TRACE ELEMENTS IN THE SOLVENT REFINED COAL PROCESS

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Abstract

Results are presented of a study of the distribution and fate of 34 trace elements in the Solvent Refined Coal Process Pilot Plant located at Fort Lewis, Washington and operated by the Pittsburg & Midway Coal Mining Co. under contract with the U.S. Energy Research and Development Administration. Neutron activation analysis was used to determine Ti, V, Ca, Mg, Al, Cl, Mn, As, Sb, Se, Hg, Br, Co, Ni, Cr, Fe, Na, Rb, Cs, K, Sc, Tb, Eu, Sm, Ce, La, Sr, Ba, Th, Hf, Ta, Ga, Zr, and Cu in feed coals, process solvent, Solvent Refined Coal (SRC-I) mineral residues, wet filter cake, sulfur, by-product solvents, process and effluent waters and by-product sulfur. A materials balance or budget was calculated for each element from the concentration data and the yields of each process fraction in the SRC process. The SRC-I and insoluble residue account for more than 90% of the input of each element, with other process fractions contributing little to the trace element balance. Except for Cl, Br, and Ti, each element was substantially lower in the SRC-I compared to the original feed coal. Two separate sets of samples were taken when the pilot plant had operated continuously for 7 days and composite samples were collected for each process fraction over a 24-hour period. The materials balance for each element (averaged for the two data sets) expressed as a percentage of the elemental input were: Ti (163), V (139), Ca (146), Mg (71), Al (97), Cl (84), Mn (136), As (106), Sb (127), Se (103), Hg (104), Br (159), Ni (133), Co (122), Cr (117), Fe (109), Na (127), Rb (119), K (100), Cs (97), Sc (120), Tb (112), Eu (100), Sm (108), Ce (110), La (108), Ba (108), Th (112), Hf (121), Ta (114), Ga (98), Zr (115), and Cu (132). The contents of all trace metals, including Hg, in plant effluent waters showed little variation from background level.

Coal liquefaction is a means of producing low sulfur, low ash fuels from coal which is a relatively dirty fuel for power generation compared to residual fuel oil. As the future energy needs of the United States are going to be met in large part by coal and coal-derived products in order to reduce dependence on petroleum, coal conversion will play an important role in the U.S. energy picture of the future. Both gasification and liquefaction processes are now under development and are at various stages of commercialization. Coal liquefaction is expected to provide chemical and refinery feedstock materials in addition to boiler fuels for energy generation, although this aspect of coal conversion is at present less attractive economically than the production of boiler fuels.

The Solvent Refined Coal Process (SRC-I process) developed by Pittsburg & Midway Coal Mining Company under contract with the U.S. Energy Research and Development Administration is presently at an advanced stage and a 50 ton/day Pilot Plant is operating at Fort Lewis, Washington. This pilot plant has undergone extensive testing and production runs of solid Solvent Refined Coal (SRC-I) have been made for power plant burning studies of the SRC-I product. The first successful commercial power generation from SRC-I was completed in the first half of 1977.

The widespread construction and use of coal conversion plants requires an evaluation of the environmental hazards associated with each process and plant. Among such hazards is the problem of potential emissions of toxic forms of some trace elements, for example As, Hg, Sb, or Se. An important objective of liquefaction processes is to remove much of the sulfur and mineral content of coal so that the resulting fuel can be burned without expensive stack scrubbers and meet stack emission specifications. It is thus important that the fate and distribution of trace elements in the SRC-I process be determined to assess the pollution potential of the fuel (SRC) and the environmental effects of emissions and effluent disposal. The distribution of trace elements present in the coal during liquefaction is also important in determining trace element materials balances in the process and to evaluate the effects of coal type, autocatalytic effects, temperature, pressure, solvent composition, degree of hydrogenation on the materials balance.

The objective of the study reported in this paper was to apply the technique of neutron activation analysis to the determination of trace elements in the SRC-I process. Neutron activation analysis was chosen as the method of trace element analysis because of the high sensitivity for many elements, good precision and accuracy, the multielement nature of the technique, and the capability of analyzing very different matrix types. This latter advantage is significant for the SRC-I project where very diverse materials are encountered, e.g. coal, SRC-I, filter aids, residues, process waters and volatile solvents.

