Phase II of the Demonstration of the Koppelman Series C Process

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EXECUTIVE SUMMARY

A pilot plant using the Koppelman Series C Process was designed, constructed, and operated near Gillette, Wyoming, as part of Phase I of this project. Construction was completed in late fall of 1993, and the shakedown was completed in early 1994. The initial series of tests performed to prove the process and to characterize the effluents was conducted during the first half of 1994. The results of those tests are described in the final report for Phase I (Merriam 1994).

This report describes the activities conducted during Phase II of the project the objective of which was to move the process, which was proven during Phase I, a step closer to commercialization. Specifically, the work was planned to lower the cost of the process by developing a high-capacity processor, increasing the already high efficiency of the process by using a feed coal preheater, increasing the bulk density of the product by using mixed particle size extrudate, and preparing a preliminary scoping design for the water treatment plant for a 500,000 ton per year commercial plant.

Thermo Ecotek announced in mid August 1995 the signing of an agreement to construct a 500,000 ton per year coal upgrading plant in the Powder River Basin of Wyoming. The plant, which is now being constructed by Thermo Ecotek, is estimated to cost \$42 million. The plant uses the Koppelman Series C Process, which was successfully demonstrated by WRI and KFx Inc in early 1994 using a pilot plant funded by matching funds from the DOE Jointly Sponsored Research Program.

In the Series C Process, coal is charged into the heated processor tubes at ambient pressure, the reactor valves are closed, and the reactor is pressurized to about 120 psig using nitrogen. The outside of the tubes, which are designed to optimize heat transfer, are heated by a flow of hot heat transfer fluid. Moisture is driven from the coal, and the condensation of the resulting steam provides uniform heating and efficient heat transfer within the coal bed. During processing, the pressure in the processor is maintained by venting gases and vapor. When the preselected time, pressure, and temperature are reached within the processor, the rate of venting is increased to depressurize the tubes. After the pressure has decreased to less than 5 psig, the bottom valves are opened, and the product is discharged from the processor into a holding bin for cooling.

Evaluation of the temperature data from the tests indicates a distinct temperature pattern within the processor during these tests. The first part of the tests is characterized by high temperature differentials between the heat transfer fluid and the coal and high heat transfer rates. The second portion of the tests is characterized by rapidly rising pressure in the processor and convergence of temperatures to the saturation temperature of steam (about 510 °F) at the pressure in the processor.

The final portion of the tests is characterized by temperatures rising above the saturation temperature and increasing to approach the temperature of the heat transfer fluid (typically 700 to 750 °F).

The analyses of the products from tests using heat transfer fluid at temperatures from 500 to 740 °F show increasing heating value from 11,868 Btu/lb at 500 °F to over 12,600 Btu/lb at 740 °F. The oxygen content of the product decreases from 13.3 wt% at 500 °F to 8.3 wt% at 740 °F. This temperature range brackets the target values of 12,100 to 12,200 Btu/lb and 7 to 10 wt% oxygen set for the product before the tests were conducted.

Processing Powder River Basin (PRB) coal removes up to 25 wt% of the sulfur from the already low-sulfur coal. The product typically contains about 0.75 lb of SO₂ per million Btus. Over 99% of the heat content of the feed coal is retained in the product while the weight of the product is condensed to about 65% of the weight of the feed coal. About 300 Btu is required to process one pound of PRB coal. Correlations of processing temperature, pressure, and heating time are used to control the characteristics of the product.

Midway through Phase II of the project we switched the emphasis of our work to support the design and operation of the commercial plant. While we had characterized the water and gas produced in the process as part of our Phase I work, the characterization was not completed in sufficient detail to provide all of the information needed for permitting and design. Consequently, we conducted more tests and analyses to generate more detailed compositions of the effluent water and gas. This report includes summaries of the results of those analyses. We also conducted studies to define the chloride content of the feed coal and to determine the rates of corrosion in various parts of the process. Those results are also summarized herein.

INTRODUCTION

PRB coal is relatively dusty and subject to self-ignition compared to bituminous coals. Dried (or processed) PRB coal is even dustier and more susceptible to spontaneous combustion than the raw coal. Also, PRB coal dried at low temperature typically readsorbs about two-thirds of the moisture removed by drying. This readsorption of moisture releases the heat of adsorption of the water which is a major cause of self-heating of low-rank coals at low temperature. PRB coal, and other low-rank coals, tend to be highly reactive when freshly mined. These reactive coals must be mixed regularly (every week or two) when fresh, but become somewhat more stable after they have aged for several weeks.

Low-temperature oxidation reduces the heating value of the coal, makes the coal less able to repel moisture (hydrophobicity), and is known to increase the unburned carbon remaining in the ash. Ingram and Rimstidt (1984) attribute increased moisture in naturally oxidized coals to increase in surface area caused by the physical effects of weathering and an increase in hydrophilic functional groups able to chemisorb water (organic acids are known to attract water to coal particles). Water molecules are generally thought to attach to polar oxygen sites in coal (this varies greatly with the different types of coal).

Many efforts have been made to overcome these problems of dust formation and self-heating while keeping the cost of processing within the very competitive limits of the markets for coal. The University of North Dakota Energy Research Center has explored the use of various drying techniques to upgrade low-rank coals (Willson et al. 1987). They found that coals dried at low temperature readsorb moisture after cooling and return to essentially the original equilibrium moisture level. In contrast, they found that the processes using temperatures high enough to alter the structure of the coal particles resulted in reduced readsorption of moisture.

They also concluded that the lowered equilibrium moisture levels resulted from the rejection of carbon dioxide by the decarboxylation reactions that occur during high-temperature drying. The readsorption of moisture by coals dried at temperatures lower than a few hundred degrees Fahrenheit and reduction of equilibrium moisture in coals dried to about 500 to 700°F is consistent with Western Research Institute (WRI) experience (Boysen et al. 1990).

Each year, over 200 million tons of coal containing about 8200 Btu/lb is shipped from the Powder River Basin of Wyoming. The high moisture content and, consequently, the low heating value of this coal causes the transportation and combustion of the coal to be inefficient. About 1900 unit train loads of coal are transported annually. When this coal is processed to remove the moisture and increase the heating value, the same bundle of energy can be shipped in fewer than 1300 train

loads per year. This will mean a savings of about 600 train loads per year, or a reduction of about 1,200,000 train-miles per year. Additional savings will also result because of the increased efficiency of combustion in large boiler systems. This increase in efficiency will reduce the carbon dioxide emissions from electrical generating systems by a huge amount.

The low heating value of PRB coal limits the markets for the coal to use in boilers specially designed for burning the low-heating value, high-moisture coal. Thus, the advantages of the low sulfur content are not fully available to potential customers having boilers designed for bituminous coal. Also, the processing used to remove water and restructure the coal removes sulfur, nitrogen, mercury, and chlorides from the coal. This precombustion cleaning is much less costly than post-combustion stack scrubbing.

BACKGROUND

Other Development Efforts

A drying process was developed for PRB coal during the early 1980s. Initial work was done by Anaconda Minerals Co., later joined by Atlantic Richfield Co., using a 4 ton/hr pilot plant at Tucson, Arizona. The process has been licensed to Kaiser Engineers. The process is a fluidized-bed drying process using conventional equipment with a proprietary product treatment step (Skinner et al. 1984). The developers conducted laboratory research to determine methods to avoid low-temperature oxidation of the product. They developed methods using cooling, controlled preoxidation, treatment with carbon dioxide, and spray application of oil or chemical solution.

