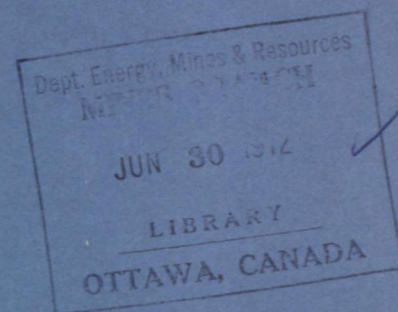


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*FIRESIDE CORROSION AND POLLUTANT  
EMISSION FROM CRUDE OIL COMBUSTION*

G. K. LEE, E. R. MITCHELL, F. D. FRIEDRICH AND R. G. DRAPER

FUELS RESEARCH CENTRE

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## Fireside Corrosion and Pollutant Emission from Crude Oil Combustion<sup>1</sup>

*A pilot-scale research boiler was used to evaluate the corrosion and pollution potential of a western Canadian mixed-blend crude oil from the Interprovincial Pipeline. It was demonstrated that this crude oil, even when deliberately contaminated with high levels of salt, can be burned successfully with moderately low excess air. In addition, problems associated with low-temperature deposits, low-temperature corrosion, and pollutant emissions were minimal. High-temperature corrosion, due to either oil ash or gas-phase oxidation, can be controlled by proper selection of boiler tube material. Low-temperature pump and screen tests on the as-received crude oil indicated that no pumping or screen-plugging problems should occur at temperatures above the maximum pour point.*

### Introduction

IN North America the demand for fossil fuels in general and low-sulphur fuels in particular is rapidly increasing. It is in this context that the Canadian Combustion Research Laboratory (CCRL) carried out a detailed evaluation of the suitability of a western Canadian mixed-blend crude oil for power generation. The evaluation included an analytical investigation of fuel properties and studies of both the fireside corrosion and pollution potential of this fuel under controlled combustion conditions in the CCRL pilot-scale research boiler.

Fuel analyses completed during the course of a 70-hr combustion test showed that the as-received crude oil contained a rather low concentration of water-soluble chloride salts; namely, 73 lb/1000 bbl of oil. Since chlorides were considered to be the most likely cause of severe high-temperature corrosion, a second 70-hr test was carried out, in which the chloride content was increased to 376 lb/1000 bbl of oil by injecting a solution of 2.7 percent sodium chloride and 0.5 percent magnesium chloride into the furnace, just above the burners.

This report describes the evaluation procedures used and the experimental results obtained during both tests.

### Test Objectives

The objectives of the analytical and combustion tests were as follows:

<sup>1</sup> This research was sponsored by Ontario Hydro and done under contract with Montreal Engineering Co. Ltd.

Contributed by the Corrosion and Deposits Division and presented at the Winter Annual Meeting, Washington, D. C., November 28-December 2, 1971, of THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS. Manuscript received at ASME Headquarters, August 3, 1971. Paper No. 71-WA/CD-2.

- 1 To determine the physical and chemical characteristics of a representative sample of the as-received crude oil, with particular attention being given to low-temperature pumpability.
- 2 To determine the optimum burner conditions for firing the crude oil with moderately low excess air (5 percent or less).
- 3 To evaluate the effect of chlorides in the crude oil on both high and low-temperature corrosion with 1 percent O<sub>2</sub> or less in the flue gas.
- 4 To characterize the particulate and gas-phase pollutants that are generated during combustion.

The high-temperature corrosion study was of particular interest because no literature was available on the behavior of various superheater tube materials at 1100 deg F while burning this crude oil with a high chloride content.

### Pilot-Scale Research Boiler

The research boiler is illustrated in Fig. 1, which shows the locations of the sampling stations selected for monitoring high and low-temperature corrosion potential and pollutant emissions. Essentially, the research boiler, which is described elsewhere,<sup>2</sup> incorporates a pressurized furnace equipped with two opposed, downward-tilting burners, an air-cooled (simulated) superheater, and a conventional air preheater.

Crude oil was supplied to each burner from a 200 gal, electrically grounded indoor storage tank. The tank was continuously pressurized with air at 2 psig to prevent the vapor to air ratio above the oil from reaching the lower explosive limit.

The combustion tests with both as-received and contaminated oil were carried out at a fuel input of 2.3 million Btu/hr, using

<sup>2</sup> Friedrich, F. D., Lee, G. K., and Mitchell, E. R., "Combustion Fouling Characteristics of Two Canadian Lignites," ASME Paper No. 71-WA/CD-3.