Material balances have been measured for the elements Ti, V, Ca, Mg, Al, Cl, Mn, As, Sb, Se, Hg, Br, Co, Ni, Cr, Fe, Na, Rb, Cs, K, Sc, Tb, Eu, Sm, Ce, La, Sr, Ba, Th, Hf, Ta, Ga, Zr and Cu. A preliminary study was carried out when the SRC-I pilot plant was operating at non-steady state conditions and the data from this study have been reported previously[1,2]. Later two material sets were collected after the pilot plant had operated continuously for at least 7 days and these are referred to as equilibrium (or steady state) sets (1 and 2) and the trace element data obtained are discussed in this paper.

The Solvent Refined Coal (SRC-I) Process

A schematic diagram of the SRC-I process is shown in Figure 1. Coal is crushed, ground and dried, mixed with a solvent (recycled in the process) to form a slurry which is hydrogenated in a reactor at 455°C at 1500 psig. After the reactor, process gases (C_1 - C_4 hydrocarbons, CO_2, H_2S, CO, H_2, etc.) are flashed off and the liquid is filtered through pre-coated rotary drum filters to remove unreacted coal and mineral matter. Light oils and process solvent are flashed off the liquid to give a solid product, SRC-I, and the solvent recycled back into the system. In this process the coal is dissolved in the solvent and, depolymerized to give smaller molecules in the presence of hydrogen.

Much of the organic sulfur is converted to H_2S and some of the FeS_2 is converted to FeS + H_2S

i.e. $FeS_2 + H_2 \rightarrow FeS + H_2S$

$$R\text{-}S\text{-}R^1 + 2H_2 \rightarrow H_2S + R\text{-}H + R^1\text{-}H$$

Approximately daily rates of production of trace elements in the 50 ton/day pilot plant are shown in Table 1. The fate of trace elements present in the coal during the process is dependent on a) the nature of the element and b) the chemical bonding of the element in the coal matrix i.e. organically bound or inorganically present as mineral species. Under the reducing process conditions (high H_2 pressure, 455°C, 1500 psig) several elements may be volatile or form volatile species, e.g. Hg^0, H_2Se, AsH_3, SbH_3, HBr, $Fe(CO)_5$, and $Ni(CO)_4$, among others. Whether such species will be formed will depend largely on the nature of the host mineral (or maceral) and whether this mineral is reactive under the liquefaction/hydrogenation conditions. In addition to the volatile species that might escape in gaseous emissions or condense with distillate products, there is the possibility of reaction with the organic matrix to form organometallic compounds, many of which are extremely toxic and some of which are volatile. Many of the transition metals (e.g. Ti, Fe, Mn, Ni, Co, etc.) form a number of stable organometallic compounds with hydrocarbons or hydrocarbon-like molecules, for example the cyclopentadienyl compounds e.g. ferrocene $Fe(C_5H_5)_2$, titanocene Ti $(C_5H_5)_2$ and the many derivatives of the metallocenes, e.g. carbonyls, hydrides, salts, etc. Many of these are toxic and relatively volatile species and Table 2 lists some compounds that, if present, could be of environmental concern.

Unfortunately we have very little information on the fate of trace elements in coal during liquefaction, although it is obvious that the final molecular species of an element may be quite different from these encountered in coal because of the highly reactive conditions and

TABLE 1

PRODUCTION OF TRACE ELEMENTS IN 50 TON/DAY SRC-I PILOT PLANT

Minor Elements	Concentration in Coal (ppm)	Production Kg/day	Trace Elements	Concentration in Coal (ppm)	Production Kg/day
Fe	2.4%	1200	As	11.6	0.6
S	3.8%	1900	Sb	1.0	0.05
Al	1.1%	540	Hg	0.113	0.006
Ti	547	28	Se	2.2	0.1
Ca	630	32	Cl	286	15
Mg	860	44	Br	5.8	0.3
K	1260	64	Ni	18.0	0.9
Na	124	6.3	Co	5.3	0.3
			Cr	10	0.5
			Cu	22	1.1

TABLE 2

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, SbOCl	$RSbH_2$, RR^1SbH, R_3Sb
Hg	Hg metal, $HgBr_2$	R_2Hg, RHg^+X^-
Se	H_2Se, Se^0	$R-Se-R^1$; $R-SeO_3H$
Fe	$Fe(CO)_5$	$Fe(C_6H_5)_2(CO)_x$
Ni	$Ni(CO)_4$	Ni-asphaltene bonds
Ti	$TiCl_4$	$Ti(C_5H_5)_2$

the complex chemical system of the dissolution/hydrogenation process.

