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SOLVENT REFINED COAL (SRC) PROCESS: TRACE ELEMENTS

**Volume 3 Pilot Plant Development Work. Part 6—The Fate of
Trace Elements in the SRC Process**

**By
Carl Steven Weiss**

**October 1980
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**The Pittsburg and Midway Coal Mining Company
Englewood, Colorado**

U. S. DEPARTMENT OF ENERGY

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PART 6 - THE FATE OF TRACE ELEMENTS IN THE SRC PROCESS

Prepared by
Carl Steven Weiss

Washington State University
Nuclear Radiation Center
Pullman, Washington 99164

Subcontractor to
The Pittsburg & Midway Coal Mining Co.
5970 South Syracuse Street
Englewood, Colorado 80111

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THE DETECTION OF TRACE ELEMENT SPECIES
IN SOLVENT REFINED COAL

ABSTRACT

by Carl Steven Weiss, Ph.D.
Washington State University, 1980

Chairman: Royston H. Filby

Due to the present global energy situation, coal usage is increasing and several coal liquefaction processes have been developed to yield a cleaner fuel from coal. A study of the forms of trace elements occurring in Solvent Refined Coal has been performed. The experimental approach has been to separate chemically the Solvent Refined Coal based on differences in the functionality and the molecular weight of the organic matrix. Analysis of the fractions separated in this manner, for various trace elements, has revealed associations of certain elements with other elements as well as with certain fractions.

The separation of Solvent Refined Coals I and II has been performed using a nine step solvent gradient separation on a silica support. The Solvent Refined Coal I solid was subjected to solvent extraction with tetrahydrofuran before the separation. The Solvent Refined Coal II was filtered prior to the separation. Each of the fractions generated was subjected to instrumental neutron activation analysis. In addition, two of the more functional fractions from the Solvent Refined Coal I silica separation were fractionated based on molecular weight using gel permeation chromatography, these fractions were also analysed by instrumental neutron activation analysis.

Atomic absorption spectroscopy was used: to determine Ca, Mg, Fe, and Be in some of the fractions generated, as an element selective detector for the effluent of a gel permeation chromatographic column.

The analysis of Solvent Refined Coal I by these methods provided data on the distribution of Ti, V, Ca, S, Al, Mn, As, Se, Cr, Fe, Ni, Zn, Sc, and Ga in the fractions generated. Because of the small trace element content of Solvent Refined Coal II only As, Se, and Cr could be detected in the silica fractions. Based on these distributions three different groups of elements have been detected based on the association of elements with each other and with certain fractions.

The first group is composed of As, Se, and Cr which are associated with silica fractions of relatively low functionality and these elements have a high percent solubility in the starting Solvent Refined Coal II oil.

The second group is composed of Ti, V, and to a lesser extent a second form of Cr. These elements are associated with fractions that have a high concentration of phenolic material. This group of elements is probably present as phenoxide complexes. These complexes may have been produced during the liquefaction process or are remnants of the original coal.

The third group is composed of Fe, Ca, K, Al, and Mg. These elements are associated with the most functional fractions. These elements are possibly present as humic acid type complexes. It is also possible that these elements are present as submicron size particulate minerals.

The integration of chromatographic methods with trace element analysis of the fractions generated is capable of discerning the presence of different forms of the elements. The methods used in this study are applicable to other important geologically occurring organic matter.

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CHAPTER 1

INTRODUCTION

Coal has served as an energy source for hundreds of years and has also been transformed into coke, necessary for steel production. During the 1800s, coal supplied the increased energy and metallurgical needs of industrialization. As early as 1819, in Great Britain, the first of a series of committees was appointed to make recommendations for minimizing the adverse environmental effects of smoke associated with coal-fired steam engines and furnaces (1). In the early part of the 20th century, petroleum and natural gas emerged as superior fuels.

Since 1900, petroleum demand has increased dramatically, becoming the dominant supplier of greatly expanded global energy needs as shown in Table I. Because of the limited global reserves of petroleum and the geographic distribution of known reserves, periods of erratic supply of petroleum to the United States have occurred. The United States, Japan, and many European countries are very susceptible to shortages because of the high percentage of energy supplied by imported oil.

Due to the current world energy situation, many energy sources are currently being developed or expanded as alternatives to petroleum. These alternatives include: conversion of solar energy, nuclear fission and fusion, coal, oil shale, tar sands, gasohol, hydroelectric, geothermal energy, and conservation. The potentials of these various alternatives have been studied and the results published (2, 3). Because of the difficulties of predicting the technical and economic success, as well as the social acceptance of any

of the aforementioned sources, coupled with the long lead times needed to bring an alternative energy source to a commercial scale, a broad based development of all feasible alternatives is needed.

The abundance of coal in the continental United States makes coal a particularly attractive alternative energy source. It is estimated that there are over 400 billion tons of coal that could be mined with present mining techniques (4). This quantity of coal can easily provide the domestic energy needs of the United States until other energy alternatives are developed during the first half of the 21st century. As the cost of petroleum increases, the economic advantages of coal usage also increase (5). However, the problems of mining and transporting coal to meet expanded coal usage are not trivial. In addition, the increased combustion of coal, or other hydrocarbon fuels, may increase the carbon dioxide concentration of the atmosphere. This may cause adverse global climate changes, commonly called the greenhouse effect. In particular, the combustion of coal releases more carbon dioxide than oil and natural gas on an energy-equivalent basis (6).

Table I. Energy Production and Consumption of the World^a

Year	Annual Energy Production and Consumption ^b			
	Coal	Oil	Natural Gas	Total
1910	12.4	2.4	0.5	15.5
1930	20.3	6.1	1.4	28.4
1950	24.1	12.2	4.2	41.9
1970	28.6	48.4	19.6	102.4

^aAdapted from: Reference (2, p. 17).

^bIn Million Barrels a Day Oil Equivalent.

In comparison to petroleum, coal has drawbacks as a source of energy. Petroleum contains a very high proportion of gases and liquids which are easily distilled, refined, and transported. Coal, a polymeric solid, normally has a higher sulfur and mineral content than petroleum. Upon the combustion of coal larger amounts of sulfur oxides, fly ash, and toxic trace elements are emitted. Sulfur oxides are involved in the formation of acid rain, and fly ash can adsorb and transport inorganic compounds. In the United States, meteorological conditions have caused localized episodes of air pollution associated at least in part with the combustion of coal.

The effects of the atmospheric pollutants sulfur and respirable particulates have been studied extensively and are reported in the literature (7). The combustion of coal is a major source of these pollutants (8, 9). In an effort to control these air pollutants, post combustion abatement processes have been developed. These mainly consist of electrostatic precipitators and baghouses designed to limit particulate emissions, as well as scrubbers designed to remove sulfur oxides and particulates from stack gases. These techniques have helped to limit emissions from coal-fired power plants. However, some problems have occurred with the more popular electrostatic precipitators. Their efficiency decreases when used in conjunction with low sulfur coal (9). As shown in Table II, their efficiency for the removal of micron and submicron size particles is lower than other available methods. In view of the facts that fly ash can adsorb and possibly stabilize some polynuclear aromatic compounds (10, 11) and the smaller sized particles tend to concentrate toxic elements, such as As, Sb, Pb, Cd, Tl, and Se (12), the reliance on electrostatic precipitators could cause major environmental impacts. With increased combustion of coal the ability of utilities using coal-fired power plants to meet federal emission requirements will be a difficult task. In fact, compromises on emission standards have been suggested to stimulate coal use.

Table II. The Percentage Efficiency for the Removal of Particles by Various Particle Collecting Equipment^a

Particle Collection Method	Particle Size Range (μm)		
	0 to 5	0 to 10	Overall
	%	%	%
Electrostatic Precipitator	72	94.5	97
Irrigated Electrostatic Precipitator	97	99	99
Wet-impingement Scrubber	96	98.5	97.9
Baghouse	99.5	100.0	99.7
Venturi Scrubber	99	99.5	99.5

^aAdapted from: Reference (9, p. 145).

As an alternative to post combustion abatement procedures the prior treatment or cleaning of coal is a logical solution. The methods include physical separation, chemical leaching, pyrolysis, catalytic and non-catalytic hydroliquefaction (with either filtration or distillation), and coal gasification.

Traditionally, coal has been cleaned using a variety of physical methods aimed at removing the mineral portions of the coal, particularly the pyritic sulfur component. The majority of these methods are based on the density difference between the heavier mineral matter and the lighter organic matter. These methods are successful at removing the larger mineral aggregates, but are not nearly as successful with the finer grained minerals. Among the constituents not easily removed by physical methods are: clay particles, finely divided pyrite, organically bound elements, and other minerals intimately associated with coal (13).

Coal gas has been produced by heating coal in an inert atmosphere, as early as the late 1700s. The Lurgi coal gasification process has operated on a commercial scale since the 1800s (14), and forms the basis for the successful Sasol Refinery in South Africa. The coal matrix is gasified as carbon monoxide by the use of steam, and then subsequent hydrogenation and Fischer-Tropsch Synthesis yield a wide range of organic compounds, principally hydrocarbons.

With the aim of establishing a domestic source of motor fuels, Germany developed and constructed coal liquefaction plants during the 1930s and 1940s. The process conditions involved high temperature and hydrogen pressure in the presence of an aromatic solvent. After World War II, little interest was shown in coal liquefaction until the 1960s (15). The product of hydroliquefaction, being a liquid (at least at elevated temperatures), can be filtered or distilled to remove the mineral matter. In addition, the reaction conditions of liquefaction facilitate sulfur removal as hydrogen sulfide. The Solvent Refined Coal processes I and II, developed by The Pittsburg & Midway Coal Mining Company, are based on hydroliquefaction. These processes have been funded for 6000 ton per day demonstration plants, the last step before a commercial size plant is built. Because of the large quantities of coal which would be consumed in a commercial plant, the fate of environmentally important elements and compounds during the process must be assessed. In catalysts used on coal liquids, certain elements have been found on the surfaces of poisoned catalysts (16). The development of catalysts not susceptible to such poisoning would improve liquefaction efficiencies. This further demonstrates the need to investigate the behavior of minor and trace elements during coal refining.

The distribution of trace elements within the Solvent Refined Coal processes, at the pilot plant stage is well documented (17, 18, 19). The concentrations of many elements are reduced to negligible amounts in the products. Other elements, particularly Ti, V, Cr, Cl, Br, Ca, and Mg in SRC-I are reduced to a lesser degree. The elements As, Se, Hg, Sb, Fe, and Ni are partially volatilized during the SRC-II process and are transported with the lighter oils. Due to these problems, an understanding of the nature of trace elements in Solvent Refined Coal (SRC) is necessary for characterizing the chemistry of trace elements in solvent refining and for the further development of environmentally acceptable coal liquefaction processes.

A study of the association of trace elements in the products SRC I and SRC-II has been performed. In order to investigate such complex materials as coal liquids, chromatographic methods of analysis are necessary. The SRC products have been separated based on accepted chromatographic procedures for the compound class separation and subsequently the molecular weight separation of the organic matrix. The complexity of coal liquefaction products makes it almost impossible to separate quantities of individual compounds. The fractions generated were subjected to trace element analysis using instrumental neutron activation analysis (INAA), and both flame and graphite furnace atomic absorption spectroscopy. In addition, a flame atomic absorption spectrophotometer has been interfaced to a gel permeation chromatographic column, providing an element selective detector for Fe and Mg. The data generated include the association of certain elements with each other and with certain fractions during the separation procedures, and the gel permeation chromatographic features of the separated materials. This information gives some insight to the behavior of certain trace elements during liquefaction, as well as into the general nature of the solvent refined coal products.

The information gathered is useful in: evaluating the environmental impact of the combustion of solvent refined coal, understanding the chemistry of inorganic elements during liquefaction, as well as providing inferences as to the nature of trace elements in the starting coal. The methods developed are suitable and directly applicable to: trace element studies of other coal liquefaction products, studies for developing catalysts suitable for the matrix of coal process liquids, oil shale, tar sands, heavy petroleum fractions, and other organic geological material.

CHAPTER 2

COAL

Coal is a polymeric organic solid, dispersed with a variety of inorganic matter. Coal originates from vegetation that was deposited over millions of years ago, in swamp areas undergoing geosyncline formation. During geological history two major eras of coal deposition are recognized. The Carboniferous era occurred between 220 and 350 million years ago, while the Tertiary era occurred between 1 and 70 million years ago. The deposited material was subsequently buried under layers of sedimentary deposits, commonly called overburden. Along with the vegetation, predominantly organic in nature, inorganic elements were deposited as: components of the plant material, detrital (existing) minerals, and minerals that were precipitated from solution. Minerals deposited during the same time period as the organic material are classified as syngenetic, while minerals deposited after the coal seam was buried are classified as epigenetic. Epigenetic minerals may form from ground water in contact with the coal seam and it is also possible that organic compounds or complexes may form in a similar manner, either before or after burial. Coal is extremely heterogeneous because of its origin and variable coalification conditions.

Detailed treatments of the geological, chemical, technological, and physical aspects of coal science have been widely published (20, 21, 22, 23, 24). More recently, publications dealing with coal conversion include detailed discussions of coal origin and composition (25, 26, 27, 28). The pertinent

points necessary for this dissertation will be summarized, but for a more detailed understanding these references are recommended.

Rank, Origin, and Composition

Over geological time, after initial biochemical decomposition of the vegetation to humic acids, pressure and temperature caused metamorphic changes forming coal (coalification). The nature of the materials deposited, the changes upon biochemical decomposition and the degree of metamorphism affect the physical and chemical properties of the coal. In order to classify the metamorphic state of a coal, various ranking systems have been developed. The main purpose of such systems is the prediction of the suitability of a coal for certain uses, based on measurable properties. These properties include swelling, dilation, agglomeration, caking, volatility, and elemental analysis.

The most useful system of classification for chemical purposes is based on elemental analysis, originally formulated by Seyler (20), and used in part by the American Society for Testing and Materials ranking system (26). The major coal ranks and their properties are presented in Table III. The progression during coalification proceeds from peat through lignite, sub-bituminous, bituminous, and anthracite (which has a structure similar to graphite). The treatment of elemental analysis data, of a variety of coal samples, presented in the form of H/C versus O/C diagrams was performed by van Krevelen (20). This type of representation gives further insight to the metamorphic changes during coalification. Wood and its components, cellulose and lignin, are plotted in Figure 2.1, along with vitrinite, an abundant portion of many coals. It is seen in Figure 2.1 that coalification proceeds through a combination of reactions being equivalent to dehydration, demethanation, and decarboxylation.

Figure 2.1.--H/C versus O/C diagram. The reactions occurring during coalification are indicated.

Table III.^a Properties of the American Society for Testing and Materials Coal Ranks

Rank	% Carbon	% Volatile Matter	Organic Acid Groups	Phenol Groups	Approximate Calific Value (BTU/lb)
Anthracite		5			
Low Volatile Bituminous	90	17			
Medium Volatile Bituminous		26		Ends	
High Volatile Bituminous (A, B, C)	80	31			12300
Sub-bituminous		35	Ends		10000
Lignite	70				7000
Peat	60				

^aAdapted from: Reference (26, p. 2-12).

