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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
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SOLVENT REFINED COAL (SRC) PROCESS: TRACE ELEMENTS

RESEARCH & DEVELOPMENT REPORT NO. 53
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VOLUME III - PILOT PLANT DEVELOPMENT WORK
PART 6 - THE FATE OF TRACE ELEMENTS IN THE SRC PROCESS

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ACKNOWLEDGMENTS

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THE FATE OF TRACE ELEMENTS IN THE SOLVENT REFINED

COAL PROCESSES SRC-I and SRC-II

ABSTRACT

by Samir Ramzy Khalil, Ph.D.
Washington State University, 1979

Chairman: Royston H. Filby

Instrumental neutron activation analysis was used to
study the distribution and fate of up to 36 elements in the
Solvent Refined Coal Process Pilot Plant located at Fort Lewis,
Washington.   The elements Ti, V, Mg, Ca, Al, Cl, Mn, As, Br, Na,
K, Sm, La, Ga, Cu, Sb, Se, Hg, Ni, Co, Cr, Fe, Rb, Cs, Sc, Tb,
Eu, Ce, Sr, Ba, Th, U, Hf, Ta, Zr and Zn were measured in feed
coal, insoluble residues, process solvent, process and effluent
waters, by-product sulfur, SRC-I solid product, liquid-liquid
separator oils and SRC-II liquid products.

The material balance was calculated for each element
from the concentration data and yields of each process fraction
for both the SRC-I and SRC-II processes.   Except for Br, average
elemental material balances for SRC-I process ranged from 71% to
141%, expressed as a percentage of the elemental input.   For the
SRC-II process, the average elemental material balances except
for Hg ranged from 82% to 119%.   Except for Ti, Cl and Br in the
SRC-I mode and Hg in the SRC-II mode, each element was substan-
tially lower in the SRC products compared to the original feed
coal.   The Br concentrations in SRC-I average 43% higher than

the feed coal and the average elemental balance was 158%. Thus an unidentified source of Br is likely. Residues from the process contained more than 80% of the trace element content found in the coal, except for Hg. More than 98.5% of the total contents of K and Fe in coal were retained in the insoluble residues. The behavior of Ti in SRC-I, which accounts for 52% to 88% of the total Ti contents in coal, was different from that of other elements (50% or less). Elements such as Hg, Se, As and Sb can form volatile compounds (such as Hg°, H_2Se, AsH_3 and SbH_3) stable under the process conditions. In one SRC-I set, Hg was partially volatilized as 5.1% of the total Hg in the coal appeared in the process water and 24.9% in the SRC-I product. In the SRC-II process, Hg is significantly volatilized and distributed among separator oils and process waters. High enhancement factors E_f, the enrichment of an element in a given fraction relative to coal and relative to K, for Hg (1290), Se (15.1), As (2.38) and Sb (3.25) in a liquid-liquid separator oil for one equilibrium set are evidence for the formation of volatile species of these elements in the SRC-II mode. Most of the Hg content of the separator oil (4.37 ppm Hg) is associated with a particulate phase which contains 940 ppm Hg rather than the hydrocarbons phase (6.71 ppb Hg). Also, higher contents of Hg, probably HgS or Hg metal, in particulate phase of the separator water (433 ppm Hg) compared to that in the aqueous phase (39 ppb Hg) were observed. The higher enhancement factors of Se (957), As (202) and Sb (27.4) in the aqueous phase of the separator water compared to that of the oil are evidence for the formation of volatile species which

are more soluble in water than in an oil phase, such as H_2Se. Corrosion of alloys or formation of carbonyls could explain the high E_f values for Ni (109), Co (30.3) and Cr (50.9) in the solid from the separator water in SRC-II mode. High concentrations of Hg, Se, As, Sb and other elements in process water were reduced to natural water values by the plant treatment process.

CHAPTER 1

INTRODUCTION

Coal is the most abundant domestic fossil fuel resource and proven reserves in the United States are estimated at 3970 billion tons (1). In light of persistent energy shortages caused principally by restricted petroleum supply, the scientific community has become increasingly aware of the problems of energy and environment that directly affect the activity of the industrial world. There will be an increasing need to develop new domestic sources of energy in an environmentally acceptable manner but because of extensive delays in bringing nuclear power plants on line and the limited domestic supplies of oil and gas, the future energy needs of the United States will be met in large part by coal. Energy from coal will continue to be extracted by direct combustion in steam boilers for the generation of electricity but converting coal to gaseous and liquid fuels in commercial quantities will be necessary to ensure the availability of conventional fuels for major users. Efforts are now under way to find efficient methods of producing clean, easily handled gaseous and liquid fuels from coal. These efforts require development of technologies for conversion and utilization of abundant fossil fuels such as oil shale and tar sands in addition to coal to replace petroleum fuels.

The processes of coal gasification, coal liquefaction and coal cleaning are expected in the future to consume a significant fraction of the coal used in the United States. These processes will produce low sulfur, low ash fuels from coal which is a relatively dirty fuel compared to residual fuel oil and other petroleum based products. Coal liquefaction, which generally involves hydrogenation of coal at elevated temperatures and pressures, shows promise of providing utility boiler fuels, chemical feedstocks and synthetic crude oils (syncrudes). There will eventually be a need to upgrade the syncrudes to produce gasoline, diesel fuel, turbine fuels and petrochemical feedstocks for uses other than electricity generation.

The current emphasis on the large scale exploitation of coal as an energy source makes a more thorough understanding of the chemistry of coal and of coal combustion increasingly important. Coal has about 10 to 30% by weight of undesirable constituents including organic and pyritic sulfur and other non-combustible minerals (2, 3). Sulfur in coal occurs in three major forms; in organic combination with the coal organic matrix, as the minerals pyrite or marcasite plus minor sulfides, or as inorganic sulfate (4, 5). Also, elemental sulfur has been found in coal by some workers (6, 7). During combustion, the organic sulfur is oxidized and evolved as SO_2 and SO_3. The sulfide sulfur is also oxidized with pyrite (FeS_2) transformed ideally to Fe_2O_3 with evolution of SO_2 and SO_3 gases. Calcium carbonate is also decomposed to CaO which may react with SO_3 to form $CaSO_4$ (7). The large scale use of coal in power production draws attention to

SO_2 emissions and associated acid rains which have a deleterious effect on surrounding vegetation (8, 9). Thus there are Federal standards (1.2 lb $SO_2/10^6$ BTU) to limit SO_2 emissions, and in most states coal cannot be burned directly without stack gas scrubbers if the sulfur content of the coal is greater than 1% (10, 11).

Large amounts of fly ash could be released under the coal combustion. The ash content in coal ranges from 7 to 16% (12). Ash is the residue remaining after complete incineration of coal. It is related to mineral matter, but is different in chemical composition from the original mineral matter and consists mainly of compounds of Si, Al, Fe and Ca with measurable contributions from compounds of Mg, Ti, Na and K (5, 6). The heat of combustion induces changes in the mineral portion of coal such as loss of water of constitution by silicate minerals, loss of CO_2 from carbonate minerals, oxidation of sulfides to oxides plus sulfur oxides, and fixation of oxides of sulfur by bases such as calcium and magnesium oxides (6). The ash constituents are predominantly silicates, oxides and sulfates with smaller quantities of other compounds (5).

The discharge of trace constituents during coal combustion is important and has potential environmental effects. The emission of harmful quantities of toxic trace elements such as Hg, As, Se, Sb, Zn and Cu is possible when substantial amounts of coal are burned and fossil fuel burning contributes significantly to total global input of some elements (13, 14, 15, 16). Coals of the same rank from different basins may vary widely in trace element contents because of different depositional influences.

Even in coals from the same basin, there are large variations in contents of most elements in the coals (16, 17). These elements are not distributed uniformly in coals due to variations in the trace element composition of the original plant material and to the geochemistry of the depositional environment and epigenetic processes occurring after formation of the coal beds (16). Several investigators have observed the enrichment of some of the hazardous volatile trace elements on the finer particulate sizes of fly ash emissions during coal combustion (18, 19, 20). This is thought to be due to condensation of Hg, As, Se, Sb, Zn and Cu species on very small particulates in the cooler stack zones. Thus the degree of emission of trace elements to the environment is a function of coal composition, trace element form and combustion conditions. Trace element forms may play an important role in coal-derived fuels.

The techniques for conversion of coal to gas and liquid hydrocarbons involve the breaking or depolymerization of the heavy hydrocarbon coal polymer into smaller molecules and the subsequent hydrogenation of the products.- Thus coal conversion processes must deal with chemical and thermal operations designed to increase the ratio of hydrogen to carbon and to remove the undesirable components (sulfur compounds, ash and trace elements) in an environmentally acceptable manner.

Coal has an H/C mole ratio of 0.8 whereas it is 1.7 for petroleum (21). Essentially, by addition of hydrogen, this ratio can be increased to produce the heavier synthetic crude liquids similar in major element composition to crude oils (22). Producing gaseous fuel requires twice as much hydrogen than heavy

fuel oil production. Hydrogen addition by various techniques also removes much of the sulfur as H_2S from coal and sulfur is then easily recovered (22). Coal liquefaction is also amenable to ash removal to produce a low sulfur and low ash fuel that can be burned without expensive stack gas scrubbers. Removal of a large fraction of the ash content will result in removal of a fraction of sulfur and significant amounts of trace elements in the coal because most trace elements are predominantly associated with the mineral matter of coal and only to a lesser degree with the organic matrix.

The fate of trace elements in coal conversion will be different compared to combustion behavior. Conversion operates in organic compound-rich reducing atmospheres, whereas combustion is basically oxidation. In coal conversion, certain elements may form more volatile species than the oxidized compounds produced by combustion (23) and in addition may form organometallic species (16). Hazardous elements possibly may be concentrated in certain process fractions and then enter the environment at concentrations higher than those of the original coal (16). In power plant flue gases, Hg, As, Se and Sb from coal combustion are likely to exist in vapor form as Hg, As_4O_6 and Sb_4O_6 (24) whereas in reducing conditions of the conversion processes volatile species such as Hg, H_2Se, AsH_3, SbH_3 and $AsCl_3$ may be formed (23). Some of the important environmental aspects of trace element behavior in the conversion process are as follows:

  a) the release of toxic trace elements in waste waters
      or other waste products

  b) the effects of trace metals forms in fuels or syncrudes
      on the incorporation into different fly ash particulate
      sizes during combustion, and

c) the formation of toxic organometallic species and
   incorporation in the products.

The effects of the nature of trace elements in feed coals on
the formation of organometallic species and their effects on
catalysts used in upgrading of the products are also important
in the liquefaction process itself, in the product composition,
and its burning characteristics (16).

The development and use of coal conversion plants there-
for requires an evaluation of the environmental hazards associated
with each process. The volatility of coal and the emission of
trace elements are of concern both environmentally and economic-
ally due to the possible release of trace elements during power
generation and conversion processes that may endanger the environ-
ment. Thus, it is important that the fate and distribution of
trace elements in the liquefaction process be determined to assess
the environmental effects of emissions and the effects of waste
disposal. The distribution of trace elements during the lique-
faction process is also important in determining the trace ele-
ments material balances of the process and in evaluating the
effects of such factors as coal type, autocatalytic effects, tem-
perature, pressure, solvent composition and degree of hydrogena-
tion on the material balance.

The objective of this study was to apply the technique
of instrumental neutron activation analysis (INAA) to the deter-
mination of trace elements in the solvent refined coal SRC-I and
SRC-II processes at the pilot plant scale. The trace element
material balances of those processes were calculated for several
equilibrium or steady state sets of materials collected after the

pilot plant had operated continuously for at least seven days. Another objective was to compare the trace element distribution and trace element contents of the SRC products in the SRC-I and SRC-II processes with those observed for petroleum products and coal. A preliminary study was carried out when the SRC plant was operating under non-steady state conditions and has been reported previously (25, 26). Two equilibrium sets of SRC-I process materials were collected after steady state operation of the pilot plant and the data on 34 elements obtained in this study have been reported in the literature (26, 27, 28). Preliminary data for SRC-II process materials obtained in this study were also reported (16). Neutron activation analysis was selected as the method of trace element analysis due to the high sensitivity for many elements present at very low concentrations, good precision and accuracy, and the capability of analyzing such different matrix types as volatile solvents, liquid oils, aqueous samples and solid coal and mineral residues samples. The multi-element nature of the technique is very useful because of the large number of potential elemental pollutants such as Se, Hg, As, Sb, Zn and Ni.

CHAPTER 2

COAL ORIGIN

Coal is a complex substance consisting of the metamorphosed remains of ancient plant vegetation. Because of variation in the degree of metamorphic change of the original plant material and the variation in the original plant and mineral constitutents, coal is not a uniform substance and no two coals are the same in every respect.

The majority of coal seams originated from plant debris that accumulated in situ as swamp peats. Peat was originally formed as a dark brown residuum produced by the partial decomposition and disintegration of mosses, sedges, trees and other plants. Peat accumulation and burial resulted in large amounts of water squeezed out of underlying layers. When these deposits become buried under thick sedimentary formations, the peat changed to lignite or brown coal (the earliest stage in the formation of coal) which resulted from the physio-chemical effects associated with increased pressure, temperature, and loss of water and volatile materials (4, 29). With deeper burial, the increase of heat and pressure continued to compress and further devolatilize the coal-forming materials. Therefore, the differing time, temperatures and pressures were responsible for the metamorphic changes. The major effect of pressure was to change the physical structure of coal, while temperature largely influenced the

chemical reactions during the coalification process (4, 29, 30, 31). Not only the maximum temperature reached but also the duration of metamorphism is important in coal formation. Physical and chemical properties of coal, such as, carbon content, calorific value, volatile matter and moisture content, are parameters that vary with the depth of burial and degree of metamorphism. The degree of metamorphism is related to "rank" (4, 5, 31). The term rank is an indication of the degree of chemical development of coal and becomes progressively higher from lignite, subbituminous, bituminous, semianthracite and anthracite to meta-anthracite. This succession of changes in the properties and structure of coal is shown in Figure (2.1) and a complete discussion of coal rank is beyond the scope of this thesis. The reader is referred to the literature (5, 32). Passing through this series, there is a darkening in color and an increase in luster of the fuels which is accompanied by a gradual rise in carbon content and calorific value and a decrease in moisture, volatile matter and oxygen contents while the proportion of hydrogen remains roughly constant until in semianthracites and anthracites it falls at an increasing rate. All these phenomena have been described by geologists under the general term "Coalification". Oxygen functional groups (e.g. -COOH, -CO and -OH) content decreases during coalification. The same coal rank may be reached either by a rapidly acting high temperature or by a longer lower temperature regime (31). The time factor plays an important factor for brown coal development while time, increase of temperature and pressure are important for bituminous and higher rank coal formations (31, 32, 33).

DECAYED   HIGH-VOLATILE   MEDIUM-   LOW-
VEGETATION   BITUMINOUS   VOLATILE   VOLATILE
(PEAT)   LIGNITE   SUBBITUMINOUS   C   B   A   BITUMINOUS   BITUMINOUS   ANTHRACITE

60 ——————————— 70 —————————— % CARBON ——————————— 80 ——————————————————————— 90 ——————————————————

————————— 0.25 ——————————— 0.4 ———————————————— 0.6 ——————— REFLECTANCE(%)———————— 1.0 ———————————— 4.0 ———

                                        VOLATILE
————————————————————————————— >35 ——————————— MATTER——31 ————————— 26 ————————————— 17——————————————— 5 ————
                                        (%)

————————————————————————————— SURFACE AREA ——
                                        (MIN)
————————— COKING PROPERTIES —————————

———————— ORGANIC ACID GROUPS ——————————————
                              (ENDS)

—————————————————————————————————————— PHENOL GROUPS ——————————————————
                                                                    (ENDS)
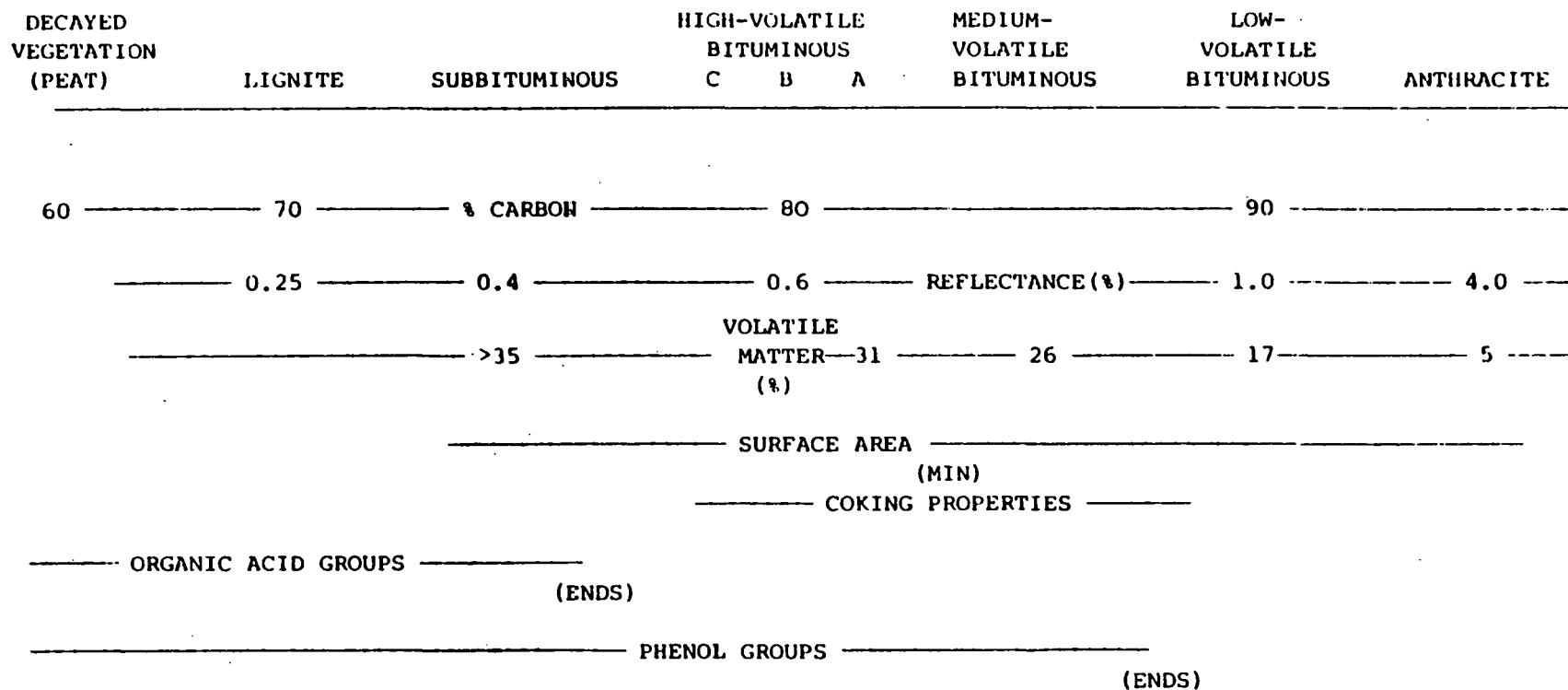
Fig. 2.1. The coal series

The coalification process can be divided into two stages:

1. A relatively short-lived biochemical stage during the peat formation where chemical changes of the accumulating plant debris are dominated by the influence of bacterial activity.

2. A longer duration metamorphic or geochemical stage in which both chemical and physical changes are governed by the effects of time, temperature and pressure.

The coalification process and the chemical characteristics of a coal seam are determined by (34):

1. The nature of the plant source materials

2. The environmental conditions prevailing in the site of of peat accumulation (e.g. minerals present, temperature, etc.)

3. The geological and geochemical history of the peat seam after burial

There have been two great coal-forming periods in the earth's history, one extending through Carboniferous and Permian times (350 to 270 million years) which is represented by mainly bituminous coals, semianthracites and anthracites, and the other mainly in the Tertiary period (70 to 3 million years) represented by lignites and brown coals (31). The older coals were derived from club mosses, ferns, seed ferns and cordaites whereas the Tertiary coals were formed from flowering plants and conifers. Although the plant types changed between these geological periods, the land plants never abandoned cellulose and lignin as their two basic structural materials. These are the substances from which vitrinite, fusinite and micrinite (35) were formed and which constitute the bulk of most coal seams.

According to Van Krevelen (4), the reaction mechanism of coalification is exceedingly complicated and it is not unexpected that the product of the process is a complicated and chemically

heterogeneous substance. Berbius (36) and Maillard (37) believed that coal formed from cellulose which is the basic constituent of wood, but Fischer and Schrader (38) postulated that coal originated exclusively from lignin. A more recent theory, however, was advanced by Enders (39) who considered that humic acids formed from both cellulose and lignin.

Cellulose is a class of linear macromolecular compounds made up of long chains of cyclohexane rings linked by oxygen bridges (29, 31). Lignin is a polyphenol built up from monomer units of phenylpropane derivatives such as coniferyl, sinapyl and coumaryl alcohols which are connected three-dimensionally (29, 31). The aromatic nuclei in the lignin structure are joined through ether and carbon-carbon bonds and have aliphatic, hydroxyl and methoxyl side chains. During the initial coalification, cellulose decomposed to products such as keto-acids which can easily condense, while phenols derived by fungi from lignin may be further oxidized by microorganisms to quinones which undergo ring cleavage to aliphatic compounds. Therefore, both cellulose and lignin degraded to mixtures of aromatic and aliphatic compounds. The net result is decomposing plant materials permeated with these oxygenated and partially unsaturated compounds which undergo condensation and polymerization (31).

Humic acids are a class of ill-defined nitrogen-containing polyphenolic compounds derived form lignin and/or cellulose materials (4, 5, 29, 31). The suggested structures of humic acids involve the linking of aromatic nuclei by oxygen and carbon-carbon bonds and also by amino acids nitrogen groups. They have

-15-

a lower aliphatic carbon content than lignin but more phenolic hydroxyl, carboxyl and quinone groups. Such groups play an important part in the incorporation of metals in coals.

In the later coalification, or geochemical stage, the elementary compositions of whole coals show an increase in carbon content and a concomitant decrease in the level of oxygen; while hydrogen remains between 5 and 6% up to the rank of the semianthracites after which this element is lost at an increasing rate. Nitrogen fluctuates between 1 and 2% throughout the whole rank series and sulfur, while variable, is generally less than 1% in most non-pyritic coals. Methane, carbon dioxide and water are regarded as the main reaction products of the geochemical stage of coalification process. Large amounts of water are lost in the early stages of coalification, but as rank rises, water becomes of decreasing importance as a product. The ratio of methane to carbon dioxide increases as coalification progresses and in the later stages the conversions to semianthracite and anthracite can be accounted for primarily by loss of the methane and a small quantity of water and increasing aromatization or polymerization (5, 29, 31, 40).

The geological, geochemical and environmental conditions in nature at the time of peat formation may influence various aspects of the ultimate seam composition. Coal from different geological provinces may exhibit differing chemical and physical characteristics because of the evolution of substances and processes in the plant and its effect on the availability of certain coal source materials (31). Older coal seams, influenced by the

effects of closely associated marine water or near marine sedi-
ments in parts of succession, may have high concentrations of
pyritic sulfur, while the younger ones generally have lower sulfur
contents reflecting formation in a fresh water environment.

Fuchs (41) has argued an alternate hypothesis. He re-
garded brown coals, formed under aerobic conditions, as the con-
clusion of one coalification process, while bituminous coals and
anthracites follow another coalification track in response to an
anaerobic biochemical environment.

Coal seams are sedimentary rock bodies (5, 35). These
consist of two basic classes of materials:

1. Mineral matter in coal which includes both the mineral
   species and the elements generally considered to be
   inorganic.

.2. Macerals, the fragmentary organic remains or products
    of plant decomposition whose evolution is discussed
    above.

The mineral and maceral materials are not uniformly distributed
through the seam. Instead, the seam often consists of a number
of layers (lithobodies), each one being compositionally dissimilar
from the adjacent layers. In an extreme case of compositional
dissimilarity, the lithobody may be an inorganic lithotype such
as a shale. Only five coal lithotypes are recognized in the
Bureau of Mines literature while six types are recognized inter-
nationally as described in Figure (2.2) (4, 35). The macerals
form the carbonaceous, combustible fraction of the coal. They
are the elementary microscopical constituents of coals and can be
grouped according to certain similarities in their petrographic
properties as shown in Table (2.1) (35), the European Stopes-
Heerlen system. The maceral names usually apply to a particular

THE BASIC COAL TYPES

I. The Humic Coals (=Banded Coals)

    A. Fusain (charcoal-like coal)
    B. Vitrain (black, vitreous coal)
    C. Clarain (striated, glossy coal)
    D. Durain (non-striated, matte coal)

II. The Liptbiolothic Coals (=Nonbanded Coals)

    A. Cannel coal
    B. Boghead coal

International Terminology

THE BASIC COAL TYPES

I. The "Banded" Coals (display anthraxylon)

    A. Bright coal--<20% opaque matter
    B. Semi-splint coal--20-30% opaque matter
    C. Splint coal-->30% opaque matter

II. The "Non=banded" Coals (no anthraxylong displayed)

    A. Cannel coal (abundant spore remains)
    B. Boghead coal (abundant algal remains)

TERMINOLOGY USED BY U.S. BUREAU OF MINES
PERSONNEL TO DESCRIBE THE GENERAL
NATURE OF A COAL SEAM OR
FRACTION THEREOF

Figure 2.2. The basic coal types

TABLE 2.1

SUMMARY OF COAL PETROGRAPHIC NOMENCLATURE

Macerals		Microlithotypes	
Maceral	Maceral group and symbol	Microlithotype	Principal groups of constituent macerals in the microlithotypes
Collinite Telinite	Vitrinite (Vt)	Vitrite	Vt
		Vitrinertite	Vt + I
Micrinite (fine-grained) Micrinite (massive)		Microite	I (micrinite dominant)
Semifusinite Fusinite Sclerotinite	Inertinite (I)	Fusite	I (except micrinite)
Cutinite Resinite Sporinite Alginite	Exinite (E)	Liptite	E
		Clarite	Vt + E
		Durite	I + E
		Duroclarite	Vt + E + I
		Clarodurite	I + E + Vt

series of genetically related materials. Also, the minerals commonly encountered in coal seams are listed in Table (2.2) (42). The minerals found in coal are classified by Nelson (43) and Gluskoter (44) as syngenetic or epigenetic. Syngenetic minerals were incorporated in the coal during the biochemical changes associated with coalification, whereas epigenetic minerals were deposited in the cleats and cracks of the coal after the coalification process was complete.

Coal is a complex mixture of various macromolecules and the detailed chemical structure of coal is not presently known. A variety of methods have been used in the study of coal structure such as X-ray diffraction, ESR, IR and NMR techniques (45, 46). Much information on coal structure has been gained from chemical degradation studies. Despite the present inadequate knowledge of coal constituents and their conformation, many significant attempts have been made to understand the structure of coal. Cartz and Hirch (47), in their X-ray diffraction studies of coal, found that variations in the molecular layers make the construction of an unambiguous coal model impossible. They conclude that the structural units of bituminous coals consist of aromatic ring systems probably containing one to three rings in low-rank vitrains and two to five rings in vitrains containing 90% carbon. The aromatic layers are believed to be linked by direct C-C linkages, aliphatic groups, and ether linkages. The layers are thought to form large sheets which are either buckled by hydro-aromatic gorups or in which adjacent aromatic ring systems are rotated relative to each other about an axis normal to the plane

TABLE 2.2

MAJOR MINERALS FOUND IN COAL*

Mineral Type	Syngenetic		Epigenetic
	Detrital	Deposited	
Clays	Kaolinite, Illite, Montomorillonite 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_2O_3 nH_2O Haematite SiO_2 Quartz	Hydrated Fe Oxides Quartz
Phosphates	Apatite	Phosphorite	
Accessory Minerals	Zircon $ZrSiO_4$ Feldspars		Chlorides NaCl Sulfates Nitrates

*Data from Mackowsky (42).

of the sheets. The sheets are also believed to contain side groups consisting of aliphatic chains and hydroxyl and quinone groups. Montgomery and Holly (48), in their oxidation studies of bituminous coals, concluded that such coals are comprised largely of eight aromatic nuclei (methylnaphthalene, benzene, biphenyl, naphthalene, phenanthrene, C_5 benzene, benzophenone and toluene) which are probably linked together by more readily oxidizable structures. One of the recent molecular structures was proposed by Given (49) as a non-planar molecule based on dihydroanthracene. His structure is consistent with highly substituted aromatics, which are not highly condensed, with functionalities which are known to be present in coal and with its elemental composition. He modified it later to an isomeric type of structure based on dihydrophenanthrene, in which no methylene bridges are involved according to the nuclear magnetic resonance studies by Brown et al (50). A more recent and more sophisticated model was presented by Wiser (51) and is shown in Figure (2.3). He used the present knowledge of coal to represent an "average" bituminous coal in a single plane showing the aromatic and hydro-aromatic components. He suggested that coal should be thought of as being composed of stacked layers rather than as being three-dimensional. The layers may then consist of several aromatic clusters, each perhaps randomly oriented in a plane different from the surrounding clusters. This diagram does not rule out the possibility of three-dimensional molecules in coal. The significance of this diagram is the location of a number of relatively weak bonds indicated by arrows which can account for the rapid breakup of coal into smaller, more soluble fragments (21).
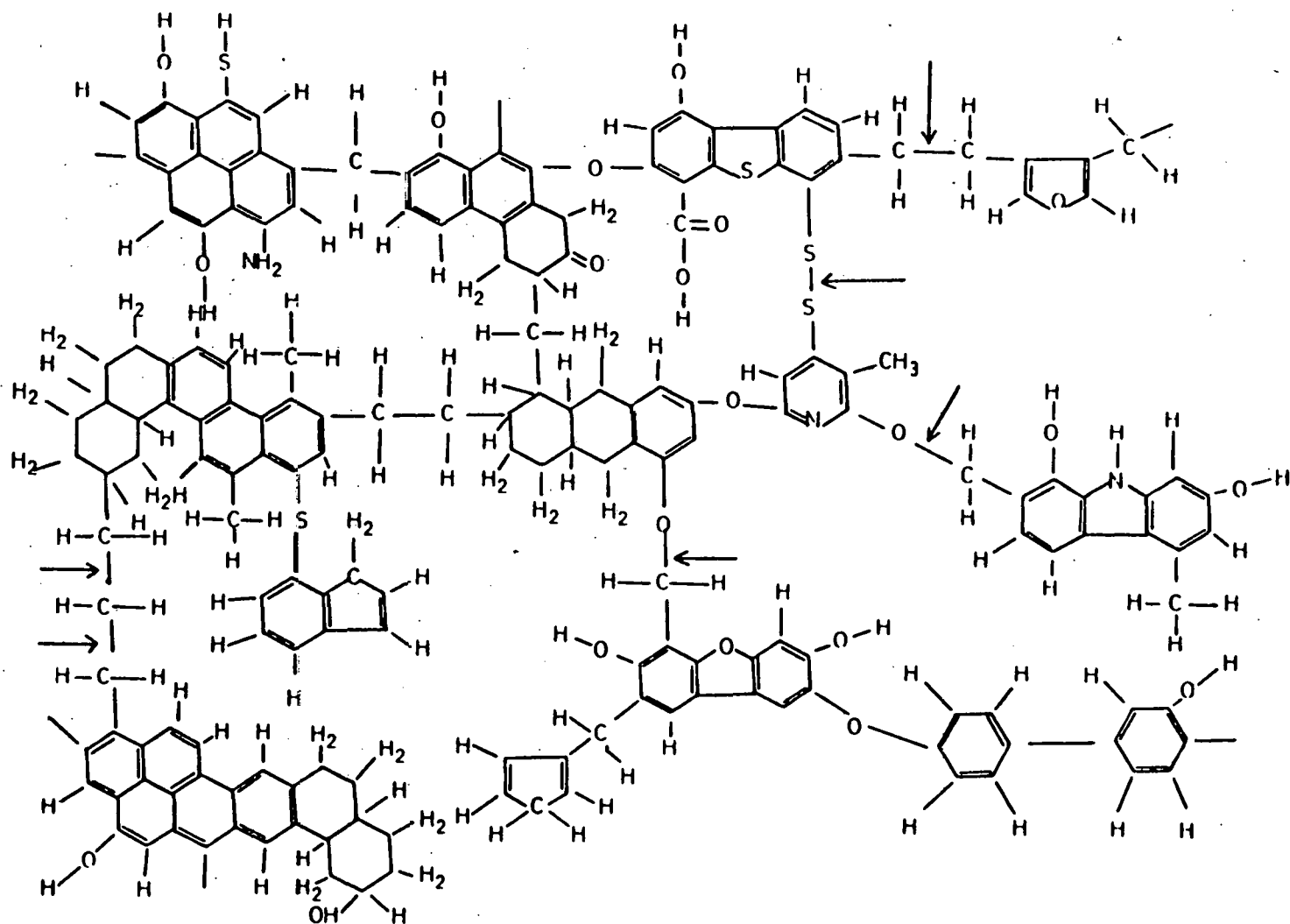
Figure 2.3. Schematic representation of structural groups and connecting bridges in bituminous coal (from reference 51)

Clusters are believed to be held together by bridges (51):

1. short aliphatic groups, probably not many longer than four carbon atoms;

2. ether linkage;

3. sulfide and disulfide; and

4. biphenyl types

Such weak linkages are important to the understanding of the mechanism of pyrolysis or liquefaction of coal.

Oxygen, sulfur and nitrogen in the organic matrix are combined in chemically functional groups or linkages. Oxygen occurs predominately as phenolic or etheric groups with lesser amounts of carboxylic acids (only in subbituminous coals) or esters and some carbonyls. Nitrogen occurs predominately as pyridine or pyrrole type rings (5, 21, 46). The variation of the functional groups of oxygen in coals are given in Figure (2.4) (4, 5). Van Krevelen (4) concludes from this information that, during the metamorphic process, in coals containing up to 70 to 80% carbon, the methoxyl groups are first lost; then the carboxyl groups decrease rapidly. At 81 to 89% carbon content, the hydroxyl groups phenolic or acidic decrease rapidly. At greater than 92% carbon content, almost all oxygen is in nonreactive stable forms. Carboxyl groups are not found in most coals above the lignite stage of development but are present in brown coals and lignites. Methoxyl groups are among the first lost during metamorphism of coal and they usually do not appear in significant amounts in hard coals. Carbonyl groups are found at all levels of coalification. The nature of oxygen, sulfur and nitrogen functional
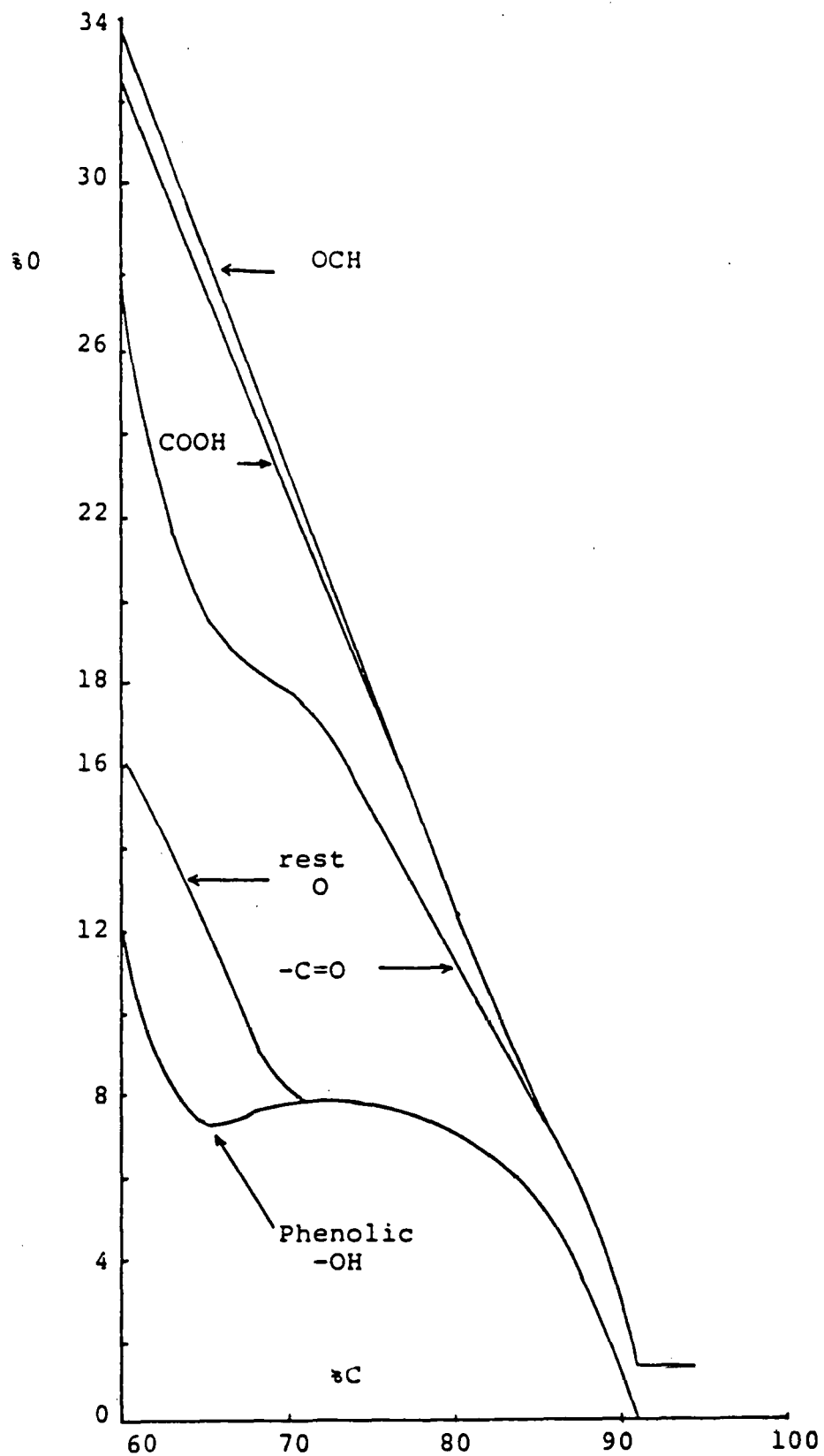
Figure 2.4.   Functional oxygen groups in
coals (from reference 4)

groups in coals is important to understanding the binding of metals in the maceral fraction of coal.