Trace Element Balances in Liquefaction

Very little information is available on the distribution of trace elements in coal conversion processes, although a number of preliminary studies have been made for gasification processes. Forney et al.[3] have studied the distribution of trace elements around the Synthane gasifier at PERC using mass spectroscopy. The results ranged from 218% recovery for F to 1103% for Pb and no reliable mass balances could be derived. Jahnig and Magee[4] presented some limited data on trace elements in SRC-I and related coals but no mass balances were calculated, nor were other process streams analyzed.

The work reported here is thus the first attempt at calculating trace element balances in the SRC-I process.

ANALYTICAL METHODS

Sample Collection and Preparation

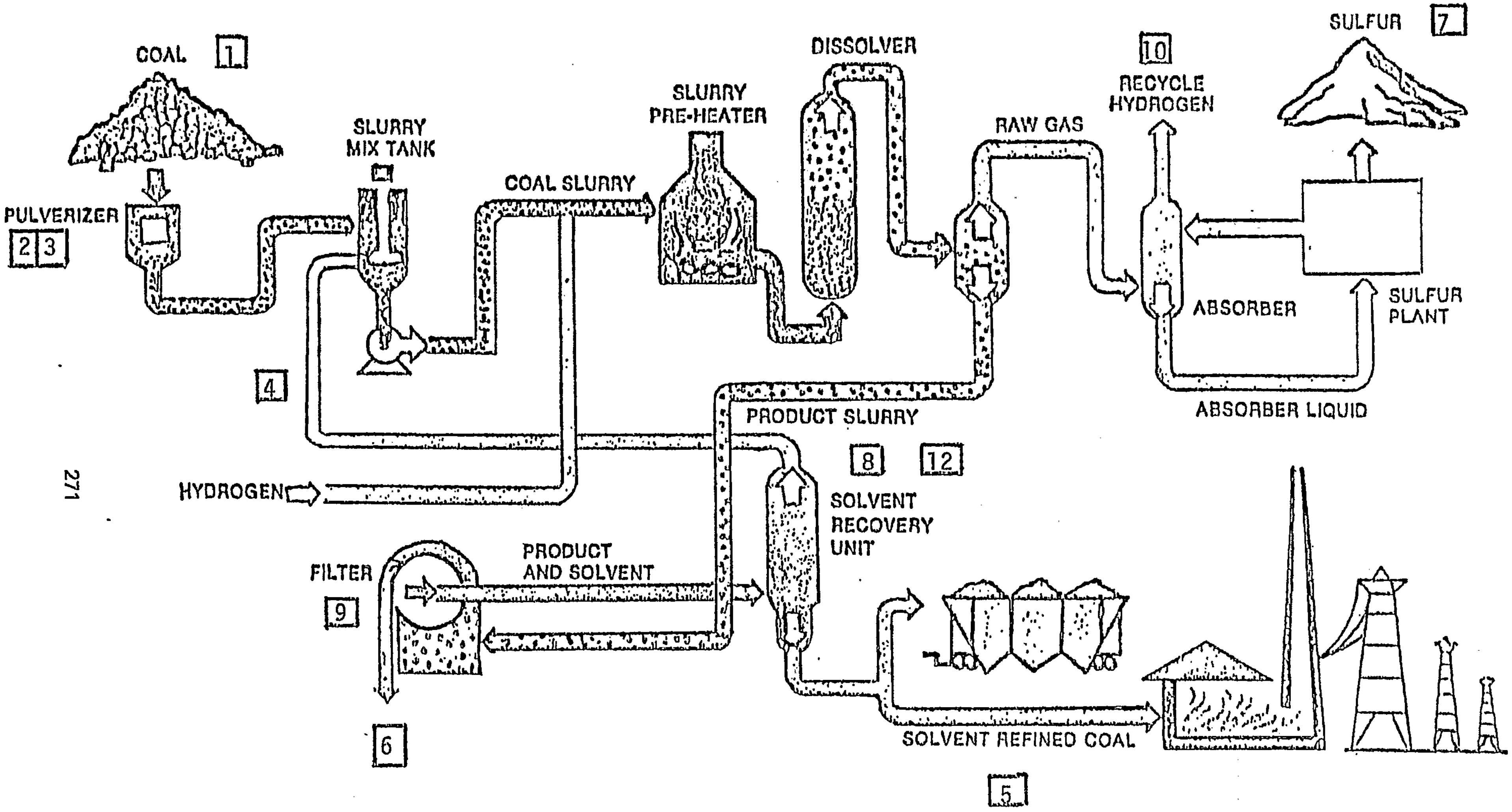
In order to evaluate the fate of elements in the coal liquefaction process, the sample collection procedure is critical. Samples collected should not only cover various important process parameters but also be representative of the process stream sampled. After discussions with pilot plant personnel, twelve different points in the pilot plant were selected as the sample collection points. These points and materials collected are listed in Table 3 and shown on Figure 1. These points effectively