In order to understand, chemically, what coal is and what transformations influence coalification, a detailed discussion of the chemical compounds thought to be involved as intermediates in the formation of coal will be presented. As previously described the main events during coal formation are: deposition, the biochemical stage, and the geological stage. Chemically speaking it is advantageous to restrict the bulk of the discussion to the material deposited and the changes occurring during the biochemical stage. The long term geochemical changes cannot be treated as rigorously, but will be briefly summarized.

Assuming that the main constituents of vegetation have not changed in nature drastically over geological time, the chemical compounds deposited in coal beds consisted predominantly of cellulose, lignins, oils, resins,

and waxes. The general structure of some of these compounds are represented in Figure 2.2, along with a model compound representative of a unit of a polymeric class of compounds called humic acids (29). At the time of deposition, and the closely associated biochemical stage, the oxidation reduction potential (pE) and the acidity (pH) of the swamp water determined the chemical and biochemical reactions which the compounds of the deposited plant material undergo. The formation of humic acids from a variety of complex reactions involving the compounds originally deposited in the swamp environment can be postulated. Various studies have been conducted on the relative stability of the deposited compounds (24, 30). It has been found that cellulose decomposes most quickly followed by lignin and the more resistant oils, waxes, and resins. The fact that cellulose decomposes most rapidly cannot preclude the importance of its decomposition products in the formation of humic acids. Other studies have shown that under certain conditions humic acids may form from a combination of cellulose and protein (31). Due to the complexity of the reactions and the environmental conditions, the view adopted here is that humic acids are the precursors of coal and are formed from cellulose, lignin, waxes, resins, and oils, or from a variety of their degradation products.

The determination of the organic structure of coal has been difficult due to its heterogeneous nature, its limited solubility in all solvents, and its limited volatility, excluding the easily driven off volatile matter. Until the advent of spectroscopic techniques suitable for the analysis of solids, the majority of structural studies had been conducted on solvent extracts, normally containing less than 30% of the starting coal and chemical or thermal fragmentation products (32). The results of such studies have been conflicting at times, but it is generally agreed upon that the skeletal structure of coal is basically aromatic. As will be presented

CELLULOSE

LIGNIN

WAX

MODEL OF A HUMIC ACID

Figure 2.2.--Chemical precursors of coal. Model of humic acid adapted from Reference (29).

later in this chapter, a variety of spectroscopic techniques have been used more recently to study the organic structure of coal. The results confirm that a large proportion of the carbon content of coal is aromatic. The aromatic nature of coal gives further evidence that lignin indirectly provides the aromatic skeletal backbone to coal. However, coal is more aromatic than lignin, so that other factors must influence the aromaticity of coal. The degradation products of both lignin and cellulose contain keto-acid groups, which provide reactive sites for the formation of chain compounds and aromatic rings (20, p. 107). These reactions may lead to the formation of humic acids, which contain higher concentrations of functional groups. The functionality of humic acids is geochemically important because it allows humic acids to complex, transport, and accumulate a variety of elements. These may be important factors in the subsequent formation of minerals (29).

During the geological stage of coalification, time, temperature, and pressure are the variables that affect the metamorphosis of the coal. In general, the effect of time and temperature are more important than pressure. The chemical changes that occur during this stage involve the loss of water and carbon dioxide. The product is a polymeric solid with entrained inorganic material.

The Organic Structure of Coal

The organic structure of coal, a polymeric solid, is extremely complex. Not only does the primary structure have to be considered, but the secondary structure produced by the interactions of the functional groups present may contribute significantly to the overall structure. Considering these factors, the determination of the organic structure of coal has been a difficult task. The nature of the secondary structure of coal has not been determined. The analysis of the total functional groups present has been

determined by a variety of methods, and is of prime importance to the development of liquefaction processes. It is also important to certain aspects of this dissertation, in particular, the binding of metals to coal, and also the possible complexing of metals during liquefaction processes.

Traditionally, functional group analyses have been performed by a variety of wet chemical methods on either solvent extracts or slurries of finely ground coal (20, 33). The functional groups of importance in coal contain oxygen, nitrogen, and sulfur. The oxygen moieties are perhaps the most widely studied functional groups. The results of a study of the oxygen functionalities present in a number of different coals is presented in Figure 2.3. As the rank of the coal increases from the humic acid precursors through the coal series, the total amount of oxygen present decreases. The methoxyl groups are lost early in the metamorphic process, followed by the loss of the carboxylic acid and carbonyl groups. The phenolic groups are more resistant to the degradation processes and are present in most bituminous coals. Etheric and heterocyclic forms of oxygen are also present. A certain proportion of the oxygen is considered nonreactive. Nitrogen occurs throughout the coal matrix, predominantly as heterocyclic pyrrole or pyridine rings. Sulfur occurs in coal in forms analogous to those previously mentioned for oxygen. In general, the oxygen and sulfur content of coal is higher than that of nitrogen, and are more significant to the complexing of minor and trace elements in coal. The functional groups found in coal are summarized in Table IV.

With the advent of instrumental methods of analysis, the identification and quantification of functional groups present in coal has improved, confirming many of the results of degradative chemical analysis. Infrared spectroscopy has perhaps been the most useful. The more recent development

Figure 2.3.--Oxygen functionalities versus carbon content of coal.
Adapted from Reference (20).

of NMR spectroscopy of solids might provide additional information, however the isotopes of oxygen, nitrogen, and sulfur with suitable magnetic spins, occur in very low abundances and the detection limits will definitely be problematic.

Table IV. Functional Groups Found in Coal^a

Element	Functional Groups
Oxygen	Phenolic, Heterocyclic Oxygen, Etheric, Ester, Ketone
Sulfur	Thiols, Heterocyclic Sulfur, Disulfides, Thioethers
Nitrogen	Aromatic Heterocyclic, Non-Aromatic Heterocyclic

^aAdapted from: Reference (28, p. 11).

The primary structure of coal has a much firmer base of information. Many chemical reactions have been used in order to identify the segments that constitute the coal polymer. In any analytical procedure that involves the disruption of the original coal matrix, the structures determined, and the conclusions as to how the fragments were interconnected will have uncertainties associated with the chemical reactions. The use of well characterized degradation reactions has yielded valuable information. A review of the reactions used has been published by Larsen et al. (34). The reactions used are: the Heredy and Neuworth depolymerization (35), Friedel-Crafts alkylation, acylation, and reductive alkylation. These methods mainly cleave the aliphatic linkages of coal, leaving the aromatic structures intact. The results of these reactions generally indicate a highly aromatic structure

for coal, but some conflicting reports have been published (36, 37). The use of trifluoroacetic acid in hydrogen peroxide has been reported to selectively oxidize aromatic rings and could be used in conjunction with the previously mentioned reactions (28).

In order to substantiate the certain assumptions about these degradation reactions, and to determine the structure of coal independently of chemical reactions spectroscopic measurements have been made on untreated coal samples. The methods used include: X-ray diffraction, IR spectroscopy, UV spectroscopy, and more recently NMR spectroscopy. The results of such studies have been reviewed by Speight (38).

Extensive X-ray diffraction studies conducted by Hirsh (39) have concluded that coal is highly aromatic. Other studies have conflicted with these results. In general, X-ray diffraction is not as useful as other spectroscopic techniques.

Mass spectrometry has also been used to analyze coal. The procedure necessitates the volatilization of a coal derived ion. The method is therefore dependent on either chemical or thermal ionization reactions. The data generated are complex, but many reports of compound types and the molecular weights of fragments have been reported (32). These studies are important as they identify the units comprising a coal molecule.

Infrared spectroscopy yields valuable information on the bonding present in coal. Not only is information obtainable about the bonding of heteroatoms, as previously mentioned, but carbon-carbon single and double bonds and carbon-hydrogen bonds are detectable. The method is applicable to solids prepared as mulls. The difficulty in quantitating the measurements from sample to sample is the only major drawback.

The use of NMR on coal solutions dates back to the late 1950s. The development of the Brown-Ladner equations (41), using certain assumptions,

enabled the quantitative determination of aliphatic versus aromatic structures. However, the limited solubility of coal and the assumptions contained in the Brown-Ladner equations limit the conclusions that can be drawn from these experiments. The recent applications of NMR to solids has contributed greatly to the structural determination of coal (42, 43). The various NMR techniques that can be used on solids are: magic angle spinning, cross polarization, and multiple pulse sequences (44). An increase in the resolution of aromatic and aliphatic carbon or hydrogen is obtainable by the use of these techniques in the appropriate nuclear magnetic resonance experiments.

The organic structure of coal can be best exemplified by Figure 2.4. This model coal molecule has been theorized by Wiser (45), based on the results of a combination of the analyses described above. The features to be recognized are: the number of aromatic rings, the number of condensed aromatic rings, the heterocyclic rings, and the types of linkages bridging the predominantly ring structures. For the sake of clarity, the presence of secondary structures has been omitted. It should be realized that free rotation about certain bonds is possible. The functional groups present may interact with each other or they may chelate metals, providing three dimensional secondary structure. The location of such groups in the two dimensional model that are possibly able to chelate metals are contained within the broken boxes indicated in Figure 2.4. Compounds containing this type of functionality have been used in the chemical analysis of metals because of their complexing ability. An example of one such compound is 8-hydroxyquinoline.

Minor and Trace Elements Occurring in Coal

Excluding the major components carbon, hydrogen, oxygen, nitrogen, and sulfur, the study of all other elements can be generalized under the topic of minor and trace elements found in coal. The main forms that minor and

Figure 2.4.--Theoretical coal molecule. Adapted from Reference (45).

trace elements exist in coals are as minerals. In lower rank coals many elements including Ca, Na, K, Sr, Mg, and Mn are present as carboxylates (46). Discrete minerals can be directly identified on the basis of optical examination, X-ray diffraction patterns, and infrared spectroscopy (47, 48, 49, 50, 51). In addition, many minerals may be separated from the coal based on their higher densities, using a float sink separation technique. The major minerals identified in coal and their possible sources are shown in Table V. In general, the detection limit of a given mineral by X-ray diffraction is limited to about 0.1% of the sample. Therefore, most studies are limited to the more abundant minerals. The chemical composition of the less abundant, and noncrystalline minerals, as well as the elements distributed throughout the mineral portion at trace levels cannot be determined directly.

The presence of elements whose chemical species cannot be determined directly can be quantitated by various analytical techniques. The association of these elements, with either the organic or mineral portion of the coal, has been based on the quantitative analysis of float sink fractions (49, 52). Float sink fractions are obtained by the physical separation of the organic matter, from the mineral matter, based on its lower density. The results of two float sink studies and a study based on the geochemistry of coal (53) are summarized in Table VI. It is shown that Ge, Be, and B are associated predominantly with the less dense organic matter, whereas Ti, V, Cr, Ni, and Cu are intermediate in terms of their associations. The elements Zn, Fe, Mn, and As all appear to be inorganically associated. These elements are probably in the form of sulfide minerals.

Table V. Major Minerals Found in Coal^a

Mineral Type	Syngenetic		Epigenetic
	Detrital	Deposited	
Clays	Kaolinite, Illite, Montmorillonite, Sericite, Chlorite	Kaolinite, Illite, Montmorillonite, Sericite, Chlorite	Illite
Carbonates		CaCO ₃ Calcite FeCO ₃ Siderite (Ca, Mg, Fe)CO ₃ Ankerite CaMgCO ₃ Dolomite	Calcite Ankerite Dolomite
Sulfides		FeS ₂ Pyrite FeS ₂ Marcasite CuFeS ₂ Chalcopyrite ZnS Sphalerite	Pyrite Marcasite Chalcopyrite Sphalerite PbS Galena
Oxides	TiO ₂ Rutile FeTiO ₃ Ilmenite SiO ₂ Quartz	Fe ₂ O ₃ nH ₂ O Haematite SiO ₂ Quartz	Hydrated Fe Oxides Quartz
Phosphates	Apatite	Phosphorite	

^aAdapted from: Reference (47).

Based on these studies, in conjunction with the chemical and geochemical behavior of the elements, the inorganic elements exist in coal:

1. Discrete minerals which can be classified as:
 - a. Syngenetic--deposited at the same time as the organic matter,
 - b. Epigenetic--deposited after the coal seam had been formed.
2. Minor components of discrete minerals by means of isomorphous substitution.
3. Chemically bound to the organic portion of the coal as:
 - a. Salts of carboxylic acids,
 - b. Discrete organometallic compounds (involving either a direct carbon bond or π - π bonding),
 - c. Metal complexes involving the heteroatoms O, S, and N.

Table VI. Organic-Inorganic Affinities of Elements in Coals

Elemental Affinity	Zubovic ^a	Gluskoter ^b	Swaine ^c
Predominantly organically combined	Ge, Be, Ga, Ti B, V	Ge, Be, B, Sb	B, Ge
Organic and Inorganic	Ni, Cr Co, Mo, Cu	Co, Ni, Cu, Cr, Se, V, Ti	Hg, Se
Predominantly inorganically combined	La, Zn	Zn, Cd, As, Mn, Mo, Hg, Pb, Fe	As, Cd, Zn, F, Zr, Fe Mn, Mo

^aReference (52). ^bReference (49). ^cReference (53).

The distribution of inorganic elements in coal has been discussed on the basis of their physicochemical properties by Zubovic (52). The uptake of elements by organic matter, presumably as complexes, is dependent on the elements' ionic radius, their known stability constants with respect to a given chelate, and their preference of bonding either to oxygen or nitrogen. In addition, the oxidation reduction potential and the acidity of the depositional environment are of importance. Many of the properties just mentioned in connection with the organic association of the elements are also important in the geochemical substitution or incorporation of elements in clays, or minerals present in aqueous solution.

The analysis of many elements in a large number of coal samples from the Illinois basin has been reported by Gluskoter et al. (54). The application of factor analysis to this data has been performed by Filby and Brown (17). Factor analysis is a statistical technique used to extract a number of factors, which in this application must be interpreted by geochemical

knowledge. These factors are derived from, and attempt to explain complex relations among many variables. In this case the variables are the concentrations of many different elements in a number of different coal samples. The factors abstracted are presented in Table VII. The association of various elements with the different factors for the most part are in agreement with the float sink studies, conducted by Zubovic (52) and Gluskoter et al. (49), and the findings of Swaine (53).

Table VII. The Association of Elements with Various Factors Determined by Factor Analysis

Factor	Elements Associated with Factor
Silicate (clay minerals)	K, Al, Si, Ti, V, Mg
Sulfide (PbS, galena)	Pb, As, Sb, Ge
Sulfide (FeS ₂ , pyrite)	Fe, Mo, Ge
Sulfide (ZnS, sphalerite)	Zn, Cd
Sulfide (NiS, CoS)	Ni, Co, Be, Ga, Sb
Carbonate	Ca, Mn, B
Phosphate (apatite)	Ca, P, F, Mn

^aAdapted from: Reference (17).