CHAPTER 3

TRACE ELEMENTS IN COAL

Coal is composed not only of those elements generally considered to be organically bound (C, H, O and N) which are important in converting coal to synthetic fuels, but it is also extremely heterogeneous and contains significant and highly variable quantities of other elements. The nature of trace elements present in coal is dependent on: (a) the element, (b) the chemical binding of the element, i.e., organically or inorganically, and (c) the nature of the mineral species if inorganically bound.

Comparison of the major, minor and trace element contents of all coal and different ranks of coal (whole-coal basis) with the average concentrations in shales, the most abundant type of sedimentary rock, are shown in Table 3.1 (52). It shows that few, if any, elements are consistently enriched in coals relative to shales. The overall picture is one of relative impoverishment of coals in minor and trace elements when compared with shales. There are several modes of origin by which trace elements could have been incorporated into coals and these can be conveniently classified depending on whether the elements are organically bound in the coal (in macerals) or inorganically bound (in minerals). Possible modes of origin are shown in Table 3.2. Although it is impossible to identify by visual methods trace element species which are organically bound, many mineral species

TABLE 3.1

AVERAGE AMOUNTS OF 25 ELEMENTS IN DIFFERENT RANKS OF COAL*
COMPARED TO THEIR AVERAGE AMOUNTS IN SHALE

Element	Anthracite	Bituminous	Subbituminous	Lignite	Shale
Al (%)	2.0	1.4	1.0	1.6	8.0
Cs (%)	.07	.33	.78	1.2	2.21
Mg (%)	.06	.08	.18	.31	1.55
Na (%)	.05	.04	.10	.21	.96
K (%)	.24	.21	.06	.20	2.66
Fe (%)	.44	2.2	.52	2.0	4.72
Mn (%)	.002	.01	.006	.015	.085
Ti (%)	.15	.08	.05	.12	.46
As (ppm)	6	25	3	6	13
Cu (ppm)	27	22	10	20	45
Hg	.15	.20	.12	.16	..4
Sb	.9	1.4	.7	.7	1.5
Se	3.5	4.6	1.3	5.3	.6
Tb	5.4	5.0	3.3	6.3	12
U	1.5	1.9	1.3	2.5	3.7
Zn	16	53	19	30	95
Ba	100	100	300	300	580
Co	7	7	2	5	19
Cr	20	15	7	20	90
Ga	7	7	3	7	19
Ni	20	20	5	15	68
Sc	5	3	2	5	13
Sr	100	100	100	300	300
V	20	20	15	30	130
Zr	50	30	20	50	160

*Amounts are presented in whole coal basis.

TABLE 3.2

ORIGIN OF METAL SPECIES IN COALS

Organically Bound (in Macerals)	Inorganically Bound (in Minerals)
a) Originally present in the source plant material	a) Brought in as detrital minerals during coal formation e.g., silica, zircon, accessory minerals
b) Complexed by amino-acids, humates, etc. during deposition of the organic source materials	b) Formed in situ during deposition of plant material by precipitation, etc. (syngenetic processes) e.t., formation of clay minerals
c) Later fixed by adsorption or ion-exchange on functional groups in lignite (-COOH or phenolic -OH) or coal (phenolic -OH)	c) Formed during movement of solutions after formation of coal (epigenetic processes) e.g., pyrite veins

have been observed in coals and can be separated by physical or chemical methods from the organic matrix. The most important minerals that occur in coal are shown in Table 2.2 and of those listed, the most important quantitatively are the clay minerals, silica and pyrite (or other FeS_2 modifications). Gluskoter (44) and Rao and Gluskoter (12, 44) have assumed that the low temperature ash produced in a radio-frequency asher at temperature below 150° C is equivalent to the mineral matter of coal. For elements that are present in coals in minor to major amounts (0.1 to 10%) it is possible to identify specific mineral species with which the elements are predominantly associated. For example, in most coals Fe is present either as pyrite FeS_2 (plus oxidized forms, $FeSO_4$ or Fe_2O_3n. H_2O) or other sulfide species such as marcasite, FeS_2 or chalcopyrite $CuFeS_2$ (16, 44). For most of the trace metals in coal, present at concentrations less than 0.1%, knowledge of the actual chemical moeities is lacking and often the species must be inferred from indirect evidence. Most trace elements are probably found in both organic and inorganic combinations (53, 54, 55). Elements such as Fe, Ca, Zn, Mg, Si, etc., may occur predominantly in mineral species of these elements; e.g., FeS_2, $CaCO_3$, ZnS, etc. However, for many elements such as Hg, As, Sb, Pb, Cd, Co, Ni, Se, etc., no specific mineral of the element may be present and the element may be distributed among several species.

Many investigators have studied the occurrence of trace and minor elements in coal (5, 17, 42, 56, 57, 58, 59). Most have commented on the probable mode of origin of various elements

especially those which occur in unusually high concentration.
The introduction and retention of trace elements in coal results
from a series of geologic and chemical processes. Three princi-
pal stages in which the elements have become enriched in the
organic matter of coal, were proposed by Goldschmidt (60) as:

1. concentration during plant growth,

2. concentration during decay of the organic substances
    by a variety of chemical processes, especially in
    humus soils,

3. concentration during mineralization of fossil remains by
    reaction with aqueous solutions after burial under
    younger sediment.

Zubovic (53) believed that the first two are the dominant pro-
cesses of accumulation and that the last process takes place only
on a very limited scale such as in isolated fragments of carbon-
ized wood and in the tops of some coal beds and therefore the
accumulation of the elements in the organic matrix is essentially
a syngenetic process.

Association with the inorganic fraction could result from
several processes (54):

1. presence of the element in the inorganic detritus
    accumulating together with the peat from which the coal
    formed,

2. sorbtion from circulating waters by this inorganic
    detritus during original peat accumulation,

3. sorbtion from ground water by mineral species during
    diagenesis,

4. precipitation from circulating waters of compounds
    stable under the physico-chemical environment of peat
    formation,

5. precipitation from ground water by reaction with com-
    pounds already present in the formation during diagenesis,
    and

6. introduction of mineral matter into coals at a late
    stage in their formation or even after their formation.

    Zubovic (53, 55) suggested that those elements associ-
ated with organic matter in coal are held as metal-organic com-
plexes and their relative affinities are correlated with those
properties that provide optimum condition for the formation and
stability of such metal-organic complexes. The chemical proper-
ties are:

1. size and charge of the ion,

2. bond configuration and coordination number,

3. tendency toward formation of covalent rather than ionic
    bonds, and

4. tendency to combine with nitrogen rather than with
    oxygen or sulfur of the donor molecule.

Generally, smaller size and higher charge increase the tendency
to form more stable complexes. The stability of such complexes
decreases as their bond configuration changes from octahedral to
planar to tetrahedral. Complexes in which the metal is bonded to
nitrogen as the donor atom are mostly covalent and most stable,
whereas those bonded to oxygen are mostly ionic and less stable.
Sulfur-to-metal bonds form the least stable metal-organic com-
plexes. The principle factors (55, 56) involved in the formation
of metal-organic complexes are:

1. Eh-pH of the coal environment,

2. availability of the metals,

3. availability of organic matter.

The first is important in producing an environment in which in-
organic compounds containing metals such as Zn, Cu and Sn are
more stable than metal-organic complexes. The second and third

factors are important in the partitioning of these elements in
that if the availability of the metals is small and the availa-
bility of organic matter is large, most of the elements would be
disseminated in the organic matter as organic complexes, whereas
few would form finely dispersed inorganic precipitates.

Trace elements in solution entering an area in which or-
ganic matter is being deposited are subjected to retention
according to the principles of coordination chemistry (55). It
can be assumed that a large variety of organic ligands is present
within such an organic environment. This environment would be
conducive to the growth of sulfate-reducing bacteria and conse-
quently reduction to H_2S, which dissociates into HS^- and $S^=$.
There would thus be competition between the organic ligands and
sulfide ions for the available metal ions, particularly the chal-
cophilic elements such as Cu, Pb, Zn, Cd, Sb, Hg and Fe. Parti-
tion of these elements between these two phases would depend on
the concentration of the sulfide ions, and organic ligands and
the relation between the stability constants of the complexes and
solubility products of their sulfides. Elements with small solu-
bility products of their sulfides and low stability constants of
their chelates would be expected to form sulfide species when H_2S
is present. The observation that chalcophilic elements have some
organic association in some coals may be an indication of the
absence of any sulfate-reducing activity at the time the element
was introduced into that particular area of the swamp. However,
elements such as Fe, Cu, Pb, Zn, etc. are most commonly encoun-
tered in coals as sulfides. Those elements having high organic

affinity in coal may be present in the absence of sulfides as chelates which their stability is directly related to the ionic potential of these elements (55). Studies of Fe species in pyro-lyzed coal residues have been made by Mossbauer spectroscopy (15). The presence of several iron species were demonstrated in whole coal and its pyrolyzed residues. Differences in isomer shifts and quadrapole splitting between pure pyrite and pyrite in coal indicate that there may be an interaction between the pyrite and the organic coal matrix (61). The association appears to break down when the coal is heated at low temperatures and any amorphous iron sulfide present in whole coal is converted to pyrite. Several authors (42, 53, 54, 56) have discussed the organic versus inorganic occurrence of trace elements in coals. Nicholls (54) approached this problem by plotting the analytical data for the concentration of a single element in coal or in coal ash against the ash content of the coal. Horton and Aubrey (62) separated three vitrain samples by sink-float techniques into different specific gravity fractions. Gluskoter et al (17), Zubovic (53) and Swaine (56) used the sink-float specific gravity separation technique. Their conclusions are shown in Table 3.3. Elements associated predominantly with the organic matrix are found in the lowest specific gravity fractions and element associated with mineral species are found in the higher specific gravity fractions. Their data provided information on those elements that have a predominantly organic affinity, a predominantly inorganic affinity and those appearing to have varying degrees of organic associa-tion. Studies by Ruch et al (58) based on a physical separation

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TABLE 3.3

ORGANIC-INORGANIC AFFINITIES OF ELEMENTS IN COALS

Elemental Affinity	Zubovic[1]	Gluskoter et al[2]	Swaine[3]
Predominantly Organic	Ge, Be, Ga, Ti, B, V	Ge, Be, B, Sb	B, Ge
Organic + Inorganic	Ni, Cr, Co, Mo, Cu	Co, Ni, Cu, Cr, Se, V, Ti	Hg, Se
Predominantly Inorganic	La, Zn	Zn, Cd, As, Mn, Mo, Hg, Pb, Fe	As, Cd, Zn, F, Zr, Fe, Mn, Mo

[1]Reference 53

[2]Reference 17

[3]Reference 56

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of the organic fractions from the mineral matter of coal, indicated that most of the elements have a partial organic and partial inorganic association. They concluded that some of the inorganic associations, especially for the chalcophilic elements, are due to sulfides while such elements as Ge, Be, B, and Zr result from their introduction into the coal-forming swamp in resistant clastic minerals. Gluskoter et al (17) have used multiple correlation matrix analysis for a large number of coals from a particular coal basin to show that some elements are organically associated and others are associated with specific minerals such as Cd in sphalerite (ZnS). Filby and Brown (63) have used multivariate factor analysis to analyze the trace element data reported by Gluskoter et al (17), on the Illinois Basin coals and have shown that twelve factors can be extracted which account for nearly all of the observed variance in the sample set. Geochemical interpretations of the extracted factors in an oblique solution have been suggested by Filby and Brown (63) and of the twelve factors, ten may be regarded as inorganic factors and are shown in Table 3.4. Comparing Tables 3.3 and 3.4, it is evident that the predominantly inorganic affinity of Zn, Cd, As, Mn, Mo and Fe reported by Gluskoter et al (17) and Swaine (56) is confirmed by the factor analysis data. No significant conclusions concerning either B or Ge were obtained from the factor analysis although neither element appeared to be strongly associated with any of the inorganic factors, hence these elements may well be organically bound as has been concluded by Zubovic (53) and others (17, 56). From these data, probable associations of some

TABLE 3.4

GEOCHEMICAL INTERPRETATION OF FACTORS FROM FACTOR
ANALYSIS OF ILLINOIS BASIN COALS

Factor Number	Associated Elements	Mineral or Process*
1	Ti, Si, Al, K, Mg, V	Silicate minerals; detrital minerals (syngenetic process)
2	As, Pb, Sb, (GE)	Galena, PbS (As, Sb in host PbS)
3	Fe, PYS**, Mo	Pyrite (syngenetic or epigenetic?)
4	SUS**, Be, Ga, Cu, Cr, ORS**	Organic factor?
5	Ca, Mn	Calcite (Ca, Mn) CO_3
6	Zn, Cd	Sphalerite, ZnS
9	Co, Ni	Millerite NiS or cobalt mineral
10	Se, Cr, V	Organic factor?
11	F, P, Mo	Fluorapatite
12	Na, Cl	NaCl--Saline factor

SOURCE: Reference (63)

NOTES: *Probable associated mineral host or geochemical process.
**PYS = pyritic sulfur; ORS = Organic sulfur; SUS = sulfate sulfur.

environmentally important elements in coal can be tentatively
assigned and are shown in Table 3.5.

The emphasis in trace element analysis of coals has been
on analytical meth·ds that are multielement, economical, effi-
cient, quick and reliable in parts-per-million (ppm) and parts-
per-billion (ppb) ranges. A wide variety of analytical tech-
niques have been used, the most important of which are atomic
absorption spectrometry (AAS), flameless AAS, spark-source mass
spectrometry (SSMS), X-ray fluorescence (XRF), optical emission
spectrometry (OES) and neutron activation analysis (NAA) (64, 65,
66, 67, 68). For the destructuve analytical techniques, different
sample digestion and dissolution methods have been used such as
low-temperature ashing at 150° C, high-temperature ashing at
500° C, Teflon acid digestion bomb, oxygen bomb, peroxide bomb or
fusion with borates. The sensitivity and detection limit for the
element of interest is very important in selecting the best
technique for analysis. Dailay and Michalson (68) have compared
the sensitivities and detection limits for many elements by
different techniques.

Coal Conversion Processes

The many processes and techniques of coal conversion have,
as a basic objective, the efficient conversion of coal to environ-
mentally acceptable and chemically useful forms. To accomplish
these objectives, high-sulfur coals must be desulfurized and
high-ash coals must be demineralized to low-sulfur, low-ash,
liquid or gaseous products. Many techniques, in various stages
of development, such as desulfurization, gasification, carbonization

TABLE 3.5

PROBABLE ASSOCIATION OF METALS IN COAL

Element	Possible Association
Ti	TiO_2, $FeTiO_3$ Most probable but organotitanium complexes possible
As	PbS host mineral (FeAsS possible but less likely)
Sb	PbS host mineral-inorganic
Cd	ZnS host mineral-inorganic
Ni, Co	Sulfide: NiS, Millerite or Co Sulfide
Pb	PbS, galena
Hg	Probably inorganic-sulfide
Se	Possibly organic and partly sulfide
Cr	Doubtful

(pyrolysis), demineralization, chemical communition and depoly-
merization (dissolution) (69), are available to produce clean
fuels or synthetic crude oils from coal.

The production of clean liquid fuels from coal is carried
out by four recognized liquefaction methods, shown in Figure 3.1,
namely (1, 22):

1. Direct Catalytic Hydrogenation (hydroliquefaction)

2. Solvent refining (noncatalytic liquid phase-dissolution
   and hydrogenation)

3. Pyrolysis

4. Liquid Hydrocarbon Catalytic Synthesis

Many techniques are available for the desulfurization of
coal (69). Pyritic sulfur may be removed from high sulfur coals
by chemical leaching with ferric chloride solutions. The removal
of organic sulfur from coal requires partial depolymerization of
the coal and hydrogenation to form hydrogen sulfide. In gasifi-
cation processes (1, 69, 70), the initial step in conversion to
gas may be either simple gasification or hydrogasification. It
entails the controlled, partial oxidation of coal to convert it
to a desired product. The essential differences between high-Btu
and low-Btu gas processes are that air is used instead of oxygen
to produce the low gas and that no shift conversion or methanation
steps are required.

Thermal decomposition of coal in the absence of air
(carbonization or pyrolysis) (70) results in the evolution of
gases and liquids. The gases are composed of mixtures of hydro-
gen, carbon monoxide, carbon dioxide, methane and higher hydro-
carbons, and water. Liquid products are condensed to tars which

Figure 3.1. Schematic diagram of four liquefaction processes

represent the products of combination of free radicals formed during the thermal decomposition of the coal.

Dissolution (70) is a more severe method of liquefying coal than is the pyrolysis method but also involves a pyrolysis step. The crushed or ground coal is dissolved in a selective solvent in the presence of hydrogen and the mineral matter is filtered off or the organic material is distilled off. After separation from the solids, the liquids can be further hydrogenated by catalytic upgrading to produce a synthetic crude oil. The solvent comprises a hydrogen donor that reacts with and hydrogenates coal free radicals which result from thermal cleavage of polymeric components in the pyrolysis step (71). Products of the various processes differ from each other. Three types of dissolution processes can be distinguished:

1. those that use no catalyst and no hydrogen, as Consol Synthetic Fuel (CSF);

2. those that use hydrogen but no catalyst, as Solvent Refined Coal (SRC) and Exxon Donor Solvent (EDS); and

3. those that use both catalyst and hydrogen, as Synthoil, H-Coal and Catalytic Coal Liquids (CCL).

In the SRC-I process (72, 73, 74) the desired product is a high pour-point liquid with ash ($<$0.12%) and sulfur content ($<$1%) lower than the feed coal and suitable for use as utility boiler fuel. The process solvent is generated in the process and is recycled. Coal dissolution occurs primarily in the plug-flow preheater and the dissolved coal is upgraded by removal of the organic oxygen and sulfur in the reactor. The solids (mineral matter, etc.) are removed by filtration, centrifugation or or solvent deashing in the SRC-I process. With a longer effective

residence time in the reactor, liquid product SRC-II is formed and the minerals and unreacted coal are separated by vacuum distillation. In processes in which a catalyst is used, e.g. H-Coal and Synthoil (73), the coal is converted to a more hydrocarbon-like liquid that can serve as a synthetic crude or fuel oil.

Another process is the Exxon donor process in which the preheater and reactor are combined into a single flow reactor. The dissolved coal is severely attacked by the action of a solvent with a high hydrogen donor capacity to yield a distillation residue. The solvent in this case must be externally rehydrogenated to restore its high donor capacity (73).

Most of the conversion processes initially involve pyrolysis of the coal since hydrogenation catalysts cannot contact the bulk of the coal matrix. Thermal analysis data (21) indicate that coal undergoes primary decomposition in the 400°-450° C range and in this temperature range the bulk of the swelling of the coal takes place resulting in significant changes in the thermal behavior of coal. In the presence of hydrogen donors solvents, e.g., decalin, tetralin, etc., bituminous coals react very rapidly with up to 80% conversion to material soluble in pyridine in one minute at 45° C. The conversion of coal depends on the type of coal, time and the nature of the solvent. Solvents which consist primarily of hydrocarbons will not dissolve the coal until it is converted into much more hydrocarbon-like species, but solvents high in phenols and polyaromatic species will dissolve the coal in shorter times.

The types of the coal-derived products of liquefaction are classified in terms of solubility classes. These are (73, 75, 76):

1. Hexane soluble materials (oils), have little or no functionality such as hydrocarbons, ethers, thioethers and non-basic nitrogen compounds. The molecular weights average 200 to 300.

2. Benzene soluble materials (asphaltenes), are predominantly mono-functional compounds as phenols or basic nitrogen compounds and ethers. The molecular weights range from 300 to 700.

3. Benzene insoluble materials (asphaltols) have multiple functionality, as polyphenols and multiple basic nitrogens or mixed functionality. The molecular weights range from 400 to >2000.

In order to convert the coal to oils, a sequence of reactions must occur with increasing heteroatom removal at each stage of the sequence. A generalized scheme is outlined below (73):

Coal ⟶ Insoluble solids ⟶ Asphaltols ⟶ Asphaltenes ⟶ Oils

The first product of coal conversion is the benzene insoluble (pyridine soluble) materials. These are subsequently converted to both benzene soluble and hexane soluble species with increasing residence time in the reactor. The asphaltols represent molecules which are high molecular weight, low in both aromatic hydrogen and carbon and high in functionality, in particular phenols. As these initial products of coal are further converted, they increase in aromatic content and lose functionality, becoming more hydrocarbon-like. The ring structures remain relatively intact and therefore the less polar less functional materials isolated from coal liquids can still reflect the structure of the original

-44-

coal (21). Conversion in either short or long contact times causes no change in the content of nitrogen. The hydrogen content is similar to the parent coal for short conversion times, but becomes less at longer times. The oxygen content and sulfur contents both are reduced slightly at short contact times but are significantly reduced with longer contact (17). Oxygen is lost primarily as CO, CO_2 and water. The loss of sulfur is kinetically parallel to that of oxygen. Therefore, it is believed that the origin of the organic sulfur in coal (e.g., -SH, -CS⁻) due to biological activity in the sediment by exchange of OH or carbonyl oxygen by sulfur (21). This fraction of organic sulfur (40 to 50%) is easily removed, while the remaining fraction is much more resistant and is probably present in heterocyclic ring structures. The increase in aromatic carbon content, as the coal is converted, can occur by one of two processes, either hydrogen elimination from hydroaromatic rings or through rearrangement of polycyclic rings to more stable aromatic rings (75).

The solvent-refining process consists mainly of conversion of insoluble coal to pyridine-soluble, toluene-insoluble material (77). The net result is loss of about 20% of the original carbon as gases and volatile liquids, loss of three-quarters of the original oxygen (mostly as water with process hydrogen), an increase in aromaticity, and some bond breakage. The conversion of coal to oil or distillate SRC products requires a large hydrogen input and results in a considerable reduction in average molecular weight and heteroatom contents. The hydrogen is required in part to saturate the fragments left when heteroatoms are removed as H_2O, H_2S and NH_3, but much of the hydrogen may be

required to reduce condensed aromatic systems that cannot be cleaved to partially hydroaromatic systems that can be cleaved especially by reforming catalysts.

The solvent Refined Coal (SRC) processes were developed by the Pittsburg & Midway Coal Mining Co. (P & M) under contract with the U.S. Department of Energy. A pilot plant at Ft. Lewis, Washington is operating to convert 50 tons per day of coal to SRC-I or SRC-II. This pilot plant has undergone extensive testing and production runs have been made for SRC-I (solid product) and SRC-II (liquid product). Schematic diagrams of the SRC-I and SRC-II processes are shown in Figures 3.2 and 3.3.

In the SRC-I process (26, 69), coal is crushed, ground and dried and is then mixed with a hydrogen-donor solvent (a coal-derived solvent recycled in the process) to form a slurry. Hydrogen is introduced and the coal is hydrogenated in a reactor at 454° C and 1500 psig. The actual degree of dissolution of coal depends on the reactivity of the particular coal. In addition to solution of the coal, several other major types of reactions occur. These are:

1. depolymerization of the coal, necessarily accompanied by the hydrogenation of the coal,

2. hydro-cracking of the coal to lower molecular weight hydrocarbons ranging from light oil to methane,

3. removal of some of the organic sulfur by hydrogenation of the sulfur to hydrogen sulfide which is converted to sulfur in the sulfur recovery unit, and

4. conversion of FeS_2 to FeS plus H_2S.

The product stream from the dissolution-hydrogenation step consists of coal solution, unreacted coal (inerts), undissolved
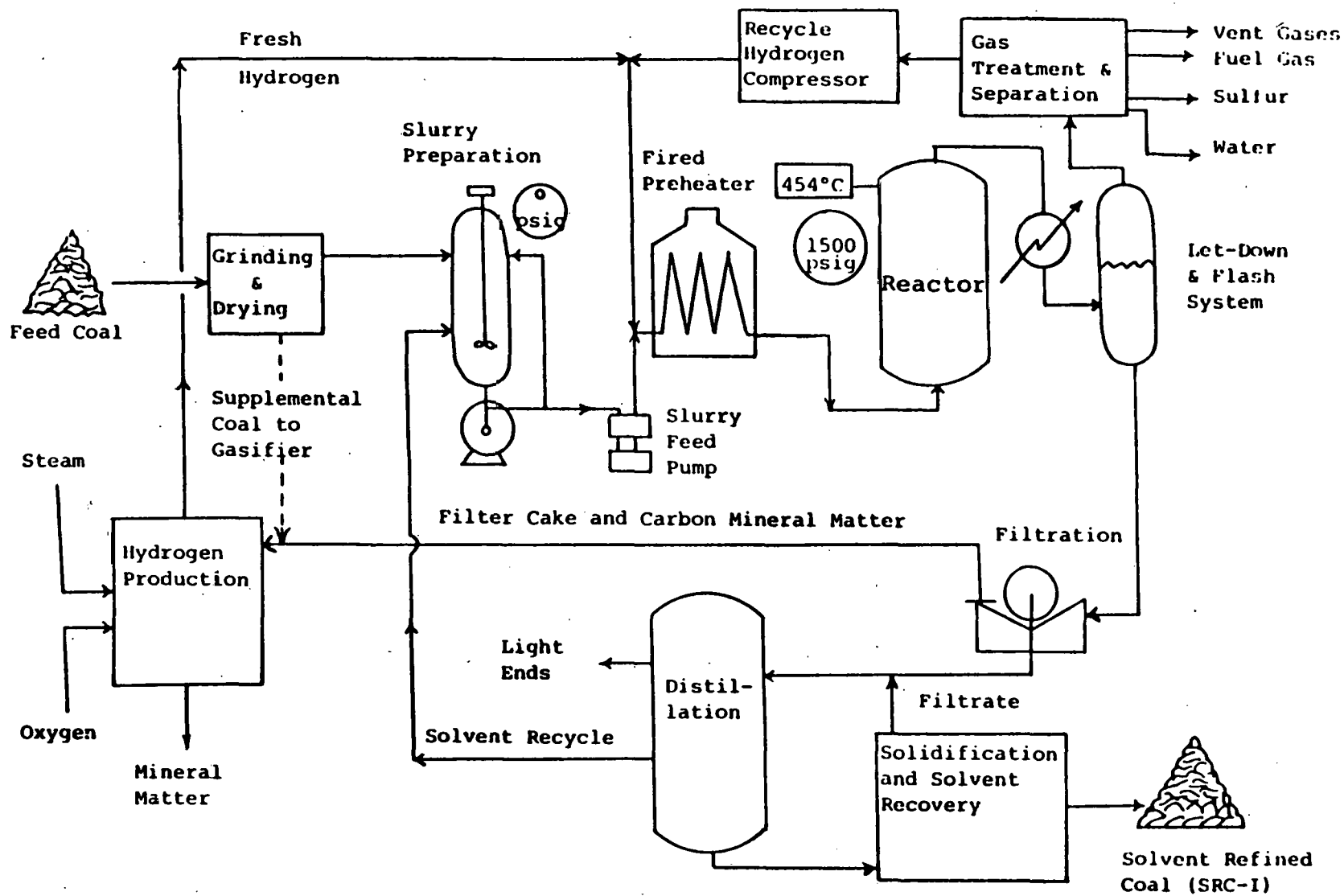
Figure 3.2.   Schematic Diagram of SRC-I Process
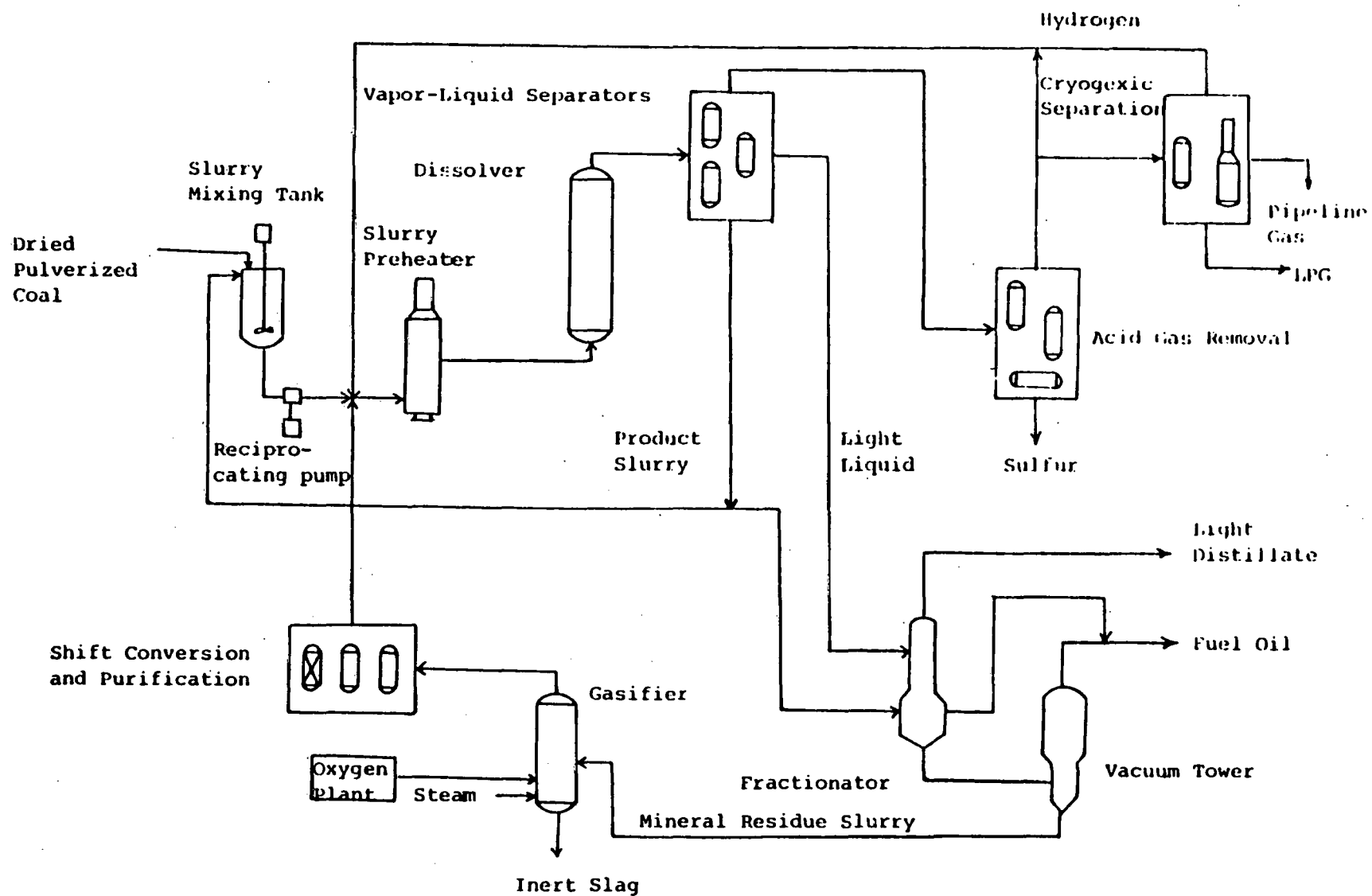
Figure 3.3. Schematic Diagram of SRC-II Process

mineral matter (ash), light hydrocarbon gases (methane-rich) and excess hydrogen. The excess hydrogen and light hydrocarbon gases are separated from the product slurry. A portion of the hydrogen stream is recycled to the dissolution reactor and the remaining hydrogen together with the light hydrocarbon gases are further processed for utilization as plant fuel. The product slurry is pumped to the filtration section where the undissolved coal solids, unreacted coal and mineral matter are separated from the coal solution. The filtrate is sent to a vacuum-flash distillation unit for removal of the solvent for recycle to the reactor. The bottoms fraction from the vacuum-flash tower is a solid SRC-I product.

The process has been modified to produce products that are in liquid form at normal temperatures and pressures, i.e., SRC-II product (78). In this process, coal is ground and slurried with an unfiltered recycle stream, then pumped, heated, and reacted as in the SRC-I process. Higher hydrogen partial pressure and longer effective residence times are utilized. The increased residence time is attained by recycling part of the reacted slurry. The separator bottoms stream is stripped to remove low boiling solvents and a portion from it recycled to slurry the coal feed. The remaining material is charged to vacuum distillation with the distillate being the desired fuel product and vacuum residual material being used as hydrogen feedstock.

In SRC-I and SRC-II processes (16, 26) a significant reduction in sulfur content compared to the original coal is achieved. In the process most of the pyrite, FeS_2 is converted to pyrrhotite, FeS:

$$FeS_2 + H_2 \longrightarrow FeS + H_2S$$
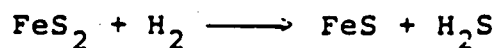
and some of the organically bound sulfur reacts to form H_2S;

$$R-S-R' + 2H_2 \longrightarrow R-H + R'-H + H_2S$$
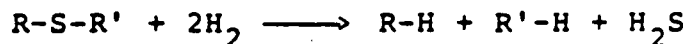
where R and R' represent organic moeities.

Trace Elements in Coal Conversion Processes

Although much research has been done on trace elements in coal, there is much less information about the forms in which such trace elements occur which is necessary to understand trace element behavior and distribution during coal conversion processes. A few preliminary studies of trace element behavior in coal conversion processes have been made. Forney et al (79) have studied the distribution of trace elements around the Synthane gasifier using spark source mass spectroscopy (SSMS). They determined 65 elements but no reliable mass balances for the process could be obtained (Ni 17% recovery and 1103% for Pb). The authors found that the greatest proportion of the elements were retained in the chars. Almost all of the chlorine was found in the water and significant amounts of mercury and selenium were also found in the process water. Keppenaal et al (80) have obtained more reliable mass balances for trace elements in Synthane gasifier process. Shults (81) reported results for 47 trace elements in COED process coal. Schultz et al (82) have made a preliminary study on the distribution of some elements in the one-half ton per day Synthoil pilot plant and trace element material balances ranging from 100% to 124% were obtained, although the authors noted that

the process run was not to be ragarded as typical of the plant
process. There have been no attempts to calculate the trace ele-
ment balances in other conversion processes. The first attempt
to calculate the trace element balances in the SRC processes was
made in this laboratory.

The amounts of trace elements produced daily with assuming
50 tons of coal converted per day in an SRC plant have been cal-
culated and are evaluated by Filby and Khalil (16). Under the
reducing process conditions (high H_2 pressure and temperature),
several elements may be volatile or form inorganic species.
These species depend largely on the nature of the host mineral
and whether this mineral is reactive under the liquefaction/
hydrogenation conditions. Also, there is the possibility of
reaction with the organic matrix to form organometallic compounds,
many of which are volatile and extremely toxic.