TABLE 3

PILOT PLANT SAMPLE COLLECTION POINTS

Sampling Point	Description	Matrix	Amount
1.	Raw coal	solid	50 gm
2.	Dried/pulverized coal	solid	50 gm
3.	Dust collector	solid	10 gm
4.	Recycle solvent	organic solvent	1000 ml
5.	Solvent refined coal	solid	100 gm
6.	Mineral residue	solid	50 gm
7.	Elemental sulfur	solid	100 gm
8.	Light ends	organic solvent	2 quart
9.	Filter-aide	solid	50 gm
10.	Process water	aqueous	350 ml
11.	Treated effluent water	aqueous	350 ml
12.	Fresh Wash Solvent	organic solvent	1000 ml

SOLVENT REFINED COAL PROCESS



11 Numbers refer to sampling points in Table 3.

covered all input, output, and other important process streams. Laboratory prepared samples were also analyzed to check any contamination of plant products by the process.

A representative sample was essential for this study. All samples should be collected when the plant is operating under a 'steady state' condition. This is very hard to achieve and as a compromise it was decided that the plant should be operating at least seven days without interruption prior to the sample collection. In order to nullify any effect of momentary fluctuation of the process conditions, all samples were collected for a period of 24 hours (every 4 hours) from each collection point. Final composites of samples were prepared by mixing samples collected during the 24-hour collection period for each point. Run conditions for equilibrium sets 1 and 2 are shown in Tables 4 and 5.

Samples collected for elemental analysis were divided into three groups depending upon sample matrix. They were a) solid samples, e.g. SRC-I, coal, residues, etc. b) organic solvents, and c) aqueous samples. Each type of sample required different procedures for the sample preparation, storage, and analysis. These procedures were:

Solid Samples: Solid samples such as SRC-I, ground coal, pyridine insolubles, etc., were collected in cleaned glass or polyethylene containers. These containers were soaked in dilute nitric acid for about 4 hours and then cleaned with double distilled water prior to use. The procedure was necessary to remove any surface contamination.

Organic Solvents: Solvents were collected in pre-cleaned brown glass containers, cleaned as above.

Aqueous Samples: Collection and shipping of aqueous samples required special attention. It is known that many elements are readily adsorbed on the wall of containers (plastic or glass) from the aqueous phase. The rate of adsorption varies from element to element and is often an irreversible process. It was found that if the aqueous samples were frozen immediately after the collection and kept frozen until analysis, the elemental adsorption process was kept to a minimum. It was also necessary that aqueous samples be free of suspended matter. In order to avoid both problems a special sample collection and shipping procedure was developed. Immediately after the collection, aqueous process streams were filtered through clean Nucleopore 0.4 μm filter in a Teflon filter assembly. The filtered samples were then quickly frozen. The aqueous filtered samples were collected in cleaned polyethylene bottles(200 ml) and in four different Playtex thin-walled polyethylene bags (each containing approx. 50 ml). These samples were shipped frozen by air freight to Washington State University.

Neutron Activation Analysis

Neutron activation analysis was used to determine the total of 34 elements, Ti, V, Mg, Ca, S, 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, Hf, Ta, and Zr in all samples. Details of the procedures have been described elsewhere[1,2].

