

EMISSIONS SURVEY CONDUCTED AT FIVE BRICK KILNS

LOCATED IN JUAREZ, CHIHUAHUA, MEXICO

March 30-31, 1993

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Test Dates:

March 29-31, 1993

Submittal Date:

April 16, 1993

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TABLE OF CONTENTS

Page

1.0	Introduction	1
1.1	Project Assignment	1
1.2	Assignment Modification	1
2.0	Process Description	2
3.0	Testing Methodology	5
3.1	Sampling Techniques	5
3.2	Sources Sampled	6
4.0	Sample Analysis	6
4.1	Analytical Techniques	6
4.1.1	Combustion Gases	6
4.1.2	Raw Materials	7
4.1.3	Propane and Fuel Oil	7
4.1.4	Volatile Organic Compounds (VOC's)	7
4.2	Summary of Results	8
4.2.1	Combustion Analyzer	8
4.2.2	Raw Materials	10
4.2.3	Propane and Fuel Oil	11
4.2.4	Volatile Organic Compounds	12
5.0	Observations and Comments	15
5.1	Test Observers	15
5.2	Combustion	15
5.3	Toxic Metal Vapors	15
6.0	Appendices	15

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1.0 Introduction

1.1 Project Assignment

On March 23, 1993, El Paso Natural Gas Company (EPNG) requested that American Environmental Testing Company, Inc. (AET) conduct emissions testing of five (5) small brick kilns in Juarez, Mexico. AET was asked to identify the organic fraction of the emissions using a modified gas chromatograph/mass spectrographic (GC/MS) modification of EPA Method 25. Two (2) samples were to be obtained from each of the kilns: The first sample after one hour into the burn, and the second about four hours later.

Also, volatile metals were to be sampled using a set of impingers and filters.

Data Chem Laboratories (Salt Lake City, Utah) was selected to conduct the analyses of the samples.

Preparation for sampling was to begin on March 29, and testing was scheduled for March 30 and 31, 1993.

After the on-site review with EPNG's Mr. Ramiro Garcia and Ms. Ana Laura of the Federacion Mexicana De Asociaciones Privadas de Salud y Desarrollo Comunitario, A.C. (FEMAP) on March 29, 1993, it was determined that the scope of work would include the following:

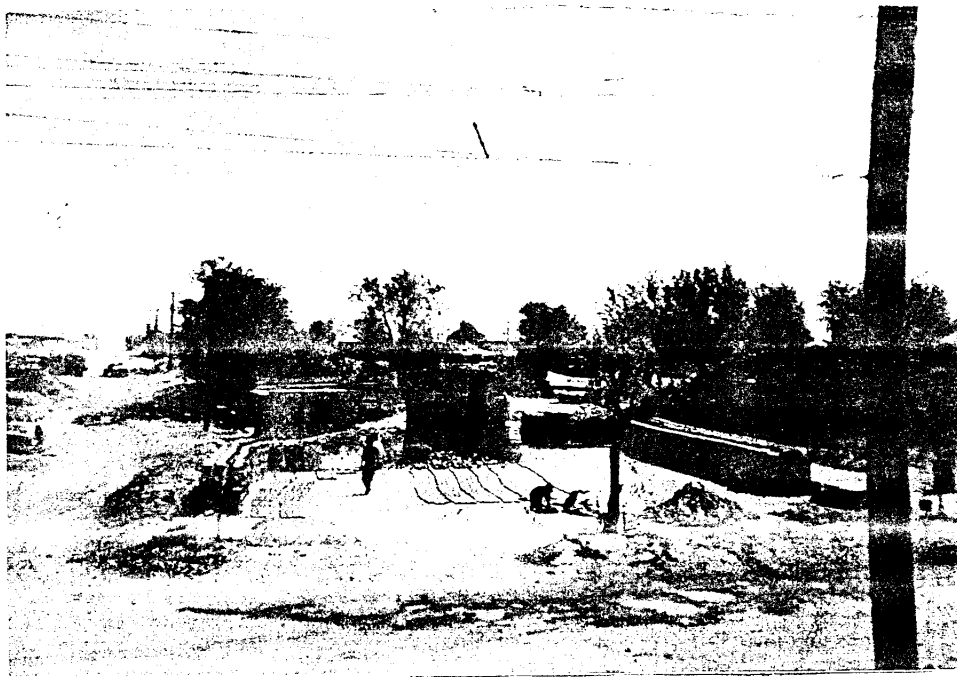
- a) Collect condensable and noncondensable organic emissions using EPA Method 25 at approximately 1 and 5 hours after the initial kiln firing. These ten samples would then be analyzed using GC/MS techniques; organic species of particular interest (air toxics and carcinogens) would be quantified.
- b) In addition, at each of the 1 and 5-hour intervals, AET would extract samples for analysis of:
 - 1 - Stack temperatures (°F)
 - 2 - Carbon monoxide (ppm CO)
 - 3 - Carbon dioxide (% CO₂)
 - 4 - Nitric oxide (ppm NO)