Although many mineral species such as SiO_2 should be
inert under the process conditions, other mineral species may
undergo chemical reactions as does pyrite and possibly other sul-
fides. Also, several elements may be volatile or form volatile
inorganic species as $Hg°$, H_2Se, AsH_3, $AsCl_3$, SbH_3, HBr, $Fe(CO)_5$
and $Ni(CO)_4$ among others. Factors governing trace metal distri-
bution are process operating conditions (13). Trace element path-
ways within conversion processes may include adsorption on parti-
culate matter, inclusion in condensates, deposition on equipment
surfaces, inclusion in by-products, inclusion in final products
and emission as fugitive pollutants (13).

There are strong indications that some of the mineral con-
stituents, such as clays and pyrite, of coals may actually be

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beneficial acting as catalysts for the liquefaction process (83). They may increase yields or alter the characteristics of the oil. Sodium ions associated with acid groups have a marked effect on the oil viscosity produced by hydrogenation (83). Pyrite, reduced to pyrrhotite or to metallic iron under the liquefaction conditions, may be an important liquefaction cocatalyst (83). Elements that are deposited on the conversion equipment can be potential hazards and may require removal to prevent interference with normal operations. For example, titanium tends to accumulate on the surface of liquefaction catalysts and deactivate them (84), or it can appear in the product oils (85). Vanadium may react with alkali in the conversion reducing atmosphere to form a vanadate slag that can cause corrosion within the units (57). Corrision from chloride-formed acids may also require treatment.

CHAPTER 4

EXPERIMENTAL TECHNIQUE

Sample Collection in Pilot Plant

In the evaluation of the fate of various elements in the coal liquefaction process, the sample collection step was regarded as critical. The objective was to obtain a representative sample and to avoid contamination of the sample during the sampling procedure. The collected samples should be representative of the important process streams, effluents and products. Also, all samples should be collected when the plant was operating under "steady state" conditions so that products would be representative of input. This condition was difficult to achieve in an operating plant and therefore samples were collected after the plant had operated for at least seven days without shutdown. All samples were collected every four hours for a period of twenty-four hours from each collection point. Final composites of samples were prepared by mixing samples collected during the twenty-four hour collection period for each point. Selective sample collection points were taken in the Pilot Plant as shown in Table 4.1 for the SRC-I and SRC-II processes. These points covered effectively all input, output, and other important process streams.

TABLE 4.1

SAMPLE TYPES FOR SRC-I AND SRC-II PROCESSES

SRC I		SRC II	
Type	Sampling Point	Type	Sampling Point
1. Ground Coal (GC)	Preparation Area	1. Ground Coal (GC)	Preparation Area
2. Pyridine Insolubles (PI)	Filter--Residue	2. Vacuum Bottoms (VB)	Vacuum Flash
3. Wet Filter Cake (WFC)	Filter--Residue		
4. Light Oil (LO)	Distillate	3. Separator 2 Oil (OS2)	Overhead Condensate
5. Recycle Solvent (PRS)	Vacuum Flash Overhead	4. Separator 3 Oil (OS3)	Overhead Condensate
6. Wash Solvent (WS)	Light Distillate	5. Total Solvent (TO) Accumulator Oil	Total Distillate Product
7. Process Water (PW)	Water Hold Tank	6. Process Water (PW)	Plant Water
8. Effluent Water (EW)	Plant Outlet	7. Effluent Water (EW)	Plant Outlet
9. Solvent Refined Coal (SRC)	Product Area		

Sample Preparation in the Pilot Plant

The samples were treated depending on their matrix type, i.e., a) solids, b) organic solvents and oils (liquids) and c) aqueous samples. Each type of sample required different procedures for the sample preparation, storage and shipment. These were:

a) _Solid Samples_, i.e. raw coal, ground coal, pyridine insolubles, wet filter cake, SRC-I and vacuum bottoms. Samples were collected in cleaned glass or polyethylene containers. These containers were soaked in dilute HNO_3 for about four hours and then were washed using double distilled water followed by acetone. This step was important to remove any surface impurity or contamination before collecting the sample.

b) _Liquid samples_, i.e., light oil, recycle solvent, wash solvent, separator oil and total solvent accumulator oil. Samples were collected in cleaned brown glass containers and were tightly capped. Brown containers, which were cleaned as those for solid samples, were selected to prevent any photodecomposition of the organic compounds.

c) _Aqueous samples_, i.e., process water, effluent water and gas-liquid separators water. These samples presented some special preparation problems. The analysis of dilute aqueous solutions is difficult because many elements

    i) are present at very low concentration,

    ii) may adsorb on the walls of the containers (plastic or glass), and

    iii) may adsorb on suspended materials in the solution.

The rate and extent of adsorption either on the container surface or on particulates varies from one element to another and depends on the pH of the solution and the presence of complexing agents. The adsorption is often an irreversible process. Therefore, it was essential to prevent trace element precipitation or adsorption on the container walls and to remove suspended material from the aqueous solution in order to obtain reliable trace element concentration in these samples. Thus water samples were filtered and then frozen immediately after collection (86). Immediately after sampling collection, the sample was filtered through a clean 0.4 μm Nucleopore (General Electric Co.) filter in a hand-pumped Teflon filter assembly. From each sample, four filtered water samples (50 ml each), were collected in separate thin-wall high purity polyethylene bags, tied and quickly frozen. These bags were kept in other thicker wall polyethylene bags to avoid any contamination of the primary container during the preparation process or their storage. Filters and frozen, filtered, samples were stored and shipped in dry ice from the pilot plant to the analytical laboratory at the Nuclear Radiation Center. All samples were kept in the freezer until prepared for neutron activation analysis.

Analytical Methodology

Sample Preparation for Irradiation

One of the most important advantages of the activation analysis technique is that a minimum of sample treatment is required prior to irradiation. Thus, contamination of the sample

and loss of volatile elements are minimized. The samples were packaged for irradiation in suitable vials which contained very low concentrations of the elements of interest to minimize the blank effect. Therefore, high purity polyethylene vials were used.

For each group of samples, different preparations were employed as follows:

a) Solid samples: After mixing, samples (about 75 to 200 mg) were accurately weighed into 2/5 dram polyethylene (Olympic Plastic Co.) vials. These vials were cleaned by soaking in dilute nitric acid for at least four hours and then cleaning with double distilled water followed by acetone. This was required to remove any surface impurities or contaminations from the vials before use. All sample preparation was performed in a clean-air hood (Agnew-Higgins Model 43) to minimize contamination for airborne dust.

b) Liquid samples: Preparation of oils and organic solvents for irradiation was dependent on the irradiation period. Two irradiation times were used in this study. For short irradiations (1 to 10 minutes) samples were taken and weighed carefully in 2/5 dram cleaned (as for solid samples) polyethylene vials. For the longer irradiations, about 2 to 3 g of liquid samples were transferred carefully with disposable syringes (washed with distilled water) to specially prepared open quartz vials. These vials were cleaned by soaking in double-distilled nitric acid for 24 hrs and subsequently washed with double-distilled water and acetone. Each quartz vial was carefully inserted into a

pretreated two-dram snap-top polyethylene vial and heat sealed. Special precautions were taken to prevent any tipping of the vials' contents during handling or irradiation. Also, the 2/5 dram vials were heat sealed and doubly encapsulated in precleaned 2 dram sealed polyethylene vials.

c) <u>Aqueous samples</u>: For the aqueous samples, the very low concentration of many elements required larger sample volumes (e.g., 50 ml) for analysis in order to get reliable results with good sensitivity and precision. As the irradiation positions in the reactor core are of limited size and the reactor neutron flux varies even over small distances, bulk samples could not be irradiated. Therefore, the concentration of aqueous samples by vacuum freeze-drying was adopted. Frozen aqueous samples which were received from the plant in thin polyethylene bags were packaged into new polyethylene bags to avoid any contamination during drying. A Virtis mechanically refrigerated freeze-dryer was used, each sample was freeze-dried and the thin polyethylene bag and its residue contents were transferred into a cleaned 2/5 dram polyethylene vial. The vial was then heat sealed and transferred to a 2 dram vial as described before.

d) <u>Standard samples</u>: Several elemental standards were used depending on the element of interest.

> i) Four mixed aqueous standard of known concentrations one containing Na, K and Br, the second containing Ba and Sr, the third containing Cr, Cs, Co, Fe and Zn, and the fourth containing Se, Sc, Ni and Rb were used. A 300 μl aliquot of each standard was dried on high purity Biosil (BioRad Laboratories) and carefully sealed in 2/5 dram vials. Also, known amounts of individual standard solutions of Cu, As, Ga, La, Au, Sb, U,

Ag, Cu and Tb were dried in Biosil and sealed in polyethylene vials. The concentrations of each element used are shown in Table 4.2.

ii) National Bureau of Standards (NBS) Standard Reference Materials (SRM's) Coal (SRM 1632) and Fly Ash (SRM 1633) were also used as reference standard samples to check the accuracy of the analytical data in this study. Orchard Leaves (NBS SRM 1571) was used as a primary standard for Hg and Mn and as a reference standard for other elements. Bovine Liver (NBS SRM 1577) Tomato Leaves (NBS SRM 1573) and Pine Needles (NBS SRM 1575) were also reference standards for Br, Hg, Cu and other elements.

iii) U.S. Geological Survey Standard Rocks GSP-1, PCC-1, AGV-1 and BCR-1 were also used as primary and/or reference standards. The rock GSP-1 was used as primary standard for Sm, Ce, Hf, Zr, Ta and Th.

iv) Specpure (Matthey) Compounds S, $CaCO_3$ and MgO were used as standards for S, Ca and Mg.

TABLE 4.2

CONCENTRATION OF ELEMENTS IN LIQUID STANDARDS

Element	Amount (µg)	Element	Amount (µg)
Mix-1			
Cr	42.12	Ag	13.28
Cs	37.41	As	24.9
Co	17.70	Au	7.1
Fe	2102.4	Cl	902.4
Zn	1224.0	Cu	21.6
Mix-2		Ga	21.9
Sc	1.869	Eu	1.883
Se	23.37	I	38.11
Ni	2510.1	La	37.52
Rb	241.7	Sb	26.14
Mix-3		Tb	9.86
Ba	1875.9	Ti	738.8
Sr	2398.2	U	27.3
Mix-4		V	30.38
Na	51.98		
K	1208.1		
Br	16.78		

Special care was taken to select each group of elements in the multielement aqueous standards (or solid reference standards) depending on their radionuclide half-lives and gamma-ray energies. All standards were prepared and packaged in cleaned 2/5 dram polyethylene vials and doubly encapsulated in two dram vials as described for solid and aqueous samples.

Irradiation of Samples

Two irradiation periods were used depending on the half-lives of the induced radionuclides measured for elemental analysis. These irradiation times and the elements determined are shown in Table 4.3. Additional information on the nuclear reactions, radionuclides, half-life, thermal cross-section and energy levels of the emitted gamma-rays are listed in Table 4.4 (87). All samples and corresponding standards were irradiated in the Washington State University TRIGA MARK III-fueled research reactor for a total integrated neutron flux of 3.6×10^{15} neutrons cm^{-2} on a rotator assembly for short irradiations, and 2.5×10^{17} neutrons cm^{-2} for long irradiations. In the reactor graphite-reflector irradiation position, the thermal neutron flux changes horizontally and vertically, therefore, samples were mounted on a rotator assembly. The assembly was rotated about a vertical axis during irradiation at the rate of 1 RPM to obtain a uniform horizontal neutron flux distribution. Samples and standards were arranged in tiers. Iron standard solutions dried on Biosil were used for the long irradiations as flux monitor, while Orchard Leaves (NBS) standard was used in the short irradiations.

TABLE 4.3

IRRADIATION PROCEDURES

Irradiation Time	Decay Time	Counting Time	Elements Determined
5-10 minutes	a) 1 minute	180 seconds	Ti, V, Mg, Ca, Al, S
	b) 30 minutes	1,000 seconds	Cl, Mn, I
8 hours	a) 14 hours	4,000 seconds	As, Br, Na, K, Sm, La, Ga, Cu, Au
	b) 21 days	80,000 seconds	Sb, Se, Hg, Ni, Co, Cr, Fe, Rb, Cs, Sc, Tb, Eu, Ce, Sr, Ba, Th, U, Hf, Ta, Zr, Zn and Ag

TABLE 4.4

NUCLEAR DATA ON NUCLIDES MEASURED

Element	Nuclear Reaction and Product	Half Life	$\sigma_{th} f$[1] (barns)	γ-Rays[2] Measured (keV)
Al	$^{27}Al(n,\gamma)^{28}Al$	2.3 m	0.24	1,779
V	$^{51}V(n,\gamma)^{52}V$	3.8 m	4.88	1,434
S	$^{36}S(n,\gamma)^{37}S$	5.07 m	.000014	3,105
Ti	$^{50}Ti(n,\gamma)^{51}Ti$	5.79 m	0.007	320
Ca	$^{48}Ca(n,\gamma)^{49}Ca$	8.8 m	0.002	3084
Mg	$^{26}Mg(n,\gamma)^{27}Mg$	9.5 m	0.0031	1,015
I	$^{127}I(n,\gamma)^{128}I$	25 m	6.40	443
Cl	$^{37}Cl(n,\gamma)^{38}Cl$	37 m	0.105	1,643
Mn	$^{55}Mn(n,\gamma)^{56}Mn$	2.56 h	13.3	847, 1,811
K	$^{41}K(n,\gamma)^{42}K$	12.4 h	0.08	1,525
Cu	$^{63}Cu(n,\gamma)^{64}Cu$	12.8 h	3.10	511
Ga	$^{71}Ga(n,\gamma)^{72}Ga$	14.1 h	2.10	834
Na	$^{23}Na(n,\gamma)^{24}Na$	15.0 h	0.53	1,368
As	$^{75}As(n,\gamma)^{76}As$	26.3 h	5.0	559
Br	$^{81}Br(n,\gamma)^{82}Br$	35.3 h	1.58	777
La	$^{139}La(n,\gamma)^{140}La$	40.2 h	8.90	1,597
Sm	$^{152}Sm(n,\gamma)^{153}Sm$	46.8 h	56.0	103
Au	$^{197}Au(n,\gamma)^{198}Au$	64.7 h	98.8	412
Ba	$^{130}Ba(n,\gamma)^{131}Ba$	12.0 d	0.009	496
U	$^{235}U(n,f)^{140}La$	12.8 d	4.16	1,596
Rb	$^{85}Rb(n,\gamma)^{86}Rb$	18.7 d	0.65	1,079
Th	$^{232}Th(n,\gamma)^{233}Th \rightarrow ^{233}Pa$	27.0 d	7.40	312
Cr	$^{50}Cr(n,\gamma)^{51}Cr$	27.8 d	0.73	320
Ce	$^{140}Ce(n,\gamma)^{141}Ce$	32.5 d	0.53	145
Hf	$^{180}Hf(n,\gamma)^{131}Hf$	42.5 d	3.52	482
Fe	$^{58}Fe(n,\gamma)^{59}Fe$	45.6 d	0.003	1,099
Hg	$^{202}Hg(n,\gamma)^{203}Hg$	46.9 d	1.19	279
Sb	$^{123}Sb(n,\gamma)^{124}Sb$	60.3 d	1.41	1,691
Sr	$^{84}Sr(n,\gamma)^{85}Sr$	64.0 d	0.004	514

Table 4.4 (continued)

Element	Nuclear Reaction and Product	Half Life	$\sigma_{th} f$[1] (barns)	γ-Rays[2] Measured (keV)
Zr	$^{94}Zr(n,\gamma)^{95}Zr$	64.0 d	0.014	757
Ni	$^{58}Ni(n,p)^{58}Co$	71.3 d	–	811
Tb	$^{159}Tb(n,\gamma)^{160}Tb$	72.1 d	46.0	879
Sc	$^{45}Sc(n,\gamma)^{46}Sc$	83.9 d	13.0	689
Ta	$^{181}Ta(n,\gamma)^{182}Ta$	115.0 d	21.0	1,121
Se	$^{74}Se(n,\gamma)^{75}Se$	120 d	0.26	265
Zn	$^{64}Zn(n,\gamma)^{65}Zn$	243 d	0.23	1,116
Ag	$^{109}Ag(n,\gamma)^{110\,m}Ag$	255 d	1.46	658
Cs	$^{133}Cs(n,\gamma)^{134}Cs$	2.05 y	28.0	797
Co	$^{59}Co(n,\gamma)^{60}Co$	5.26 y	37.0	1,333
Eu	$^{151}Eu(n,\gamma)^{152}Eu$	12.7 y	2,820	1,408

[1] $\sigma_{th} f$--product of thermal neutron (n,γ) capture cross section (barns) and isotopic fraction of target nuclide. All reactions involved are (n,γ) reactions except the fast-neutron reaction, $^{58}Ni(n,p)^{58}Co$ used to measure Ni.

[2] Energies in keV taken from Filby et al. (87).

Post-irradiation Treatment

Samples and standards were left after irradiation for a suitable decay period (depending on the half-lives of the radio-nuclides as shown in Tables 4.3 and 4.4) to allow unwanted short-lived nuclides to decay. The polyethylene vials containing standards and solid or freeze dried aqueous samples were washed with water to remove any outer contamination and were transferred to new non-irradiated two dram vials for counting. For short irradiation samples, solid, liquid or aqueous samples and their corresponding standards were transferred immediately to new two dram vials after the entrapped air was flushed out with a syringe to remove the major part of the ^{41}Ar activity. For long irradiations of liquid samples, samples were carefully transferred from the quartz vials to clean glass petri dishes (5 cm diameter). The quartz vials were rinsed with the minimum amount of benzene to transfer any remaining sample to the petri dish. Powdered silica was slowly added on the petri dish containing the irradiated oil or organic solvent and mixed carefully to form a homogeneous gel. The dish was then sealed and stored at 4° C. Standards were also transferred to glass petri dishes to ensure the same counting geometry in a similar manner except water was used in making the silica gel.

Radionuclide Activity Measurements

Ge (Li) gamma-ray spectroscopy was used for all gamma-ray emitting radionuclides activity determinations. The gamma-ray spectrometer consisted of a Ge (Li) detector (Princeton Gamma-Tech;

volume, 60 cm^3), Princeton Gamma-Tech Preamplifier (Model RG-11), Tennelec 203 BLR amplifier, Nuclear Data Model 2200 4096 channel analyzer and a Kennedy 3112 7-track magnetic tape unit. The system resolution was 2.3 keV measured at the ^{60}Co 1332.5 keV line and the peak/Compton ratio was 30:1.

For the determination of Ti, V, Al, Mg, Ca and S, the analyzer was set to record a 0 to 4096 keV gamma-ray spectrum in 2048 channels. Samples and standards were allowed to decay for 2 min and then were counted for 300 seconds on the gamma-ray spectrometer for ^{51}Ti, ^{52}V, ^{28}Al, ^{27}Mg, ^{49}Ca and ^{37}S. The start and end times of each count relative to the time at the end of the irradiation were noted. For the determination of Cl, Mn, and I, the gamma-ray spectrometer was calibrated to record 0-2048 keV in 1 keV/channel. After 30 min decay time, to allow the short-lived nuclides ^{28}Al, ^{27}Mg and ^{49}Ca to decay, samples and standards were counted for at least 1000 seconds for ^{38}Cl, ^{56}Mn and ^{128}I. All spectra were recorded on 7-track magnetic tape.

For long irradiations all samples and standards were trans-ferred to appropriate counting vials or dishes and were counted for approximately 4000 seconds to measure ^{24}Na, ^{42}K, ^{82}Br, ^{153}Sm, ^{64}Cu, ^{76}As, ^{72}Ga, ^{198}Au and ^{140}La radionuclides. After a decay period of not less than 17 days, samples and corresponding stan-dards were counted again for 10,000 to 80,000 seconds to determine ^{141}Ce, ^{75}Se, ^{203}Hg, ^{233}Pa (for Th), ^{51}Cr, ^{181}Hf, ^{131}Ba, ^{85}Sr, ^{134}Cs, ^{58}Co (for Ni), ^{110m}Ag, ^{160}Tb, ^{95}Zr, ^{46}Sc, ^{86}Rb, ^{59}Fe, ^{65}Zn, ^{182}Ta, ^{60}Co, ^{152}Eu, ^{140}La (for U) and ^{124}Sb. The gamma-ray spec-tra were recorded on magnetic tape.

Computation of Analytical Results

In all INAA procedures described above, gamma-ray spectra were transferred from 7-track tape to 9-track IBM magnetic tape and gamma-ray peak areas of all nuclides were computed by the FOURIER spectrum analysis program on the IBM 360-67 computer. The computer programs were previously developed at W.S.U. to identify the radionuclides present from their characteristic gamma-ray energies (88, 89, 90), calculate net gamma-ray peak areas in sample and standard spectra and convert net peak areas to the appropriate elemental wieghts by direct comparison to known standards, thus calculating the concentration of elements in the original samples. The concentrations were calculated from

$$ C = \frac{A_{sa} \ W_{st}}{A_{st} \ W_{sa}} $$

where   C = concentration of element in sample (μg/g)

A_{sa} = peak area/sec of nuclide of interest of sample

A_{st} = peak area/sec of nuclide in standard

W_{st} = weight (μg) of element in standard

W_{sa} = weight (g) of sample

All peak areas (A_{sa} and A_{st}) were corrected for decay to a common point in time. The statistical error associated with radio-activity counting was also calculated by the FOURIER program and the standard deviation of each concentration value calculated. For the very short half-lived radionuclides, such as ^{51}Ti, ^{52}V, ^{28}Al, ^{27}Mg, ^{49}Ca and ^{37}S, decay during counting corrections were applied using Hoffman and Van Camerik method (91).

Accuracy and Precision

National Bureau Standards Reference Materials (SRM's) Coal (SRM 1632) and Coal Fly Ash (SRM 1633) were analyzed with the samples and other standards to evaluate the accuracy and precision of every irradiation run. The analytical concentration values for 28 element in SRM 1632 and SRM 1633 standards are shown in Tables 4.5 and 4.6 respectively. The data shown represent three separate irradiations and the averages of two determinations for each irradiation. The comparison of these average values, the average results from a four laboratory comparison which indicates analyses by Washinton State University (26, 92, 93) and the certified NBS values are also shown in Tables 4.5 and 4.6. It is clear that the results of this study agree very well with the reported and certified values. The results for many elements presented at an Environmental Protection Agency, National Bureau of Standards Conference in Research Triangle Park, N.C., 1973, showed the superiority of activation analysis over other techniques (92, 93, 94). It can be concluded that the INAA method used in this study has satisfactory accuracy and precision. No oil-type NBS standards were available with accurate certified values to be used in this study.

Blank corrections were done for all irradiations. This correction was essential for aqueous samples due to their low elemental concentrations. Blank corrections were applied for vials and polyethylene bags for aqueous samples. A study of the effect of blank values on final analyses was made by using three methods for preparation and counting of coal and fly ash (NBS) standards. These are:

1. samples in 2/5 irradiated vials were transferred to non-irradiated 2 dram vials and counted,

2. samples were transferred after irradiation to a petri dish using water to form a homogeneous gel and counted, and

3. samples were weighed into polyethylene 3 x 4 cm thin wall bags which were transferred after irradiation to non-irradiated 2/5 dram vials and inserted into 2 dram vials for counting.

Tables 4.5 and 4.6 show results obtained from the three methods which indicate no significant difference from different blank values effect. The neutron flux differences between sample and standard due to their different irradiation tiers were corrected by using factors calculated from flux monitors counting. Errors may result if overlapping peak energies are very close and unresolvable, as for 279.1 keV of ^{203}Hg and 279.3 keV of ^{75}Se in mercury determination and for 1115.5 keV of ^{65}Zn and 1120.5 keV of ^{46}Sc for zinc determination. Because there are no other peaks for these mercury and zinc nuclides, appropriate corrections were made for the overlapping peaks by obtaining the interfering peak area from that of another peak of the interfering nuclide (e.g., 264.7 keV of ^{75}Se and 889.3 keV of ^{46}Sc) (89). As presented in the nuclear data table, the 1015 keV ^{27}Mg peak energy was used for magnesium determination because ^{56}Mn 846.7 keV peak overlaps with the highest intensity peak 843.8 keV for magnesium nuclide. Also, the 889.3 keV gamma-ray energy peak was better than 1120.5 keV peak for ^{46}Sc determination due to ^{65}Zn overlapping peak (89). For ^{64}Cu analysis, 511.0 keV/1368.4 keV ^{24}Na peak area correction had been made (88).

TABLE 4.5

ELEMENTAL CONCENTRATIONS IN NBS STANDARD COAL (SRM 1632) AND COMPARISON OF THE AVERAGE
VALUES WITH AVERAGE OF 4-LABORATORY AND NBS VALUES

Element	Coal[1*]	Coal[2*]	Coal[3*]	Average[+]	4-Laboratory Average[**]	NBS Value[**]
As	6.35 + 0.14	6.25 + 0.12	6.55 + 0.15	6.41 ± 0.17	5.5 + 0.4	6.5 + 1.4
Sb	3.91 + 0.10	2.82 + 0.10	4.00 + 0.15	3.72 ± 0.66	3.8 + 1.3	3.9 + 1.3
Se	3.10 + 0.07	2.90 + 0.08	2.85 + 0.12	2.91 ± 0.21	3.4 + 0.2	3.4 + 0.2
Br	19.1 + 0.4	19.5 + 0.3	19.6 + 0.4	19.4 ± 0.23	19.3 + 1.6	19.3 + 1.9
Ni	17.8 + 2.8	12.2 + 2.3	17.2 + 4.3	16.4 ± 3.8	18.0 + 3.0	18.0 + 4.0
Co	5.75 + 0.28	5.64 + 0.38	5.32 + 0.33	5.56 ± 0.25	5.7 + 0.3	5.7 + 0.4
Cr	20.4 + 1.6	17.8 + 1.9	19.2 + 2.0	19.4 ± 1.1	19.8 + 0.8	19.7 + 0.9
Fe (%)	0.88 + 0.01	0.86 + 0.01	0.82 + 0.01	0.85 ± 0.04	0.85 + 0.03	0.84 + 0.04
Na	393 + 3	383 + 3	392 + 3	390 ± 7	414 + 19	414 + 20
Rb	20.9 + 0.9	19.7 + 1.0	21.1 + 1.8	20.8 ± 0.9	21.0 + 2.0	21.0 + 2.0
Cs	1.31 + 0.05	1.50 + 0.03	1.34 + 0.09	1.36 ± 0.11	1.4 + 0.1	1.4 + 0.1
K (%)	0.286 + 0.007	0.286 + 0.005	0.279 + 0.007	0.283 ± 0.004	0.28 + 0.03	0.28 + 0.03
Sc	3.73 + 0.01	3.51 + 0.01	3.49 + 0.01	3.59 ± 0.17	3.8 + 0.2	3.7 + 0.3
Tb	0.22 + 0.01	0.24 + 0.01	0.21 ± 0.02	0.22 ± 0.02	0.23 + 0.05	0.23 + 0.05
Eu	0.33 + 0.06	0.33 + 0.05	0.30 + 0.07	0.32 ± 0.02	0.31 + 0.02	0.33 + 0.04
Sm	1.68 + 0.01	1.48 ± 0.01	1.63 + 0.01	1.60 ± 0.10	1.7 + 0.1	1.7 + 0.2
Ce	20.1 + 0.1	17.9 + 0.1	18.0 + 0.1	18.8 ± 1.3	19.5 + 1.0	19.5 + 1.0
La	10.7 + 0.1	10.2 + 0.2	10.5 + 0.2	10.5 ± 0.2	10.7 + 0.5	10.7 + 1.2
Sr	162 + 8	166 + 8	150 + 13	159 ± 10	156 + 14	161 + 16
Ba	358 + 11	322 + 14	349 + 27	347 ± 27	353 + 25	353 + 30
Th	3.10 + 0.01	3.19 + 0.02	2.90 + 0.04	3.04 ± 0.14	3.2 + 0.2	3.2 + 0.2
U	1.32 + 0.19	0.90 + 0.18	1.49 + 0.41	1.30 ± 0.24	1.41 + 0.07	1.41 + 0.2
Hf	0.98 + 0.02	0.95 + 0.02	0.94 + 0.03	0.96 ± 0.04	0.85 + 0.12	0.96 + 0.05
Ta	0.25 + 0.02	0.25 + 0.02	0.23 + 0.02	0.24 ± 0.03	0.22 + 0.02	0.24 + 0.04

Table 4.5 (continued)

Element	Coal	Coal	Coal	Average[+]	4-Laboratory Average[**]	NBS Values[**]
Ga	5.47 + 0.26	5.24 + 0.41	5.28 + 0.26	5.35 ± 0.20	–	5.4 + 0.3
Zr	33.2 + 5.9	29.1 + 4.9	34.5 + 9.0	32.9 ± 6.2	–	–
Cu	16.9 + 0.5	22.9 + 4.0	15.0 + 0.5	18.3 ± 4.1	–	18.0 + 2.0
Zn	38.2 + 2.7	26.0 + 2.7	34.5 + 2.8	33.0 ± 6.3	30.0 + 10.0	30.0 + 10.0

[1]Counted in 2/5 dram irradiated vials.

[2]Counted in petri dish.

[3]Counted in thin wal polyethylene bags.

*Average of two determinations plus counting statistical error.

**Reference

[+] $\bar{X} \pm S_{\bar{x}}$ where $\bar{X}$ is average of six values.

TABLE 4.6

ELEMENTAL CONCENTRATIONS IN NBS STANDARD FLY ASH (SRM 1633) AND COMPARISON OF THE AVERAGE
VALUES WITH AVERAGE OF 4-LABORATORY AND NBS VALUES

Element	Fly Ash 1*	Fly Ash 2*	Average[+]	4-Laboratory Average**	NBS value**
As	56.2 + 0.3	58.7 + 0.3	57.5 ± 1.6	60.7 + 2.4	58.0 + 4.0
Sb	6.27 + 0.23	7.05 + 0.21	6.66 ± 0.46	6.9 + 0.5	6.9 + 0.6
Se	9.57 + 0.44	10.2 + 0.3	9.89 ± 0.56	10.2 + 1.3	10.2 + 1.4
Br	7.62 + 0.39	8.04 + 0.38	7.83 ± 0.31	12.0 + 4.0	12.0 + 4.0
Ni	120 + 16	119 + 13	120 ± 4	92.0 + 6.0	98.0 + 9.0
Co	36.0 + 0.3	38.4 + 0.2	37.2 ± 1.4	41.8 + 1.3	41.5 + 1.2
Cr	124 + 2	127 + 1	126 ± 2	128 + 5	127 + 6
Fe (%)	6.10 + 0.04	6.26 + 0.06	6.18 ± 0.10	6.25 ± 0.30	6.20 + 0.30
Na	2990 + 8	2940 + 10	2965 ± 31	3200 + 300	3200 + 400
Rb	102 + 5	134 + 6	118 ± 18	125 + 10	125 + 10
Cs	7.69 + 0.12	7.77 + 0.09	7.73 ± 0.10	8.9 + 1.0	8.6 + 1.1
K (%)	1.59 + 0.01	1.63 + 0.01	1.61 ± 0.02	1.72 + 0.03	1.61 + 0.15
Sc	26.3 + 0.1	26.1 + 0.1	26.2 ± 0.3	27.3 + 1.0	27.0 + 1.0
Tb	2.01 + 0.07	1.50 + 0.06	1.75 ± 0.3	1.9 + 0.3	1.9 ± 0.3
Eu	2.44 + 0.05	2.37 + 0.04	2.41 ± 0.08	2.3 + 0.1	2.5 + 0.4
Sm	12.6 + 0.1	12.9 + 0.1	12.8 ± 0.2	12.4 + 0.9	12.4 ± 0.9
Ce	146 + 1	142 + 1	144 ± 3	146 + 10	146 + 15
La	75.5 + 0.4	79.5 + 0.5	77.5 ± 2.4	82.0 + 2.0	82.0 + 2.0
Sr	1360 + 42	1420 + 37	1390 ± 53	1700 + 300	1700 + 300
Ba	2640 + 73	2540 + 70	2590 ± 70	2700 + 200	2700 + 200
Th	23.3 + 0.1	24.3 + 0.1	23.8 ± 0.6	25.4 + 1.5	24.8 + 2.2
U	11.7 + 1.4	10.5 + 1.4	11.1 ± 0.9	12.0 + 0.5	12.0 + 0.5
Hf	8.27 + 0.11	7.58 + 0.09	7.93 ± 0.44	7.0 + 1.1	7.9 + 0.4

Table 4.6 (continued)

Element	Fly Ash 1	Fly Ash 2	Average	4-Laboratory Average	NBS value
Ta	1.81 + 0.09	1.56 + 0.08	1.69 ± 0.15	1.7 + 0.1	1.8 + 0.3
Ga	25.6 + 0.3	29.6 + 0.6	27.5 ± 2.4	--	--
Zr	301 + 30	273 + 32	285 ± 29	301 + 20	301 + 20
Cu	126 + 15	112 + 13	119 ± 11	--	--
Zn	226 + 3	--	226 ± 3	216 + 25	216 + 25

[1]Counted in 2/5 dram irradiated vials.

[2]Counted in petri dish

*Average of two determination plus counting statistical error.

**Reference (26)

$\overline{X} \pm S_{\overline{x}}$ where $\overline{X}$ is average of four values.

During irradiation, the nuclide of interest may be formed by competing nuclear reactions shown by other elements present in the sample. For magnesium determination, $^{26}Mg(n,\gamma)^{27}Mg$ reaction was used while correction was made due to the interfering $^{27}Al(n,p)^{27}Mg$ reaction. Also the interfering reaction $^{235}U(n,f)$ was considered for its fission products (Ce, La, Zr and Ba) to be correct for these element determinations. For uranium determination, ^{140}La fission product (Table 4.4) was used and 21 days decay time was used to allow the activity from the original lanthanium element content to be vanished. Low error was observed for oils analyses due to the losses of volatile species during preparation and irradiation times.

CHAPTER 5

RESULTS AND DISCUSSION

The Solvent Refined Coal Pilot Plant has been operating since 1974 and produces either solid SRC-I or liquid SRC-II products under controlled process conditions. Several sets of samples were taken in material balance runs during development and production of SRC-I and SRC-II in the pilot plant to provide information on the major, minor and trace elements. These sample sets were carefully selected to represent steady-state conditions as closely as possible although it was recognized that true steady-state conditions could not be achieved. Different feed coals, i.e., Illinois No. 6, Kentucky 9/14 and Pittsburg Seam No. 2 coals were used in the liquefaction processes. Major component material balances, process run conditions and product yields have been reported in Pittsburg & Midway Coal Mining Co. monthly progress reports (95). Sample sets from some of these runs were chosen to study the fate and behavior of trace elements in the SRC-I and SRC-II processes.

Trace Elements in the SRC-I Process

Preliminary studies were carried out using neutron activation analysis of materials obtained during scale-up from bench scale to the SRC pilot plant. Data from the first sample set from the SRC-I process (laboratory work-ups and pilot plant streams) have been reported by Filby et al (26, 27). The data

for 22 elements in samples from this set, which did not represent steady state pilot plant operation, indicated that the INAA technique was suitable for trace element analysis and that satisfactory accuracy and precision could be obtained on these very different matrix types.

Trace Elements in Equilibrium Sets

It is important to study the distribution of trace elements in the coal liquefaction process and to calculate the material balance of each element in the process. Three sample sets (designated equilibrium sets) were obtained in different runs after the plant had operated continuously for seven days without shut down to approximate steady-state conditions. Samples were then collected for a 24-hour period every four hours from each collection point and composite samples made for each point. The concentrations of up to 36 major, minor and trace elements in SRC-I process materials were determined by INAA. The complete data for equilibrium set 1 (Illinois coal) are shown in Appendix A. The error terms listed for each elemental determination in Appendix A are those obtained from the gamma-spectrometry counting statistics of the measurement and are standard deviations for a single measurement. The larger errors observed, greater than 20% relative standard deviation, are those associated with measurements close to the detection limit. Less-than values were computed for some elements that were below detection limits but do not represent the actual sensitivities of the method for the element in question but are often the result of high background in the region of the pertinent gamma-ray peak. Because of the

large number of data obtained from the three sets, only those from equilibrium set 1 are reported here; the additional data have been reported by Filby et al (26, 27, 28, 96). The yields of important components for the three pilot plant runs are given in Table 5.1. Summaries of the analytical data for Ti, V, Ca, Mg, Al, Mn, Cl, As, Sb, Se, Hg, Br, Ni, Co, Cr, Fe, Na, Rb, Cs, K, Sc, Tb, Eu, Sm, Ce, La, Sr, Ba, Th, Hf, Ta, Ga, Zr, Zn and Cu for all three sets are shown in Tables 5.2, 5.3 and 5.4. Data were obtained for raw and/or ground coal (GC), solvent refined coal (SRC-I), pyridine insolubles (PI), wet filter cake (WFC), process recycle solvent (PRS), light oil (LO), wash solvent (WS), sulfur (S), process water (PW) and effluent water (EW). The input materials for the process were feed coal and process recycle solvent and the remaining materials represent process streams, products or wastes. The wet filter cake (WFC) is the solid material filtered from the reacted coal solution after hydrogenation. It contains principally mineral matter, insoluble high molecular weight organic material with some unreacted coal and some entrained coal solution. The pyridine insolubles (PI) is the residue from the solid wet filter cake (WFC) after removal of the soluble organic matter with pyridine. Therefore the pyridine insoluble samples represent the insoluble material fraction of the SRC-I process and contain mineral matter, mineral reaction products, a small amount of unreacted coal, and high molecular weight pyridine-insoluble organic matter. Process solvent (PRS), light oil (LO) and wash solvent (WS) are liquids condensed from overhead streams or flashed off the reacted, filtered coal solution.

