Final Technical Report

Project Title: Alternative Fuel Source Study – An Energy Efficient and Environmentally Friendly Approach
Award Number: DE-FG36-05GO85011

Recipient: Auburn University
Project Location: Auburn University Wilmore Laboratories (Chemical and Materials), Auburn University Harbert Hall (Civil Engineering), Auburn University Funchess Hall (Agriculture), Lafarge North America Roberta Plant, Calera, AL

Reporting Period: August 1, 2005 to August 31, 2010
Date of Report: December 5, 2010
Written by: Ralph Zee, Anton Schindler, Steve Duke, Tom Burch, and David Bransby of Auburn University, Don Stafford of Lafarge North America.

Task A: Survey of Alternate Waste Materials

The objective of this project is to conduct research to determine the feasibility of using alternate fuel sources for the production of cement. Successful completion of this project will also be beneficial to other commercial processes that are highly energy intensive. During this report period, we have completed all the subtasks in the preliminary survey. Literature searches focused on the types of alternative fuels currently used in the cement industry around the world. Information was obtained on the effects of particular alternative fuels on the clinker/cement product and on cement plant emissions. Federal regulations involving use of waste fuels were examined. Information was also obtained about the trace elements likely to be found in alternative fuels, coal, and raw feeds, as well as the effects of various trace elements introduced into system at the feed or fuel stage on the kiln process, the clinker/cement product, and concrete made from the cement.

When embarking on any research project, it is important to assemble as much of the relevant information as possible and present it in a convenient form so that the researchers may assimilate it rapidly. The accompanying bibliography contains listings for scientific papers deemed pertinent to various aspects of this project. The bibliography is intended to be a resource for those who need to familiarize themselves with previous work on specific topics related to this project.

Most of the information sources cited in this bibliography are papers from scientific journals and conference proceedings. Some are government papers that have been made publicly available, while others are publications from industry groups such as the Portland Cement Association. The listings are ordered by topic. In cases where a paper is appropriate for multiple topics, it is listed under each topic, with a notation that it is duplicated elsewhere in the bibliography. Within each topic, the citations are listed alphabetically [or chronologically]. Capsule summaries are provided for each information source.

The topics include:

I. The use of a variety of waste materials as substitutes for traditional fuels;

II. The use of waste materials as substitutes for raw materials in the cement industry;
III. Trace metals found in cement and in cement kiln dust, a significant by-product of the cement manufacturing process;
IV. Trace metals found in concrete, especially their leaching behavior;
V. Trace metals found in coal, the traditional fuel used for cement manufacture in the US;
VI. Trace metals found in scrap tires and information about the combustion of scrap tires as fuel, especially with respect to emissions;
VII. Trace metals found in poultry litter and information about the combustion of poultry litter as fuel, especially with respect to emissions;
VIII. Trace metals found in waste plastics;
IX. Mercury emissions from combustion processes, which are of special environmental concern;
X. NO_x emissions from combustion processes, which are of special environmental concern;
XI. The effects of trace elements, including metals, on the kiln process, on the cement produced, and on the concrete made from that cement.
XII. Definitions for the abbreviations used in the citations and the capsule summaries.

The following is a bibliography with summary for alternate energy sources appropriate for use in the cement industry. The list is arranged by topics.

Waste Fuels in Cement Manufacturing: Annotated Bibliography

I. Wastes as Fuel

Lamb, C.W., F.M. Miller, A. Roth, B. Dellinger, and S. Sidhu. “Detailed Determination of Organic Emissions from a Preheater Cement Kiln Co-Fired with Liquid Hazardous Wastes.” *Hazardous Waste & Hazardous Materials* 11, no. 1 (1994): 201-216.

> This article presents data on stack emissions from the use of waste fuels in a cement kiln. The fuel mix examined includes coal, liquid hazardous wastes, and tires. Results for the fuel mix were compared to results from the use of coal alone. Emissions rates of organics, metals, and specific gaseous pollutants were measured. Destruction and Removal Efficiencies (DREs) were calculated for specific hazardous wastes.
>
> Inputs and outputs for six compounds (monochlorobenzene, 1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene, sulfur hexafluoride, carbon tetrachloride, and tetrachloroethylene) were monitored and DREs were calculated for them. Complete destruction is assumed to occur when the DRE exceeds “six nines” (99.9999%). “Five nines” (99.999% DRE) was consistently achieved for all compounds except monochlorobenzene. “Six nines” was only achieved for tetrachloroethylene and carbon tetrachloride.
>
> A comparison of organic emissions between burns using coal and burns using liquid hazardous waste fuel found that emissions were significantly higher for ethylbenzene, 1,1,1-trichloroethane, trichloroethane [sic], and Total PCDDs/PCDFs. Higher emissions were also observed for benzene, carbon

tetrachloride, chloroform, phenol, styrene, and tetrachloroethane [sic]. Although the experimental section indicates that metals emissions were measured, no metals data are reported.

Sarofim, Adel F., David W. Pershing, Barry Dellinger, Michael P. Heap, and Warren D. Owens. “Emissions of Metal and Organic Compounds from Cement Kilns Using Waste Derived Fuels.” *Hazardous Waste & Hazardous Materials* 11, no. 1 (1994): 169-192. (duplicated in another section)

This article examines data from plants burning Waste Derived Fuels (WDF) for both organic and metal emissions. The authors review the cement making process, the fate of metals introduced into the process, and the destruction of organic compounds in the cement kiln.

Data are obtained from certificate of compliance tests for cement kilns burning WDF. Mass balances are calculated for those data sets which are sufficiently complete. Most of the data in these cases are within 30% closure, with the largest errors for the two most volatile metals, Hg and Tl. Although metal inputs and emissions data are presented graphically, *no tables of metals data are presented*. Metals emissions increase with metals input, but Pb emissions seems to also be dependent on the amount of Cl present in the system as well as the total amount of Pb present.

Destruction and Removal Efficiencies (DREs) for organic compounds introduced at the discharge (front) end of the kiln and mid-kiln appear to be >99.9999%. DREs for organics introduced at the precalciner, however, are considerably lower for some compounds, apparently because of insufficiently high temperatures or insufficient exposure time to the temperatures necessary for destruction (1073-1173°C). It is also possible that there is some pyrolysis and/or formation of organic and chlorinated organic compounds occurring in the preheater tower.

Guo, Qizhong, and James O. Eckert, Jr. “Heavy Metal Outputs from a Cement Kiln Co-Fired with Hazardous Waste Fuels.” *Journal of Hazardous Materials* 51 (1996): 47-65. (duplicated in another section)

This article examines data from a real-world kiln equilibration test for a cement kiln co-fired with Hazardous Waste Fuel (HWF). These data are used to derive equations for predicting metal outputs at steady state operating conditions. (It is assumed that some kiln dust will be wasted and some recycled.)

The CKD and the stack emissions are found to be enriched in the more volatile metals while the clinker is found to be enriched in the less volatile metals. Metal outputs for non-steady state conditions are also analyzed, and metals in clinker are predicted to be higher under these conditions than for steady-state operation.

Metal inputs and outputs from the steady state compliance testing are reported.

Coal: Mass feed rate-5.23 Mg/h; thermal feed rate-106 x 10^9 J/h; As-19.8 g/h; Be-11.9 g/h; Cd-0.654 g/h; Cr-87.6 g/h; Pb-54.0 g/h

HWF: Mass feed rate-14.5 Mg/h; thermal feed rate-383 x 10^9 J/h; As-9430 g/h; Be-1190 g/h; Cd-7120 g/h; Cr-43,700 g/h; Pb-46,300 g/h

Raw materials: Mass feed rate-132 Mg/h; As-54.9 g/h; Be-79.0 g/h; Cd-97.2 g/h; Cr-2130 g/h; Pb-468 g/h

Recycled CKD: Mass feed rate-10.9 Mg/h; As-1230 g/h; Be-56.8 g/h; Cd-1950 g/h; Cr-3600 g/h; Pb-15,500 g/h

Wasted CKD: Production rate-16.3 Mg/h; As-2150 g/h; Be-117 g/h; Cd-4570 g/h; Cr-6220 g/h; Pb-33,000 g/h

Clinker: Production rate-69.6 Mg/h; As-7040 g/h; Be-611 g/h; Cd-120 g/h; Cr-33,600 g/h; Pb-855 g/h

Stack emissions: As-0.622 g/h; Be-0.403 g/h; Cd-41.5 g/h; Cr-19.6 g/h; Pb-283 g/h

Metal concentrations for CKD during operation at two different HWF feed rates and with no HWF feed are compared.

Metals in CKD at maximum intended HWF feed rate (rate not given): As-90.0 ppm, Be-8.6 ppm, Cd-394 ppm, Cr-409 ppm, Pb-2740 ppm

Metals in CKD at normal HWF feed rate (rate not given): As-2.30 ppm, Be-0.852 ppm, Cd-8.84 ppm, Cr-38.6 ppm, Pb-386 ppm

Metals in CKD at no HWF feed rate (based on 2 sampling periods): As-ND-8.0 ppm, Be-0.27-0.70 ppm, Cd-3.7-15.4 ppm, Cr-14.8-39.0 ppm, Pb-44.0-192 ppm

Carrasco, F., N. Bredin, Y. Gningue, and M. Heitz. “Environmental Impact of the Energy Recovery of Scrap Tires in a Cement Kiln.” *Environmental Technology* 19 (1998): 461-474.

This article presents emissions data from the use of scrap tires as a partial replacement for coal in a Quebec cement plant. The authors use a modeling software package to predict the impact of the emissions on the area surrounding the plant.

Eckert, James O., Jr., and Qizhong Guo. “Heavy Metals in Cement and Cement Kiln Dust from Kilns Co-Fired with Hazardous Waste-Derived Fuel: Application of EPA Leaching and Acid-Digestion Procedures.” *Journal of Hazardous Materials* 59 (1998): 55-93.
(duplicated in another section)

This article examines the use of TCLP procedure as an accurate predictor of the leaching of metals from concrete samples in real-world conditions.

The authors perform the standard TCLP procedure for raw cement and cement kiln dust and on cement paste samples. Comparisons indicate that metals are more easily leached from the raw cement than from set cement.

Standard TCLP results for raw cement: Be (ND-29.72 ppb); Al (4.84 ppb-out of range); Ti (0.40-466.58 ppb); V (ND-6.35 ppb); Cr (14.14-986.21 ppb); Mn (ND-6.79 ppb); Co (1.84-9.17 ppb); Ni (ND-104.44 ppb); Zn (ND-41.50 ppb); Cu (ND-8.63 ppb); As (ND-0.97 ppb); Se (ND-25.46 ppb); Rb (1.98-824.92 ppb); Cd (ND-2.30 ppb); Cs (ND-17.33 ppb); Ba (426.95-4108.91 ppb); Pb (ND-17.24 ppb)

Standard TCLP results for CKD: Be (1.78 ppb); Al (15.62 ppb); Ti (19.07 ppb); V (13.88 ppb); Cr (217.93 ppb); Mn (ND); Co (4.72 ppb); Ni (31.82 ppb); Zn (26.48 ppb); Cu (6.49 ppb); As (4.36 ppb); Se (144.93 ppb); Rb (3954.18 ppb); Cd (0.28 ppb); Cs (393.99 ppb); Ba (830.38 ppb); Pb (111.04 ppb)

TCLP results for cement paste (set cement): Be (2.1-11.9 ppb); Al (227.7-658.1 ppb); Ti (0.4-2.0 ppb); V (ND-0.4 ppb); Cr (11.9-62.6 ppb); Mn (ND-1.1 ppb); Co (4.2-19.4 ppb); Ni (29.9-50.8 ppb); Zn (21.7-79.2 ppb); Cu (5.5-13.5 ppb); As (ND-0.2 ppb); Se (ND-1.1 ppb); Rb (45.0-521.8 ppb); Cd (ND-0.3 ppb); Cs (0.4-14.7 ppb); Ba (1710.9-3487.1 ppb); Pb (ND-1.4 ppb)

The authors also perform several variations on the standard TCLP procedure on raw cement samples which include multiple exposures to the leaching solution, extended exposure time, and the use of chlorinated water for a leaching solution. Comparisons of these data indicate that As, Co, Zn, Cu, Ga, and Ba are leached more strongly with multiple exposures to a leaching solution, that Ti, Co, Ni, Cu, Ga, Se, and Ba are leached more strongly with longer exposure time, and that Cr, Ni, Ga, Rb, and Ba are leached more strongly with a chlorinated water leaching solution.

The authors point out that the pH of a cement leachate solution tends to be high, because of the buffering capacity of the cement. They speculate that, under real-world conditions (multiple exposures, extended exposure time, and/or exposure to chlorinated water), the buffering effect could diminish resulting in increased metal leaching.

The authors also analyze cement and kiln dust samples by microwave-assisted acid digestion and demonstrate that there are correlations between acid-soluble metals and TCLP results for only a few metals.

Acid soluble metals in raw cement: Be (ND-29.72 ppb); Al (4.84 ppb-out of range); Ti (0.40-466.58 ppb); V (ND-6.35 ppb); Cr (14.14-986.21 ppb); Mn (ND-6.79 ppb); Co (1.84-9.17 ppb); Ni (ND-104.44 ppb); Zn (ND-41.50 ppb); Cu (ND-8.63 ppb); As (ND-0.97 ppb); Se (ND-25.46 ppb); Rb (1.98-824.92 ppb); Cd (ND-2.30 ppb); Cs (ND-17.33 ppb); Ba (426.95-4108.91 ppb); Pb (ND-17.24 ppb)

Acid soluble metals in CKD: Be (0.678-1.311 ppm); Al (2076.671-2962.433 ppm); Ti (118.545-259.44 ppm); V (4.581-17.173 ppm); Cr (4.776-28.007 ppm); Mn (21.721-356.724 ppm); Co (0.788-2.310 ppm); Ni (3.222-13.722 ppm); Zn (4.060-280.280 ppm); Cu (1.381-31.893 ppm); As (0.370-4.403 ppm); Se (ND-1.645 ppm); Rb (0.160-3.050 ppm); Cd (ND-0.961 ppm); Cs (ND-0.188 ppm); Ba (18.214-61.307 ppm); Pb (0.129-23.181 ppm)

The authors also analyze cement and kiln dust samples by XRF and demonstrate that the acid digestion methods used to obtain “total metals” results actually oonly obtain partial metals recovery and should be reported as “recoverable metals” or “acid-soluble metals” not “total metals”. Moreover, the “total metals” results obtained by XRF have little or no correlation to the “acid-soluble metals” results or to the TCLP results.

XRF metals in raw cement: SiO_2 (20.06-21.27%); Al_2O_3 (4.35-5.87%); Fe_2O_3 (1.56-4.24%); MnO (0.01-0.3%); MgO (0.89-3.32%); CaO (64.75-68.67%); Na_2O (0.11-0.41%); K_2O (0.1-0.74%); TiO_2 (0.18-0.37%); P_2O_5 (0.06-0.23%); Al (23022.4-31067.0 ppm); Ti (1078.9-2217.8 ppm); V (44.0-167.0 ppm); Cr (58.0-315.0 ppm); Mn (77.4-2323.4 ppm); Co (7.0-19.0 ppm); Ni (29.0-91.0 ppm); Cu (8.0-198.0 ppm); Zn (24.0-2522.0 ppm); As (ND at 5 ppm-29.0 ppm); Pb (ND at 5 ppm-140.0 ppm)

XRF metals in CKD: SiO_2 (15%); Al_2O_3 (5.57%); Fe_2O_3 (2.19%); MnO (0.02%); MgO (0.82%); CaO (43.63%); Na_2O (0.36%); K_2O (2.96%); TiO_2 (0.41%); P_2O_5 (0.14%); Al (29479.3 ppm); Ti (2457.6 ppm); V (134 ppm); Cr (81.0 ppm); Mn (154.9 ppm); Co (25.0 ppm); Ni (49.0 ppm); Cu (175.0 ppm); Zn (573.0 ppm); As (46.0 ppm); Pb (525.0 ppm)
Levendis, Yiannis A., Ajay Atal, Bonnie Courtemanche, and Joel B. Carlson. “Burning Characteristics and Gaseous/Solid Emissions of Blends of Pulverized Coal with Waste Tire-Derived Fuel.” *Combustion Science and Technology* 131 (1998): 147-185.

This article examines the combustion characteristics and emissions of various combinations of coal and ground tires burned in a drop-tube furnace*, not in a cement kiln*. Combinations varied from 100% coal through blends to 100% tire crumbs. Flame temperatures were about 1150°C. Emissions examined included SO_2, NO_x, PAHs, and particulates.

Prisciandaro, M., G. Mazziotti, and F. Veglio. “Effect of Burning Supplementary Waste Fuels on the Pollutant Emissions by Cement Plants: A Statistical Analysis of Process Data.” *Resources, Conservation and Recycling* 39 (2000): 161-184.

This article presents data on stack emissions from Italian cement plants burning coke plus shredded tires or a liquid fuel made from waste oil. Results are compared between the emissions produced burning coke alone and those produced burning coke plus waste fuel. Most of the article consists of statistical analysis of the data obtained.

In Plant 1, coal was partially replaced (16%) with shredded tires. When tires were burned with the coal, SO_2, NO_x, CO, and Zn gaseous emissions were significantly higher than when coal alone was burned, although environmental limits were not exceeded. In Plant 2, coal was partially replaced (20%) with waste oils. When the waste oils were burned with the coal, SO_2 and NO_x gaseous emissions were significantly lower than when coal alone was burned. Clinker production was found to be the same, regardless of the fuel burned, hence productivity was not impaired by the use of alternative fuels.

Trezza, M.A., and A.N. Scian. “Burning Wastes as an Industrial Resource: Their Effect on Portland Cement Clinker.” *Cement and Concrete Research* 30 (2000): 137-144.

This article reports the results of a laboratory simulation of the use of waste fuel in the cement industry. Used car oils are ashed, the ashes are mixed with raw feed dust, and clinkers are produced in a muffle furnace. Clinkers produced with the fuel ashes are compared with clinkers produced without ashes.

Clinker analyses: DTA-TG results indicated that the addition of the fuel oil ashes caused a widening of the temperature range of clinkering and a shift to lower solidification temperatures. Blaine tests indicate that addition of ashes resulted in more-easily milled material (more finely ground material for the same milling time). Free lime content did not appear to change. XRD did not show the formation of new phases, although observed crystallinity passed through a maximum as the amount of added ashes increased. Changes in pyrometric cone equivalent temperature indicated that the clinkering mechanism had changed with the additional of the fuel ashes.

Hydrated clinker analyses: Calorimetry results indicated a faster early hydration reaction with increased amount of added ashes. Compressive strength was found to increase with added ashes, while porosity decreased.

Carrasco, F., N. Bredin, and M. Heitz. “Atmospheric Pollutants and Trace Gases: Gaseous Contaminant Emissions as Affected by Burning Scrap Tires in Cement Manufacturing.” *Journal of Environmental Quality* 31 (2002): 1484-1490.

This article uses the same emissions data from the use of scrap tires in a Quebec cement plant that were presented in an earlier paper. The authors also use the same modeling software package to predict the impact of the emissions on the area surrounding the plant. There is somewhat more discussion of the meaning of the emissions data.

When tires were burned with coal, CO emissions were 37% higher, SO_2 emissions were 24% higher, HCl emissions were 48% higher, and NO_x emissions were 11% lower, than when coal was burned alone. Metals emissions (from stacks) were 61% higher for Fe, 33% higher for Al, 487% higher for Zn, 127% higher for Pb, 339% higher for Cr, 100% higher for Mn, 74% higher for Cu, and 22% lower for Hg. Particulate emissions were 7% higher. Emissions for organic compounds were 14% lower for PAHs, 8% lower for naphthalene, 37% lower for chlorobenzene, and 45% lower for dioxins and furans. All emissions were within Quebec standard permit limits.

Miller, B.B., R. Kandiyoti, and D.R. Dugwell. “Trace Element Emissions from Co-Combustion of Secondary Fuels with Coal: A Comparison of Bench-Scale Experimental Data with Predictions of a Thermodynamic Equilibrium Model.” *Energy & Fuels* 16 (2002): 956-963.
(duplicated in another section)

This article examines the co-combustion of coal, four biomass fuels (wood-bark, straw, pulp sludge, and paper sludge), and three waste fuels (agricultural waste, sewage sludge, and plastic waste) in a suspension-firing reactor (intended to simulate a section of a fluidized bed combustor), *not in a cement kiln*. Temperatures in the reactor were 800°C and 900°C. Trace metals are analyzed in the original fuels and in ashes resulting from their combustion. The focus of the article is in the enrichment of the trace metals in the combustion ash.

Exact m*etals data for the original fuels were not given (although ranges were reported)*, nor were metals data for the various ash samples. The volatilization (or conversely the retention of a metal in the ash) was found to depend, not only on the metal's volatility but also on the type of fuel burned. This was ascribed at least partially to the differences between the metal compounds found in the different types of fuels. Paper sludge had the highest degree of volatilization while sewage sludge had the lowest.

Trace metals in fuels, ranges:

Wood-bark: Less than 1 ppm (As, Be, Cd, Co, Hg, Se, Sb, Tl), 1 to 10 ppm (Ni, Mo, Pb, V), 10-100 ppm (Cr, Cu, Sr), greater than 100 ppm (Ba, Mn, Zn)

Straw: Less than 1 ppm (As, Be, Cd, Co, Hg, Ni, Mo, Sb, Tl, V), 1 to 10 ppm (Cr, Cu, Pb), 10-100 ppm (Ba, Mn, Zn)

Columbian coal: Less than 1 ppm (Be, Cd, Hg, Sb, Tl), 1 to 10 ppm (As, Co, Cu, Ni, Mo, Pb, Se), 10-100 ppm (Ba. Cr, Mn, Sr, V, Zn)

Polish coal: Less than 1 ppm (Cd, Hg, Mo, Tl), 1 to 10 ppm (As, Be, Co, Sb, Se), 10-100 ppm (Cr, Cu, No, Pb, Sr, V, Zn), greater than 100 ppm (Ba, Mn)

Sewage sludge: Less than 1 ppm (Be, Hg,Tl), 1 to 10 ppm (As, Cd, Co, Sb), 10-100 ppm (Ni, Mo, Pb, V), greater than 100 ppm (Ba, Cr, Cu, Mn, Sr, Zn)

Paper sludge: Less than 1 ppm (As, Be, Cd, Co, Hg, Se, Tl), 1 to 10 ppm (Ni, Mo, Sb, V), 10-100 ppm (Cr, Cu, Mn, Pb, Sr), greater than 100 ppm (Ba, Zn)

Agricultural waste: Less than 1 ppm (As, Be, Cd, Co, Hg, Pb, Sb, Se, Tl), 1 to 10 ppm (Cr, Mo, V), 10-100 ppm (Ba, Ni, Sr, Cu), greater than 100 ppm (Mn, Zn)

Pulp sludge: Less than 1 ppm (As, Be, Co, Hg, Mo, Sb, Se, Tl), 1 to 10 ppm (Cd, Pb, V), 10-100 ppm (Ba, Cr, Cu, Ni, Sr), greater than 100 ppm (Mn, Zn)

Plastic waste: Less than 1 ppm (As, Be, Hg, Se, Tl), 1 to 10 ppm (Cd, Co, Ni, Mo, Sb, V), 10-100 ppm (Cr, Cu, Mn, Pb, Sr), greater than 100 ppm (Ba, Zn)

Hartlieb, Nicola, Matthias Achternbosch, and Klaus-Rainer Brautigam. “Co-Incineration of Wastes in Cement Kilns—Determination of Input Pathways of Trace Elements in Cement by Material Flow Analysis.” *Fresenius Environmental Bulletin* 12, no. 6 (2003): 629-635.(duplicated in another section)

This article attempts to use a material flow analysis model to determine the sources of trace elements in cement. Ranges of trace elements found in various materials and the relative contributions those materials are presumed to make to the final clinker/cement product are used to test the model with measured values in cement being compared to values calculated using the model.

Measured values of trace metals in cement: As (ND-13.6 ppm); Cd (ND-0.8 ppm); Co (4-17 ppm); Cr (23-59 ppm); Cu (9-43 ppm); Mn (255-1268 ppm); Ni (13-39 ppm); Pb (10-48 ppm); Sb (ND-15 ppm); Sn (ND-10.6 ppm); V (30-96 ppm); Zn (48-291 ppm)

The authors conclude that wastes used as raw materials and/or fuels could be a significant source of trace elements in cement. Industry data on the relative amounts of Zn, V, Sb, and Cr in the various cement raw materials and fuels are presented graphically. *No experimental data are reported*.

Mokrzycki, Eugeniusz, Alicja Uliasz-Bocheńczyk, and Mieczysław Sarna. "Use of Alternative Fuels in the Polish Cement Industry." *Applied Energy* 74 (2003): 101-111.

This article describes the use of waste fuels in two Lafarge Cement Polska plants. It covers gaseous and dust emissions and heavy metals detected in the clinker as a result of the use of two different waste fuels, one derived from municipal waste, the other from industrial waste.

With the industrial waste-derived fuel (PASi), HCl and CO emissions were higher, metal, SO_2, NO_x, and dust emissions were similar, and amounts of Zn and Cu trapped in the clinker were higher, than without the waste fuel. With the municipal waste-derived fuel (PASr), dust emissions were much higher, NO_2 and SO_2 emissions were much lower, CO and HCl emissions were similar, and amounts of Zn, Cu, and Mn trapped in the clinker were higher, than without the waste fuel. Except for dust emissions from the use of PASr, emissions were within government permissable limits.

Mokrzycki, Eugeniusz, and Alicja Uliasz-Bocheńczyk. "Alternative Fuels for the Cement Industry." *Applied Energy* 74 (2003): 95-100.

This article is basically a survey of the types of waste fuels that can be used in the cement industry. The authors break down the types of waste fuels into sub-types based on physical characteristics, like size and stickiness, and there are a couple of useful diagrams, but there is not any experimental data.

Waste fuels are broken down into five classes: Class 1-Gaseous alternative fuels; Class2-Liquid alternative fuels; Class 3-Pulverized, granulated or finely-crushed solid alternative fuels; Class4-Coarse-crushed solid alternative fuels; and Class5-Lump alternative fuels. Solid alternative fuels are broken down into four groups: Group 1-Solid, dry fuels of relative fine size, which do not adhere; Group 2-Solid, dry fuels of coarse size, which do not adhere; Group 3-Solid, dry fuels which tend to stick; and Group 4-Mixtures of different lumpy fuels. Solid alternative fuels are also broken into three categories: Vegetable compounds or natural products; Synthetic products; and Others. Liquid alternative fuels are broken down into two divisions: Liquid substitute fuels-Easily decomposed, slightly toxic and Liquid substitute fuels-Stable, toxic. The diagrams show where various types of alternative fuels can be introduced into the kiln system and what the temperatures are at the various locations and how long materials are retained at these temperatures.

Abad, Esteban, Karell Martinez, Josep Caixach, and Josep Rivera. “Polychlorinated Dibenzo-*p*-dioxin/Polychlorinated Dibenzofuran Releases into the Atmosphere from the Use of Secondary Fuels in Cement Kilns during Clinker Formation.” *Environmental Science and Technology* 38 (2004): 4734-4738.

> This article presents data on PCDD/PCDF emissions from three cement plants in Spain burning meat meal and/or used tires. Emissions were also obtained from these plants burning conventional fuel (petroleum coke) alone. Results were compared between the use of conventional fuel with waste fuel and between the different types of waste fuels.

Lorber, K.E., A.M. Ragossnig, and H. Tesch. “Co-Incineration of Industrial Wastes in Fluidised [sic] Bed Utility Boilers.” *Proceedings of the Biennial Congress of the Institute of Waste Management of Southern Africa, WasteCon 2004* (2004): 115-124.

> This article is about use of industrial wastes as fuels, *not in the cement industry but in industrial boilers*. The waste fuels compared are In-Plant Residues from chipboard manufacture, “Alternative Standard Fuel”—a combination of waste wood, package waste, and sewage sludge, and several Refuse Derived Fuels. A combination of the Alternative Standard Fuel with the In-Plant Residues is compared to fuel oil, hard coal, and lignite, and the Refuse Derived Fuels are then compared to the ASF-IPR combination, in terms of elemental constituents and combustion emissions.
>
> When the amounts of trace elements are expressed in terms of energy content (mg/MJ) instead of mass (mg/kg), the Alternative Standard Fuel is found to be lower in S than fossil fuels but higher in Cr, Hg, Ni, and Pb and significantly higher in Cl, F, and Zn. In turn, the RDF mixtures are significantly higher in Cl, Cd, Co, Cr, Pb, and Zn than the Alternative Standard Fuel, and thus, significantly higher than fossil fuels. In the flue gas emissions, HCl, $S0_2$, Pb, Zn, Cr, and PCDD/PCDF were higher for the RDF fuels than for the Alternative Standard Fuels. In the filter ashes, Cd, Co, Cr, Pb, Zn, and PCDD/PCDF were higher for the RDF fuels than for the Alternative Standard Fuels. The authors were able to obtain satisfactory mass balances for Cl, Zn, Cu, and Pb. Other trace elements were problematic because of low concentrations, unstable process conditions, and heterogeneity of samples.

Lorber, K.E., H.J. Glinz, and H. Tesch, “Utilisation [sic] of Sieve Rejects from Mechanical-Biological Pre-Treatment of Household Waste in Cement Industry.” *Proceedings of the Biennial Congress of the Institute of Waste Management of Southern Africa, WasteCon 2004* (2004): 705-715.

> This article describes the use of a particular type of Refuse Derived Fuel in a cement plant. This fuel, called “MBT-Sieve Rejects”, is characterized and results of analysis from material obtained in summer and in winter are presented. MBT-Sieve Rejects material is rich in plastics, textiles, paper, and cardboard. Data from trial burns using the MBT-Sieve Rejects fuel are also presented, with analyses of inputs and outputs, including gaseous emissions.
>
> Higher amounts of Cr, Hg, Pb, and Cl are found in the ESP dust when the MBT-Sieve Rejects fuel is burned compared to the baseline. Higher amounts of Pb

and Zn are found in the cyclone dust and in the clinker. Gaseous emissions of NO_x, SO_2, and HCl also were increased over baseline levels, although all were within emissions limits. The fuel used for the baseline burn was coal + plastics-RDF. The MBT-Sieve Rejects fuel was higher in pollutant elements than the plastics-RDF, so a better quality coal was burned during the test burns than was burned for the baseline (presumably so that emissions wouldn't exceed regulatory limits). This creates problems trying to do a direct comparison of metal emissions between the test burns and the baseline.

Pipilikaki, P., M. Katsioti, D. Papageorgiou, D. Fragoulis, and E. Chaniotakis. "Use of Tire Derived Fuel in Clinker Burning." *Cement & Concrete Composites* 27 (2005): 843-847.

This article examines the use of tire derived fuel in the cement industry in Greece. Clinker and dust samples produced using pet-coke, coal, and tire derived fuel (TDF) are compared with clinker and dust samples produced from the use of just pet-coke and coal. Tire derived fuel (tire crumb) was burned not whole tires. The TDF was burned only in the precalciner at a replacement value of 6% of the total fuel.

For the samples obtained from the TDF burns (compared to those from the baseline, non-TDF, burns):

Clinker and kiln inlet dust had two times the zinc content. Sulfate was higher in the clinker but lower in the cooling tower dust. Chloride was higher in the cooling tower dust but lower in the electrostatic filter dust. Sodium, potassium and total chromium amounts were about the same. There were no apparent differences in the XRD patterns and the clinker microstructure, implying similar mineralogical composition. Cement compressive strengths were similar, but the TDF burn sample had an increased setting time, attributed to the higher amount of zinc present.

Trezza, M.A., and A.N. Scian. "Waste Fuels: Their Effect on Portland Cement Clinker." *Cement and Concrete Research* 35 (2005): 438-444.

This article reports the results of a laboratory simulation of the use of waste fuel in the cement industry. Three different materials (pyrolitic carbon, petroleum waste, and a trademarked waste fuel) are ashed, the ashes are mixed with raw feed dust in varying proportions, and clinkers are produced in a muffle furnace. Clinkers produced with the fuel ashes are compared with clinkers produced without ashes. Effects of the proportion of ashes mixed in before clinkering are also examined.

Clinker analyses: XRD analyses indicated lower crystallinity for the samples prepared with ashes from pyrolitic carbon and petroleum waste but similar or higher crystallinity for the samples prepared with ashes from the waste fuel mixture. Blaine tests showed that the sample prepared with petroleum waste ashes had no change in hardness, while both other sets of samples showed some increase in hardness. Pyrometric cone equivalent temperatures indicated that the ashes from pyrolytic carbon and petroleum waste were acting as a flux, while the ashes from the waste fuel mixture lowered the viscosity to such an extent that, in an industrial situation, the kiln's refractory lining could be damaged. DTA-TG tests supported these findings.

Hydrated clinker analyses: The added ashes samples showed slower hydration at early ages than the control sample. Compressive strengths were comparable.

Yuan, Chung-Shin, Hsun-Yu Lin, Chun-Hsin Wu, and Ming-Han Liu. "Partition and Size Distribution of Heavy Metals in the Flue Gas from Municipal Solid Waste Incinerators in Taiwan." *Chemosphere* 59 (2005): 135-145.

This article is about the fate of heavy metals as a result of the combustion of municipal wastes in incinerators, *not in a cement kiln*. Particulate matter from the flue gas was captured and analyzed for heavy metals. Impinger solutions were used to capture emissions of mercury and other volatile metals emitted in gaseous form instead of particulate form.

Flue gas was sampled at the inlets and outlets of the APCDs. Removal efficiencies of greater than 90% were observed for Pb, Cd, Zn, Cu, and Cr since these metals were present mainly in the solid phase (particulates) with a solid/gas ratio of greater than 12.3. Hg was not removed as efficiently because it was more likely to occur in gaseous form with a solid/gas ratio of 0.15 to 1.04. Finer particles (formed by homogeneous nucleation) contained more Pb, Cd, Zn, and Cu. Coarser particles (formed by ash formation) contained more Cr and Hg.

Levendis, Yiannis A., Ajay Atal, Bonnie Courtemanche, and Joel B. Carlson. "Burning Characteristics and Gaseous/Solid Emissions of Blends of Pulverized Coal with Waste Tire-Derived Fuel." *Combustion Science and Technology* 131 (1998): 147-185.

This article examines the combustion characteristics and emissions of various combinations of pulverized coal and ground tires burned in a drop-tube furnace*, not in a cement kiln*. Combinations varied from 100% coal through blends to 100% tire crumbs. Flame temperatures were about 1150°C. NO_x, SO_2, CO, CO_2, particulate, and PAH emissions were examined.

NO_x emissions were lower for the ground tires than for the pulverized coal, with emissions for mixtures being proportionate to the relative amounts. SO_2 emissions were higher for the tires than for the coal, with emissions for mixtures being proportionate to the relative amounts. CO emissions were fairly low but were higher for tires and for coal, with emissions for mixtures being close to those for tires alone. CO_2 emissions were lower for tires than for coal, with emissions for mixtures being proportionate to the relative amounts. Particulate emissions were higher for tires than for coal, with emissions for mixtures being proportionate to the relative amounts. PAH emissions were an order of magnitude higher for tires than for coal, but emissions for mixtures were close to those of coal alone.

Willitsch, Friedrich, Gernot Sturm, Friedrich Wurst, and Theodor Prey. "Alternnative [sic] Fuels in the Cement Industry." PMT-Zyklontechnik GmbH publication. Online. Accessed 8 March 2006.

http://greenbusinesscentre.com/Documents/Alternative%20fuels%20in%20Cement%20Industry.pdf

> This document has not been published in a refereed journal and is not a government or an industry publication. The authors have made presentations using similar content, however, at “green” conferences and have made their presentation slides, as well as this document available on the Web site for the Confederation of Indian Industry’s “Green Business Centre”.
>
> The paper discusses their company’s approach to using a variety of waste materials as fuel for cement kilns. There are diagrams and practical details (“how we do it”) but little hard data on the results of using the waste fuels. The authors’ first language clearly is not English, and their syntax becomes indecipherable in the section discussing gaseous emissions. It is virtually impossible to determine whether or not emissions increase significantly with the use of waste fuels, based on the statements made, and there are no helpful tables or diagrams. The authors do state that gaseous emissions of metals and organics are below legal limits.

II. Wastes as Raw Materials

Gadayev, Anatoly, and Boris Kodess. “By-Product Materials in Cement Clinker Manufacturing.” *Cement and Concrete Research* 29 (1999): 187-191.

> This article examines the use of chlorine-containing and sulfate-containing industrial wastes as raw materials in cement manufacture. Various industrial by-products containing calcium carbonate, calcium chloride, and alkali chlorides were added to raw mix and burned to form clinkers, which were compared to clinkers prepared from the raw mix alone.
>
> The high chlorine content of the first waste resulted in the formation of alkali chlorides, which effectively reduced the production of alite. The presence of excess alkali chlorides also led to the formation of kiln rings and increased amounts of cement kiln dust, creating process problems. The high sulfate content of the second waste also lowered the amount of alite produced and led to kiln ring formation and increased dust.

Caponero, Jefferson, and Jorge A.S. Tenório. “Laboratory Testing of the Use of Phosphate-Coating Sludge in Cement Clinker.” *Resources, Conservation and Recycling* 29 (2000): 169-179.

> This article describes the results of laboratory production of clinker using waste sludge from a phosphate coating process as a raw material, along with raw meal. Clinkers made with different levels of sludge were compared to clinker made with raw meal alone.
>
> Comparisons showed that up to 7% sludge could be added to the raw meal with no damage to the clinkerization process. No atypical phases were observed in any sample. Zn (found in the sludge at percent levels) was incorporated into the clinker at an average of 75%. [setting time concern?] P (also present in the

sludge at percent levels) was also incorporated into the clinker, although the percentage incorporated was not calculated. [strength concern?]

.

Espinosa, Denise C.R., and Jorge A.S. Tenório. "Laboratory Study of Galvanic Sludge's Influence on the Clinkerization Process." *Resources, Conservation and Recycling* 31 (2000): 71-82.

This article describes an experimental procedure to create clinker in the laboratory. The procedure is used to create clinkers using galvanic sludge as a raw material, along with raw meal. Clinkers made with different levels of sludge were compared to clinker made with raw meal alone. Leaching tests were also done on the clinkers to determine the amount of chromium loss.

Comparisons showed that up to 2% sludge could be added to the raw meal with no effect on the clinkerization process. At 3% and 5% sludge additions, there was a decrease in the temperatures of C_3S formation and of liquid phase formation. At 8% sludge addition, C_3S formation and liquid phase formation could not be observed experimentally. No significant loss of Cr (present in the sludge at percent levels) was observed during the clinkering process in the laboratory, with Cr content in the clinker proportional to the amount of sludge added. Leaching tests of cement made from the experimental clinkers showed that leachable Cr and leachable Cr^{6+} were below Brazilian legal limits.

Dalton, Jennifer L., Kevin H. Gardner, Thomas P. Seager, Mindy L. Weimer, Jean C.M. Spear, and Bryan J. Magee. "Properties of Portland Cement Made of Contaminated Sediments." *Resources, Conservation and Recycling* 41 (2004): 227-241.

This article describes the results of laboratory and pilot scale production of clinker using material dredged from the New York/New Jersey harbor as a partial substitute for raw meal. Clinkers were produced with different amounts of dredged material and compared with clinker produced with raw meal alone.

Decreased alite and increased belite were observed in the clinkers produced with dredged material, suggesting that the quartz present in the sediments requires more burning time than raw meal. Free choride present in the clinkers was below the ACI limits for cement, and there was little difference in chloride content between all the clinkers. However, chloride present in the sediments is expected to create process and maintenance issues.

Kolovos, K. G. "Waste Ammunition as Secondary Mineralizing Raw Material in Portland Cement Production." *Cement and Concrete Composites* 28 (2006): 133-143.

This article examines the use of waste ammunition materials (WAMs) as raw materials in cement manufacture. Three types of waste ammunition materials (crushed airgun pellets and fragments, crushed bullets and fragments, and cartridge cases were ground and mixed together in three different proportions. The three WAM mixes were then added to raw mix (in amounts from 0.5 to 2.0% w/w) and burned to form clinkers, which were compared to clinkers prepared from the raw mix alone.

The three WAMs had different chemical compositions: the airgun pellets were 99% Pb and almost 1% Sb, the bullets were 96% Pb, 2.5% Sn, and almost 1% Fe, and the cartridge cases were 70% Cu and 28% Zn. All three materials were present in the three ammunition mixes, but in different proportions, so that the compositions of the three mixes had different amounts of the metals Pb, Sb, Sn, Fe, Cu, and Zn, although all were present.

All three mixes acted as mineralizers, improving the burnability of the raw meal. That is, the clinkering temperatures for all three mixes in all measured proportions were lowered as compared to the control. All mixes produced clinkers with typical structures, with well crystallized alite, belite, calcium aluminate and ferrite and no detection of undesirable compounds. Spectroscopy results showed that Pb was preferentially found in the silicate phases while Cu, Zn, Sn, and Sb were selectively found in the interstitial material. Pb was incorporated into clinker at an average of about 46%, with the remainder presumably volatilized. Cu and Zn were incorporated at 84-100% and 73-100, respectively. Sn and Sb seemed to be incorporated at 100%.

Lower proportions (0.5-1.0%) of added WAM mixes had little effect on cement paste hydrations, while the higher proportions (1.5-2.0%) slowed down hydration. Compressive strength at 1 day was the same as the control but higher at 2, 7, and 28 days. The optimum amount of added WAM for increased compressive strength was 1.0% for all three mixes. There was a slight increase in setting time proportional to the amount of added WAM mix. There was no effect on the water demand of the cement paste. Leaching tests showed that leached Pb was in the ppb range. Very little Cu, Zn, and Sn and no Sb, Hg, Cd, Cr, As, and Bi were found in the leachate solutions, even at 90 days.

Shih, Pai-Huang, Juu-En Chang, Hsing-Cheng Lu, and Li-Choung Chiang. “Reuse of Heavy Metal-Containing Sludges in Cement Production.” *Cement and Concrete Research* 35 (2005): 2110-2115.

This article examines the use of two industrial heavy metal-containing sludges as raw materials in cement manufacture. Two sludges, one from surface finishing and one from electroplating, were added to raw mix and clinkered in the laboratory. The clinkers obtained were compared to ordinary portland cement.

Comparisons of XRD patterns showed that the major crystalline phases found in ordinary portland cement were also present in the clinker made with surface finishing sludge, but that most of them were absent in the clinkers made with high percentages of electroplating sludge. This difference was attributed to the high (percent) levels of heavy metals (Ni, Cr, Cu, and Pb) present in the electroplating sludge. Clinkers with 10% and 15% electroplating sludge had XRD patterns similar to those of ordinary portland cement.

Higher percentages of heavy metals inhibited the formation of C_3S, while lower percentages seemed to enhance its formation. The volatile metal Pb evaporated during sintering (20% retention in the clinker), but less volatile metals Cr, Ni, and Cu were trapped in the clinker (90% retention for Cr and Ni, nearly 100% for Cu).

Leachate tests were performed on hydrated samples of clinkers made with surface finishing sludge and two levels of electroplating sludge. The only metal detected in any leachate was Cr, which was detected in the leachate from the two samples made from clinkers prepared with electroplating sludge. The amounts of Cr detected in the leachates were below regulatory limits.

III. Cement and Cement Kiln Dust, Trace Metals in Cement and Cement Kiln Dust

Delles, J.B., H.M. Kanare, S.T. Padiyara, and D.J. Broton. “Trace Metals in Cement and Cement Kiln Dust from North American Cement Plants.” Portland Cement Association, SP110, 1991.

> This publication seems to contain the original data from the same study described in the publication above. The study was conducted by personnel of Construction Technology Laboratories, Inc. on behalf of the Portland Cement Association.
>
> Cement and cement kiln dust (CKD) samples supplied by cement plants in North America were analyzed for acid-soluble metals and for leachable metals. The report briefly describes the sampling and analysis processes and gives details about quality assurance procedures and the statistical analysis of the analysis results. No information about the plants supplying the samples is provided.
>
> Acid-soluble and leachable metals data are presented for 94 cement and 95 CKD samples in several tables. Side-by-side scatter plots for acid-soluble metals are given for cement and CKD samples from plants burning fossil fuels only and plants burning waste fuels.
>
> Cement samples: For most of the analyte metals, there seems to be no significant difference. Cr is an exception, with significantly higher concentration in the samples from plants burning waste fuels. For some metals, there were too many Not Detected (ND) samples to make a comparison.
>
> CKD samples: Cd, Cr, Pb Se had significantly higher concentration in the samples from plants burning waste fuels. As before, for some metals, there were too many ND samples to make a comparison.
>
> Side-by-side histogram plots for leachable metals and acid-soluble metals are given for the cement and CKD samples. In addition, X-Y plots of leachable metals vs. acid-soluble metals are also given. These plots are meant to show if there is any correlation between the two. There is apparently no systematic correlation.

An Analysis of Selected Trace Metals in Cement and Kiln Dust. Portland Cement Association, SP109T, 1992.

> This publication summarizes the results of a study of trace metals in cement and cement kiln dust (CKD). The study was undertaken by the Portland Cement

Assocation as a follow-up to an earlier study of trace elements in CKD by the U. S. Bureau of Mines published in 1982.

The samples came from 79 cement plants in the United States and 10 in Canada, but there is no identifying information about the plants or about the conditions under which the samples were produced. There is also no information about the analyses performed. [It is possible that this report is a repackaging of some of the data reported in the following report by Delles, et al.]

Cement and CKD samples are analyzed for acid-soluble metals and leachable metals. No consistent relationship can be observed between the two. A correlation can be made between the metals in CKD and the extent of CKD recycling in a plant.

Acid-soluble metals in cement: Hg (ND-0.039 mg/kg), Se (0.62-2.23 mg/kg), Tl (0.01-2.68 mg/kg), Cd (0.03-1.12 mg/kg), Pb (1-75 mg/kg), Sb (0.7-4.0 mg/kg), Ag (6.75-19.90 mg/kg), As (5-71 mg/kg), Ni (10-129 mg/kg), Ba (91-1402 mg/kg), Be (0.32-3.05 mg/kg), Cr (25-422 mg/kg)

Acid-soluble metals in CKD: Hg (0.004-25.500 mg/kg), Se (2.68-307.00 mg/kg), Tl (1.40-776.00 mg/kg), Cd (0.1-59.6 mg/kg), Pb (34-7390 mg/kg), Sb (0.3-3.4 mg/kg), Ag (4.80-40.70 mg/kg), As (2-159 mg/kg), Ni (1-60 mg/kg), Ba (35-767 mg/kg), Be (0.13-3.54 mg/kg), Cr (8-293 mg/kg)

TCLP metals leached from cement: Hg (0.0001-0.0050 mg/L), Se (0.001-0.025 mg/L), Tl (0.002-0.028 mg/L), Cd (0.0003-0.0123 mg/L), Pb (0.002-0.029 mg/L), Sb (0.003-0.063 mg/L), Ag (0.003-0.12 mg/L), As (0.005-0.084 mg/L), Ni (0.06-0.17 mg/L), Ba (0.49-4.27 mg/L), Be (0.0001-0.0030 mg/L), Cr (0.07-1.54 mg/L)

TCLP metals leached from CKD: Hg (0.0002-0.0223 mg/L), Se (0.006-1.711 mg/L), Tl (0.01-4.50 mg/L), Cd (0.0001-0.2200 mg/L), Pb (0.002-9.718 mg/L), Sb (0.003-0.031 mg/L), Ag (0.03-0.17 mg/L), As (0.003-0.636 mg/L), Ni (0.06-0.32 mg/L), Ba (0.12-9.19 mg/L), Be (0.0001-0.0029 mg/L), Cr (0.01-1.29 mg/L)

A comparison of the results of this study with those of the Bureau of Mines study in 1982 found that Sb, As, Cd, and Ni had higher maximum and average concentrations in the earlier study, Cr had a higher maximum in the current study but the average values were similar, and Pb and Ag had higher maximum and average values in the current study. The other metals included in the current study were not included in the earlier study due to limited detectability.

Appendix A contains the complete data set from which the above data ranges are taken. Appendix B contains a tabulation of data from the earlier study by the U.S. Bureau of Mines on trace elements in CKD. Appendix C contains a brief discussion of the cement-making process.

United States Environmental Protection Agency. Office of Solid Waste. *Report to Congress on Cement Kiln Dust: Volume II: Methods and Findings (December 1993)*. Washington, D.C.

This document is a report from the US EPA to Congress on cement kiln dust, from the point of view of whether of not CKD is hazardous to the environment, especially CKD produced in plants burning hazardous waste. The report discusses how CKD is generated, its characteristics, how it is managed, and the environmental impact of CKD management practices.

The portion of the report of most relevance is Chapter 3, “CKD Generation and Characteristics”. The EPA collected and analyzed CKD samples from 20 cement-production facilities.

Metals data are tabulated and are compared with data from earlier Portland Cement Company and Bureau of Mines studies.

Trace metals in “as generated” (fresh) CKD, EPA survey data: Sb (1.77-27.2 ppm); As (2.1-20.3 ppm); Ba (11.0-779.0 ppm); Be (0.158-1.6 ppm); Cd (0.89-80.7 ppm); Cr (11.5-81.7 ppm); Pb (5.1-1490.0 ppm); Hg (0.005-14.4 ppm); Ni (6.9-39.0 ppm); Se (2.5-109.0 ppm); Ag (1.1-22.6 ppm); Tl (0.99-108.0 ppm); V (6.6-204.0 ppm)

Trace metals in “as managed” (weathered) CKD, EPA survey data: Sb (1.581-10.9 ppm); As (2.1-19.8 ppm); Ba (39.8-360.0 ppm); Be (0.175-1.5 ppm); Cd (0.62-27.4 ppm); Cr (9.6-110.0 ppm); Pb (40.6-863.0 ppm); Hg (0.009-0.830 ppm); Ni (6.3-54.7 ppm); Se (1.4-43.9 ppm); Ag (0.348-17.2 ppm); Tl (1.1-14.6 ppm); V (7.6-120.0 ppm)

CKD metals data are also compared with data obtained for native soils data, which were reported in an earlier EPA publication.

Native soils: Sb (2-10 ppm); As (1-50 ppm); Ba (100-3000 ppm); Be (0.1-40 ppm); Cd (0.01-0.7 ppm); Cr (1-1000 ppm); Cu (2-100 ppm); Pb (2-200 ppm); Mn (20-3000 ppm); Hg (0.01-0.3 ppm); Ni (5-500 ppm); Se (0.1-2 ppm); Ag (0.01-5 ppm); Tl (NA); V (20-500 ppm); Zn (10-300 ppm); Sr (50-1000 ppm)

For “as generated” CKD, Cd, Cr, and Pb were higher from facilities burning HWF. For “as managed” CKD, As, Ba, Cd, Cr, Hg, Pb, and Se were higher from facilities burning HWF.

Samples from 11 facilities were analyzed for chlorinated dioxins and furans. A number of these compounds were found at low concentrations in samples from all facilities, including both the facilities burning Hazardous Waste Fuels and the facilities burning only fossil fuels.

Samples were also analyzed for volatile organic compounds, semi-volatile organic compounds, pesticides, PCBs, and radionuclides. Several radionuclides were detected but results were considered within normal range.

Clinker samples from 18 cement facilities, 11 of which burned HWF, were collected and analyzed.

Trace metals in (fresh) clinker from plants burning only fossil fuels, EPA survey data: Sb (ND-16.5 ppm); As (3.8-25.4 ppm); Be (ND-2.4 ppm); Cd (ND); Cr

(26.1-138 ppm); Pb (0.77-21 ppm); Hg (ND); Ni (13.1-82 ppm); Se (ND-0.52 ppm); Ag (ND-8.2 ppm); Tl (ND-0.19 ppm)

Trace metals in (fresh) clinker from plants burning HWF, EPA survey data: Sb (5.3-27.9 ppm); As (1.4-14.7 ppm); Be (0.86-2.7 ppm); Cd (ND); Cr (44.3-150 ppm); Pb (0.68-33.1 ppm); Hg (ND-0.07 ppm); Ni (20.1-91.1 ppm); Se (ND-1.6 ppm); Ag (ND-9.9 ppm); Tl (ND-0.54 ppm)

Wheeler, Bradner D. "Analysis of Contaminated Soils and Hazardous Waste Fuels by XRF Spectroscopy." *Spectroscopy* 8, no. 5 (1993): 34-39.

This article examines the use of XRF spectroscopic methods to determine elemental compositions of environmentally significant samples such as soils, waste fuels, and cement kiln dust. XRF is shown to be an appropriate technique for analysis of metals in soils, Hazardous Waste Fuels, and cement kiln dust, based on its shorter sample preparation time and the accuracy and precision of the technique.

Metal results for a kiln dust sample analyzed by XRF are included.

CKD: MgO-1.46%, Al_2O_3-2.78%, SiO_2-14.30%, K_2O-2.73%, CaO-42.20%, TiO_2-0.10%, Mn_2O_3-0.05%, Fe_2O_3-2.06%, Ni-60 ppm, Cu-16 ppm, Zn-75 ppm, Br-74 ppm, Rb-470 ppm, Sr-510 ppm, Zr-1200 ppm, Mo-30 ppm, Pb-370 ppm

Owens, Warren D., Adel F. Sarofim, and David W. Pershing. "The Use of Recycle for Enhanced Volatile Metal Capture." *Fuel Processing Technology* 39, nos. 1-3 (1994): 337-356.
(duplicated in another section)

This article discusses the enrichment of volatile metals such as mercury in cement kiln dust (CKD). There is some mathematical modeling of the process, but there is no experimental data although the authors cite data from the Portland Cement Association study of 1991.

The title is misleading as it seems to suggest that the authors are advocating the recycle of CKD to reduce volatile metal emissions. However, the opposite seems to be true, that is, the authors advocate using a bypass to waste a fraction of the CKD instead of recycling it, in order to remove some of the volatile metals from the system. The authors seem to think that this is a way to reduce metal emissions, when in fact, it just changes their form from gaseous emissions to solid waste.

The authors discuss the use of carbon to trap (and thus reduce) mercury emissions in industrial boilers. They use some more mathematical modeling to suggest that there is some application of the recycle idea to the boilers that will help reduce mercury emissions. One interesting piece of information is that HCl in gaseous emissions favors the formation of $HgCl_2$ which can be removed by impinger solutions (and possibly by dust collectors?) while the presence of SO_2 in gaseous emissions favors the formation of Hg which will be volatilized and go up the stack.

Sarofim, Adel F., David W. Pershing, Barry Dellinger, Michael P. Heap, and Warren D. Owens. “Emissions of Metal and Organic Compounds from Cement Kilns Using Waste Derived Fuels.” *Hazardous Waste & Hazardous Materials* 11, no. 1 (1994): 169-192. (duplicated in another section)

> This article examines data from plants burning Waste Derived Fuels (WDF) for both organic and metal emissions. The authors review the cement making process, the fate of metals introduced into the process, and the destruction of organic compounds in the cement kiln.
>
> Data are obtained from certificate of compliance tests for cement kilns burning WDF. Mass balances are calculated for those data sets which are sufficiently complete. Most of the data in these cases are within 30% closure, with the largest errors for the two most volatile metals, Hg and Tl. Although metal inputs and emissions data are presented graphically, *no tables of metals data are presented*. Metals emissions increase with metals input, but Pb emissions seems to also be dependent on the amount of Cl present in the system as well as the total amount of Pb present.
>
> Destruction and Removal Efficiencies (DREs) for organic compounds introduced at the discharge (front) end of the kiln and mid-kiln appear to be >99.9999%. DREs for organics introduced at the precalciner however are considerably lower for some compounds, apparently due to insufficiently high temperatures or insufficient exposure time to the temperatures necessary for destruction (1073-1173°C). It is also possible that there is some pyrolysis and/or formation of organic and chlorinated organic compounds occurring in the preheater tower.

Guo, Qizhong, and James O. Eckert, Jr. “Heavy Metal Outputs from a Cement Kiln Co-Fired with Hazardous Waste Fuels.” *Journal of Hazardous Materials* 51 (1996): 47-65. (duplicated in another section)

> This article examines data from a real-world kiln equilibration test for a cement kiln co-fired with Hazardous Waste Fuel (HWF). These data are used to derive equations for predicting metal outputs at steady state operating conditions. (It is assumed that some kiln dust will be wasted and some recycled.)
>
> The CKD and the stack emissions are found to be enriched in the more volatile metals while the clinker is found to be enriched in the less volatile metals. Metal outputs for non-steady state conditions are also analyzed, and metals in clinker are predicted to be higher under these conditions than for steady-state operation.
>
> Metal inputs and outputs from the steady state compliance testing are reported.
>
> Coal: Mass feed rate-5.23 Mg/h; thermal feed rate-106 x 10^9 J/h; As-19.8 g/h; Be-11.9 g/h; Cd-0.654 g/h; Cr-87.6 g/h; Pb-54.0 g/h
>
> HWF: Mass feed rate-14.5 Mg/h; thermal feed rate-383 x 10^9 J/h; As-9430 g/h; Be-1190 g/h; Cd-7120 g/h; Cr-43,700 g/h; Pb-46,300 g/h
>
> Raw materials: Mass feed rate-132 Mg/h; As-54.9 g/h; Be-79.0 g/h; Cd-97.2 g/h; Cr-2130 g/h; Pb-468 g/h

Recycled CKD: Mass feed rate-10.9 Mg/h; As-1230 g/h; Be-56.8 g/h; Cd-1950 g/h; Cr-3600 g/h; Pb-15,500 g/h

Wasted CKD: Production rate-16.3 Mg/h; As-2150 g/h; Be-117 g/h; Cd-4570 g/h; Cr-6220 g/h; Pb-33,000 g/h

Clinker: Production rate-69.6 Mg/h; As-7040 g/h; Be-611 g/h; Cd-120 g/h; Cr-33,600 g/h; Pb-855 g/h

Stack emissions: As-0.622 g/h; Be-0.403 g/h; Cd-41.5 g/h; Cr-19.6 g/h; Pb-283 g/h

Metal concentrations for CKD during operation at two different HWF feed rates and with no HWF feed are compared.

Metals in CKD at maximum intended HWF feed rate (rate not given): As-90.0 ppm, Be-8.6 ppm, Cd-394 ppm, Cr-409 ppm, Pb-2740 ppm

Metals in CKD at normal HWF feed rate (rate not given): As-2.30 ppm, Be-0.852 ppm, Cd-8.84 ppm, Cr-38.6 ppm, Pb-386 ppm

Metals in CKD at no HWF feed rate (based on 2 sampling periods): As-ND-8.0 ppm, Be-0.27-0.70 ppm, Cd-3.7-15.4 ppm, Cr-14.8-39.0 ppm, Pb-44.0-192 ppm

Eckert, James O., Jr., and Qizhong Guo. “Heavy Metals in Cement and Cement Kiln Dust from Kilns Co-Fired with Hazardous Waste-Derived Fuel: Application of EPA Leaching and Acid-Digestion Procedures.” *Journal of Hazardous Materials* 59 (1998): 55-93.
(duplicated in another section)

This article examines the use of TCLP procedure as an accurate predictor of the leaching of metals from concrete samples in real-world conditions.

The authors perform the standard TCLP procedure for raw cement and cement kiln dust and on cement paste samples. Comparisons indicate that metals are more easily leached from the raw cement than from set cement.

Standard TCLP results for raw cement: Be (ND-29.72 ppb); Al (4.84 ppb-out of range); Ti (0.40-466.58 ppb); V (ND-6.35 ppb); Cr (14.14-986.21 ppb); Mn (ND-6.79 ppb); Co (1.84-9.17 ppb); Ni (ND-104.44 ppb); Zn (ND-41.50 ppb); Cu (ND-8.63 ppb); As (ND-0.97 ppb); Se (ND-25.46 ppb); Rb (1.98-824.92 ppb); Cd (ND-2.30 ppb); Cs (ND-17.33 ppb); Ba (426.95-4108.91 ppb); Pb (ND-17.24 ppb)

Standard TCLP results for CKD: Be (1.78 ppb); Al (15.62 ppb); Ti (19.07 ppb); V (13.88 ppb); Cr (217.93 ppb); Mn (ND); Co (4.72 ppb); Ni (31.82 ppb); Zn (26.48 ppb); Cu (6.49 ppb); As (4.36 ppb); Se (144.93 ppb); Rb (3954.18 ppb); Cd (0.28 ppb); Cs (393.99 ppb); Ba (830.38 ppb); Pb (111.04 ppb)

TCLP results for cement paste (set cement): Be (2.1-11.9 ppb); Al (227.7-658.1 ppb); Ti (0.4-2.0 ppb); V (ND-0.4 ppb); Cr (11.9-62.6 ppb); Mn (ND-1.1 ppb); Co

(4.2-19.4 ppb); Ni (29.9-50.8 ppb); Zn (21.7-79.2 ppb); Cu (5.5-13.5 ppb); As (ND-0.2 ppb); Se (ND-1.1 ppb); Rb (45.0-521.8 ppb); Cd (ND-0.3 ppb); Cs (0.4-14.7 ppb); Ba (1710.9-3487.1 ppb); Pb (ND-1.4 ppb)

The authors also perform several variations on the standard TCLP procedure on raw cement samples which include multiple exposures to the leaching solution, extended exposure time, and the use of chlorinated water for a leaching solution. Comparisons of these data indicate that As, Co, Zn, Cu, Ga, and Ba are leached more strongly with multiple exposures to a leaching solution, that Ti, Co, Ni, Cu, Ga, Se, and Ba are leached more strongly with longer exposure time, and that Cr, Ni, Ga, Rb, and Ba are leached more strongly with a chlorinated water leaching solution.