- 5 - Nitrogen dioxide (ppm NO₂)
- 6 - Oxygen (% O₂)
- 7 - Sulfur dioxide (ppm SO₂)

2.0 Process Description

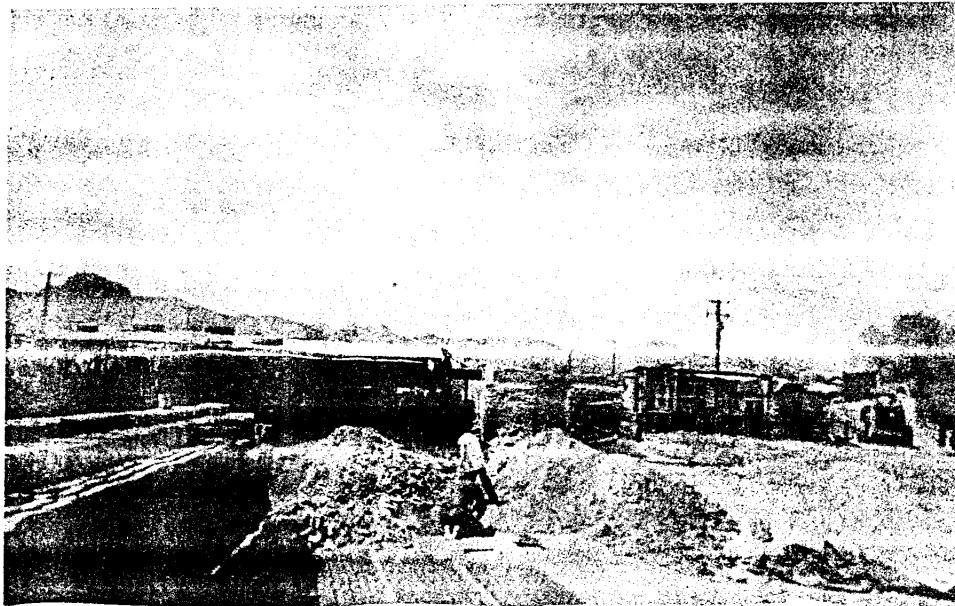
The kilns tested are used to fire adobe-like bricks from various local clay, sand and organic materials; the finished bricks are used in the Juarez building trades. Photograph 1 shows the piles of raw materials being mixed with water to be formed into the selected brick shape, the bricks being air dried and the firing kiln in the background.