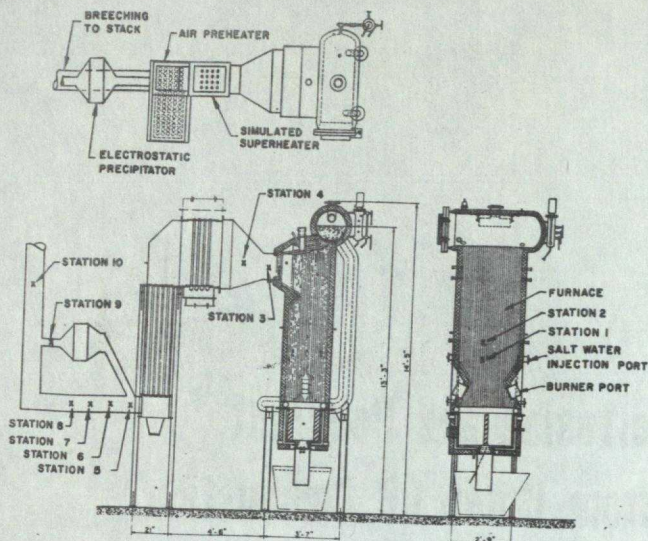


Fig. 1 Pilot-scale research boiler showing location of sampling stations

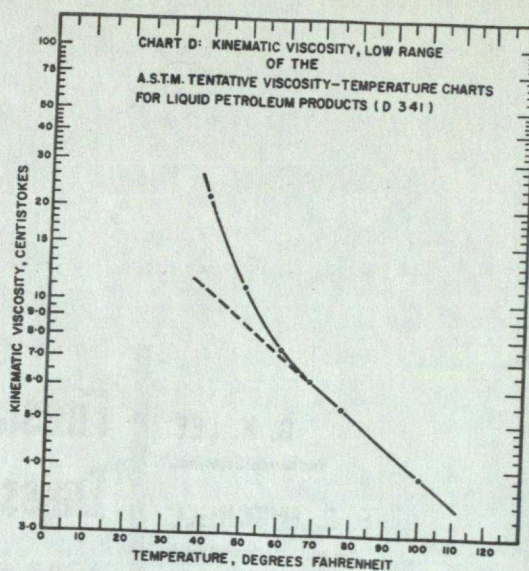


Fig. 2 Viscosity-temperature relationship for mixed blend crude oil

Table 1 Analysis of as-received crude oil

Property	Method of Determination	Result
1. Gravity, °API	D 287 (Hydrometer)	36.9
specific, 60/60°F	D 287	0.840
2. Reid vapour pressure, lb	D 323	7.7
3. Sulphur, % wt.	D 129	0.51
4. Pour point, °F	D 97	25
5. Gross calorific value, corrected for sulphur, Btu/lb	D 240	19003
6. Water and sediment, % wt	D 96	0.40
7. Ash, % wt	D 482	0.022
8. Total water-soluble chlorides as NaCl, lb/1000 bbl	USBM RI 3517	73
9. Water-soluble phenols		nil
10. Water-soluble mercaptans		nil
11. Explosiveness at 70°F, %	3-GP-0/99.1 (modified)	100
12. Viscosity, 100°F, SUS	D 445-D 2161	38.7
13. Viscosity, centistokes at 100°F	D 445	
77°F		3.83
68°F		5.40
60°F		6.25
50°F		7.41
40°F		10.98
21.68		
14. Elemental analysis		
Carbon, % wt	calculated	86.1
Hydrogen, % wt	calculated	13.4
Sulphur, % wt	D 129	0.51
Vanadium, ppm	D 1548	2.4
V <sub>2</sub> O <sub>5</sub>		4.4
Nickel, ppm		4.4
Iron, ppm		2.8
Sodium, ppm	D 1318	54
Calcium, ppm	Atomic absorption	11
Magnesium, ppm	Atomic absorption	1.6
15. Distillation range - by USBM Routine Method Bul. 490		
Distillation at 758 mm Hg		
Cut Temp. °F	Recovery, % vol.	
80	First drop	
122	3.1	
167	5.3	
212	9.9	
257	15.6	
302	20.5	
347	25.2	
392	29.3	
437	33.6	
482	38.3	
527	43.1	
572	48.1	
600	53.3	
Residuum	43.9	
Loss	2.8	