The authors point out that the pH of a cement leachate solution tends to be high, due to the buffering capacity of the cement. They speculate that, under real-world conditions (multiple exposures, extended exposure time, and/or exposure to chlorinated water), the buffering effect could diminish resulting in increased metal leaching.

The authors also analyze cement and kiln dust samples by microwave-assisted acid digestion and demonstrate that there are correlations between acid-soluble metals and TCLP results for only a few metals.

Acid soluble metals in raw cement: Be (ND-29.72 ppb); Al (4.84 ppb-out of range); Ti (0.40-466.58 ppb); V (ND-6.35 ppb); Cr (14.14-986.21 ppb); Mn (ND-6.79 ppb); Co (1.84-9.17 ppb); Ni (ND-104.44 ppb); Zn (ND-41.50 ppb); Cu (ND-8.63 ppb); As (ND-0.97 ppb); Se (ND-25.46 ppb); Rb (1.98-824.92 ppb); Cd (ND-2.30 ppb); Cs (ND-17.33 ppb); Ba (426.95-4108.91 ppb); Pb (ND-17.24 ppb)

Acid soluble metals in CKD: Be (0.678-1.311 ppm); Al (2076.671-2962.433 ppm); Ti (118.545-259.44 ppm); V (4.581-17.173 ppm); Cr (4.776-28.007 ppm); Mn (21.721-356.724 ppm); Co (0.788-2.310 ppm); Ni (3.222-13.722 ppm); Zn (4.060-280.280 ppm); Cu (1.381-31.893 ppm); As (0.370-4.403 ppm); Se (ND-1.645 ppm); Rb (0.160-3.050 ppm); Cd (ND-0.961 ppm); Cs (ND-0.188 ppm); Ba (18.214-61.307 ppm); Pb (0.129-23.181 ppm)

The authors also analyze cement and kiln dust samples by XRF and demonstrate that the acid digestion methods used to obtain “total metals” results actually only obtain partial metals recovery and should be reported as “recoverable metals” or “acid-soluble metals” not “total metals”. Moreover, the “total metals” results obtained by XRF have little or no correlation to the “acid-soluble metals” results or to the TCLP results.

XRF metals in raw cement: SiO_2 (20.06-21.27%); Al_2O_3 (4.35-5.87%); Fe_2O_3 (1.56-4.24%); MnO (0.01-0.3%); MgO (0.89-3.32%); CaO (64.75-68.67%); Na_2O (0.11-0.41%); K_2O (0.1-0.74%); TiO_2 (0.18-0.37%); P_2O_5 (0.06-0.23%); Al (23022.4-31067.0 ppm); Ti (1078.9-2217.8 ppm); V (44.0-167.0 ppm); Cr (58.0-315.0 ppm); Mn (77.4-2323.4 ppm); Co (7.0-19.0 ppm); Ni (29.0-91.0 ppm); Cu (8.0-198.0 ppm); Zn (24.0-2522.0 ppm); As (ND at 5 ppm-29.0 ppm); Pb (ND at 5 ppm-140.0 ppm)

XRF metals in CKD: SiO_2 (15%); Al_2O_3 (5.57%); Fe_2O_3 (2.19%); MnO (0.02%); MgO (0.82%); CaO (43.63%); Na_2O (0.36%); K_2O (2.96%); TiO_2 (0.41%); P_2O_5 (0.14%); Al (29479.3 ppm); Ti (2457.6 ppm); V (134 ppm); Cr (81.0 ppm); Mn (154.9 ppm); Co (25.0 ppm); Ni (49.0 ppm); Cu (175.0 ppm); Zn (573.0 ppm); As (46.0 ppm); Pb (525.0 ppm)

Hartlieb, Nicola, Matthias Achternbosch, and Klaus-Rainer Bräutigam. "Co-Incineration of Wastes in Cement Kilns—Determination of Input Pathways of Trace Elements in Cement by Material Flow Analysis." *Fresenius Environmental Bulletin* 12, no. 6 (2003): 629-635.
(duplicated in another section)

This article attempts to use a material flow analysis model to determine the sources of trace elements in cement. Ranges of trace elements found in various materials and the relative contributions those materials are presumed to make to the final clinker/cement product are used to test the model with measured values in cement being compared to values calculated using the model.

Measured values of trace metals in cement: As (ND-13.6 ppm); Cd (ND-0.8 ppm); Co (4-17 ppm); Cr (23-59 ppm); Cu (9-43 ppm); Mn (255-1268 ppm); Ni (13-39 ppm); Pb (10-48 ppm); Sb (ND-15 ppm); Sn (ND-10.6 ppm); V (30-96 ppm); Zn (48-291 ppm)

The authors conclude that wastes used as raw materials and/or fuels could be a significant source of trace elements in cement. Industry data on the relative amounts of Zn, V, Sb, and Cr in the various cement raw materials and fuels are presented graphically. *No experimental data are reported*.

Kanare, Howard. "Comparison of Trace Metal Concentrations in Cement Kiln Dust, Agricultural Limestone, Sewage Sludge, and Soil." Portland Cement Association, R&D SN2080, 1999.

This article compares trace metal concentrations in a soil additive (agricultural limestone) with two waste products (cement kiln dust (CKD) and sewage sludge) and with soil. The comparison is part of an evaluation of the suitability of cement kiln dust to be used as a soil additive.

Aglime samples are acid-digested (in some cases, with microwave assistance) prior to analysis by AAS (either flame or graphite furnace AAS). Aglime TCLP samples are also analyzed.

Nitric acid-soluble metals in aglime samples: Sb (ND); As (ND-9.3 mg/kg); Ba (9.4-210 mg/kg); Be (ND-1 mg/kg); Cd (ND-0.84 mg/kg); Cr (ND-18.9 mg/kg); Pb (ND-4.8 mg/kg); Hg (ND-0.03 mg/kg); Ni (ND-6.5 mg/kg); Se (ND-0.54 mg/kg); Ag (2.7-8.8 mg/kg); Tl (ND-0.8 mg/kg)

TCLP metals in aglime samples: Sb (ND-0.08 mg/L); As (ND); Ba (0.01-2 mg/L); Be (ND-0.004 mg/L); Cd (ND-0.009 mg/L); Cr (ND-0.02 mg/L); Pb (ND); Hg (ND-0.0005 mg/L); Ni (ND-0.04 mg/L); Se (ND-0.04 mg/L); Ag (0.01-0.04 mg/L); Tl (ND)

Only aglime samples have actually been analyzed for this paper. Metals results given for CKD, sewage sludge, and soil have been taken from other publications.

Metals in CKD: Sb (ND-3.4 mg/kg); As (2.0-159 mg/kg); Ba (36-1402 mg/kg); Be (ND-1.8 mg/kg); Cd (ND-49.8 mg/kg); Cr (8-257 mg/kg); Pb (37-1504 mg/kg); Hg (ND-25.5 mg/kg); Ni (1-60 mg/kg); Se (ND-121 mg/kg); Ag (5.3-41 mg/kg); Tl (ND-776 mg/kg)

Metals in sewage sludge: Sb (ND-572 mg/kg); As (1.1-230 mg/kg); Ba (23-3104 mg/kg); Be (1-30 mg/kg); Cd (1-3410 mg/kg); Cr (10-99000 mg/kg); Pb (13-26000 mg/kg); Hg (0.6-56 mg/kg); Ni (2-5300 mg/kg); Se (1.7-17.2 mg/kg); Ag (ND-1252 mg/kg); Tl (ND-5 mg/kg)

Metals in soil: Sb (ND-8.8 mg/kg); As (ND-97 mg/kg); Ba (10-5000 mg/kg); Be (ND-15 mg/kg); Cd (ND mg/kg); Cr (1-2000 mg/kg); Pb (10-700 mg/kg); Hg (ND-4.6 mg/kg); Ni (ND-700 mg/kg); Se (ND-4.3 mg/kg); Ag (ND); Tl (ND)

IV. Concrete, Trace Metals in Concrete

Guo, Qizhong. “Increases of Lead and Chromium in Drinking Water from Cement-Mortar-Lined Pipes: Initial Modeling and Assessment.” *Journal of Hazardous Materials* 56 (1997): 181-213.

This article examines the effects of various parameters on the leaching of Pb and Cr from cement mortar of the type used to line drinking water pipes. The motivation for this study is the increase in the use of Hazardous Waste Fuels (HWF) in cement plants and the absence of standards on limits for Pb and Cr in cement-mortar pipe linings.

The author reviews the literature on heavy metals in cement and cement kiln dust (CKD). Heavy metals will be higher in cements from HWF-burning kilns. As more drinking water pipes are lined with cement mortar or concrete, leachability becomes more important. The author reviews the literature on leaching of metals from cement mortar and concrete.

The author develops a mathematical model to estimate when drinking water standards for heavy metals are likely to be exceeded for water exposed to cements containing these metals. In his model, the author considers the initial wetting process, dissolution, diffusion, and advection of metals in the lining, accumulation of metals in the static pipe water, and dilution of metals by the flowing water.

Based on the modeling results, the author finds that drinking water standards are likely to be exceeded by cement with Cr solubility larger than 540 ppb or Pb solubility larger than 70 ppb. The author recommends that the maximum allowable amount of Cr in cement be reduced and that cement kiln dust not be recirculated when the HWF has the maximum allowable amount of Pb (since recycling kiln dust results in higher amounts of more volatile metals such as Pb ending up in the clinker).

Hillier, S.R., C.M. Sangha, B.A. Plunkett, and P.J. Waldren. “Long-Term Leaching of Toxic Trace Metals from Portland Cement Concrete.” *Cement and Concrete Research* 29 (1999): 515-521.

> This article examines the long-term leaching of trace metals from concrete made from Portland cement and flint aggregate.
>
> Concrete sample cubes are leached with de-ionized water for time periods varying from 1.5 hr to 256 days. The leachates are analyzed using an AAS method for determination of metals in Refuse-Derived Fuel (ASTM E885-88). V is the only metal detected in the leachate samples.
>
> Leachate results: Sb-Not Detected (15 µg/L); As-Not Detected (3 µg/L); Be-Not Detected (3 µg/L); Cd-Not Detected (15 µg/L); Cr-Not Detected (84 µg/L); Pb-Not Detected (15 µg/L); Hg-Not Detected (6 µg/L); Ni-Not Detected (9 µg/L); Se-Not Detected (6 µg/L); V-120 µg/L at 64 days, 180 µg/L at 256 days for poorly-cured (1-day) concrete cubes; Not Detected (6 µg/L) for well-cured (28-day) cubes
>
> The metal content of the Portland cement was also analyzed by AAS using a lithium tetraborate fusion method (ASTM E886-94) to prepare the samples.
>
> Cement results: Sb-Not Detected (5 µg/g); As-19.9 µg/g; Be-1.4 µg/g; Cd-Not Detected (5 µg/g); Cr-72.7 µg/g; Pb-75.3 µg/g; Hg-Not Detected (12 µg/g); Ni-72.0 µg/g; Se-Not Detected (2 µg/g); V-44.1 µg/g

Marion, Anne-Marie, Michel De Lanève, and Alain De Grauw. “Study of the Leaching Behaviour of Paving Concretes: Quantification of Heavy Metal Content in Leachates Issued from Tank Test Using Demineralized Water.” *Cement and Concrete Research* 35 (2005): 951-957.

> This article examines the leaching of heavy metals from concrete samples made from porphyry aggregate, river sand, and either Portland cement or blast furnace slag cement. The cement used to make the concrete was made using alternative fuels and industrial by-products to partially replace fossil fuels and normal raw materials. The leachate solvent used was de-ionized water.
>
> Leachates were changed at the end of each measuring period. Metal content decreased strongly with increased immersion time for concrete samples made from both cements.
>
> Concentrations of metals in leachates are reported for one of the concrete samples.
>
> Leachates from concrete made with Portland cement (1 day, 3 days, 7 days, 14 days, 36 days, 64 days): As (<0.015, <0.015, <0.015, <0.015, <0.015, <0.015 µg/L); Cd (0.025, 0.011, 0.006, 0.003, 0.001, <0.001 µg/L); Cr (6.2, 3.7, 1.8, 0.94, 0.33, 0.21 µg/L); Cu (no values given); Hg (0.029, 0.015, 0.005, <0.003, <0.001, <0.001 µg/L); Mn (<0.060, <0.060, <0.060, <0.060, <0.060, <0.060 µg/L); Ni (0.88, 0.57, 0.28, 0.16, 0.29, 0.19 µg/L); Pb (0.15, 0.10, 0.058, 0.033, 0.018, 0.010 µg/L); Sb (0.015, 0.11, 0.071, 0.048, 0.016, 0.015 µg/L); Zn (0.17, 0.067,

0.042, 0.015, 0.016, 0.009 µg/L); Se (<0.60, <0.60, <0.60, <0.60, <0.60, <0.60 µg/L); Ag (<0.005, <0.005, <0.005, <0.005, <0.005, <0.005 µg/L); Ba (143, 90, 53, 32, 14, 8.3 µg/L), pH (11.9, 11.8, 11.8, 11.6, 11.4, 12.0).

Concentrations of metals in a 24 hr "average" leachate (calculated from the leached quantities for all samples, averaged over the total 64 day leaching period) are reported for both types of concretes.

24 hour "average" leachate from concrete made with Portland cement: As (<0.002-0.006 µg/L); Cd (<0.001-0.002 µg/L); Cr (0.31-0.71 µg/L); Cu (<0.004-0.015 µg/L); Hg (<0.002-<0.002 µg/L); Mn (<0.006-<0.006 µg/L); Ni (0.19-0.45 µg/L); Pb (<0.001-0.027 µg/L); Sb (0.011-0.028 µg/L); Zn (0.014-0.020 µg/L); Se (<0.060-<0.060 µg/L); Ag (<0.001-<0.001 µg/L); Ba (6.4-22 µg/L).

24 hour "average" leachate from concrete made with blast furnace slag cement: As (<0.002-0.007 µg/L); Cd (<0.001-<0.001 µg/L); Cr (0.13-0.29 µg/L); Cu (<0.004-<0.004µg/L); Hg (<0.002-<0.002 µg/L); Mn (<0.006-0.008 µg/L); Ni (0.096-0.28 µg/L); Pb (<0.001-<0.001 µg/L); Sb (0.010-0.068 µg/L); Zn (0.005-0.022 µg/L); Se (<0.060-<0.060 µg/L); Ag (<0.001-0.003 µg/L); Ba (8.0-8.8 µg/L).

Bulk metal concentrations in both types of concretes are reported. There is no systematic relationship observed between bulk metals in the cement and concrete samples and the metals detected in the concrete sample leachates.

Portland cement: As (7.1-11 mg/kg); Cd (0.51-1.5 mg/kg); Cr (74-121 mg/kg); Cu (22-60 mg/kg); Hg (0.71-3.5 mg/kg); Mn (234-465 mg/kg); Ni (56-84 mg/kg); Pb (12-145 mg/kg); Sb (4.4-9.4 mg/kg); Zn (91-514 mg/kg); Se (4.0-9.9 mg/kg); Ag (0.49-0.61 mg/kg); Ba (205-577 mg/kg).

Blast furnace slag cement: As (2.9-5.9 mg/kg); Cd (0.53-0.89 mg/kg); Cr (45-71 mg/kg); Cu (15-30 mg/kg); Hg (<0.19-0.44 mg/kg); Mn (746-1117 mg/kg); Ni (36-45 mg/kg); Pb (15-56 mg/kg); Sb (1.5-13 mg/kg); Zn (75-199 mg/kg); Se (2.6-5.1 mg/kg); Ag (0.30-0.74 mg/kg); Ba (534-689 mg/kg).

Concrete prepared from Portland cement: As (1.8-12 mg/kg); Cd (0.14-0.28 mg/kg); Cr (55-64 mg/kg); Cu (18-30 mg/kg); Hg (4.6-7.3 mg/kg); Mn (382-465 mg/kg); Ni (17-26 mg/kg); Pb (11-27 mg/kg); Sb (1.6-2.1 mg/kg); Zn (56-94 mg/kg); Se (<0.01-4.5 mg/kg); Ag (0.33-0.74 mg/kg); Ba (327-400 mg/kg).

Concrete prepared from blast furnace slag cement: As (1.4-1.8 mg/kg); Cd (0.08-0.17 mg/kg); Cr (24-31 mg/kg); Cu (9.3-12 mg/kg); Hg (8.7-9.9 mg/kg); Mn (341-383 mg/kg); Ni (9.3-12 mg/kg); Pb (8.6-12 mg/kg); Sb (0.64-1.6 mg/kg); Zn (30-38 mg/kg); Se (<0.01-<0.01 mg/kg); Ag (0.27-0.58 mg/kg); Ba (366-393 mg/kg).

V. Coal, Metals in Coal

Danihelka, P., Z. Volna, J.M. Jones, and A. Williams. "Emission of Trace Toxic Metals During Pulverized Fuel Combustion of Czech Coals." *International Journal of Energy Research* 27 (2003): 1181-1203.

> This article studies examine metal emissions from combustion of Czech coals in heating and power stations, *not in cement kilns*. The authors also examine the effect of Cl on the volatility of metal such as Zn, Cu, Pb, Hg, and Tl.
>
> The authors found that high levels of Cl in coal increased the amount of some metals, such as Ni, Cu, Zn, Cd, Sn, Sb, Pb, Hg, and Tl, found in the particulate emissions. The more thermodynamically stable the metal chloride, the more likely that the metal will be found in the particulate emissions. Affinities for Cl follow the order Tl > Cu > Zn > Pb > Co > Mn > Sn > Hg.
>
> Analysis results for coal samples, range: Ash (12.7%-37.0%), Moisture (5.6%-22.2%), C (44.4%-67.4%), H (2.9%-4.2%), N (0.5%-1.0%), O (6.6%-10.5%), S (0.3%-1.1%), Cl (ND at 0.08%-0.12%), Volatile carbon daf (19.1%-45.4%), and heat value (17.3-29.8 MJ/kg).
>
> Metals results for coal samples, range: V (44-101 ppm), Cr (18.2-69.3 ppm), Mn (70-301 ppm), Fe (1192-9633 ppm), Co (ND at 5.1 ppm-7.7 ppm), Ni (18.3-38.8 ppm), Cu (18.3-48.9 ppm), Zn (13.6-56.4 ppm), As (1.1-23.1 ppm), Se (ND at 0.5 ppm-1.5 ppm), Cd (0.1-0.3 ppm), Sn (0.9-2.4 ppm), Sb (0.7-1.2 ppm), Hg (0.027-0.135 ppm), Tl (ND at 0.7 ppm-1 ppm), and Pb (8.2-103 ppm).
>
> Metals results for bottom ash samples, range: V (112.4-407.6 ppm), Cr (11.6-382.5 ppm), Mn (432.8-9046 ppm), Fe (58260-69450 ppm), Co (ND at 8 ppm-35.2 ppm), Ni (72.5-686 ppm), Cu (54-130.6 ppm), Zn (21.5-72.3 ppm), As (1.1-10.8 ppm), Se (ND at 0.5 ppm-1 ppm), Cd (ND at 0.3 ppm-1.1 ppm), Sn (1.6-3.7 ppm), Sb (ND at 0.6 ppm-1.7 ppm), Hg (ND at 0.002 ppm-0.008 ppm), Tl (ND at 1.4 ppm-1.7 ppm), and Pb (5-179.7 ppm).
>
> Metals results for fly ash samples, range: V (163.3-295.4 ppm), Cr (101.5-176 ppm), Mn (402.3-1168 ppm), Fe (48370-81220 ppm), Co (ND at 21 ppm-32 ppm), Ni (70.9-172.3 ppm), Cu (90.2-151 ppm), Zn (60.3-140.5 ppm), As (5.3-46.6 ppm), Se (2-7.9 ppm), Cd (ND at 0.1 ppm-1 ppm), Sn (2.5-7.7 ppm), Sb (ND at 0.7 ppm-5 ppm), Hg (0.013-0.24 ppm), Tl (ND at 1.7 ppm-3 ppm), and Pb (10.7-79 ppm).
>
> Metals results for particulate emissions, range: V (140-421 ppm), Cr (ND), Mn (ND-1870 ppm), Co (ND-58 ppm), Ni (13-27591 ppm), Cu (17-2289 ppm), Zn (ND-16880 ppm), As (ND-788 ppm), Se (160-966 ppm), Cd (1-33 ppm), Sn (ND-85 ppm), Sb (ND-57692 ppm), Hg (ND-5 ppm), Tl (ND-2 ppm), and Pb (ND-416 ppm).
>
> .

Diehl, S.F., M.B. Goldhaber, and J.R. Hatch. "Modes of Occurrence of Mercury and Other Trace Elements in Coals from the Warrior Field, Black Warrior Basin, Northwestern Alabama." *International Journal of Coal Geology* 59 (2004): 193-208.

> This article examines trace elements in coal samples from the Black Warrior Basin, Alabama.

Although most of the coal samples mined in this region are low in the potentially toxic elements Hg, As, Mo, Se, Cu, and Tl, samples that have high pyrite content or that arise from seams near faults are enriched in them. Amounts of the metals in the pyrites can be as high as 100 times the metals in the non-pyrite coal.

The authors believe that the enrichment arises from a tectonic phenomenon in the Alleghanian age. The authors also believe that some of the metals-rich pyrites can be removed in a “coal-cleaning” procedure, since the pyrites are coarser grained than the coal.

Finkelman, Robert G. “Trace Elements in Coal: Environmental and Health Significance.” *Biological Trace Element Research* 67 (1999): 197-204.

This article discusses trace elements found in U.S. coal, specifically their likely origins and their environmental impact when the coal is burned for fuel.

A table summarizes arithmetic and geometric means and maximum values for all the elements in the entire periodic table with respect to US coals. Data were obtained from the US Geological Survey.

Sample data (arithmetic mean, geometric mean, maximum): As (24, 6.5, 2200 ppm), Ba (170, 93, 22000 ppm), Cd (0.47, 0.02, 170 ppm), Cl (614, 79, 8800 ppm), Cr (15, 10, 250 ppm), Co (6.1, 3.7, 500 ppm), Cu (16, 12, 280 ppm), Pb (11, 5.0, 1900 ppm), Mg (0.11, 0.07, 1.5%), Mn (43, 19, 2500 ppm), Hg (0.17, 0.10, 10 ppm), Mo (3.3, 1.2, 280 ppm), P (430, 20, 58000 ppm), K (0.18, 0.10, 2.0%), Na (0.08, 0.04, 1.4%), Sr (130, 90, 2800 ppm), S (1.8, 1.3, 25%), Tl (1.2, 0.00004, 52 ppm), Ti (0.08, 0.06, 0.74%), V (22, 17, 370 ppm), and Zn (53, 13, 19000 ppm).

Ikävalko, E., T. Laitinen, M. Pärkkä, and I. Yliruokanen. “Intercomparison of Trace Element Determination in Samples from a Coal-Fired Power Plant.” *International Journal of Environmental Analytical Chemistry* 61 (1995): 207-224.

This article describes a round-robin analysis of samples designed to test the accuracy of analyses of coal, fly ash, by-product from fly-ash desulfurization, and solutions used for removing metals from gaseous emissions. HNO_3 and $K_2Cr_2O_7$ solutions of containing trace metals were prepared in the laboratory. Coal, fly ash, and desulfurization by-product samples were taken from a plant and prepared in the laboratory to ensure as much uniformity as possible.

The focus was on lab-to-lab performance. XRF and NAA were comparable, in terms of performance, to AAS and ICP-AES, except in having higher detection limits. Cold vapor AAS for mercury analysis had a high relative standard deviation. Results from analyses using the Au-film mercury analyzer were similar, but there were too few labs using this technique to do a valid comparison. A comparison of digestion methods showed that the acid composition was more important than heating. A combination of HNO_3 and HF gave the best results.

Coal data (range): Al (19700-21000 ppm), As (4.50-14.8 ppm), Cd (0.06-0.20 ppm), Co (2.00-10.4 ppm), Cr (19.0-63.8 ppm), Cu (10.0-32.2 ppm), Hg (0.04-0.13 ppm), Mn (49.0-91.1 ppm), Ni (2.00-25.1 ppm), and Pb (4.30-20.3 ppm).

Miller, B.B., R. Kandiyoti, and D.R. Dugwell. "Trace Element Emissions from Co-Combustion of Secondary Fuels with Coal: A Comparison of Bench-Scale Experimental Data with Predictions of a Thermodynamic Equilibrium Model." *Energy & Fuels* 16 (2002): 956-963.
(duplicated in another section)

This article examines the co-combustion of coal, four biomass fuels (wood-bark, straw, pulp sludge, and paper sludge), and three waste fuels (agricultural waste, sewage sludge, and plastic waste) in a suspension-firing reactor (intended to simulate a section of a fluidized bed combustor), *not in a cement kiln*. Temperatures in the reactor were 800°C and 900°C. Trace metals are analyzed in the original fuels and in ashes resulting from their combustion. The focus of the article is in the enrichment of the trace metals in the combustion ash.

Exact metals data for the original fuels were not given (although ranges were reported), nor were metals data for the various ash samples. The volatilization (or conversely the retention of a metal in the ash) was found to depend, not only on the metal's volatility but also on the type of fuel burned. This was ascribed at least partially to the differences between the metal compounds found in the different types of fuels. Paper sludge had the highest degree of volatilization while sewage sludge had the lowest.

Trace metals in fuels, ranges:

Wood-bark: Less than 1 ppm (As, Be, Cd, Co, Hg, Se, Sb, Tl), 1 to 10 ppm (Ni, Mo, Pb, V), 10-100 ppm (Cr, Cu, Sr), greater than 100 ppm (Ba, Mn, Zn)

Straw: Less than 1 ppm (As, Be, Cd, Co, Hg, Ni, Mo, Sb, Tl, V), 1 to 10 ppm (Cr, Cu, Pb), 10-100 ppm (Ba, Mn, Zn)

Columbian coal: Less than 1 ppm (Be, Cd, Hg, Sb, Tl), 1 to 10 ppm (As, Co, Cu, Ni, Mo, Pb, Se), 10-100 ppm (Ba. Cr, Mn, Sr, V, Zn)

Polish coal: Less than 1 ppm (Cd, Hg, Mo, Tl), 1 to 10 ppm (As, Be, Co, Sb, Se), 10-100 ppm (Cr, Cu, No, Pb, Sr, V, Zn), greater than 100 ppm (Ba, Mn)

Sewage sludge: Less than 1 ppm (Be, Hg,Tl), 1 to 10 ppm (As, Cd, Co, Sb), 10-100 ppm (Ni, Mo, Pb, V), greater than 100 ppm (Ba, Cr, Cu, Mn, Sr, Zn)

Paper sludge: Less than 1 ppm (As, Be, Cd, Co, Hg, Se, Tl), 1 to 10 ppm (Ni, Mo, Sb, V), 10-100 ppm (Cr, Cu, Mn, Pb, Sr), greater than 100 ppm (Ba, Zn)

Agricultural waste: Less than 1 ppm (As, Be, Cd, Co, Hg, Pb, Sb, Se, Tl), 1 to 10 ppm (Cr, Mo, V), 10-100 ppm (Ba, Ni, Sr, Cu), greater than 100 ppm (Mn, Zn)

Pulp sludge: Less than 1 ppm (As, Be, Co, Hg, Mo, Sb, Se, Tl), 1 to 10 ppm (Cd, Pb, V), 10-100 ppm (Ba, Cr, Cu, Ni, Sr), greater than 100 ppm (Mn, Zn)

Plastic waste: Less than 1 ppm (As, Be, Hg, Se, Tl), 1 to 10 ppm (Cd, Co, Ni, Mo, Sb, V), 10-100 ppm (Cr, Cu, Mn, Pb, Sr), greater than 100 ppm (Ba, Zn)

Nguyen, T.H., J. Boman, and M. Leermakers. "EDXRF and ICP-MS Analysis of Environmental Samples." *X-Ray Spectrometry* 27 (1998): 265-276.

This article examines the environmental impact of coal mining on the environment.

Samples of Vietnamese coal and water (groundwater, run-off, and river water), soil and sediment, vegetation (spinach and sea pine trees), and fish were analyzed for trace elements. Trace element concentrations were higher in the environmental samples taken in the vicinity of the mines compared to non-adjacent samples.

Trace elements in Vietnamese coal analyzed by EDXRF (mean): P (2400 ppm), S (3700 ppm), K (2000 ppm), Ca (5400 ppm), Ti (1100 ppm), V (12 ppm), Cr (10.4 ppm), Mn (140 ppm), Fe (15800 ppm), Co (4.9 ppm), Ni (7.5 ppm), Cu (4.4 ppm), Zn (4.4 ppm), As (4.3 ppm), Se (1.5 ppm), Br (4 ppm), Rb (11 ppm), Sr (48 ppm), and Pb (2.1 ppm).

Trace elements in Vietnamese coal analyzed by ICP-MS (mean): Be (0.6 ppm), Ti (1000 ppm), V (10 ppm), Cr (9 ppm), Mn (180 ppm), Co (3.7 ppm), Ni (6.8 ppm), Cu (5.3 ppm), Zn (5.2 ppm), As (3.6 ppm), Se (1.8 ppm), Sr (52 ppm), Nb (1.1 ppm), Mo (0.9 ppm), Cd (0.1 ppm), Sn (0.5 ppm), Ba (0.8 ppm), Hg (0.08 ppm), Pb (1.8 ppm), Th (2.1 ppm), U (1.3 ppm).

Rauf, M.A., M. Ikram, and N. Ayub. "Determination of Major and Trace/Toxic Metals in Coal Samples by Atomic Absorption Spectroscopy and Neutron Activation Analysis." *Journal of Trace and Microprobe Techniques* 20, no.1 (2002): 91-103.

This article presents metals analysis results for Pakistan coal samples.

Pakistan mined coal:
Proximate analysis: Moisture (2.7-8.5%), Ash (7.6-40.7%), Volatile matter (25.0-33.8%), Fixed C (25.9-50.8%), Total S (4.4-5.7%)
Trace elements analyzed by AAS: Ca (700-1900 ppm), Cr (2.90-68.0 ppm), Fe (12700-72000 ppm), Mg (400-3200 ppm), Ni (1.60-74.80 ppm), Pb (Below detection limit-45.40 ppm), Zn (28.60-181.40 ppm)
Trace elements analyzed by NAA: Co (3.20-15.00 ppm), Cr (4.70-64.00 ppm), Fe (14500-72800 ppm), Mn (18.00-145.00 ppm), Na (225.00-3150.00 ppm), Zn (31.00-200.00 ppm), Ce (8.20-63.00 ppm), Cs (Below detection limit-2.40 ppm), Eu (0.10-1.00 ppm), Hf (0.20-46.00 ppm), Rb (Below detection limit-15.00 ppm), Sb (Below detection limit-0.60 ppm), Sc (0.90-11.50 ppm), Tb (Below detection limit-1.25 ppm), Th (1.00-12.00 ppm), Yb (0.20-7.20 ppm)

Thar coalfield coal:
Proximate analysis: Moisture (6.1-12.4%), Ash (6.5-20.0%), Volatile matter (31.3-40.8%), Fixed C (34.1-49.7%), Total S (3.4-5.4%)

Trace elements analyzed by AAS: Ca (Below detection limit-800 ppm), Cr (0.96-43.00 ppm), Fe (200-64800 ppm), Mg (2700-3100 ppm), Ni (25.60-87.60 ppm), Pb (16.40-78.00 ppm), Zn (9.00-255.00 ppm)
Trace elements analyzed by NAA: Co (0.50-15.60 ppm), Cr (1.30-73.00 ppm), Fe (600.00-62000.00 ppm), Mn (42.00-200.00 ppm), Na (1700.00-5250.00 ppm), Zn (12.00-275.00 ppm), Ce (Below detection limit-70.60 ppm), Cs (Below detection limit-0.80 ppm), Eu (Below detection limit-1.60 ppm), Hf (0.10-3.50 ppm), Rb (Below detection limit), Sb (Below detection limit-0.25 ppm), Sc (0.40-13.80 ppm), Tb (Below detection limit-1.30 ppm), Th (0.30-5.40 ppm), Yb (0.20-5.00 ppm)

Wooden coal [probably charcoal, possibly lignite or sawdust briquettes]:
Proximate analysis: Moisture (4.0-11.7%), Ash (2.1-9.7%), Volatile matter (49.8-61.8%), Fixed C (29.6-38.0%), Total S (2.7-3.7%)
Trace elements analyzed by AAS: Ca (Below detection limit), Cr (Below detection limit-11.75 ppm), Fe (11.00-283.00 ppm), Mg (0.16-0.50 ppm), Ni (11.50-19.20 ppm), Pb (7.70-14.60 ppm), Zn (0.30-4.10 ppm)
Trace elements analyzed by NAA: Co (Below detection limit-0.22 ppm), Cr (0.10-19.50 ppm), Fe (18.00-332.00 ppm), Mn (7.00-38.00 ppm), Na (10.00-99.00 ppm), Zn (5.00-9.00 ppm), Ce (Below detection limit-0.70 ppm), Cs (Below detection limit-0.30 ppm), Eu (Below detection limit), Hf (Below detection limit), Rb (Below detection limit-9.00 ppm), Sb (Below detection limit-0.08 ppm), Sc (Below detection limit-0.20 ppm), Tb (Below detection limit), Th (Below detection limit-0.10 ppm), Yb (Below detection limit-0.02 ppm)

Reddy, M. Srnivasa, Shaik Basha, H.V. Joshi, and B. Jha. “Evaluation of the Emission Characteristics of Trace Metals from Coal and Fuel Oil Fired Power Plants and Their Fate During Combustion.” *Journal of Hazardous Materials B* 123 (2005): 242-249.

This article examines trace metal emissions from burning coal and fuel oil in power plant combustors, *not a cement kiln*.

Metals in coal, fuel oil, bottom ash, fly ash, flue gases and stack particulates were analyzed, and mass balances for metals were calculated for plants. Mass balances for the fuel-oil fired plant were “acceptable” (no definition as to what constituted acceptable) but were below 50% for the coal fired plant for all trace metals except As (84% mass balance) and Hg (76% mass balance). Trace metal emissions were higher for the coal fired plant than for the fuel-oil fired plant. Total Hg was the predominant metal in the flue gas for both fuels.

Proximate and ultimate analyses results for fuel oil (sample#1, sample#2, sample#3): Gross calorific value (9941 kcal/l, 9714.3 kcal/l, 9265.4 kcal/l), moisture (0.05%, 0.05%, 0.04%), ash (0.033%, 0.031%, 0.029%), C (89.1%, 86.8%, 87.4%), H (2.5%, 2.4%, 2.5%), N (0.42%, 0.39%, 0.41%), S (0.38%, 0.35%, 0.37%), and O (7.51%, 6.97%, 7.65%).

Trace metals for fuel oil: As (13.2 ±3.5 ppm), Cd (1.85 ±0.54 ppm), Co (2.3 ±0.65 ppm), Cr (3.2 ±0.98 ppm), Cu (8.9 ±1.5 ppm), Fe (7439 ±95 ppm), Hg (0.02 ±0.001 ppm), Mn (16.8 ±3.2 ppm), Ni (9.9 ±1.6 ppm), Pb (22.4 ±3.1 ppm), Se (4.8 ±0.86 ppm), and Zn (14.2 ±3.2 ppm).

Proximate and ultimate analyses results for coal (sample#1, sample#2, sample#3): Gross calorific value (4337.2 kcal/kg, 4215.3 kcal/kg, 4289.6 kcal/kg), moisture (7.8%, 8.2%, 7.9%), ash (34.67%, 32.51%, 36.25%), C (41.5%, 38.4%, 40.6%), H (3.33%, 3.21%, 3.79%), N (0.94%, 0.78%, 0.84%), S (0.76%, 0.68%, 0.71%), and O (11%, 10.2%, 9.9%).

Trace metals for coal: As (41.9 ±2.4 ppm), Cd (4.31 ±0.6 ppm), Co (4.1 ±1.1 ppm), Cr (21 ±2.8 ppm), Cu (43 ±4.4 ppm), Fe (9432 ±89 ppm), Hg (0.2 ±0.007 ppm), Mn (98.5 ±11.5 ppm), Ni (16 ±4.2 ppm), Pb (29.4 ±8.6 ppm), Se (12.1 ±3.1 ppm), and Zn (30 ±12.4 ppm).

Wang, Jie, Chunqi Li, Kinya Sakanishi, Tetsuya Nakazato, Hiroaki Tao, Toshimasa Takanohashi, Takayuki Takarada, and Ikuo Saito. “Investigation of the Remaining Major and Trace Elements in Clean Coal Generated by Organic Solvent Extraction.” *Fuel* 84 (2005): 1487-1493.

This article examines the effectiveness of thermal extraction methods using organic solvents to create “Hyper-coal” or “clean coal”.
N-methyl-2-pyrrolidone (NMP) was found to be a more effective extraction solvent than 1-methylnaphthalene (1-MN), yielding a higher amount of coal extracted. The Illinois coal sample was more effectively extracted by both solvents than the Wyodak coal. Acid pretreatment improved NMP extraction effectiveness for the Wyodak coal but not extraction with 1-MN. No pretreatment effect was observed for the Illinois coal with either solvent. Both extraction solvents reduced the metals in the extracted coal (compared to the original samples), but 1-MN was more effective than NMP.

Ultimate analysis, Wyodak coal: Ash (8.8%), C (75.0%), H (5.4%), N (1.1%), S (0.5%), and O (18.0%).
Major [sic] elements, Wyodak coal: Na (1.28 ppth), Mg (2.70 ppth), Al (7.26 ppth), Ca (13.6 ppth), and Fe (4.21 ppth).
Trace elements, Wyodak coal: Li (8.68 ppm), Be (0.30 ppm), V (14.4 ppm), Cr (6.11 ppm), Mn (25.4 ppm), Co (1.72 ppm), Ni (5.4 ppm), Ga (3.62 ppm), As (3.83 ppm), Se (1.6 ppm), Sr (315 ppm), Cd (0.083 ppm), Ba (390 ppm), Hg (0.147 ppm), and Pb (6.28 ppm).

Ultimate analysis, Illinois No. 6 coal: Ash (15.3%), C (76.9%), H (5.5%), N (1.9%), S (5.6%), and O (10.1%).
Major [sic] elements: Na (1.86 ppth), Mg (0.84 ppth), Al (12.1 ppth), Ca (9.6 ppth), and Fe (27.9 ppth).
Trace elements, Illinois No. 6 coal: Li (17.3 ppm), Be (0.71 ppm), V (40.2 ppm), Cr (45.3 ppm), Mn (85.3 ppm), Co (5.23 ppm), Ni (35.5 ppm), Ga (3.67 ppm), As (4.12 ppm), Se (5.69 ppm), Sr (31.6 ppm), Cd (0.74 ppm), Ba (76.9 ppm), Hg (0.116 ppm), and Pb (9.47 ppm).

Xu, Minghou, Rong Yan, Chuguang Zheng, Yu Qiao, Jun Han, and Changdong Sheng. “Status of Trace Element Emission in a Coal Combustion Process: A Review.” *Fuel Processing Technology* 85 (2003): 215-237.

This is a review article (no original research). The topic is trace element emissions during coal combustion in conventional burners, *not in cement kilns*.

A mechanism for the distribution of a trace element among the various forms of emissions is presented: Vaporized metals are formed at the high temperature region near the flame, then condense or nucleate at lower temperature regions further away from the flame, forming a suspended aerosol and particles. The vaporized species then convert into various solid and/or liquid forms which influences their partitioning behavior.

Trace elements with concentrations greater than 50 ppm: Ba (for most coals, 20-100 ppm), B (for most coals, 5-400 ppm), F (for most coals, 20-500 ppm), Mn (for most coals, 5-300 ppm), P (for most coals, 10-3000 ppm), Sr (for most coals, 15-500 ppm), Ti (for most coals, 10-2000 ppm), and Zn (for most coals, 5-300 ppm).

Trace elements with concentrations from 10-50 ppm: As (for most coals, 0.5-80 ppm), Cl (for most coals, 50-2000 ppm), Cr (for most coals, 0.5-60 ppm), Cu (for most coals, 0.5-50 ppm), Pb (for most coals, 2-80 ppm), Li (for most coals, 1-80 ppm), Ni (for most coals, 0.5-50 ppm), Rb (for most coals, 2-20 ppm), V (for most coals, 2-100 ppm), and Zr (for most coals, 5-200 ppm).

Trace elements with concentrations from 1-10 ppm: Sb (for most coals, 0.05-10 ppm), Be (for most coals, 0.1-15 ppm), Cd (for most coals, 0.1-3 ppm), Cs (for most coals, 0.3-5 ppm), Co (for most coals, 0.5-30 ppm), Ga (for most coals, 1-20 ppm), Ge (0.5-50 ppm), Mo (for most coals, 0.1-10 ppm), Nb (for most coals, 1-20 ppm), Sc (for most coals, 1-10 ppm), Se (for most coals, 0.2-4 ppm), Tl (for most coals, <0.2-1 ppm), Th (for most coals, 0.5-10 ppm), and U (for most coals, 0.5-10 ppm).

Trace elements with concentrations below 1 ppm: Hg (for most coals, 0.02-1 ppm) and Ag (for most coals, 0.02-2 ppm).

Xu, Yan-Hua, Akira Iwashita, Tsunenori Nakajima, Hiroyuki Yamashita, Hirokazu Takanashi, and Akira Ohki. “Effect of HF Addition on the Microwave-Assisted Acid-Digestion for the Determination of Metals in Coal By Inductively Coupled Plasma-Atomic Emission Spectrometry.” *Talanta* 66 (2005): 58-64.

This article investigates the necessity for using HF in the digestion of coal samples prior to metals analysis by ICP-AES. `

Analysis of Standard Reference Materials showed that a two-stage digestion using HNO_3 and H_2O_2 was effective without the addition of HF. Twenty-four standard Japanese coals were digested by the two-stage method and the extracts were analyzed.

Japanese standard coals, ash: 1.58-14.97%.
Japanese standard coals, metal oxides in ash: Al_2O_3 (9.18-36.75%), Fe_2O_3 (2.18-15.95%), CaO (0.33-20.63%), MgO (0.26-6.84%), and MnO (0.01-2.46%).

Yan, Rong, D. Gauthier, and G. Flamant. “Partitioning of Trace Elements in the Flue Gas from Coal Combustion.” *Combustion and Flame* 125 (2001): 942-954.

This article studies the partitioning of trace elements in flue gases from coal burned in a combustor, *not in a cement kiln*.

The identities of the dominant species of the various trace elements were found to be dependent on combustion temperature, the amount of oxygen present, and the amount of ash in the coal.

Proximate analysis, low-ash coal: Water (11%), ash (15%), and volatile matter (24%).
Elementary and halogen analysis, low-ash coal: C (64.08%), H (3.115%), O (6.764%), N (1.513%), S (0.534%), F (0.01%), Cl (0.01%), Br (3 x 10^{-5}%), I (2 x 10^{-6}%)
Ash analysis, low-ash coal: SiO_2 (6.94%), Al_2O_3 (4.67%), CaO (0.23%), MgO (0.040%), K_2O (0.080%), Na_2O (0.027%), Fe_2O_3 (0.534%), Mn_3O_4 (0.0040%), P_2O_5 (0.147%), TiO_2 (0.320%)
Trace elements, low-ash coal: As (0.1 ppm), Cd (0.5 ppm), Co (3 ppm), Cr (0.5 ppm), Cu (8 ppm), Hg (0.6 ppm), Ni (5 ppm), Pb (18 ppm), Sb (0.1 ppm), Se (0.5 ppm), Sn (0.2 ppm), Te (0.5 ppm), Tl (0.5 ppm), V (6 ppm), Zn (14 ppm), Ag (0.5 ppm), B (8 ppm), Ba (147 ppm), Be (0.5 ppm), Ce (17 ppm), Cs (2.5 ppm), Ga (5 ppm), Ge (5 ppm), La (10 ppm), Li (1 ppm), Mo (0.5 ppm), Nb (3 ppm), Rb (20 ppm), Sc (3 ppm), Sr (159 ppm), Ta (0.15 ppm), Th (3.5 ppm), U (10 ppm), Y (50 ppm), and Zr (4 ppm).

Proximate analysis, high-ash coal: Water (2.03%), ash (31.36%), and volatile matter (25.24%).
Elementary and halogen analysis, high-ash coal: C (56.50%), H (2.81%), O (5.61%), N (0.95%), S (0.80%), F (0.02%), Cl (0.01%), Br (3 x 10^{-5}%), I (2 x 10^{-6}%)
Ash analysis, high-ash coal: SiO_2 (16.94%), Al_2O_3 (9.00%), CaO (1.50%), MgO (0.04%), K_2O (1.20%), Na_2O (0.30%), Fe_2O_3 (2.00%), Mn_3O_4 (0.003%), P_2O_5 (0.01%), TiO_2 (0.01%)
Trace elements, high-ash coal: As (20 ppm), Cd (2 ppm), Co (7 ppm), Cr (20 ppm), Cu (25 ppm), Hg (0.2 ppm), Ni (20 ppm), Pb (30 ppm), Sb (2 ppm), Se (2.5 ppm), Sn (5 ppm), Te (2.5 ppm), Tl (5 ppm), V (40 ppm), Zn (75 ppm), Ag (0.1 ppm), B (60 ppm), Ba (100 ppm), Be (2 ppm), Ce (20 ppm), Cs (2.5 ppm), Ga (5 ppm), Ge (5 ppm), La (10 ppm), Li (20 ppm), Mo (3 ppm), Nb (3 ppm), Rb (20 ppm), Sc (3 ppm), Sr (100 ppm), Ta (0.15 ppm), Th (3 ppm), U (1.5 ppm), Y (10 ppm), and Zr (50 ppm).

VI. Tires, Trace Metals in and/or Combustion of

AB2588 Emissions Testing at California Portland Cement Company's Colton Plant: Coal Firing and Coal With Tires Firing (September 1999), by Arlene C. Bell, Delta Air Quality Services, Incorporated (prepared for submittal to South Coast Air Quality Management District). Orange, CA.

This document summarizes gaseous emissions data from a cement plant, comparing a test burn of coal + tires to baseline results from a burn of coal alone.

Gaseous and particulate stack emissions were tested for organic and inorganic components. During the test burn, tires replaced coal at about 11-12%, with a corresponding reduction in coal feed compared to the baseline burn of coal only. However, kiln feed was also reduced by about 11% compared to the baseline burn. During the test burn, stack emissions of NO_x were reduced by about 50%, while CO emissions increased by about 150%.

During the test burn, total particulates and PM_{10} were higher than for the baseline, while non-methane hydrocarbons were lower. Some volatile organic species were higher, some were lower, and others were not detected. All the PAH species that were detected were lower for the test burn than for the baseline burn.

PCDD/PCDFs were higher for all the detected isomers. The hexa-, hepta-, and octachlorobiphenyl congeners were all higher for the test burn, while the mono-, di-, tri-, tetra-, and penta- congeners were all lower. The nona- and deca-congeners were not detected for both the test burn and the baseline burn.

HCl and HF emissions were higher for the test burn than for the baseline burn. Total Cr, Mn, Hg, P, and Zn were higher, while Ba, Cd, Cu, Pb, and Ni were lower. Sb, As, Be, Se, Ag, and Tl were not detected for both the test burn and the baseline burn.

Amari, Takeshi, Nickolas J. Themelis, and Iddo K. Wernick. “Resource Recovery from Used Rubber Tires.” *Resources Policy* 25 (1999): 179-188.

This article describes the ways in which scrap tires can be used: fuel, pyrolysis to produce secondary products, retreading. There are no original data reported, just data taken from the literature.

The compounds that make up tires are described and discussed, and the devulcanization process is discussed. There is also a discussion as to the energy-effectiveness of using tires as fuel vs. recovering and recycling the rubber. According to the authors, less than 40% of the energy content of tires can be recovered as fuel energy.

Retreading is stated to be the best use in term of new material and energy required. It is pointed out, however, that burning tires for fuel is preferable environmentally if the only alternative is landfilling.

Literature data are reported for Proximate and Ultimate analyses and for metals in ash for coal and three types of tire rubber samples (1.25 cm “fuzz”, 5 cm pieces with metal, and 5 cm pieces with most metal removed magnetically).

Coal, Proximate and Ultimate analyses: Energy content (28.23 MJ/kg), moisture (7.76%), ash (11.05%), volatiles (34.05%), C (67.69%), H (4.59%), N (1.13%), O (5.47%), and S (2.30%).
Coal, metals in ash: SiO_2 (47.98%), Al_2O_3 (20.70%), Fe_2O_3 (18.89%), TiO_2(0.82%), CaO (3.30%), MgO (0.79%), Na_2O (0.48%), K_2O (2.06%), SO_3 (4.33%), P_2O_5 (0.62%), and ZnO (0.02%).

Rubber, 1.25 cm “fuzz”, Proximate and Ultimate analyses: Energy content (32.10 MJ/kg), moisture (2.26%), ash (16.48%), volatiles (64.66%), C (69.74%), H (6.30%), N (0.45%), O (3.40%), and S (1.30%).
Rubber, 1.25 cm “fuzz”, metals in ash: SiO_2 (18.21%), Al_2O_3 (6.99%), Fe_2O_3 (30.93%), TiO_2(6.01%), CaO (5.99%), MgO (0.73%), Na_2O (1.07%), K_2O (0.55%), SO_3 (8.35%), P_2O_5 (0.56%), and ZnO (20.60%).

Rubber, 5 cm, with metal, Proximate and Ultimate analyses: Energy content (31.05 MJ/kg), moisture (0.75%), ash (23.19%), volatiles (54.23%), C (67.00%), H (5.81%), N (0.25%), O (1.64%), and S (1.33%).
Rubber, 5 cm, with metal, metals in ash: SiO_2 (5.16%), Al_2O_3 (1.93%), Fe_2O_3 (0.35%), TiO_2(0.14%), CaO (0.56%), MgO (0.10%), Na_2O (0.13%), K_2O (0.14%), SO_3 (0.99%), P_2O_5 (0.10%), and ZnO (5.14%).

Rubber, 5 cm, without metal, Proximate and Ultimate analyses: Energy content (32.58 MJ/kg), moisture (1.02%), ash (8.74%), volatiles (67.31%), C (72.15%), H (6.74%), N (0.36%), O (9.67%), and S (1.23%).
Rubber, 5 cm, without metal, metals in ash: SiO_2 (22.00%), Al_2O_3 (9.09%), Fe_2O_3 (1.45%), TiO_2(2.57%), CaO (10.64%), MgO (1.35%), Na_2O (1.10%), K_2O (0.92%), SO_3 (15.38%), P_2O_5 (1.03%), and ZnO (34.50%).

Literature data are also reported for Proximate and Ultimate analyses for 5 different types of tires.

Fiberglass-belted, Proximate and Ultimate analyses: Energy content (32.47 MJ/kg), moisture (0.0%), ash (11.70%), C (75.80%), H (6.62%), N (0.20%), O (4.39%), and S (1.29%).
Steel-belted, Proximate and Ultimate analyses: Energy content (26.67 MJ/kg), moisture (0.0%), ash (25.20%), C (64.20%), H (5.00%), N (0.10%), O (4.40%), and S (0.91%).
Nylon-belted, Proximate and Ultimate analyses: Energy content (34.64 MJ/kg), moisture (0.0%), ash (7.20%), C (78.90%), H (6.97%), N (not detected at level of 0.10%), O (5.42%), and S (1.51%).
Polyester-belted, Proximate and Ultimate analyses: Energy content (34.28 MJ/kg), moisture (0.0%), ash (6.50%), C (83.50%), H (7.08%), N (not detected at level of 0.10%), O (1.72%), and S (1.20%).
Kevlar-belted, Proximate and Ultimate analyses: Energy content (39.20 MJ/kg), moisture (0.0%), ash (2.50%), C (86.50%), H (7.35%), N (not detected at level of 0.10%), O (2.11%), and S (1.49%).

Atal, Ajay, and Yiannis A. Levendis. “Comparison of the Combustion Behaviour [sic] of Pulverized Waste Tyres [sic] and Coal.” *Fuel* 74, no. 11 (1995): 1570-1581.

This article examines the combustion behavior of tire crumb and pulverized coal in a drop-tube furnace, *not a cement kiln*. Most of the paper is not relevant to our purposes, however, as it focuses on the physical behavior of the tire crumbs vs. pulverized coal during combustion and/or pyrolysis.

A good introduction summarizes the environmental and economic aspects of using tires or tire crumb as fuel.

About 250 million tires are disposed of in the USA every year, with about 200 million of these being landfilled. The number of accumulated tires in landfills could be as high as 3 billion. Storage of discarded tires is a fire hazard and tire fires release toxic pollutants. Tire dumps provide breeding opportunities for mosquitoes. Landfilled whole tires tend to move to the surface, interfering with settling.

Waste tires have a high heat value (28-37 MJ/kg), comparable to coal. They have a much higher volatile mass content (about 60%) than coal (about 30%), so incineration leads to about 90% mass reduction in waste materials (ash) that must be landfilled. Tires have low moisture content but higher chlorine and zinc content than coal. High temperatures (up to 1200°C) are required to minimize the formation of pollutants such as NO_x, PAHs, and PCDDs/PCDFs.

Whole tires require incinerator residence times of up to 1 hour to completely combust while allowing for the temperature control necessary to minimize NO_x emissions. Shredding or grinding tires reduces the residence times required and the smaller the particles the easier it is to achieve complete combustion. However, grinding increases the cost of the fuel. Cryogenically ground waste tires can cost as much as 3-5 times as much as pulverized coal.

Bituminous coal sample, analysis: Fixed C (51.9%), volatiles (34.4%), ash (13.7%), N (1.4%), and S (1.4%).

Waste tyre [sic] sample, analysis: Fixed C (33.6%), volatiles (58.7%), ash (7.7%), N (not available), and S (not available).

SBR (styrene-butadiene rubber crumbs) sample, analysis: Fixed C (26.3%), volatiles (65.0%), ash (8.7%), N (<0.5%), and S (1.7%).

Atal, Ajay, Yiannis A. Levendis, Joel Carlson, Yuriy Dunayevskiy, and Paul Vouros. “On the Survivability and Pyrosynthesis of PAH During Combustion of Pulverized Coal and Tire Crumb.” *Combustion and Flame* 110 (1997): 462-478.

This article examines the emissions of Polynuclear Aromatic Hydrocarbons from the combustion of tire crumb and pulverized coal in a drop-tube furnace, *not a cement kiln*.

PAHs were not detected in combustion emissions under fuel-lean conditions, but they were detected under fuel-rich conditions.

PAH species in the emissions were compared with PAHs in the original fuels. PAHs emitted were not the same ones present in the original sample but were products of pyrosynthesis during the combustion process.

Deuterated PAHs were adsorbed onto the samples of the original fuels. The deuterated species did not survive the combustion process under oxidative conditions.

Bituminous coal, analysis: Fixed C (51.9%), volatiles (34.4%), ash (13.7%), C (71.9%), H (4.7%), N (1.36%), O (7.0%), S (1.36%), and heating value (29 MJ/kg).

Ground tire, analysis: Fixed C (21.7%), volatiles (52.3%), ash (26.0%), C (60.9%), H (5.3%), N (0.28%), O (7.1%), S (2.46%), and heating value (29 MJ/kg).

California Integrated Waste Management Board. *Final Report: Environmental Factors of Waste Tire Pyrolysis, Gasification, and Liquefaction (July 1995),* by CalRecovery, Inc., Hercules, CA.

This is a report from a study about the recovery of materials and/or energy from waste tires by pyrolysis, gasification, or liquefaction, *not by combustion*. For this reason, most of the report is not relevant to our current purposes.

Table 3-1 compares analysis results for tires to those for waste plastics, waste oil, Municipal Solid Waste, and waste paper.

Whole tires, proximate analysis: Volatile matter (79.78%), fixed carbon (4.69%), ash (14.39%), moisture (1.14%)

Shredded tires, proximate analysis: Volatile matter (83.98%), fixed carbon (4.94%), ash (9.88%), moisture (1.20%)

Waste plastics, proximate analysis: Volatile matter (85.84%), fixed carbon (1.84%), ash (5.08%), moisture (7.24%)

Municipal Solid Waste (MSW), proximate analysis: Volatile matter (58.67%), fixed carbon (10.68%), ash (6.07%), moisture (24.58%)

Mixed paper, proximate analysis: Volatile matter (56.85%), fixed carbon (8.76%), ash (10.17%), moisture (24.22%)

Whole tires, ultimate analysis, dry basis: C (74.50%), H (6.00%), O (3.00%), S (1.50%), N (0.50%), Cl (1.00%), ash (13.50%)

Shredded tires, ultimate analysis, dry basis: C (77.60%), H (10.40%), O (0.00%), S (2.00%), N (not given), Cl (not given), ash (10.00%)

Waste plastics, ultimate analysis, dry basis: C (77.49%), H (12.76%), O (3.51%), S (0.18%), N (0.03%), Cl (0.55%), ash (5.48%)

Municipal Solid Waste (MSW), ultimate analysis, dry basis: C (45.65%), H (6.08%), O (37.10%), S (0.20%), N (1.12%), Cl (0.81%), ash (9.04%)

Mixed paper, ultimate analysis, dry basis: C (39.38%), H (5.94%), O (40.95%), S (0.09%), N (0.08%), Cl (0.15%), ash (13.42%)

Whole tires, trace metals analysis: Pb (51.50 mg/kg), Zn (45,500 mg/kg), Sb (not given), As (2.90 mg/kg), Cd (4.80 mg/kg), Hg (0.30 mg/kg), Mo (not given), Se (not given), Sn (not given)

Shredded tires, trace metals analysis: Pb (51.50 mg/kg), Zn (45,500 mg/kg), Sb (not given), As (2.90 mg/kg), Cd (4.80 mg/kg), Hg (0.30 mg/kg), Mo (not given), Se (not given), Sn (not given)

Waste plastics, trace metals analysis: Pb (199 mg/kg), Zn (73 mg/kg), Sb (10.70 mg/kg), As (2.20 mg/kg), Cd (0.40 mg/kg), Hg (0.02 mg/kg), Mo (not given), Se (0.002 mg/kg), Sn (151 mg/kg)

Municipal Solid Waste (MSW), trace metals analysis: Pb (354.4 mg/kg), Zn (870.8 mg/kg), Sb (2.7 mg/kg), As (9.7 mg/kg), Cd (10.4 mg/kg), Hg (0.4 mg/kg), Mo (23.0 mg/kg), Se (0.5 mg/kg), Sn (3.8 mg/kg)

Mixed paper, trace metals analysis: Pb (13.0 mg/kg), Zn (96.0 mg/kg), Sb (11.1 mg/kg), As (0.50 mg/kg), Cd (0.30 mg/kg), Hg (0.05 mg/kg), Mo (not given), Se (0.002 mg/kg), Sn (87.0 mg/kg)

Whole tires, heating value: 15,000 BTU/lb, 34,875 kJ/kg

Shredded tires, heating value: 11,330 BTU/lb, 26,342 kJ/kg

Waste plastics, heating value: 15,306 BTU/lb, 35,586 kJ/kg

Municipal Solid Waste (MSW), heating value: 6,756 BTU/lb, 15,708 kJ/kg

Mixed paper, heating value: 5,265 BTU/lb, 12,241 kJ/kg

California Integrated Waste Management Board. Policy, Research and Technical Assistance Committee. *Tires As a Fuel Supplement: Feasibility Study (January 1992),* by Bob Boughton, Tom Dietsch, Martha Gildart, and Fred Jager. Sacramento, CA. [received from CIWMB upon request]

This is a report from a feasibility study about the use of tires as a fuel supplement in California. The report reviews the production of waste tires and ways to reduce it, as well as the other uses of waste tires. The specific application of tire burning in the cement industry is also reviewed.

Appendix A contains a comparison of elemental analysis data for tires, western coal, Municipal Solid Waste/Refuse Derived Fuel, and biomass. The tire data may be for whole tires, since the table does not specify TDF or tire shreds. However, the Fe number looks pretty low. The values for S, Cl, and Zn are all higher for the tires than for the western coal sample, the Zn value dramatically so.

