

Development of Cleaner-Burning Brick Kilns in Ciudad Juarez, Chihuahua, Mexico

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ABSTRACT

The following results provide a comparison between net airborne contamination produced by the traditional form of kiln used in Northern Mexico and by those modified according to a design by Dr. Robert Marquez. What has become known as the MK style kiln was intended to significantly reduce contaminant emissions. The concept involves covering the kiln with a dome and channeling the output of an active kiln through a second, identical loaded kiln for its additional filtration of the effluents. Kilns of a pair are connected via clay brick channels. The roles are reversed after the initial kiln is refilled. Significant reductions in the particulate and gaseous emissions were achieved in the prototype system, but a connectional problem with recent kiln pairs has also limited the degree of operational success. The problem did not mask the potential of the MK kiln, as will be shown. Additional anticipated benefits to the owners of MK kilns, such as reduced operating cycles and decreased quantities of fuel, also have been verified. Key measurements made during all of the burns were of aerosol densities and buoyancies in the flues, kiln temperatures, and, on a number of occasions, chemical analyses of both aerosol and gaseous effluents. Continuous time histories of aerosol densities for most burns (of a total of ~40) provide a basis for examining features and the effects of differing styles of

operation with respect to burn efficiency and net contaminant masses. Covering the active kiln with a dome produces a net reduction in dry aerosol effluent mass of a factor between 5 and 10, whereas the addition of a filter kiln produces a net reduction of about a factor of 2. The use of used motor oil as a fuel further reduced aerosol contamination by ~1 order of magnitude.

INTRODUCTION

Previous studies have considered aspects of Mexican brick-making kiln construction: economic factors and general qualitative performance, as well as concerns with the implicit health problems caused by the resulting air contamination. A summary is given in two reports by Blackman and colleagues.^{1,2}

A typical traditional kiln in this region is open topped, has a surface area of ~10 m², and is fired with scrap wood as the dominant fuel. There are hundreds of brick-making kilns within Ciudad Juarez alone. Reduction of the contamination produced by these kilns is a major environmental objective on both sides of the border with El Paso, TX. Other large Mexican cities are also involved in the search for approaches to cleaner-burning kilns.

Roughly 8 yr ago, Robert Marquez, then a doctoral student at New Mexico State University (NMSU), sought a kiln design that would significantly reduce effluent emissions.^{3,4} These emissions include massive quantities of soot, a fractal particulate material consisting of aggregations of tiny graphitic carbon "spherules"⁵ bearing much smaller quantities of hazardous substances and various gases, many of which are also hazards to health.

The basic idea was to explore the absorptive possibilities of the material at hand, that is, clay, to capture the effluents. Two steps were needed to channel the flow through raw clay. First, to channel the flow through clay, it was necessary to cover the traditionally open-topped kiln. This step alone led to the greater reduction in harmful effluent emissions, because the kiln became more thermally efficient and burned cleaner, whereas a small exhaust flue allowed adequate flow. Second, the flue was covered and the effluent from the kiln was fed, by way of connecting flow channels, through a twin kiln filled with

IMPLICATIONS

Two facts concerning brick-making kilns or ladrilleras put them in the environmental spotlight: they normally produce copious effluents, which are known (if not well quantified) hazards to public health, and they tend to proliferate in regions of high population density. Ciudad Juarez is not the only city with this problem. In the interest of mitigating air contamination from this type of source, basic operating properties and effluents of brick-making kilns in this region have been characterized in a study of several years duration.

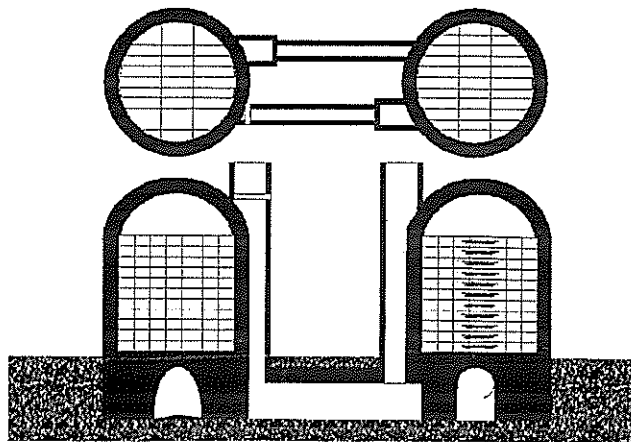


Figure 1. Outline sketches of the reversible MK kiln pair in side and plan views. As it is drawn, the active kiln is on the left, and the flow is channeled down the flue and into the base of the filter kiln. The filtered output exits through the filter kiln flue.

unfired bricks, which served as a passive filter element to further reduce the emissions. The active and passive roles of the two kilns are reversed in the succeeding burn, and so on. A simple sketch of a twin kiln pair is shown in Figure 1. These coupled kiln pairs are referred to as MK-type kilns, whereas either of the two kilns operated without coupling is referred to as an MK-domed kiln.

To obtain satisfactory performance, it is essential to preserve the effluent flow rate when coupling the kilns. This has proved to be a difficult design issue. This problem surfaced after the measurements on the first prototype systems for which the active kiln and the filter were not identical. All of the succeeding systems constructed through the end of 2005 displayed an undesirable degree of flow restriction.

This report examines the performance of several open-top kilns, two MK kiln prototypes, and two series of MK-type kilns constructed in Ciudad Juarez, one with funding from the U.S. Department of Energy and the other funded by El Paso Electric Corp. under an emissions trading agreement with the U.S. government.^{6,7}

EXPERIMENTAL WORK

Dry Aerosols

Densities/Fluxes. Two basic approaches to measurement of the dry aerosol flux were used. Both incorporated continuous monitoring by means of nephelometry and semi-continuous, time-integrated calibration using flow-matched directly in-line filters.^{8,9}

Nephelometers measure the intensity of light scattered from a given volume through a selected range of angles. Normally this means that a statistical number of particles contribute essentially simultaneously. Other than providing the maximum detection sensitivity, this approach can be designed to require minimal or no significant interference with particle motion and densities. Nephelometer measurements can be linear with density over several decades, a feature that is important in the highly variable kiln effluent flows.

The primary system used for the measurements of this kiln study was specified by an author (C.W.B.) and

developed by MIE Corp. of Bedford, MA (jointly sponsored by U.S. Environmental Protection Agency [EPA] and the U.S. Army). It has been applied in arrays to a wide variety of aerosols in various field studies by the U.S. government. It is designated the RAS-1. In its field form, the sensitive volume is external to the unit in airflow unimpeded by the unit body. For the kiln studies of aerodynamically small particles, it has been used both in semiopen fashion and in a flow circuit with the sensitive volume enclosed.

In the former nephelometer sampling configuration, the optical unit mounts directly atop the flue, whether of the active or the filter kiln. The aerosol flows past the optically active volume and exits through a variable-speed fan. This configuration is possible because of the small sizes of the soot particles and the low flow rates (<3 m/sec). This unit mounts above an expanded wire screen and faces the flow. Although the RAS units are particularly tough with respect to temperature (and other parameters), one cannot sample an entire burn in the flue of the active kiln in this fashion. However, it can sample throughout the burn in the flue of the filter kiln.

By far the more usual sampling configuration has been with a triplet of measurements that are easily shifted from one flue to the other. In this scheme the nephelometer is remotely located. The other two colocated measurement systems are the dosimetric filters and the buoyancy sensor. For the MK-type kilns, these systems clip over the rim of the flue and sample from the flue center, although position is adjustable and lateral uniformity of the variables is explored in each case within the $\sim 0.37 \text{ m}^2$ (2' \times 2') port.

