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Project Summary

Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with an EPA Heavy Oil Low-NO_x Burner

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The report discusses emission results obtained from sampling the flue gas from a 16-MW (55 million Btu/hr) enhanced oil recovery steam generator equipped with an EPA heavy oil low-NO_x burner firing high-nitrogen (about 1 percent) Kern County crude oil. The tests consisted of a comprehensive flue gas monitoring program to characterize emissions from the steamer with the burner operation set to achieve NO_x levels below 85 ppm (at 3 percent O_2) with low CO and smoke emissions. In addition, an extended 30-day flue gas monitoring program was conducted to measure low-NO_x burner performance under typical unattended steamer operation. Emission measurements for the comprehensive tests included:

- **Continuous monitoring of flue gas emissions.**
- **Source assessment sampling system (SASS) testing with subsequent laboratory analysis of samples to give total flue gas organics in two boiling point ranges, specific quantitation of the semivolatile organic priority pollutant species, and flue gas concentrations of 73 trace elements.**
- **Volatile organic sampling train (VOST) testing with subsequent laboratory analysis to give volatile organic priority pollutant species emissions.**
- **EPA methods 5 and 8 sampling for particulate and SO_x emissions.**
- **Controlled condensation system (CCS) sampling, also for SO_x emissions.**
- **Emitted particle size distribution measurements using Andersen impactors.**
- **N_2O emission sampling.**

During the comprehensive tests, NO_x emissions averaged 70 ppm at 3 percent O_2 with CO levels generally below 30 ppm. SO_2 emissions measured with a continuous monitor ranged between 500 and 750 ppm at 3 percent O_2. Measurements of SO_2 by EPA Method 8 (and subsequently by controlled condensation) indicated generally good agreement with the continuous emission analyzer. The average of two particulate emission measurements was 27ng/J (96mg/dscm). The average condensible particulate emission level was 14 ng/J (50 mg/dscm). Two particle size distribution measurements were performed. Results indicate that 90 percent of the particulate matter had a mean particle diameter less than 1.4 and 11μm, respectively, for the two tests.

Total organic emissions from the steamer were relatively low, at 300 μg/dscm (85 pg/J), and relatively evenly distributed between the semivolatile (boiling point about 100 to 300°C) and nonvolatile (boiling point greater than about 300°C) categories. Of the volatile organic priority pollutants, emissions of benzene, toluene, and ethylbenzene were quantitated in the 2 to 60 μg/dscm (0.4 to 20 ppb) range. Of the semivolatile organic priority pollutants, emissions of naphthalene and phenol at about 1 μg/dscm (0.3 ppb) were measured.

Extended 30-day continuous monitoring of flue gas emissions confirmed the bur-

ner's ability to maintain NO_x emissions below 80 ppm. The average for this duration was calculated at about 70 ppm at 3 percent O_2. CO emissions were also low, generally less than 30 ppm at 3 percent O_2, throughout the test program.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in two separate volumes of the same title (see Project Report ordering information at back).

Introduction

Remaining petroleum reserves in older fields often require enhanced oil recovery (EOR) techniques for continued production. One EOR technique involves steam flooding of oil fields to lower the viscosity of heavy crude so it can be recovered. The steam for injection is most often raised by crude-oil-fired steam generators, termed steamers. In Kern County, California, the aggregate NO_x emissions from these steamers have received recent regulatory attention since that area is currently in borderline attainment of the NO_2 ambient air quality standard.

Over the past several years, EPA has sponsored the development of a low-NO_x burner capable of achieving NO_x levels below 85 ppm with low CO and smoke generation while burning high nitrogen fuel oils such as the Kern County crude. These programs have led to the recent full-scale demonstration of a burner prototype in an operating steamer. This steamer, equipped with a full-scale 16-MW (55 million Btu/hr) burner prototype, was tested under the Combustion Modification Environmental Assessment (CMEA) program. Results of these tests are presented in this report.