RESULTS AND DISCUSSION

The elements Ti, V, Ca, Mg, Al, Cl, Mn, As, Sb, Se, Hg, Br, Ni, Co, Fe, Cr, Na, Rb, K, Cs, Sc, Tb, Sm, Ce, La, Sr, Ba, Th, Eu, Hf, Ta, Ga, Zr and Cu were determined in the samples from the two equilibrium sets and from the SRC-I process pilot plant. The concentrations obtained in the important process fractions are shown in Tables 6 and 7 for Equilibrium Set 1. Due to lack of space the concentration data for equilibrium set 2 are not included, neither are the error values associated with each determination. In most cases, however, the relative standard deviations of each value (counting statistics) are less than 10% and in many cases are less than 5%.

Several points should be made concerning the concentration data. The concentration of each element in SRC-I is much lower than in the feed coal, except for Br which is the only element to show an increase. The percentage reduction in the SRC-I relative to the ground feed coal for equilibrium sets 1 and 2 are shown in Table 8. Bromine shows an increase in both equilibrium sets and it is not clear where the source of Br lies. Another point of interest, pertinent to the question of materials balances,

TABLE 4

RUN CONDITIONS FOR EQUILIBRIUM SETS

CONDITION	SET 1	SET 2	
RAW COAL FEED	3422.	3488.	#/HR
WATER REMOVED FROM COAL	233.	219.	#/HR
NET DEHUMIDIFIED COAL FEED	3188.	3269.	#/HR
MOISTURE FREE COAL FEED	3129.	3241.	#/HR
SOLVENT FEED FROM AREA 04	4635.	4240.	#/HR
SLURRY RECYCLE FEED	0.	0.	#/HR
SLURRY FEED TO PREHEATER	7823.	7509.	#/HR
SOLV.& REC. SLURRY TO DEH. COAL RATIO	1.45	1.30	
PERCENT SLURRY RECYCLE	0.0	0.0	PCT.
RECYCLE/TOTAL FEED RATIO	0.00	0.00	
HYDROGEN-RICH GAS FEED	201.	164.	#/HR
GAS FEED PURITY-MOL. PCT. H2	97.6	98.7	
HYDROGEN FEED	164.	140.	#/HR
HYDROGEN FEED	30855.	26306.	SCFH
SLURRY PREHEATER INLET PRESSURE	1623.	1631.	PSIG
SLURRY PREHEATER OUTLET TEMPERATURE	742.	752.	DEGF
DISSOLVER A PRESSURE	1545.	1498.	PSIG
DATE	3/1/76	5/14/76	

TABLE 5

YIELD DATA FOR EQUILIBRIUM RUNS

Product	Yield % MFC Equil. Set 1	 Equil. Set 2
H2	-2.75	-1.92
N2	0.02	0.00
C1	2.54	1.91
CO	0.02	0.79
C2	1.00	0.76
CO2	1.38	1.65
C3	1.16	0.92
C4	0.54	0.48
H2S	1.65	1.92
LT. OIL	2.53	2.90
H2O	5.00	5.00
WSH SOLV	7.77	3.11
PROC SOL	-8.90	-6.93
SRC	69.48	71.13
ASH	11.88	12.31
UNREA. C	6.12	6.00
COAL	-100.03	-100.02
TOTAL	0.00	0.00

TABLE 6

CONCENTRATIONS OF SEVEN ELEMENTS IN SRC-I STREAMS

Element	GC	SRC	PI	WFC	LO	PRS	WS	S
Ti (ppm)	530.1	465.0	3350	1490	2.04	19.1	0.92	<90.0
V (ppm)	30.1	4.63	195.2	140.6	0.050	0.445	0.052	8.2
Ca (ppm)	330	72.8	6300	3015	<10	<10	<5	<600.0
Mg (ppm)	1160	89.0	4000	4345	<10	<10	<7	<300.0
Mn (ppm)	34.0	20.3	185.0	140.0	0.18	2.09	0.2	8.0
Al (%)	1.18	0.02	7.72	5.5	50 ppm	43.9ppm	11.6ppm	<6 ppm
Cl (ppm)	260.1	159.5	759.6	1641.0	16.9	127	92.2	<40.0

GC	Ground coal	PI	Pyridine insolubles
WFC	Wet filter cake	LO	Light oil
PRS	Process recycle solvent	WS	Wash solvent
		S	Sulfur