More recently scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX) has been used to examine the occurrence of minor and trace elements in whole coal samples (55, 56). This technique is capable of detecting submicron size particles, as well as determining the physical distribution of mineral particles with respect to other minerals and the organic portion of the coal. The results of this study indicate that some elements

that show organic affinity during float sink separations are actually particulate minerals that are associated physically, rather than chemically, with the organic materials. The forms of a number of elements are listed in Table VIII.

Table VIII. The Forms of Some Elements in Coal as Determined by Scanning Electron Microscopy with Energy Dispersive X-ray Analysis

Forms	Elements
Solid solution in pyrite	As, Hg
Probably as an accessory sulfide in the organic matrix	Sb
Organically associated	Be
Clays	Cr
Chalcopyrite	Cu
Clays, organic associations, sulfides	Ga
Organic association	Ge
Organically associated, as PbSe, in pyrite	Se
Titanium oxides, organically associated, clays	Ti

^aAdapted from: Reference (56).

The difficulty in making generalizations about the distribution of elements in coal must be stressed. Due to its heterogeneous nature, local variations within a coal seam occur, and the differences between two coal seams of the same rank can be great.

Liquefaction of Coal

The study and development of coal liquefaction processes has expanded greatly over the last decade. The basic processes under investigation are based on German technology of the 1930s and 1940s. The liquefaction process may be viewed as a depolymerization process and is illustrated in Figure 2.5. The solvolysis of coal is based on thermal fragmentation, in the presence of a highly aromatic solvent derived from the coal. Because of the elevated temperatures, free radicals are created in the coal matrix. These free radicals are stabilized by hydrogen available from the tetralin type donor solvent, diatomic hydrogen or from hydrogen sulfide. If the free radicals are not stabilized they may interact with each other creating high molecular weight materials similar to coke. Some of the mineral components of the coal have been found to have a catalytic effect on the conversion to liquids (57), however this may be only the result of the physical dispersion of the coal by the mineral matter (58).

Figure 2.5. General reactions occurring during hydrol liquefaction.

A more chemically meaningful explanation of the hydroliquefaction of coal can be adapted from the work of Schwager et al. (59), and is presented in Figure 2.6. Of particular importance is the fact that benzene insoluble materials may form from the less functional lower molecular weight benzene soluble materials. The nature of these materials will be discussed in more detail in Chapter 3.

Figure 2.6. The generalized chemical reactions occurring during hydroliquefaction.

Attempts to develop coal liquefaction processes using added catalysts have been made. Many difficulties have been encountered with the poisoning of these catalysts by both organic and inorganic materials present during liquefaction (16, 60). The status of the major catalytic and non-catalytic coal liquefaction processes under development are presented in Table IX.

The coal liquefaction products used in this study were produced via the SRC process operating in a 50 ton per day pilot plant scale. A schematic diagram of the SRC-I process is presented in Figure 2.7. The coal is first ground and dried, and then mixed with the process solvent to create a slurry. The slurry is then heated in the preheater, before being brought into the reactor for the actual hydrogenation. After the reactor, a pressure let down

system separates the gaseous products from the solvent refined coal. These gaseous products are then treated and separated yielding hydrogen (which is recycled), hydrocarbon gases, elemental sulfur, and water. The SRC is then filtered to remove the mineral matter and unreacted coal. The process solvent is distilled off and reused in the initial slurry preparation. The liquid product is then solidified, yielding a material similar to coal but with reduced sulfur and ash content. The SRC-II process is similar to the SRC-I process, however a portion of the product is recycled increasing the mean residence time of the coal in the reactor. In addition, the product is distilled, rather than filtered, to separate the mineral matter and unreacted coal.

Table IX. Status of Major Coal Liquefaction Processes^a

Process	Description	Status
Solvent Refined Coal	Hydrogenation with solvent; no catalyst; solid or liquid product	50 ton/day pilot plant operating; 6000 ton/day demonstration plants being designed
H-Coal	Hydrogenation with solvent and catalyst; liquid product	3 ton/day pilot plant; 600 ton/day under construction
Exxon Donor Solvent	Hydrogenation with solvent; external catalyst; liquid product	250 ton/day pilot plant under construction
Gulf Catalytic Coal Liquids	Hydrogenation with solvent and catalyst; liquid product	120 lb/day pilot plant; development discontinued
Synthoil	Hydrogenation with solvent and catalyst; liquid product	1/2 ton/day process development unit discontinued
COED	Pyrolysis process; no hydrogenation or catalyst; liquid product	Discontinued

^aAdapted from: Reference (61).

Figure 2.7.--Schematic diagram of the Solvent Refined Coal I process.

CHAPTER 3

CHEMICAL ANALYSIS AND THE NATURE OF COAL LIQUEFACTION PRODUCTS

The analysis of coal liquefaction products (CLP) ranges from the determination of the percent material soluble in a given solvent to the quantification of trace constituents at the part per million level. The analysis performed depends upon the goal of the overall research problem. For the purposes of liquefaction process development, the determination of percent conversion is of importance. This includes determination of: C_1 to C_6 gases, oils soluble in alkane solvents, material insoluble in alkanes but soluble in simple aromatic solvents, and insoluble material. There are a variety of such procedures which yield classes of organic compound types. These analyses contribute to the understanding of the major compounds present in CLP. More selective spectroscopic and chromatographic techniques must be used in conjunction with the solvent separation procedures to characterize specifically what classes of compounds are present. The combination of separation and characterization techniques oriented towards the organic compounds present in percent quantities will be discussed under the topic of the general analysis of CLP. The application of these techniques to studies of coal liquids will be discussed under the topic of the nature of coal liquefaction products.

The techniques used to analyze CLP for trace constituents include almost all conventional trace analytical techniques available. The major problem with the application of most techniques to CLP is the interference of the complex sample matrix.

The analyses performed during this research project include both general analysis techniques, and trace element analysis. The integration of the results of these methods depend on a basic understanding of and the limitations of many different analytical methods.

General Analysis of Coal Liquefaction Products

The general methods of analysis of CLP have been included in a variety of books, symposium proceedings, and articles dealing primarily with coal liquefaction processes and their chemistry (28, 62, 63). The methods used will be briefly reviewed, but for a more detailed treatment these references are recommended. The object of the discussion, presented here, is to indicate the general nature of the compounds constituting coal liquids as determined by such analyses.

During the hydrogenation of coal various gases are formed. These include low molecular weight hydrocarbons, carbon monoxide, carbon dioxide, water, and hydrogen sulfide. The analysis of these gases are handled by trapping in suitable aqueous solutions with subsequent titrimetric, spectroscopic or gas chromatographic analysis. Gas chromatographic analysis may also be used on product gases directly during process conditions or during subsequent let down procedures.

It is important to realize that the initial separation of CLP must be performed on a preparative scale, in order to provide sufficient material for the more sophisticated spectroscopic and chromatographic techniques. In some cases the separation of CLP based on their volatility, utilizing atmospheric as well as vacuum distillation techniques, is useful for preliminary separation of large quantities of these materials. However, the use of elevated temperatures may change the chemical nature of the sample.

The structural parameters of importance when analyzing coal liquids have been presented by Whitehurst (64). The functional groups, molecular weight, and the degree of aromaticity present are the most important parameters. A typical solvent separation scheme, based on non-aqueous solvents is shown in Figure 3.1. This scheme has been derived from a variety of schemes previously developed for the separation and analysis of crude petroleum, and CLP. The major factor controlling the solubility of a compound in a particular solvent is its functionality, or its overall polarity. Minor effects due to the compounds molecular weight and its structural similarity to the solvent employed also contribute to the compounds solubility.

Figure 3.1. Solvent separation schemes.

More complex solvent separation schemes employ a variety of acids and bases to neutralize and further separate the functional groups. However, the use of such reagents in a study aimed at determining the nature of trace elements in CLP would further complicate the interpretation of results. The possibility of metal cation exchange in acidic media, and the dissolution of colloidal silicates in a basic media exist under such conditions.

Because of the complexity of coal liquids there has been some discussion as to the role that easily soluble coal derived compounds have on the solubility of more functional but less soluble compounds. In order to avoid such difficulties the use of preparative liquid chromatography has been employed in place of, or in addition to solvent separations (65).

In summary, the preparative separation of compounds contained in CLP, based on functionality, may be obtained by various solvent separations and by preparative liquid chromatography. Mass spectrometry (MS) has also been employed for such analyses. The data obtained by MS are massive and the interpretation of the data is complicated, therefore the reader is referred to the literature (28, 66, 67).

In order to obtain information on the molecular weight of CLP and fractions separated from CLP viscometry, vapor phase osmometry, gel permeation chromatography (GPC), and MS have been used. The most useful technique is GPC, which may be used on an analytical scale providing a molecular weight distribution of the compounds present, rather than a number average or weight average molecular weight. In addition, preparative GPC may be employed to isolate compounds of particular molecular weight ranges for further characterization. It must be stressed that the mechanism of GPC operates on the separation by molecular size. Therefore, not only does the primary (two dimensional) structure, but also the secondary (three dimensional) structure

effect the GPC separation. For example, two compounds of identical molecular weight, but with different structural configurations may elute at different volumes from a GPC system.

In order to characterize the functionality and aromaticity of the compounds found in CLP, or their fractions, spectroscopic methods including IR, UV, and both ^1H and ^{13}C NMR spectroscopy are useful. As in the case of the structural studies of coal the NMR techniques are the most useful. The use of IR spectroscopy is especially helpful in the investigation of the functional groups present in CLP.

The Nature of Coal Liquefaction Products

A variety of studies have been conducted using combinations of the aforementioned separation and characterization techniques. According to studies conducted by Farcasiu et al. (65, 68), the initial products of coal liquefaction are highly functional compounds with molecular weights greater than 2000. These high molecular weight compounds are then converted to a variety of compounds of lower molecular weight, ranging from about 300 to 900. Other studies confirm these results. Table X summarizes the results obtained by Schwager et al. (59, 69). The chemical characteristics of a number of different CLP were studied. The authors indicate that in all cases, except the FMC COED product, the C/H ratio of the carbenes and carboids are higher than that of the starting coal. They indicate that the carbenes and carboids are possibly, in part, products of polymerization reactions involving the free radicals thermally fragmented from the starting coal.

The molecule in Figure 3.2 indicates the general structural characteristics found in a preasphaltene molecule. This compound can be viewed as being similar to units found in the starting coal as well as an intermediate in the conversion to lower molecular weight compounds during coal liquefaction.

Table X. The Chemical Characteristics of Solvent Fractions of Various Coal Liquefaction Products^a

Solvent Fraction & Chemical Property	Coal Liquefaction Product				
	Pittsburg & Midway SRC	Catalytic, Inc. SRC	Synthoil	HRI H-Coal	FMC Coed
Oil					
% of SM ^b	42	4	61	71	26
C/H	0.92	1.09	0.76	0.81	0.73
% S	0.34	0.57	0.43	0.05	1.08
% O	0.86	1.09	1.65	0.83	2.87
% N	0.54	0.41	0.60	0.45	0.42
Molecular Weight	202	264	243	222	267
f _a ^c	d	0.76	0.46	d	0.43
Resin					
% of SM ^b	19	15	22	13	48
C/H	1.02	1.12	0.94	1.05	0.96
% S	0.13	0.00	0.14	0.14	1.26
% O	5.00	2.64	3.52	2.27	7.18
% N	1.40	0.84	1.30	1.13	1.06
Molecular Weight	226	370	305	270	325
f _a ^c	d	0.75	0.62	d	0.63
Asphaltene					
% of SM ^b	21	45	13	10	15
C/H	1.16	1.32	1.12	1.23	1.06
% S	1.11	0.12	0.66	0.64	2.58
% O	6.35	4.23	3.93	4.96	7.11
% N	1.45	1.25	1.63	1.61	1.70
Molecular Weight	471	560	715	513	458
f _a ^c	0.66	0.67	0.63	0.67	0.58

Table X--(Continued)

Solvent Fraction & Chemical Property	Coal Liquefaction Products				
	Pittsburg & Midway SRC	Catalytic, Inc. SRC	Synthoil	HRI H-Coal	FMC Coed
Carbene					
% of SM ^b	0.6	2	0.6	0.6	1
C/H	1.28	1.49	1.23	1.44	1.13
% S	0.67	0.26	0.74	0.94	1.31
% O	4.54	3.83	3.64	4.90	9.82
% N	1.49	1.11	1.72	1.93	1.69
Molecular Weight	d	d	d	d	d
f ^c _a	0.74	0.72	0.63	0.70	0.81
Carboid					
% of SM ^b	17	34	3	5	10
C/H	1.44	1.54	1.29	1.47	1.15
% S	1.19	0.34	2.07	0.97	1.85
% O	7.50	6.92	2.28	6.56	12.08
% N	1.00	0.96	1.64	1.51	1.95
Molecular Weight	600	1026	938	1020	394
f ^c _a	0.77	0.83	0.71	0.75	0.84

^aAdapted from: References (59, 69).^bStarting Material.^cFraction of carbon that is aromatic.^dNo value reported.

Figure 3.2.--Preasphaltene molecule. Adapted from Reference (64).

The chemical interactions occurring in coal liquids have been studied by a number of the techniques previously mentioned (70, 71). These same techniques have been applied to compounds thought to be simple models of the more complex compounds occurring in coal liquids (72). In addition, calorimetry has been used in studies attempting to relate the interactions present to thermodynamic heats of reaction (73, 74).

The most widely studied compound types have been the asphaltenes. Much is known about the nature of petroleum asphaltenes and Yen (75) has presented some views on the similarities and differences between petroleum and coal derived asphaltenes. The conclusions are: coal derived asphaltenes have a higher fraction of aromatic carbon, but have a lower proportion of condensed aromatic ring systems; the molecular weights of petroleum asphaltenes are about 10 times greater than that of coal derived asphaltenes; coal derived asphaltenes are more reactive and more polar than petroleum derived asphaltenes. The oxygen content of coal derived asphaltenes was also shown to be higher than that of petroleum derived asphaltenes.

In an investigation of petroleum asphaltenes, Speight et al. (76) have specifically addressed the topics of asphaltene aromaticity, molecular weight, and heteroatom content. Various structural types are suggested. Of most interest to this dissertation is the discussion of the heteroatoms present, in particular the oxygen functional groups. A variety of investigations utilizing IR spectroscopy of the starting asphaltenes, have been conducted. Two proposed compound types, involving oxygen functionalities are,

a dihydroxynaphthalene, and a hydroquinone. These compounds have the ability to chelate metals, especially those that have an affinity for oxygen and can also contribute electrons into, or extend the aromatic delocalized electron cloud. Due to the higher concentration of oxygen in coal derived asphaltenes, in relation to those derived from petroleum, similar structures may be present in coal liquids. The presence of ortho-dihydroxybenzene structures in coal liquids has been proposed (77).