Specific gravity of residuum: 0.923 at 60/60 °F

\* Analysis of Contaminated Crude Oil

The crude oil used in the second test was the same as that described above, except that total water-soluble chlorides, (Item 9) were increased by the addition of NaCl and MgCl<sub>2</sub> to a total of 373 lb/1000 bbl.

two pressure-atomizing burners. This corresponds to 92 percent of the research boiler's full-load rating. Specified control parameters for these tests were as follows:

- 1 Excess air levels: 5 percent or less.
- 2 Smoke number: 0.5 Ringelmann or less.
- 3 CO in flue gas: 0.1 percent or less.
- 4 Surface temperature of the high-temperature corrosion probe: 1100 deg F ± 50 deg F.

### Fuel Analysis

The crude oil blend provided for the combustion tests was that normally supplied by the Interprovincial Pipeline to Toronto from western Canada. Random samples, taken from 12 of the 50 barrels in the shipment, had specific gravity readings ranging from 37.10 deg API to 37.15 deg API. A composite of the random samples was then used to conduct an explosiveness analysis in accordance with the Canadian Government Specifications 3-GP-0/99-1 (Modified).<sup>3</sup> This analysis yielded an explosiveness reading of 100 percent at 70 deg F, which emphasizes the need for stringent precautions to control evaporation losses during bunkering and storage.

The analytical data for both the as-received and contaminated crude oil are given in Table 1. Referring to item 13 of Table 1, it is important to note that the relationship of kinematic viscosity versus temperature deviates from linearity at temperatures below 65 deg F, when plotted on Chart D-ASTM 341, shown in Fig. 2. This nonlinearity is generally conceded to be due to the oil, which contained 3.5 percent by weight wax, becoming non-Newtonian because of molecular agglomeration or crystallization.

Screen plugging tests revealed that the pour point is very dependent upon the previous temperature history of the crude oil; the maximum pour point being +30 deg F and the minimum pour point being -45 deg F.<sup>4</sup> These results indicated that care must be taken to overcome problems of pumping from storage if the oil temperature drops below the maximum pour point.

### Performance Parameters

The principal parameters measured during the combustion performance tests are listed next. The first 8 parameters were

<sup>3</sup> Private communication, Quality Engineering Test Establishment, Department of National Defence.

<sup>4</sup> Private communication, Fuels and Lubricants Laboratory, National Research Council of Canada.



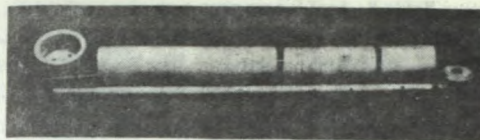


Fig. 3 High-temperature corrosion probe, ready for assembly

Table 2 Operating data—combustion tests with crude oil

Operating Parameter	Untreated Crude Oil		Crude Oil Contaminated with Chloride	
	Average	Range	Average	Range
Total time operated on crude oil:	70 hr., 25 min.		72 hr.	
Total crude oil burned, imp. gal.:	1,015.0		1,030.0	
Firing rate, Igph	14.41	13.5 - 15.25	14.3	-
Fuel pressure at burners, psig	288	250 - 330	210	200 - 230
Fuel temp. at burners, °F	86	83 - 92	91	86 - 95
Steam flow, lb/hr	1388	1332 - 1466	1276	1136 - 1400
Steam pressure in drum, psig	75	67 - 81	56	50 - 62
Feedwater temp., °F	175	145 - 189	160	145 - 180
Steam temp. in condenser, °F	250	-	253	-
Steam pressure in condenser, psig	26	-	27	-
Air temp. into condenser, °F	84	-	80	-
Air temp. out of condenser, °F	152	-	150	-
Air temp. to burners, °F	415	380 - 420	395	385 - 410
Primary air pressure at burner, in. W.G.	3.3	2.1 - 5.3	1.85	1.6 - 2.1
Secondary air pressure at burner, in. W.G.	7.5	7.1 - 8.0	6.85	6.12 - 7.6
Furnace pressure, in. W.G.	1.8	1.7 - 2.1	1.6	1.4 - 1.7
Flue gas temp. at high-temp. corrosion probe, °F	1200	1160 - 1230	1183	1130 - 1210
Surface temp. of high-temp. corrosion probe, °F	1112	1075 - 1135	1150	1100 - 1190
Final flue gas temp. °F	609	585 - 630	575	560 - 590
Excess air, %	4.22	-	3.69	-

monitored continuously while the remainder were measured intermittently.