Tires: N (<0.1-0.8%); S (0.9-2.1%); C (64-87%); H (5-7%); O (1-5%); Ash (2-25%); Cl (0.07-0.2%); Al (8506 µg/MJ); As (61-120 µg/MJ); Cd (110-184 µg/MJ); Cr (98-2457 µg/MJ); Cu (921 µg/MJ); Fe (122,835 µg/MJ); Pb (1167-1996 µg/MJ); Mn (798 µg/MJ); Hg (1.5-15 µg/MJ); Ni (104 µg/MJ); Zn (460,631-2,333,866 µg/MJ); Heating value (14000 BTU/lb)

Western coal: N (0.3-1.4%); S (0.4-1.0%); C (30-72%); H (4-5%); O (9-26%); Ash (8-11%); Cl (0.04%); Al (no data); As (20-537 µg/MJ); Cd (2-179 µg/MJ); Cr (186-1385 µg/MJ); Cu (233-1026 µg/MJ); Fe (no data) µg/MJ); Pb (88-476 µg/MJ); Mn (287-3472 µg/MJ); Hg (2-9 µg/MJ); Ni (104-534 µg/MJ); Zn (186-8825 µg/MJ); Heating value (12500 BTU/lb)

MSW/RDF: N (0.3-0.8%); S (0.1-0.4%); C (27-33%); H (4%); O (26%); Ash (13-20%); Cl (0.3-0.8%); Al (no data); As (23-2392 µg/MJ); Cd (17-3538 µg/MJ); Cr (280-125623 µg/MJ); Cu (1946-180,039 µg/MJ); Fe (no data); Pb (877-136,663 µg/MJ); Mn (1059-48022 µg/MJ); Hg (<130-362 µg/MJ); Ni (90-51,564 µg/MJ); Zn (3018-303,716 µg/MJ); Heating value (6000 BTU/lb)

Biomass: N (0.1-4.5%); S (0.01-0.7%); C (13-72%); H (3-7%); O (3-47%); Ash (0.2-17%); Cl (no data); Al (no data); As (no data); Cd (no data); Cr (no data); Cu (no data); Fe (no data); Pb (no data); Mn (no data); Hg (no data); Ni (no data); Zn (no data); Heating value (6500-8500 BTU/lb)

Appendix B contains gaseous emissions test data from two cement plants co-burning tires and coal, comparing data from coal alone to coal + tires. Some values are lower for coal + tires, some are higher.

RMC Lonestar plant in Davenport, coal alone: kiln feed rate (200 tons/hr), NO_x (207 lbs/hr), SO_x (43 lbs/hr), PM (no data), CO (257 lbs/hr), THC (no data), benzene (0.403 lbs/hr), dioxins/furans (5.50×10^{-9} lbs/hr), formaldehyde (0.507 lbs/hr), PCB (0.000288 lbs/hr), PAHs (3.65×10^{-5}-1.22×10^{-4} lbs/hr), Al (0.00560 lbs/hr), As (1.35×10^{-5} lbs/hr), Ba (0.000839 lbs/hr), Be (1.36×10^{-5} lbs/hr), Cd (0.000125 lbs/hr), Ca (no data), Cr(VI) (6.31×10^{-5} lbs/hr), Cr(III) (no data lbs/hr), Cr (total) (0.000387 lbs/hr), Co (0.0011lbs/hr), Cu (0.025 lbs/hr), Fe (0.069 lbs/hr), Pb (0.0011 lbs/hr), Mg (0.17 lbs/hr), Mn (0.018 lbs/hr), Hg (0.21 lbs/hr), Mo (0.0017 lbs/hr), Ni (0.0028 lbs/hr), P (no data), Se (0.00016 lbs/hr), Si (0.061lbs/hr), Na (0.18 lbs/hr), Sr (0.00055 lbs/hr), Ti (0.00082 lbs/hr), V (0.00055 lbs/hr), Zn (0.0097 lbs/hr), Zr (0.00055 lbs/hr)

RMC Lonestar plant in Davenport, coal and tires: kiln feed rate (189 tons/hr), NO_x (162 lbs/hr), SO_x (45 lbs/hr), PM (no data), CO (244 lbs/hr), THC (no data), benzene (0.09 lbs/hr), dioxins/furans (4.4×10^{-9} lbs/hr), formaldehyde (11.8 lbs/hr), PCB ($9.0 v 10^{-6}$ lbs/hr), PAHs (3.8×10^{-7}-1.6×10^{-5} lbs/hr), Al (0.033 lbs/hr), As (7.7×10^{-5} lbs/hr), Ba (0.0061 lbs/hr), Be (0.00028 lbs/hr), Cd (0.0017 lbs/hr), Ca (0.68 lbs/hr), Cr(VI) (5.5×10^{-6} lbs/hr), Cr(III) (0.0003 lbs/hr), Cr (total) (no data), Co (0.000406 lbs/hr), Cu (0.000956 lbs/hr), Fe (0.150 lbs/hr), Pb (0.00527 lbs/hr), Mg (0.0156 lbs/hr), Mn (0.00968 lbs/hr), Hg (1.06×10^{-5} lbs/hr), Mo (0.000381 lbs/hr), Ni (0.00687 lbs/hr), P (no data), Se ($9.07 v 10^{-5}$ lbs/hr), Si (0.0749 lbs/hr), Na (no data), Sr (no data), Ti (0.00209 lbs/hr), V ($1.29 v 10^{-5}$ lbs/hr), Zn (0.00248 lbs/hr), Zr ($2.06 v 10^{-5}$ lbs/hr)

Southwestern Portland Cement plant in Victorville, coal alone: kiln feed rate (224 tons/hr), NO_x (6.26 lbs/hr), SO_x (4 lbs/hr), PM (11 lbs/hr), CO (250 lbs/hr), THC (11.5 lbs/hr), benzene (0.66 lbs/hr), dioxins/furans (5.91×10^{-7} lbs/hr), formaldehyde (0.0468 lbs/hr), PCB (no data), PAHs (1.18 x 10^{-5}-5.00 x 10^{-3} lbs/hr), Al (no data), As (.000310 lbs/hr), Ba (no data), Be (3.68 x 10^{-5} lbs/hr), Cd (0.00290 lbs/hr), Ca (no data), Cr(VI) (3.67 x 10^{-5} lbs/hr), Cr(III) (no data), Cr (total) (0.00118 lbs/hr), Co (no data), Cu (0.00409 lbs/hr), Fe (no data), Pb (0.00822 lbs/hr), Mg (no data), Mn (0.00423 lbs/hr), Hg (0.00148 lbs/hr), Mo (no data), Ni (0.000633 lbs/hr), P (0.0730 lbs/hr), Se (0.000243 lbs/hr), Si (no data), Na (no data), Sr (0.0640 lbs/hr), Ti (no data), V (no data), Zn (0.0560 lbs/hr), Zr (no data)

Southwestern Portland Cement plant in Victorville, coal and tires: kiln feed rate (216.7 tons/hr), NO_x (487.8 lbs/hr), SO_x (0.3 lbs/hr), PM (6.3 lbs/hr), CO (538 lbs/hr), THC (6.40 lbs/hr), benzene (0.15 lbs/hr), dioxins/furans (9.81 x 10^{-7} lbs/hr), formaldehyde (0.00933 lbs/hr), PCB (no data), PAHs (1.84 x 10^{-7}-1.15 x 10^{-3} lbs/hr), Al (no data), As (0.000120 lbs/hr), Ba (no data), Be (4.99 x 10^{-5} lbs/hr), Cd (0.000151 lbs/hr), Ca (no data), Cr(VI) (2.41 x 10^{-5} lbs/hr), Cr(III) (no data), Cr (total) (0.000775 lbs/hr), Co (no data), Cu (0.000646 lbs/hr), Fe (no data), Pb (0.000647 lbs/hr), Mg (no data), Mn (0.00367 lbs/hr), Hg (0.0193 lbs/hr), Mo (no data), Ni (0.000211 lbs/hr), P (0.0280 lbs/hr), Se (0.000120 lbs/hr), Si (no data), Na (no data), Sr (0.000499 lbs/hr), Ti (no data), V (no data), Zn (0.0193 lbs/hr), Zr (no data)

Granger, John E., and Gregory A. Clark. “Fuel Characterization of Coal/Shredded Tire Blends.” In *Proceedings: 1991 Conference on Waste Tires as a Utility Fuel, September 1991*. Palo Alto, Calif.: Electric Power Research Institute, 1991.

This article is a summary for a presentation given at a conference on using tires as fuel in the utility business. The authors compare analyses of three types/sizes of tire-derived fuel (½-in “fuzz”, 2-in with metal, 2-in without metal) with coal and with each other. The “2-in with wire” sample is the closest approximation to whole tires, in that the metal from the steel belts is not removed for most of the analyses (it was removed prior to analysis for minor/trace elements). Pieces of all three TDF types are irregularly sized and many of the “fuzz” samples still adhere to belt fabric.

Coal, Proximate analysis and heating value: Total moisture (7.76%); volatile matter (34.05%); fixed carbon (47.14%); ash (11.05%); heating value (12148 BTU/lb)

Tire-derived fuel, ½-in “fuzz”, Proximate analysis: Total moisture (2.26%); volatile matter (64.66%); fixed carbon (16.60%); ash (16.48%); heating value (13813 BTU/lb)

Tire-derived fuel, 2-in without metal, Proximate analysis: Total moisture (1.02%); volatile matter (67.31%); fixed carbon (22.93%); ash (8.74%); heating value (14019 BTU/lb)

Tire-derived fuel, 2-in with metal, Proximate analysis: Total moisture (0.75%); volatile matter (54.23%); fixed carbon (16.85%); ash (23.19%); heating value (13362 BTU/lb)

Coal, Ultimate analysis: Moisture (7.76%); C (67.69%); H (4.59%); N (1.13%); S (2.30%); ash (11.05%); Cl (0.01%); O (by diff.) (5.47%)

Tire-derived fuel, ½-in “fuzz”, Ultimate analysis: Moisture (2.26%); C (69.74%); H (6.30%); N (0.45%); S (1.30%); ash (16.48%); Cl (0.07%); O (by diff.) (3.40%)

Tire-derived fuel, 2-in without metal, Ultimate analysis: Moisture (1.02%); C (72.15%); H (6.74%); N (0.36%); S (1.23%); ash (8.74%); Cl (0.09%); O (by diff.) (9.67%)

Tire-derived fuel, 2-in with metal, Ultimate analysis: Moisture (0.75%); C (67.00%); H (5.81%); N (0.25%); S (1.33%); ash (23.19%); Cl (0.03%); O (by diff.) (1.64%)

Coal, ashes: SiO_2 (47.98%); Al_2O_3 (20.70%); Fe_2O_3 (18.89%); TiO_2 (0.82%); CaO (3.30%); MgO (0.79%); Na_2O (0.48%); K_2O (2.06%); SO_3 (4.33%); P_2O_5 (0.62%); ZnO (0.02%)

Tire-derived fuel, ½-in “fuzz”, ashes: SiO_2 (18.21%); Al_2O_3 (6.99%); Fe_2O_3 (30.93%); TiO_2 (6.01%); CaO (5.99%); MgO (0.73%); Na_2O (1.07%); K_2O (0.55%); SO_3 (8.35%); P_2O_5 (0.56%); ZnO (20.60%)

Tire-derived fuel, 2-in without metal, ashes: SiO_2 (22.00%); Al_2O_3 (9.09%); Fe_2O_3 (1.45%); TiO_2 (2.57%); CaO (10.64%); MgO (1.35%); Na_2O (1.10%); K_2O (0.92%); SO_3 (15.38%); P_2O_5 (1.03%); ZnO (34.50%)

Tire-derived fuel, 2-in “with metal” (actually steel belt removed), ashes: SiO_2 (5.16%); Al_2O_3 (1.93%); Fe_2O_3 (0.35%); TiO_2 (0.14%); CaO (0.56%); MgO (0.10%); Na_2O (0.13%); K_2O (0.14%); SO_3 (0.99%); P_2O_5 (0.10%); ZnO (5.14%); Metal (85.28%)

Coal, ashes: As_2O_3 (<0.10%); NiO (<0.06%); Cr_2O_3 (<0.06%); MoO_3 (<0.06%); V_2O_5 (<0.10%); CoO (<0.06%); MnO_2 (<0.06%); CuO (<0.10%); ZnO (0.02%); PbO (<0.06%); SnO_2 (<0.06%); ZrO_2 (<0.06%)

Tire-derived fuel, ½-in “fuzz”, ashes: As_2O_3 (<0.10%); NiO (<0.06%); Cr_2O_3 (<0.06%); MoO_3 (<0.06%); V_2O_5 (<0.10%); CoO (<0.06%); MnO_2 (0.10%); CuO (0.10%); ZnO (19.37%); PbO (0.06%); SnO_2 (<0.06%); ZrO_2 (<0.06%)

Tire-derived fuel, 2-in without metal, ashes: As_2O_3 (<0.10%); NiO (<0.06%); Cr_2O_3 (<0.06%); MoO_3 (<0.06%); V_2O_5 (<0.10%); CoO (<0.06%); MnO_2 (<0.06%); CuO (0.10%); ZnO (33.74%); PbO (<0.06%); SnO_2 (<0.06%); ZrO_2 (<0.06%)

Tire-derived fuel, 2-in “with metal” (actually steel belt removed), ashes: As_2O_3 (<0.10%); NiO (<0.06%); Cr_2O_3 (<0.06%); MoO_3 (<0.06%); V_2O_5 (<0.10%); CoO (<0.06%); MnO_2 (<0.06%); CuO (0.10%); ZnO (33.16%); PbO (0.40%); SnO_2 (<0.06%); ZrO_2 (<0.06%)

Gray, Terry. “Tire Derived Fuel: An Environmentally Friendly Resource.” *Rubber Recycling Symposium, in conjunction with the 74th Annual Meeting of the Rubber Association of Canada, 1994.* Toronto, Ont., March 3, 1994.

> This is a summary of a symposium presentation and is largely a general discussion of the use of tires as fuel. The discussion of gaseous emissions includes data from facilities burning TDF, compared to baseline data (no TDF). These facilities include utility boilers for a paper mill, Ohio Edison and Wisconsin Power and Light and three cement kilns.
>
> Champion International Mill, utility boiler, baseline: NO_x (0.274 lb/MM BTU), SO_x (0.508 lb/MM BTU), particulates (0.053 lb/MM BTU), total H (0.00117 lb/MM BTU), Be (1.06 x 10^{-6} lb/MM BTU), Cd (0.60 x 10^{-6} lb/MM BTU), Cr (12.1 x 10^{-6} lb/MM BTU), Pb (<10^{-6} lb/MM BTU), Zn (0.00026 lb/MM BTU)
>
> Champion International Mill, utility boiler, 14.5% TDF: NO_x (0.273 lb/MM BTU), SO_x (0.510 lb/MM BTU), particulates (0.056 lb/MM BTU), total H (0.00118 lb/MM BTU), Be (0.73 x 10^{-6} lb/MM BTU), Cd (0.78 x 10^{-6} lb/MM BTU), Cr (6.36 x 10^{-6} lb/MM BTU), Pb (<10^{-6} lb/MM BTU), Zn (0.000256 lb/MM BTU)
>
> Ohio Edison, utility boiler, baseline: SO_x (5.30 lb/MM BTU), NO_x (0.601 lb/MM BTU), particulates (0.0631 lb/MM BTU), Pb (96.3 x 10^{-6} lb/MM BTU)
>
> Ohio Edison, utility boiler, 10% tires: SO_x (5.71 lb/MM BTU), NO_x (0.436 lb/MM BTU), particulates (0.0564 lb/MM BTU), Pb (96.3 x 10^{-6} lb/MM BTU)
>
> Ohio Edison, utility boiler, 20% tires: SO_x (5.34 lb/MM BTU), NO_x (0.387 lb/MM BTU), particulates (0.0453 lb/MM BTU), Pb (91.2 x 10^{-6} lb/MM BTU)
>
> Wisconsin Power and Light, utility boiler, baseline: Particulates (0.52 lb/MM BTU), SO_x (1.14 lb/MM BTU), NO_x (0.79 lb/MM BTU), CO (1.52 lb/hr), hydrocarbons (5.16 lb/hr), HCl (25.77 lb/hr), HF (1.86 lb/hr)
>
> Wisconsin Power and Light, utility boiler, 7% TDF: Particulates (0.14 lb/MM BTU), SO_x (0.87 lb/MM BTU), NO_x (0.91 lb/MM BTU), CO (7.26 lb/hr), hydrocarbons (10.27 lb/hr), HCl (19.89 lb/hr), HF (1.34 lb/hr)
>
> Florida Crushed Stone, cement kiln, baseline: Particulates (56.80 lbs/hr), SO_2 (595.15 lbs/hr), acetone (0.02 lbs/hr), benzene (0.08 lbs/hr), toluene (0.01 lbs/hr), chloromethane (<0.01 lbs/hr), volatile organics (total) (0.15 lbs/hr), semi-volatile organics (C16-C18) (5.01 lbs/hr), Al (6.86 lbs/hr), As (<0.004 lbs/hr), Ba (0.02 lbs/hr), Cd (<0.005 lbs/hr), Cr (0.02 lbs/hr), Co (0.005 lbs/hr), Cu (0.03 lbs/hr), Fe (1.39 lbs/hr), Pb (0.13 lbs/hr), Mg (0.50 lbs/hr), Hg (0.04 lbs/hr), Mo (0.02 lbs/hr), Ni (<0.02 lbs/hr), Se (<0.004 lbs/hr), Ag (<0.009 lbs/hr), Ti (0.22 lbs/hr), V (<0.02 lbs/hr), Zn (3.12 lbs/hr), dioxins/furans (10.550 x 10^{-6} lbs/hr)
>
> Florida Crushed Stone, cement kiln, 14% TDF: Particulates (52.21 lbs/hr), SO_2 (551.30 lbs/hr), acetone (0.02 lbs/hr), benzene (0.15 lbs/hr), toluene (0.20 lbs/hr), chloromethane (0.03 lbs/hr), volatile organics (total) (0.44 lbs/hr), semi-volatile organics (C16-C18) (0.90 lbs/hr), Al (8.13 lbs/hr), As (<0.004 lbs/hr), Ba (0.02 lbs/hr), Cd (<0.005 lbs/hr), Cr (0.01 lbs/hr), Co (<0.002 lbs/hr), Cu (0.03 lbs/hr),

Fe (1.30 lbs/hr), Pb (0.04 lbs/hr), Mg (0.55 lbs/hr), Hg (0.01 lbs/hr), Mo (0.02 lbs/hr), Ni (<0.02 lbs/hr), Se (<0.004 lbs/hr), Ag (<0.009 lbs/hr), Ti (0.26 lbs/hr), V (<0.02 lbs/hr), Zn (1.68 lbs/hr), dioxins/furans (1.837 x 10^{-6} lbs/hr)

Ashgrove Cement, cement kiln, baseline: particulates (5.27 lbs/hr), SO_2 (<1.5 lbs/hr), chlorides (0.268 lbs/hr), total hydrocarbons (3.0 lbs/hr), PAHs (0.0058 lbs/hr), As (0.2 µg), Cd (3.0 µg), Cr (30 µg), Ni (30 µg), Zn (35 µg), Cu (37 µg), Pb (not detected), Fe (400 µg), Ba (not detected), V (not detected)

Ashgrove Cement, cement kiln, 9-10% TDF: (4.83 lbs/hr), SO2 (<1.2 lbs/hr), chlorides (0.197 lbs/hr), total hydrocarbons (3.3 lbs/hr), PAHs (0.0053 lbs/hr), As (0.2 µg), Cd (2.0 µg), Cr (not detected), Ni (not detected), Zn (35 µg), Cu (13 µg), Pb (not detected), Fe (200 µg), Ba (not detected), V (not detected)

Tillbury Cement, cement kiln, baseline (test 1, test 2): particulates (64.2, 67.9 mg/DSCF), HCl (2, 3 mg/DSCF), SO_x as SO_2 (3, 3 mg/DSCF), NO_x as NO_2 (877, 930 mg/DSCF), O_2 (13.3, 13.0 vol %), CO_2 (14.3, 14.8 vol %), Pb (0.013, 0.011 mg/DSCF), Sb (0.00045, 0.00034 mg/DSCF), Cu (0.0089, 0.0070 mg/DSCF), Mn (0.0019, 0.016 mg/DSCF), V (0.0009, 0.0010 mg/DSCF), Zn (0.046, 0.068 mg/DSCF), As (0.0011, 0.0013 mg/DSCF), Cr (0.0067, 0.0077 mg/DSCF), Co (0.00094, 0.00091 mg/DSCF), Ni (0.013, 0.011 mg/DSCF), Se (0.0015, 0.00035 mg/DSCF), Te (0.00023, 0.00019 mg/DSCF), Tl (<0.0059, <0.0063 mg/DSCF), Cd (0.0015, 0.0015 mg/DSCF), Hg (0.010, 0.007 mg/DSCF)

Tillbury Cement, cement kiln, 7% TDF (test 1, test 2): particulates (32.4, 31.6 mg/DSCF), HCl (<1, <1 mg/DSCF), SO_x as SO_2 (3, 4 mg/DSCF), NO_x as NO_2 (1062, 1123 mg/DSCF), O_2 (12.5, 13.0 vol %), CO_2 (14.5, 14.7 vol %), Pb (0.0016, 0.0024 mg/DSCF), Sb (0.00045, 0.00028 mg/DSCF), Cu (<0.001, <0.001 mg/DSCF), Mn (0.012, 0.0083 mg/DSCF), V (0.00035, 0.00032 mg/DSCF), Zn (0.039, 0.049 mg/DSCF), As (0.00051, 0.0022 mg/DSCF), Cr (0.0330, 0.0099 mg/DSCF), Co (0.00036, 0.00025 mg/DSCF), Ni (0.0135, 0.0065 mg/DSCF), Se (<0.0001, <0.0001 mg/DSCF), Te (0.00021, 0.00030 mg/DSCF), Tl (<0.0031, <0.0031 mg/DSCF), Cd (0.00075, 0.00058 mg/DSCF), Hg (<0.0019, <0.0019 mg/DSCF)

Hansen, Eric R. “Changing Process Priorities When Firing Alternate Fuels.” In *2003 IEEE Cement Industry Technical Conference*. Dallas, Texas: The Institute of Electrical and Electronics Engineers, Inc., Industry Applications Society, and the Portland Cement Association, 2003. 219-230.
(duplicated in another section)

This article describes the challenges presented by the substitution of alternate fuels for fossil fuels such as coal, with specific emphasis on whole tires. These challenges are categorized as lower flame temperature, difficulty in metering the alternate fuel feed (due to “lumpiness”), variable heating values of the alternate fuels (both because of “lumpiness” and because of inherent variability of fuels such as municipal waste), and difficulty with ignition. These challenges lead to loss of production, inferior clinker quality and/or poor kiln stability.

The author maintains that all of these problems can be minimized by shifting the process control emphasis from feed/fuel control to excess air (oxygen) control.

He states that many alternate fuel problems are related to localized reducing conditions around the fuel "lumps" themselves, but that increasing the oxygen supply too much creates problems itself. Careful monitoring of emissions of CO and SO_2 should allow the determination of the minimum requirement for kiln oxygen, and changes in the process can then be made to better control the oxygen level, thus reducing the problems associated with the fuel. Such process changes include using a bluff body burner, conversion to semi-indirect firing, improvements in the primary fuel flow uniformity, and better mixing of the kiln gases to reduce stratification which results in buildup.

Horvath, Michael. "Results of the Ohio Edison Whole-Tire Burn Test." In *Proceedings: 1991 Conference on Waste Tires as a Utility Fuel, September 1991.* 6.1-6.19. Palo Alto, Calif.: Electric Power Research Institute, 1991.

This article is a summary for a presentation given at a conference on using tires as fuel in the utility business.

Emissions results for co-firing tires with coal in a power plant boiler *(not a cement kiln)* are reported for levels of tires ranging from 0% to 20%. At 20% tires, when steady state was reached, emission rates were equivalent to coal for SO_2, 5% lower for Pb, 28% lower for particulates, and 36% lower for NO_x.

Emissions, 0% tires: SO_2 (ave., 5.30 lb/MM BTU), NO_x (ave., 0.601 lb/MM BTU), particulates (ave., 0.0631 lb/MM BTU), Pb (ave., 96.3 x 10^{-6} lb/MM BTU)

Emissions, 5% tires: SO_2 (ave., 5.73 lb/MM BTU), NO_x (ave., 0.510 lb/MM BTU), particulates (ave., 0.0717 lb/MM BTU), Pb (ave., 99.3 x 10^{-6} lb/MM BTU)

Emissions, 10% tires: SO_2 (ave., 5.71 lb/MM BTU), NO_x (ave., 0.436 lb/MM BTU), particulates (ave., 0.0564 lb/MM BTU), Pb (ave., 96.3 x 10^{-6} lb/MM BTU)

Emissions, 15% tires: SO_2 (ave., 5.47 lb/MM BTU), NO_x (ave., 0.443 lb/MM BTU), particulates (ave., 0.0815 lb/MM BTU), Pb (ave., 96.6 x 10^{-6} lb/MM BTU)

Emissions, 20% tires: SO_2 (ave., 5.34 lb/MM BTU), NO_x (ave., 0.387 lb/MM BTU), particulates (ave., 0.0453 lb/MM BTU), Pb (ave., 96.12 x 10^{-6} lb/MM BTU)

Fly ash and bottom ash samples were also analyzed for the TCLP metals, using the TCLP method and for "total metals" in the bottom ash. No data were obtained for "total metals" in the fly ash.

No differences could be seen in the data from the bottom ash samples, regardless of the amount of tires burned. Fly ash showed higher TCLP results for Cd and Pb for increasing amounts of tires. [It is important to note that there is not necessarily a relationship between "total metals" and TCLP metals.]

Human Health Evaluation of Cement Kiln Emissions from Coal Supplmented with Natural Gas and Coal Supplemented with Tires (March 2003), by J. Scott Klingensmith, Flatirons Technology, Inc. (prepared for CEMEX, Inc.). Boulder, CO.

This document describes two sets of emissions tests for test burn of tires co-burned in coal and coal co-burned with natural gas in a cement kiln in Lyons, Colorado. The Coal + TDF emissions are compared to those from Coal + Natural Gas (referred to as Fossil Fuels). The Coal +TDF emissions were significantly higher for formaldehyde, acetaldehyde and CO and significantly lower for NO_x and SO_x. Interestingly, the Zn emissions were NOT significantly higher (maybe because they were looking at metals in the particulate emissions?).

Emissions, Fossil Fuels only: particulates (M29 train) (8.76 lb/hr), particulates (M26A train) (9.52 lb/hr), NO_x (517.7 ppm), SO_x (26.2 ppm), total hydrocarbons (0.5 ppm), CO (50.3 ppm), HCl (0.66 lb/hr), Pb (0.0011 lb/hr), VOCs (0.2 lb/hr), total PAHs (0.2×10^{-6} lb/hr), total dioxins/furans (0.02 ng/mg^3), total PCBs (not detected), formaldehyde (0.05 lb/hr), acetaldehyde (0.07 lb/hr), chloromethane (not detected), carbon disulfide (0.031 lb/hr), acetone (not detected), methylene chloride (0.004 lb/hr), benzene (0.003 lb/hr), toluene (not detected), tetrachloroethene (not detected), bromomethane (0.005 lb/hr), 1,4-dioxane (0.026 lb/hr), ethanol (0.005 lb/hr), propylene (not detected), Sb (not detected), As (0.0000177 lb/hr), Ba (0.00931 lb/hr), Be (0.0000111 lb/hr), Cd (0.000717 lb/hr), Cr (0.000796 lb/hr), Co (0.000325 lb/hr), Cu (0.000744 lb/hr), Pb (0.00111 lb/hr), Mn (0.0073 lb/hr), Hg (0.00669 lb/hr), Ni (0.000882 lb/hr), Se (0.00177 lb/hr), Ag (0.000162 lb/hr), Tl (0.00344 lb/hr), Zn (0.00946 lb/hr)

Emissions, 19.2% TDF: particulates (M29 train) (9.68 lb/hr), particulates (M26A train) (9.07 lb/hr), NO_x (391.2 ppm), SO_x (15.7 ppm), total hydrocarbons (1.8 ppm), CO (120.2 ppm), HCl (0.63 lb/hr), Pb (0.0019 lb/hr), VOCs (0.9 lb/hr), total PAHs (1.0×10^{-6} lb/hr), total dioxins/furans (<0.02 ng/mg^3), total PCBs (not detected), formaldehyde (0.10 lb/hr), acetaldehyde (0.26 lb/hr), chloromethane (0.005 lb/hr), carbon disulfide (0.010 lb/hr), acetone (0.177 lb/hr), methylene chloride (0.013 lb/hr), benzene (0.101 lb/hr), toluene (0.008 lb/hr), tetrachloroethene (0.012 lb/hr), bromomethane (0.006 lb/hr), 1,4-dioxane (not detected), ethanol (not detected), propylene (0.007 lb/hr), Sb (not detected), As (0.000469 lb/hr), Ba (0.0107 lb/hr), Be (0.0000111 lb/hr), Cd (0.00161 lb/hr), Cr (0.00115 lb/hr), Co (0.00022 lb/hr), Cu (0.00147 lb/hr), Pb (0.00192 lb/hr), Mn (0.00856 lb/hr), Hg (0.00723 lb/hr), Ni (0.00119 lb/hr), Se (0.00390 lb/hr), Ag (0.00012 lb/hr), Tl (0.00535 lb/hr), Zn (0.0117 lb/hr)

Karell, Marc A., and Michael H. Blumenthal. “Air Regulatory Impacts of the Use of Tire-Derived Fuel.” *Environmental Progress* 20, no. 2 (2001): 80-86.

This article examines emissions from burning Tire Derived Fuel. Federal regulations, both current (2001) and expected are discussed. The authors mention the attractiveness of tires as fuels to the cement industry. *No actual air emissions data are reported*.

Bituminous coal, Ultimate analysis: C (75.8%), H (5.1%), O (8.2%), N (1.5%), S (1.6%), Cl (not listed), ash (7.8%), heating value (13,560 BTU/lb)

Passenger tires, Ultimate analysis: C (89.48%), H (7.61%), O (<0.01%), N (0.27%), S (1.88%), Cl (0.07%), ash (3.9%), heating value (15,843 BTU/lb)

> Truck tires, Ultimate analysis: C (89.65%), H (7.5%), O (<0.01%), N (0.25%), S (2.09%), Cl (0.06%), ash (5.5%), heating value (14,968 BTU/lb)
>
> TDF, Ultimate analysis: C (89.51%), H (7.59%), O (<0.01%), N (0.27%), S (1.92%), Cl (0.07%), ash (4.2%), heating value (15,688 BTU/lb)
>
> TDF, 96+% Wire Removed, Proximate Analysis: Moisture (0.62%), ash (4.78%), volatile matter (66.64%), fixed carbon (27.96%)
>
> TDF, 96+% Wire Removed, Ultimate Analysis: Moisture (0.62%), ash (4.78%), C (83.87%), H (7.09%), N (0.24%), S (1.23%), O by difference (2.17%)
>
> TDF, 96+% Wire Removed, Elemental Mineral Analysis (oxide form): zinc oxide (1.52%), calcium oxide (0.378%), iron oxide (0.321%), chlorine (0.149%), chromium oxide (0.0097%), fluoride (0.0010%), cadmium oxide (0.0006%), lead oxide (0.0065 %)
>
> TDF, 96+% Wire Removed, Heat value: HHV (16,250 BTU/lb), HV Ave (15,500 BTU/lb)
>
> TDF, 96+% Wire Removed, Combustion characteristics: Flash point (tires ignite) (288-343°C); carbon begins to burn (450°C); carbon completely burnt (650°C)

Keefe, Brian P., and Robert E. Shenk. “An Innovative Solution for Waste Utilization.” In *2003 IEEE Cement Industry Technical Conference*. Dallas, Texas: The Institute of Electrical and Electronics Engineers, Inc., Industry Applications Society, and the Portland Cement Association, 2003. 197-206.
(duplicated in another section)

> This article describes a combustion chamber designed to minimize problems associated with burning alternate fuels such as whole tires and allow higher substitutions of alternate fuel for fossil fuels in the precalciner. The bottom of the chamber, onto which the fuel is dropped, consists of a rotating disk. Hot kiln gases are piped in to combust the fuel. Hot gases from the combustion process are then used in the preheater/precalciner, while the ash and residue are swept into the kiln as the disk rotates.
>
> A working model of the chamber was installed at a Norwegian cement plant. The unit has been operated routinely at a precalciner fuel substitution rate of 40%. The chamber has been tested with up to 60% substitution but this could not be sustained due to problems with sulfur, alumina-iron balance, and other problems. CO and SO_2 emissions were “not significantly influenced” by burning these higher levels of tires, and NO_x emissions decreased. Although the plant generally burns shredded tires, the unit has been tested with whole tires. These required longer burn times, which was accommodated by decreasing the rotation speed of the disk.

Mukherjee, Arun B., Ursula Kääntee, and Ron Zevenhoven. “The Effects of Switching from Coal to Alternative Fuels on Heavy Metals Emissions from Cement Manufacturing.” In *Chemistry of Trace Elements in Fly Ash*. Eds., Kenneth S. Sajwan, Ashok K. Alva, and Robert F. Keefer. New York: Kluwer, 2003.

(duplicated in another section)

> This article is from a book compilation of papers presented at the Sixth International Conference on Biogeochemistry of Trace Elements, 2001. It discusses the use of scrap tires in Finland. Although Finland already (as of the presentation of this paper) recycled 90% of its scrap tires in road construction, there was still interest in burning tires as fuel for the cement process.
>
> Emissions from the Finnsementti Oy cement plant in Parainen, Finland, were monitored. The plant was using shredded tires to replace coal as the secondary fuel in the preheating system. Gas phase emissions and particulate emissions were sampled and analyzed. *Data are reported for clusters of metals, not for individual metals.* Emission of the more volatile and more toxic metals (Hg, Cd, Tl) decreased, while those of other metals increased. All metals emissions were below regulatory limits. The authors also state that the emissions of Hg and Tl shifted from the gas phase to particulates for the scrap tire fuel, making the emissions easier to control.
>
> 100% coal/petcoke: Hg (27 µg/m), Cd+Tl (15 µg/m),
> As+Cr+Cu+Mn+Ni+Pb+Sb+Sn+V (26 µg/m)
>
> 10% car tire scrap and 90% coal/petcoke: Hg (3 µg/m), Cd+Tl (13 µg/m),
> As+Cr+Cu+Mn+Ni+Pb+Sb+Sn+V (76 µg/m)

Schmidthals, Holger. "The Pre-Combustion Chamber for Secondary Fuels—Development Status of a New Technology." In *2003 IEEE Cement Industry Technical Conference*. Dallas, Texas: The Institute of Electrical and Electronics Engineers, Inc., Industry Applications Society, and the Portland Cement Association, 2003. 207-218. (duplicated in another section)

> This article describes a technology designed to minimize problems associated with burning alternate fuels such as whole tires or wood chunks. The fuel is dropped into a pre-combustion chamber where hot gases from the clinker cooler are piped in. The hot gases convert the fuel to a mixture of combustible gases, ash and coke, and, in the case of whole tires, metal wires. The combustible gases are then piped into the precalciner to be burnt there and the ash and coke are lifted out and sent to the precalciner as well, while the metal wires are allowed to drop into the kiln to be incorporated with the clinker.
>
> A pilot-scale working model of the chamber yielded good results, and two industrial-scale chambers have been installed at Swiss and German cement plants with acceptable results for tire combustion. Results for the latter installation can be summarized: (1) Volatiles are almost completely released by the gasification. (2) Separation efficiency of the solids (ash, coke vs. metal wires) is very high. (3) Energy flow into the kiln is even. (4) No impact on kiln operation by CO. (5) Kiln operation is more stable than it had been with direct introduction of tires into the kiln. The author thinks this technology could also be suitable for combustion of other difficult wastes such as carpet waste or car parts.

Schrama, Hans, Michael Blumenthal, and Edward C. Weatherhead. "A Survey of Tire Burning Technology for the Cement Industry." In *1995 IEEE Cement Industry Technical*

Conference. San Juan, Puerto Rico: The Institute of Electrical and Electronics Engineers, Inc., Industry Applications Society, 1995. 283-306.

This document discusses the logistics of burning tires at a cement plant. Analyses of three different types of rubber fuels are presented.

Tire Chip Fuel (containing bead and cord wire), Proximate analysis: Moisture (0.70%), ash (11.74%), volatile matter (61.68%), fixed carbon (25.88%)

Tire-Derived Fuel (relatively wire free), Proximate analysis: Moisture (0.62%), ash (4.78%), volatile matter (66.64%), fixed carbon (27.96%)

Rubber-Derived Fuel (metal and cord free), Proximate analysis: Moisture (0.52%), ash (4.33%), volatile matter (67.26%), fixed carbon (27.89%)

Tire Chip Fuel (containing bead and cord wire), Ultimate analysis: Moisture (0.70%), ash (11.74%), C (78.35%), H (6.62%), N (0.22%), S (1.15%), O (1.22%)

Tire-Derived Fuel (relatively wire free), Ultimate analysis: Moisture (0.62%), ash (4.78%), C (83.87%), H (7.09%), N (0.24%), S (1.23%), O (2.17%)

Rubber-Derived Fuel (metal and cord free), Ultimate analysis: Moisture (0.52%), ash (4.33%), C (84.21%), H (7.21%), N (0.24%), S (1.20%), O (2.29%)

Tire Chip Fuel (containing bead and cord wire), Elemental mineral analysis (oxide form): Fe (8.320%), Zn (1.398%), Ca (0.348%), Cl (0.137%), Cr (0.0089%), Pb (0.0060%), F (0.0009%), Cd (0.0006%)

Tire-Derived Fuel (relatively wire free), Elemental mineral analysis (oxide form): Fe (0.321%), Zn (1.520%), Ca (0.378%), Cl (0.149%), Cr (0.0097%), Pb (0.0065%), F (0.0010%), Cd (0.006%)

Rubber-Derived Fuel (metal and cord free), Elemental mineral analysis (oxide form): Fe (0.225%), Zn (1.350%), Ca (0.278%), Cl (0.119%), Cr (0.0037%), Pb (0.0043%), F (0.0090%), Cd (0.0003%)

Tire Chip Fuel (containing bead and cord wire), Heat value: HHV (14,950 BTU/lb), HVave (14,260 BTU/lb)

Tire-Derived Fuel (relatively wire free), Heat value: HHV (16,250 BTU/lb), HVave (15,500 BTU/lb)

Rubber-Derived Fuel (metal and cord free), Heat value: HHV (17,500 BTU/lb), HVave (16,050 BTU/lb)

Transportation costs, tire or TDF storage needs, and methods of introduction of tires or TDF into the kiln are discussed. The authors suggest that a kiln be operated with tires or TDF for a minimum of 30 days prior to testing to stabilize the kiln and acclimate the kiln operators to the new fuel regime.

The suggested sampling plan includes sampling at 1-hr intervals during the stack test period and at normal plant sampling intervals for the remainder of the trial run period. Sampling should include the kiln feed, kiln dust, clinker, coal, and all other fuels. Fuels should be analyzed for ultimate analysis and mineral ash content, as well as testing the tires/TDF for proximate analysis and heat value. Kiln dust samples should be analyzed for heavy metals, including zinc. Parameters that should be monitored include kiln feed rate, feed rates and proportions for the various fuels, clinker production and dust production, kiln shell temperatures, and damage to the kiln brick and/or coating. Gaseous emissions should also be monitored.

Results of a survey of 23 North American cement plants burning tires or TDF were presented for several parameters. Preheater/precalciner kilns burning whole tires were burning tires and substitution rates of 2.5-30%, while those burning shredded tires (whether tire chip fuel, tire-derived fuel, or rubber-derived fuel) had substitution rates of 6-10%. Some plants reported reduced production, and two had stopped burning tires as a consequence. The factors limiting tire substitution rates were buildups, reduced production, and the necessity of higher kiln O_2 levels.

Kilns burning whole tires showed a decrease in NO_x emissions (attributed to localized reducing conditions) and a local CO spike each time a whole tire entered the kiln system (attributed to the rubber temporarily using up all the available oxygen for combustion, i.e., localized reducing conditions). For some plants, this meant that the kiln had to operate at higher oxygen levels. Little change was observed in SO_2 emissions, in early or late strength or in setting time.

United States Environmental Protection Agency. National Risk Management Research Laboratory. *Air Emissions from Scrap Tire Combustion (October 1997),* by Joel I. Reisman. Research Triangle Park, NC.

This is a report on air emissions from combustion of scrap tires under various circumstances. The relevant section is Section 3.0 “Tires as Fuel”.

Gaseous emissions data from power plant (utilities) boilers, cement and lime kilns, pulp and paper mills, and other industrial boilers are reported. Overall, particulate and NO_x emissions tended to decrease as the amount of TDF fuel replacement increased. There was no discernable relationship between SO_2 emissions and amount of TDF fuel replacement. There were not enough data on CO emissions available to form any inferences.

The author points out that the smaller particulates produced by combustion of TDF as compared to coal will affect the performance of the Air Pollution Control Devices being used. Fabric filters and electrostatic precipitators are more effective than venturi scrubbers in removal of the smaller particulates found in TDF stack gases.

The author also points out that the size (whole, chunk, shred, or crumb) and type (wire-in or wire-removed) of TDF combusted will affect the gaseous emissions. Smaller pieces require shorter residence times and possibly lower temperatures to completely combust. Larger pieces make control of combustion temperatures and atmosphere (oxidizing or reducing) more difficult which makes NO_x control more difficult.

Power plant boilers data:

Facility A, 100% tires: particulates (2.2×10^{-6} lb/MMBTU), SO_x (1.4×10^{-5} lb/MMBTU), NO_x (9.8×10^{-5} lb/MMBTU), CO (7.2×10^{-5} lb/MMBTU)

Facility B, baseline: particulates (0.21 lb/MMBTU), SO_x (1.41 lb/MMBTU), NO_x (0.78 lb/MMBTU), CO (not tested)

Facility B, 5% TDF: particulates (0.015 lb/MMBTU), SO_x (1.80 lb/MMBTU), NO_x (0.58 lb/MMBTU), CO (not tested)

Facility B, 10% TDF: particulates (0.009 lb/MMBTU), SO_x (1.53 lb/MMBTU), NO_x (0.30 lb/MMBTU), CO (not tested)

Facility C, baseline: particulates (0.52 lb/MMBTU), SO_x (1.14 lb/MMBTU), NO_x (0.79 lb/MMBTU), CO (1.52 lb/MMBTU)

Facility C, 7% TDF: particulates (0.14 lb/MMBTU), SO_x (0.87 lb/MMBTU), NO_x (0.91 lb/MMBTU), CO (7.26 lb/MMBTU)

Facility D, baseline: particulates (0.063 lb/MMBTU), SO_x (5.30 lb/MMBTU), NO_x (0.601 lb/MMBTU), CO (not tested)

Facility D, 5% TDF: particulates (0.0717 lb/MMBTU), SO_x (5.73 lb/MMBTU), NO_x (0.510 lb/MMBTU), CO (not tested)

Facility D, 10% TDF: particulates (0.0564 lb/MMBTU), SO_x (5.71 lb/MMBTU), NO_x (0.436 lb/MMBTU), CO (not tested)

Facility D, 15% TDF: particulates (0.0815 lb/MMBTU), SO_x (5.47 lb/MMBTU), NO_x (0.443 lb/MMBTU), CO (not tested)

Facility D, 20% TDF: particulates (0.0453 lb/MMBTU), SO_x (5.34 lb/MMBTU), NO_x (0.387 lb/MMBTU), CO (not tested)

Facility E, baseline: particulates (0.083 lb/MMBTU), SO_x (0.021 lb/MMBTU), NO_x (0.19 lb/MMBTU), CO (not tested)

Facility E, 7% TDF: particulates (0.310 lb/MMBTU), SO_x (0.074 lb/MMBTU), NO_x (0.125 lb/MMBTU), CO (not tested)

Facility F, 2% TDF: particulates (0.17 lb/MMBTU), SO_x (5.78 lb/MMBTU), NO_x (not tested), CO (not tested)

Cement and lime kilns data:

Cement kiln 1, baseline: particulates (0.969 lb/MMBTU), SO_2 (0.276 lb/MMBTU), CO (0.046 ppm), aliphatic [organic] compounds (0.0011 lb/MMBTU), Ni (30 µg), Cd (3.0 µg), Cr (30 µg), Pb (not detected), Zn (35 µg), As (0.2 µg), Cl (0.268 lb/hr), Cu (37 µg), Fe (400 µg)

Cement kiln 1, 9-10% TDF: particulates (0.888 lb/MMBTU), SO_2 (0.221 lb/MMBTU), CO (0.036 ppm), aliphatic [organic] compounds (0.0009 lb/MMBTU), Ni (not detected), Cd (2.0 µg), Cr (not detected), Pb (not detected), Zn (35 µg), As (0.2 µg), Cl (0.197 lb/hr), Cu (13 µg), Fe (200 µg)

Cement kiln 2, baseline: acenaphthalene (2.76 x 10^{-6} lb/MMBTU), acenaphthylene (0.22 x 10^{-6} lb/MMBTU), anthracene (2.46 x 10^{-6} lb/MMBTU), benzo(b)anthracene (9.88 x 10^{-6} lb/MMBTU), benzoic acid (10.46 x 10^{-6} lb/MMBTU), benzo(a)pyrene (2.04 x 10^{-6} lb/MMBTU), benzo(g,h,i)perylene (not detected), bis(2-chloroethoxy)methane (222.42 x 10^{-6} lb/MMBTU), butylbenzylphthalate (5.98 x 10^{-6} lb/MMBTU), dibenz(g,h)phthracene (106.69 x 10^{-6} lb/MMBTU), di-n-butylphthalate (2.23 x 10^{-6} lb/MMBTU), 1,2-dichlorobenzene (3.21 x 10^{-6} lb/MMBTU), 2,4-dinitrotoluene (13.37 x 10^{-6} lb/MMBTU), fluorene (7.65 x 10^{-6} lb/MMBTU), hexachlorobenzene (73.49 x 10^{-6} lb/MMBTU), naphthalene (340.00 x 10^{-6} lb/MMBTU), 2-nitroaniline (4.67 x 10^{-6} lb/MMBTU), N-nitrosodiphenylamine (90.81 x 10^{-6} lb/MMBTU), pyrene (4.97 x 10^{-6} lb/MMBTU), 1,2,4-trichlorobenzene (17.45 x 10^{-6} lb/MMBTU), 4,6-dinitro-2-methylphenol (5.53 x 10^{-6} lb/MMBTU), 4-methylphenol (19.55 x 10^{-6} lb/MMBTU), 2-nitrophenol (194.99 x 10^{-6} lb/MMBTU), 4-nitrophenol (not detected), pentachlorophenol (not detected), phenol (32 x 10^{-6} lb/MMBTU), 2,4,5-trichlorophenol (not detected)

Cement kiln 2, 11% TDF: acenaphthalene (2.01 x 10^{-6} lb/MMBTU), acenaphthylene (not detected), anthracene (not detected), benzo(b)anthracene (not detected), benzoic acid (not detected), benzo(a)pyrene (not detected), benzo(g,h,i)perylene (3.00 x 10^{-6} lb/MMBTU), bis(2-chloroethoxy)methane (173.45 x 10^{-6} lb/MMBTU), butylbenzylphthalate (not detected), dibenz(g,h)phthracene (47.67 x 10^{-6} lb/MMBTU), di-n-butylphthalate (not detected), 1,2-dichlorobenzene (not detected), 2,4-dinitrotoluene (9.97 x 10^{-6} lb/MMBTU), fluorene (7.03 x 10^{-6} lb/MMBTU), hexachlorobenzene (40.42 x 10^{-6} lb/MMBTU), naphthalene (178.94 x 10^{-6} lb/MMBTU), 2-nitroaniline (not detected), N-nitrosodiphenylamine (47.60 x 10^{-6} lb/MMBTU), pyrene (2.38 x 10^{-6} lb/MMBTU), 1,2,4-trichlorobenzene (2.57 x 10^{-6} lb/MMBTU), 4,6-dinitro-2-methylphenol (not detected), 4-methylphenol (9.13 x 10^{-6} lb/MMBTU), 2-nitrophenol (169.18 x 10^{-6} lb/MMBTU), 4-nitrophenol (49.62 x 10^{-6} lb/MMBTU), pentachlorophenol (not detected), phenol (161.04 x 10^{-6} lb/MMBTU), 2,4,5-trichlorophenol (not detected)

Cement kiln 2, 14% TDF: acenaphthalene (2.06 x 10^{-6} lb/MMBTU), acenaphthylene (not detected), anthracene (not detected), benzo(b)anthracene (not detected), benzoic acid (not detected), benzo(a)pyrene (not detected), benzo(g,h,i)perylene (10.33 x 10^{-6} lb/MMBTU), bis(2-chloroethoxy)methane (275.75 x 10^{-6} lb/MMBTU), butylbenzylphthalate (not detected), dibenz(g,h)phthracene (67.17 x 10^{-6} lb/MMBTU), di-n-butylphthalate (not detected), 1,2-dichlorobenzene (not detected), 2,4-dinitrotoluene (9.00 x 10^{-6} lb/MMBTU), fluorene (7.12 x 10^{-6} lb/MMBTU), hexachlorobenzene (53.46 x 10^{-6}

lb/MMBTU), naphthalene (159.20 x 10^{-6} lb/MMBTU), 2-nitroaniline (5.02 x 10^{-6} lb/MMBTU), N-nitrosodiphenylamine (49.92 x 10^{-6} lb/MMBTU), pyrene (2.23 x 10^{-6} lb/MMBTU), 1,2,4-trichlorobenzene (not detected), 4,6-dinitro-2-methylphenol (not detected), 4-methylphenol (15.28 x 10^{-6} lb/MMBTU), 2-nitrophenol (172.12 x 10^{-6} lb/MMBTU), 4-nitrophenol (29.77 x 10^{-6} lb/MMBTU), pentachlorophenol (not detected), phenol (306.71 x 10^{-6} lb/MMBTU), 2,4,5-trichlorophenol (not detected)

Lime kiln, baseline: anthracene (3.7 x 10^{-6} lb/MMBTU), phenanthrene (51.9 x 10^{-6} lb/MMBTU), fluoranthene (8.6 x 10^{-6} lb/MMBTU), pyrene (6.6 x 10^{-6} lb/MMBTU), benzo(a)anthracene (1.1 x 10^{-6} lb/MMBTU), chrysene (1.1 x 10^{-6} lb/MMBTU), benzo(b)fluoranthene (0.8 x 10^{-6} lb/MMBTU), benzo(k)fluoranthene (0.3 x 10^{-6} lb/MMBTU), As (1.9 x 10^{-6} lb/MMBTU), Cu (3.2 x 10^{-6} lb/MMBTU), Zn (28.8 x 10^{-6} lb/MMBTU), Fe (231.7 x 10^{-6} lb/MMBTU), Ni (5.6 x 10^{-6} lb/MMBTU), Cr (83.3 x 10^{-6} lb/MMBTU), Cd (1.4 x 10^{-6} lb/MMBTU), Pb (4.1 x 10^{-6} lb/MMBTU), V (5.7 x 10^{-6} lb/MMBTU), Ba (24.9 x 10^{-6} lb/MMBTU)

Lime kiln, 15% TDF: anthracene (1.8 x 10^{-6} lb/MMBTU), phenanthrene (29.1 x 10^{-6} lb/MMBTU), fluoranthene (8.8 x 10^{-6} lb/MMBTU), pyrene (6.2 x 10^{-6} lb/MMBTU), benzo(a)anthracene (1.1 x 10^{-6} lb/MMBTU), chrysene (1.1 x 10^{-6} lb/MMBTU), benzo(b)fluoranthene (0.8 x 10^{-6} lb/MMBTU), benzo(k)fluoranthene (0.4 x 10^{-6} lb/MMBTU), As (3.5 x 10^{-6} lb/MMBTU), Cu (2.9 x 10^{-6} lb/MMBTU), Zn (427.7 x 10^{-6} lb/MMBTU), Fe (168.3 x 10^{-6} lb/MMBTU), Ni (3.5 x 10^{-6} lb/MMBTU), Cr (318.6 x 10^{-6} lb/MMBTU), Cd (1.3 x 10^{-6} lb/MMBTU), Pb (1.3 x 10^{-6} lb/MMBTU), V (3.8 x 10^{-6} lb/MMBTU), Ba (52.1 x 10^{-6} lb/MMBTU)

United States Environmental Protection Agency. *Pilot Scale Evaluation of the Potential for Emissions of Hazardous Air Pollutants from Combustion of Tire-Derived Fuel (April 1994),* by Paul M. Lemieux. Research Triangle Park, NC.

This article describes the use of a rotary kiln incinerator simulator to examine emissions from the incineration of scrap tire material. The TDF (wire-free crumb) is co-incinerated with natural gas to minimize effects from impurities in the second fuel.

TDF, Proximate analysis: Moisture (0.84%), volatile matter (65.52%), ash (7.20%), fixed carbon (26.44%)

TDF, Ultimate analysis: Moisture (0.84%), C (76.02%), H (7.23%), Kjeldahl N (0.34%), S (1.75%), total halogens (calc. as Cl) (0.31%), ash (7.20%)

TDF, metals: Cd (<5 ppm), Cr (<5 ppm), Fe (295 ppm), Pb (51 ppm), Zn (2.14%)

TDF, heating value: 7666 kJ/kg

The author examines gaseous emissions, fly ash, and bottom ash for organic and inorganic materials.

Metals, Stack emissions, baseline conditions: Sb (0.18 µg/m^3), As (1.12 µg/m^3), Be (not detected), Cd (0.41 µg/m^3), Cr (0.65 µg/m^3), Pb (8.05 µg/m^3), Mn (2.82 µg/m^3), Ni (0.71 µg/m^3), Se (0.83 µg/m^3), Zn (286.94 µg/m^3)

Metals, Stack emissions, 17% TDF, steady-state conditions: Sb (2.11 µg/m^3), As (37.16 µg/m^3), Be (0.05 µg/m^3), Cd (1.06 µg/m^3), Cr (3.88 µg/m^3), Pb (65.96 µg/m^3), Mn (5.79 µg/m^3), Ni (3.51 µg/m^3), Se (4.50 µg/m^3), Zn (35,465 µg/m^3)

Metals, Fly ash, 17% TDF (run 3, run 6): Al (2.8, 1.9 wt%), Ca (3.1, 2.9 wt%), Cr (0.002, 0.01 wt%), Co (0.005, 0.01 wt%), Cu (0.002, 0.0001 wt%), Fe (0.86, 0.83 wt%), Pb (0.001, 0.0009 wt%), Mg (0.86, 0.95 wt%), Ni (0.007, 0.003 wt%), P (0.001, 0.0001 wt%), K (0.58, 0.58 wt%), Si (32, 32 wt%), Na (0.68, 1.2 wt%), Sr (0.002, 0.01 wt%), S (0.0004, 0.0003 wt%), Ti (0.15, 0.084 wt%), Zn (2.4, 5.2 wt%), Zr (0.01, 0.01 wt%)

Most experiments were conducted with TDF being fed continuously. One experiment was conducted in batch mode (300 g batches being loaded every 10 minutes), to simulate the feeding of whole tires. Another experiment used continuous TDF feed but ramped the kiln air flow rate up and down every 10 minutes to simulate the local reducing conditions caused by whole tire feeding.

Some gaseous emissions data (CO, total hydrocarbons (THC), and PAHs) were dramatically different for the batch-feed experiment when compared to data from the other experiments done in continuous-feed mode, while data from the experiment in which the kiln air flow rate was ramped up and down were similar to the other continuous-feed experiments. Gaseous emissions in the batch-feed experiments followed a pattern of a high emissions “spike” followed by settling to background levels.

Range for continuous-feed experiments, Kiln exit: CO (16-59 ppm), THC (-1-3 ppm)

Batch-feed experiment, Kiln exit: CO (700 ppm), THC (43 ppm)

Range for continuous-feed experiments, Secondary Combustion Chamber exit: CO (12-20 ppm), THC (-2-0 ppm), PAH (404-3,289 ng/m^3)

Batch-feed experiment, Secondary Combustion Chamber exit: CO (70 ppm), THC (6 ppm), PAH (214,000 ng/m^3)

VII. Poultry Litter, Trace Metals in and/or Combustion of

Abelha, P., I. Gulyurtlu, D. Boavida, J. Seabra Barros, I. Cabrita, J. Leahy, B. Kelleher, M. Leahy, and A.M. Henihan. “Combustion of Poultry Litter in a Fluidised [sic] Bed Combustor.” *Fuel* 82 (2003): 687-692.

This article examines the combustion of poultry litter in a fluidized bed combustor, *not a cement kiln*. A comparison is made between the combustion of poultry litter alone and its co-combustion with peat in a 50-50 mixture. Aspects of the combustion process were examined, and the emissions and ash content were analyzed.

It was found that, as long as the moisture content of the poultry litter was below 25%, there were no combustion problems. Higher levels of moisture created blocking of the screw feeder used to load the litter into the combustor, leading to unstable burning. Proximate and Ultimate analysis data are reported for the chicken litter. Proximate (as received): Moisture-43%, Volatile matter-38.9%, Fixed carbon-1.7%, Ash-16.4%. Ultimate (dry basis): C-28.17%, H-3.64%, N-3.78%, S-0.55%, Cl-0.63%, O-34.43%. HHV was reported as 106.20 kJ/kg.

Large quantities of ash were created when the poultry litter was burned. Metals data for the poultry litter ash (*not the unburned litter*) are given for K (3.1%), Mn (596 ppm), Zn (209 ppm), Cu (71 ppm), and Cr (1112 ppm). HCl was emitted during the burning process (56 ppm when 100% chicken litter was burned). This was attributed to the high levels of Cl present in the litter. Cl present in the ash (no amount given) accounted for about 70% of the Cl in the litter. Changes in air staging in the combustor reduced gaseous emissions of NOx, CO, and volatile organics.

Cang, Long, Yu-jun Wang, Dong-mei Zhou, and Yuan-hua Dong. “Heavy Metals Pollution in Poultry and Livestock Feeds and Manures under Intensive Farming in Jiangsu Province, China.” *Journal of Environmental Sciences* 16, no. 3 (2004): 371-374.

This article analyzes 97 animal feeds and manures (including poultry manures) from Jiangsu Province for heavy metals and calculates the yearly heavy metal loading for soils to which these manures would be applied.

Analysis results showed that most feed samples contained metals concentrations exceeding the national standard. Levels of metals in manures (<0.2 µg/kg-1726.3 mg/kg) were considerably higher than those in feeds (<0.2 µg/kg-472.25 mg/kg).