Koppelman was awarded U.S. Patents 4,728,339 and 5,071,477, which are the technical basis for the K-Fuel® Series B process planned for commercialization by Heartland Fuels Corporation.

Lien (1991) discusses the problems and progress AMAX has experienced with a McNally dryer at the AMAX Belle Ayr mine. In this low-temperature process, coal is dried by contact with a hot stream of fluidizing gas. The gas is composed partly of flue gas from combustion of coal and partly from recycled gas. The hot drying gas contains less than 5% oxygen. The dried coal, which contains 12 to 13 wt % moisture, enters the cooler at a temperature of 180 to 190°F, where it is cooled to about 100°F by contact with air. The cooled product is mixed with 2 to 4 gallons of number 6 fuel oil per ton to control product dustiness and inhibit readsorption of moisture. Lien discusses the problems of upsets in the process caused by loss of feed and the experience with degradation of particles in the dryer. He also states that a major concern has been the stability of the product.

The Syncoal Process is used at a Clean Coal I demonstration plant located at Western Energy Company's Rosebud mine near Colstrip, Montana. In the process, coal is passed through two vibrating fluidized-bed reactors, where it is contacted by hot gas to dry the coal and remove carboxyl groups and volatile sulfur compounds. The dried coal is further desulfurized by pneumatically stratifying the product to separate pyrite-rich ash (Western Energy Company 1992).

The Carbondry Process (Simmons and Simmons 1992) has been tested at the pilot plant scale at Carbontec's facility at Bismarck, North Dakota. The process involves a hot oil first-stage drying unit and a flue gas drying unit. The process uses a coating of oil on the surface of particles to protect against readsorption of moisture and spontaneous heating. Published data indicates that the product made from PRB coal using the process contains about 6 to 10 wt % moisture and has a heating value ranging from 11,200 to about 11,700 Btu/lb.

The ENCOAL LFC Process is used at a commercial demonstration facility located at Triton Coal Company's Buckskin mine north of Gillette, Wyoming, (McPherson 1992). In that process, coal is roasted to drive off moisture, coal liquids, and sulfur compounds. The plant, which was built using an award from Clean Coal III, produces a crude coal liquid and solid process derived fuel.

Koppelman's Earlier Development Work

Since its inception in 1984, K-Fuel Inc. (KFI) has worked to develop processes for the production of clean-burning, high-Btu fuel from low-rank coals, wood waste materials, and biomass products. This effort is based on the technology described in U.S. Patents 4,728,339 and 5,071,477. These patents are for an apparatus and process to treat organic carbonaceous materials containing residual moisture to effect a physical and/or chemical modification whereby the residual moisture content is substantially reduced. The upgraded product resulting from this high-pressure, controlled thermal restructuring process possesses increased heating value.

Early development work was conducted at Stanford Research Institute (SRI) in Palo Alto, California. Later, some of the equipment was relocated to the present KFI pilot plant near Gillette, Wyoming. In 1986, KFI constructed the Series A pilot plant near Gillette using equipment relocated from SRI and additional equipment. The Series A Process involves crushing and feeding coal into a continuous, high-pressure unit where the coal is converted using moderately severe conditions of temperature and pressure.

In 1990, a small batch pilot plant was constructed at the Gillette facility to test the Series B Process. The Series B Process involves loading coal into a reactor at atmospheric pressure, heating

the coal using high-pressure steam, depressuring the reactor, and discharging the K-Fuel®. Tests using this unit were successfully conducted during 1991 and 1992. The Series B Process is the technical basis for the commercial K-Fuel® plant that Heartland Fuels Corporation is presently planning to construct.

For the past several years, Edward Koppelman has been testing the Series C Process using bench-scale equipment at the pilot plant. The Series C Process involves loading coal into a reactor at atmospheric pressure, pressurizing the reactor with nitrogen, heating the coal indirectly by transferring heat into the reactor in a very efficient manner, depressurizing the reactor, and discharging the product. The successful conclusion of these bench-scale tests has resulted in the need to construct and operate larger-scale test facilities.

Koppelman has conducted bench-scale tests using the Series C Process to show that subbituminous Powder River Basin (PRB) coal can be converted to a higher-value product having the characteristics of a low-sulfur bituminous coal. In the Series C process, PRB coal (Table 1) with a heating value of 8367 Btu/lb is upgraded to a higher-rank fuel with a heating value of about 12,400 Btu/lb by removing all of the moisture and by reducing the oxygen content of the coal from about 29 wt % (dry basis) to about 7 wt %. The sulfur content of the low-sulfur PRB coal is further reduced in the process, resulting in a product containing about 0.56 lb of SO₂/million Btu (Table 2).

Table 1. Analyses of Raw Coal Used for the Bench-Scale Tests

PROXIMATE ANALYSIS			ULTIMATE ANALYSIS		
	As Received	Dry Basis		As Received	Dry Basis
Moisture, wt %	28.91	—	Moisture	28.91	—
Ash, wt %	4.81	6.76	Carbon	42.26	59.45
Volatile, wt %	32.17	45.25	Hydrogen	1.98	2.79
Fixed C, wt %	34.11	47.99	Nitrogen	1.12	1.57
Total, wt %	100.0	100.0	Sulfur	0.26	0.37
			Ash	4.81	6.76
H.H.V., Btu/lb	8367	11,770	Oxygen	20.66	29.06
Sulfur	0.26	0.37	Total	100.00	100.00
MAF Btu		12,624	lb SO ₂ per million Btu = 0.63		

Note: Moisture is not included in the hydrogen and oxygen values

Table 2. Properties of Products from Series C Bench-Scale Tests

PROXIMATE ANALYSES				
Sample	4FT87	4FT89	4FT91	4FT92
Moisture, wt %	0.00	0.00	0.00	0.00
Ash, wt %	7.41	7.56	7.40	7.75
Volatiles, wt %	39.67	36.58	38.68	37.90
Fixed C, wt %	52.92	55.86	53.92	54.35
Total, wt %	100.00	100.00	100.00	100.00
H.H.V., Btu/lb	12,337	12,611	12,450	12,422
Sulfur, wt %	0.35	0.34	0.35	0.35
MAF Btu	13,324	13,642	13,445	13,466
lb SO₂ per million Btu	0.57	0.54	0.56	0.56
ULTIMATE ANALYSES				
Moisture, wt %	0.00	0.00	0.00	0.00
Carbon, wt %	79.39	79.77	79.08	80.07
Hydrogen, wt %	3.46	3.41	3.47	3.60
Nitrogen, wt %	1.63	1.79	1.75	1.73
Sulfur, wt %	0.35	0.34	0.35	0.35
Ash, wt %	7.41	7.56	7.40	7.75
Oxygen, wt %	7.76	7.13	7.93	6.50
Total, wt %	100.00	100.00	100.00	100.00

Note: Moisture is not included in the hydrogen and oxygen values

OBJECTIVES OF PHASE II OF THIS PROJECT

One objective of Phase I of this project was to demonstrate the feasibility of the Koppelman Series C process by constructing a 1,000-lb batch test unit and conducting tests to further develop the design basis for a commercial plant, while producing samples of the product for testing and evaluation. A second objective was to characterize the gaseous and water emissions from the process by determining the quantity and composition of those respective emissions. These objectives were accomplished during Phase I and were reported in the final report for Phase I (Merriam 1994).

This report describes the activities conducted during Phase II of the project, the objective of which was to move the process, proven during Phase I, a step closer to commercialization. Specifically, the work was planned to lower the cost of the process by developing a high-capacity processor, increasing the already high efficiency of the process by using a feed coal preheater, increasing the bulk density of the product by using mixed particle size extrudate, and preparing a preliminary scoping design for the water treatment plant for a 500,000 ton per year commercial plant.

