	3,165,480	55,523	1,545,480
V	0.97	6.58	3,315,200	22,481,200	2,419,200	16,405,200
Au	0	0.42	0	11,776,000	0	10,223,360
TOTAL			124,433,011	708,505,483	80,128,724	459,828,645

available; 1978 values range between $120 million and $668 million for aluminum and between $3.3 million and $22.5 million for vanadium. Gold with a maximum $11.8 million value follows as the third most valuable residue metal of the class.

The eight elements of Class I represent a total value of $124.5 million at the minimum level and $708.5 million at the maximum level. In other words, at 50 million tons coal input, the available metallic residue could assign a credit value of $2.50 to $14.20 per ton of coal.

Ten elements of strategic significance, Ni, Hg, Cr, Sn, Bi, Co, Ag, In, Mn, and Ge, were listed under Class II. Because Hg was included in the group of elements thought to be partially or completely volatilized in the final residual material, no economic value was assigned to it. The concentrations of these elements were very low (generally <1 ppm). The data in Table 27 show that no reserves of Co, Mn, Ni, and Sn are projected to be available in the year 2000 and that the reserves of other elements would only be meager.

Table 27. Expected demand for class II metals in 2000, ratio reserves to demand and hypothetical reserves from coal liquefaction residues (scenarios).

Metal	Demand in 2000	Ratio Reserves to Demand in 2000	Range of Hypothetical Reserves (tons) from Coal Liquefaction Residues Depending upon System and Coal Used and Amount of Coal Input (million tons per year) for Liquefaction				
			1	3	10	30	50
Bi	2,250 (tons)	6	0.088-0.693	0.263-2.079	0.876-6.930	2.628-20.79	4.38-34.65
Cr	1,100,000 (tons)	2	3.12-38.00	9.36-84.00	31.20-280.00	93.60-840.00	156.00-1,400
Co	21,500 (tons)	0	0.68-8.40	2.04-25.20	6.80-84.00	20.40-252.00	34.00-420.00
Ge	41 (tons)	11	0.218-4.914	0.653-14.742	2.176-49.14	6.528-147.42	10.88-245.70
In	1,520,000 (troy oz)	7	0.00-5,632*	0.00-16,928*	0.00-56,448*	0.00-169,344*	0.00-282,240*
Mn	2,130,000 (tons)	0	9.24-56.1	27.72-168.3	92.4-561.0	277.2-1,683	462.0-2,805
Ni	385,000 (tons)	0	0.935-29.40	2.805-88.2	9.35-294.0	28.05-882.0	46.75-1,470
Ag	230,000,000 (troy oz)	7	1,024-14,784*	3,104-44,352*	10,336-147,840*	31,008-443,520*	51,680-739,200*
Sn	71,700 (tons)	0	0.42-2.016	1.26-6.048	4.2-20.16	12.6-60.48	21.0-100.8

*Troy oz

Table 28. Minimum and maximum hypothetical reserves and total value in 1978 and 1974 for class II metals.

	Reserves as percent of demand in 2000 at 50 million tons/year coal input		Total value in 1978 dollars at 1978 prices		Total value in 1974 dollars at 1974 prices	
Metal	Minimum Hypothetical	Maximum Hypothetical	Minimum	Maximum	Minimum	Maximum
Bi	0.19	1.54	29,959	237,000	73,672	582,813
Cr	0.01	0.13	65,988	590,000	33,072	296,800
Co	0.16	1.95	435,200	5,376,000	235,280	2,906,400
Ge	26.5	600.00	3,438,080	77,740,000	2,894,080	65,454,480
In	0	18.6	--	2,385,000	--	1,247,500
Mn	0.02	0.13	670	174,000	416	107,993
Ni	0.01	0.38	205,700	6,468,000	162,690	5,115,500
Ag	0.02	0.32	274,938	3,933,000	243,413	3,481,632
Sn	0.03	0.14	224,532	1,079,000	166,433	798,940
TOTAL			4,675,067	97,982,000	3,809,056	79,992,058

An examination of the amount of these metals in liquefaction residue materials at different levels of coal input show that, at the 50 million tons of coal level, the quantity of metals available in the residue will be large enough to be possibly of economic interest.

For example, the processing of 50 million tons of coal could result in 11 to 246 tons of Ge in the residue material. Since in year 2000 only about 41 tons of Ge is projected to be needed to meet the demand, the recovery of this metal could result in quantities far exceeding the total demand (Table 28). Similarly, processing of a given type of coal could result in up to 282,240 troy ounces of indium in the residue, and its recovery could account for more than 18 percent of the total projected demand in year 2000. For the recovery of Cr, Mn, Ni, Ag, and Sn, the available residues may not be of much significance.

To establish the economic value of metals present in the residue material, the 1978 published average price for each metal was used (USBM, 1979, 1977, 1978). In terms of economic value, the germanium in the coal residue could be assigned a value of $3.5 million to $77.7 million. Even though no large quantities of Co, Ni, and Ag have been identified in the residues, the assigned economic value for each of these metals ranges between $4 million to $6 million. This suggests that the recovery of these metals could be of economic as well as of strategic significance.

The total estimated value of the identified nine metals at 1978 prices could range between $4.7 million and $98.0 million and could be credited with $0.1 to $1.95 per ton of coal input.

Recovery of Class I and II elements could therefore represent an economic value between $129.2 million and $806.5 million. Because this calculation assumes at least 50 million tons of coal liquefaction, the presence of these 17 metals alone could account for an economic value ranging between $2.50 and $16.10 per ton of coal input. Any increase in price of these metals will obviously make the residue material even more valuable. The actual contribution of metal recovery toward overall economic improvement of the process will depend upon the cost of recovery, which could be considerable.

The amount of ore to be processed constitutes only a small fraction of the coal tonnage input and ranges between 1.2 percent and 7 percent. In other words, the dollar values stated above translate into $208 to $230 per ton of "ore" processed. Therefore, metals recovery from coal liquefaction residues could contribute positively to the economy of the processes of liquefaction if the cost of metals recovery could be kept lower than $208 to $230 per ton of ore processed. The strategic importance of recovery of metals from the residues could remain unaffected by costs.

The single most valuable metal found in coal liquefaction residues was aluminum, having a total value ranging from $121 million to $668 million. Vanadium and germanium were the next most valuable metals.

Under Class III the elements S, Mg, and U were identified. There are substantial quantities of lower grade ores, or secondary sources, available for recovery of these metals. Therefore, the use of residues of coal liquefaction to recover these metals is not likely to be of much economic significance.

For all elements analyzed, Table 29 shows the calculated values of the minimum and maximum amounts of each metal present in the residue from 50 million tons of coal input.

Table 29. Minimum and maximum hypothetical metal amount available from liquefaction residues of 50 million tons of coal input (tons/year).

Metal	Minimum	Maximum	Metal	Minimum	Maximum
1. Al	114,000.0	560,000.0	31. In	0	8.82
2. Ca	34,650.0	609,000.0	32. La	66.0	595.0
3. Fe	144,000.0	1,417,500.0	33. Li	72.0	1,039.5
4. K	6,600.0	95,700.0	34. Lu	1.02	9.45
5. Mg	174.0	162,000.0	35. Mn	462.0	2,805.0
6. Na	2,975.0	142,000.0	36. Mo	4.93	280.0
7. P	0	25,500.0	37. Nd	78.0	875.0
8. Si	258,000.0	1,400,000.0	38. Ni	46.75	1,470.0
9. Ti	6,600.0	33,600.0	39. Pb	69.6	899.0
10. Ag	1.615	23.1	40. Pd	0	0.347
11. As	16.8	976.0	41. Pr	15.6	300.0
12. Au	0	1.98	42. Pt	0	74.25
13. B	1,189.0	10,360.0	43. Rb	32.0	1,036.0
14. Ba	600.0	48,000.0	44. Sb	4.93	98.0
15. Be	5.44	280.0	45. Sc	31.8	182.7
16. Bi	4.38	34.65	46. Sm	21.0	84.0
17. Cd	3.315	21.105	47. Sn	21.0	100.8
18. Ce	156.0	1,228.0	48. Sr	240.0	17,200.0
19. Co	34.0	420.0	49. Ta	1.62	7.975
20. Cr	156.0	1,400.0	50. Tb	1.92	18.2
21. Cs	14.4	81.2	51. Th	24.0	140.0
22. Cu	96.0	1,291.0	52. Tl	4.74	101.5
23. Dy	8.4	63.0	53. Tm	0.46	6.93
24. Er	6.8	63.0	54. U	5.59	173.60
25. Eu	2.94	23.45	55. V	320.0	2,170.0
26 Ga	37.8	185.85	56. W	5.82	162.0
27. Gd	13.2	161.00	57. Y	66.0	535.5
28. Ge	0	245.70	58. Yb	6.6	50.4
29. Hf	6.6	178.00	59. Zn	60.0	3,480.0
30. Ho	2.16	18.585	60. Zr	306.0	1,680.0

SUMMARY

To determine the metals and their concentrations in the residues of coal liquefaction processes, 18 sets of residues representing 6 separate processes were analyzed. The concentrations were normalized to 1 million tons coal input. Metallic residue was determined; C, H, N, S, Br, Cl, F, Hg, I, Se, Te, and O were omitted from further calculations. Between 12,000 and 63,000 tons of metallic residues remained, depending upon process applied and coal used.

Mineralogical analysis of the metallic residue showed that most metals in coal liquefaction residues are not present as independent minerals but are isomorphous substitutes for other elements in crystalline structures of other minerals such as silicates. Mineralogically, the residues differ entirely from conventional ores, and necessitate the development of new beneficiation technology for liberating these metals. In the absence of such technology, the economic analysis carried out here must remain an entirely hypothetical one; however, economic background data are generated upon which the economic feasibility of technology developed in the future can be measured.

The economic analysis was based upon 1974 import statistics and reserves and demand development forecasts by the U.S. Bureau of Mines to the year 2000. First, the metals were grouped into the following three categories:

(A) Metals having at least 25 percent of total demand imported in 1974 and thus of high strategic value.

(B) Metals having expected demand growth of at least 100 percent by year 2000 and therefore of high economic significance.

(C) Metals having reserves to demand ratio of less than 20 and hence of potential economic and strategic importance.

Data on metals obtained from chemical analysis of liquefaction residues were then compared with the three categories described above, and the elements were grouped into three classes with decreasing economic and strategic priority: Class I, metals belonging to all three categories A, B, and C; Class II, metals belonging to categories A and C; and Class III, metals in categories B and C.

Based upon the available data and with the help of a simple computer program, the tonnages of each metal present in the liquefaction residues from 1 to 50 million tons of coal input were calculated. Seventeen of the 22 metals classified as most significant were chosen for economic evaluation. The dollar values of these metals in residues of 50 million tons of coal at 1978 prices were calculated for the minimum and the maximum amounts of metal present, taking into account the liquefaction process applied and the coal used. The dollar value ranged from $129 million to $807 million. In other words a credit value of $2.50 to $16.10 per ton of coal input or $208 to $230 per ton of metallic residue could be attributed to these 17 metals.

Aluminum with a total value ranging from $121 million to $668 million accounted for 84 to 94 percent of the total value of metals.

APPENDIX A

LITERATURE REVIEW OF CHEMICAL STUDIES OF LIQUEFACTION PROCESSES

The following literature review summarizes the studies that have been conducted on elemental analysis of samples from various liquefaction processes. Table A1 presents a comparison of some literature results for feed coals and residues with those results obtained at the Illinois State Geological Survey (ISGS). Table A2 is a compilation of various literature results of analyses of liquefaction products.

SYNTHOIL PROCESS

Yavorsky and Akhtar (1974) reported on the analysis of a SYNTHOIL product that was ashed at 500°C. The elements determined were, in order of descending concentration, Fe, Si, Al, K, Na, Ca, Mg, Mo, and Co. The concentrations ranged from 67.4 ppm for Fe to <0.1 ppm for Co and <0.2 ppm for Mo (Table A2).

Schwager and Yen (1976) examined a SYNTHOIL product that had been extracted with various solvents into an oil, a resin, an asphaltene, a carbene, and a carboid fraction. The asphaltene fraction and a benzene-insoluble fraction were semiquantitatively analyzed for Si, Fe, Al, Ti, B, Ca, and Mg. Concentrations in the asphaltene fraction ranged from a high of 180 ppm Si to a low of 1 ppm Mg, and in the benzene-insoluble fraction ranged from a high of 1800 ppm Si to a low of 29 ppm Mg. Results show that the metals were generally concentrated in the asphaltene and carboid fractions.

Schultz et al. (1977) and Lett et al. (1977) reported on experimental run FB-55 of the SYNTHOIL process; the feed coal was of a run-of-mine western Kentucky HvBb coal. Splits of samples from this experimental run were obtained by ISGS and analyzed. The results from these two reports and the ISGS results for the feed coal and centrifuge residue are given in Table A1. Lett et al. (1977) indicated a precision in their data of ±50 percent. Schultz et al. (1977) gave relative standard deviations of from ±2 to ±13 percent. The ISGS values have a relative standard deviation range of ±10 to 20 percent. Considering these ranges most of the values in the tables are in agreement. Schultz et al. (1977) found that the liquid product was cleaner than the feed coal with respect to the trace element content, especially when the heating values of the feed coal (10,830 Btu/lb) and centrifuged liquid product (14,700 Btu/lb) were considered. The centrifuge residue was the major sink for the trace elements determined; very low concentrations of these trace elements were contained in the aqueous fractions. The scrubber effluent and vapor knock-out trap also contained only small concentrations of the trace elements determined. Material balances were done for the PDU and some of its subunits; the values ranged from 92 to 140 percent. Percentages higher than 100 were obtained for Cu, Ni, and Cr. An explanation given for the higher percentages for Cu, Cr, and Ni was that erosion of the stainless steel alloys and bronze valves used in the PDU may have contaminated the samples.

Lett et al. (1977) examined the feed coal, recycle oil, feed paste, gross liquid product, centrifuged liquid product, centrifuge residue, scrubber influent, scrubber effluent-aqueous fraction, and scrubber effluent-organic fraction from the PERC PDU. All the samples, except for the scrubber fractions, were ashed in a low-temperature plasma asher. It was mentioned that some significant losses of very volatile elements such as Hg, Sb, S, and the halogens, might occur from the ashing. For example, the sample preparation for the spark-source mass spectrometry (SSMS) analyses resulted in an 80 to 90 percent

TABLE A1 - Comparison of results from Schultz et al. (1977); Lett et al. (1977); and ISGS for sample run FB-55

	Feed Coal (ppm)^{a}			Centrifuge Residue (ppm)^{a}		
Element	Schultz et al. (1977)	Lett et al. (1977)^{b}	ISGS	Schultz et al. (1977)	Lett et al. (1977)^{b}	ISGS
Li		23.	16. (AA)		60.	46. (AA)
Be		1.0	1.2 (OEP)		2.4	2.8 (OEP)
B		87.	100. (OED)		370.	200. (OED)
Na		250.	230. (NAA)		40.	650. (NAA)
Al		2.3%	2.3% (XRF)		4.5%	4.5% (XRF)
Al		1.4% (AA)				
Si		3.3%	3.8% (XRF)		7.0%	8.0% (XRF)
Si		2.8% (GA)				
P		130.	120. (XRF)		575.	200. (XRF)
S		1.8%	5.2% (ASTM)		5.3%	6.0% (ASTM)
K		.23%	.17% (NAA)		.85%	.5% (NAA)
K		0.2% (AA)	.19% (XRF)			0.49% (XRF)
Ca		.42%	.43% (XRF)			
Ca		0.3% (AA)				
Sc		∿9	3.5 (NAA)		∿8.	8.3 (NAA)
Ti		1000.	1000. (XRF)		1400.	2000. (XRF)
V		16.	40. (OED)		39.	96. (OED)
V			26. (OEP)			77. (OEP)
Cr	21. (AA)	13.	21. (NAA)	84. (AA)	67.	60. (NAA)
Cr			28. (OED)			98. (OED)
Mn	57. (AA)	44.	66. (NAA)	180. (AA)	240.	180. (NAA)
Mn			64. (OEP)			200. (OEP)
Co		2.4	5.3 (NAA)		13.	9.3 (NAA)
Co			7.0 (OED)			19. (OED)
Co			5.7 (OEP)			14. (OEP)
Ni	9.3 (AA)	15	10. (AA)	54. (AA)	83.	30. (AA)
Ni			<10. (NAA)			34. (NAA)
Ni			24. (OED)			75. (OED)
Ni			16. (OEP)			49. (OEP)
Cu	10. (AA)	6.8	10. (AA)	45. (AA)	47.	40. (AA)
Cu			9.4 (OED)			40. (OED)
Cu			10. (OEP)			32. (OEP)
Zn		31.	52. (AA)		105.	140. (AA)
Ga		2.3	3.8 (NAA)		9.9	9.8 (NAA)
Ge		2.7	4.3 (OED)		10.	5.6 (OED)
As		3.9	7.1 (NAA)		10.	7.2 (NAA)
Se		4.0	1.6 (NAA)		10.	5.0 (NAA)
Br		≤0.2	0.8 (NAA)		≤6.	1.5 (NAA)
Rb		23.	25. (NAA)		84.	41. (NAA)

loss of chlorine in some samples. Therefore, the scrubber unit may collect some of the more volatile elements such as chlorine. The centrifuged liquid product was a much cleaner fuel than the feed coal with regard to most of the elements determined. Lett et al. (1977) also found that the concentrations of the trace and minor elements in the centrifuged liquid product and centrifuge residue could be estimated from their ash contents. This was not true for sulfur and a few volatile elements.

TABLE A1 - (Continued)

	Feed Coal (ppm)[a]			Centrifuge Residue (ppm)[a]		
Element	Schultz et al. (1977)	Lett et al. (1977)[b]	ISGS	Schultz et al. (1977)	Lett et al. (1977)[b]	ISGS
Sr		60.	46. (NAA)		270.	190. (NAA)
Sr			46. (OED)			130. (OED)
Zr		22.	42. (OEP)		74.	120. (OEP)
Mo		3.7	6.9 (OED)		12.	19. (OED)
Cd	.32(AA)	≤0.4	<0.4 (AA)	1.0(AA)	≤1.8	<1.1 (AA)
Sn		0.45	0.95 (OED)		3.0	3.1 (OED)
Sn			2.0 (XES)			7.3 (XES)
Sb		0.24	0.27 (NAA)		1.0	0.8 (NAA)
Te		≤0.3	0.7 (XES)		≤0.6	2.1 (XES)
I		≤0.25	2.1 (XES)		≤0.5	4.2 (XES)
Cs		0.93	1.4 (NAA)		6.4	3.6 (NAA)
Ba		130.	130. (XES)		400.	420. (XES)
La		6.6	10. (NAA)		26.	26. (NAA)
Hf		1.2	0.46 (NAA)		3.9	1.4 (NAA)
W		1.4	0.9 (NAA)		≤1.6	1.8 (NAA)
Au		≤0.4	0.002 (NAA)			
Tl		2.9	1.5 (OED)		7.2	3.2 (OED)
Pb	4.6 (AA)	6.7	<4.3 (AA)	18. (AA)	18.	<12. (AA)
Ce		19.	18. (NAA)		59.	39. (NAA)
Sm		1.1	1.8 (NAA)		4.5	4.8 (NAA)
Eu		0.2	0.32 (NAA)		0.8	1.0 (NAA)
Tb		0.3	0.40 (NAA)		0.6	1.0 (NAA)
Dy		1.1	1.5 (NAA)		3.9	3.0 (NAA)
Yb		0.3	0.63 (NAA)		1.3	1.4 (NAA)
Lu		0.1	0.08 (NAA)		0.2	0.27 (NAA)
Th		3.1	2.9 (NAA)		14.	9.0 (NAA)
U		1.8	1.2 (NAA)		5.3	2.1 (NAA)
Fe		3.6%(AA)	3.6% (AA)		10.%(AA)	10.% (AA)
Fe			3.5% (NAA)			7.7% (NAA)
Fe			2.5% (XRF)			9.7% (XRF)

[a] Values in Table A1 are in parts per million unless indicated otherwise.

[b] Values by Lett et al. (1977) were done by spark source mass spectrometry unless noted.

Note:
(AA) = Atomic Absorption Spectrophotometry
(ASTM) = American Society for TEsting and Materials Method
(BA) = Gravimetric Analysis
(NAA) = Neutron Activation Analysis
(OED) = Optical Emission Spectroscopy - Direct Reading
(OEP) = Optical Emission Spectroscopy - Photographic
(XES) = Energy-dispersive X-ray fluorescence Spectrometry
(XRF) = Wavelength-dispersive X-ray fluorescence Spectrometry

COED PROCESS

Hildebrand, Cushman, and Carter (1976) have reported trace element values on two process streams from a pilot plant operation. The two streams were the stage liquor and the product separator liquor. Fifty-five elements were analyzed by spark source mass spectrometry. For most of the elements detected, the product separator liquor had higher concentrations than the stage liquor.

TABLE A2 - Product data (as received basis) (all concentrations are reported in ppm)

Process	Reference	Ag	Al	As	Au	B	Ba	Be	Bi	Br	Ca	Cd	Ce	Cl	Co
SRC	Koppenaal and Manahan(1976)		65	1						6.2				167	0.8
	Coleman, et al.(1978)		171								2370	2.8			19.2
			77.8								93.5	0.5			12.0
			32								5486	0.3			5.0
			107								1297	0.3			4.8
											105				
	Coleman, et al.(1977)		147									<.07			<2
	Fruchter, et al.(1977)			2.1			.14			4.7			0.4		.26
	Jahnig(1975)	.02	96	1.4	<.4	57	.22		<.2	3.8	140	<.1			.35
		.09	130	0.5	<.2	43	.55		<.1	3.9	77	<.1			.23
	Filby, et al.(1976)			1.39			2.48			3.95			.553		.31
	Filby, et al.(1977)		200	2.0			5.75			7.74	72.8		.45	159.5	.22
Synthoil	Yavorsky and Akhtar(1974)		29.1								2.3				<.1
	Schultz, et al.(1977)											.077			
	Lett, et al.(1977)		2100	1.8		30	9.4	.31		≤.3	250	≤.15	1.1	12	1.4
Gulf Research and Development	Given, et al.(1975)					.15		.0004							.12
						.12		.01							.01
						.03		.0009							.004

Process	Reference	Cr	Cs	Cu	Dy	Er	Eu	F	Fe	Ga	Gd	Ge	Hf	Hg	Ho
SRC	Koppenaal and Manahan(1976)														
	Coleman, et al.(1978)	5.7		3.2					11797						
		11.2		3.6					714						
		11.9		0.8					738						
		3.7		1.4					3300						
				12.4											
	Coleman, et al.(1977)	5.9		<9.5					423						
	Fruchter, et al.(1977)	7.5	.012			.065	.025		270		.14		.054	.02	.030
		6.0							300						
	Jahnig(1975)	1.1		2.4				<100	64			<.4		.05	
		1.2		3.2				<100	161			<.2		.01	
	Filby, et al.(1976)	2.68	.023				.013		680					.025	
	Filby, et al.(1977)	1.64	.02	2.07			.055		300	1.79			.084	39.6	
Synthoil	Yavorsky and Akhtar(1974)								67.4						
	Schultz, et al.(1977)	7.6		2.7											
	Lett, et al.(1977)	4.9	.43	3.4	.02	.02	.03		5500	1.1	.15	.78	0.1		0.2
Gulf Research and Development	Given, et al.(1975)	.05		.02											
		.12		.03											
		.05		.01											

TABLE A2 - (Continued)

Process	Reference	I	K	La	Li	Lu	Mg	Mn	Mo	Na	Nb	Nd	Ni	P	Pb
SRC	Koppenaal and Manahan(1976)						196	1.7		2.6					
	Coleman, et al.(1978)		22.3				58.9	4.4					16.4		12.8
			27.2				29.0	39.6					13.8		23.7
			40.9				8.3	8.7					7.7		4.9
			33.5				8.0	3.6					3.3		2.1
							24.3						12.0		
	Coleman, et al.(1977)		113				93	21.6					23		<.5
	Fruchter, et al.(1977)			0.10		.014				8.8		.27	<6		
													2.1		
	Jahnig(1975)		5.		<.02		21	2.9	1.7	27	<2.0		3.1		<.4
			17		<.02		12	1.9	1.4		<1.0		6.4		<.2
	Filby, et al.(1976)		315			.004				9.55			2.7		
	Filby, et al.(1977)		4.72	.13			89.0	20.3		4.23			<3.0		
Synthoil	Yavorsky and Akhtar(1974)		5.0				2.2		<0.2	2.9					
	Schultz, et al.(1977)							11					6.6		1.1
	Lett, et al.(1977)	≤.1	670	1.6	∿3.	.05	220	11	2.5	60	1.9	1.0	5.3	50	.57
Gulf Research and Development	Given, et al.(1975)							.05	.08	5			.15		.02
								.12	.01	2.5			.08		
								.05		.9			.03		

Process	Reference	Pd	Pr	Rb	Rh	Ru	S	Sb	Sc	Se	Si	Sm	Sn	Sr	Ta
SRC	Koppenaal and Manahan(1976)														
	Coleman, et al.(1978)														
	Coleman, et al.(1977)														
	Fruchter, et al.(1977)		.045					.066	0.45	0.17		.11		.96	.043
	Jahnig(1975)							.25		2.	600	.36	51	<.8	<2.
								.30		<1.	900	.16	5.5	<.5	<.9
	Filby, et al.(1976)			.57				.074	.13	.148		.040		4.4	
	Filby, et al.(1977)			<.5				.06	.57	.12		.29		<6.0	.046
Synthoil	Yavorsky and Akhtar(1974)										63.34				
	Schultz, et al.(1977)														
	Lett, et al.(1977)	≤.07	0.2	10	≤.02	≤.01	2900	.06	∿.2	1.1	3200	0.2	.11	12.	
Gulf Research and Development	Given, et al.(1975)														

TABLE A2 - (Continued)

Process	Reference	Tb	Te	Th	Ti	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
SRC	Koppenaal and Manahan(1976)				96				2.8					
	Coleman, et al.(1978)													
	Coleman, et al.(1977)												7.6	
	Fruchter, et al.(1977)	.026		.19			.016	.54				.094	8.1	
	Jahnig(1975)		1.4	<.8	280			<4.	17	<1.		0.39	5.3	3.7
			0.6	<.5	120			<2.	14	<.7		.025	1.9	2.0
	Filby, et al.(1976)	.014		.055										
	Filby, et al.(1977)	.045		.22	465.0				4.63					16.0
Synthoil	Yavorsky and Akhtar(1974)													
	Schultz, et al.(1977)													
	Lett, et al.(1977)		≤.2	.48	150	.41	.02	.24	2.0	.2	1.7	.08	13.	4.8
Gulf Research and Development	Given, et al.(1975)				5				.06				.12	
					6				.25				.12	
					0.5				.004				.05	

A preliminary effort was made to assess the potential for toxicity or bioaccumulation hazards in aquatic systems. Al, As, B, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, and Zn in the process streams were at levels high enough to be toxic to aquatic biota. The elements were rated for their potential toxicity as follows:

(1) Low potential—As, B, Cu, and Mg

(2) Medium potential—Al, Co, Hg, and Mn

(3) High potential—Cr, Fe, Ni, Pb, and Zn

Al, As, Cd, Co, Cr, Cu, Fe, Ge, Hg, Mg, Mn, Ni, Pb, Se, Sn, Ti, and Zn were also at high enough concentrations to produce potentially hazardous bioaccumulations. These elements were rated as to their potential for detrimental bioaccumulation in aquatic systems as follows:

(1) Low potential—Cd, Ge, and Mg

(2) Medium potential—Al, As, Co, Hg, and Ti

(3) High potential—Cr, Cu, Fe, Mn, Ni, Pb, Se, Sn, and Zn

Hildebrand et al. (1976) considered the results to be preliminary.

Schwager and Yen (1976) reported semiquantitative results for Si, Fe, Al, Ti, B, Ca, and Mg in an asphaltene fraction and a benzene-insoluble fraction of a FMC-COED product. The values obtained ranged from 210 ppm Si to a 5 ppm Mg in the asphaltene fraction and from 280 ppm Ca to a 10 ppm Ti in the benzene-insoluble fraction. The authors reported that the metals tended to be more concentrated in the asphaltene and carboid fractions.

H-COAL PROCESS

No information on trace elements in the liquid products was found. Some information was found for elemental depositions on used catalysts.

Kang and Johanson (1976) reported that typical contaminants on used catalysts were Ti, Fe, Ca, Na, and sometimes Al, and that Ti deposition increased with the age of the catalyst for an Illinois No. 6 coal. Very little Ti was deposited when a Wyodak coal was used. About 5 percent of the Ti present in the Illinois coal was deposited on the catalyst. The authors proposed that Ti was present as organometallic complexes in the Illinois bituminous coal. Other elements determined in the catalysts were Al, Sb, As, Ba, Be, B, Ca, Cr, Co, Cu, Ga, Ge, Fe, Pb, Mg, Mn, Mo, Nb, Ni, Si, Ti, V, Zn, Zr, C, and S.

Jahnig (1974b) reported values for C, S, V, Ni, Ti, B, Ca, and Fe on a spent catalyst from the H-COAL process. The values reported (from a paper presented by Johnson et al. [1972]) were from a run of an Illinois coal. Jahnig reported some of the product oil is recycled into the system such that any trace elements collected in the oil will concentrate there.

SOLVENT REFINED COAL PROCESS (SRC)

Coleman et al. (1977) reported on some samples obtained from the Southern Services, Inc. pilot plant in Wilsonville, Alabama. The samples consisted of the SRC, THF-insoluble SRC, THF-soluble SRC, and 3 different molecular-weight fractions of the THF-soluble SRC. The THF-soluble SRC was separated into 3 molecular weight groupings by using gel-permeation chromatography and was analyzed for the 12 elements, Mg, Al, K, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb. The detection limits of Cr, Co, Ni, Cu, Cd, and Pb were too high relative to the levels of these elements in the samples to allow quantitative results to be obtained for all the samples. For the other elements, concentrations in the SRC ranged from 423 μg/g Fe to 7.6 μg/g Zn. The concentrations of Cd and Pb were reported to be <0.07 μg/g and <0.5 μg/g, respectively. A comparison of the THF-insoluble SRC with the THF-soluble SRC showed that Mg, Al, K, Cr, Mn, Cd, Pb, and Fe were concentrated in the insoluble portion and Co, Ni, Cu, and Zn were more or less evenly distributed between the two samples. A National Bureau of Standards sample, SRM 1632, was analyzed in the study and reported for comparison. All the analyses in the report were done by flameless atomic absorption analysis.

Koppenaal and Manahan (1976) reported on an SRC product of a Kentucky No. 9 coal. As, Br, Co, Mn, V, Al, Cl, Mg, Na, and Ti were determined; results ranged from 0.8 ppm for Co to 196 ppm for Mg. The authors speculated that various types of organometallics could be present, such as metal-porphyrins, metal-carbonyls, metallocenes, arene carbonyls, metal alkyls, organo hydrides, and metal chelates.

Coleman et al. (1978) reported on SRC samples obtained from the pilot plant at Wilsonville, Alabama, for a Pittsburgh No. 8 coal, an Amax coal, a Monterey coal, a Western Kentucky No. 9 and 14 coal, and an Illinois No. 6 coal. The samples (SRC, THF-soluble SRC, THF-insoluble SRC, and 3 different molecular weight fractions) were analyzed for Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Pb, and Cd. The authors found that in some cases Al, Ca, and Fe in the SRC were somewhat soluble in THF. The concentration of Co was found to be higher in the THF-soluble SRC than in the THF-insoluble SRC from four of the five coals tested. They postulated that the metals found in the THF-soluble fraction were probably metal chelates or organically bound metals.

Fruchter et al. (1977) reported on some SRC samples acquired from the Pittsburgh and Midway Coal Mining Company. The sample types analyzed were the feed coal (a Kentucky high-sulfur bituminous coal), SRC, mineral residue, process solvent, and process NAPTHA. Thirty-six elements were determined. The SRC and the light oil were generally low in trace elements. The light oil did show some Zn, Br, Cr, and As. Bromine did not show any decrease in the SRC. U, Ta, Cr, and Zn did show a decrease in the SRC but still remained in significant amounts. Most of the trace elements were found in the mineral residue.

Schwager and Yen (1976) reported values for Si, Fe, Al, Ti, B, Ca, and Mg on a SRC sample that had been extracted with various solvents to give a benzene-insoluble sample and an asphaltene fraction. The values obtained ranged from 55 ppm Si to 1 ppm Ti for the asphaltene fraction and from 420 ppm Al to 18 ppm B in the benzene-insoluble fraction.

Jahnig (1974a) reported on two samples of SRC that had been analyzed by the Pittsburgh and Midway Coal Mining Company. These samples were from two runs of the same coal (one run at 1000 psi and the other run at 2000 psi), and were analyzed for 43 elements. The SRC contained significant concentrations of V, Ni, Ti, Na, Zn, Fe, Cu, Mn, and Co. Titanium was one of the most concentrated elements in the SRC with one value reported to be 300 ppm. The K content of the SRC was quite low. Three possible explanations for the high Fe content were that an iron carbonyl compound was formed and retained in the SRC, that pyrite was converted to a finely divided or colloidal form, and that equipment was corroding. Jahnig pointed out that if some trace elements are found in a process stream that is recycled in the system, those trace elements in this stream will tend to be concentrated.