Chicken feed: Zn (35.76-399.36 mg/kg), Cu (6.09-50.50 mg/kg), Cr (6.57-162.36 mg/kg), Ba (4.58-36.74 mg/kg), Mn (57.29-472.25 mg/kg), Sr (12.15-75.63 mg/kg), Ti (6.49-48.55 mg/kg), Pb (3.07-14.41 mg/kg), Cd (0.08-2.81 mg/kg), Ni (0.12-91.80 mg/kg), Co (0.11-1.31 mg/kg), Mo (0.26-5.56 mg/kg), As (<4-138.0 µg/kg), Hg (<0.2-33.4 µg/kg)

Chicken manure: Zn (175.3-964.7 mg/kg), Cu (20.7-569.7 mg/kg), Cr (38.76-269.11 mg/kg), Ba (28.21-180.24 mg/kg), Mn (207.1-1117.3 mg/kg), Sr (48.24-299.21 mg/kg), Ti (31.6-351.89 mg/kg), Pb (2.92-20.31 mg/kg), Cd (0.31-11.32 mg/kg), Ni (6.91-31.4 mg/kg), Co (0.24-5.71 mg/kg), Mo (1.20-6.75 mg/kg), As (<4-553 µg/kg), Hg (1.2-77.3 µg/kg)

Duck feed: Zn (138.5-173.3 mg/kg), Cu (18.21-23.5 mg/kg), Cr (11.56-13.44 mg/kg), Ba (11.32-11.64 mg/kg), Mn (128.53-186.47 mg/kg), Sr (9.10-11.13 mg/kg), Ti (10.71-11.15 mg/kg), Pb (2.38-10.90 mg/kg), Cd (0.04-0.97 mg/kg), Ni (1.57-3.14 mg/kg), Co (0.40-0.53 mg/kg), Mo (0.13-0.64 mg/kg), As (<4-8 µg/kg), Hg (9.6-17.5 µg/kg)

Duck manure: Zn (434.8-446.4 mg/kg), Cu (41.69-52.21 mg/kg), Cr (44.74-44.96 mg/kg), Ba (79.53-84.44 mg/kg), Mn (574.2-578.1 mg/kg), Sr (47.14-49.45 mg/kg), Ti (45.07-55.05 mg/kg), Pb (4.27-4.74 mg/kg), Cd (0.27-0.29 mg/kg), Ni

(10.22-10.59 mg/kg), Co (0.95-1.79 mg/kg), Mo (1.17-2.44 mg/kg), As (6-6 µg/kg), Hg (7.5-50.5 µg/kg)

Goose feed: Zn (33.79-159.59 mg/kg), Cu (7.67-17.90 mg/kg), Cr (3.76-7.16 mg/kg), Ba (4.50-4.90 mg/kg), Mn (32.75-136.28 mg/kg), Sr (3.14-12.17 mg/kg), Ti (2.89-11.79 mg/kg), Pb (6.99-9.29 mg/kg), Cd (0.31-0.75 mg/kg), Ni (0.99-1.50 mg/kg), Co (0.024-0.172 mg/kg), Mo (<0.1-1.956 mg/kg), As (<4-61 µg/kg), Hg (<0.2-0.3 µg/kg)

Goose manure: Zn (66.33-88.51 mg/kg), Cu (11.78-17.64 mg/kg), Cr (45.14-64.35 mg/kg), Ba (187.7-217.4 mg/kg), Mn (421.7-601.5 mg/kg), Sr (59.19-65.01 mg/kg), Ti (821.4-1264.6 mg/kg), Pb (16.86-19.55 mg/kg), Cd (1.05-1.75 mg/kg), Ni (32.23-32.74 mg/kg), Co (8.37-10.51 mg/kg), Mo (0.21-1.08 mg/kg), As (6-7 µg/kg), Hg (<0.2-44.7 µg/kg)

Dove feed: Zn (25.32-31.64 mg/kg), Cu (4.06-6.75 mg/kg), Cr (6.16-9.77 mg/kg), Ba (1.49-8.87 mg/kg), Mn (15.49-57.35 mg/kg), Sr (1.49-3.01 mg/kg), Ti (2.84-5.29 mg/kg), Pb (3.16-4.01 mg/kg), Cd (0.04-0.16 mg/kg), Ni (1.99-4.77 mg/kg), Co (<0.01-0.49 mg/kg), Mo (<0.1-1.33 mg/kg), As (<4 µg/kg), Hg (<0.2-2.4 µg/kg)

Dove manure: Zn (142.16-242.2 mg/kg), Cu (18.15-26.51 mg/kg), Cr (56.02-168.58 mg/kg), Ba (34.29-43.21 mg/kg), Mn (111.5-287.0 mg/kg), Sr (80.34-95.00 mg/kg), Ti (46.27-53.74 mg/kg), Pb (0.53-37.57 mg/kg), Cd (0.23-0.42 mg/kg), Ni (10.96-21.8 mg/kg), Co (0.01-2.06 mg/kg), Mo (1.54-3.49 mg/kg), As (6-21 µg/kg), Hg (19.0-118.3 µg/kg)

Collins, Eldridge, R., Jr., James C. Barker, Lewis E. Carr, Herbert L. Brodie, and John H. Martin, Jr. *Poultry Waste Management Handbook*. Ithaca, NY: NRAES (Natural Resource, Agriculture, and Engineering Service), 1999.

This article examines the management of poultry waste in many aspects. There are separate sections on environmental regulations, storage, treatment, and land application equipment, as well as the analysis of poultry waste.

The chapter relevant to this work is Chapter One, which contains a discussion of manure and several tables of data for different types of poultry wastes.

Manure characteristics, as excreted:

Commercial layer: Density (62 lbs/ft^3), Total Solids (25%), Volatile Solids (19%), Total Kjehldahl N (27 lbs/ton), NH_3 N (6.6 lbs/ton), P_2O_5 (21 lbs/ton), K_2O (12 lbs/ton), Ca (41 lbs/ton), Mg (4.3 lbs/ton), S (4.3 lbs/ton), Na (3.6 lbs/ton), Cl (20 lbs/ton), Fe (2.0 lbs/ton), Mn (0.16 lbs/ton), B (0.05 lbs/ton), Zn (0.14 lbs/ton), Cu (0.02 lbs/ton)

Broiler: Density (64 lbs/ft^3), Total Solids (26%), Volatile Solids (19%), Total Kjehldahl N (26 lbs/ton), NH_3 N (6.7 lbs/ton), P_2O_5 (16 lbs/ton), K_2O (12 lbs/ton), Ca (10 lbs/ton), Mg (3.5 lbs/ton), S (2.0 lbs/ton), Na (3.5 lbs/ton), Cl (18 lbs/ton), Fe (1.9 lbs/ton), Mn (0.20 lbs/ton), B (0.06 lbs/ton), Zn (0.084 lbs/ton), Cu (0.02 lbs/ton)

Turkey: Density (63 lbs/ft^3), Total Solids (25%), Volatile Solids (19%), Total Kjehldahl N (28 lbs/ton), NH_3 N (8.1 lbs/ton), P_2O_5 (24 lbs/ton), K_2O (12 lbs/ton), Ca (27 lbs/ton), Mg (3.1 lbs/ton), S (3.3 lbs/ton), Na (2.8 lbs/ton), Cl (18 lbs/ton), Fe (3.2 lbs/ton), Mn (0.10 lbs/ton), B (0.06 lbs/ton), Zn (0.62 lbs/ton), Cu (0.03 lbs/ton)

Duck: Density (62 lbs/ft^3), Total Solids (27%), Volatile Solids (16%), Total Kjehldahl N (28 lbs/ton), NH_3 N (7.4 lbs/ton), P_2O_5 (23 lbs/ton), K_2O (17 lbs/ton), Ca (29 lbs/ton), Mg (4.1 lbs/ton), S (3.6 lbs/ton), Na (3.5 lbs/ton), Cl (20 lbs/ton), Fe (2.8 lbs/ton), Mn (0.17 lbs/ton), B (0.06 lbs/ton), Zn (0.48 lbs/ton), Cu (0.03 lbs/ton)

Litter characteristics, as removed from production houses (typical litter base is sawdust, wood shavings, or peanut hulls):

Broiler [chicken], whole litter: Density (32 lbs/ft^3), Total Solids (79%), Volatile Solids (63%), Total Kjehldahl N (71 lbs/ton), NH_3 N (12 lbs/ton), P_2O_5 (69 lbs/ton), K_2O (47 lbs/ton), Ca (43 lbs/ton), Mg (8.8 lbs/ton), S (12 lbs/ton), Na (13 lbs/ton), Cl (13 lbs/ton), Fe (1.2 lbs/ton), Mn (0.79 lbs/ton), B (0.057 lbs/ton), Zn (0.71 lbs/ton), Cu (0.53 lbs/ton)

Broiler [chicken], manure cake: Density (34 lbs/ft^3), Total Solids (60%), Volatile Solids (47%), Total Kjehldahl N (46 lbs/ton), NH_3 N (12 lbs/ton), P_2O_5 (53 lbs/ton), K_2O (36 lbs/ton), Ca (34 lbs/ton), Mg (7.0 lbs/ton), S (9.2 lbs/ton), Na (10 lbs/ton), Cl (not available), Fe (1.2 lbs/ton), Mn (0.69 lbs/ton), B (0.044 lbs/ton), Zn (0.60 lbs/ton), Cu (0.41 lbs/ton)

Roaster [chicken], whole litter: Density (29 lbs/ft^3), Total Solids (76%), Volatile Solids (59%), Total Kjehldahl N (69 lbs/ton), NH_3 N (16 lbs/ton), P_2O_5 (70 lbs/ton), K_2O (47 lbs/ton), Ca (41 lbs/ton), Mg (8.4 lbs/ton), S (14 lbs/ton), Na (13 lbs/ton), Cl (not available), Fe (1.6 lbs/ton), Mn (0.76 lbs/ton), B (0.047 lbs/ton), Zn (0.68 lbs/ton), Cu (0.49 lbs/ton)

Cornish [chicken], whole litter: Density (30 lbs/ft^3), Total Solids (68%), Volatile Solids (53%), Total Kjehldahl N (59 lbs/ton), NH_3 N (12 lbs/ton), P_2O_5 (57 lbs/ton), K_2O (59 lbs/ton), Ca (41 lbs/ton), Mg (22 lbs/ton), S (not available), Na (not available), Cl (not available), Fe (not available), Mn (1.1 lbs/ton), B (not available), Zn (0.92 lbs/ton), Cu (0.61 lbs/ton)

Cornish [chicken], manure cake: Density (34 lbs/ft^3), Total Solids (54%), Volatile Solids (42%), Total Kjehldahl N (62 lbs/ton), NH_3 N (17 lbs/ton), P_2O_5 (39 lbs/ton), K_2O (39 lbs/ton), Ca (30 lbs/ton), Mg (14 lbs/ton), S (not available), Na (not available), Cl (not available), Fe (not available), Mn (0.67 lbs/ton), B (not available), Zn (0.50 lbs/ton), Cu (0.46 lbs/ton)

Breeder [chicken], whole litter: Density (50 lbs/ft^3), Total Solids (69%), Volatile Solids (29%), Total Kjehldahl N (37 lbs/ton), NH_3 N (8.0 lbs/ton), P_2O_5 (58 lbs/ton), K_2O (35 lbs/ton), Ca (83 lbs/ton), Mg (8.2 lbs/ton), S (7.8 lbs/ton), Na (8.3 lbs/ton), Cl (not available), Fe (1.2 lbs/ton), Mn (0.69 lbs/ton), B (0.034 lbs/ton), Zn (0.62 lbs/ton), Cu (0.23 lbs/ton)

Turkey poult, whole litter: Density (23 lbs/ft^3), Total Solids (80%), Volatile Solids (62%), Total Kjehldahl N (40 lbs/ton), NH_3 N (9.6 lbs/ton), P_2O_5 (43 lbs/ton), K_2O (27 lbs/ton), Ca (26 lbs/ton), Mg (5.1 lbs/ton), S (6.1 lbs/ton), Na (4.7 lbs/ton), Cl (1.8 lbs/ton), Fe (2.0 lbs/ton), Mn (0.53 lbs/ton), B (0.038 lbs/ton), Zn (0.46 lbs/ton), Cu (0.39 lbs/ton)

Grower [turkey], whole litter: Density (32 lbs/ft^3), Total Solids (73%), Volatile Solids (53%), Total Kjehldahl N (55 lbs/ton), NH_3 N (12 lbs/ton), P_2O_5 (63 lbs/ton), K_2O (40 lbs/ton), Ca (38 lbs/ton), Mg (7.4 lbs/ton), S (8.5 lbs/ton), Na (7.6 lbs/ton), Cl (12 lbs/ton), Fe (1.4 lbs/ton), Mn (0.80 lbs/ton), B (0.052 lbs/ton), Zn (0.66 lbs/ton), Cu (0.60 lbs/ton)

Grower [turkey], manure cake: Density (32 lbs/ft^3), Total Solids (55%), Volatile Solids (44%), Total Kjehldahl N (45 lbs/ton), NH_3 N (20 lbs/ton), P_2O_5 (47 lbs/ton), K_2O (30 lbs/ton), Ca (26 lbs/ton), Mg (5.4 lbs/ton), S (6.3 lbs/ton), Na (5.5 lbs/ton), Cl (not available), Fe (1.2 lbs/ton), Mn (0.56 lbs/ton), B (0.038 lbs/ton), Zn (0.47 lbs/ton), Cu (0.48 lbs/ton)

Breeder [turkey], whole litter: Density (50 lbs/ft^3), Total Solids (78%), Volatile Solids (34%), Total Kjehldahl N (35 lbs/ton), NH_3 N (7.6 lbs/ton), P_2O_5 (47 lbs/ton), K_2O (18 lbs/ton), Ca (72 lbs/ton), Mg (4.6 lbs/ton), S (7.4 lbs/ton), Na (4.3 lbs/ton), Cl (not available), Fe (1.0 lbs/ton), Mn (0.43 lbs/ton), B (0.031 lbs/ton), Zn (0.50 lbs/ton), Cu (0.40 lbs/ton)

Duck, whole litter: Density (50 lbs/ft^3), Total Solids (37%), Volatile Solids (24%), Total Kjehldahl N (17 lbs/ton), NH_3 N (3.6 lbs/ton), P_2O_5 (21 lbs/ton), K_2O (13 lbs/ton), Ca (22 lbs/ton), Mg (3.3 lbs/ton), S (3.0 lbs/ton), Na (3.0 lbs/ton), Cl (not available), Fe (1.3 lbs/ton), Mn (0.37 lbs/ton), B (0.021 lbs/ton), Zn (0.32 lbs/ton), Cu (0.04 lbs/ton)

Litter characteristics, as removed from open stockpiles [i.e., weathered or composted]:

Broiler: Density (33 lbs/ft^3), Total Solids (61%), Volatile Solids (43%), Total Kjehldahl N (33 lbs/ton), NH_3 N (6.9 lbs/ton), P_2O_5 (77 lbs/ton), K_2O (32 lbs/ton), Ca (63 lbs/ton), Mg (8.2 lbs/ton), S (10 lbs/ton), Na (6.6 lbs/ton), Cl (13 lbs/ton), Fe (1.8 lbs/ton), Mn (0.70 lbs/ton), B (0.039 lbs/ton), Zn (0.63 lbs/ton), Cu (0.29 lbs/ton)

Turkey: Density (24 lbs/ft^3), Total Solids (61%), Volatile Solids (44%), Total Kjehldahl N (32 lbs/ton), NH_3 N (5.5 lbs/ton), P_2O_5 (70 lbs/ton), K_2O (30 lbs/ton), Ca (45 lbs/ton), Mg (7.1 lbs/ton), S (7.4 lbs/ton), Na (5.7 lbs/ton), Cl (8.0 lbs/ton), Fe (2.1 lbs/ton), Mn (0.76 lbs/ton), B (0.042 lbs/ton), Zn (0.63 lbs/ton), Cu (0.42 lbs/ton)

Duck: Density (50 lbs/ft^3), Total Solids (49%), Volatile Solids (32%), Total Kjehldahl N (22 lbs/ton), NH_3 N (34 lbs/ton), P_2O_5 (41 lbs/ton), K_2O (22 lbs/ton), Ca (34 lbs/ton), Mg (5.2 lbs/ton), S (4.5 lbs/ton), Na (5.4 lbs/ton), Cl (not available), Fe (1.5 lbs/ton), Mn (0.56 lbs/ton), B (0.031 lbs/ton), Zn (0.50 lbs/ton), Cu (0.05 lbs/ton)

Gupta, Gian, and William Gardner. “Use of Clay Mineral (Montmorillonite) for Reducing Poultry Litter Leachate Toxicity (EC50).” *Journal of Hazardous Materials B* 118 (2005): 81-83.

> This article examines the ability of clay mineral to adsorb heavy metals from poultry litter leachate, thus reducing its toxicity, possibly making the litter more attractive as an agricultural supplement. Montmorillonite, a type of clay, was mixed with poultry litter in varying proportions, and the mixtures were agitated with water. The resulting leachates were tested for toxicity after 1 day and 7 day periods.
>
> It was observed that the presence of the montmorillonite decreased the observed toxicity of the poultry litter leachate. *No metals data were obtained for either the litter or the leachates. [Metals data are quoted from an earlier paper by one of the authors. However, when I examined that earlier paper, I could find no metals data reported for poultry litter, only data for soils to which litter had been applied.]*

Henihan, A.M., M.J. Leahy, J.J. Leahy, E. Cummins, and B.P. Kelleher. “Emissions Modeling of Fluidised [sic] Bed Co-Combustion of Poultry Litter and Peat.” *Bioresource Technology* 87 (2003): 289-294.

> This article examines gaseous emissions from co-combustion of poultry litter with peat in a fluidized bed combustor, *not in a cement kiln*. Modeling software is used to examine how the gaseous emissions would disperse in the area around the combustor.
>
> Proximate and Ultimate analysis data are reported for the poultry litter. Proximate: Moisture-43.01%, Volatile matter-38.91%, Fixed carbon-1.66%, Ash-16.42%. Ultimate: C-39.57%, H-5.11%, N-5.31%, S-0.77%, Cl-0.88%, O-48.27%. HHV was reported as 10620 MJ/kg. Gaseous emissions data used in the modeling came from an earlier set of experiments. *No metals data are reported for the litter*.

Hseu, Zeng-Yei. “Evaluating Heavy Metal Contents in Nine Composts Using Four Digestion Methods.” *Bioresource Technology* 95 (2004): 53-59.

> This article examines the effectiveness of four digestion techniques (nitric acid, sulfuric acid, nitric acid/perchloric acid, dry ashing) in the analysis heavy metals in nine composts (including poultry litter) and two standard reference materials. Atomic absorption was used to analyze the solutions produced by the digestion procedures.
>
> The author found that no single digestion technique was best for all the metals analyzed. The author suggested that the choice of a digestion method would probably be influenced by safety, cost, and time effectiveness, in addition to the results of these experiments.
>
> In the analysis of Standard Reference Material SRM 1573a (tomato leaves), nitric acid gave the highest recovery for Cr, dry-ashing gave the highest recoveries for Cd, Cu, and Ni, nitric-perchloric acid mixture gave the highest recovery for Mn, and sulfuric acid gave the highest recovery for Zn. Recoveries for all methods

were 76% or higher for all metals analyzed except for Pb which was not present in the sample.

In the analysis of Standard Reference Material BCR 146 (sewage sludge), dry-ashing gave the highest recoveries for Mn and Pb, nitric-perchloric acid mixture gave the highest recoveries for Cu and Zn, and sulfuric acid gave the highest recoveries for Cd and Ni. Recoveries for all methods were 63% or higher for all metals analyzed except for Cr which was not present in the sample.

In the analysis of poultry litter, nitric acid gave the highest value for Cd, dry-ashing gave the highest values for Cr and Mn, nitric-perchloric acid mixture gave the highest values for Cu, Ni, and Pb, and sulfuric acid gave the highest value for Zn.

Metals data for poultry litter are reported: Cd (6-7 ppm), Cr (5-7, 15 ppm), Cu (90-140 ppm), Mn (240-620 ppm), Ni (15, 34 ppm), Pb (6-9, 16 ppm), and Zn (630-780 ppm).

Ihnat, Milan, and Leta Fernandes. “Trace Elemental Characterization of Composted Poultry Manure.” *Bioresource Technology* 57 (1996): 143-156.

This article examines the effect of composting on metals content of poultry manure. Comparisons are made between total metals, water-extractable metals, and nitric acid-extractable metals. Composting is done with barley/oat straw or sphagnum peat moss.

Total concentrations for 21 trace elements in poultry manure, in the composting materials, and in the composted manure are reported. Concentrations for the manure: Al (645 ppm), Ba (17.4 ppm), Ca (79900 ppm), Cd (0.48 ppm), Cr (7.3 ppm), Cu (54.3 ppm), Fe (1530 ppm), K (21500 ppm), Mg (7720 ppm), Mn (465 ppm), Mo (7.69 ppm), Na (4320 ppm), Ni (7 ppm), P (22720 ppm), Pb (2.3 ppm), Rb (25.4 ppm), S (4580 ppm), Sr (56 ppm), Ti (17.2 ppm), V (5.2 ppm), and Zn (550 ppm).

Total concentrations for trace/minor elements in the composted manure were necessarily lower than those for the original manure, of course, because of the dilution of the manure by the composting materials. Some changes in the extractable concentrations of several elements were observed with length of composting time. Some of these changes were deemed artifacts, but others might have been caused by changes in the forms of the extractable elements in the composted manures, rendering them more or less extractable.

Jackson, B.P., P.M. Bertsch, M.L. Cabrera, J.J. Camberato, J.C. Seaman, and C.W. Wood. “Trace Element Speciation in Poultry Litter.” *Journal of Environmental Quality* 32 (2003): 535-540.

This article examines a method to determine the amounts of different arsenic species found in poultry litter. Some arsenic (and other metal) species are more water soluble than others, so the metal species present will affect whether metals will remain in the soil after land application of poultry litter or will be removed by leaching.

The trace elements Ni, Cu, and As were found to be readily soluble from poultry litter. 50% of the poultry litter samples had the organo-arsenic compound ROX (3-nitro-4-hydroxyphenylarsonic acid) as the major As species, while 50% had As (V) as the major As species. Other unidentified As species were observed, presumably breakdown products of ROX.

Total concentrations for other trace/minor elements in poultry litter samples are reported: Na (10810 ppm), Mg (7162 ppm), Al (3169 ppm), P (17100 ppm), K (33020 ppm), Ca (22420 ppm), Mn (449.3 ppm), Fe (2189 ppm), Ni (11.09 ppm), Cu (479.2 ppm), Zn (372.7 ppm), As (15.65 ppm), Se (1.183 ppm), Sr (82.62 ppm), Cd (0.252 ppm), Ba (21.61 ppm), Pb (2.06 ppm), and U (5.601 ppm).

Jackson, Brian P., and Paul M. Bertsch. “Determination of Arsenic Speciation in Poultry Wastes by IC-ICP-MS.” *Environmental Science and Technology* 35 (2001): 4868-4873.

This article examines a method to determine the amounts of six arsenic species found in poultry litter. An ion chromatograph is coupled to an inductively coupled plasma-mass spectrometer instrument. Water extracts from a poultry litter sample are analyzed by three methods, each using a different ion chromatography column.

All three methods showed that the major As species in the water extracts was ROX, with trace concentrations of dimethyl arsenic acid (DMA) and As (V) detected. Two methods also detected other arsenic species, which were believed to be metabolites of ROX.

Total concentrations for trace metals in the poultry litter sample were also reported: V (3.63ppm), Cr (2.59 ppm), Mn, (274.52 ppm), Fe (497.06 ppm), Co (0.68 ppm), Ni (7.97 ppm), Cu (656.09 ppm), Zn (246.88 ppm), As (16.79 ppm), Se (0.95 ppm), Cd (0.10 ppm), Ba (17.69 ppm), Pb (0.74 ppm), and U (2.17 ppm).

Keener, Kevin M., and Kenneth E. Anderson. “Characterization of Poultry Manure for Potential Co-Combustion with Coal in a Co-Fired Electricity Generation Plant.” *Final Reports (November 2003)*, by North Carolina State University College of Agriculture and Life Sciences, Waste Management Programs, Animal and Poultry Waste Management Center. Raleigh, NC.

This paper describes the analysis of pullet and layer manure as a preliminary step to evaluating suitability for co-combustion with coal to produce electricity. Ultimate analysis of coal: C (78.5%), H (5.9%), N (1.5%), S (0.9%), Cl (not determined), ash (5.5%), O by difference (8.2%). Moisture content: 5%. Energy content: 30672 kJ/kg.

Ultimate analysis of pullet manure: C (31.2%), H (3.8%), N (4.4%), S (0.6%), Cl (0.89 literature value), ash (33.0%), O by difference (25.4%). Moisture content: 27.8%. Energy content: 9995 kJ/kg.

Minor/trace elements in pullet manure: N (68.7 ppth), P (35.0 ppth), K (65.5 ppth), Ca (121.4 ppth), Mg (18.6 ppth), S (14.3 ppth), Fe (1.2 ppth), Mn (0.9 ppth), Zn (1.0 ppth), Cu (0.1 ppth), B (0.1 ppth), Na (13.1 ppth).
Ash composition, pullet manure: SiO_2 (6.4%), Al_2O_3 (1.1%), TiO_2 (0.08%), Fe_2O_3 (1.4%), CaO (29.6%), MgO (5.7%), K_2O (15.0%), Na_2O (3.5%), SO_3 (5.4%), P_2O_5 (23.0%), SrO (0.04%), BaO (0.02%), Mn_3O_4 (0.3%).

Ultimate analysis of layer manure: C (31.9%), H (3.6%), N (5.3%), S (0.5%), Cl (0.89 literature value), ash (31.8%), O by difference (25.4%). Moisture content: 40.0%. Energy content: 10920 kJ/kg.
Minor/trace elements in layer manure: N (78.7 ppth), P (27.4 ppth), K (40.1 ppth), Ca (185.3 ppth), Mg (10.1 ppth), S (6.4 ppth), Fe (0.6 ppth), Mn (0.6 ppth), Zn (0.7 ppth), Cu (0.1 ppth), B (0.1 ppth), Na (6.4 ppth).
Ash composition, layer manure: SiO_2 (4.5%), Al_2O_3 (1.0%), TiO_2 (0.1%), Fe_2O_3 (0.9%), CaO (43.8%), MgO (3.3%), K_2O (8.5%), Na_2O (1.6%), SO_3 (0.5%), P_2O_5 (14.2%), SrO (0.04%), BaO (0.02%), Mn_3O_4 (0.4%).

Miller, B., D. Dugwell, and R. Kandiyota. "The Fate of Trace Elements During the Co-Combustion of Wood-Bark with Waste." *Energy & Fuels* 20 (2006): 520-531. (duplicated in another section)

This article examines four waste fuels: wood-bark (from the debarking plant of a paper mill), agricultural waste (chicken litter, manure, and wood chips), pulp sludge (from the paper industry), and plastic waste (from a recycling process). The fuels were combusted in a suspension-firing reactor (intended to simulate a section of a fluidized bed combustor), *not in a cement kiln*. Temperatures in the reactor were 800°C and 900°C.

The original fuels were analyzed to determine their elemental composition, ash and moisture content, and their Lower Heating Value (LHV).

Elemental analysis, Wood-bark, dry, ash-free: C (53.1%), H (6.00%), N (0.45%), O (40.3%), S (0.07%), Cl (0.01%), P (0.04%), ash (6.9%), moisture (3.0%), LHV (18.6 MJ/kg)

Elemental analysis, Agricultural waste, dry, ash-free: C (50.2%), H (6.23%), N (4.11%), O (37.3%), S (0.63%), Cl (0.39%), P (1.06%), ash (12.8%), moisture (4.0%), LHV (15.7 MJ/kg)

Elemental analysis, Pulp sludge, dry, ash-free: C (48.5%), H (6.49%), N (1.31%), O (42.9%), S (0.52%), Cl (0.12%), P (0.08%), ash (3.6%), moisture (4.3%), LHV (18.2 MJ/kg)

Elemental analysis, Plastic waste, dry, ash-free: C (67.9%), H (10.0%), N (0.35%), O (20.4%), S (0.38%), Cl (0.98%), P (0.01%), ash (10.2%), moisture (2.6%), LHV (29.7 MJ/kg)

Minor elements, Wood-bark, dry basis: Na (1.35 g/kg), K (2.26 g/kg), Mg (0.79 g/kg), Ca (7.98 g/kg), Al (2.99 g/kg), Fe (1.52 g/kg), Si (9.7 g/kg)

Minor elements, Agricultural waste, dry basis: Na (4.03 g/kg), K (27.1 g/kg), Mg (4.28 g/kg), Ca (16.4 g/kg), Al (0.35 g/kg), Fe (0.54 g/kg), Si (3.6 g/kg)

Minor elements, Pulp sludge, dry basis: Na (3.06 g/kg), K (0.87 g/kg), Mg (2.04 g/kg), Ca (2.37 g/kg), Al (2.32 g/kg), Fe (0.84 g/kg), Si (9.9 g/kg)

Minor elements, Plastic waste, dry basis: Na (1.91 g/kg), K (0.25 g/kg), Mg (1.18 g/kg), Ca (9.43 g/kg), Al (24.9 g/kg), Fe (1.71 g/kg), Si (9.4 g/kg)

Trace elements, Wood-bark, dry basis: As (0.44 ppm), Ba (156 ppm), Be (0.07 ppm), Cd (0.20 ppm), Co (0.72 ppm), Cr (26 ppm), Cu (87 ppm), Hg (0.033 ppm), Ni (10.0 ppm), Mn (414 ppm), Mo (1.26 ppm), Pb (3.1 ppm), Sb (0.21 ppm), Se (<0.8 ppm), Sr (51 ppm), Ti (94 ppm), Tl (0.09 ppm), V (2.8 ppm), Zn (150 ppm)

Trace elements, Agricultural waste, dry basis: As (0.34 ppm), Ba (13.3 ppm), Be (0.18 ppm), Cd (0.36 ppm), Co (0.40 ppm), Cr (8.8 ppm), Cu (38.2 ppm), Hg (0.95 ppm), Ni (10.6 ppm), Mn (240 ppm), Mo (9.1 ppm), Pb (0.86 ppm), Sb (0.08 ppm), Se (<0.8 ppm), Sr (19.0 ppm), Ti (26.3 ppm), Tl (0.007 ppm), V (1.0 ppm), Zn (252 ppm)

Trace elements, Pulp sludge, dry basis: As (0.50 ppm), Ba (45 ppm), Be (<0.03 ppm), Cd (1.99 ppm), Co (0.45 ppm), Cr (25 ppm), Cu (14.7 ppm), Hg (0.083 ppm), Ni (10.1 ppm), Mn (137 ppm), Mo (0.97 ppm), Pb (2.3 ppm), Sb (0.17 ppm), Se (<0.8 ppm), Sr (13.1 ppm), Ti (40 ppm), Tl (0.13 ppm), V (5.3 ppm), Zn (200 ppm)

Trace elements, Plastic waste, dry basis: As (0.31 ppm), Ba (263 ppm), Be (0.11 ppm), Cd (4.1 ppm), Co (4.6 ppm), Cr (33 ppm), Cu (65 ppm), Hg (0.055 ppm), Ni (5.5 ppm), Mn (26 ppm), Mo (1.10 ppm), Pb (35 ppm), Sb (3.5 ppm), Se (<0.8 ppm), Sr (17.1 ppm), Ti (2,993 ppm), Tl (0.03 ppm), V (2.3 ppm), Zn (501 ppm)

The four fuels were combusted in various combinations. The wood-bark and the agricultural waste were also combusted alone, but it was not possible to combust the pulp sludge or the plastic waste alone, as they could not be fed to the reactor unless mixed with wood-bark.

Although the combustion ashes were analyzed for metal content, the exact metals data are not reported. “Retention values” for each metal are plotted as a function of the concentration of the metal in the original fuel vs. its concentration in the combustion ash of a particular fuel combination.

The retention value of a metal was found to depend, not only on the metal’s inherent volatility, but also on the type of fuel burned.

Cd: Highest retention value was for wood-bark, 60% retention. Retention decreased as other fuels were substituted for the woodbark, proportionate to the amount of the substitution. Retention for agricultural waste burned by itself was 15% at 800°C and 5% at 900°C.

Cr: There was some Cr loss for all fuels, but there seemed to be a higher degree of retention for the fuel combinations than for the individual fuels.

Pb: Most of the Pb in the fuels was volatilized during combustion. There seemed to be little effect from combining the fuels.

Mn: Most of the Mn in the fuels was retained in the ashes for most fuel combinations. However, the addition of the pulp sludge to the wood-bark led to losses of 50%, and the addition of both agricultural waste and plastic waste at a 10% level to wood-bark led to similar losses. The chlorine content of these fuels was suggested as being related to the Mn loss.

Hg: Almost complete volatilization (1-10% retention) was observed for Hg in the combustion of wood-bark, agricultural waste, and their combinations. However, the addition of pulp sludge or plastic waste led to a higher retention (20-30%) of Hg in the ashes. The sulfur content of these fuels is suggested as being related.

Ni: Retention of Ni was high for most fuels and fuel combinations. Two bark/agricultural waste combinations had retention values of 60-65%, however.

Se: Amounts of Se were either below or close to the experimental quantitation limit, which prevented drawing any conclusions about its retention.

Zn: “Substantial” volatilization of Zn was observed for all fuel combinations.

Nicholson, F.A., B.J. Chambers, J.R. Williams, and R.J. Unwin. “Heavy Metal Contents of Livestock Feeds and Animal Manures in England and Wales.” *Bioresource Technology* 70 (1999): 23-31.

This article reports metals analysis results for 183 livestock feeds and 85 animal manures.

Concentrations of trace metals are reported for commercial poultry feeds: three broiler feeds (starter, grower, finisher), three turkey feeds (various, grower, finisher), and one layer feed. Trace metal concentrations in broiler feeds: Zn (148 ppm, 118 ppm, 135 ppm), Cu (31.7 ppm, 36.1 ppm, 32.6 ppm), Ni (2.0 ppm, 2.0 ppm, 2.1 ppm), Pb (ND, ND, ND at 1.00 ppm detection limit), Cd (0.19 ppm, 0.16 ppm, 0.12 ppm), As (0.23 ppm, 0.25 ppm, 0.15 ppm), and Cr (1.77 ppm, 1.44 ppm, 0.22 ppm). Trace metal concentrations in turkey feeds: Zn (155 ppm, 120 ppm, 108 ppm), Cu (27.8 ppm, 26.5 ppm, 19.9 ppm), Ni (1.8 ppm, 2.0 ppm, 1.7 ppm), Pb (ND, ND, ND at 1.00 ppm detection limit), Cd (0.15 ppm, 0.14 ppm, 0.19 ppm), As (0.35 ppm, 0.28 ppm, ND at 0.10 ppm detection limit), and Cr (2.08 ppm, 1.13 ppm, 0.72 ppm). Trace metal concentrations in layer feed: Zn (153 ppm), Cu (23.0 ppm), Ni (2.6 ppm), Pb (ND at 1.00 ppm detection limit), Cd (0.39 ppm), As (ND at 0.10 ppm detection limit), and Cr (0.76 ppm). Trace metal concentrations are also reported for components of home-mixed poultry feeds.

Concentrations of trace metals in poultry manures are considerably higher than those found in the feeds, indicating a biological concentration effect. Trace metals concentrations in poultry/turkey manure: Zn (378 ppm), Cu (96.8 ppm), Ni (5.4 ppm), Pb (3.62 ppm), Cd (0.42 ppm), As (9.01 ppm), and Cr (17.17 ppm). Trace metals concentrations in layer manure: Zn (459 ppm), Cu (64.8 ppm), Ni (7.1 ppm), Pb (8.37 ppm), Cd (1.06 ppm), As (0.46 ppm), and Cr (4.57 ppm).

Sims, J.T., and D.C. Wolf. “Poultry Waste Management: Agricultural and Environmental Issues.” In *Advances in Agronomy, Vol. 52*, ed. Donald L. Sparks, 2-72. San Diego: Academic Press, Inc., 1994.

> This review article examines the management of poultry waste in many aspects. There are separate sections on poultry waste generation, the impact of land application on water quality, pesticides, antibiotics, and heavy metals in poultry wastes, and N and P management.
>
> Summaries of values for trace elements in poultry wastes, as reported in the literature, as well as data for N, NH_3, P, and S, are given in several tables.

Sistani, K.R., G.E. Brink, S.L. McGowen, D.E. Rowe, and J.L. Oldham. “Characterization of Broiler Cake and Broiler Litter, the By-Products of Two Management Practices.” *Bioresource Technology* 90 (2003): 27-32.

> This article describes differences between broiler cake and broiler litter: how they are collected and their chemical characteristics. Broiler litter is collected by a process called “total cleanout” and involves removal of all the material in the broiler house. Broiler cake is essentially the top layer of material, which includes fresh manure, spilled feed and water, and some bedding material. It is collected mechanically by a machine which passes material over a grate and removes only the solidified portion. This process conserves bedding materials, reducing costs to the farmer, and is becoming more prevalent.
>
> Broiler feed, litter and cake samples were analyzed.
>
> Analysis results for broiler feed: Total C (410 ppth), Total N (31.4 ppth), Total P (6.93 ppth).
> Trace/minor metals results for broiler feed: Ca (10.1 ppth), Mg (1.8 ppth), K (9.0 ppth), Cu (210 ppm), Fe (202 ppm), Mn (169 ppm), Zn (139 ppm).
>
> Analysis results for broiler litter: Total C (320 ppth), Total N (32.8 ppth), Total P (18.77 ppth).
> Trace metals results for broiler litter: Ca (26.2 ppth), Mg (6.1 ppth), K (30.3 ppth), Cu (662 ppm), Fe (1055 ppm), Mn (556 ppm), Zn (436 ppm).
>
> Analysis results for broiler cake: Total C (343 ppth), Total N (37.6 ppth), Total P (19.17 ppth).
> Trace metals results for broiler cake: Ca (99.1 ppth), Mg (24.4 ppth), K (125.7 ppth), Cu (2763 ppm), Fe (3818 ppm), Mn (2307 ppm), Zn (1848 ppm).

Tiquia, S.M., and N.F.Y. Tam. “Fate of Nitrogen During Composting of Chicken Litter.” *Environmental Pollution* 110 (2000): 535-541.

> This article studies the losses of ammonia nitrogen in chicken litter during the composting process. Chicken litter was composted over a period of months. Samples were analyzed during the composting period to monitor losses (or gains) of organic matter and nitrogen.

Organic matter in the composted litter decreased by 9% during the composting period, attributed to conversion of the organic C to CO_2. Total N in the composted litter decreased by 59% during the composting period, attributed to volatilization loss of ammonia.

Analysis results for the original chicken litter: Total N (33.9 ppth), Total P (16.9 ppth), Total C (491.4 ppth), ash (141 ppth), Total K (20.3 ppth), Total Cu (85 ppm), and Total Zn (197 ppm).

Zhu, S., and S.W. Lee. “Co-Combustion Performance of Poultry Wastes and Natural Gas in the Advanced Swirling Fluidized Bed Combustor (SFBC).” *Waste Management* 25 (2005): 511-518.

This article examines the co-combustion of poultry litter, poultry manure, and sawdust with natural gas in a fluidized bed combustor, *not a cement kiln*. Burning characteristics and gaseous emissions are compared.

In this fluidized bed system, CO emissions were observed to be dependent on the excess air, not on fuel characteristics. NO_x emissions, however, were observed to increase both with an increase of excess air and with an increase in N content of the waste fuel. At optimal operating conditions, combustion efficiencies for sawdust, poultry litter, and poultry manure were 95%, 89%, and 83%, respectively.

Proximate analysis of sawdust: Moisture (8.7%), Volatiles (72.39%), Fixed C (16.94%), ash (1.97%). Ultimate analysis of sawdust: C (49.5%), H (6.35%), O (41.08%), N (0.89%), S (0.02%), ash (2.16%). LHV of sawdust: 12618 kJ/kg.

Proximate analysis of poultry litter: Moisture (15.02%), Volatiles (40.35%), Fixed C (13.71%), ash (30.92%). Ultimate analysis of poultry litter: C (29.34%), H (4.16%), O (25.80%), N (4.22%), S (0.1%), ash (36.38%). LHV of poultry litter: 6030 kJ/kg.

Proximate analysis of poultry manure: Moisture (13.55%), Volatiles (39.5%), Fixed C (12.7%), ash (33.44%). Ultimate analysis of poultry manure: C (32.45%), H (2.82%), O (20.34%), N (5.6%), S (0.12%), ash (38.68%). LHV of poultry manure: 5800 kJ/kg.

Metals data are not reported in this paper.

VIII. Plastics, Trace Metals in and/or Combustion of

Boavida, D., P. Abelha, I. Gulyurtlu, and I. Cabrita. “Co-Combustion of Coal and Non-Recyclable Paper and Plastic Waste in a Fluidized Bed Reactor.” *Fuel* 82 (2003): 1931-1938.

This paper examines the effect of substituting a fuel derived from the paper and plastic fraction of municipal waste for coal in a fluidized bed reactor, *not a cement kiln*. Processed Engineered Fuel (first abbreviated PEF, then PRF) typically contains 70-90% paper but can be higher in plastic. The authors state that the

PRF combusted for this paper was high in plastics, but they do not indicate the percentage.

Proximate analysis, Coal, as received: Moisture (3.8 %), ash (6.0 %), volatile matter (33.5 %), fixed carbon (56.7 %)

Proximate analysis, High-plastics PRF [sic], as received: Moisture (6.8 %), ash (15.6 %), volatile matter (67.5 %), fixed carbon (10.1 %)

Proximate analysis, Coal, dry basis: C (74.5 %), H (5.9 %), N (2.1 %), S (0.1 %), O (11.2 %), ash (6.2 %)

Proximate analysis, High-plastics PRF [sic], dry basis: C (39.0 %), H (5.8 %), N (0.7 %), S (0.1 %), O (37.7 %), ash (16.7 %)

Gross calorific value, Coal: 30.4 MJ/kg

Gross calorific value, High-plastics PRF [sic]: 15.9 MJ/kg

The PRF is usually obtained in palletized form, but the pellets were too large to feed into the reactor. Shredded PRF (“fluff”) and “fluff” PRF re-pelletized to a smaller size were co-combusted with coal in the reactor. The authors found that, with the “fluff” material, it was difficult to control the combustion, apparently due to an inability to sufficiently control the feed rate. Repelletizing the “fluff” to a smaller pellet size than the original fuel pellets allowed control over the feed rate and the combustion process.

The fuels, the ashes, and the flue gases were analyzed for heavy metals and HCl.

Heavy metals and HCl, 100% coal, fuel: Pb (9 µg/g), Ni (17 µg/g), Cu (18 µg/g), Cr (12 µg/g), Cd (0 µg/g), V (2 µg/g), Zn (15 µg/g), Mn (44 µg/g), Hg (5834 ppb), HCl (<0.05 wt %)

Heavy metals and HCl, 60% coal + 40% PRF, fuel: Pb (12 µg/g), Ni (17 µg/g), Cu (37 µg/g), Cr (14 µg/g), Cd (1 µg/g), V (4 µg/g), Zn (104 µg/g), Mn (54 µg/g), Hg (27.4 ppb), HCl (0.08 wt %)

Heavy metals, 100% coal, bed ash + cyclone ash: Pb (96 µg/g), Ni (314 µg/g), Cu (177 µg/g), Cr (123 µg/g), Cd (0 µg/g), V (22 µg/g), Zn (140 µg/g), Mn (255 µg/g), Hg (2907.42 ppb)

Heavy metals, 60% coal + 40% PRF, bed ash + cyclone ash: Pb (232 µg/g), Ni (465 µg/g), Cu (502 µg/g), Cr (208 µg/g), Cd (9 µg/g), V (23 µg/g), Zn (1475 µg/g), Mn (573 µg/g), Hg (1031.32 ppb)

Heavy metals and HCl, 100% coal, flue gas: Pb (0.034 mg/N m^3), Ni (ND), Cu (0.045 mg/N m^3), Cr (0.124 mg/N m^3), Cd (ND), V (ND), Zn (0.344 mg/N m^3), Mn (0.084 mg/N m^3), Hg (3.0×10^{-4} mg/N m^3), HCl (<0.42 mg/N m^3)

Heavy metals and HCl, 60% coal + 40% PRF, flue gas: Pb (ND), Ni (0.003 mg/N m^3), Cu (0.020 mg/N m^3), Cr (0.062 mg/N m^3), Cd (ND), V (ND), Zn (0.224 mg/N m^3), Mn (0.044 mg/N m^3), Hg (7.6 x 10^{-5} mg/N m^3), HCl (<0.41 mg/N m^3)

Campbell, Petra E., Sharon McCahey, Brian C. Williams, and Mark L. Beekes. “Coal and Plastic Waste in a PF Boiler.” *Energy Policy* 28 (2000): 223-229.

This paper describes the use of a European Union simulation program, ECLIPSE, to compare the economics of adding 5% plastics from municipal solid waste to the coal burned in an industrial boiler, *not a cement kiln*. *No data from actual combustion processes are presented.*

The simulation indicates that (energy-equivalent) substitution of plastic waste for coal reduces power production, attributed to the high moisture content of the plastics. Reduction in power production would necessarily reduce the efficiency of the fuel substitution, hence, its economic feasibility. Costs for processing the plastic wastes to make it suitable for combustion would also affect the cost of the substitution. Tipping fees and costs for transportation would also impact the economic situation.

The ECLIPSE simulation indicates little difference in the gaseous emissions, possibly because of the low substitution rate (5%). HCl emissions seemed to double, however.

Ultimate analysis, Coal, dry, ash-free: H (5.21%), C (82.44%), S (1.85%), N (1.82%), O (8.65%), Cl (0.03%)

Ultimate analysis, Plastics from MSW, dry, ash-free: H (10.05%), C (70.41%), S (0.05%), N (0.41%), O (18.33%), Cl (0.75%)

Proximate analysis, Coal: Moisture, as received (7.97%), Ash, dry basis (13.53%)

Proximate analysis, Plastics from MSW: Moisture, as received (56.0%), Ash, dry basis (6.6%)

Heating values, Coal: LHV, as received (25.955 MJ/kg), HHV, as received (27.041 MJ/kg)

Heating values, Plastics from MSW: LHV, as received (14.608 MJ/kg), HHV, as received (15.444 MJ/kg)

Courtemanche, Bonnie, and Yiannis A. Levendis. “A Laboratory Study on the NO, NO_2, SO_2, CO and CO_2 Emissions from the Combustion of Pulverized Coal, Municipal Waste Plastics and Tires.” *Fuel* 77, no. 3 (1998): 183-196.
(duplicated in another section)

This article examines emissions from combustion of coal, tire crumbs, and waste plastics in a drop furnace, *not a cement kiln*. Coal, waste tire crumb, poly(styrene), poly(ethylene), poly(methylmethacrylate), poly(propylene), and poly(vinyl chloride) were tested as pulverized materials.

Under these conditions (i.e., in the drop furnace), NO_x production was correlated with N content of the fuel, with coal combustion generating three to four times more NO_x than tire crumb and up to ten times more NO_x than the plastics (which contained no N). There was a strong dependence on gas-temperature, with higher gas temperatures producing higher NO_x emissions for all fuels.

A nitrogen-free atmosphere was used to evaluate the conversion of fuel-N to NO_x. For all fuels, less than two-thirds of the fuel-N was converted to NO_x. Higher conversion rates were observed under fuel-lean conditions and lower conversion rates under fuel-rich conditions. Atmospheric N contributed 20% of the NO_x for coal, 30% for tires, and 100% for the plastics.

SO_2 emissions were comparable for coal and tire crumb. SO_2 emissions were higher in the absence of atmospheric N, especially under fuel-rich conditions. The authors observed little effect of gas-temperature on SO_2 emissions. In most cases, 60-100% of the S present in the fuels was converted to SO_2. More SO_2 emissions were observed in the nitrogen-free atmosphere than in air.

CO emissions were mild in the fuel-lean region but exponentially higher in the fuel-rich region. CO_2 emissions were proportional to the amount of C in the fuel.

Ernst, Tobias, Ralf Popp, and Rudi van Eldik. “Quantification of Heavy Metals for the Recycling of Waste Plastics from Electrotechnical Applications.” *Talanta* 53 (2000): 347-357.

This article compares three analytical methods (EDXRF, AAS, ICP-AES) to determine lead, cadmium, and antimony in waste plastics from technical waste. Several samples of high-impact polystyrene and acrylonitrile butadiene styrene and a single sample of polycarbonate were analyzed. Some samples were not analyzed for all three metals. This was attributed to interferences from other sample components.

The samples were digested or wet-ashed prior to analysis. Sulfuric acid wet-ashing combined with ICP-AES gave the lowest numbers for all samples when compared to the other techniques. The authors found that the presence of bromine in the form of brominated flame retardants interfered with the determination of Pb by XRF for some samples.

Pb in electrotechnical plastics samples: High-impact polystyrene (70-98 µg/g), acrylonitrile butadiene styrene (182-229, 64-88, 371-651 µg/g)

Sb in electrotechnical plastics samples: High-impact polystyrene (5.76-6.19, 2.62-2.74 mole %), acrylonitrile butadiene styrene (2.71-2.77, 3.69-3.94, 2.91-3.00, 1.69-1.77 mole %)

Cd in electrotechnical plastics samples: High-impact polystyrene (238-285, 77-86 µg/g), acrylonitrile butadiene styrene (107-123, 9945-11340 µg/g), polycarbonate (2760-3070 µg/g)

Figi, Renato, Peter Lienemann, and Peter Richner. “Determination of Traces of Fluorine, Chlorine, Bromine, Cadmium and Lead in Plastic Materials.” *Technological and Environmental Chemistry* 52 (1995): 35-44.

> This article describes the development of a method to evaluate plastic samples for F, Cl, Br, Cd, and Pb so that decisions can be made concerning their disposal.
>
> The samples were first analyzed non-destructively using semi-quantitative XRF to screen for Cl, Br, Cd, and Pb. The XRF detection limit for F is too high (50 times higher than the Swiss limit for disposal without special precautions), so it cannot be used as a screening technique for F for disposal purposes. Only semi-quantitative results could be obtained by XRF since the technique used was not sensitive enough to obtain good quantitative results for these analytes in plastics.
>
> Following the XRF screen, samples were digested with NaOH. The digests were then quantititatively analyzed by potentiometry for F^- and Br^- and by ion chromatography for Cl^-. Spiked samples gave spike recoveries ranging from 88% to 120%.
>
> Polyethylene foil: F (11.2 µg/g), Cl (94.7 µg/g), Br (11.6 µg/g)
>
> Foil containing PVC: Cl (56.9 mg/g)
>
> Toy: Br (0.69 mg/g)
>
> Track and field flooring: Br (1.20 mg/g)
>
> Plastic cable: Cl (241 mg/g), Br (1.88 mg/g)
>
> The samples were also digested with concentrated HNO_3, and the digests were quantitatively analyzed by atomic absorption for Cd and Pb. Spiked samples gave spike recoveries ranging from 87% to 101%.
>
> Polyethylene foil: Cd (not detected), Pb (not detected)

Fink, H., U. Panne, M. Theisen, R. Niessner, T. Probst, and X. Lin. “Determination of Metal Additives and Bromine in Recycled Thermoplasts from Electronic Waste by TXRF Analysis.” *Fresenius Journal of Analytical Chemistry* 368 (2000): 235-239.

> This article proposes a method for the analysis of metals and bromine in waste plastics from discarded electronic equipment. Over a hundred thermoplastic samples were analyzed for Ti, Zn, Br, Cd, Sn, Sb, and Pb, elements of concern with respect to recycling which are likely to be found in thermoplastic additives.
>
> The samples were cryogenically ground, then the particles were dissolved or suspended in an organic solvent which was deposited onto a sample holder. The dried sample film was then analyzed by XRF.
>
> Analysis results are presented graphically, *but no numerical data are supplied*. The authors state that the concentrations of any single element varied widely

between samples. Zn, Sn, Cd, and Pb were found in concentrations below 1%. Ti, Be, and Sb were found in concentrations between 1% and 10%. A peak value of 25% was found for Br.

About half of the samples had brominated flame retardants and most of these had SbO_3 as well. Most plastic samples with white pigments were found to contain TiO_2, while Zn was found as a pigment (ZnO) and in stabilizers. Sn was also found in stabilizers as well. Cd and Pb were only found in a few samples.

Fink, Johannes Karl. “Pyrolysis and Combustion of Polymer Wastes in Combination with Metallurgical Processes and the Cement Industry.” *Journal of Analytical and Applied Pyrolysis* 51 (1999): 239-252.

This paper is a review which discusses the use of polymer wastes as a substitute for coke, coal, or oil used as fuels in metallurgical processing. Most of the papers reviewed are in European publications, including conference proceedings. Some are in languages other than English.

The author points out that the non-polymer components of polymeric wastes, particularly metals found in automobile shredder waste and electronic scrap, can cause problems in blast furnaces and other metallurgical processes. Special precautions must be taken. Although wastes can be introduced with the ore and other fuels, they can also be pre-degraded into liquid or gaseous fuels that are injected into the furnace.

The author briefly discusses the use of polymer wastes as fuels in the cement industry. He points out that shredded material could lead to clogging of fuel lines if the materials were not uniform in size. He also mentions that several plants report decreases in some gaseous emissions (SO_2) and increases in others (CO and dust).

Frankenhaeuser, M., H. Manninen, I. Kojo, J. Ruuskanen, T. Vartiainen, R. Vesterinen, and J. Virkki. “Organic Emissions from Co-Combustion of Mixed Plastics with Coal in a Bubbling Fluidized Bed Boiler.” *Chemosphere* 27 (1993): 309-316.

This article examines co-combustion of mixed plastics (4% chlorine) with coal in a fluidized bed boiler, *not a cement kiln*. The effect of limestone injection was also examined.

Coal analysis: LHV, dry (29.4 MJ/kg), specific C (27.4 g/MJ), Ash (7.6%)

Mixed plastics: LHV, dry (39.0 MJ/kg), specific C (19.7 g/MJ), Ash (2.0%)

Coal analysis, major elements: C (80.5%), H (4.8%), N (1.3%), S (0.5%), Cl (0.1%), Al (1.04%), Ca (0.25%), Fe (0.39%), Si (1.6%)

Mixed plastics, major elements: C (77.0%), H (13.1%), N (0.7%), S (-), Cl (3.9%), Al (0.04%), Ca (0.11%), Fe (0.03%), Si (0.1%)

Limestone, major elements: C (11.1%), H (-), N (-), S (-), Cl (-), Al (0.47%), Ca (36.6%), Fe (0.25%), Si (1.4%)

Coal analysis, trace metals: Cd (4 ppm), Cr (20 ppm), Cu (-), Hg (-), Ni (20 ppm), Pb (40 ppm), Sn (-), Ti (500 ppm), Zn (20 ppm)

Mixed plastics, trace metals: Cd (80 ppm), Cr (15 ppm), Cu (6 ppm), Hg (-), Ni (10 ppm), Pb (70 ppm), Sn (-), Ti (10,500 ppm), Zn (30 ppm)

Limestone, trace metals: Cd (-), Cr (44 ppm), Cu (-), Hg (-), Ni (10 ppm), Pb (10 ppm), Sn (20 ppm), Ti (300 ppm), Zn (10 ppm)

Plastic waste was substituted for coal in amounts varying from 0-70% thermal substitution (0-51% by weight). Tests were run with the substitution amounts increasing incrementally to the maximum, then decreasing. Limestone injection was used in the second (decreasing) series of experiments.

Increasing plastic content of the fuel did not seem to correlate with any changes in emissions. Limestone injection seemed to correlate with increases in metal emissions but that effect is attributed to the presence of metals in the limestone itself.

Flue gas, coal alone: CO (331, 409 mg/N m^3), SO_2 (1395, 271 mg/N m^3), NO_x (248, 234 mg/N m^3), N_2O (101, 106 mg/N m^3), HCl (81, 134 mg/N m^3), HF (8.2, ND mg/N m^3), Hg (1.2, 0.4 mg/N m^3), Pb (0.05, 0.07 mg/N m^3), Cu (0.04, 0.02 mg/N m^3), Ni (ND, ND mg/N m^3)

Flue gas, 10% plastic waste: CO (351, 235 mg/N m^3), SO_2 (1325, 598 mg/N m^3), NO_x (211, 214 mg/N m^3), N_2O (83, 65 mg/N m^3), HCl (191, 604 mg/N m^3), HF (4.4, ND mg/N m^3), Hg (0.6, 1.0 mg/N m^3), Pb (0.07, 0.07 mg/N m^3), Cu (0.03, ND mg/N m^3), Ni (ND, ND mg/N m^3)

Flue gas, 36% plastic waste: CO (388 mg/N m^3), SO_2 (460 mg/N m^3), NO_x (231 mg/N m^3), N_2O (47 mg/N m^3), HCl (397 mg/N m^3), HF (3.3 mg/N m^3), Hg (0.8 mg/N m^3), Pb (0.06 mg/N m^3), Cu (0.02 mg/N m^3), Ni (ND mg/N m^3)

Flue gas, 51% plastic waste: CO (487, 311 mg/N m^3), SO_2 (258, 275 mg/N m^3), NO_x (229, 234 mg/N m^3), N_2O (41, 33 mg/N m^3), HCl (461, 953 mg/N m^3), HF (3.3, ND mg/N m^3), Hg (1.1, 0.4 mg/N m^3), Pb (0.08, 0.06 mg/N m^3), Cu (ND, 0.08 mg/N m^3), Ni (0.2, ND mg/N m^3)

Fly ash, coal alone: Ca (3.25, 10.4%), Cl (0.08, 0.39%), S (1.54, 1.72%), Cd (2, 1 ppm), Cr (140, 76 ppm), Cu (160, 90 ppm), Hg (-), Ni (160, 90 ppm), Pb (130, 210 ppm), Sn (20, 30 ppm), Ti (2500, 4300 ppm), Zn (650, 200 ppm)

Fly ash, 10% plastic waste: Ca (2.84, 10.4%), Cl (0.11, 1.17%), S (1.48, 1.87%), Cd (1, 1 ppm), Cr (94, 87 ppm), Cu (140, 160 ppm), Hg (-), Ni (120, 90 ppm), Pb (100, 130 ppm), Sn (10, 70 ppm), Ti (3600, 16,000 ppm), Zn (360, 230 ppm)

Fly ash, 36% plastic waste: Ca (3.99%), Cl (0.19%), S (1.28%), Cd (1 ppm), Cr (130 ppm), Cu (100 ppm), Hg (-), Ni (140 ppm), Pb (110 ppm), Sn (20 ppm), Ti (8900 ppm), Zn (420 ppm)

Fly ash, 51% plastic waste: Ca (5.06, 12.2%), Cl (0.39, 1.45%), S (1.50, 1.98%), Cd (2, 1 ppm), Cr (130, 99 ppm), Cu (120, 110 ppm), Hg (-), Ni (150, 100 ppm), Pb (170, 130 ppm), Sn (50, 80 ppm), Ti (14,000-19,000 ppm), Zn (460, 260 ppm)

Limestone injection seemed to result in to increase the PCDD/PCDF emissions.

PCDD/PCDF, coal alone: Gas (0.01, 0.04 ng/N m^3), Dust (0.01, 0.02 ng/N m^3), Ash (0.03, 0.04 ng/N m^3)

PCDD/PCDF, 10% plastic waste: Gas (0.004, 0.06 ng/N m^3), Dust (0.009, 0.01 ng/N m^3), Ash (0.01, 0.5 ng/g)

PCDD/PCDF, 36% plastic waste: Gas (0.003 ng/N m^3), Dust (0.008 ng/N m^3), Ash (0.07 ng/g)

PCDD/PCDF, 51% plastic waste: Gas (0.02, 0.01 ng/N m^3), Dust (0.01, 0.03 ng/N m^3), Ash (0.2, 0.6 ng/g)

Frankenhauser, M., M. Hiltunen, H. Manninen, J. Palonen, J. Ruuskanen, and T. Vartiainen. “Emissions from Co-Combustion of Used Packaging with Peat and Coal.” *Chemosphere* 29 (1994): 2057-2066.

This article examines co-combustion of packaging waste from several sources (pre- and post-consumer) with a standard coal/peat mixture in a fluidized bed boiler, *not a cement kiln*. The effect of limestone injection was also examined.

Proximate analysis, peat: Moisture (58%), volatiles in d.s. (73%), ash in d.s. (1.9%)

Proximate analysis, coal: Moisture (11%), volatiles in d.s. (27%), ash in d.s. (12%)

Proximate analysis, LPB (packaging offcuts): Moisture (24%), volatiles in d.s. (87%), ash in d.s. (1.9%)

Proximate analysis, MB/FP (printed packaging scrap): Moisture (20%), volatiles in d.s. (80%), ash in d.s. (10%)

Proximate analysis, RDF: Moisture (46%), volatiles in d.s. (73%), ash in d.s. (9.9%)

Proximate analysis, MP (mixed plastics): Moisture (39%), volatiles in d.s. (80%), ash in d.s. (18%)

Ultimate analysis, peat: C (52%), H (5.4%), N (1.3%), S (0.1%), O (39%), Cl (0.03%), Ca (0.14%), HHV (20.1 MJ/kg), LHV (19.0 MJ/kg)

Ultimate analysis, coal: C (74%), H (4.1%), N (1.4%), S (0.7%), O (7.8%), Cl (0.10%), Ca (0.34%), HHV (29.6 MJ/kg), LHV (28.7 MJ/kg)

Ultimate analysis, LPB (packaging offcuts): C (49%), H (7.2%), N (0.2%), S (0.0%), O (42%), Cl (0.06%), Ca (0.12%), HHV (20.5 MJ/kg), LHV (19.0 MJ/kg)

Ultimate analysis, MB/FP (printed packaging scrap): C (48%), H (6.8%), N (0.5%), S (0.0%), O (33%), Cl (0.18%), Ca (1.42%), HHV (20.2 MJ/kg), LHV (18.7 MJ/kg)

Ultimate analysis, RDF: C (49%), H (6.6%), N (1.0%), S (0.2%), O (31%), Cl (0.75%), Ca (1.37%), HHV (19.1 MJ/kg), LHV (17.7 MJ/kg)

Ultimate analysis, MP (mixed plastics): C (65%), H (8.8%), N (0.8%), S (0.1%), O (5.3%), Cl (1.29%), Ca (0.55%), HHV (33.7 MJ/kg), LHV (31.8 MJ/kg)

Metals, peat: Al (0.1%), Cd (<1 ppm), Cu (-), Hg (<1 ppm), Pb (30 ppm), Sn (-), Zn (20 ppm)

Metals, coal: Al (1.8%), Cd (<1 ppm), Cu (-), Hg (<1 ppm), Pb (40 ppm), Sn (-), Zn (30 ppm)

Metals, LPB (packaging offcuts): Al (0.2%), Cd (<1 ppm), Cu (-), Hg (<1 ppm), Pb (40 ppm), Sn (-), Zn (20 ppm)

Metals, MB/FP (printed packaging scrap): Al (3.1%), Cd (<1 ppm), Cu (30 ppm), Hg (<1 ppm), Pb (30 ppm), Sn (-), Zn (220 ppm)

Metals, RDF: Al (1.0%), Cd (<1 ppm), Cu (20 ppm), Hg (<1 ppm), Pb (210 ppm), Sn (10 ppm), Zn (280 ppm)

Metals, MP (mixed plastics): Al (1.0%), Cd (26 ppm), Cu (20 ppm), Hg (<1 ppm), Pb (190 ppm), Sn (30 ppm), Zn (230 ppm)

Fuel efficiency, based on CO emissions, seemed to be enhanced by the substitution of waste fuels for the peat/coal mixture, especially with the limestone addition. Low sulfur waste fuels lowered the emissions of SO_2. Limestone addition did not seem to have an effect on HCl emissions. Heavy metal gaseous emissions did not change much from the baseline conditions to the waste fuel substitutions. PCDD/PCDF emissions did not correlate with the amount of Cl in the fuels but increased with the limestone injection. Injection of sulfur seemed to decrease Hg gaseous emissions.