During the Phase II project, we altered our emphasis to give top priority to support for the commercial plant being built by Thermo Ecotek. We conducted additional tests using the Series C pilot plant to collect water and gas samples for use in specifying the metallurgy to be used in the commercial plant. We also gave top priority to determining the chloride content of PRB coal and to interpreting the results of corrosion coupons that had been placed in the pilot plant during Phase I.

Construction of a 500,000 TPY Commercial Coal Upgrading Plant Using the Koppelman Series C Process

Thermo Ecotek announced in mid August 1995 the signing of an agreement to construct a 500,000 ton per year coal upgrading plant in the Powder River Basin of Wyoming. The plant, which is now being constructed by Thermo Ecotek, is estimated to cost \$42 million. The plant uses the Koppelman Series C Process which was successfully demonstrated by WRI and KFx Inc. (KFx Inc. is the successor organization to K-Fuel Inc.) in early 1994 using a pilot plant funded by matching funds from the DOE Jointly Sponsored Research (JSR) Program.

In the early 1990s KFx Technology tested the Koppelman Series C Process using bench-scale equipment. In 1993 Western Research Institute, using matching funds from the DOE JSR Program, participated in the design of a demonstration plant using a 1000-lb batch processor, a 2 million Btu per hour heater, and associated product and effluent cooling and collection equipment. WRI assumed the lead role for shakedown and operation of the pilot plant and was also responsible for analysis and transfer of data. The pilot plant was successfully operated in the first half of 1994. The data obtained from the testing program was used to design the commercial plant.

WRI is presently working with KFx Inc. to improve the process by increasing the throughput and reducing the cost of future plants that will use the improved version of the Koppelman Series C Process.

Description of the Series C Pilot Plant

The pilot plant constructed as part of this project in the fall of 1993 consists of coal feed and product discharge systems, a batch processor, a hot oil heating system, and effluent measurement and control systems (Figure 1).

Figure 1. Process Flow Diagram for the Koppelman Series C Pilot Plant

In the pilot plant, crushed and sized coal is fed into a tote bin, and the weight of the feed coal charge is obtained from load cell readings. The coal is drained from the tote bin through a feed screw into a bucket elevator where it is lifted into a feed bin above the 40-ft-tall reactor system. The coal drains by gravity through an open valve into the top of the reactor and flows into the open end of vertical tubes that penetrate the upper tube sheet of the processor. The coal fills the reactor by piling up on a closed slide gate valve (Figure 2) located below the tubes and above a closed pressure containment valve at the bottom of the reactor. When the coal charge is within the reactor tubes, the seats in the valve at the top of the reactor are cleaned by a blast of nitrogen gas, and the valve is then closed by a pneumatic operator upon receiving an electrical signal from the programmable logic controller (PLC) that controls the system. The air is swept from the processor by displacement using nitrogen gas, and the pressure is then increased to about 120 psig with nitrogen.

The processor is heated to the temperature for the individual tests (design 800 °F) by a flow of 400 gallons per minute of Therminol VP-1, which flows continuously through a 2 million Btu/hr (net heat transferred) heater fired with propane. The heat load to the processor is controlled by varying the firing rate of propane flowing to the heater to maintain a constant temperature of the heat transfer fluid leaving the heater. When a charge of cold coal enters the preheated processor, the temperature of the oil leaving the processor drops, and the heater firing rate is increased to maintain the set-point temperature of the hot oil leaving the heater. The heater is designed for a 2.8 MM Btu/hr heat release rate with a hot oil flow of 400 gal/min. After the coal is heated, the temperature of the heat transfer fluid leaving the processor remains substantially the same as the inlet temperature, and the firing rate of the heater is reduced by the temperature set-point controller.

As the coal is heated by transfer of heat through the tubes, the water on the coal is evaporated into the lower portion of the coal charge, where it again condenses as it heats cooler coal. After evaporating and condensing several times, the condensate from the moisture in the coal is drained from the bottom of the processor through an automatically controlled vent valve. When the coal has been heated sufficiently to alter the structure and increase the heating value, the reactor is depressurized by draining gas and condensate from the processor. When the pressure in the processor is below 5 psig, the slide gate valve and the pressure-containing valve at the bottom of the processor are opened. The product falls from the reactor into a nitrogen-blanketed product collection bin. The product is then transferred by a screw conveyor to a storage bin where it is held in a nitrogen atmosphere until it is cool enough to be exposed to air (about 250 °F). The product is then weighed, sampled, and held for evaluation.

Condensate drained from the processor is cooled by contact with cold water in a flash tank, filtered to remove coal dust and most of the coal tars, and transferred to a storage tank. The gas that flows with the condensate from the processor is vented from a gas-water separator, which also acts as a holding tank for the water, through a gas meter equipped with electronic readout for rate determination, and into the stack of the hot oil heater for incineration.

Temperatures within the processor are measured by thermocouples (TC) located throughout the reactor. One group of 11 thermocouples is located within the center tube, with the first TC at the top and the other 10 spaced at 3-ft intervals. A second group of four thermocouples is located in a tube on the north side of the reactor and are spaced at depths of 5, 10, 15, and 20 feet into the tube. A third group of four thermocouples is located in a tube in the south side of the reactor and are spaced at 5-, 10-, 15-, and 20-ft depths. Four additional thermocouples are located in the cylindrical and conical portion of the processor below the tubes. The temperature of the coal in the feed bin and the temperature of the product in the collection bin are also recorded. Temperatures are also recorded in the heat transfer fluid lines at the inlet and outlet of the heater, the inlet and outlet of the processor, and at the expansion tank. We also record temperatures in the effluent gas and water lines.

Pressures are recorded using pressure transducers taking measurements from the top and the bottom of the processor and in the flash tank. Pressures are measured, but not recorded, at the heat transfer fluid circulating pump suction and discharge, on both sides of the filter in the pump suction line, as well as in the cooling water system, the nitrogen system, and the propane supply system.

Temperatures and pressures in the system are recorded at intervals that can be varied from fractions of a second to 60 seconds using a computer-based data acquisition system. The timer, which controls the programmable logic controller (PLC), is used to establish a time-based series of data. The temperature and pressure readings are grouped by location and are continuously visible on a terminal located near the processor. The values may be printed by touching a print screen button or by designating the time or events that initiate an automatic print command. Printed data are collected at the end of each test and used to evaluate the data from the tests. Some of the temperature and pressure data are used in the summary calculations that describe the individual tests. The rate of water production is measured by a continuous reading of the level in the flash tank. An electronic signal from the gas meter is used to acquire the rate of gas production during tests.

Samples of coal and product are collected from the raw coal charges and the cooled product from the tote bin and are analyzed following ASTM procedures. Water samples are collected from the cooled sample line and analyzed following established EPA protocols. Gas samples are taken from the effluent gas sample line located in the gas line near the gas meter and are analyzed using a gas chromatograph.

WRI SUPPORT FOR DESIGN AND OPERATION OF THE COMMERCIAL PLANT

Earlier characterization of the water and gas from the Series C process was reported in the final report for Phase I (Merriam 1994). However, we had to conduct more detailed characterization of the water and gas to acquire more complete data for the design basis for the commercial plant. We also conducted an assessment of the chlorine content of PRB coal to use in specifying the metallurgy

for the effluent processing systems. Corrosion testing started in Phase I was accelerated to supply data for use in specifying the metallurgy for the commercial plant.