The acid base structure of coal derived asphaltenes has been reported by Sternberg, Raymond, and Schweighardt (70). The asphaltenes of a coal derived liquid were separated into acidic and basic components by the precipitation of the bases, by treatment with HCl gas. The acidic and basic components were studied by ^1H NMR. The acidic components revealed a broad peak at 5.35 parts per million downfield from tetramethylsilane. On adding D_2O this signal disappeared, indicating exchangeable hydroxyl protons were present in the acidic fraction. When the basic component was added incrementally to the acidic component the hydroxyl resonance shifted towards the aromatic region, indicating interaction of the acidic proton with an aromatic base. Various other experiments were conducted including the molecular weight determination of the whole asphaltene, the acidic component, and the basic component. These measurements indicate a ratio of two to five for the acidic to basic components in the undissociated asphaltene. The use of ortho-phenyl-phenol with the basic fraction indicated the same interaction as was found in the case of mixing the acidic and basic fractions, based on the NMR spectra obtained. A variety of these type of studies have been conducted by Schweighardt et al. (71, 72), mainly using NMR in conjunction with chromatographic methods.

Studies of the molecular weights of coal derived asphaltenes have been reported (78, 79). They indicate a concentration dependence of the molecular weight of asphaltenes, in various different solvents, as determined by vapor phase osmometry. These results conform to the expectations derived from the previously mentioned acid base study.

The more complex preasphaltenes have been more difficult to characterize because of their complexity. They are presumed to be constructed of units similar to asphaltene type compounds, with a variety of bridging groups creating larger molecules, that are polymeric. These compounds may be intermediates in the formation of asphaltenes from coal, or they may also form from polymerizing reactions of asphaltenes. The difficulty in studying the preasphaltenes has to do with their high molecular weight and behavior in solution. Nuclear magnetic resonance experiments are not easily performed on compounds, like these, whose tumbling time is slow.

Trace Elements in Coal Liquefaction Products

A variety of methods for determining trace elements in CLP have been reported. A d.c. arc emission spectrograph was used to analyze 14 minor and trace elements in the products of a catalytic hydrogenation process (80). Instrumental neutron activation analysis and graphite furnace atomic absorption spectroscopy have been used to determine the fate of over 30 elements in the SRC pilot plant in Tacoma, Washington, operating in both SRC-I and SRC-II modes (17, 18, 19, 81). Semiquantitative analysis was performed on some of the solvent fractions for the five coal liquids presented in Table X (59, 69). Graphite furnace atomic absorption spectroscopy, in conjunction with GPC chromatographic separations, was used to analyze an SRC produced at Wilsonville, Alabama (82, 83). The distribution of trace elements in the Synthoil pilot plant have been analyzed by atomic absorption spectroscopy (62).

A combination of techniques including neutron activation analysis, X-ray fluorescence spectroscopy, and mass spectrometry have been used by Fruchter et al. (67) to analyze oil shale and solvent refined coal. A combination of electron spectroscopy for chemical analysis, X-ray diffraction and IR spectroscopy has been used to identify the chemical forms possibly present in a non-catalytically produced coal liquid (84). Spark source mass spectrometry and atomic absorption spectroscopy have been used to determine trace elements in a process development unit at the Pittsburgh Energy Technology Center (85). The use of mineralogical characterization techniques have been used in conjunction with a variety of trace element techniques in order to determine metals in liquefaction residues (86). An investigation of the nature of certain non-hydrocarbon constituents in petroleum substitutes has used a combination of separation techniques with INAA and AAS to determine over 30 elements (61).

The most valuable investigation to date, with respect to this dissertation, is "The Fate of Trace Elements in the Solvent Refined Coal Processes SRC-I and SRC-II" (18). Some of the results of the INAA of SRC-I and SRC-II products (18) are presented in Table XI. The low reduction of the concentration of Ti during the SRC-I process is apparent. Other elements whose concentrations are not reduced by greater than 90% in the SRC-I process include V, Ca, Cl, Mn, As, Hg, Br, Cr, and Ga. In the SRC-II process the concentrations of almost all of the elements determined are reduced to negligible values in the product with respect to the starting coal. However, there has been some concern about the volatilization of Hg, Se, As, Sb, and to a lesser extent Cr, Co, Ni, and Fe, causing these elements to be transported with volatile oils during pressure let down, as indicated in Table XII. The transport of Hg is likely due to the volatility of Hg^0

produced during the hydrogenation process. Similarly, H_2Se and As_4^0 are possible volatile forms that could be mobilized during hydrogenation (19), although the generation of volatile hydrides of these elements must also be considered. The transport of Cr, Co, Ni, and Fe is possible during portions of the process due to the formation of volatile carbonyls, since carbon monoxide is a component of the reaction gases.

In summary, many of the coal liquefaction processes under development have been studied with respect to their trace element distributions. In many of these studies Ti appears to behave uniquely, and has been found to be highly associated with the product (18) or highly associated with the organic material in the residue of such products (84). Environmentally important elements such as Hg, As, Se, and Sb behave significantly different from the other elements during liquefaction. Most of the other elements are greatly depleted during solvent refining, due to their presence as minerals that are easily filtered.

Table XI. The Percentage of Elements in Coal During Solvent Refining^a

Element	% Reduction ^b	
	Solvent Refined Coal I	Solvent Refined Coal II
Ti	12	99.6
V	85	99.9
Ca	88	c
Mg	92	c
Al	98	100
Cl	38	98.9
Mn	40	99.9
As	84	99.4
Sb	92	99.9
Se	94	96.9
Hg	65	78.8
Br	-70	99.8
Ni	c	99.9
Co	96	99.9
Cr	88	99.7
Fe	99	100
K	100	99.9
Sc	78	100
Ce	98	100
Th	89	100
Ga	50	99.9
Cu	90	c

^aAdapted from: Reference (18). ^bPercentage reduction of an element
 $= 100 - 100([X] \text{ in the Solvent Refined Coal}) / ([X] \text{ in the original coal})$.

^cData not available.

Table XII. Enhancement Factors for Elements in Separator #2 Oil in the Solvent Refined Coal II Process^a

Element	Enhancement Factor ^b
Hg	1290
Se	15.1
As	2.38
Sb	3.25
Cr	2.29
Co	1.42
Fe	1.48
Ni	8.76
La	1.03
K	1.00
Al	1.11
Sc	0.79

^aAdapted from: Reference (18). ^bEnhancement factor for element

$$X = ([X] \text{ oil} / [K] \text{ oil}) / ([X] \text{ coal} / [K] \text{ coal}).$$

CHAPTER 4

EXPERIMENTAL PROCEDURES

The experimental procedures used during the course of this research project were a combination of separation methods and trace element analytical methods, the aim being to determine the distribution of trace elements during the separation of the organic material. The separations are based on solubility, functionality (as determined by a chromatographic separation), and by molecular weight. The SRC-I sample used during this study was a composite sample produced from the liquefaction of different batches of Kentucky No. 9/14 coal. The sample was obtained from the Pittsburgh & Midway pilot plant at Fort Lewis in Tacoma, Washington, shipment sample #681. The SRC-II sample was a total product oil, shipment sample #1137, also obtained from Pittsburgh & Midway.

Solubility of Solvent Refined Coal I in Organic Solvents

The method for dissolving SRC-I for the initial gel permeation chromatography study, including the use of an atomic absorption (AA) spectrophotometer as an element specific detector, involved a one step extraction with tetrahydrofuran (THF). The ratio of SRC-I to THF was 1 g to 10 ml and the extraction was performed in a 250 ml Erlenmeyer flask. The slurry was then transferred to two 100 ml centrifuge tubes, centrifuged, and the supernatant then filtered through an all glass Millipore filter apparatus using a Fluoropore 0.2 μ m filter (Millipore Corporation). In all cases the yield of the THF soluble material was measured.

The solutions prepared for the preliminary preparative gel permeation chromatographic separation for INAA and all subsequent procedures were processed by a slightly different method, based on the published procedure of Schweighardt and Thames (87). The first step of the procedure was to place approximately 2.5 g of SRC-I and 200 ml of the appropriate solvent, contained in a 250 ml glass centrifuge bottle, in an ultrasonic bath, while stirring with a glass rod for 10 minutes. The resulting slurry was then centrifuged at 2000 revolutions per minute for 20 minutes. The supernatant was then filtered through an all glass Millipore filter. In the preliminary study a 0.2 μ m filter was used, while in the silica separation scheme a 0.5 μ m filter was used. Table XIII shows the various solvents used during the different segments of the study. The solvents used were all Baker Analyzed Reagent grade solvents, with the exception of the THF used in the silica separation scheme, and the solubility separation. In these cases the THF was MCB Omni-Solv chromatographic solvent, without preservative. For quantitative recovery of the solvent separated material a 13 mm Swinny stainless steel filter apparatus, with a 0.5 μ m filter obtained from Millipore was used to process a 75 mg sample of SRC-I.

Table XIII. Solvents Used During the Various Separation Procedures

Procedure	Solvents	Method ^a
GPC and GPC-AA	Tetrahydrofuran	1
GPC for INAA	Pentane	2
	Toluene	
	Tetrahydrofuran	2
Silica Separation Scheme	Tetrahydrofuran	2
Solubility Separation	Tetrahydrofuran	2
	Pyridine	

^a1--employed stirring bar, 2--employed ultrasonic.

Gel Permeation Chromatography

Gel permeation chromatography was used throughout this study because of the useful information obtained by molecular weight separations and because it is a relatively chemically inert chromatographic stationary phase. The packings used, the column dimensions, and the exclusion limits are shown in Table XIV.

The Bio-Beads S (Bio-Rad Laboratories) and Controlled-Pore Glass (Electro-Nucleonics, Inc.) packing materials were used in all glass columns equipped with teflon fittings (Laboratory Data Control). The Bio-Beads columns were packed as a wet slurry, as was the Controlled-Pore Glass (CPG) column. The CPG packing material was silylated, using dimethyldichlorosilane, to reduce adsorption. The Waters columns (Waters Associates, Inc.) were constructed of stainless steel and packed by the manufacturer and used as received. In all cases THF was used as the solvent for GPC separations.

Table XIV. Characteristics of the Gel Permeation Columns Used in This Study

Packing Material	Column Dimensions	Exclusion Limit
Biobeads S-X2 and S-X8 (two columns in series)	2.5 cm x 1 m (each column)	14 000 ^a
Bio-Beads S-X1	2.5 cm x 25 cm	14 000 ^a
Bio-Beads S-X2	2.5 cm x 25 cm	2 700 ^a
Bio-Beads S-X1 and S-X2 (two columns in series)	2.5 cm x 25 cm (each column)	14 000 ^a
Controlled-Pore Glass 75Å	9 mm x 1 m	> 10 000 ^b
Waters μ STYRAGEL 1000Å and 500Å (two columns in series)	7.8 mm x 30 cm (each column)	> 20 000 ^c

^aBio-Rad Laboratories. ^bElectro-Nucleonics, Inc. ^cWaters Associates, Inc.

The Bio-Beads and CPG columns were used in the chromatographic system illustrated in Figure 4.1. The pump was a Minipump obtained from Laboratory Data Control. The injection valve was an eight port Altex teflon injection valve with a removable, variable sample loop. The UV monitor was an Isco model UA-5 using a 280 nm filter with photodiode detection. The Waters μ STYRAGEL columns were used on an analytical liquid chromatograph (Waters ALC/GPC-244), equipped with a U6K variable injection valve. The detector used for this chromatograph was a UV absorbance detector operating at 280 nm. All GPC columns were calibrated using polystyrene molecular weight standards obtained from Waters. In addition, rubrene (molecular weight = 532), obtained from Aldrich Chemicals, and Baker Analyzed Reagent grade toluene were used as standards for the lower molecular weight range where polystyrene standards were not available.

The molecular weight calibration curve, consisting of a plot of the log of the molecular weight of the standard versus the elution vol of the standard for the $10^3\text{\AA}$ and $500\text{\AA}$ μ STYRAGEL columns in series is shown in Figure 4.2. The calibration curve for the preparative Bio-Beads S-X1 and S-X2 columns in series is shown in Figure 4.3. The calibration curve for the CPG column is shown in Figure 4.4. The main differences between the μ STYRAGEL and the Bio-Beads column series are: the increased relative vol separating the standards of high molecular weight on the Waters μ STYRAGEL columns (greater than 3000 and up to 35 000), the increased relative vol separating the rubrene and the 2400 molecular weight polystyrene standard on the Bio-Beads columns, the increased loading obtainable on the Bio-Beads columns, and the visual observation of absorption on the all glass columns containing Bio-Beads.

Figure 4.1.--Chromatographic system for Bio-Beads and Controlled-Pore Glass columns.

Figure 4.2.--Calibration curve for μ STYRAGEL columns.

Figure 4.3.--Calibration curve for Bio-Beads columns.

Figure 4.4.--Calibration curve for Controlled-Pore Glass columns.

In general, the experimentally derived exclusion limits were slightly different than those quoted by the manufacturers. This is not unusual especially in the case of the soft gels, whose properties are dependent upon the solvent used. In addition, it must be stressed that GPC operates on differences in molecular size, not on molecular weight. This aspect of GPC separations as they relate to the analysis of CLP has been discussed in the literature (88).

Silica Separation

After preliminary trace element analysis, using an AA spectrophotometer as a detector for gel permeation column effluents, and the INAA of fractions obtained from GPC separations, it was decided that further separation of the compound types was needed to separate different trace element species. A step gradient solvent separation procedure on a silica stationary phase was selected. This procedure was selected because it was well documented, can be performed on a preparative scale, and its ability to separate CLP based on differences in functionality (65). The solvents used for the silica separation are: hexane, 15% toluene in hexane, chloroform, 4% ethyl ether in chloroform, 3% ethanol in ethyl ether, methanol, 3% ethanol in chloroform, 3% ethanol in tetrahydrofuran, and 3% ethanol in pyridine. Initially, the separation was performed on 50 mg of THF soluble SRC-I, on two SEP-PAK silica cartridges obtained from Waters, and used in series. The solvent vol of each cartridge is approximately 2 ml, and is conveniently used with a Luer lock syringe. A 10 ml aliquot of each solvent was used to elute the separate fractions. The value of this separation was demonstrated initially by means of a GPC separation on Bio-Beads S-X1, which showed that fractions 7, 8, and 9 all contained high molecular weight material. Based on the preliminary study, it was hoped that the high molecular weight material, that contained

the majority of the trace elements, was sufficiently separated on the silica to reveal different distributions of trace elements. In addition, graphite furnace AA spectroscopy was used to determine the distribution of Be in these fractions. Based on these results a separation which would provide sufficient material for other analyses was developed.