- 1 CO<sub>2</sub> by infrared analyzer; Station 3.
- 2 CO by infrared analyzer; Station 3.
- 3 O<sub>2</sub> by paramagnetic analyzer; Station 3.
- 4 SO<sub>2</sub> by modified West-Gaeke method; Station 7.
- 5 NO<sub>2</sub> by modified Saltzman reagent; Station 7.
- 6 NO<sub>x</sub> by modified Saltzman reagent; Station 7.
- 7 Smoke density by self-standardizing photometric cell; Station 10.
- 8 Flame temperature by radiometer. This provides a relative indication of the average flame temperature across the flame envelope. Maximum or peak flame temperature is estimated to be about 3000 deg F; Station 1.
- 9 Acid dewpoint and rate of acid buildup (RBU) by BCURA dewpoint meter; Station 8.
- 10 SO<sub>3</sub> by a modified Shell-Thornton method, was measured both in the furnace and in the breeching; Station 2.
- 11 Particulate matter was sampled using a cyclone with high drop in pressure followed by a millipore filter system. The samples were weighed to establish particulate loading and ashed to determine combustible content. Size distribution of particles was determined by Coulter counter; Station 5.
- 12 Electrostatic precipitator performance was measured by passing part of the flue gas through a small electrostatic precipitator for several hours. Inlet and outlet dust loadings were measured in each case to establish the efficiency of precipitation; Station 9.
- 13 Low-temperature corrosion potential was measured by three mild-steel probes inserted simultaneously into the breeching and maintained at three different temperatures for 55 hr during each test. The probes were then washed to remove water-soluble corrosion products and the wash water was analyzed to determine the loss of iron due to reaction with sulphur and chlorine; Station 6.
- 14 High-temperature corrosion potential was measured using the probe design shown in Fig. 3. At the start of each test, a new probe was placed in the gas stream between the furnace screen tubes and the test air heater and was maintained at a metal temperature of 1100 deg F ± 50 deg F during the test. Both probes held five test specimens, one each of the following alloys: SA 192, T-1, T-11, T-22, and 321. Each specimen was weighed beforehand. Upon removal, the test specimens were gently scraped



Fig. 4 High-temperature corrosion probe after the test with as-received crude oil

Table 3 Typical values for flue gas analysis, smoke density, and flame temperature

Parameter	Untreated Crude Oil		Treated Crude Oil	
	Average Value	Range	Average Value	Range
1. CO <sub>2</sub> in dry flue gas, %	14.34	13.6 - 14.8	14.31	13.8 - 14.7
2. CO in dry flue gas, %	0.055	0.00 - 0.12	0.01	0.00 - 0.04
3. O <sub>2</sub> in dry flue gas, %	0.95	0.75 - 1.15	0.82	0.56 - 1.15
4. SO <sub>2</sub> in dry flue gas, ppm	320	215 - 380	275	235 - 305
5. NO <sub>2</sub> in dry flue gas, ppm	0	-	0	-
6. NO <sub>x</sub> in dry flue gas, ppm	168	-	161	-
NO in dry flue gas, ppm (by difference)	168	-	161	-
7. Smoke density, Ringelmann No.	0.4	0.3 - 0.6	0.35	0.3 - 0.6
8. Avg. temp. in flame envelope, °F	2575	2475 - 2650	2506	2400 - 2580

to remove loose deposition and corrosion products. These products were analyzed by the X-ray diffraction method and the specimens were then reweighed and examined metallographically; Station 4.

## Experimental Data

**Combustion Performance Tests.** Preliminary combustion tests, using a single burner, demonstrated that the as-received crude oil can be readily pumped at room temperature by flooding the pump suction, and can be pressure-atomized at 300 psig with nozzles designed for No. 2 fuel oil. It was also observed that a 60-deg hollow-spray oil nozzle produced a flame with a conical angle of about 120 deg. In the narrow furnace of the research boiler, this caused flame impingement and heavy coke buildup on the furnace water walls. The impingement problem was corrected by using a 30-deg solid-spray oil nozzle. This produced a flame with an orange, highly luminous core and yellow-white, partially nonluminous outer edges. The color pattern suggested that during atomization the low-gravity, highly volatile components in the crude oil are swirled to the outer edges of the oil spray while the heavier, more viscous fractions remain in the core.