Composition of Water Produced Using the Series C Pilot Plant

We had characterized the water from the process during Phase I but had not spent sufficient time and money to perform analyses in sufficient detail to serve as a complete design basis for a commercial water treatment plant. During Phase II, we conducted six special tests in the 1000-lb batch pilot plant to obtain water analyses to use for firming up the design basis. Water samples were collected and conveyed to Energy Labs under chain of custody control for complete analyses for Wyoming Livestock and Agriculture Standards and also for the Resource Conservation Recovery Act (RCRA) toxicity characteristic leaching procedure (TCLP). The results of these analyses are shown in Tables 3 and 4.

Preliminary Design of the Water Treatment System for the Commercial Plant

The simplified process flowsheet (Figure 3) shows the quantity of water produced by a plant that produces 500,000 tons of product per year. The water is produced as a boiling liquid at its saturation temperature and must be cooled to condense the flashing vapors and separate the water from the gas (Figure 4). The final treatment steps and the final disposition of the treated water will be determined after the analyses are complete.

Composition of Gas from the Series C Pilot Plant

Samples of the gas produced during Series C tests 73 and 74 (Tables 5 and 6) were analyzed for permanent and combustion gases. Samples were taken in Mylar gas sample bags and shipped to WRI for analyses. Gas samples were withdrawn from the bags and were injected into the gas chromatograph (GC) column using a gas-tight syringe. Permanent and combustion gases and methane were analyzed on a Hewlett-Packard 5840A GC equipped with a thermal conductivity detector and a 7 m long by 3 mm dia. stainless steel column packed with Chromosorb 102. The initial column oven temperature of -50 °C was maintained for 6 min, then increased at a rate of 25 °C per min to a temperature of 180 °C. High-purity helium flowing at a rate of 28 cc per min was used as carrier gas.

Hydrocarbon gases were analyzed using a Hewlett-Packard 5840A gas chromatograph with a flame ionization detector using a 3 m long by 3 mm dia. stainless steel column packed with Chemipak C18. The initial column oven temperature of 100 °C was maintained for 3 min, then was increased at a rate of 25 C/minute until a temperature of 180 °C was reached. High-purity helium flowing at a rate of 28 cc/minute was used as carrier gas. Hydrocarbon gases were quantified relative to the methane concentration for each sample. The hydrocarbon concentrations were then added to the combustion gas analyses, and the result was renormalized to 100%.

Table 3. Wyoming Water Standards and Sample Values

Constituent —	Class I Domestic	Class II Agriculture	Class III Livestock	CSER 70 —	CSER 71 —	CSER 72 —	CSER 73 —	CSER 74 —
Nitrate as N	10.0	—	—	<5	<5	<5	<5	<5
Nitrite as N	1.0	—	10.0	<5	<5	~5	<5	<5
Oil & Grease	<1	10.0	10.0	2400	4700	3800	3800	3900
Ortho Phosphate	—	—	—	0.22	0.12	0.16	<0.1	<0.1
Phenol	0.001	—	—	500	1300	900	1100	1000
Potassium	—	—	—	6	6	5	5	4
Selenium	0.01	0.02	0.05	<0.005	<0.005	<0.005	<0.005	<0.005
Silica Oxide	—	—	—	10.8	10.2	9.5	9.5	8.6
Silver	—	—	<0.005	<0.005	<0.005	<0.005	<0.005	
Sodium	—	—	—	64	59	52	53	50
Strontium	—	—	—	1.1	0.9	0.9	0.9	0.9
Sulfate	250	200	2000	142	128	104	99	98
Toluene	—	—	—	<0.1	<0.1	<0.1	<0.1	<0.1
TOC	—	—	—	1700	2000	1300	1400	1280
TOH	—	—	—	<0.010	<0.010	<0.010	<0.010	<0.010
TDS	500	2000	5000	1110	1060	1070	972	968
TSS	—	—	—	262	180	341	424	440
Uranium	5.0	5.0	5.0	<0.003	<0.0003	<0.0003	<0.0003	<0.0003
Vanadium	—	0.1	0.1	~0.10	<0.10	~0.10	<0.10	<0.10
Xylene	—	—	—	<0.1	<0.1	<0.1	~0.1	<0.1
Zinc	5.0	2.0	25.0	0.18	0.23	0.26	0.21	0.14
pH	6.5-9.0 S.U.	4.5-9.0 S.U.	6.5-8.5 S.U.	5.0 S.U.	4.8 S.U.	4.8 S.U.	4.9 S.U.	4.8 S.U.
SAR	—	8.0 Unitless	—	2.07	2.08	2.2	1.99	2.0
RSC	—	1.25 meq/l	—	1.40	-1.34	0.39	-0.20	0.17
Radium226	5.0 pCi/l	5.0 pCi/l	5.0 pCi/l	0.5+0.4 pCi/l	0.6+0.5 pCi/l	0.5+0.4 pCi/l	0.2+0.2 pCi/l	0.5+0.4 pCi/l
Gross Alpha	15.0 pCi/l	15.0 pCi/l	15.0 pCi/l	<1.0 pCi/l	<1.0 pCi/l	<1.0 pCi/l	~1.0 pCi/l	<1.0 pCi/l

Table 4. Toxicity Characteristic Constituents, Regulatory Levels, and Sample Levels (mg/l)

EPA No.	Constituent	R.L.2	CSER 70	CSER 71	CSER 72	CSER 73	CSER 74
D004	Arsenic	5.0	0.077	0.069	0.056	0.062	0.042
D005	Barium	100.0	0.4	0.4	0.4	0.3	0.2
D018	Benzene	0.5	<0.1	<0.1	<0.1	<0.1	<0.1
D006	Cadmium	1.0	<0.001	<0.001	<0.001	<0.001	<0.001
D019	Carbon Tetrachloride	0.5	—	—	<0.1	—	—
D020	Chlordane	0.03	—	—	<0.2	—	—
D021	Chlorobenzene	100.0	—	—	<0.1	—	—
D022	Chloroform	6.0	<0.1	<0.1	<0.1	<0.1	<0.1
D007	Chromium	5.0	<0.01	0.01	<0.01	<0.01	<0.01
D023	o-Cresol	200.0	30.1	47.9	51.3	59.9	49.0
D024/25	m- & p-Cresol	200.0	135.0	180.0	213.0	246.0	244.0
D026	Cresol	200.0	165.1	227.9	264.3	305.9	293.0
D016	2,4-D	10.0	—	—	<0.4	—	—
D027	1,4-Dichlorobenzene	7.5	—	—	<0.1	—	—
D028	1,2-Dichloroethane	0.5	—	—	<0.1	—	—
D029	1, I-Dichloroethylene	0.7	—	—	<0.1	—	—
D030	2,4-Dinitrotoluene	0.13	—	—	<5.0	—	—
D012	Endrin	0.02	—	—	<0.04	—	—
D031	Heptachlor	0.008	—	—	<0.02	—	—
D032	Hexachlorobenzene	0.13	—	—	<5.0	—	—
D033	Hexachloro-1,3-butadiene	0.5	—	—	<5.0	—	—
D034	Hexachloroethane	3.0	—	—	<5.0	—	—
D008	Lead	5.0	0.01	0.02	0.01	0.01	<0.01
D013	Lindane	0.4	—	—	<0.02	—	—
D009	Mercury	0.2	0.03	<0.01	0.03	<0.01	<0.01-
D014	Methoxychlor	10.0	—	—	<0.2	—	—
D035	Methyl Ethyl Ketone	200.0	4.98	26.4	37.7	55.5	40.8
D036	Nitrobenzene	2.0	—	—	<5.0	—	—
D037	Pentachlorophenol	100.0	—	—	<25.0	—	—
D038	Pyridine	5.0	—	—	<10.0	—	—
D010	Selenium	1.0	<0.005	<0.005	<0.005	<0.005	<0.005
D011	Silver	5.0	<0.005	<0.005	<0.005	<0.005	<0.005
D039	Tetrachloroethylene	0.7	—	—	<0.1	—	—
D015	Toxaphene	0.5	—	—	<2.0	—	—
D040	Trichloroethylene	0.5	—	—	<0.1	—	—
D041	2,4,5-Trichlorophenol	400.0	—	—	<5.0	—	—
D042	2,4,6-Trichlorophenol	2.0	—	—	<5.0	—	—
D017	2,4,5-TP Silvex	1.0	—	—	<0.08	—	—
D043	Vinyl chloride	0.2	—	—	<0.1	—	—