Filby, Shah, and Sautter (1976) analyzed the feed coal, SRC, filter cake, pyridine-insolubles, recycle process solvent, light ends, and process water from the 50-ton/per day SRC pilot plant at Ft. Lewis, WA. The samples, taken during a nonequilibrium pilot plant run, were analyzed for 22 elements by neutron activation analysis. The analyses showed that most of the trace elements were found in the SRC, pyridine-insolubles, and wet filter cake. (The pyridine-insolubles are that portion of the wet filter cake that are insoluble in pyridine.) It was noted that 75 percent of the original weight of the coal could be accounted for with the SRC and the pyridine-insoluble portion. The SRC appeared to be cleaner than the feed coal. Elemental balances were done on the process with the assumptions that all the K was present in inorganic combination and that the SRC yield was 60 percent. The mass balances thus obtained ranged from 59.7 percent for As to 189 percent for Se. The high elemental balance for Se was presumed to be due to a source such as the solvent or to some contamination problem. The low values for As and Hg were postulated to be due to possible losses by volatility. The authors reported good balances for K, Cs, Rb, Fe, and the rare earths, which they expected to be found entirely in the inorganic fraction of coal. From the elemental balance, the concentration of Br appeared to be quite high in the SRC (67.5 percent of the total Br in the SRC); it was the only element enriched in the SRC relative to the coal. An effort was made to calculate the percentage of an element that was in an organic form in the coal and the SRC. It was assumed that K was in an inorganic form and that the pyridine-insoluble fraction was totally inorganic material. By using these assumptions and the elemental data for the coal, SRC, and pyridine-insoluble portion normalized to K, the organic and inorganic associations were computed. Calculations showed that As, Sb, Se, Hg, Br, Ni, Cr, Co, and Na were predominantly organically bound in the SRC. Rb, Cs, Th, Sr, Ba, and the rare earths were found to be predominantly inorganically bound in the SRC. The same calculations were done on the coal. When the results from the calculations on the SRC were compared with those on the coal, the authors concluded that As, Sb, Se, Hg, Ni, Co, Cr, and Na appeared to "either preserve some original coal organic forms in the SRC or form new organometallic species and are incorporated during liquefaction."

Filby, Shah, and Sautter (1977) analyzed the feed coal, process solvent, SRC, mineral residue, wet filter cake, sulfur, by-product solvent, process and effluent waters, and by-product sulfur for two sets of samples for 34 trace elements by neutron activation analysis. The samples were collected from the Ft. Lewis, WA, pilot plant after the pilot plant had been running continuously for 7 days. The SRC and the insoluble residue accounted for more than 90 percent of each element from the input stream. The SRC was much cleaner than the feed coal for all the elements except Cl, Br, and Ti. Bromine showed an enrichment in the SRC relative to the feed coal. Ti showed only a 12 percent reduction in the SRC relative to the feed coal. Three possible explanations for the high concentration of titanium in the SRC were: (a) that extremely fine particles of TiO_2 passed through the rotary drum filters; (b) that Ti was present as a solvent-soluble organometallic compound; and (c) that Ti is present in an inorganic form in the coal but is converted to an oil-soluble or an organometallic compound during the hydrogenation step. Material balance calculations were attempted on the sample sets. Some assumptions made to facilitate the calculations were that the recycle process solvent contributed 5 percent to the mass balance, that the residue component of the SRC could be based on the pyridine-insoluble fraction, that 100 percent of the K is in the pyridine-insoluble fraction, and that only the coal contributes to the trace element input. The material balance values ranged from 53 percent for Mg to 259 percent for Rb in the first data set and from 82 percent for Cl to 293 percent for Ca in the second data set. For both data sets, most of the material balance values were from 85 to 150 percent. The authors believed that this range of values was excellent, considering the assumptions that were made and the difficulty in obtaining representative samples. It was noted that Sb, Hg, and Se showed good material balances, which showed that these more volatile elements could be accounted for. Ten percent of the Hg in the first data set was accounted for in the recycle process water. A high As concentration was obtained for the pyridine-insoluble fraction in the second data set, which caused a high material balance value; however, the As value for the first data set was good. The high value for As in the second set was not explained. Both data sets showed high material balance values for Br (possibly from the solvents). High material balances for Ti (149 percent for set one and 176 percent for set two) and high values for Ni and Cr in the second set of data (CR at 272 percent and Ni at 248 percent) were felt to possibly be from equipment corrosion. Some aqueous samples were analyzed in this study. It was found that some Hg, Se, As, and Cu were in the process waters from both sets. The treated effluent water appeared to be quite low in these trace elements. The bio-sludge of the second data set was examined and found to contain 6.3 ppm Se and 8.7 ppm Hg, which indicated good removal of these two elements from the process waters of both sets.

CATALYTIC HYDROGENATION

Given et al. (1975) reported on a catalytic hydrogenation process being used at Gulf Research and Development Co. In this process the coal was fed into a continuous flow reactor at 400°C and a hydrogen pressure of 300 psi. A proprietary catalyst was used in the experiment. Two different coals were used in this process. A third coal was processed in a batch autoclave at the same temperature and pressure in the presence of the proprietary catalyst. For the runs with these three coals, the feed coal, its solid residue, and its oil product were analyzed for B, Co, V, Ni, Ti, Mo, Na, Pb, Zn, Mn, Cr, Cu, Cd, Be, Th, Bi, Ge, and Ga. Th, Bi, Ge, and Ga were not detected in any of the samples. The oil product was reported to be much cleaner than its feed coal. The oils contained 0.1 to 0.2 percent sulfur. It was noted that two of the three oil products were enriched in Ti relative to the other elements, and that one explanation for the high Ti content could be that Ti is in the oil in organometallic compounds.

Mezey (1977) reported on the data given by Given et al. (1975). He observed that the largest portion of the trace elements remained in the residue.

CHEMICAL DATA ON LIQUEFACTION PRODUCTS

In the course of the present study, certain liquefaction products in a run were analyzed. Table A2 lists various literature results of the chemical analysis of products from certain processes.

SAMPLE PRE-TREATMENT LOG

LAB. NO.	SAMPLE DESCRIPTION	PROCESS NAME	SAMPLING DATE	"AS RECEIVED" SAMPLE		TETRAHYDROFURAN EXTRACTION				
						EXTRACTED RESIDUE (A)			EXTRACT (B)	
				DATE AND HTA	DATE AND LTA	EXTRACTION DATE AND YIELD	DATE AND HTA	DATE AND LTA	DISTILLATION COMPLETION DATE	DATE AND HTA
C19660	ILLINOIS NO. 6 COAL	CLEAN COKE	03/ /77	03/23/77 19.37%	21.18%	--	--	--	--	--
C19661	VAPOR STRIPPER BOTTOMS	CLEAN COKE	03/ /77	03/23/77 14.28%	--	09/19/77 30.68%	10/14/77 75.58%	82.52%	11/28/77	01/16/78 .14%
C19876	CONCENTRATED VAPOR-STRIPPER RESIDUE	CLEAN COKE	07/ /77	10/14/77 16.08%	--	09/19/77 25.66%	10/14/77 45.22%	49.03%	11/08/77	11/10/77 6.27%
C19963	CHAR FROM ILLINOIS NO. 6 COAL	FMC COED		11/28/77 13.07%		--	--	--	--	--
C18903	COAL FROM P-2 FEED, -100 MESH	H-COAL	09/30/75	10/13/75 11.53%	10/19/75 14.21%	--	--	--	--	--
C18941	VACUUM STILL BOTTOMS	H-COAL	11/26/75	05/07/76 16.65%	--	02/25/76 22.95%	05/26/76 63.36%	04/23/76 67.70%	04/15/76	05/13/76 1.00%
C19194	P-2 FEED COAL	H-COAL	04/06/76	06/04/76 11.63%	04/07/76 13.92%	--	--	--	--	--
C19196	VACUUM STILL BOTTOMS	H-COAL	04/06/76	10/21/76 17.36%	--	06/03/76 27.22%	06/04/76 58.03%	04/06/76 66.05%	08/09/76	02/25/77 .98%
C19916	FEED COAL ILLINOIS NO. 6	H-COAL	09/08/77	10/14/77 11.72%	13.84%	--	--	--	--	--
C19917	UNFILTERED VACUUM STILL BOTTOMS	H-COAL	09/08/77	10/14/77 28.04%	--	12/05/77 40.23%	02/17/78 68.55%	81.39%	01/ /78	02/17/78 .26%
C20021	FEED COAL WYODAK SEAM	H-COAL	12/11/77	02/17/78 8.99%	12.17%	05/10/78 88.61%	8.98%	--	--	.72%
C20022	VACUUM STILL BOTTOMS	H-COAL	12/11/77	02/17/78 21.53%	--	02/10/78 66.02%	44.74%	68.97%	03/13/78	05/05/78 .57%

SAMPLE PRE-TREATMENT LOG

LAB. NO.	SAMPLE DESCRIPTION	PROCESS NAME	SAMPLING DATE	"AS RECEIVED" SAMPLE: DATE AND HTA	"AS RECEIVED" SAMPLE: DATE AND LTA	TETRAHYDROFURAN EXTRACTION — EXTRACTED RESIDUE (A): EXTRACTION DATE AND YIELD	EXTRACTED RESIDUE (A): DATE AND HTA	EXTRACTED RESIDUE (A): DATE AND LTA	EXTRACT (B): DISTILLATION COMPLETION DATE	EXTRACT (B): DATE AND HTA
C19590	PULVERIZED LIGNITE	LIGNITE	01/06/76	01/25/77 8.56%	10.77%	--	--	--	--	--
C19591	MINERAL RESIDUE V-8 BOTTOMS	LIGNITE	06/23/76	01/25/77 34.72%	36.65%	--	--	--	--	--
C19592	SOLVENT REFINED LIGNITE F-1 BOTTOMS	LIGNITE	06/22/76	01/25/77 .15%	--	--	--	--	--	--
C19702	FEED COAL MONTEREY	SRC-ALA	10/13/75	07/19/77 11.32%	13.97%	--	--	--	--	--
C19703	MINERAL RESIDUE	SRC-ALA	10/13/75	07/19/77 65.50%	71.73%	--	--	--	--	--
C19704	SOLVENT REFINED COAL	SRC-ALA	10/13/75	07/19/77 .39%	--	--	--	--	--	--
C19705	FEED COAL ILLINOIS NO.6	SRC-ALA	12/06/74	07/19/77 11.22%	14.52%	--	--	--	--	--
C19706	MINERAL RESIDUE	SRC-ALA	04/01/75	07/19/77 43.58%	10/14/77 46.83%	--	--	--	--	--
C19707	SOLVENT REFINED COAL	SRC-ALA	12/06/74	07/19/77 .19%	--	--	--	--	--	--
C19708	FEED COAL W. KENTUCKY NOS.9&14	SRC-ALA	04/19/76	07/19/77 9.26%	12.11%	--	--	--	--	--
C19709	MINERAL RESIDUE	SRC-ALA	04/19/75	07/19/77 53.17%	60.23%	--	--	--	--	--
C19710	SOLVENT REFINED COAL	SRC-ALA	04/19/76	07/19/77 .12%	--	--	--	--	--	--

SAMPLE PRE-TREATMENT LOG

LAB. NO.	SAMPLE DESCRIPTION	PROCESS NAME	SAMPLING DATE	"AS RECEIVED" SAMPLE: DATE AND HTA	"AS RECEIVED" SAMPLE: DATE AND LTA	TETRAHYDROFURAN EXTRACTION: EXTRACTED RESIDUE (A): EXTRACTION DATE AND YIELD	EXTRACTED RESIDUE (A): DATE AND HTA	EXTRACTED RESIDUE (A): DATE AND LTA	EXTRACT (B): DISTILLATION COMPLETION DATE	EXTRACT (B): DATE AND HTA
C19711	FEED COAL AMAX WYODAK	SRC-ALA	11/22/75	07/19/77 7.42%	10.67%	--	--	--	--	--
C19712	MINERAL RESIDUE	SRC-ALA	11/22/75	07/19/77 33.34%	40.43%	--	--	--	--	--
C19713	SOLVENT REFINED COAL	SRC-ALA	11/22/75	07/19/77 .26%	--	--	--	--	--	--
C19714	FEED COAL PITTSBURGH NO.8	SRC-ALA	07/21/75	07/19/77 8.81%	10.64%	--	--	--	--	--
C19715	MINERAL RESIDUE	SRC-ALA	07/21/75	07/19/77 56.67%	10/14/77 58.70%	--	--	--	--	--
C19716	SOLVENT REFINED COAL	SRC-ALA	08/21/75	07/19/77 .14%	--	--	--	--	--	--
C19141	GROUND AND DEHUMIDIFIED COAL, 1000 HRS.	SRC-WASH	03/02/76	05/12/76 9.97%	04/16/76 12.99%	--	--	--	--	--
C19142	MINERAL RESIDUE, COMPOSITE, 1000 HRS.	SRC-WASH	03/02/76	05/05/76 70.14%	--	05/14/76 100-%	05/17/76 69.82%	03/02/76 79.77%	05/25/76	--
C19143	SOLVENT REFINED COAL, COMPOSITE, 1000 HRS.	SRC-WASH	03/02/76	05/05/76 .12%	--	05/10/76 .25%	--	--	06/01/76	06/04/76 .19%
C19486	SOLVENT REFINED COAL JULY-AUGUST COMPOSITE	SRC-WASH	09/20/76	10/26/76 .17%	--	--	--	--	--	--
C19487	MINERAL RESIDUE JULY-AUGUST COMPOSITE	SRC-WASH	09/20/76	10/26/76 67.20%	--	--	--	--	--	--
C19488	GROUND COAL JULY-AUGUST COMPOSITE	SRC-WASH	09/20/76	10/27/76 11.59%	13.99%	--	--	--	--	--

SAMPLE PRE-TREATMENT LOG

						TETRAHYDROFURAN EXTRACTION				
						EXTRACTED RESIDUE (A)			EXTRACT (B)	
				"AS RECEIVED" SAMPLE		EXTRACTION			DISTILLATION	
LAB. NO.	SAMPLE DESCRIPTION	PROCESS NAME	SAMPLING DATE	DATE AND HTA	DATE AND LTA	DATE AND YIELD	DATE AND HTA	DATE AND LTA	COMPLETION DATE	DATE AND HTA
C19899	GROUND COAL - COMPOSITE SAMPLE W. KENTUCKY NOS. 9&14	SRC-WASH	08/26/77	10/14/77 9.55%	11.48%	--	--	--	--	--
C19902	SRC-II VACUUM BOTTOMS COMPOSITE SAMPLE	SRC-WASH	08/26/77	10/14/77 25.19%	--	04/05/78 40.18%	05/05/78 40.62%	45.35%	04/10/78	05/05/78 .09%
C19915	OIL FROM VAC. FLASH CONDENSATE DRUM. COMPOSITE SAMPLE	SRC-WASH	08/26/77	--	--	--	--	--	--	--
C20014	GROUND COAL ILLINOIS NO. 6	SRC-WASH	10/31/77	01/16/78 12.56%	14.75%	--	--	--	--	--
C20015	SRC-II VACUUM BOTTOMS	SRC-WASH	10/31/77	01/16/78 27.93%	--	01/25/78 38.76%	02/17/78 71.27%	81.46%	02/15/78	05/05/78 .11%
C20016	FEED COAL - 24 HR. COMPOSITE PITTSBURGH SEAM	SRC-WASH	11/15/77	01/16/78 12.32%	14.43%	--	--	--	--	--
C20017	VACUUM FLASH DRUM BOTTOMS	SRC-WASH	11/15/77	01/16/78 25.52%	--	04/05/78 63.15%	05/05/78 37.98%	43.54%	04/06/78	05/05/78 .58%
C20019	FEED COAL - 24 HR. COMPOSITE PITTSBURGH SEAM	SRC-WASH	12/05/77	02/17/78 12.83%	14.55%	05/31/78 95.11%	12.75%	--	--	.30%
C20020	VACUUM BOTTOMS - 24 HR. COMP.	SRC-WASH	12/05/77	02/17/78 26.70%	--	04/17/78 44.67%	05/09/78 58.15%	62.51%	04/17/78	05/09/78 .11%
C19276	FEED COAL	SYNTHOIL	05/17/76	10/21/76 16.85%	05/25/76 22.00%	--	--	--	--	--
C19349	CENTRIFUGE RESIDUE	SYNTHOIL	05/17/76	10/21/76 47.81%	--	08/24/76 53.62%	10/21/76 72.91%	83.92%	01/17/77	10/14/77 1.12%
C19512	CENTRIFUGE LIQUID PRODUCT	SYNTHOIL	05/17/76	--	--	--	--	--	--	--

APPENDIX B

SAMPLE PRE-TREATMENT LOG

LAB. NO.	SAMPLE DESCRIPTION	PROCESS NAME	SAMPLING DATE	"AS RECEIVED" SAMPLE		TETRAHYDROFURAN EXTRACTION				
						EXTRACTED RESIDUE (A)			EXTRACT (B)	
						EXTRACTION			DISTILLATION	
				DATE AND HTA	DATE AND LTA	DATE AND YIELD	DATE AND HTA	DATE AND LTA	COMPLETION DATE	DATE AND HTA
C18804	CATALYST	H-COAL	/ /	--	--	--	--	--	--	--
C18805	SPENT CATALYST	H-COAL	/ /	10/03/78 83.05%	--	--	--	--	--	--
C19371	'DICALCITE 600' FILTER AID	SRC-WASH	/ /	--	--	--	--	--	--	--
C19372	'SPEED PLUS' FILTER AID	SRC-WASH	/ /	--	--	--	--	--	--	--
C19373	'SPEEDEX' FILTER AID	SRC-WASH	/ /	--	--	--	--	--	--	--
C19374	'CELITE 545' FILTER AID	SRC-WASH	/ /	--	--	--	--	--	--	--
C19375	'FIBRA FLO 11-C' FILTER AID	SRC-WASH	/ /	--	--	--	--	--	--	--
C19718	FILTER AID	SRC-ALA	/ /	--	--	--	--	--	--	--

APPENDIX C

CHEMICAL PROCEDURES

The following ashing and analytical chemical procedures were developed, or adapted, and used for the analyses of whole coal, liquefaction residues, and the ash of both kinds of samples. For each procedure the sample preparation, operating parameters of instruments, interferences, accuracy obtained on reference standards, and precision are described.

Results from the determination of an element by more than one method were compared for agreement, absence of bias, and consistency. Those results for an element determined by the method or methods judged to be reliable (Table 3) were used in the calculations and discussion of the behavior of the element in coal liquefaction.

The analysts associated with the development of each method are as follows: AA—J. Steele, J. Ashby; OED—G. Dreher, S. Hampton; OEP—G. Dreher, E. Hopke; INAA—R. Cahill; NAA-RC—J. Frost, L. Camp, M. Seifrid, R. Nevitt, R. Koszykowski; XRF—R. Henderson, E. Fruth, M. Seifrid, J. Kuhn; XES—R. Henderson, J. Kuhn; ISE—J. Thomas, R. Gracon; and ASTM—L. Kohlenberger, T. Sharton, J. Kuhn, B. Cardott, R. Gracon.

PREPARATION OF 500°C TEMPERATURE ASH (HTA)

Approximately 2 grams of whole coal or liquefaction residue, as received, was placed in an acid-washed 30 ml Vycor brand crucible that had been previously dried at 100°C for several hours, cooled to room temperature, and accurately weighed. The crucible and sample were placed in a moisture oven at 100°C to 110°C for 2 hours. The dried sample was removed from the moisture oven and placed in a desiccator to cool. The sample was then carefully weighed, covered with a Vycor brand crucible cover, and placed in a room temperature, muffle furnace that had been adjusted to obtain a maximum temperature of 500°C in approximately 2 hours. The sample remained in the muffle furnace at 500°C for 20 to 24 hours, or until no carbonaceous material remained. The sample was then placed in a desiccator to cool. After it had cooled, the sample was weighed and then ground in a mullite mortar with pestle. The ground sample was placed in a 3 dram glass vial, dried at 110°C for several hours, and stored in a desiccator until used.

PREPARATION OF THF-INSOLUBLE SLURRIED RESIDUE SAMPLES

A weighed portion of the liquefaction residue sample was placed in a polyethylene beaker and just covered with reagent grade THF. The ingredients were mixed periodically until slurrying was effected. The mixture was vacuum-filtered in portions through Whatman No. 1 filter paper and rinsed several times with fresh THF. Both the filtrate and the filter cake were kept. The filter cake was air-dried and weighed and then ground in a porcelain mortar with pestle and designated the "A" fraction. The filtrate, the THF-soluble fraction, was poured out in thin layers onto Teflon-coated metal sheets and the solvent was evaporated at ambient temperature. The amorphous solid remaining was chipped from the Teflon-coated sheet, stored in a glass jar, and designated the "B" fraction.

PREPARATION OF 150°C LOW-TEMPERATURE ASH (LTA)

Whole coal samples and samples of THF-insoluble liquefaction residues were low-temperature ashed on a L.F.E. Corporation Model LTA-504 radio-frequency asher in which oxygen is passed through a radio-frequency field and an "activated" oxygen-plasma is produced. A split of 10 grams of coal sample was divided among three Pyrex boats to yield a density of sample in the boat of about 70 mg cm^{-2}. The samples were then dried in a vacuum desiccator for about 24 hours. Before ashing was begun, each chamber was washed with a 10 percent HCl solution, rinsed with acetone, and rinsed again with distilled water. A vacuum of 0.5 torr was introduced to insure dryness.

Samples were placed in the oxidation chamber and ashing was commenced at a pressure of about 1 torr, a radio-frequency power of about 35 watts per chamber, and an oxygen flow-rate of 20 cc per minute. Ashing temperature was monitored with a Raynger Model LTA-28 infrared remote thermometer, and at all times was kept below 150°C by regulation of the radio-frequency power.

Because the rate of ashing depends primarily on the proportion of surface area exposed, the samples were stirred twice a day. Each time that it was taken out to be stirred, the sample was weighed; ashing was then resumed until the next measurement showed a loss in weight of less than 10 milligrams or a gain in weight began. The sample was allowed to cool under vacuum for approximately 10 minutes prior to weighing.

The percentage of LTA was determined from the ratio of the final weight of LTA to the initial weight of dry coal by using data from three boats:

$$\frac{\text{sum of final LTA weights}}{\text{sum of initial dry coal or residue weights}} \times 100 = \%\text{LTA}.$$

ATOMIC ABSORPTION SPECTROMETRY (AA)

A Perkin-Elmer Model 306 atomic absorption spectrometer was used to determine Cd, Cu, Fe, Li, Ni, Pb, and Zn in the liquefaction feed coal and residue samples. Absorbance signals were recorded on a strip chart recorder. For all the elements except Li, non-atomic background correction was made simultaneously with a deuterium arc background corrector. Single element hollow cathode lamps were used for all seven elements except for occasional use of electrodeless discharge lamps for Cd and Pb. Table C1 lists the conditions used and the

TABLE C1 - Operating Parameters for Atomic Absorption Spectroscopy

Element	Current or Power	Wave-length (nm)	Slit (nm)	Flame oxidant/fuel	Typical Sensitivity (ppm/0.0044 Abs)	Solution Concentration Range (ppm)	Detection Limits in Ash (ppm)	Estimated Relative Standard Deviation
Cd	8ma	228.8	0.7	Air/C_2H_2	0.023	0.003 to 1.8	1.5	--
Cu	10ma	324.7	0.7	Air/C_2H_2	0.07	0.005 to 4	2.5	±6%
Fe	30ma	302.1	0.2	N_2O/C_2H_2	1.4	50 to 750	0.1	±4%
Li	15ma	670.8	1.4	Air/C_2H_2	0.04	.02 to 0.5	.003	±12%
Ni	18ma	232.0	0.2	Air/C_2H_2	0.1	0.007 to 3.5	3.5	±7%
Pb	10ma	283.3	0.7	Air/C_2H_2	0.5	0.03 to 20	15	±14%
Zn	15ma	213.9	0.7	Air/C_2H_2	0.14	0.004 to 0.8	2	±5%

TABLE C2 - Results by atomic absorption spectroscopy for seven elements in reference materials SRM-1632a and SRM-1635

Element	This Study (ppm)	SRM-1632a Certified Values (ppm)	This Study (ppm)	SRM-1635 Certified Values (ppm)
Cd	<0.76	0.17 ± 0.02	<0.16	0.03 ± 0.01
Cu	16	16.5 ± 1	3.5	3.6 ± 0.3
Fe	11400	11,100 ± 200	2500	2390 ± 50
Li	36	---	1.5	---
Ni	16	19.4 ± 1	1.4	1.74 ± 0.1
Pb	15	12.4 ± 0.6	2.7	1.9 ± 0.2
Zn	27	28 ± 2	4.8	4.7 ± 0.5

estimated relative standard deviations of the analyses. Table C2 gives results of our study for the seven elements determined by AA on the National Bureau of Standards SRM-1632a and SRC-1635 samples and the certified values for those elements for the two standards.

All reagents used were ACS reagent grade or better. Standards were prepared from high purity metals or compounds, and the standards were matrix-matched to the samples with regard to H_3BO_3, HF, and aqua regia content. All glassware and plasticware were washed with a 10 percent v/v solution of HNO_3 and rinsed several times with deionized water before being used. Approximately 0.1 gm of the ashed sample was accurately weighed and placed in a 60 mL linear polyethylene screw cap bottle. The sample was wetted with 1.0 mL of 1:1 distilled HCl, and the resulting solution was evaporated to dryness on a steam bath. The dried sample was wetted with 0.7 mL of aqua regia (1:3:1 - HNO_3:HCl:H_2O), followed by 0.5 mL of HF. The bottle was tightly capped and placed on a steam bath for at least 2 hours. The dissolved sample was removed from the steam bath and allowed to cool to ambient temperature. Then 10 mL of a solution of 50 gm H_3BO_3 per liter of deionized H_2O was added to the dissolved sample, and the resulting solution was shaken vigorously to ensure thorough mixing. The solution was transferred to a 50 mL volumetric flask, and 0.2 mL of a solution of 0.5 gm Cs per mL of H_2O was added as an ionization suppressant. The sample solution was diluted to volume with deionized water and returned to the digestion bottle for storage.

OPTICAL EMISSION SPECTROSCOPY (OE)

Preparation of Synthetic Standards for Direct-Reading and Photographic Optical Emission Spectroscopy

A set of synthetic standards was prepared for use in determining trace element concentrations of the liquefaction samples. The synthetic standard matrix was prepared using the mean values of the concentrations of major

TABLE C3 - Composition of optical emission spectroscopy synthetic standards and weights of components used

Final Std. Conc. (ppm)	Weight of Synthetic Matrix (gm)	SiO_2 Spex Time Saver Std. (mg)	SiO_2 Spex Time Saver Std. (ppm)	Al_2O_3 Spex Time Saver Std. (mg)	Al_2O_3 Spex Time Saver Std. (ppm)	Spex Mix #1000 (1.27%) (mg)	SiO_2 (mg)	Al_2O_3 (mg)
1000	.90000	--	--	--	--	79	14.5	6.5
330	.90000	--	--	--	--	26	51	23
100	.90000	69	1000	31	1000	--	--	--
33	.90000	69	333	31	333	--	--	--
10	.90000	69	100	31	100	--	--	--
3.3	.90000	69	33.3	31	33.3	--	--	--
1.0	.90000	69	10.0	31	10.0	--	--	--

elements in coal samples as determined by X-ray fluorescence spectrometry. The mean values used are:

Constituent	Concentration (%)
SiO_2	40.30
Al_2O_3	18.14
$CaCO_3$	14.59
K_2CO_3	2.20
Na_2CO_3	0.94
Fe_2O_3	23.19
MgO	0.63
	99.99

Alumina and silica "Spex Time Saver Standards" (Spex Industries, Inc., Metuchen, NJ) containing 1000, 333, 100, and 33 parts per million of 49 different elements were added to the synthetic matrix in the proportion to keep the SiO_2:Al_2O_3 ratio (2.22:1) constant. Standards were prepared containing 100, 33, 10, 3.3, and 1.0 ppm of the 49 elements. To make 1000 and 333 ppm standards, Spex Mix No. 1000, containing 1.27 percent of each of 49 elements, was used and silica and alumina in the appropriate ratio were added. The composition of each standard and the weights of the components used are given in Table C3.

To ensure homogeneity, each standard mixture was thoroughly ground in an agate mortar with pestle under absolute ethanol.

Direct-Reading Optical Emission Spectrometry (OED)

A 50 mg portion of the 500°C ash of a sample was mixed in a ratio of 1 part ash to 3 parts by weight of a 2:1:1 by weight mixture of SP-2X graphite powder, NaCl, and K_2SO_4 (salts are spectroscopically pure, from Spex Industries, Metuchen, NJ) in a 1 inch long by 1/2 inch diameter polystyrene vial containing two 1/8 inch diameter methacrylate balls. The contents of the vial were mixed for 1 minute using a Wig-L-Bug agitator. After mixing was complete, 16.5 mg portions of the sample mixture were weighed into each of four graphite electrodes for direct current arc excitation.

A d.c. anode excitation procedure was followed. After a 2 second gas flush of the arc gap, the arc is initiated at approximately 6 amperes for 10 seconds, then the current is increased to approximately 15 amperes for 52 seconds.

Standards were mixed and arced in a similar manner; one standard electrode is arced after every two sample electrodes. Periodically, single electrodes of an ash mixture of NBS SRM 1632 and an ash mixture of SRM 1633 are arced to check the accuracy for the synthetic coal ash standards.

The relative intensities of the lines of the elements from the standards are operated upon by a linear least squares regression computer routine to compute the slope and intercept of the working curve for each element and to relate relative intensity to concentration. The slopes and intercepts are then applied to the respective samples relative intensity data to calculate concentrations by weight of the various elements in a given sample.

The wavelengths used, detection limits, and average relative standard deviations are listed in Table C4. A list of operating parameters is given in Table C5.

TABLE C4 - Wavelengths, detection limits, and average relative standard deviations for elements determined by direct-reading optical emission spectroscopy

Element	Wavelength (Å)	Detection limit in 500°C ash (mg/gm)	Average relative std. deviation(%)
B	2498	1	±9
Be	2349	0.3	±15
Co	3454	0.3	±6
Cr	4254	0.6	±8
Cu	3274	0.3	±7
Ge	2651	1	±16
Mo	3170	3.3	±10
Ni	3415	0.6	±6
Sr	4607	1	±11
Sn	3034	3.0	±16
Tl	3776	0.3	±16
V	3184	3.3	±9
Zn	2139	3.3	±15
Zr	3392	3.3	±16

TABLE C5 - Operating parameters for direct-reading and photographic optical emission spectroscopic techniques

	Direct-Reading	Photographic
Instrument	Jarrell-Ash Model 750 Atomcounter .75 m direct-reading spectrometer	Jarrell-Ash 3.4 m Ebert spectrograph
Arc current (d.c.)	6-15 A. (see text)	14 A.
Arc voltage		210 V
Arc gap	6 mm	6 mm
Exposure time	62 sec.	65 sec.
Atmosphere and flow rate	80% argon, 20% oxygen @10 SCFH	80% argon, 20% oxygen @14 SCFH
Sample electrode	Nat. L-3979 thin-wall crater electrode	Nat. L-3903 crater electrode (ASTM#S-13)
Counter electrode	Nat. L-4036 pointed counter electrode (ASTM#C-1)	Nat. L-4036 pointed counter electrode (ASTM#C-1)
Electrode Charge	16.5 mg	20 mg
Entrance slit width	10 μm	10 μm
Exit slit width	50 μm	--
Photographic emulsion	--	Eastman Kodak SA-1
Photographic developer	--	Eastman Kodak D-19
Step sector	--	6 step, 2:1 step ratio

Photographic Optical Emission Spectroscopy (OEP)

Forty mg of sample was mixed with 10 mg of spectroscopically pure barium nitrate and 150 mg of National brand SP-2X graphite powder in a polystyrene vial that was

1/2 inch in diameter and 1 inch in depth, and contained two methacrylate balls, 1/8 inch in diameter. The vial was agitated in a Wig-L-Bug mixer for 1 minute. Twenty mg of the mixture was taken for the electrode charge. Analyses were made by using the operating parameters given in Table C5. The elements determined, analytical wavelengths used, and average relative standard deviations of the determinations are given in Table C6. The percent transmittance values of the spectrographic lines selected for measurement were determined by standard densitometry. Relative intensities were determined via Hurter-Driffield emulsion calibration curves by using a computerized spline function routine to fit the Hurter-Driffield curves, which spaced points every 2 percent transmittance. The working curves of relative intensity vs. concentration for each element were fitted by either first or second-degree least squares regressions or by a combination of the two.