The preparative silica separation, needed for the scheme illustrated in Figure 4.5 was performed on a Waters PrepLC/System 500 liquid chromatograph, using one radially compressed silica cartridge, containing approximately 325 g of high quality porous silica and obtained from Waters. A precolumn was used to introduce the sample onto the silica column as suggested by a Waters procedure (89). The sample was first dissolved in THF, centrifuged, and filtered as previously described. The solution was then evaporated to approximately 50 ml in a 500 ml round bottom flask, 100 ml of pyridine and approximately 75 ml of 100/120 mesh glass beads were then added. The mixture was evaporated to dryness and then loaded into the stainless steel precolumn. The purpose of this extensive sample preparation procedure was to ensure the activity of the chromatographic silica. If a direct injection of 25 ml of a 10% THF soluble SRC-I solution was attempted, the column would immediately be deactivated by the THF and the more functional sample compounds. By using the precolumn loading procedure this problem was avoided. The sample material was progressively washed onto the silica column, from the precolumn, preventing column overloading.

In the case of SRC-II a slightly different separation scheme was used as illustrated in Figure 4.6. The volatile material that distilled over during the vacuum distillation, was not analyzed by INAA because of the difficulty of irradiating highly volatile and flammable compounds for any length of time.

Figure 4.5.--Silica separation scheme for Solvent Refined Coal I.

Figure 4.6.--Silica separation scheme for Solvent Refined Coal II.

The SRC-I fractions separated on silica were evaporated to between 1 and 3 ml, transferred to a 25 ml volumetric flask and diluted with THF. Forty percent of this material was then evaporated stepwise, first in a 10 ml glass beaker and then into a 2/5 dram polyethylene vial containing approximately 60 mg of Bio-Beads S-X8. The S-X8 was needed to adsorb the sample in the bottom of the vial to ensure reproducible irradiation and counting geometry for INAA. Because of the amount of material contained in fractions 3, 5, and 6 and the high activity obtained from irradiating these samples for only 10 minutes, a second set of these fractions was prepared using only 4% of the separated material. Fractions 8 and 9 were evaporated to a dry powder in 50 ml round bottom flasks on a rotary evaporator, because of the difficulty of drying them in the 2/5 dram vial. All evaporations, except those performed on the rotary evaporator were conducted in an Agnew-Higgins Laminar/Flow Ultra Clean Work Station.

Fractions 7 and 8 of SRC-I were further fractionated on the Bio-Beads GPC column series, on a preparative scale. The purpose was twofold. First, to determine the molecular weight distribution of trace element species found in these fractions, and secondly, to evaluate the possible contamination of these materials by either the solvents used or by the silica stationary phase. Presumably these contaminants would occur with the lower molecular weight fractions. In addition to the six fractions collected during the normal elution vol range of the GPC columns, a seventh fraction was collected. This fraction contained material that was adsorbed to the packing material and eluted in between preparative chromatograms, as well as from exhaustive elution at the end of every third chromatographic run. A total of 12 chromatographic runs were performed, on each of the silica fractions 7 and 8, in order to obtain a sufficient quantity of material for INAA.

Silica fraction 9 and the THF insoluble, pyridine soluble portion of SRC-I were not further separated because of: the expense of pyridine, the difficulty of safely working with pyridine in large quantities, the high UV absorbance of pyridine affected the chromatographic detectors, and the visually observed high proportion of fraction 9 adsorbed onto the Bio-Beads material.

The solvents were removed from the SRC-II fractions leaving fractions 1 through 5 as viscous oils. The oils were transferred to 2 ml quartz cuvettes for irradiation. At least 50% of each of the separated oils were irradiated. Fractions 6 through 9 were evaporated as previously described for the SRC-I samples, using the entire amount of material separated.

Trace Element Analysis

Instrumental Neutron Activation Analysis

Instrumental neutron activation analysis was used to analyze the starting materials and the chromatographically separated fractions. The detection limits, multielement capability, and relative lack of matrix interferences make this procedure ideal for a study involving the distribution of trace elements during a separation procedure.

The principles of INAA have been widely published (90, 91) and only the basic principles will be covered here. The samples and standards were irradiated simultaneously in the Washington State University modified TRIGA reactor. The elements of interest have isotopes which undergo a reaction that may be generalized as the reaction

where X represents the element of interest and A represents the mass number

of the isotope undergoing the reaction. The product isotope $A+1X$ undergoes radioactive decay, emitting a γ -ray that is detectable by conventional means. The activity of the isotope produced at the end of the irradiation is determined by the relationship

$$A_t = N\sigma\phi(1-e^{-0.693t/T})$$

where A_t = induced activity (disintegrations/s)

N = number of atoms of A X present

σ = thermal neutron capture cross section (cm^2)

ϕ = thermal neutron flux (neutrons $\text{cm}^{-2}\text{s}^{-1}$)

t = irradiation time

T = half life of product isotope

The quantification of the trace element contents of the samples is based on the relationship

$$[X] = \frac{A_{\text{sample}} W_{\text{std}}}{A_{\text{std}} W_{\text{sample}}}$$

where $[X]$ = concentration of element in sample ($\mu\text{g/g}$)

A_{sample} = γ -ray peak area/s of $A+1X$ in the sample

A_{std} = γ -ray peak area/s of $A+1X$ in the std

W_{sample} = weight (g) of the sample

W_{std} = weight (μg) of X in the std

All γ -ray peak areas were corrected for decay to a common point of time. The equation for the determination of $[X]$ is derived from the equations for the induced activity of ^{A+1}X in the sample and standard. This is performed by taking the ratio of the equation for the induced activity in the sample and dividing it by the equation for the induced activity of the standard. Since the samples and standards are irradiated simultaneously, variations in the neutron flux are accounted for. The errors reported for the values determined by INAA are based on the counting statistics. The isotope measured, the half life, and the γ -ray measured are listed in Table XV.

Two irradiation periods were used, the first was for 10 minutes and the second for 8 hours, at a neutron flux of 6×10^{12} neutrons $\text{cm}^{-2}\text{s}^{-1}$. Since the same samples were used for both irradiations, the 10 minute irradiation was performed first. A minimum decay time of 3 weeks was allowed before re-irradiating the samples for 8 hours. The irradiation and counting procedures used, along with the elements determined, are presented in Table XVI.

The detection system used was a Nuclear Data 6620 computer based γ -ray spectrometer as illustrated in Figure 4.7. The detectors used were high resolution Ge(Li) detectors. Typical specifications are 2.26 keV full width at half maximum at 1332 keV, and 12% efficiency in the detection of γ -rays.

The standards used for the elements determined are listed in Table XVII. In addition, a number of the National Bureau of Standards Standard Reference Materials (SRM), and U.S. Geological Survey Standard Rocks were analyzed for elements other than those used as standards. Other reference materials were analyzed as samples, in order to verify the accuracy of the analytical procedure. The results of these analyses with respect to the reported values are presented in the Appendix.

Table XV. The Characteristics of the Isotopes Used for Instrumental Neutron Activation Analysis^a

Isotope	Half Life	γ -Ray Measured (keV)
²⁸ Al	2.3 min	1779
⁵² V	3.8 min	1434
³⁷ S	5.07 min	3105
⁵¹ Ti	5.79 min	320
⁴⁹ Ca	8.8 min	3084
²⁷ Mg	9.5 min	1015
¹²⁸ I	25 min	443
³⁸ Cl	37 min	1643
⁵⁶ Mn	2.56 h	847
⁴² K	12.4 h	1525
⁶⁴ Cu	12.8 h	511
⁷² Ga	14.1 h	834
²⁴ Na	15.0 h	1368
⁷⁶ As	26.3 h	559
⁸² Br	35.3 h	777
¹⁴⁰ La	40.2 h	1597
¹²² Sb	64.3 h	564
¹³¹ Ba	12.0 d	496
⁸⁶ Rb	18.7 d	1079

Table XV--(Continued)

Isotope	Half Life	γ -Ray Measured (keV)
^{233}Pa (from ^{233}Th)	27.0 d	312
^{51}Cr	27.8 d	320
^{141}Ce	32.5 d	145
^{181}Hf	42.5 d	482
^{59}Fe	45.6 d	1099
^{203}Hg	46.9 d	279
^{85}Sr	64.0 d	514
^{58}Co (for Ni)	71.3 d	811
^{46}Sc	83.9 d	889
^{75}Se	120 d	265
^{65}Zn	243 d	1116
^{134}Cs	2.05 year	797
^{60}Co	5.26 year	1333

^aAdapted from: Reference (92).

Table XVI. Irradiation and Counting Procedures for Instrumental Neutron Activation Analysis

Irradiation Time	Decay Time	Counting Time	Elements Determined
5-10 min	1 min 30 min	180 s 1000 s	Ti, V, Ca, Al, S, Mg, Cl, Mn, I
8 h	36 h	4000 s	As, K, La, Ga, Na, Cu, Br
	21 d	80000 s	Sb, Se, Hg, Ni, Co, Cr, Fe, Cs, Rb, Sc, Ce, Sr, Ba, Hf, Zn, Th

Table XVII. Standards Used for Instrumental Neutron Activation Analysis

Material	Element(s) Used as Standards
Solution of Ti and V	Ti, V
NBS Coal SRM 1632 ^a	Al, Br, Ga, Na, Se
CaCO ₃ ^b	Ca
MgO ^b	Mg
Reagent Grade S Powder	S
Solution of I and Cl	I, Cl
NBS Orchard Leaves SRM 1571 ^a	Cu, As, Sb, K, Rb, Zn, Mn, Hg
NBS Fly Ash SRM 1633 ^a	Ba, Sr, La, Cs
USGS Standard Rock GSP-1 ^c	Ce, Th, Hf, Sc
USGS Standard Rock DTS-1 ^c	Fe, Ni, Co, Cr

^aNational Bureau of Standards Standard Reference Material.

^b"Specpure", Johnson, Matthey & Co., Limited.

^cU.S. Geological Survey Standard Rocks.

Figure 4.7.--Schematic diagram of γ -ray spectrometer.

The quantities of the elements determined after the 10 minute irradiation were computed by the PEAKANAL program in use at the Nuclear Radiation Center (NRC) at Washington State University. For the elements determined during the 3 minute counting period a correction for the decay during counting is included in this program according to the procedure of Hoffman and Van Camerik (93). The amounts of the elements determined after the 8 hour irradiation were calculated using the FOURIER program in use at the NRC. The program generates a smoothed background spectrum, and then subtracts this background spectrum from the original spectrum. The background corrected spectrum is then used to calculate the amounts of the various elements determined by the previously mentioned relationship.

Atomic Absorption Spectroscopy

Atomic absorption spectroscopy was used to determine the elements Ca, Mg, Fe, and Be during the course of this study. The analytical wavelengths and slit widths used for each element are presented in Table XVIII. The instrument used was a Varian model AA-5. The elements Ca, Mg, and Fe were determined using an air acetylene flame with a premix laminar flow burner. Beryllium was determined using a graphite furnace atomizer in the step voltage mode.

Table XVIII. The Analytical Wavelengths and Slit Widths Used for Atomic Absorption Analyses

Element	Wavelength (μm)	Slit Width (μm)
Ca	422.7	200
Mg	285.2	500
Fe	248.3	200
Be	235	300

During the preliminary study Fe and Mg were determined in the effluents of GPC columns, by directly interfacing the effluent line to the nebulizer of the flame AA spectrophotometer. This provided a continuous monitoring of the chromatographic effluent for the selected element.

The relative absorbances of Ca and Mg were determined in fractions 7, 8, and 9 from the silica separation by flame AA spectroscopy. Magnesium was also determined in the effluent of the Controlled-Pore Glass GPC column after injecting silica fraction 8. Since no Mg signal was obtained, the solvent flow to the column was stopped and manually reversed in order to backflush the adsorbed material.

The relative absorbances of Be in the silica fractions, obtained from the initial SEP-PAK silica separation and the preparative silica separation, were determined by graphite furnace AA. The conditions used are presented in Table XIX.

Table XIX. The Instrumental Conditions for the Graphite Furnace Atomic Absorption Determination of Beryllium

Heating Cycle	Voltage	Time
Dry	7.0	60 s
Ash	8.5	60 s
Atomize	10.0	2.5 s

CHAPTER 5

RESULTS AND DISCUSSION

Analysis of the Starting Materials

Instrumental neutron activation analysis was used to analyze the starting SRC products, as well as the chromatographic fractions generated throughout the study. The composite SRC-I sample, produced from a Kentucky coal, was analyzed for all elements detectable by INAA but particular attention was given to the elements Ti, V, Al, Ca, and Mn. The results of the analysis of the original coal and for the SRC-I sample for these elements are presented in Table XX. As concluded in previous studies (17, 18), Ti, V, and Mn are not depleted substantially in SRC-I relative to the original coal.

Table XX. The Analysis of the Original Coal and Solvent Refined Coal I by Instrumental Neutron Activation Analysis

Element ($\mu\text{g/g}$)	Coal (Kentucky No. 9/14) ^a	Solvent Refined Coal I ^b
Ti	509.1 $\pm$ 92.1	223 $\pm$ 11
V	33.7 $\pm$ 1.4	6.1 $\pm$ 0.2
Al	11600 $\pm$ 200	102 $\pm$ 5
Ca	1630 $\pm$ 230	73 $\pm$ 15
Mn	37.0 $\pm$ 0.5	16.6 $\pm$ 0.1

^aCoal values from Reference (17).

^bSolvent Refined Coal I values from samples run during this study.

Both SRC-I and SRC-II starting materials were analyzed by INAA. The concentrations of the elements determined are presented in Table XXI.

Preliminary Study

A preliminary study was conducted to obtain a limited data base for further fractionation of the SRC-I. Gel permeation chromatography was initially conducted on two 1 m columns, an S-X2 and an S-X8, connected in series. The chromatogram obtained for the THF soluble portion of SRC-I, approximately 75% of the SRC-I, is shown in Figure 5.1. Because of the difficulty of maintaining the nonrigid Bio-Beads packing material under the pressure and flow conditions (90 psi and 2.0 ml/min) of these long columns, the use of a single 30 cm column of S-X1 was investigated. The chromatogram obtained is also shown in Figure 5.1. The differences between the chromatograms are slight. It was decided that the increased stability of the packing material and the decreased separation time favored the use of the shorter column. Examination of these chromatograms shows that there is a significant amount of material greater than 1000. This is indicative of benzene insoluble material, which is highly functional and constitutes approximately 30% of a West Kentucky SRC (68).