TABLE 5.1

COMPONENTS AND YIELDS FOR SRC-I PROCESS RUNS

Component	Equilibrium set #1	Yields % MFC* Equilibrium set #2	Equilibrium set #3
H_2	-2.75	-1.92	-2.40
N_2	0.02	0.00	0.00
C_1 hydrocarbons	2.54	1.91	2.20
C_2 hydrocarbons	1.69	0.76	1.10
C_3 hydrocarbons	1.16	0.92	1.00
C_4 hydrocarbons	0.54	0.48	0.40
CO	0.02	0.79	-0.20
CO_2	1.38	1.65	1.90
H_2S	1.65	1.92	1.40
Light oil (60-190°C)	2.53	2.90	5.70
H_2O	5.00	5.00	5.00
Wash solvent (190°-250°C)	7.77	3.11	
Process solvent (250° - 450°C)	-8.90	-6.93	4.60
SRC-I	69.48	71.13	65.00
Ash	11.88	12.31	9.10
Unreacted Coal	6.12	6.00	5.20
TOTAL	100.03	100.02	100.00

SOURCE: Pittsburg & Midway Coal Mining Co. progress reports reference (95).

*MFC=moisture free coal.

The recycle process solvent is recycled back into the system and thus is an input material of variable composition although a steady-state composition is eventually attained. Light oil has a boiling range of 60 to 190° C, wash solvent has a boiling range of 190 to 250° C and process solvent has a boiling range of 250 to 450° C at atmospheric pressure. The mineral residue (MR) comprises material collected on the rotary drum filters after washing with wash solvent (WS). Process water is the water produced as a reaction product from oxygen in the coal during the conversion process plus some quench water used in the process. Effluent water comprises process water, run-off waters, wash waters and cooling waters after flocculation and biological treatment designed to remove soluble organic compounds, sulfur compounds and trace elements. The effluent water is diluted before discharge. Certain samples, e.g., the sulfur fraction derived from H_2S, were not collected for all equilibrium sets due to technical problems in the plant during sampling.

Tables 5.2, 5.3 and 5.4 show that all elements are significantly concentrated in the residues from the SRC-I process (i.e., pyridine insolubles and wet filter cake) compared to the original coal. Also, the concentrations of all trace elements (except Br) in the SRC-I product are lower than that in feed coal (GC) but the degree of depletion is different for each element. For example, the very high concentration of K in the coal (1550 ppm) compared to the low concentration of K in SRC-I (4.72 ppm) is due to efficient removal of inorganic species of K in the SRC-I process. Potassium is a major component in some of the minerals present in coal such as clay minerals and silicate minerals. The data thus

TABLE 5.2

SUMMARY OF TRACE ELEMENT DATA IN SRC-I STREAMS [a]
(EQUILIBRIUM SET 1)

Element (ppm)	GC	SRC	PI	WFC	LO	PRS	WS	S	PW	EW
Ti	530	465	3,350	1,490	2.04	19.1	0.92	<90	<0.2	<0.1
V	30.1	4.63	195	141	0.050	0.445	0.052	8.2	<0.002	0.02
Ca	330	72.8	6,300	3,020	<10	<10	<5	<600	<1	4.4
Mg	1160	89.0	4,000	4,350	<10	<10	<7	<300	<2	1.9
Mg	34.0	20.3	185	140	0.18	2.09	0.2	8.0	0.02	0.01
Al	1.18**	0.02**	7.72**	5.50**	50.0	43.9	11.6	<6	0.54	0.25
Cl	260	160	760	1,640	16.9	127	92.2	<40	32.4	1.7
As	12.5	2.00	85.7	62.1	0.011	0.24	0.011	<2	0.006	<0.001
Sb	0.76	0.06	7.21	5.35	<0.4*	8.2*	<0.4*	<0.1	0.66*	2.0*
Se	2.00	0.12	16.5	11.3	0.052	0.024	0.014	<1.5	0.16	0.0012
Hg	113*	39.6*	508*	346*	18.5*	1.45*	10.5*	<100*	106*	3.2*
Br	4.56	7.74	12.0	20.7	0.015	1.0	0.02	<3	15.6*	31.8*
Ni	14.9	<3.0	142	82.4	<0.03	0.4	<0.03	<28	<0.004	0.013
Co	5.88	0.22	40.7	26.5	<3*	40.7*	1.43*	110	0.2*	0.41*
Cr	13.7	1.64	106	69.2	0.037	3.59	0.041	<2	0.007	0.15
Fe	2.11**	0.03**	16.8**	11.7**	2.90	211	11.2	<0.1	0.30	1.25
Na	137	4.23	1,020	623	0.60	0.50	0.45	3120	0.70	8.3
Rb	<4	<0.5	66.5	37.1	<0.01	0.02	<0.01	<9	0.78*	0.52*
Cs	0.75	0.02	5.08	3.20	1.06*	<1.2*	0.91*	<0.2	0.04*	0.02*

Table 5.2 (continued)

Element (ppm)	GC	SRC	PI	WFC	LO	PRS	WS	S	PW	EW
K	1,550	4.72	11,100	6,660	<0.1	0.25	<0.1	179	0.2	1.26
Sc	2.59	0.57	14.8	9.26	0.15*	32.8*	0.19*	<0.02	0.13*	0.01*
Tb	0.39	0.045	2.06	1.34	<0.13*	3.75*	<0.13*	<0.1	0.01*	0.01*
Eu	0.26	0.055	1.48	0.96	<0.01	<0.01	<0.01	<0.01	0.01*	0.01*
Sm	2.62	0.29	16.9	8.16	<0.01	0.02	<0.01	0.61	0.08*	<0.06*
Ce	20.9	0.45	156	1C2	<0.004	<0.004	<0.003	<2	<0.2*	<0.2*
La	7.55	0.13	59.8	35.2	<0.01	0.01	<0.01	1.80	0.27*	0.5*
Sr	88.6	<6	456	453	<0.6	<0.2	0.74	<45.0	<0.01	<0.04
Ba	53.0	5.75	347	185	<0.1	1.14	<0.07	<39.0	<0.02	<0.04
Th	2.00	0.22	12.8	7.70	<0.001	0.012	<0.001	<0.2	0.05*	<0.01*
Hf	0.51	0.084	3.30	2.20	<0.001	0.003	<0.001	<0.2	0.02*	<0.01*
Ta	0.14	0.046	0.71	0.42	<0.4*	2.53*	<0.3*	<0.2	0.02*	0.01*
Ga	3.56	1.79	19.4	11.3	<0.01	0.06	<0.01	<1.5	<1*	<4*
Zr	62.9	16.0	500	246	0.07	0.71	<0.1	<61.0	0.02	0.04
Cu	19.9	2.07	189	138	0.03	0.68	0.03	<1	<12*	<10*

NOTE: GC = Ground Coal; WFC = Wet Filter Cake; PRS = Process Recycle Solvent; PW = Process Water; PI = Pyridine Insolubles; LO = Light Oil; WS = Wash Solvent; S = Sulfur; EW = Effluent Water.

*Values in ppb.

**Values in percent.

[a]Error terms are not given in order to reduce space, see Appendix A.

TABLE 5.3

SUMMARY OF TRACE ELEMENT DATA IN SRC I STREAMS [a]
(EQUILIBRIUM SET 2)

Element (ppm)	GC	SRC	PI	WFC	LO	PRS	WS	PW	EW
Ti	660	490	4,480	<1,500	2.50	15.0	1.8	<0.3	<0.2
V	29.2	13.7	226	103	0.44	0.80	0.32	<0.001	0.009
Ca	660	123	10,200	10,300	<12	9.7	<6	<10	9.6
Mg	<2,400	96.0	5,290	4,550	10.5	<8	7.2	<17	4.2
Mn	35.7	14.2	219	147	<0.1	1.27	0.16	0.04	0.03
Al	1.58**	0.042**	6.84**	2.84**	74	41.6	56.4	0.40	0.25
Cl	289	99.0	668	147	300	38.9	115	17.0	3.70
As	20.1	2.27	388	3.24	2.58*	243*	68.6*	10.7*	<5*
Sb	1.43	0.06	9.05	6.38	1.86*	9.20*	--	1.0*	0.66*
Se	3.03	0.080	14.1	8.64	0.023	0.036	0.012	914*	0.37*
Hg	114*	46.7*	497*	33.8*	3.40*	<1*	10.2*	20.7*	5.5*
Br	3.72	4.93	10.1	12.3	0.018	0.75	0.048	18.3*	<10*
Ni	12.4	<2	170	142	0.04	0.22	<0.04	14.0*	10.0*
Co	5.20	0.25	32.2	24.4	1.8*	37.6*	1.20*	0.43*	0.36*
Cr	14.8	5.50	200	141	<5*	2.42	0.018	11.3*	10.1*
Fe	2.38**	0.026**	13.7**	9.37**	0.30	57.5	7.0	1.34	0.41
Na	173	6.30	1,040	710	0.04	1.18	0.33	5.10	<10
Rb	11.8	0.21	76.7	54.1	<0.01	<0.02	<0.01	0.77*	1.36*
Cs	0.91	<0.2	4.93	3.34	0.84*	1.53*	1.02*	0.04*	0.06*

Table 5.3 (continued)

Element (ppm)	GC	SRC	PI	WFC	LO	PRS	WS	PW	EW
K	2,030	2.27	11,200	7,600	0.20	<0.5	0.22	0.73	<1
Sc	2.48	0.36	18.5	12.3	0.13*	24.5*	0.10*	0.12*	0.12*
Tb	0.32	0.030	2.41	1.64	<0.1*	1.7*	<0.2*	<0.01*	<0.01*
Eu	0.20	0.027	1.06	0.77	<0.001	<0.001	<0.001	0.012	0.015
Sm	1.65	0.117	10.4	7.47	<0.01*	10.1*	0.15*	<0.1*	<0.1*
Ce	20.8	0.36	131	94.6	<0.005	0.03	<0.004	<0.2*	6.5*
La	6.56	0.09	37.4	25.9	<0.001*	9.30*	<0.001*	<0.7*	<0.01
Sr	158	<4	<74	271	<0.1	<0.2	<0.1	<0.02	<0.01
Ba	62.5	<2	409	390	<0.1	0.18	<0.1	<0.02	<0.01
Th	1.90	0.19	12.6	9.30	<0.001	0.015	<0.001	<0.04*	0.09*
Hf	0.59	0.069	4.32	3.00	<0.001	0.004	<0.001	0.04*	0.02*
Ta	0.17	0.05	1.07	0.81	<0.5*	3.20*	<0.4*	0.02*	<0.2*
Ga	3.26	<1.5	13.1	10.3	<0.1*	34.3*	<0.1*	<0.004	<0.004
Zr	79.0	6.40	422	373	<0.1	0.34	<0.1	0.02	0.02
Cu	14.3	1.15	93.0	93.7	0.02	0.23	0.02	0.24	0.025

NOTE: GC = Ground Coal; WFC = Wet Filter Cake; PRS = Process Recycle Solvent; PW = Process Water; PI = Pyridine Insolubles; LO = Light Oil; WS = Wash Solvent; EW = Effluent Water.

*Values in ppb.

**Values in percent.

[a]Error terms are not given in order to reduce space.

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TABLE 5.4

SUMMARY OF TRACE ELEMENT DATA IN SRC I STREAMS[a]
(EQUILIBRIUM SET 3)

Element (ppm)	GC	SRC	WFC	LO	PRS	WS	PW	EW
Ti	600	311	1,450	<1.3	5.01	<0.9	<0.6	<0.3
V	37.4	7.94	127	<0.01	0.19	<0.01	<0.003	0.038
Ca	1,320	82.0	4,660	<10	<9	<6	<6	11.7
Al	0.90**	80.0	3.62**	0.92	1.30	<0.2	0.70	0.23
Cl	293	113	1,110	6.19	66.8	89.3	<1.02	7.97
Mn	23.6	8.9	84.0	<0.001	1.23	0.11	<0.002	0.042
As	5.70	2.17	11.0	0.010	0.38	0.015	0.66	<4*
Sb	2.00	0.17	5.00	<1	6.80*	<2.0	<1.0*	0.49*
Se	3.00	0.070	7.80	0.023	0.019	0.017	0.021	0.85*
Hg	30.0*	<0.14	107*	7.43*	<0.1*	5.66*	12.1*	0.31*
Br	5.20	6.60	18.1	0.018	0.52	0.011	0.007	0.038
Ni	12.6	1.23	31.3	<0.14	<0.4	<0.2	<0.1	0.039
Co	2.80	0.24	7.80	0.010	0.037	0.015	0.007	0.67*
Cr	12.8	3.68	47.3	0.012	4.51	0.020	0.016	<0.003*
Fe	1.65**	214	4.91**	0.86	107	7.59	0.35	0.17
Na	238	5.63	645	0.78	0.38	0.42	0.11	86.9
Rb	15.0	<0.13	59.8	<0.02	<0.07	--	<0.02	<0.002
Cs	0.87	<0.005	2.40	2.89*	3.71*	5.43*	2.25*	<0.001

Table 5.4 (continued)

Element (ppm)	GC	SRC	WFC	LO	PRS	WS	PW	EW
K	1,830	9.20	6,810	<0.1	<0.1	0.08	0.047	<3.4
Sc	1.90	0.13	4.30	0.063*	5.49*	<0.1*	0.039*	<0.03*
Tb	0.14	0.010	0.32	<0.6*	<2*	<1*	<0.5*	<0.02*
Eu	0.13	0.010	0.56	1.40*	2.00*	2.31*	1.11*	<0.02*
Sm	1.00	0.050	2.80	<0.046*	2.59*	<0.05*	<0.04*	<0.11*
Ce	9.60	0.16	34.2	<7*	<0.01	<9*	<7*	0.34*
La	4.82	0.10	18.0	<0.7	2.87*	<0.7*	<0.3*	<1.5*
Sr	37.0	<1.5	60.0	<0.3	<0.6	<0.5	<0.3	<0.02
Ba	74.0	2.12	102	<0.3	<0.7	<0.6	<0.2	<0.03
Th	1.40	0.060	3.40	<0.7*	5.25*	<1*	<0.7*	<0.04*
Hf	0.48	0.020	1.14	<0.7*	<2*	<1*	<0.6*	<0.04*
Ta	0.15	0.022	0.26	<0.9*	3.36*	<2*	<0.7	0.057*
Ga	3.08	1.26	6.40	6.15*	0.017	<2*	0.49*	<0.02
Zr	64.0	5.10	173	<0.2	--	0.24	<0.14	--
Cu	6.15	--	80.5	0.037	0.28	9.61*	8.93*	<0.01*
Zn	60.3	<1	<33	<0.02	0.50	0.054	<0.02	0.26

NOTE: GC = Ground Coal; WFC = Wet Filter Coal; PRS = Process Recyle Solvent; PW = Process Water; LO = Light Oil; WS = Wash Solvent; EW = Effluent Water.

*Values in ppb.

**Values in percent.

[a]Error terms are not given in order to reduce space.

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indicate that most of the mineral matter is removed from the coal and concentrated in the insoluble residue which accounts for the decreased elemental concentrations in SRC-I compared to coal. Corresponsdingly, the light oils, wash solvent and recycle process solvent values show that the distillate fractions have very low trace element concentrations as would be expected from the mineral-inorganic nature of most of the trace elements.

Comparison of trace element concentrations in SRC-I to the concentrations in corresponding ground coal are presented in Tables 5.2, 5.3 and 5.4 for the three equilibrium sets. Illinois coals were used for all runs. Table 5.5 shows the concentration ratio for each element between SRC-I and ground coal and the percentage reduction of each element in SRC-I with respect to its content in the feed coal. It is clear that most elements in all runs are efficiently removed from coal with 75% or more reduction. Except for Cl, Br and Ti, all elements are significantly depleted (50% or more) in the SRC-I product and many elements show 90% or greater reduction. Some depletion differences for certain elements were observed from one set to another. Chromium shows greater reduction (88%) in equilibrium set 1 while the percentage reduction was lower in the equilibrium sets 2 (63%) and 3 (71%). Vanadium in set 2 and As in set 3 showed lower reduction than in the other two sets. Also, the Ta depletion was higher in set 3 than for sets 1 and 2. Gallium decreased by 81% in set 2 but only 50% and 59% reductions were observed in sets 1 and 3 respectively. The reduction of Cl, Mn and Hg were within the 40-71% range. These differences in behavior are presumably related to

TABLE 5.5
TRACE ELEMENT REDUCTION IN SRC-I RELATIVE TO CCAL

Element	Equilibrium Set #1		Equilibrium Set #2		Equilibrium Set #3	
	SRC/Coal	% Reduction	SRC/Coal	% Reduction	SRC/Coal	% Reduction
Ti	0.88	12	0.79	26	0.52	48
V	0.15	85	0.47	53	0.21	79
Ca	0.12	88	0.19	81	0.06	94
Mg	0.08	92	--	--	--	--
Al	0.02	98	0.03	97	0.01	99
Cl	0.62	38	0.34	66	0.39	61
Mn	0.60	40	0.40	60	0.38	62
As	0.16	84	0.11	89	0.38	62
Sb	0.08	92	0.04	96	0.09	91
Se	0.06	94	0.03	97	0.02	98
Hg	0.35	65	0.41	59	--	--
Br	1.70	+70	1.33	+33	1.27	+27
Ni	--	--	--	--	0.10	90
Co	0.04	96	0.05	95	0.09	91
Cr	0.12	88	0.37	63	0.29	71
Fe	0.01	99	0.01	99	0.01	99
Na	0.03	97	0.04	96	0.02	98
Rb	--	--	0.02	98	--	--
Cs	0.03	97	--	--	--	--
K	0.003	100	0.001	100	0.005	100
Sc	0.22	78	0.15	85	0.07	93
Tb	0.12	88	0.09	91	0.07	93
Eu	0.21	79	0.14	86	0.08	92
Sm	0.11	89	0.07	93	0.05	95
Ce	0.02	98	0.02	98	0.02	98
La	0.02	98	0.01	99	0.02	98
Th	0.11	89	0.10	90	0.04	96
Hf	0.16	84	0.12	88	0.04	96
Ta	0.33	67	0.29	71	0.15	85
Ga	0.50	50	0.19	81	0.41	59
Zr	0.25	75	0.08	92	0.08	92
Ba	0.11	89	--	--	0.03	97
Cu	0.10	90	0.08	92	--	--

the forms in which these elements exist in coal and/or possible mineral transformations during the liquefaction process. There is a wide range of SRC/Coal values as shown in Table 5.5. Values between 0.001 and 0.03 are found for K, Na, Cs and Fe, while Ti, Cl and Hg have values higher than 0.3.

Titanium was the only element that was consistantly depleted less than 50% relative to feed coal for all sets. The high content of Ti in SRC-I has been noted by other authors (97). The anomalously high Ti content of SRC-I and its distinct behavior from other elements is discussed later and a possible explanation proposed. In all equilibrium sets, there are increases in the Br concentration in SRC-I relative to feed coal. The reason for the Br increase may be an unknown source of contamination. The relatively large increases (70, 33, and 27% for sets 1, 2 and 3 respectively) rule out a simple concentration effect due to removal of mineral matter, assuming that all the Br in the original coal is organically bound and remains so in the SRC product. The relatively low concentrations of Br in the process solvents (1.0, 0.75 and 0.52 ppm for sets 1, 2 and 3 respectively) also indicate that make-up solvent is not a source of Br contamination in the process. As discussed later, in the SRC-II process, Br behaved normally and the material balance closed well. A possible explanation is that the filtration step in SRC-I process, which is eliminated in the SRC-II mode, may be the source of contamination. However, the concentration of Br in the filteraid materials used on the rotary filters could not be determined because of the very high Na content in these samples.

Materials Balance for SRC-I Equilibrium Sets

To study the fate of the trace elements in the SRC-I process and their distribution, it is necessary to evaluate the material balance for each element from various important process streams, effluents and products relative to their input. Also, consideration of material balances for the elements reveals whether significant losses occur in the process, either as fugitive emissions to the environment or in process units not sampled. Therefore, element concentrations in all process fractions (Tables 5.2, 5.3 and 5.4) and the weight yields of each fraction calculated as a percentage of the input moisture free coal (MFC) (95) have been used to calculate the material balance for each element in the process. The yields of SRC-I, process solvent (PRS), light oil (LO), wash solvent (WS), recycle process water (RPW) and sulfur (S) in each equilibrium set are shown in Table 5.1. The process solvent yields shown in Table 5.1 are negative because some make-up solvent had to be added during the process. As the process solvent has a variable composition some build-up of trace elements will occur and the process recycle solvent may be a sink for some elements. Thus the elemental contributions of the process recycle solvent to the overall mass balance are difficult to quantify and a yield of 5% moisture free coal has been arbitrarily assigned to this fraction. The uncertainties in overall material balances due to this assigned yield are very small because of the low trace element concentrations in the process recycle solvent. Several filtered residues were collected from the SRC-I process and represent the insoluble fraction of the reacted coal. These are pyridine insoluble and wet filter

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cake (described above) mineral residue (MR) and ash of pyridine insoluble data which are shown in Appendix A. The mineral residue comprises materials collected on the rotary drum filters after washing with wash solvent. The mineral residue, however, still contains some soluble organic material and a significant amount of filteraid used to coat the drums. This is indicated by the high Na contents of the mineral residue compared to the pyridine insoluble (Appendix A). All filteraid materials contain very high Na concentrations (up to 3.2% Na). Thus contamination of the mineral residue with soluble material and filteraid made this material unsuitable for use in the material balance calculations. Therefore, the pyridine insoluble was chosen to represent the residue component in the material balance calculation because a) solvent-soluble material has been removed, in contrast to the wet filter cake, b) no elements have been lost by ashing (very important for Hg, Se and As) compared to the pyridine insolubles ash and c) the pyridine insolubles are not contaminated with filteraid as in the case of the mineral residue because this fraction was obtained by laboratory filtration of the reacted coal solution. The yields of ash (basically mineral matter) and unreacted coal are reported in Table 5.1 but no fractional yields of the pyridine insolubles in any equilibrium set were determined. Schmid (98) indicated that simulated pilot plant studies in the laboratory gave pyridine insoluble yields of 14.9% MFC. The assumption was made in this work that the K content of the pyridine insolubles fraction represents 100% of K content of the input coal. This implies that K is present in

inorganic (or other insoluble) and non-volatile forms. The assumption is reasonable because K is a component of some common coal minerals, e.g., illite, biotite, muscovite and jarosite (Table 2.2) and forms few organo-potassium compounds stable under the process conditions. The K minerals present in the coal and common inorganic K salts are not volatile under the process conditions. Further justification is provided by the K data. The two major products of the process are SRC-I and residue and the K content of SRC-I is very low (4.72 ppm in equilibrium set 1) compared to the input coal (1550 ppm). Thus the pyridine insoluble yields were calculated from the K contents and were found to be 13.9% MFC for equilibrium set 1 and 18.1% MFC for set 2. In case of equilibrium set 3, no pyridine insoluble was obtained and the wet filter cake was used for the material balance in this equilibrium set. Since the feed coal in all sets was Illinois coal, and the K concentrations in pyridine insoluble in equilibrium sets 1 and 2 were almost the same (11,100 ppm in set 1 and 11,200 ppm in set 2). It was assumed that the K content of the pyridine insolubles in set 3 was the same. Therefore the computed pyridine insoluble yield was 16.4% MFC and 26.8% MFC for wet filter cake in equilibrium set 3. The higher percentage yields of the wet filter cake than pyridine insoluble is due to the solvent soluble materials in the wet filter cake fraction. The proportions of each output fraction (total = 1.0 MFC) and the weighted contributions of each element in each fraction are shown in Tables 5.6, 5.7 and 5.8 for all sets. The material balance for each element in percent MFC are given in the last column in these Tables. In

TABLE 5.6

MATERIAL BALANCE FOR TRACE ELEMENTS (EQUILIBRIUM SET 1) IN SRC-I PROCESS

Material	SRC	PI	PRS	LO	WS	Sulfur	RPW	Total	Coal	Mat. Bal.
Fraction (ppm)	0.695	0.139	0.05	0.023	0.05	0.016	0.05	1.02	1.00	(percent)
Ti	323	465	--	--	--	--	--	788	530	149 ± 20
V	3.22	27.1	--	--	0.01	0.13	--	30.5	30.1	101 ± 6
Ca	50.6	876	--	--	--	--	--	927	633	146 ± 65
Mg	61.9	556	--	--	--	--	--	618	1,160	53.3 ± 14
Al (%)	0.014	1.07	--	--	--	--	--	1.08	1.18	92.2 ± 10.4
Cl	111	106	6.35	0.39	4.61	--	1.6	229	260	88.2 ± 5.3
Mn	14.1	25.7	--	--	--	0.13	--	40.1	34.0	118 ± 5
As	1.39	11.9	0.012	--	--	--	--	13.3	12.5	106 ± 5
Sb	0.042	1.00	--	--	--	--	--	1.04	0.76	137 ± 11
Se	0.083	2.30	0.001	0.001	--	--	--	2.38	2.0	119 ± 11
Hg (ppb)	27.5	70.6	0.072	0.43	0.53	--	5.3	104	113	92.5 ± 15.0
Br	5.38	1.66	0.05	--	--	--	--	7.09	4.56	156 ± 9
Ni	--	19.8	0.07	--	--	--	--	19.9	14.9	133 ± 32
Co	0.15	5.65	0.002	--	--	1.76	--	7.56	5.88	129 ± 5
Cr	1.14	14.7	0.18	--	0.002	--	--	16.0	13.7	117 ± 6
Fe (%)	0.021	2.34	0.001	--	--	--	--	2.36	2.11	112 ± 9
Na	2.94	142	0.03	0.01	0.022	50.0	0.04	195	137	142 ± 6
Rb	--	9.24	--	--	--	--	--	9.24	11.8	78.3 ± 10.1
Cs	0.014	0.71	--	--	--	--	--	0.724	0.75	96.0 ± 7.4
K	3.28	1,540	--	--	--	2.8	--	1,546	1,546	100 ± 6
Sc	0.396	2.05	0.002	--	--	--	--	2.45	2.59	94.5 ± 4.1
Tb	0.031	0.286	--	--	--	--	--	0.32	0.39	81.3 ± 5.6
Eu	0.038	0.206	--	--	--	--	--	0.244	0.26	93.9 ± 4.9
Sm	0.202	2.35	--	--	--	0.010	--	2.55	2.62	97.9 ± 4.9
Ce	0.313	21.7	--	--	--	--	--	22.0	20.9	105 ± 5
La	0.090	8.31	--	--	--	0.029	--	8.43	7.55	112 ± 6
Sr	--	63.4	--	--	--	--	--	63.4	88.6	71.6 ± 16.2
Ba	4.00	43.2	0.06	--	--	--	--	52.3	53.0	98.6 ± 24.8
Th	0.153	1.78	--	--	--	--	--	1.93	2.00	96.7 ± 4.7

Table 5.6 (continued)

Material	SRC	PI	PRS	LO	WS	Sulfur	RPW	Total	Coal	Mat. Bal.
Fraction (ppm)	0.695	0.139	0.05	0.023	0.05	0.016	0.05	1.02	1.00	(percent)
Hf	0.058	0.459	--	--	--	--	--	0.517	0.51	101 ± 7
Ta	0.032	0.099	--	--	--	--	--	0.131	0.14	93.6 ± 17.2
Ga	1.24	2.69	0.003	--	--	--	--	3.93	3.56	110 ± 7
Zr	11.1	69.5	--	--	--	--	--	80.6	62.9	128 ± 24
Cu	1.44	26.3	0.34	--	--	--	--	27.8	19.9	140 ± 15

NOTE: Values for each element are contributions for each process fraction weighted for yield (Coal = 1).

-- = indicates insignificant contribution.

TABLE 5.7

MATERIAL BALANCE FOR TRACE ELEMENTS (EQUILIBRIUM SET 2) IN SRC-I PROCESS

Material	SRC	PI	PRS	LO	WS	Sulfur	RPW	Total	Coal	Mat. Bal.
Fraction (ppm)	0.711	0.187	0.05	0.03	0.05	0.016	0.05	1.09	1.00	(percent)
Ti	348	811	1.00	--	--	--	--	1,160	660	176 ± 54
V	9.71	40.8	0.04	0.01	--	--	--	51.6	29.2	177 ± 13
Ca	87.5	1,843	--	--	--	--	--	1,931	658	293 ± 109
Mg	68.3	957	--	--	--	--	--	1,025	1,160	88.4 ± 33.0
Al (%)	0.03	1.24	0.002	--	--	--	--	1.27	1.24	102 ± 19
Cl	70.4	121	1.95	9.00	3.50	--	--	206	250	82.3 ± 6.4
Mn	10.1	39.6	0.064	--	0.005	--	--	49.8	34.8	143 ± 10
As	1.61	70.2	0.012	--	0.002	--	--	71.8	20.1	357 ± 27
Sb	0.043	1.64	0.001	--	--	--	--	1.68	1.43	118 ± 10
Se	0.057	2.55	0.002	0.001	--	--	0.046	2.66	3.03	87.7 ± 8.1
Hg (ppb)	33.2	89.9	+-	--	0.31	--	1.04	124	114	109 ± 19
Br	3.51	1.84	0.04	0.001	0.001	--	--	5.39	3.72	145 ± 13
Ni	--	30.7	0.011	--	--	--	--	30.71	12.4	248 ± 57
Co	0.178	5.82	0.002	--	--	--	--	6.00	5.20	115 ± 9
Cr	3.91	36.2	0.12	--	--	--	--	40.2	14.8	272 ± 20
Fe (%)	0.0185	2.48	--	--	--	--	--	2.50	2.38	105 ± 11
Na	4.48	189	--	--	--	--	0.26	194	173	112 ± 8
Rb	0.149	13.9	--	--	--	--	--	14.0	11.8	119 ± 10
Cs	--	0.89	--	--	--	--	--	0.89	0.91	97.8 ± 8.0
K	1.61	2,020	--	--	--	--	--	2,030	2,030	100 ± 6
Sc	0.256	3.35	0.001	--	--	--	--	3.61	2.48	145 ± 10
Tb	0.021	0.436	--	--	--	--	--	0.457	0.32	143 ± 13
Eu	0.019	0.192	--	--	--	--	--	0.211	0.20	105 ± 8
Sm	0.083	1.88	--	--	--	--	--	1.96	1.65	119 ± 9
Ce	0.24	23.7	--	--	--	--	--	23.9	20.8	115 ± 9
La	0.064	6.78	--	--	--	--	--	6.84	6.56	104 ± 8
Ba	--	74.0	--	--	--	--	--	74.0	62.5	118 ± 15
Th	0.135	2.28	--	--	--	--	--	2.42	1.40	127 ± 9

Table 5.7 (continued)

Material	SRC	PI	PRS	LO	WS	Sulfur	RPW	Total	Coal	Mat. Bal.
Fraction (ppm)	0.711	0.187	0.05	0.03	0.05	0.016	0.05	1.09	1.00	(percent)
Hf	0.049	0.78	|--	--	--	--	--	0.82	0.59	141 ± 11
Ta	0.036	0.194	--	--	--	--	--	0.23	0.17	135 ± 18
Ga	--	2.37	0.002	--	--	--	--	2.37	3.26	12.6 ± 7.0
Zr	4.55	76.4	--	--	--	--	--	81.0	79.0	102 ± 16
Cu	0.818	16.8	0.011	--	--	--	0.012	17.6	14.3	123 ± 22

NOTE: Values for each element are contributions for each process fraction weighted for yield (Coal = 1).

-- = indicates insignificant contribution.

TABLE 5.8

MATERIAL BALANCE FOR TRACE ELEMENTS (EQUILIBRIUM SET 3) IN SRC-I PROCESS

Material	SRC	WFC	LO	RPS	WS	RPW	Total	Coal	Mat. Bal.
Fraction (ppm)	0.65	0.268	0.057	0.05	0.046	0.05	1.12	1.00	(percent)
Ti	202	389	--	0.251	--	--	591	600	98.5 ± 14.5
V	5.16	33.9	--	0.010	--	--	39.1	37.4	104 ± 6
Ca	53.3	1,248	--	--	--	--	1,301	1,320	98.6 ± 25.0
Al	52.0	9,700	0.053	0.065	--	0.035	9,752	9,040	108 ± 6
Cl	73.5	296	0.353	3.34	4.11	--	377	293	129 ± 6
Mn	5.79	22.5	--	0.062	0.005	--	28.4	23.6	120 ± 5
As	1.41	2.95	0.001	0.019	0.001	0.003	4.38	5.70	76.9 ± 3.2
Sb	0.111	1.34	--	--	--	--	1.45	2.00	72.5 ± 3.8
Se	0.046	2.09	0.001	0.001	0.001	0.001	2.14	3.00	71.3 ± 4.2
Hg (ppb)	--	28.7	0.424	--	0.260	0.610	29.9	30.0	99.9 ± 12.6
Br	4.29	4.85	0.001	0.026	0.001	--	9.17	5.20	173 ± 9
Ni	0.80	8.39	--	--	--	--	9.19	12.6	72.9 ± 15.8
Co	0.156	2.09	0.001	0.002	0.001	--	2.25	2.80	81.2 ± 3.7
Cr	2.39	12.7	0.001	0.226	0.001	0.001	15.3	12.8	120 ± 5
Fe (%)	0.014	1.32	--	0.001	--	--	1.34	1.65	80.7 ± 4.1
Na	3.66	173	0.045	0.019	0.019	0.005	177	238	74.2 ± 3.6
Rb	--	16.0	--	--	--	--	16.0	15.0	107 ± 10
Cs	--	0.643	--	--	--	--	0.64	0.87	74.0 ± 4.0
K	5.98	1,825	--	--	0.004	0.003	1,831	1,830	100 ± 5
Sc	0.085	1.15	--	--	--	--	1.24	1.90	65.1 ± 3.0
Tb	0.007	0.086	--	--	--	--	0.092	0.14	65.9 ± 4.6
Eu	0.007	0.150	--	--	--	--	0.157	0.13	121 ± 7
Sm	0.03	0.75	--	--	--	--	0.78	1.00	78.3 ± 3.7
Ce	0.104	9.17	--	--	--	--	9.27	9.60	96.6 ± 4.7
La	0.065	4.82	--	--	--	--	4.89	4.82	101 ± 6
Th	0.039	0.911	--	--	--	--	0.95	1.40	67.9 ± 3.2
Hf	0.013	0.306	--	--	--	--	0.319	0.48	66.4 ± 3.6
Ta	0.014	0.070	--	--	--	--	0.084	0.15	56.1 ± 9.7
Ga	0.82	1.72	--	0.001	--	--	2.54	3.08	82.3 ± 4.5
Zr	3.32	46.4	--	--	0.011	--	49.7	64.0	77.6 ± 8.5

these calculations, the assumption is made that the only contribution to the trace element input is the coal. However, this assumption does not take into account contributions from the process recycle solvent, hydrogen gas (both probably small) or from equipment and construction material corrosion and erosion (possibly important for some elements, e.g., Cr, Ni, Co and V used in high temperature alloys .

The SRC plus pyridine insoluble fractions account for 81% to 89% by weight of the original coal but vary depending on the coal type. The remaining 11% to 19% is comprised of product gases (CO, H_2S, CO_2, CH_4, etc.), water, and light hydrocarbons and derivatives generated during the coal hydrogenation.