Table C6. Wavelengths and relative standard deviations of elements determined by photographic optical emission spectroscopy

Element	Wavelength (Å)	Relative Standard deviation (%)
Be	3131	±9
Bi	--	--
Cr	2843	±16
Co	3454	±16
Cu	3274	±15
Ge	3039	±21
Pb	3683	±14
Mn	2801	±14
Ni	3493	±19
Ag	3382	±19
Sn	3034	±13
V	3118	±14
Zn	3345	±24
Zr	3392	±20

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

Approximately 1 gm of feed coal or residue, as received, was weighed into a two-fifths dram polyethylene vial and the vial was heat-sealed. The samples and standards were activated in the Advanced TRIGA Mark II reactor at the University of Illinois. The irradiation times, decay intervals, count intervals, nuclides observed, limits of detection for the elements determined, and the average error with which they were determined are shown in Table C7. Irradiation and counting times were chosen to optimize the determination of certain elements. Liquid products and THF-soluble fractions were analyzed in the same manner except that longer counting periods were used. Gamma activities of the samples were compared to those of a multielemental standard that consisted of a Whatman 41 filter paper onto which a portion of a solution containing the several elements had been spotted and evaporated. The mixed standard solution was prepared from reagent grade elements or compounds of them. In addition to the prepared standards, a sample of National Bureau of Standards SRC-1632 was occasionally analyzed to check accuracy. Results obtained on NBS-1632 for those elements that were determined by measurement of isotopes with intermediate or long half-lives and the literature values for those elements are given in Table C8. A block diagram of the counting systems used for a portion of this study is shown in Figure C1. Much of the work was performed on 10.0 percent Ge(Li) detector with a resolution that ranged from 2.2-2.8 keV/channel measured at the 1333 keV transition line of ^{60}Co. Data reduction was accomplished with the IBM 360/75 computer facilities at the University of Illinois.

Table C7 - Detection limits and nuclear properties of isotopes used for the analysis of coal.

Element	Isotope Produced	Half Life	Cross Section (barns)	Counting Period*	Major gamma-rays utilized (keV)	Limit of Detection (ppm)	Average Relative Standard Deviation %
Ag	^{110m}Ag	253 day	3.5	D	657, 937	1.0	30
As	^{76}As	26.4 hr	4.5	C	559, 657	0.2	20
Au	^{198}Au	65 hr	99	C	411	0.01	40
Ba	^{131}Ba	12 day	8.8	C, D	496, 216	30	10
Ba	^{139}Ba	83 min	0.35	A, B	166	200	20
Br	^{82}Br	35.3 hr	3.0	B, C	554, 777	0.5	15
Ce	^{141}Ce	33 day	0.6	D	145	0.5	15
Cl	^{38}Cl	37 min	0.40	A	1642	20	15
Co	^{60}Co	5.26 yr	37	D	1173, 1333	0.5	5
Cr	^{51}Cr	27.8 day	17	D	320	1	10
Cs	^{134}Cs	2.05 yr	31	D	797, 569	0.05	15
Dy	^{165}Dy	2.35 hr	700	A, B	95, 361, 633	0.1	10
Eu	^{152}Eu	9.3 hr	2800	A, B, C	122, 344, 963	0.10	5
Eu	^{152}Eu	12.5 yr	5900	D	1408	0.05	5
Fe	^{59}Fe	45 day	1.1	D	1099, 1292	200	10
Ga	^{72}Ga	14.2 hr	5.0	B, C	834, 630	0.5	15
Hf	^{181}Hf	42.5 day	10	D	481, 133	0.05	15
I	^{128}I	25 min	6.2	A	443	0.5	25
In	^{116m}In	54 min	160	B	417, 1097	0.01	30
K	^{42}K	12.4 hr	1.2	B, C	1525	30	10
La	^{140}La	40.2 hr	8.9	C	1596, 487, 329	0.1	5
Lu	^{177}Lu	6.7 day	2100	C	208	0.05	15
Mn	^{56}Mn	2.58 hr	13.3	A, B	846, 1811	0.1	5
Mo	^{99}Mo	67 hr	0.15	C	141	5.0	20
Na	^{24}Na	15 hr	0.53	A, B, C	1368	0.5	5
Ni	^{58}Co	71 day	0.2	D	810	5.0	30
Rb	^{86}Rb	18.7 day	0.7	D	1079	1.0	20
Sb	^{122}Sb	2.7 day	6.5	C	564	0.2	20
Sb	^{124}Sb	60.3 day	2.5	D	1691	0.1	10
Sc	^{46}Sc	83.8 day	13	D	889, 1120	0.01	5
Se	^{75}Se	120 day	30	D	136, 264	0.1	15
Sm	^{153}Sm	47 hr	210	C	103	0.05	5
Sr	^{87m}Sr	2.8 hr	1.3	A, B	388	5.0	10
Sr	^{85}Sr	64 day	1.0	D	514	50	20
Ta	^{182}Ta	115 day	21	D	155, 222, 1221	0.01	10
Tb	^{160}Tb	72 day	46	D	879, 1178	0.05	10
Th	^{233}Pa	27 day	7.4	D	312	0.2	10
U	^{239}Np	56 hr	2.7	C	277, 228	0.1	20
W	^{187}W	23.8 hr	38	B, C	480, 686	0.2	30
Yb	^{175}Yb	4.2 day	55	C	396, 282	0.5	25
Yb	^{169}Yb	32 day	5500	D	198, 110	0.1	10
Zn	^{65}Zn	245 day	0.5	D	1115	5.0	30
Zn	^{69}Zn	13.8 hr	0.1	B, C	439	50	25

*Counting Period	Irradiation	Flux (n.cm^{-2}• sec^{-2})	Decay Interval	Count Interval
A	15 min	2.0×10^{12}	30 min	500 sec
B	15 min	2.0×10^{12}	3 hr	4000-10,000 sec
C	2 hr	4.1×10^{12}	24 hr	4000-7000 sec
D	2 hr	4.2×10^{12}	30 day	6-10 hr

Table C8 - Comparison of data for NBS SRM 1632 selected literature values*.

Element**	This Study	NBS[d]	Ondov et al., 1975	Rowe & Steinnes, 1976	Selected Literature Values[e]
Fe(%)	.98 ± .28(12)[a]	.87 ± .03	.84 ± .04	.90 ± .01	.86 ± .05(14)[c]
K(%)	.29 ± .06(13)		.28 ± .03	.298	.29 ± .03(13)
Na	414 ± 88(13)		414 ± 20	380	379 ± 24(13)
Ag	.4 ± .3(4)	(≤.1)[b]	.06 ± .03		
As	5.9 ± .26(11)	5.9	6.5	6.5 ± 1.2	5.85 ± .6(13)
Au	.007 ± .001(3)				.001(1)
Ba	341 ± 58(12)		352 ± 30	338 ± 14	336 ± 32(140
Br	19.5 ± 1.6(12)		19.3 ± 1.9	19.5 ± .3	18.5 ± 2.1(12)
Ce	21 ± 2.6(12)		19.5 ± .1	19.5 ± .7	19.5 ± 1.1(10)
Co	6.4 ± 1.2(12)	(6)	5.7 ± .4	5.7 ± .12	5.8 ± .4(13)
Cr	22 ± 4.3(12)	20.2 ± .5	19.7 ± .9	20.8	20 ± 1.5(15)
Cs	1.85 ± .22(12)		1.4 ± 1	1.52 ± .11	1.78 ± .48(10)
Eu	.44 ± .11(13)		.33 ± .04	.30 ± .02	.33 ± .06(11)
Ga	6.0 ± 1.3(13)			5.8 ± .4	5.3 ± .5(6)
Hf	1.3 ± .3(11)		.96 ± .05	.83	.97 ± .1(11)
La	11.3 ± 1.1(13)		10.7 ± 1.2	11.4	10.9 ± 1.6(12)
Lu	.15 ± .03(12)		.14 ± .01	.11	.12 ± .01(8)
Mo	4.3 ± 1.7(10)				3 ± 1(8)
Ni	18 ± 5(12)	15 ± 1	18 ± 4	16.4	15 ± 2.3(10)
Rb	25 ± 7(12)		21 ± 2	18.3 ± 1.6	20.4 ± 2.3(12)
Sb	3.8 ± 1(11)		3.9 ± 1.3	3.0	3.6 ± 1.0(14)
Sc	4.5 ± .7(9)		3.7 ± .3	3.8 ± .05	3.8 ± .23(8)
Se	3.8 ± .7(11)	2.9 ± .3	3.4 ± .2	3.0 ± .3	3.1 ± .4(13)
Sm	2.0 ± .25(13)		1.7 ± .2	1.38 ± .10	1.5 ± .3(10)
Sr	153 ± 29(12)		161 ± 16	161 ± 9	141 ± 23(10)
Ta	.27 ± .03(12)		.24 ± .04	.27	.26 ± .05(10)
Tb	.30 ± .07(11)		.23 ± .05	.27	.29 ± .07(4)
Th	3.4 ± .4(12)	(3.0)	3.2 ± .2	3.12	3.2 ± .2(11)
U	1.6 ± .2(12)	1.4 ± .1	1.4 ± .07	1.46 ± .2	1.43 ± .26(12)
W	.76 ± .15(12)		.75 ± .17	.79 ± .17	.76 ± .08(6)
Yb	.85 ± .12(11)		.7 ± .1	.84	.77 ± .12(9)
Zn	37 ± 9(10)	37 ± 4	30 ± 10	37 ± 6	35 ± 3.3(12)

(*) Date from counts C and D only - see Table C7.

(**) Parts per million unless otherwise indicated.

(a) Numbers in parentheses in this column indicate number of determinations.

(b) Numbers in parentheses in this column are informational values.

(c) Number in parentheses in this column are number of laboratory averages used.

(d) National Bureau of Standards certified values.

(e) The selected literature values are as follows: NBS certified values; Ondov et al., 1975; Rowe and Steinnes, 1976; Chattopadhyay and Jervis, 1974; Millard and Swanson, 1975; Maenhaut and Zoller, 1976; Hancock, 1976; Klein et al., 1975; Simms, Rickey, and Mueller, 1976; Sheibley, 1974; Nadkarni, 1975; Ruch, Gluskoter, and Shimp, 1974; Ruch et al., 1975; and Nadkarni and Morrison, 1974.

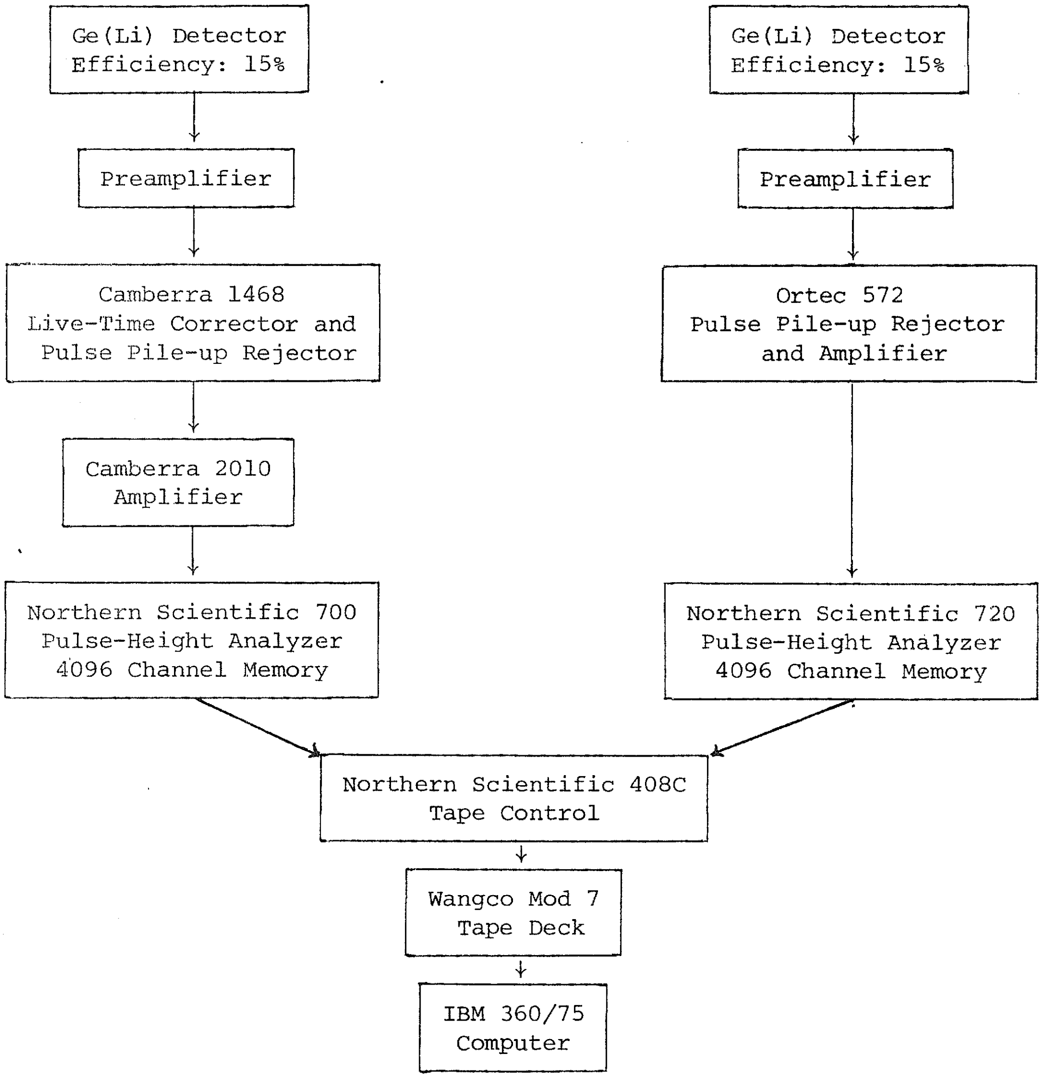


Figure Cl. Block Diagram of INAA System.

NEUTRON ACTIVATION ANALYSIS WITH RADIOCHEMICAL SEPARATIONS (NAA-RC)

Determination of Platinum, Palladium, and Gold

The levels of concentration of some noble metals in residues from the coal liquefaction processes were determined. Gold could be detected in some of the feed coals and resultant residues by instrumental neutron activation analysis. A radiochemical procedure was developed for the determinations of palladium and platinum in the ashes of the coal and residue samples. Since gold follows the other noble metals in a radiochemical separation, it was determined as well.

The project first used low-temperature ashes of the coal samples. It was found that, despite many various attempts to purify the platinum separated, the 77 keV γ-ray peak of ^{197}pt ($t_{\frac{1}{2}}$=19 hr.) was swamped by 77 keV γ-ray activity from 65 hr ^{197}Hg. This activity indicated the presence of a larger percentage of mercury than had been present in the coal sample that was ashed. We determined that the low-temperature coal ash samples were contaminated with mercury from a source in the low-temperature ashing laboratory. The source of contamination was removed, but, in the meantime, the project for the determination of the noble metals used 500°C coal ash samples.

The procedure was adapted from the work of Nadkarni and Morrison (1974) on the determination of noble metals in geological materials, and of Govaerts, Gijbels, and Hoste (1975) on the determination of noble metals in copper by neutron activation analysis.

For each experimental run, two or three samples (0.2 to 0.25 gm of 500°C ash) of palladium, platinum, and gold standards were irradiated in the University of Illinois Advanced TRIGA reactor for 2 hours at a flux of 2.7 x 10^{12} thermal neutrons cm^{-2} sec^{-1}. Samples were sealed in cleaned two-fifths dram polyethylene snap-cap vials. The palladium and platinum mixed standard was 700 μL containing 80.7 μg/mL of Pd as $(NH_4)_2PdCl_4$ and 88.9 μg/mL of Pt as $(NH_4)_2PtCl_6$ in 1N HCl solution, sealed in a quartz ampoule. The gold standard was 250 μL of solution containing 1.18 mg/mL of Au as $AuCl_3$ in ∿2N HCl, sealed in a polyethylene vial.

After a decay period of 24 hours, the sample was transferred to a nickel crucible in which 1 mL of carrier solution (21 mg Pd, 22 mg Pt, and 1.7 mg Au) had been evaporated. Sodium hydroxide (2 gm) and 3 gm of sodium peroxide were added, and the mixture fused at red heat for about 10 minutes.

The crucible was cooled in ice. The melt was loosened and poured into a beaker with 75 mL of water, and the crucible was rinsed with 8N HCl. The slurry was acidified with 8N HCl and heated almost to boiling, until a clear green or yellow-green solution was obtained. Distilled water was then added to increase the volume to 300 to 350 mL, to decrease the acidity to about pH 2, and to ensure that silica would remain in solution. A few grams of zinc powder were added to the warm solution to give a rapid precipitation of the noble metals. Hydrochloric acid was added to dissolve the excess zinc. The precipitate was separated by vacuum filtering onto a Millipore filter (0.45 μm type HA filter, 47 mm in diameter) and dissolved in a few mL of aqua regia. To remove the nitric acid, 10 mL of concentrated HCl was added and the solution boiled to near dryness. This step was repeated. The small amount of solution remaining was taken up in 40 mL of 1N HCl. Gold was extracted with three 20 mL portions of ethyl acetate; the organic fraction was collected in a 100 mL glass bottle for γ-ray counting. The aqueous solution remaining was heated to evaporate traces of ethyl acetate, then cooled in an ice bath, and 3 mL of a 1 percent solution of dimethylglyoxime in ethanol was added. After 30 minutes the precipitate of palladium dimethylglyoximate was filtered off onto a tared Millipore filter, rinsed with 0.01 N HCl, and finally with hot water. A cardboard backing supported the filter membrane when its radioactivity was counted.

The filtrate remaining was heated to 80°C on a hot plate, and 5 gm of ammonium chloride was added. The mixture was heated until ammonium chloride began to crystallize. The cooled mixture was vacuum filtered to collect the ammonium hexachloroplatinate on a tared Millipore filter. The precipitate was washed with 0.25 N NH_4Cl solution, then again with a very small amount of water. The filter membrane was mounted onto a labelled cardboard holder for γ-ray counting.

Fifty μL of the irradiated gold standard was diluted 200 times in a volumetric flask. Aliquots of the gold dilution and of the irradiated palladium and platinum standard were diluted together 20 times in a volumetric flask. To 250 μL of this mixed dilute standard (1.01 μg Pd, 1.11 μg Pt, and 0.0735 μg Au) was added 1 mL of mixed carrier and sufficient 1N HCl to give 40 mL of solution.

The noble metal separations were carried out on this solution as they were on the samples and began with the ethyl acetate extraction of gold.

The detector was a 3 x 3 inch NaI (Tl) crystal connected to a Nuclear-Chicago 400 channel pulse-height analyzer, equipped with a printer and a plotter for read-out of data.

Palladium was measured on the same day that the radiochemical work was done, *via* the 22.2 keV X-ray of ^{109m}Ag ($T_{1/2}$=40 sec.) produced in the decay of ^{109}Pd ($t_{1/2}$=13.5 hr.); and platinum *via* the 77 keV gold X-ray produced in the decay of ^{197}Pt ($t_{1/2}$=19 hr.) in the ammonium hexachoroplatinate precipitate. Gold was easily measured *via* the 412 keV γ-ray of ^{198}Au ($t_{1/2}$=64.8 hr.) and also in the ethyl acetate fraction's ^{199}Au ($t_{1/2}$=3.15 days) produced by β-decay of ^{199}Pt ($t_{1/2}$=30 min.). However, the strongest peak, that from the 158 keV γ-ray of ^{199}Au, was not large enough to be reliably seen and measured above the high background in the region of the gold; so platinum could not be measured *via* its gold daughter.

The radiochemical yields of palladium and platinum were determined from the weight of the air-dried precipitates of palladium dimethylglyoximate and ammonium hexachloroplatinate, respectively. The chemical yield of gold was determined by reactivation of an aliquot (evaporated in a two-fifths dram polyethylene vial) of the ethyl acetate solution. Yields were typically 60 to 85 percent for platinum, and 55 to 75 percent for gold.

The accuracy of the method was checked using the platinum ore reference material SARM 7 of South Africa and the rock standard W-1 of the U.S. Geological Survey. These results are shown in Table C9. Accurate results were obtained on SARM 7 which contains the noble metals at the ppm level of concentration. W-1 and the ash samples of the coals and coal liquefaction residues contain palladium, platinum, and gold at the ppb level of concentration. In these samples, adequate

Table C9 - Concentrations of palladium, platinum and gold in geological reference materials.

	Palladium		Platinum		Gold	
	Found*	Lit. Value	Found*	Lit. Value	Found*	Lit. Value
W-1 (ppb)	12 ± 8(4)	25(1), 16 ± 2(2) 11.5 ± 0.3(3) 17.7 ± 0.4(4)	49 ± 12(4)	12(1), 17 ± 3(2) 16, 22(6) 17.0 ± 0.3(4)	4.7 ± 2.2(4)	3.7(1), 4.6 ± 0.7(2) 5.8 ± 0.2(3) 4.7 ± 0.5(4)
SARM 7 (ppm)	1.82 ± .31(10)	1.53 ± .032(5)	3.93 ± .49(6)	3.74 ± .045(5)	.32 ± .13(12)	0.31 ± .015(5)
NBS 1632 (ppb)	6.2 ± 3.5(3)		10, <340	186 ± 2.3(7) 270 ± 20(9)	2.1 ± .4(3)	0.99 ± 0.16(7) 146(8) 0.85 ± 0.03(9) 200(11)
NBS 1633 (ppb)	--		<150, <60	451 ± 11(7) 1380 ± 280(9)	48.11	4.84 ± 0.13(7) 2.75 ± 0.2(9) 8 ± 2(10) 1700(11)

*Number in brackets is the number of determinations.

1 Flanagan, 1974
2 Nadkarni and Morrison, 1974
3 Crockett, Keays, and Hsieh, 1968
4 Ahmad, Ahmad, and Morris, 1977
5 Steele, Levin, and Copelowitz, 1975
6 Haffty and Riley, 1968
7 Nadkarni and Morrison, 1976
8 Sheibley, 1975
9 Nadkarni, 1978
10 Chattopadhyay, 1976
11 Weaver, 1978

counting statistics, accuracy, and precision were obtained for gold. The method was not always sufficiently sensitive to determine palladium—for some samples counting statistics were so low that only a limit of detection could be given. Platinum was the element least satisfactorily determined. In every sample there was interference from mercury such that sharp peaks with the proper half-life could not be obtained for platinum in the samples. Counting the samples on 2 successive days and subtracting a peak area for mercury interference did not give a very accurate or precise value for platinum; so nearly all of the platinum values on the coals and liquefaction residues are reported at their detection limits.

Determination of Rare Earth Elements and Yttrium in the Ash of Coals and Their Residues from Liquefaction Processes.

Several of the rare earth elements were determined on coals and their residues from liquefaction processes by instrumental neutron activation analysis. Not determined, but considered to be important, were erbium, holmium, thulium and the related element yttrium. Erbium, holmium, and thulium can be determined in most geologic materials by thermal neutron activation analysis and Ge (Li) spectrometry, if the rare earth element group is separated and analyzed. No suitable isotope exists for gamma-ray measurement of yttrium but ^{90}Y can be beta-counted if yttrium is separated from the rare earth elements.

Numerous reports in the literature describe group separations of the rare earth elements and yttrium from geologic materials, either before (Abdel-Rassoul, Herpers, and Herr, 1971; Zielinski, 1975; Randa, 1976) or after (Graver, Lukens, and MacKenzie, 1970; Rey, Wakita, and Schmitt, 1970; Denechaud, Helmke, and Haskin, 1970; Brunfelt, Roelandts, and, Steinnes, 1974; Porritt and Porritt, 1977) thermal neutron irradiation. Rocks and other geologic materials are commonly brought into solution by means of an alkaline fusion (Abdel-Rassoul, Herpers, and Herr, 1971; Randa, 1976; Graber, Lukens, and MacKenzie, 1970; Rey, Wakita, and Schmitt, 1970; Denechaud, Helmke, and Haskin, 1970; Frunfelt, Roelandts, and Steinnes, 1974; Porritt and Porritt, 1977), though treatment with hydrofluoric and perchloric acids is sometime employed (Zielinski, 1975). Separation of the group of rare earth elements is usually accomplished by one or more precipitations as hydroxides, fluorides, and oxalates, with separation by ion-exchange sometimes included (Abdel-Rassoul, Herpers, and Herr, 1971; Zielinski, 1975; Rey, Wakita, and Schmitt, 1970; Brunfelt, Roelandts, and Steinnes, 1974). Some schemes include special steps for the removal of silica, iron, and scandium.

In the radiochemical procedure adapted from the above literature for this work, ash samples (usually 500°C ash, although a few low temperature ash samples were analyzed) were fused with sodium hydroxide and sodium peroxide, the rare earth elements, and yttrium separated by precipitations of their hydroxides and fluorides, with lanthanum as carrier. The ash of the coals and liquefaction process residues were used because the ash, unlike coals, can be quickly brought into solution. The adapted procedure produced a rare earth element group pure enough for analysis by Ge (Li) spectrometry; also the procedure was short enough that the samples could be measured on the same day as the radiochemical separation was made for the gamma-ray activity of 7.52 hr ^{171}Er.

Thirteen rare earth elements (i.e., all the stable rare earth elements except dysprosium) were determined on the separated rare earth element group precipitate. Accuracy and precision of measurement were better than those obtained in the instrumental neutron activation determination of lanthanum, cerium, samarium, europium, terbrium, ytterbrium and lutetium, and were much better for the latter three elements. Because a rapid radiochemical procedure was necessary, separation of yttrium from the rare earth elements was not attempted. The group precipitate provided a simple matrix, concentrated in yttrium,

Table C10. Nuclear and Counting Data for Radiochemical Determination of Rare Earth Elements.

Element	Product Nuclide	Half-life of Product	γ-rays (keV) Measured	Count No.	Amount (μg) of Element in 200 μl of Std.
La	^{140}La	40.2 h	1596.2, 487.0, 328.7	1	13.89
Ce	^{143}Ce	32.88 h	293.2	1	30.92
	^{141}Ce	32.5 d	145.4	2	
Pr	^{142}Pr	19.2 h	1575.4	1	4.904
Nd	^{147}Nd	11.1 d	531, 91.1	2	56.83
Sm	^{153}Sm	47 h	103.2, 69.7	1	5.429
Eu	^{152m}Eu	9.2 h	121.8, 963.1, 841.8, 344.3	1	1.155
	^{152}Eu	12.4 y	1408.1, 779.1, 1086.0, 121.8, 344.3	2	
Gd	^{159}Gd	18 h	363.3	1	2.435
	^{153}Gd	242 d	103.2, 97.4	2	
Tb	^{160}Tb	72.1 d	879.3, 1178.1, 86.7	2	2.774
Ho	^{166}Ho	26.9 h	80.6, 1379.4	1	4.906
Er	^{171}Er	7.52 h	308.2, 295.9	1	18.33
Tm	^{170}Tm	127 d	84.3	2	5.338
Yb	^{175}Yb	4.2 d	396.1, 282.6	1,2	5.483
	^{169}Yb	32 d	177.0, 197.9, 307.7	2	
Lu	^{177}Lu	6.74 d	208.4	1,2	2.781
Sc					4.639
Y					31.79
Dy					4.867

that could be conveniently measured therein by energy-dispersive X-ray fluorescence spectroscopy.

Experimental procedures

Standards. A cerium standard was made by dissolving ceric ammonium nitrate in dilute sulfuric acid, to give a concentration of 30.9 μg Ce/200 μL. Dilute nitric acid stock solutions of the other rare earth elements, scandium, and yttrium were prepared from spectroscopically pure oxides, and a mixed standard, in dilute nitric acid, was prepared from the stock solutions, such that in 200 μL there was the amount of each element listed in Table C10. The amounts selected were the average amounts expected in the coal ash samples for the weight taken. Dysprosium, although not measured, was included because it is separated with the rest of the rare earth elements. Scandium was included because it follows the rare earth elements in the radiochemical separation; though it does not follow quantitatively, the 889.2 keV and 1120.5 keV peaks of ^{46}Sc were major peaks in the spectra of all samples and standards.

Irradiation. Three weighed samples (0.25 g of ash, 0.2 g of the reference standards BCR-1, AGV-1 or IAEA Soil 5) were heat-sealed in cleaned two-fifths dram polyethylene snap-cap vials. One-half mL of the cerium standard and one-half mL of the mixed rare earth element standard were also sealed in polyethylene vials. Samples and standards were irradiated in the Univeristy of Illinois Advanced TRIGA reactor for 2 hours at a thermal neutron flux of 1.4×10^{12} n cm^{-2} sec^{-1}. The vials were placed in a rotary specimen assembly that rotated at 1 rpm during irradiation to ensure equal neutron flux for all specimens. Samples and standards were allowed to decay for 24 hours before radiochemical work was begun.

Radiochemical group separation of the rare earth elements and yttrium. Each irradiated sample was transferred to a nickel crucible. Lanthanum carrier (0.5 mL, 10.2 mg La^{+++}) was added and the mixture evaporated to dryness on a hot plate. The mixture was then fused for 10 minutes at red heat with 2 gm of sodium hydroxide and 3 gm of sodium peroxide. The fusion cake was taken up in water. The mixture was acidified with concentrated hydrochloric acid and heated until a clear yellow solution was obtained.

Concentrated ammonium hydroxide was added to bring the pH range to 9 to 10 to precipitate lanthanum and the other rare earth element hydroxides. The mixture was centrifuged and the supernatant discarded. The precipitate was rinsed two or three times with water containing a small amount of ammonium hydroxide, each time followed by centrifugation and discard of the supernatant.

The precipitate was dissolved in 3 to 5 mL of concentrated hydrochloric acid, and 5 mL of concentrated hydrofluoric acid was added. The mixture in the centrifuge tube was heated gently to obtain a good digested precipitate of the rare earth element fluorides. The mixture was centrifuged and the supernatant discarded. Twice the precipitate was washed with 25 ml portions of water containing a drop or two of concentrated HF, the mixture was centrifuged, and the supernatant was discarded.

The fluoride precipitate was dissolved in 15 mL of 6 M HNO_3 containing 0.225 g of dissolved H_3BO_3. The hydroxide, fluoride, and hydroxide precipitation steps were repeated; a minimum of washing of the precipitates was included. To the final centrifuged hydroxide precipitate a few ml of water were added to make a slurry. This was vacuum-filtered onto a tared Millipore filter. The filter paper was placed on a stiff cardboard support for gamma-ray activity measurements.

Later, when the precipitate had completely air-dried, it was weighed to obtain an estimate of radiochemical yield or evidence of efficiency of separation of the rare earth elements from silica and alumina. The group separation of the rare earth elements from silica and alumina proved to be excellent; iron was not detected in the spectra.

Treatment of the Standard. Lanthanum carrier (0.5 mL) was put in a beaker and diluted to about 10 mL with 1 N HCl. Two hundred µL of the irradiated cerium standard and 200 µL of the irradiated mixed rare earth element standard were added; the solution was stirred and allowed to stand for 5 to 10 min. Concentrated ammonium hydroxide was added to take the pH range to 9 to 10. The mixture was allowed to stand for 15 minutes; the hydroxide precipitate was filtered onto a tared Millipore filter that was then mounted for gamma-ray counting.

Determination of radiochemical yield. After all measurements had been made, the filter papers, and their precipitates of samples and standards, and a theoretical lanthanum carrier sample, deposited on a Millipore filter, were sealed in 2 dram cleaned polyethylene vials and irradiated for 5 min at a flux of 0.7 x 10^{12} thermal n cm^{-2} sec^{-1}. After a decay period of a few days, the radiochemical yield of lanthanum was determined from the 1596 keV gamma-ray of ^{40}La, measured on a NaI(Tl) detector. Radiochemical yields were generally above 90 percent for the standard and 65 to 90 percent for the samples.

Measurements of the rare earth elements and yttrium

Most of the γ-ray counting was done on a Ge(Li) coaxial detector of 75.7 cm^3 active volume, a measured resolution of 1.05 keV (FWHM) at 122.1 keV, 2.0 keV (FWHM) at 1332 keV, and an efficiency of 17.6 percent and peak/Compton ratio of 48 at 1332 keV. During a four-week period that this detector was not available, counting was done on a Ge(Li) detector with volume 55 cm^3, a measured resolution of 1.10 keV (FWHM) at 122.1 keV, and 1.9 keV (FWHM) at 1332 keV, and an efficiency of 14.5 percent and peak/Compton ratio of 42 at the latter energy. Unfortunately the resolution of the latter detector was erratic during this period—it degraded at times by 10 to 20 percent. This led to imprecision in peak areas, particularly at the low energy end of the gamma-ray spectrum.

Each detector is coupled via a pre-amplifier, amplifier, and live-time corrector and pulse-pile-up rejector unit to a 4096 channel analyzer. Data are fed to a magnetic tape and analyzed by a computer reduction program, as outlined in the description of instrumental neutron activation analysis.

The samples and standard in a set were counted on the day after irradiation, immediately following radiochemical separation, for 6,000 to 8,000 seconds. About 15 days later they were counted for 30,000 to 40,000 seconds to measure the activity of long-lived isotopes.