Preliminary trace element analysis was made with a flame AA spectrophotometer as an element specific chromatographic detector for Fe and Mg. The data are presented in Figure 5.2 for the GPC separation of the THF soluble portion of SRC-I. The chromatograms indicate that these elements are present in the high molecular weight material, although Mg appears to a greater extent in the lower molecular weight material. These results were used to determine the collection points for chromatographic fractions for further analysis by INAA. In order to increase the column loading, the SRC-I was first extracted with pentane and then toluene. These extractions remove the less functional,

Table XXI. The Concentration of Elements in Solvent Refined Coals I and II by Instrumental Neutron Activation Analysis

Element ($\mu\text{g/g}$)	Solvent Refined Coal I	Solvent Refined Coal II
S	8.4 ± 0.8^a	b
Mg	< 60	b
Cl	137 ± 5	b
K	5.0 ± 2.7	1.6 ± 0.1
Cu	2.7 ± 0.2	0.100 ± 0.013
Ga	1.06 ± 0.05	0.007 ± 0.002
As	1.95 ± 0.04	0.042 ± 0.001
Br	6.9 ± 0.1	0.043 ± 0.002
La	0.18 ± 0.02	0.006 ± 0.001
Sb	0.17 ± 0.03	0.003 ± 0.0007
Ba	15 ± 4	< 0.38
Rb	< 1.7	< 0.034
Th	0.26 ± 0.02	0.001 ± 0.0002
Cr	2.8 ± 0.1	0.216 ± 0.003
Ce	0.53 ± 0.05	0.005 ± 0.001
Hf	0.08 ± 0.01	0.001 ± 0.0002
Fe	394 ± 13	10.6 ± 0.3
Hg	< 0.005	0.015 ± 0.002
Sr	$< 18.$	< 0.41
Ni	< 6.3	< 0.11
Sc	0.74 ± 0.01	< 2
Se	0.15 ± 0.03	0.091 ± 0.002
Zn	< 0.9	0.124 ± 0.007

Table XXI--(Continued)

Element ($\mu\text{g/g}$)	Solvent Refined Coal I	Solvent Refined Coal II
Cs	< 0.06	< 0.001
Co	0.31 ± 0.01	0.006 ± 0.0003

^aValue expressed in mg/g. ^bSolvent Refined Coal II was not irradiated to determine this element.

lower molecular weight material and accounted for approximately 25% of the starting material. The remaining material was then extracted with THF and the soluble portion amounted to 50% of the original SRC-I. The material was collected in five fractions. The results of the analysis of these fractions for Ti, V, Al, Mn, and Ca are presented in Table XXII. The quantities of these elements are fractionated primarily with the higher molecular weight material. There are some differences as to how the quantities of these elements decrease on proceeding to the lower molecular weight fractions.

Table XXII. Trace Element Analysis of Gel Permeation Chromatography Fractions of Benzene Insoluble, THF Soluble Solvent Refined Coal I

Fraction ^a	Micrograms of Element		
	Ti	V	Mn
1	15.3 ± 0.5	0.780 ± 0.006	1.50 ± 0.02
2	7.9 ± 0.2	0.380 ± 0.003	0.54 ± 0.01
3	2.9 ± 0.2	0.180 ± 0.002	0.100 ± 0.002
4	0.9 ± 0.2	0.110 ± 0.002	0.037 ± 0.002
5	0.7 ± 0.1	0.060 ± 0.001	0.030 ± 0.002

^aFraction 1 is the excluded high molecular weight material, and the molecular weight of the fraction decreases with increasing fraction number.

Figure 5.1.--Preliminary Bio-Beads separation of tetrahydrofuran soluble SRC-I.

Figure 5.2.--Atomic absorption detection for magnesium and iron in gel permeation chromatographic effluent.

These elements may be present as high molecular weight organometallic compounds or as organic complexes. Humic acids, known to be precursors of coal, have the ability to complex many metals, primarily as carboxylates (29). As the coal rank increases the relative concentration of the carboxylic acid groups in the coal decreases. During solvent refining, hydrogenation may mobilize certain elements or restore complexing sites in the organic matter. These materials would elute as high molecular weight compounds. The presence of organometallic complexes in the high molecular weight material separated from SRC-I (Wilsonville SRC-I pilot plant) was suggested by Coleman et al. (82, 83), based on a similar GPC separation. However, these elements may also be present as submicron particulate inorganic minerals that are present in coal and would not be filtered out of the SRC-I product during the process. Among submicron size particles found in coal are various clays. Clays adsorb functional organic compounds (94) and may be suspended in a colloidal state by the organic coating. These colloidal entities would also elute as high molecular weight compounds during the GPC separation.

Solubility and Trace Element Distribution of Solvent Refined Coals I and II

The THF soluble portion of SRC-I, approximately 75% by weight, the THF insoluble pyridine soluble portion of SRC-I, approximately 25%, and the insoluble portion, less than 1%, were separated and analyzed. A Swinny filter apparatus, equipped with a 0.5 μ m filter, was used to process 75 mg of SRC-I with THF and pyridine so that complete recovery and analysis of the entire material could be performed. The trace element data for SRC-I separated in this manner are shown in Table XXIII. Chromium does not balance well, and based on other studies performed in this laboratory (61), it appears that the pyridine insoluble material was contaminated. High recovery

of Al, Fe, and Co are apparent and are possibly due to contamination by the materials used in the sample preparation. It is apparent that Ti and V are almost completely soluble in the solvents used. The further significance of this data is discussed later in this chapter.

Table XXIII. The Weight Distribution of Elements During Solvent Separation of Solvent Refined Coal I and the Percentage Recovery

Element (ng)	Solvent Separation					% Recovery ^a
	Tetrahydrofuran Soluble		Tetrahydrofuran Insoluble Pyridine Soluble		Pyridine Insoluble	
Ti ^b	3.5 ±	0.3	11.7 ±	0.4	< 0.6	91
V	182 ±	2	280 ±	4	18 ± 1	105
Al	4680 ±	60	4100 ±	100	4650 ± 70	180
Ca	1200 ±	400	2400 ±	700	< 1600	65
S ^b	272 ±	38	341 ±	56	< 76	97
Mn	277 ±	2	758 ±	3	169 ± 2	97
As	47 ±	1	75 ±	1	8 ± 1	89
Ga	21 ±	1	38 ±	1	< 3	75
Ce	< 6		23 ±	1	9 ± 3	89
Th	1.0 ±	0.2	14.0 ±	0.4	< 2	75
Cr	89 ±	3	129 ±	4	504 ± 8	351
Hf	1.0 ±	0.3	4.0 ±	0.4	< 2	83
Sc	5.0 ±	0.1	35.0 ±	0.2	2.0 ± 0.1	75
Fe ^b	6.0 ±	0.3	8.0 ±	0.3	25.0 ± 0.7	132
Co	11.0 ±	0.4	15.0 ±	0.5	12.0 ± 0.7	165
Sb	2.0 ±	0.5	7.0 ±	0.7	3.0 ± 0.6	100

^a% Recovery = 100(the sum of the weight of the element in each solvent fraction)/(the weight of the element in 75 mg of SRC-I).

^bElement in µg.

As part of the silica separation scheme of SRC-II, the starting oil was filtered through a 0.5 μm filter before chromatographically separating the oil. This procedure was performed in order to detect any elements that might have been transported with the SRC-II product oil during processing but formed a precipitate in the final product oil. In addition, it is standard practice in liquid chromatography to filter the sample prior to the actual chromatographic procedure. The insoluble material was analyzed by INAA and the results compared to the original unfiltered oil. For each element detected, the percentage of the element found to be insoluble in the unfiltered SRC-II oil was calculated and the results are shown in Table XXIV. For the elements Fe, Th, Sc, Zn, and Co, at least 50% of the total quantity of each element present in the unfiltered oil was found in the insoluble material. It is possible that these elements are transported as volatile carbonyls during the SRC-II process, as proposed by Khalil (18). These elements may then form precipitates in the final product, possibly as sulfides. Greater than 75% of the amounts of Se, Cr, Hf, Sb, and As in the unfiltered oil were found to be soluble. It is possible that these elements form volatile inorganic or organic species which are transported during the SRC-II process and remain soluble in the product oil.

Silica Separation Scheme

In order to separate SRC-I and SRC-II based on the differences in functionality present, preparative liquid chromatography on a silica support was performed. The overall separation schemes are shown diagrammatically in Figures 4.5 and 4.6.

The types of organic compounds occurring in each of the nine fractions, as determined by Farcasiu (65), are presented in Table XXV. The sixth, seventh, eighth, and ninth fractions are highly functional, high

molecular weight compounds that are difficult to characterize. In general, the aromatic-OH content increases with increasing fraction number. The weight distributions of SRC-I and SRC-II obtained from the silica separations are presented in Table XXVI. The relative absence of material in fractions 6 through 9, in SRC-II compared to SRC-I, results from the distillate nature of SRC-II. Whether the small amount of high molecular weight material in fractions 6 through 9 in SRC-II actually distilled over during the process or condensed from lighter fractions is not determinable. The greater amounts of fractions 1, 2, and 4 in SRC-II compared to those found in SRC-I is due to the higher conversion to resins and oils in the SRC-II process, in addition to the concentration of the more volatile material by distillation.

Table XXIV. The Percentage of Elements found to be Insoluble in Solvent Refined Coal II

Element	% Insoluble ^a
As	13
Sb	25
Th	100
Cr	6
Hf	20
Fe	109
Sc	100
Se	2
Zn	131
Co	50

^a% Insoluble = 100(ng of the element in the precipitate/g of oil filtered)/(ng/g of the element in the unfiltered oil).

Table XXV. The Characteristic Compounds Present in the Fractions Generated from the Step Gradient Solvent Silica Separation^a

Fraction	Solvent	Characteristic Compounds Present
1	Hexane	Saturates
2	15% Toluene in Hexane	Aromatics
3	Chloroform	Polar Aromatics--Heterocyclics
4	4% Ethyl Ether in Chloroform	Monophenols
5	3% Ethanol in Ethyl Ether	Basic Nitrogen Heterocyclics
6	Methanol	Highly Functional Compounds
7	3% Ethanol in Chloroform	Polyphenols
8	3% Ethanol in Tetrahydrofuran	Increasing Oxygen Content
9	3% Ethanol in Pyridine	Increasing Basicity of Nitrogen

^aAdapted from: Reference (65).

Table XXVI. The Weight Distribution of Solvent Refined Coals I and II During the Silica Solvent Separation

Fraction (g)	Solvent Refined Coal I	Solvent Refined Coal II
1	0.050	2.204
2	0.050	2.482
3	0.550	0.807
4	0.189	1.922
5	1.375	0.837
6	0.275	0.048
7	0.150	0.016
8	0.363	0.064
9	0.100	0.027

The distributions of trace elements, detected by INAA in the silica solvent separated fractions, are presented in Tables XXVII through XXIX for SRC-I and in Table XXX for SRC-II. Many of the elements normally determined by INAA were not detected in these fractions because of the small amounts present, especially in the case of SRC-II. For a few elements the recoveries after the silica separation were extremely high. The recoveries for Br and Co were greater than 300% and the source of this contamination could not be determined. The poor detection limits for many elements in fractions 5 and 6 are caused by high ^{24}Na and ^{38}Cl activities from Na and Cl extracted from the silica by the ethanol and methanol used as eluants. The high ^{24}Na and ^{38}Cl activities contribute large Compton continuum backgrounds in the γ -ray spectra of the irradiated fractions. Relatively large quantities of Ca are present in fractions 5 and 6. This is due to the extraction of Ca by the ethanol and methanol. Verzele et al. (95) have measured the trace element content of chromatographic silica and of silica extracted by various acids. They found that Na, Cl, Ca, and Mg are the elements present in the highest concentrations in chromatographic silica. These elements were also found to be extractable to varying degrees. The activities from Na and Cl interfered with, and prevented, the determination of Cu. The determination of Hg in the fractions was not possible because of the contamination of the starting solutions upon filtration. The low recoveries of Al, Mn, and Fe are possibly due to their presence as colloidal materials that precipitated on concentrating the silica solvent fractions.

In order to clearly display the separation of different trace element species obtained by the silica separation of SRC-I, the results of some of the elements detected are presented in Figures 5.3 through 5.6 in the form of bar graphs. The distributions of the elements As, Se, and Cr obtained by the silica separation of SRC-II are also displayed in Figures 5.7 and 5.8.

Table XXVII. The Distribution of Titanium, Vanadium, Calcium, Sulfur, and Aluminum in the Solvent Refined Coal I fractions obtained from the Silica Solvent Separation

Fraction	Micrograms of Element				
	Ti	V	Ca	S	Al
1	< 0.46	0.004 ± 0.001	< 1.7	< 85.3	0.35 ± 0.04
2	< 0.26	< 0.001	< 1.1	90 ± 21	0.17 ± 0.02
3	< 8.9	< 0.060	< 19	3040 ± 610	< 1.2
4	< 2.8	0.046 ± 0.006	< 8.0	780 ± 160	1.1 ± 0.2
5	< 14	0.69 ± 0.04 ^a	77 ± 22 ^a	3520 ± 120	8.0 ± 0.7 ^a
6	< 66	1.02 ± 0.05 ^a	65 ± 20 ^a	< 2830	12 ± 1 ^a
7	7.3 ± 1.4	3.00 ± 0.03	< 9.8	420 ± 160	2.2 ± 0.2
8	37.8 ± 1.9	1.96 ± 0.02	21.0 ± 5.2	1010 ± 190	4.9 ± 0.2
9	24.7 ± 4.2	0.78 ± 0.01	56.6 ± 7.1	< 540	4.0 ± 0.2
Total ^b	69.8 ± 4.8	5.79 ± 0.07	77.6 ± 8.8	8860 ± 690	12.72 ± 0.40
Starting Material	88.8 ± 4.1	4.30 ± 0.06	d	5630 ± 690	40.0 ± 0.8
% Recovery ^c	79	135	d	120	31

^aConsidered contamination and not included in totals. ^bLess than values not included in totals.

^c% Recovery = 100(Total)/(Starting Material). ^dNot determined.

Table XXVIII. The Distribution of Manganese, Arsenic, Antimony, Selenium, and Chromium in the Solvent Refined Coal I fractions obtained from the Silica Solvent Separation

Fraction	Nanograms of Element				
	Mn	As	Sb	Se	Cr
1	14 ± 1	< 4	35 ± 3	7 ± 2	52 ± 5
2	6 ± 1	< 4	< 3	< 11	16 ± 3
3	60 ± 10	< 39	< 30	110 ± 20	50 ± 30
4	9 ± 3	10 ± 2	< 3	16 ± 2	23 ± 3
5	76 ± 6	230 ± 20	< 30	100 ± 20	670 ± 40
6	90 ± 20	< 860	28 ± 8	70 ± 20	900 ± 300
7	91 ± 4	98 ± 6	4 ± 1	9 ± 3	260 ± 20
8	820 ± 6	240 ± 10	38 ± 4	< 26	910 ± 20
9	694 ± 5	250 ± 20	9 ± 3	< 31	430 ± 30
Total ^a	1860 ± 30	820 ± 30	110 ± 10	320 ± 40	3300 ± 300
Starting Material	5900 ± 4	860 ± 30	c	c	2300 ± 100
% Recovery ^b	31	95	c	c	143

^aLess than values not included in totals. ^b% Recovery = 100(Total)/(Starting Material).

^cNot determined.