In this case, the nephelometer flow circuit starts in the entrance port of a relatively large-diameter stainless steel tube. For use with open-top kilns, the stainless tube is $\sim 2 \text{ m}$ long. Two triangular, movable feet ride the kiln surface. The isokinetically sampling port faces into the kiln flue from a distance of $\sim 38 \text{ cm}$. For both flues of the MK-type kilns, the stainless tube is in the form of a "U". This U-tube, which, again, is flow matched and faces the flow within the flue, connects to a 3.175-cm flexible plastic tube that connects with a condenser system usually at ground level. An ice bath surrounds the condenser chamber. The large-diameter system is aspirated with the intake side of a squirrel-cage blower. Various instruments sample through taps in the main flow line; the nephelometer (dry aerosol) tap, of course, samples in the line after the condenser. Flows for all of the other tap connections (CO, other gases, moisture, etc.) are much smaller than the main flow.

Before entering the nephelometer, the flow is heated with a tape wound about the sampling line. The nephelometer flow pump is protected from moisture in the flow by a preceding aerosol filter. Smaller sampling systems with heaters and condensers have been used for simultaneous sampling through the walls of both flues.

Another type of nephelometer used has quite different design parameters; several nephelometers based on the model 2050B by Meteorology Research, Inc. (MRI) of Altadena, CA, have been modified⁷ so that they also accommodate a wide range of aerosols. These systems were used for comparative measurements at times. Although

the MRI systems are always remotely located, the temporal profiles, adjusted for flow delay, are essentially the same.

Gravimetry. Matched-flow filters sampling directly in the rising flow provide the most basic measure of the time-averaged density in the flues. The time integral of the dry aerosol mass accumulated and the time integral of the nephelometer signal are proportional. This is strictly true if the size distribution and the bulk optical properties do not vary significantly with time. Both are good assumptions for the kiln dry aerosols, with rare exceptions, such as the ash encountered in just one sawdust burn. Obtaining areal density profiles atop open kilns involves moving the colocated filter and nephelometer port. Typically between 20 and 40 gravimetric filter samples are obtained for calibration during the course of a kiln burn.

Buoyant Flow. Several sensor systems have been used to measure flow from the kilns. Two were propeller sensors (Young and Omega) mounted in larger tubes, and one was a manometric sensor developed primarily for the measurement of smaller air flows without sensitivity to various environmental factors.^{9,10} All were operated together in a wind tunnel in an early stage of the kiln study project. Agreement for the two propeller sensors was well within 10% (typically about half that). The signal for the manometric sensor is relative, and the unit is used with on-site calibration. This sensor uses a phase-sensitive amplifier and was rarely used, because the flow generally stabilizes fairly quickly, and the propeller-based sensors do a better job of spatially averaging the flow.

Gases

Polyaromatic Hydrocarbons. Polyaromatic hydrocarbons (PAHs) are formed during the combustion of all types of materials used to fuel the kilns. Quantitative measurements of these compounds were made during one burn. The nephelometer calibration filters were used to quantify the presence of PAHs.

The compounds from three filters were extracted using ultrasonic extraction (EPA method 3550B). The filters were folded, introduced in 10 mL of methylene chloride (MC), and exposed to the tip of the ultrasonic device. The resultant solution was passed through a column packed with fiberglass beads (3-cm diameter) and anhydrous sulfate to remove any water and particulate matter from the MC. The extract was divided into two samples. The first sample was exchanged with acetonitrile and analyzed using high-performance liquid chromatography (HPLC).

The analysis of the second sample was performed using gas chromatography (GC)/mass spectrometry. The peaks on the chromatograms were quantified against a Supelco EPA 610 PAH mixture containing the 16 EPA priority PAHs (PAH-16). This standard was serially diluted to produce a set of five standards that covered the PAH concentration range observed. The PAH-16 set was composed of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene,

dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene.

Volatile Organic Compounds. Volatile organic compounds (VOCs) are also present in the aerosol effluents. There were two attempts to identify and measure VOCs. One was a qualitative analysis performed during a burn made with an MK kiln. The sample was collected by drawing kiln effluent through a preconditioned and cleaned VOCARB 4000 trap using a vacuum pump with constant sampling period. The compounds trapped were identified with GC/mass spectrometry.

The second attempt was made using active carbon filters during a different burn. The filters were placed in the sampling line just downstream from the aerosol filters. Because the dosage for saturation is not well known and is different for the various substances of interest, sets of three filters were placed in series so that extrapolations could be made to the original concentrations. Four sets of filters were used: two sets for oil-fired portions of the burn and the other two sets for wood-fired portions of the burn. Of these, one set in each case was taken just after the aerosol filter, and the second set was taken down the pump line, after the condenser. These were analyzed via GC/mass spectrometry by the Soil, Water, and Air Testing Laboratory at NMSU.

Metals. The fuels for the kilns could include significant concentrations of metals. The particulate emissions of burns made with used motor oil were captured on filters and analyzed. The samples were analyzed using EPA method 6010B with inductively coupled plasma. The target metals were the eight hazardous metals categorized by the Resource and Conservation Recovery Act: arsenic, barium, cadmium, chromium, selenium, mercury, silver, and lead. The analyses of the samples were made by Applied Environmental Services, Inc./Archana, Inc.

General Characteristics of the Burns

The principal (most massive) kiln contaminant effluents are soot and CO, that is, if we exclude CO₂. As will be shown, the former two track fairly closely. In this section, soot will be used to indicate the relationship between the source and the contaminants.

Three parameters form a reference frame to characterize the aerosols of a kiln burn. The three equally important, multiplicative quantities compose the flux; they are as follows: (1) the dry aerosol density, (2) the effluent flow rate or buoyancy, and (3) the kiln output cross-sectional area. From the complete record of the flux, the total mass of the effluent is determined. Tables in the following sections summarize the results. Before proceeding to this, however, observations on general kiln function are in order.

The typical traditional kiln in this region has a surface area of ~10 m² and can hold ~6000 bricks of normal size. The maximum size is partly dictated by the strength of the kiln, that is, the necessity of holding the bulging kiln together. Some are lashed about the middle level with a steel cable. Some kilns are much larger and accommodate loads of 16,000 bricks.

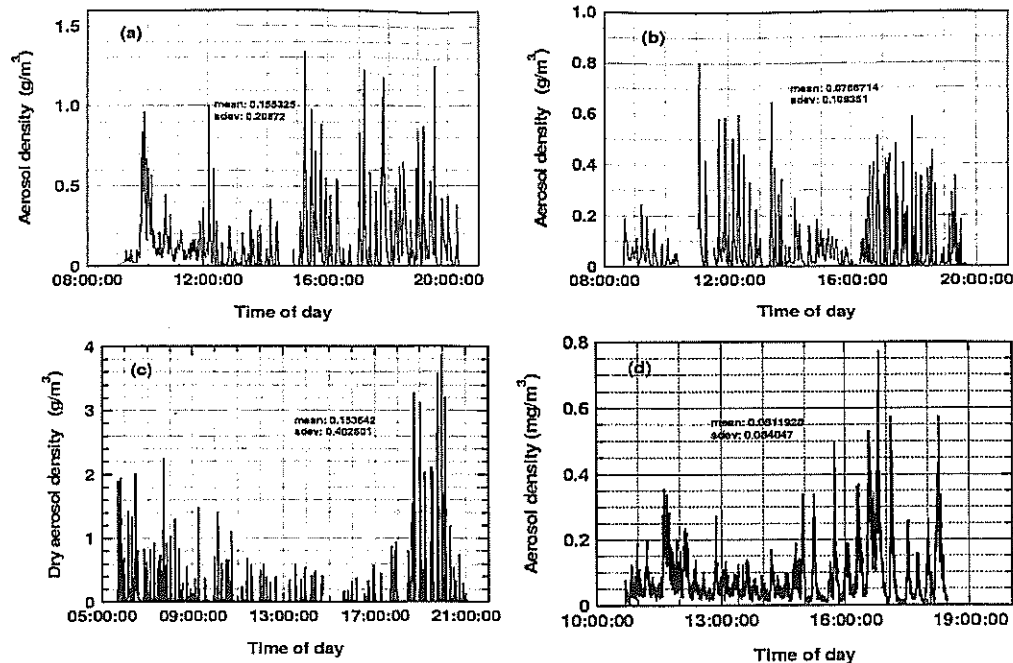


Figure 2. Smoke densities for four burns. Burn of plot c was for open kiln. Burns of plots a, b, and d were for MK kilns. Profiles reveal general magnitudes and temporal patterns. Variations are largely functions of moisture in fuel, kiln-loading procedures, and operator judgment.