Gaseous emissions, peat/coal mixture: Dust (58 Nm^3/s), CO (62 Nm^3/s), hydrocarbons (13 Nm^3/s), SO_x as SO_2 (500 Nm^3/s), NO_x as NO_2 (150 Nm^3/s), HCl (47 Nm^3/s), Cd (0.059 mg/Nm^3), Cu (2.2 mg/Nm^3), Hg (<0.001 mg/Nm^3), Pb (0.23 mg/Nm^3), Sn (0.09 mg/Nm^3), Zn (4.3 mg/Nm^3), PCDD/PCDF (0.010 ng I-TEQ/Nm^3), PCB (0.019 ng TEF/Nm^3), PAH (2.0 µg/Nm^3), chlorobenzene (22 µm/Nm^3), bromobenzene (12 µm/Nm^3), toluene (0.13 µm/Nm^3)

Gaseous emissions, peat/coal + 12% LPB: Dust (27 Nm^3/s), CO (100 Nm^3/s), hydrocarbons (7 Nm^3/s), SO_x as SO_2 (430 Nm^3/s), NO_x as NO_2 (160 Nm^3/s), HCl (49 Nm^3/s), Cd (0.060 mg/Nm^3), Cu (1.8 mg/Nm^3), Hg (0.003 mg/Nm^3), Pb (0.69 mg/Nm^3), Sn (0.05 mg/Nm^3), Zn (4.0 mg/Nm^3), PCDD/PCDF (0.005 ng I-

TEQ/Nm^3), PCB (0.011 ng TEF/Nm^3), PAH (0.4 µg/Nm^3), chlorobenzene (7.8 µm/Nm^3), bromobenzene (24 µm/Nm^3), toluene (0.29 µm/Nm^3)

Gaseous emissions, peat/coal + 8% MB/FP: Dust (130 Nm^3/s), CO (55 Nm^3/s), hydrocarbons (-), SO_x as SO_2 (180 Nm^3/s), NO_x as NO_2 (160 Nm^3/s), HCl (53 Nm^3/s), Cd (0.062 mg/Nm^3), Cu (2.9 mg/Nm^3), Hg (0.001 mg/Nm^3), Pb (0.27 mg/Nm^3), Sn (0.09 mg/Nm^3), Zn (11 mg/Nm^3), PCDD/PCDF (0.010 ng I-TEQ/Nm$^{3)}$, PCB (0.057 ng TEF/Nm^3), PAH (1.3 µg/Nm^3), chlorobenzene (23 µm/Nm^3), bromobenzene (23 µm/Nm^3), toluene (0.22 µm/Nm^3)

Gaseous emissions, peat/coal + 9% MB/FP + limestone: Dust (5 Nm^3/s), CO (57 Nm^3/s), hydrocarbons (7 Nm^3/s), SO_x as SO_2 (150 Nm^3/s), NO_x as NO_2 (160 Nm^3/s), HCl (37 Nm^3/s), Cd (0.062 mg/Nm^3), Cu (2.9 mg/Nm^3), Hg (<0.001 mg/Nm^3), Pb (0.08 mg/Nm^3), Sn (0.01 mg/Nm^3), Zn (5.2 mg/Nm^3), PCDD/PCDF (0.010 ng I-TEQ/Nm^3), PCB (0.019 ng TEF/Nm^3), PAH (1.4 µg/Nm^3), chlorobenzene (2.7 µm/Nm^3), bromobenzene (93 µm/Nm^3), toluene (0.68 µm/Nm^3)

Gaseous emissions, peat/coal + 11% RDF: Dust (64 Nm^3/s), CO (71 Nm^3/s), hydrocarbons (9 Nm^3/s), SO_x as SO_2 (390 Nm^3/s), NO_x as NO_2 (170 Nm^3/s), HCl (130 Nm^3/s), Cd (0.042 mg/Nm^3), Cu (2.1 mg/Nm^3), Hg (<0.001 mg/Nm^3), Pb (1.22 mg/Nm^3), Sn (0.05 mg/Nm^3), Zn (3.1 mg/Nm^3), PCDD/PCDF (0.015 ng I-TEQ/Nm^3), PCB (0.010 ng TEF/Nm^3), PAH (1.2 µg/Nm^3), chlorobenzene (1.2 µm/Nm^3), bromobenzene (57 µm/Nm^3), toluene (0.44 µm/Nm^3)

Gaseous emissions, peat/coal + 11% RDF + limestone: Dust (62 Nm^3/s), CO (49 Nm^3/s), hydrocarbons (5 Nm^3/s), SO_x as SO_2 (130 Nm^3/s), NO_x as NO_2 (170 Nm^3/s), HCl (83 Nm^3/s), Cd (0.033 mg/Nm^3), Cu (2.1 mg/Nm^3), Hg (0.002 mg/Nm^3), Pb (0.53 mg/Nm^3), Sn (0.03 mg/Nm^3), Zn (4.4 mg/Nm^3), PCDD/PCDF (0.009 ng I-TEQ/Nm^3), PCB (0.009 ng TEF/Nm^3), PAH (1.6 µg/Nm^3), chlorobenzene (12 µm/Nm^3), bromobenzene (92 µm/Nm^3), toluene (0.15 µm/Nm^3)

Gaseous emissions, peat/coal + 18% RDF + limestone: Dust (58 Nm^3/s), CO (55 Nm^3/s), hydrocarbons (9 Nm^3/s), SO_x as SO_2 (130 Nm^3/s), NO_x as NO_2 (190 Nm^3/s), HCl (71 Nm^3/s), Cd (0.051 mg/Nm^3), Cu (1.9 mg/Nm^3), Hg (0.002 mg/Nm^3), Pb (0.88 mg/Nm^3), Sn (0.01 mg/Nm^3), Zn (2.4 mg/Nm^3), PCDD/PCDF (0.012 ng I-TEQ/Nm^3), PCB (0.003 ng TEF/Nm^3), PAH (0.6 µg/Nm^3), chlorobenzene (6.0 µm/Nm^3), bromobenzene (110 µm/Nm^3), toluene (0.30 µm/Nm^3)

Gaseous emissions, peat/coal + 20% RDF + limestone + sulfur: Dust (15 Nm^3/s), CO (62 Nm^3/s), hydrocarbons (6 Nm^3/s), SO_x as SO_2 (370 Nm^3/s), NO_x as NO_2 (160 Nm^3/s), N_2O (23 Nm^3/s), HCl (120 Nm^3/s), Cd (0.037 mg/Nm^3), Cu (2.1 mg/Nm^3), Hg (<0.001 mg/Nm^3), Pb (0.17 mg/Nm^3), Sn (0.01 mg/Nm^3), Zn (5.0 mg/Nm^3), PCDD/PCDF (0.010 ng I-TEQ/Nm^3), PCB (0.014 ng TEF/Nm^3), PAH (0.8 µg/Nm^3), chlorobenzene (4.8 µm/Nm^3), bromobenzene (120 µm/Nm^3), toluene (0.36 µm/Nm^3)

Gaseous emissions, peat/coal + 14% MP: Dust (7 Nm^3/s), CO (51 Nm^3/s), hydrocarbons (3 Nm^3/s), SO_x as SO_2 (140 Nm^3/s), NO_x as NO_2 (170 Nm^3/s), HCl

(47 Nm^3/s), Cd (0.073 mg/Nm^3), Cu (2.9 mg/Nm^3), Hg (<0.001 mg/Nm^3), Pb (0.74 mg/Nm^3), Sn (0.02 mg/Nm^3), Zn (5.3 mg/Nm^3), PCDD/PCDF (0.002 ng I-TEQ/Nm^3), PCB (0.007 ng TEF/Nm^3), PAH (0.5 µg/Nm^3), chlorobenzene (25 µm/Nm^3), bromobenzene (16 µm/Nm^3), toluene (0.11 µm/Nm^3)

Carbon content of the fly ash decreased with substitution of waste fuels for peat/coal mixture. Limestone addition increased the amount of S and Cl retained on the fly ash. The substitution of waste fuels for peat/coal led to significantly higher heavy metals in the fly ash, especially for Hg and Cd. Without limestone, the amount of PCDD/PCDF in the fly ash increased with increasing amount of Cl in the waste fuels. The addition of limestone greatly increased the amount of PCDD/PCDF.

Fly ash, peat/coal mixture: Total C (20%), Al (10%), Ca (3.3%), S (0.9%), Cl (0.05%), Cd (1 ppm), Cu (180 ppm), Hg (1 ppm), Pb (180 ppm), Sn (30 ppm), Zn (290 ppm), PCDD/PCDF (10 pg/g I-TEQ), PCB (0.9 pg/g TEF), PAH (3.2 µg/g), chlorobenzene (0.2 µg/g), bromobenzene (Not Detected), chlorophenol (Not Detected)

Fly ash, peat/coal + 12% LPB: Total C (24%), Al (10%), Ca (3.1%), S (1.0%), Cl (0.04%), Cd (1 ppm), Cu (180 ppm), Hg (1 ppm), Pb (180 ppm), Sn (30 ppm), Zn (210 ppm), PCDD/PCDF (8.3 pg/g I-TEQ), PCB (0.7 pg/g TEF), PAH (5.4 µg/g), chlorobenzene (0.2 µg/g), bromobenzene (Not Detected), chlorophenol (0.04 µg/g)

Fly ash, peat/coal + 8% MB/FP: Total C (17%), Al (13%), Ca (5.9%), S (1.3%), Cl (0.07%), Cd (2 ppm), Cu (220 ppm), Hg (1 ppm), Pb (190 ppm), Sn (20 ppm), Zn (390 ppm), PCDD/PCDF (25 pg/g I-TEQ), PCB (0.9 pg/g TEF), PAH (5.1 µg/g), chlorobenzene (0.5 µg/g), bromobenzene (Not Detected), chlorophenol (0.01 µg/g)

Fly ash, peat/coal + 9% MB/FP + limestone: Total C (12%), Al (12%), Ca (15%), S (2.7%), Cl (0.35%), Cd (2 ppm), Cu (270 ppm), Hg (7 ppm), Pb (190 ppm), Sn (30 ppm), Zn (350 ppm), PCDD/PCDF (2.6 pg/g I-TEQ), PCB (1.9 pg/g TEF), PAH (0.8 µg/g), chlorobenzene (0.7 µg/g), bromobenzene (Not Detected), chlorophenol (Not Detected)

Fly ash, peat/coal + 11% RDF: Total C (17%), Al (12%), Ca (4.6%), S (1.1%), Cl (0.10%), Cd (4 ppm), Cu (330 ppm), Hg (2 ppm), Pb (600 ppm), Sn (60 ppm), Zn (970 ppm), PCDD/PCDF (34 pg/g I-TEQ), PCB (1.0 pg/g TEF), PAH (4.9 µg/g), chlorobenzene (0.2 µg/g), bromobenzene (4.1 µg/g), chlorophenol (0.01 µg/g)

Fly ash, peat/coal + 11% RDF + limestone: Total C (12%), Al (10%), Ca (14%), S (2.9%), Cl (0.75%), Cd (10 ppm), Cu (400 ppm), Hg (2 ppm), Pb (650 ppm), Sn (50 ppm), Zn (850 ppm), PCDD/PCDF (98 pg/g I-TEQ), PCB (2.6 pg/g TEF), PAH (1.8 µg/g), chlorobenzene (0.3 µg/g), bromobenzene (Not Detected), chlorophenol (0.01 µg/g)

Fly ash, peat/coal + 18% RDF + limestone: Total C (10%), Al (9%), Ca (17%), S (3.6 %), Cl (1.4%), Cd (17 ppm), Cu (540 ppm), Hg (3 ppm), Pb (910 ppm), Sn (110 ppm), Zn (1130 ppm), PCDD/PCDF (920 pg/g I-TEQ), PCB (5.4 pg/g TEF), PAH (6.3 µg/g), chlorobenzene (0.7 µg/g), bromobenzene (Not Detected), chlorophenol (0.11 µg/g)

Fly ash, peat/coal + 20% RDF + limestone + sulfur: Total C (9%), Al (10%), Ca (17%), S (4.2 %), Cl (1.1%), Cd (14 ppm), Cu (780 ppm), Hg (3 ppm), Pb (1050 ppm), Sn (100 ppm), Zn (1270 ppm), PCDD/PCDF (910 pg/g I-TEQ), PCB (6.5 pg/g TEF), PAH (1.3 µg/g), chlorobenzene (0.8 µg/g), bromobenzene (Not Detected), chlorophenol (0.11 µg/g)

Fly ash, peat/coal + 14% MP: Total C (15%), Al (7%), Ca (17%), S (3.5%), Cl (1.5%), Cd (36 ppm), Cu (340 ppm), Hg (2 ppm), Pb (510 ppm), Sn (80 ppm), Zn (590 ppm), PCDD/PCDF (430 pg/g I-TEQ), PCB (1.3 pg/g TEF), PAH (2.4 µg/g), chlorobenzene (0.4 µg/g), bromobenzene (Not Detected), chlorophenol (0.05 µg/g)

Gimeno Adelantado, J.V., V. Peris Martinez, F. Bosch Reig, M.T. Doménech Carbó, and F. Bosch Mossi. “Analysis of Toxic Elements in Plastic Components for Toys: Multi-Elemental Determination by X-Ray Fluorescence.” *Analytica Chimica Acta* 276 (1993): 39-45.

This article proposes a method for determining toxic metals in plastic materials to be used in toys. Samples were obtained of components of children’s toys in a variety of colors.

The samples were decomposed using molten sodium hydroxide, and metals were precipitated from the resulting solution and filtered out. The filters were then analyzed by XRF.

Heavy metals, plastic toy samples: Sb (18-42 µg/g), Ba (30-5100 µg/g), Cr(III) (0.07-0.31 µg/g), Cd (7.5-31 µg/g), Hg (1.10-1.96 µg/g), Pb (1.10-240 µg/g), As (III) (12-215 µg/g)

Kim, Dongsu, Sunghye Shin, Seungman Sohn, Jinshik Choi, and Bongchan Ban. “Waste Plastics as Supplemental Fuel in the Blast Furnace Process: Improving Combustion Efficiencies.” *Journal of Hazardous Materials* B94 (2002): 213-222.

This article describes experiments to investigate the use of waste plastics to supplement fossil fuels such as pulverized coal and natural gas in a blast furnace, *not in a cement kiln*.

The authors used laboratory equipment to simulate a blast furnace and test the effects of particle size, blast temperature, and level of oxygen enrichment on the combustion of recycled polyethylene (PE) and pulverized coal. The combustion efficiency of mixtures of recycled PE and pulverized coal was also tested.

Three particle sizes (1.0-1.5 mm, 3.0-5.0 mm, and 8.0-10.0 mm) were examined. As might be expected, larger particles took longer to combust. Because the fuel is injected into the system, this means that the combustion took place over a longer distance in the injection tube and continued to occur closer to the entrance to the blast chamber. Increasing the blast temperature and the level of oxygen enrichment speeded up the process.

The authors found that the addition of plastics decreased the efficiency of coal combustion. Altering the experimental conditions to combust the mixture at a greater distance from the blast chamber improved its combustion efficiency.

Knopf, Hans J. “Energy Recovery from Plastic Wastes in Cement Kilns.” In *Recycling and Recovery of Plastics*. Eds., Johannes Brandrup, et al. New York: Hanser Publishers, 1995.

This document is a book chapter reviewing the use of waste fuels in cement kilns. There is a brief summary of the physical and chemical processes taking place in the precalcinator and kiln. *Despite the title, most of the chapter is about the use for fuel of Automobile Shredder Waste and Refuse-Derived Fuel (RDF) with a plastic component, not about waste plastics as such.* The papers reviewed are largely German-language publications.

In one study reviewed, an initial trial burn of automobile shredder waste had numerous stoppages due to blockage of the fuel feeding system, attributed to inhomogeneous feed materials. There was also an increase in customer complaints about the cement color. Later trials found that it was necessary to limit the amount of shredder waste to 6% of the thermal input in order to limit the total chlorine input. Despite the fact that this limit eliminated blockages due to alkali chloride condensation, there was still damage to the kiln refractory brickwork, attributed to the alkali chlorides.

In another study, the high level of volatile components of RDF meant that adjustments had to be made to the flame size, shape, and temperature profile when using this fuel. The higher level of chlorine in RDF vs. coal led to the installation of an alkali bypass to control the amount of alkali chloride circulating in the kiln system. Use of the bypass allowed the substitution of RDF for coal at levels up to 50%.

Although trial burns of waste plastic materials are mentioned, few details are given, apparently because the information was not published.

Calorific values and composition for fuels:

Hard Coal: Calorific value (29,500 kJ/kg), ash (13.5%), water (1-10%), volatiles (6-30%), C (81-92%), H (4-5%), O (1.4-10%), N (1.2-1.7%), S (0.6%), Cl (0.10-0.16%), F (0.001-0.035%), Cd (0.4-10 mg/kg), Pb (20-270 mg/kg), Cu (16-60 mg/kg), Zn (20-210 mg/kg), Ni (15-95 mg/kg), Cr (5-80 mg/kg), Hg (0.4-1.5 mg/kg)

Firewood: Calorific value (15,070 kJ/kg), ash (0.05%), water (12-25%), volatiles (70-85%), C (50.4%), H (6.4%), O (43.3%), N (0.1%), S (0.3%), Cl (0.08-0.13%), F (--), Cd (0.4-0.7 mg/kg), Pb (0-50 mg/kg), Cu (11-17 mg/kg), Zn (13-27 mg/kg), Ni (0-13 mg/kg), Cr (0-4 mg/kg), Fe (20-60 mg/kg), Hg (--)

Household waste: Calorific value (8,200 kJ/kg), ash (25-33%), water (25-30%), volatiles (10-20%), C (30-40%), H (4-5%), O (15-30%), N (0.3-0.5%), S (0.2-0.7%), Cl (0.5-1.5%), F (0.005-0.025%), Cd (10-40 mg/kg), Pb (600-2,500 mg/kg), Cu (450-2,500 mg/kg), Zn (440-3,500 mg/kg), Ni (50-200 mg/kg), Cr (200-880 mg/kg), Fe (25,000-75,000 mg/kg), Hg (2-7 mg/kg)

RDF: Calorific value (16,000-17,600 kJ/kg), ash (16-25%), water (4-12%), volatiles (50-72%), C (43-50%), H (5-6.5%), O (36-42%), N (0.5-1.0%), S (0.3-0.7%), Cl (0.4-0.7%), F (0.001-0.07%), Cd (2-9 mg/kg), Pb (100-320 mg/kg), Cu (100-1,050 mg/kg), Zn (350-790 mg/kg), Ni (15-60 mg/kg), Cr (80-250 mg/kg), Fe (1,500-9,000 mg/kg), Hg (0.5-3.0 mg/kg)

PDF (paper-derived fuel: Calorific value (13,000-17,410 kJ/kg), ash (4.6%), water (6.2-12.5%), volatiles (75-84%), C (38-45%), H (4-6%), O (33-37%), N (0.15-0.20%), S (0.08-0.3%), Cl (0.1-4.0%), F (0.001-0.012%), Cd (1-5 mg/kg), Pb (80-250 mg/kg), Cu (20-100 mg/kg), Zn (100-500 mg/kg), Ni (1-7 mg/kg), Cr (10-30 mg/kg), Fe (100-700 mg/kg), Hg (0.2 mg/kg)

Scrap tires: Calorific value (27,090-33,600 kJ/kg), ash (12.5-18.6%), S (1.3-2.2%), alkalis (K2O equiv) (<0.1%), Cl (0.2%), Zn (9,300-20,500 ppm), Cr (97 ppm), Ni (77 ppm), Pb (60-760 ppm), Cd (5-10 ppm), Tl (0.2-0.3 ppm)

RDF: Calorific value (18,850 kJ/kg), C (50%), H (7%), O (26%), N (1%), S (0.2%), Cl (0.8%), Ash (15%), Loss on Ignition (2.0%), silicon dioxide (41.0%), aluminium oxide (20.0%), iron trioxide (3.5%), calcium oxide (24.0%), magnesium oxide (3.0%), sodium oxide (2.5%), Pb (244 ppm), Cd (4 ppm), Hg (0.4 ppm), Ni (140 ppm), Cr (300 ppm), Zn (1,350 ppm), V (35 ppm)

Polyolefins: Calorific value (41,000 kJ/kg), volatiles (--), ash (--), particle size (2.0-2.8 mm), degree of combustion (92%)

Petroleum coke: Calorific value (32,369 kJ/kg), volatiles (4.11%), ash (0.7%), particle size (2.3 mm), degree of combustion (56%)

Landsberger, S., and D.L. Chichester. "Characterization of Household Plastics for Heavy Metals Using Neutron Activation Analysis." *Journal of Radioanalytical and Nuclear Chemistry* Articles 192, no. 2 (1995): 289-297.

This article examines the use of neutron activation analysis to determine amounts of heavy metals and halogens in 64 samples of household plastics. Heavy metals are found in plastics due to their presence in pigments, stabilizers and fillers. Amounts vary widely, even for plastics of the same color and/or intended for the same use.

Heavy metals, plastics samples, ranges: Ag (ND-53.0 ppb), Al (ND-39,400 ppm), As (ND-841 ppb), Au (ND-7.66 ppb), Ba (ND-15,227 ppm), Br (ND-65.8 ppm), Ca (ND-70,800 ppm), Cd (ND-4,802 ppm), Cl (ND-41,764 ppm), Co (ND-72.6 ppm), Cr (ND-1,034 ppm), Cs (ND-408 ppb), Cu (ND-474 ppm), Fe (ND-13,806 ppm), In (ND-15.4 ppb), Mn (ND-120 ppm), Mo (ND-122 ppm), Na (ND-1,900 ppm), Ni (ND-6.75 ppm), Sb (ND-306 ppm), Sc (ND-3.45 ppm), Se (ND-1,101 ppm), Si (ND-35,616 ppm), Sm (ND-1.81 ppm), Sn (ND-37.1 ppm), Sr (ND-125 ppm), Th (ND-5.13 ppm), Ti (ND-25,000 ppm), U (ND-923 ppb), V (ND-24.9 ppm), W (ND-804 ppb), Zn (ND-354 ppm)

Marshall, John, Jeff Franks, Ian Abell, and Chris Tye. “Determination of Trace Elements in Solid Plastic Materials by Laser Ablation-Inductively Coupled Plasma Mass Spectrometry.” *Journal of Analytical Atomic Spectrometry* 6 (March 1991): 145-150.

> This article examines the use of laser ablation-ICP-MS for determination of metals and phosphorus in various plastics. Samples of polypropylene, polyester, poly(vinyl chloride), nylon, and polyethylene were analyzed.
>
> Semi-quantitative analysis using carbon-13 as an internal standard was performed on two samples.
>
> Polyester sample, semi-quantitative analysis: Li (0.2 µg/g), Al (590 µg/g), P (90 µg/g), Mn (76 µg/g), Co (25 µg/g), Zn (30 µg/g), Ge (2 µg/g), Mo (2.3 µg/g), Sn (18 µg/g), Sb (160 µg/g), Pb (3.2 µg/g)
>
> Polypropylene sample, semi-quantitative analysis: Li (0.2 µg/g), Al (240 µg/g), P (18 µg/g), Ti (120 µg/g), Mn (30 µg/g), Fe (30 µg/g), Co (12 µg/g), Cu (20 µg/g), Zn (300 µg/g), Zr (41 µg/g), Cd (2.7 µg/g), Sn (33 µg/g), Ba (340 µg/g), Pb (6.5 µg/g)
>
> Quantitative analyses were performed for several samples using external standards with similar matrices.
>
> Polyester sample, quantitative analysis: Al (357 µg/g), Si (720 µg/g), P (93 µg/g), Co (32 µg/g), Zn (45 µg/g), Sb (155 µg/g)
>
> Polypropylene sample, quantitative analysis: Al (105 µg/g), Si (600 µg/g), P (60 µg/g), Co (7 µg/g), Zn (205 µg/g), Sb (Not Detected)
>
> P in pigmented polyethylene samples: Sample A (297 µg/g), sample B (314 µg/g), sample C (139 µg/g), sample D (227 µg/g), sample E (361 µg/g)
>
> Ni in pigmented polyethylene samples: Sample A (204 µg/g), sample B (162 µg/g), sample C (210 µg/g), sample D (80 µg/g), sample E (1 µg/g)
>
> Mg in pigmented polypropylene samples: Sample A (11 µg/g), sample B (6.3 µg/g), sample C (23 µg/g), sample D (17 µg/g), sample E (29 µg/g)

Menad, N., Bo. Björkman, and Eric G. Allain. “Combustion of Plastics Contained in Electric and Electronic Scrap.” *Resources, Conservation and Recycling* 24 (1998): 65-85.

> This article reviews the challenges related to recycling plastic waste from electric and electronic materials. The authors describe the types of plastics found in these wastes, their decomposition processes during combustion, and the environmental problems likely to arise (PCBs in old equipment, halogenated flame retardants, Cd from Ni-Cd batteries, PbO in cathode ray tubes, etc.). *This is an overview article and does not contain specific data relevant to combustion in a cement kiln.*

Miller, B. B., R. Kandiyoti, and D.R. Dugwell. “Trace Element Emissions from Co-Combustion of Secondary Fuels with Coal: A Comparison of Bench-Scale Experimental Data with Predictions of a Thermodynamic Equilibrium Model.” *Energy & Fuels* 16 (2002): 956-963.
(duplicated in another section)

This article examines the co-combustion of coal, four biomass fuels (wood-bark, straw, pulp sludge, and paper sludge), and three waste fuels (agricultural waste, sewage sludge, and plastic waste) in a suspension-firing reactor (intended to simulate a section of a fluidized bed combustor), *not in a cement kiln*. Temperatures in the reactor were 800°C and 900°C. Trace metals are analyzed in the original fuels and in ashes resulting from their combustion. The focus of the article is in the enrichment of the trace metals in the combustion ash.

Exact metals data for the original fuels were not given (although ranges were reported), nor were metals data for the various ash samples. The volatilization (or conversely the retention of a metal in the ash) was found to depend, not only on the metal’s volatility but also on the type of fuel burned. This was ascribed at least partially to the differences between the metal compounds found in the different types of fuels. Paper sludge had the highest degree of volatilization while sewage sludge had the lowest.

Trace metals in fuels, ranges:

Wood-bark: Less than 1 ppm (As, Be, Cd, Co, Hg, Se, Sb, Tl), 1 to 10 ppm (Ni, Mo, Pb, V), 10-100 ppm (Cr, Cu, Sr), greater than 100 ppm (Ba, Mn, Zn)

Straw: Less than 1 ppm (As, Be, Cd, Co, Hg, Ni, Mo, Sb, Tl, V), 1 to 10 ppm (Cr, Cu, Pb), 10-100 ppm (Ba, Mn, Zn)

Columbian coal: Less than 1 ppm (Be, Cd, Hg, Sb, Tl), 1 to 10 ppm (As, Co, Cu, Ni, Mo, Pb, Se), 10-100 ppm (Ba. Cr, Mn, Sr, V, Zn)

Polish coal: Less than 1 ppm (Cd, Hg, Mo, Tl), 1 to 10 ppm (As, Be, Co, Sb, Se), 10-100 ppm (Cr, Cu, No, Pb, Sr, V, Zn), greater than 100 ppm (Ba, Mn)

Sewage sludge: Less than 1 ppm (Be, Hg,Tl), 1 to 10 ppm (As, Cd, Co, Sb), 10-100 ppm (Ni, Mo, Pb, V), greater than 100 ppm (Ba, Cr, Cu, Mn, Sr, Zn)

Paper sludge: Less than 1 ppm (As, Be, Cd, Co, Hg, Se, Tl), 1 to 10 ppm (Ni, Mo, Sb, V), 10-100 ppm (Cr, Cu, Mn, Pb, Sr), greater than 100 ppm (Ba, Zn)

Agricultural waste: Less than 1 ppm (As, Be, Cd, Co, Hg, Pb, Sb, Se, Tl), 1 to 10 ppm (Cr, Mo, V), 10-100 ppm (Ba, Ni, Sr, Cu), greater than 100 ppm (Mn, Zn)

Pulp sludge: Less than 1 ppm (As, Be, Co, Hg, Mo, Sb, Se, Tl), 1 to 10 ppm (Cd, Pb, V), 10-100 ppm (Ba, Cr, Cu, Ni, Sr), greater than 100 ppm (Mn, Zn)

Plastic waste: Less than 1 ppm (As, Be, Hg, Se, Tl), 1 to 10 ppm (Cd, Co, Ni, Mo, Sb, V), 10-100 ppm (Cr, Cu, Mn, Pb, Sr), greater than 100 ppm (Ba, Zn)

Miller, B., D. Dugwell, and R. Kandiyota. “The Fate of Trace Elements During the Co-Combustion of Wood-Bark with Waste.” *Energy & Fuels* 20 (2006): 520-531. (duplicated in another section)

This article examines four waste fuels: wood-bark (from the debarking plant of a paper mill), agricultural waste (chicken litter, manure, and wood chips), pulp sludge (from the paper industry), and plastic waste (from a recycling process). The fuels were combusted in a suspension-firing reactor (intended to simulate a section of a fluidized bed combustor), *not in a cement kiln*. Temperatures in the reactor were 800°C and 900°C.

The original fuels were analyzed to determine their elemental composition, ash and moisture content, and their Lower Heating Value (LHV).

Elemental analysis, Wood-bark, dry, ash-free: C (53.1%), H (6.00%), N (0.45%), O (40.3%), S (0.07%), Cl (0.01%), P (0.04%), ash (6.9%), moisture (3.0%), LHV (18.6 MJ/kg)

Elemental analysis, Agricultural waste, dry, ash-free: C (50.2%), H (6.23%), N (4.11%), O (37.3%), S (0.63%), Cl (0.39%), P (1.06%), ash (12.8%), moisture (4.0%), LHV (15.7 MJ/kg)

Elemental analysis, Pulp sludge, dry, ash-free: C (48.5%), H (6.49%), N (1.31%), O (42.9%), S (0.52%), Cl (0.12%), P (0.08%), ash (3.6%), moisture (4.3%), LHV (18.2 MJ/kg)

Elemental analysis, Plastic waste, dry, ash-free: C (67.9%), H (10.0%), N (0.35%), O (20.4%), S (0.38%), Cl (0.98%), P (0.01%), ash (10.2%), moisture (2.6%), LHV (29.7 MJ/kg)

Minor elements, Wood-bark, dry basis: Na (1.35 g/kg), K (2.26 g/kg), Mg (0.79 g/kg), Ca (7.98 g/kg), Al (2.99 g/kg), Fe (1.52 g/kg), Si (9.7 g/kg)

Minor elements, Agricultural waste, dry basis: Na (4.03 g/kg), K (27.1 g/kg), Mg (4.28 g/kg), Ca (16.4 g/kg), Al (0.35 g/kg), Fe (0.54 g/kg), Si (3.6 g/kg)

Minor elements, Pulp sludge, dry basis: Na (3.06 g/kg), K (0.87 g/kg), Mg (2.04 g/kg), Ca (2.37 g/kg), Al (2.32 g/kg), Fe (0.84 g/kg), Si (9.9 g/kg)

Minor elements, Plastic waste, dry basis: Na (1.91 g/kg), K (0.25 g/kg), Mg (1.18 g/kg), Ca (9.43 g/kg), Al (24.9 g/kg), Fe (1.71 g/kg), Si (9.4 g/kg)

Trace elements, Wood-bark, dry basis: As (0.44 ppm), Ba (156 ppm), Be (0.07 ppm), Cd (0.20 ppm), Co (0.72 ppm), Cr (26 ppm), Cu (87 ppm), Hg (0.033 ppm), Ni (10.0 ppm), Mn (414 ppm), Mo (1.26 ppm), Pb (3.1 ppm), Sb (0.21 ppm), Se (<0.8 ppm), Sr (51 ppm), Ti (94 ppm), Tl (0.09 ppm), V (2.8 ppm), Zn (150 ppm)

Trace elements, Agricultural waste, dry basis: As (0.34 ppm), Ba (13.3 ppm), Be (0.18 ppm), Cd (0.36 ppm), Co (0.40 ppm), Cr (8.8 ppm), Cu (38.2 ppm), Hg (0.95 ppm), Ni (10.6 ppm), Mn (240 ppm), Mo (9.1 ppm), Pb (0.86 ppm), Sb (0.08

ppm), Se (<0.8 ppm), Sr (19.0 ppm), Ti (26.3 ppm), Tl (0.007 ppm), V (1.0 ppm), Zn (252 ppm)

Trace elements, Pulp sludge, dry basis: As (0.50 ppm), Ba (45 ppm), Be (<0.03 ppm), Cd (1.99 ppm), Co (0.45 ppm), Cr (25 ppm), Cu (14.7 ppm), Hg (0.083 ppm), Ni (10.1 ppm), Mn (137 ppm), Mo (0.97 ppm), Pb (2.3 ppm), Sb (0.17 ppm), Se (<0.8 ppm), Sr (13.1 ppm), Ti (40 ppm), Tl (0.13 ppm), V (5.3 ppm), Zn (200 ppm)

Trace elements, Plastic waste, dry basis: As (0.31 ppm), Ba (263 ppm), Be (0.11 ppm), Cd (4.1 ppm), Co (4.6 ppm), Cr (33 ppm), Cu (65 ppm), Hg (0.055 ppm), Ni (5.5 ppm), Mn (26 ppm), Mo (1.10 ppm), Pb (35 ppm), Sb (3.5 ppm), Se (<0.8 ppm), Sr (17.1 ppm), Ti (2,993 ppm), Tl (0.03 ppm), V (2.3 ppm), Zn (501 ppm)

The four fuels were combusted in various combinations. The wood-bark and the agricultural waste were also combusted alone, but it was not possible to combust the pulp sludge or the plastic waste alone, as they could not be fed to the reactor unless mixed with wood-bark.

Although the combustion ashes were analyzed for metal content, the exact metals data are not reported. “Retention values” for each metal are plotted as a function of the concentration of the metal in the original fuel vs. its concentration in the combustion ash of a particular fuel combination.

The retention value of a metal was found to depend, not only on the metal’s inherent volatility, but also on the type of fuel burned.

Cd: Highest retention value was for wood-bark, 60% retention. Retention decreased as other fuels were substituted for the woodbark, proportionate to the amount of the substitution. Retention for agricultural waste burned by itself was 15% at 800°C and 5% at 900°C.

Cr: There was some Cr loss for all fuels, but there seemed to be a higher degree of retention for the fuel combinations than for the individual fuels.

Pb: Most of the Pb in the fuels was volatilized during combustion. There seemed to be little effect from combining the fuels.

Mn: Most of the Mn in the fuels was retained in the ashes for most fuel combinations. However, the addition of the pulp sludge to the wood-bark led to losses of 50%, and the addition of both agricultural waste and plastic waste at a 10% level to wood-bark led to similar losses. The chlorine content of these fuels was suggested as being related to the Mn loss.

Hg: Almost complete volatilization (1-10% retention) was observed for Hg in the combustion of wood-bark, agricultural waste, and their combinations. However, the addition of pulp sludge or plastic waste led to a higher retention (20-30%) of Hg in the ashes. The sulfur content of these fuels is suggested as being related.

Ni: Retention of Ni was high for most fuels and fuel combinations. Two bark/agricultural waste combinations had retention values of 60-65%, however.

Se: Amounts of Se were either below or close to the experimental quantitation limit, which prevented drawing any conclusions about its retention.

Zn: “Substantial” volatilization of Zn was observed for all fuel combinations.

Mirza, Ruksana. “A Review of the Role of Plastics in Energy Recovery.” *Chemosphere* 38 (1999): 207-231.

This article reviews data reported for test burns of plastics at energy-from-waste (EFW) facilities, *not cement kilns*, around the world. Data for some studies are presented in tabular form; for other studies, data are summarized in the text.

Wurtzburg trials data:

Heavy metals, Plastic waste, Condition B(7.5% plastics): Cd (0.023 g/kg), Hg (0.002 g/kg), Pb (0.166 g/kg), Cu (0.022 g/kg), Sb (0.077 g/kg), Cr (0.029 g/kg), Be (<0.0001 g/kg), Zn (0.338 g/kg), Mn (0.004 g/kg), Ni (0.002 g/kg), Se (<0.005 g/kg), Sn (0.029 g/kg)

Heavy metals, Plastic waste, Condition C (15% plastics): Cd (0.036 g/kg), Hg (0.0002 g/kg), Pb (0.645 g/kg), Cu (0.029 g/kg), Sb (0.031 g/kg), Cr (0.046 g/kg), Be (<0.0001 g/kg), Zn (0.542 g/kg), Mn (0.009 g/kg), Ni (0.023 g/kg), Se (<0.005 g/kg), Sn (0.028 g/kg)

Heavy metals, Flue gases, Before APCD (Cyclone), Condition A (baseline): Cd (0.30-1.57 mg/m^3), Hg (0.10-0.75 mg/m^3), Pb (2.80-10.10 mg/m^3), Cu (1.74-3.84 mg/m^3), Sb (1.01-2.75 mg/m^3), Cr (0.06-1.08 mg/m^3), Sn (0.43-2.57 mg/m^3), particulates (2.96-9.77 mg/m^3)

Heavy metals, Flue gases, Before APCD (Cyclone), Condition B (7.5% plastics): Cd (0.38-0.98 mg/m^3), Hg (0.48-1.1 mg/m^3), Pb (1.57-2.70 mg/m^3), Cu (1.43-2.08 mg/m^3), Sb (1.38-1.66 mg/m^3), Cr (0.10-0.16 mg/m^3), Sn (0.49-0.89 mg/m^3), particulates (1.52-3.76 mg/m^3)

Heavy metals, Flue gases, Before APCD (Cyclone), Condition C (15% plastics): Cd (1.21-1.31 mg/m^3), Hg (0.16-0.47 mg/m^3), Pb (4.29-6.78 mg/m^3), Cu (4.14-5.27 mg/m^3), Sb (2.98-5.47 mg/m^3), Cr (0.74-0.76 mg/m^3), Sn (1.70-2.59 mg/m^3), particulates (2.60-3.67 mg/m^3)

HCl Emissions, Condition A (baseline): Before APCD (Cyclone) (358-631 mg/m^3), After APCD (11-41 mg/m^3)

HCl Emissions, Condition B (7.5% plastics): Before APCD (Cyclone) (1465-4739 mg/m^3), After APCD (15-17 mg/m^3)

HCl Emissions, Condition C (15% plastics): Before APCD (Cyclone) (806-1095 mg/m^3), After APCD (18-19 mg/m^3)

PCDD/F in flue gases, Condition A (baseline): Before APCD (Cyclone) (1.29-4.34 ng/m^3), After APCD (0.0117-1.59 ng/m^3)

PCDD/F in flue gases, Condition B (7.5% plastics): Before APCD (Cyclone) (2.89-6.53 ng/m^3), After APCD (0.0179-1.63 ng/m^3)

PCDD/F in flue gases, Condition C (15% plastics): Before APCD (Cyclone) (2.76-4.2 ng/m^3), After APCD (0.0158-0.91 ng/m^3)

Heavy metals in solid residues, Condition A (baseline): Cd (0.345-0.5045 g/kg), Hg (0.0057-0.0089 g/kg), Sb (0.836-1.248 g/kg), Pb (8.93-14.518 g/kg), Cr (0.655-0.833 g/kg), Cu (3.605-10.539 g/kg), Sn (1.25-1.782 g/kg)

Heavy metals in solid residues, Condition B (7.5% plastics): Cd (0.3554 g/kg), Hg (0.0044 g/kg), Sb (0.643 g/kg), Pb (6.481 g/kg), Cr (0.671 g/kg), Cu (2.892 g/kg), Sn (0.946 g/kg)

Heavy metals in solid residues, Condition C (15% plastics): Cd (0.3796 g/kg), Hg (0.0035 g/kg), Sb (1.047 g/kg), Pb (11.632 g/kg), Cr (0.618 g/kg), Cu (3.921 g/kg), Sn (1.676 g/kg)

Miscellaneous analytes in solid residues, Condition A (baseline): Cl (246-354 g/kg), Total Organic Carbon (19.9-135.9 g/kg), PCDD/F (1.1807-2.4557 µg/kg)

Miscellaneous analytes in solid residues, Condition B (7.5% plastics): Cl (286-357 g/kg), Total Organic Carbon (19-91.3 g/kg), PCDD/F (1.1109-1.8684 µg/kg)

Miscellaneous analytes in solid residues, Condition C (15% plastics): Cl (282-358 g/kg), Total Organic Carbon (14.1-73.9 g/kg), PCDD/F (0.9079-1.2348 µg/kg)

South East London Combined Heat and Power emissions data:

Baseline data: Particulates (1.51, 1.37 mg/m^3), HCl (11.3, 3.1 mg/m^3), SO_2 (21, 7 mg/m^3), CO (20, 9 mg/m^3), Cd (0.001, <0.001 mg/m^3), Hg (0.002, 0.006 mg/m^3), As (<0.001, <0.001 mg/m^3), Cr (0.003, 0.001 mg/m^3), Cu (0.002, 0.001 mg/m^3), Mn (<0.001, <0.001 mg/m^3), Ni (0.001, <0.001 mg/m^3), Pb (0.006, 0.005 mg/m^3), Sn (<0.001, <0.001 mg/m^3), PCDD/Fs (0.01, 0.06 mg/m^3)

Added plastics data: Particulates (1.28, 1.6 mg/m^3), HCl (8.3, 8.7 mg/m^3), SO_2 (18, 13 mg/m^3), CO (5, 4 mg/m^3), Cd (0.002, 0.001 mg/m^3), Hg (0.003, 0.011 mg/m^3), As (<0.001, <0.001 mg/m^3), Cr (0.01, 0.002 mg/m^3), Cu (0.002, 0.002 mg/m^3), Mn (0.002, 0.001 mg/m^3), Ni (0.015, 0.001 mg/m^3), Pb (0.009, 0.009 mg/m^3), Sn (<0.001, <0.001 mg/m^3), PCDD/Fs (0.014, 0.005 mg/m^3)

Pittsfield study:

This study compared PCDD/PCDF production for burns of waste with no poly(vinyl chloride) (PVC) content versus. waste spiked with 2% PVC. The researchers found that the PVC content did not have an effect on the PCDD/PCDF emissions.

Ebara study:

This study compared two trial burns: one with waste plastics from MSW and one with plastic pellets. No baseline burns were done without plastics.

Summary of gaseous emissions data: CO (22 ppm); NO_x (100 ppm); HCl (87 ppm); total hydrocarbons (1.4 ppm), PCDD/PCDF (0.1 ng-TEQ/Nm^3); dust (<1 mg/Nm^3)

University of Florida study:

This work studied the correlation between PVC content of incinerated waste and emissions of chlorinated organic compounds. PVC was spiked into institutional waste at levels of 0.7%-4.7%. Emissions of HCl, CO, and VOCs were measured at the stack.

Valid VOC results were only obtained for about half of the tests; reasons for this are not known. Only 6 of the runs yielding valid VOC results were made with PVC-spiked waste. *Unfortunately, although the data are reported for these tests, there is no indication in the table as to which data belong to which run.* The text states that HCl emissions increased with increasing PVC content in the waste and that dichlorobenzenes emissions correlate to the amounts of chlorobenzene and HCl present in the emissions.

A subsequent analysis of these data by other researchers indicates that the data were not obtained under steady state conditions and that the conclusions drawn are thus unreliable.

Nakano, Kazuhiko, and Toshihiro Nakamura. “Preparation of Calibrating Standards for X-Ray Fluorescence Spectrometry of Trace Metals in Plastics.” *X-Ray Spectrometry* 32 (2003): 452-457.

This article discusses the preparation and use of calibration standards for quantitative analysis of some trace metals in plastics using XRF.

Standards for calibration were prepared from polyester resin and from polyurethane resin. The resins were combined with toluene solutions of organometallic forms of the desired metal species. Disks were cast using the resin/organometallic solutions and were then used as calibration standards for the XRF instrument. Metals added were V, Cr, Co, Ni, Ge, and Sb.

Method blanks were also cast from the polymer resins without the addition of the organometallics. Zn and Fe were detected in both resins and Co was detected in the polyester disk.

After calibration curves were prepared and analyzed, 20 samples of plastic materials were quantitatively analyzed for the metals. Good agreement was observed with results obtained using Atomic Absorption Spectrometry.
Polyethylene 1: Ni (22.4 ppm), Sb (82.2 ppm)
Polyethylene 2: Co (20.7 ppm), Sb (227 ppm)
Polypropylene 1: Cr (4.66 ppm), Ni (6.43 ppm), Sb (40.1 ppm)
Polypropylene 2: Ni (8.60 ppm)

Polypropylene 3: Cr (1.79 ppm)
Polystyrene: Cr (1.30 ppm)
Acrylonitrile-butadiene-styrene copolymer: Co (91.5 ppm), Ni (24.8 ppm), Sb (33.4 ppm)
Polyethylene terephthalate 1: Ge (53.2 ppm)
Polyethylene terephthalate 2: Ge (53.7 ppm)
Polyethylene terephthalate 3: Ge (55.2 ppm)
Polyethylene terephthalate 4: Ge (not detected)
Polyethylene terephthalate 5: Ge (52.0 ppm)
Polyethylene terephthalate 6: Ge (59.1 ppm)
Polyethylene terephthalate 7: Ge (not detected)
Polyethylene terephthalate 8: Ge (51.8 ppm)
Polyethylene terephthalate 9: Ge (56.6 ppm)
Polyethylene terephthalate 10: Ge (33.8 ppm)
Polyethylene terephthalate 11: Ge (55.7 ppm)
Polyethylene terephthalate 12: Ge (53.9 ppm)
Polyethylene terephthalate 13: Ge (37.3 ppm)

Resano, M., Miguel A. Belarra, J.R. Castillo, and Frank Vanhaecke. "Direct Determination of Phosphorus in Two Different Plastic Materials (PET and PP) by Solid-Sampling-Graphite Furnace Atomic Asorption Spectrometry." *Journal of Analytical Atomic Spectrometry* 15 (2000): 1383-1388.

This article describes the determination of phosphorus in two plastics by solid sampling graphite furnace AAS. Analysis of P (used as an additive) is difficult by more conventional techniques due to losses during sample digestion, high detection limits, and possible interferences. Solid sampling bypasses the sample digestion stage and its losses, and graphite furnace AAS allows larger amounts of sample to be analyzed, lowering detection limits.

Polyethyleneterephthalate (PET) and polypropylene (PP) samples were analyzed as small pieces suspended in water. Modifiers (Pd and ascorbic acid) were added to the samples to improve the analysis performance. Good agreement was observed with analyses obtained using ICP-MS and ICP-AES.

P in polyethyleneterephthalate: 47.7 µg/g

P in polypropylene: 1054 µg/g

Vanhaecke, Frank, Martín Resano, and Luc Moens. "Electrothermal Vaporisation [sic] ICP-Mass Spectrometry (ETV-ICP-MS) for the Determination and Speciation of Trace Elements in Solid Samples—A Review of Real-Life Applications from the Author's Lab." *Analytical and Bioanalytical Chemistry* 374 (2002): 188-195.

This article describes the use of electrothermal vaporization from a graphite furnace as a means of volatilizing solid samples for ICP-MS analysis.

Temperature programs were used to separate the volatilization of a target element or elements from the matrix and from other analytes. Plastics and samples of biological origin were analyzed using this method. Results were in good agreement with reference values for these samples.

Polyethyleneterephthalate: Co (49.3 µg/g), Mn (29.6 µg/g), P (19.5 µg/g), Ti (46.1 µg/g)

Polyethylene: Al (18.3 µg/g), Ba (286 µg/g), Cd (21.6 µg/g), Cu (13.0 µg/g), Mn (4.59 ng/g), Pb (13.8 µg/g), Tl (503 µg/g)

Vehlow, Jürgen, Britta Bergfeldt, Hans Hunsinger, Helmut Seifert, and Frank E. Mark. "Bromine in Waste Incineration. Partitioning and Influence on Metal Volatilisation [sic]." *ESPR-Environmental Science & Pollution Research* 10 no. 5 (2003): 329-334.

This article describes tests at a pilot-scale incinerator, *not a cement kiln*, in which plastics containing brominated flame retardants were mixed with MSW and burned. The plastics tested were those expected to have high Br content, including plastic foams from the building trade and waste from electrical and electronic equipment (WEEE).

The baseline fuel for this pilot incinerator was said to represent Central European MSW and consisted of 75% shredded and homogenized residential waste and 25% pelletized RDF. The first test burn was done with 12% plastic waste (mixture of plastic from consumer, commercial, and industrial sectors) and 0.25% total Br. The second test burn was done with 22% plastic waste (mixed WEEE) and 1% total Br).

The test plastics and the incinerator gaseous emissions, fly ash, and bottom ash were analyzed to obtain approximate mass balances for Cl, Br, and metal species. Data are *not reported in tabular form*, however, but are presented graphically. More than 90% of the organic Br ended up in the gaseous emissions, mostly as HBr. At high Br levels, Br_2 was detected. However, as long as there was an excess of SO_2 present, no Br_2 was detected, only HBr. Br enhanced the volatilization of metals such as K, Zn, Cd, Sn, Sb, and Pb similarly to Cl. Most of the volatilized metals ended up in the fly ash.

Wurst, F., and T. Prey. "Dioxin Emissions When Using Alternative Fuels in the Cement Industry." *ZKG International* 56 no. 4 (2003): 74-77.

This article describes the test burns of chlorine-containing alternative fuels at a cement plant. The alternative fuels included waste plastics, a high-calorie fraction from mechanical-biological waste treatment, and an alternative fuel produced from domestic refuse by mechanical-thermal processing.

Emissions results showed no correlation between the amount of chlorine input into the system from the alternative fuel being tested and PCDD/PCDF emissions. There was also no correlation between fuel chlorine input and PCB emissions. However, there was a good correlation between fuel chlorine content and the chlorine content of the dust collected at the filters

IX. Mercury Emissions

Owens, Warren D., Adel F. Sarofim, and David W. Pershing. “The Use of Recycle for Enhanced Volatile Metal Capture.” *Fuel Processing Technology* 39, nos. 1-3 (1994): 337-356.
(duplicated in another section)

> This article purports to be about how industries using coal-fired boilers can benefit from a process similar to the one used by cement kilns use to entrap volatile metals in the clinker—the recycle of cement kiln dust. However, the authors seem to fixate on the use of the bypass, which actually removes volatile metals from the system by wasting the CKD. (However, this doesn’t really reduce metal emissions, it just changes their form from gaseous to solid.) It is not altogether clear how the industrial boilers can emulate the cement kiln’s recycle process (possibly the use of a bypass to loop the flue gas back into the boiler so it passes over the ash?). One interesting and possibly useful item is the mention of the use of carbon to trap (and thus reduce) mercury emissions.

Laudal, D., B. Nott, T. Brown, and R. Roberson. “Mercury Speciation Methods for Flue Gas.” *Fresenius Journal of Analytical Chemistry* 358 (1997): 397-400.

> This article examines the mercury species in flue gas from coal burned in a power plant combustor, *not a cement kiln*. A baghouse is used as an air pollution control device. Dust samples collected from the bags, as well as impinger solutions, are analyzed to determine the mercury species present in the flue gas.

Chang, Moo Been, Hsiu Tung Wu, and Chien Kun Huang. “Evaluation on Speciation and Removal Efficiencies of Mercury from Municipal Solid Waste Incinerators in Taiwan.” *The Science of the Total Environment* 246 (2000): 165-173.

> This article examines the mercury emissions from two municipal solid waste incinerators, *not cement kilns*. The authors sample the stack gases and capture the mercury using liquid and fabric scrubbers and analyze the scrubbers to determine the various mercury species emitted.

Laudal, Dennis L., Jeffrey S. Thompson, John H. Pavlish, Lynn A. Brickett, and Paul Chu. “Use of Continuous Mercury Monitors at Coal-Fired Utilities.” *Fuel Processing Technology* 85 (2004): 501-511.

> This article examines mercury emission data obtained using semicontinuous emission monitors at coal-burning power plants, *not cement kilns*. Emissions before and after the various pollution control devices employed at the plants are compared. Factors affecting the performance of the monitoring devices are also examined.

X. NO_x Emissions

McQueen, A.T., S.J. Bortz, M.S. Hatch, and R.L. Leonard. “Cement Kiln NO_x Control.” *IEEE Transactions on Industry Applications* 31, no. 1 (1995): 36-44.

> This article seems to be a review of the methods used to control NO_x emissions in cement manufacture. The various methods are compared in terms of feasibility, effectiveness, cost, and effect on clinker quality. There is also a discussion of NO_x formation mechanisms and regulations concerning NO_x emissions.

Young, G.L., and M. von Seebach. “NO_x Abatement in Kiln Plants in the Cement Industry.” *ZKG International* 51, no. 6 (1995):304-321

> This article discusses NO_x formation reactions in the cement kiln system. It uses statistical analysis to show that determination of NO_x emission limits requires data measurements over several days. It also discusses several NO_x control techniques for the cement plant.

Davis, Richard A. “Nitric Oxide Formation in an Iron Oxide Pellet Rotary Kiln Furnace.” *Journal of the Air & Waste Management Association* 48 (1997): 44-51.

> This article is about a model for NO_x formation in an iron oxide pellet rotary kiln furnace, *not in a cement kiln*. The kiln temperature is about 1330°C. Simulations were made using different pellet bed mass flow rates, O_2 partial pressures, and temperatures.

Courtemanche, Bonnie, and Yiannis A. Levendis. “A Laboratory Study on the NO, NO_2, SO_2, CO and CO_2 Emissions from the Combustion of Pulverized Coal, Municipal Waste Plastics and Tires.” *Fuel* 77, no. 3 (1998): 183-196.

> This article examines emissions from combustion of coal, tire crumbs, and waste plastics in a drop furnace, *not a cement kiln*. Effects of various operating parameters on the NO_x, SO_2, CO, and CO_2 emissions are studied.

Lietti, Luca, Gianpiero Groppi, and Cristiano Ramella. “NH_3 Oxidation during the Catalytic Combustion of Biomasses-Related Fuels Over Mn-Substituted Hexaaluminates.” *Catalysis Letters* 53 (1998): 91-95.

> This article examines the catalysis of NH_3 oxidation to NO_x by a Mn-substituted hexaaluminate. The fuels burned are biomass-derived, and they are burned in a laboratory setting using a microreactor, *not a cement kiln*. Although significant amounts of NO_x are formed, at high temperatures, gas-phase reactions between NH_3 and NO_x in the presence of O_2 reduce NO_x formation.

Sugiyama, Hideko, Sachiko Kagawa, Hidehiro Kamiya, and Masayuki Horio. “Chlorine Behavior in Fluidized Bed Incineration of Refuse-Derived Fuels.” *Environmental Engineering Science* 15, no. 1 (1998): 97-105.

> This article examines the fate of chlorine in a fluidized bed incinerator burning Refuse Derived Fuel, *not in a cement kiln*. Bed temperatures are around 970-1070°C. Almost 40% of the chlorine is captured by the bottom ash. It is also

observed that the presence of chlorine seems to activate CaO as a catalyst for oxidation of NH_3 to NOx in the fluidized bed incinerator.

Smart, J.P., B.G. Jenkins, and W.L. van de Kamp. “An Investigation into NO_x Emissions from the High-Temperature Rotary Cement Kiln.” *Journal of the Institute of Energy* 72, no. 492 (1999): 99-109.

This article reports the results of a study of NO_x emissions made using a cement kiln simulator. Fuels used were bituminous coals and petroleum coke. In these studies, thermal NO_x formation was the dominant formation mechanism.

Smart, J.P., B.G. Jenkins, and W.L. van de Kamp. “Studies on NO_x Emission from an Experimental Rotary Cement Kiln Fired with Mono and Multi-Channel Burners.” *ZKG International* 52, no. 8 (1999): 420-422, 425-432.

This article seems to be the same as the earlier one by the same authors. The data might be different, but it’s difficult to tell.

Lissianski, Vitali V., Vladimir M. Zamandky, and Peter M. Maly. “Effect of Metal-Containing Additives on NO_x Reduction in Combustion and Reburning.” *Combustion and Flame* 125 (2001): 1118-1127.

This article describes a study of the effect of sodium and potassium carbonates, calcium acetate and fly ash on NO_x emissions in a combustor, *not a cement kiln*. Co-injections with the fuel reduced NO_x, while injections further away reduced it less. Modeling was done to see if the mechanism of the reduction could be determined.

Sullivan, Neal, Anker Jensen, Peter Glarborg, Marcus S. Day, Joseph F. Grcar, John B. Bell, Christopher J. Pope, and Robert J. Kee. “Ammonia Conversion and NO_x Formation in Laminar Coflowing Nonpremixed Methane-Air Flames.” *Combustion and Flame* 131 (2002): 285-298.

This article discusses NO_x formation from NH_3 in a methane air flame, *not a cement kiln*. The NH_3/methane mixture is intended as a model for biomass fuels. Flue-gas sampling is used to measure stable species in the gaseous emissions. A computed model shows good agreement with the experimental measurements.

Kouprianov, V.I., and W. Permchart. “Emissions from a Conical FBC Fired with a Biomass Fuel.” *Applied Energy* 74 (2003): 383-392.

This article examines the gaseous emissions from the combustion of mixed sawdust using a conical Fluidized Bed Combustor, *not a cement kiln*. Effects of various operating parameters on the emissions of CO, NO_x, and CO2 are studied.

Wei, Xiaolin, Xiahai Han, Uwe Schnell, Jörg Maier, Holger Wörner, and Klaus R.G. Hein. “The Effect of HCl and SO_2 on NO_x Formation in Coal Flames.” *Energy & Fuels* 17 (2003): 1392-1398.

This article investigates the effect of HCl and SO_2 on NO_x formation in a combustion reactor burning coal, *not a cement kiln*. HCl is shown to reduce NO_x formation, while the effect of SO_2 is less pronounced.

XI. Element Effects on Kiln Process, Clinker, Cement, and Concrete

Gartner, E.M. "The Effects of Minor and Trace Elements on the Manufacture and Use of Portland Cement." SN2064, Portland Cement Association.

This is a fairly lengthy review of minor/trace elements in cement (possibly an earlier version of the Bhatty book). Likely origins, amounts, and effects are discussed for most of the elements in the periodic table. Environmental hazards and volatilities are also discussed.

Miller, F.M. "Minor Elements in Cement Clinker." SN2061, Portland Cement Association.

This is a brief review of minor/trace elements in cement. Likely origins, amounts, and effects are discussed for some common minor/trace elements.

Jawed, Inam, and Jan Skalny. "Alkalies [sic] in Cement: A Review. I. Forms of Alkalies [sic] and Their Effect on Clinker Formation." *Cement and Concrete Research* 7 (1977): 719-730.

This article is a review of the literature on the effect of alkali sulfates on the crystal structure of clinker minerals and their hydraulic reactivity. The literature about the effects of alkalis on the kiln melt and the phase composition of the clinker is also reviewed.

Jawed, Inam, and Jan Skalny. "Alkalies [sic] in Cement: A Review. II. Effects of Alkalies [sic] on Hydration and Performance of Portland Cement." *Cement and Concrete Research* 8 (1978): 37-52.

This article is a review of the literature on the effect of alkali compounds in clinker on the hydration of the Portland cement made from that clinker. The literature on the effects on engineering and mechanical properties of the cement is also reviewed.

Halicz, L., Y. Nathan, and L. Ben-Dor. "The Influence of P2O5 on Clinker Reactions." *Cement and Concrete Research* 14 (1983): 11-18.

This article describes laboratory experiments in which phosphate rock, raw meal containing Israeli oil shale (at various concentrations), and laboratory grade $CaCO_3$ and SiO_2 are burned to make clinker. The effects of the amount of P_2O_5 present on the alite, belite, and C_2S/C_3S ratio are examined.

Suderman, R.W. "CCL Raw Mix Prep[a]ration Seminar: Influence of Trace Elements on Cement Quality." Given October 25-28, 1983, November 15-18, 1983.