Table XXIX. The Distribution of Nickel, Scandium, Iron, Zinc, and Gallium in the Solvent Refined Coal I fractions obtained from the Silica Solvent Separation

Fraction	Nanograms of Element				
	Ni	Sc	Fe ^a	Zn ^a	Ga
1	< 214	b	2.1 ± 0.3	0.18 ± 0.02	< 5
2	< 202	b	1.2 ± 0.3	0.07 ± 0.01	< 6
3	< 2000	b	< 10.6	b	< 54
4	< 191	b	1.4 ± 0.3	0.25 ± 0.02	< 11
5	< 2100	4.0 ± 0.3	14.1 ± 3.0	1.78 ± 0.17	< 184
6	b	b	b	b	< 412
7	519 ± 78	2.0 ± 0.1	b	b	< 64
8	890 ± 120	23.0 ± 0.3	8.3 ± 0.9	4.08 ± 0.10	144 ± 19
9	530 ± 200	36.0 ± 0.3	28.8 ± 2.6	7.71 ± 0.21	357 ± 29
Total ^c	1940 ± 240	65 ± 1	55.9 ± 4.1	14.07 ± 0.29	501 ± 35
Starting Material	e	98 ± 3	109.6 ± 8.3	9.08 ± 0.45	451 ± 37
% Recovery ^d	e	66	51	155	111

^aValues for element in micrograms. ^bBlank value accounted for all of measured value.

^cLess than values not included in totals. ^d% Recovery = 100(Total)/(Starting Material).

^eNot determined.

Table XXX. The Distribution of Arsenic, Selenium, and Chromium in the Solvent Refined Coal II fractions obtained from the Silica Solvent Separation

Fraction	Nanograms of Element		
	As	Se	Cr
1	< 2	134 ± 4	< 20
2	70 ± 10	567 ± 10	< 33
3	83 ± 2	348 ± 5	8 ± 2
4	76 ± 3	68 ± 3	345 ± 5
5	117 ± 9	56 ± 2	2079 ± 7
6	22 ± 5	35 ± 1	289 ± 3
7	8 ± 2	5 ± 1	155 ± 2
8	9 ± 2	4 ± 1	99 ± 2
9	8 ± 2	8 ± 1	87 ± 2
Total ^a	388 ± 18	1225 ± 13	3062 ± 10
Starting Material	455 ± 72	1077 ± 23	3084 ± 27
% Recovery ^b	85	114	99

^aLess than values not included in totals. ^b% Recovery = 100(Total)/(Starting Material).

Figure 5.3.--Weight distribution of titanium and vanadium. The fractions were obtained from the silica solvent separation of Solvent Refined Coal I. (Non-shaded areas indicate less than values)

Figure 5.4.--Weight distribution of calcium and sulfur. The fractions were obtained from the silica solvent separation of Solvent Refined Coal I. (Non-shaded areas indicate less than values)

Figure 5.5.--Weight distribution of arsenic and selenium. The fractions were obtained from the silica solvent separation of Solvent Refined Coal I. (Non-shaded areas indicate less than values)

Figure 5.6.--Weight distribution of chromium and iron. The fractions obtained from the silica solvent separation of Solvent Refined Coal I. (Non-shaded areas indicate less than values)

Figure 5.7.--Weight distribution of arsenic and selenium. The fractions were obtained from the silica solvent separation of Solvent Refined Coal II.

Figure 5.8.--Weight distribution of chromium. The fractions were obtained from the silica solvent separation of Solvent Refined Coal II.

Some generalizations can be made about the distribution of elements in the fractions obtained from the silica solvent separation of SRC-I. The largest quantities of Ti, V, Ca, Mn, Ni, Sc, Fe, Zn, and Ga occur in fractions 7, 8, and 9, which contain highly functional phenolic material. Atomic absorption spectroscopy was used to detect Ca, Mg, and Be in the silica fractions. The measurements were semi-quantitative and in agreement with the distribution of Ca as determined by INAA. The results also indicated the Mg distribution was similar to that of Ca. The determination of Be by graphite furnace AA indicated the presence of Be predominantly in fractions 8 and 9. For the most part S is distributed according to the weight distribution of SRC-I, showing no preferential association with any particular fraction. The elements Fe, Cr, Se, and As have bimodal distributions with a significant quantity of each element present in fraction 5. Fraction 5 is considered to be the more functional asphaltene material which has been found to have a relatively high concentration of basic nitrogen (65). A large amount of Se is found in fraction 3, a fraction consisting of compounds of relatively low functionality. The association of these elements with each other and with particular silica fractions is discussed and summarized later in this chapter.

The distributions of As, Se, and Cr in the silica fractions obtained from SRC-II indicate the presence of less functional forms of these elements. In particular, Cr is found almost exclusively in fraction 5, which might indicate association with the basic nitrogen compounds present, as indicated in the analysis of SRC-I. In addition, As occurs in fraction 5, but is also present in fraction 3 indicating a less functional form is present. The distribution of Se is unique, and it is possible that it occurs as an inorganic or organic compound of very low functionality.

In most of the gel permeation chromatograms of the SRC-I silica solvent fractions that will follow, there are various peaks in the low molecular weight ranges. These peaks are due to the solvents used in the silica separation.

The analytical scale gel permeation chromatograms, obtained on the μ STYRAGEL columns, of silica fractions 7, 8, and 9 of SRC-I are presented in Figure 5.9. There is a slight increase in the molecular weight of the UV absorbance maxima A, B, and C with increasing fraction number. Fraction 8 has the largest amount of very high molecular weight material.

The gel permeation chromatograms of the SRC-I silica solvent fractions 7, 8, and 9, on the Bio-Beads columns, are presented in Figure 5.10. These columns do not separate the very high molecular weight material, but there is good separation of materials between molecular weights 500 and 3000 based on the standards used. For silica fractions 7 and 8 the fraction collection cut points for the preparative separation of samples analyzed for trace elements are indicated.

The molecular weight separations obtained by preparative GPC of silica fraction 8 were checked using analytical GPC on the μ STYRAGEL columns. Also, the distribution of high molecular weight material was measured in each of the preparative fractions. The UV chromatograms obtained are presented in Figure 5.11. The results confirm the separation of compounds by molecular weight on the preparative GPC columns. This is indicated by the decrease in molecular weight corresponding to the absorbance maxima of each of the fractions. Very high molecular weight material was found only in the preparative GPC fractions 5 and 6. The nature of this material is unknown, and is difficult to analyze because of the small quantities present.

Figure 5.9.--Analytical gel permeation chromatograms of silica fractions obtained from Solvent Refined Coal I.

S-X1 + S-X2 Bio-Beads

Figure 5.10.--Gel permeation chromatograms of silica fractions obtained from Solvent Refined Coal I.

Figure 5.11.--Analytical gel permeation chromatograms of preparative gel permeation fractions.

In an attempt to characterize the small amount of high molecular weight material in the analytical GPC chromatogram of silica fraction 8, AA spectroscopy was used as an element selective detector for Mg in the effluent from the Controlled-Pore Glass GPC column. The only signal for Mg that was obtained was when the flow to the column was reversed, backflushing the column. The chromatogram of Mg response and the chromatogram of the UV response is presented in Figure 5.12. The results show that Mg is not chemically bound with the small amount of high molecular weight material, peak A, nor with the bulk of the organic matter, peak B. The Mg is associated with the material strongly adsorbed on the column. This could indicate the presence of colloidal Mg minerals, possibly clays, or highly functional organic complexes similar to Mg humates.

The data for Ti, V, Ca, S, Al, Mn, As, Cr, Ni, and Fe in the preparative GPC fractions of silica fraction 8 of SRC-I are presented in Tables XXXI and XXXII. The distributions of Ti, V, Ca, and Fe are presented in the form of bar graphs in Figures 5.13 and 5.14. A large fraction of the Ti is in the high molecular weight fractions, and to a lesser degree As, Cr, and Ni are also found in these fractions. However, V and S are present in significant quantities in the intermediate molecular weight fractions. The major portion of the Ca, Al, Mn, and Fe are found in the adsorbed fraction. The significance of the association of these elements with each other will be discussed later in this chapter.

The data for Ti, V, As, Cr, and Fe in the preparative GPC fractions of silica fraction 7 of SRC-I are presented in Table XXXIII. The distribution of Ti is similar to that obtained on the GPC separation of silica fraction 8. The largest quantity of V occurs in the highest molecular weight fraction. The quantities of the other elements present are very low and few conclusions can be drawn. As previously stated, silica fraction 9 was not fractionated.

Figure 5.12.--Controlled-Pore Glass Chromatograms of silica fraction 8 obtained from Solvent Refined Coal I.

Table XXXI. The Distribution of Titanium, Vanadium, Calcium, Sulfur, and Aluminum in the Solvent Refined Coal I fractions obtained from the Gel Permeation Chromatographic Separation of Silica Solvent Fraction 8

Fraction ^a	Nanograms of Element				
	Ti	V	Ca	S ^b	Al
Adsorbed	1950 ± 320	79 ± 2	13200 ± 1400	235 ± 58	5910 ± 60
1	2850 ± 350	62 ± 2	4670 ± 1100	< 170	2780 ± 80
2	990 ± 220	82 ± 1	2850 ± 610	153 ± 35	1260 ± 30
3	1800 ± 280	95 ± 2	1810 ± 520	130 ± 42	580 ± 50
4	1540 ± 220	83 ± 1	2600 ± 650	147 ± 37	4010 ± 90
5	3700 ± 180	107 ± 1	1180 ± 390	154 ± 27	1060 ± 30
6	4250 ± 400	105 ± 2	4700 ± 1300	257 ± 83	3240 ± 110

^aThe adsorbed fraction is the material collected between chromatographic runs and by exhaustive elution of the columns. Fraction 1 is the lowest molecular weight and molecular weight increases with increasing fraction number.

^bValues for Sulfur in micrograms.

Table XXXII. The Distribution of Manganese, Arsenic, Chromium, Nickel, and Iron in the Solvent Refined Coal I fractions obtained from the Gel Permeation Chromatographic Separation of Silica Solvent Fraction 8

Fraction ^a	Nanograms of Element				
	Mn	As	Cr	Ni	Fe ^b
Adsorbed	1199 ± 6	13 ± 2	323 ± 3	361 ± 31	12.2 ± 0.3
1	289 ± 3	11 ± 3	165 ± 2	295 ± 29	4.3 ± 0.2
2	155 ± 1	9 ± 2	85 ± 2	143 ± 21	4.0 ± 0.2
3	128 ± 1	11 ± 1	98 ± 2	< 140	1.7 ± 0.2
4	106 ± 1	19 ± 2	130 ± 2	164 ± 32	1.9 ± 0.2
5	111 ± 1	23 ± 1	178 ± 3	210 ± 26	2.8 ± 0.2
6	189 ± 2	32 ± 2	115 ± 2	511 ± 36	6.3 ± 0.2

^aThe adsorbed fraction is the material collected between chromatographic runs and by exhaustive elution of the columns. Fraction 1 is the lowest molecular weight and molecular weight increases with increasing fraction number.

^bValues for Iron in micrograms.

Figure 5.13.--Weight distribution of titanium and vanadium. The fractions were obtained from gel permeation separation of silica fraction 8 of Solvent Refined Coal I.

Figure 5.14.--Weight distribution of calcium and iron. The fractions were obtained from gel permeation separation of silica fraction 8 of Solvent Refined Coal I.

Table XXXIII. The Distribution of Titanium, Vanadium, Arsenic, Chromium, and Iron in the Solvent Refined Coal I fractions obtained from the Gel Permeation Chromatographic Separation of Silica Solvent Fraction 7

Fraction ^a	Nanograms of Element				
	Ti	V	As	Cr	Fe ^b
Adsorbed	< 630	7 ± 1	< 4	34 ± 2	1.2 ± 0.1
1	< 1850	59 ± 5	7 ± 2	140 ± 2	4.1 ± 0.2
2	< 650	70 ± 1	10 ± 3	97 ± 3	1.6 ± 0.2
3	600 ± 240	119 ± 2	12 ± 1	60 ± 2	1.7 ± 0.2
4	1580 ± 240	280 ± 2	17 ± 1	133 ± 3	3.8 ± 0.2
5	1670 ± 280	325 ± 3	16 ± 1	128 ± 2	2.2 ± 0.2
6	1810 ± 210	363 ± 3	19 ± 1	80 ± 2	1.7 ± 0.2

^aThe adsorbed fraction is the material collected between chromatographic runs and by exhaustive elution of the columns. Fraction 1 is the lowest molecular weight and molecular weight increases with increasing fraction number.

^bValues for Iron in micrograms.

The data obtained on the distribution of trace elements in SRC-I and SRC-II, by several separation procedures indicate that three different groups of trace element species may be proposed. The basis, for these groupings, is the association of the elements with each other during the separation procedures. The groups and the associated elements, during each separation procedure, are presented in Table XXXIV.

Table XXXIV. The Association of Various Elements During the Separations Performed

Separation	Group I	Group II	Group III
Solubility ^a	As, Se, Cr	Ti, V, Cr, As, Al, Ca, Mn, S	Fe, K, Al
Silica Separation ^b	Cr, Se, As, Fe	Ti, V, Cr, Ni, As, Al	Fe, Ca, Al, Mg
GPC Separation ^c	V	Ti, V, Ni, Cr, As	Fe, Ca, Al, Mg, Mn

^aGroup I--determined by the majority of the element being soluble in tetrahydrofuran or soluble in the SRC-II oil, Group II--determined by the majority of the element being soluble in tetrahydrofuran and pyridine, Group III--determined by the majority of the element being insoluble in pyridine.

^bGroup I--determined by having appreciable amounts in fractions 1-5, Group II--determined by having appreciable amounts in fractions 7 and 8, Group III--determined by having appreciable amounts in fraction 9.

^cGroup I--determined by having appreciable amounts in the relatively low molecular weight fractions, Group II--determined by having appreciable amounts in the high molecular weight fractions, Group III--determined by having appreciable amounts in the adsorbed material.

The first group may be considered as species of relatively low functionality, and low molecular weight. The second group is associated with the functional material, soluble in THF to an extent of approximately 30% and essentially totally soluble in pyridine. This second group of elements also occurs in fractions 7 and 8 in the silica separation, and in the two

highest molecular weight fractions in the GPC separation. The exception, based on the molecular weight separation of silica fraction 8, is V which appears as intermediate molecular weight compounds. The most highly functional compounds constitute the third group, being predominantly insoluble in pyridine and distributed primarily in fraction 9 during the silica separation.

The analyses of SRC-II and its various fractions supports many of the associations of the elements in SRC-I. The most noteworthy elements are As, Se, and Cr which occur in the SRC-II filtered oil, and are also distributed in the relatively low functional fractions 1-5 in the silica separation. These elements, especially As and Se, are probably discrete inorganic or organic compounds which are transported during the SRC-II process and remain in the product.