Summary and Conclusions

Source Description

The tests were performed on a crude-oil-fired steamer retrofitted with the low-NO_x burner illustrated in Figure 1. The burner consists of a large, 13 m^3 (460 ft^3), refractory-lined chamber. Steam-atomized oil and combustion air are well mixed in this chamber at a stoichiometric ratio of about 0.6 to 0.65. Primary air to the chamber is preheated by a regenerative chamber design in which the air passes through an inner shell before being injected into the chamber. Secondary combustion air is injected both radially and axially in the interface connecting the burner to the steamer. This staged combustion low-NO_x burner enhances the decay of total fixed nitrogen species (NH_3 and HCN primarily), formed early in the mixing zone from fuel nitrogen, to N_2 prior to injection of secondary combustion air. The large refractory-lined combustor volume provides both the long residence time (about 0.6 sec) and the high temperature (about 1,400 °C) required for the decay of the fixed nitrogen species.

Test Program and Burner Operation

The test program called for a comprehensive evaluation of steamer flue gas emissions with the burner operation set to achieve NO_x levels below 85 ppm with low CO and smoke emissions. In addition, the test program called for a continuous 30-day emission monitoring program to monitor the longer-term NO_x control capability of the burner under typical steamer operation.

Table 1 summarizes the steamer/burner operating conditions during the comprehensive tests on February 1, 1984. The burner fired Kern County crude with a nitrogen and sulfur content of 1.04 and 1.06 percent, respectively. Measurement of primary and secondary airflows indicated a first-stage combustor stoichiometry in the range of 0.61 to 0.65, with an estimated