A comparison of the material balances for each element calculated from all process fractions in the three equilibrium sets is shown in Table 5.9. The material balances are based on assumption of 100% balance for K in coal. For equilibrium set 1, the values range from 53% (Mg) to 156% (Br). Except for Br (156%) and Mg, all values lie within the range of 81% to 150% with an average of 111 ± 6%. For set 2, the values range from 82% (C̄l) to 357% (As). Except for As (357%), Ca (293%), Cr (272%), Ni (248%), Ti (176%) and V (177%), all balances lie within the range 83% to 145% with an average of 114 ± 6%. For equilibrium set 3, the values range from 56% (Ta) to 351% (Cu). Except for Cu (351%) and Br (173%), all balances lie within the range 65% to 129% with an average of 89 ± 5%. Except for the high values noted, the ranges for the 3 sets may be regarded as excellent given the assumptions made and the errors associated with obtaining representative samples from the process streams in a large operating pilot plant.

TABLE 5.9

MATERIALS BALANCES FOR SRC-I EQUILIBRIUM SETS

Element	Set #1 (%)	Set #2 (%)	Set #3 (%)	Average (%)
Ti	149	176	99	141
V	101	177	104	127
Ca	146	293*	99	123
Mg	53	88	-	71
Al	92	102	108	101
Cl	88	82	129	100
Mn	118	143	120	127
As	106	357*	77	92
Sb	137	118	73	109
Se	119	88	71	93
Hg	93	109	100	100
Br	156	145	173	158
Ni	133	248*	73	103
Co	129	115	81	108
Cr	117	272*	120	119
Fe	112	105	81	99
Na	142	112	74	109
Rb	78	119	107	101
Cs	96	98	74	89
K	100	100	100	100
Sc	95	145	65	102
Tb	81	143	66	97
Eu	94	105	121	107
Sm	98	119	78	98
Ce	105	115	97	106
La	112	104	101	106
Ba	99	118	-	109
Th	97	127	68	97
Hf	101	141	66	103
Ta	94	135	56	95
Ga	110	73	82	88
Zr	128	102	78	103
Cu	140	123	-	132

NOTE: Materials balances as % MFC (moisture free coal).

*Values not considered for the average calculations.

There are a number of explanations for the high values observed for some elements. The high value for As in set 2 is probably due to an anomalous analysis since the other equilibrium sets give good balances for As. If the materials balance for As in set 2 is based on the mineral residue value (81.2 ppm) rather than the apparently anomalous value in the pyridine insolubles, a material balance of 83.6% is obtained. Evidently, the wet filter cake (and derived pyridine insolubles) was not representative for As when the sample was taken. The Sb and Se balances closed well in all sets. The high balances for Ni, Cr, and V in set 2 may be due to corrosion in the construction materials during sampling since problems were encountered in the pilot plant at that time. However the balances are good in the two other equilibrium sets. Bromine in all sets is consistently high which may be due to a source of contamination. These finding are discussed later. For Hg, which may be appreciably volatile as Hg° under the process conditions, the material balances are 93%, 109% and 100% for sets 1, 2 and 3, respectively, indicating that the Hg balance is excellent for all sets within experimental error. However, Hg was observed in the process water (106 ppb) and the light oil (18.5 ppb) fractions indicating some transport of volatile species in overhead streams. This is discussed later. The anomalous value for Cu in set 3 could arise from the erosion of bronze valves in the plant. It can be seen that the alkali metals (Na, K, Cs and Rb), the rare earth elements (La, Ce, Sm, Eu and Tb) and Fe show acceptable material balances for all equilibrium sets in SRC-I process.

Trace Elements in the SRC-II Process

To produce a liquid product in the SRC-II mode, the solvent refining process is modified by using a higher hydrogen partial pressure and by recycling part of reacted coal solution to the reactor to give a longer effective residence time. The filtration procedure is not used in this process but the reacted coal solution, after removal of lighter fractions, is charged to a vacuum distillation system. Total products are naphtha, middle distillate and heavy distillate fractions and vacuum bottoms (VB) residual material. As for the SRC-I process, the trace element behavior in the process was investigated in this study.

Trace Element in Equilibrium Sets

In the trace element distribution study, five material balance sample sets (designated equilibrium sets) were obtained on different dates after the plant had operated for at least seven days on each occasion. Sample materials were collected for 24 hr periods every 4 hours and composited. These materials were: ground coal (GC), vacuum bottom (VB), total solvent accumulator oil (SRC-II or TO), oil from separator No. 2 (OS2), oil from separator No. 3 (OS3), recycle process water (PW) and effluent water (EW), Table 4.1. Although the process produces a number of distillate fractions, for material balance purposes all distillate fractions were collected as total solvent accumulator oil. Individual separator oils were also collected and analyzed. The total solvent accumulator oil (TO) thus represents the SRC-II products and is designated SRC-II in the following text. Elemental concentrations for the SRC-II process materials were

determined by INAA and complete data for equilibrium set SR-15 are shown in Appendix B. The analytical data for the other four equilibrium sets materials were reported by Filby et al (16, 96). The components and yields for all SRC-II runs are given in Table 5.10. Summaries of the analytical data for total accumulator oil, process water, vacuum bottoms and ground coal for the five equilibrium sets are presented in Tables 5.11 to 5.15. The feed coals, Illinois No. 6 and Pittsburg seam No. 2, were used in order to study their reactivities in the SRC-II process. Pittsburg seam coals were less reactive than the Illinois coals (95). Contents of trace elements in these coal samples compared with the average concentrations in Illinois Basin coals reported by Gluskoter et al (17) are given in Table 5.16. Table 5.16 shows that there are large variations in most elemental contents in the coals, even in coals from the Illinois Basin (17). The variations among coals are due to differences in the trace element composition of the original plant materials, the geochemistry of the depositional environment, and epigenetic process occuring after formation of the coal beds (16). No information was available on the forms of the trace elements in the coals used in these SRC-II studies. Feed coal samples were collected every four hours separately and were analyzed separately from the total 24 hr composite sample for 4 of these sets to determine input coal homogeneity. Appendix B shows the analytical data for equilibrium set SR-15. The variation in concentrations of Ti, Ni, Hg, Zr and Cu indicate the heterogeneity of the feed coal during the collection period. The 24 hr composite sample is

TABLE 5.10

COMPONENTS AND YIELDS FOR SRC-II PROCESS RUNS

Component	Yields % MFC*									
	Eq. set SR-11		Eq. set SR-12		Eq. set SR-15		Eq. set SR-17		Eq. set SR-20	
H_2	-3.1		-3.2		-3.6		-5.1		-3.7	
C_1 hydrocarbons	4.0		8.0		5.1		4.8		5.0	
C_2 hydrocarbons	3.3		4.1		3.0		3.4		3.1	
C_3 hydrocarbons	2.5		3.2		2.6		2.7		2.4	
C_4 hydrocarbons	1.2		1.3		1.4		1.1		0.8	
CO	0.2		0.6		0.1		-0.4		-0.3	
CO_2	1.9		1.3		1.0		1.1		1.8	
H_2S	2.8		1.2		1.1		1.6		3.9	
H_2O plus losses	9.8		7.8		5.3		10.5		4.1	
Naphtha (IBP--177°C)	6.9		6.5		3.5		5.9		6.0	
Middle dist. (177°-288°C)	17.4	33.9	15.7	27.3	19.7	34.2	13.6	24.4	18.7	33.7
Heavy Dist. (288°-454°C)	9.6		5.1		11.0		4.9		9.0	
SRC vacuum bottom	27.6		27.6		30.2		33.7		29.7	
Unreacted coal	4.4	43.5	9.7	48.4	7.7	49.8	10.6	55.9	13.9	49.2
Ash	11.5		11.1		11.9		11.6		5.6	
TOTAL	100.0		100.0		100.0		100.0		100.0	

*MFC--moisture free coal.

TABLE 5.11

SUMMARY OF TRACE ELEMENT DATA IN SRC-II STREAMS
(EQUILIBRIUM SET SR-11) [a]

Element (ppm)	GC	VB	TO	OS2	OS3	PW	EW
Ti	655	1,390	2.72	5.45	<0.8	<2	<0.6
V	34.3	76.7	0.040	0.305	<0.01	0.89	0.65
Ca	0.47**	1.08**	<7	<15	<9	11.3	12.6
Mg	1,580	3,480	<15	<27	<13	<11	<5
Al	1.26**	2.77**	9.68	79.0	0.85	<2	<0.2
Cl	194	398	2.21	1.53	0.23	<0.2	<0.02
Mn	37.3	94.0	0.035	0.266	0.003	<0.01	<0.01
As	2.02	4.30	0.013	0.058	0.034	<9*	<6*
Sb	0.42	0.91	0.55*	4.45*	<0.22*	0.92*	0.48*
Se	3.56	7.26	0.15	0.22	0.057	0.021	1.97*
Hg	0.13	0.24	0.027	0.78	4.60*	1.20*	0.66*
Br	3.29	5.40	6.65*	11.1*	8.71*	0.052	0.031
Ni	24.2	36.3	0.030	0.19	<0.02	0.016	0.035
Co	3.72	8.34	2.34*	31.1*	1.45*	0.41*	0.39*
Cr	28.9	69.6	0.082	0.26	0.015	<6*	<4*
Fe	1.54**	3.68**	3.39	120	0.73	0.36	0.36*
Na	684	1,560	0.38	3.00	0.064	104	41.3*
Rb	19.6	63.0	0.01	0.14	<7*	1.51*	<2*
Cs	1.21	2.80	1.76*	8.24*	1.27*	<0.06*	0.07*
K	2,220	4,860	1.49	14.1	0.091	<7	2.81
Sc	2.98	6.66	1.27*	12.3*	0.061*	0.113*	0.092*
Tb	0.22	0.44	0.070*	0.65*	<0.05*	<0.02*	<0.02*
Eu	0.23	0.54	0.18*	1.06*	0.042*	<0.05*	<0.05*
Ca	11.2	27.7	5.34*	0.056	<3*	0.92*	0.75*
Sm	1.04	2.12	0.60*	9.17*	0.019*	<0.29*	<0.22*
La	6.33	13.6	3.03*	0.030	0.27*	<2.9*	<2.8*
Sr	<19	<46	<0.1	<0.2	<0.1	<0.06	<0.01
Ba	96.7	578	0.18	0.54	<0.2	<0.02	28.8*
Th	2.06	4.94	1.11*	10.2*	<0.3*	0.087*	0.066*
U	2.88	6.51	3.20*	4.65*	<1.76*	<0.4*	<0.4*

Table 5.11 (continued)

Element (ppm)	GC	VB	TO	OS2	OS3	PW	EW
Hf	0.57	1.33	0.29*	2.83*	<0.22	<0.04*	<0.03*
Ta	0.16	0.31	0.33*	1.00*	<0.14	<0.04*	<0.03*
Ga	3.44	6.83	4.05*	20.5**	0.14*	<0.04*	<0.02*
Zr	36.2	103	--	0.24	--	<0.01	--
Cu	<0.3	2.19	0.012	0.099	3.03*	<0.01	<3*
Zn	<1.3	<2.5	0.036	0.27	0.018	0.033	0.062

NOTE: GC = ground coal; VB = vacuum bottle; TO = total accumulator oil; OS2 = oil from separator 2; OS3 = oil from separator 3; PW = process water; EW = effluent water.

*Values in ppb.

**Values in percent.

[a]Error terms are not given in order to reduce space, see Appendix A.

TABLE 5.12

SUMMARY OF TRACE ELEMENT DATA IN SRC-II STREAMS
(EQUILIBRIUM SET SR-12)[a]

Element (ppm)	GC	VB	TO	OS2	OS3	PW	EW
Ti	822	1,770	0.8	1.00	<1.1	<1.3	<0.5
V	21.3	39.8	0.021	<6*	<0.5	<0.02	<0.04
Ca	0.58**	1.31**	<7	<7	<10	<4	15.3
Mg	1,930	3,280	<15	<15	<17	<8	2.64
Al	1.38**	2.80**	5.20	5.10	1.80	<1.6	<2.4
Cl	917	2,230	<1.4	<1.5	1.50	141	<6
Mn	37.3	85.5	0.021	0.010	0.023	<0.02	<0.02
As	6.00	15.1	0.023	0.020	0.11	0.029	<6*
Sb	0.30	0.54	0.58*	0.69*	0.48*	1.28*	0.39*
Se	1.35	3.04	0.039	0.054	0.024	0.47	0.76*
Hg	170	94.0	0.023	0.040	0.038	0.096	0.22*
Br	13.3	26.2	7.47*	11.3*	6.90*	0.61	45.6*
Ni	8.62	19.6	<0.02	<0.02	<0.03	0.031	4.23*
Co	2.69	6.24	1.89*	2.15*	2.39*	1.04*	0.55*
Cr	15.1	35.8	0.032	0.016	0.023	0.051	<7*
Fe	1.49**	3.50**	3.4(	3.54	0.97	0.85	0.76
Na	743	1,560	0.13	0.15	0.26	0.38	0.051
Rb	13.8	24.1	2.40*	<6*	<9*	3.48*	1.19*
Cs	0.87	1.90	0.81*	1.08*	1.38*	<0.06*	<0.6*
K	1,580	3,220	0.32	0.36	1.12	0.028	<4
Sc	2.67	5.57	0.29*	0.29*	0.066*	0.33*	0.27*
Tb	0.19	0.45	<0.05*	<0.07*	<0.08*	<0.03*	0.039*
Eu	0.21	0.44	0.055*	0.082*	0.074*	<0.06*	<0.07*
Sm	1.00	2.41	3.28*	0.12*	0.044*	<0.1*	<0.2*
Ce	16.2	27.5	1.14*	<3*	<3*	--	1.29*
La	7.00	14.0	0.98*	1.01*	<0.24*	<0.6	<3*
Sr	<46	343	<0.08	<0.1	<0.1	<0.03	74.3*
Ba	103	233	<0.09	<0.15	<0.24	<0.08	<0.03
Th	1.80	3.75	0.33*	0.39*	<0.35*	0.28*	0.22*
U	0.46	<3	<0.7*	<1.5*	<3*	<1*	<0.6*
Hf	0.65	1.34	0.13*	<0.23*	<0.26*	0.16*	0.055*
Ta	0.15	0.33	0.098*	<0.17*	<0.21*	<0.05*	<0.04*
Ga	2.94	6.30	0.70*	0.43*	0.14*	<1.6*	<24*
Zr	50.3	59.7	--	--	--	--	--
Cu	10.7	<1	8.24*	4.21*	3.55*	15.2*	<6*
Zn	<1	<2	0.016	0.017	0.033	0.036	0.069

NOTE: GC = ground coal; VB = vacuum bottoms; TO = total accumulator oil; OS2 = oil from separator2; OS3 = oil from separator 3; PW = process water; EW = effluent water.

*Values in ppb.

**Values in percent.

[a]Error terms are not given in order to reduce space, see Appendix A.

TABLE 5.13

SUMMARY OF TRACE ELEMENT DATA IN SRC-II STREAMS
(EQUILIBRIUM SET SR-15) [a]

Element (ppm)	GC	VB	TO	OS2	OS3	PW	EW
Ti	822	1,460	<1.4	12.8	1.87	<3	<0.4
V	19.1	37.0	<0.01	0.34	0.005	<0.05	<0.12
Ca	0.68**	1.15**	98	57.0	<9	<8	12.7
Mg	1,430	3,000	<6	22.0	<11	<18	<4
Al	1.31**	2.73**	<0.5	225	0.22	<5	<0.22
Cl	840	1,620	0.538	12.5	4.39	305	<4
Mn	30.2	72.9	0.010	1.13	0.006	<0.03	<0.02
As	9.41	17.5	0.064	0.27	0.16	0.039	<6*
Sb	0.33	1.05	1.85*	10.8*	<0.5*	1.20*	0.33*
Se	1.68	2.92	0.064	0.54	0.045	1.31	0.34*
Hg	0.21	0.11	0.057	4.74	0.014	0.16	0.30*
Br	13.3	27.1	9.18*	0.084	0.013	1.07	0.037
Ni	7.06	38.1	0.034	0.66	0.033	0.062	0.014
Co	2.93	6.26	1.35*	0.078	0.94*	2.00*	0.53*
Cr	16.9	40.8	0.021	0.51	0.011	0.12	<5*
Fe	1.91**	3.69**	2.43	514	0.11*	0.97	0.62
Na	812	1,610	0.095	12.2	0.036	0.36	42.7
Rb	19.6	38.2	<7*	0.46	<8*	<5*	1.31*
Cs	1.38	2.84	0.47*	0.016	<0.3*	0.13*	<0.09*
K	1,680	3,400	0.22	30.8	<0.02	0.037	2.26
Sc	2.62	5.40	0.23*	37.6*	<0.02*	0.39*	0.25*
Tb	0.16	0.30	<0.06*	0.60*	<0.06*	<0.03*	0.020*
Eu	0.21	0.46	0.078*	3.49*	0.14*	0.045*	<0.06*
Sm	3.41	3.94	0.052*	0.042	<0.07*	<0.14*	0.17*
Ce	14.2	29.4	<4*	0.30	<5*	<2*	0.78*
La	6.79	14.3	0.91*	0.11	<0.23*	0.041*	<3*
Sr	149	279	<0.12	1.83	<0.14	<0.03	<0.02
Ba	107	205	0.082	1.95	<0.14	<0.11	0.019
Th	2.05	4.24	<0.4*	0.028	<0.4*	0.25*	0.17*
U	0.88	2.49	<1.5*	8.73*	<1.4*	<1.3*	<0.5*
Hf	0.74	1.44	<0.3*	9.56*	<0.3*	0.076*	0.062*
Ta	0.17	0.35	<0.2*	2.14*	<0.3*	<0.04*	<0.04*
Ga	2.51	6.09	0.31*	31.8*	<0.4*	<2.2*	<22*
Zr	21.1	39.4	ND	0.41	ND	ND	ND
Cu	<6	2.95	5.88	287	3.12	0.018	<4*
Zn	47.9	<2	0.021	1.63	0.027	0.092	0.12

NOTE: GC = ground coal; VB = vacuum bottoms, TO = total accumulator oil; OS2 = oil from separator 2; OS3 = oil for separator 3; PW = process water, EW = effluent water.

*Values in ppb.

**Values in percent.

[a] Error terms are not given in order to reduce space.

TABLE 5.14

SUMMARY OF TRACE ELEMENT DATA IN SRC-II STREAMS
(EQUILIBRIUM SET SR-17)

Element (ppm)	GC	VB	TO	OS2	OS3	PW	EW
Ti	757	1,550	<0.6	4.86	<0.2	<2	<0.5
V	15.3	34.2	0.014	0.15	<0.7	<0.02	<0.6
Ca	0.48**	0.92**	2.32	36.1	<3	<5	10.1
Mg	1,220	2,220	<3	7.81	<2	<4	<5
Al	1.23**	2.43**	5.04	76.3	<0.6	<1	<0.2
Cl	991	1,660	<2	2.92	<1.2	210	4.85
Mn	38.7	62.9	<0.02	0.24	<0.01	<0.02	<0.02
As	8.77	13.8	0.012	0.10	0.11	0.033	<1.9*
Sb	0.33	0.98	0.49*	7.79*	<0.3*	0.38*	0.12*
Se	1.45	3.02	0.081	0.14	0.028	0.68	0.19*
Hg	0.15	0.043	0.012	0.48	6.49*	0.16	0.52*
Br	14.3	24.6	0.013	0.040	8.93*	0.96	7.98*
Ni	9.92	22.0	0.027	0.22	<0.02	0.020	7.64*
Co	2.80	5.74	3.35*	0.027	1.22*	1.24*	0.089*
Cr	16.0	34.1	0.021	0.20	0.012	0.050	<0.9*
Fe	1.68**	3.33**	3.41	119	0.16	1.06	0.083
Na	726	1,370	0.34	5.20	0.037	0.46	6.26
Rb	18.7	35.6	<7*	0.088	<6*	<3.4*	<1.1*
Cs	1.19	2.74	0.71*	6.56*	0.47*	<0.07*	<0.02*
K	1,550	3,110	0.69	0.012	<0.02*	0.092	<0.7*
Sc	2.47	5.19	0.66*	0.015	0.022*	0.30*	0.011*
Tb	0.11	0.38	--	0.80*	<0.04*	<0.04*	<0.01*
Eu	0.20	0.42	0.13*	1.49*	0.062*	0.042*	<0.04*
Sm	1.09	2.22	0.19*	4.30*	<0.04*	<0.15*	<0.08*
Ce	13.7	27.9	<4*	0.073	<3*	<2*	0.38*
La	6.84	13.3	2.18*	0.044	<0.2*	0.15*	<1*
Sr	189	272	<0.1	0.88	<0.1⁻	<0.04	<9*
Ba	106	170	<0.1	0.63	<0.1	0.044	<15*
Th	1.91	4.06	0.503*	0.013	<0.3*	0.26*	<0.02*
U	0.70	1.48	<1*	0.019	<1*	<0.6*	<0.4*
Hf	0.69	1.38	0.17*	3.76*	<0.2*	0.080*	<0.02*
Ta	0.15	0.33	<0.2*	1.10*	<0.2*	0.060*	0.041*
Ga	2.72	6.27	<1*	0.020	<0.3*	1.69*	<5*
Zr	25.4	47.7	ND	0.13	ND	ND	ND
Cu	<0.8	<1.20	8.56*	0.091	2.66*	18.2*	<2*
Zn	<0.9	2	0.032	<0.02	0.020	0.028	0.024

NOTE: GC = ground coal; VB = bacuum bottoms; TO = total accumulator oil; OS2 = oil from separator2; OS3 = oil from separator 3; PW = process water; EW = effluent water. Error terms are not given in order to reduce space.

*Values in ppb.

**Values in percent.

TABLE 5.15

SUMMARY OF TRACE ELEMENT DATA IN SRC-II STREAMS
(EQUILIBRIUM SET SR-20)

Element (ppm)	GC	VB	TO	OS2	OS3	PW	EW
Ti	787	1,540	0.63	<0.4	<0.3	<0.5	<0.4
V	41.3	88.7	0.69	3.06*	2.30*	<0.01	<0.06
Ca	0.61**	1.21**	<2	<2	9.17	<2	13.9
Mg	1,370	3,290	<4	<3	<2	<4	1.73
Al	1.34**	2.97**	5.84	<2	<2	<0.8	<2
Cl	294	550	<3	<3	6.18	69.6	5.28
Mn	64.0	150	0.017	<0.01	<0.02	<0.01	<0.01
As	3.38	6.64	0.035	0.015	0.042	0.018	<4*
Sb	0.32	0.75	0.96*	1.82*	<0.4*	0.55*	0.25*
Se	3.78	8.48	0.12	0.13	0.067	2.25	0.38*
Hg	0.034	<0.1	0.018	0.050	5.61*	0.054	0.062*
Br	2.31	7.16	0.029	0.011	6.50*	0.38	0.027
Ni	17.6	35.5	0.084	<0.03	<0.03	0.025	7.07*
Co	3.84	8.83	5.61*	4.94*	2.89*	1.66*	0.41*
Cr	37.1	86.0	0.22	<4*	9.35*	0.11	<6*
Fe	1.65**	3.51**	9.37	1.02	0.14	0.67	0.053
Na	548	1,250	3.82	0.19	0.029	<1	34.5
Rb	20.4	38.3	<9*	<9*	<8*	<8*	3.22*
Cs	1.21	2.69	1.42*	1.26*	1.25*	0.13*	<0.1*
K	2,130	4,780	1.07	0.11	0.033	<0.6	<2.6
Sc	3.01	6.79	1.45*	0.087*	0.014*	0.16*	0.21*
Tb	0.23	0.44	0.12*	<0.2*	<0.2*	<0.04*	—
Eu	0.24	0.54	0.22*	0.15*	0.12*	0.05*	<0.06*
Sm	2.79	5.51	0.60*	0.046*	<0.07*	<0.07*	<0.14*
Ce	11.6	28.8	1.69*	<3*	<3*	12.8*	1.14*
La	5.75	13.3	3.35*	<0.4*	<0.2*	<0.6*	<2.2*
Sr	<18	<45	<0.2	<0.2	<0.2	<0.03	<0.01
Ba	118	637	<0.2	<0.1	<0.1	<0.1	<0.04
Th	2.00	4.89	1.41*	<0.4*	<0.4*	0.17*	0.18*
U	3.36	7.18	<1.4*	<1.2*	<1.1*	<1.5*	<0.5*
Hf	0.59	1.43	0.37*	<0.3*	<0.3*	<0.08*	0.064
Ta	0.13	0.32	0.19*	<0.3*	<0.3*	<0.04*	0.071*
Ga	2.91	6.68	3.18*	<0.5*	<0.3	0.90	<17*
Zr	47.8	113	ND	ND	ND	ND	<13
Cu	1.89	12.9	0.051	3.44*	1.72*	14.6*	<4*
Zn	<1.4	504	0.10	0.037	0.033	0.031	0.076

NOTE: GC = ground coal; VB = vacuum bottoms; TO = total accumulator oil; OS2 = oil from separator 2; OS3 = oil from separator 3; PW = process water; EW = effluent water; ND = not detected. Error terms are not given in order to reduce space.

*Values in ppb.

**Values in percent.

TABLE 5.16

CONTENTS OF 20 TRACE ELEMENTS IN THREE COALS USED IN LIQUEFACTION (SRC-II)
COMPARED WITH AVERAGE OF ILLINOIS BASIN COALS

Element (μg/g)	Kentucky[*] Coal	Pittsburg[1] Seam Coal	Illinois[2] Coal	Illinois Basin[**] Average	Illinois Basin Coals[**] Standard Deviation
Ti	480	822	655	600	200
V	108	21.3	34.3	32.0	13.0
Ca	2,660	5,760	4,700	6,700	4,800
Mg	1,070	1,930	1,580	500	200
Al	10,000	13,800	12,600	12,000	3,900
Fe	13,800	14.900	15,400	20,000	6,300
Na	208	743	684	500	400
K	1,870	1,580	2,220	1,700	700
As	6.70	6.00	2.02	14.0	20.0
Sb	2.24	0.30	0.42	1.30	1.40
Se	3.00	1.35	3.56	2.20	1.00
Hg	0.237	0.170	0.13	0.20	0.19
Co	2.95	2.69	3.72	7.30	5.30
Ni	8.20	8.62	24.2	21.0	10.0
Cr	14.6	15.1	38.9	18.0	9.70
Cu	6.70	10.7	-	14.0	6.60
Sc	2.19	2.67	2.98	2.70	1.10
La	5.30	7.00	6.33	6.80	2.80
Rb	34.5	13.8	19.6	19.0	9.90
Cs	0.85	0.87	1.21	1.40	0.73

[*]From reference 99. [**]From reference 17 [1]Equilibrium not on 13 [2]

therefore a better representative sample for the trace element input than individual coal samples.

From Tables 5.11 to 5.15, it can be seen that all trace elements are concentrated in the vacuum bottoms residual material while much lower concentrations are observed in the total accumulator oil and process water. Table 5.17 shows the concentration ratios between the total accumulator oil (SRC-II) and ground coal, (Oil/Coal) and the percentage reduction for each trace element in the SRC-II compared to the feed coal. All elements, except Hg, Se and Cl, are almost completely depleted in SRC-II relative to coal (greater than 99%) in all equilibrium sets. The depletion of Br in SRC-II relative to coal is similar to that of other elements. The elements Sb, As, V and Ti are very highly depleted (>99%) in SRC-II accumulator oil. The concentration of Se is reduced by 97% while Hg reduction is not greater than 93%. The average reduction of Hg when Pittsburg coal was used is 84 ± 10%. The reasons for the different behavior of Hg and Se compared to the other elements in SRC-II are discussed later.

Materials Balance for SRC-II
Equilibrium Sets

From the equilibrium run conditions and yields (Table 5.10), it can be seen that the vacuum bottoms yields range from 43.5% (SR-11) to 55.9% (SR-17) of the moisture free coal (MFC). The SRC-II (total distillate) yields range from 24.4% (SR-17) to 33.9% MFC (SR-11) while process water yields range from 4.1% (SR-20) to 10.5% MFC (SR-17). The average yields of the SRC-II total distillate oil is 33.8% MFC for Illinois coal and 28.5% MFC

TABLE 5.17

TRACE ELEMENT REDUCTION IN SRC-II RELATIVE TO COAL

Element	Equilibrium Set SR-11		Equilibrium Set SR-12		Equilibrium Set SR-15	
	Oil/Coal $\times 10^2$	% Reduction	Oil/Coal $\times 10^2$	% Reduction	Oil/Coal $\times 10^2$	%Reduction
Ti	0.42	99.6	--	--	--	--
V	0.12	99.9	0.1	99.9	--	--
Ca	--	--	--	--	1.40	98.6
Al	0.08	100	0.04	100	--	--
Cl	1.10	98.9	--	--	0.06	100
Mn	0.09	99.9	0.06	100	0.03	100
As	0.64	99.4	0.38	99.6	0.68	99.3
Sb	0.13	99.9	0.19	99.8	0.57	99.4
Se	3.10	96.9	2.90	97.1	3.80	96.2
Hg	21.2	78.8	13.5	86.5	27.2	72.8
Br	0.2	99.8	0.06	100	0.07	99.9
Ni	0.13	99.9	--	--	0.48	99.5
Co	0.06	99.9	0.07	100	0.05	100
Cr	0.28	99.7	0.21	99.8	0.12	99.9
Fe	0.02	100	0.02	100	0.01	100
Na	0.06	99.9	0.02	100	0.01	100
Rb	0.05	99.9	0.02	100	--	--
Cs	0.15	99.8	0.09	99.9	0.03	100
K	0.07	99.9	0.02	100	0.01	100
Sc	0.04	100	0.01	100	0.01	100
Tb	0.03	100	--	--	--	--
Eu	0.08	99.9	0.03	100	0.04	100
Sm	0.06	99.9	0.33	99.7	0.01	100
Ce	0.05	100	0.01	100	--	--
La	0.05	100	0.01	100	0.10	100
Th	0.05	100	0.02	100	--	--
Hf	0.05	100	0.02	100	--	--
Ta	0.21	99.8	0.07	99.9	--	--
Ga	0.12	99.9	0.02	100	0.01	100

for the Pittsburg seam coal. At the same time, the light hydro-carbons (C_1-C_4), CO, CO_2 and H_2S account for 13% MFC of Illinois coal and range from 21% to 28% MFC for Pittsburg coal. In Table 5.10 separate yields for ash, unreacted coal and SRC vacuum bottom fractions are reported but the vacuum bottoms fraction analyzed comprises these three individual fractions, hence the vacuum bottoms yields were obtained by adding the three individual yields in Table 5.10.

From the elemental concentrations in each process fraction (Tables 5.11 to 5.15) and the percentage yields (as MFC) for each fraction (Table 5.10), the elemental material balances for each element in the total accumulator oil, process water and vacuum bottoms relative to feed coal (coal = 100%) and material balances normalized to K = 100% are given in the last two columns of Tables 5.18 to 5.22. The K-normalized percentages were calculated by assuming the K found in vacuum bottoms represents all the K in the feed coal. This assumption is valid since less than 0.1% MFC of K content were observed in the total accumulator distillate oils (TO) as shown in Table 5.17. In these calculations, the elemental contributions from sulfur and gases were not taken into consideration because they were assumed small compared to the very large contributions of all elements in vacuum bottoms, although this may not be true for Hg (see later). In the SRC-II equilibrium sets, sulfur and gas samples were not collected. Different volumes of gases from the recycel condensate separator passed through standard charcoal filters were collected after this work was completed and preliminary analyses show very small or background levels for all elements except Hg (99).

TABLE 5.18

MATERIALS BALANCE FOR SRC-II PROCESS (SR-11)**

Material	TO	PW	VB	Total	Coal*	Material Balance	
Fraction	0.339	0.098	0.435	0.872	1.00	Total % MFC	Normalized % MFC***
Ti	0.92	-	604	605	655	92.4 + 11.6	97.0 + 13.2
V	0.014	0.087	33.4	33.5	34.3	97.6 + 6.7	102 + 9
Ca	-	1.11	4,700	4,701	4,730	99.4 + 10.4	104 + 12
Mg	-	-	1,514	1,514	1,580	95.8 + 21.7	101 + 23
Al (%)	-	-	1.21	1.21	1.26	95.4 + 5.1	100 + 8
Cl	0.75	-	173	174	194	89.6 + 8.1	94.0 + 9.8
Mn	0.012	-	40.9	40.9	37.3	110 + 6	115 + 8
As	0.004	-	1.87	1.87	2.02	92.8 + 9.4	97.4 + 11.1
Sb	-	-	0.40	0.40	0.42	94.2 + 8.4	98.9 + 10.3
Se	0.039	0.002	3.16	3.20	3.56	89.9 + 4.9	98.3 + 7.1
Hg (ppb)	9.25	0.12	103	112	129	87.2 + 5.2	91.5 + 7.3
Br	0.002	0.005	2.35	2.36	3.29	71.6 + 9.7	75.1 + 10.9
Ni	0.010	0.002	15.7	15.7	24.2	65.1 + 9.2	68.3 + 10.3
Co	-	-	3.63	3.63	3.72	97.5 + 5.0	102 + 8
Cr	0.03	-	30.3	30.3	28.9	105 + 5	110 + 8
Fe (%)	-	-	1.60	1.60	1.54	104 + 5	109 + 8
Na	0.13	10.2	678	688	684	101 + 5	106 + 8
Rb	-	-	27.4	27.4	19.6	140 + 15	147 + 17
Cs	-	-	1.22	1.22	1.21	101 + 5	106 + 8
K	0.51	-	2,113	2,113	2,218	95.3 + 5.1	100 + 7
Sc	-	-	2.90	2.90	2.98	97.2 + 4.9	102 + 8
Tb	-	-	0.191	0.191	0.219	87.0 + 6.1	91.3 + 8.0
Eu	-	-	0.233	0.233	0.234	99.7 + 17.4	105 + 19
Ce	-	-	12.1	12.1	11.2	104 + 5	109 + 8
Sm	-	-	0.92	0.92	1.04	88.7 + 4.6	93.1 + 6.9
La	-	-	5.92	5.92	6.33	93.5 + 5.2	98.1 + 7.6
Th	-	-	2.15	2.15	2.06	104 + 5	109 + 8
Hf	-	-	0.58	0.58	0.57	102 + 6	107 + 8

Table 5.18 (continued)

Material	TO	PW	VB	Total	Coal	Material Balance	
Fraction	0.339	0.098	0.435	0.872	1.00	Total % MFC	Normalized % MFC
Ta	-	-	0.136	0.136	0.155	87.9 + 9.3	92.3 + 10.9
Ga	0.001	-	2.97	2.97	3.44	86.4 + 6.0	90.7 + 7.9
Zr	-	-	44.8	44.8	36.2	124 + 21	130 + 23
U	0.001	-	2.83	2.83	2.88	98.4 + 17.3	103 + 19

NOTES: TO=total accumulator oil; PW=process water; VB=vacuum bottom; MFC=moisture free coal.

*Illinois coal.

**Concentration values in ppm

***Normalized to K = 100%.

TABLE 5.19

MATERIALS BALANCE FOR SRC-II PROCESS (SR-12)**

Material	TO	PW	VB	Total	Coal*	Material Balance	
Fraction	0.273	0.078	0.484	0.835	1.00	Total % MFC	Normalized % MFC
Ti	-	-	855	855	822	104 + 13	106 + 14
V	0.006	-	19.3	19.3	21.3	90.5 + 9.2	91.8 + 10.5
Ca	-	-	6,314	6,314	5,760	110 + 10	111 + 12
Mg	-	-	1,588	1,588	1,930	82.2 + 15	83.5 + 16
Al (%)	-	-	1.35	1.35	1.38	98.3 + 5.7	99.9 + 7.8
Cl	-	11.0	1,077	1,088	917	119 + 8	121 + 11
Mn	0.006	-	41.4	41.4	37.3	111 + 6	113 + 8
As	0.006	0.002	7.30	7.31	6.00	122 + 7	124 + 10
Sb	-	-	0.26	0.26	0.30	86.5 + 8.9	87.9 + 10.1
Se	0.011	0.037	1.47	1.52	1.35	112 + 7	115 + 9
Hg (ppb)	6.25	7.51	45.5	59.3	170	34.9 + 1.8	35.4 + 2.6
Br	0.002	0.047	12.7	12.7	13.1	97.1 + 5.9	98.8 + 8.0
Ni	-	0.002	9.49	9.49	8.62	110 + 30	112 + 31
Co	0.001	-	3.02	3.02	2.69	112 + 6	114 + 8
Cr	0.009	0.004	17.3	17.3	15.1	115 + 6	117 + 9
Fe (%)	-	-	1.70	1.70	1.49	114 + 6	116 + 9
Na	0.036	0.030	755	755	743	102 + 5	103 + 8
Rb	-	-	11.7	11.7	13.8	84.5 + 11.2	85.8 + 12.2
Cs	-	-	0.92	0.92	0.87	105 + 6	108 + 8
K	0.086	0.002	1,556	1,556	1,580	98.5 + 5.2	100 + 7
Sc	-	-	2.70	2.70	2.67	101 + 5	103 + 7
Tb	-	-	0.216	0.216	0.185	117 + 8	119 + 10
Eu	-	-	0.214	0.214	0.210	102 + 18	104 + 20
Sm	-	-	1.17	1.17	1.00	117 + 6	119 + 9
Ce	-	-	13.3	13.3	16.2	82.2 + 4.1	83.4 + 6.1
La	-	-	6.78	6.78	7.00	96.8 + 5.3	98.3 + 7.5
Th	-	-	1.82	1.82	1.80	101 + 5	102 + 8
Hf	-	-	0.65	0.65	0.65	100 + 6	101 + 8

Table 5.19 (continued)

Material	TO	PW	VB	Total	Coal	Material Balance	
Fraction	0.273	0.078	0.484	0.035	1.00	Total % MFC	Normalized % MFC
Ta	-	-	0.16	0.16	0.15	107 + 10	108 + 12
Ga	-	-	3.05	3.05	2.94	104 + 7	105 + 9
Zr	-	-	28.9	28.9	50.3	57.4 + 13.1	58.4 + 13.6
Ba	-	-	113	113	103	109 + 26	111 + 27

NOTES: TO-total a-cumulator oil; PW-process water; VB-vacuum bottom; MFC=moisture free coal.