The boiler was then fired using two opposed burners equipped with 30-deg solid-spray nozzles. The resulting highly turbulent, bright yellow flame did not contact the furnace walls and was remarkably stable at excess oxygen levels between 0.7 and 1.0 percent. A firing rate of about 14 Igph, (92 percent of full-load rating) provided the furnace exit temperature necessary to maintain the high-temperature corrosion probe at 1100 deg F ± 50 deg F.

Having established that all of the specified control parameters could be easily and safely maintained, two continuous combustion tests of 70 hr, 25 min and 72-hr duration were conducted with as-received and contaminated crude oil, respectively. Typical operating data from each test, given in Table 2, reflect two important operational considerations:



Table 4 Electrostatic precipitator performance

Crude Oil Test	Particulate Matter Loading at Electrostatic Precipitator		Loss on Ignition (LOI) % wt Precipitator Inlet	Dust Collection Efficiency % wt*
	Inlet	Outlet		
As received	25	0.3	80.4	99
Contaminated	30	0.4	78.0	99

\*Gas inlet temperature at the precipitator = 300°F.

1 Late autumn conditions with overnight temperatures dropping to 35 deg F caused a gradual decrease in temperature of the oil supply after sunset each day which caused a slow, but measurable, increase in firing rate. This effect, which was compensated for by reducing the oil pressure, is critical with gear pumps where increases in oil viscosity are associated with increases in flow rate.

2 The fireside pressure drop across the furnace screen tubes, simulated superheater and the air preheater remained constant, indicating little or no fouling of these heat-transfer surfaces. Consequently, soot blowing was unnecessary and temperatures throughout the waterside and the fireside of the boiler circuit were relatively steady.

In general, the combustion and boiler performance with crude oil were extremely good and no operational difficulties were encountered. Crude oil is, in all respects, a premium fuel for steam generation.

**Flue Gas Analysis, Smoke Density, and Flame Temperature.** Average and range values for these parameters are summarized in Table 3. Excess oxygen was kept below 1 percent while CO averaged 0.05 and 0.01 percent in the tests with as-received and contaminated crude oil, respectively. The difference in CO level is probably due to minor changes in combustion aerodynamics which are magnified by the very short residence time in the furnace of the pilot-scale research rig. It is anticipated that with the longer residence time available in a utility generator, well-designed burners should achieve 0.6 percent excess oxygen with less than 0.005 percent CO.

The SO<sub>2</sub> concentration merely reflects the sulfur content of the fuel and is not significantly affected by changes in firing conditions.

Nitrogen-oxide concentrations are fairly low compared to values reported in the literature, and it is significant that all nitrogen oxides are in the form of NO rather than NO<sub>2</sub>. These low NO levels are likely due to the low excess air levels. However, somewhat higher NO levels could be expected from a large generator, under the same firing conditions, because the flame temperature would be higher.

Faint smoke was visible from time to time in the breeching but the stack was clear.

**Acid Dewpoint, SO<sub>2</sub> Concentration, and Rate of Acid Buildup.** During both tests, (a) repeated measurements demonstrated that no acid dewpoint existed, although a water dewpoint was detected below 115 deg F; (b) SO<sub>2</sub> levels were consistently less than 2 ppm; and (c) there was no measurable rate of acid buildup. This is consistent with the trace levels of SO<sub>2</sub> that were found.

These results clearly indicate that the combination of low-sulfur oil and low-excess-air firing virtually eliminates the formation of SO<sub>3</sub>.

**Particulate-Matter Loading in Flue Gas and Electrostatic Precipitator Performance.** These data are summarized in Table 4. Soot loadings at the inlet of the electrostatic precipitator were relatively low and collection of soot by the precipitator was relatively efficient. In addition, the combustible content of the soot, being lower than is normally experienced in residual-oil fired systems, indicated good burnout. Size analyses, conducted on soot samples taken at the precipitator inlet, indicated that over 70 percent by weight of the particles were less than 30 $\mu$  while over 40 percent by weight were less than 10 $\mu$ . The soot sample collected at the precipitator outlet was too small to permit a particle count but a

Table 5 Low-temperature corrosion probe data

Crude Oil	Probe No.	Temp., °F	Water-soluble Deposit Composition, mg/55 hr					
			Fe	Ca	Mg	Na	Cl	SO <sub>4</sub>
As received	1	180	3.1	16.4	2.2	1.1	1.0	28.2
	2	220	3.5	15.0	0.5	0.4	2.2	24.2
	3	260	2.6	10.4	0.8	0.4	2.0	31.0
Contaminated	4	180	5.9	15.4	0.1	0.8	4.1	25.6
	5	220	5.2	10.8	0.3	0.9	3.7	23.3
	6	260	0.4	14.8	2.2	2.2	3.3	24.9

comparative microscopic examination of soot collected at both the inlet and outlet of the precipitator showed no observable differences in particle size distribution.