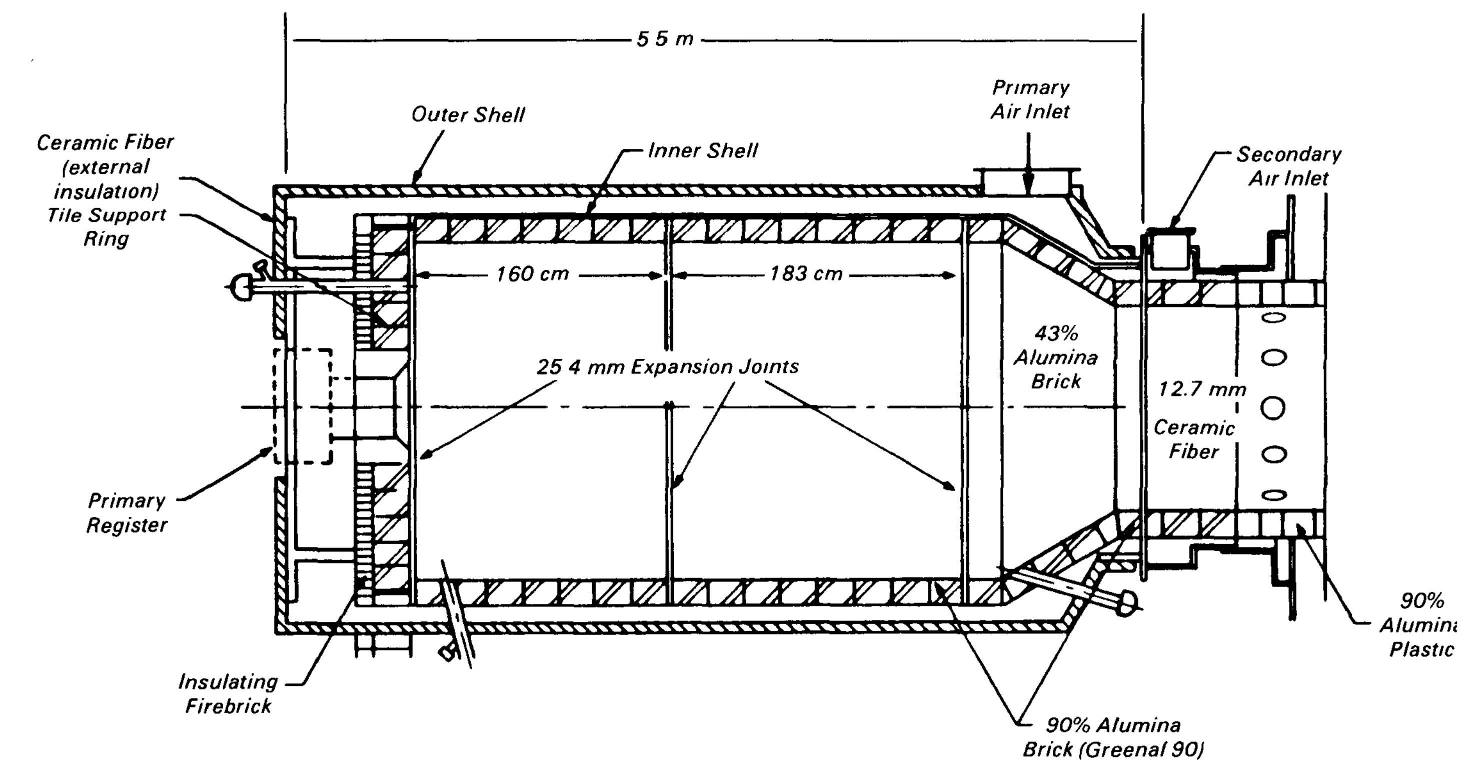

Figure 1. *EPA low-NO_x burner*

bulk gas residence time of 0.65 sec. Steamer operation was uninterrupted during this test.

Emission Measurements and Results—Comprehensive Tests

The sampling and analysis procedures used in this test conformed to an extended EPA Level 1 protocol. Emission measurements included:

- Continuous monitoring for O_2, CO_2, CO, NO_x, and SO_2.
- SASS sampling for trace element and semi- and non-volatile organic emissions.
- VOST for volatile organic emissions.
- EPA Method 5 sampling for solid and condensible particulate emissions.
- EPA Method 8 sampling for SO_x emissions in conjunction with Method 5.
- Particle size distribution measurements using Andersen impactors.
- CCS for SO_x emissions.
- Grab sampling for laboratory gas chromatographic analysis of N_2O.

All sampling took place at the stack, downstream of the steamer economizer. The analysis protocol for the SASS train samples included:

- Analyzing methylene chloride extracts of particulate and XAD-2 resin for total organic content in two boiling point ranges: semivolatile organics with boiling points between 100 and 300°C (nominally C_7 to C_{16} organics) by total chromatographable organic (TCO) analysis and nonvolatile organics with boiling points greater than 300°C (nominally C_{16+} organics) by gravimetry.
- Obtaining infrared (IR) spectra of the gravimetric residues of the extract samples.
- Analyzing the organic sorbent module extract samples for the semivolatile organic priority pollutants, including several polynuclear aromatic hydrocarbon (PAH) species, by gas chromatography/mass spectrometry (GC/-MS) according to EPA Method 625.
- Analyzing particulate, XAD-2 resin, and impinger solutions for 73 trace elements using primarily spark source mass spectrometry (SSMS) and atomic absorption spectroscopy.

VOST train samples were analyzed by thermal desorption, purge and trap GC/MS for the volatile organic priority pollutant compounds as outlined in the EPA VOST protocol.

Table 2 summarizes the emissions measured during the comprehensive tests. Emissions of NO_x, CO, and SO_2 were relatively constant throughout these tests. NO_x emissions averaged about 70 ppm dry corrected to 3 percent O_2, well below the burner target of 85 ppm. CO emissions averaged 24 ppm. SO_2 emissions, as determined by both the continuous monitor and the average of two Method 8 determinations, are shown in the table: the two agree within 10 percent. Average SO_3 emissions by Method 8 were about 9 ppm (3 percent O_2), corresponding to about 1.4 percent of total SO_x (SO_2 + SO_3) emissions: this is a significantly lower fraction than is typical for oil-fired sources. Subsequent measurements using CCS gave SO_2 emissions of 600 ppm (average of two measurements) with SO_3 emissions of 49 ppm: in these subsequent test, SO_3 accounted for about 7.5 percent of the total SO_x emitted, more typical for oil-fired sources.

Table 2 shows that particulate emissions were 146 mg/dscm (average of two measurements) with about 35 percent of the particulate being condensible. Total organic emissions from the steamer were quite low, at 300 μg/dscm. These were roughly equally split among the semi- and nonvolatile boiling point ranges.

Of the volatile organic priority pollutants, benzene and alkyl substituted benzenes were detected at concentrations below about 20 ppb. No other volatile organic priority pollutants were detected. Of the semivolatile organic priority pollutants, naphthalene and phenol were detected at concentrations of 0.3 and 0.2 ppb, respectively. The dimethyl phthalate noted in Table 2 is most likely a contaminant.