Burn cycles tend to be 14–18 hr fuelled by scrap wood, broken-up pallets, or sawdust. Occasionally the material is plywood, varnished or painted, adding extra ingredients to the effluent smoke. Not all of the burns follow similar temporal patterns, although there are features that do appear and also features that are characteristic of specific types of wood fuels.

Aerosol densities for continuously monitored burns follow the feeding cycle, which usually varies with thickness of the wood. Heavy pieces, such as pallet wood, burn longer, and the intervals between feedings are also longer; typically between 10 and 15 min. Bundles of thin material are consumed quite rapidly, and the mean feeding interval is likely to be only several minutes. Operator choices vary greatly, and some operators make it a rule to feed a large quantity of material only once every half hour. The smoke tends to peak early in these cycles and to diminish even more rapidly later in the burns. Density decay portions of the feeding cycles generally fit well with exponential forms. Stoking generally provokes smoke, especially early in the total burn cycle.

A general feature of the burns is that early in the overall burn cycle the smoke density does not return to near zero values. It remains somewhat elevated during the first several hours. This appears to be the result of moist wood fuel and of having lower temperatures in the firebox in the early stages of the burn. Later in the burn, the densities return to essentially zero between feedings/stokings. This can be seen in all but one of the four examples of Figure 2 and was true for most of the other burns. Occasionally, as with the exception here, it appears that the fuel wood was quite dry.

Figure 2 illustrates the variation in the time dependence of the smoke density, especially during midburn. Inevitably the final hours show strong smoke activity. An author (A.S.L.) has suggested that this final burst of smoke

results from the removal but incomplete vaporization of carbon from the bricks as the kiln rises to the temperatures that will bake the bricks most remote from the fire. This thesis is supported by laboratory simulations of the process. When the burns are incomplete, the bricks in those remote regions of the kiln are still black. The most definite indicator of incompleteness of the firing process is found in the time profiles of temperature obtained from thermocouples inserted through the wall of the active kiln at three levels.

As the firebox heats, the density rises, and so does the plume buoyancy or vertical flow. The buoyancy is closely approximated by the form $b_0[1 - \exp(-t/c_0)]$. Once the value reaches b_0 , it rarely changes by more than a few percent and does not fluctuate strongly (the response time of the detector is ~ 2 sec). Four examples of plume buoyancy development are given in Figure 3. The MK kilns, with their small, well-defined, and relatively uniformly filled flues, permit a simpler determination of the buoyancy time dependence than the open-top kilns.

The manner in which the temperatures rise in the various parts of the kiln is a generally consistent feature of kiln burns at a given site. However, operator savvy determines how evenly the temperatures develop and in what pattern. Usually the operators heat the arches near the feed port and then progress toward the rear. Some operators consistently manage burns well, whereas others never manage to obtain the relatively uniform temperatures needed to bake the entire load to completion. Poor results were also obtained by operators of open kilns who clamped the burns down by covering the kiln before the temperatures were well developed. In these cases, the bricks were not of high quality (either not baked or weakly baked and of light, not red, color).

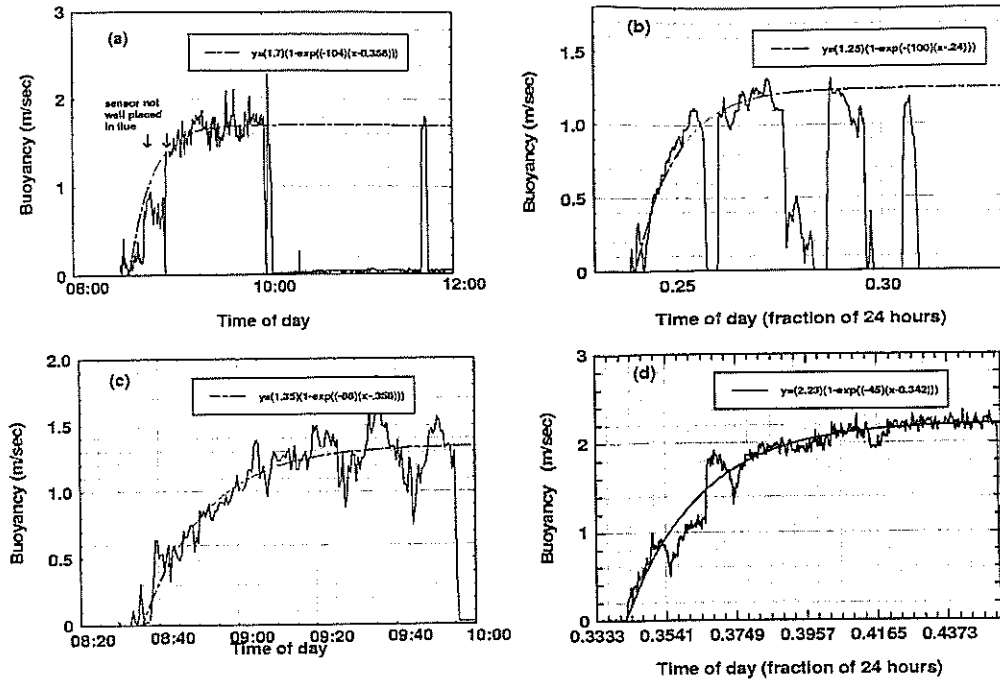


Figure 3. Development of kiln output flow rates or buoyancies. Burn of plot b was for open kiln. Burns of plots a, c, and d were for MK kilns.

From his studies, Marquez³ has suggested that an increase of 40–60 °C/hr is a target rate. Two examples of temperature profiles are shown in Figure 4. Figure 4a represents a satisfactorily managed burn and Figure 4b a poorly managed burn. For the burn shown in Figure 4a, the temperatures above the feed port rise more quickly and mature earlier than those elsewhere, but the operator then shifted the location of the fuel fed to achieve uniform interior temperatures. In contrast, all three of the

burns measured at the site of Figure 4b had the same characteristic inadequate temperature rise rate on the side of the kiln opposite the feed port. It was intended that the operators could judge the progress of the burn in each region of the kiln by means of the thermocouple readings. Flue temperatures, an inexact composite of the kiln-top temperatures for the domed kilns, were also recorded.

Successful coupling between the active and filter kilns has been elusive. Very few cases after the first prototypes yielded strong flow in the flue of the filter kiln; none came close to equalling the flow of the active kiln. For many kiln pairs, only a minimal flow, typically ~0.6 m/sec, could be achieved, as is shown in Figure 5. Flow in a few reached 1 m/sec. For several others, not even a measurable flow (~0.2 m/sec) could be achieved.

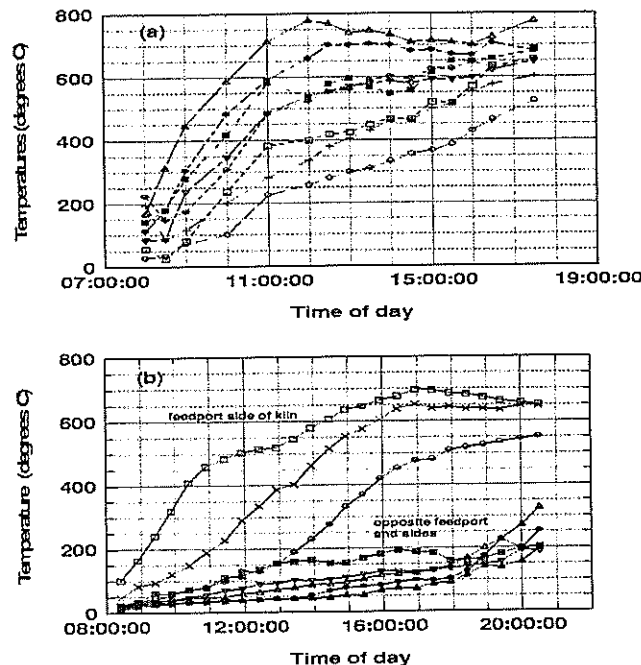


Figure 4. Kiln rim temperature time profiles for (a) a well-managed burn and (b) one not well managed.