This document is a handout from a seminar on the influence of some common trace elements (Mg, alkalis, sulfates, P_2O_5, some metals) in raw materials on the

> cement produced. The author briefly mentions the most likely origins, amounts, and effects for each of these elements.

Grzeszczyk, S., and L. Kucharska. “The Influence of Alkalis on Rheological Properties of Fresh Cement Pastes.” *Cement and Concrete Research* 18 (1988): 1-8.

> This article describes laboratory experiments in which alkali metals are added either to the raw meal before clinker burning or, after burning and grinding, in the makeup water. The effects on the rheological properties of fresh cement pastes made from the clinkers are compared.

Kakali, G., V. Kasselouri, and G. Parissakis. “Hydration and Strength Development of Cements Produced from Raw Mixes Containing MoO_3, Nb_2O_5, WO_3 and ZrO_2.” *Cement and Concrete Research* 19 (1989): 968-972.

> This article describes laboratory experiments in which a metal oxide is added to raw meal (at various concentrations) and burned to make clinker. The effects of the added metal on the hydration, compressive strength, and setting time of the resulting cements are examined.

Kakali, G., V. Kasselouri, and G. Parissakis. “Investigation of the Effect of Mo, Nb, W, and Zr Oxides on the Formation of Portland Cement Clinker.” *Cement and Concrete Research* 20 (1990): 131-138.

> This article describes laboratory experiments in which a metal oxide is added to raw meal (at various concentrations) and burned to make clinker. The effects of the added metal on the thermogravimetry, crystal structure, and mineralogy of the resulting clinkers are examined.

Kakali, G., V. Kasselouri, and G. Parissakis. “Investigation of the Effect of Mo, Nb, W, and Zr Oxides on the Formation of Portland Cement Clinker.” *Cement and Concrete Research* 20 (1990): 131-138.

> This article describes laboratory experiments in which a metal oxide is added to raw meal (at various concentrations) and burned to make clinker. The effects of the added metal on the thermogravimetry, crystal structure, and mineralogy of the resulting clinkers are examined.

Ichikawa, M., and Y. Komukai. “Effect of Burning Conditions and Minor Components on the Color of Portland Cement Clinker.” *Cement and Concrete Research* 23 (1993): 933-938.

> This article describes laboratory experiments in which one or more metal oxides are added to raw meal (at various concentrations) and burned to make clinker. Burning conditions are also varied. The effects of the added metals and the changes in burning conditions on clinker color are examined.

Bhatty, Javed I., *Role of Minor Elements in cement Manufacture and Use*, RD109T, Skokie, Ill.: Portland Cement Association, 1995.

This book is a fairly comprehensive review of minor/trace elements in cement. Likely origins, amounts, and effects are discussed for most of the elements in the periodic table. Elements are discussed as part of their periodic table Group. There is a brief discussion of the role of waste materials in the manufacture of cement, whether as feed or as fuel. There are also definitions of “major”, “lesser”, “minor”, and “trace” elements.

Kakali, G., and G. Parissakis. “Investigation of the Effect of Zn Oxide on the Formation of Portland Cement Clinker.” *Cement and Concrete Research* 25, no.1 (1995): 79-85.

This article describes laboratory experiments in which ZnO is added to raw meal (at various concentrations) and burned to make clinker. The effects of the added metal on the differential scanning calorimetry and crystal structure of the resulting clinkers are examined.

Kasselouri, V., and Ch. Ftikos. “The Effect of V_2O_5 on the C_3S and C_3A Formation.” *Cement and Concrete Research* 25, no. 4 (1995): 721-726.

This article describes laboratory experiments in which V_2O_5 is added (at various concentrations) to mixtures of pure compounds, and the mixtures are fired to produce C_3S or C_3A (depending on the mixture composition). The material produced is analyzed to determine the amount of C_3S or C_3A produced and its form.

Kakali, G., G. Parissakis, and D. Bouras. “A Study of the Burnability and the Phase Formation of PC Clinker Containing Cu Oxide.” *Cement and Concrete Research* 26, no. 10 (1996): 1473-1478.

This article describes laboratory experiments in which CuO is added to raw meal (at various concentrations) and burned to make clinker. The effects of the added metal on the differential scanning calorimetry, amount of free lime, as an indicator of reactivity, crystal structure, and mineralogy of the resulting clinkers are examined.

Murat, M., and F. Sorrentino. “Effect of Large Additions of Cd, Pb, Cr, Zn to Cement Raw Meal on the Composition and the Properties of the Clinker and the Cement.” *Cement and Concrete Research* 26, no. 3 (1996): 377-385.

This article describes laboratory experiments in which a metal chloride is added to raw meal (at various concentrations) and burned to make clinker. The clinkers produced are analyzed to determine the effects of the dopants on crystal structure and mineralogy. The amounts of the dopants present in the clinkers are also determined to evaluate the extent to which the metals volatilize during clinkerization. The effects of the added metal on the setting time, compressive strength, and hardening behavior of the resulting cements are also examined.

Ichikawa, M., and M. Kanaya. “Effects of Minor Components and Heating Rates on the Fine Textures of Alite in Portland Cement Clinker.” *Cement and Concrete Research* 27, no. 7 (1997): 1123-1129.

This article describes laboratory experiments in which a minor constituent, such as a metal oxide, P_2O_5, or SO_3, is added to raw meal (at various concentrations) and burned to make clinker. The alite in the clinkers produced is analyzed to determine its phase ration and grain structure.

Kasselouri, V., and Ch. Ftikos. “The Effect of MoO_3 on the C_3S and C_3A Formation.” *Cement and Concrete Research* 27, no. 6 (1997): 917-923.

This article describes laboratory experiments in which MoO_3 is added (at various concentrations) to mixtures of pure compounds, and the mixtures are fired to produce C_3S or C_3A (depending on the mixture composition). The material produced is analyzed to determine the amount of C_3S or C_3A produced and its form.

Tsivilis, S., and G. Kakali. “A Study on the Grindability of Portland Cement Clinker Containing Transition Metal Oxides.” *Cement and Concrete Research* 27, no. 5 (1997): 673-678.

This article describes laboratory experiments in which a metal oxide is added to raw meal (at various concentrations) and burned to make clinker. The effects of the added metal on the clinker grindability are examined. The clinkers are also examined for effects on crystal structure.

Kakali, G., S. Tsivilis, and A. Tsialtis. “Hydration of Ordinary Portland Cements Made from Raw Mix Containing Transition Element Oxides.” *Cement and Concrete Research* 28, no.3 (1998): 335-340.

This article describes laboratory experiments in which a metal oxide is added to raw meal (at various concentrations) and burned to make clinker. The effects of the added metal on the hydration process, products, compressive strength, and setting time of the resulting cements are examined.

Altun, İ. Akın. “Effect of CaF_2 and MgO on Sintering of Cement Clinker.” *Cement and Concrete Research* 29 (1999): 1847-1850.

This article describes laboratory experiments in which CaF_2 or MgO is added (at various concentrations) to a mixture of limestone, sand, and loam and burned to make clinker. The clinkers produced are analyzed for alite, belite, and free lime, and results are compared to clinkers produced without additions.

Katyal, N.K., S.C. Ahluwalia, and R. Parkash. “Effect of Barium on the Formation of Tricalcium Silicate.” *Cement and Concrete Research* 29 (1999): 1857-1862.

This article describes laboratory experiments in which $BaCO_3$ is added (at various concentrations) to $CaCO_3$ and quartz, and the mixtures are fired to produce C_3S. The material produced is analyzed to determine the amount of C_3S produced and its form and the amount of free lime remaining.

Katyal, N.K., S.C. Ahluwalia, and Ram Parkash. “Effect of TiO_2 on the Hydration of Tricalcium Silicate.” *Cement and Concrete Research* 29 (1999): 1851-1855.

This article describes laboratory experiments in which TiO_2 is added (at various concentrations) to $CaCO_3$ and quartz, and the mixtures are fired to produce C_3S. The C_3S produced is ground and hydrated to produce pastes which are then analyzed to determine the effect of the amount of TiO_2 on hydration rate.

Stephan, D., H. Maleki, D. Knöfel, B. Eber, and R. Härdtl. "Influence of Cr, Ni, and Zn on the Properties of Pure Clinker Phases. Part I. C_3S." *Cement and Concrete Research* 29 (1999): 545-552.

This article describes laboratory experiments in which a metal oxide is added (at various concentrations) to $CaCO_3$ and SiO_2, and the mixtures are fired to produce C_3S. The material produced is analyzed to determine the amount of C_3S produced and its form and the amount of free lime remaining. Hydration products of the C_3S produced are also analyzed.

Stephan, D., H. Maleki, D. Knöfel, B. Eber, and R. Härdtl. "Influence of Cr, Ni, and Zn on the Properties of Pure Clinker Phases. Part II. C_3A and C_4AF." *Cement and Concrete Research* 29 (1999): 651-657.

This article describes laboratory experiments in which a metal oxide is added (at various concentrations) to $CaCO_3$ and Al_2O_3 or to $CaCO_3$, Al_2O_3, and Fe_2O_3, followed by firing of the mixtures to produce C_3A or C_4AF, respectively. The product is then analyzed to determine the amount and form of C_3A or C_4AF produced and the amount of free lime remaining. Hydration products of the C_3A or C_4AF produced are also analyzed.

Stephan, D., R. Mallmann, D. Knöfel, and R. Härdtl. "High Intakes of Cr, Ni, and Zn in Clinker. Part I. Influence on Burning Process and Formation of Phases." *Cement and Concrete Research* 29 (1999): 1949-1957.

This article describes laboratory experiments in which a metal oxide (at various concentrations) is added to one of three different raw meals and burned to make clinker. The effects of the added metal on free lime (a measure of reactivity), crystal structure, and mineralogy of the resulting clinkers are examined.

Stephan, D., R. Mallmann, D. Knöfel, and R. Härdtl. "High Intakes of Cr, Ni, and Zn in Clinker. Part II. Influence on the Hydration Properties." *Cement and Concrete Research* 29 (1999): 1959-1967.

This article describes laboratory experiments in which cements made from clinkers produced by experiments in the earlier paper are made into pastes. The effects of the added metal on the heat evolution during hydration, on setting time and strength and on the hydration products formed are examined.

Katyal, N.K., S.C. Ahluwalia, and R. Parkash. "Effect of Cr_2O_3 on the Formation of C_3S in $3CaO{:}1SiO_2{:}xCr_2O_3$ System." *Cement and Concrete Research* 30 (2000): 1361-1365.

This article describes laboratory experiments in which Cr_2O_3 is added (at various concentrations) to $CaCO_3$ and quartz, and the mixtures are fired to produce C_3S. The material produced is analyzed to determine the amount of C_3S produced and its form and the amount of free lime remaining.

Juel, Iver, and Ebbe Jøns. “The Influence of Earth Alkalis on the Mineralogy in a Mineralized Portland Cement Clinker.” *Cement and Concrete Research* 31 (2001): 893-897.

> This article describes laboratory experiments in which an alkaline earth metal oxide is added to raw meal (at various concentrations) and burned to make clinker. The clinkers produced are analyzed to determine the effects on belite structure.

Kolovos, K., P. Loutsi, S. Tsivilis, and G. Kakali. “The Effect of Foreign Ions on the Reactivity of the CaO-SiO_2-Al_2O_3-Fe_2O_3 System. Part I. Anions.” *Cement and Concrete Research* 31 (2001): 425-429.

> This article describes laboratory experiments in which salts containing a variety of anions are added (at various concentrations) to pure compounds simulating raw meal composition, and the mixtures are burned to make clinker. The clinkers produced are analyzed to determine the effects of the dopants on free lime content, as a measure of reactivity, and on the crystal structure of the clinkers. The amount of the dopant anion in the clinker is also determined to evaluate its volatility under clinkering conditions.

Barros, A.M., J.A.S. Tenório, and D.C.R. Espinosa. “Chloride Influence on the Incorporation of Cr_2O_3 and NiO in Clinker: A Laboratory Evaluation.” *Journal of Hazardous Materials* B93 (2002): 221-232.

> This article describes laboratory experiments in which a metal oxide is added to raw meal (at various concentrations) and burned to make clinker. The effect of chloride content on the loss of Cr and Ni during the burning process is studied using thermogravimetry. The clinkers produced are analyzed for the metals and the amounts added to the meal are compared to the amounts found in the clinkers.

Kolovos, K., P. Loutsi, S. Tsivilis, and G. Kakali. “The Effect of Foreign Ions on the Reactivity of the CaO-SiO_2-Al_2O_3-Fe_2O_3 System. Part II. Cations.” *Cement and Concrete Research* 32 (2002): 463-469.

> This article describes laboratory experiments in which salts containing a variety of cations are added (at various concentrations) to pure compounds simulating raw meal composition, and the mixtures are burned to make clinker. The clinkers produced are analyzed to determine the effects of the dopants on free lime content, as a measure of reactivity, and on the crystal structure of the clinkers.

Andrade, F.R.D., V. Maringolo, and Y. Kihara. “Incorporation of V, Zn, and Pb into the Crystalline Phases of Portland Clinker.” *Cement and Concrete Research* 33 (2003): 63-71.

> This article describes laboratory experiments in which a metal oxide or nitrate is added to raw meal (at various concentrations) and burned to make clinker. The clinkers produced are analyzed to determine the partition of the metals among the various crystal phases of the clinker.

Prodjosantoso, A.K., and B.J. Kennedy. “Heavy Metals in Cement Phases: On the Solubility of Mg, Cd, Pb and Ba in $Ca_3Al_2O_6$.” *Cement and Concrete Research* 33 (2003): 1077-1084.

> This article describes laboratory experiments in which metal carbonates and metal nitrates are mixed together and heated to create metal-doped aluminates. The C_3A samples are then studied using X-ray diffraction to determine the substitution patterns for the dopants in the aluminate crystal structure.

Barros, A.M., D.C.R. Espinosa, and J.A.S. Tenório. “Effect of Cr_2O_3 and NiO Additions on the Phase Transformations at High Temperatures in Portland Cement.” *Cement and Concrete Research* 34 (2004): 1795-1801.

> This article describes laboratory experiments in which a metal oxide and an alkali chloride are added (at various concentrations) to high purity reactants simulating raw meal and heated in a differential thermal analysis apparatus to study the effect of the added metals on the phase transformation processes.

Barros, A.M., J.A.S. Tenório, and D.C.R. Espinosa. “Evaluation of the Incorporation Ratio of ZnO, PbO and CdO into Cement Clinker.” *Journal of Hazardous Materials* B112 (2004): 71-78.

> This article describes laboratory experiments in which a metal oxide and an alkali chloride are added to raw meal (at various concentrations) and burned to make clinker. The clinkers produced are analyzed for the metals and the amounts added to the meal are compared to the amounts found in the clinkers. The effect of chloride content on the loss of Zn during the burning process is also studied using thermogravimetry.

Kolovos, K.G., S. Tsivilis, and G. Kakali. “Study of Clinker Dopped [sic] with P and S Compounds.” *Journal of Thermal Analysis and Calorimetry* 77 (2004): 759-766.

> This article describes laboratory experiments in which S and P containing salts are added (at various concentrations) to pure compounds simulating raw meal composition, and the mixtures are burned to make clinker. The clinkers produced are analyzed to determine the effects of the dopants on free lime content and on clinker texture. Differential thermal analysis is used to evaluate the effects of the dopants on the phase transformations of the mixtures.

XII. Abbreviations

AAS: Atomic absorption spectroscopy
Aglime: Agricultural limestone
APCD: Air pollution control device
ASF: Alternative Standard Fuel
ASTM: American Society for Testing of Materials
BTU: British thermal units
C_2S: Dicalcium silicate ($2CaO.SiO_2$)
C_3A: Tricalcium aluminate ($3CaO.Al_2O_3$)

C_3S: Tricalcium silicate ($3CaO.SiO_2$)
C_4AF: Tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$)
CKD: Cement kiln dust
DAF: Dry and ash-free
DRE: Destruction and Removal Efficiency
DSCF: Dry standard cubic foot
DTA-TG: Differential thermal analysis-thermogravimetry
EDXRF: Energy dispersive X-ray fluorescence
EPA: Environmental Protection Agency
ESP: Electrostatic precipitator [dust collection device]
ETV: Electrothermal vaporization
Fluff: Shredded PRF
FBC: Fluidized bed combustor
HHV: High heating value or Higher heating value
HWF: Hazardous Waste Fuel
ICP-AES: Inductively coupled plasma-atomic emission spectroscopy
ICP-MS: Inductively coupled plasma-mass spectrometry
IPR: In-Plant Residues
LHV: Low heating value or Lower heating value
LPB: Liquid Packaging Board (milk container packaging)
MB/FP: Mixed Board and Flexible Packaging (printed packaging scrap)
MBT-Sieve: Mechanical-Biological Treatment [plant]-Sieve
MJ: Megajoule
MMBTU: Million British thermal units
MP: Mixed plastics
MSW: Municipal Solid Waste
NAA: Neutron activation analysis
ND: Not Detected
NO_x: Nitrogen Oxides
PAH: Polynuclear aromatic hydrocarbon
PCA: Portland Cement Association
PCB: Polychlorinated biphenyl
PCDD: Polychlorinated dibenzo-*p*-dioxin
PCDD/F: Polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans
PCDF: Polychlorinated dibenzofuran
PDF: Paper-derived fuel
Pet-coke: Petroleum coke
PM: Particulate matter
PM_{10}: Particulate matter up to 10 μm in size (“large” particulates)
PPB: Part per billion
PPM: Part per million
PPTh: Part per thousand
PEF: Processes Engineered Fuel
PRF: Processed Refuse Fuel
PVC: Polyvinylchloride
RDF: Refuse Derived Fuel
ROX: Roxarsone (3-nitro-4-hydroxyphenylarsonic acid)
SBR: Styrene-butadiene rubber
SFBC: Swirling fluidized bed combustor
SO_x: Sulfur oxides
SRM: Standard Reference Material

TCLP: Toxicity Characteristic Leaching Procedure
TDF: Tire Derived Fuel
TEF: Toxic Equivalence Factor (factor used to express all exposures to members of a group of toxic compounds in terms of the index compound)
TEQ: Toxicity Equivalence (method of relating the toxicity of various dioxin/furan congeners to the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin)
THC: Total hydrocarbons
VOC: Volatile Organic Compound
WDF: Waste Derived Fuel
XRD: X-ray diffraction
XRF: X-ray fluorescence

A goal of this research is to determine the suitability of waste fuels as substitutes for coal in the cement manufacturing process. One area of concern is that waste fuels may contain higher quantities of certain trace elements than are found in coal, and that these trace elements might have negative effects on cement manufacturing and/or products.

We began by examining the scientific literature to learn what trace elements were likely to occur in coal and in the waste fuels of interest (scrap tires, waste plastics, and broiler litter). Soon, we decided it would benefit the project to focus on the elements that would have the most pronounced effects on the kiln process, on the clinker/cement produced, and on concrete produced from that cement.

We then began searching the literature for information on the effects of various elements on cement, concrete, and/or the kiln process. We started with the standard texts on cement, H.F.W. Taylor's *Cement Chemistry* and *Lea's Chemistry of Cement and Concrete*. We continued with the journal literature and industry publications. The data collected were compiled in a spreadsheet, with the source(s) of the data identified.

The spreadsheet data were then used to identify the elements that have negative effects. We will be analyzing feeds, fuels, and products for these elements during the baseline period and the trial burns in the hope of correlating changes in the amounts of these elements with changes observed in the process and/or products. The eventual goal is to use a comparison of the relative amounts of these elements in a given waste fuel and in coal as a predictor of a waste fuel's suitability for use in cement manufacture.

	Kiln Process--Bad Effects	Kiln Process--Good Effects	Clinker and/or Cement--Bad Effects	Clinker and/or Cement--Good Effects	Concrete--Bad Effects	Concrete--Good Effects
Non-metals						
Br	No information available, but HBr and Br2 probably have the same effects as HCl and Cl2 in terms of corrosivity to the kiln.				No specific information, but bromides probably act similar to chlorides (in terms of both good and bad effects).	
	(3) Alkali bromides concentrate in kiln dust.				(5) Halo-aluminates may cause setting problems.	
	(5) Br expected to behave similarly to Cl.					
	(3) Br2 is formed under oxidative conditions and will be emitted in stack gases.					
Cl	HCl and Cl2 corrode the kiln system	(34) Chlorides can be "important mineralizers".	(3, 34) The presence of chlorides favors formation of spurrite.		(5, 34) Chloride in concrete promotes corrosion of steel reinforcement.	(5) Cl accelerates hardening of cement pastes.
	(3. 5, 10, 34) Chlorides of volatile metals cycle in the kiln dust and lead to kiln ring formation and/or clogging in the preheater/precalciner system.	(10) Chlorides can help remove alkali sulfates by forming alkali chlorides which volatilize and move into the kiln gas.	(5) Excessive amount of Cl can deplete the alkali available for the clinker.		(5) Halo-aluminates may cause setting problems.	
	(10, 34) Chlorides of volatile metals may escape in the stack gases.		(18) With 6% and more CaCl2 in the raw mix, the clinker produced contains mostly alinite and little alite.			
	(3, 5) Chlorides in the stack gases cause "condensation plumes" which are difficult to remove.		(4) Amounts of 4-6% of Cl in the raw mix cause low-viscosity chloride-rich melts in the clinker modulation zone, disrupting the normal nodulization process and leading to creation of rings, cakes, and big balls.			
	(5) High chloride levels can cause rapid deterioration of the refractory bricks in the kiln.					
	(4) Amounts of 4-6% of Cl in the raw mix cause low-viscosity chloride-rich melts in the clinker modulation zone, disrupting the normal nodulization process and leading to creation of rings, cakes, and big balls.					

	(24) Cl- is described as having high volatility during heating.					
F	No information available, but HF and F2 probably have the same effects as HCl and Cl2.	(10) Fluoride acts as a mineralizer.	(34) Fluorides favor formation of spurrite and silicosulfate.	(27) At high burning temperatures, fluoride can lead to formation of fluorosilicates: some of these increase late strength, while others decrease setting time.	(10) Portland cements produced from clinkers containing 0.2% F or more can have slow setting and hardening characteristics at low temperatures (5°C).	(5) Good 28 day strengths can be obtained from F-containing clinker.
	(3, 5, 27, 34) Fluorides of volatile metals can cycle in the kiln dust similar to chlorides and can also be deposited.	(10) Fluoride additions reduce the viscosity of the melt (but lead to unstable products instead of C3S).	(27) At low burning temperatures, fluoride can lead to formation of fluoroaluminate compounds which require careful sulfate optimization to avoid setting problems.	(3) Most fluoride ends up in the clinker (good or bad?).	(3) Fluoroaluminates lead to rapid setting.	(3) There is an optimum value for fluoride content in clinker associated with early strength and another with later strength.
	(34) Amounts of CaF2 of a "few tenths of a percent" are "deleterious".	(5) Amounts of 0.5% or less seldom produce harmful effects and act as mineralizer, allowing clinker to be burned at lower temperatures.	(27) Fluoride increases decomposition of alite, but this may be avoided by rapid clinker cooling.	(3) Presence of Al and F "beyond the threshold level" produces C3S with a rhombohedral symmetry, associated with improved hydraulic properties.		
	(10) Fluoride additions reduce the viscosity of the melt but lead to unstable products instead of C3S.	(24) F- is an effective mineralizer at 1450°C, probably due to easy diffusion of F- in solid state and to lower viscosity of melt.	(3, 5) Excessive amounts of fluorosilicates may cause decomposition of alite.			
	(3, 10) Use of fluoride as a mineralizer may give rise to buildup of excessive coating in the kiln.		(1) Added CaF2 resulted in decrease in alite and increase in belite.			
			(1) Amount of free lime decreases with increase in CaF2 added (bad or good?).			
N	(5) Kiln N believed to contribute significantly to NOx formation.			(5) Clinker N is probably in the form of nitrides.		
P, P205	(34) Amounts of P2O5 of a "few tenths of a percent" are "deleterious".	(24) The effectiveness of P as mineralizer depends on its ionic form.	(34) Phosphates are "undesirable constituents of clinker".	(34) Phosphates inhibit the formation of spurrite.	(5, 33) Amounts of P2O5 greater than 2.5% (presumably in cement) cause strength to decrease.	(5, 27) At lower levels of P (to 0.5%?), there is a slight decrease in water necessary for normal consistency.

	(24) PO4-3 is described as having moderate volatility during heating.	(24) HPO4-2 is described as having low volatility during heating.	(10) Amounts higher than 0.3% inhibit formation of C3S, with a loss of 10% C3S for each additional 1% of P2O5.	(10) Amounts of up to 0.3% enter the C2S and improve its hydraulic properties.	(27) Phosphate in excessive quanitities (greater than 2.5%?) can cause severe set retardation.	(5, 27) P at lower levels (to 0.5%?) leads to slightly lower heat of hydration at all ages (good or bad?).
		(26) P added as HPO4-2 dissolves in melt and has "positive effect on burnability".	(34) Clinkers typically contain 0.2% of P2O5, but higher amounts lead to decreased formation of alite.	(27) P2O5 appears to stabilize reactive forms of belite.	(27) P at lower levels (to 0.5%?) leads to some tendency to paste shrinkage.	(5) Levels of P2O5 below 2.5% can be tolerated when F is added to form fluoroapatite (Cl may also help).
			(34) Amounts of P2O5 higher than 2.5% lead to the presence of free lime.			(3) P2O5 in clinker can reduce the negative effects of alkali on strength.
			(34) At a clinkering temperature of 1500°C, mixes with more than a few % P2O5 do not yield C3S, although the tolerance is increased if F- is present.			
			(27) Amounts of P2O5 over 2.5% make alite unstable and cause it to decompose into free lime and C2S.			
			(26) P (added as PO3-3 or H2PO4-) preferentially accumulates in the belite, stabilizing beta-C2S and hindering further binding of free lime.			
P, P2O5 (cont.)			(7) For P2O5 concentrations above 1% in clinker, there is a decrease in alite (C3S) and an increase in belite (C2S), proportional to the amount of P2O5. Addition of silica improves the ratio.			
			(8) Increases in P lower both the viscosity and the surface tension of interstitial liquid in the clinkering process, leading to an increase in the M1 form of alite (bad or good?).			
			(3) High concentrations of P2O5 decompose C3S to C2S.			

S	(5, 34) Sulfates of alkali metals and some other metals are volatile like chlorides and end up cycling in the kiln dust and can lead to kiln ring formation and clogging in the preheater/precalciner.	(34) Sulfates can be "important mineralizers".	(27) In sulfite (not sulfate) form, S can catalyze alite decomposition.		(5) Excess SO3 can lead to expansion of the cement paste (depending on amount of aluminate present) (although it can be "rather unreactive").	
	(4) High amounts of SO3 lead to high-viscosity melt of alkali sulfates, leading to broad size distribution of clinker, with numerous cakes, balls, and lumps.	(34) Sulfates may "depress the liquidus temperature" .	(18) As amount of SO3 increases, the amount of alite decreases.		(12) Large amounts of SO3 present in clinker encourage alkalis present to go into solution during hydration.	
	(24) S-2 is described as having high volatility during heating.	(24) SO4-2 is described as having low volatility during heating.	(4) High amounts of SO3 (lead to high-viscosity melt of alkali sulfates and) lead to broad size distribution of clinker, with numerous cakes, balls, and lumps.			
	(3) SO2 gas formed can escape in the stack gases.	(26) S (added as S-2 or SO4-2) dissolves in the melt and has "positive effect on burnability".	(8) Increases in S lower both the viscosity and the surface tension of interstitial liquid in the clinkering process, leading to an increase in the M1 form of alite (bad or good?).			
		(11) The presence of sulfur leads to reduction in alkali volatility during clinker formation.	(11) In the absence of alkalis and MgO, Al+3 and SO4-2 prevent the formation of C3S.			
			(11) Addition of SO3 caused large "amoeba-like" alite crystals and belite crystals without lamellae. C3A content decreased, and clinker pores became larger.			
Metals and Metalloids						
Ag						
Al						
As	(3, 5) As2O3 is fairly volatile, with a tendency to end up in kiln dust.	(3) Substantial fraction of As present will end up in clinker (good or bad?).	(3) 0.15% As+5 decreases rate of C3S formation.		(3) As2O3 as an admixture slightly retards paste hydration.	(3) As leaching rate is very low.

B	(25) The presence of B oxide at 1450°C appears to decrease reactivity (as measured by free lime appearance).		(27) B can stabilize beta C2S and increase its hydraulic reactivity, but it decreases C3S.	(27) B can stabilize beta C2S in an alumina- and iron-poor system (good or bad?).	(27) The effect of B addition can be highly unpredictable.	(27) 0.5% B2O3 improves strength performance.
			(3) B2O3 reacts with C2S to form C2S and free lime. Too much B2O3 can cause C3S to disappear completely.		(27) B retards setting time, but not predictably at all.	
					(3, 5) Boron oxide added to cements in quantities as low as 0.04% can be deleterious to the cementing properties.	
Ba		(3) Raw mixes with higher than normal amounts of Ba have a decrease in clinkerization temperature and increase in clinker production rate.	(5) Excessive amounts of BaO increase free lime content of clinker.	(21) Addition of BaCO3 "significantly reduced the time and temperature of formation of C3S"; up to 0.5% BaO "exerted the maximum mineralizing action on C3S formation".	(27) Ba leads to lower strength on autoclaving.	(10) Amounts of 0.3% in clinker increase the 28 day strength by 20%; amounts of 0.5% increase it by 10%; amounts of 0.7% don't increase it at all.
			(21) More than 1.8% BaO led to decomposition of C3S into C2S and CaO (free lime).	(21) With up to 2% BaO, triclinic form of C3S was stabilized; with up to 4% BaO, monoclinic form of C3S was stabilized (good or bad?).	(27) Ba is associated with higher paste shrinkage at all ages.	(27) Ba appears to reduce water demand slightly.
			(13) BaO reacts with sulfate in clinkers to form barite, making the sulfate unavailable for hydration.	(3) Raw mixes with higher than normal amounts of Ba "improve the mineralogical composition of the resulting clinker".	(5) Ba is reported to produce small increases of cement paste shrinkage.	(27) Ba is claimed to markedly increase normal strengths.
			(13) Higher amounts of BaO in clinker leads to decomposition of alite to form belite and free lime.			(5) Ba may increase strength of cements "appreciably".
			(3) Excessive amounts of Ba in raw mix can increase free lime content of clinker.			(3) Ba is "an effective activator of hydraulicity and strength".
Be				(5) Due to stability and low volatility of its oxides, Be will probably be retained in clinker		

				(good or bad?).		
Bi				(5) The oxides of Bi are not very volatile, so they will probably be retained in clinker (good or bad?).		
Ca					(34) Ca adversely affects resistance to sulfate attack ; also the final strength can be reduced.	(34) CaCl2 is used to speed up setting and hardening of concrete (added after the process?).
Cd	(5, 34) Cd compounds are volatile and cycle in the kiln dust and can be deposited in the preheater/precalciner.	(5) Cd improves burnability although it doesn't lower temperature of liquid phase formation.			(5) High concentrations of CdO decrease strength of C3S pastes.	(5) Cd is not readily leachable from concrete.
	(25) Cd+2 is described as having high volatility when heated.				(28) Cd in clinker retards setting time.	(28) There is no leachable Cd after one month.
					(28) Cd in clinker decreases slightly compressive strength.	
Co	(25) Co+3 is described as having moderate volatility when heated.		(5) Co can impart a strong color to cement.		(27) Co marginally reduces late strength.	
			(5) Co reduces hydraulic activity of alite to some extent.		(27) Co marginally increases water demand.	
			(5) Co increases the hardness of clinker.		(18) Co oxide (added in raw mix) slightly retards hydration during the first 2 days (but effect becomes negligible at 28 days).	
Cr	(5) Cr is somewhat volatile and may be found in kiln dust.	(27) Small amounts of added Cr improve burnability of poorly burnable mixes.	(29) (pure C3S) Up to 0.5% Cr added prior to clinkering, free lime content decreases; with more Cr, free lime rises "extremely".	(27) Cr may stabilize beta C2S (good or bad?).	(27) Cr increases early strength but decreases 28 day strengths.	(34) High levels of Cr give high early strengths.
	(25) Cr+6 is described as having moderate volatility when heated.	(5) Cr improves burnability at concentrations of 1%.	(30) (pure C3A) 5.0% Cr led to slightly higher free lime content.	(30) (pure C4AF) Cr has no effect on free lime.	(27) Cr may result in high heat of expansion.	(5, 27) Cr may result in lower autoclave expansion.
	(25) The presence of Cr oxide at 1450°C appears to decrease reactivity (as measured by free lime appearance).	(31) Up to 0.5%, Cr results in decrease in free lime, implying improvement in burnability.	(31) Between 0.5% and 2.5%, Cr results in increase in free lime, implying decomposition of alite.	(31) A level of 2.5% Cr gives a much higher porosity of clinker (improves grindability?).	(3, 5, 27) Cr may result in higher sulfate expansion.	(5) Cr-rich cements tend to have high compressive strengths at early

						ages.
	(3) Cr in raw materials reduces viscosity of clinker melt (bad or good?).	(2) Cr2O3 increases the amount of liquid phase but doesn't change the temperature of liquid phase formation (good or bad?).	(31) At 2.5% Cr, belite composition is higher than alite (although not sure if this meant stabilization of belite or destabilization/decomposition of alite).	(22) A level of up to 2% Cr2O3 improves crystal size of C3S, with maximum at 1%.	(3, 27) Cr may result in increased 24 hr paste shrinkage.	(3, 5) Cr(VI) accelerates cement hydration.
	(3) Cr can be found in the CKD.	(3) 1% Cr2O3 improves clinker burnability.	(22) Beyond solubility limit at 1450°C, partial decomposition of C3S, with formation of CaCrO4.		(5, 28) Cr is readily leached from cement pastes or concretes.	(28) Cr in clinker shortens setting time.
			(22) C3S was in triclinic form up to 2% Cr2O3; at amounts of 2-4% and above, it converted to monoclinic form (good or bad?).		(18) Cr oxide (added in raw mix) slightly retards hydration during the first 2 days (but effect becomes negligible at 28 days).	(28) Cr in clinker leads to increased early strengths.
			(2) Cr2O3 acts as inhibitor of C2S formation.		(30) (C4AF) 2.5% Cr prevents hydration and there is no final setting of the paste within 20 hours.	(29) (C3S) Cr speeds up hydration at levels between 0.5% and 2.5%, even accounting for free lime.
					(30) (C3A) 2.5% Cr lowered the heat of hydration "significantly".	(32) With 2.5% Cr in feed, cement increased onset of hydration.
					(32) With level of 2.5% Cr in feed, cement had expansion reaction during hydration.	(32) With 2.5% Cr in feed, cement had accelerated setting.
					(32) With 2.5% Cr in feed, cement had lower strength at 7 and 28 days.	
					(3) 0.11-1.32% Cr2O3 in raw feed as flux improved 8-hour and 24-hour strengths, but 28-day strengths decreased.	
					(3) Cr+6 chromates "markedly affect the hydration characteristics of the paste".	
Cs	(3, 5) Cs is expected to behave similarly to K, forming stable (and volatile) sulfates and chlorides, leading to kiln rings and clogging.					

Cu	(5) Cu compounds can be volatile and may appear in kiln dust.	(5) CuO acts as a flux and decreases the initial temperature of liquid formation slightly.	(5, 27) High levels of Cu2O "strongly inhibit" formation of alite and beta C2S.	(5) Cu++ appears to stabilize monoclinic alite (good or bad?).	(5, 27) Soluble Cu (added with the cement?) is a retarder.	(27) Cu is associated with low sulfate expansion.
		(16) CuO in an amount as low as 0.5% in the raw meal lowers the clinkerization temperature.	(5, 27) At less than 2% Cu2O, gamma C2S and free lime are the chief products.	(16) CuO promotes formation and development of alite crystals at lower temperature.	(18) Cu oxide (added in raw mix) causes delay in hydration, even at 28 days .	(27) Cu is associated with low water requirements.
		(16) CuO acts as a mineralizer and a flux, its action beginning at 1100°C.	(5) Cu+2 severely retards hydration of pure C3A.	(16) CuO alters the crystallization process during clinker cooling (good or bad?).	(27) Cu is associated with low heat of hydration (good or bad?).	(5) Cu+2 is not readily leachable from concretes, even when added at amounts up to 5%.
		(25) Cu++ is described as having low volatility when heated.	(3) Under reducing conditions, Cu2O adversely affects both alite and belite formations.	(3) A small amount of Cu present as CuO stabilizes alite.		
		(25) The presence of Cu oxide at 1200°C "greatly increases reactivity" (as measured by free lime disappearance).				
		(25) The presence of Cu oxide at 1450°C increases reactivity (as measured by free lime disappearance).				
		(3) CuO decreases melt temperature "considerably".				
		(3) 1% CuO is "effective in reducing free lime at much lower melt temperatures."				
Fe			(34) Fe+2 replaces Ca+2 in the solid phases during clinkering (seems to be controlled by O2 control, not by feed materials and/or fuel).		(34) The replacement of Ca+2 by Fe+2 impairs strength development and makes setting time harder to control.	
			(27) Fe+2 can catalyze alite decomposition (presence of MgO can prevent this).			
Ge				(3, 5) Ge is not volatile and would likely remain in the clinker (good or bad?).	(3) Ge can displace Si, leading to formation of C2G and C3G. C3G is hydraulic, but C2G is not.	

Hg	(5) Hg is very volatile and probably escapes up stack, either as salts or metal vapor.				(5) Hg++, if present as HgO, is readily leached from concrete (HgS less leachable).	
In	(5) In is another volatile metal (like Pb) which will concentrate in the kiln dust and may escape up the stack.	(5) In improves burnability at amounts up to 1%.	(3) In is a volatile metal and largely ends up in the kiln dust.			
Li		(25) The presence of Li oxide at 1200°C "greatly increases reactivity" (as measured by free lime disappearance?).	(3) Li2O inhibits conversion of C2S to C3S.			(5) When added to the cement, Li retards rate of alkali-aggregate reaction.
		(3) Li2O (formed at elevated kiln temperatures) lowers temperature of formation of initial liquid phase.				(3) As an admixture, Li reduces alkali-silica reactivity (ASR) in concrete. It might do the same if present in clinker.
Mg	(34) Amounts of MgO of a "few percent" are "deleterious".	(34) MgO lowers the viscosity of the melt (which favors alite formation).	(10) Amounts of MgO greater than 5% leads to crystallization of periclase (associated with "long term unsoundness").	(34) MgO lowers the viscosity of the melt (which favors alite formation).	(34) Levels of MgO 0.5% and higher reduce early strength.	
		(34) MgO in the clinkering process "depresses the liquidus temperatures and increase the Al2O3/Fe2O3 ratio in the liquid".	(33) Mg has minor effects on color.	(34) MgO stabilizes the M3 alite and slows down decomposition of alite in the clinker cooling process.	(33) Amounts of MgO in the feed over 2% result in "uncombined" MgO, which will form Mg(OH)2 over time, expanding and creating cracking in hardened concrete.	
		(3, 5) MgO in small quantities improves burnability.	(9) Substitution of Mg for Al and Fe in C4AF changes the color from yellowish brown to dark grey.	(8) Increases in Mg lower the viscosity and raise the surface tension of interstitial liquid in the clinkering process, leading to an increase in the M3 form of alite (good or bad?).	(33) Mg has minor effects on strength.	
		(34) MgO in the clinkering region lowers the temperature at which melting begins and slightly decreases the viscosity (good or bad?).	(1) Added MgO resulted in decrease in alite and increase in belite.		(5) Presence of large crystals of periclase leads to destructive expansion of concrete due to formation of Mg(OH)2.	

Mn	(25) Mn+4 is described as having moderate volatility when heated.		(34) The presence of Mn results in darker colored clinkers.	(5) At low concentrations, Mn can stabilize monoclinic form of alite (good or bad?).	(33) Mn will adversely affect strengths in amounts greater than 0.5%.	(5) At levels of 0.7% or more, in presence of F, Mn can give a high early-strength cement.
			(10) Mn substitutes for ferric oxide, reducing viscosity in the melt, which can lead to large crystals of alite, which is "unhelpful [to] strength development".	(3) Alite content increases with Mn addition.	(27) Mn causes slightly reduced strength at some ages.	
			(5, 27, 33) Mn has an influence on color.		(18) Mn oxide (added in raw mix) slightly retards hydration during the first 2 days (but effect becomes negligible at 28 days).	
			(5, 27) Mn is associated with a tendency to increase the ferric phase, decreasing C3A and increasing free lime "marginally".			
Mo	(15) The presence of Mo oxide causes a 2-stage solidification process of the melt during cooling (good or bad?).	(34) Mo lowers the viscosity of the melt (which favors alite formation).	(15) The presence of MoO3 causes alite crystals that are bigger and more roundish in shape, probably due to decreased viscosity of the melt (good or bad?).	(34) Mo lowers the viscosity of the melt (which favors alite formation).	(34) Amounts 3.0% and higher of Mo significantly reduce the 28 day strength.	(34) Amounts of up to 0.5% of Mo increase the 28 day strength.
		(25) Mo+6 is described as having low volatility when heated.	(15) The presence of MoO3 causes changes in the form of belite crystals (good or bad?).	(19) MoO3 in amounts up to 3% (maybe higher) promotes C3S formation and increases crystal size; at amounts up to 1% (over 1%, increases transformation from triclinic to monoclinic form (good or bad?)).	(18) Mo oxide (added in raw mix) slightly retards hydration during the first 2 days (but effect becomes negligible at 28 days).	(14) Added MoO3 has no effect on setting process.
		(25) The presence of Mo oxide at 1450°C increases reactivity (as measured by free lime disappearance).		(19) MoO3 in amounts up to 3% (maybe higher) promotes C3A formation and increases crystal size at amounts up to 1%.		
		(15) The presence of Mo oxide doesn't cause significant changes in the temperatures of heating reactions.		(14) Added MoO3 has no effect on clinker grinding process.		

		(28) The presence of Mo oxide causes decreased viscosity of the melt (good or bad?).				
Na, K	(5, 10, 34) Na and K form volatile compounds with halides and with sulfate, which overloads the kiln dust with volatile compounds, leading to the formation of kiln rings and clogging in the preheater/precalciner.	(34) Alkalis may "depress the liquidus temperature".	(34) K_2O favors formation of spurrite.	(8) Increases in Na raise the viscosity and lower the surface tension of interstitial liquid in the clinkering process, leading to an increase in the M3 form of alite (good or bad?).	(34) Alkalis in the kiln process lead to forms of aluminate in the clinker that have "undesirable effects on the rheology" of fresh concrete.	(33) As alkali sulfates increase in the cement, the setting time of the concrete decreases (good or bad?).
	(34) Amounts of alkalis of a "few tenths of a percent" are "deleterious".	(34) K_2O and Na_2O lower the temp of the formation of the melt (same as above?).	(33) Alkali sulfates can cause flow problems for dry cement, due to reaction with traces of water, leading to formation of double-salts whose shape reduces the flow of the powder.		(5, 10) Alkalis in the concrete lead to destructive reactions with certain aggregates.	(12) Increased alkali content leads to decreased bleeding of pastes (good or bad?).
	(10, 34) Alkalis not present as sulfates increase the viscosity of the melt, inhibiting formation of C_3S.	(10) Alkalis as sulfates decrease the viscosity of the melt, thus promoting formation of C_3S.	(33) As alkali content increases, demand for gypsum (optimum SO_3 content) increases.		(5, 10, 33, 34) Higher levels of alkalis as sulfates increase early strength but "at the expense" of later strength.	
Na, K (cont.)	(5) Excess Na (not present as sulfate) reduces burnability.	(11) Alkali oxides lower melt viscosity, favoring aggregation and leading to clinkers with uniform grain size.	(5) Excess Na (not present as sulfate) increases free lime and aluminate content of clinker.		(33) Alkalis increase compressive strength at 3 days but markedly depress it at 28 days; a change or 0.1% will make a 1 Mpa (145 psi) change in strength.	
	(11) Alkalis with sulfate change the surface tension and lead to phase separation, decreasing aggregation and producing tiny grains of clinker "dust".	(11) Presence of alkalis in raw materials decreases the rate of clinkering reactions.	(5) Excess K (not present as sulfate) increases free lime and decreases the alite content of clinker.		(6) Alkalis "built into" the clinker increase reactivity of the C_3A with respect to hydration. Increased reactivity with water leads to taking up more water, leading to changes in the rheology of the resulting paste. Alkalis introduced into the clinker reduce the effectiveness of gypsum to control the paste rheology.	
			(11) Free alkali reacts with C_3A, displacing CaO, leading to excess free lime. This leads to "latent unsoundness".		(12) Alkalis accelerate the hydration process (bad or good?) Extra gypsum is required to achieve "proper retardation".	

			(11) "Very small changes in Na, K, and SO3 contents may cause relatively large changes in the amount of C3S and C3A."		(12) Presence of alkalis leads to rapid hardening or "flash setting".	
			(11) Syngenite, a potassium calcium sulfate, leads to formation of lumps in cement duirng storage.		(12) Increased alkali content leads to increased shrinkage.	
			(11) Increased alkali content leads to reduced solubilty of CaO, leading to decreased formation of C3S.			
			(11) Over 0.33% Na2O causes C2S to change from triclinic to monclinic form and C3A to change from cubic to orthorhombic (bad or good?).			
Ni	(5) Ni compounds are somewhat volatile and may end up in kiln dust.	(31) Ni results in decrease in free lime, implying improvement in burnability.	(29) (C3S) With Ni added prior to clinkering, free lime rises, but not stoichiometrically.	(27) Ni can stabilize monoclinic alite (good or bad?).	(27) Ni in clinker seems to have very little effect on hydration.	(3, 5, 27) Water soluble Ni (added to cement?) is a strong accelerator for cement hydration.
	(25) Ni+2 is described as having moderate volatility when heated.	(2) NiO lowers the temperature of liquid formation.		(5) Ni levels of 0.5 to 1.0% stabilize alite.		(18) Ni oxide (added to cement raw mix) does not affect hydration rate of cement.
	(2) NiO causes small increase in temperature of C2S formation.			(30) (C4AF) Ni has no effect on free lime content.		(29) (C3S) Ni speeds up hydration at 2.5%, but probably due to free lime.
				(31) At 2.5% Ni, there is no significant change in ratio of alite to belite.		(30) (C4AF) 2.5% Ni leads to higher heat evolution (good or bad?).
				(30) (C3A) Ni has no effect on free lime content.		(30) (C3A) 2.5% Ni has no effect on heat liberation.
						(3) Ni substitution in alite enhances 1-day and 5-year compressive strengths.
						(3) Ni compounds added to cement tend to give high early

						strengths.
Pb	(5, 34) Pb compounds will concentrate in the kiln dust, especially if chloride or sulfate is present.		(3) Pb compounds are volatile and accumulate in the kiln dust.	(5) Pb can be retained in clinker (under some circumstances) and at low levels (0.001-0.007%) doesn't affect properties of the cement.	(34) Pb salts slow down the setting time of concrete but this may refer to additives after the kiln process.	(10) If Pb in clinker is <0.1%, no effect on setting time or hardening (no info if amount is >0.1%).
	(34) Volatile Pb compounds may also escape in the stack gases.				(27) Amounts of Pb of 0.2% or higher (possible when high PbO kiln dusts are recycled!) retard setting time.	(27) Amounts of Pb of 0.2% or higher (possible when high PbO kiln dusts are recycled!) ncrease 28 day strengths.
	(25) Pb+2 is described as having high volatility when heated.				(5) Pb added to cement at levels as low as 0.25 can seriously retard setting.	(5) Leachability of Pb compounds from concrete is found to be very low, even added at levels of 5%.
					(28) When Pb is trapped in clinker, delays in setting time are observed.	(28) Not much Pb is leached out.
						(3) If present in clinker below 70 ppm, there are no adverse effects on the cement.
						(3) Pb added to cement enhances workability (while retarding the hydration) of pastes.
Rb	(3, 5) Rb is expected to behave similarly to K, forming stable (and volatile) sulfates and chlorides, leading to kiln rings and clogging.				(27) Rb may contribute to strength reduction at most ages.	
					(27) Rb may contribute to increased paste shrinkage.	
					(27) Rb may contribute to increased concrete expansion.	
					(27) Rb may contribute to reduced freeze-thaw durability.	

					(27) Rb may contribute to increased water requirement.	
Sb	(5) There is a tendency for Sb to concentrate in kiln dust.					
Se	(3, 5) Selenates form, similar to sulfates, which probably concentrate in kiln dust and may escape in the stack gases.					
Sn				(3, 5) Sn is "reasonably involatile" and likely to remain in clinker (good or bad?).		
Sr	(34) Amounts of SrO of a "few percent" are "deleterious".		(34) SrO increases the free lime present at clinkering temperatures.	(34) Small contents of SrO favor alite formation.	(27) Sr is associated with slightly lower strengths at most ages.	(27) Sr is associated with lower heat of hydration at 28 days (good or bad?).
Sr (cont.)	(10) Amounts between 0.01% and 0.21% are not expected to cause problems, but larger amounts such as 3.7% SrO make it difficult to reduce free lime and convert C3S to (CSr)2S and free lime.		(27) Greater than 3% SrO increases free lime levels "markedly".	(33) Clinkers containing up to 0.5% SrO have been made with no adverse effects.	(27) Sr is associated with higher autoclave expansion.	
	(5) Sr may reduce burnability.		(5) Excessive amounts of SrO increase free lime content of clinker.	(13) Increases in Sr concentration correlate with increases in transition from beta to alpha prime polymorph of belite (good or bad?).	(27) Sr is associated with higher sulfate expansion.	
			(13) Higher amounts of SrO in clinker leads to decomposition of alite to form belite and free lime.		(27) Sr is associated with increased concrete shrinkage.	
			(3) Sr in belite inhibits alite formation.		(5) Sr is marginally deleterious to strength and other physical properties.	
			(3) Sr in raw feed favors free lime formation.		(27) Sr is associated with lower heat of hydration at 28 days (good or bad?).	
Te	(3, 5) Tellurates, similar to sulfates, form and probably concentrate in kiln dust and may escape in the stack gases.					

Ta		(25) The presence of Ta oxide at 1450°C increases reactivity (as measured by free lime disappearance).				
Ti		(10) TiO2 may act as a mineralizer, increasing alite crystal size.	(34) Increase in TiO2 produces a decrease in alite.	(3, 5) TiO2 expected to concentrate in the clinker (good or bad?).	(10) Amounts of TiO2 up to 1% inhibit early strength but may improve strength after 3 days.	(10) Amounts of TiO2 up to 1% inhibit early strength but may improve strength after 3 days.
		(25) Ti+4 is described as having low volatility when heated.	(34) The presence of TiO2 produces darker colored clinkers.		(27) Ti may lead to increased water demand.	(5) 1-2% TiO2 in clinker can give improved cement strength.
		(25) The presence of Ti oxide at 1450°C increases reactivity (as measured by free lime disappearance).	(27, 33) TiO2 can influence color.		(18) Ti oxide (added in raw mix) slightly retards hydration during the first 2 days (but effect becomes negligible at 28 days).	(23) Amounts of TiO2 above 2% speed up hydration of C3S.
		(3) About 1% TiO2 reduces melt temperature by 50-100°C.	(3) Increase in TiO2 produces a sharp reduction in alite with an equal gain in belite.		(23) 1% of TiO2 inhibits hydration up to 1 day; up to 2% slows down hydration for about 2 days, then goes on to exceed degree of normal hydration.	(3) 1% TiO2 clinker yields 20% higher 3-day and 90-day strengths.
					(3) TiO2 in clinker produces slower initial setting.	
Tl	(5, 10, 34) Tl is another volatile metal (like Pb) which will concentrate in the kiln dust and may escape in the stack gases.		(3) Tl is the most volatile element after Hg in the kiln and will concentrate in the kiln dust, leading to build-up if dust is recycled.			
	(10) Tl halides and sulfates will circulate in the kiln dust and may lead to clogging.					
V	(10) Low levels of V compounds could lead to shorter refractory lining life.	(25) V+5 is described as having low volatility when heated.	(5) The presence of V results in large alite crystals (good or bad?).	(27) V is believed to stabilize beta C2S (good or bad?).	(10) An amount of 0.2% of V leads to 10% reduction in the 28 day strength.	(33) V is advantageous in low amounts, less than 0.2%.
	(3, 5) Very high levels of V can cause rapid deterioration of refractory linings of kilns.	(3) V decreases the melt viscosity (good or bad?).	(3) Higher concentrations of V2O5 can adversely affect grindability.	(5, 27) V is believed to improve grindability.	(33) V has an adverse effect on strength at concentrations higher than 0.2%.	(27) V is believed to improve strength.
				(5) V apparently causes an increase in hydraulic activity of alite at levels of about 1.5%.	(3, 5, 27) V may be associated with higher sulfate expansions.	
				(20) V2O5 in amounts up to 0.5% enhances	(27) V may lead to increased water demand.	

				C3S formation and increases crystal size.		
				(20) V2O5 in amounts up to 3.5% (maybe higher) enhances C3A formation and in amounts up to 0.5% increases crystal size.	(18) V oxide (added in raw mix) slightly retards hydration during the first 2 days (but effect becomes negligible at 28 days).	
				(3) V2O5 can reduce the free lime in clinker (good or bad?).		
W		(25) W+6 is described as having low volatility when heated.	(15) The presence of WO3 causes alite crystals that are bigger and more roundish in shape, probably due to decreased viscosity of the melt (good or bad?).	(14) Added WO3 has no effect on clinker grinding process.		(14) Added WO3 has no effect on setting process.
		(25) The presence of W oxide at 1450°C increases reactivity (as measured by free lime disappearance).	(15) The presence of WO3 causes changes in the form of belite crystals (good or bad?).	(3) Addition of W+6 decreased clinker dusting and "improved granulometric composition".		
		(15) The presence of W oxide doesn't cause significant changes in the temperatures of heating reactions.				
		(15) The presence of W oxide causes decreased viscosity of the melt (good or bad?).				
Zn	(5, 34) Zn compounds cycle in the kiln dust and can be deposited in the preheater/precalciner (but can be retained in the clinker if the kiln dust is recycled).	(5) Zn can improve burnability.	(27) "Appreciable" amounts of Zn present in raw materials lead to "drastically reduced" levels of C3A.	(30) (C4AF) Zn has no effect on free lime content.	(10) Amounts of Zn between 0.01% and 0.2% can cause setting time problems (another reference refers to delays); up to 0.5% of ZnO seems to have no other effect on hydraulic properties, but no info about amounts over 0.5%.	(27) ZnO enhances late strengths (Zn in raw mix or added to cement?).
Zn (cont.)	(27) Most of the Zn may be volatilized in systems with low amounts of liquid phase; ends up in kiln dust or emitted in the stack gases.	(17) ZnO lowers the clinkerization temperature, the amount depending on amount of ZnO present (no more change above 3%).	(27) "Appreciable" amounts of Zn present in raw materials lead to reduction of free lime levels (good or bad?).	(31) A level of 2.5% Zn showed small increase in alite and small decrease in belite (good or bad?).	(34) Zn salts slow down the setting time of concrete but I think this may refer to additives after the kiln process.	(5) Zn gives higher strength cements.

	(29) (C3S) 25% of Zn added prior to clinkering evaporated.	(17) ZnO promotes the combination of free lime, not only in the melt but also in solid.	(27) "Appreciable" amounts of Zn present in raw materials lead to color changes.		(27) When Zn added to the mix (not to the cement), retardation is "slight".	(5) Zn reduces early strengths but gives higher later strengths.
	(3) Volatility of Zn for preheater kilns "could be 10-20%".	(31) Zn results in a decrease in free lime, implying improvement in burnability.	(17) More than 3% ZnO in raw mix changes color of clinker to brown.		(27) "Appreciable" amounts of Zn present in raw materials extend setting times.	(5) Zn++ is leached only very slowly.
		(25) Zn+2 is described as having low volatility when heated.	(29) (pure C3S) At low levels, there is no relationship between Zn added prior to clinkering and amount of free lime present; between 0.5% and 5.0%, free lime increases linearly with level of Zn.		(5) Zn can increase shrinkage.	(28) Not much ZnO is leached out.
		(3) ZnO additions accelerate clinker formation.	(30) (pure C3A) Only 2.5% and 5.0% Zn led to higher free lime content.		(5) Zn has severe retarding influence on cement hydration	(30) (C4AF) 2.5% Zn has no effect on hydration.
			(31) At a level of 2.5% Zn, the porosity of clinker is much lower (decreases grindability?).		(28) ZnO retards setting time.	(32) Amounts of 2.5% Zn in feed produce low strength after 1 day, but higher strength after 28 days.
			(9) Substitution of Zn for Al and Fe in C4AF changes the color from yellowish brown to dark grey.		(28) ZnO reduces strength.	
			(3) Zn doping causes alite and C2AF to increase at the expense of belite and C3A.		(18) Zn oxide (added to raw mix) delays formation of Ca(OH)2 but only during first day.	
			(3) Up to 1% ZnO in raw mix decreases free lime "considerably" (bad or good?).		(29) (C3S) Zn slows down hydration at levels between 0.5% and 2.5%, despite the free lime; however the total amount of heat is higher.	
					(30) (C3A) 2.5% Zn lowered the heat of hydration "significantly".	
					(32) 2.5% Zn in feed, cement had substantial delay in hydration process.	
					(32) 2.5% Zn in feed, cement had delayed setting process.	