Trace element analyses of SASS samples indicate that sodium, chlorine (condensed chlorides), copper, iron, nickel, and zinc are emitted at the highest levels with emissions exceeding 100 μg/dscm. The most likely source of the sodium and chlorine is the residual brine in the crude oil fuel. Sodium levels in the fuel were quite high, about 120 μg/g. Figure 2 illustrates the particle size distributions resulting from two separate Andersen impactor measurements. The data indicate that 90 percent of the total particulate mass had a mean particle diameter of less than 1.4 μm for run 1 and 11 μm for run 2.

Table 1. *Steamer/Burner Operation*

	Range		Average[a]	
Fuel flow, l/min (bbl/day)	23.4 to 24.1	(212 to 218)	23.8	(215)
Heat input, MW (10^6 Btu/hr)	16.4 to 16.8	(55.8 to 57.4)	16.6	(56.6)
Fuel temperature, °C (°F)	129 to 132	(264 to 269)	130	(267)
Feedwater flow, l/min (10^3 bbl/day)	380 to 400	(3.4 to 3.6)	390	(3.5)
Steam pressure, MPa (psig)	7.03 to 9.10	(1,020 to 1,320)	8.41	(1,220)
Steam temperature, °C (°F)	279 to >300	(525 to >570	—	—
Stack temperature, °C (°F)	232 to 254	(450 to 490)	242	(468)
Burner primary airflow, m^3/s (scfm)	2.71 to 2.87	(5,740 to 6,080)	2.80	(5,940)
Secondary airflow, m^3/s (scfm)	2.38 to 2.95	(5,040 to 6,260)	2.65	(5,630)
First stage stoichiometry	0.61 to 0.65		0.64	
First stage residence time,[b] sec		—	0.65	
Fuel/Oil analysis, percent weight				
Carbon		—	86.2	
Hydrogen		—	11.3	
Sulfur[c]	1.00 to 1.10		1.06	
Nitrogen[c]	1.00 to 1.09		1.04	
Ash		—	0.03	
Moisture		—	0.57	
Oxygen		—	0.4	
Gross heating value, MJ/kg (Btu/lb)		—	42.78	(18,430)
Specific gravity (API) at 16°C (60°F)		—	12.6	

[a]Spans the entire 1-day period of comprehensive testing.
[b]Assumes a combustor temperature of 1,430°C (2,600°F).
[c]Analyses of sulfur and nitrogen were performed in triplicate.

Emission Measurements and Results—30-Day Monitoring

The sampling and analysis protocol for this portion of the test program consisted of continuous monitoring of flue gas for O_2, CO_2, CO, NO_x, and SO_2 with certification of NO_x analyzer readings using EPA Method 7. Flue gas was monitored from January 21 to February 24, 1984. Figures 3 through 5 illustrate the emission data collected. Apart from two periods when the steamer was shut down, one for inspection and another due to electrical

Table 2. Summary of Flue Gas Emissions

Component	Flue gas concentration[a] ppm[b]	mg/dscm	ng/J[c]
Criteria pollutant and other gas-phase species:			
NO_x (as NO_2)	69	140	39
CO	24	29	8.1
SO_2			
– Continuous monitor	556	1,560	435
– Method 8[d]	606	1,640	456
SO_3			
– Method 8[d]	8.7	29	8.1
Particulate			
– Solid[d]	–	96	27
– Condensible[d]	–	50	14
Total particulate[d]	–	146	41
N_2O	7	12	3.5
Total organics:			
Semivolatile organics (C_7 to C_{16}) by TCO	–	0.17	0.050
Nonvolatile organics C_{16+}) by gravimetry	–	0.13	0.035
Total C_{7+}	–	0.30	0.085
Volatile organic priority pollutants:			
Benzene	0.018	0.060	0.017
Toluene	0.00083	0.0032	0.0009
Ethylbenzene	0.00039	0.0017	0.0005
Semivolatile organic priority pollutants:			
Naphthalene	0.0003	0.0014	0.0004
Phenol	0.0002	0.0007	0.0002
Dimethyl phthalate	0.0004	0.0036	0.0010