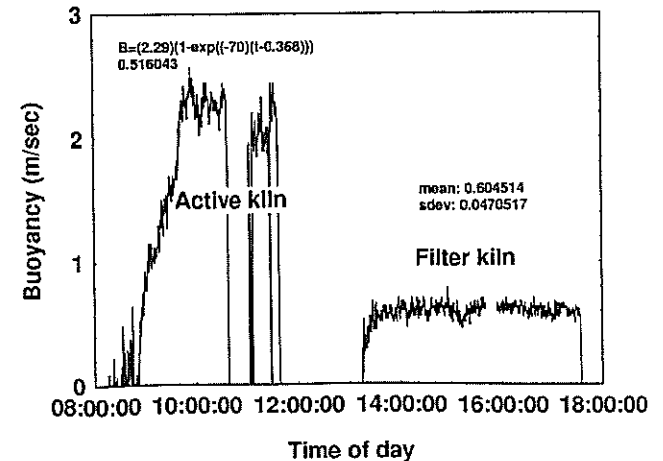


Figure 5. Typical example of coupling problem: reduced flow in output (filter) kiln flue.

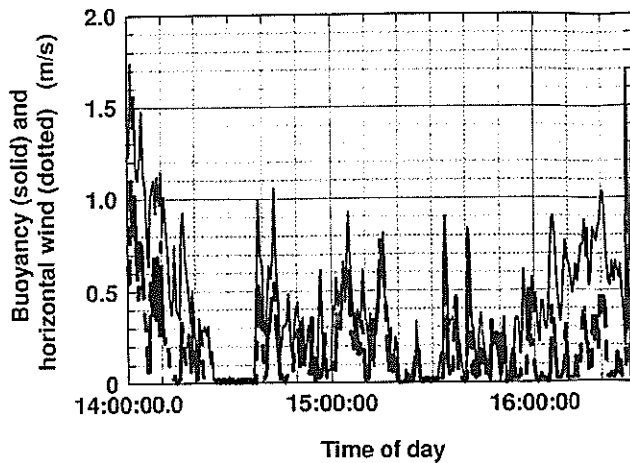


Figure 6. Wind-driven enhancement of flow-through filter kiln for weak flow coupling (high flow impedance).

There are two indicators of the source of the problem. Hydrostatic pressures were measured in the two kilns. For one kiln pair, for which the coupling was weak, the pressure was slightly higher in the base of the filter kiln than in the flue of the active kiln. A second observation is closely related: when weak coupling (or relatively high flow impedance) prevents a strong draft, the flow is increased by the flue-top vacuum created by the horizontal wind. This wind-buoyancy correlation, which is quite strong, as shown in Figure 6, was observed for several minimally coupled kiln pairs.

One burn produced a rather striking manifestation of the flow impedance problem. Several hours into a burn (September 6, 2002) with an MK kiln pair, the operator was trying to convince the measurement team to further delay the transfer of the flow to the filter kiln. It must be assumed that he was aware of the flow impedance problem. The transfer decreased the buoyant flow to approximately one third of that of the ~ 2 m/sec measured in the active flue. After approximately half an hour, a strong cyclic oscillation of the flames in the feed port entrance was observed. Each of the two phases of the cycle took ~ 1.5 sec. The flames rushed out of the port and then rushed inward (as when the flow out of the kiln is free and normal). This was not a weak phenomenon; the rushing noise for each phase was distinct and sharp. Although it would be very difficult to compute such a phenomenon, it is assumed that this kiln system was serving as a giant Helmholtz resonator. Two other kiln pairs having similar flow parameters showed weaker oscillations in the feed port at about the same frequency.

It should be noted that a variety of operational differences can affect the results; these include stacking patterns in the kilns for the bricks to be baked, brick sizes,

temporal and spatial fuel feeding patterns, and when and how open kilns are covered as the burn advances. With these and other lesser variations, such as the effects of crosswinds, one could desire many more than the ~ 40 measurement sets of this study. However, parameters of the most basic interest have become clear. The issues involved are important with regard to planning for both new kilns and for the renovation of existing colonies of kilns.

RESULTS AND DISCUSSION

Results will be presented by type of fuel for the various kiln types. First we will examine the performance of kilns fired with wood. Then we will present results from domed MK kilns and fully functional MK kiln pairs, also with fuel from the same category. After this, because its vastly higher surface-to-volume ratio manifests distinctly different burn characteristics, sawdust-fuelled kiln results will be presented. Finally, we will examine the potential reduction in contaminant effluents for used motor oil as a kiln fuel. Several burns allocated major time intervals to used motor oil as a fuel. For others, minor intervals were involved (the latter were edited out of the wood fueled results).

Quantitative Results, Aerosols: Kiln Performance for Wood Fuel

Open-Top Kilns. The burns selected were typical and represent the most complete datasets. Table 1 lists the key parameters and the significant variances.

In the following tables, the symbol ρ represents the dry aerosol density; the subscript p , the peak value; $\langle \rangle$, the average; δ , the variance; τ , the duration of the burn; and M , the total effluent mass. Three burns were used for this table.

All three constituents of the flux, the density, the buoyancy, and the active portion of the uncovered area, are variable throughout the burn for open kilns. The average flux is given in the table for the reader's convenience, but it varies during the burn. As an example, Figure 7 shows how the active surface area varied with time for two open-kiln burns. Again, we see that latitude available to the operator is significant.

Domed MK Kilns. There are a number of completed burns for this category, which gains importance because of the coupling problem between MK kiln pairs. Flow impedance was sufficient so that many burns were completed with only a short attempt to couple the flow through the second kiln. Six burns are represented in this group. Other burns, which were more complicated by the coupling attempt, also support in a general way the data provided

Table 1. Open kiln parameters.

Parameter	$\langle \rho \rangle$ (g/m ³)	ρ_p	$\langle \rho \rangle / \rho_p$	$\delta \rho$	B (m/sec)	$\langle \tau \rangle / \tau_{min} / \tau_{max}$ (hr)	$\langle \text{Flux} \rangle$ (g/min)	M (kg)
Open, wood	0.176	2.13	0.083	0.053	0.95	18.0/15.5/20.6	25.9	25.6
Plus or minus (%)	30	46			26	12	13	7