1 - USEPA Hazardous Waste Number 2 - Regulatory Level

Figure 3. Simplified Process Flowsheet for the Preliminary Design of a Water Treatment Plant

Figure 4. Gas-Water Separation System Proposed for the Preliminary Design

Table 5. Composition of Gas Produced During Test CSER73 (mol%)

TIME	1123	1124	1125	1126	1127	1128	1129	1130	1133	1135
Interval, min	0	1	2	3	4	5	6	7	10	12
Hydrogen	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0	0.0
Nitrogen	71.575	70.011	68.114	70.574	70.270	72.074	73.342	70.693	72.7	36.9
Oxygen	6.276	0.000	0.660	9.315	4.042	8.173	10.241	6.019	1.9	5.4
Argon	0.000	0.000	0.000	0.397	0.000	0.375	0.473	0.000	0.0	0.1
Carbon Monoxide	0.674	0.998	1.064	0.525	0.901	0.676	0.563	0.907	1.0	3.1
Carbon Dioxide	19.792	26.519	27.327	16.959	22.048	16.303	13.731	19.351	20.8	42.6
Methane	0.549	0.863	0.998	0.548	0.900	0.734	0.648	0.976	1.1	3.9
Ethylene	0.036	0.048	0.046	0.045	0.048	0.039	0.028	0.053	0.1	0.2
Ethane	0.074	0.104	0.110	0.145	0.125	0.097	0.070	0.146	0.2	0.6
Propanes	0.732	1.078	1.206	1.263	1.319	1.034	0.792	1.545	1.8	6.1
Butanes	0.009	0.000	0.000	0.000	0.030	0.025	0.000	0.040	0.0	0.2
Pentanes	0.008	0.007	0.002	0.006	0.008	0.008	0.001	0.012	0.0	0.1
C6+	0.005	0.005	0.000	0.011	0.002	0.004	0.001	0.006	0.0	0.0
Hydrogen Sulfide	0.240	0.315	0.395	0.187	0.275	0.382	0.079	0.221	0.3	0.7
Methyl mercaptan	0.030	0.042	0.061	0.024	0.033	0.062	0.018	0.033	0.0	0.1
Ethyl mercaptan	0.000	0.000	0.007	0.000	0.000	0.008	0.000	0.000	0.0	0.0
Thiophene	0.000	0.000	0.011	0.000	0.000	0.006	0.013	0.000	0.0	0.0

Table 6. Composition of Gas Produced During Test CSER74 (mol%)

TIME	1520	1521	1522	1523	1524	1525	1526	1527	1528	1529	1530
Interval, min	0	1	2	3	4	5	6	7	8	9	10
Hydrogen	0	0	0	0	0	0	0	0	0	0	0
Nitrogen	70.631	70.179	72.458	69.693	74.661	69.766	71.494	74.792	33.553	77.699	47.05
Oxygen	9.514	6.616	10.212	4.752	14.091	3.673	6.992	14.986	2.108	6.186	4.923
Argon	0.434	0.254	0.463	0	0.63	0	0.294	0.669	0	0	0
Carbon Monoxide	0.629	0.78	0.556	0.901	0.319	0.971	0.806	0.27	0.28	0.591	2.573
Carbon Dioxide	17.571	20.593	14.997	22.531	9.25	23.306	18.361	8.342	63.324	13.962	37.586
Methane	0.425	0.604	0.456	0.749	0.314	0.841	0.723	0.305	0.256	0.563	2.854
Ethylene	0.031	0.037	0.025	0.045	0.017	0.049	0.039	0.018	0.014	0.03	0.164
Ethane	0.05	0.069	0.048	0.09	0.035	0.106	0.083	0.05	0.033	0.068	0.403
Propanes	0.455	0.674	0.461	0.903	0.359	1.07	0.865	0.515	0.35	0.67	3.784
Butanes	0.008	0	0	0.009	0	0	0	0	0	0	0.093
Pentanes	0.004	0.005	0	0.007	0.002	0.008	0.005	0	0.002	0	0.01
C6+	0.001	0.002	0	0.004	0.001	0.003	0.002	0	0.002	0	0
Hydrogen Sulfide	0.226	0.172	0.284	0.282	0.038	0.189	0.298	0.054	0.069	0.208	0.505
Methyl Mercaptan	0.02	0.016	0.031	0.035	0	0.019	0.037	0	0.008	0.021	0.055
Ethyl Mercaptan	0	0	0	0	0	0	0	0	0	0	0
Thiophene	0	0	0	0	0	0	0	0	0	0	0

Sulfur-containing gases were analyzed using a Hewlett-Packard 5840A GC equipped with a flame photometric detector while using a 2 m long by 3 mm dia. Teflon column packed with Carbopak BHT 100. The initial column oven temperature of 20 °C was maintained for 3 minutes and was then increased at a rate of 25 °C/min to a temperature of 140 °C. Nitrogen flowing at a rate of 50 cc/min was used as carrier gas. The GC used to analyze for sulfur containing gases was calibrated between 500 and 10,000 ppm using a certified standard gas containing 10,000 ppm of hydrogen sulfide. The response factors determined for the H₂S were also used for the other sulfur species. These factors are probably not exactly correct but are the best approximation that can be made without purchasing certified gases containing the other standards.

Most of the samples from these tests contained some oxygen. The Mylar gas sample bombs without septums are difficult to use without causing oxygen contamination. Some of the sample bombs with septums seemed less likely to be contaminated with oxygen. We cannot determine how much of this oxygen is the result of air contamination during the sampling process and how much is actually present in the process gas. Therefore, the results are reported both "as analyzed" and on an air-free basis. Air-free analyses were calculated assuming that all the oxygen in the sample resulted from air contamination.

Air-free analyses were calculated by multiplying the area of the oxygen peak in the chromatogram by appropriate factors to obtain the areas of nitrogen and argon peaks corresponding to the oxygen area for an air sample. Nitrogen and argon areas were then reduced by the respective product numbers, and the results were renormalized to 100%.

The detection limit for hydrogen in these analyses was approximately 2%. Hydrogen values reported as 0.000% should be viewed as less than 2%.

Chloride Content Of Powder River Basin Coals

The work (Satchwell 1995) described in this section was conducted to determine chlorine content of the Powder River Basin Coal deposits, particularly the coal deposits in vicinity of Gillette, Wyoming. This data will be used as a basis for specifying metallurgy in the commercial plant that is to be located at the Fort Union Mine site, approximately 6 miles northeast of Gillette, Wyoming.

Surveys of the chlorine content of PRB coal were conducted using available sources of analyses. This data was obtained from Geological Survey of Wyoming documents, U.S. Geological Survey documents, and Western Research Institute reports.