[a]Average flue gas O_2 and CO_2 were 2.7 and 13.1 percent, respectively.
[b]Corrected to 3 percent O_2.
[c]Heat input basis.
[d]Average of two separate measurements.

problems, operation throughout this test period was relatively steady. O_2 levels, shown in Figure 3, were maintained at about 3 percent. Only at the start and end of the 30-day test period did the O_2 increase to over 4 percent. It is not known if this increase was caused by a change in primary or secondary combustion airflow. NO_x emission levels, shown in Figure 4, were below 80 ppm corrected to 3 percent O_2 throughout. Average NO_x for the entire test period was about 70 ppm. CO emissions were generally below 30 ppm. However, there were no CO readings after day 23. SO_2 emissions ranged between 500 and 750 ppm corrected to 3 percent O_2. The notable increase in SO_2 during the last days of testing may have been caused by an increase in sulfur content of the crude.

Quality Assurance

Results of several quality assurance (QA) activities performed in conjunction with this test program are discussed in the report. Conclusions are that the quality of data obtained is of an acceptable level in terms of the stated project QA objectives.

Summary

Emissions from a crude-oil-fired steamer equipped with the EPA low-NO_x burner were tested. Field testing of the steamer over a 30-day monitoring period supports the capability of the burner to maintain NO_x levels below 80 ppm with CO emissions below 30 ppm. Particulate emissions were in the range typical of other EOR steamers. Total organic emissions were relatively low. Low concentrations of several aromatics (benzene, toluene, ethylbenzene, phenol, and naphthalene) were quantitated.