Between the Ge (Li) spectrometry measurements the rare earth element hydroxide precipitates of samples and standard on the Millipore filter papers were analyzed for yttrium content by energy-dispersive X-ray fluorescence spectroscopy with the apparatus described for that method. A tin secondary target was used in the measurement of the 14.93 keV Kα X-ray lines of yttrium.

It became apparent that the results for yttrium were inconsistent because the geometry of the sample presented for counting was too variable—the precipitates were not uniformly and evenly deposited on the filter papers.

Better determination of yttrium was attempted by using samples of the whole coals and the liquefaction process residues and the 500°C ash of these coals and residues. Measurements were made as described in the section on determination of elements by energy-dispersive X-ray fluorescence spectroscopy. For use in the analysis of the coals, two standards with concentrations 10 and 50 ppm yttrium were prepared by addition of an appropriate amount of a synthetic rare earth standard mix (Spex Industries Inc.) to a weighed amount of a mineral-matter-free coal (a coal sample from which the mineral matter had been removed by sequential treatment with nitric, hydrofluoric and hydrochloric acids). Yttrium was not detected in the mineral-matter-free coal by energy-dispersive X-ray fluorescence spectroscopy, and it was run as a blank in the analyses. For standards for the analysis of the 500°C ash samples, amounts of the synthetic rare earth standard mix were added to portions of a synthetic coal ash matrix standard prepared for use in optical emission spectroscopy, to give mixtures containing 33 and 100 ppm yttrium. A correction for interference from rubidium was made in the analyses of both the coal samples and the coal-ash samples.

Discussion of γ-ray measurement of the samples

Table C10 lists the radionuclides and their γ-ray lines measured on the separated rare earth element precipitates. Some comments are in order concerning the accuracy and precision of the γ-ray measurements.

Lanthanum. Agreement of results obtained from the three photopeaks of lanthanum was excellent. An average relative standard deviation of the results was about 0.6 percent.

Cerium. Results from ^{143}Ce for the reference standards analyzed were high and variable. The area from the 145.4 keV photopeak of ^{141}Ce was used in the calculation of the cerium concentrations reported.

Praseodymium. Counting statistics were good for the 1575.4 keV line.

Neodymium. Results from the 531 and 91.1 keV lines of ^{147}Nd agreed satisfactorily (within 10 percent in nearly all cases and usually within 5 percent). The concentration obtained from the 531 keV photopeak is considered the more reliable as the 91.1 keV photopeak was usually analyzed as one peak of a doublet, and sometimes of a triplet.

Samarium. The two peaks of ^{153}Sm measured gave concentration values in excellent agreement.

Europium. Results from the four measured γ-ray lines of ^{152m}Eu agreed well. Occasionally the peak for the 963.1 keV γ-ray occurred as part of a doublet, giving a result differing significantly from the other three. Similarly, if the 1086.0 keV or the 121.8 keV photopeak of ^{152}Eu occurred in a doublet, the concentration calculated would vary significantly from the results from the other four lines. Usually, however, the five lines gave results that agreed well. The concentration obtained from ^{152m}Eu was usually slightly higher than that obtained from ^{152}Eu, an effect thought to be associated with dead-time error. Because the results from ^{152}Eu agreed best with the literature values for the reference standards analyzed, it is the result by ^{152}Eu that is reported.

Gadolinium. Sufficient ^{153}Sm remained in the samples and standard, when they were counted for the longer-lived isotopes, and interfered with the 103.2 keV line of ^{153}Gd, to cause low results. Results from ^{159}Gd and the 97.4 keV line of ^{153}Gd usually agreed satisfactorily; when they did not, the result from the 97.4 keV line was used because of the better counting statistics for that photopeak.

Terbium. The concentrations calculated from the areas of the 879.3 and 1178.1 keV photopeaks of ^{160}Tb agreed well. The 86.7 keV photopeak (usually part of a doublet) usually gave a somewhat higher result and in such cases was not used in calculating the concentration value reported.

Holmium. If sufficient holmium was present in a sample to give reasonable counting statistics for the 1379.4 keV line of ^{166}Ho, the concentration calculated would agree satisfactorily with that from the 80.6 keV peak. Otherwise, the result reported is from the 80.6 keV photopeak only.

Erbium. Neither of the 308.2 and 295.9 keV photopeaks of ^{171}Er is very good for determination of the concentration of erbium. Both are relatively weak lines. The 295.9 keV peak was often not completely separated from the 293.2 keV peak of ^{143}Ce and sometimes did not have satisfactory counting statistics. The concentration value obtained from the larger 308.2 keV peak is reported; the uncertainty in a value is usually 20 percent or more.

Thulium. Only the 84.3 keV peak of ^{170}Tm exists for the γ-ray measurement of thulium in thermal neutron activation analysis. The peak is in a crowded region of the spectrum, even for the relatively clean spectrum of the separated rare earth element group. The detectors used had quite good resolution in this region but even so the 84.3 keV photopeak was not completely resolved and was usually a doublet with the 86.7 keV peak of ^{160}Tb, and occasionally the 84.3 and 86.7 keV photopeaks; the 91.1 keV photopeak of ^{147}Nd appeared as a triplet. Multiplets are not analyzed well by the computer reduction program. The area for the ^{170}Tm peak in all spectra was corrected for the scattered background contribution from the 85 keV X-ray of lead, as determined from several background spectra. Because of these errors associated with the measurement of the 84.3 keV peak, the values reported for thulium are not considered too accurate or precise (average relative standard deviation of 25 percent, and may be low, particularly at low thulium concentrations, for then the correction for the lead X-ray was a large fraction of a small area ill-defined from the 86.7 keV photopeak of ^{160}Tb.

Ytterbium. Reported values are the average of the concentrations obtained from the 396.1 and 282.6 keV photopeaks of ^{175}Yb, counted some 15 days after irradiation. The two results usually agreed closely; their average agreed with the literature values for the analyzed reference standards BCR-1, AGV-1 and IAEA Soil 5 (Table C11). The 396.1 and 282.6 keV peaks were observed in the first count of the samples, but because of the greater number of peaks and the higher background in that spectrum the statistical uncertainties in the peaks were greater and the agreement between them less. The average of the results from the 177.0, 197.9 and 307.7 keV photopeaks of ^{169}Yb was usually

Table C11. Results in ppm of the Radiochemical Determination of Rare Earth Elements and Yttrium in Reference Standards.

	BCR-1		AGV-1		IAEA Soil 5	
	This Work[a]	Lit.[b]	This Work	Lit.[b]	This Work	Lit.[c]
La	31.1 ± 2.5(5)	(26)	45 ± 3 (2)	(35)	31.9 ± .3 (4)	28.1 ± 1.5
Ce	53.6 ± 1.6(5)	53.9	74.7 ± 5.2(3)	63	58.2 ± 1.4 (4)	59.7 ± 3.0
Pr	7.6 ± .8 (5)	(7)	9.1 ± 1.3(3)	(7)	7.38 ±.38 (4)	(6.9, 3.0)
Nd	34.6 ± 2.4(3)	29	39.6 ± 1.5(4)	39	32.1 ± 1.3 (4)	29.9 ± 1.6
Sm	6.83 ± .17(3)	6.6	6.10 ± .37(3)	5.9	5.65 ± .05 (4)	5.42 ± .39
Eu	1.96 ± .08(5)	1.94	1.68 ± .06(4)	1.7	1.17 ± .05 (4)	1.18 ± .08
Gd	6.5 ± 1.7(3)	6.6	4.8 ± 2.2(3)	(5.5)	4.2 ±.36 (4)	(5.0, 64.8)
Tb	1.02 ± .05(5)	1.0	.66 ± .04(5)	.70	.67 ± .01 (4)	.665 ± .075
Ho	1.26 ± .04(3)	(1.2)	.68 ± .03(3)	(.6)	.81 ± .06 (4)	(.75, .88)
Er	4.00 ± .29(5)	3.59	2.0 ± .29(3)	(1.2)	2.3 ± .97 (4)	2.2[d]
Tm	.51 ± .29(5)	.6	.18 ± .01(3)	(.4)	.29 ±.05 (4)	(.34, .495)
Yb	3.27 ± .13(5)	3.36	1.66 ± .06(5)	1.7	2.14 ± .05 (4)	2.24 ± .20
Lu	.50 ± .02(5)	.55	.27 ± .03(3)	.28	.34 ± .02 (4)	.34 ± .04
Y[e]	47 ± 14 (5)	37.1	22.4 ± 2.9(4)	21.3	25.3 ± 5.9 (4)	(21 ± 7)

a. Values are the mean and standard deviation based on the number of determinations given in parenthesis.

b. Literature values are from Flanagan (1976). Values are recommended, averages, or (value of magnitude only).

c. Literature values are from Dybczyński, Tugsavul, and Suschny (1978). The reported uncertainties are confidence levels of the mean for a significance level of $\alpha = 0.05$. Values in parenthesis for praseodymium, gadolinium, holmium and thulium were the only result reported for those elements. The literature value for yttrium is the mean and standard deviation of the results reported.

d. Value from Laul, Nielson, and Wogman (1977).

e. The yttrium values are from determinations on the radiochemically--separated rare earth element fraction precipitates.

significantly lower than the reported result from ^{175}Yb. One or another of the peak areas was often discrepant; this indicated interference from the 197.0 keV line of ^{160}Tb, the 309.6 keV line of ^{160}Tb, or possibly the 177.0 keV peak of ^{177m}Lu.

Lutetium. The 208.4 keV peak of ^{177}Lu was evident in both counts 1 and 2, but the statistical uncertainty was lower for the peak in count 2, and the concentration determined from count 2 gave better agreement with the literature values for lutetium in BCR-1, AGV-1 and IAEA Soil 5. The lutetium concentration reported is that determined in a sample from count 2 on the 208.4 keV peak of ^{177}Lu.

Based on the results obtained for the three reference standards as listed in Table C11 and on the results of duplicate analyses of eight coals and liquefaction process residues, calculations of determinations of the rare earth elements in the present work are made with a precision of measurement and are expressed as average relative standard deviation: La, 6%; Ce, 4%; Pr, 8%; Nd, 5%; Sm, 4%; Eu, 4%; Gd, 25%; Tb, 5%; Ho, 6%; Er, 20%; Tm, 25%; Yb, 4%; and Lu, 6%.

Discussion of the energy-dispersive X-ray fluorescence spectroscopy measurement of yttrium

The results for yttrium from analysis of the precipitate of rare earth element group, as illustrated by the results for BCR-1, AGV-1, and IAEA Soil 5, are reasonably accurate, but have a precision, expressed as average relative standard deviation, of only about 25 percent. The lack of precision is due to the lack of uniformity of deposition of the rare earth hydroxide precipitates on the filter papers, as stated.

No good reference standards were available to check the accuracy of the analyses of the whole coals and residues and their 500°C ashes for yttrium. The determination of yttrium in coal ash gave results of satisfactory precision that generally agreed satisfactorily with those from the rare earth element fraction precipitates. The whole coal or liquefaction process samples gave results that were generally lower than those by the other two measurements. The determination of yttrium in a whole coal is not a sensitive measurement because of the low concentration of the yttrium.

The yttrium values listed in the table of analytical results for the coal liquefaction project are those from the determinations considered most reliable. Usually they are the results from analysis of the activated rare earth element precipitates, the result from analysis of the 500°C ash, or an average of the two. In a few cases the results from analysis of the whole coal or liquefaction process sample appeared to be the most reliable.

Discussion of results for rare earth elements and yttrium in coals and coal liquefaction process samples

The results are presented in the complete table of analytical data. The results from the radiochemical separation procedure on low temperature ash samples agree, within experimental error, with the results from determinations made on 500°C ash samples. Moreover results, by the radiochemical separation procedure and by instrumental neutron activation analysis, for the seven elements (La, Ce, Sm, Eu, Tb, Yb, Lu) determined by the two methods show no consistent differences that would indicate these elements are lost in ashing of coal. Therefore, it is believed that determination of the rare earth elements on the ashed samples gives a valid estimate of their concentrations in the whole coal sample.

The significance of the results of the study of the rare earth elements in coal samples and liquefaction residues is discussed in Appendix L.

DETERMINATION OF MERCURY

From 0.6 to 1.0 gm of feed coal, liquefaction residue, or product sample is accurately weighed into a two-fifths dram polyethylene snap-cap vial. A 1 mL aliquot of a 10.04 mg/mL standard solution of Hg^{+2} (as nitrate) is sealed in a similar polyethylene vial. Samples and standard are simultaneously irradiated for 2 hours in the University of Illinois Advanced TRIGA reactor at the flux of $1.4 \times 10^{12} n \cdot cm^{-2}\ sec^{-1}$. One day is allowed for radiation levels to decrease by the preferential decay of shorter-lived radioisotopes such as ^{24}Na, ^{31}Si, and ^{56}Mn, to permit the safe handling of the samples.

A method modified from that of Rook, Gills, and LaFleur (1971) is used to determine mercury. Each sample is mixed 1:1 with 60-mesh Norton Alundum RR (Al_2O_3), transferred to a 4-inch porcelain boat (Fisher Combax, size A), and covered with Alundum. The boat, previously impregnated with 2 mg Hg^{+2} carrier, is placed in a 1-inch diameter Vycor tube and the contents then combusted slowly in a tube furnace at 900° to 1000°C. An oxygen or air flow of about 50 to 75 mL per minute is maintained through the tube. The gaseous and volatilized products are collected in a cold trap that is cooled by dry ice/acetone mixture. The combustion process requires several hours to ensure controlled burning and efficient transfer of volatile products to the trap. (CAUTION: The use of oxygen as an oxidant is not recommended for liquefaction product samples because of their highly volatile nature. All samples should be burned very gradually; THERE IS DANGER OF VIOLENT EXPLOSION.) After combustion of the sample is complete, the cold trap is warmed to room temperature and the mercury is washed out with dilute HNO_3. The solution is heated to 80°C, and the ^{82}Br interference is removed by precipitation of AgBr while the more soluble $HgBr_2$ remains in solution. The Hg^{++} solution is decanted, and the 77 keV γ-ray activity that is due to Hg is counted with a NaI(Tl) detector. The mercury standard is treated identically to the samples. Radiochemical yields are determined by re-irradiation and range from 50 to 90 percent. The average relative standard deviation is 15 percent, and the detection limit is 0.005 ppm for a 1 gram sample and 2 hour irradiation. Analyses of NBS SRM-1632 standard coal using this method gave a Hg value of 0.13 ± 03 and is in excellent agreement with the certified value (0.13±02 ppm).

Wavelength-Dispersive X-ray Fluorescence Analysis (XRF)

The wave-length dispersive X-ray equipment consists of a Phillips' vacuum spectrometer equipped with a Mark I electronics panel and a chromium target X-ray tube. X-ray fluorescence analyses were done on the 500°C ashes of the residues and products for P, Mg, K, Ca, Fe, Ti, Al, and Si. Determinations of the same eight elements were also made on the whole coal samples and unashed residues and products when insufficient ash was available for analysis.

Because the matrix inference problems presented by coal ash are like those of rocks, the dilution technique of Rose, Adler, and Flanagan (1962), developed primarily for silicate rock samples, was used to analyze coal ash samples.

A 125 mg aliquot of dried 500°C ash sample was weighed into a graphite crucible containing 1.000 gm of lithium tetraborate. A depression made in the lithium tetraborate prior to addition of the ash sample prevented contact of the sample with the crucible wall. Next, 125 mg of lanthanum oxide was added as a heavy-element absorber, and the contents of the crucible were mixed as thoroughly as possible with a glass stirring rod, without scraping the crucible bottom or wall. The mixture was fused in a furnace for 15 minutes at 1000°C, removed, covered with a second crucible, and allowed to cool to room temperature. The resulting pellet was weighed to determine loss of weight on fusion and was placed in the tungsten carbide grinding vial of a No. 6 Wig-L-Bug with 2 percent by weight of Somar mix (a commercial grinding and plasticizing agent). The sample was ground for 3 minutes, transferred to a die, and pressed into a disk at 40,000 psi. When backed with a layer of pressed Somar mix, the pressed disk was semi-permanent and was used for the quantitative determination of major and minor elements by X-ray analysis. Table C12 demonstrates the accuracy of this method for the determination of Si, Ti, Al, Fe, Mg, Ca, K, and P in coal ash samples.

Interferences due to matrix effects in the X-ray fluorescence analysis of whole coal samples are much less of a problem than they are in the analysis of coal ash samples because coal contains mainly organic compounds. The concentration of a constituent such as pyrite rarely falls below 0.2 percent or exceeds 5.0 percent of bituminous and higher rank coals. The concentration of other inorganic elements varies much less. Matrix effects are not absent, but in most cases they are small and corrections for them are easily made.

Table C12. Comparison of ISGS X-ray fluorescence analyses of coal ash with BCURA* analyses (in percent).

	BCURA No. 4		BCURA No. 5		BCURA No. 7		BCURA No. 10		BCURA Slag		Ave. diff.
Oxide	X-RF	Reported*	X-RF	Reported*	X-RF	Reported*	X-RF	Reported*	X-RF	Reported*	
SiO_2	53.28	53.41	29.27	29.43	20.01	20.37	44.03	44.49	51.45	51.58	0.25
TiO_2	1.65	1.70	0.65	0.70	0.26	0.34	1.18	1.19	0.96	0.96	0.04
Al_2O_3	34.11	33.88	19.73	19.82	10.03	10.33	29.93	30.02	28.20	28.45	0.19
Fe_2O_3	5.83	5.76	39.02	39.24	62.16	62.31	13.56	13.82	6.27	5.99	0.17
MgO	0.66	0.71	1.18	1.29	0.58	0.63	2.05	2.00	2.33	2.26	0.06
CaO	0.73	0.77	2.47	2.54	2.31	2.30	1.24	1.29	7.89	7.91	0.04
K_2O	2.45	2.38	1.94	1.95	1.38	1.39	3.68	3.71	2.84	2.81	0.03
P_2O_5	0.48	0.41	0.14	0.14	0.17	0.15	0.77	0.77	0.09	0.05	0.03

*British Coal Utilization Research Association (Dixon et al., 1964).

To form the whole coal disk that is subjected to X-rays, 2.000 gm of air-dried coal was placed in the tungsten carbide grinding vial of a No. 6 Wig-L-Bug. The coal was ground for 3 minutes, transferred to a die and 0.2 gm of Somar mix added and, with a backing of a layer of Somar mix, pressed into a disk at a pressure of 40,000 psi. The whole coal disk was dried in the vacuum chamber of the X-ray spectrometer. Determinations of all elements except Fe, Ti, and V were performed in vacuum to avoid scattering of X-rays from water adsorbed on the surface of the whole coal disk.

Relative standard deviations for wavelength dispersive X-ray fluorescence analyses of whole coal in this study are: Si, 2.0%; Ti, 3.2%; Al, 3.1%; Fe, 1.9%; Mg, 4.4%; Ca, 1.6%; K, 4.5%; and P, 25%.

Operating parameters of the X-ray fluorescence spectrometer for the analysis of coal and coal ash samples are listed in Table C13.

Table C13. X-ray fluorescence settings for the analysis of coal and coal ash.

						Pulse height analyzer	
Element	X-ray	20 angle	Background 20	Crystal	Vacuum	Base	Window
Si	KL_3 & KL_2	108.01	111.01	EDDT	yes	7	17
Al	KL_3 & KL_2	142.44	145.95	EDDT	yes	5	12
Ti	KL_3 & KL_2	86.12	89.12	LiF	no	5	18
Fe	KL_3 & KL_2	57.51	60.51	LiF	no	5	25
Ca	KL_3	44.85	47.95	EDDT	yes	14	30
K	KL_3 & KL_2	50.32	53.90	EDDT	yes	14	21
Mg	$KL_{2\,3}$	136.69	139.69	ADP	yes	4	8
V	KL_3 & KL_2	76.93	80.93	LiF	no	5	16
S	KL_3 & KL_2	75.24	78.38	EDDT	yes	12	18
Cl	KL_3	64.94	67.94	EDDT	yes	11	19
P	KL_3 & KL_2	110.99	113.99	Ge	yes	9	15

Energy-Dispersive X-ray Fluorescence Analysis (XES)

Determinations of Cd, Sn, Te, I, Cs, Ba, La, Ce, and Y were made on ashed and unashed feed coal, and residue and profuct samples by energy-dispersive X-ray fluorescence spectrometry. No results for Cd, Sb, I, Cs, La by XES were reported because the results by AA and INAA for these elements were considered to be significantly more accurate and precise. The specific procedure for Y is described in the section on rare earth analyses by NAA-RC.

Table C14. XES accuracy data.

		Y	Ba	Sn	Te
AGV-1	accepted	21.3^1	1208^1	4.2^1	$<1.0^1$
	found	23.3	1635	5.0	5.8
BCR-1	accepted	37.1^1	675^1	2.6^1	$<1.0^1$
	found	41.6	846	2.0	3.1
W-1	accepted		160^1	3.2^1	$<1.0^1$
	found		209	1.1	<1.0
NBS-SRM 1632	accepted	7.5^3		3.4^4	0.6^2
	found	7.8		3.3	1.6

[1] Flanagan, 1976.
[2] Gladney and Rock, 1975.
[3] Simms, et al., 1976.
[4] ISGS, unpublished optical emission data.

The instrumentation consists of a Kevex Si (Li) detector with a resolution of 155 eV (FWHM) at 5.9 KeV, a 300 mCi ^{241}Am excitation source, and a Tracor Northern 1700 multichannel analyzer.

Determinations of trace elements of high atomic number were made by XES on both the 500°C ash and the whole coal or other unashed sample. The ash was ground to pass a -200 mesh sieve and 0.500 gm (1.000 gm when unashed coal or product was used) was placed in a polyethylene cup. The mouth of the cup was sealed with a piece of Mylar film (0.00015 inch thick). The cup was inverted and tapped so that the sample settled as a uniform layer on the Mylar. The sample was then placed in an aluminum sample holder and exposed to monochromatic radiation generated from a secondary target of Dy.

Standards were coals and ashes previously analyzed by other methods. The standards were analyzed in the same manner as, and in sequence with, the samples. Count rates obtained on samples and standards were corrected for background and a blank. For each element, a plot was made of concentration versus net count rate for standards with a range of concentrations of the element. The concentration of an element in a sample was then calculated as the product of net count rate for the sample and the slope of the curve of concentration versus count rate for the standards.

The relative standard deviations of the measurements by energy-dispersive X-ray fluorescence analyses are: (on whole coal samples) Ba, 15%; Sn, 25%; Te, 50%; and Y, 25% (on ash samples) Ba, 10%; Sn, 20%; Te, 25%; and Y, 20%.

Table C14 lists the results obtained with the method for Y, Ba, Sn, and Te on some reference materials.

Determination of Fluorine with the Fluoride Ion—Selective Electrode (ISE)

One gram of feed coal or liquefaction residue, weighed to the nearest 0.5 mg and contained in a fused quartz sample holder, is placed in a combustion bomb containing 5 mL of a 1M sodium hydroxide solution. The bomb is pressurized to about 28 atmospheres with oxygen and is fired. At least 15 minutes are allowed to elapse before the bomb is depressurized slowly over a period of about 1 minute. Three 5 mL aliquots of demineralized water are used to rinse the bomb contents into a 50 mL plastic beaker. The beaker contents are stirred while the pH is adjusted to 5.0 to 5.2 with 0.25M H_2SO_4. (This reduces the initially high HCO_3^- content sufficiently to minimize its possible interference in the fluoride determination.) Five mL of a 1M citrate ionic-strength-adjustment buffer are added to the beaker contents to buffer the solution at a pH of about 6.0, and to release most of the fluoride from complexes with iron, aluminum, and hydrogen ions. The total volume is adjusted to 50 mL with deionized water in a plastic volumetric flask, and the contents returned to the plastic beaker for a measurement. The potential is determined with the fluoride ion-selective electrode. One mL of a solution 0.01M in F^- (190 ppm) is added to the beaker contents and the potential is again determined. The fluoride content in the coal is calculated from the ΔE resulting from the known fluoride addition. With care, the reproducibility of the method is about ±5 percent, relative in the concentration range of 5 ppm to 1000 ppm.

The error is not large in the above method when the ash content is as great as 20 percent. However, when the ash content surpasses 20 percent, the residue that remains in the bomb after the soluble material has been washed out following combustion is fused in a nickel crucible with 3 gm of powdered sodium hydroxide, and the fusion mixture is taken up in deionized water. The pH is adjusted to 5.0 to 5.2 (the solution volume is much larger in this case, 200 mL total solution); then 20 mL of the 1M citrate ionic-strength-adjustment buffer solution is added. The volume is adjusted to 200 mL and the potential is determined. After addition of 5 mL of 0.01M F^- solution ΔE is again determined and the fluoride concentration of the combustion bomb residue is determined. The result of this determination is added to that obtained for the combustion bomb washings. Owing to the small sample size and the high dilution factor, the detection limit of fluoride in the fusion method is 10 ppm.

AMERICAN SOCIETY FOR TESTING AND MATERIALS COAL ANALYSES PROCEDURES (ASTM)

The following ASTM procedures were used for the feed coal and residues: moisture, Method D3173; ash (750°C), Method D3174; carbon and hydrogen, Method D3178; total sulfur, Method D3177; and nitrogen, a modified micro-version of D3179.

These procedures, modified and reapproved periodically, are described in the ASTM Annual Book of Standards, part 26, every year.

ASTM methods for determining Giesler plasticity (D2639), free-swelling index (D720), volatility (D3175), forms of sulfur (D2492), and oxygen by difference (D3178) were attempted for the residue samples and were found to be inappropriate for this type of sample. The residue samples apparently retain little of the physical properties of the coals from which they are derived.

			AL(XRF) (%)	C(ASTM) (%)	CA(XRF) (%)	FE(NAA) (%)	FE(XRF) (%)	H(ASTM) (%)	K(NAA) (%)	K(XRF) (%)	MG(XRF) (%)	N(ASTM) (%)
C19660	CLEAN CUKE	AS IS		63.%		1.6%		4.8%	.30%			1.2%
C19660	CLEAN CUKE	HTA	1.7%		1.1%		1.7%			.30%	.08%	
C19661	CLEAN CUKE	AS IS		77.%		-		5.6%	.21%			.11%
C19661	CLEAN CUKE	HTA	1.3%		.71%		1.4%			.24%	.06%	
C19963	FMC CUED	AS IS		77.%				2.0%	.037%			.77%
C19963	FMC CUED	HTA	.51%		2.4%		.63%			.048%	.44%	
C18903	H-CUAL-1	AS IS		67.%		1.6%		4.9%	.18%			
C18903	H-CUAL	HTA	1.0%		.56%		1.4%			.14%	.054%	
C18941	H-CUAL	AS IS		73.%		2.1%		5.9%	.23%			1.5%
C18941	H-CUAL	HTA	1.5%		.73%		2.0%			.22%	.10%	
C19194	H-CUAL-2	AS IS		69.%		2.1%		5.4%	.17%			1.7%
C19194	H-CUAL	HTA	1.0%		.46%		1.4%			.19%	.03%	
C19196	H-CUAL	AS IS		72.%		2.0%		6.0%	.21%			1.6%
C19196	H-CUAL	HTA	1.5%		.67%		2.0%			.24%	.02%	
C19916	H-CUAL-3	AS IS		69.%		1.5%		5.0%	.13%			1.5%
C19916	H-CUAL	HTA	1.0%		.59%		1.6%			.14%	.020%	
C19917	H-CUAL	AS IS		64.%		3.7%		4.4%	.33%			.92%
C19917	H-CUAL	HTA	2.3%		1.3%		.86%			.37%	.071%	
C20021	H-CUAL-4	AS IS		55.%		.33%		6.4%	.035%			1.0%
C20021	H-CUAL	HTA	.81%		.86%		.43%			.03%	.28%	
C20022	H-CUAL	AS IS		62.%		1.1%		4.9%	.052%			1.0%
C20022	H-CUAL	HTA	2.1%		2.9%		.99%			.06%	.63%	
C19590	LIGNITE	AS IS		55.%		.64%		5.6%	.018%			.69%
C19590	LIGNITE	HTA	.42%		1.5%		.52%			.02%	.33%	
C19591	LIGNITE	AS IS		61.%		2.2%		4.0%	.043%			.40%
C19591	LIGNITE	HTA	1.8%		5.3%		2.2%			.06%	1.3%	
C19702	SRC-ALA-1	AS IS		67.%		1.0%		5.4%	.16%			1.1%
C19702	SRC-ALA	HTA	.96%		.32%		1.3%			.16%	.05%	
C19703	SRC-ALA	AS IS		30.%		7.0%		2.0%	.67%			.40%
C19703	SRC-ALA	HTA	4.8%		1.7%		10.%			.96%	.35%	
C19705	SRC-ALA-2	AS IS		55.%		1.4%		5.7%	.18%			.97%
C19705	SRC-ALA	HTA	.96%		.55%		1.2%			.14%	.05%	
C19706	SRC-ALA	AS IS		51.%		3.1%		2.4%	.42%			.75%
C19706	SRC-ALA	HTA	3.0%		1.6%		3.4%			.48%	.19%	
C19708	SRC-ALA-3	AS IS		69.%		1.4%		4.9%	.16%			1.4%
C19706	SRC-ALA	HTA	1.0%		.09%		1.4%			.16%	.02%	
C19709	SRC-ALA	AS IS		41.%		7.2%		2.6%	.74%			.71%
C19709	SRC-ALA	HTA	4.4%		.72%		7.2%			.82%	.30%	

			AL(XRF) (%)	C(ASTM) (%)	CA(XRF) (%)	FE(NAA) (%)	FE(XRF) (%)	H(ASTM) (%)	K(NAA) (%)	K(XRF) (%)	MG(XRF) (%)	N(ASTM) (%)
C19711	SRC-ALA-4	AS IS		60.%		.28%		5.8%	.011%			.88%
C19711	SRC-ALA	HTA	.54%		1.3%		.26%			.012%	.18%	
C19712	SRC-ALA	AS IS		59.%		.74%		3.4%	.12%			.87%
C19712	SRC-ALA	HTA	2.6%		3.6%		.80%			.14%	.70%	
C19714	SRC-ALA-5	AS IS		76.%		.94%		5.3%	.078%			1.2%
C19714	SRC-ALA	HTA	.86%		.55%		.94%			.08%	.06%	
C19715	SRC-ALA	AS IS		39.%		2.7%		2.2%	.42%			.56%
C19715	SRC-ALA	HTA	4.2%		1.5%		2.9%			.42%	.38%	
C19141	SRC-WASH-1	AS IS		71.1%		3.4%		6.1%	.16%			1.9%
C19141	SRC-WASH	HTA	1.2%		.046%		2.2%			.13%	.025%	
C19142	SRC-WASH	AS IS		28.%		17.%		2.2%	.96%			.50%
C19142	SRC-WASH	HTA	7.3%		.41%		16.%			.83%	.085%	
C19488	SRC-WASH-2	AS IS		70.%		2.2%		5.2%	.16%			1.5%
C19488	SRC-WASH	HTA	1.2%		.20%		2.4%			.15%	.04%	
C19487	SRC-WASH	AS IS		28.%		12.%		1.7%	.90%			.54%
C19487	SRC-WASH	HTA	5.7%		1.1%		12.%			.83%	.12%	
C19899	SRC-WASH-3	AS IS		74.%		1.2%		5.4%	.12%			1.2%
C19899	SRC-WASH	HTA	.93%		.26%		1.3%			.16%	.021%	
C19902	SRC-WASH	AS IS		67.%		3.4%		3.7%	.34%			1.6%
C19902	SRC-WASH	HTA	2.4%		.69%		3.5%			.42%	.030%	
C20014	SRC-WASH-4	AS IS		70.%		1.9%		5.0%	.15%			1.2%
C20014	SRC-WASH	HTA	1.1%		.38%		1.3%			.18%	.02%	
C20015	SRC-WASH	AS IS		64.%		3.8%		4.0%	.33%			1.4%
C20015	SRC-WASH	HTA	2.5%		1.1%		2.8%			.40%	.04%	
C20016	SRC-WASH-5	AS IS		72.%		1.4%		5.2%	.11%			1.2%
C20016	SRC-WASH	HTA	1.1%		.61%		1.2%			.13%	.05%	
C20017	SRC-WASH	AS IS		69.%		3.7%		3.7%	.25%			1.4%
C20017	SRC-WASH	HTA	2.3%		1.1%		2.9%			.28%	.08%	
C20019	SRC-WASH-6	AS IS		71.%		1.4%		5.2%	.15%			1.2%
C20019	SRC-WASH	HTA	1.2%		.46%		1.4%			.15%	.06%	
C20020	SRC-WASH	AS IS		66.%		3.5%		4.1%	.23%			1.4%
C20020	SRC-WASH	HTA	2.3%		1.1%		2.9%			.28%	.03%	
C19276	SYNTHOIL	AS IS		62.%		3.7%		5.3%	.18%			1.3%
C19276	SYNTHOIL	HTA	1.4%		.47%		3.1%			.18%	.003%	
C19349	SYNTHOIL	AS IS		46.%		7.7%		3.9%	.50%			.77%
C19349	SYNTHOIL	HTA	4.5%		1.5%		9.7%			.49%	<.003%	

			NA(NAA) (%)	P(XRF) (%)	S(ASTM) (%)	SI(XRF) (%)	TI(XRF) (%)	AG(NAA) (PPM)	AG(OEP) (PPM)	AS(NAA) (PPM)	B(OED) (PPM)	BA(NAA) (PPM)
C19660	CLEAN COKE	AS IS	.13%		2.9%			.18		5.4		280.
C19660	CLEAN COKE	HTA		.01%		3.9%	.10%		<.19		130.	
C19661	CLEAN COKE	AS IS	.092%		.93%			-		2.1		-
C19661	CLEAN COKE	HTA		.009%		3.0%	.07%		<.14		100.	
C19963	FMC COED	AS IS	.77%		.61%					13.		260.
C19963	FMC COED	HTA		.0023%		1.1%	.023%		<.13		230.	
C18903	H-COAL-1	AS IS	.04%		3.3%					3.1		41.
C18903	H-COAL	HTA		.0030%		2.4%	.064%		<.09		200.	
C18941	H-COAL	AS IS	.049%		1.7%			<0.1		2.5		78.
C18941	H-COAL	HTA		.006%		3.4%	.085%		<.06		210.	
C19194	H-COAL-2	AS IS	.03%		3.2%			.05		3.0		66.
C19194	H-COAL	HTA		.005%		2.3%	.07%		<.04		110.	
C19196	H-COAL	AS IS	.05%		1.9%			-		3.9		
C19196	H-COAL	HTA		.005%		3.7%	.09%		<.14		290.	
C19916	H-COAL-3	AS IS	.032%		2.5%			-		4.5		48.
C19916	H-COAL	HTA		.0010%		2.3%	.05A%		<.11		210.	
C19917	H-COAL	AS IS	.078%		2.5%			-		4.7		120.
C19917	H-COAL	HTA		<.001%		5.5%	.14%		<.27		340.	
C20021	H-COAL-4	AS IS	.038%		.76%			<.4		2.2		320.
C20021	H-COAL	HTA		.02%		1.1%	.01%		<.48		49.	
C20022	H-COAL	AS IS	.090%		.73%			<.1		3.6		830.
C20022	H-COAL	HTA				2.6%	.16%		<1.1		120.	
C19590	LIGNITE	AS IS	.41%		.65%			<.4		7.7		760.
C19590	LIGNITE	HTA		.02%		.67%	.02%		<.08		124.	
C19591	LIGNITE	AS IS	1.1%					.18		27.		3600.
C19591	LIGNITE	HTA		.09%		3.4%	.07%		<.33		300.	
C19702	SRC-ALA-1	AS IS	.10%		3.9%			-		1.9		65.
C19702	SRC-ALA	HTA		.02%		2.5%	.06%		<.11		250.	
C19703	SRC-ALA	AS IS	.51%		4.7%			.96		8.1		400.
C19703	SRC-ALA	HTA		.12%		15.%	.22%		<.63		520.	
C19705	SRC-ALA-2	AS IS	.023%		2.5%			.27		3.2		46.
C19705	SRC-ALA	HTA		<.0004%		2.2%	.06%		<.11		190.	
C19706	SRC-ALA	AS IS	.27%		2.3%			<.5		7.1		230.
C19706	SRC-ALA	HTA		.009%		11.%	.19%		<.42		240.	
C19708	SRC-ALA-3	AS IS	.014%		2.8%			-		8.7		45.
C19708	SRC-ALA	HTA		.01%		1.8%	.06%		<.09		100.	
C19709	SRC-ALA	AS IS	.31%		4.4%			-		19.		260.
C19709	SRC-ALA	HTA		.03%		12.%	.17%		<.51		180.	