TABLE 7

EQUILIBRIUM SET 1, RAW MATERIALS & PRODUCTS

	GC	SRC	PI	WFC	LO	PRS	WS	S	PW	EW
As (ppm)	12.5	2.00	85.7	62.1	0.011	0.24	0.011	<2.0	0.006	<0.001
Sb (ppm)	0.76	0.06	7.21	5.35	<0.4*	8.2*	<0.4*	<0.1	0.66*	2.0*
Se (ppm)	2.0	0.12	16.5	11.3	51.6*	24.0*	14.4*	<1.5	0.16	0.0012
Hg (ppb)	113	39.6	508	346	18.5	1.45	10.5	<100	106	3.2
Br (ppm)	4.56	7.74	12.0	20.7	0.015	1.0	0.02	<3.0	15.6	31.8
Ni (ppm)	14.9	<3.0	142	82.4	<0.03	0.4	<0.03	<28.0	<0.004	0.013
Co (ppm)	5.88	0.22	40.7	26.5	< 3.0*	40.7*	1.43*	110	0.2*	0.41*
Cr (ppm)	13.7	1.64	106	69.2	37.3*	3590*	41.3*	<2.0	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 (ppm)	137	4.23	1020	623	0.60	0.50	0.45	3120	0.70	8.3
Rb (ppm)	<4.0	<0.5	66.5	37.1	<0.01	0.02	<0.01	<9.0	0.78*	0.52*
Cs (ppm)	0.75	0.02	5.08	3.20	1.06*	<1.2*	0.91*	<0.2	0.04*	0.02*
K (ppm)	1550	4.72	11100	6660	<0.1	0.25	<0.1	179	0.2	1.26
Sc (ppm)	2.59	0.57	14.8	9.26	0.15*	32.8*	0.19*	<0.02	0.13*	0.01*
Tb (ppm)	0.39	0.045	2.06	1.34	<0.13*	3.75*	<0.13*	< 0.1	0.01*	0.01*
Eu (ppm)	0.26	0.055	1.48	0.96	<0.01	<0.01	<0.01	<0.01	0.01*	0.01*
Sm (ppm)	2.62	0.29	16.9	8.16	< 0.01	0.02	< 0.01	0.61	0.08*	<0.06*
Ce (ppm)	20.9	0.45	156.0	102	<0.004	<0.004	<0.003	<2.0	<0.2*	<0.2*
La (ppm)	7.55	0.13	59.8	35.2	<0.01	0.01	<0.01	1.80	0.27*	0.5*
Sr (ppm)	88.6	<6.0	456.0	453	<0.6	<0.2	0.74	<45.0	<0.01	<0.04
Ba (ppm)	53.0	5.75	347.0	185.0	<0.1	1.14	<0.07	<39.0	<0.02	<0.04
Th (ppm)	2.00	0.22	12.8	7.70	<0.001	0.012	<0.001	<0.2	0.05*	<0.01*
Hf (ppm)	0.51	0.084	3.30	2.20	<0.001	0.003	<0.001	<0.2	0.02*	<0.01*
Ta (ppm)	0.14	0.046	0.71	0.42	<0.4*	2.53*	<0.3*	<0.2	0.02*	0.01*
Ga (ppm)	3.56	1.79	19.4	11.3	<0.01	0.06	<0.01	<1.5	<1*	<4*
Zr (ppm)	62.9	16.0	500.0	246	0.07	0.71	<0.1	<61.0	0.02	0.04
Cu (ppm)	19.9	2.07	189	138	0.03	0.68	0.03	<1.0	<12*	<10*

Note *Values in ppb: **Values in ppm PW Process Water EW Treated Effluent Water

TABLE 8

TRACE ELEMENT REDUCTION SRC COMPARED TO COAL

Element	SRC/G.Coal	% Reduction	Element	SRC/G.Coal	% Reduction
Ti	0.88	12	Ti	0.74	16
V	0.15	85	V	0.47	53
Ca	0.22	78	Ca	0.22	78
Mg	0.08	92	Mg		
Al(%)	0.02	98	Al(%)	0.03	97
Cl	0.61	39	Cl	0.34	66
Mn	0.60	40	Mn	0.40	60
As	0.16	84	As	0.07	93
Sb	0.08	92	Sb	0.04	96
Se	0.06	94	Se	0.03	97
Hg	0.35	65	Hg	0.41	59
Br	1.70	+70	Br	1.33	+33
Ba	0.11	89	Ba		
Th	0.11	89	Th	0.10	90
Hf	0.16	84	Hf	0.12	88
Ta	0.39	61	Ta	0.29	71
Ga	0.50	50	Ga	0.19	81
Zr	0.25	75	Zr	0.08	92
Cu	0.10	90	Cu	0.08	92
Na	0.03	97	Na	0.04	96
Rb			Rb	0.02	98
Cs	0.03	97	Cs		
K	0.003	100	K	0.001	99.9
Ni			Ni		
Co	0.04	96	Co	0.05	95
Cr	0.12	88	Cr	0.37	63
Fe	0.01	99	Fe	0.01	99
Sc	0.22	78	Sc	0.15	85
Tb	0.12	88	Tb	0.09	91
Eu	0.21	79	Eu	0.14	86
Sm	0.11	89	Sm	0.07	93
Ce	0.02	98	Ce	0.02	98
La	0.02	98	La	0.01	99