The data in Table 7 represents the results from analyses of twenty samples of coal from the Fort Union formation in the Powder River Coal Basin performed by the Geological Survey of Wyoming (See Figure 5). Sample numbers 35, 36, and 37 represent a Badger coal bed sample and two School coal bed samples from the Dave Johnson strip mine located in the Glenrock field of Converse County. Three samples, designated as sample numbers 38, 39, and 40, of the Anderson-Canyon bed (Wyodak) were collected from the Belle Ayr strip mine located in Campbell County. Sample numbers 41, 42, and 43 designate samples of the Wyodak strip mine also located in Campbell County. Coal samples from the Dietz and Monarch beds, sample numbers 44 to 48, were collected from the Big Horn strip mine in Sheridan County. Monarch bed coal samples from the Welch strip mine in Sheridan County are designated as sample numbers 49 to 54.

Table 7. Chlorine Content in the Powder River Basin Coal Deposits ¹

Sample Number	Ash	Cl ²	Cl on a Whole Coal Basis
yr. - location	wt. %	% of Ash	ppm
74 - 35	12.9	< 0.1	< 129
74 - 36	21.7	< 0.1	< 217
74 - 37	11.3	< 0.1	< 113
74 - 38	7.6	< 0.1	< 76
74 - 39	6.3	< 0.1	< 63
74 - 40	7.1	< 0.1	< 71
74 - 41	8.7	< 0.1	< 87
74 - 42	10.4	< 0.1	< 104
74 - 43	7.5	< 0.1	< 75
74 - 44	7.9	< 0.1	< 79
74 - 45	18.0	< 0.1	< 180
74 - 46	6.0	< 0.1	< 60
74 - 47	5.4	< 0.1	< 54
74 - 48	7.4	< 0.1	< 74
74 - 49	10.0	< 0.1	< 100
74 - 50	10.2	< 0.1	< 102
74 - 51	10.2	< 0.1	< 102
74 - 52	9.9	< 0.1	< 99
74 - 53	26.2	< 0.1	< 262
74 - 54	14.0	< 0.1	< 140

1 - From Glass, G. B., 1975, "Analyses and Measured Sections of 54 Wyoming, Coal Samples," The Geological Survey of Wyoming, Laramie Wyoming, pg. 30-33.

2 - Measured by USGS laboratories using X-ray fluorescence analysis

< - Means less than.

Figure 5. Location of Sources of Coal Samples Taken for Chlorine Analysis

Since the characteristics of coal change with depositional environment, only sample numbers 38 to 43, shown by the shaded area in Table 7, should be used as given. The chlorine data in the shaded region has a sample mean of less than 79.3 ppm, a sample standard deviation of 14.4, and a range from 63 to 104. However, the reader is cautioned not to use this data as the sole basis for design calculations because the accuracy is limited by the small sample size.

Table 8 is a comparison of five coal samples from the Belle Ayr strip mine. This data was supplied from analyses performed by the AMAX Coal Company and the Geological Survey of Wyoming. This chloride data has a sample mean of 122 ppm, a sample standard deviation of 100, and a range from 63 to 300. Again, the reader is cautioned not to use this data for design calculations because of the small sample size.

Table 8. Comparison of Chloride Analyses from the Belle Ayr Strip Mine

Source of Analysis	Coal Name	Location	Chlorine, ppm
AMAX ¹	Anderson-Canyon Coal	Belle Ayr Strip Mine	300
AMAX ²	Anderson-Canyon Coal	Belle Ayr Strip Mine	100
WGS ³	Anderson-Canyon Coal	Belle Ayr Strip Mine	< 76
WGS ³	Anderson-Canyon Coal	Belle Ayr Strip Mine	< 63
WGS ³	Anderson-Canyon Coal	Belle Ayr Strip Mine	< 71

< - Means less than.

1 - Supplied by AMAX Coal Company, From Glass, G. B., 1975, "Analyses and Measured Sections of 54 Wyoming, Coal Samples," The Geological Survey of Wyoming, Laramie Wyoming, pg. 172.

2 - Supplied by AMAX Coal Company, From Merriam, N. W. et. al, 1990, "Development of an Advanced Continuous Mild Gasification Process for the Production of Co-products," DOE/MC/24268-3075, Western Research Institute, Laramie, Wyoming, pg. 4.

3 - From Glass, G. B., 1975, "Analyses and Measured Sections of 54 Wyoming, Coal Samples," The Geological Survey of Wyoming, Laramie Wyoming, pg. 30-33.

A final source of chlorine concentration data was available from the U.S. Geological Survey, Coal Quality (COALQUAL) Database. The initial search in the database was performed using only the following qualifiers: State - Wyoming, Coal Region - Powder River Basin, Coal Formation - Fort Union, and County - Campbell. This search revealed 204 entries. This data included coals of all rank, all depths, and blank entries for chlorine. The search was then narrowed to include only subbituminous rank coals, depths less than or equal to 220 feet, and only entries with actual chlorine concentration values. The results of this search found 33 entries. The results of this search are given in Table 9. This table represents the largest data set pertinent to the coal mining operations that could supply coal to the commercial plant.

Table 9. Chlorine Content of Subbituminous Coals in Campbell County¹

Sample #	Latitude deg:min:sec	Longitude deg:min:sec	Ash ² wt %	Chlorine ³ ppm
1	44:57:15	105:38:09	17.30	70
2	44:58:20	105:47:37	13.80	70
3	44:58:42	105:47:37	12.90	100
4	44:09:48	105:21:41	6.82	1100
5	44:52:32	105:46:45	10.10	100
6	44:32:42	105:34:48	10.26	70
7	44:32:42	105:34:48	6.29	100
8	44:32:42	105:34:48	6.93	70
9	44:32:42	105:34:48	13.62	100
10	44:32:54	105:31:36	4.95	70
11	43:32:13	105:15:36	5.10	70
12	44:20:34	105:27:33	5.39	230
13	43:48:58	105:19:07	5.93	70
14	43:49:10	105:16:59	12.80	70
15	43:49:10	105:16:59	6.75	70
16	43:50:39	105:15:32	----	70
17	43:50:39	105:15:32	4.70	100
18	43:50:39	105:15:32	8.20	70
19	43:50:39	105:15:32	4.60	70
20	43:50:39	105:15:32	9.79	85
21	43:50:02	105:18:09	7.70	70
22	43:52:02	105:18:09	5.47	70
23	43:57:06	105:19:27	19.10	70
24	43:57:06	105:19:27	9.70	70
25	43:57:06	105:19:27	6.11	87
26	43:58:52	105:18:24	7.70	70
27	43:58:52	105:18:24	7.36	70
28	43:59:48	105:20:00	8.60	70
29	43:59:48	105:20:00	7.89	70
30	44:29:10	105:31:55	4.83	70
31	44:32:54	105:31:36	6.56	90
32	43:48:58	105:19:07	10.00	70
33	44:29:10	105:31:55	5.41	78

1 - From USGS Coal Quality (COALQUAL) CD-ROM Database: Version 1.3

2 - Ash measured using ASTM method D-3178

3 - Measured by USGS laboratories using X-ray fluorescence analysis

The results of the statistical analysis are given in Table 10. The 95% and 99% confidence intervals on the population mean and standard deviation were determined using one-sided t-tests from the data presented in Table 9. The 95% and 99% confidence intervals for the ranges were determined using Chebyshev's Theorem. This theorem states that at least $(1 - 1/K^2)$ of any observation of any data set lies within K standard deviations of the mean of the data.