*Pittsburg Coal.

**Concentration values in ppm

***Normalized to K = 100%.

TABLE 5.20

MATERIAL BALANCE FOR SRC-II PROCESS (SR-15)**

Material	TO	PW	VB	Total Coal*		Material Balance	
Fraction	0.342	0.053	0.498	0.893	1.00	Total % MFC	Normalized % MFC***
Ti	-	-	728	728	822	88.6 + 10.3	87.9 + 11.3
V	-	-	18.4	18.4	19.1	96.5 + 8.7	95.7 + 10.1
Ca	33.5		5,725	5,759	6,820	84.5 + 7.1	84.0 + 8.0
Mg	-	-	1,493	1,493	1,430	104 + 16	103 + 17
Al (%)	-	-	1.36	1.36	1.31	104 + 6	103 + 8
Cl	0.18	16.2	805	822	840	97.8 + 5.7	97.1 + 7.7
Mn	0.003	-	36.3	36.3	30.2	120 + 7	119 + 9
As	0.022	0.002	8.72	8.74	9.41	92.9 + 4.9	92.2 + 7
Sb	-	-	0.52	0.52	0.33	158 + 14	156 + 16
Se	0.022	0.070	1.45	1.54	1.68	92.0 + 5.6	91.3 + 7.4
Hg (ppb)	19.4	8.32	54.3	82.0	206	39.8 + 2.2	39.5 + 3.1
Br	0.003	0.057	13.5	13.6	13.3	102 + 6.9	101 + 9
Ni	0.012	0.003	19.0	19.0	7.06	269 + 63	267 + 64
Co	-	-	3.12	3.12	2.93	106 + 8	105 + 10
Cr	0.007	0.006	20.3	20.3	16.9	120 + 12	119 + 14
Fe (%)	-	-	1.84	1.84	1.91	96.2 + 5.0	95.4 + 7.2
Na	0.032	0.019	802	802	812	98.8 + 5.0	98.0 + 7.4
Rb	-	-	19.0	19.0	19.6	97.1 + 7.9	96.3 + 9.4
Cs	-	-	1.41	1.41	1.38	103 + 6	102 + 8
K	0.077	0.002	1,692	1,692	1,680	101 + 5	100 + 7
Sc	-	-	2.69	2.69	2.62	103 + 5	102 + 7
Tb	-	-	0.15	0.15	0.16	94.0 + 7.7	93.2 + 9.2
Eu	-	-	0.23	0.23	0.21	108 + 23	107 + 24
Sm	-	-	1.96	1.96	3.41	57.5 + 3.0	57.1 + 4.3
Ce	-	-	14.6	14.6	14.2	103 + 5	102 + 7
La	-	-	7.12	7.12	6.79	105 + 6	104 + 8
Th	-	-	2.11	2.11	2.05	103 + 5	102 + 7
Hf	-	-	0.72	0.72	0.74	97.2 + 5.2	96.5 + 7.4

Table 5.20 (continued)

Material	TO	PW	VB	Total Coal*		Material Balance	
						Total % MFC	Normalized % MFC***
Fraction	0.342	0.053	0.498	0.893	1.00		
Ta	-	-	0.18	0.18	0.17	103 + 10	102 + 11
Ga	-	-	3.03	3.03	2.51	121 + 10	120 + 12
Zr	-	-	19.6	19.6	21.2	92.6 + 21	91.9 + 21.4
Sr	-	-	139	139	149	93.3 + 6.4	92.6 + 8.1
Ba	0.028	-	102	102	107	95.4 + 9.9	94.6 + 11.1

NOTES: TO=total accumulator oil; PW=process water; VB=vacuum bottom; MFC=moisture free coal.

*Pittsburg coal.

**Concentration values in ppm.

***Normalized to K = 100%.

TABLE 5.21

MATERIAL BALANCE FOR SRC-II PROCESS (SR-17)**

Material	TC	PW	VB	Total	Coal*	Material Balance	
Fraction	0.244	0.105	0.559	0.908	1.00	Total % MFC	Normalized % MFC***
Ti	-	-	868	868	757	115 + 13	102 + 13
V	0.003	-	19.1	19.1	15.3	125 + 11	136 + 12
Ca	0.57	-	5,140	5,141	4,800	107 + 11	95.5 + 11
Mg	-	-	1,240	1,240	1,230	102 + 25	90.4 + 23
Al (%)	-	-	1.36	1.36	1.23	111 + 7	98.8 + 8.0
Cl	-	22.1	929	951	991	96.0 + 5.7	86.0 + 6.8
Mn	-	-	35.2	35.2	38.7	90.9 + 4.8	80.9 + 6.1
As	0.003	0.003	7.70	7.71	8.77	87.9 + 5.5	78.3 + 6.1
Sb	-	-	0.55	0.55	0.33	164 + 14	146 + 15
Se	0.020	0.072	1.69	1.78	1.45	123 + 7	111 + 9
Hg (ppb)	2.93	17.2	24.0	44.2	149	29.7 + 9.2	26.4 + 8.4
Br	0.003	0.101	13.8	13.9	14.3	96.9 + 5.1	86.4 + 6.5
Ni	0.007	0.002	12.3	12.3	9.92	124 + 27	110 + 25
Co	0.001	-	3.21	3.21	2.80	115 + 9	102 + 12
Cr	0.003	0.005	19.1	19.1	16.0	119 + 12	106 + 12
Fe (%)	-	-	1.86	1.86	1.68	111 + 6	98.6 + 7.3
Na	0.082	0.048	765	765	726	105 + 5	94.0 + 6.9
Rb	-	-	19.9	19.9	18.7	106 + 8	94.8 + 8.9
Cs	-	-	1.53	1.53	1.19	129 + 9	115 + 10
K	0.17	0.01	1,740	1,740	1,550	112 + 6	100 + 7
Sc	-	-	2.90	2.90	2.47	117 + 6	105 + 8
Tb	-	-	0.21	0.21	0.11	190 + 16	169 + 17
Eu	-	-	0.23	0.23	0.20	118 + 26	105 + 24
Sm	-	-	1.24	1.24	1.09	114 + 6	101 + 7
Ce	-	-	15.6	15.6	13.7	114 + 6	101 + 7
La	-	-	7.43	7.43	6.84	109 + 6	96.8 + 7
Th	-	-	2.27	2.27	1.91	119 + 6	106 + 8
Hf	-	-	0.77	0.77	0.69	112 + 6	100 + 8

Table 5.21 (continued)

Material	TO	PW	VB	Total	Coal	Material Balance	
Fraction	0.244	0.105	0.559	0.908	1.00	Total % MFC	Normalized % MFC
Ta	-	-	0.19	0.19	0.15	124 + 11	110 + 12
Ga	-	-	3.51	3.51	2.72	129 + 9	115 + 10
Zr	-	-	26.7	26.7	25.4	105 + 19	93.5 + 18
Sr	-	-	152	152	189	80.5 + 5.1	71.7 + 6.0
Ba	-	0.005	95.0	95.0	106	89.7 + 9.3	79.9 + 9.3

NOTES: TO=total accumulator oil; PW=process water; VB=vacuum bottom; MFC=moisture free coal.

*Pittsburg coal.

**Concentration values in ppm.

***Normalized to K = 100%.

TABLE 5.22

MATERIAL BALANCE FOR SRC-II PROCESS (SR-20)

Material	TO	PW	VB	Total	Coal*	Material Balance	
						Total % MFC	Normalized % MFC***
Fraction	0.337	0.041	0.492	0.870	1.00		
Ti	0.21	-	755	755	787	96.0 + 12.2	86.7 + 12.0
V	0.23	-	43.6	43.8	41.3	106 + 7	95.8 + 7.6
Ca	-	-	5,970	5,970	6,110	97.7 + 8.8	88.3 + 9.1
Mg	-	-	1,620	1,620	1,370	118 + 19	107 + 18
Al (%)	-	-	1.46	1.46	1.34	109 + 8	98.7 + 8.8
Cl	-	2.85	271	274	294	93.0 + 8.1	84.0 + 8.5
Mn	0.006	-	73.8	73.8	64.0	115 + 6	104 + 8
As	0.012	0.001	3.28	3.28	3.38	97.0 + 5.8	87.6 + 7.0
Sb	-	-	0.37	0.37	0.33	115 + 11	104 + 11
Se	0.039	0.092	4.17	4.30	3.78	114 + 6	103 + 8
Hg (ppb)	5.90	2.20	-	8.10	34.0	24.0 + 3.3	21.7 + 3.3
Br	0.010	0.016	3.52	3.55	2.31	154 + 26	139 + 24
Ni	0.028	0.001	17.5	17.5	17.6	99.4 + 13.9	89.9 + 13.4
Co	0.002	-	4.35	4.35	3.84	113 + 5.9	102 + 7.6
Cr	0.075	0.004	42.3	42.4	37.1	114 + 5.9	103 + 7.6
Fe (%)	-	-	1.73	1.73	1.65	105 + 5.5	94.9 + 7.1
Na	1.29	-	614	615	549	112 + 6	101 + 8
Rb	-	-	18.8	18.8	20.4	92.4 + 9.4	83.5 + 9.6
Cs	-	-	1.32	1.32	1.21	109 + 6	98.5 + 8
K	0.36	-	2,352	2,352	2,130	111 + 5	100 + 7
Sc	-	-	3.34	3.34	3.01	111 + 6	100 + 7
Tb	-	-	0.215	0.215	0.231	93.3 + 6.4	84.3 + 7.3
Eu	-	-	0.27	0.27	0.24	112 + 20	101 + 19
Sm	-	-	2.71	2.71	2.79	97.2 + 5.0	87.8 + 6.5
Ce	0.001	0.001	14.2	14.2	11.6	123 + 6	111 + 8
La	0.001	-	6.52	6.52	5.75	113 + 6	102 + 8
Th	-	-	2.41	2.41	2.00	120 + 6	108 + 8
Hf	-	-	0.70	0.70	0.59	120 + 7	108 + 8

Table 5.22 (continued)

Material	TO	PW	VB	Total	Coal	Material Balance	
Fraction	0.337	0.041	0.492	0.870	1.00	Total % MFC	Normalized % MFC
Ta	-	-	0.158	0.158	0.134	118 + 13	107 + 13
Ga	-	-	3.29	3.29	2.91	113 + 7	102 + 9
Zr	-	-	55.6	55.6	47.8	116 + 18	105 + 18
Ba	-	-	313	313	118	266 + 32	240 + 32

NOTES: TO=total accumulator oil; PW=process water; VB=vacuum bottom; MFC=moisture free coal.

*Illinois coal.

**Concentration values in ppm.

***Normalized to K = 100%.

For the equilibrium set SR-11, the elemental balances lie within the range of 91-115% MFC (average of 101 ± 5%) except for Br (75%), Ni (68%), Zr (130%) and Rb (147%). For set SR-12 all elemental balances lie within the range of 83-124% MFC (average 105 ± 6%) except for Hg (35) and Zr (58%). In set SR-15, the balance lies within the range of 84-120% MFC (average 100 ± 5%) except for Hg (40), Sm (57%), Sb (156%) and Ni (267%). For equilibrium set SR-17 balance lies within range of 80-115% MFC (average of 98 ± 5%) except for Hg (26), Sb (146%) and Tb (169%). In equilibrium set SR-20, elemental balances lie within the range of 84-111% MFC (98 ± 5% average) except for Ba (240%) and Hg (22%). These values for all sets are excellent considering the errors associated with obtaining representative samples.

In Table 5.18 Zr balance in SR-11 was somewhat high, possibly due to the high detection limit of Zr by INAA method. At the same time, the low balance of Zr in set Sr-12 may be due to the anomalously high value (50.3 ppm) of Zr in Pittsburg coal while it is 21.1 and 25.4 ppm in SR-15 and SR-17 equilibrium sets for this type of coal. Also, the Tb value in coal (set SR-17) and the Sm value in coal (set SR-15) are anomalous compared to the Tb and Sm concentrations in the other two sets of Pittsburgh feed coal. Comparison between SR-11 and SR-20 equilibrium runs, when Illinois coal was used, shows that the Rb value in vacuum bottom for set SR-11 is not a representative value. The average of Br content in Illinois coal is 3.86 ± 0.65 ppm, from Tables 5.2, 5.3 and 5.4, indicating an incorrect value for Br in set SR-20 coal. The low value of Br in set SR-11 may indicate losses in the process. Antimony concentrations in Pittsburg coal are

0.30, 0.33 and 0.33 ppm in equilibrium sets SR-12, 15 and 17, and the values of Sb in vacuum bottom indicate non-homogeneity of the Sb contents in vacuum bottoms. The material balances for Hg in all equilibrium sets show that Hg fails to close in all cases. The low values of Hg (Table 5.23) may be due to losses in process streams or from fugitive plant emissions. Preliminary data for gas samples from the recycle condensate vessel indicate that some Hg may enter the desulfurization unit but there is no evidence of emission of Hg to the environment. However, there is evidence for the concentration of Hg in overhead streams through volatilization of Hg from coal during the liquefaction process. For such environmentally important elements as As, Sb, Fe, Cr, Ni, Co, Se, etc. the material balances are satisfactory. The alkali metals (K, Na, Cs and Rb), Fe and the rare earth elements all close well.

Trace Elements in Process and Effluent Waters

The trace element contents of important aqueous phases from the SRC-I and SRC-II processes were measured in order to determine the pollution potential of plant effluent water. In both SRC-I and SRC-II processes, water is produced as a reaction product (from oxygen in coal) of the hydrogenation of the coal and it is also used as a quenching agent. These process waters contain trace elements from a number of possible sources (original coal, corrosion products, etc.) in addition to H_2S and organic compounds soluble in water. Because the process waters contain phenols, sulfur compounds and trace elements, they must be treated to remove such toxic compounds prior to discharge to the environment. The treatment process used in the SRC-I and SRC-II processes

TABLE 5.23

MATERIALS BALANCES FOR SRC-II EQUILIBRIUM SETS

Element	SR-11 (%)	SR-12 (%)	SR-15 (%)	SR-17 (%)	SR-20 (%)	Average (%)
Ti	97	106	88	102	87	97
V	102	92	96	136	96	104
Ca	104	111	84	96	88	95
Mg	101	84	103	90	107	97
Al	100	100	103	99	99	100
Cl	94	121	97	86	84	96
Mn	115	113	119	81	104	106
As	97	124	92	78	88	96
Sb	99	88	156	146	104	119
Se	94	115	91	111	103	103
Hg	92	35	40	26	22	43
Br	75	99	101	86	139	100
Ni	68	112	267*	110	90	95
Co	102	114	105	102	102	105
Cr	110	117	119	106	103	111
Fe	109	116	95	99	95	103
Na	106	103	98	94	101	100
Rb	147	86	96	95	84	101
Cs	106	108	102	115	99	106
K	100	100	100	100	100	100
Se	102	103	102	105	100	102
Tb	91	119	93	169	84	111
Eu	105	104	107	105	101	104
Sm	93	119	57	101	88	92
Ce	109	83	102	101	111	101
La	98	98	104	97	102	100
Th	109	102	102	106	108	105
Sr	-	-	93	72	-	82
Ba	-	111	95	80	240*	95
Hf	107	101	97	100	108	103
Ta	92	108	102	110	107	104
Ga	91	105	120	115	102	107
Zr	130	58	92	94	105	96

NOTE: Materials balances as % MFC (moisture free coal).

*Values not considered for the average calculations.

is flocculation with aluminum hydroxide, biodegradation of organic species followed by filtration through activated charcoal filters. Process water, effluent waters and Hamer Marsh water (discharge site) were analyzed for all equilibrium sets collected from the SRC-I and SRC-II processes. Process waters from separators No. 2 and 3 in the SRC-II process were also analyzed because these are derived from condensation of different overhead streams. The analytical data for equilibrium set 1 of SRC-I and set SR-15 of SRC-II are shown in Appendices A and B. For the other equilibrium sets, results are reported in Filby et al (26, 96). No direct comparisons between the process waters and effluent waters can be made because effluent waters contain run-off waters, wash waters and cooling waters used in the plant in addition to process waters. It can be seen from Appendices A and B that Se, Hg, As, Sb, Cu and Cl concentrations are significantly higher in process water than in effluent water. However, these elements are reduced by the treatment process to essentially background levels in effluent waters as shown by comparison with concentrations in the Hamer Marsh water. This means that the treatment process is effective in reducing toxic trace element levels. In the SRC-II process, high concentrations of As, Cl, Se, Hg, Br, Ni, Cr, and Cu are found in the effluent water and the process water water and separators No. 2 and 3 waters while effluent waters have background levels (Hamer Marsh water) of these elements. The Hg and Se in SRC-I and SRC-II process waters have higher relative values (compared to coal) than all other elements measured. It is probable that these elements form volatile species as Hg^o, HgS, H_2Se and Se^o and/or organometallic species which condense in

the cool condensate zone region. This is discussed in detail later.

A comparison of the trace elements levels in the effluent water with the median values for U.S. rivers (100), mean Pacific Northwest rivers (101) and Environmental Protection Agency (EPA) drinking water standards (102) is shown in Table 5.24. There is a remarkably close agreement between plant effluent water and the median concentrations for U.S. rivers. The effluent water exceeds EPA drinking water standards only for Hg and Zn while the other element levels are lower than the EPA limits.

Trace Elements Behavior During Hydrogenation

The objective of this study was not to identify the chemical species of the trace elements in the liquefaction products or to determine reaction mechanisms but to define trace element behavior during hydrogenation. The distribution of the trace elements in the liquefaction products and material balances are considered as a necessary first step in the study of their chemistry during hydroliquefaction.

In order to understand the chemical transformations of trace elements in the Solvent Refined Coal Processes, it is important to know the forms in which trace elements exist in feed coal and how these species behave during liquefaction. In spite of much work done on trace elements in coal (5, 17, 56, 57, 58, 59) there is little information on the nature of trace element species in coal and their reactions under coal conversion conditions. Trace elements can occur in coal in several modes, basically in

TABLE 5.24

COMPARISON OF TRACE ELEMENTS IN PLANT EFFLUENT WATER WITH
U.S. RIVER WATERS AND EPA DRINKING WATER STANDARDS

Element (mg/l)	Plant effluent[a]	Median U.S. rivers[b]	Mean Pacific N.W. rivers[c]	EPA Drinking water[d]
Ti	<0.2	0.009	0.009	0.1
V	0.009	0.001	0.013	0.1
Ca	9.6	15	-	-
Mg	4.2	4.1	-	10
Al	0.25	0.24	0.03	0.01
Cl	3.7	7.8	-	-
Mn	0.03	0.012	0.0028	0.05
As	<0.005	0.0004	0.0007	0.05
Sb	0.0006	--	-	0.01
Se	0.0004	<0.02	-	0.01
Hg	0.00055	0.00008	-	0.002
Br	<0.01	0.021	-	3
Ba	<0.01	0.054	0.027	1.0
Th	0.09*	0.02*	-	-
Zn	0.06	0.01	0.04	5
Ga	<0.004	<0.001	-	-
Zr	0.02	0.003	-	1
Cu	<0.025	0.01	0.009	0.1
Na	8.3	6.3	-	-
Rb	0.0014	0.0015	-	5
Cs	0.0006	0.0002	-	-
K	<1	2.3	-	-
Co	0.00036	0.0009	0.008	0.05
Cr	0.010	0.0002	0.006	0.05
Fe	0.41	0.67	0.032	0.3

*Values in g/l

[a] From equilibrium set #2 (SRC-I)

[b] Reference 100

[c] Reference 101

[d] Reference 102

either organic forms (bound in macerals), or inorganic forms (bound in minerals) and most trace elements are probably found in coal in both combinations (17, 53, 58). Although it is impossible to identify by visual methods elemental species which are organically bound, many mineral species have been identified in coals and the most important minerals, i.e., the clay minerals, silica and pyrite, can be identified microscopically (42, 44). Elements that are present in major or minor amounts in coals, such as Fe, Ca, Mg, Zn and Si, specific mineral species, e.g., pyrite (FeS_2), marcosite (FeS_2), chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and calcite ($CaCO_3$) may be readily identified (Table 2.2). For most trace elements such as As, Hg, Se, Co, Ni, etc., the actual chemical moieties with which the elements of interest are associated are not known, and the element may be distributed among several mineral species. Thus, behavior during liquefaction cannot be predicted.

In the Solvent Refined Coal processes (SRC-I or SRC-II) the original distribution of trace element forms in coal could be changed. Elements present in the organic matrix of coal may be converted to inorganic components during the dissolution (depolymerization) of coal and the hydrogenation of the depolymerized organic matrix. Also elemental transfer from inorganic forms to the organic matrix may occur if reactive functional groups in coal are able to coordinate with the element to give chelate-type complex compounds under the process conditions. Many of these species may be toxic, volatile or potentially harmful to catalysts (13, 16). Some elements can form either organic or

inorganic volatile compounds, stable under the conditions used in the SRC process (e.g., $Hg°$, H_2Se, AsH_3, etc.). Mineral species such as silica, silicates and many sulfides should be unchanged under the process conditions while other mineral species may react with hydrogen. For example, pyrite (FeS_2) is converted to pyrrhotite

$$FeS_2 + H_2 \rightleftharpoons FeS + H_2S$$
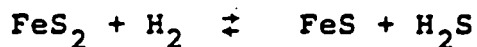
In addition to chemical changes, some physical characteristics, e.g., grain size of minerals, may change.

Most of the elements showed satisfactory balances for both SRC-I and SRC-II processes (Tables 5.9 to 5.23) in spite of the assumptions made. All elemental balance calculations were based on the major input and output streams in the process without taking into consideration the very small contributions from the recycle process solvent, hydrogen gas, product gases or from corrosion/erosion of the construction materials. The elements As, Sb, Se, Hg and Br, which may be considered as the important environmental volatile pollutants, balanced well except for Hg in SRC-II and Br in SRC-I process.

In the SRC-I process, volatilization of trace elements from coal into overhead streams during the hydrogenation process could occur despite satisfactory material balances. Such volatile species would likely condense in the light oil and/or process waters. Some volatile species may be released in flares but no data are available because no gas samples from the SRC-I process were obtained during collection of the equilibrium sets.

To illustrate the relative enrichment of volatile ele-
ments in light oils or process waters, enhancement factors, E_f,
wer calculated. The enhancement factor is defined as:

$$E_f = \frac{\text{Element concentration in oil or water}}{\text{Element concentration in coal}} \cdot \frac{\text{Potassium concentration in coal}}{\text{Potassium concentration in oil or water}}$$

The enhancement factor, E_f, thus is a measure of the enrichment
of an element in a given fraction relative to coal and relative
to K. Thus elements with $E_f > 1.0$ show enhancement relative to K,
which is taken as a typical non-volatile element.

Table 5.25 shows the enhancement factors of some trace
elements in the SRC-I process (normalized to E_f for K=1.0) in
light oil and process water fractions. The high E_f values of Hg,
Se, Br, As and Sb in light oil and process water fractions give
strong evidence for the formation of volatile species of these
elements. Recently, it was shown (103) that Se in coal may
exist as the mineral clausthalite, PbSe. During hydrogenation
this may react with hydrogen to form H_2Se which is more soluble
in water than in a hydrocarbon phase as indicated by $E_f = 838$ for
Se in process water and $E_f = 78.3$ for Se in light oil. Thus the
following reaction may take place:

$$PbSe + H_2 \rightarrow Pb + H_2Se$$

or

$$PbSe + H_2S \rightarrow PbS + H_2Se.$$
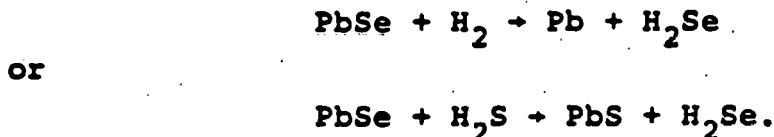
TABLE 5.25

ENHANCEMENT FACTORS FOR ELEMENT IN LIGHT OIL AND RECYCLE PROCESS WATER IN SRC-I PROCESS (SET 2)

Element	Concentration in Coal (ppm)	Concentration in light oil (ppb)	Enhancement factor, E_f*	Concentration in process water (ppb)	Enhancement factor, E_f**
As	20.1	2.83	1.43	10.7	1.48
Sb	1.43	1.84	13.0	1.00	1.94
Se	3.03	23.4	78.3	914	838
Hg	0.114	3.40	302	20.7	502
Br	3.72	18.2	49.6	13.8	13.7
Ni	12.4	40.0	32.6	14.0	3.13
Co	5.20	1.80	3.51	0.43	0.23
Cr	14.8	--	--	11.3	2.12
Fe	23,800	300	0.128	1,340	0.15
Na	172	40.0	2.35	5100	82.1
Sc	2.48	130	0.53	0.12	0.134
K	2030	200	1.00	730	1.00

*Enhancement factor for element X, $E_f = \dfrac{(X)oil \cdot (K)coal}{(X)coal \cdot (K)oil}$

**Enhancement factor for element X, $E_f = \dfrac{(X)water \cdot (K)coal}{(X)coal \cdot (K)water}$

The high E_f values for Hg in light oil (302) and process water (502) fractions indicate that volatile Hg species condensed in these two fractions under the process conditions. The distribution of Hg among the various process fractions is distinctly different from the distribution of non-volatile elements such as K and Fe (see Tables 5.9, 5.23). Although the material balance for Hg in SRC-I was good for all equilibrium sets, Hg is partially converted to a) a volatile species as evidenced by the fact that 5.1% MFC (Table 5.6) of the total Hg appears in process water, and b) an SRC soluble form (organic or inorganic) that accounts for 24.9% MFC (Table 5.6) of the total Hg in the system. Similar behavior, but less pronounced, was found for As and Sb, Table 5.25.

The elements are depleted in SRC-I relative to coal to different degrees. Potassium is depleted to the greatest extent in all equilibrium sets. To illustrate the differences in depletion among the elements, the SRC/Coal concentration ratios have been normalized to K=1.0 and the data are shown in Table 5.26. The differences in behavior are open to a number of interpretations and it is difficult to distinguish among them. Possible interpretations are:

a) different minerals or mineral reaction species may have different particle sizes and therefore different degrees of retention on the filters,

b) organometallics (85) or solvent soluble species may form, thus passing through the filters, and

c) volatile species may pass through the filters and be incorporated into the SRC-I.

TABLE 5.26

CONCENTRATION RATIO OF SRC RELATIVE TO COAL FOR SRC-I PROCESS

Element	Equilibrium Set 1		Equilibrium Set 2		Equilibrium Set 3	
	(SRC/Coal)	(SRC/Coal)$_{norm}$*	(SRC/Coal)	(SRC/Coal)$_{norm}$*	(SRC/Coal)	(SRC/Coal)$_{norm}$*
Ti	0.88	288	0.74	664	0.52	103
V	0.15	50.5	0.47	420	0.21	42.1
Ca	0.12	37.8	0.19	167	0.06	12.3
Mg	0.08	25.2	--	--	--	--
Al	0.02	5.57	0.03	23.8	0.01	1.76
Cl	0.62	202	0.34	305	0.39	76.5
Mn	0.60	196	0.40	356	0.38	74.8
As	0.16	52.5	0.11	101	0.38	75.6
Sb	0.08	25.9	0.04	37.5	0.09	16.9
Se	0.06	19.7	0.03	23.6	0.02	4.63
Hg	0.35	115	0.41	366	--	--
Br	1.70	557	1.33	1185	1.27	252
Ni	--	--	--	--	0.10	19.4
Co	0.04	12.3	0.05	43.0	0.09	17.0
Cr	0.12	39.3	0.37	332	0.29	57.1
Fe	0.01	4.67	0.01	9.77	0.01	2.58
Na	0.03	10.1	0.04	32.6	0.02	4.70
Rb	--	--	0.02	15.9	--	--
Cs	0.03	8.76	--	--	--	--
K	0.003	1.0	0.001	1.0	0.005	1.0
Sc	0.22	72.3	0.15	130	0.07	13.6
Tb	0.12	37.9	0.09	83.8	0.07	14.2
Eu	0.21	69.5	0.14	121	0.08	15.3
Sm	0.11	36.3	0.07	63.4	0.05	9.92
Ce	0.02	7.07	0.02	14.5	0.02	3.31
La	0.02	5.65	0.01	12.3	0.02	4.12
Th	0.11	36.1	0.10	89.4	0.04	8.51
Hf	0.16	54.1	0.12	105	0.04	8.27
Ta	0.33	108	0.29	263	0.15	29.1
Ga	0.50	165	0.19	167	0.41	81.2
Zr	0.25	83.5	0.08	72.4	0.08	15.8
Cu	0.10	34.2	0.08	71.9	--	--
Ba	0.11	35.6	--	--	0.03	5.69

*Normalized to potassium ratio equal to 1.00.

Potassium is very efficiently retained in insoluble residues
(pyridine insolubles 11,200 ppm, and wet filter cake 7600 ppm)
compared to the original coal (2030 ppm) (Table 5.3). At the
same time, the low concentrations of K in SRC-I (2.27 ppm), light
oil (0.20 ppm) and process water (0173 ppm) (Tables 5.3 and 5.25)
confirm the presence of K in easily filterable minerals in coal
such as silicates or clay minerals. Pyrite (FeS_2) the principal
Fe mineral in coal is converted under the hydrogenation condition
to pyrrhotite (FeS). The low concentrations in SRC-I (260 ppm),
light oil (0.30 ppm), and process water (1.34 ppm) compared to
the coal (2.38%) (Table 5.3) indicate that Fe (as FeS and other
species) are well retained in the mineral residues. The other
elements shown in Table 5.26 probably exist in other minerals
having different mean particle sizes. Thus elements present in
fine grained minerals will show lower retention than those pre-
sent in coarser size mineral fractions. Comparison between the
wet filter cake and pyridine insolubles fractions (Tables 5.2 and
5.3) show that the Cl and Br concentrations in the pyridine insol-
ubles are lower than in the wet filter cake while the reverse is
true for the other elements. This indicates that Cl and Br are
probably concentrated in the soluble fraction of the wet filter
cake. However, the concentrations of Cl and Br in the light oil
fraction are very low. Thus Cl and Br may be associated with the
organic fraction of the wet filter cake but present in relatively
involatile organic compounds.

The behavior of Ti is very different from other elements
in the process. The Ti in SRC-I accounts for 52% to 88% of the

total Ti content in coal with an average of 71% ± 18%. Several

explanations for this behavior are possible, e.g. (26),

a) Ti is present in the original coal as an extremely
finely divided oxide, TiO_2 (rutile), which passes through
the filtration system whereas other minerals do so to a
much lesser extent.

b) Ti minerals present in the coal (probably rutile, TiO_2
or ilmenite, $FeTiO_3$) are converted to finely divided
forms in the SRC-I reactor.

c) Ti is present as an organotitanium species in the coal
and this species is soluble in the process solvent (16,
85, 104).

d) Ti present as an inorganic mineral species, i.e., rutile
TiO_2 or ilmenite $FeTiO_3$ reacts to form soluble organo-
titanium species during the hydrogenation reaction (16,
105).

Titanium in coal may exist partly as a mineral species

and partly as an organic species (see Table 5.5). This agrees

with the findings of Ruch et al (106) and with the conclusion of

Miller and Given (107) that organically bound Ti forms can occur

in coal. Several authors have postulated that Ti may be present

in coal partly as organotitanium species (16, 85, 104) or that

Ti in the inorganic forms in coal can be converted to organoti-

tanium compounds (16, 105). The very high ratio of Ti in the

SRC-I product (Table 5.26) may be explained by formation of solu-

ble organotitanium species during the hydrogenation reaction

since it is known that under reducing conditions and in the pre-

sence of Cl_2, TiO_2 can form reactive $TiCl_4$ at temperatures as

low as 500° C. If $TiCl_4$ is produced, reactions with condensed

aromatic hydrocarbon species could produce organo-titanium com-

pounds associated with the high molecular weight fractions of the

SRC-I (e.g., asphaltenes) (108). A recent study of the

distribution of Ti as a function of SRC-I fraction molecular weight obtained by a combination of gel permeation chromatography (GPC) and adsorption chromatography indicated that the highest molecular weight organic material is associated with much of the Ti in the SRC-I (108). Thus the behavior of Ti may involve a combination of processes (a) through (d).

For the SRC-II process, material balances for five equilibrium sets shows that most of the trace elements balance well in spite of neglecting the contributions of gases and equipment corrosion. Although the Hg balance in the SRC-I process was good, it does not close in the SRC-II process, and volatilization of mercury is more serious than in SRC-I. The analysis of vapor samples from the recycle condensate separator showed that significant amounts of Hg were released into the desulfurization unit in the liquefaction process (99). Also, Hg was observed in other process streams through volatilization of Hg from the coal into the overhead stream of the second pressure let-down vessel (see Figure 5.1). Thus Hg appears in the liquid-liquid separator No. 2. This can be seen clearly when the observed high concentration of Hg in the separator 2 oil from SRC-II process is compared to that in other SRC-II oils and a light distillate oil from the SRC-I process (Table 5.27). The concentration of Hg in the separator 2 oil (776 ppb) is greater than that of the original coal (129 ppb) (Table 5.18) and Hg is apparently present in the oil in particulate form as either Hg or HgS as shown by the data in Table 5.28. The separator 2 oil is thus the source of the relatively high Hg (27.3 ppb) and Se (115 ppb) contents in the
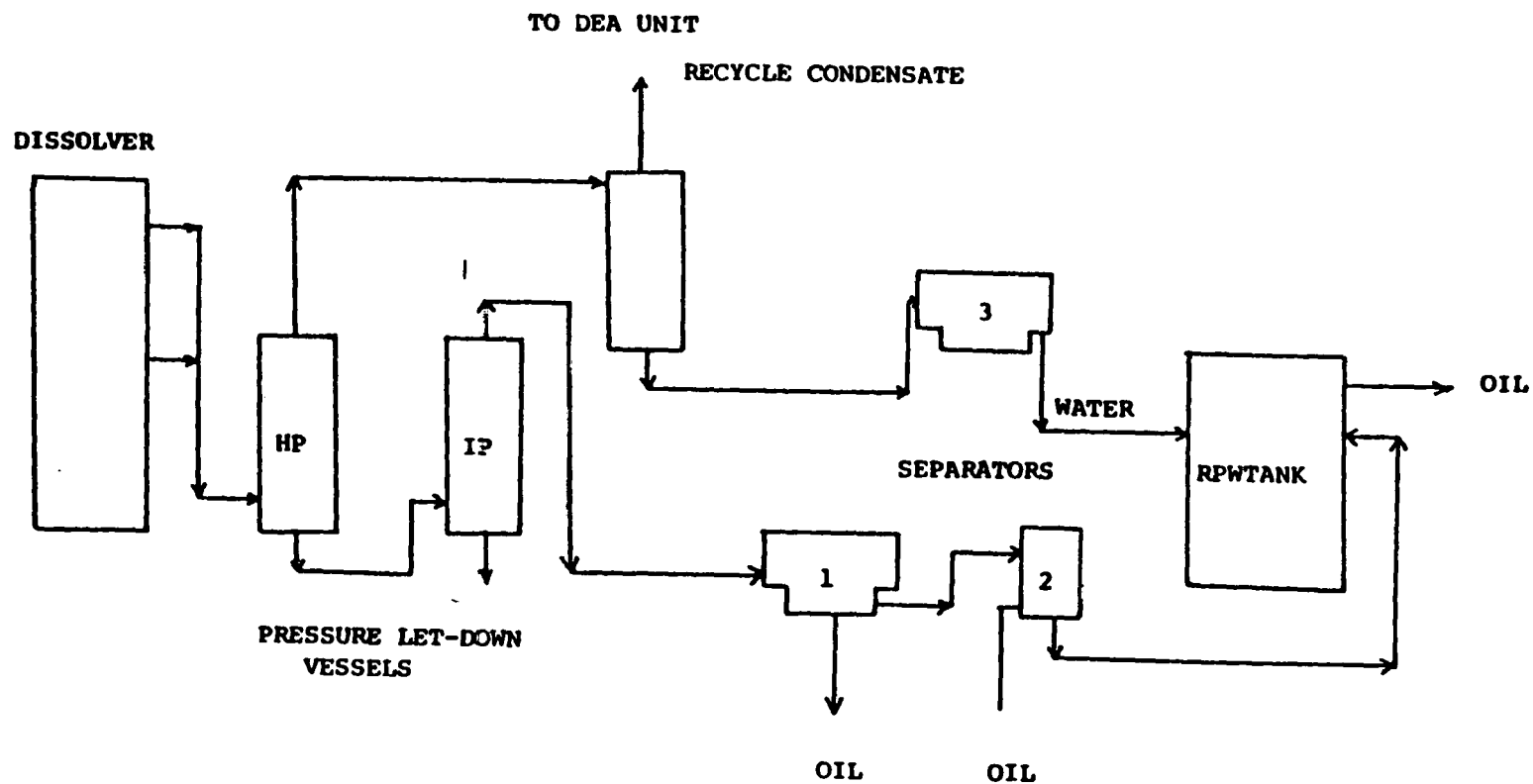
Figure 5.1.   Simplified schematic diagram of overhead streams in SRC-II

TABLE 5.27

TRACE ELEMENTS IN SRC-I AND SRC-II
DISTILLATE FRACTIONS (SR-11)

Element (ppb)	Separator #2 Oil*	Separator #3 Oil*	Solvent Acc. Oil	Light Oil SRC-I**
As	57.7	32.9	12.7	2.85
Sb	4.45	<0.2	0.55	1.86
Se	214	57.1	115	23.0
Hg	776	4.60	27.3	3.40
Br	11.1	8.71	6.65	18.0
Ni	189	<20	30.3	40.0
Co	31.1	1.45	2.34	1.8
Fe (ppm)	120	0.73	3.39	0.30
Cr	14.0	14.5	81.8	<5

*SRC II data from Equilibrium Set # SR-11.