is that only SRC and fractions derived from the mineral residues (i.e. mineral residue, pyridine insolubles) show significant concentrations of trace elements.

The high concentrations of Ti in the SRC-I are only slightly lower than in the original coal. In SRC-I from equilibrium set 1 the concentration is 465 (in set 2 it is 490 ppm) and this represents only a 12% reduction compared to coal (10% for set 2). It is not known why Ti behaves so differently from all other metals studied but possible explanations are:

a) Ti is present in coal as an extremely finely divided oxide (TiO_2) which passes through the rotary drum filters.

b) Ti is present as an organometallic species in coal, soluble in the process solvent.

c) Ti is present in an inorganic combination (i.e. mineral form) but reacts to form an oil-soluble compound ($TiCl_4$) or an organometallic species) during the hydrogenation reaction.

There is some evidence[5] that suggests the presence of an organometallic species in SRC-I, but the form of Ti in SRC-I is outside the scope of this paper.

Materials Balance Calculations

One of the main objectives of this study was to determine the fate of trace elements in the SRC-I process and to determine a materials balance for each element, particularly those known to be, or suspected of being toxic. To do this, it is necessary to know the elemental concentration of each process fraction and the weight yield (in % from original coal) of each fraction. The run data shown in Table 5 provides information on the yields of SRC-I, Light Oils (LO), Wash Solvent (WS), Process Water (PW), and Sulfur (from H_2S yields). However, it is difficult to assign a contribution to the recycle process solvent yields so that we have arbitrarily assigned a value of 5% for this fraction. In quantitative terms, the recycle process solvent contribution to the overall materials balances is negligible and the error associated with the assigned yield is small. A more difficult problem concerns the contribution of the filtered residue to the materials balance. Several residues were analyzed viz: pyridine insolubles (PI), mineral residue, wet filter cake (WFC) and ash of pyridine insolubles. We have chosen to base the "residue" component of the materials balance on the pyridine insolubles because a) the solvent-soluble material has been washed out compared to the filter cake, and b) no elements have been lost by ashing (very important for Hg, Se, and As) as compared to the ash of the pyridine insolubles. The pyridine insolubles thus represent inorganic mineral matter and any unreacted coal. However, we did not have run data on pyridine insolubles. Consequently we computed the PI contribution by assuming that 100% of K from the coal is in the PI and this appears reasonable considering the very low K content of SRC-I compared to the input coal. When computed in this way the PI yield per unit of coal is 13.9% for Run 1 and 18.1% for equilibrium set 2. The proportions of each fraction (coal = 1.0) for the two equilibrium sets are shown in Table 9. The material balance for each element in percent of input from coal are given in Table 10.

In these calculations we have assumed that the only contributions to the trace element input is the coal. This assumption naturally does not take into account contributions from the recycle process solvent (small), H_2 gas (small) or from corrosion and wear of the construction materials (possibly important for some elements). For equilibrium set 2 the balances range from a low value of 82.3% (Cl) to a high of 293% for Ca. Except for Ca, Ni, Ti, V, and Cr all balances lie within the range 83 - 145% which may be regarded as excellent given the assumptions made and the errors associated with obtaining representative samples of the process streams. For equilibrium set 1 the values range from 53% (Mg) to 259% (Rb). Except for Mg (53%), Rb (259%) and Br (172%) all values lie within the range 85 - 150% which may be considered excellent.