Table 10. Statistical Analysis of Chlorine Values from USGS Data

Statistical Terms	0% Confidence Interval	95% Confidence Interval	99% Confidence Interval
Population Mean, μ , (ppm)	112.4	165.4	189.0
Population Standard Deviation, μ , (ppm)	179.6	226.7	251.0
Range ¹ (ppm)	0 - 1100	0 - 916	0 - 1908
Range ² (ppm)	—	0 - 1179	0 - 2432
Range ³ (ppm)	—	0 - 1311	0 - 2699

1 - Ranges using 0% confidence interval of the population mean and standard deviation

2 - Ranges using 95% confidence interval of the population mean and standard deviation

3 - Ranges using 99% confidence interval of the population mean and standard deviation

As the actual data shows, it would not be prudent to use the 95% confidence interval with the sample mean and standard deviation for design, since the range does not encompass all of the actual chlorine values (0 - 916 compared to actual range of 70 - 1100). The question design personnel should ask is what quantity and duration of chlorine can the system handle. The most conservative approach that can be taken is that design personnel can be 99% confident that all chlorine values of coals that could supply material to the commercial plant will be between 0 to 2699 ppm.

Corrosion Testing in the Series C Process

Powder River Basin coal contains about 30% water. In the Series C Process water is removed when pressure is relieved into a flash tank. Previous work had shown that produced water can range in pH of about 3.5 to 4.0, and can contain substantial quantities of chlorides. Realizing that depending upon the materials, issues such as general corrosion, pitting and crevice corrosion, and stress corrosion cracking are possible, a corrosion testing effort of limited scope was implemented. Two corrosion test racks were installed in the flash tank. Samples of several alloys were installed in one of the reactor tubes, and a special test fixture was constructed for installation in the throat of a valve at the reactor outlet. Installation of the racks took place sometime in November prior to plant startup in December 1993. Corrosion racks exposed in the flash drum, and the samples exposed in

the reactor tube were sent back to WRI for a quick analysis on November 17, 1995. This section of this report deals with the results (Sethi 1995) obtained.

Test Materials Used for Corrosion Studies

Materials exposed in the reactor tube included 316 ss, Inconel 625, alloy 31, alloy 59, and alloy 1925. Composition of these alloys are given in Table 11. These samples, in the form of 2.75 x 1 x 0.125 in. flats, were strapped to a 0.250 in. dia. thermowell installed into one of the processing tubes of the reactor. These samples were neither electrically isolated from one another nor from the process. Expected environment was wet/dry cycles, exposure to coal-derived liquids, and in the long run, potential for carburization.

Selection of materials for inclusion on the corrosion racks to be exposed in the flash drum was dictated by the expected pH and chloride content of the produced water. Materials were selected in consultation with Mr. Jim Crum of INCO International and included 316L ss, Incoloy 825, 25S6Mo, 904L ss, Hastelloy C-276, and INCO's alloy 686. Compositions of these alloys are given in Table 12. Duplicate samples of each of the alloy in the form of 2-in. dia. discs were assembled into corrosion racks after recording their initial weights. In addition to the disc samples, corrosion racks also carried four U-bend samples, two each of 316 ss and Incoloy 825 to assess their stress corrosion cracking performance. Rack construction followed established National Association of Corrosion Engineers (NACE) procedures and guidelines for electrical isolation using Teflon spacers.

Exposure Conditions

Test racks installed in December 1993, prior to plant operations, were exposed in the reactor tube for 66 tests and were removed on July 19, 1995. Test racks were exposed for 74 tests in the flash drum, while about 60,000 lbs was processed. They were removed on November 14, 1995.

A typical test involves loading the coal in the reactor, pressurization, heating to desired temperature, venting or flashing as needed to maintain pressure, flashing into the drum, and cooldown. The time required for these tests is approximately 25 to 45 minutes. Total exposure time for the samples exposed in the reactor tube is thus quite short. Similarly, exact exposure time for the samples exposed in the flash drum cannot be ascertained. One of the corrosion test racks was installed at the bottom of the drum, and depending on the location of the drain, once submerged in the produced water, it may have been exposed to water for the entire duration the rack was in place—about two years. Temperature of the water may have varied from ambient to about 200 °F. The second corrosion rack was installed in the flash drum at an inspection port nozzle. This rack was exposed to vented gases at 150 to 200 °F for about 15 to 20 minutes during venting after each test.

Table 11. Alloy Composition of Materials Exposed as Spacers on the TC Probe in the Reactor

Alloy	Ni	Cr	C	Mn	Si	Cu	Mo	P	S	N	Fe	Other
1925	25.0	20.5	0.020	1.00	0.50	1.00	6.00	0.030	0.005	0.20	Bal	
31	31.0	27.0	0.015	2.00	0.30	1.40	7.00	0.020	0.010	0.20	Bal	
59	Bal	23.0	0.010	0.50	0.10		16.5	0.015	0.005		1.50	0.3 Co 0.4 Al
316	10.2	16.4	0.02	1.60	0.50		2.10			0.05	Bal	
625	Bal	21.5	0.05	0.10	0.10		9.00				4.00	3.6 Nb

Table 12. Alloy Composition of Materials Exposed in the Flash Drum

ID	Alloy	Cr	Ni	Mo	Si	Mn	Co	S	Cu	P	C	Fe	Other
RML	316L	16.68	12.49	2.38	0.57	1.54	0.20	0.021	0.30	0.021	0.023	Bal	
FL	825	22.33	43.60	2.84	0.09	0.39		0.004	1.96		0.020	Bal	0.84 Ti 0.04 Al
NX	904L	20.02	27.12	4.62	0.47	1.49		0.001	1.38	0.023	0.010	Bal	
NCE	25S6Mo	20.00	25.00	6.00					1.00			Bal	Nominal Comp.
NCN	C276	15.73	56.56	16.08	0.06	0.48	1.08	0.001		0.011	<.01	5.84	3.98 W 0.18 V
NCL	686	20.48	57.63	16.38		0.24	0.02		<.01		0.005	1.04	3.88 W 0.03 Nb 0.22 Al

Evaluation of Samples Exposed in the Reactor Tube

Weight loss/gain data for the samples exposed are summarized in Table 11. Please note that a total of eleven samples were sent for installation, and only ten were sent back for evaluation. Exposure locations for these samples were about one foot apart along the length of the reactor tube. The lower three samples were heavily coated with coal-derived liquids on the entire exposed surface. The rest of the samples had a similar coating in the crevice created by the metal strap used for installation on the thermowell tube. These samples were weighed in the as received condition, cleaned with soap and water, and reweighed. Areas where coal-derived liquid deposits were present still had material adhering to the surfaces and required further cleaning. A brass wire brush was used for further cleaning, and samples were weighed again. Weight loss/gain data displayed in Table 13 uses the weights after final cleaning using a wire brush.

In general, all materials showed a weight loss. It is not clear whether this should be attributed to any corrosion losses because, with the exception of Inconel 625 exposed near the bottom of the reactor which had a bluish tinge, no obvious corrosion scale was present on other samples. Examination of all of these samples showed “ding” markings on one of their long edges, presumably caused by the falling coal. It is possible that the weight loss is a reflection of this erosive action of the coal as the reactor tube was filled. It should be pointed out that there are no reactor parts that will experience this type of impaction under normal operation. It is also possible that the weight change was caused by the abrasive action of the coal as the reactor was emptied. In such a case the weight loss data reflect potential wear of the reactor tubes.