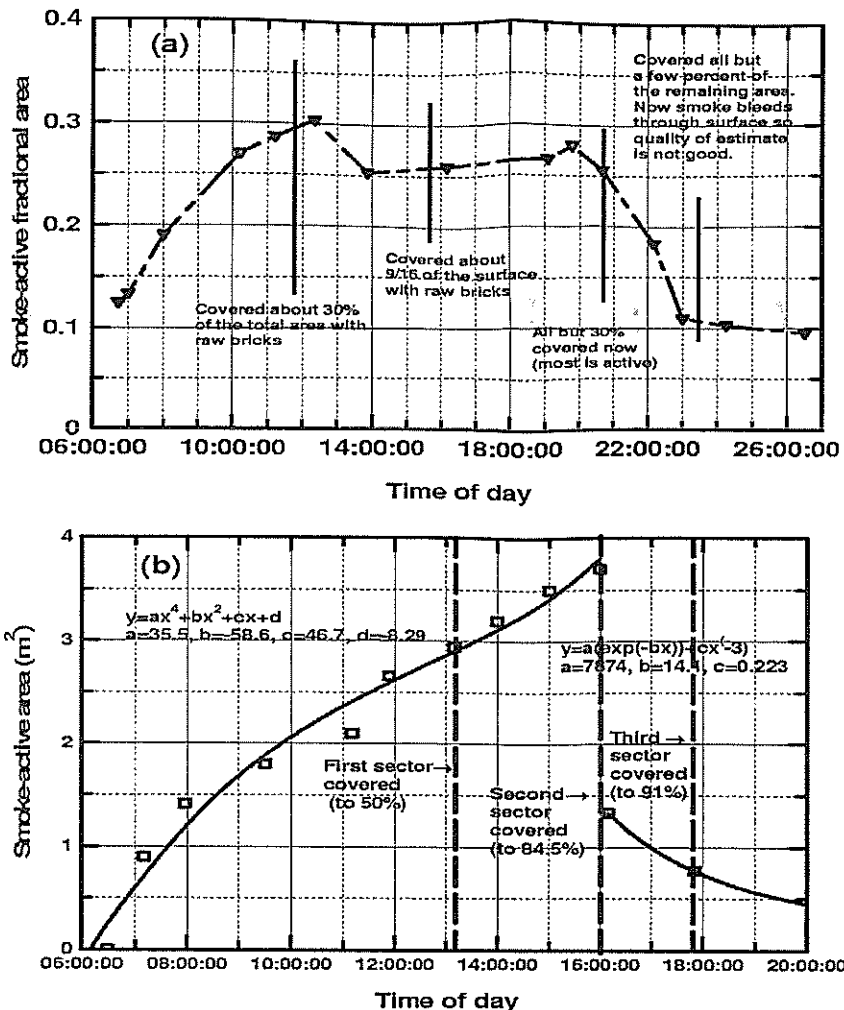


Figure 7. Open-top kilns: examples of variation with time for smoke-active surface area. Initially there is growth followed by a partial covering of the surface using unbaked bricks. This is usually followed by increased covering. After each covering the flow shifts into the remaining open area and usually expands. Covering procedures actually vary widely as can be seen from the two examples.

in Table 2. Dry aerosol densities have not changed drastically for the kilns with small (usually ~0.4 m²) exit flues. The flow has increased somewhat, but with a decrease in cross-sectional exit area that was always between a factor of 10 and 20, the product $\langle F \rangle = \langle \rho \rangle A \langle B \rangle$ is much smaller than for the open kiln. We have heard it said by the kiln workers that the smoke from the domed-kiln exit flues was just as thick as from the open kilns themselves. This is approximately true, as can be seen from the accompanying tables, but what is not as often considered is that this smoke comes from a much smaller cross-sectional area. The average reduction is a factor of at least five. As can also be deduced from the two tables, some

burns have produced a reduction of a factor of 10. In addition, the burns are shorter, further reducing the total aerosol mass. For the owners, this means savings in fuel costs.

Type MK Kiln Pairs. When the flow from an active kiln is channelled through a similar kiln, an additional reduction in the contamination level is expected. Despite the difficulty of coupling, there exist several cases that can approximate a fully functional kiln pair. For example, the first prototype did function well; that is, the flow velocity in both flues was essentially the same and was quickly

Table 2. Domed kiln parameters.

Parameter	$\langle \rho \rangle$ (g/m ³)	ρ_p	$\langle \rho \rangle / \rho_p$	$\delta \rho$	B_{active} (m/sec)	$B_{passive}$	$\langle \tau \rangle / \tau_{min} / \tau_{max}$ (hr)	M (kg)
MK, domed, wood	0.137	0.95	0.144	0.061	1.66	0.465	12.4/10/16	4.6
Plus or minus (%)	45	47			16	68	16	42

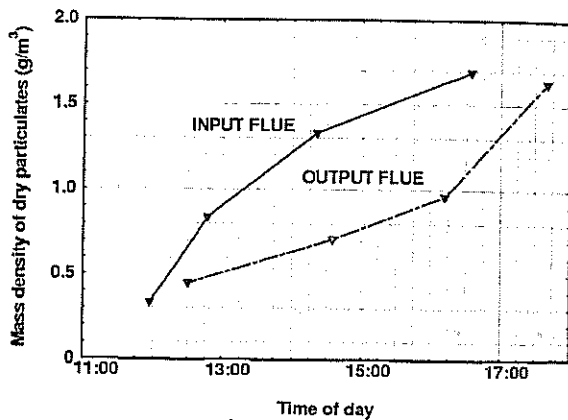


Figure 8. Densities for kiln smoke sampled in flue of active kiln and in flue of filter (passive) kiln: an early prototype.

established in the second flue. Average densities over several intervals for a burn using that system are shown in Figure 8. For this burn, all of the filter samples were obtained during feeding intervals. The results suggest roughly a factor of two reduction in aerosols from use of the filter kiln. A second example of data for a moderately well coupled kiln pair (roughly two-thirds active kiln flue flow speed in the filter kiln flue) also indicates that a factor of two is reasonable. In the latter case, continuous data were taken before, during, and after a 2-hr coupling interval. Other, more intermittent, data taken during several burns provide additional support for a factor of two for aerosol filtration efficiency.

Size Distributions for Open and Filter Kilns. The distribution of particle sizes affects the persistence of the smoke in the atmosphere and the health hazard. For kiln burns, either open or domed-and-filtered, there were only two relatively brief occurrences of ash deposition. A look at the particle size distributions produced show why virtually all of the material remains airborne; there are virtually no effluent particles with significant settling rates.

Size distributions were obtained for two burns using 60-channel optical sizing spectrometers. In a number of other cases, particle morphology has been examined using electron microscopy of polycarbonate filters. Virtually the entire effluent aerosol is soot, fractal particulate graphitic carbon. The massive agglomerates sometimes seen in smokestack effluents have not been found, either on the filters, which are sampled directly in the flow at flow-matched rates, or among the channels of the size spectrometers.

Optical sizing spectrometers developed by Particle Measuring Systems were used for this work. Two units provide radii in 8 ranges of 15 channels each (including a certain amount of overlap) from ~ 0.07 to $16 \mu\text{m}$. The responses of these systems have been calibrated for the indices of soot. The more sensitive of the two light scattering spectrometers is an "active cavity" system (ASASP-X), and the second measures outside the laser cavity (CSASP). In fact, all of the significant quantities of the effluent aerosol were covered by the smallest two size ranges (30 channels) of the ASASP-X system; that is, there

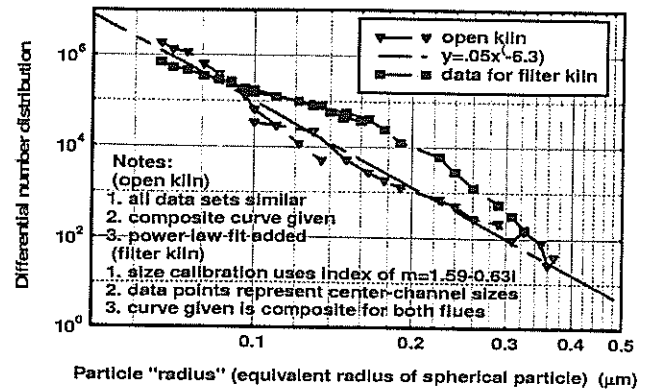


Figure 9. Optically detected (Particle Measuring Systems, Inc. ASASP-X and CSAS) sphere-equivalent particle sizes obtained during kiln burns.

was no large component. One of the two burns characterized using in situ size spectroscopy was a domed MK kiln with two smaller filter kilns, and the other was an open-top conventional kiln. Sampling for the former was done in both the active and passive kiln output flues. In both cases, sampling was conducted over several hours during the mid-to-late portions of the burn and for each, numerous 5-min samples were obtained. The objectives were to determine how the distributions vary between flues and between kiln types and to determine the existence of any large, quickly settling component.