					(3) Over 1% ZnO in raw mix retards hydration and reduces strength.	
Zr	(15) The presence of Zr oxide causes a 2-stage solidification process of the melt during cooling (good or bad?).	(25) Zr+4 is described as low volatility when heated.	(3) Zr2O3 changes size and shape of alite crystals and modifies type of belite crystal.	(14) Added ZrO2 has no effect on clinker grinding process.	(14) Added ZrO2 retards setting, independent of concentration at levels studied.	(27) Zr may be responsible for "modestly higher strengths at most ages"
		(15) The presence of Zr oxide doesn't cause significant changes in the temperatures of heating reactions.	(3) ZrO3 produces a color change in clinker.		(3) ZrO in raw mixes produces a "significant retarding effect and a subsequent delay in strength" for cement pastes.	(27) Zr may slightly reduce water needed.
						(5) Zr may increase early strengths somewhat.
						(18) Zr oxide (added to cement raw mix) does not affect hydration rate of cement.
						(27) Zr has been associated with high heat of hydration at 7 days (good or bad?).
						(3) Smaller ZrO additions to raw mix increases early compressive strength.
		(33) Influence of additives (1%) on sintering at 1300°C= CuO=Co2O3=ZnO>TiO2> CdO> MnO>V2O5>Cr2O3		(35) Effect on grindability of clinker, more grindable to less: MnO>Cr2O3>>Ni2O3>ZrO2>CuO> Co2O3>>V2O5>MoO3> TiO2>>ZnO		(34) Elements (again probably additives) which accelerate setting time, in order of effectiveness: Ca+2>Sr+2>Ba+2>Li+>K+>Na+~Cs+> Rb+
		(24) Effectiveness of anions in reduction of free lime at 1200°C, decreasing order: Cl->SO4-2>S-2>HPO4-2>SiF6-2>F-> PO4-3				

		(24) Effectiveness of anions in reduction of free lime at 1450°C, decreasing order: SO4-2>F->HPO4-2>SiF6-2>S-2>Cl-> PO4-3				

1. Altun, I. A., "Effect of CaF2 and MgO on Sintering of Cement Clinker." *Cement and Concrete Research*. 29 (1999): 1847-1850.
2. Barros, A.M., Espinosa, D.C.R., Tenorio, J.A.S. "Effect of Cr2O3 and NiO Additions on the Phase Transformations at High Temperature in Portland Cement" *Cement and Concrete Research* 34 (2004): 1795-1801.
3. Bhatty, J. I. *Role of Minor Elements in Cement Manufacture and Use*. RD109T. Skokie, Ill.: Portland Cement Association, 1995.
4. Gadayev, A., Kodess, B. "By-product Materials in Cement Clinker Manufacturing" *Cement and Concrete Research*. 29 (1999): 187-191.
5. Gartner, E.M. "The Effects of Minor and Trace Elements on the Manufacture and Use of Portland Cement." Portland Cement Association. R&D SN2064. [no date]
6. Grzeszczyk, S., Kucharska, L. "The Influence of Alkalis on Rheological Properties of Fresh Cement Pastes." *Cement and Concrete Research*. 18 (1988): 1-8.
7. Halicz, L., Nathan, Y. "The Influence of P2O5 on Clinker Reactions." *Cement and Concrete Research*. 14 (1983): 11-18.
8. Ichikawa, M., Kanaya, M. "Effects of Minor Components and Heating Rates on the Fine Textures of Alite in Portland Cement Clinker." *Cement and Concrete Research*. 27:7 (1997): 1123-1129.
9. Ichikawa, M., Komukai, Y. "Effect of Burning Conditions and Minor Components on the Color of Portland Cement Clinker." *Cement and Concrete Research*. 23 (1993): 933-938.
10. Jackson, Peter J. "Portland Cement: Classification and Manufacture." *Lea's Chemistry of Cement and Concrete*. Fourth edition. Ed. Peter C. Hewlett. New York: Wiley, 1998.
11. Jawed, I., Skalny, J. "Alkalies [sic] in Cement: A Review. I. Forms of Alkalies [sic] and Their Effect on Clinker Formation." *Cement and Concrete Research*. 7 (1977): 719-730.
12. Jawed, I., Skalny, J. "Alkalies [sic] in Cement: A Review. II. Effects of Alkalies [sic] on Hydration and Performance of Portland Cement." *Cement and Concrete Research*. 8 (1978): 37-52.
13. Juel, I., Jons, E. "The Influence of Earth Alkalis on the Mineralogy in a Mineralized Portland Cement Clinker." *Cement and Concrete Research*. 31 (2001): 893-897.
14. Kakali, G., Kasselouri, V., Parissakis, G. "Hydration and Strength Development of Cements Produced from Raw Mixes Containing MoO3, Nb2O5, WO3, and ZrO2." *Cement and Concrete Research*. 19 (1989): 968-972.
15. Kakali, G., Kasselouri, V., Parissakis, G. "Investigation of the Effect of Mo, Nb, W, and Zr Oxides on the Formation of Portland Cement Clinker." *Cement and Concrete Research*. 20 (1990): 131-138.
16. Kakali, G., Parissakis, G., Bouras, D. "A Study On the Burnability and the Phase Formation of PC Clinker Containing Cu Oxide" *Cement and Concrete Research*. 26:10 (1996): 1473-1478.
17. Kakali, G., Parissakis, G. "Investigation of the Effect of Zn Oxide on the Formation of Portland Cement Clinker" *Cement and Concrete Research*. 25:1 (1995): 79-85.
18. Kakali, G., Tsivilis, S., Tsialtas, A. "Hydration of Ordinary Portland Cements Made From Raw Mix Containing Transition Element Oxides" *Cement and Concrete Research*. 28:3 (1998): 335-340.
19. Kasselouri, V., Ftikos, Ch. "The Effect of MoO3 on the C3S and C3A Formation" *Cement and Concrete Research*. 27:6 (1997): 917-923.
20. Kasselouri, V., Ftikos, Ch. "The Effect of V2O5 On the C3S and C3A Formation" *Cement and Concrete Research*. 25:4 (1995): 721-726.
21. Katyal, N.K., Ahluwalia, S.C., Parkash, R. "Effect of Barium On the Formation of Tricalcium Silicate" *Cement and Concrete Research*. 29 (1999): 1857-1862.
22. Katyal, N.K., Ahluwalia, S.C., Parkash, R. "Effect of Cr2O3 On the Formation of C3S in 3CaO:1SiO2:xCr2O3 System" *Cement and Concrete Research*. 30 (2000): 1361-1365.
23. Katyal, N.K., Ahluwalia, S.C., Parkash, R. "Effect of TiO2 On the Hydration of Tricalcium Silicate" *Cement and Concrete Research*. 29 (1999): 1851-1855.
24. Kolovos, K., Loutsi, P., Tsivilis, S., Kakali, G. "The Effect of Foreign Ions On the Reactivity of the CaO-SiO2-Al2O3-Fe2O3 System. Part I. Anions" *Cement and Concrete Research*. 31 (2001): 425-429.
25. Kolovos, K., Tsivilis, S., Kakali, G. "The Effect of Foreign Ions On the Reactivity of the CaO-SiO2-Al2O3-Fe2O3 System. Part II. Cations" *Cement and Concrete Research*. 32 (2002): 463-469.
26. Kolovos, K.G., Tsivilis, S., Kakali, G. "Study of Clinker Dopped [sic] With P and S Compounds" *Journal of Thermal Analysis and Calorimetry*. 77 (2004): 759-766.
27. Miller, F.M. "Minor Elements in Cement Clinker." Portland Cement Association. R&D SN2061. [no date]
28. Murat, M., Sorrentino, F. "Effect of Large Additions of Cd, Pb, Cr, Zn, to Cement Raw Meal on the Composition and the Properties of the Clinker and the Cement" *Cement and Concrete*

Research. 26:3 (1996: 377-385.

29. Stephan, D., Maleck, H., Knofel, D., Eber, B.; Hardtl, R. "Influence of Cr, Ni, and Zn On the Properties of Pure Clinker Phases. Part I. C3S" *Cement and Concrete Research*. 29 (1999): 545-552.
30. Stephan, D., Maleck, H., Knofel, D., Eber, B.; Hardtl, R. "Influence of Cr, Ni, and Zn On the Properties of Pure Clinker Phases. Part II. C3A and C4AF" *Cement and Concrete Research*. 29 (1999): 651-657.
31. Stephan, D., Mallmann, R., Knofel, D., Hardtl, R. "High Intakes of Cr, Ni, and Zn In Clinker. Part I. Influence On Burning Process and Formation of Phases" *Cement and Concrete Research*. 29 (1999): 1949-1957.
32. Stephan, D., Mallmann, R., Knofel, D., Hardtl, R. "High Intakes of Cr, Ni, and Zn In Clinker. Part II. Influence On the Hydration Properties" *Cement and Concrete Research*. 29 (1999): 1959-1967.
33. Suderman, R.W. "CCL Raw Mix Prepration [sic] Seminar: Influence of Trace Elements on Cement Quality." Presented Oct. 25-28, 1983, Ste. Adele, Quebec, and Nov. 15-18, 1983, Calgara,
34. Taylor, H.F.W. *Cement Chemistry*. 2nd edition. London: Thomas Telford, 1997.
35. Tsivilis, S., Kakali, G., "A Study on the Grindability of Portland Cement Clinker Containing Transition Metal Oxides" *Cement and Concrete Research*. 27:5 (1997): 673-678.

Task B: Selection of Two Alternate Sources of Fuel

Based on the preliminary survey of the literature and other factors including logistics, economics, and compatibility of fuel and cement kiln, the team has identified broiler litter and light plastic as the two alternate test fuels. We have begun developing the test plan, analysis plan and design of the modification of the Roberta Cement Plant to accept these alternate fuels.

The team is also developing a comprehensive plan to sample the cement product from control experiments as well as trial burns with the alternate fuels. At this point, we have developed the analysis plan for the principal chemical properties of the cement. During each of the three-day trial burns, cement will be sampled to evaluate the impact of the fuel composition on the performance of the cement and concrete made with this cement. Cement will be sampled from the following burn phases: (1) coal only burn process without the use of waste tires or any other alternate fuels, (2) coal and ~10% waste tires, (3) coal, ~10% waste tires and ~10% broiler litter as alternate fuel, and (4) coal, ~10% waste tires and ~10% light plastics as alternate fuel. Table B-1 provides a summary of the principal chemical analyses to be performed.

Table B-1: Testing to evaluate the chemical properties of cement

Test	Specification	Tested by
Chemical Composition: Silicon dioxide (SiO_2) Aluminum oxide (A1203) Ferric oxide (Fe_20_3) Magnesium oxide (MgO) Sulfur (S) → Calculate $S0_3$ Calcium oxide (CaO) Free CaO Loss on ignition (LO I) Insoluble residue Sodium Oxide (Na_20) Potassium Oxide (K_2O)	ASTM C 114 X-ray Fluorescence (XRF)	Lafarge (Roberta Plant) and Auburn University
Clinker Phase Composition: C_3S, C_2S, C_3A, C_4AF	ASTM C 150 (Determined by Bogue formulae)	Lafarge (Roberta Plant) and Auburn University
Clinker Phase Composition: C_3S, C_2S, C_3A, C_4AF	Rietveld Analysis	Lafarge (CTS Montreal)

The purpose of the sampling and analysis plan is to ensure that relevant and pertinent information about the effects of using alternative fuels in the cement manufacturing process will be obtained. One focus is on trace elements of concern to cement manufacture, especially the amounts of these elements in alternative fuels relative to those in coal. Attempts will be made to correlate the presence or absence of these trace elements to changes in the kiln process, clinker production, clinker composition, properties of the cement produced, properties of the concrete made from this cement, and gaseous plant emissions. The project team is determining what streams should be sampled and when and how often sampling should take place. It is also determining what tests will be most cost- and time-efficient and most effective at providing the necessary data.

In developing the Sampling and Testing Plans, it is necessary to focus on the primary purpose of these experiments: to evaluate any effects, negative or positive, of using alternative fuel sources in the cement kiln on the quality of the cement product produced and on the process itself.

One part of the development of the Sampling Plan is to identify what specific materials need to be sampled. Cement product must be sampled, since product from experimental conditions in which coal is partially replaced by one or more alternative fuels will be compared to product from baseline conditions where coal is burned alone. The fuels themselves must all be sampled, since any differences in product between the experimental conditions and the baseline will be ascribed to differences between the fuels. All raw material feed streams must be sampled to rule out differences between products that arise, not from differences in the fuels, but from changes in the raw materials themselves. Intermediate products and by-products should also be sampled to track changes in the kiln process as well as changes in the product. Another part of the development of the Sampling Plan is to determine when and how these materials should be sampled to best observe and track changes. Samples will be taken before, during, and after the test burns as well as during the baseline period. Natural products such as coal, limestone/clay, and natural gypsum have a normal range of variation in terms of the analytes of interest. Wherever possible, these sample streams will be composited to average out this normal variation. Composites will be prepared from grab samples taken at regular intervals throughout the day or over several days. In some cases, it will not be possible to obtain sample composites. Grab samples will be obtained for these sample streams.

One part of the development of the Testing Plan is to compare the performance of cement product from experimental conditions in which coal is partially replaced by one or more alternative fuels to that from baseline conditions where coal is burned alone. Standard physical tests for cement and concrete will be used to compare cement product from baseline and experimental conditions to identify any changes in physical performance. Chemical analyses for cement will also be used to compare product from the baseline and the test burns to identify changes in chemical composition and to correlate changes in physical performance with changes in chemical composition. In addition to the standard analyses performed routinely, the cement, clinker, cement kiln dust, and raw materials will also be analyzed for a select group of trace elements believed to have an effect on the quality of cement product and/or kiln process based on a survey of the literature. All fuel materials will be tested to compare their performance as fuels. They will also be tested for the same list of trace elements as the kiln products and raw materials. An attempt will be made to correlate changes in the cement product and/or the kiln process with changes observed in the amounts of these trace elements.

The installation of the monitoring system is complete. One pollutant (VOC) has not been certified yet due to low emission concentrations. All other pollutants (NO_x, SO_2, opacity) are certified. VOC certification should be complete by the end of February. Conceptual design of the injection system is complete. The kiln injection point has been identified. Detailed engineering is underway.

Approval to conduct test burns of alternate fuels in the Roberta Plant was acquired from Alabama Department of Environmental Management (ADEM). A copy of the approval is attached on the next page

Based on the preliminary survey of the literature and other factors including logistics, economics, and compatibility of fuel and cement kiln, the team identified broiler litter and light plastic as the two alternate test fuels to be used in this project. Lafarge North America has conducted a detailed market survey and logistic costs for different alternate fuels in the region centered at Calera Alabama and this information was used in the process that resulted in the selection of broiler litter and plastics as the first two sources. This survey information contains sensitive data and Lafarge company plans and is therefore not included in this progress report.

During the reporting quarter, we finalized the sampling and test plan, and continued the design of the modification of the Roberta Cement Plant to accept these alternate fuels.

In developing the Sampling and Testing Plans, the team focused on the primary purpose of these experiments: to evaluate any effects, negative or positive, of using alternative fuel sources in the cement kiln on the quality of the cement product produced and on the process itself. The purpose of the sampling and testing plan is to ensure that relevant and pertinent information about the effects of using alternative fuels in the cement manufacturing process will be obtained. One focus is on trace elements of concern to cement manufacture, especially the amounts of these elements in alternative fuels relative to those in coal. Attempts will be made to correlate the presence or absence of these trace elements to changes in the kiln process, clinker production, clinker composition, properties of the cement produced, properties of the concrete made from this cement, and gaseous plant emissions.

The sampling and testing plans are given below in a series of table (Table B-2)

ADEM

ALABAMA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
POST OFFICE BOX 301463 36130-1463 ◆ 1400 COLISEUM BLVD. 36110-2059
MONTGOMERY, ALABAMA
WWW.ADEM.STATE.AL.US
(334) 271-7700

ONIS "TREY" GLENN, III, P.E.
DIRECTOR

BOB RILEY
GOVERNOR

Facsimiles: (334)
Administration: 271-7950
General Counsel: 394-4332
Communication: 394-4383
Air: 279-3044
Land: 279-3050
Water: 279-3051
Groundwater: 270-5631
Field Operations: 272-8131
Laboratory: 277-6718
Mining: 394-4326

September 16, 2005

MR TRAVIS REED
ENVIRONMENTAL MANAGER
LAFARGE BUILDING MATERIALS
P O BOX 182
CALERA AL 35040

Dear Mr. Reed:

The Department has received and evaluated the information submitted in your letter dated June 20, 2005, concerning the proposed pilot project which would involve the utilization of varied alternate fuel sources for the rotary kiln at the Roberta Plant in Calera, Alabama.

In your letter, you have requested the ability to run a 7 to 10-day trial for each proposed alternate fuel stream. The Department understands that, while Lafarge has currently decided upon only two streams to introduce into the kiln system, your facility wishes to test several fuel sources. Lafarge will be expected to utilize its monitoring systems (COMS, CEMS, kiln operating parameters, baghouse performance characteristics, etc.) during the pilot study.

Please note that this test project shall last no longer than three months from the first day of the project. Please contact the Department so as to inform us of the start date of the project. Lafarge will be expected to record the dates and times that each test fuel source is used. Prior to the beginning of the pilot study, Lafarge shall submit to the Department its proposed schedule, including each type of alternate fuel stream to be used during the trial.

If you have any questions concerning this matter, please call Amy Graham at (334) 270-5677.

Sincerely,

Ronald W. Gore, Chief
Air Division

RWG:aeg

Birmingham Branch
110 Vulcan Road
Birmingham, Alabama 35209-4702
(205) 942-6168
(205) 941-1603 [Fax]

Decatur Branch
2715 Sandlin Road, S.W.
Decatur, Alabama 35603-1333
(256) 353-1713
(256) 340-9359 [Fax]

Mobile Branch
2204 Perimeter Road
Mobile, Alabama 36615-1131
(251) 450-3400
(251) 479-2593 [Fax]

Mobile – Coastal
4171 Commanders Drive
Mobile, Alabama 36615-1421
(251) 432-6533
(251) 432-6598 [Fax]

Printed on Recycled Paper

Tables B-2. Sampling Plan

Table I: Analyzing the chemical composition of *Raw Materials*

Item #	Material Analyzed	Test	Sampling Frequency	Sample Method	Sampling Period	Tested by	Routine?
1	***Fly Ash***	LOI, moisture, and XRF element scan	1 / week	Grab samples	2 weeks before burn, during burn period (3-5 days), and 1 week after burn	Lafarge, Roberta Plant	Yes
2	***High Calcium Fines***						
3	***Limestone/Clay***						
4	***Furnace Slag***						
5	***Sand***						
6	***Fly Ash***	Trace elements, Table B (excluding Na, K, Mg, Mg)	Single	Grab sample	during burn period	Wyoming Analytical Laboratory	No
7	***High Calcium Fines***						
8	***Limestone/Clay***						
9	***Furnace Slag***						
10	***Sand***						
11	***Preheater/Precalciner Feed Stream***	LOI and moisture	4 / day	Grab samples	12 days before burn, during burn period (3-5 days), 6 days after burn	Lafarge, Roberta Plant	No
12	***Preheater/Precalciner Feed Stream***	XRF element scan	4 / day	Grab samples	12 days before burn, during burn period (3-5 days), 6 days after burn	Lafarge, Roberta Plant	Yes
13	***Preheater/Precalciner Feed Stream***	Trace elements, Table B (excluding Na, K, Mg, Mg)	4 composites before burn, 1-2 during burn, 2 after burn	3-day composites prep. from 4 X-daily grab samples (each composite analyzed in triplicate)	12 days before burn, during burn period (3-5 days), 6 days after burn	Wyoming Analytical Laboratory	No
14	***Gypsum***	LOI, moisture, and XRF	1 / week	Grab samples	Before and during grinding	Lafarge, Roberta	Yes

		element scan				Plant	
15	***Gypsum***	Trace elements, Table B (excluding Na, K, Mg, Mg)	1 composite before grinding, 1 during grinding	3-day composites prep. from twice-daily grab samples (each composite analyzed in triplicate)	3 days before grinding, 3 days during grinding	Wyoming Analytical Laboratory	No

Table II: Analyzing the chemical composition of *Fuel Sources (Coal, Tires, Broiler Litter, and Plastics)*

Item #	**Material Analyzed**	**Test**	**Sampling Frequency**	**Sample Method**	**Sampling Period**	**Tested by**	**Routine?**
1	*Pulverized Coal*	Proximate Analysis	4 composites before burn, 1-2 during burn, 2 after burn	3-day composites prep. from twice-daily grab samples (each composite analyzed in triplicate)	12 days before burn, during burn period (3-5 days), 6 days after burn	Wyoming Analytical Laboratory	No
2	*Pulverized Coal*	Ultimate Analysis				Wyoming Analytical Laboratory	No
3	*Pulverized Coal*	Total Cl				Wyoming Analytical Laboratory	No
4	*Pulverized Coal*	Total S				Wyoming Analytical Laboratory	No
5	*Pulverized Coal*	Ash Analysis: Trace elements, Table B (excluding S, Cl)				Wyoming Analytical Laboratory	No
6	*Pulverized Coal*	Combustion Analysis				Wyoming Analytical Laboratory	No
7	*Tires*	Proximate Analysis	1 composite before burn, 1 during burn, 1	composites prep. from 8 discrete radial-section	3 days before burn, during burn period, and 3 days after	Wyoming Analytical Laboratory	No

8	*Tires*	Ultimate Analysis	after burn	samples removed from random tires (each composite analyzed in triplicate)	burn	Wyoming Analytical Laboratory	No
9	*Tires*	Total Cl				Wyoming Analytical Laboratory	No
10	*Tires*	Total P				Wyoming Analytical Laboratory	No
11	*Tires*	Ash Analysis: Trace elements, Table B (excluding S, Cl)				Wyoming Analytical Laboratory	No
12	*Tires*	Combustion Analysis				Wyoming Analytical Laboratory	No
13	*Broiler Litter*	Proximate Analysis	4 / day	Grab samples	During burn period (3-5 days)	Wyoming Analytical Laboratory	No
14	*Broiler Litter*	Ultimate Analysis				Wyoming Analytical Laboratory	No
15	*Broiler Litter*	Total Cl				Wyoming Analytical Laboratory	No

16	*Broiler Litter*	Total S				Wyoming Analytical Laboratory	No
17	*Broiler Litter*	Ash Analysis: Trace elements, Table B (excluding S, Cl)				Wyoming Analytical Laboratory	No
18	*Broiler Litter*	Combustion Analysis				Wyoming Analytical Laboratory	No
19	*Plastics*	Proximate Analysis.	4 / day	Grab samples	During burn period (3-5 days)	Wyoming Analytical Laboratory	No
20	*Plastics*	Ultimate Analysis				Wyoming Analytical Laboratory	No
21	*Plastics*	Total Cl				Wyoming Analytical Laboratory	No
22	*Plastics*	Total S				Wyoming Analytical Laboratory	No
23	*Plastics*	Ash Analysis: Trace elements, Table B (excluding S, Cl)				Wyoming Analytical Laboratory	No

24	*Plastics*	Combustion Analysis				Wyoming Analytical Laboratory	No

Table III: **Analyzing the chemical composition of *Cement Kiln Dust (CKD)***							
Item #	**Material Analyzed**	**Test**	**Sampling Frequency**	**Sample Method**	**Sample Period**	**Tested by**	**Routine?**
1	*CKD*	Si, Al, Fe, Ca, Mg, S, Na, K, Cl	2 / day	Grab samples	3 days before burn, during burn period, and 3 days after burn	Lafarge, Roberta Plant	Yes
2	*CKD*	Trace elements, Table B (excluding Na, K, Mg, S, Cl)	2 / day	Grab samples	3 days before burn, during burn period, and 3 days after burn	Wyoming Analytical Laboratory	No

Table IV: Analyzing the chemical composition of *Clinker*

Item #	Material Analyzed	Test	Specification	Sampling Frequency	Sample Method	Sampling Period	Tested by	Routine?
1	*Clinker*	***Chemical Composition:*** Silicon dioxide (SiO_2) Aluminum oxide (Al_2O_3) Ferric oxide (Fe_2O_3) Magnesium oxide (MgO) Sulfur (S) → Calc. SO_3 Calcium oxide (CaO) Free CaO Sodium Oxide (Na_2O) Potassium Oxide (K_2O) LSF (calc) T Alkalis (calc)	ASTM C 114 and X-ray Fluorescence (XRF)	8-12 / day	Grab samples	3 days before burn, during burn period, and 3 days after burn	Lafarge, Roberta Plant	Yes
2	*Clinker*	***Clinker Phase Composition:*** C_3S, C_2S, C_3A, C_4AF	ASTM C 150 (Calculated by Bogue formulae)	N/A	N/A	N/A	Lafarge, Roberta Plant	Yes
3	*Clinker*	***Clinker Phase Composition:*** C_3S, C_2S, C_3A, C_4AF	Rietveld Analysis	1 / day	Daily Composite, prep.from grab samples	3 days before burn, during burn period, and 3 days after burn	Lafarge, CTS	No
4	*Clinker*	***Trace Element Content of Clinker:*** Trace elements, Table B (excluding Na, K, Mg, S)	XRF				Wyoming Analytical Laboratory	No

Table V: Analyzing the chemical composition of *Cement*								
Item #	**Material Analyzed**	**Test**	**Specification**	**Sampling Frequency**	**Sample Method**	**Sampling Period** [1]	**Tested by**	**Routine?**
1	*Cement*	***Chemical Composition:*** Phosphorus Pentoxide (P_2O_5) Titanium dioxide (TiO_2)	ASTM C 114 and X-ray Fluorescence (XRF)	12 / day	Grab samples	3 days before burn, during burn period, and 3 days after burn	Lafarge, Roberta Plant	Yes
2	*Cement*	***Clinker Phase Composition:*** C_3S, C_2S, C_3A, C_4AF	ASTM C 150 (Calculated by Bogue formulae)	N/A	N/A	3 days before burn, during burn period, and 3 days after burn	Lafarge, Roberta Plant	Yes

3	*Cement*	***Chemical Composition:*** Silicon dioxide (SiO_2) Aluminum oxide (Al_2O_3) Ferric oxide (Fe_2O_3) Magnesium oxide (MgO) Sulfur (S) → Calc. SO_3 Calcium oxide (CaO) Free CaO Loss on ignition (LOI) Insoluble residue Sodium Oxide (Na_2O) Potassium Oxide (K_2O) Equiv. Na2O	XRF, other	1 / day	Daily Composite, prep. from grab samples	3 days before burn, during burn period, and 3 days after burn	Lafarge, Roberta Plant	Yes
4	*Cement*	***Chemical Composition:*** Insoluble residue		Single	Daily composite, prep. from grab samples	During burn period	Lafarge, Roberta Plant	Yes
5	*Cement*	***Additional Chemical Analysis:*** Anhydrite (Calcium Sulfate, $CaSO_4$) Sodium Sulfate (Na_2SO_4) Potassium Sulfate (K_2SO_4) Aphthitalite ($Na_2SO_4 \cdot 3K_2SO_4$) Calcium langbeinite ($2CaSO_4 \cdot K_2SO_4$)	Differential Scanning Calorimetry (DSC) or X-ray Diffraction (XRD)	2 / day	Grab samples	3 days before burn, during burn period, and 3 days after burn	Lafarge, CTS	No

6	*Cement*	***Additional Chemical Analysis:*** Total organic carbon (TOC)	TOC Analyser	1 / day	Daily composite, prep. from grab samples	3 days before burn, during burn period, and 3 days after burn	Wyoming Analytical Laboratory	No
7	*Cement*	***Trace Element Content of Cement:*** Trace elements, Table B (excluding Na, K, Mg, S)	NAA and/or XRF	1 / day	Daily composite, prep. from grab samples	3 days before burn, during burn period, and 3 days after burn	Wyoming Analytical Laboratory	No

Notes:

[1] Roberta Plant has agreed to set aside a portion of the clinker prepared during the test burn so it can be tracked through the cement grinding process.

Table VI: Testing the physical properties of *Cement*

Item #	Material Analyzed	Test	Specification	Sampling Frequency	Sample Method	Sampling Period[2]	Tested by	Routine
1	*Cement*	***Standard ASTM C150 Requirements:*** Air content of mortar (%) Blaine specific surface area (m^2/kg)	ASTM C 185 ASTM C 204	1 / day	Composite	3 days before burn, during burn period, and 3 days after burn	Lafarge, Roberta Plant	Yes
2	*Cement*	***Standard ASTM C150 Requirements:*** Calcium Sulfate (% expansion)	ASTM C 1038	Single	Composite	during burn period	Lafarge, Roberta Plant	Yes
3	*Cement*	***Standard ASTM C150 Requirements:*** Autoclave expansion (%) Compressive strength (psi): 1, 3, 7, 28d Consistency (Mortar flow times) Time of setting: Gillmore test: Initial and Final set Vicat test: Initial and Final set	ASTM C 151 ASTM C 109 ASTM C 230 ASTM C 266 ASTM C 191	1 / day	Composite	3 days before burn, during burn period, and 3 days after burn	Lafarge, Roberta Plant, and Auburn Univ[1]	Yes
4	*Cement*	***Additional Properties:*** 325 mesh Pack set % NC PMFS H_2O F set Lime Saturation					Lafarge, Roberta Plant	Yes

		Factor						
5	*Cement*	***Additional Testing for Phase I:*** Particle size distribution Heat of hydration under isothermal conditions (1, 3, and 7 days) Heat of hydration (kJ/kg): 3, 7, 28 days	Laser Diffraction TamAir Calorimeter ASTM C 186				Lafarge, CTS	No
6	Cement	***Additional Testing for Phase I:*** Drying shrinkage of paste prisms	ASTM C 596				Auburn University[1]	No

Notes:

[1] 1 sample prior to burn, 1 sample during burn period, and 1 sample after burn

[2] Roberta Plant has agreed to set aside a portion of the clinker prepared during the test burn so it can be tracked through the cement grinding process.

Table VII: Testing the properties of *Concrete* performed by Auburn University and Lafarge Concrete Lab at Atlanta Plant

Item #	Test	Specification	Material Type	Concrete Age (days)	Sampling Frequency	Sample Method [4]	Sample Size
1	***Fresh Properties:*** Setting time Total air content Air void distribution (air void analyser[1])	ASTM C 403 ASTM C 231 -	Mortar Concrete Mortar	Early-age Fresh State Fresh State	1/ trial burn	Discrete at end of trial burn	2 x (4 - 55 gal. drums)
2	***Heat Development:*** Heat of hydration under semi-adiabatic conditions	RILEM	Concrete	0.1 to 7			
3	***Physical Properties:*** Compressive strength Splitting tensile strength Drying shrinkage development Permeability (RCPT)	ASTM C 39 ASTM C 496 ASTM C 157 ASTM C 1202	Concrete Concrete Concrete Concrete	1, 3, 7, 28, 91 1, 3, 7, 28, 91 4 to 448 91 and 365			
4	***Durability Issues:*** Freezing and thawing resistance Alkali-silica reaction susceptibility[2] Delayed-ettringite formation susceptibility[2]	ASTM C 666 ASTM C 1293 -	Concrete Concrete Concrete	91 days Long-Term Long-Term			
5	***Interactions with Chemical Admixtures:***[3] Air entraining admixtures Type A Water-reducing admixtures Type B Retarding admixtures	Repeat the tests shown above under: Fresh Properties, Heat Development, and Physical Properties					

	Type C Accelerating admixtures Type F Water-reducing, high range admixtures		

Notes:

[1] Phase II – Additional equipment required for these tests.

[2] Phase II – Subcontracted to the University of Texas at Austin

[3] Phase II – Three standard concrete mixtures will be developed to evaluate the response of the cement:

(1) Cement only, w/c = 0.40 (For AEA, Type A, B, and C Admixtures)
(2) Cement only, w/c = 0.32 (For AEA, Type B, C and F Admixtures)
(3) Cement with 30% Class C fly ash replacement, w/cm = 0.40 (For AEA, Type A, B, and C Admixtures)

[4] Roberta Plant has agreed to set aside a portion of the clinker prepared during the test burn so it can be tracked through the cement grinding process.

Table VIII: Analyzing *Emissions*

Item #	Material Analyzed	Test	Spec.	Frequency	Sample Method	Period for which Data Are Needed	Tested by	Routine?
1	Main Stack emissions	CO NO_x Opacity SO_2 VOC	CEMS	Continuous-	Real - Time	12 days before burn, during burn (3-5 days), 6 days after burn	Lafarge, Roberta Plant	Yes
2	Coal Stack emissions	NO_x Opacity SO_2 VOC	CEMS	Continuous-	Real - Time	12 days before burn, during burn (3-5 days), 6 days after burn	Lafarge, Roberta Plant	Yes

Table IX: ASTM Methods	
Method Number	**Method Title**
C39	Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens
C109	Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)
C151	Standard Test Method for Autoclave Expansion of Hydraulic Cement
C157	Standard Test Method for Length Change of Hardened Hydraulic-Cement, Mortar, and Concrete
C185	Standard Test Method for Air Content of Hydraulic Cement Mortar
C186	Standard Test Method for Heat of Hydration of Hydraulic Cement
C191	Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle
C204	Standard Test Method for Fineness of Hydraulic Cement by Air Permeability Apparatus
C230	Standard Specification for Flow Table for Use in Tests of Hydraulic Cement
C231	Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method
C266	Standard Test Method for Time of Setting of Hydraulic-Cement Paste by Gillmore Needles
C403	Standard Test Method for Time of Setting of Concrete Mixtures by Penetration Resistance
C471M	Standard Test Methods for Chemical Analysis of Gypsum and Gypsum Products [Metric]
C496	Standard Test Method for Splitting Tensile Strength of Cylindrical Concrete Specimens
C596	Standard Test Method for Drying Shrinkage of Mortar Containing Hydraulic Cement
C666	Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing
C1038	Standard Test Method for Expansion of Hydraulic Cement Mortar Bars Stored in Water
C1202	Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration
C1271	Standard Test Method for X-ray Spectrometric Analysis of Lime and Limestone
C1293	Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction
C1301	Standard Test Method for Major and Trace Elements in Limestone and Lime by Inductively Coupled Plasma-Atomic

	Emission Spectroscopy (ICP) and Atomic Absorption (AA)
D2361	Standard Test Method for Chlorine in Coal
D2795	Standard Test Methods for Analysis of Coal and Coke Ash
D3172	Standard Practice for Proximate Analysis of Coal and Coke
D3176	Standard Practice for Ultimate Analysis of Coal and Coke
D3683	Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption
D3684	Standard Test Method for Total Mercury in Coal by the Oxygen Bomb Combustion/Atomic Absorption Method
D4208	Standard Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method
D4326	Standard Test Method for Major and Minor Elements in Coal and Coke Ash By X-Ray Fluorescence
D5142	Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures
D5468	Standard Test Method for Gross Calorific and Ash Value of Waste Materials
D5865	Standard Test Method for Gross Calorific Value of Coal and Coke
D6349	Standard Test Method for Determination of Major and Minor Elements in Coal, Coke, and Solid Residues from Combustion of Coal and Coke by Inductively Coupled Plasma—Atomic Emission Spectrometry
D6357	Test Methods for Determination of Trace Elements in Coal, Coke, & Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission, Inductively Coupled Plasma Mass, & Graphite Furnace Atomic Absorption Spectrometries
D6721	Standard Test Method for Determination of Chlorine in Coal by Oxidative Hydrolysis Microcoulometry
D6722	Standard Test Method for Total Mercury in Coal and Coal Combustion Residues by Direct Combustion Analysis
E711	Standard Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter
E775	Standard Test Methods for Total Sulfur in the Analysis Sample of Refuse-Derived Fuel
E776	Standard Test Method for Forms of Chlorine in Refuse-Derived Fuel
E777	Standard Test Method for Carbon and Hydrogen in the Analysis Sample of Refuse-Derived Fuel
E778	Standard Test Methods for Nitrogen in the Analysis Sample of Refuse-Derived Fuel

E830	Standard Test Method for Ash in the Analysis Sample of Refuse-Derived Fuel
E870	Standard Test Methods for Analysis of Wood Fuels
E885	Standard Test Methods for Analyses of Metals in Refuse-Derived Fuel by Atomic Absorption Spectroscopy
E897	Standard Test Method for Volatile Matter in the Analysis Sample of Refuse-Derived Fuel
E949	Standard Test Method for Total Moisture in a Refuse-Derived Fuel Laboratory Sample

Table X: Problematic Minor/Trace Elements

Analyte	Analysis Technique
As	XRF
Ba	
Cd	
Cl	
Cr	
Cu	
Hg	
K	
Mg	
Na	
P	
Pb	
S	
Sr	
Ti	
V	
Zn	

Table XI: Fuels Analysis

Test	Analyte
Proximate Analysis	Volatile Matter, Fixed Carbon, % Ash, % Moisture
Ultimate Analysis	C, H, O, S, N, Ash
Ash Analysis	Trace elements from Table B
Combustion Analysis	BTUs

Table XII: Abbreviations Used

Abbreviation	**Definition**
% NC	% Normal Consistency
AEA	Air entraining agent
ASTM	American Society for Testing and Materials
C_2S	Dicalcium silicate
C_3A	Tricalcium aluminate
C_3S	Tricalcium silicate
C_4AF	Tetracalcium aluminoferrite
CEMS	Continuous emissions monitoring system
CKD	Cement kiln dust
F set	Fast set
LOI	Loss on ignition
LSF	Lime saturation factor
NAA	Neutron activation analysis
PMFS H_2O	Paste Mortar Fault Set Water requirement
RCPT	Rapid chloride permeability test
T Alkalis	Total alkalis
TOC	Total organic carbon
VOC	Volatile organic compounds
XRF	X-ray fluorescence

We have selected broiler litter and plastics are the two alternate sources for testing. One area of concern for using broiler litter is Avian influenza. According to all the available scientific literature, there is no documented case of transmission of this disease via broiler litter. We have inquire Dr. Hoerr, director of the Alabama State Diagnostic Laboratories. He stated “Considering the thousands of poultry farms in Alabama and the tonnage of litter produced, reports of human disease stemming from direct exposure to litter appear to be sparse, if they even exist.” He also recommended safety precautions as follows: “Potential risks can be managed by personal protective equipment including coveralls, gloves and protective footwear; N95 or equivalent respirator and safety glasses; and good personal hygiene that includes showering and changing to clean clothing prior to departing the workplace.”

The installation of the monitoring system is complete. One pollutant (VOC) has not been certified yet due to low emission concentrations. All other pollutants (NO_x, SO_2, opacity) are certified. Figure B-1 is a photograph showing the installed devices on the stack.

Figure B-1. Photograph showing emission monitoring devices installed on the stack.

Task C: Test Two Selected Alternate Sources of Fuel

Two test-burns with alternative fuels have been completed. A summary of the time of each burn and the plant conditions are presented in Table C-1. Two waste-plastic fuel streams were combined and approximately 300 tons were burned. One source was automotive flooring trim scrap materials (Source: Collins and Aikman) and the other was automotive trim scrap (Source: Color Fi). Since the flooring material had a low density, blending of the two materials resolved some material handling problems. The fuels and equipment used at the Roberta Plant is shown in Figure C-1.

The broiler litter test burn utilized coal, tires, and broiler litter as the fuel. The time-history data of the alternative fuel to total fuel substitution rate by heat equivalency basis for all four completed burns are shown in Figure C-2.

Figure C-1: Fuels and equipment used at the cement plant

Table C-1: Summary of Plant Conditions during Each Trial Burn

Item	Burn Type			
	Coal Only (C)	**Coal and Tires (C+T)**	**Coal, Tires, and Plastics (C+T+P)**	**Coal, Tires, and Broiler Litter (C+T+BL)**
Period	April 18 to 21, 2006	July 11 to 14, 2006	April 3 to 7, 2007	June 19 to 22, 2007
Kiln Feed Rate (tons/hr)	250 to 310	90 to 330	260 to 330	215 to 345
Clinker Production Rate (tons/hr)	160 to 200	100 to 200	170 to 240	127 to 249
Coal Feed Rate (tons/hr)	18 to 20	10 to 20	10 to 20	11 to 18
Tire Feed Rate (tons/hr)	-	0.0 to 1.4	0.3 to 4.0	0.1 to 1.0
Tire-to-Fuel Replacement Rate (%) [a]	-	1 to 10	2.0 to 8.0	0.1 to 4.4
Plastics Feed Rate (tons/hr)	-	-	2.5 to 3.5	-
Plastics-to-Fuel Replacement Rate (%) [a]	-	-	12 to 22.5	-
Broiler Litter Feed Rate (tons/hr)	-	-	-	1.7 to 3.0
Broiler Litter-to-Fuel Replacement Rate (%) [a]	-	-	-	5.0 to 7.5

[a] Reported as an energy replacement basis

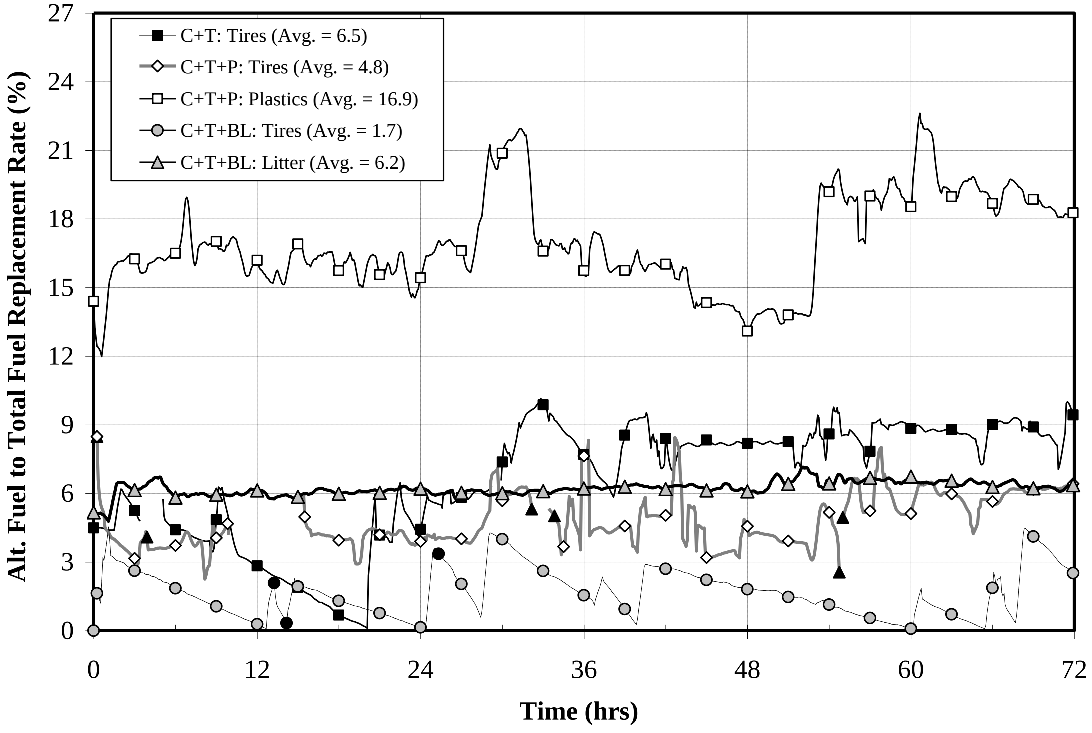


Figure C-2: Alternative fuel to total fuel substitution rate by heat equivalency basis

A summary of the proximate and ultimate analyses of the fuels used for these burns is summarized in Tables C-2. Unfortunately, the coal source used by the cement plant was changed between the Coal and Tires (C+T) and Coal, Tires, and Plastics (C+T+P) Burns. The plant switched back to its original source for the Coal, Tires, and Broiler Litter (C+T+BL) Burn. These decisions were made with production and economic issues in mind. The quantity of scrap tires that could be burned was limited by the development of sulfur build-ups within the system, which limited the amount of airflow, and effectively choked the system.

Table C-2: Proximate and Ultimate Analysis of Fuels

Test	**Parameter**	**C Burn**	**C+T Burn**		**C+T+P Burn**			**C+T+BL Burn**		
		Coal	**Coal**	**Tires**	**Coal**	**Tires**	**Plastics**	**Coal**	**Tires**	**Broiler Litter**
Proximate Analysis	**Ash (wt. %)**	22.45	16.74	13.72	24.54	14.56	0.32	17.65	12.21	20.61
	Fixed Carbon (wt. %)	49.58	54.81	24.60	47.68	26.38	8.75	53.61	49.41	33.75
	Moisture (wt. %)	1.04	1.17	0.14	1.06	0.07	0.32	0.64	0.09	29.06
	Volatile Matter (wt. %)	27.97	28.45	61.68	27.78	59.06	2.95	28.73	38.28	45.64
Ultimate Analysis	**Carbon (wt. %)**	67.61	73.09	72.34	64.68	75.94	8.06	69.8	78.98	40.89
	Hydrogen (wt. %)	3.61	4.66	7.05	3.93	6.53	64.23	3.59	5.44	4.86
	Nitrogen (wt. %)	1.10	1.22	0.36	1.08	0.52	1.27	0.59	0.06	4.30
	Oxygen (wt. %)	3.95	3.14	4.98	4.11	0.46	0.22	6.77	1.84	28.66
	Sulfur (wt. %)	1.28	1.15	1.54	1.66	2.00	17.46	1.55	1.47	0.68
Dry Basis Heat Value [1] (BTU/lb)		11698	12624	14467	11369	14687	12754	12431	15501	6875

The low density of the plastics affected the ability of the equipment to feed this fuel into the precalciner. The average density of the plastics was measured to be only 5.26 lb/ft^3 (84.3 kg/m^3). The introduction of waste plastics into the system was affected by the ability of the fuel feed equipment to convey the low-density material into the precalciner. Note that both the scrap tires and waste plastics had higher energy contents than the coal. Broiler litter (ash) obtained from a nearby farm had a low heat value compared to the other alternative fuels. The average density of the broiler litter was measured to be 41.7 lb/ft^3 (667.7 kg/m^3). Broiler litter, though low in energy content, handled easily and did not cause any problems while in use.

The Continuous Emissions Monitoring System (CEMS) is a certified device that measures various plant emissions in accordance with Alabama Department of Environmental Management (ADEM) and Environmental Protection Agency (EPA) requirements. Hourly average emissions in tons per hour (tph) were determined from the CEMS data over the entire three days for each trial burn period. The average emissions for all the trial burns are shown in Table C-3, along with the allowable daily average emissions allowed by the plant permit. The percent change in average emissions for each trial burn is compared to that of the Coal Only (C) Burn. The average hourly ADEM limits for NOx, SO_2, and VOC were calculated from the permitted monthly emissions by assuming production over 30 days/month at an average clinker production rate of 185 tons/hr.

The largest difference is seen in the SO_2 data: a very large increase for both the C+T and C+T+BL Burns but not much for the C+T+P Burn. Once the SO_2 emissions of the C and CTP Burns are compared to the ADEM daily average limit, it can be concluded that the SO_2 emissions for the trial burns are all significantly less than the daily average emissions allowed by the plant permit. Personnel at the cement plant, believe that the apparent increase in SO_2 readings for the C+T and C+T+BL Burns are a result of normal process variations (oxygen, feed composition, temperatures etc.). The values in Table C-3 indicate that the NO_x emissions were the lowest for the C and C+T+BL Burns. Theses data further indicate that the VOC emissions were the lowest for the C and C+T+P Burns. All the plant emissions were under the average limits set by ADEM. It is encouraging to notice that the average CO levels were lower for the trial burns that used alternative fuels.

Table C-3: Summary and Comparison of Emission Results

Parameter	**ADEM Average Limit** [1]	**C Burn**	**CT Burn**		**CTP Burn**		**CTB Burn**	
		Value[1]	**Value**[1]	**Diff.** [2] **(%)**	**Value**[1]	**Diff.** [2] **(%)**	**Value**[1]	**Diff.** [2] **(%)**
NO_x	166	82	121	47.9	105	28.5	81	-0.66
SO_2	152	0.04	1.124	2711	0.041	2.2	0.625	1464.5
VOC	3.60	2.31	3.42	48.2	2.61	13.0	3.55	53.6
CO	200	76.8	54.1	-29.2	56.7	-26.1	37.9	-34.8

Notes: [1] Units of 10^{-5} tons/tons of clinker. [2] Percent Difference relative to C burn

Task D: Analysis and Initiation of Long-term Concrete Testing

Concrete mixtures were made from the cement collected from the plastic and broiler litter test burns. Two concrete mixture designs were made and tested at Auburn University. The primary mixture design, referred to as Mix A, had a water-to-cement ratio of 0.44, and used No. 57 crushed limestone and a natural river sand as aggregate. The secondary mixture design, referred to as Mix B, had a water-to-cement ratio in of 0.37, and used No. 78 crushed limestone and a natural river sand as aggregate. In an attempt to eliminate the variability in aggregates, enough of each aggregate type was collected on the same day to make all the concrete for all burns. Mix A was also produced by the cement plant's specialty laboratory. The aggregate used by the cement plant's concrete laboratory for Mix A was collected and provided by personnel at Auburn University.

Concrete was made using Mix A and Mix B mixture proportions. Concrete from cement from each burn was made in 6.5 ft^3 (0.184 m^3) batches under laboratory-controlled conditions. The properties measured for concrete from Mix A are presented in Figures D-1 and D-2 and those for Mix B are presented in Figures D-3 and D-4.

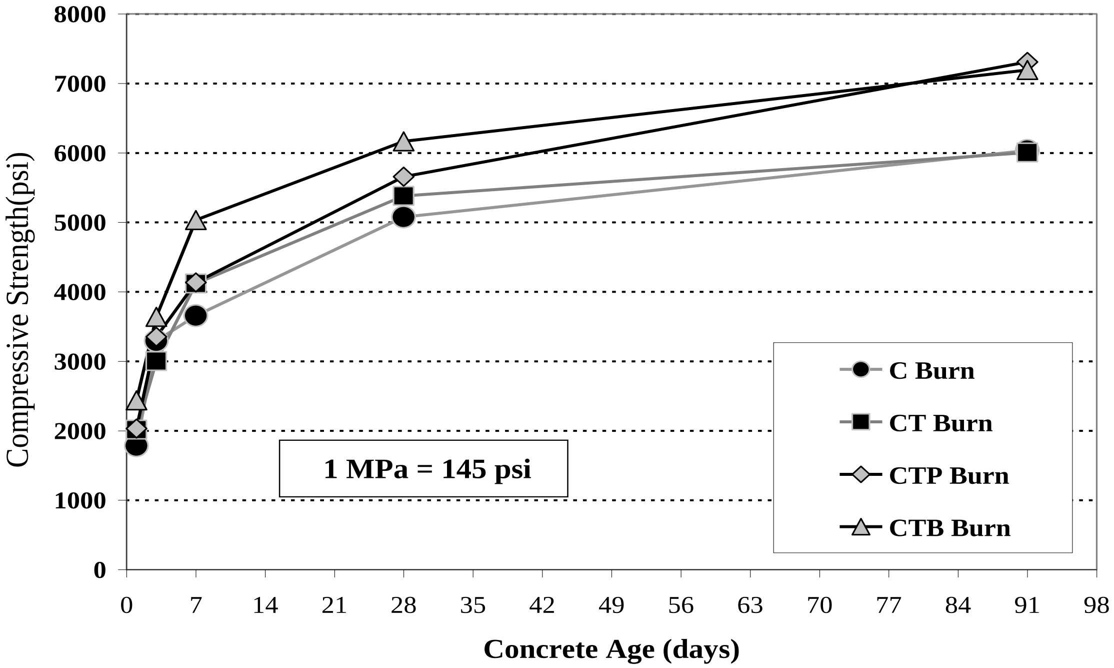


Figure D-1: Mix A (*w/c* = 0.44) - Compressive Strength of Concrete

The total air content and the slump are lower for the CTB burn compared to the C Burn. However, this change may be attributed to the amount of time elapsed between batches and thus differences in laboratory conditions.

The compressive strength of the concrete is observed to be higher for cement from the C+T+P and C+T+BL Burns compared to the C and C+T Burns. However, because of changes in plant conditions, it is not possible to attribute this result solely to changes in fuel types. The lower air contents of the C+T, C+T+P, and C+T+BL concretes for Mix B may also explain some of the increased later-age compressive strength values obtained for these cements.

According to ASTM C 496, the acceptable range of results of splitting tensile strength test within a single laboratory is 14 percent. Based on this range, there is little to no significant difference in the splitting tensile strengths of concrete made from the cement collected from these trial burns.

According to ASTM C 157, the allowable percent length change difference between drying shrinkage results is 0.0266. This value is percentage of length change, not relative difference between the results for each burn. Based on this allowable value, there was no significant difference in the drying shrinkage of the cements collected from the trial burns.

The 91-day permeability results are similar, especially after considering that the within-test repeatability for ASTM C 1202 is on the order of 1000 Coulombs. From this data it may be concluded that the concrete made from each of these cements has similar permeability levels.

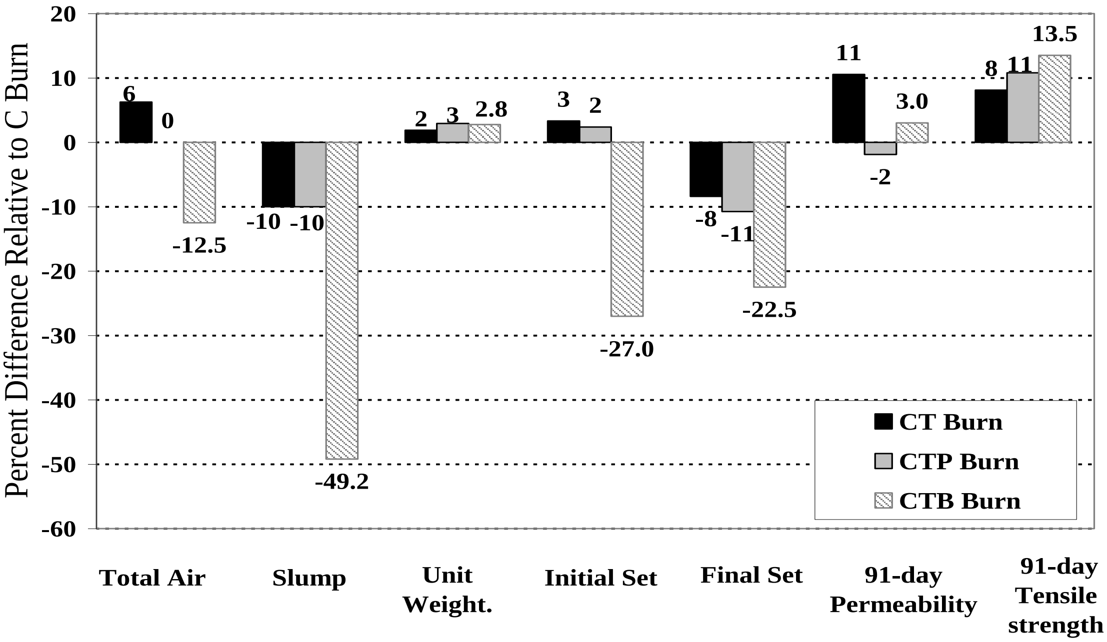


Figure D-2: Mix A (*w/c* = 0.44) - Properties of Concrete

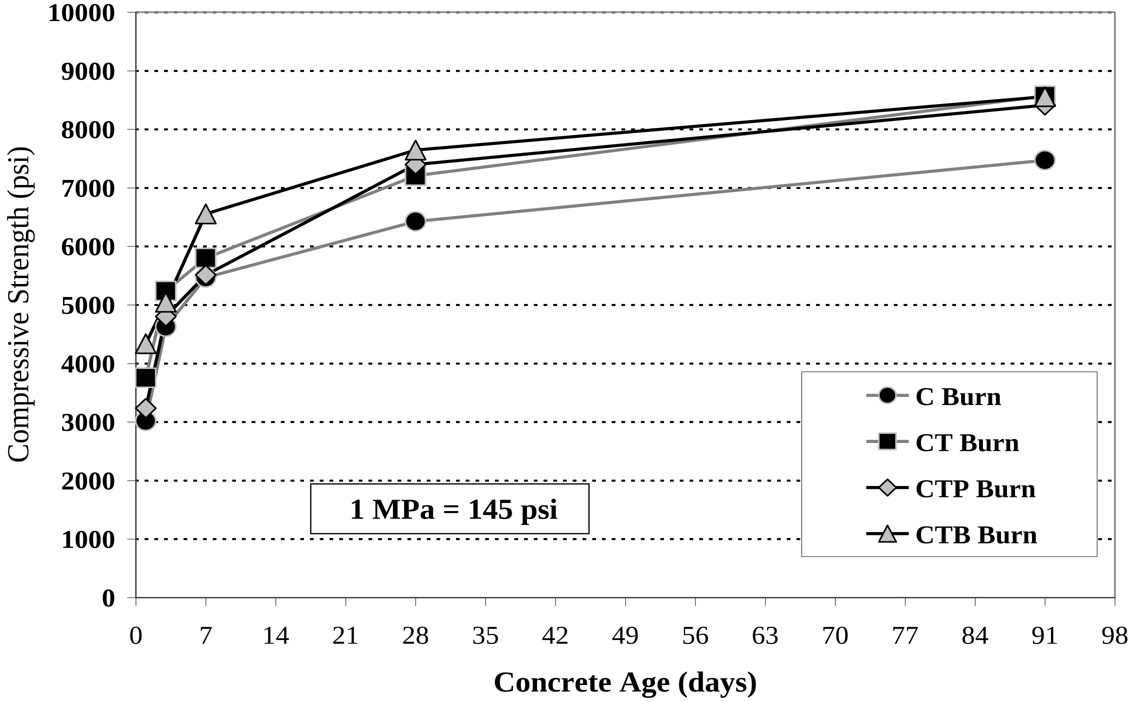


Figure D-3: Mix B (*w/c* = 0.37) - Compressive Strength of Concrete

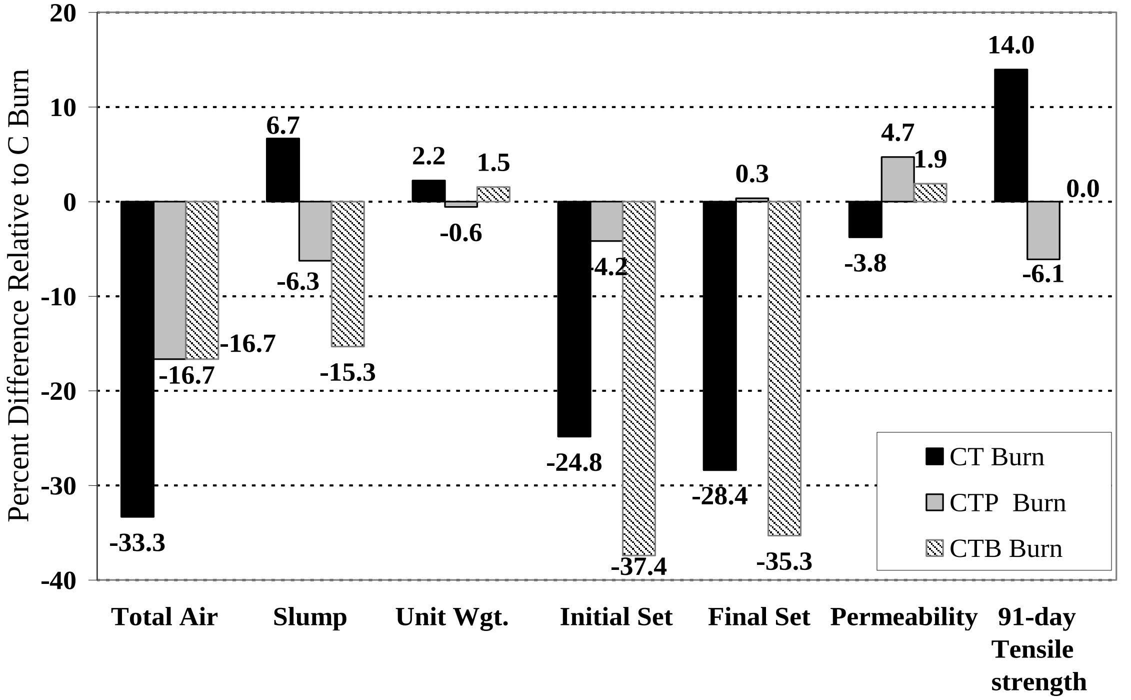


Figure D-4: Mix B (*w/c* = 0.37) - Properties of Concrete

Table D-1. Physical Properties of Concrete made with the Cement Produced by Burning Coal and Tires

Property	AUR		CPR
	Mix w/c=0.44	Mix w/c=0.37	Mix w/c=0.44
Total Air Content (%)	4.25	4.00	3.20
Slump (mm)	89.0	165.1	25.4
Unit Weight (kg/m^3)	2439.0	2427.1	2447.6
Setting Time (Min)			
Initial Set	218	239	247
Final Set	273	290	NC
Semi-Adiabadic Heat of Hydration			
τ (hrs)	CIP	CIP	NC
β	CIP	CIP	NC
α_u	CIP	CIP	NC
H_u (kJ/g)	CIP	CIP	NC
E (kJ/mol)	CIP	CIP	NC
Compressive Strength (MPa)			
1 day	13.9	25.9	15.1
3 days	20.7	36.1	21.9
7 days	28.4	38.6	32.9
28 days	37.1	49.7	42.3
91 days	41.4	CIP	CIP
Splitting Tensile Strength (MPa)			
1 day	2.0	3.0	NC
3 days	2.3	3.7	NC
7 days	2.8	3.9	NC
28 days	3.2	4.3	NC
91 days	3.4	CIP	NC
Drying Shrinkage Development (% Length Change)			
7 days	-0.019	-0.017	NC
28 days	-0.023	-0.027	NC
448 days	CIP	CIP	NC
Rapid Chloride Ion Penetration Test Electrical Conductance (Coulombs)			
91 days	2928	CIP	CIP
365 days	CIP	CIP	CIP
Freeze-Thaw Resistance	CIP	CIP	NC

Notes:

CIP - Collection in Progress	AUR - Auburn University Result
NC - Not Collected	CPR - Cement Plant Result

Task E: Development and Testing of a Cement Burn Simulator

The drop tube furnace, because of its custom design, is taking several months to be manufactured by ATS. Delivery is set for August 11. A single solid fuel particle injection system was designed and built that using a vibrating syringe. Fuel samples were obtained and readied for use with the burn simulator. Wood chip samples were ground, screened into size fractions, and dried for storage. Coal samples were obtained from Lafarge; these were screened into size fractions. Optical mounts were designed and set up in the Shop Building Chemical Engineering laboratory. A review of literature was conducted to determine appropriate light wavelengths and camera frame rates and resolution that will be used for spatial temperature visualization (these reviews are attached to this report in Attachments E-A and E-B below). Existing cameras, potential CMOS and CCD cameras, and pyrometers were invested; specification and quotes have been obtained. However, we are determining if it prudent to set up the furnace system (after it arrives in August), run it, and do preliminary visualizations and analyses with existing equipment. These preliminary results would provide a firm basis for selection of gas and product analysis equipment and visualization system components.

ATTACHMENT E-A:

Internal Memo

Theoretical calculation of desired frame rate of camera for purposes of imaging burning coal and biomass particles

To: Steve Duke

From: Josh Thompson

Date: June 2008

Introduction

In another report, the general theory of ratio thermometry was examined along with current and past research efforts in integrating new technology into this practice. The study showed that digital cameras can produce true temperature profiles of burning objects with the support of optical fibers and filters, frame grabbers and computer software. As a continuation of this study, the behavior of single particles interacting with a fluid medium is addressed to aid in visualization system design and camera and lens selection.

Theory and Approach

Because there are currently many unknown factors associated with coal combustion that will take place in our actual experimentation, the simplicity of this study has been reduced to only account the medium as stagnant air at what will be assumed standard conditions of 20 °C and 101 kPa. In addition it will be assumed that the particle has reached its terminal velocity before entering the viewing window of the camera. The area of a pixel is assumed to be square, as all cameras chosen in the previous report had. Also, exact values of the density of wood and coal that will be used in the experiments are not known; however, the density of biomass and the density of coal change very little. The density value of coal used in the calculations was taken from data acquired by Levendis et al. (2007); the value of the wood was taken from data acquired by Demirbas et al. (2003). Two other conditions to consider when evaluating the terminal velocity calculations are the “no-slip” condition and wall effects with respect to the particle.