Photograph 1



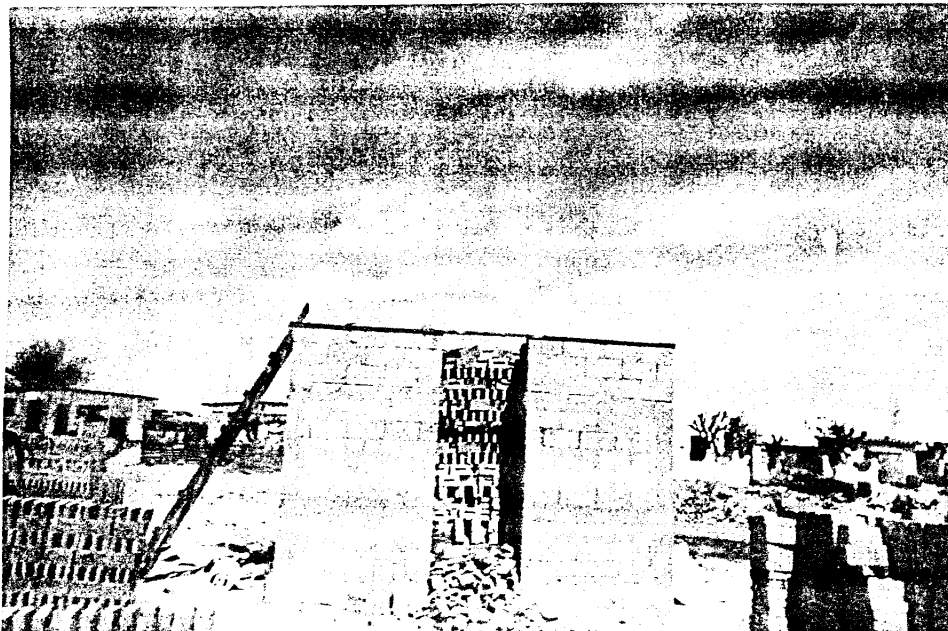
Photograph 2 is a closer view of the mixing and drying processes.

Photograph 2



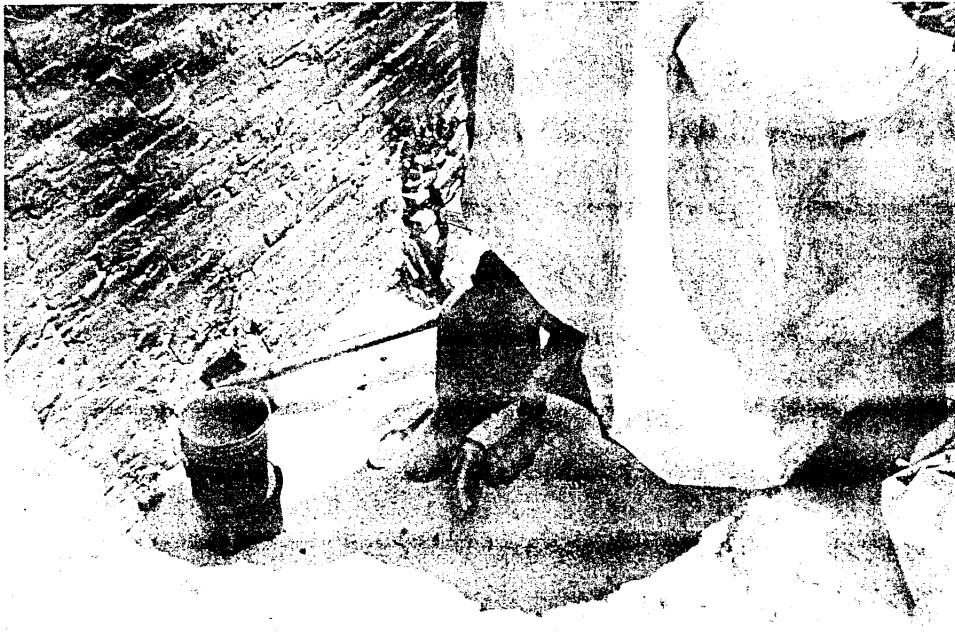
After being air dried, the bricks are then hand stacked into the kiln, where various fuels are burned to dry, fire and cure the bricks (Photograph 3).

Photograph 3



Photographs 4 and 5 show one of the brickmakers hand-feeding sawdust into the firing chambers of one of the kilns. A small vacuum/blower mixes air with the sawdust and charges it to the burners beneath the bricks.

