

# TRACE ELEMENT DISTRIBUTION IN THE THREE TON PER DAY H-COAL PROCESS DEVELOPMENT UNIT

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## Introduction

Current research in coal conversion has identified a number of processes that potentially could produce clean burning fuel from coal. The shifting of combustion sources from oil to coal has accentuated the need for a clean burning fuel oil derived from coal. Scientists have studied possible degradation of the environment by tracking trace elements in coal burning power plants, in coal liquefaction pilot plants of various sizes, and in bench scale units (1,2,3,4,5). A study made of the Savannah River coal-fired power plant has given insight into trace element buildup in the environment surrounding the plant (1). The Synthane (coal gasification) process was studied, utilizing isotope dilution Spark Source Mass Spectrometry (SSMS) (2). Determination of trace metals in Solvent Refined Coal by means of INAA (Instrumental Neutron Activation Analysis) revealed much lower elemental concentrations in the SRC product than in the feed coal (3,4). The trace element studies of the Synthoil 1/2 ton per day coal liquefaction Process Development Unit also showed that trace element concentrations are lower in the product oil (CLP) than in the feed coal (5,6). In order to further our knowledge of the fate of the trace metals in coal hydro-liquefaction processes, a study was conducted of the H-Coal Process Development Unit (PDU) located in Trenton, N.J.

## Experimental

In the H-Coal process, dried pulverized coal, clean oil tank material, and hydroclone overflow are reacted with hydrogen at pressures up to 3500 psig and temperatures up to 850°F (7). The PDU is unique in that a substantial amount of the liquid products are recycled to the slurry mix tank so equilibrium conditions can be maintained. The products of the process are the atmospheric overhead, which is a light distillate material, and the vacuum still bottoms. The vacuum still bottoms is a viscous material that becomes a semiliquid upon cooling. The severity of the reactor conditions determines the relative amounts of the individual products made (7). The reactor design uses the fluidized bed concept (8). Since the catalyst is in constant motion, spent catalyst may be extracted and fresh catalyst injected into the reactor while the PDU is in operation. Figure 1 shows the flow diagram of the HRI PDU #130 unit.

A sampling exercise was conducted at the H-Coal PDU in Trenton, N.J., the goal of which was to obtain representative, uncontaminated samples for trace element characterization. Factors considered in planning the sampling of the plant included transportation of the trace clean containers to the sampling site, transportation of the samples back to PETC, environmental conditions at the plant, and the PDU design. The flow rates and process streams sampled are listed in Table 1. The feed coal for the run sampled was Burning Star Illinois No. 6.

All liquid samples were collected in soft glass containers with teflon lid spacers where required. Coal samples were taken in polyethylene bags whose tops were sealed with rubber bands. The coal filled bags were placed in tared one-gallon paint cans that were then sealed. Cleaning the soft glass containers was accomplished by detergent washing, rinsing with distilled water, soaking in dilute hydrochloric acid, rinsing with deionized distilled water, and air drying. All liquid samples were drawn directly into the heated clean soft glass containers. Sample temperatures of up to 500oF were encountered when taking some of the liquid samples; so the containers had to be heated to prevent cracking. The head spaces of the precleaned sample containers were purged with nitrogen to prevent exposure of the bulk samples to air after the samples were taken.

Elemental analyses performed on a wide variety of coals has shown the presence of over half the elements in the periodic table (10). Sample inhomogeneity (5) and complex coal matrices (2) play an important role in the precision of analysis. Atomic absorption spectroscopy, both flame and flameless, has been employed successfully for the analyses of coal and coal by-products (11,12) and was therefore selected for this study. To obviate possible matrix effects, the method of standard additions was used, along with deuterium arc background correction. Small amounts of standard solutions of the elements of interest were added to separate aliquots of the sample for each element. The total concentration of each element after the addition was in no case more than three times the concentration in the original solution. Absorbance readings obtained for the sample and the three additions were entered into a desk top calculator programmed to calculate a correlation coefficient, an intercept, and a slope by the method of linear least squares. Concentration levels in the original sample were calculated using these values plus the sample weights, volumes, etc. This method was used with all samples. Method blanks were carried through all steps of the sample preparation with each set of samples.