			NA(NAA) (%)	P(XRF) (%)	S(ASTM) (%)	SI(XRF) (%)	TI(XRF) (%)	AG(NAA) (PPM)	AG(OEP) (PPM)	AS(NAA) (PPM)	B(OED) (PPM)	BA(NAA) (PPM)
C19711	SRC-ALA-4	AS IS	.06%		.62%			-		1.2		360.
C19711	SRC-ALA	HTA		.03%		.90%	.05%		<.07		33.	
C19712	SRC-ALA	AS IS	.27%		.55%			-		3.0		1400.
C19712	SRC-ALA	HTA		.24%		6.8%	.22%		<.32		140.	
C19714	SRC-ALA-5	AS IS	.065%		1.8%			-		5.3		108.
C19714	SRC-ALA	HTA		.02%		1.6%	.05%		<.08		88.	
C19715	SRC-ALA	AS IS	1.0%		.22%			.34		8.4		440.
C19715	SRC-ALA	HTA		.06%		16.%	.10%		<.55		240.	
C19141	SRC-WASH-1	AS IS	.01%		3.4%			-		13.		38.
C19141	SRC-WASH	HTA		.0061%		1.5%	.051%		<.04		88.	
C19142	SRC-WASH	AS IS	.16%		9.3%			-		110.		
C19142	SRC-WASH	HTA		.092%		10.%	.25%		<.27		250.	
C19488	SRC-WASH-2	AS IS	.020%		3.8%			.25		23.		
C19488	SRC-WASH	HTA		.01%		2.2%	.06%		<.09		90.	
C19487	SRC-WASH	AS IS	.34%		7.3%			.60		66.		350.
C19487	SRC-WASH	HTA		.09%		15.%	.20%		<.52		160.	
C19899	SRC-WASH-3	AS IS	.02%		2.4%			-		6.7		43.
C19899	SRC-WASH	HTA		.0033%		2.0%	.058%		.52		96.	
C19902	SRC-WASH	AS IS	.044%		2.4%			-		15.		110.
C19902	SRC-WASH	HTA		.0066%		5.4%	.15%		<.24		240.	
C20014	SRC-WASH-4	AS IS	.06%		3.6%			.73		1.9		65.
C20014	SRC-WASH	HTA		.01%		2.7%	.07%		<.67		180.	
C20015	SRC-WASH	AS IS	.13%		2.1%			-		3.8		150.
C20015	SRC-WASH	HTA		.03%		6.0%	.15%		<1.5		380.	
C20016	SRC-WASH-5	AS IS	.07%		2.3%			-		6.1		77.
C20016	SRC-WASH	HTA		.03%		2.4%	.07%		<.65		90.	
C20017	SRC-WASH	AS IS	.15%		2.0%			-		14.		200.
C20017	SRC-WASH	HTA		.06%		4.9%	.14%		<1.4		170.	
C20019	SRC-WASH-6	AS IS	.05%		2.7%			<.2		6.0		130.
C20019	SRC-WASH	HTA		.02%		2.5%	.07%		<.68		100.	
C20020	SRC-WASH	AS IS	.13%		2.2%			.2		16.		200.
C20020	SRC-WASH	HTA		.05%		4.8%	.14%		<1.4		240.	
C19276	SYNTHOIL	AS IS	.024%		5.2%					7.5		120.
C19276	SYNTHOIL	HTA		.02%		2.8%	.09%		<.13		100.	
C19349	SYNTHOIL	AS IS	.065%		6.0%			-		7.2		470.
C19349	SYNTHOIL	HTA		.02%		8.0%	.20%		<.37		200.	

			BA(XES) (PPM)	BE(UEP) (PPM)	BI(UEP) (PPM)	BR(NAA) (PPM)	CD(AA) (PPM)	CE(NAA) (PPM)	CL(NAA) (PPM)	CU(NAA) (PPM)	CO(UED) (PPM)	CO(OEP) (PPM)
C19660	CLEAN COKE	AS IS				16.		24.	4100.	6.4		
C19660	CLEAN COKE	HTA	260.	1.1	<.23		<.36	18.			4.9	4.1
C19661	CLEAN COKE	AS IS				12.		13.	3300.	-		
C19661	CLEAN COKE	HTA	180.	.72	<.17		<.26	14.			3.6	3.2
C19963	FMC COED	AS IS	260.			2.0		7.0	92.	1.6		
C19963	FMC COED	HTA	310.	.65	<.6		<.49	9.6			2.4	1.4
C18903	H-COAL-1	AS IS	46.			3.2		9.4	370.	9.4		
C18903	H-COAL	HTA	46.	1.1	<.6		<.27	10.			7.2	8.0
C18941	H-COAL	AS IS	71.			4.7		14.	590.	8.0		
C18941	H-COAL	HTA	75.	1.3	<.8		<.58	16.			13.	10.
C19194	H-COAL-2	AS IS	52.			3.2		15.	330.	4.5		
C19194	H-COAL	HTA		.93	<.6		<.35	14.			6.7	5.1
C19196	H-COAL	AS IS	83.			4.3		20.	400.	4.8		
C19196	H-COAL	HTA	78.	1.0	<.9		<.41	16.			4.7	5.5
C19916	H-COAL-3	AS IS				3.2		11.	420.	3.1		
C19916	H-COAL	HTA	43.	.84	<.6		<.23	12.			3.4	3.5
C19917	H-COAL	AS IS				7.0		28.	580.	9.1		
C19917	H-COAL	HTA	110.	1.8	<1.		<.54	26.			9.4	9.5
C20021	H-COAL-4	AS IS	260.			2.1		13.	50.	3.2		
C20021	H-COAL	HTA	330.	.20	<.4		<.4				3.2	3.6
C20022	H-COAL	AS IS	800.			2.7		36.	150.	12.		
C20022	H-COAL	HTA	780.	.76	<1.		<.96	36.			11.	13.
C19590	LIGNITE	AS IS	860.			3.4		6.1	29.	.99		
C19590	LIGNITE	HTA	1000.	.28	<.10		<.16	4.0			1.7	.50
C19591	LIGNITE	AS IS	4000.			3.6		24.		4.2		
C19591	LIGNITE	HTA	4000.	1.2	<.41		.63	23.			6.6	3.4
C19702	SRC-ALA-1	AS IS				6.1		7.9	920.	3.0		
C19702	SRC-ALA	HTA	67.	1.3	<.13		.48	9.5			3.5	2.6
C19703	SRC-ALA	AS IS				21.		56.	4100.	18.		
C19703	SRC-ALA	HTA	370.	6.4	<.78		2.0	50.			20.	17.
C19705	SRC-ALA-2	AS IS				2.0		9.9	310.	2.7		
C19705	SRC-ALA	HTA	50.	.86	<.6		<.21	11.			2.9	2.5
C19706	SRC-ALA	AS IS				5.2		33.	530.	7.7		
C19706	SRC-ALA	HTA	240.	2.3	<2.		<.80	35.			10.	10.
C19708	SRC-ALA-3	AS IS				3.9		16.	280.	1.6		
C19708	SRC-ALA	HTA	62.	.74	<.5		<.17	15.			1.5	1.2
C19709	SRC-ALA	AS IS				9.7		74.	1200.	17.		
C19709	SRC-ALA	HTA	260.	1.9	<3.		<.98	58.			16.	17.

			BA(XES) (PPM)	BE(UEP) (PPM)	BI(OEP) (PPM)	BR(NAA) (PPM)	CD(AA) (PPM)	CE(NAA) (PPM)	CL(NAA) (PPM)	CO(NAA) (PPM)	CO(UED) (PPM)	CO(OEP) (PPM)
C19711	SRC-ALA-4	AS IS				1.1		14.	35.	1.9		
C19711	SRC-ALA	HTA	400.	.13	<.4		<.14	13.			2.1	1.6
C19712	SRC-ALA	AS IS				2.1		33.	140.	3.6		
C19712	SRC-ALA	HTA	1600.	.50	<2.		<.61	33.			5.0	2.7
C19714	SRC-ALA-5	AS IS				13.		10.	1100.	2.3		
C19714	SRC-ALA	HTA	120.	.28	<.4		<.16	8.3			2.2	1.6
C19715	SRC-ALA	AS IS				28.		38.	2300.	8.1		
C19715	SRC-ALA	HTA	520.	1.0	<3.		<1.0	37.			8.8	8.6
C19141	SRC-WASH-1	AS IS	34.			3.7		29.	190.	9.5		
C19141	SRC-WASH	HTA	37.	2.7	<.5		<.34	20.			8.1	6.7
C19142	SRC-WASH	AS IS	300.			6.0		150.	810.	47.		
C19142	SRC-WASH	HTA	270.	9.2	<4.		<2.4	125.			46.	39.
C19488	SRC-WASH-2	AS IS	48.			4.7		19.	330.	6.4		
C19488	SRC-WASH	HTA	48.	1.4	<.6		<.28	28.			9.	7.4
C19487	SRC-WASH	AS IS	290.			7.0		100.	1100.	44.		
C19487	SRC-WASH	HTA	260.	5.8	<3.		<1.6	160.			38.	42.
C19899	SRC-WASH-3	AS IS	44.			5.6		9.1	640.	2.9		
C19899	SRC-WASH	HTA	42.	1.0	<.5		<.18	11.			2.9	4.0
C19902	SRC-WASH	AS IS	120.			14.		29.	1470.	8.1		
C19902	SRC-WASH	HTA	100.	2.1	<1.		<.49	32.			7.9	8.1
C20014	SRC-WASH-4	AS IS	63.			2.9		15.	200.	3.8		
C20014	SRC-WASH	HTA	62.	.63	<.6		<.56	15.			3.8	4.1
C20015	SRC-WASH	AS IS	150.			5.7		38.	420.	8.7		
C20015	SRC-WASH	HTA	140.	1.6	<1.		<1.2	33.			8.8	9.6
C20016	SRC-WASH-5	AS IS	100.			12.		17.	1100.	2.7		
C20016	SRC-WASH	HTA	100.	.51	<.6		<.55	17.			2.9	2.5
C20017	SRC-WASH	AS IS	220.			29.		32.	2200.	6.6		
C20017	SRC-WASH	HTA	210.	1.1	<1.		<1.1	33.			6.5	7.0
C20019	SRC-WASH-6	AS IS	98.			12.		15.	880.	3.3		
C20019	SRC-WASH	HTA	100.	.55	<.6		<.57	10.			2.3	2.5
C20020	SRC-WASH	AS IS	220.			27.		27.	1900.	6.0		
C20020	SRC-WASH	HTA	210.	1.1	<1.		<1.2	24.			5.4	5.9
C19276	SYNTHOIL	AS IS	130.			.9		19.	48.	5.6		
C19276	SYNTHOIL	HTA	130.	1.2	<.8		<.40	18.			7.0	5.7
C19349	SYNTHOIL	AS IS	420.			1.5		39.	140.	9.3		
C19349	SYNTHOIL	HTA	370.	2.8	<2.		<1.1	51.			19.	14.

			CR(NAA) (PPM)	CR(UED) (PPM)	CS(NAA) (PPM)	CU(AA) (PPM)	CU(UED) (PPM)	CU(DEP) (PPM)	DY(NAA) (PPM)	ER(RC) (PPM)	EU(NAA) (PPM)	F(ISE) (PPM)
C19660	CLEAN COKE	AS IS	33.		2.8				1.3		.48	130.
C19660	CLEAN COKE	HTA		22.		12.	13.	9.5		.88	.30	
C19661	CLEAN COKE	AS IS	-		1.5				1.0		.23	110.
C19661	CLEAN COKE	HTA		21.		11.	12.	9.2		.58	.24	
C19963	FMC CUED	AS IS	6.0		.25				1.1		.20	21.
C19963	FMC CUED	HTA		6.0		7.9	6.7	7.7		.74	.19	
C18903	H-COAL-1	AS IS	28.		1.3				1.0		.21	69.
C18903	H-COAL	HTA		18.		7.2	7.6	8.7	10.	.73	.22	
C18941	H-COAL	AS IS	25.		1.7				1.5		.28	100.
C18941	H-COAL	HTA		29.		13.	12.	13.		.93	.31	
C19194	H-COAL-2	AS IS	25.		1.3				.7		.29	68.
C19194	H-COAL	HTA		28.		9.0	11.	10.		.97	.29	
C19196	H-COAL	AS IS	25.		2.3				1.2		.32	100.
C19196	H-COAL	HTA		19.		14.	10.	12.		.85	.32	
C19916	H-COAL-3	AS IS	16.		1.2				1.0		.25	55.
C19916	H-COAL	HTA		14.		9.7	9.2	8.6		.97	.24	
C19917	H-COAL	AS IS	40.		3.4				2.5		.75	110.
C19917	H-COAL	HTA		40.		23.	25.	21.		1.1	.53	
C20021	H-COAL-4	AS IS	8.8		<.6				1.6		.31	44.
C20021	H-COAL	HTA		7.7		17.	17.	12.				
C20022	H-COAL	AS IS	19.		.80				2.8		.82	120.
C20022	H-COAL	HTA		20.		46.	43.	36.		1.7	.77	
C19590	LIGNITE	AS IS	3.0		.11				.46		.07	16.
C19590	LIGNITE	HTA		2.2		3.2	2.1	2.7		.34	.07	
C19591	LIGNITE	AS IS	14.		.43				.95		.38	40.
C19591	LIGNITE	HTA		11.		15.	8.1	18.		1.8	.36	
C19702	SRC-ALA-1	AS IS	21.		1.2				1.0		.19	91.
C19702	SRC-ALA	HTA		25.		11.	12.	8.1		.52	.18	
C19703	SRC-ALA	AS IS	160.		6.7				4.1		.75	350.
C19703	SRC-ALA	HTA		160.		82.	83.	59.		2.3	.94	
C19705	SRC-ALA-2	AS IS	23.		1.3				1.2		.20	52.
C19705	SRC-ALA	HTA		20.		7.8	8.7	7.4		.60	.20	
C19706	SRC-ALA	AS IS	64.		3.0				3.3		.74	210.
C19706	SRC-ALA	HTA		69.		36.	38.	34.		2.1	.72	
C19708	SRC-ALA-3	AS IS	17.		1.2				1.4		.31	61.
C19708	SRC-ALA	HTA		16.		13.	14.	10.		.76	.27	
C19709	SRC-ALA	AS IS	87.		5.1				4.2		1.0	210.
C19709	SRC-ALA	HTA		78.		44.	44.	40.		1.8	.92	

			CR(NAA) (PPM)	CR(UED) (PPM)	CS(NAA) (PPM)	CU(AA) (PPM)	CU(UED) (PPM)	CU(UEP) (PPM)	DY(NAA) (PPM)	ER(RC) (PPM)	EU(NAA) (PPM)	F(ISE) (PPM)
C19711	SRC-ALA-4	AS IS	6.0		.14				1.1		.28	51.
C19711	SRC-ALA	HTA		5.7		16.	14.	12.		.56	.28	
C19712	SRC-ALA	AS IS	36.		1.4				2.0		.60	140.
C19712	SRC-ALA	HTA		36.		35.	32.	32.		1.5	.60	
C19714	SRC-ALA-5	AS IS	12.		.7				.76		.17	65.
C19714	SRC-ALA	HTA		9.4		5.3	5.3	4.7		.26	.14	
C19715	SRC-ALA	AS IS	61.		3.1				3.0		.68	210.
C19715	SRC-ALA	HTA		62.		26.	26.	27.		.99	.60	
C19141	SRC-WASH-1	AS IS	24.		.6				2.2		.70	70.
C19141	SRC-WASH	HTA		22.		21.	19.	16.		1.5	.54	
C19142	SRC-WASH	AS IS	140.		4.0				7.2		2.6	350.
C19142	SRC-WASH	HTA		150.		170.	160.	110.		6.9	3.0	
C19488	SRC-WASH-2	AS IS	18.		1.3				1.8		.54	90.
C19488	SRC-WASH	HTA		22.		17.	19.	13.		1.1	.53	
C19487	SRC-WASH	AS IS	140.		6.5				2.8		2.5	200.
C19487	SRC-WASH	HTA		150.		120.	140.	108.		5.9	2.5	
C19899	SRC-WASH-3	AS IS	15.		1.1				1.1		.23	51.
C19899	SRC-WASH	HTA		12.		6.6	6.3	7.6		.49	.19	
C19902	SRC-WASH	AS IS	45.		3.2				2.6		.65	110.
C19902	SRC-WASH	HTA		35.		20.	20.	19.		1.4	.49	
C20014	SRC-WASH-4	AS IS	27.		1.7				1.1		.27	100.
C20014	SRC-WASH	HTA		31.		10.	11.	9.5		.77	.28	
C20015	SRC-WASH	AS IS	66.		3.4				2.0		.68	160.
C20015	SRC-WASH	HTA		61.		22.	24.	22.		1.7	.67	
C20016	SRC-WASH-5	AS IS	13.		1.1				.78		.23	77.
C20016	SRC-WASH	HTA		13.		13.	13.	12.		.72	.28	
C20017	SRC-WASH	AS IS	41.		2.3				1.6		.47	150.
C20017	SRC-WASH	HTA		31.		24.	23.	22.		1.3	.58	
C20019	SRC-WASH-6	AS IS	17.		1.1				1.1		.19	69.
C20019	SRC-WASH	HTA		12.		16.	16.	13.		.65	.19	
C20020	SRC-WASH	AS IS	32.		2.1				1.7		.43	160.
C20020	SRC-WASH	HTA		27.		19.	25.	19.		1.2	.44	
C19276	SYNTHOIL	AS IS	22.		1.5				1.6		.34	63.
C19276	SYNTHOIL	HTA		28.		10.	9.4	10.		.72	.35	
C19349	SYNTHOIL	AS IS	60.		3.6				3.0		1.0	200.
C19349	SYNTHOIL	HTA		98.		40.	40.	32.		2.3	.96	

			GA(NAA) (PPM)	GE(OED) (PPM)	HF(NAA) (PPM)	HG(RC) (PPM)	HO(RC) (PPM)	I(NAA) (PPM)	IN(NAA) (PPM)	LA(NAA) (PPM)	LI(AA) (PPM)	LU(NAA) (PPM)
C19660	CLEAN CUKE	AS IS	5.2		1.5	.09		2.3	.02	10.		.15
C19660	CLEAN COKE	HTA		.43			.31			12.	16.	.09
C19661	CLEAN COKE	AS IS	3.8		.72	.05		1.7	<.05	7.8		.09
C19661	CLEAN COKE	HTA		.36			.15			7.1	13.	.08
C19963	FMC COED	AS IS	2.8		.62	.23		<1.0	<.3	4.3		.10
C19963	FMC COED	HTA		<.40			.24			6.3	2.0	.10
C18903	H-COAL-1	AS IS	4.0		.72	.11		1.0	.17	6.4		.13
C18903	H-COAL	HTA		5.1	10.	.73	.22			5.5	18.	.080
C18941	H-COAL	AS IS	3.3		.83	.03		.7		7.5		.17
C18941	H-COAL	HTA		5.4			.29			8.3	17.	.11
C19194	H-COAL-2	AS IS	3.8		.63	.21		<.5	-	7.6		.10
C19194	H-COAL	HTA		5.7			.30			8.0	11.	.10
C19196	H-COAL	AS IS	4.9		1.1	.05		4.	.02	9.4		.12
C19196	H-COAL	HTA		6.0			.30			8.6	17.	.12
C19916	H-COAL-3	AS IS	3.3		.58	.12		<.5	.02	5.6		.09
C19916	H-COAL	HTA		3.5			.26			5.8	14.	.09
C19917	H-COAL	AS IS	7.4		1.6	.12		1.0	<.2	14.		.25
C19917	H-COAL	HTA		4.1			.54			15.	34.	.19
C20021	H-COAL-4	AS IS	3.3		.65	.13		<.5	.03	7.4		.10
C20021	H-COAL	HTA		<1.							3.6	
C20022	H-COAL	AS IS	7.1		2.5	.15		.71	-	20.		.24
C20022	H-COAL	HTA		<3.			.61			20.	8.7	.22
C19590	LIGNITE	AS IS	2.3		.75	.16		<.5	<.14	3.0		.04
C19590	LIGNITE	HTA		.73			.12			3.8	1.5	.04
C19591	LIGNITE	AS IS	6.6		3.4	.03		-	<.10	12.		.11
C19591	LIGNITE	HTA		2.5			.45			15.	8.4	.20
C19702	SRC-ALA-1	AS IS	3.3		.50	.10		1.8	.01	4.8		.07
C19702	SRC-ALA	HTA		2.4			.17			5.4	2.6	.06
C19703	SRC-ALA	AS IS	12.		2.6	.09		2.6		21.		.36
C19703	SRC-ALA	HTA		14.			.70			25.	22.	.33
C19705	SRC-ALA-2	AS IS	3.0		.67	.24		1.0	.01	4.8		.08
C19705	SRC-ALA	HTA		2.1			.19			5.1	12.	.08
C19706	SRC-ALA	AS IS	8.6		1.9	.11		1.9	-	17.		.26
C19706	SRC-ALA	HTA					.67			18.	41.	.27
C19708	SRC-ALA-3	AS IS	3.2		.60	.26		.6	.014	9.2		.10
C19708	SRC-ALA	HTA		3.3			.21			9.6	12.	.09
C19709	SRC-ALA	AS IS	10.		2.3	.06		1.5	-	32.		.33
C19709	SRC-ALA	HTA		21.			.46			24.	31.	.31

			GA(NAA) (PPM)	GE(UEU) (PPM)	HF(NAA) (PPM)	HG(RC) (PPM)	HO(RC) (PPM)	I(NAA) (PPM)	IN(NAA) (PPM)	LA(NAA) (PPM)	LI(AA) (PPM)	LU(NAA) (PPM)
C19711	SRC-ALA-4	AS IS	1.6		.93	.09		.1	.024	7.2		.08
C19711	SRC-ALA	HTA		<.22			.19			7.2	1.8	.07
C19712	SRC-ALA	AS IS	7.0		3.4	.05		.7	-	19.		.20
C19712	SRC-ALA	HTA		<.99			.24			23.	12.	.19
C19714	SRC-ALA-5	AS IS	2.7		.58	.09		1.1	.015	5.4		.06
C19714	SRC-ALA	HTA		.63			.07			3.3	8.2	.05
C19715	SRC-ALA	AS IS	9.6		2.4	.05		1.7	.26	20.		.25
C19715	SRC-ALA	HTA		3.6			.34			15.	32.	.24
C19141	SRC-WASH-1	AS IS	3.2		.66	.13		2.6	.1	14.		.18
C19141	SRC-WASH	HTA		7.2			.48			12.	19.	.16
C19142	SRC-WASH	AS IS	21.		3.8	.07		1.1	<1.	76.		1.4
C19142	SRC-WASH	HTA		28.			2.1			74.	120.	.82
C19488	SRC-WASH-2	AS IS	3.2		.47	.21		1.0	.02	13.		.15
C19488	SRC-WASH	HTA		5.1			.3			14.	18.	.16
C19487	SRC-WASH	AS IS	14.		2.2	.07		2.2		60.		.73
C19487	SRC-WASH	HTA		22.			1.6			69.	93.	.77
C19899	SRC-WASH-3	AS IS	3.0		.62	.26		.34	-	6.4		.09
C19899	SRC-WASH	HTA		6.5			.15			6.1	6.6	.06
C19902	SRC-WASH	AS IS	8.0		1.6	.17		.45	.02	18.		.24
C19902	SRC-WASH	HTA		18.			.36			14.	17.	.18
C20014	SRC-WASH-4	AS IS	3.8		.86	.10		1.5	<.14	6.6		.10
C20014	SRC-WASH	HTA		9.3			.22			7.3	7.7	.10
C20015	SRC-WASH	AS IS	8.6		1.6	.10		3.4	<.14	15.		.24
C20015	SRC-WASH	HTA		18.			.49			17.	17.	.23
C20016	SRC-WASH-5	AS IS	2.7		.80	.11		3.7	.022	7.0		.09
C20016	SRC-WASH	HTA		1.5			.20			9.1	9.2	.09
C20017	SRC-WASH	AS IS	6.6		1.9	.02		3.7	.05	14.		.18
C20017	SRC-WASH	HTA		3.1			.39			17.	19.	.18
C20019	SRC-WASH-6	AS IS	3.0		.90	.15		1.2	<.03	6.1		.09
C20019	SRC-WASH	HTA		1.2			.15			6.8	9.2	.07
C20020	SRC-WASH	AS IS	5.4		1.8	.03		2.3	.037	14.		.20
C20020	SRC-WASH	HTA		3.0			.34			14.	24.	.14
C19276	SYNTHOIL	AS IS	4.0		.49	.21		0.6	-	11.		.09
C19276	SYNTHOIL	HTA		4.3			.24			11.	16.	.09
C19349	SYNTHOIL	AS IS	9.8		1.4	-		<.5	.073	26.		.27
C19349	SYNTHOIL	HTA		5.6			.70			32.	46.	.26

			MN(NAA) (PPM)	MN(UEP) (PPM)	MO(UED) (PPM)	ND(NAA) (PPM)	NI(AA) (PPM)	NI(NAA) (PPM)	NI(UED) (PPM)	NI(UEP) (PPM)	PB(AA) (PPM)	PD(RC) (PPB)
C19660	CLEAN COKE	AS IS	70.					23.				
C19660	CLEAN COKE	HTA		56.	2.0	8.9	13.		16.	13.	18.	<2.7
C19661	CLEAN COKE	AS IS	51.					18.				
C19661	CLEAN COKE	HTA		41.	1.2	6.3	11.		14.	12.	22.	<2.5
C19963	FMC COED	AS IS	40.					<4.				
C19963	FMC COED	HTA		44.	4.7	5.0	2.1		2.6	2.5	6.4	<2.3
C18903	H-COAL-1	AS IS	72.					15.				
C18903	H-COAL	HTA		52.	6.0	16.3	7.5		12.	12.	6.4	4.7
C18941	H-COAL	AS IS	86.			7.0		19.				
C18941	H-COAL	HTA		77.	8.8	9.1	15.		21.	17.	16.	5.8
C19194	H-COAL-2	AS IS	54.					9.				
C19194	H-COAL	HTA		50.	7.7	9.3	11.		21.	14.	18.	47.
C19196	H-COAL	AS IS	83.			-		-				
C19196	H-COAL	HTA		82.	7.6	9.0	32.		20.	28.	13.	
C19916	H-COAL-3	AS IS	76.					11.				
C19916	H-COAL	HTA		50.	5.6	6.8	8.7		9.2	11.	12.	1.3
C19917	H-COAL	AS IS	150.					20.				
C19917	H-COAL	HTA		110.	13.	16.	22.		24.	29.	33.	1.3
C20021	H-COAL-4	AS IS	70.					12.				
C20021	H-COAL	HTA		36.	1.3		8.2		7.9	7.4	5.9	1.6
C20022	H-COAL	AS IS	120.					28.				
C20022	H-COAL	HTA		89.	7.4	22.	18.		18.	20.	15.	2.2
C19590	LIGNITE	AS IS	95.					<4.				
C19590	LIGNITE	HTA		27.	.96	2.6	1.8		1.3	.76	2.2	<1.4
C19591	LIGNITE	AS IS	220.					9.8				
C19591	LIGNITE	HTA		130.	4.4	11.	9.9		13.	10.	8.7	<7.4
C19702	SRC-ALA-1	AS IS	36.					18.				
C19702	SRC-ALA	HTA		28.	7.0	5.4	16.		18.	14.	6.8	<2.7
C19703	SRC-ALA	AS IS	270.					110.				
C19703	SRC-ALA	HTA		180.	46.	27.	100.		110.	96.	46.	<26.
C19705	SRC-ALA-2	AS IS	90.					-				
C19705	SRC-ALA	HTA		45.	3.9	5.6	8.2		10.	10.	10.	4.4
C19706	SRC-ALA	AS IS	280.					49.				
C19706	SRC-ALA	HTA		180.	19.	20.	47.		53.	62.	33.	12.
C19708	SRC-ALA-3	AS IS	28.					14.				
C19708	SRC-ALA	HTA		23.	4.5	8.4	7.0		8.3	7.7	8.5	1.8
C19709	SRC-ALA	AS IS	140.					66.				
C19709	SRC-ALA	HTA		130.	20.	32.	61.		57.	63.	42.	9.5