Photograph 4

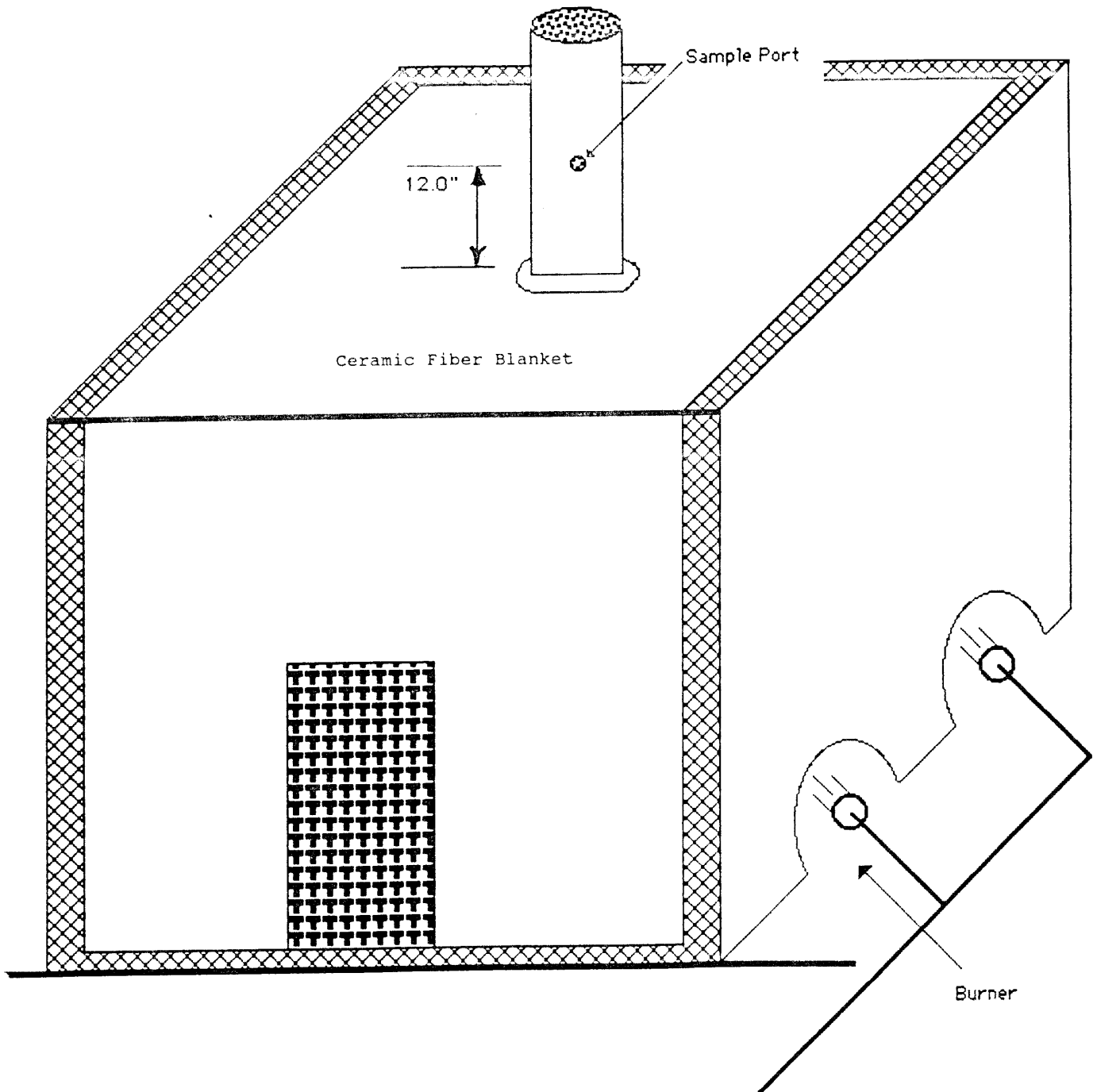


Products of combustion and other emissions from the hot bricks rise from the kiln bed and exit the top of the kiln.

Photograph 5



Figure 1:
Sketch of Brick Kiln and Improved Sampling Arrangement



Samples of the raw clay, an unfired brick, and each of the fuels were collected for analysis at Data Chem Laboratories, as well.