**SRC I data from Equilibrium Set #2.

total accumulator oil. The oil from separator No. 3 had lower Se and Hg concentrations than that of separator No. 2 (Table 5.27).

To indicate possible concentration of volatile elemental species in overhead streams of the SRC-II process, the data in Appendix B for equilibrium set SR-15 separators No. 2 and 3 oils, total solvent accumulator oil, and process waters have been used to compute the enhancement factors, E_f, defined as in the SRC-I process section. Thus a value of $E_f > 1$, indicates that the element is concentrated in the fraction (i.e., more volatile) relative to K while $E_f < 1$ indicates that the element is less volatile than K. The values of the E_f are shown in Tables 5.29 through 5.33 and Figures 5.2 and 5.3. The high elemental contents in separator No. 2 oil relative to that in separator No. 3 (Table 5.27) indicate that the volatile species of Hg, Se, As and Sb from coal were condensed from the overhead stream from the second pressure let-down vessel and collected in the separator No. 2 oil of the equilibrium set SR-15 (4.37 ppm in Table 5.28). Also, high concentrations of several other trace elements (Se, As, Sb, Co and Ni) are seen in this oil from equilibrium set SR-15 compared to the oil from separator No. 3. This oil of SR-15 set separator No. 2 was filtered, after separation of an aqueous phase, and some of the filtered oil was washed with distilled water for 10 minutes. Data for all fractions of this sample are presented in Table 5.28. Almost all the anomalously high element content in the separator No. 2 oil could be associated with the particulate phase (940 ppm Hg, 67 ppm Se and 44 ppm As) rather than the filtered oil (6.71 ppb Hg, 84.7 ppb Se and 15.7 ppb As).

TABLE 5.28

TRACE ELEMENT CONCENTRATIONS IN SEPARATOR #2 OIL AND FRACTIONS (SR-15)

Element (ppb)	Oil from Separator #2	Aqueous	Filtrate Oil	Filtered Solid	Washed Oil	Wash Water
As	310 ± 3	1140 ± 5	15.3 ± 0.8	43.5 ± 0.2	6.18 ± 0.45	4.97 ± 0.21
Sb	16.7 ± 0.9	10.4 ± 0.6	11.1 ± 0.9	1850 ± 105	3.60 ± 0.36	3.73 ± 0.27
Se	391 ± 3	89.8 ± 1.1	84.7 ± 1.4	66.8* ± 0.4	80.8 ± 10.0	2.52 ± 0.31
Hg	4370 ± 80	5.43 ± 0.14	6.71 ± 0.21	940* ± 17	5.52 ± 0.15	0.15 ± 0.02
Br	139 ± 4	1140 ± 12	101 ± 3	7450 ± 192	84.1 ± 2.2	15.6 ± 0.5
Ni	940 ± 81	1150 ± 52	<82	147* ± 9	119 ± 14	<25
Co	65.8 ± 0.7	21.6 ± 0.3	1.97 ± 0.18	14.0* ± 0.1	0.68 ± 0.09	0.12 ± 0.03
Cr	526 ± 6	134 ± 3	63.8 ± 2.7	101* ± 1	50.8 ± 1.7	4.27 ± 0.66
Fe	418* ± 1	2.34* ± 0.15	<0.4*	87,900*± 878	0.13* ± 0.03	<0.13*
Na	11.1* ± 0.04	39.7* ± 0.1	0.284* ± 0.005	1690* ± 6	0.34* ± 0.01	0.72* ± 0.004
Rb	245 ± 29	<54	<31	23.6* ± 3.9	<17	<14
Cs	11.7 ± 0.4	<1.0	2.25± 0.17	2730 ± 56	0.28 ± 0.07	0.84 ± 0.05
K	24.8* ± 0.4	5.32* ± 0.38	<0.12*	4280* ± 65	<0.12*	0.084* ± 0.016
Sc	34.0 ± 0.1	47.6 ± 0.1	0.15 ± 0.01	6630 ± 17	0.1н ± 0.01	0.032 ± 0.003
Tb	4.83 ± 0.25	<0.56	<0.2	1030 ± 43	<0.11	<0.07
Eu	3.09 ± 0.10	0.36 ± 0.04	0.96 ± 0.09	512 ± 14	0.426 ± 0.036	0.21 ± 0.02
Sm	13.4 ± 0.2	1.07 ± 0.19	<0.4	4250 ± 11	<0.3	<0.1
Ce	190 ± 2	12.0 ± 1.1	<6.1	13.7* ± 0.2	<4	<1.3
La	101 ± 2	<7	<1.2	16.8* ± 0.2	<1.0	<0.6
Sr	1890 ± 163	<376	<249	352* ± 19	<129	<68

Table 5.28 (continued)

Element (ppb)	Oil from Separa- tor #2	Aqueous	Filtrate Oil	Filtered Solid	Washed Oil	Wash Water
Ba	2080 ± 469	<1540	<544	391* ± 76	<311	<268
Th	25.9 ± 0.4	23.9 ± 0.3	<0.8	5460 ± 55	<0.5	<0.25
U	<20	27.2 ± 7.0	<11	4710 ± 1110	<7	<6
Hf	9.31 ± 0.33	11.5 ± 0.3	<0.6	1560 ± 46	<0.4	<0.2
Ta	3.43 ± 0.26	2.98 ± 0.20	<0.6	344 ± 31	<0.3	0.74 ± 0.07
Ga	44.8 ± 1.8	<18	2.85 ± 0.53	9060 ± 310	3.84 ± 0.53	<0.87
Zr	433 ± 118	647 ± 126	--	112* ± 20	--	--
Cu	244 ± 2	424 ± 3	10.3 ± 0.41	40.1* ± 0.3	19.4 ± 0.5	2.33 ± 0.09
Zn	<38	<16	45.6 ± 6.0	<5700	21.9 ± 3.1	<5.3
Ag	<3.4	<2.7	1.74 ± 0.37	<.85	<0.60	<0.3
Au	<0.22	0.151 ± 0.040	< .09	<7.5	0.84 ± 0.02	<0.03

*Values in ppm.

From Table 5.29, the enhancement factors, E_f, for Hg (1290), Se (15.1), As (2.38) and Sb (3.25) indicate that the volatile species of these elements are concentrated in separator 2 oil relative to K (Figure 5.2). Also, the high E_f for the solid phase of the separator 2 oil compared to K (Table 5.29) indicates that the volatile species of Hg, Se, As, and Sb may be associated in sludges of SRC-II mode and may result in buildup of highly undesirable solid deposits in the liquid-liquid separators. Total accumulator oil is also enriched for Hg, Se, As, Sb, Ni, Co and Cr as indicated by the higher E_f values of these elements compared to K as shown in Table 5.30. The source of the element enrichment in the total accumulator oil is probably the separator 2 oil which is emortied to the total accumulator or may be due to corrosion of construction materials.

The enhancement factors of the trace elements in process waters and their associated particulates from separators No. 2 and 3 waters and recycle process water tanks were computed for equilibrium set SR-12 rather than SR-15 because of the uncertainty in K concentrations (less than values) of those fractions for equilibrium set SR-15 (see Appendix B). Tables 5.31 and 5.32 and Figure 5.3 show that the enhancement factors of Hg, Se, Sb, As, Co, Cr and Ni are high relative to K in both aqueous and solid phases of separators No. 2 and 3 waters. It can be seen that the enrichments of Se, As and Sb in the aqueous phase are higher than those in the solid phase and this may be due to the formation of water soluble species such as H_2Se, AsH_3 and SbH_3 which are condensed in the separators' water tanks. Higher

TABLE 5.29

ENHANCEMENT FACTORS FOR ELEMENTS IN SOLID AND LIGHT OIL
FROM SEPARATOR #2 OIL IN SRC-II PROCESS (SR-15)

Element (ppm)	Concentration in Coal	Concentration in Solid	Enhancement** Factor, E_f	Concentration in Separator 2 Oil	Enhancement*** Factor, E_f
As	8.37	43.5	1.94	0.31	2.38
Sb	0.33	1.85	2.09	0.017	3.25
Se	1.66	66.8	15.0	0.39	15.1
Hg	0.22	940	1,610	4.37	1,290
Br	13.1	7.45	0.212	0.14	0.681
Ni	6.9	147	7.93	0.94	8.76
Co	2.98	14.0	1.75	0.060	1.42
Cr	14.8	101	2.54	0.53	2.29
Fe	18,200	87,900	1.80	418	1.48
Mn	30.2	144	1.78	1.13	2.37
Na	783	1,690	0.80	11.1	0.912
Rb	25.1	23.6	0.40	0.25	0.628
Cs	0.93	2.73	1.09	11.7*	0.809
K	1,600	4,280	1.000	24.8	1.000
Sc	2.77	6.63	0.892	0.034	0.790
Tb	0.34	1.03	1.13	4.83*	0.916
Eu	0.22	0.512	0.855	3.09*	0.891
Sm	0.94	2.45	0.971	13.4*	0.917
La	6.31	16.8	0.991	0.101	1.03
Sr	139	352	0.943	1.89	0.874
Ba	104	391	1.40	2.08	1.28
Th	2.07	5.46	0.986	0.026	0.805
Hf	0.69	1.56	0.850	9.31*	0.874
Ta	0.22	0.344	0.582	3.43*	1.00
Ga	3.10	9.06	1.09	0.045	0.929
Zr	20.0	112	2.09	0.43	1.39
Ti	822	687	0.311	12.8	1.00
V	19.1	36.3	0.708	0.34	1.16
Mg	1,430	2,890	0.753	22.0	0.989
Ca	6,820	6,080	0.332	57.0	0.538
Al	13,100	23,200	0.661	225	1.11
Cl	840	761	0.338	12.5	0.957

*Values in ppb.

**Enhancement factor for element X, $E_f = \dfrac{(X)\ solid\ \cdot\ (K)\ coal}{(X)\ coal\ \cdot\ (K)\ solid}$.

***Enhancement factor for element X, $E_f = \dfrac{(X)\ oil\ \cdot\ (K)\ coal}{(X)\ coal\ \cdot\ (K)\ oil}$.

$$E_f = \frac{[\text{Element}]\ \text{oil}\ [K]\ \text{coal}}{[\text{Element}]\ \text{coal}\ [K]\ \text{oil}}$$
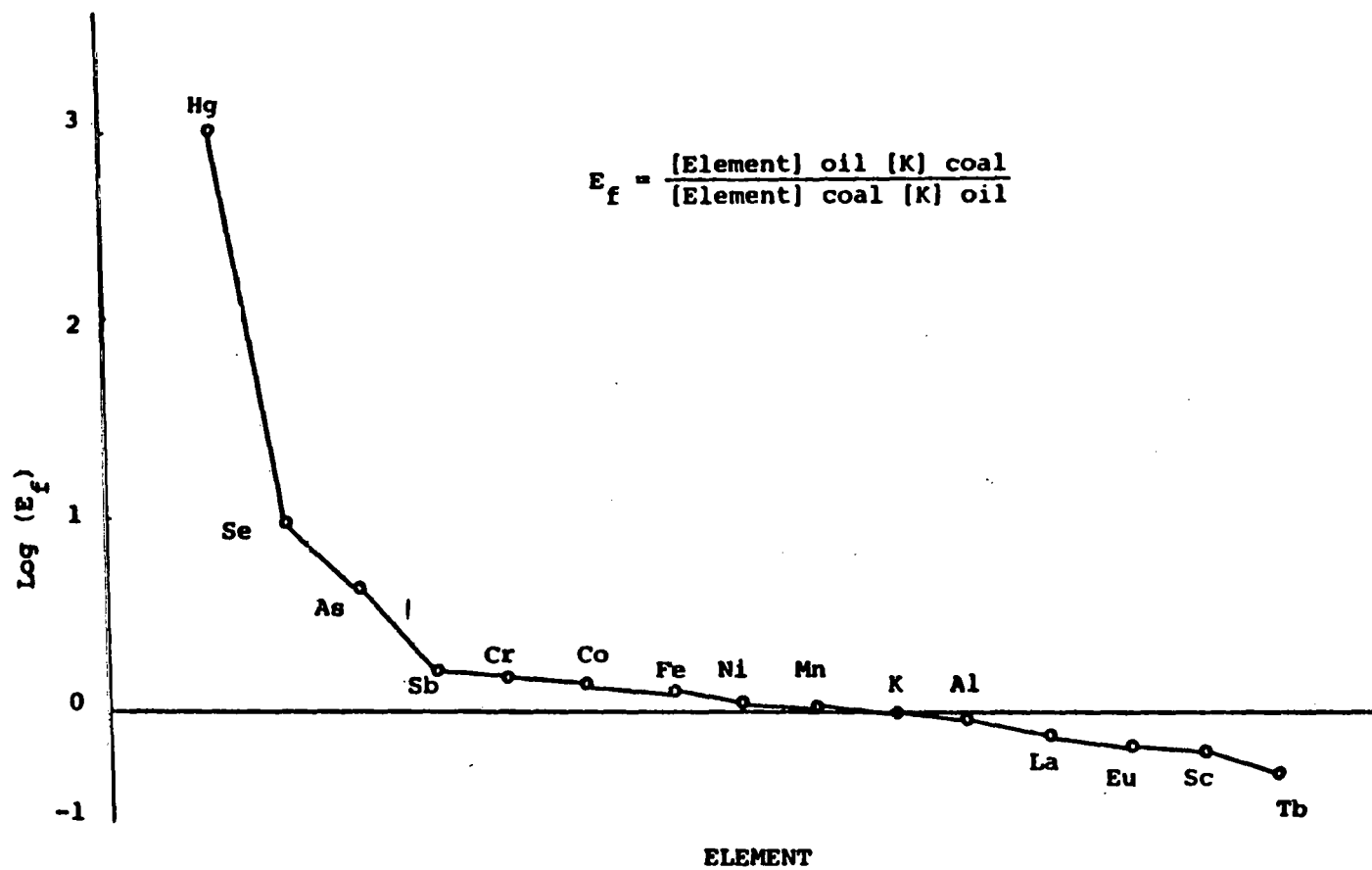
Figure 5.2. Enhancement factors for elements in separator 2 oil

TABLE 5.30

ENHANCEMENT FACTORS FOR ELEMENTS IN TOTAL SOLVENT
ACCUMULATOR OIL IN SRC-II PROCESS (SR-15)

Element (ppm)	Concentration in Coal	Concentration in Total Accumulator Oil	Enhancement** Factor, E_f
As	8.37	0.064	54.4
Sb	0.33	1.85*	39.9
Se	1.66	0.064	274
Hg	0.22	56.6*	1,848
Br	13.1	9.18*	4.99
Ni	6.90	0.034	35.1
Co	2.98	1.35*	3.23
Cr	14.8	0.021	10.1
Fe	18,200	2.43	0.951
Mn	30.6	0.010	2.33
Na	783	0.094	0.855
Cs	930	0.47*	3.62
K	1,600	0.22	1.000
Sc	2.77	0.23*	0.584
Eu	0.22	0.078*	2.49
Sm	0.94	0.052*	0.394
La	6.31	0.90*	1.02
Ga	3.10	0.31*	0.714

*Values in ppb.

**Enhancement factor for element X, $E_f = \dfrac{(X)\ oil\ \cdot\ (K)\ coal}{(X)\ coal\ \cdot\ (K)\ oil}$

TABLE 5.31

ENHANCEMENT FACTORS FOR ELEMENTS IN FILTERED
WATER AND ITS PARTICULATE FROM SEPARATOR
#2 WATER IN SRC-II PROCESS (SR-12)

Element (ppm)	Concentration in coal	Concentration in Separator #2 Water	Enhancement Factor, E_f	Concentration in solid	Enhancement Factor
As	8.4	0.23	202	9.97	10.3
Sb	0.45	1.70*	27.4	0.13	2.59
Se	1.64	0.21	957	6.20	33.2
Hg	196*	0.039	1,440	433	19,385
Ni	4.50	0.024	38.6	10.5	20.5
Co	2.50	1.30*	3.81	0.71	2.47
Cr	14.6	11.3*	5.68	3.87	2.33
Fe	12,900	0.98	0.557	3,020	2.05
K	1,520	0.21	1.000	173	1.000
Sc	2.25	0.77*	2.50	0.17	0.643
Eu	0.18	0.069*	2.80	0.024	1.17
Sm	0.82	1.82*	16.3	0.080	0.858
La	5.89	0.86*	1.07	0.52	0.775
Th	1.63	0.41*	1.86	0.17	0.904
Hf	0.53	0.16*	2.26	0.047	0.784

*Values in ppb.

**Enhancement factor for element X, $E_f = \dfrac{(X)\ water\ \cdot\ (K)\ coal}{(X)\ coal\ \cdot\ (K)\ water}$.

***Enhancement factor for element X, $E_f = \dfrac{(X)\ solid\ \cdot\ (K)\ coal}{(X)\ coal\ \cdot\ (K)\ solid}$.

TABLE 5.32

ENHANCEMENT FACTORS FOR ELEMENTS IN FILTERED
WATER AND ITS PARTICULATE FROM SEPARATOR #3
WATER IN SRC-II PROCESS (SR-12)

Element (ppm)	Concentration in Coal	Concentration in Separator #3 Water	Enhancement Factor, E_f	Concentration in solid	Enhancement Factor, E_f
As	8.40	6.91*	14.4	0.26	3.77
Sb	0.45	0.90*	35.2	0.030	8.04
Se	1.64	0.50	5,376	0.87	64.4
Hg	196*	20.8*	1,860	0.29	178
Ni	4.50	0.028	108	4.04	109
Co	2.50	1.04*	7.29	0.62	30.3
Cr	14.6	0.062	74.9	6.12	50.9
Fe	12,900	1.01	1.37	1,510	14.2
K	1,520	0.087	1.00	12.5	1.00
Sc	2.25	0.24*	1.89	0.020	1.10

*Values in ppb.

**Enhancement factor for element X, $E_f = \dfrac{(X)\ water\ \cdot\ (K)\ coal}{(X(coal\ \cdot\ (K)\ water}$.

***Enhancement factor for element X, $E_f = \dfrac{(X)\ solid\ \cdot\ (K)\ coal}{(X)\ coal\ \cdot\ (K)\ solid}$.
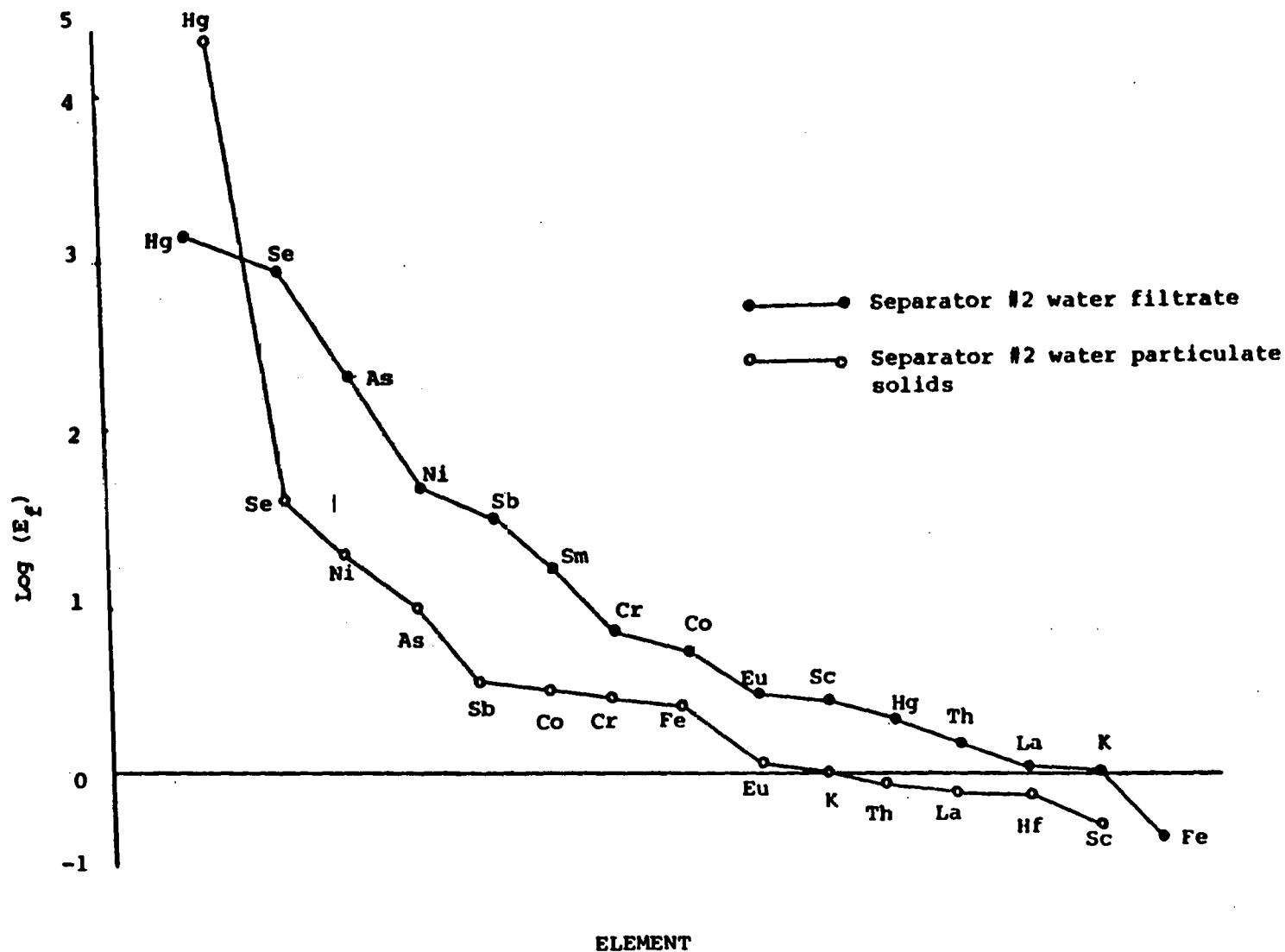
Figure 5.3. Enhancement factors for elements in separator 2 water

concentrations of Hg in separator 2 water (39 ppb in process
water and 433 ppb in solid) were observed than that in separator
3 water (20.8 ppb in water phase and 290 ppb in solid). The
high E_f values for Hg in these water fractions indicate that the
volatile species of Hg were condensed in these two separators'
water tanks under the process conditions. The formation of H_2Se
from PbSe (103) which is more soluble in water than in oil phase
is indicated by the higher E_f of Se in water (957 and 5376 in
separator 2 and 3 waters repectively) than that in separator 2
oil (E_f=15.0) and total accumulator oil (E_f=274). The enhancement
of Se and Hg were also observed in less degree in the process
water from the recycle process water tank in SRC-II mode as shown
in Table 5.33. Three possible mechanisms for the volatization
of Hg in the SRC-II process are shown in Table 5.34. The
second proposed mechanism appears more likely than the first
from previous work on the mechanism of sublimation of HgS (109).
These proposed mechanisms assume that Hg is present in the coal
as a sulfide, HgS (110). The volatilization of organic Hg
species (mechanism 3) cannot be ruled out, particularly if Hg is
bound organically in coal. Thermodynamic data on sublimation of
HgS and As_2S_3 (109) suggest that vapor pressures at 450° C are
similar. But from the data in Tables 5.29 through 5.33 it is
evident that As is much less volatile than Hg and that simple sul-
fide sublimation cannot explain the observed behavior under SRC-
II conditions. The high enhancement factors of Co, Cr and Ni in
separator 2, total accumulator oils in separator 2 and 3 process
waters, and associated particulates may be due either to

TABLE 5.33

ENHANCEMENT FACTORS FOR ELEMENT IN PROCESS WATER AND ITS PARTICULATE IN SRC-II PROCESS (SR-15)

Element	Concentration in Coal (ppm)	Concentration in Process Water (ppb)	Enhancement Factor, E_f*	Concentration in solid (ppm)
As	8.37	39.0	0.201	0.072
Sb	0.33	1.20	0.157	--
Se	1.66	1310	34.1	1.73
Hg	0.22	157	31.1	0.87
Br	13.3	1070	3.53	0.64
Ni	6.90	62.2	0.39	0.50
Co	2.98	2.00	0.029	0.15
Cr	14.8	115	0.336	0.41
Fe	18,200	969	0.002	--
Na	783	356	0.020	--
K	1600	37.0	1.000	--
Sc	2.77	0.39	0.006	0.0076

*Enhancement factor for element X, $E_f = \dfrac{(X)water \cdot (K)coal}{(X)coal \cdot (K)water}$

TABLE 5.34

POSSIBLE MECHANISM FOR Hg VOLATILIZATION IN SRC-II PROCESS

Dissolver Reaction (450-500°C)	Volatile Species	Cool Zone Condensate
(1) $HgS_{(s)}$ ⟶	HgS vap ⟶	HgS solid
(2) $HgS_{(s)} + H_2$ ⟶	$Hg°$ vap $+ H_2S$ ⟶	$Hg_{(s)}$
		⟶ $HgS_{(s)}$
(3) Coal - Hg - Solvent ⟶	R-Hg-R' $\xrightarrow{\quad H_2S \quad}$	$HgS_{(s)}$

corrosion/erosion of high temperature alloy construction materials by hot gases (e.g., H_2S, H_2O, H_2) or may also have resulted from the formation of carbonyls of these elements, either by reaction of CO in product gases with Co, Cr and Ni in coal, or with the dissolver and pipe alloys. If carbonyls are formed, they may subsequently decompose to give the metallic element which reacts with H_2S to form metal sulfides, or form substituted carbonyls with reactive organic species, i.e.

$$NiS_{coal} + H_2 + 4CO \rightleftarrows Ni(CO)_4 + H_2S \rightleftarrows NiS + 4CO + H_2$$

$$Ni_{structural\ materials} + 4CO \rightleftarrows NI(CO)_4$$
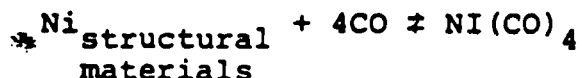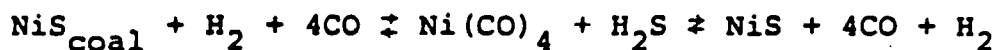
Carbonyls can form a large number of substituted carbonyls with hydrocarbons or may react to give ferrocene type compounds.

Table 5.35 shows some possible volatile forms and organo-metallic species of As, Sb, Se, Hg, Fe, Ni, Co, Cr and Ti that may be produced during SRC-I and SRC-II liquefaction processes. Many of these proposed forms can readily form from either organic or inorganic compounds under the conditions used in the process. The Hg°, $Ni(CO)_4$, $(C_6H_6)_2Cr$ and many other species listed in this Table may be quite stable under the process conditions, or may form at lower temperatures on cooling. Reactions may occur at lower temperatures to form substituted species such as carbonyls, Tables 5.29 to 5.33. In the SRC-II process the volatility order is $Hg > Se > As > Sb$.

TABLE 5.35

POSSIBLE ENVIRONMENTALLY IMPORTANT FORMS OF
SOME TRACE ELEMENTS DURING LIQUEFACTION

Element	Volatile Species	Organic Species
As	AsH_3, $AsCl_3$, $AsBr_3$	$RAsH_2$, RR^1AsH R_3As, $R_4As^+X^-$
Sb	SbH_3, $SbCl_3$, $SbBr_3$	$RSbH_2$, RR^1SbH, R_3Sb
Hg	Hg metal, HgS	R_2Hg, RHg^+X^-
Se	H_2Se, Se^o	$R-Se-R^1$; $R-SeO_3H$
Fe	$Fe(CO)_5$, $Fe_2(CO)_9$	$Fe(C_6H_5)_2(CO)_x$; $Fe(C_5H_5)_2$
Ni	$Ni(CO)_4$	Ni-asphaltene bonds
Cr	$Cr(CO)_6$	$Cr(C_6H_6)(CO)_3$;, $(C_6H_6)_2Cr$
Ti	$TiCl_4$	$Ti(C_5H_5)_2Cl_2$

SOURCE: Filby, Shah, Hunt, Khalil and Sautter (26).

NOTE: R and R^1--aliphatic or aromatic groups.

Comparison of Trace Elements in SRC-I and
SRC-II Products with Other Fuels

In order to evaluate the trace element releases expected
from power generation using coal-derived SRC-I or SRC-II, it is
necessary to compare the trace element levels of these products
with conventional power plant fuels, coal and residual fuel oil.
A comparison of the trace element concentrations of SRC-I (26),
a blend of heavy and middle distillates (1:5.75 ratio by weight)
from the SRC-II process which resembles a residual fuel oil, with
an Illinois No. 6 coal, a residual fuel oil from a relatively low
trace element crude oil (111), and crude shale oil (97) are shown
in Table 5.36. Shale oil values are single determinations while
the residual fuel oil concentrations are means of 13 residual
fuel oils (111). It can be seen that the trace element levels
of SRC-I are much lower than those of coal except for Ti. Also
the SRC-II blend has very low concentrations of trace elements
compared to the residual fuel oil and coal. Both liquefaction
process products were lower in sulfur than the feed coal. The
SRC-I shows an enrichment of Br relative to coal and the Ti con-
tent in SRC-I is much higher than that of the other oils and the
SRC-II blend. For Hg and Fe, the SRC-II product and residual
fuel oil concentrations are similar but much lower than for coal.
The Cr content of SRC-II is higher than crude shale oil and resi-
dual oil and this may be due to the corrosion of the plant con-
struction materials. The concentrations of Na, Ni and V are
higher in residual fuel oil than both SRC products, while As, Br,
Sb, Se, Hg, Cr and Fe are higher in SRC-I than residual oil. It

TABLE 5.36

COMPARISON OF TRACE ELEMENTS IN SRC-I, SRC-II
MATERIALS WITH COAL AND FUEL OIL

Element (ppm)	SRC-I	SRC-II[a]	Illinois coal	Crude shale oil[b]	Residual fuel oil[c]
As	2.10	0.015	16.3	15.6	0.055
Sb	0.136	0.0026	1.10	0.008	0.004
Se	0.122	0.0284	2.52	0.86	0.09
Hg	0.043	0.0034	0.114	0.200	0.004
Br	5.69	0.092	4.14	0.079	0.22
Cl	130	16.9	275	--	40
V	9.51	0.179	29.7	--	87
Ni	1.82	0.099	13.7	0.88	12.5
Co	0.314	0.0030	5.54	0.37	0.32
Cr	4.19	2.57	14.3	0.04	0.070
Fe	0.044	0.0004	2.25	0.003	0.0005
Ti	326	<10	595	<10	<10
S	0.74	0.23	4.34	--	1.1
Na	13.5	0.512	155	19.4	33
Rb	0.21	<0.014	7.69	--	--
Cs	0.02	0.0003	0.83	<0.002	--
K	8.44	0.403	1,790	--	--

[a] Heavy/middle distillate ratio 1:5.75.

[b] Crude shale oil, reference (97).

[c] Residual fuel oil, reference (111).

should be noted that commercially availabel fuel oils show wide ranges of composition (111) as will SRC products from different coals. The As concentration in fuel oil is 4 times its concentration in SRC-II while crude oil and coal As contents are very high. From the viewpoint of toxic trace element concentrations, the SRC-II fuel blend appears to be an excellent substitute for petroleum derived fuel oil and SRC-I appears to be a suitable substitute for coal in coal-fixed power plants. Although the trace element levels in the coal-derived SRC products are lower than in the feed coals, it is difficult to predict their environmental impact on burning since different chemical forms may result in different distributions on fly ash particle size ranges from coal and SRC products.

CHAPTER 6

CONCLUSIONS

Neutron activation analysis is a very sensitive, non-destructive technique for analysis of many elements. This multi-element technique is accurate, precise and involves minimal sample pre-treatment thus avoiding many possible sources of error common in trace elements analysis. The range and scope of INAA methods combined with high resolution Ge(Li) gamma-ray spectroscopy allows complex spectra to be resolved with very few overlapping peaks. Therefore, INAA can be considered an excellent analytical technique for elemental analysis in such difficult and very different matrices encountered in coal conversion processes. The technique is particularly suitable because of the very low concentrations of many of the fractions. This technique has been applied to the simultaneous determination of up to 34 elements comprising major, minor and trace constituents in materials from the Solvent Refined Coal (SRC-I and SRC-II) processes and to the study of the distribution and fate of these elements in the processes. The SRC processes produce fuels with lower sulfur, ash and trace element contents relative to the original coal and thus are desirable power plant fuels. Except for Ti, Br and Cl, the elements V, Ca, Mg, Al, Mn, As, Sb, Se, Hg, Co, Cr, Fe, Na, Rb, Cs, K, Sc, Tb, Eu, Sm, Ce, La, Sr, Ba, Th, Hf, Ta, Ga, Zr and Cu were significantly lower in SRC-I relative to the

feed coal. The Br concentrations in SRC-I were higher than in the feed coal and must be due to some other source of Br not identified in this study. In the SRC-II process the total distillate accumulator (major SRC-II product) has much lower trace element contents than the feed coal and it appears to be an excellent substitute for petroleum-derived residual fuel oil. Except for Hg in the SRC-II process, elemental material balances close well when the major output streams of the processes are considered, assuming that the only contribution to the trace elements input is the coal. The results of this study indicate that the contributions to the overall material balance of the trace elements from the recycle process solvent and hydrogen gas are not significant. Erosion of high temperature alloys by hot gases may be the cause of the high values obtained for some of the Cr, Co and Ni material balances. Formation of carbonyls of these elements (and subsequent incorporation in products) may have resulted either by reaction of CO in product gases with Co, Ni and Cr in coal or with dissolver and pipe alloys. For the environmentally important elements As, Sb and Se, the material balances were satisfactory in both SRC-I and SRC-II processes indicating no significant losses in the processes. In the SRC-I and SRC-II processes, the original distribution of trace element forms in coal could be changed during the dissolution of coal and hydrogenation of the organic polymeric species. Some elements can form either organic or inorganic volatile compounds stable under the conditions used in the process (e.g., Hg°, H_2Se, AsH_3). Most mineral species such as silicates and many sulfides should

not react while other mineral species such as pyrite may react with hydrogen. Enhancement factors E_f, normalized for $K=1.0$, for Hg, Se, As, and Sb in light oil and process water fractions gives evidence for the formation of volatile species of these elements. Although the material balance for Hg in SRC-I process was good, Hg is partially converted to volatile species (5.1% MFC of the total Hg appears in process water) and a solvent soluble form (24.9% MFC in SRC-I). In the SRC-II process, Hg is significantly volatilized and is distributed among oils (particularly separator No. 2 oil), process waters and their particulates (sludges) originated from the overhead streams from the dissolver. No observable pattern correlating Hg loss from the coal with coal type, or process conditions such as H_2 partial pressure, or residence time, can be observed. Also, Hg may be lost in gas streams from the recycle condensate vessel to the desulfurization unit in SRC-II process but there is no evidence for loss in SRC-I mode. The anomalously high elemental content (especially for Hg, Se and As) in solid phase of separator No. 2 oil indicated that the volatile element species may be concentrating in SRC-II sludges and may result in buildup of highly undesirable solid deposits in the liquid-liquid separators. Variation in the depletion of elements (other than Hg, Se, As and Sb) in SRC-I compared to coal may be due to occurrence in different minerals with different particle sizes, formation of organometallic or solvent soluble species or volatile species. Potassium and iron are very efficiently retained in insoluble residues while some other elements may exist in fine grain size minerals or mineral reaction

species which are retained less efficiently on the filters in SRC-I mode. The behavior of Ti in SRC-I process is different from the other elements. The Ti in SRC-I is probably present in both inorganic and organic combination and the organically bound Ti is probably associated with the high molecular weight fraction of SRC-I (the asphaltenes). Process waters concentrate Hg, Se, As, Sb and other volatile elements which are reduced by the treatment process to essentially background levels in effluent waters.