These samples did not show any signs of pitting on their exposed flat surfaces. No aggravated corrosion was evident in the crevices created by the straps used for installation. If the weight loss experienced by the samples is indeed indicative of the abrasive action of the coal, then it is recommended that if and when a reactor tube is removed or replaced, a thorough metallurgical evaluation be undertaken.

Evaluation of Samples Exposed in the Flash Drum

Prior to their arrival at WRI, these racks had been cleaned by washing with a solvent. Racks were disassembled, and individual samples were cleaned by washing with soap and water. No adherent deposits were left on any of the samples. Samples were then weighed. Weight change data for the samples exposed on the two racks are displayed in Tables 14 and 15. Table 14 shows the weight change data for samples exposed at the bottom of the flash drum, whereas Table 15 shows similar data for samples exposed in the same vessel in an inspection nozzle. In both the tables a weight gain is shown by all of the exotic alloys tested. Type 316 L ss samples do show a weight loss, however the change is not consistent on a given test rack in that only one of the samples shows a loss while the other does not.

Table 13. Weight Loss Data for Samples Exposed on the TC Probe in the Reactor

Material	Sample ID	Location	Initial Weight (g)	As Received (g)	Cleaned ¹ (g)	Final Weight ² (g)	Weight Loss (mg)
Alloy 59	59-1	11	40.69875	40.70248	40.69617	40.69619	2.56
Alloy 31	31-1	10	Sample was not returned				
Alloy 1925	1925-1	9	37.96270	37.96005	37.95863	37.95823	4.47
Alloy 59	59-2	8	39.85732	39.85447	39.85421	39.85233	4.99
Alloy 31	31-4	7	39.77662	39.77270	39.77198	39.77200	4.62
Alloy 1925	1925-2	6	38.12919	38.12907	38.12724	38.12769	2.50
Alloy 59	59-3	5	41.07979	41.07834	41.07681	41.07729	2.50
Alloy 31	31-3	4	39.96522	39.96211	39.96103	39.96108	4.14
Alloy 1925	1925-3	3	38.15493	38.16604	38.16172	38.15312	1.81
Type 316 ss	316	2	42.48378	42.49530	42.49232	42.48209	1.76
Inconel 625	IN	1 (Bottom)	47.96171	47.96028	47.95904	47.95409	2.62

¹ Weights of samples after cleaning with soap and water

² Weights of samples after cleaning using a brass wire brush

Table 14. Weight Loss Data for Samples Exposed at the Bottom of the Flash Tank

Material	Sample ID	Location	Initial Weight (g)	Final Weight (g)	Weight Loss (mg)
316 L	RML 462	1	17.69221	17.69231	-0.10
25S6Mo	NCE 75	2	56.33162	56.33196	-0.34
825	FL 563	3	31.92280	31.92311	-0.31
904 L	NX 877	4	41.11483	41.11477	0.06
C276	NCN 359	5	34.73728	34.73730	-0.02
686	NCL 55	6	42.94242	42.94246	-0.04
316 L	RML 463	7	17.70412	17.70377	0.35
25S6Mo	NCE 76	8	56.26395	56.26418	-0.23
825	FL 564	9	31.77502	31.77536	-0.34
904 L	NX 878	10	40.75274	40.75298	-0.24
C276	NCN 360	11	34.89530	34.89564	-0.34
686	NCL 56	12	43.18516	43.18566	-0.50

Table 15. Weight Loss Data for Samples Exposed in the Inspection Port Nozzle of the Flash Tank

Material	Sample ID	Location	Initial Weight (g)	Final Weight (g)	Weight Loss (mg)
316 L	RML 466	1	17.73620	17.73139	4.81
25S6Mo	NCE 79	2	56.06642	56.06647	-0.05
825	FL 567	3	31.98673	31.98688	-0.15
904 L	NX 879	4	41.03533	41.03550	-0.17
C276	NCN 363	5	34.81261	34.81263	-0.02
686	NCL 59	6	43.07103	43.07134	-0.31
316 L	RML 467	7	17.57623	17.57622	0.01
25S6Mo	NCE 80	8	56.46665	56.46675	-0.10
825	FL 568	9	32.00645	32.00663	-0.18
904 L	NX 880	10	41.34620	41.34597	0.23
C276	NCN 364	11	34.97129	34.97200	-0.71
686	NCL 60	12	43.10826	43.10866	-0.40

Samples were examined for pitting and crevice corrosion. Results are displayed in Tables 16 and 17 for the two corrosion racks. Because of limited exposure, data displayed in the two tables should be considered tentative. Pits, if present, were shallow and small and often hard to distinguish from other surface inhomogeneities. Longer exposures are needed to better characterize the alloy performance. Similarly, there was no evidence of aggravated crevice corrosion on any of the samples. Results described as discoloration of the crevice area in Tables 14 and 15 merely refer to the fact that crevice areas were stained either with corrosion product or with process fluids that could not be removed by soap and water washing.

U-bend samples exposed on the two corrosion racks were examined for stress corrosion cracking under low-power microscope and by using a scanning electron microscope. No evidence of cracking was seen in the 316 ss and alloy 825 samples.

Summary of Corrosion Testing Results

Corrosion samples were exposed in the KFX coal upgrading pilot facility. Overall exposure to process streams over a two-year period was quite short, in that about 74 tests of about 25-40 minutes each were conducted.

Based on the evaluation of samples exposed in the flash drum, it is concluded that general corrosion of materials as deduced by weight loss was quite low. The extent of pitting and crevice corrosion could not be assessed conclusively. No stress corrosion cracks were observed in the U-bend samples exposed. However, it should be noted that localized corrosion processes involve incubation periods, and hence relatively short exposure duration precludes any definitive and conclusive corrosion performance of any of the alloy in the process fluids and streams.

Samples exposed in the reactor tube showed definite weight loss. There is no evidence that the weight loss occurred by corrosive process. It is speculated that the loss may be due to the mechanical action of moving and falling coal.

If plant operations are to continue, it is recommended that corrosion racks in the flash drum be reinstalled. It is also recommended that if and when a reactor tube is replaced, a thorough evaluation of the tube be performed.

Table 16. Pitting and Crevice Corrosion Data for Samples Exposed at the Bottom of the Flash Tank

Material	Sample ID	Location	Pitting Corrosion	Crevice Corrosion
316 L	RML 462	1	Small Pits	Discolored
25S6Mo	NCE 75	2	No	Discolored
825	FL 563	3	No	Discolored
904 L	NX 877	4	No	Discolored
C276	NCN 359	5	?	Discolored on one side
686	NCL 55	6	?	Discolored
316 L	RML 463	7	No	Discolored
25S6Mo	NCE 76	8	No	No
825	FL 564	9	No	Discolored
904 L	NX 878	10	No	Discolored
C276	NCN 360	11	?	Discolored
686	NCL 56	12	?	No

Table 17. Pitting and Crevice Corrosion Data for Samples Exposed in the Inspection Port Nozzle of the Flash Tank

Material	Sample ID	Location	Pitting Corrosion	Crevice Corrosion
316 L	RML 466	1	Yes?	Discolored on one side
25S6Mo	NCE 79	2	No	Discolored
825	FL 567	3	No	Discolored
904 L	NX 879	4	No	Discolored
C276	NCN 363	5	?	Discolored
686	NCL 59	6	?	No
316 L	RML 467	7	No	Discolored
25S6Mo	NCE 80	8	?	No
825	FL 568	9	No	Discolored
904 L	NX 880	10	No	No
C276	NCN 364	11	?	No
686	NCL 60	12	?	No

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