Sampling of the MK kiln system was via a 38-cm-diameter stainless tube directly in the port. This tube, connected to a flex tube of the same diameter, was aspirated by a squirrel cage. The size sampling systems tapped into this flow. Because the channels operated in succession, the density was subject to change. The composite plot shows a slightly humped number density distribution in the vicinity of $0.2 \mu\text{m}$, which indicates a favored state of agglomeration for the elemental spherule forms. No significant differences in distribution were observed for the flue of the active kiln and the filter kiln. Apparently the soot size distribution was not altered by more

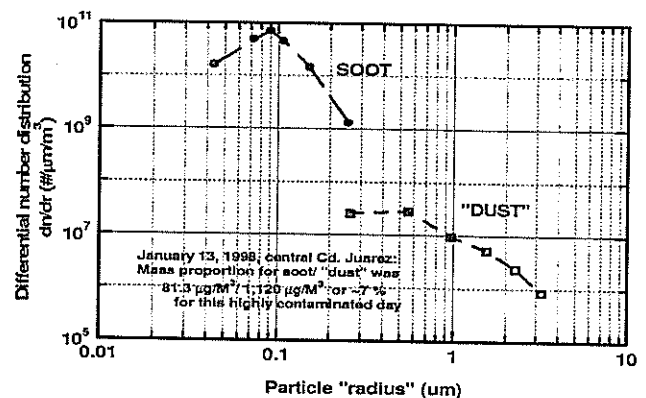


Figure 10. Typical ambient particle size distributions for the city of Juarez, Chihuahua. Actual counts from projections of scanning electron microscope photos. The composite form of the differential number distribution compared with that obtained using the same optical counters as for the kiln study was essentially coincident. The optical systems are not considered accurate for absolute numbers but excellent for form of the distributions.

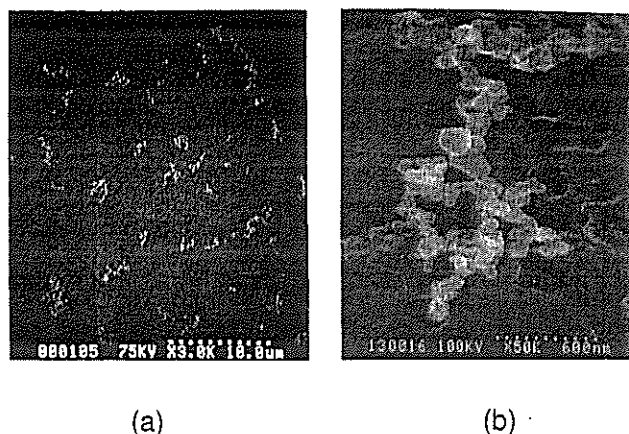


Figure 11. Photos of soot particles at two magnifications (a, 3K; b, 50K). Morphology is quite similar and distinct from that of other aerosols for the soots of various materials whether products of internal or external combustion.

than doubling the path of flow, but the total density had decreased.

Sampling atop the open kiln did show a somewhat different size distribution, and the reason is not apparent. In this case, the sampling system was near the top of the kiln, and, because of the proximity, an in-line condenser and heater were used to remove any condensed moisture. The aggregate forms for both distributions can be seen in Figure 9. The primary difference between the two is that there is no sign of the change in slope at 0.2 μm for the open kiln. Number and mass distributions from both measurement sets show a monotonic, relatively rapid decrease with increasing size. The values of the slopes throughout the range of radii indicate that all of the particle sizes statistically represented will have long mean lifetimes in the atmosphere.

Clearly, the optical probe cannot precisely characterize the fractal forms by means of the single scattering detector but simply give an idea of the size through the effective scattering cross-section. The general size range of the soot has been separated in air quality measurements in the same city using the same instrumentation. An example in terms of the ambient mass distribution is shown in Figure 10. The latter analysis was obtained through direct counting from filter substrates using observable differences in morphology supported by selective X-ray (EDAX) analyses. There is no difficulty separating the soot component in this process, which, although tedious, showed that the shapes of the distributions as determined by the two independent techniques were very close.¹¹ On an absolute basis, the magnitudes from the Particle Measuring Systems, Inc. counter are much less

reliable, because the single particle counting efficiency is dependent on a very complicated optical selection-rejection scheme. Analyses of the filters involve no such difficulty and provide absolute densities for known sample volumes.

Soot agglomerates are shown in Figure 11. The morphology of soot does not vary widely with source and can be statistically described using a single parameter called the radius of gyration (~ 1.7). It appears that, as the component "spherules" condense in the cooler regions, they connect before growth is complete. Probably because of electrostatic forces, the probability of linear connection is highest, although multiple connections are also likely. Similarity to soot from other sources, such as internal combustion engines, illustrates how nearly generic soot is.^{12,13}

Quantitative Results, Aerosols: Kiln Performance for Sawdust as a Fuel

Sawdust, with a very high surface area-to-volume ratio, burns very rapidly in the heated firebox. This means that it must be fed almost continuously; it almost explodes in the feed port later in the burn. As a consequence, the aerosol density average is much closer to the peak value. Furthermore, from the rapidity of the combustion (near explosion), it would seem very difficult to heat the rear of the kiln arches as the burn cycle progresses. Table 3 provides the results for this fuel. There were only five of these burns, and one involved mixed wood and sawdust fuels, rendering the data more or less useless.

As can be seen, the mass of the dry particulate effluent is significantly greater than for pallets, woodworking shop scraps, and heavy cardboard tubes. The open kiln burn using sawdust was among the first monitored and not quite to time of completion. Sawdust may be a less expensive fuel, but it is clearly not a good choice for reducing contaminant effluent mass.

Quantitative Results, Aerosols: Kiln Performance Used Motor Oil as a Fuel

An alternative approach to the reduction of aerosol contaminants from kilns is through the use of petroleum burners. Because fuel cost is an issue, an optimum choice is used motor oil. Working with Ciudad Juárez kilns, we have explored the potential for this fuel through the use of a fairly eclectic mix of burner designs over the past 6 yr. Most designs were produced by Dr. Marquez or Don Enrique Chavez, the latter an innovative Juárez kiln owner and codesigner and owner of the first and most successful of the MK kilns. Three additional oil burners of distinctly different designs were developed elsewhere and borrowed for brief tests of their functionality.

Table 3. Sawdust as used in both domed and open kilns.

Sawdust: MK, Domed and Open	$\langle \rho \rangle$ (g/m^3)	ρ_p	$\langle \rho \rangle / \rho_p$	$\delta \rho$	B/B_{active} (m/sec)	$\langle \tau \rangle / \tau_{\text{min}} / \tau_{\text{max}}$ (hours)	M (kg)
Domed	0.51	2.45	0.21	0.015	1.07	15.3/15.0/15.5	19.8
Plus or minus (%)	3	39			19		14
Open	0.7	~ 1.5	0.47		~ 0.5	~ 14	> 50 ; ~ 70 –100

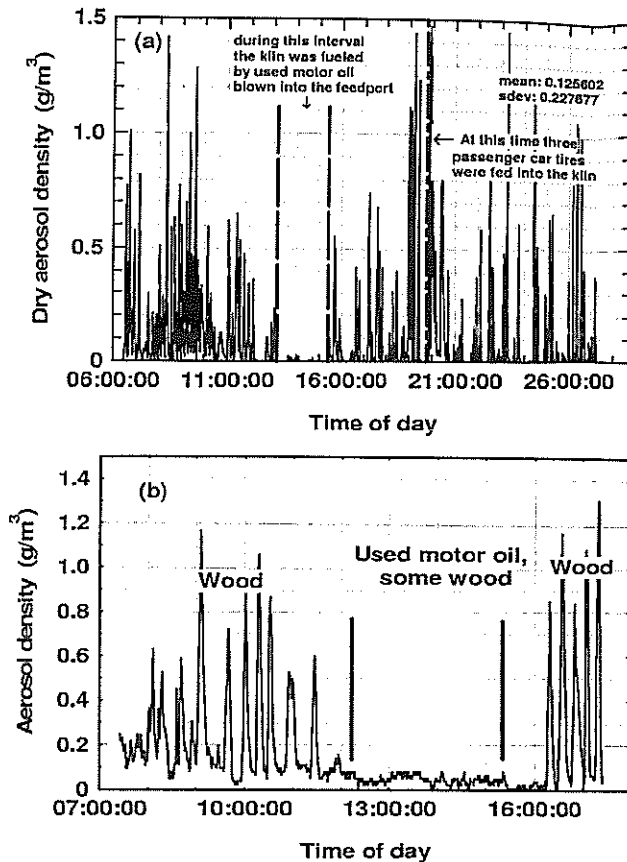


Figure 12. Dry aerosol density reduction through use of used motor oil as a fuel for brick kilns: (a) dry aerosol density and (b) aerosol density.