3.2 Sources Sampled

Samples were collected from the kilns on March 30 and 31, 1993. The kilns were fired using various fuels and/or techniques, as follows:

- a) Kiln 1: The combustion cycle in this kiln was initiated using paper and wood kindling. Then a sawdust-air mixture was blown into the combustion chamber for the approximately twenty-four-hour firing cycle.
- b) Kiln 2: Combustion was initiated with the same materials as Kiln 1. As soon as the temperature was high enough, used crankcase oil was injected and burned to provide the required heat cycle; the firing time is nearly the same length as the sawdust-fired kiln process.
- c) Kiln 3: Combustion was initiated by burning old tires, followed by firing with propane for the entire duration of the firing cycle.
- d) Kiln 4: This kiln firing was started and sustained by burning wood and sawdust materials containing various plastic laminates and organic coatings and binders.
- e) Kiln 5: This kiln, referred to as the "Ecological Kiln," was fired with propane by naturally aspirated fuel burners (provided by EPNG).

4.0 Sample Analysis

4.1 Analytical Techniques

4.1.1 Combustion Gases

AET used a COSA 6000 EN Analyzer to determine temperatures and compositions of the stack gases. The analyzer pumped a sample from the kiln exhaust gases and measured the temperature and various gaseous constituents using absorption and electrochemical cells. The COSA 6000 EN has internal calibration

circuits that cycle each time the instrument is started.

4.1.2 Raw Materials

Samples of an air-dried brick, the clean sawdust and the contaminated wood were collected and transported to Data Chem Laboratories for chemical analysis. EPNG requested that these materials be analyzed for those metals that the EPA has identified as potentially harmful to either humans or the environment. Representative samples of these materials were digested using a variety of oxidizing acids and heat. The resultant solutions were aspirated into an inductively coupled plasma arc atomic absorption spectrophotometer (ICPA-AA) for analysis.

4.1.3 Propane and Used Motor Oil

Samples of the propane and used crankcase oil also were sampled and sent for analysis by Data Chem. The propane fuel was analyzed using a gas chromatograph (GC) with a flame ionization detector (FID) and a standard alkane column.

The crankcase oil was analyzed for "EP Toxicity" metals using atomic absorption spectroscopy. Sulfur content was determined using iodometric analysis (LECO Sulfur Analyzer). The heating value of the oil was determined with a Parr Oxygen Bomb Calorimeter.

4.1.4 Volatile Organic Compounds (VOC's)

VOC's emitted from the kilns were collected using EPA Method 25 condensation loops and teflon-coated bags for noncondensable organic species. The VOC's were condensed with a dry ice/acetone bath. The loops were delivered to the laboratory packed in dry ice to preserve sample integrity.

A 10-ml aliquot of each sample bag was analyzed by direct injection in a VG Trio-1 gas chromatograph/mass spectrometer system.

A blank was injected before the sample using 10 ml of room air with 50 ul of 1.1 ug/ml difluorobenzene in helium. A 100-ul aliquot of sample #EM-0851 was also analyzed for early saturated peaks. The first loop of the guard column was immersed in liquid nitrogen and was removed after injection.

The following instrumental conditions were used for the analysis:

Gas Chromatograph

Injection Mode: 10 ml

Column: 30 cm of 0.32-mm i.d. DB-5 1-um thick film

Carrier Gas: Helium at 10 psi

Oven Temperature: 40°C for 4 min, ramped to 320°C at 10°C/min - hold for 3 minutes

GC/MS Interface: Direct to MS source at 250°C

Mass Spectrometer

Scanning: 21-420 AMU at 400 AMU/sec

Ionization Mode: Electron impact at 70 eV

4.2 Summary of Results

4.2.1 Combustion Analyzer

Results obtained on-site using the COSA 6000 EN Combustion Gas Analyzer are summarized in Table 1.