			MN(NAA) (PPM)	MN(UEP) (PPM)	MO(OED) (PPM)	ND(NAA) (PPM)	NI(AA) (PPM)	NI(NAA) (PPM)	NI(OED) (PPM)	NI(OEP) (PPM)	PB(AA) (PPM)	PD(RC) (PPB)
C19711	SRC-ALA-4	AS IS	20.					9.9				
C19711	SRC-ALA	HTA		16.	.51	7.1	4.4		3.9	3.3	3.8	.79
C19712	SRC-ALA	AS IS	59.					20.				
C19712	SRC-ALA	HTA		56.	1.7	17.	16.		17.	17.	20.	3.2
C19714	SRC-ALA-5	AS IS	38.					7.9				
C19714	SRC-ALA	HTA		25.	.78	4.5	3.7		4.8	4.7	4.6	.44
C19715	SRC-ALA	AS IS	120.					43.				
C19715	SRC-ALA	HTA		120.	5.2	19.	30.		38.	48.	26.	6.5
C19141	SRC-WASH-1	AS IS	44.			-		29.				
C19141	SRC-WASH	HTA		39.	4.1	12.	24.		34.	20.	16.	<4.5
C19142	SRC-WASH	AS IS	170.			-		185.				
C19142	SRC-WASH	HTA		150.	30.	82.	170.		140.	120.	100.	<42.
C19488	SRC-WASH-2	AS IS	44.					29.				
C19488	SRC-WASH	HTA		43.	6.2	17.	21.		53.	17.	8.3	<.6
C19487	SRC-WASH	AS IS	200.					190.				
C19487	SRC-WASH	HTA		200.	21.	92.	120.		200.	110.	28.	<2.5
C19899	SRC-WASH-3	AS IS	34.					12.				
C19899	SRC-WASH	HTA		27.	4.8	5.7	7.2		7.4	11.	7.4	1.7
C19902	SRC-WASH	AS IS	91.					40.				
C19902	SRC-WASH	HTA		72.	13.	16.	19.		21.	26.	18.	6.4
C20014	SRC-WASH-4	AS IS	39.					22.				
C20014	SRC-WASH	HTA		37.	4.5	8.9	16.		17.	20.	8.3	1.4
C20015	SRC-WASH	AS IS	120.					36.				
C20015	SRC-WASH	HTA		93.	10.	18.	35.		36.	44.	18.	9.8
C20016	SRC-WASH-5	AS IS	33.					5.2				
C20016	SRC-WASH	HTA		37.	.96	8.8	6.0		6.4	8.2	7.0	2.7
C20017	SRC-WASH	AS IS	75.					19.				
C20017	SRC-WASH	HTA		73.	2.2	17.	16.		17.	26.	13.	20.
C20019	SRC-WASH-6	AS IS	37.					15.				
C20019	SRC-WASH	HTA		34.	.96	6.2	5.5		6.6	8.9	7.5	<1.3
C20020	SRC-WASH	AS IS	70.					26.				
C20020	SRC-WASH	HTA		70.	2.9	13.	19.		20.	23.	16.	<4.4
C19276	SYNTHOIL	AS IS	70.					<11.				
C19276	SYNTHOIL	HTA		64.	6.9	11.	10.		24.	16.	<4.3	3.2
C19349	SYNTHOIL	AS IS	180.					34.				
C19349	SYNTHOIL	HTA		200.	19.	29.	30.		75.	49.	<12.	<2.6

			PT(RC) (PPM)	RB(NAA) (PPM)	SB(NAA) (PPM)	SC(NAA) (PPM)	SE(NAA) (PPM)	SN(OED) (PPM)	SN(XES) (PPM)	SR(NAA) (PPM)	SR(OED) (PPM)	TA(NAA) (PPM)
C19660	CLEAN COKE	AS IS		38.	.66	4.9	3.8			100.		.32
C19660	CLEAN COKE	HTA	<.13					1.2	3.9		45.	
C19661	CLEAN COKE	AS IS		24.	.33	2.9	1.8			39.		.16
C19661	CLEAN COKE	HTA	<.20					1.0	3.1		31.	
C19963	FMC COED	AS IS		4.	1.9	2.5	<1.0		<1.0	560.		.08
C19963	FMC COED	HTA	<1.3					.72	1.1		550.	
C18903	H-COAL-1	AS IS		13.	.86	3.7	3.1		1.8	14.		.15
C18903	H-COAL	HTA	<.2					.73	0.6	16.3	18.	
C18941	H-COAL	AS IS		22.	1.0	4.0	2.6		2.4	17.		.19
C18941	H-COAL	HTA	<.69					1.8	1.9		26.	
C19194	H-COAL-2	AS IS		16.	1.3	4.5	2.3		1.7	29.		.13
C19194	H-COAL	HTA	<.005					1.1			30.	
C19196	H-COAL	AS IS		29.	1.9	3.6	3.1		<1.0	28.		.17
C19196	H-COAL	HTA						1.2	0.7		25.	
C19916	H-COAL-3	AS IS		13.	1.5	2.9	2.3			16.		.13
C19916	H-COAL	HTA	<.04					1.8	1.9		17.	
C19917	H-COAL	AS IS		32.	1.6	7.6	4.8			51.		.40
C19917	H-COAL	HTA	<3.7					5.0	3.7		44.	
C20021	H-COAL-4	AS IS		6.3	.31	2.0	2.1		<1.0	190.		.11
C20021	H-COAL	HTA	<.018					1.1	1.5		140.	
C20022	H-COAL	AS IS		5.3	1.5	6.9	3.7		<1.0	580.		.32
C20022	H-COAL	HTA	<.032					2.4	3.1		350.	
C19590	LIGNITE	AS IS		1.9	.44	.99	1.0		2.0	420.		.15
C19590	LIGNITE	HTA	<.2					.62	3.1		260.	
C19591	LIGNITE	AS IS		4.6	1.4	3.9	3.7		8.4	1720.		.46
C19591	LIGNITE	HTA	<.06					3.2	12.		970.	
C19702	SRC-ALA-1	AS IS		14.	.51	2.1	3.2			73.		.13
C19702	SRC-ALA	HTA	<.04					1.0	2.0		40.	
C19703	SRC-ALA	AS IS		69.	2.6	11.	18.			280.		.55
C19703	SRC-ALA	HTA	<.26					4.5	7.2		240.	
C19705	SRC-ALA-2	AS IS		11.	.95	2.9	2.4			16.		.10
C19705	SRC-ALA	HTA	<.24					2.1	4.2		18.	
C19706	SRC-ALA	AS IS		43.	3.3	7.7	6.2			110.		.39
C19706	SRC-ALA	HTA	<.058					3.3	7.1		87.	
C19708	SRC-ALA-3	AS IS		14.	2.3	2.6	3.1			94.		.17
C19708	SRC-ALA	HTA	<.57					1.6	2.6		68.	
C19709	SRC-ALA	AS IS		79.	9.1	9.2	11.			170.		.41
C19709	SRC-ALA	HTA	<.65					9.3	7.9		150.	

			PT(RC) (PPM)	RB(NAA) (PPM)	SB(NAA) (PPM)	SC(NAA) (PPM)	SE(NAA) (PPM)	SN(UED) (PPM)	SN(XES) (PPM)	SR(NAA) (PPM)	SR(UED) (PPM)	TA(NAA) (PPM)
C19711	SRC-ALA-4	AS IS		1.3	.44	2.3	1.2			270.		.14
C19711	SRC-ALA	HTA	<.040					1.3	1.7		150.	
C19712	SRC-ALA	AS IS		24.	1.0	6.9	3.2			760.		.64
C19712	SRC-ALA	HTA	<.34					7.4	7.0		560.	
C19714	SRC-ALA-5	AS IS		14.	.43	2.0	1.3			150.		.14
C19714	SRC-ALA	HTA	<.037					1.4	1.6		110.	
C19715	SRC-ALA	AS IS		43.	1.7	8.6	4.2			490.		.46
C19715	SRC-ALA	HTA	<.19					5.2	8.5		460.	
C19141	SRC-WASH-1	AS IS		12.	1.6	6.0	2.8		1.2	68.		.12
C19141	SRC-WASH	HTA	<.034					.92	0.7		91.	
C19142	SRC-WASH	AS IS		88.	10.	20.	21.		11.	490.		.57
C19142	SRC-WASH	HTA	<.59					8.8	6.9		590.	
C19488	SRC-WASH-2	AS IS		15.	1.5	3.7	2.5		<1.0	66.		.16
C19488	SRC-WASH	HTA	<.11					1.3	1.5		56.	
C19487	SRC-WASH	AS IS		91.	11.	15.	17.		6.7	430.		.58
C19487	SRC-WASH	HTA	<.48					7.2	9.5		280.	
C19899	SRC-WASH-3	AS IS		13.	4.2	2.4	3.0		<1.0	-		.16
C19899	SRC-WASH	HTA	<.013					2.3	1.4		19.	
C19902	SRC-WASH	AS IS		38.	11.	6.7	8.4		1.5	64.		.44
C19902	SRC-WASH	HTA	<.054					6.4	4.8		56.	
C20014	SRC-WASH-4	AS IS		19.	.68	3.0	2.5		<1.0	-		.20
C20014	SRC-WASH	HTA	<.011					2.9	1.2		27.	
C20015	SRC-WASH	AS IS		46.	1.2	7.4	7.0		<1.0	43.		.37
C20015	SRC-WASH	HTA	<.02					7.2	2.2		71.	
C20016	SRC-WASH-5	AS IS		14.	.41	2.7	1.9		3.5	110.		.17
C20016	SRC-WASH	HTA	<.034					11.	3.4		110.	
C20017	SRC-WASH	AS IS		34.	.85	6.3	4.2		<1.0	250.		.41
C20017	SRC-WASH	HTA	<.013					6.8	4.0		230.	
C20019	SRC-WASH-6	AS IS		14.	.37	2.8	2.3		2.7	160.		.22
C20019	SRC-WASH	HTA	<.060					4.4	5.5		130.	
C20020	SRC-WASH	AS IS		31.	.86	5.6	3.6		2.3	210.		.40
C20020	SRC-WASH	HTA	<.088					2.9	4.4		210.	
C19276	SYNTHOIL	AS IS		27.	.29	3.7	1.7		2.0	49.		.17
C19276	SYNTHOIL	HTA	<.007					.95	2.5		46.	
C19349	SYNTHOIL	AS IS		41.	.8	8.3	5.0		<1.0	190.		.37
C19349	SYNTHOIL	HTA	<.04					3.1	7.3		130.	

			TB(NAA) (PPM)	GD(RC) (PPM)	TE(XES) (PPM)	TH(NAA) (PPM)	PR(RC) (PPM)	TL(OED) (PPM)	TM(RC) (PPM)	U(NAA) (PPM)	V(OED) (PPM)	V(OEP) (PPM)
C19660	CLEAN COKE	AS IS	.30			4.0				1.4		
C19660	CLEAN COKE	HTA	.18	1.9	<1.0		2.8	1.3	.05		30.	24.
C19661	CLEAN COKE	AS IS	.15			2.0				.9		
C19661	CLEAN COKE	HTA	.14	1.6	<1.0		1.4	.93	.03		21.	18.
C19963	FMC COED	AS IS	.12		1.6	1.4				1.4		
C19963	FMC COED	HTA	.15	1.6	<1.0		1.2	1.4	.08		16.	11.
C18903	H-COAL-1	AS IS	.18		<1.0	1.6				3.0		
C18903	H-COAL	HTA	.16	.9	<0.5	16.3	1.2	1.5	.07		22.	26.
C18941	H-COAL	AS IS	.2		1.0	1.7				3.2		
C18941	H-COAL	HTA	.22	1.9	<0.5		1.8	2.0	.09		37.	35.
C19194	H-COAL-2	AS IS	.4		<1.0	2.0				2.4		
C19194	H-COAL	HTA	.20	1.0			1.8	1.8	.10		24.	34.
C19196	H-COAL	AS IS	.60		<1.0	3.1				5.0		
C19196	H-COAL	HTA	.23	1.4	1.0		2.1	1.9	.10		41.	39.
C19916	H-COAL-3	AS IS	.15			2.1				2.2		
C19916	H-COAL	HTA	.16	2.0	<1.0		1.4	1.3	.04		23.	26.
C19917	H-COAL	AS IS	.37			5.2				5.4		
C19917	H-COAL	HTA	.38	4.6	1.3		3.6	3.0	.25		58.	64.
C20021	H-COAL-4	AS IS	.15		1.7	2.0				.81		
C20021	H-COAL	HTA	.17		<1.0			1.0			23.	17.
C20022	H-COAL	AS IS	.36		4.0	6.3				2.5		
C20022	H-COAL	HTA	.48	3.8	2.1		5.1	2.4	.22		57.	74.
C19590	LIGNITE	AS IS	.07		5.1	1.4				<.4		
C19590	LIGNITE	HTA	.05	1.0	2.1		.67	.69	.02		7.9	1.6
C19591	LIGNITE	AS IS	.27		17.	4.5				1.4		
C19591	LIGNITE	HTA	.31	1.9	7.7		2.5	2.3	.16		40.	9.8
C19702	SRC-ALA-1	AS IS	.10			1.4				1.9		
C19702	SRC-ALA	HTA	.13	.89	<1.0		1.2	1.1	.04		25.	20.
C19703	SRC-ALA	AS IS	.65			7.4				8.1		
C19703	SRC-ALA	HTA	.61	2.4	1.5		5.8	8.1	.18		130.	110.
C19705	SRC-ALA-2	AS IS	.16			1.8				3.0		
C19705	SRC-ALA	HTA	.15	.88	<1.0		1.1	1.5	.07		30.	31.
C19706	SRC-ALA	AS IS	.45			5.1				7.5		
C19706	SRC-ALA	HTA	.52	4.6	1.1		3.9	4.6	.21		81.	89.
C19708	SRC-ALA-3	AS IS	.16			2.0				2.1		
C19708	SRC-ALA	HTA	.16	.82	<1.0		2.4	1.1	.07		38.	35.
C19709	SRC-ALA	AS IS	.62			6.8				7.6		
C19709	SRC-ALA	HTA	.59	4.4	1.7		4.7	6.4	.38		220.	200.

			TB(NAA) (PPM)	GD(RC) (PPM)	TE(XES) (PPM)	TH(NAA) (PPM)	PR(RC) (PPM)	TL(OED) (PPM)	TM(RC) (PPM)	U(NAA) (PPM)	V(OED) (PPM)	V(OEP) (PPM)
C19711	SRC-ALA-4	AS IS	.15			2.3				.61		
C19711	SRC-ALA	HTA	.18	2.2	<1.0		1.5	.80	.04		19.	12.
C19712	SRC-ALA	AS IS	.42			6.8				2.6		
C19712	SRC-ALA	HTA	.42	4.5	3.6		4.2	2.3	.16		80.	39.
C19714	SRC-ALA-5	AS IS	.12			1.4				.77		
C19714	SRC-ALA	HTA	.10	.79	<1.0		.71	.34	.05		14.	13.
C19715	SRC-ALA	AS IS	.41			5.7				4.0		
C19715	SRC-ALA	HTA	.42	3.7	2.3		2.8	1.8	.06		81.	80.
C19141	SRC-WASH-1	AS IS	.76		<1.0	2.7				1.7		
C19141	SRC-WASH	HTA	.38	2.6	<0.5		3.1	2.4	.11		32.	34.
C19142	SRC-WASH	AS IS	4.6		5.2	14.				13.		
C19142	SRC-WASH	HTA	1.9	11.	2.0		17.	9.2	.75		180.	170.
C19488	SRC-WASH-2	AS IS	.43		<1.0	2.3				2.3		
C19488	SRC-WASH	HTA	.34	3.5	<0.5		3.1	1.9	.15		50.	37.
C19487	SRC-WASH	AS IS	2.1		4.7	15.				7.5		
C19487	SRC-WASH	HTA	1.6	17.	2.0		15.	7.8	.62		240.	220.
C19899	SRC-WASH-3	AS IS	.14		1.9	1.6				1.7		
C19899	SRC-WASH	HTA	.14	1.1	<1.0		1.4	.96	.05		38.	43.
C19902	SRC-WASH	AS IS	.41		2.3	4.6				5.0		
C19902	SRC-WASH	HTA	.34	3.7	<1.0		2.8	2.7	.11		110.	110.
C20014	SRC-WASH-4	AS IS	.20		1.7	2.8				1.7		
C20014	SRC-WASH	HTA	.19	1.9	<1.0		1.5	.67	.09		31.	36.
C20015	SRC-WASH	AS IS	.44		2.8	5.7				4.5		
C20015	SRC-WASH	HTA	.47	3.1	<1.0		3.7	1.1	.22		72.	94.
C20016	SRC-WASH-5	AS IS	.17		1.2	2.0				<.5		
C20016	SRC-WASH	HTA	.19	1.4	<1.0		1.9	.75	.083		17.	23.
C20017	SRC-WASH	AS IS	.44		1.9	4.7				<.5		
C20017	SRC-WASH	HTA	.37	2.7	<1.0		3.8	1.1	.17		37.	44.
C20019	SRC-WASH-6	AS IS	.16		2.0	2.2				.45		
C20019	SRC-WASH	HTA	.12	.51	<1.0		1.4	.98	.08		15.	21.
C20020	SRC-WASH	AS IS	.26		2.8	4.1				<1.0		
C20020	SRC-WASH	HTA	.28	1.8	<1.0		3.0	1.9	.20		31.	41.
C19276	SYNTHOIL	AS IS	.43		1.8	3.1				1.3		
C19276	SYNTHOIL	HTA	.22	1.0	0.7		2.5	1.5	.09		40.	26.
C19349	SYNTHOIL	AS IS	1.0		2.1	9.0				2.1		
C19349	SYNTHOIL	HTA	.62	2.4	1.9		7.2	3.2	.30		96.	77.

			W(NAA) (PPM)	Y(RC) (PPM)	YB(NAA) (PPM)	ZN(AA) (PPM)	ZR(OEP) (PPM)	SM(NAA) (PPM)	MOIST (%)	ASH (%)	FE(AA) (%)	AU(RC) (PPB)
C19660	CLEAN COKE	AS IS	.35		.80			1.6	1.7%	19.%		
C19660	CLEAN COKE	HTA		7.9	.59	130.	37.	2.1			1.9%	6.5
C19661	CLEAN COKE	AS IS	1.0		.63			1.2	.3%	14.%		
C19661	CLEAN COKE	HTA		5.8	.44	85.	27.	1.1			1.5%	6.9
C19963	FMC COED	AS IS	<1.		.44			.70	5.3%	13.%		
C19963	FMC COED	HTA		6.7	.60	4.3	22.	1.0			.66%	1.3
C18903	H-COAL-1	AS IS	1.2		.36			1.1	2.5%	12.%		
C18903	H-COAL	HTA		6.0	.53	55.	32.	1.1			1.5%	72.
C18941	H-COAL	AS IS	1.9		.57			1.5	.3%	17.%		
C18941	H-COAL	HTA		7.6	.73	69.	30.	1.5			2.1%	56.
C19194	H-COAL-2	AS IS	.92		.42			1.7	2.6%	12.%		
C19194	H-COAL	HTA		8.7	.66	62.	25.	1.6			1.5%	.76
C19196	H-COAL	AS IS	2.2		.6			2.4	0.1%	17.%		
C19196	H-COAL	HTA		8.1	.71	63.	39.	1.6			1.9%	
C19916	H-COAL-3	AS IS	1.5		.63			1.5	2.8%	12.%		
C19916	H-COAL	HTA		11.	.50	63.	24.	1.4			1.8%	7.7
C19917	H-COAL	AS IS	4.5		1.0			3.8	.1%	28.%		
C19917	H-COAL	HTA		15.	1.3	120.	57.	2.8			4.1%	100.
C20021	H-COAL-4	AS IS	2.2		.69			1.6	20.%	9.0%		
C20021	H-COAL	HTA		7.5		20.	15.				.52%	.46
C20022	H-COAL	AS IS	5.5		1.1			3.8	.5%	22.%		
C20022	H-COAL	HTA		14.	1.4	50.	74.	3.9			1.2%	2.4
C19590	LIGNITE	AS IS	2.9		.33			.41	17.5%	8.6%		
C19590	LIGNITE	HTA		4.8	.23	.74	7.3	.50			.51%	44.9
C19591	LIGNITE	AS IS	13.		.92			1.3		35.%		
C19591	LIGNITE	HTA		18.	1.2	4.7	45.	2.0			2.3%	
C19702	SRC-ALA-1	AS IS	.26		.40			1.0	2.5%	11.%		
C19702	SRC-ALA	HTA		5.1	.41	82.	22.	1.0			1.4%	1.7
C19703	SRC-ALA	AS IS	1.0	18.	2.0			5.5	1.5%	66.%		
C19703	SRC-ALA	HTA			2.1	370.	100.	3.9			8.3%	8.8
C19705	SRC-ALA-2	AS IS	.23		.41			1.2	20.%	11.%		
C19705	SRC-ALA	HTA		5.1	.57	46.	29.	.99			1.3%	1.4
C19706	SRC-ALA	AS IS	1.3		1.5			4.3	7.9%	44.%		
C19706	SRC-ALA	HTA		21.	1.8	200.	82.	3.6			4.1%	39.
C19708	SRC-ALA-3	AS IS	.83		.64			1.5	1.0%	9.3%		
C19708	SRC-ALA	HTA		5.2	.50	12.	28.	1.5			1.5%	11.
C19709	SRC-ALA	AS IS	2.0		2.0			5.3	1.7%	53.%		
C19709	SRC-ALA	HTA		21.	2.0	85.	120.	3.4			7.7%	15.

			W(NAA) (PPM)	Y(RC) (PPM)	YB(NAA) (PPM)	ZN(AA) (PPM)	ZR(OEP) (PPM)	SM(NAA) (PPM)	MOIST (%)	ASH (%)	FE(AA) (%)	AU(RC) (PPB)
C19711	SRC-ALA-4	AS IS	.39		.47			1.5	12.%	7.4%		
C19711	SRC-ALA	HTA		5.0	.45	7.6	17.	1.3			.29%	.84
C19712	SRC-ALA	AS IS	.71		1.2			3.1	1.8%	33.%		
C19712	SRC-ALA	HTA		12.	1.2	19.	29.				.76%	11.
C19714	SRC-ALA-5	AS IS	.29		.30			.82	.6%	8.8%		
C19714	SRC-ALA	HTA		3.2	.32	8.2	21.	.51			1.0%	1.2
C19715	SRC-ALA	AS IS	1.0		1.7			3.5	.7%	57.%		
C19715	SRC-ALA	HTA		22.	1.4	50.	86.	2.2			3.0%	39.
C19141	SRC-WASH-1	AS IS	.5	9.8	1.3			3.1	1.2%	10.%		
C19141	SRC-WASH	HTA			1.0	25.	20.	2.7			2.3%	2.5
C19142	SRC-WASH	AS IS	2.6	61.	5.4			15.	0.5%	70.%		
C19142	SRC-WASH	HTA			5.6	120.	93.	15.			16.%	<150.
C19488	SRC-WASH-2	AS IS	.55		.83			2.5	2.3%	12.%		
C19488	SRC-WASH	HTA		11.	.98	30.	31.	2.5			2.5%	2.7
C19487	SRC-WASH	AS IS	2.6		3.5			11.	2.3%	67.%		
C19487	SRC-WASH	HTA		43.	4.5	120.	150.	12.			12.%	8.5
C19899	SRC-WASH-3	AS IS	.50		.44			1.2	1.4%	9.6%		
C19899	SRC-WASH	HTA		4.7	.40	42.	30.	1.0			1.4%	1.8
C19902	SRC-WASH	AS IS	1.3		1.1			3.3	.1%	25.%		
C19902	SRC-WASH	HTA		15.	1.1	96.	68.	2.4		41.%	3.7%	<7.0
C20014	SRC-WASH-4	AS IS	.50		.92			1.2	.8%	13.%		
C20014	SRC-WASH	HTA		6.5	.63	66.	31.	1.2			1.6%	5.7
C20015	SRC-WASH	AS IS	1.3		1.1			2.9	.2%	28.%		
C20015	SRC-WASH	HTA		15.	1.5	150.	69.	3.1			3.3%	2.0
C20016	SRC-WASH-5	AS IS	1.0		.7			1.2	4.1%	12.%		
C20016	SRC-WASH	HTA		7.5	.60	16.	36.	1.4			1.4%	.32
C20017	SRC-WASH	AS IS	1.3		1.2			2.7	.2%	26.%		
C20017	SRC-WASH	HTA		12.	1.2	36.	79.	2.8			3.2%	.89
C20019	SRC-WASH-6	AS IS	.36		.40			1.0	5.6%	13.%		
C20019	SRC-WASH	HTA		5.7	.39	18.	36.	1.0			1.6%	.36
C20020	SRC-WASH	AS IS	1.1		.76			2.4	.1%	27.%		
C20020	SRC-WASH	HTA		12.	.88	41.	56.	2.4			3.3%	.56
C19276	SYNTHOIL	AS IS	1.0		.67			1.9	5.8%	17.%		
C19276	SYNTHOIL	HTA		9.5	.61	52.	42.	1.8			3.6%	.57
C19349	SYNTHOIL	AS IS	1.8		1.4			4.8	3.6%	48.%		
C19349	SYNTHOIL	HTA		19.	1.8	140.	120.	5.0			10.%	4.6

ALL CONCENTRATIONS HAVE BEEN CALCULATED TO THE AS RECEIVED BASIS. THE VALUES LISTED ARE IN PARTS PER MILLION UNLESS OTHERWISE INDICATED.

APPENDIX E - ELEMENTAL CONCENTRATIONS IN FEED COALS AND LIQUEFACTION RESIDUES (500°C ASH-BASIS)

		Concentration															
		%											ppm				
Process	Sample Number	Al	Ca	Fe	K	Mg	Na	N	P	S	Si	Ti	Ag	As	Au	B	Ba
CLEAN COKE	C19660(feed coal)	8.8	5.7	8.9	1.5	0.41	0.67	6.3	0.052	15	20	0.52	<0.98	28	0.034	670	1300
	C19661(residue)	9.1	5.0	10	1.6	0.42	0.64	0.77	0.063	6.5	21	0.49	<0.98	15	0.045	700	1300
COED	C19963(residue)	3.9	18	4.9	0.33	3.4	5.9	6.2	0.018	4.9	8.4	0.18	<0.99	99	0.0099	1800	2200
H-COAL-1	C18903(feed coal)	8.7	4.9	13	1.4	0.47	0.35	--	0.026	29	21	0.56	<0.78	27	0.62	1700	380
	C18941(residue)	9.0	4.4	12	1.4	0.60	0.29	9.0	0.036	10	20	0.51	<0.36	15	0.34	1300	450
H-COAL-2	C19194(feed coal)	8.6	4.1	12	1.5	0.26	0.26	15	0.043	28	20	0.60	<0.34	26	0.0065	950	450
	C19196(residue)	8.6	3.9	11	1.3	0.12	0.29	9.2	0.029	11	21	0.52	<0.81	22	--	1700	460
H-COAL-3	C19916(feed coal)	8.5	5.0	14	1.1	0.17	0.27	13	0.009	22	20	0.49	<0.94	38	0.066	1800	390
	C19917(residue)	8.2	4.6	14	1.2	0.25	0.28	3.3	<0.004	8.9	20	0.50	<0.96	17	0.36	1200	410
H-COAL-4	C20021(feed coal)	9.0	9.6	4.7	0.36	3.1	0.42	14	0.22	11	12	0.73	<5.3	24	0.0051	550	3400
	C20022(residue)	9.8	13	5.1	0.26	2.9	0.42	4.7	--	3.4	12	0.74	<5.1	17	0.011	560	3700
LIGNITE	C19590(feed coal)	4.9	18	6.5	0.22	3.9	4.8	8.7	0.23	8.2	7.8	0.23	<0.93	90	<0.057	1400	10000
	C19591(residue)	5.2	15	6.4	0.15	3.7	3.2	1.2	0.26	--	9.8	0.20	<0.95	78	0.0060	860	11000
SRC-ALA-1	C19702(feed coal)	8.5	2.8	11	1.5	0.44	0.88	10	0.18	35	22	0.53	<0.97	17	0.015	2200	580
	C19703(residue)	7.3	2.6	13	1.2	0.53	0.78	0.62	0.18	7.3	23	0.34	<0.96	12	0.013	790	590
SRC-ALA-2	C19705(feed coal)	8.6	4.9	12	1.4	0.45	0.21	11	<0.004	28	20	0.53	<0.98	29	0.012	1700	430
	C19706(residue)	6.9	3.7	8.4	1.0	0.44	0.62	1.9	0.021	5.7	25	0.44	<0.96	16	0.089	550	540
SRC-ALA-3	C19708(feed coal)	11	0.97	15	1.7	0.22	0.15	15	0.11	30	19	0.65	<0.97	94	0.12	1100	580
	C19709(residue)	8.3	1.4	14	1.5	0.56	0.58	1.4	0.056	8.4	23	0.32	<0.96	36	0.028	340	490
SRC-ALA-4	C19711(feed coal)	7.3	18	3.7	0.15	2.4	0.81	14	0.40	9.5	12	0.67	<0.94	16	0.011	440	5100
	C19712(residue)	7.8	11	2.3	0.39	2.1	0.81	2.7	0.72	1.7	20	0.66	<0.96	9.0	0.033	420	4500
SRC-ALA-5	C19714(feed coal)	9.8	6.2	11	0.90	0.68	0.74	14	0.23	21	18	0.57	<0.91	60	0.014	1000	1300
	C19715(residue)	7.4	2.6	5.1	0.74	0.67	1.8	0.99	0.11	0.39	28	0.32	<0.97	15	0.069	420	850
SRC-WASH-1	C19141(feed coal)	12	0.46	26	1.5	0.25	0.10	19	0.061	34	15	0.51	<0.40	130	0.025	880	360
	C19142(residue)	10	0.58	23	1.3	0.12	0.23	0.72	0.13	13	14	0.36	<0.38	160	<0.21	360	410
SRC-WASH-2	C19488(feed coal)	10	1.7	20	1.3	0.35	0.17	13	0.086	34	19	0.52	<0.78	200	0.023	780	410
	C19487(residue)	8.5	1.6	18	1.3	0.18	0.51	0.82	0.13	11	22	0.30	<0.77	98	0.013	240	410
SRC-WASH-3	C19899(feed coal)	9.7	2.7	14	1.5	0.22	0.21	13	0.035	25	21	0.61	5.4	70	0.019	1000	450
	C19902(residue)	9.5	2.7	13	1.5	0.12	0.17	6.4	0.026	9.5	21	0.60	<0.95	60	<0.028	950	440
SRC-WASH-4	C20014(feed coal)	8.8	3.0	13	1.3	0.16	0.48	10	0.080	31	21	0.56	<5.3	15	0.045	1400	500
	C20015(residue)	9.0	3.9	12	1.3	0.14	0.47	5.0	0.11	7.5	21	0.54	<5.4	14	0.0072	1400	530
SRC-WASH-5	C20016(feed coal)	8.9	5.0	11	0.97	0.41	0.57	10	0.24	19	19	0.57	<5.3	50	0.0026	730	750
	C20017(residue)	9.0	4.3	13	1.0	0.31	0.59	5.5	0.24	7.9	19	0.55	<5.5	55	0.0035	670	820
SRC-WASH-6	C20019(feed coal)	9.4	3.6	11	1.2	0.47	0.39	9.9	0.16	22	19	0.55	<5.3	47	0.0028	780	850
	C20020(residue)	8.6	4.1	12	0.96	0.11	0.49	5.2	0.19	8.2	18	0.52	<5.2	60	0.0021	900	790
SYNTHOIL	C19276(feed coal)	8.3	2.8	21	1.1	0.018	0.14	8.2	0.12	33	17	0.53	<0.77	45	0.0034	590	750
	C19349(residue)	9.4	3.1	19	1.0	0.006	0.14	1.7	0.042	13	17	0.42	<0.77	15	0.0096	420	880

APPENDIX E - ELEMENTAL CONCENTRATIONS IN FEED COALS AND LIQUEFACTION RESIDUES (500°C ASH-BASIS) (Continued)