Further study is needed to identify:

1. the chemical species, i.e., organic or inorganic forms of trace elements in coals and coal products,

2. the organometallic species of trace elements in SRC-I and SRC-II processes, particularly Ti species in SRC-I,

3. the volatile species of Hg, Se, As, Sb and other elements in liquefaction processes, especially in fugitive gases and overhead streams,

4. the source of the high Br concentrations in SRC-I process,

5. the distribution of trace elements in distillate oil fractions, i.e., naphtha, middle distillate and heavy distillate fractions and their chemical species in each fraction, and

6. the formation of carbonyls of Co, Ni and Cr from coal or from construction materials.

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APPENDIX A

SRC-I

TRACE ELEMENT DATA FOR EQUILIBRIUM SET 1

TABLE A-1

SRC-I, EQUILIBRIUM SET 1, RAW MATERIALS AND PRODUCTS

Element (ppm)	Raw Coal	Ground Coal	Solvent Refined Coal	Mineral Residue	Sulfur
Ti	546 ± 122	530 ± 55	465 ± 16	2,600 ± 335	<90
V	25.2 ± 1.1	30.1 ± 0.8	4.63 ± 0.08	225 ± 5	8.20 ± 0.10
Ca	633 ± 264	--	72.8 ± 22.3	4,900 ± 800	<600
Mg	858 ± 150	1,160 ± 200	89.0 ± 25.0	5,200 ± 600	<300
Al (%)	1.07 ± 0.02	1.18 ± 0.04	0.020± 0.001	7.47 ± 0.29	--
Cl	286 ± 6	260 ± 7	160 ± 3	988 ± 78	<40
Mn	32.8 ± 0.4	34.0 ± 0.4	20.3 ± 0.2	174 ± 2	8.00 ± 0.31
As	11.6 ± 0.1	12.5 ± 0.1	2.00 ± 0.03	97.6 ± 1.4	<2
Sb	0.98 ± 0.06	0.76 ± 0.04	0.060± 0.009	5.84 ± 0.20	<0.1
Se	2.18 ± 0.19	2.00 ± 0.10	0.12 ± 0.03	14.8 ± 0.5	<1.5
Hg (ppb)	<130	113 ± 14	39.6 ± 4.0	540 ± 70	<160
Br	5.79 ± 0.14	4.56 ± 0.14	7.74 ± 0.10	5.67 ± 1.33	<3
Ni	18.0 ± 4.0	14.9 ± 2.62	<3	89.2 ± 11.3	<28
Co	5.25 ± 0.08	5.88 ± 0.06	0.22 ± 0.01	38.8 ± 0.3	110 ± 1
Fe (%)	2.40 ± 0.12	2.11 ± 0.09	0.030± 0.001	15.5 ± 0.7	<0.1
Na	124 ± 1	137 ± 1	4.23 ± 0.09	1,830 ± 15	3,120 ± 24
Rb	3.57 ± 0.80	<4.0	<0.5	62.2 ± 4.2	<9
Cs	<0.2	0.75 ± 0.03	0.020± 0.006	4.93 ± 0.13	<0.2
K	1,260 ± 17	1,550 ± 20	4.72 ± 0.95	10,200 ± 185	179 ± 7
Sc	2.10 ± 0.01	2.59 ± 0.01	0.570± 0.002	14.3 ± 0.1	<0.02
Tb	0.43 ± 0.02	0.39 ± 0.01	0.045± 0.003	2.41 ± 0.06	<0.1
Eu	0.26 ± 0.01	0.26 ± 0.01	0.055± 0.002	1.41 ± 0.02	<0.01
Sm	2.59 ± 0.02	2.62 ± 0.02	0.290± 0.004	13.1 ± 0.3	0.61 ± 0.15
Ce	24.2 ± 0.2	20.8 ± 0.1	0.45 ± 0.02	139 ± 1	<2
La	7.52 ± 0.09	7.55 ± 0.11	0.13 ± 0.01	52.3 ± 1.0	1.80 ± 0.31
Cr	10.4 ± 0.3	13.7 ± 0.2	1.64 ± 0.04	117 ± 1	<2

Table A-1, continued

Element (ppm)	Raw Coal	Ground Coal	Solvent Refined Coal	Mineral Residue	Sulfur
Sr	97.2 ± 19.4	88.6 ± 12.4	<6.0	808 ± 70	<45
Ba	31.0 ± 8.1	53.0 ± 7.7	5.75 ± 1.23	259 ± 32	<39
Th	1.51 ± 0.03	2.00 ± 0.02	0.220± 0.004	11.8 ± 0.1	<0.2
Hf	0.34 ± 0.03	0.51 ± 0.02	0.084± 0.006	2.73 ± 0.08	<0.2
Ta	0.10 ± 0.02	0.14 ± 0.02	0.046± 0.005	0.71 ± 0.09	<0.2
Ga	2.69 ± 0.07	3.56 ± 0.09	1.79 ± 0.04	17.7 ± 0.8	<1.5
Zr	66.5 ± 11.1	62.9 ± 7.9	16.0 ± 3.3	442 ± 42	<61
Cu	22.4 ± 2.2	19.9 ± 1.6	2.07 ± 0.20	176 ± 13	<1

TABLE A-2

SRC-I, EQUILIBRIUM SET 1, LAB PREPARED SAMPLES

Element (ppm)	Wet Filter Cake	Pyridine Insolubles	Ash of Pyridine Insolubles	Vacuum Bottoms
Ti	1,490 ± 162	3,350 ± 409	4,470 ± 417	450 ± 10
V	141 ± 4	195 ± 5	376 ± 8	4.00 ± 0.07
Ca	3,020 ± 568	6,300 ± 1,000	10,500 ± 1,300	63.7 ± 24.5
Mg	4,350 ± 6	4,000 ± 800	7,490 ± 1,160	56.2 ± 28.5
Al (%)	5.50 ± 0.52	7.72 ± 0.75	20.2 ± 0.75	0.043 ± 0.001
Cl	1,640 ± 267	760 ± 67	<400	17.8 ± 1.6
Mn	140 ± 1	185 ± 2	254 ± 2	7.20 ± 0.11
As	62.1 ± 1.0	85.7 ± 1.6	119 ± 2	1.30 ± 0.03
Sb	5.35 ± 0.24	7.21 ± 0.29	11.7 ± 0.4	<0.2
Se	11.3 ± 0.8	16.5 ± 1.1	<4	<0.2
Hg (ppb)	346 ± 30	508 ± 65	-	<90
Br	20.7 ± 1.0	12.0 ± 1.6	<7	1.15 ± 0.05
Ni	82.4 ± 18.2	142 ± 22	-	<3
Co	26.5 ± 0.3	40.7 ± 0.4	61.5 ± 0.6	0.29 ± 0.01
Cr	69.2 ± 1.3	106 ± 2	147 ± 2	1.34 ± 0.09
Fe (%)	11.7 ± 0.6	16.8 ± 0.8	22.3 ± 1.1	0.011 ± 0.001
Na	623 ± 6	1,020 ± 11	1,720 ± 16	23.3 ± 0.2
Rb	37.1 ± 4.2	66.5 ± 5.5	107 ± 8	<0.5
Cs	3.20 ± 0.16	5.08 ± 0.22	7.54 ± 0.30	<0.04
K	6,660 ± 140	11,100 ± 255	17,900 ± 344	<6
Sc	9.26 ± 0.04	14.8 ± 0.1	25.5 ± 0.1	0.820 ± 0.004
Tb	1.34 ± 0.08	2.06 ± 0.09	4.07 ± 0.13	0.084 ± 0.005
Eu	0.96 ± 0.03	1.48 ± 0.03	2.42 ± 0.05	0.055 ± 0.002
Sm	8.16 ± 0.16	16.9 ± 0.3	29.2 ± 0.53	0.370 ± 0.004
Ce	102 ± 1	156 ± 1	249 ± 2	0.87 ± 0.05
La	35.2 ± 0.7	59.8 ± 1.30	104 ± 2	0.14 ± 0.01
Sr	453 ± 60	456 ± 78	646 ± 89	<6
Ba	185 ± 37	347 ± 75	524 ± 79	6.53 ± 1.92
Th	7.70 ± 0.11	12.8 ± 0.1	21.1 ± 0.2	0.45 ± 0.01
Hf	2.20 ± 0.12	3.30 ± 0.15	4.40 ± 0.22	0.16 ± 0.01
Ta	0.42 ± 0.09	0.71 ± 0.12	1.02 ± 0.16	0.066 ± 0.007
Ga	11.3 ± 0.6	19.4 ± 1.2	31.9 ± 1.3	1.15 ± 0.05
Zr	246 ± 45	500 ± 73	714 ± 100	<8
Cu	138 ± 7	189 ± 10	291 ± 13	1.42 ± 0.10

TABLE A-3

SRC-I, EQUILIBRIUM SET 1, PLANT SOLVENTS AND AQUEOUS SAMPLES

Element (ppb)	Light Oil	Process Recycle Solvent	Wash Solvent	Recycle Process Water	Effluent Water	Hamer Marsh Water
Tl(ppm)	2.04 ± 0.53	19.1 1.2	0.92 ± 0.31	<0.2	<0.08	<0.06
V	50.0 ± 3.0	450 ± 10	52.0 ± 3.0	<2	20.0 ± 1.0	10.0 ± 0.3
Ca(ppm)	<9	<8	<5	<1	4.40 0.30	4.60 0.30
Mg(ppm)	<10	<10	<7	<2	1.90 0.30	1.40 0.30
Al(ppm)	50.0 ± 1.0	43.9 ± 0.8	11.6 ± 0.5	0.54 0.02	0.25 ± 0.01	0.200 0.004
Cl(ppm)	16.9 ± 0.2	127 ± 1	92.2 ± 0.4	32.4 ± 0.4	1.70 0.05	2.60 0.04
Mn(ppm)	0.18 ± 0.01	2.09 ± 0.2	<0.2	0.020 0.002	0.010 0.001	0.012 0.001
As	11.0 ± 0.3	240 ± 2	11.0 0.3	6.30 0.12	<1	<1
Sb	<0.4	8.20 0.38	<0.4	0.66 0.02	2.00 0.03	2.60 0.04
Se	51.6 ± 1.1	24.0 1.3	14.4 0.8	159 2	1.20 0.04	0.90 0.03
Hg	18.5 ± 0.8	1.45 0.20	10.5 0.5	106 3	3.20 0.08	3.00 0.03
Br	15.0 ± 1.0	1000 6	20.0 1.0	15.6 0.3	31.8 0.6	22.9 0.5
Ni	<30	400 30	<30	4.00 0.50	13.0 0.5	12.0 0.5
Co	<3	40.7 0.4	1.43 0.11	0.20 0.01	0.41 ± 0.01	0.34 0.02
Cr	37.3 ± 1.3	3,590 10	41.3 1.1	7.40 ± 0.11	153 1	137 1
Fe(ppm)	2.90 ± 0.09	211 ± 4	11.2 0.3	0.30 0.01	1.25 0.02	0.82 0.02
Na(ppm)	0.600 ± 0.004	0.500 0.004	0.450 0.004	0.700 0.003	8.30 0.04	6.70 0.03
Rb	<10	20.0 5.0	<10	0.78 0.20	0.52 0.13	0.31 0.08
Cs	1.06 ± 0.12	<1.2	0.91 0.09	0.040 0.004	0.022 0.004	0.030 0.003
K (ppm)	<1	0.25 0.05	<1	0.20 0.02	1.26 0.11	0.93 0.07
Sc	0.15 ± 0.01	32.8 0.1	0.19 0.01	0.130 0.001	0.010 0.001	0.020 0.001
Tb	<0.13	3.75 0.15	<0.13	0.010 0.002	0.010 0.002	<0.005
Eu	<0.001	<0.001	<0.001	0.010 0.002	0.008 0.003	0.006 0.001
Sm	<10	20.0 1.0	<10	0.080 0.010	<0.06	<0.06
Ce	<4	<4	<3	<0.2	<0.2	1.50 0.04
La	<1	10.0 0.6	<1	0.27 0.05	<0.5	<0.5
Sr	<600	<200	740 30	<10	40.0 2.0	<10
Ba	<100	1,140 40	<70	<20	<40	<40
Th	<1	12.0 0.1	<1	0.050 0.006	<0.01	<0.01
Hf	<1	3.00 0.10	<1	0.020 ± 0.005	<0.01	0.010 0.003
Ta	<0.4	2.53 0.20	<0.3	0.020 0.004	0.010 0.003	<0.02
Ga	<100	60.0 1.0	<100	<1	<4	<4
Zr	70.0 20.0	710 90	<100	20.0 ± 1.0	40.0 2.0	60.0 2.0
Cu	30.0 1.0	680 4	30.0 1.0	<12	<10	<10

TABLE A-4

SRC-I, EQUILIBRIUM TEST 1, F... RAID MATERIALS

Element (ppm)	Celite-545 basecoat	Fibra Flo 11C basecoat	Celite 6000	Speed Plus	Speedex
Ti	1,540 ± 225	1,520 ± 295	1,450 ± 246	--	750 ± 250
V	158 ± 4	197 ± 5	448 ± 5	--	391 ± 4
Ca (%)	0.35 ± 0.09	0.37 ± 0.09	3.55 ± 0.18	--	2.31 ± 0.18
Mg (%)	0.64 ± 0.12	1.43 ± 0.14	0.47 ± 0.08	--	0.34 ± 0.10
Al (%)	2.83 ± 0.10	2.98 ± 0.11	2.61 ± 0.05	--	3.45 ± 0.11
Cl	--	--	--	--	202 ± 75
Mn	72.1 ± 3.3	91.5 ± 3.1	57.9 ± 2.5	50.5 ± 2.3	87.3 ± 2.0
As	<17	<25	<20	<20	<18
Sb	1.57 ± 0.0	1.74 ± 0.06	3.0 ± 0.06	2.73 ± 0.06	2.73 ± 0.09
Se	0.78 ± 0.12	1.62 ± 0.13	2.11 ± 0.10	0.60 ± 0.10	--
Hg (ppb)	--	--	--	272 ± 40	--
Br	<30	<30	<30	<30	<30
Ni	29.6 ± 2.1	146 ± 15	77.2 ± 2.5	73.0 ± 2.5	71.9 ± 4.4
Co	2.82 ± 0.03	8.43 ± 0.08	2.92 ± 0.03	3.47 ± 0.04	2.81 ± 0.04
Cr	67.1 ± 0.5	167 ± 1	106 ± 1	108 ± 1	107 ± 1
Fe (%)	1.20 ± 0.05	1.31 ± 0.06	1.10 ± 0.05	1.13 ± 0.05	1.24 ± 0.06
Na (%)	3.12 ± 0.02	3.21 ± 0.03	2.47 ± 0.02	2.28 ± 0.02	2.58 ± 0.02
Rb	28.0 ± 0.7	34.5 ± 1.2	28.7 ± 0.8	20.8 ± 0.6	20.6 ± 1.0
Cs	1.80 ± 0.03	1.90 ± 0.04	1.58 ± 0.02	1.45 ± 0.02	1.48 ± 0.05
K	5,670 ± 700	7,090 ± 980	5,980 ± 764	2,260 ± 478	4,460 ± 585
Sc	4.51 ± 0.01	4.51 ± 0.02	3.51 ± 0.01	4.40 ± 0.01	3.82 ± 0.02
Tb	0.41 ± 0.01	0.28 ± 0.02	0.34 ± 0.01	0.41 ± 0.01	0.39 ± 0.02
Eu	0.32 ± 0.01	0.22 ± 0.01	0.34 ± 0.01	0.22 ± 0.004	0.24 ± 0.04
Sm	4.69 ± 0.61	2.04 ± 0.36	<2	<2	4.56 ± 0.61
Ce	23.1 ± 0.1	25.6 ± 0.2	21.1 ± 0.1	25.4 ± 0.1	24.0 ± 0.2
La	4.91 ± 1.44	16.5 ± 3.1	<7	11.5 ± 2.3	9.46 ± 2.10
Sr	88.1 ± 11.0	--	258 ± 10	170 ± 10	--
Ba	296 ± 8	293 ± 12	415 ± 8	318 ± 7	301 ± 13
Th	4.74 ± 0.02	3.86 ± 0.03	3.20 ± 0.02	4.05 ± 0.02	3.84 ± 0.03
Hf	1.30 ± 0.02	1.28 ± 0.03	1.11 ± 0.02	1.10 ± 0.02	1.06 ± 0.03
Ta	0.32 ± 0.02	0.35 ± 0.03	0.28 ± 0.02	0.27 ± 0.02	0.25 ± 0.03
Ga	<25	<25	<25	<25	<25
Zr	129 ± 8	144 ± 15	203 ± 8	210 ± 10	161 ± 15
Cu	114 ± 28	139 ± 18	85.6 ± 13.2	104 ± 23	148 ± 27

APPENDIX B

SRC-II

TRACE ELEMENT DATA FOR EQUILIBRIUM SET SR-15

TABLE B-1

SRC-II, EQUILIBRIUM SET SR-15, RAW MATERIAL AND PRODUCTS

Element (ppm)	Ground Coal Zero hr	Ground Coal 4 hr	Ground Coal 8 hr	Ground Coal 12 hr
Ti	735 ± 69	660 ± 54	808 ± 52	751 ± 53
V	18.8 ± 1.1	18.4 ± 1.3	17.7 ± 1.1	18.6 ± 1.2
Ca	6,120 ± 323	6,710 ± 390	6,650 ± 376	4,850 ± 292
Mg	1,670 ± 224	931 ± 153	1,280 ± 176	1,680 ± 142
S (%)	2.71 ± 0.96	<2.8	<2.5	2.26 ± 0.90
Al (%)	1.29 ± 0.03	1.33 ± 0.03	1.31 ± 0.03	1.38 ± 0.03
Cl	1,010 ± 26	966 ± 17	154 ± 19	861 ± 20
Mn	35.0 ± 0.5	33.4 ± 0.4	33.7 ± 0.4	30.8 ± 0.4
I	3.7 ± 1.00	0.89 ± 0.22	1.46 ± 0.37	<1.7
As	7.24 ± 0.07	8.86 ± 0.08	8.13 ± 0.09	8.60 ± 0.09
Sb	0.36 ± 0.05	0.52 ± 0.05	0.33 ± 0.05	0.47 ± 0.05
Se	1.60 ± 0.02	1.47 ± 0.03	1.27 ± 0.02	1.04 ± 0.02
Hg (ppb)	176 ± 44	184 ± 46	140 ± 36	92.0 ± 30.0
Br	13.3 ± 0.2	13.2 ± 0.2	13.2 ± 0.2	12.1 ± 0.2
Ni	8.6 ± 1.00	8.30 ± 1.30	8.20 ± 0.90	6.20 ± 0.80
Co	3.03 ± 0.02	2.91 ± 0.02	2.81 ± 0.02	2.05 ± 0.01
Cr	18.7 ± 0.1	17.6 ± 0.1	16.6 ± 0.1	11.9 ± 0.1
Fe (%)	2.22 ± 0.02	2.04 ± 0.01	1.74 ± 0.01	1.36 ± 0.01
Na	784 <4	820 ± 4	771 ± 4	771 ± 4
Rb	25.8 ± 0.6	19.9 ± 0.7	18.6 ± 0.4	15.8 ± 0.4
Cs	0.87 ± 0.01	0.91 ± 0.01	0.86 ± 0.01	0.64 ± 0.01
K	1,500 ± 22	1,710 ± 25	1,600 ± 27	1,450 ± 25
Sc	3.36 ± 0.01	3.18 ± 0.01	3.04 ± 0.01	2.19 ± 0.01
Tb	0.27 ± 0.01	0.18 ± 0.01	0.18 ± 0.01	0.11 ± 0.01
Eu	1.04 ± 0.01	1.11 ± 0.01	1.20 ± 0.01	1.01 ± 0.01
Sm	1.04 ± 0.01	1.11 ± 0.01	1.20 ± 0.01	1.01 ± 0.01
Ce	14.3 ± 0.1	14.3 ± 0.1	13.5 ± 0.1	9.40 ± 0.10
La	5.91 ± 0.08	6.59 ± 0.09	6.41 ± 0.10	6.05 ± 0.09
Sr	144 ± 3	145 ± 4	144 ± 3	105 ± 3
Ba	112 ± 3	115 ± 4	104 ± 3	89.0 ± 3.0
Th	2.11 ± 0.01	2.14 ± 0.01	2.02 ± 0.01	1.45 ± 0.01
U	0.70 ± 0.05	0.57 ± 0.07	0.36 ± 0.03	0.46 ± 0.04
Hf	0.70 ± 0.01	0.69 ± 0.01	0.67 ± 0.01	0.48 ± 0.01
Ta	0.19 ± 0.01	0.19 ± 0.01	0.19 ± 0.01	0.13 ± 0.01
Ga	4.43 ± 0.40	3.31 ± 0.34	4.04 ± 0.49	3.92 ± 0.44
Zr	24.5 ± 2.6	32.1 ± 3.8	31.2 ± 3.0	11.2 ± 1.8
Cu		<2		1.05 ± 0.00
Zn	16.4 ± 0.2	19.6 ± 0.3	20.7 ± 0.2	<0.5
Ag	<0.1	<0.2	<0.1	<0.1
Au (ppb)	<8	<8	<10	<8

Ground Coal 16 hrs	Ground Coal 20 hrs	Ground Coal 24 hrs composite	Vacuum Bottom 24 hrs composite
703 ± 51	624 ± 52	822 ± 67	1,460 ± 97
17.5 ± 1.1	19.1 ± 0.9	19.1 ± 1.2	37.0 ± 1.5
5,710 ± 318	5,540 ± 278	6,820 ± 326	11,500 ± 545
1,610 ± 165	1,170 ± 184	1,430 ± 185	3,000 ± 277
3.89 ± 0.85	4.01 ± 0.82	2.86 ± 0.71	<4.3
1.27 ± 0.03	1.30 ± 0.01	1.31 ± 0.03	2.73 ± 0.07
862 ± 24	770 ± 10	840 ± 18	1,620 ± 39
35.4 ± 0.5	30.6 ± 0.2	30.2 ± 0.4	72.9 ± 0.8
<2.9	<1.3	1.30 ± 0.50	3.80 ± 1.13
7.60 ± 0.09	7.32 ± 0.08	7.40 ± 0.08	14.1 ± 0.1
0.44 ± 0.05	0.32 ± 0.04	0.43 ± 0.05	0.82 ± 0.05
1.39 ± 0.05	1.24 ± 0.02	1.33 ± 0.03	1.96 ± 0.03
164 ± 44	128 ± 39	263 ± 46	41.0 ± 10.0
13.4 ± 0.2	12.1 ± 0.2	12.2 ± 0.2	23.7 ± 0.2
4.5 ± 1.20	7.50 ± 0.8	11.1 ± 1.5	13.7 ± 1.2
2.96 ± 0.02	2.24 ± 0.01	2.60 ± 0.02	4.23 ± 0.02
14.0 ± 0.1	13.9 ± 0.1	15.7 ± 0.1	26.5 ± 0.1
1.49 ± 0.01	1.44 ± 0.01	1.82 ± 0.01	2.65 ± 0.02
806 ± 4	787 ± 4	747 ± 4	1,390 ± 6
18.1 ± 0.8	15.7 ± 0.5	14.3 ± 0.6	27.8 ± 0.8
0.91 ± 0.02	0.68 ± 0.01	0.78 ± 0.01	1.24 ± 0.01
1,710 ± 31	1,540 ± 27	1,460 ± 28	2,920 ± 44
2.50 ± 0.01	2.41 ± 0.01	2.78 ± 0.01	4.42 ± 0.01
0.23 ± 0.01	0.16 ± 0.01	0.17 ± 0.01	0.32 ± 0.01
0.21 ± 0.01	0.18 ± 0.01	0.20 ± 0.01	0.34 ± 0.01
1.11 ± 0.01	1.07 ± 0.01	1.02 ± 0.01	1.78 ± 0.01
13.7 ± 0.1	10.0 ± 0.1	12.3 ± 0.1	18.0 ± 0.1
6.39 ± 0.10	5.69 ± 0.08	5.72 ± 0.09	11.3 ± 0.1
141 ± 5	108 ± 3	134 ± 4	215 ± 4
94.0 ± 8.0	92.0 ± 4.0	94.0 ± 6.0	158 ± 6
1.91 ± 0.01	1.56 ± 0.01	1.90 ± 0.01	2.86 ± 0.01
0.70 ± 0.09	0.51 ± 0.06	0.72 ± 0.11	1.01 ± 0.09
0.59 ± 0.01	0.57 ± 0.01	0.66 ± 0.01	0.99 ± 0.01
0.18 ± 0.01	0.14 ± 0.01	0.15 ± 0.01	0.26 ± 0.01
3.04 ± 0.42	2.78 ± 0.46	3.31 ± 0.39	5.96 ± 0.59
17.9 ± 3.7	20.4 ± 1.9	23.6 ± 3.8	28.0 ± 3.7
2.13 ± 0.005	1.16 ± 0.003	3.31 ± 0.01	0.714 ± 0.002
<1.4	<0.5	16.3 ± 0.2	39.9 ± 0.3
<0.1	<0.1	<0.1	<0.1
<10	<8	<8	<8

TABLE B-2

SRC-II, EQUILIBRIUM SET SR-15, PLANT OILS

Element (ppb)	Oil From Separator #2	Oil From Separator #3	Oil From Recycle Process Water Tank	Total Accumulator Oil
Ti(ppm)	12.8 ± 1.5	1.87 ± 0.36	<1	<1.4
V(ppm)	0.34 ± 0.02	0.005 ± 0.001	<0.004	<0.006
Ca(ppm)	57.0 ± 7.0	<9	131 ± 7	98.0 ± 7.0
Mg(ppm)	22.0 ± 5.9	<10	<4	<5.6
S (%)	0.37 ± 0.04	0.58 ± 0.04	<0.03	<0.05
Al(ppm)	225 ± 3	0.22 ± 0.20	<0.2	<0.5
Cl(ppm)	12.5 ± 1.0	4.39 ± 0.61	0.53 ± 0.10	0.54 ± 0.11
Mn(ppm)	1.13 ± 0.02	<0.006	<0.004	0.010 ± 0.003
I (ppm)	<0.1	<0.03	<0.02	<0.03
As	273 ± 2	156 ± 1	79.0 ± 1.0	64.0 ± 1.0
Sb	10.8 ± 0.7	<0.5	0.40 ± 0.11	1.85 ± 0.19
Se	544 ± 4	45.0 ± 1.0	62.0 ± 1.0	64.0 ± 1.0
Hg	4,740 ± 178	14.1 ± 1.1	15.3 ± 1.4	56.6 ± 2.5
Br	84.0 ± 2.0	12.9 ± 0.5	9.67 ± 0.48	9.18 ± 0.48
Ni	656 ± 59	33.0 ± 8.0	<30	34.0 ± 8.0
Co	77.8 ± 0.8	0.94 ± 0.08	0.87 ± 0.07	1.35 ± 0.07
Cr	514 ± 4	11.4 ± 1.1	19.8 ± 1.0	21.0 ± 0.8
Fe (ppm)	514 ± 4	0.11 ± 0.03	0.53 ± 0.04	2.43 ± 0.07
Na(ppm)	12.2 ± 0.1	0.036 ± 0.001	0.066 ± 0.001	0.095 ± 0.001
Rb	455 ± 30	<8	<7	<7
Cs	16.1 ± 0.5	<0.3	<0.3	0.47 ± 0.07
K(ppm)	30.8 ± 0.3	<0.02	0.062 ± 0.012	0.22 ± 0.02
Sc	37.6 ± 0.1	<0.02	0.070 ± 0.005	0.23 ± 0.01
Tb	0.60 ± 0.10	<0.06	<0.06	<0.06
Eu	3.49 ± 0.14	0.14 ± 0.03	0.071 ± 0.018	0.078 ± 0.017
Sm	42.0 ± 0.2	<0.07	<0.0	0.052 ± 0.012
Ce	299 ± 3	<4.9	<4.7	<4.3
La	106 ± 1	<0.2	<0.3	0.90 ± 0.13
Sr	1,830 ± 148	<135	<132	<118
Ba	1,950 ± 145	<144	<143	82 ± 23
Th	28.1 ± 0.3	<0.4	<0.05	<0.3
U	8.73 ± 1.58	<1.4	<1.4	<1.5
Hf	9.56 ± 0.28	<0.3	<0.3	<0.3
Ta	2.14 ± 0.23	<0.3	<0.2	<0.2
Ga	31.8 ± 1.2	<0.4	<0.4	0.31 ± 0.09
Zr	410 ± 112	-	-	-
Cu	287 ± 36	3.12 ± 0.36	3.21 ± 0.36	5.88 ± 0.47
Zn	1,630 ± 21	27 ± 3	27 ± 2	21 ± 2
Ag	<5.4	<0.8	<0.8	<0.7
Au	<0.1	0.032 ± 0.008	0.24 ± 0.01	0.078 ± 0.007

TABLE B-3

SRC-II, EQUILIBRIUM SET SR-15, AQUEOUS SAMPLES

Element (ppb)	Effluent Water	Water From Separator No (3)	Water from Recycle Process Watertank	Water Charge to Reactivator
Ti (ppm)	<0.4	<4.4	<3	<0.8
V (ppm)	<0.1	<0.09	<0.05	<0.1
Ca (ppm)	12.7 ± 0.9	<10	<8	13.9 ± 1.5
Mg (ppm)	<3.6	<21	<18	<7
S (%)	<0.01	0.55 ± 0.07	0.39 ± 0.04	<0.02
Al (ppm)	<0.2	<13	<5	<1.5
Cl (ppm)	<4.4	292 ± 15	305 ± 15	8.43 ± 0.44
Mn (ppm)	<0.02	<0.01	<0.03	<0.01
I (ppm)	<0.02	<0.13	<0.1	<0.03
As	<6.3	16.1± 0.4	39.0 ± 0.5	<6.4
Sb	0.33 ± 0.03	0.49 ± 0.06	1.20 ± 0.08	0.79 ± 0.04
Se	0.34 ± 0.04	1,040 ± 10	1,310 ± 10	3.88 ± 0.06
Hg	0.30 ± 0.01	19.1 ± 0.5	157 ± 3	0.40 ± 0.01
Br	36.7 ± 2.1	1,280 ± 6	1,070 ± 5	52.9 ± 2.8
Ni	14.0 ± 1.3	32.3 ± 2.3	62.2 ± 2.8	3.96 ± 1.00
Co	0.53 ± 0.02	1.29 ± 0.03	2.00 ± 0.04	0.68 ± 0.02
Cr	<5	105 ± 1.6	115 ± 2	<7
Fe (ppm)	0.62 ± 0.02	0.96 ± 0.04	0.97 ± 0.04	0.59 ± 0.01
Na (ppm)	42.7 ± 4.2	0.380 ± 0.003	0.356 ± 0.003	61.5 ± 6.0
Rb	1.31 ± 0.32	<4.3	<5	<1.8
Cs	<0.09	0.17 ± 0.02	0.13 ± 0.02	<0.1
K (ppm)	2.26 ± 0.65	0.039 ± 0.001	0.037 ± 0.002	5.20 ± 1.18
Sc	0.248 ± 0.002	0.24 ± 0.0	0.39 ± 0.01	0.252 ± 0.002
Tb	0.020 ± 0.006	<0.03	<0.03	<0.02
Eu	<0.05	0.044 ± 0.005 —	0.045 ± 0.004	<0.05
Sm	0.17 ± 0.04	<0.1	<0.1	<0.2
Ce	0.78 ± 0.04	7.59 ± 0.31	<2	1.08 ± 0.06
La	<3	1.31 ± 0.20	0.041 ± 0.007	<3
Sr	<13	<23	<32	67.2 ± 3.3
Ba	19.3 ± 4.4	<79	<110	<30
Th	0.17 ± 0.01	0.24 ± 0.02	0.25 ± 0.03	0.21 ± 0.01
U	<0.5	<1	<1.3	0.82 ± 0.19
Hf	0.062 ± 0.008	0.038 ± 0.0-1	0.076 ± 0.015	0.044 ± 0.006
Ta	<0.04	<0.05	<0.04	<0.03
Ga	<22	2.11 ± 0.51	<2	<30
Zr	-	-	-	<13
Cu	<4	13.6 ± 1	18.2 ± 1	<6
Zn	117 ± 1	24.5 ± 0.9	91.5 ± 3.0	<0.9
Ag	<0.4	<0.1	<0.1	<0.1
Au	0.084 ± 0.019	<0.05	<0.05	<0.07

TABLE B-4

SRC-II, EQUILIBRIUM SET SR-15, WATER PARTICULATE SAMPLES

Element (ppm)	Effluent Water	Solids	Separator #3 Water	Solids	Recycle Process Water	Solids	Water Charge to Reactivator	Solids
As	0.048	0.007	0.086	0.010	0.072	0.008	1.40	0.03
Sb	0.013	0.06	0.02		0.01		0.70	0.09
Se	0.053	0.005	29.4	0.4	1.73	0.03	1.25	0.03
Hg	0.20	0.01	1		0.87	0.02	5.76	0.11
Br	6.98	0.07	0.78	0.09	0.64	0.07	3.66	0.16
Ni	3.11	0.18	3.38	0.98	0.50	0.11	2.82	0.41
Co	0.025	0.002	0.48	0.01	0.15	0.01	1.17	0.02
Cr	0.30	0.01	3.93	0.08	0.41	0.03	11.4	0.2
Fe	100	2	1,290	418	176		2,120	675
Na	46.5	1.1	46		32		294	3
Rb		0.2	1.4		0.3		2.11	0.18
Cs		0.01	0.04		0.01		0.12	0.01
K		11	8		5		304	13
Sc(ppb)	4.22	0.11	10.6	0.7	7.55	0.17	375	2
Tb		0.002	0.02		0.004		0.024	0.002
Eu(ppb)		3	4.96	1.86	8		21.3	1.8
Sm(ppb)	1.84	0.32	10		6.36	1.67	196	4
Ce	0.038	0.004	0.18	0.03	0.039	0.012	1.50	0.02
La	0.017	0.002	0.04		0.04		0.76	0.04
Sr		1.3	10		2.6		8	
Ba		2.3	11.3	3.1	3.5		11.4	1.7
Th (ppb)	5.19	0.57	12.4	2.2	7		454	3
U	—	0.04	0.058	0.017	0.05		0.089	0.025
Hf		0.003	—		—		0.094	0.004
Ta		0.004	26.0	2.8	0.02		0.2	
Ga		0.09	0.09		0.06		1.48	0.06
Zr	—		—		—		4.34	1.02
Cu	4.82	0.52	8		3.7		53.3	0.8
Zn	6.80	1.36	1		2.6		286	7
Ag	0.0024	0.0008	0.63	0.01	0.028	0.002	0.14	0.01
Au(ppb)		1.3	2		2		6	