Table 1: Generic Components of Combustion Gases

<u>Kiln #/hr</u>	<u>Primary Fuel</u>	<u>Temp Stack F</u>	<u>O₂ %</u>	<u>CO₂ %</u>	<u>CO ppm</u>	<u>NO ppm</u>	<u>NO₂ ppm</u>	<u>SO₂ ppm</u>
1/1.0	Sawdust	103	16.3	4.3	1915	12	0	11
1/1.5	Sawdust	121	15.2	5.3	1626	16	0	11
1/6.0	Sawdust	116	16.2	4.4	649	15	0	1
1/6.5	Sawdust	115	15.9	4.6	685	12	0	1
2/1.0	Oil	141	10.2	8.6	329	29	1	11
2/1.5	Oil	120	7.0	11.1	1987	26	0	54
2/6.0	Oil	148	16.3	3.7	785	15	0	2
2/6.5	Oil	154	16.9	3.8	809	12	0	2
3/1.0	Propane	99	7.4	8.9	3543	40	0	40
3/1.5	Propane	110	7.0	9.2	4683	42	0	60
3/5.5	Propane	124	12.3	6.9	1853	84	0	3
3/6.0	Propane	130	9.0	9.5	2194	103	0	8
4/1.0	Contamin-	64	14.5	5.9	2671	47	0	19
4/1.5	ated wood	81	15.6	4.9	3920	36	0	18
4/5.5	and	134	6.6	13.3	29267	80	0	226
4/6.0	sawdust	119	6.8	13.1	27351	43	0	105
5/1.0	Propane,	118	13.0	7.3	331	21	0	9
5/1.3	Ecological	115	12.7	7.6	255	22	0	6
5/2.0	Kiln	123	13.3	7.1	304	19	0	0
5/2.5	& special burner*	124	13.5	6.9	288	21	0	0

* Times expressed in hours after initial firing of kiln. Stack temperatures are expressed in degrees Fahrenheit. Concentrations of pollutants are in parts per million (ppm) by volume.

4.2.2 Raw Materials

Results from the ICPA-AA analyses are listed in Table 2.

Table 2: Raw Material Analysis

	<u>Brick</u>	<u>Sawdust</u>	<u>Wastewood</u>
Aluminum	21,000	150	160
Antimony	ND	ND	ND
Arsenic	ND	ND	ND
Barium	160	10	12
Beryllium	ND	ND	ND
Cadmium	ND	ND	ND
Calcium	72,000	2,000	1,200
Chromium	16	ND	2
Cobalt	6	ND	ND
Copper	10	5	2
Iron	14,000	210	300
Lead	ND	ND	ND
Lithium	20	ND	ND
Manganese	6,700	210	190
Molybdenum	290	72	37
Nickel	10	ND	ND
Phosphorus	360	ND	80
Potassium	5,000	500	600
Selenium	ND	ND	ND
Silver	ND	ND	ND
Sodium	620	20	170
Strontium	210	7	7
Thallium	50	ND	ND
Vanadium	33	ND	ND
Zinc	38	11	13
Mercury	ND	ND	0.10

All samples are reported in ppm by weight. ND means "not detected."

4.2.3 Propane and Fuel Oil

Results of the propane analysis by GC are given in Table 3.

Table 3: Constituents in Propane, in Order of Quantity Present

1. Propane
2. Methyl propane
3. Butane
4. Butene
5. Pentene
6. Methylbutane
7. C6 - alkanes
8. Methylcyclopentane
9. Benzene
10. Cyclohexane
11. C7 - alkanes
12. Methylcyclohexane
13. Dimethyl disulfide
14. C8 - alkanes
15. Toluene
16. C2 - alkylcyclohexanes
17. c9 - alkanes
18. Hexamethyl cyclotrisiloxane
19. Methyl propyl disulfide
20. Ethylbenzene
21. Xylenes
22. Diethyl disulfide
23. C3 - alkylbenzenes
24. Octamethyl cyclotetrasiloxane
25. Dimethyl trisulfide
26. Decamethyl cyclopentasiloxane

Results of the crankcase oil analysis are provided in Table 4.

Table 4: Crankcase oil analysis

BTU's	=	21,936
%S	=	3.4%
%Ash	=	2.1%
%H ₂ O	=	0.8%
ppm As	=	436
ppm Cd	=	54
ppm Cr	=	73
ppm Cu	=	25
ppm Hg	=	1.4
ppm Se	=	5.1
ppm Pb	=	1,114

4.2.4 Volatile Organic Compounds

Results of the GC/MS analysis on the noncondensable Teflon-lined bags are given in Tables 5 through 9. See Table 10 for results of the GC/MS analysis of the condensable VOC loops.