		Concentration																		
		ppm																		
Process	Sample Number	Be	Bi	Br	Cd	Ce	Cl	Co	Cr	Cs	Cu	Dy	Er	Eu	F	Ga	Gd	Ge	Hf	Hg
CLEAN COKE	C19660(feed coal)	5.7	<1.2	83	<1.9	110	21000	23	110	14	59	6.7	4.5	2.0	670	27	9.8	2.2	7.7	0.46
	C19661(residue)	5.0	<1.2	84	<1.8	95	23000	24	150	11	75	7.0	4.1	1.6	770	27	11	2.5	5.0	0.35
COED	C19963(residue)	5.0	<4.6	15	<3.7	64	700	14	46	1.9	57	8.4	5.7	1.5	160	21	12	<3.1	4.7	1.8
H-COAL-1	C18903(feed coal)	9.5	<5.2	28	<2.3	84	3200	71	200	11	68	8.7	6.3	1.9	600	35	7.8	44	6.2	0.95
	C18941(residue)	7.8	<4.8	28	<3.5	90	3500	62	160	10	76	9.0	5.6	1.8	600	20	11	32	5.0	0.18
H-COAL-2	C19194(feed coal)	8.0	<5.2	28	<3.0	120	2800	47	230	11	86	6.0	8.3	2.5	580	33	8.6	49	5.4	1.8
	C19196(residue)	5.8	<5.2	25	<2.4	100	2300	29	130	13	69	6.9	4.9	1.8	580	28	8.1	35	6.3	0.29
H-COAL-3	C19916(feed coal)	7.2	<5.1	27	<2.0	98	3600	28	130	10	78	8.5	8.3	2.1	470	28	17	30	4.9	1.0
	C19917(residue)	6.4	<3.6	25	<1.9	96	2100	33	140	12	82	8.9	3.9	2.3	390	26	16	15	5.7	0.43
H-COAL-4	C20021(feed coal)	2.2	<4.4	23	<4.4	140	560	37	92	<6.7	170	18	--	3.4	490	37	--	<11	7.2	1.4
	C20022(residue)	3.5	<4.6	13	<4.5	170	700	56	91	3.7	190	13	7.9	3.8	560	33	18	<14	12	0.70
LIGNITE	C19590(feed coal)	3.3	<1.2	40	<1.9	59	340	12	30	1.3	31	5.4	4.0	0.82	190	27	12	8.5	8.8	1.9
	C19591(residue)	3.5	<1.2	10	1.8	68	--	14	36	1.2	39	2.7	5.2	1.1	120	19	5.5	7.2	9.8	0.086
SRC-ALA-1	C19702(feed coal)	11	<1.1	54	4.2	77	8100	27	200	11	92	8.8	4.6	1.6	800	29	7.9	21	4.4	0.88
	C19703(residue)	9.8	<1.2	32	3.1	81	6300	28	240	10	110	6.3	3.5	1.3	530	18	3.7	21	4.0	0.14
SRC-ALA-2	C19705(feed coal)	7.7	<5.3	18	<1.9	93	2800	24	190	12	71	11	5.3	1.8	460	27	7.8	19	6.0	2.1
	C19706(residue)	5.3	<4.6	12	<1.8	78	1200	21	150	6.9	83	7.6	4.8	1.7	480	20	11	--	4.4	0.25
SRC-ALA-3	C19708(feed coal)	8.0	<5.4	42	<1.8	170	3000	15	180	13	130	15	8.2	3.1	660	35	8.9	36	6.5	2.8
	C19709(residue)	3.6	<5.6	18	<1.8	120	2300	31	160	9.6	80	7.9	3.4	1.8	390	19	8.3	39	4.3	0.11
SRC-ALA-4	C19711(feed coal)	1.8	<5.4	15	<1.9	180	470	25	79	1.9	190	15	7.5	3.8	690	22	30	<3.0	13	1.2
	C19712(residue)	1.5	<6.0	6.3	<1.8	99	420	11	110	4.2	99	6.0	4.5	1.8	420	21	13	<3.0	10	0.15
SRC-ALA-5	C19714(feed coal)	3.2	<4.5	150	<1.8	100	12000	23	120	7.9	58	8.6	3.0	1.8	740	31	9.0	7.2	6.6	1.0
	C19715(residue)	1.8	<5.3	49	<1.8	66	4100	15	110	5.5	46	5.3	1.7	1.1	370	17	6.5	6.4	4.2	0.088
SRC-WASH-1	C19141(feed coal)	27	<5.0	37	<3.4	250	1900	81	230	6.0	190	22	15	6.2	700	32	26	72	6.6	1.3
	C19142(residue)	13	<5.7	8.6	<3.4	200	1200	63	210	5.7	210	10	9.8	4.0	500	30	16	40	5.4	0.10
SRC-WASH-2	C19488(feed coal)	12	<5.2	41	<2.4	200	2800	62	170	11	140	16	9.5	4.6	780	28	30	44	4.1	1.8
	C19487(residue)	8.6	<4.5	10	<2.4	190	1600	66	220	9.7	180	4.2	8.8	3.7	300	21	25	33	3.3	0.10
SRC-WASH-3	C19899(feed coal)	10	<5.2	59	<1.9	110	6700	34	140	12	72	12	5.1	2.2	530	31	12	68	6.5	2.7
	C19902(residue)	8.3	<4.0	56	<1.9	120	5800	32	160	13	78	10	5.6	2.3	440	32	15	71	6.4	0.67
SRC-WASH-4	C20014(feed coal)	5.0	<4.8	23	<4.5	120	1600	31	230	14	81	8.8	6.1	2.2	800	30	15	74	6.8	0.80
	C20015(residue)	5.7	<3.6	20	<4.3	130	1500	32	230	12	81	7.2	6.1	2.4	570	31	11	64	5.7	0.36
SRC-WASH-5	C20016(feed coal)	4.1	<4.9	97	<4.5	140	8900	22	110	8.9	100	6.3	5.8	2.1	630	22	11	12	6.5	0.89
	C20017(residue)	4.3	<3.9	110	<4.3	130	8600	26	140	9.0	90	6.3	5.1	2.1	590	26	11	12	7.4	0.078
SRC-WASH-6	C20019(feed coal)	4.3	<4.7	94	<4.4	97	6900	21	110	8.6	120	8.6	5.1	1.5	540	23	4.0	9.4	7.0	1.2
	C20020(residue)	4.1	<3.7	100	<4.5	95	7100	22	110	7.9	79	6.4	4.5	1.6	600	20	6.7	11	6.7	0.11
SYNTHOIL	C19276(feed coal	7.1	<4.7	5.3	<2.4	110	280	36	150	8.9	58	9.5	4.3	2.0	370	24	5.9	26	2.9	1.2
	C19349(residue)	5.9	<4.2	3.1	<2.3	94	290	29	170	7.5	78	6.3	4.8	2.0	420	20	5.0	12	2.9	--

APPENDIX E - ELEMENTAL CONCENTRATIONS IN FEED COALS AND LIQUEFACTION RESIDUES (500°C ASH-BASIS) (Continued)

		Concentration																
		ppm																
Process	Sample Number	Ho	I	In	La	Li	Lu	Mn	Mo	Nd	Ni	Pb	Pd	Pr	Pt	Rb	Sb	Sc
CLEAN COKE	C19660(feed coal)	1.6	12	0.10	57	83	0.62	330	10	46	84	93	<0.014	14	<2.8	200	3.4	25
	C19661(residue)	1.1	11.9	<0.35	52	91	0.60	320	8.4	44	96	150	<0.008	9.8	<6.4	170	2.3	20
COED	C19963(residue)	1.8	<38	<2.3	41	15	0.77	320	36	38	18	49	<0.018	9.2	<9.9	31	15	19
H-COAL-1	C18903(feed coal)	1.7	8.7	1.5	52	100	0.91	540	52	55	100	56	0.041	10	<1.7	110	7.5	32
	C18941(residue)	1.7	6.0	--	47	100	0.84	490	53	55	108	96	0.035	11	<4.1	130	6.0	24
H-COAL-2	C19194(feed coal)	2.6	<4.3	--	67	95	0.86	450	66	80	130	150	0.40	15	<0.043	140	11	39
	C19196(residue)	1.7	<29	0.12	52	98	0.69	480	44	52	154	75	--	12	--	170	11	21
H-COAL-3	C19916(feed coal)	2.2	<17	0.17	49	120	0.77	540	48	58	85	100	0.011	12	<0.34	110	13	25
	C19917(residue)	1.9	3.6	<0.71	52	120	0.78	460	46	57	85	120	0.0046	13	<13	110	5.7	27
H-COAL-4	C20021(feed coal)	--	<17	0.33	82	40	1.1	590	14	--	99	66	0.018	--	<0.20	70	4.4	22
	C20022(residue)	2.8	3.3	--	93	40	1.1	490	34	100	98	70	0.010	24	<0.15	25	5.1	32
LIGNITE	C19590(feed coal)	1.4	4.7	<1.6	40	18	0.47	710	11	30	15	26	<0.016	7.8	<2.3	22	5.1	12
	C19591(residue)	1.3	2.0	<0.29	39	24	0.45	500	13	32	31	25	<0.021	7.2	<0.17	13	4.0	11
SRC-ALA-1	C19702(feed coal)	1.5	20	0.088	45	23	0.57	280	62	48	150	60	<0.024	11	<0.35	120	4.5	19
	C19703(residue)	1.1	5.0	--	35	34	0.52	340	70	41	160	70	<0.040	8.9	<0.40	140	4.0	17
SRC-ALA-2	C19705(feed coal)	1.7	8.9	0.089	44	110	0.71	600	35	50	84	89	0.039	9.8	<2.1	98	8.5	26
	C19706(residue)	1.5	5.5	--	40	94	0.61	530	44	46	120	76	0.028	8.9	<0.13	99	7.6	18
SRC-ALA-3	C19708(feed coal)	2.3	7.6	0.15	100	130	1.0	280	49	91	100	92	0.019	26	<6.2	150	25	28
	C19709(residue)	0.87	3.6	--	53	58	0.60	250	38	60	120	79	0.018	8.8	<1.2	150	17	17
SRC-ALA-4	C19711(feed coal)	2.6	2.7	0.32	97	24	1.0	240	6.9	96	52	51	0.011	20	<0.54	18	5.9	31
	C19712(residue)	0.72	3.0	--	63	36	0.58	170	5.1	51	53	60	0.010	13	<1.0	42	3.0	21
SRC-ALA-5	C19714(feed coal)	0.80	12	0.17	49	93	0.62	360	8.9	51	60	52	0.0050	8.1	<0.42	160	4.9	23
	C19715(residue)	0.60	3.7	0.46	31	56	0.43	210	9.2	34	70	46	0.011	4.9	<0.34	76	3.0	15
SRC-WASH-1	C19141(feed coal)	4.8	26	1.0	130	190	1.7	420	41	120	270	160	<0.045	31	<0.34	120	16	60
	C19142(residue)	3.0	2.1	<1.4	110	170	1.6	230	43	120	220	140	<0.060	24	<0.84	130	14	29
SRC-WASH-2	C19488(feed coal)	2.6	11	0.17	120	160	1.3	380	53	150	260	72	0.0052	27	<0.95	130	13	32
	C19487(residue)	2.4	4.2	--	96	140	1.1	300	31	140	230	42	<0.0037	22	<0.71	140	16	22
SRC-WASH-3	C19899(feed coal)	1.6	3.5	--	65	69	0.79	320	50	60	98	77	0.018	15	<0.14	140	44	25
	C19902(residue)	1.4	1.8	0.079	63	67	0.83	320	52	64	110	71	0.025	11	<0.21	150	44	27
SRC-WASH-4	C20014(feed coal)	1.8	12	<1.1	55	61	0.80	300	36	71	150	66	0.011	12	<0.088	150	5.4	24
	C20015(residue)	1.8	13	<0.50	57	61	0.84	380	36	64	135	64	0.035	13	<0.072	160	4.3	26
SRC-WASH-5	C20016(feed coal)	1.6	30	0.18	65	75	0.73	280	7.8	71	52	57	0.022	15	<0.28	110	3.3	22
	C20017(residue)	1.5	14	0.20	61	74	0.71	290	8.6	67	76	51	0.078	15	<0.051	130	3.3	25
SRC-WASH-6	C20019(feed coal)	1.2	9.4	<0.23	50	72	0.62	280	7.5	48	70	58	<0.010	11	<0.47	110	2.9	22
	C20020(residue)	1.3	8.2	0.14	52	90	0.64	260	11	49	82	60	<0.016	11	<0.33	120	3.2	21
SYNTHOIL	C19276(feed coal)	1.4	4.7	--	65	95	0.53	400	41	65	91	<26	0.019	15	<0.042	160	1.7	22
	C19349(residue)	1.5	<1.0	0.15	61	96	0.55	400	40	61	98	<25	0.0054	15	<0.084	86	1.7	17

APPENDIX E - ELEMENTAL CONCENTRATIONS IN FEED COALS AND LIQUEFACTION RESIDUES (500°C ASH-BASIS) (Continued)

		Concentration																
		ppm																
Process	Sample Number	Se	Sm	Sn	Sr	Ta	Tb	Te	Th	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
CLEAN COKE	C19660(feed coal)	20	9.6	13	370	1.7	1.2	<5.2	21	6.7	0.26	7.2	140	1.8	41	3.6	670	190
	C19661(residue)	13	8.1	14	250	1.1	1.0	<7.0	14	6.5	0.21	6.3	140	7.0	41	3.7	600	190
COED	C19963(residue	<7.7	6.5	5.5	4200	0.61	1.0	<7.7	11	11	0.61	11	100	<7.7	51	4.0	33	170
H-COAL-1	C18903(feed coal)	27	9.5	5.8	140	1.3	1.5	<4.3	14	13	0.61	26	210	10	52	3.9	480	280
	C18941(residue)	16	9.0	11	130	1.1	1.3	<3.0	10	12	0.54	19	220	11	46	3.9	410	180
H-COAL-2	C19194(feed coal)	20	14	9.5	250	1.1	2.6	<8.6	17	15	0.86	21	250	7.9	75	4.6	530	210
	C19196(residue)	18	12	5.5	150	0.98	2.4	<5.6	18	11	0.58	29	230	13	47	3.8	360	220
H-COAL-3	C19916(feed coal)	20	12	16	140	1.1	1.3	<8.5	18	11	0.34	19	210	13	94	4.8	540	200
	C19917(residue)	17	12	16	170	1.4	1.3	4.6	19	11	0.89	19	220	16	53	4.1	430	200
H-COAL-4	C20021(feed coal)	23	18	15	1800	1.2	1.8	<11	22	11	--	9.0	220	24	83	7.7	220	170
	C20022(residue)	17	18	13	2200	1.5	2.0	9.8	29	11	1.0	12	300	26	65	5.8	230	340
LIGNITE	C19590(feed coal)	12	5.3	22	4000	1.8	0.70	25	16	8.1	0.23	<4.7	56	34	56	2.9	8.6	85
	C19591(residue)	11	4.8	22	3900	1.3	0.84	22	13	6.6	0.46	4.0	72	37	52	3.1	14	130
SRC-ALA-1	C19702(feed coal)	28	8.8	13	500	1.1	1.0	<8.8	12	9.7	0.35	17	200	2.3	45	3.5	720	190
	C19703(residue)	27	7.2	8.9	400	0.84	0.96	2.2	11	12	0.27	12	180	1.5	27	3.1	560	150
SRC-ALA-2	C19705(feed coal)	21	9.8	28	150	0.89	1.4	<8.9	16	13	0.62	27	270	2.0	45	4.4	410	260
	C19706(residue)	14	9.1	12	230	0.89	1.1	2.5	12	11	0.48	17	200	3.0	48	3.8	460	190
SRC-ALA-3	C19708(feed coal)	33	16	23	880	1.8	1.7	<11	22	12	0.76	23	390	9.0	56	6.2	130	300
	C19709(residue)	21	8.2	16	300	0.77	1.1	3.2	13	12	0.71	14	400	3.8	39	3.8	160	230
SRC-ALA-4	C19711(feed coal)	16	19	20	2800	1.9	2.2	<13	31	11	0.54	8.2	210	5.3	67	6.2	100	230
	C19712(residue)	9.6	9.3	22	2000	1.9	1.3	11	20	6.9	0.48	7.8	180	2.1	36	3.6	57	87
SRC-ALA-5	C19714(feed coal)	15	7.5	17	1500	1.6	1.3	<11	16	3.9	0.57	8.7	150	3.3	36	3.5	93	240
	C19715(residue)	7.4	5.0	12	840	0.8	0.73	4.0	10	3.2	0.11	7.1	140	1.8	39	2.7	88	150
SRC-WASH-1	C19141(feed coal)	28	29	8.1	800	1.2	3.8	<5.0	27	24	1.1	17	330	5.0	98	12	250	200
	C19142(residue)	30	21	11	770	0.81	2.7	2.9	20	13	1.1	19	250	3.7	87	7.9	170	130
SRC-WASH-2	C19488(feed coal	22	22	12	530	1.3	3.3	<4.3	20	16	1.3	20	380	4.7	95	7.8	260	270
	C19487(residue)	25	17	12	530	0.86	2.8	3.0	22	12	0.92	11	340	3.9	64	6.0	180	220
SRC-WASH-3	C19899(feed coal)	31	12	19	200	1.7	1.5	<20	17	10	0.52	18	420	5.2	49	4.4	440	310
	C19902(residue)	33	11	22	240	1.7	1.5	<4.0	18	11	0.44	20	440	5.2	60	4.4	380	270
SRC-WASH-4	C20014(feed coal)	20	9.6	16	220	1.6	1.6	<14	22	5.3	0.72	14	270	4.0	52	6.2	530	250
	C20015(residue)	25	11	17	200	1.3	1.6	<3.6	20	3.9	0.79	16	300	4.7	54	5.4	540	250
SRC-WASH-5	C20016(feed coal)	15	11	58	890	1.4	1.5	<8.1	16	6.1	0.67	<4.1	160	8.1	61	5.3	130	290
	C20017(residue)	16	11	21	940	1.6	1.6	<3.9	18	4.3	0.67	<2.0	160	5.1	47	4.7	140	310
SRC-WASH-6	C20019(feed coal)	18	7.8	39	1100	1.7	1.1	<7.8	17	7.6	0.62	3.5	140	2.8	44	3.1	140	280
	C20020(residue)	13	9.0	14	790	1.5	1.0	<3.7	15	7.1	0.75	<3.7	140	4.1	45	3.1	150	210
SYNTHOIL	C19276(feed coal)	10	11	10	280	1.0	1.9	4.2	18	8.9	0.53	7.7	200	5.9	56	3.8	310	250
	C19349(residue)	10	10	11	340	0.77	1.7	4.0	19	6.7	0.63	4.4	180	3.8	40	3.4	290	250

APPENDIX F

HOTELLING T^2 TEST FOR ASH

The "t" test is a univariate statistical test designed to test the hypothesis that the means of two sample populations are equal against the hypothesis that they are not equal. Thus:

$$H_0: \mu_1 = \mu_2$$

against

$$H_1: \mu_1 \neq \mu_2.$$

In making the "t" test it is assumed that the samples were drawn at random from normally distributed populations having equal variances.

Univariate statistical tests have been extended to multivariate data by extending the concept of the normal distribution "to include situations in which observational units consist of many variables" (Davis, 1973). The extension of the "t" test to multivariate data is Hotelling's T^2 test, which tests the hypothesis that two mean vectors of two independent random samples are equivalent against the hypothesis that they are not, or:

$$H_2: \mu_1 = \mu_2$$

against

$$H_3: \mu_1 \neq \mu_2.$$

The assumption is made that the samples were drawn from multivariate normal populations having the same variance-covariance matrix. The resulting T^2 test statistic can be applied to special tables of the T^2 distribution, or it can be converted to an F value, which allows the use of conventional F tables. The conversion equation used when testing the equivalence of two mean vectors is:

$$F = \frac{n_1 + n_2 - m - 1}{(n_1 + n_2 - 2)m} T^2 \qquad (1)$$

where n_1 and n_2 are the numbers of samples in the two sample sets, and m is the number of variables (2). The degrees of freedom are m and $(n_1 + n_2 - m - 1)$.

For purposes of the T^2 test it seems appropriate to group all of the feed coals together and all of the residues together. There are, in this study, 17 sets of feed coals and residues and the feed coals could be tested directly against the residues. However, it is beneficial to test the two groups separately against a "standard" population, not only to test their equivalence to each other, but also to test their equivalence to coals of the United States. The "standard" population of coals has been derived from file data of the Illinois State Geological Survey. There are 172 coals in the "standard" population comprised of 120 coals from the Interior Province, 20 coals from the Eastern Province, and 32 coals from the Western Province. Data for 13 elements (Fe, Na, As, Be, Br, Co, Cr, Cu, Mn, Ni, Sb, Se, and V) in these coals were used in testing against the liquefaction feed coals and residues. The same 13 variables were used in each of the three populations. The sample sets were

Table F1. Results of Hotelling's T^2 test on feed coals and residues of liquefaction processes.

	As Received Basis			Ash Basis		
Test Population	T^2 Value	F Value	F Test Statistic (5%)	T^2 Value	F Value	F Test Statistic (5%)
Feed Coals	21.15	1.52	2.24	16.45	1.18	2.24
Residues	249.34	17.95	2.24	24.38	1.76	2.24

tested on the as received basis and on the 500°C ash basis. Table F1 gives the Hotelling's T^2 value, the corresponding F value, and the F test statistics for the numbers of degrees of freedom (13 and 175) involved. If the calculated F value is larger than the F test statistic, then the hypothesis that the two population mean vectors are equivalent is rejected.

The statistical tests will tell only what something is not and will not give conclusive information about what something is. Table F1 does tell us that on the as received basis the mean vectors of the residues and feed coals are not equivalent. However, on the ash basis, the data indicate that the hypothesis that the two mean vectors are equivalent is not disproven by the T^2 test, or that the 500°C ashes of the residues are not different from the ashes of the feed coals.

APPENDIX G

RESULTS OF REPLICATE 500°C ASH DETERMINATIONS OF COALS AND LIQUEFACTION RESIDUE SAMPLES

Whole Coal			Liquefaction Residue		
Sample Number	Mean, %	RSD, %	Sample Number	Mean, %	RSD, %
C-19660	19.37(4)	0.39	C-19661	14.26(5)	0.64
C-18903	11.39(9)	0.77	C-19876	16.09(3)	0.21
C-19194	11.64(2)	0.08	C-19963	13.06(4)	1.59
C-19916	11.72(5)	0.38	C-18941	16.65(4)	0.92
C-20021	8.99(7)	0.73	C-19196	17.36(3)	1.38
C-19590	8.56(10)	0.66	C-20022	21.52(3)	0.76
C-19702	11.32(6)	0.15	C-19706	43.58(2)	0.06
C-19705	11.22(6)	0.76	C-19709	53.17(2)	0.25
C-19708	9.26(7)	0.39	C-19712	33.34(2)	0.06
C-19711	7.42(10)	0.40	C-20015	27.93(2)	0.03
C-19714	8.81(7)	0.41	C-20020	26.72(2)	4.11
C-19141	9.97(6)	0.54	C-19349	47.81(2)	0.23
C-19488	11.59(6)	0.22		Average...	0.85
C-19899	9.56(5)	0.14			
C-20014	12.56(4)	0.52			
C-20016	12.32(4)	1.63			
C-20019	12.82(4)	3.16			
C-19276	16.85(3)	0.14			
	Average...	0.64			

( ) = number of determinations

APPENDIX H

CHEMICAL COMPOSITION OF FILTER-AIDS AND EFFECT OF FILTER-AIDS ON COMPOSITION OF LIQUEFACTION RESIDUES

Seven of the 18 liquefaction runs studied, the 5 SRC-Alabama runs and SRC-Wash-1 and SRC-Wash-2, involved a filtration at elevated temperatures to separate the final liquid mixture from the solid residue. This involved the use of a filter mat, composed mainly of diatomaceous earth mixed with lesser amounts of asbestos, that was coated over a perforated rotating drum. The liquid was filtered through the mat into the interior of the drum while the solid residue was continuously scraped off the drum. The data from those seven runs showed that Si was significantly elevated in most of the residues, relative to its concentration in the feed coals. Scanning electron microscopy studies revealed that some of the filter-aid material was in the residues samples.

Some representative samples of the filter-aid materials used in the two plants were chemically analyzed for 49 elements. These samples were not necessarily from the same batch of filter-aids as used in the run from which we obtained samples of feed coal and residue for analysis. The results are shown in Table H1.

Data from runs that did not use filter-aids indicated that Si (Figure 2.24) was not a mobile element and is neither volatilized nor mechanically enriched or depleted in going through the liquefaction process from feed coal to residue. With the assumption that the behavior of silicon would not differ significantly in runs using filter-aids and based upon the "apparent" Si enrichment, calculations were done to correct the concentrations of elements in the residues from these runs for the contribution made by the filter-aid materials.

For instance, in run SRC-ALA-3 the residue has a Si concentration of 23 percent on the 500°C ash basis and the concentration of Si in the feed coal ash is 19 percent (Appendix E). If one assumes that the enrichment of 4 percent absolute in the silicon comes solely from the filter-aid, in which the Si concentration is about 38 percent, the following equation gives the amount of silicon contributed to the residue from the contaminating filter-aid.

$$X\ (19\%) + [100 - X]\ (38\%) = 100\ (23\%)$$

where X = % residue material derived from feed coal,
and $100 - X$ = % residue material derived from filter-aid.

Solving for X we get 79 percent; thus 21 percent by weight of the material in the residue is assumed to be derived from the filter-aid.

In the same manner the percentage of filter-aid materials in the residue necessary to correct for "zero mobility" of Si was calculated for the other five runs. The calculated values are given in Table H2.

By using the values for percentage of filter-aid in residue from Table H2, one can calculate (assuming Si immobility) a corrected concentration in

Table H1. Chemical analysis of filter-aid material.

Sample Number	Sample Description	%								ppm			
		Al	Ca	Fe	K	Mg	P	Si	Ti	Ag	As	B	Ba
C19371	SRC-Wash (DICALCITE 600)	1.7	3.8	0.99	.35	.53	.14	39	.10	2.0	4.7	300	340
C19372	SRC-Wash (SPEED PLUS)	1.7	1.8	1.0	.35	.45	.10	40	.09	1.6	2.5	180	310
C19373	SRC-Wash (SPEEDEX)	1.4	2.1	0.93	.34	.41	.07	40	.09	2.3	6.5	220	290
C19374	SRC-Wash (CELITE 545)	2.1	0.27	1.2	.49	.45	.07	41	.13	1.4	3.8	150	290
C19375	SRC-Wash (FIBRA FLO 11-C)	2.4	0.32	1.2	.57	2.3	.07	38	.14	1.4	7.0	150	290
C19718	SRC-Ala	1.8	0.18	1.1	.42	2.3	.06	38	.10	<2.0	<1.5	190	220

Sample Number	Sample Description	ppm											
		Be	Br	Cd	Ce	Co	Cr	Cs	Cu	Eu	Ga	Ge	Hf
C19371	SRC-Wash (DICALCITE 600)	<1.0	<2.0	<4.0	19	17	140	1.0	53	.40	5.2	<14	1.0
C19372	SRC-Wash (SPEED PLUS)	<1.0	<2.0	16.0	25	7.4	110	1.1	41	.70	5.5	<15	1.2
C19373	SRC-Wash (SPEEDEX)	<1.0	3.1	15.0	16	6.3	140	1.1	54	.40	---	<15	1.1
C19374	SRC-Wash (CELITE 545)	<1.0	7.0	<4.0	22	5.2	68	1.3	24	.70	6.3	<15	1.4
C19375	SRC-Wash (FIBRA FLO 11-C)	<1.0	4.0	<3.0	24	11	180	1.3	27	.40	4.5	<15	1.5
C19718	SRC-Ala	<1.0	3.8	<4.0	17	7.3	140	1.3	18	.40	7.2	<15	1.1

Sample Number	Sample Description	ppm												
		Hg	La	Li	Lu	Mn	Mo	Na%	Ni	Pb	Rb	Sb	Sc	Se
C19371	SRC-Wash (DICALCITE 600)	.04	7.0	7.5	.17	68	120	1.5	91	<47	25	3.8	3.9	1.0
C19372	SRC-Wash (SPEED PLUS)	.03	11	5.0	.36	49	37	1.6	74	<47	27	3.0	5.4	.80
C19373	SRC-Wash (SPEEDEX)	.07	10	6.1	.20	50	52	2.0	96	<47	28	4.4	3.6	2.4
C19374	SRC-Wash (CELITE 545)	.02	9.0	9.8	.24	72	23	2.3	42	<47	38	2.0	5.3	<1.0
C19375	SRC-Wash (FIBRA FLO 11-C)	.04	10	10.0	.16	120	32	2.3	180	<47	37	1.9	5.3	2.0
C19718	SRC-Ala	---	10	7.2	.12	97	10	3.0	140	<47	31	1.4	4.5	.80

Sample Number	Sample Description	ppm											
		Sn	Sr	Ta	Tb	Te	Th	Tl	U	V	Yb	Zn	Zr
C19371	SRC-Wash (DICALCITE 600)	5	280	.20	.24	<1.0	3.4	<10	8.4	380	1.1	120	38
C19372	SRC-Wash (SPEED PLUS)	3	160	.25	.42	<1.0	4.3	<10	15	290	2.0	110	18
C19373	SRC-Wash (SPEEDEX)	3.7	200	.26	.26	<1.0	3.2	<10	9.1	330	1.0	120	17
C19374	SRC-Wash (CELITE 545)	2.2	82	.30	.36	<1.0	5.3	<10	9.0	160	1.3	45	41
C19375	SRC-Wash (FIBRA FLO 11-C)	3.6	100	.34	.23	<1.0	4.5	<10	11	210	.90	70	34
C19718	SRC-Ala	2.5	75	.20	.29	<1.0	3.8	<10	4.5	130	.80	34	20

Table H2. Calculated amount of filter-aid material in residues of SRC-ALA and SRC-WASH runs.

Run	Residue sample no.	% Filter-aid in residue
SRC-ALA-1	C-19703	6
SRC-ALA-2	C-19706	28
SRC-ALA-3	C-19709	21
SRC-ALA-4	C-19712	31
SRC-ALA-5	C-19715	50
SRC-WASH-1	C-19142	<1
SRC-WASH-2	C-19487	14

the residue. Aluminum in run SRC-ALA-3 will serve to illustrate the correction. The Al concentration in the residue is calculated by:

$$Al_{(RES + FA)} = Al_{(FA)} (0.21) + Al_{(RES)} (0.79)$$

where: $Al_{(RES + FA)}$ = measured Al concentration in residue = 8.3%;
$Al_{(FA)}$ = measured Al concentration in filter-aid = 1.8%; and
$Al_{(RES)}$ = Al concentration in residue unaffected by filter-aid.

Solving for $Al_{(RES)}$, the result is 10.0 percent Al. The gain/loss value can then be calculated and is found to be -9 percent, a value which is a less-pronounced loss than the -23 percent loss actually measured (with no consideration for filter-aid contributions). The above procedure was followed to calculate corrected residue values for all elements that had filter-aid data available. The results are shown in Table H3. The gain/loss values were then calculated and averaged for each element and are shown in Table H4.

No filter-aid data were available for a number of elements. For N and S, it was assumed that their concentrations in the filter-aid were negligible with respect to the filter-aid. For the remaining elements lacking filter-aid data, no conclusions could be drawn, and their mobility behavior was assumed to parallel those runs not using filter-aids.

In the Al example discussed above, as with most of the elements, the concentrations observed in the filter-aids are considerably less than the concentrations found in the residues. This situation results in a dilution effect where losses are enhanced and gains are inhibited. For the elements Mg and Na though, the above situation is reversed; they are more concentrated in the filter-aid than in the residue, and results show inhibited losses and enhanced gains.

From the discussion above we conclude that, in general, the presence of filter-aids in the residues has increased the apparent mobility of most of the elements. Before correcting for the filter-aids, 21 of 47 elements showed 4 or more losses and 3 of 47 elements showed 3 or more gains. After correcting for the filter-aids, only 13 elements showed similar losses and 5 elements

Table H3. Elemental concentrations in feed coals and corrected liquefaction residues (500°C ash basis) for sets using filter aid.