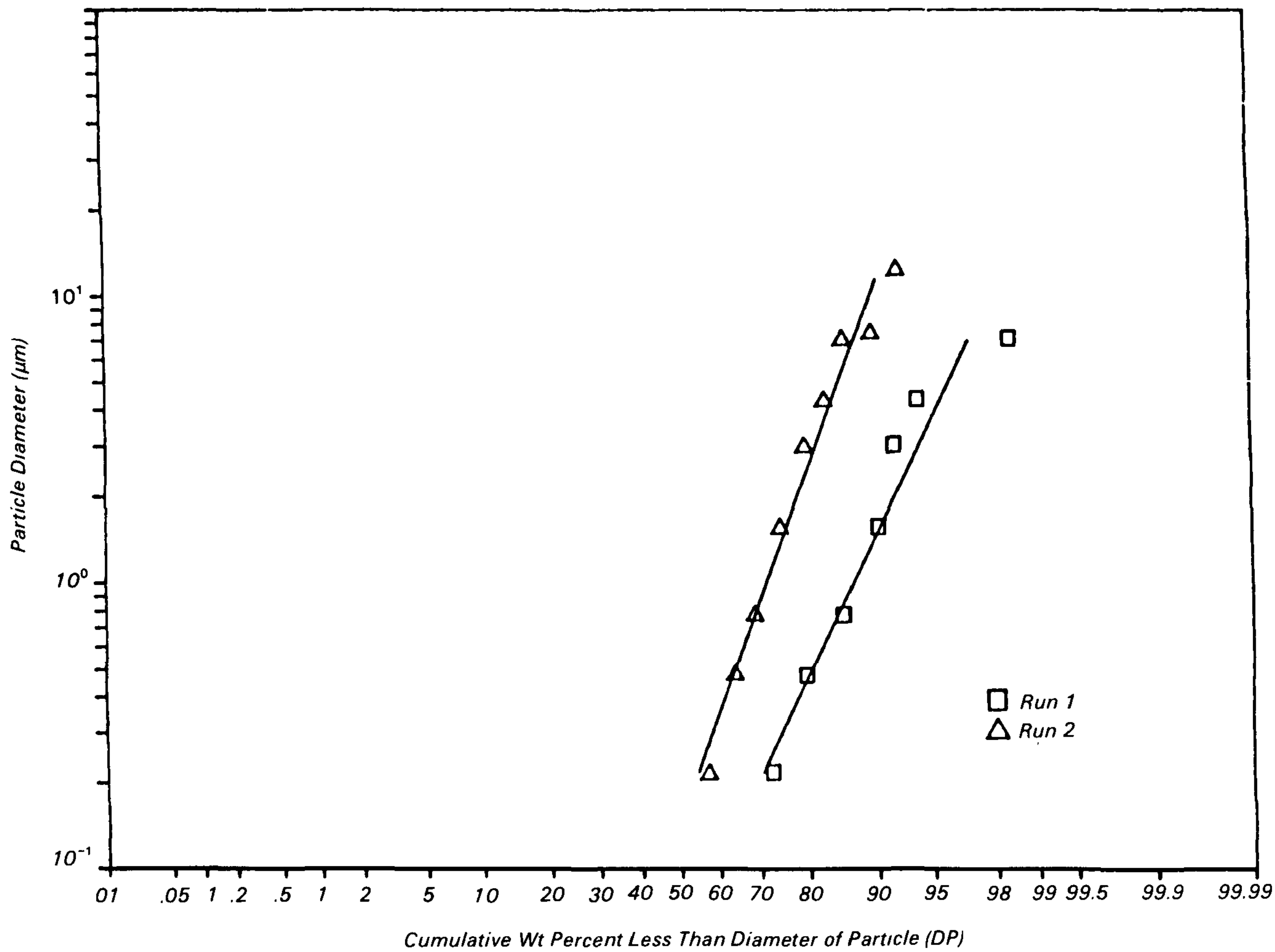

Figure 2. *Particle size distribution.*

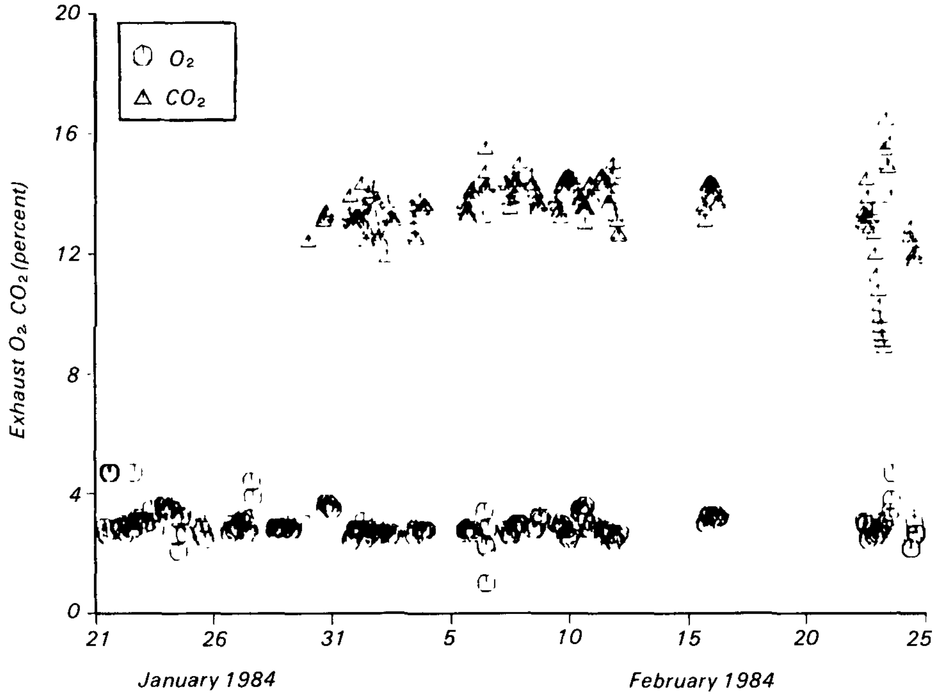

Figure 3. *Flue gas O_2 and CO_2 for the extended test period*

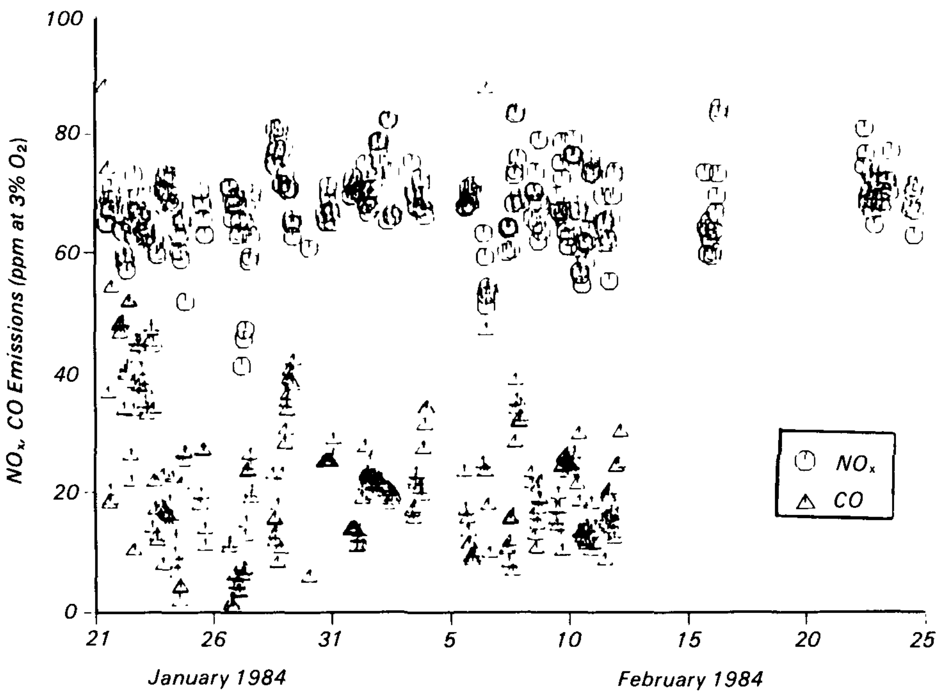

Figure 4. *Flue gas NO_x and CO for the extended test period*

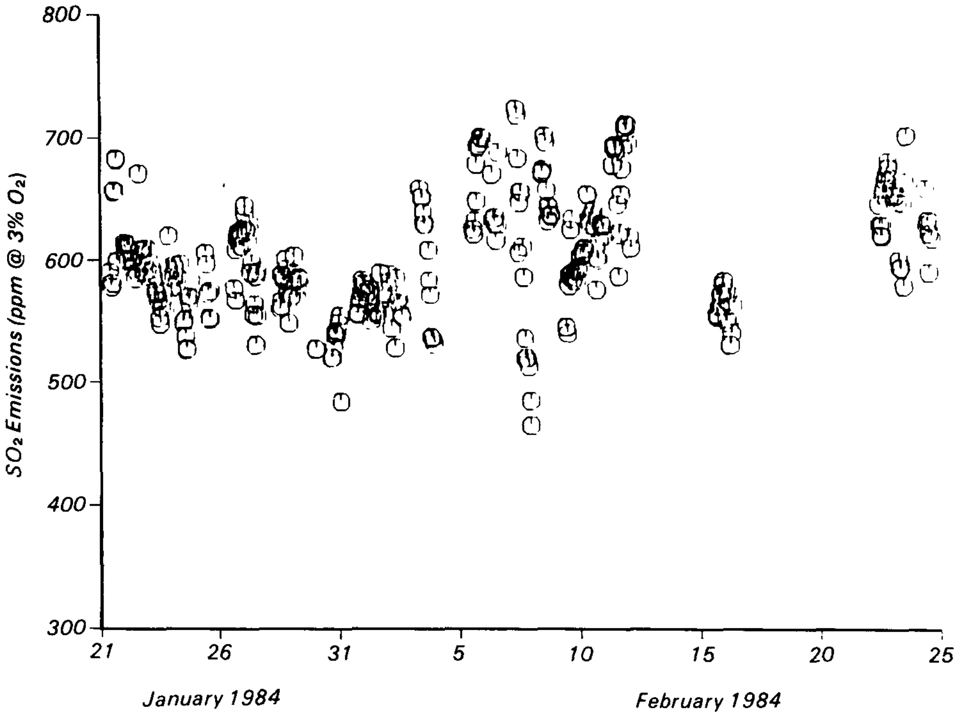

Figure 5. *Flue gas SO_2 for the extended test period.*

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The complete report consists of two volumes, entitled "Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with an EPA Heavy Oil Low-NO_x Burner,"

"Volume I. Technical Results," (Order No. PB 86-191 475/AS; Cost: $16.95)

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