Table 5: Kiln 1 - Sawdust - VOC's identified in bag sample

<u>1.0-hr Sample</u>	<u>6.5-hr Sample</u>
1. Methanol	1. Acetone
2. Acetaldehyde	2. Benzene
3. Acetone	3. N,N - dimethylacetamide
4. Methylene chloride	4. Hexamethyl cyclotrisiloxane
5. Unidentified nitrate	5. Octamethyl cyclotetrasiloxane
6. Benzene	6. Unidentified terpene
7. N,N - dimethylacetamide	
8. Hexamethyl cyclotrisiloxane	
9. Octamethyl cyclotetrasiloxane	
10. Decamethyl cyclopentasiloxane	
11. Terpenes	

Table 6: Kiln 2 - Crankcase Oil - VOC's identified in bag sample

<u>1.0-hr Sample</u>	<u>5.0-hr Sample</u>
1. Methanol	1. Propane
2. Acetaldehyde	2. Acetone
3. Acetone	3. Methylene chloride
4. Benzene	4. N,N - dimethylacetamide
5. Toluene	5. Hexamethyl cyclotrisiloxane
6. N,N - dimethylacetamide	6. Unidentified alkane
7. Hexamethyl cyclotrisiloxane	7. Terpenes
8. Octamethyl cyclotetrasiloxane	
9. Unidentified terpene	

Table 7 Kiln 3 - Propane - VOC's identified in bag sample

<u>1.0-hr Sample</u>	<u>5.0-hr Sample</u>
1. Formaldehyde	1. Acetone
2. Methanol	2. Furan
3. Acetaldehyde	3. Iodomethane
4. Acetone	4. Unidentified nitrate
5. Methylene chloride	5. Butanal
6. Unidentified nitrate	6. Methyleneethyl ketone or methylpropenol acetate
7. Benzene	7. Benzene
8. Toluene	8. Toluene
9. N,N - dimethyl acetamide	9. N,N - dimethyl acetamide
10. Hexamethyl cyclotrisiloxane	10. Hexamethyl cyclotrisiloxane
11. Octamethyl cyclotetrasiloxane	11. Octamethyl cyclotetrasiloxane

Table 8: Kiln 4 - Contaminated Waste Wood - VOC's identified in bag sample

<u>1.0-hr Sample</u>	<u>5.0-hr Sample</u>
1. Methanol	1. Furan
2. Acetaldehyde	2. Unidentified nitrogen compound
3. Acetone	3. Propenenitrile
4. Methylene chloride	4. Unidentified nitrates
5. Unidentified nitrate	5. Benzene
6. Methyl propanal	6. Thiophene
7. Nitromethane	7. Toluene
8. Benzene	8. Ethylbenzene
9. Toluene	9. Xylenes
10. N,N - dimethyl acetamide	10. N,N - dimethyl acetamide
11. Hexamethyl cyclotrisiloxane	11. Ethynyl benzene
12. Octamethyl cyclotetrasiloxane	12. Hexamethyl cyclotrisiloxane
13. Terpenes	13. Octamethyl cyclotetrasiloxane
14. Unidentified alkene	14. Terpenes

Table 9: Kiln 5 - Propane - VOC's identified in bag sample

<u>1.0-hr Sample</u>
1. Acetone
2. Furan
3. Benzene
4. Toluene
5. Ethylbenzene
6. Xylene
7. N,N - dimethylacetamide
8. Hexamethyl cyclotrisiloxane
9. Octamethyl cyclotetrasiloxane
10. Terpene

5.0 Observations and Comments

5.1 Test Observers

Representatives of the following organizations were present during the kiln tests:

1. FEMAP - Federacion Mexicana de Asciaciones Privadas de Salud y Desarrollo Comunitaria, A.C.
2. Comite Municipal de Ecologia-Area Atmosfera
3. Secretaria de Ecologia del Estado de Mexico
4. Empresas de Solidaridad.

5.2 Combustion

AET noticed that very little attention was being paid by the brickmakers to the problem of incomplete combustion in the kilns. Large amounts of carbon monoxide (CO) were present in combustion gases emitted from the first four kilns tested. CO exposure likely posed a serious threat to the brickmakers, nearby residents and other people passing by the kilns.

5.3 Toxic Metal Vapors

There was some mercury present in the wastewood fuel. Exposure to mercury vapors should be avoided.

6.0 Appendix

Data Chem Laboratory Reports