		Concentration									
		%									
Process	Sample Number	Al	Ca	Fe	K	Mg	Na	N	P	S	Ti
SRC-ALA-1	C19702(feed coal)	8.5	2.8	11	1.5	0.44	0.88	10	0.18	35	0.53
	C19703(residue)	7.7	2.8	13.8	1.2	0.42	0.64	.66	0.19	8	0.36
SRC-ALA-2	C19705(feed coal)	8.6	4.9	12	1.4	0.45	0.21	11	<.004	28	0.53
	C19706(residue)	8.9	5.1	11.2	1.2	0	0	2.6	0.006	8	0.57
SRC-ALA-3	C19708(feed coal)	11	0.97	15	1.7	0.22	0.15	15	0.11	30	0.65
	C19709(residue)	10.0	1.7	17.4	1.8	0.10	0	1.8	.055	11	0.38
SRC-ALA-4	C19711(feed coal)	7.3	18	3.7	0.15	2.4	0.81	14	0.40	9.5	0.67
	C19712(residue)	10.5	15.9	2.8	0.38	2.0	0	3.9	1.02	3	0.91
SRC-ALA-5	C19714(feed coal)	9.8	6.2	11	0.74	0.68	0.74	14	0.23	21	0.57
	C19715(residue)	13.0	5.0	9.1	1.4	0	0.60	2.0	0.16	1	0.54
SRC-WASH-1	C19141(feed coal)	12	0.46	26	1.5	0.25	0.10	19	0.061	34	0.51
	C19142(residue)	10	0.58	23	1.3	0.12	0.23	0.7	0.13	13	0.36
SRC-WASH-2	C19488(feed coal)	10	1.7	18	1.3	0.35	0.17	13	.086	34	0.52
	C19487(residue)	9.6	1.6	23	1.4	0.07	0.28	1.0	0.14	13	0.33

		Concentration											
		ppm											
Process	Sample Number	As	B	Ba	Br	Ce	Co	Cr	Cs	Cu	Eu	Ga	Ge
SRC-ALA-1	C19702(feed coal)	17	2200	580	54	77	27	200	11	92	1.6	29	21
	C19703(residue)	13	830	610	34	85	29	250	11	116	1.4	19	21
SRC-ALA-2	C19705(feed coal)	29	1700	430	18	93	24	190	12	71	1.8	27	19
	C19706(residue)	22	690	660	15	102	26	160	9.1	108	2.2	25	-
SRC-ALA-3	C19708(feed coal)	94	1100	580	42	170	15	180	13	130	3.1	35	36
	C19709(residue)	45	380	560	22	150	37	170	12	96	2.2	22	45
SRC-ALA-4	C19711(feed coal)	16	440	5100	15	180	25	79	1.9	190	3.8	22	<3
	C19712(residue)	12	520	6400	7	140	13	97	5.5	135	2.4	27	0
SRC-ALA-5	C19714(feed coal)	60	1000	1300	150	100	23	120	7.9	58	1.8	31	7.2
	C19715(residue)	29	650	1480	94	115	23	80	9.7	74	1.8	27	0
SRC-WASH-1	C19141(feed coal)	130	880	360	37	250	81	230	6.0	180	6.2	32	72
	C19142(residue)	160	360	410	9	200	63	210	5.7	210	4.0	30	40
SRC-WASH-2	C19488(feed coal)	200	780	410	41	200	62	170	11	140	4.6	28	44
	C19487(residue)	113	250	430	11	220	75	230	11	203	4.2	24	36

		Concentration											
		ppm											
Process	Sample Number	Hf	Hs	La	Li	Lu	Mn	Mo	Ni	Pb	Rb	Sb	Sc
SRC-ALA-1	C19702(feed coal)	4.4	.88	45	23	0.57	280	62	150	60	120	4.5	19
	C19703(residue)	4.2	-	37	36	0.55	356	74	160	71	150	4.2	18
SRC-ALA-2	C19705(feed coal)	6.0	2.1	44	110	0.71	600	35	84	89	98	8.5	26
	C19706(residue)	5.7	-	52	128	0.80	700	57	110	87	130	10	23
SRC-ALA-3	C19708(feed coal)	6.5	2.8	100	130	1.0	280	49	100	92	150	25	28
	C19709(residue)	5.2	-	64	72	0.73	290	45	120	88	180	21	20
SRC-ALA-4	C19711(feed coal)	13	1.2	97	24	1.0	240	6.9	52	51	18	5.9	31
	C19712(residue)	14	-	87	49	0.79	200	2.9	14	66	50	3.7	78
SRC-ALA-5	C19714(feed coal)	6.6	1.0	49	93	0.62	360	8.9	60	52	160	4.9	23
	C19715(residue)	7.3	-	52	105	0.74	320	8.4	0	45	120	4.6	26
SRC-WASH-1	C19141(feed coal)	6.6	1.3	130	190	1.7	420	41	270	160	120	16	60
	C19142(residue)	5.4	-92	110	170	1.6	230	43	220	140	130	14	29
SRC-WASH-2	C19488(feed coal)	4.1	1.8	120	160	1.3	380	53	260	72	130	13	32
	C19487(residue)	3.6	-94	110	162	1.2	340	27	250	41	160	18	25

		Concentration											
		ppm											
Process	Sample Number	Se	Sn	Sr	Ta	Tb	Th	Tl	U	V	Yb	Zn	Zr
SRC-ALA-1	C19702(feed coal)	28	13	500	1.1	1.0	12	9.7	17	200	3.5	720	190
	C19703(residue)	28	9.3	420	0.88	1.0	11	12	13	183	3.2	590	160
SRC-ALA-2	C19705(feed coal)	21	28	150	0.89	1.4	16	13	27	270	4.4	410	260
	C19706(residue)	19	16	290	1.2	1.4	15	11	22	230	5.0	630	260
SRC-ALA-3	C19708(feed coal)	33	23	880	1.8	1.7	22	12	23	390	6.2	130	300
	C19709(residue)	26	20	360	0.92	1.3	15	12	17	470	4.6	190	290
SRC-ALA-4	C19711(feed coal)	16	20	2800	1.9	2.2	31	11	8.2	210	6.2	100	230
	C19712(residue)	14	31	2860	2.7	1.8	27	5.5	9.3	200	4.9	67	120
SRC-ALA-5	C19714(feed coal)	15	17	1500	1.6	1.3	16	3.9	8.7	150	3.5	93	240
	C19715(residue)	14	22	1600	1.4	1.2	16	0	9.7	150	4.6	140	280
SRC-WASH-1	C19141(feed coal)	28	8.1	800	1.2	3.8	27	24	17	330	12	250	200
	C19142(residue)	30	11	770	0.81	2.7	20	13	19	250	7.9	170	130
SRC-WASH-2	C19488(feed coal)	22	12	530	1.3	3.3	20	12	20	380	7.8	260	220
	C19487(residue)	29	13	590	0.96	3.2	25	17	11	350	6.5	190	310

Table H4. Average % gain/loss after correction for Si.

Al	+6	Co	+16	Rb	+34
Ca	+10	Cr	+2	Sb	-3
Fe	+2	Cs	+24	Sc	-17
K	+30	Cu	+15	Se	-1
Mg	-87	Eu	-15	Sn	+6
N	-86	Ga	-13	Sr	+5
Na	-51	Ge	-33	Ta	-10
P	+42	Hf	-6	Tb	-12
S	-73	Hg	-93	Th	-7
Ti	-15	La	-9	U	-12
As	-28	Li	+19	V	-6
B	-47	Lu	-4	Yb	-9
Ba	+16	Mn	-5	Zn	+7
Br	-48	Mo	-5	Zr	-7
Ce	-2	Ni	-20		

showed similar gains. This behavior compares very favorably with those sets not using filter-aids, where 13 elements showed 4 or more losses and 5 elements showed 3 or more gains.

In those sets using filter-aids, the following elements show, after correction, moderate to high incidences of loss: N, S, Mg, Na, Ti, As, B, Br, Eu, Hg, Sc, Ta, and Zn. The level of loss for all but one (Ta) of the 13 elements, when averaged for the seven sets, was also found to be significant.

APPENDIX I

LITERATURE REVIEW OF MINERALOGICAL STUDIES OF LIQUEFACTION PROCESSES

IMPORTANCE OF MINERAL MATTER IN COAL LIQUEFACTION PROCESSES AND RESULTING RESIDUES

The characterization of minerals in coal liquefaction residues is necessary to assess the beneficial and detrimental effects that the mineral matter may have both on the liquefaction process and on the ultimate disposal of the residue. Beneficial effects of mineral matter to coal liquefaction include the possible catalysis of hydrogenation reactions and sulfur removal. Tarrer et al. (1977) ranked various types of mineral matter according to their performance as catalysts for hydrogenation and desulfurization in experiments on liquefaction systems. In a study of lignite in liquefaction systems, Given et al. (1975) reported that the highest liquefaction yields were obtained from a lignite with the greatest amount of mineral matter. Granoff et al. (1978), Granoff and Thomas (1978), Gray (1978), Mukherjee and Chowdhury (1976), and Henley (1975), and others, performed experiments to determine the individual catalytic effects of different minerals present in coal liquefaction residue on the liquefaction processes. Some researchers have reported that the presence of pyrite and other iron-bearing minerals aids in the hydrogenation of coal during liquefaction (Tarrer et al., 1977; Mukherjee and Chowdhury, 1976; Granoff et al., 1978; and Granoff and Thomas, 1978.

Possible detrimental effects of mineral matter associated with coal liquefaction processes include the poisoning of catalysts and the leaching of harmful elements from residue after disposal (Griffin et al., 1978). Certain minerals may cause undue abrasive or chemical wear in coal liquefaction plants as well as clogging (Harris and Yust, 1978) and buildup in reactor vessels (Walker et al., 1977). Therefore, the characterization of mineral matter in liquefaction residues is important in assessing their positive and negative effects in specific conversion processes.

X-RAY DIFFRACTION IN THE ANALYSIS OF COAL AND COAL LIQUEFACTION RESIDUES

A number of studies of coal and coal liquefaction residues have used X-ray diffraction to identify the mineral matter. Rao and Gluskoter (1973) and Ward (1977) obtained quantitative data on quartz, pyrite, and calcite in low-temperature ashes of coals. Walker et al. (1977) performed quantitative X-ray diffraction analysis on mineral matter in coal and coal liquefaction residues. Granoff et al. (1978) used quantitative X-ray diffraction in the analysis of the low-temperature ash of feed coals in a study of the catalytic effects of mineral matter on coal liquefaction. Granoff et al. used the technique of Rao and Gluskoter with nickel oxide as an internal standard. A qualitative X-ray diffraction study of mineral matter was made by Griffin et al. (1978) for solid coal wastes including liquefaction residue.

Previous studies of the clay minerals in the low-temperature ash of coals include the following. Environmental interpretations from the clay mineral composition of the Herrin (No. 6) Coal were made by Gluskoter (1967) and Rao and Gluskoter (1973). Rao and Gluskoter (1973), and Ward (1977) presented relative quantitative data for clay minerals in the Herrin (No. 6) and Harrisburg and Springfield (No. 5) Coals, respectively. Stepusin (1978) studied vertical variations in clay minerals in Illinois coals from the underclay through the roof rocks.

SCANNING ELECTRON MICROSCOPY IN THE ANALYSIS OF COAL AND COAL LIQUEFACTION RESIDUE

In recent years electron microscopy has proven useful for characterizing coal and coal liquefaction residue. Sutherland (1975) used the electron microprobe to determine organic sulfur concentrations in coal. Boateng and Phillips (1976) used the microprobe and the scanning electron microscopy (SEM) to examine surfaces of coal for iron and sulfur distribution. Other studies using the electron microprobe in the determination of organic and inorganic sulfur in coal were conducted by Harris et al. (1977), Solomon and Manzione (1977), and Raymond and Gooley (1978). Augustyn et al. (1976) examined fractured and polished surfaces of coal for coal structure and composition of the mineral constituents with the SEM. Gluskoter (Gluskoter and Lindahl, 1973, and Gluskoter, 1977) used the SEM for the characterization of mineral matter in coal. Other studies involving the SEM and coal discuss the occurrence and distribution of pyrite in coal (Greer, 1977, 1978; and Scheihing et al., 1978; in situ analysis of inorganic trace element sites in coal (Finkelman, 1978; and Finkelman and Stanton, 1978), correlated Mössbauer-SEM studies of the mineralogy of coal and coal conversion products using an automated SEM (Lee et al., 1978), and microstructural studies of chemically desulfurized coals (Rebagay and Shou, 1978). Only a few studies have been devoted to the examination of coal liquefaction residues with the SEM. Russell (1977) described the mineral composition of liquefaction residues from several coal liquefaction processes. Harris and Yust (1978) identified the constituents of a carbonaceous plug from a Solvent-Refined Coal Liquefaction Plant. Liquefaction residues and liquefaction reactor solids were characterized through the use of several techniques including SEM, X-ray diffraction, and optical microscopy by Walker et al. (1977).

APPENDIX J

PROCEDURES FOR X-RAY DIFFRACTION ANALYSIS

QUANTITATIVE DETERMINATION OF NONCLAY MINERALS

Sample Preparation

Prior to X-ray diffraction analysis of coals and THF-extracted coal liquefaction residues, the mineral matter must be isolated. Organic material may be removed by an oxidizing agent (such as hydrogen peroxide) (Ward, 1974) or by the more widely accepted method of low temperature ashing as described in Appendix C.

Preparation of Standards

The method of quantitative X-ray diffraction using internal standards involves preparing standard mixtures of varying composition for each mineral to be analyzed, and constructing standard graphs from diffraction data for each mineral. The minerals quantified for the coals were quartz, calcite, and pyrite, and for the residues, quartz, calcite, and pyrrhotite. This method of quantitative analysis is not suitable for clay minerals. Minerals chosen for standards ideally should be crystallographically identical to the minerals found in the coals and liquefaction residues. Fulfilling this requirement and securing monomineralic materials for standards can be difficult. A synthesized pyrrhotite (Shiley et al., 1979) was used as a standard for pyrrhotite from liquefaction residues. This pyrrhotite shows Mössbauer spectroscopic parameters and X-ray diffraction patterns very similar to those from the pyrrhotite in the liquefaction residues. Natural pyrrhotite could not be used for a standard because it is not available in quantity in monomineralic form.

Standard mixtures were made for calcite, quartz, pyrite, and pyrrhotite using a clay matrix. The matrix of the standards for the coal minerals was made to approximate the composition of clays in Illinois coals from which the largest number of samples for this study were taken. Kaolinite, illite, and montmorillonite that were fractionated by sedimentation techniques were used for the clay matrix. Montmorillonite (an expandable clay) is not ordinarily found in Illinois coals. The expandable clays that occur are a heterogenous mixed-layer material. Montmorillonite was used because it was not possible to find a similar mixed-layer material suitable for a standard. Clay minerals compose approximately 50 percent of the low temperature ash of Illinois Basin coals, and it was determined from analyses by Rao and Gluskoter (1973) in what proportions the clays should be added to create the matrix: kaolinite, 12 percent; illite, 20 percent; and expandables, 18 percent, by weight.

For the coal LTA, ten mixtures of varying amounts of calcite, quartz, and pyrite were prepared with a 50 percent by weight clay matrix. Standard minerals were ground to -325 mesh before being added to the standard mixture. Ten mixtures of varying amounts of pyrrhotite with the same clay matrix were prepared for the residue LTA. The liquefaction residues were analyzed by X-ray diffraction and found to contain the same clay minerals as the coals, although the proportions of those clays were not determined. The calcite and quartz standard curves constructed for the coal LTA were also used to determine the calcite and quartz in the residue LTA. Twenty percent by weight of 0.3 μm

Linde A alumina (Al_2O_3) was added as an internal standard to each of the standard mixtures. Al_2O_3 was chosen as an internal standard over other minerals, such as fluorite (as used by Rao and Gluskoter, 1973) for several reasons: (1) the smaller Al_2O_3 particle size minimizes orientation effects, (2) extremely pure Al_2O_3 is available, and (3) alumina produces a minimal amount of X-ray diffraction peak interference. The main objection to the use of CaF_2 is the interference of the (111) fluorite peak with that of the (111) peak of sphalerite and the (111) peak of pyrite. The standard mixtures (including Al_2O_3) were ground together by hand in absolute alcohol with an agate or mullite mortar and pestle.

Standard mixtures were run on a Phillips Norelco X-ray diffractometer at 2° 2Θ per minute using copper Kα radiation and a graphite monochromator. A cavity powder mount was used for the samples. In constructing standard curves for calcite, quartz, pyrite, and pyrrhotite, the following peaks were used for area measurements: (104) calcite, (101) quartz, (200) pyrite, (200) pyrrhotite (hexagonal) and (104) Al_2O_3. Each standard was run 3 times and the areas of the above mentioned peaks were determined. The ratios of the (104) calcite, (101) quartz, (200) pyrite, and (200) pyrrhotite to the internal standard peak, (104) Al_2O_3, were calculated. The ratios of the measurements on the three replicates were averaged. Standard graphs were constructed for each mineral by plotting the percentage of the mineral versus the ratio of its peak area to the (104) Al_2O_3 peak area.

PREPARATION OF UNKNOWNS

Twenty percent by weight of Al_2O_3 was added to the low temperature ash of coal and residue samples. These mixtures were ground by hand in absolute alcohol for approximately 20 minutes. All of the samples passed through a -200-mesh sieve (U.S. Standard sieve series). The samples were oven-dried at about 35°C, reground slightly, and mounted in a cavity powder mount. The unknowns were run three times with repacking of the sample each time. The (104) calcite, (101) quartz, (200) pyrite, (200) pyrrhotite, and (104) Al_2O_3 peaks were measured and peak area ratios calculated in the same manner as was done for the standards. The percentage of each mineral was then read from the standard curve.

Further information on the methods described above can be found in Russell and Rimmer (1979). For a general discussion of X-ray diffraction procedures and theory see Klug and Alexander (1974).

QUANTITATIVE ANALYSIS OF CLAY MINERALS

Clay minerals may account for approximately 50 percent of the mineral matter in low temperature ashes of coals (Rao and Gluskoter, 1973; Ward, 1977) and an even greater weight percentage in liquefaction residues (as a result of the loss of sulfur during the conversion of pyrite to pyrrhotite). Despite this abundance of clay minerals, there have been relatively few attempts to quantify clay minerals in coals and liquefaction residues.

Sample Pretreatment

The low temperature ash of the coal and the residue samples is used for the clay mineral analysis. The less than 2 μm fraction of the clay minerals must be separated from the other minerals in the low temperature ash for analysis. The sodium dithionite-citrate-bicarbonate method of iron removal (Jackson, 1975) adapted by Ward (1977), which was used in this study, enables the dispersion of the clay fraction within the low temperature ash. Ward's method (1977) is basically a three-step process involving the removal of soluble ions and the removal of carbonates and acid-soluble iron compounds, followed by the removal of soluble ferrous iron after reduction from the ferric state.

Advantages of clay dispersion by iron removal are that the clay structures are not attacked and the method is fairly rapid and relatively free of analytical difficulties. Jackson (1975) provides further discussion of this method.

Sample Preparation

Once the clays were dispersed, the <2 µm fraction was isolated. The suspensions were thoroughly agitated, then allowed to settle for 21 minutes. At this time the top 0.5 cm of suspension was removed by pipette. According to Stokes' law this contains the less than 2 µm fraction.

The method of slide preparation used in this study was that of centrifuging the <2 µm fraction onto a ceramic tile (Kinter and Diamond, 1956). The method provides excellent orientation and is especially good when only a small amount of sample is available. One problem with the method is that mullite present in the ceramic tile produces a diffraction peak at 16.3° 2θ which may interfere with the $(002)_{10}/(003)_{17}$ and $(005)_{27}/(002)_{10}$ reflections of mixed-layer clays. However, this study does not differentiate the mixed-layer clays and hence, the mullite presents no problem.

X-ray Diffraction Analysis of Clay Minerals

Ceramic tiles were run on a Phillips Norelco X-ray diffractometer at 2° 2θ per minute using copper Kα radiation with a graphite monochromator. Because of the amount of time used for preparation of the tiles and the small amount of low temperature ash of each sample available, only one tile was prepared for most samples. Several samples were prepared twice to check for reproducibility of the analyses.

Each ceramic tile was X-rayed after solvation with ethylene glycol for 48 hours and again after heating to 350°C for 1 hour.

The relative percentages of kaolinite plus chlorite (K + C), illite (I), and expandables (EX) in the less than 2 µm fraction are determined by a procedure modified from Griffin (1971). Calculations are based on the relative intensities of the 7 Å and 10 Å peaks obtained from X-ray diffraction patterns of ethylene glycol and heat-treated samples. Peak heights were used in the determinations since experience has shown that this figure provides better reproducibility of data than peak areas. The modified formulas (Ward, 1977) used to determine the relative amounts of clays present are:

$$\%(K + C) = \frac{7\ \text{Å}h/2.5}{(7\ \text{Å}h/2.5 + 10\ \text{Å}h)} \times 100$$

$$\%(I + Ex) = 100 - \%(K + C)$$

$$\%I = \frac{10\ \text{Å}g}{10\ \text{Å}h} \times \frac{7\ \text{Å}h}{7\ \text{Å}g} \times \%\ (I + Ex)$$

$$\%Ex = \%(I + Ex) - \%I$$

where:

% (K + C) = percentage of kaolinite + chlorite

% I = percentage of illite

% Ex = percentage of expandable clay minerals

and: 7 Åh = intensity of 7 Å peak after heating slide to 375°C for one hour

7 Åg = intensity of 7 Å peak following exposure of sample to ethylene glycol vapor for 2 days

10 Åh = intensity of 10 Å peak after heating slide to 375°C for one hour

10 Åg = intensity of 10 Å peak following exposure of sample to ethylene glycol vapor for 2 days

A detailed account of the clay minerals analysis appears in Russell and Rimmer (1979).

APPENDIX K

PROCEDURES FOR SCANNING ELECTRON MICROSCOPY OF MINERALS IN LIQUEFACTION SAMPLES

SEM STUDY OF MINERALS

The scanning electron microscope (SEM) with a resolution of 100 to 200 Å on the average and 50 Å or better in some cases can be used to study the surface features of specimens. With the SEM, the morphology and interrelationships of minerals in coal and coal liquefaction residues can be studied. The scanning electron microscope used in this study was a Cambridge Mark II A Stereoscan with ancillary energy-dispersive X-ray analyzer.

PREPARATION OF SPECIMENS FOR SEM

Pretreatment of Samples

Coal and tetrahydrofuran extracted liquefaction residues were low temperature ashed before preparation for observation with the SEM.

Preparation of Low Temperature Ash (LTA)

Observation of the heavy minerals in coal and residue LTA is aided by the bromoform separation of the heavy (pyrite, pyrrhotite, calcite) minerals from the light (clays and quartz). The clay minerals cling to the surfaces of particles of other mineral matter after low temperature ashing and make it difficult to observe the heavy minerals if they are not separated. Bromoform separation of the LTA of coal was accomplished by gravity using a separatory funnel according to the methods of Müller (1967) and Carver (1971). There was some difficulty in the separation of heavy and light minerals from the liquefaction residues. The heavy minerals in the residues are intimately associated with the clay minerals and during gravity separation very few heavies settle out. Some success in concentrating the heavy minerals of the liquefaction residue was attained using a method modified slightly from Barsdate (1962). LTA (about 0.05 to 0.1 g) of liquefaction residue was added to a 15 mL glass centrifuge tube containing bromoform. The tubes were centrifuged for 15 to 20 minutes at 3000 to 4000 rpm. Heavy material that segregated at the bottom of the tubes was removed with a hypodermic needle, taking care to expel air slowly from the needle as it was being lowered through the light mineral layer. The heavy minerals were then emptied from the hypodermic onto filter paper, washed in acetone to remove all traces of bromoform, and were then mounted for SEM work using the techniques described below. After removal of the heavies, the light mineral fraction was poured off, filtered, and washed with acetone. Bromoform-separated fractions were not used for analytical purposes other than SEM examination.

Sample Mounting Techniques

Two different mounting techniques, one for the heavy fraction and another for the light, were employed in observing the morphology of the LTA of coals and residues. The heavy mineral fraction was mounted on SEM stubs coated with Kodaflat®, a print flattener manufactured by Kodak and useful as a thin adhesive coating. After mounting, the heavy minerals were cleaned in ethyl alcohol in a mild sonic bath for several seconds to remove surface debris from the minerals. Inevitably, some particles were lost from the adhesive in cleaning.

The light mineral fraction (principally clays) of the LTA of coals and residues was dispersed in distilled water with a minute amount of sodium hexametaphosphate to aid in dispersion. The suspension was agitated in an ultrasonic bath for 2 minutes and 1 to 3 drops deposited on a copper SEM stub and allowed to dry. A method similar to this that has been used for clays is described by Walker (1978). Addition of sodium hexametaphosphate in some cases caused the detection by energy-dispersive X-ray analysis of sodium and phosphorous in the clays.

To investigate the interrelationships of particles, the LTA or heavy minerals of the coal and residue were embedded in epoxy and a 1 cm diameter chip made. The surfaces of the chips were polished to expose sections through the particles and finished with 0.5 µm Buehler Finish-pol®. The chips were cleaned in an ultrasonic unit. Some polished epoxy chips were etched in HCL to enhance structures and clarify relationships of the minerals (Russell and Rimmer, 1979).

All samples were coated with chromium by vacuum evaporation. Au is commonly used as a coating and has a better secondary emission coefficient than Cr; however, the Au Mα line interferes with the sulfur Kα line in X-ray analysis and would hinder detection of sulfur.

APPENDIX L

CONCENTRATION OF RARE EARTH ELEMENTS AND YTTRIUM IN COALS AND COAL LIQUEFACTION PROCESS SAMPLES AND THE GEOCHEMICAL SIGNIFICANCE OF THE RESULTS

The rare earth elements are interesting because of their characteristic group behavior in different types of geologic materials. The distribution of the rare earth elements with respect to each other has been useful in elucidating the source material and the geochemical changes undergone by a sample (Haskin and Schmitt, 1967). A study of the relative distribution of rare earth elements in coals can provide information on the association of the rare earth elements with the primary constituents of coal and on geochemical changes that occurred during coal formation.

Data obtained on concentrations of the rare earth elements and yttrium in some samples from the coal liquefaction residues project are illustrated in Figure L1. The concentration, on the 500°C ash basis, of each element relative to its concentration in chondritic meteorites (Evensen, Hamilton, and O'Nions, 1978) is plotted vs. the ionic radius of the element, for a set of samples from the SRC-Washington liquefaction plant. Data obtained by instrumental neutron activation analysis are also plotted. Agreement between the results for lanthanum, cerium, samarium, europium, terbium, ytterbrium, and lutetium by neutron activation analysis with radiochemical separation and the corresponding results by instrumental neutron activation analysis is generally satisfactory. This observation is also true for the other sets of samples analyzed. The graph of the data resembles closely the plots of the data from other sets of samples and is used to illustrate two conclusions drawn from the study;

(a) The rare earth elements and yttrium present in the feed coal of a liquefaction process are generally essentially retained in the residue from the process. Also they are generally essentially retained in the residue when it undergoes extraction with tetrahydrofuran. This indicates that the rare earth elements and yttrium are associated largely with the inorganic or nonvolatile fraction of coal.

(b) The relative rare earth abundance pattern for coal ash closely resembles the pattern of a composite of 40 North American shale samples illustrated in Figure L2, and the concentrations of the rare earth elements in coal ash are in the same range as those in shales. This indicates that probably the rare earth elements in the clastic sediments in the coal-forming basin are incorporated, with no further partitioning, into the mineral matter portion of the coal.

Close examination of Figures L1 and L2, however, shows further partitioning to be significant for europium. Figure L2 shows europium to be slightly enriched in shale vs. chondrite in comparison to the shale/chondrite concentrations of the heavier rare earth elements. The concentration of europium in coal ash is based on the data for the nineteen sets of coal liquefaction samples studied and as illustrated in Figure L1; it is about the same as the concentration of the heavier rare earth elements, relative to their concentrations in chondrites. This likeness may indicate anomalous chemical behavior of europium, which is fairly easily reduced to the +2 state from the ordinarily trivalent state of the rare earth cations. In the anaerobic environment existing in the peat bog, europium may be reduced and selectively removed from the rest of the rare earth elements.

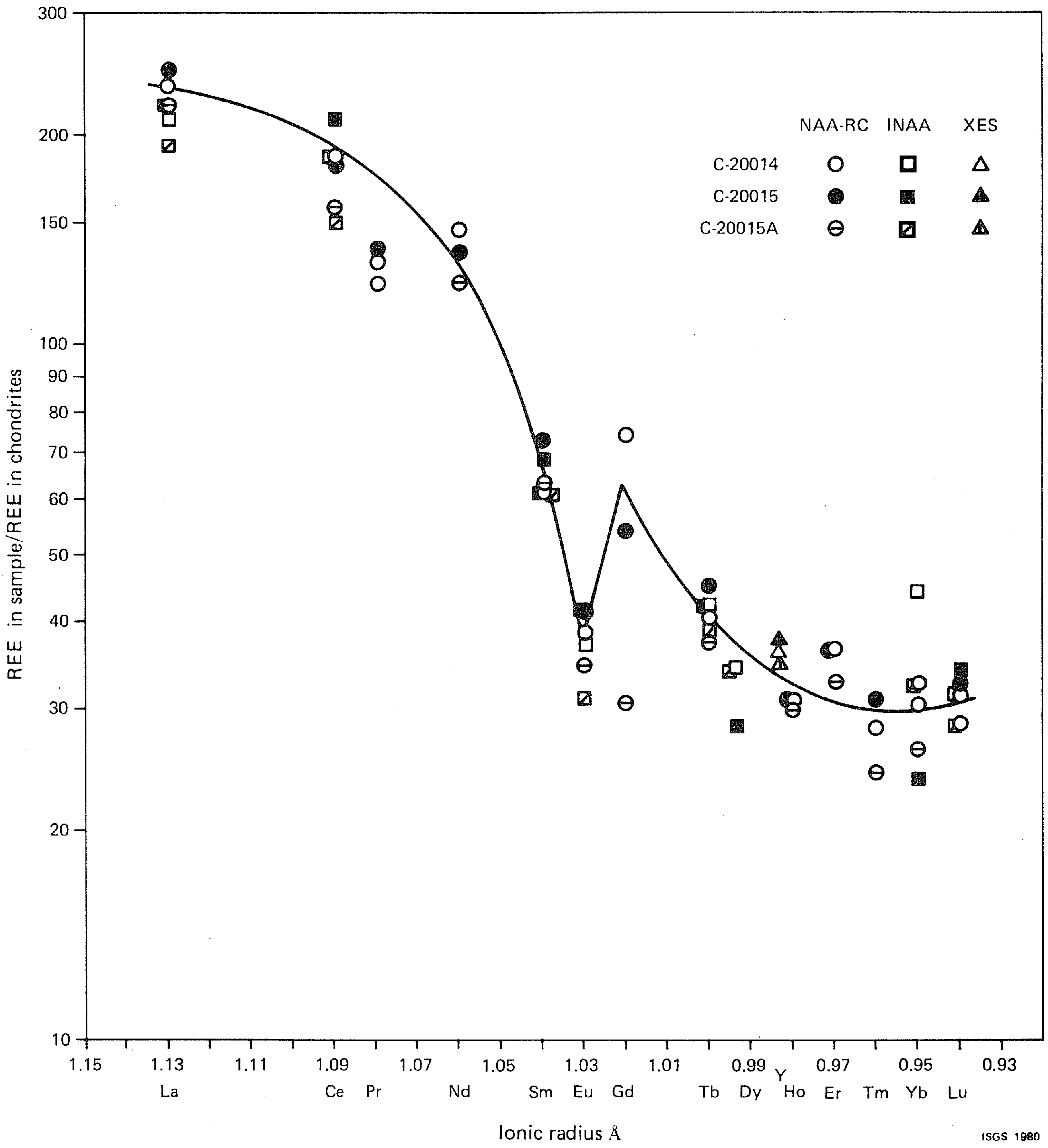


Figure L1. Relative abundance pattern of the rare earth elements (REE) and yttrium in the 500°C ash of three samples from a run from the SRC-Washington plant.

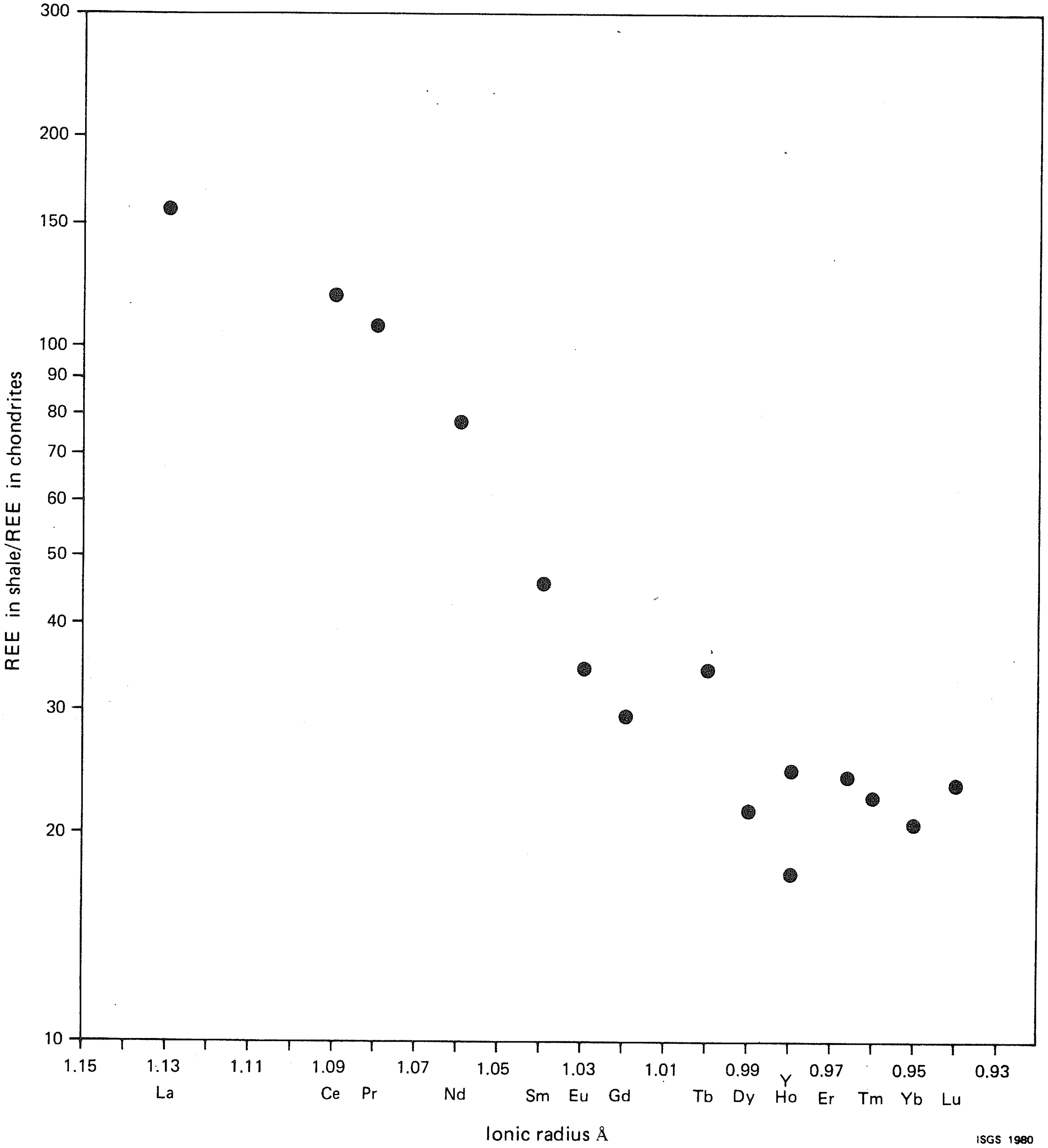


Figure L2. Relative abundance pattern of the rare earth elements (REE) and yttrium in the composite of 40 North American shales.

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