Of particular significance are the materials balances for Hg, As, Se, Sb and Br. For Hg, a volatile element, the materials balances are 98% and 109% for sets 1 and 2 and this shows that all the Hg in the process is accounted for. It should be noted that the recycle process water of equilibrium set 1 accounts for 10% of the total. Mercury is the only element

TABLE 9

PROCESS FRACTION CONTRIBUTIONS
TO MATERIALS BALANCES

Process Fraction	Contribution Equilibrium Set 1	Equilibrium Set 2
Coal	1.00	1.00
SRC	0.695	0.711
PI	0.139	0.187
PRS	0.05	0.05
LO	0.023	0.03
WS	0.05	0.05
RPW	0.05	0.05
S	0.016	0.016
TOTAL	1.02	1.09

for which the RPW accounts for more than 1% of the total. Arsenic, antimony and selenium in equilibrium set 1 all balance well. For set 2 the very high As value is accounted for by an anomalously high concentration of As in the PI. This is being investigated. For Sb, and Se the balance is again good. For both sets, Br is high and there may be an external source of Br (probably solvents). Titanium is also high, 149% and 176% for sets 1 and 2 respectively. This may be due to corrosion of equipment or some other source. The high values for set 2 for Cr, Ni, and B may be due also to equipment corrosion. These three elements balance normally for equilibrium set 1.

Aqueous Environmental Samples

Several aqueous samples were analyzed in this study to determine the buildup of trace elements in the process water, treated effluent water and Hamer Marsh water (into which the plant effluent drains). Although there are significant concentrations of Hg, Se, As, and Cu in both process waters, these elements had been reduced to very low levels in the treated effluent water and in Hamer Marsh water. The efficient removal of these elements in the biotreatment plant appears to be primarily responsible for the low elemental concentrations in the plant effluent. High values of Se (6.3 ppm) and Hg (8.7 ppm) are found in the bio-sludge of equilibrium set 2 indicating the efficient removal of Hg and Se. Table 11 shows the concentrations of some important elements in samples from equilibrium set 2 because the set 1 samples did not include the biosludge. The analytical data for aqueous samples from set 1 are similar to those of set 2.

ACKNOWLEDGMENTS

This work was supported under a contract with Pittsburg & Midway Coal Mining Company

TABLE 10

MATERIALS BALANCES FOR EQUILIBRIUM SETS

Element	Set 1(%)	Set 2(%)	Element	Set 1(%)	Set 2(%)
Ti	149	176	Na	142	112
V	101	177	Rb	259	119
Ca	146	293	Cs	97	98
Mg	53	88	K	100	100
Al	92	102	Sc	95	145
Cl	85	82	Tb	81	143
Mn	129	143	Eu	94	105
As	106	-	Sm	97	119
Sb	137	118	Ce	105	115
Se	119	88	La	112	104
Hg	98	109	Ba	99	118
Br	172	145	Th	97	127
Ni	133	248	Hf	101	141
Co	129	115	Ta	94	135
Cr	117	272	Ga	110	86
Fe	112	105	Zr	128	102
			Cu	140	123

TABLE 11

SRC PILOT PLANT, AQUEOUS SAMPLES, EQUI. SET 2

	Process Water	Treated Effluent Water	Hamer Marsh Water	Bio-Sludge*
As (ppb)	10.7	<1.0	<5.0	<12.0
Sb (ppb)	1.0	0.64	0.5	1.21
Se (ppb)	914.3	0.37	0.45	6.28
Hg (ppb)	20.7	5.5	0.38	8.75
Br (ppb)	18.3		28.1	8.57
Ni (ppb)	14.0	16.0	7.0	12.0
Co (ppb)	0.43	0.36	0.26	4.48
Cr (ppb)	11.30	10.1	6.2	47.33
Fe (ppm)	1.34	0.41	0.36	12,000
Na (ppm)	5.1	8.0	42.4	9630
Rb (ppb)	0.77	1.36	0.91	2.66
Cs (ppb)	0.04	0.06	0.05	0.19
K (ppm)	0.73	<.10	<8	<200.0

*Note: All concentrations in the BioSludge are in ppm, not ppb

under an inter-agency agreement between the U.S. Energy Research and Development Administration (ERDA) and the Environmental Protection Agency (EPA). The authors would like to express their appreciation to Mr. S. R. Khalil for much of the analytical work and to Mr. C. A. Palmer for assistance in the computer reduction of data. The cooperation of Mr. R. E. Perrussel at the SRC Pilot Plant is gratefully acknowledged.

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