**Low-Temperature Corrosion Probes.** The composition of the water-soluble products from these corrosion probes, given in Table 5, shows that virtually all of the anions (Cl and SO<sub>4</sub>) are neutralized by cations (Mg, Ca, and Na) normally present in the oil. But, it should be noted that iron corrosion can still occur when surface temperatures are low enough to allow condensation of liquid salt solution. Examination of the probe heads after cleaning revealed that the exposed surfaces were uniformly covered with tiny pits that contained chlorides. These pits were of a superficial nature.

The amount of water-soluble iron and sulfate removed from the probes indicates that wastage of mild steel surfaces in low-temperature boiler regions would be very low while burning this crude oil. Furthermore, the absence of an acid dewpoint confirms that corrosion due to condensed sulfuric acid will be no problem.

**High-Temperature Corrosion Probes.** The temperature of each probe was measured by a thermocouple silver-soldered to the middle specimen, which was made of SA 192 carbon steel. The middle specimen was included for temperature control rather than corrosion study since this material is not intended for high-temperature service. However, after each test the control specimen was cleaned of loose deposits, reweighed, and examined metallographically as were the others.

Fig. 4 shows the high-temperature corrosion probe after termination of the test on the as-received crude oil. The thin, uniform deposit layer, though loosely bonded, covered a tightly adherent scale that could not be removed by scraping. This condition was essentially duplicated on the probe that had been exposed to the contaminated crude oil.

X-ray diffraction analyses of the loose deposits revealed that only sodium sulfates and iron oxides were present, regardless of whether as-received or contaminated crude oil was burned. It is significant that neither chlorides nor vanadates were detected in these deposits. The sodium sulfates are a reaction product of the salt and sulfur in the oil but the iron oxides result from gas-phase oxidation of the ring surfaces in the 1200 deg F gas stream.

Metallographic examination of the fireside surfaces of each specimen showed that, in terms of scale thickness, the 321 stainless steel specimen was the most resistant to surface corrosion with the degree of resistance gradually deteriorating for the T-22, T-11, T-1, and SA 192 specimens, respectively. No intergranular corrosion or severe surface pitting was observed on any specimen. In general, all specimens exhibited a weight increase, after exposure, that was roughly proportional to the scale thickness.

The metallographic examinations and the X-ray diffraction analyses strongly indicate that the surface scale or corrosion layer on each specimen resulted from gas-phase oxidation at 1150 deg F rather than from liquid-phase corrosion by molten oil ash.

## Conclusions

The crude oil provided for this evaluation contained highly volatile components; this imposes requirements for precautions to prevent storage tank explosions. Low-temperature tests indicated no problems due to plugging of screens or in pumping the

fuel above the maximum pour point.

In all respects, the sample crude oil tested represents a premium, low-pollution fuel for power generation. General combustion performance, in terms of ignitibility, flame stability, and burnout, was equivalent to, or better than, No. 2 fuel oil. The deposition, corrosion, and pollution characteristics of this crude will not be changed significantly by the addition of over five times the normal salt level.

Particulate emission will be low compared to typical values for residual fuel oil, and  $\text{SO}_2$  emission will, of course, be proportional to the sulfur content of the crude oil. Burning with moderately low excess air will practically eliminate the emission of  $\text{SO}_2$  and will limit nitrogen-oxides emission to fairly low levels of  $\text{NO}$ .

It appears that corrosion potential will be low for, though corrosion rates established during short-term tests cannot be extrapolated to several thousand hours, no alarming quantities of oil-ash corrosion products were found at either high temperature or low temperature. The 321 stainless steel will corrode but slightly; however, the SA 192 carbon steel and "T" series alloys

will scale substantially, as would be expected at 1150 deg F. Metallurgical studies indicated that 316 stainless steel will also be a suitable alloy for this superheater application.

### Acknowledgments

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