The Nature of Titanium and Associated Elements in Solvent Refined Coal I

The behavior of Ti in the SRC-I process appears unique because of its relatively low depletion in SRC-I compared to the original coal. Because Ti will contribute to the fly ash from SRC-I combustion and because it may act as a catalyst poison in the upgrading of SRC-I (96, 97), its chemistry is of particular interest. It has been previously discussed (17) that Ti may occur in SRC-I as:

1. A finely divided titanium dioxide in the original coal that is not filtered during the SRC-I process.
2. An organically associated form found in the original coal that survives the liquefaction process and remains in the product.
3. An organically associated form produced during the liquefaction process and remains in the product.

At this point it is worthwhile to review some of the information available about the nature of Ti in coal, in particular in relation to the

fate of Ti during liquefaction. In float sink separations Ti has been found to have a partial organic association (49, 52), while other studies have indicated an inorganic association (56). It is possible that Ti occurs completely as an oxide, some forms being so finely divided that they may be separated with the lighter specific gravity fractions because of an organic coating of the oxide particles. The presence of different crystalline forms of titanium oxides in coal has been reported (55, 56), but this does not preclude the presence of organo-titanium or organic titanium complexes.

Eskenazy (98) has shown that Ti is adsorbed from aqueous solutions by peat, a more stable Ti organic complex is formed on prolonged contact time, compared to complexes formed initially. In the same study it was found that Al(III) reduced the rate of Ti adsorption probably through a competitive reaction. Miller and Given (46) found that a significant proportion of the Ti in the lighter specific gravity fractions of low rank coals was acid soluble. These findings indicate that some of the Ti present in coal is not in the form of oxides which are insoluble in most acids, but possibly occur as organic complexes.

The fate of these organic complexes, present in the precursors of bituminous coals; during coalification is speculative. The complexes may survive as initially formed or they may be transformed to other organic complexes. During coalification decarboxylation reactions occur, eliminating some of the primary functional groups responsible for complexation in peat and low rank coals. Whether or not the carboxyl groups present as chelating groups are affected is uncertain, as is the fate of the complexed element. The release of the carboxyl groups result in the formation of metal carbonates if water is present.

Finkleman (56), using SEM-EDX, was only able to account for about 50% of the Ti present in Appalachian coal in mineral species. It is possible that finely divided, organically dispersed, titanium dioxide or clays containing Ti were not detected by the SEM-EDX procedure. However, the author contends that this is not likely in the amounts necessary to account for the discrepancy between the SEM-EDX results and the results of the optical emission spectroscopic analysis.

In summary, there is chemical evidence that peat can complex Ti from aqueous solution, low rank coals may contain organo-titanium complexes, and that bituminous coal contains titanium oxides and may contain quantities of Ti not accountable as minerals.

The formation of a Ti organic complex during liquefaction requires a source of Ti which will be reactive under hydrogenation conditions. Titanium oxides are extremely stable, and even though the formation of titanium tetrachloride by reaction of titanium dioxide and diatomic chlorine is known to occur (99, 100), the concentration of HCl present during liquefaction is not sufficient to generate a significant concentration of $TiCl_4$ in the vapor phase. Table XXXV illustrates some of the possible reactions of titanium dioxide, and the free energies (ΔG°_{700}) of these reactions, under hydro-liquefaction temperature. Thus it does not seem likely from thermodynamic considerations that Ti will be mobilized from titanium dioxide as volatile $TiCl_4$ during liquefaction.

It is possible that clays containing Ti may provide a source of Ti during hydrogenation, but considering the high charge/radius ratio of the Ti(IV) ion, exchange reactions are unlikely. Reduction during hydrogenation may create a lower oxidation state of Ti which might be exchangeable.

Table XXXV. The Possible Reactions, and Their Free Energies, of Titanium Dioxide During Hydroliquefaction^a

Reaction	Thermodynamic Free Energy at 700°(kcal/mol)
$\text{TiO}_2 \rightleftharpoons \text{Ti} + \text{O}_2(\text{g})$	195
$\text{Ti} + 4\text{HCl} \rightleftharpoons \text{TiCl}_4(\text{g}) + 2\text{H}_2(\text{g})$	-65
$2\text{H}_2 + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{g})$	-99
$\text{TiO}_2 + 4\text{HCl}(\text{g}) \rightleftharpoons \text{TiCl}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g})$	31

^aAdapted from: Reference (101).

Considering an organo-titanium as a source of Ti during hydrogenation, it is logical to assume some rearrangement of the original complex may occur but the formation of a mobile Ti ion or the formation of an entirely different type complex is unlikely.

In a study of catalyst deactivation during the catalytic hydrogenation of coal, Ti was found on the surface of the deactivated catalyst (16). More recent investigations of catalyst deactivation during the hydrotreating of coal derived liquids have obtained similar reports (96, 97). Data obtained by an SEM-equipped electron microprobe system in one such study (97) indicates that Ti is found predominantly in the innermost portion of the material deposited on the catalyst. This behavior is distinctly different from that of Si and Ca (which may be present as clay minerals), and from Fe and S (which are probably present as pyrrhotite, FeS). The catalyst in this study was partially regenerated by burning the deposited carbonaceous material, which was found to be similar to coke. The discussion indicates that "the mineral matter is secondary in the direct deactivation of the catalyst" (97). However, the role of the deposited mineral matter, in the regeneration of

the catalyst may involve the formation of coke on the regenerated catalyst. This may limit the lifetime of the regenerated catalyst.

The question as to exact chemical form of Ti in coal liquids cannot presently be answered by direct spectroscopic or other instrumental methods. The distribution of Ti with certain elements and certain chromatographic fractions, as determined by the present study, in conjunction with the known chemistry of Ti represents a logical approach to the question posed.

Considering the relatively high phenol content of fractions 7, 8, and 9 obtained by silica chromatography (65), the possibility of titanium phenoxide should be considered. This has been suggested from IR measurements (84) and from the chemistry of phenols thought to be remnants of the original plant material from which coals have been derived (28). Table XXXVI lists reactions of various metal ions with catechol together with the formation constants for such reactions. Titanium has the highest formation constant of any element found in the literature. The elements V and Al also show highly favorable formation constants with catechol. This is a possible explanation for the association of V, and to a lesser extent Al, with Ti during some of the separations performed. It is possible that the formation of thermodynamically stable titanium phenoxides may result in the mobilization of Ti from titanium dioxide.

Dimers of titanium phenoxide have been reported in the literature (102). This may explain the presence of the higher molecular weight peak in the analytical GPC separation of silica fraction 8 as shown in Figure 5.9. Fraction 8 contains a high concentration of phenolic material and contains the largest amount of Ti relative to the other silica fractions. Pyridine is among the solvents that interact strongly with the acidic titanium phenoxides (103). This may explain the complete solubility of Ti, present in SRC-I, in pyridine, as indicated in Table XXIII.

Table XXXVI. The log of the Formation Constant for Various Ions with Catechol^a

Ion	log (Formation Constant)
Mg(II)	5.7 ^b
Mn(II)	13.6 ^c
Fe(II)	13.5 ^c
Ni(II)	14.4 ^c
VO(II)	33.5 ^c
Ti(IV)	45.8 ^d
Al(III)	37.6 ^d

^aAdapted from: Reference (104). ^bFirst Formation Constant.

^cSecond Formation Constant. ^dThird Formation Constant.

The unique penetration of Ti into catalyst pores (96) can be explained by the presence of titanium phenoxides. The possible role of titanium phenoxide as a catalyst poison as well as its importance in the formation of pre-asphaltenes during hydroliquefaction is a technically important aspect of liquefaction development.

The Nature of Iron and Associated Elements in Solvent Refined Coal I

The elements Fe, K, Ca, Mg, and Al appear to be associated with each other during the variety of separations performed during this study. The possibilities exist that these elements may be present as discrete humic acid complexes or as finely divided minerals, especially clays, with adsorbed organic matter, which are similar to or actually are humic acids. In the original formation of coal both of these species may be present.

During coalification it is not clear what happens to the humic acid complexes. In the liquefaction process the humic acids, or the coalification products of humic acids probably do not survive in their original forms. The products probably are highly functional compounds with a high aromatic-OH concentration.

During both coalification and liquefaction, clays undergo only minor changes due to temperature, pressure, and possible cation exchange reactions. The compound types found in silica fractions 7, 8, 9, being highly phenolic, resemble a class of compounds referred to as tannates. Tannates have been used as peptizing agents in drilling fluids, preventing the flocculation of clays (94). It is possible that Fe, Ca, Mg, and Al are present in mineral forms that interact with phenolic compounds forming species that are soluble, to a limited extent, in the solvents used during this study. The minerals present in coal liquefaction products have been determined by Ruch et al. (86). Table XXXVII summarizes the minerals present and some of the elements found as substituents and impurities in these minerals. The presence of many of these minerals, especially clays, in submicron size particles could account for the occurrence of Fe and the elements associated with Fe.

The Nature of Arsenic and Selenium in Solvent Refined Coal I and II

Based on the silica separations of SRC-I and SRC-II, As and Se appear in fractions of relatively low functionality. In coal both As and Se have been found associated with sulfides, in particular with pyrite (56, 86). During hydroliquefaction it is likely that As and Se may form volatile sulfides or hydrides.

During the SRC-II process the transport of As, Se, Hg, and Sb have been reported by Filby et al. (19). The limited conclusions that can be drawn from the present study are in agreement with the chemical forms

proposed for the volatility of these elements in the SRC-II process. After the let down procedure these elements may precipitate in various forms, but according to the filtration performed in this study As, Se, and Sb remain soluble in the SRC-II product. These elements may form inorganic compounds that are soluble in the SRC-II product oil or may be organically bound. In addition, Cr also appears in a soluble form, possibly due to its affinity for heterocyclic nitrogen compounds present in silica solvent fraction 5.

Table XXXVII. Minerals Found in Coal Liquefaction Products and their Associated Elements^a

Mineral	Common Substitutions and Impurities
Calcite CaCO_3	Substitutions: Mg, Fe^{2+} , Mn, Sr, Ba, Co, Ni, Zn for Ca
Feldspar (K, Na) $[\text{AlSi}_3\text{O}_8]$ and $\text{Na}[\text{AlSi}_3\text{O}_8]-\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$	Substitutions: Ba for K; Fe^{3+} Ti for Al; Mg, Fe^{2+} , Sr, Mn for Ca Impurities: Fe^{2+}
Illite $\text{K}_{1-1.5}\text{Al}_4[\text{Si}_{7-6.5}\text{Al}_{1-1.5}\text{O}_{20}](\text{OH})_4$	Substitutions: octahedral: Fe^{3+} , Fe^{2+} , Mg, Ti, Ca Interlayer: Na, Ca
Kaolinite $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$	Substitutions: Fe, Mg, Ti for Al Impurities: Ca, Na, K
Quartz SiO_2	Substitutions: Al^{3+} for Si Impurities: Li, Na, Ti, Mg
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

^aAdapted from: Reference (86).

CHAPTER 6

SUMMARY AND CONCLUSIONS

The study performed was an attempt to characterize the various elements found in trace quantities in Solvent Refined Coal. The approach taken was to separate chemically the organic matrix based on functionality and molecular weight and then analyze the separated material for various elements.

Initially, solvent extraction was used to separate SRC-I based on functionality, followed by gel permeation chromatography to separate the material by molecular weight. Instrumental neutron activation analysis and atomic absorption spectroscopy were used to analyze the various fractions. In addition, an atomic absorption spectrometer was used as an element selective detector for the effluent of gel permeation chromatographic columns. The results indicated that further fractionation of SRC-I was needed to detect different trace element species.

A step gradient liquid chromatographic solvent separation on a silica support was selected (65). This procedure was chosen because the fractions generated from the separation had been well characterized with respect to their organic nature. The overall separation procedure used a preliminary solvent extraction and included a preparative GPC separation. The numerous fractions generated were subjected to INAA to determine their trace element content. Atomic absorption spectroscopy was also used during different parts of this study.

The analysis of SRC-I, by these methods, was given prime importance because of the detectable levels of many trace elements, with respect to the levels found in SRC-II. The results of the analysis of the various fractions generated from SRC-I indicated different distributions, by weight, for certain elements. The association of elements with each other and with certain fractions have led to the proposal of three different groups of elements.

The first group consists of As, Se, and Cr which appear to occur as less functional compounds. In the case of As and Se these compounds might be inorganic or organic in nature. Chromium appears to be associated with heterocyclic nitrogen compounds.

The second group consists of Ti, V, and to a lesser extent a second form of Cr. These elements are likely to occur as phenoxide complexes, based on their presence in the silica solvent fractions containing highly phenolic material. The elements Ti, V, and Cr are not reduced substantially during the SRC-I process. In particular, Ti has been implicated as a catalyst poison in attempts to upgrade coal liquids. Particular attention was given to the analysis and distribution of Ti. It appears that Ti may in part be present in the original coal as a phenoxide complex which survives the liquefaction process. The possibilities that titanium phenoxides are the source of catalyst poisoning by titanium and that titanium phenoxides may be an intermediate in the conversion of coal to oil products are technically important aspects of coal liquefaction development.

The third group of elements consists of Fe, Ca, Mg, Al, and K. These elements may be present as humic acid type complexes. They may also be present as particulate minerals, especially clays, which may interact with the phenolic material produced during liquefaction.

The analysis of SRC-II was also performed using the combination of separation techniques and trace element analytical techniques. Because of the low levels of most elements present in SRC-II only Se, As, and Cr could be detected. Their distribution is similar to that found in the separation of SRC-I. Both As and Se occur in less functional forms than in SRC-I. Chromium occurs in a form similar to that found in SRC-I.

Further areas of study, based on the results of this dissertation are:

1. The chemistry of simple model compounds of the more complex titanium phenoxides proposed to be present in SRC,
2. Fractionation of CLP on other chromatographic systems (in particular, reverse phase chromatography),
3. The use of radiotracers to characterize the formation of metal organic complexes under liquefaction conditions, or the exchange of metals in chromatographically separated fractions of a CLP,
4. Extension of the GPC separation to SRC-II,
5. Extension of the separation schemes designed during this study to petroleum heavy ends, oil shale, tar sands, and other geologically occurring organic matter.

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APPENDIX

Table XXXVIII. The Ratio of the Accepted Values for the National Bureau of Standards Standard Reference Materials Coal 1632 and 1632a to the Values Determined by Instrumental Neutron Activation Analysis During This Study

Element	Coal	Coal A
Ce	1.16	1.15
Se	b	0.93
Th	1.11	1.05
Cr	1.18	1.04
Hf	1.12	1.1
Ba	1.07	a
Sr	0.75	a
Zr	a	a
Cs	0.81	0.93
Ni	1.10	0.56
Tb	0.58	a
Sc	0.83	0.87
Rb	1.01	0.92
Fe	0.91	0.90
Zn	0.92	a
Ta	0.92	a
Co	1.0	1.07
Eu	0.81	1.00
U	2.7	2.3
Sb	1.89	0.89

^aNo accepted value for comparison. ^bUsed as standard.