Analysis of 19 coals in one study (10) and 11 coals in another (13) showed trace element concentrations varied widely between coals from the western and the eastern United States. Details of sample preparation in the determination of trace elements in coal and coal-derived materials have been previously described (9). Briefly the sample is ashed and extracted with dilute hydrochloric acid or dilute nitric acid. Remaining residues are dissolved using a fusion procedure. The dissolved ash is then combined with the acid extract. Four aliquots of the combined solution are taken, standard solution is added to three of the aliquots, and the solutions are analyzed as described above.

Experience has shown that the concentration of chromium, copper, manganese, and nickel in coal is usually greater than one part per million. The exact concentration of each of these elements in a specific coal depends largely on the geographic origin and the type of coal.

Cadmium is usually present in coal at concentration levels below one part per million (9). Lead concentrations are normally much higher. Although flame AA is quite sensitive to cadmium (0.025  $\mu\text{g/ml}$  for 1% absorption), the sensitivity for lead is only 0.5  $\mu\text{g/ml}$  for 1% absorption. Solvent extraction was used to increase the sensitivity of the Pb determination by increasing its concentration. Iodide complexes of Pb and Cd were formed in ascorbic acid media,

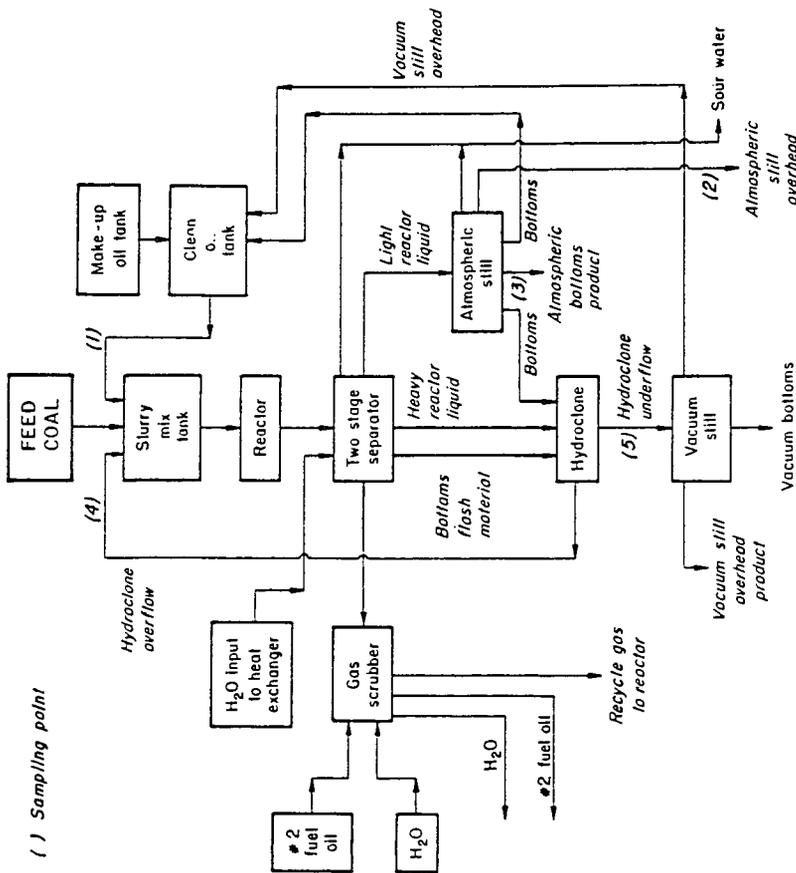


Figure 1. HRI PDU #130 FLOW DIAGRAM

followed by extraction into MIBK (Methyl Isobutyl Ketone). Acidified MIBK was used to establish the instrumental base line. Blank solutions were carried through all steps of the analytical procedure.

#### Discussion

The recoveries of the determined trace elements, as indicated by the material balances around the slurry mix tank and the product separation unit, demonstrate the success of the sampling procedures and analytical methods employed in this study. The trace elements entering the PDU are accounted for within the precision of the data presented. Material balances (i.e., total input versus total output) ranged from 69% to 137% and are shown in Table II. Incomplete recoveries of Cu, Cr, Mn, and Pb may be indicative of an elemental buildup in the process streams analyzed. Statistical analysis of the available data do not indicate such a buildup, although further work may need to be done in this area.