The Marquez-Chavez type of burner introduces a gravity-fed iron pipe into the firebox. This tube is concentric with another, which stands on short legs. The firebox is initially heated with wood, and the operator slides the oil burner in on runners. When the inner tube is at a sufficiently high temperature, the oil drips onto the inner wall of the outer tube, is vaporized, and blasts out of upward-directed holes in the outer tube producing fierce jets. From this point, the system should be self-sustaining, but, after some time, the jets tend to clog. On no occasion

was a burn completed entirely through the use of an oil burner. Nevertheless, enough data have been obtained to show that such a system can drastically reduce the aerosol contaminant mass (which is still generic fractal soot). The jet cleaning process is not extensive but disrupts the burn. It is apparent that this is not an insuperable problem.

On a number of occasions the Marquez-Chavez designs have been tested during wood-fed burns. The resulting data provide a ready comparison of the aerosol densities for the two fuels. This can be seen in Figure 12. The dramatic reduction in density during use of the oil burner can be seen.

Development of firebox temperatures sufficiently high to fire the oil burner involves the use of wood. This elevates the effluent mass total for the oil burner by approximately that percentage of the burn (because oil produces far less smoke). Usually heating of the firebox requires ~2 hr. In addition, occasional supplementary feeding (priming) and stoking produce smoke, which might be further reduced or eliminated for a mature design.

The quantitative results are shown in Table 4. Comparisons are found in the upper portion of the table, whereas a brief summary is given at the bottom. These results show that the oil burner can be expected to produce an order of magnitude reduction in the aerosol effluent density. Any supplemental stoking and priming reduce the effectiveness by producing wood smoke.

When used motor oil burners are used with MK kilns, the ratio expressing the net reduction in aerosol (soot) contamination produced by each of the two (relative to an ordinary open-top kiln) can be represented by their product: $R_{total} = R_{MK,wood} \times R_{oil}$. If the mean aerosol contaminant reduction factor for an MK-domed kiln is typically between 5 and 10 and, for a well-coupled MK kiln pair, is an additional factor of 2, then the continuous use of a successful used motor oil burner would reduce the aerosol contamination by roughly an additional factor of 10 (reasonable, as can be seen from the table, even with the initial wood component). A total reduction factor of 100 from, say, 30 kg, means a value that would permit the final stage use of a reusable (water-cleaned) filter with which to effectively eliminate the aerosol contamination.

Table 4. Used motor oil as used in both domed and open kilns.

Date	Oil Burn Interval (hr)	$\langle \rho_{oil} \rangle / \langle \rho_{wood} \rangle$	Open or MK
March 15, 2004	12:00–7:00 p.m.	0.0444	MK
	4:30–6:00 p.m.	0.0134	
	1:20–3:20 p.m.	0.0193	
November 21, 2003	12:40–3:20 p.m.	0.0650	MK
September 24, 2003	12:12–3:18 p.m.	0.178 ^a	MK
June 17, 2003	9:00–9:55 a.m.	0.0634	MK
July 19, 2002	1:40–3:00 p.m.	0.053	Open
October 7, 1999	Total oil burn	0.285 ^a	MK
	Without feeding, stoking	0.172	
Summary	All, unselective	Exclude 1st	All but 2 ^a
$\langle \rho_o \rangle / \langle \rho_w \rangle$	0.115 ± 77%	0.0808 ± 61%	0.0565 ± 15%

Notes: ^aThese two burns were more compromised by the use of wood than the others.

Table 5. PAHs/particulates ratio ($\mu\text{g/g}$) found in filters taken from an oil burn.

PAHs	Wood	Active	Filter
Naphthalene			
Acenaphthylene		127	
Acenaphthene			
Fluorene	2161	1105	299
Phenanthrene	1172	1235	182
Anthracene	1343	242	195
Fluoranthene		1173	377
Pyrene	2186	2222	337
Benzo(b)anthracene	1826	714	581
Chrysene	934	403	333
Benzo(b)fluoranthene	580	4078	2581
Benzo(k)fluoranthene	916	1024	735
Benzo(a)pyrene	1856	990	581
Dibenzo(a,h)anthracene	952	518	300
Benzo(g,h,i)perylene	1044	425	273
Indeno(1,2,3-cd)pyrene	1832	953	368

Quantitative Results: Gaseous Effluents

Gaseous effluents were sampled only for selected burns of the total series. For these cases, the effluents from the active and filter (passive) kiln were sampled every hour. Three of the collected filters were analyzed to determine the presence of semivolatile compounds. The PAHs with low molecular weight were detected with GC/mass spectrometry, and the PAHs with high molecular weight were detected by HPLC. The PAH/particulate ratios, given in micrograms per gram, are shown in Table 5. The values for most of the compounds are higher for the sample taken during the wood feeding (Table 5, column 2). However, the amounts of fluoranthene, pyrene, benzo(b)fluoranthene, and benzo(k)fluoranthene are larger when oil is used as a fuel (Table 5, column 3). When the same fuel is used, a noticeable reduction is achieved with the use of the filter kiln (Table 5, columns 3 and 4).

VOCs are formed in all of the incomplete combustion processes. One goal of the examination of the gaseous effluents of the MK system was to identify the volatile organic compounds present during an oil burn. Samples were collected using adsorbent traps (VOCARB 4000 and activated carbon), which were desorbed using a purge and trap device connected to a GC/mass spectrometry. This test was carried out on only one burn. Figure 13 shows qualitative differences between the compounds found in the VOCARB 4000 trap for the active and filter kilns. It is evident from this figure that, although more compounds are present in the chromatogram of the active kiln, there is a decrease in the intensity of the principal peaks for the filter kiln sample. This can be observed for benzene, toluene, naphthalene, and acenaphthylene, to mention some examples. Figure 13 does show new peaks in the region of compounds with higher masses (30–40 min) for the filter kiln sample. The research suggests that catalysis by the filter bricks might be causing the formation of new compounds. Some peaks on the chromatogram of the active kiln require further identification.

Figure 14 shows two chromatograms derived from the analyses of the emissions from the filter kiln. There is a consistent reproducibility of the types of compounds

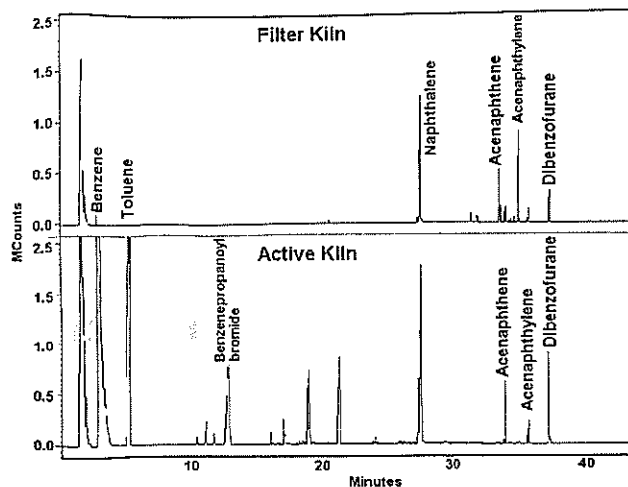


Figure 13. VOCs found on VOCARB 4000 sampling traps used during the oil burn on March 15, 2004. The two samples were taken simultaneously from 5:30 p.m. to 5:50 p.m. of a burn cycle that started at 8:00 a.m. and terminated at 8:00 p.m.

present in the traps. There is also a slight decrease in the intensity with time as the temperature of the kiln increases.