Table I. HRI PDU #130 PROCESS STREAMS AND FLOW RATES

PERIOD 14A

<u>Process Streams</u>	<u>Lb/Hr*</u>	<u>Kg/Hr</u>	<u>Nature of Samples</u>
Feed Coal	335.2	152.0	Plant grind (98% through -50 mesh)
Hydroclone Overflow	359.3	163.0	Viscous oil held at 500°F (ash = 9.3%)
Clean Oil Tank Material	321.7	145.9	Comb. of vacuum still overhead & atmospheric still bottoms
Slurry Mix	1,016	460.9	Mixture of feed coal, atmospheric still bottoms, vacuum still overhead, & hydroclone overhead (ash = 7.2%)
Hydroclone Underflow	278.3	126.2	Viscous oil held at 500°F (ash = 13.7%)
Atmospheric Still Overhead	49.9	22.6	Light oil
Atmospheric Still Bottoms (COT)	250.7	113.7	Liquid feed to the clean oil tank
Injected Feed Water	2.3	1.0	Tap water
Sour Water	33.1	15.0	Comb. of feed water and water generated in the PDU
Vacuum Still Overhead (COT)	44.8	20.3	Liquid feed to the clean oil tank
Atmospheric Still Bottoms (product)	8.5	3.9	Sample stream outlet used for continuous sampling
Vacuum Still Overhead (product)	1.0	0.5	Sample stream outlet used for continuous sampling
Vacuum Still Bottoms	234.1	106.2	Product of run 130-88 period 14A
Atmospheric Still Bottoms (hydroclone)	60.0	27.2	Liquid feed to the hydroclone
Overhead Flash Material	89.8	40.8	Very light oil
Makeup Oil	34.8	15.8	Oil used when the PDU is not at equilibrium

\*Feed Rates as supplied by plant personnel.

Table II. RECOVERIES OF TRACE ELEMENTS IN THE H-COAL PDU.

#130 RUN 130-88 PERIOD 14A

	(Weight in mg)					
	<u>Cu</u>	<u>Cr</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Cd</u>
Slurry Mix Tank						
Inputs	2,900	6,100	17,200	3,500	3,300	40
Outputs	2,900	6,600	21,000	3,500	3,200	46
% Recovery	102	109	120	100	98	113
Product Separation Unit						
Inputs	2,900	6,600	21,000	3,500	3,200	46
Outputs	2,900	5,900	19,700	3,500	2,900	56
% Recovery	97	89	94	101	90	122
Complete Plant						
Inputs	1,400	2,900	9,300	1,600	1,700	27
Outputs	1,000	2,300	9,800	1,400	1,200	36
% Recovery	76	81	105	85	69	137

Appendix

TRACE ELEMENT ANALYSIS OF PROCESS STREAMS

From HRI PDU #130 PERIOD 14A

<u>PROCESS STREAMS:</u>	ug/gm					
	<u>Cu</u>	<u>Cr</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Cd</u>
Feed Coal	8.9	19	61	11	11	0.18
Hydroclone Overflow	8.4	20	48	12	9.6	0.08
Clean Oil Tank Material	0.6	0.2	0.9	0.1	0.1	0.002
Slurry Mix	6.2	14	45	7.7	7.0	0.10
Hydroclone Underflow	9.9	22	92	13	11	0.34
Atmospheric Still Overhead	0.036	0.022	0.015	0.017	0.003	0.04 <sup>-2</sup>
Atmospheric Still Bottoms	1.1	0.2	0.8	0.1	0.068	≤0.01 <sup>-4</sup>
Vacuum Still Overhead	0.4	0.003	0.01	≤0.01 <sup>-2</sup>	0.019	≤0.01 <sup>-4</sup>
Injected Feed Water	0.028	≤0.006	0.007	0.001	≤0.001	0.01 <sup>-2</sup>
Sour Water	1.2	0.029	0.021	0.032	≤0.001	0.004

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