The same MK kiln burn provided data for a comparison of the gaseous effluents for wood and used motor oil. Figure 15 shows the chromatogram representing the analyses of the activated carbon traps. The figure presents the chromatographic region for which the differences between the two fuels are evident (20–35 min). The chlorinated compounds, furan and dioxins, are of greater concern and, thus, were priority targets in this study. Some of these compounds were observed in both fuels.

To gain a better understanding of the potential problems associated with the use of used motor oil, the oil itself, the emissions, and the residue from the oil burner were all analyzed. The concentrations of metals present in

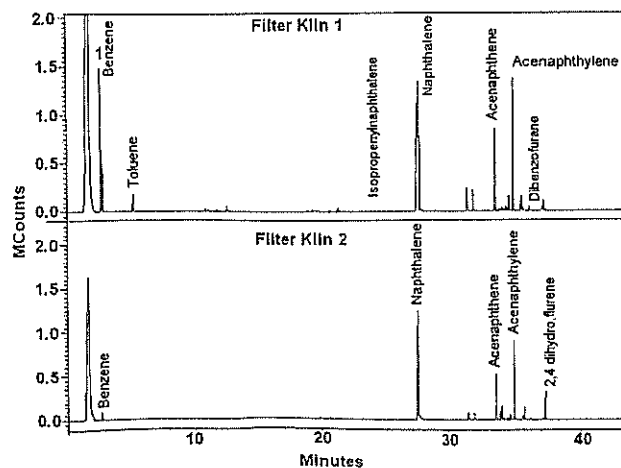


Figure 14. VOCs found on VOCARB 4000 sampling traps used during the oil burn on March 15, 2004. The chromatograms are very similar on the two samples. Filter kiln 1 represents the compounds trapped at 5:00 p.m. when the temperature of the kiln was at 16.28 mV. Filter kiln 2 represents the compounds trapped at 5:30 p.m.; the overall temperature of the kiln was at 16.65 mV.

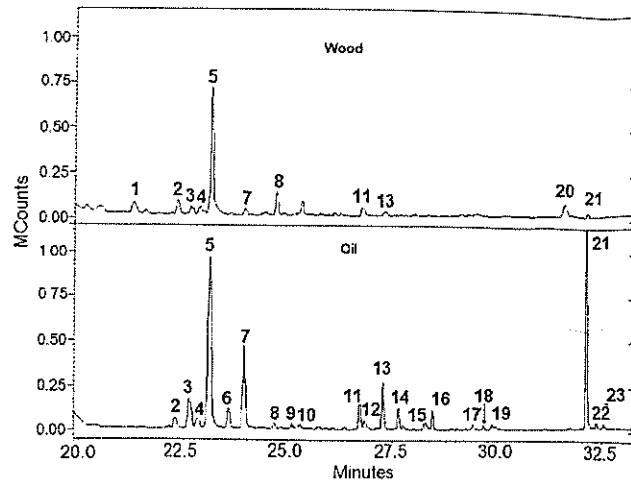


Figure 15. Differences between the compounds found in the wood (top) and the oil (bottom) burns.

the unburned (50-gal drum) oil were Pb (135 ppm) and Cd (28 ppm). Cr and Ba were not analyzed for the lack of the hollow cathode lamps at the time of the analysis. Table 6 shows the concentration of metals (micrograms per cubic meter) produced as effluents during the oil burn. The filters were exposed to the emissions for 20 min. The concentration of lead is seen to be somewhat reduced through the use of the filter kiln. Although the concentration of Pb released to the atmosphere is low, it is too large when compared with the $1.5 \mu\text{g}/\text{m}^3$ in 3 months stated in the Mexican regulation (NOM-026-SSA1-1993). The concentration of Ba is also reduced $\sim 50\%$. The average concentration of Pb in the residue was $66.25 \text{ mg}/\text{kg}$ and $5.5 \text{ mg}/\text{kg}$ for Cd. The results indicate that the use of the burner can be a potential danger for the brick-makers, because they will be exposed to residue with high concentrations of toxic metals.

CO emissions from the kilns, by contrast with those of the gases described above, represent a major constituent of the effluent mass. Measurements were made by means of a calibrated flow-through system for two burns with consistent results. Measurements were made at roughly 1-min intervals throughout the burns. Two facets of these results were notable, first, that the CO concentration and the aerosol density tracked very closely, as can be seen in Figure 16, although the ratio between the two quantities did vary over a burn. Second, the net masses of the two primary effluents were nearly equal. For example, values for a burn with a few minor operational interruptions were $M_{\text{CO}} = 21 \text{ kg}$ and $M_{\text{dry aerosol}} = 24 \text{ kg}$.

Table 6. Metal concentrations in the emissions of the active and filter kiln.

Variable	Pb ($\mu\text{g}/\text{m}^3$)	Cr ($\mu\text{g}/\text{m}^3$)	Cd ($\mu\text{g}/\text{m}^3$)	Ba ($\mu\text{g}/\text{m}^3$)
Active kiln	2.41	NA	ND	28.85
Filter kiln	1.43	NA	ND	14.36
Difference	0.980	NA	ND	14.49

Notes: ND = not detected. The concentrations are below the instrument detection limit. NA = not analyzed (lack of hollow cathode lamp).

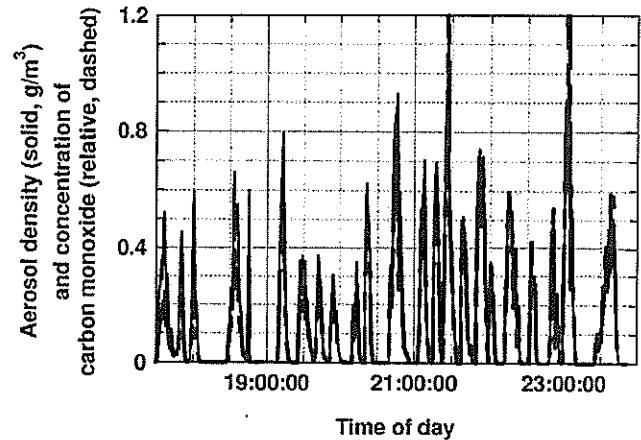


Figure 16. Correlation of CO with dry aerosol effluent for a burn.

CONCLUSIONS AND RECOMMENDATIONS

Two primary objectives have been served by this study; both open and MK-modified kilns have been characterized. The potential of the MK-type kilns for reduction of effluent contamination is demonstrated, that is, a reduction factor of typically $5\times$ to $10\times$ for the domed kiln and an additional $2\times$ when the filter kiln is functional, although it is clear that the connections between kilns of a pair cannot be taken for granted. If the flow impedance is too high, coupling will be insufficient, and the cleansing effects for both soot and, perhaps more importantly, the gases will be lost. Also, without a functional filter kiln the bricks for the succeeding burn will not be dried to the same degree (lengthening that burn). Finally, information that should encourage exploration into the use of used motor oil as a fuel has been presented. The suggestion (taken from the section on used motor oil) is tantalizing that the contaminants might be reduced to a value that would permit the final stage use of a (reusable?) filter with which to effectively eliminate kiln contamination. Because there is a strong impetus to build more kilns, it is important to promptly correct the design faults and to institute the changes that prevent sufficient coupling between kiln pairs.

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