There are two ways to calculate its terminal velocity and to validate either method a Reynolds number calculation is necessary. If Re < 0.1, then the following equation holds true (BSL, Eqn. 2.6-16, pg. 61):

$$\frac{4}{3}\pi R_P^3 \rho_P g = \frac{4}{3}\pi R_P^3 \rho_A g + 6\pi \mu_A R_P v_t \tag{1}$$

where R_P is the radius of the particle (m), ρ_P is the density of the particle (kg/m^3), ρ_A is the density of air (kg/m^3), μ_A is the viscosity of air (N·s/m^2), g is gravity (m/s^2), and v_t is the terminal velocity (m/s). Eqn. (1) leads to an explicit solution of:

$$v_t = \frac{2}{9\mu_A} R_P^2 g(\rho_P - \rho_A) \tag{2}$$

If Re > 0.1, then the friction factor cannot be simplified as it is in (1). This leads to an implicit solution due to the third term in (1) changing to:

$$F = f(\pi R_P^2)(0.5\rho_A v_t^2) \tag{3}$$

where

$$f = \left(\sqrt{\frac{24}{Re}} + 0.5407\right)^2 \tag{4}$$

Eqn. (3) is valid for the range of 0.1 < Re < 6000. Because the particle under consideration is 100 µm, it can be assumed that there is no need to investigate solutions regarding Re > 6000. With the altered force equation, the velocity equation can now be written as:

$$v_t = \left[\frac{8}{3}\frac{R_P g}{f \rho_A}(\rho_P - \rho_A)\right]^{1/2} \tag{5}$$

Once the terminal velocity of the particle is found, two parameters must be defined in order to calculate a theoretical frame rate for the camera: number of pixels defining the length of the particle (magnification); and the number of frames to capture the falling particle. Magnification in this case can be thought of as a means to accurately record the temperature profile of the particle if it were aflame; however, this assumes there are no blooming effects that will alter the recording of the image to translate to a temperature. In this case the following levels of magnification (number of pixels for particle diameter) will be observed: 5, 10, 15, 25 and 50 pixels. The number of frames considered will be: 5, 10, 15, 25 and 50 frames. By using the following calculation, a theoretical required frame rate can be calculated, assuming that the exposure time is sufficient:

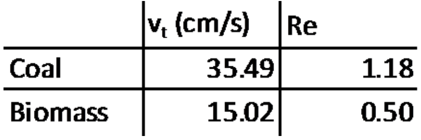
$$Frame\ rate = v_t \times N_f \times \frac{M}{SR \times D_P} \tag{6}$$

where N_f is the number of frames desired for the viewing area, M is the magnification number as defined previously, SR is the vertical spatial resolution of the camera, and D_p is the diameter of the particle.

Results and Discussion

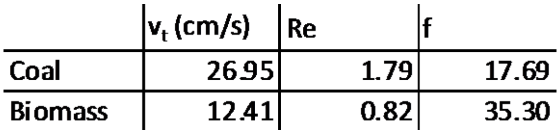
Terminal velocity can be first found in explicit form based on (2). The following are density values for the substances under study and the mediating fluid: coal[1], 1180 kg/m^3; biomass[2], 500 kg/m^3; and air, 1.20 kg/m^3. Table 1 has the results of the velocity and the Reynolds number. As seen, the assumption of Re < 0.1 is not valid in the case of this particle flow through air medium. Therefore, (1) and (2) are not valid, and (3) through (5) must be used to find the terminal velocity of the particle. Table 2 shows the results, which do meet the assumptions required for (3) through (5).

Table 1: Coal and Biomass Terminal Velocity Calculations via (2)



	v_t (cm/s)	Re
Coal	35.49	1.18
Biomass	15.02	0.50

Table 2: Coal and Biomass Terminal Velocity Calculations via (4) and (5)



	v_t (cm/s)	Re	f
Coal	26.95	1.79	17.69
Biomass	12.41	0.82	35.30

To consider the validation of the results in Table 2, the “no-slip” condition and wall effects must be examined in order to ensure these numbers are correct. Because the considerations made in the calculations assumed that the air was stagnant, the “no-slip” condition applies and, therefore, does not require any further calculations for its consideration. However, no assumptions can be made about wall effects, and the significance is determined by the ratio of the diameter of the particle to the diameter of the wall and by the Reynolds number. When the ratio of diameters is examined, the result of D_p/D_W is 1.57E-03; from this value, it can be inferred that wall effects are negligible in calculating the terminal velocity.

Figures 1 and 2 show the change in frame rate required for the camera with varying velocity. Each line has a constant magnification of 2 µm/pixel and varying number of frames. The change in velocity was done under the presumption that a down- or an up-flow of air can be used to alter the velocity of the particle. Considering previous assumptions made about the “no-slip” condition, there is no real need to recalculate the particle’s velocity at each air velocity change. The variation in velocity is mainly used to examine the possible range of frame rate speed needed for the camera under consideration for purchase.

---

[1] Demirbas, A. *Combustion characteristics of different biomass fuels.* Prog. Energy Combust. Sci., 30 (2004), pg. 223

[2] Bejerano, P.A.; Levendis, Y.A. *Single-coal-particle combustion in O_2/N_2 and O_2/CO_2 environments. Combust. Flame, 153 (2008),pg. 273*

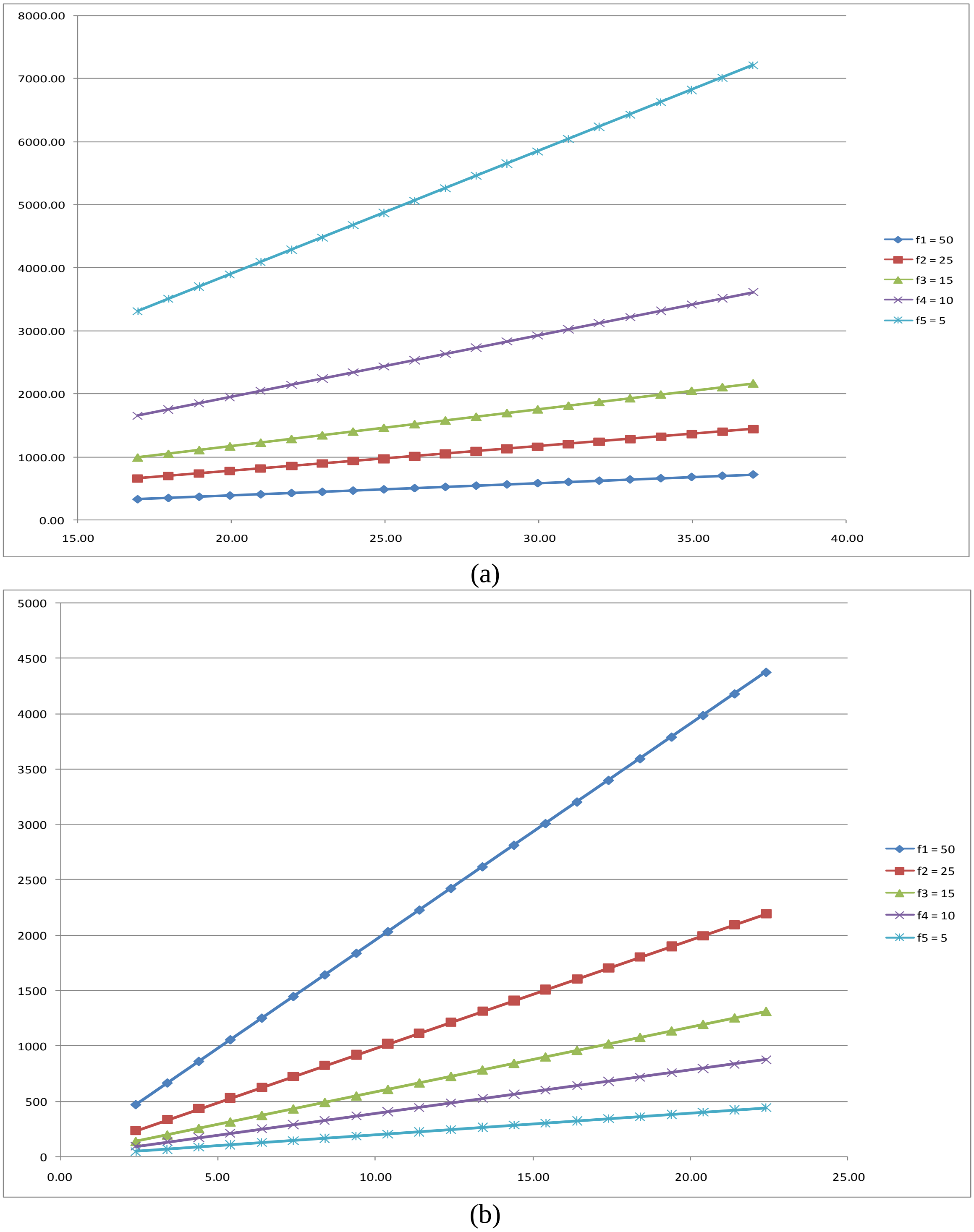
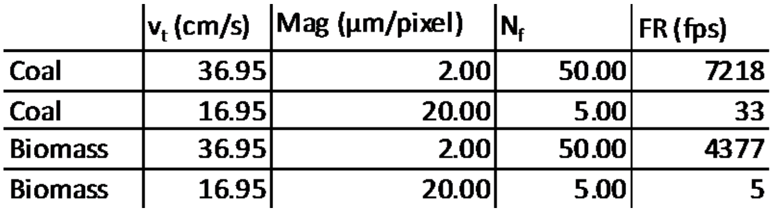


Figure 1: Frame rate speed vs. velocity with changing number of frames for the viewing length; (a) is coal and (b) is biomass.

Table 3 has the minimum and maximum frame rate speeds; the minimum is at the lowest magnification and velocity whereas the maximum is at the highest magnification and velocity. It can be seen there is a significant difference between the two substances. From this, it can be deduced that a camera is needed with a wide range of frame rate capabilities. The magnification is not determined by the camera and does not need to be considered when selecting a camera.

Table 3: Minimum and maximum theoretical frame rates for both coal and biomass.



	v_t (cm/s)	Mag (μm/pixel)	N_f	FR (fps)
Coal	36.95	2.00	50.00	7218
Coal	16.95	20.00	5.00	33
Biomass	36.95	2.00	50.00	4377
Biomass	16.95	20.00	5.00	5

Conclusion

From the results, it is clear that a camera with a wide range of frame rate speeds is needed in order to obtain adequate data. It can be proposed that for pure accuracy of temperature measurement, a slower camera can be used with a high quantum efficiency to assure its accuracy; consequently, a high speed camera can be used to measure reaction rates for both coal and biomass. This is sufficient because it will allow enough time-elapsed measurements of either particle in order to maintain continuous data of the reaction rate (the temperature change over the vertical pathway).

It should also be noted that the accuracy of the high speed camera, which will definitely have lower quantum efficiency than that of a slower camera, can be checked with respect to the results of the slower camera and/or an optical pyrometer. Any noticeable difference (e.g., within 10% difference) can be reported for the sake of accuracy with these scientific measurements.

Currently, our laboratory already has a slower CCD camera with high quantum efficiency. It is capable of reaching speeds of 200 fps, which is sufficient for few measurements of temperature; however, a few high speed cameras were recommended in the last report that will be capable to take the 50 measurements or more that our group wishes to have in order to possibly record optimal reaction rates of both coal and biomass. Attached is a price quote given for the pco.1200 hs CMOS camera. Currently, there are two other cameras that come close to meeting these specifications that were both included in the last report. The IDT M3 camera is currently being researched more for a price quote. The Redlake M3 camera, though similar to the pco.1200 hs, has windowing options that are not sufficient for our applications.

When windowing the spatial resolution of the camera, the frame rate speed is increased; however, it should be noted that we wish to record the coal particle temperature profile over the vertical length and windowing in only one dimension, and not both, is desired for this purpose. The Redlake camera states on its data sheet that it windows in both dimensions, but not just one. The IDT M3 camera shows on its data sheet that it can be windowed in only one dimension; therefore, a price quote has been requested to compare to the pco.1200 hs camera. Once these two can be compared, a request can be made for either camera.

ATTACHMENT E-B:

Internal Memo

Imaging Progress Report: CCD Camera and Pyrometer literature research, use in drop-tube furnaces and other considerations

To: Steve Duke

From: Josh Thompson

Date: June 2008

Introduction

When a solid object emits radiation, it produces a full spectrum of light, some visible and some not. This is the main governing principle of how CCD cameras and pyrometers are used with respect to non-contact measuring. The main difference between the two apparatuses is the range of the wavelengths being emitted that can be captured optically. CCD cameras operate within the limits of visible light radiation, for the most part, whereas a pyrometer uses near- to mid-infrared light radiation to determine temperature profiles of an object. Many researchers have used either imaging tool along with physical, chemical, and engineering principles to determine accurate temperature profiles.

Research Efforts and Applications

Li et al. [6]

There are many efforts in research currently to use color and monochrome CCD cameras to determine temperatures by non-contact measurements within furnaces; the application ranges from laboratory to industrial scale. In determining a calibration method for CCD cameras, Zhihong Li et al. used the wavelengths of 689.8, 630 and 578.2 nm. Their apparatus consisted of an endoscope, a monochrome CV-M50IR CCD camera, a Matrox Meteor-II frame grabber and appropriate software. The calibration was done using a black-body furnace of known emissivity over the temperature range to be used in the studies. However, the methodology used seems unreliable and very experiment-specific. For instance, there is a six term empirical correlation of gray body values relating to temperatures. It also uses an equation developed by Hottel and Broughton (1932), in which absorptivity is equated with emissivity.

Haung et al. [7]

A 500-kW furnace is used as the burning apparatus for the coal. The imaging apparatus is composed of optical filters at 650 and 700 nm, a monochrome CCD camera, a frame grabber and appropriate software. The paper lists reasons for picking the wavelengths:

1. Wavelengths should be selected to avoid the radiation from gas molecules and intermediate radicals, e.g., CO_2, H_2O, OH, CH, C_2, and CN.
2. Wavelengths should be in a region where the outputs of the CCD camera can be expected to vary sufficiently in view of sensitivity and SNR.

3. Choice of wavelengths should be expected to prevent the camera from saturation (unless there is an anti-blooming mechanism).
4. Two wavelengths (or three) should be chosen close to each other so that the differences between the emissivities and optical transmissions effects are negligible.

Lou et al. [13]
An industrial-sized furnace was used for the purpose of 3D temperature distribution observations for coal combustion. The main governing principle, as in Haung et al., is Wien's approximation to Planck's radiation law. A blackbody furnace was used as a method of calibrating the system. Because the spectral range is within the visible light area, the coal particles are assumed to be gray bodies; therefore, calculation of emissivity will produce the same value for whatever wavelength that is observed. Several cameras are used; the images are sent to a frame maker that composes a video signal before being recorded on a computer. The camera used is a Samsung SCC-833P color CCD camera.

More research is done in this group to also determine emissivity and other radiative properties of the particulate medium in the industrial-sized boiler. For these experiments, the wavelengths used are 700, 546.1 and 435.8 nm. However, the blue region does not provide suitable data to use in determination of the true temperature and emissivity of the coal particle flames due to difficulty to record the low intensity values in the blue region.

Hain et al. [14]
Some other considerations to make when selecting a camera for use in thermal imaging of coal and other fuel combustions; these suggestions were developed through research done by Hain et al.:

1. Scientific CMOS cameras have a good image quality. However, the image quality of scientific CCD cameras is still better. Thus, for high precision measurements a CCD camera should be applied.
2. Intensified CMOS cameras further reduce the image quality and spatial resolution. However, their high sensitivities allow measurements at low illuminations with moderate SNR.
3. For time resolved data acquisition, a CMOS camera without an intensifier is the best choice as long as the signal strength is acceptable.

Lu and Yan [10]
A 500 kW coal-fired combustion facility is used as the burning apparatus. A system for image recording is set up in the follow arrangement:

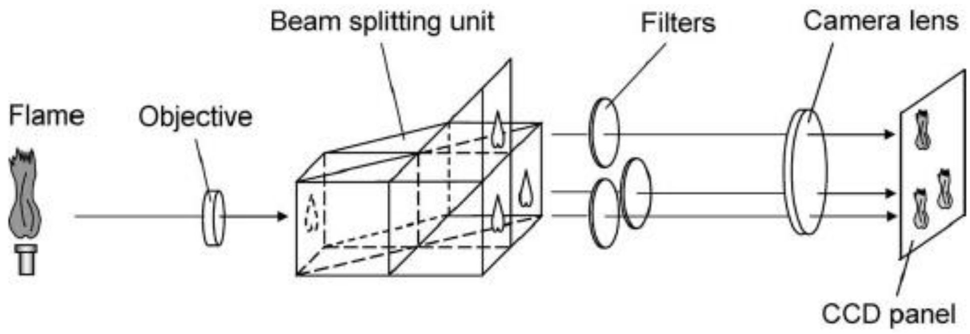


Figure 1: Optical system set-up from Lu and Yan [10].

The underlying principle of this experimental procedure is to capture three images at different wavelengths and then using the empirical equation developed by Hottel and Broughton (1932) to determine the true temperature. This empirical equation lies in the range of 550 to 850 nm due to the known constant parameter, α:

$$\varepsilon_{\lambda} = 1 - exp\left({}^{kl}/_{\lambda\alpha}\right) \tag{1}$$

The main reason that emissivity is not considered constant over the wavelength range for this paper is as follows: "the emissivity of the flame is considered to be unevenly distributed in consideration of the fuel blends being fired." Also the wavelengths are considered carefully to be 700, 632 and 550 nm and the authors explain why these are chosen:

1. Visible and infrared wavelengths can be used in a two-color system, but visible wavelengths are preferred because the rate of change of the spectral radiance with respect to temperature is greater in the visible spectral range than in the infrared spectral range, resulting in a higher sensitivity and SNR of the image signal.
2. The wavelengths must be far from the absorption bands of gas molecules and free radicals in the reaction zone of the flame.
3. The bandwidths of the filters should be as narrow as possible to acquire a single-wavelength radiation and, meanwhile, allow enough light passing through.
4. The pair of the selected wavelengths should be separated to achieve a higher SNR of two image signals.

Governing equations and general theory related to our research efforts

Planck's Law and Wien's Approximation

The radiation of a black body object follows Planck's radiation law:

$$I(\lambda, T) = \frac{2hc^{2}}{\lambda^{5}}\left(e^{\frac{hc}{\lambda kT}} - 1\right)^{-1} \tag{2}$$

where I is the monochromatic radiation intensity of the object, λ is the wavelength, T is the absolute temperature. By assuming an object is a gray body and using Wien's radiation approximation, the equation can be reduced to:

$$I(\lambda,T) = \frac{\varepsilon_\lambda(\lambda,T)C_1 e^{-\frac{C_2}{(\lambda T)}}}{\lambda^5 \pi} \qquad (3)$$

where ε_λ is the emissivity of the object at a specific wavelength, λ (nm), and temperature, T (K), and C_1 and C_2 are Planck's constants of 1.911 x 10^8 W·µm^{4}·m^{-2}·sr^{-1} and 1.4388 x 10^4 µm·K, respectively. Wien's approximation is valid when the product of the wavelength and the temperature is less than 3000, $\lambda \cdot T \leq 3000$ µm·K [DeWitt & Nutter, pg 486]. It should also be noted that from Wien's approximation that a theoretical maximum intensity relationship of wavelength and temperature can be found by taking the derivative of (3) and setting it equal to zero [DeWitt & Nutter, pg. 43]:

$$\lambda_{\max T} = 2897.7\ \mu m \cdot K \qquad (4)$$

CCD camera operation

For its relation to the current project, the assumptions stated to obtain (3) are valid for the range of temperatures (1400 to 1600K) and wavelengths (400 to 700nm) that will be examined. Unless the emissivity of an object is explicitly known, then using (3) for direct calculations is not possible due to the complexity of obtaining such a value. Therefore, like many researchers have adopted, ratio thermometry can be used to obtain the temperature based on the relative intensities at two different wavelengths.

For a CCD camera, radiation intensity can be expressed in pixel, or gray, values as follows [Lu et al., 991, "Concurrent meas. of temp. and soot conc.", 2002]:

$$P_\lambda = f(I) = f(\lambda,T) = RS_\lambda \frac{\varepsilon_\lambda(\lambda,T)C_1 e^{-\frac{C_2}{(\lambda T)}}}{\lambda^5} \qquad (5)$$

$$\frac{P_{\lambda 1}}{P_{\lambda 2}} = \frac{R_1 S_{\lambda 1}\varepsilon_{\lambda 1}(\lambda_1,T)\lambda_1^{-5} C_1 e^{-\frac{C_2}{\lambda T}}}{R_2 S_{\lambda 2}\varepsilon_{\lambda 2}(\lambda_2,T)\lambda_2^{-5} C_1 e^{-\frac{C_2}{\lambda T}}} \qquad (6)$$

where R_i is the instrument constant representing effects of radiation attenuation, observation distance, lens properties, etc., that can be obtained through calibration of an object at a known temperature (see below) and $S_{\lambda i}$ is the spectral sensitivity of the imaging system. By calibration of the system, (6) can be simplified to exclude emissivity by assuming the ratio of the two emissivities is at unity in the range under consideration and also assuming that the optical system parameters can be grouped together and solve for one value during calibration. Therefore, T (K) can be solved implicitly:

$$T_i = \frac{C_2\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)}{ln\left(\frac{P_i(\lambda_1,T)}{P_i(\lambda_2,T)}\right) + ln\left(\frac{S_{\lambda 2}}{S_{\lambda 1}}\right) + ln\left(\frac{\lambda_1}{\lambda_2}\right)} \qquad (7)$$

where P_i represents the pixel value of each pixel at the specific temperature and wavelength and the ratio of $S_{\lambda 2}/S_{\lambda 1}$ is a constant represented by the optical system factors that affect the measurement of the temperature and can be solved for through calibration. It is important to note that this ratio can change with observation distance, lens, etc., and therefore, whichever setup is used for calibration must be used for experimentation.

Some approaches to obtain pixel values at different wavelengths are to use a beam splitter or to use a color camera. When picking wavelengths for either application, the follow criteria are important to consider [DeWitt & Nutter, pg. 485]: 1) the ratio of signals in each is sensitive to temperature changes; 2) some knowledge of the emissivity value in each wavelength region is available; and 3) values are known for the relative absorptions of intervening media in each wavelength region.

The ratio of signals can be examined before any measurements by analyzing the ratio of the intensities of a blackbody at the respective wavelengths and estimated temperatures. Looking at the following figure, it is apparent that the radiation intensity varies greatly over both the wavelength and the temperature:

Though Fig. 2 is for a blackbody radiation example, the radiation exhibited by fuel particles will be similar, but with less intensity (obviously, due to emissivity). However, for the purposes of our experimentation, it is not necessary to know the emissivity of the particles at different wavelengths. As Mitchell and McLean [12] demonstrated, the emissivity of burning pulverized fuels is equal to each at wavelengths in the visible light portion of the spectrum; therefore, when using ratio thermometry, it is not necessary to know the emissivity of the object.

There are techniques for determining emissivity if ever a need should arise. In Lou et al. there is an experimental technique explained for finding emissivity of flames at various temperatures. The use is through finding intensities of known blackbody furnaces and comparing them to the flame intensity; this is done with wavelengths in the red, green and blue regions of the visible spectrum. However, observations made by the group show that at the temperatures they considered (1373 to 1673 K), the blue region did not provide sufficient data to be used in the results and discussion.

Lastly, values of intervening media must be known so wavelengths that can skew the data are not chosen. When combusting fuel, there are three molecules to consider as absorbing media, H_2O, CO_2 and NO_x. Provided by the Energy Information Administration (www.eia.doe.gov), water vapor has absorption bands at 600, 720, 820 and 940 nm and carbon dioxide and nitrous oxide do not have any absorption bands near the visible light spectrum.

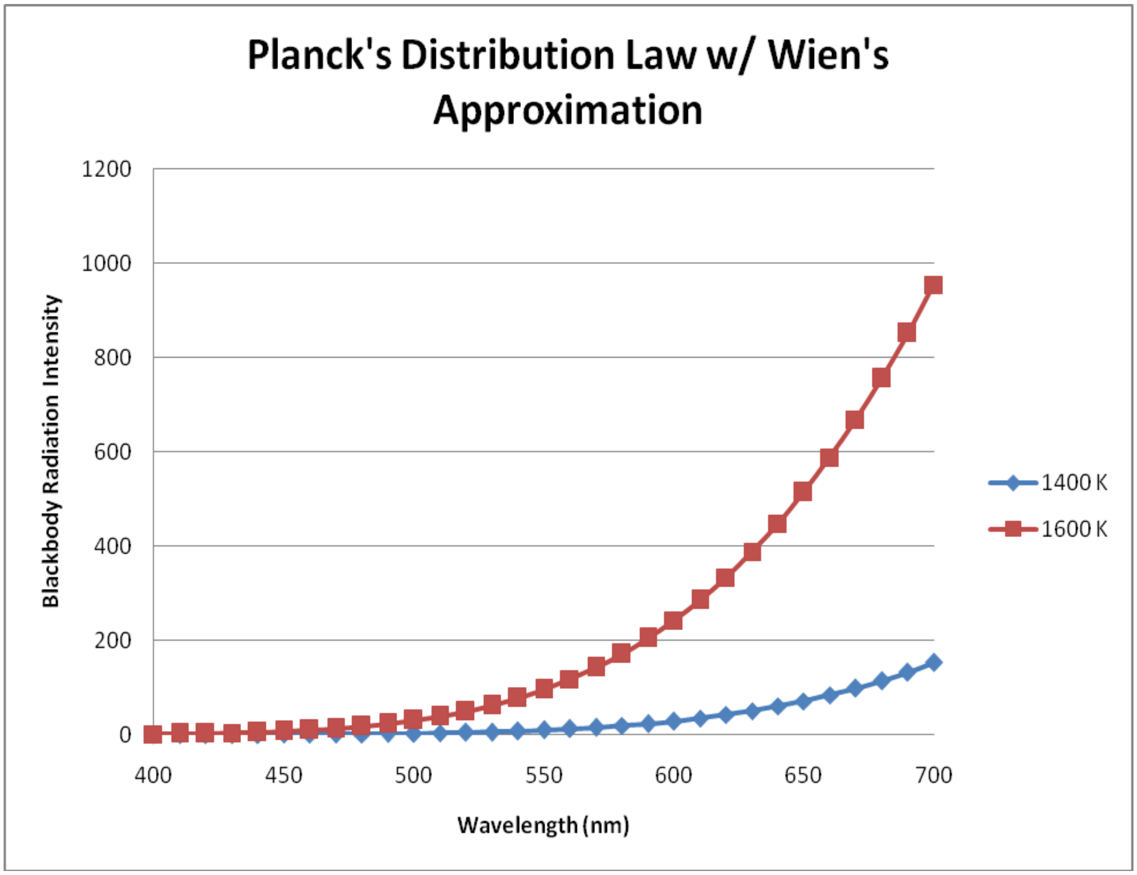


Figure 2: Variance of intensity of wavelength and temperature using Eqn. (3).

Conclusion

Based on the theory studied and the literature research done so far, it can be recommended that the wavelengths that should be examined are: ~430, ~550, and 700 nm. Generally speaking, though, these wavelengths can be changed to better match the application – and also fuel type – being observed. Currently, there are a few cameras to consider for the non-contact measurement applications we wish to pursue:

CCD Cameras

These cameras are high sensitivity and lower frame rate.

- **UNIQ UP-1830CL (Attachment 1)**
- **ILI GE1830 (Attachment 2)**
- **DALSTAR 2M30-SA (Attachment 3)**
- **Cooke Dicam Pro (Attachment 4)**
- **Toshiba IK-TF9 (Attachment 5)**

CMOS Cameras

These cameras have lower sensitivity than CCD cameras, but much higher frame rates.

- **Cooke Corp. pco.1200 hs (Attachment 6)**
- **Redlake MotionPro X5 (Attachment 7)**
- **Redlake MotionScope M3 (Attachment 8)**

Of the five CCD cameras listed, the Toshiba camera is most likely the best option for use. It currently uses new technology; instead of using one CCD chip, it uses 3 CCD chips for image capture. It has a very high resolution and very small pixel size, giving the greatest accuracy of measurement of the five. It is capable of both windowing and binning to increase its frame rate, from 20 fps up to 40 fps.

Of the three CMOS cameras, the pco.1200 hs camera is the best option. It was used in Hain et al. [14] and as shown, it had many similarities to the CCD camera used as far as signal variation and SNR variation with the illuminance of light used. It is capable of 636 fps at a resolution of 1.3 Megapixels. Also, its peak quantum efficiency of 25% is at 520 nm, well within the range of the visible spectrum.

This paper covers how the research group has done temperature measurements of single particles in a drop tube furnace.
[1] P.A. Bejarano, Y.A. Levendis. *Single-coal-particle combustion in O2/N2 and O2/CO2 environments*. Combustion and Flame, 153 (2008), 270-287.

This paper covers most of the theory behind non-contact temperature measurements and also development of a three-color pyrometer (though for our purposes we will focus on using CCD cameras, having the necessary background is useful).
[2] Y.A. Levendis, K.R. Estrada, and H.C. Hottel. *Development of multicolor pyrometers to monitor the transient response of burning carbonaceous particles.* Rev. Sci. Instrum., 63 (1992), 3608-3622.

A textbook with comprehensive coverage of radiation heat transfer. Gives in-depth explanations into Planck's law, Wien's approximation theory, and other pertinent information for combustion of coal in furnaces.
[3] H.C. Hottel, A. Sarofim. *Radiative Transfer*. McGraw-Hill, New York, 1967.

A textbook with comprehensive coverage in radiation heat transfer, principles of radiation thermometry, including applications with pyrometers. May be useful with applying thermometry in the visible spectrum with CCD cameras.
[4] D.P. DeWitt, G.D. Nutter. *Theory and Practice of Radiation Thermometry*. John Wiley & Sons, Inc., New York, 1988.

Paper covering different fluidized beds for transfer of coal particles of <100 microns.
[5] R.J. Hamor, I.W. Smith. *Fluidizing feeders for providing fine particles at low, stable flows*. Fuel, 50 (1971), 394-404.

Extensive calibration method for a color CCD camera for the specific use of non-contact flame thermometry.
[6] Li et. al. *Calibration and Experimental Research of a Multiple-wavelength Flame Temperature Instrumentation System*. J. Thermal Sci., 13 (2004), 371-375.

Covers two-color method and use of it with a monochromatic CCD camera.
[7] Y. Haung, Y. Yan, G. Riley. *Vision-based measurement of temperature distribution in a 500-kW model furnace using the two-colour method*. Measurement, 28 (2000), 175-183.

Covers three-color method and integration with a color CCD camera. Also covers algorithm development for determining temperatures based on pixel values.
[8] Dong et. al. *Simulation study on radiative imaging of combustion flame in furnace*. J. Zhejiang Univ. Sci. A, 8 (2007), 1853-1857.

Contains physical and theoretical information on the operation and application of CCDs. Also helps in deciding what factors to look for when picking a camera to use.
[9] J.D.E. Beynon, D.R. Lamb. *Charge-coupled devices and their applications*. McGraw-Hill, London, 1980.

Explanations on experimental measurement using both pyrometers and CCD color cameras.
[10] G. Lu, Y. Yan. *Temperature Profiling of Pulverized Coal Flames Using Multicolor Pyrometric and Digital Imaging Techniques*. IEEE Transactions on Instrumentation and Measurement, 55 (2006), 1303-1308.
[11] Lu et al. *Concurrent Measurement of Temperature and Soot Concentration of Pulverized Coal Flames*. IEEE Transactions on Instrumentation and Measurement, 51 (2002), 990-995.

Validates gray body assumption that emissivity is constant in the visible light range.
[12] R. Mitchell and W. McLean. *On the temperature and reaction rate of burning pulverized fuels*. Proc. Combust. Inst., 19 (1982), 1113-1122.

Detailed experimental set up and theory on measuring flame emissivity and radiation properties in an industrial-sized furnace. Can possible be used for laboratory scale applications.
[13] Lou et al. *Measurements of the flame emissivity and radiative properties of particulate medium in pulverized-coal-fired boiler furnaces by image processing of visible radiation*. Proc. Combust. Inst., 31 (2007), 2771-2778.

Quantitative comparisons using gray-values of images with CCD, CMOS, and intensified CMOS cameras.
[14] R. Hain, C.J. Kähler, C. Tropea. *Comparison of CCD, CMOS and intensified cameras*. Exp. Fluids, 42 (2007), 403-411.

The furnace is a modified version of the ATS (Applied Testing Systems) Series 3240 Split Tube Furnace. The temperature rating for the furnace is 1450°C. It has three independent heating zones: 2600 watts per zone and 55 amps/8000 watts total. The retort is a quartz tube with stainless steel integral type flanges with water cooling. The retort caps are stainless steel and include radiation shields. The heating elements are controlled with Eurotherm Model 2408 PID controllers. The controllers and the power supplies for the heating elements are housed in an electrical cabinet (on wheels, approximate size 2 feet x 2 feet and 4 feet high).

The controller system and the power supply for the heating elements required a designated electrical circuit (60A, 208V). The footprint of the furnace and the controller unit are large and necessitated considerable demolition and construction in the Shop Building laboratory for safe and appropriate positioning of the system. Thus the decision was made to relocate the furnace system and all of the burn simulator project equipment and personnel to laboratory Wilmore 184. The relocation was accomplished in December, with some laboratory modification continuing into early January. The Wilmore 184 laboratory has a 3 x 5 foot walk-under vent hood, with the hood stack connected to the building's extensive fume hood. Just beside the vend hood is an unused electrical junction box with appropriate electrical power. This space was cleared of another experiment.

The furnace is approximately 4 feet high, 2 feet wide and 2 feet deep. It weighs approximately 200 pounds. It was equipped with a spacer and bracket for vertical mounting. It is a split tube furnace with three 9 inch windows that allow viewing of the internal retort tube. For structural integrity, two of the windows had to be installed on one side of the furnace box and one on the other. Most split tube furnaces include hinges that allow the furnace to be easily opened: the hinges could not be used for our furnace to make space for the visualization windows. Thus latching clamps hold each half of the split furnace together. The size and weight of the furnace, need for access to the visualization windows, and the lack of hinges to access to the furnace tube necessitated design of a mount system that could be moved and turned to make it easy for furnace maintenance and for positioning of the furnace for camera and instrumentation access. We selected a industrial steel open cage heavy duty cart (Little Giant Mfr. Model # OT-2448-6PPY from Grainger) as a mounting base and designed a steel railed bracket to attach the manufacturer supplied furnace bracket to the cage.

With the furnace retorts now available we began adapting the needle vibrator injection system for delivery of individual 100 micrometer particles of coal, wood, and switch grass. Previously we conducted experiments and determined unique needle diameters and vibration intensities needed for consistent delivery for each type of material. We obtained samples of pet coke (which is now being used by the Lafarge Roberta plant) and prepared particles for use in our system. We obtained SEM images to characterize these particles in the same manner that we have prepared and characterized the coal, wood, and switch grass.

We developed designs and commissioned our glass shop to make a prototype water-cooled nozzle that will be inserted through the retort top flange. The purpose of the nozzle is to keep the particle at temperatures lower than the combustion temperature as it drops through the top portion of the furnace where we do not have visualization access. The tip of the cooled nozzle is at the top of the visualization window. A series of pictures were taken to illustrate the major components in Figures E-1 to E8.

Figure E-1. The Wilmore laboratory set up is shown. The furnace is mounted to the open cage cart. The blue electrical cabinet is the controller: the three displays are for the independent furnace zones. An existing high spped CCD camera is also shown.

Figure E-2. The furnace is seen here on its side.

Figure E-3. The furnace is shown highlighting one of the three visualization windows.

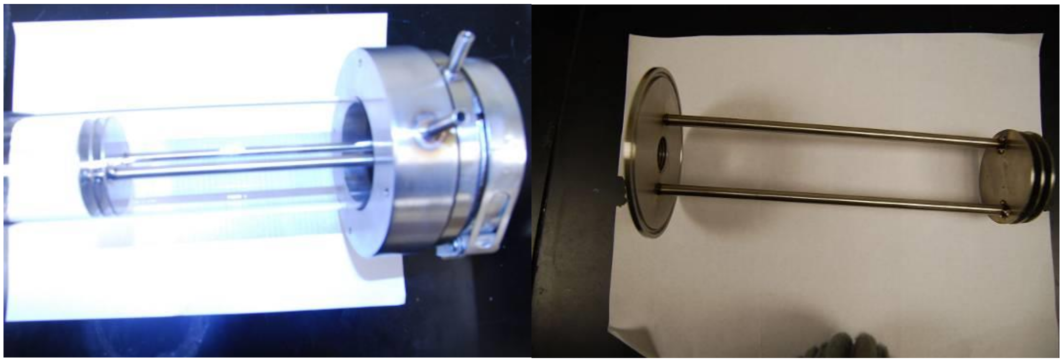


Figure E-4. A portion of the quartz retort along with the water cooled flange is shown at left. The retort cap with radiation shields is shown at right.

The furnace a drop tube underwent the bake out procedure as specified by the manufacturer ATS. Several of the flanges and an injector nozzle tip are cooled with water. A water manifold was designed for this purpose and installed; it can be seen on the photographs of the simulator that follow.

The temperature is controlled through digital and manual controllers. The manuals provided with the equipment did not give complete information on set point and heating rate selection; thus considerable effort was put into mapping out appropriate procedures for heating schemes. Additional information and guidance was provided by the controller manufacturer and the furnace manufacturer.

A glass particle injector nozzle was designed and constructed for injection of particles into the heated retort tube. The injector has a center tube that is jacketed and water cooled. This allows particles to stay cool as they fall through the injector. Particles leave the injector approximately 11 inches into the furnace drop tube positioning them in a view window where they are exposed to the elevated temperatures and begin combustion.

Safe practices, warning signage, and a remote control room video camera were set up.

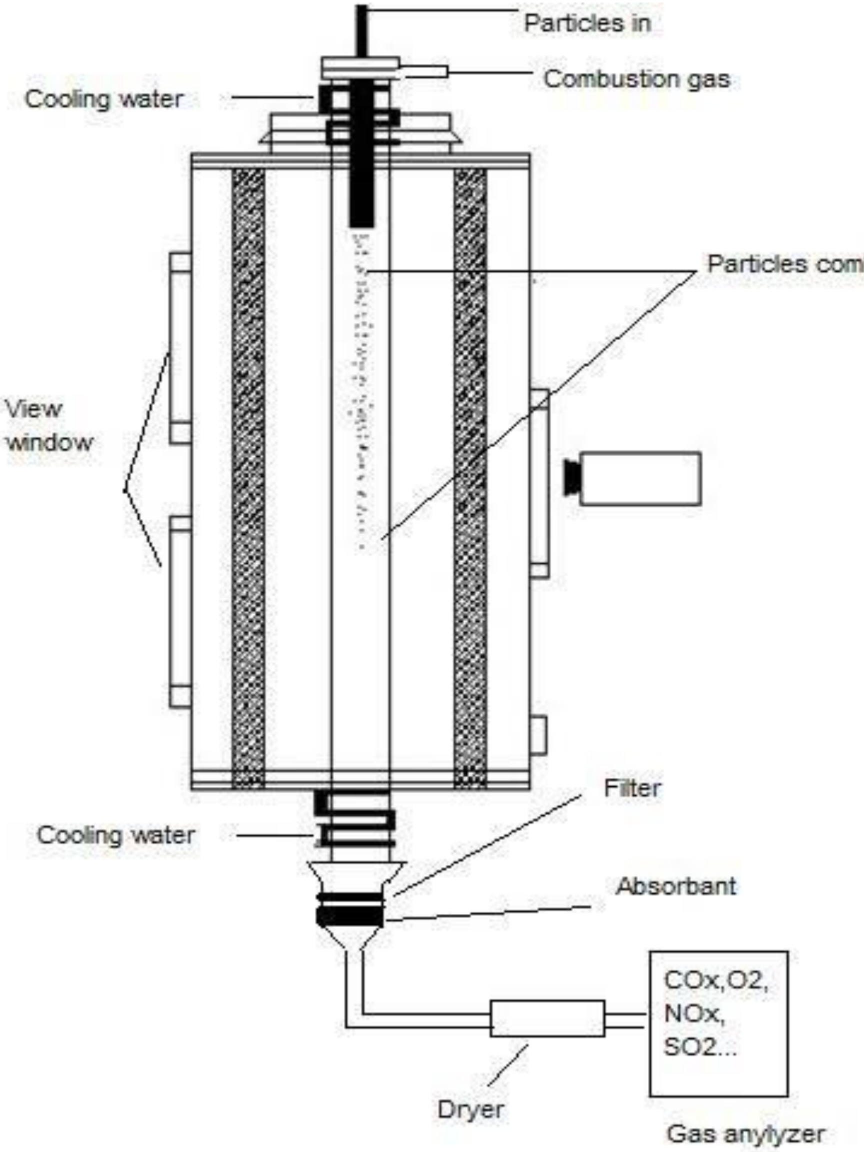


Figure E-5: Schematic of the Auburn Burn Simulator. The effluent portion of the apparatus is presently being designed and the equipment is being selected (filter, dryer, gas analyzer)

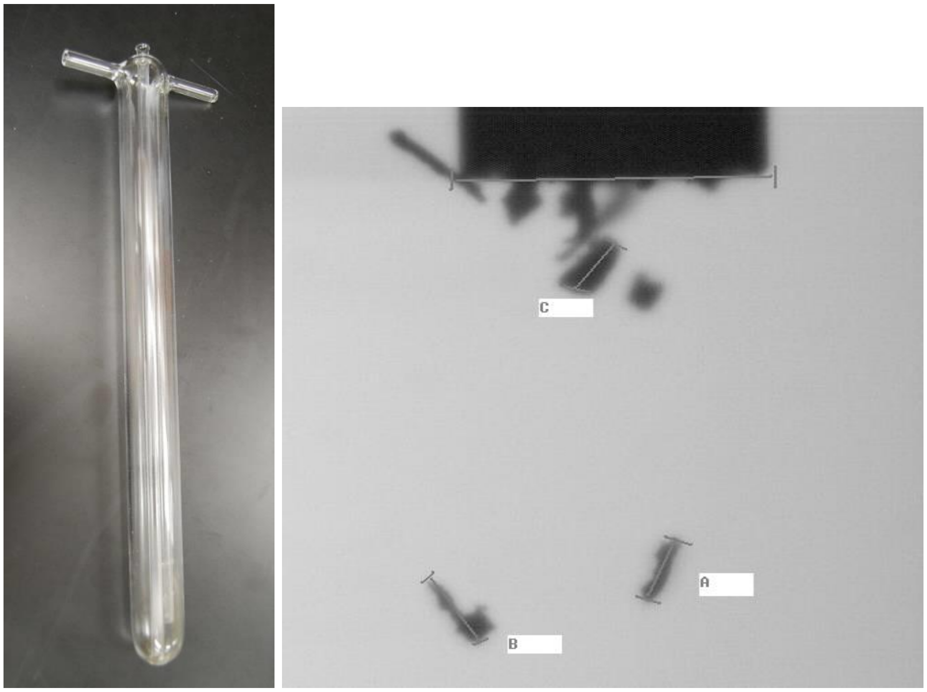


Figure E-6: The glass particle injector (shown here without its stainless steel harness and inconel radiation shields) and vibrating needle single particle dropper

Figure E-7: The furnace shown here operating at 900°C. The controller shows the temperature in the three zones. One of the windows in the furnace is seen. The black tubes to the right of the furnace are part of the water cooling for the flanges.

Figure E-8: The furnace at 900°C. One of the windows is shown demonstrating that it is possible to see through the window, through both sides of the quartz internal retort, and out one of the back windows (seen in the lower third of the front window).

Images were obtained for coal, wood, and switch grass 100 micron particles undergoing combustion in the drop tube furnace. The images demonstrated that combustion was occurring the furnace tube at the locations as predicted, however the clarity and resolution of the images were poor and blurred. Images were obtained at shorter exposure times and the blur remained. Additional studies revealed that the quartz furnace retort tube was manufactured such that it contained a wavy front surface that had ripples and curvature that inhibited focus at high magnifications. We worked through the Auburn university glass shop and designed and purchased a new quartz glass retort with smooth inner and outer walls. The diameter of the new retort was 61 mm and the original retort was 63 mm, necessitating adjustment of the retort flanges and selection of thicker o-ring seals. Images of resolution targets and cool (non-combusting) particles show that the new retort allows clear high resolution imaging. The retort glass underwent a series of heating tests in the furnace and is now deemed safe to operate at more than 900 C. Imaging of combusting particles is now underway.

The glass particle injection nozzle described in the previous quarterly report proved to be unreliable. The water jacket cracked during several experiment; causes for the cracks were determined and mitigated and the nozzle is now functional. However a stainless steel nozzle was designed and fabricated in our machine shop. The nozzle is shown in Figure E-9. The injection tube has a 6 mm inside diameter and it is inside of a concentric outer water jacket. The stainless steel nozzle includes radiation shields; the top of the nozzle was designed to accommodate attachment to the retort water cooled flanges as shown in Figure E-10. More than 30 experiments at 900 C have been conducted with the SS nozzle and it has proved to be reliable.

Figure E-9: Stainless steel nozzle for burn simulator furnace particle injection

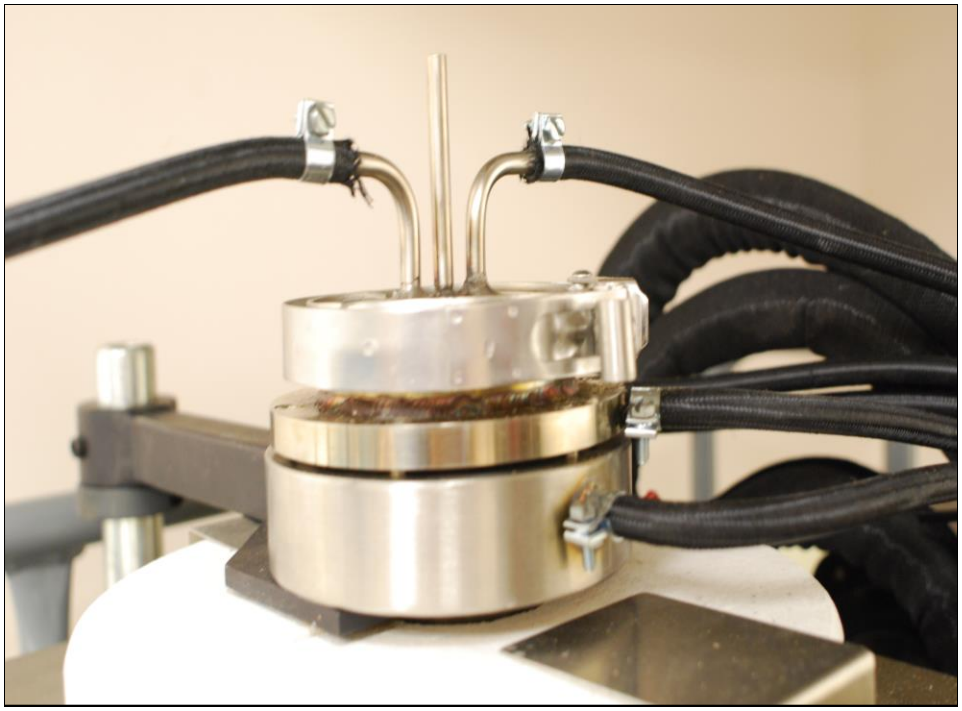


Figure E-10: Stainless steel injection nozzle shown atop retort and connected to cooling water

An oxygen analyzer was selected, purchased, and has been tested. The analyzer is the Advanced Micro Instruments Model 60 sensor. The analyzer can measure oxygen concentration for inlet and effluent streams for the furnace tube. It was determined that the GC is the appropriate analyzer for measuring the gaseous products of combustion since these will occur at very low concentration and volumes. We have obtained system suggestions and quotes from three vendors (one has visited our labs) and we are in the process of setting up a bid request to purchase a two-column system.

The inlet combustion gas system for the burn simulator furnace was designed and installed. This system allows control of the gas composition and flow through the clear furnace retort tube. The gas system allows combination of air (house compressed air, dried), oxygen, carbon dioxide, and nitrogen. The oxygen concentration is measured on the inlet and outlet of the furnace tube using the analyzer described in the previous quarterly report. The effluent system includes a venturi vacuum to allow the inlet gas to be pulled through the retort. Figure E-11 shows a photograph of the gas flow control system. Figure E-12 shows a schematic diagram of the gas system.

Figure E-11: Combustion gas flow control system.

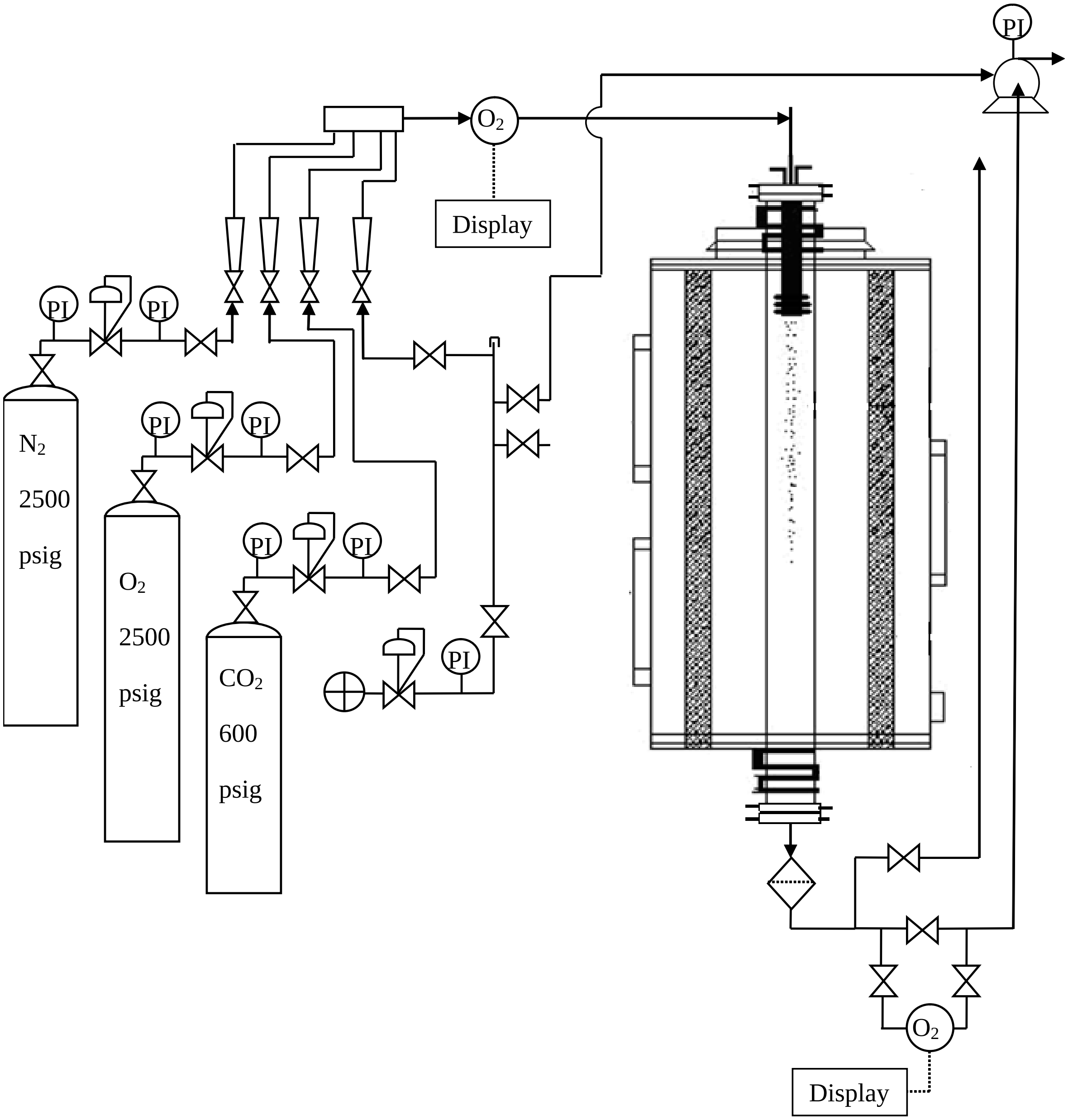


Figure E-12: Schematic diagram of the combustion gas flow control system.

A filter system was selected, ordered and installed in the furnace effluent system for collection of solid material (char). A stainless steel Millipore filter holder is attached below the retort flange. Glass fiber filters were selected and we have shown these to be effective at capturing coal and switch grass char resulting from combustion at 900 C. We are in the process of analyzing char particles using the SEM. Figure E-13 shows a photograph of the filter holder attached to the furnace.

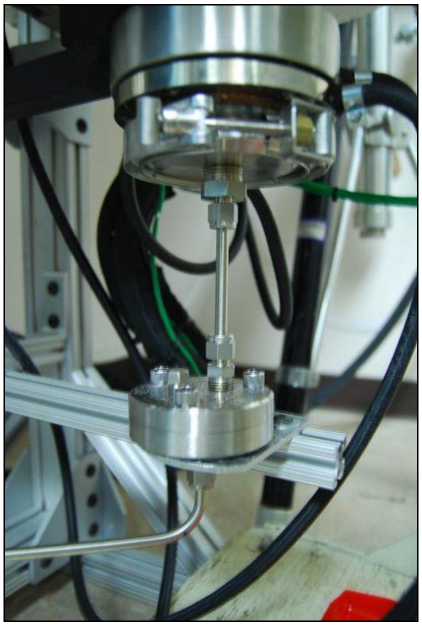


Figure E-13: Filter holder for collection of effluent particles after combustion.

The gas flow system composition control necessitated an upgrade to the particle injection system. Previously particles were dropped into an open tube at the top of the water cooled nozzle (described in the previous quarterly report). Air was drawn into the open tube as a result of the effluent vacuum, or gasses were emitted from this open tube for positive pressure runs. An injection T fitting was designed to allow the gas to flow into the nozzle but also to provide a tube sealed with a septum through which the particle injection needles could pierce. Figure E-14 shows a photograph of the particle injection fitting. The septum dampened the vibration of the injection needles, so new vibration settings and needle diameters were selected for each particle type and size.

Figure E-14: Sealed particle injection system.

Unfortunately there were two setbacks. We purchase a color CCD video camera and worked with it and the manufacturer for more than a month but were unable to get the camera to connect to the Firewire and software. It turned out that there were two problems: the particular camera was defective and there was a known problem with use of the camera with the type PCs in our research lab. We returned the camera to the vendor and have recently received a similar camera but of a different brand. We are presently acquiring images with the new camera (AVT Guppy F-033c). A second setback was that in the process of installing the filter holder we broke the glass furnace retort: it was repaired in our Auburn university glass shop but the furnace was out of operation for about three weeks. To remedy this in the future we have commission the glass shop to make two additional retort tubes so that if one breaks or needs cleaning was can use the spares.

Task F: Three Additional Test Burns with Alternate Sources of Fuel

A test burn was completed that used wood chips as fuel. This test burn was conducted between 7 AM on October 16, 2007 and 7 AM on October 19, 2007. This test burn was successfully completed and the plant operated well during this period.

A test burn was done that used switchgrass as fuel. Due to a limited supply of switchgrass, this burn lasted only 2 days. The drought conditions Alabama experienced in 2007 limited the availability of this biofuel. This test burn was conducted between 9 AM on November 27, 2007 and 9 AM on November 29, 2007. The bales of switchgrass had to be shredded and this was a labor intensive process. This test burn was successfully completed and the plant operated well during this period.

The synergistic burn was conducted between 5 PM on April 2, 2008 and 5 PM on April 5, 2008. Fuel for the kiln during this burn consisted of coal, tires and a blend of wood chips and waste plastics. The alternative solid fuel (ASF) blend consisted of wood chips, wire stripping and textile fluff that was fed through the granular processing system. A blend of plastic bottles, automotive head liners, door panels and dashboards, and polyester and nylon fibers were shredded into the plant's Keith bin and was targeted to make up approximately 45% of the ASF fuel stream. This test burn was successfully completed and the plant operated well during this period. The alternative fuel to total fuel replacement rates are shown in the figure below. It may be seen that the highest replacement rate by energy was achieved for the plastics (8 to 14 percent) that was part of the synergistic burn. A diagram representing the replacement rate is given in Figures F-1 and F-2.

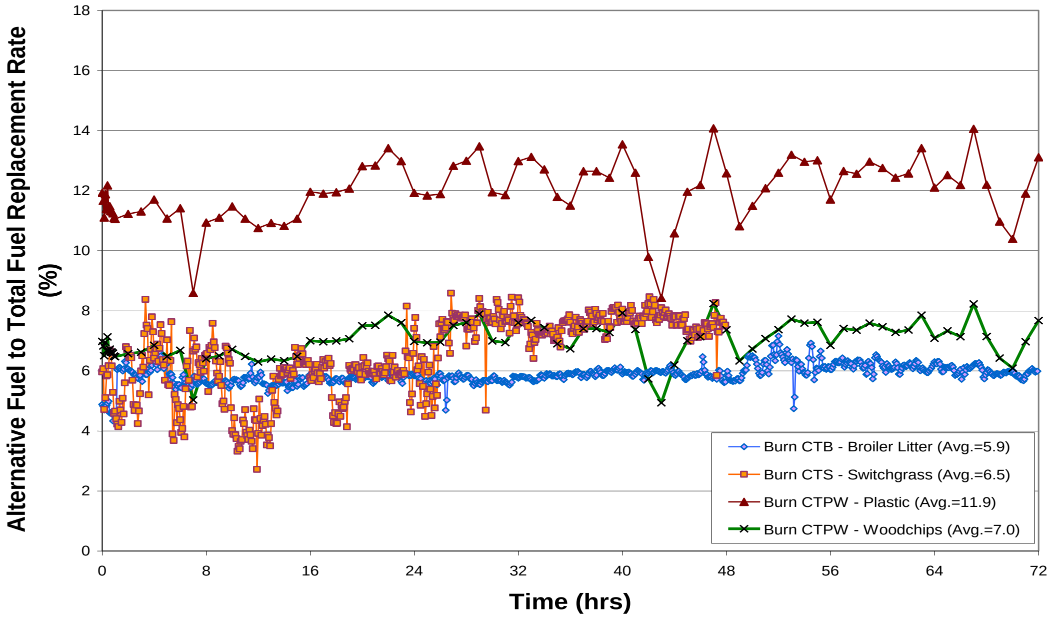


Figure F-1. Alternative fuel replacement rates (Energy Basis)

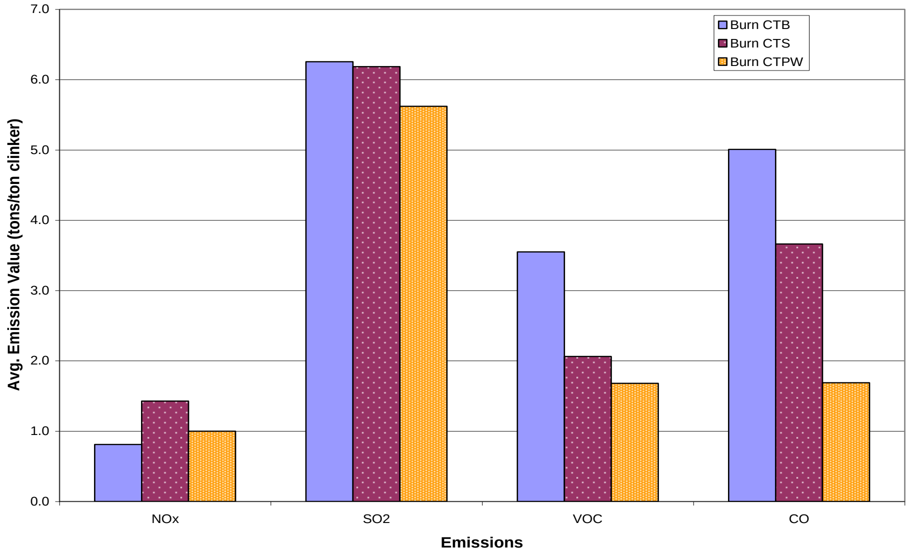


Figure F-2: Comparison of average emissions for trial burns

Task G: Feasibility Analysis of Commercially Available Gasification Technologies

Sean O'Grady and Kevin McQuigg from Primenergy provided an electronic copy of the completed gasification feasibility study to the project team via email on August 6, 2008. They traveled to the Lafarge Roberta plant for a presentation and face-to-face discussion of their findings on August 12. The full report was presented as hardcopy and as electronic files and was including in an earlier progress report and will not be included here. Additional engineering drawings and a power point presentation are also available. The economic analysis was presented as an Excel file to allow project team members ability to change price and financing assumed values. The project team agreed that the study was conducted appropriately and that the findings and the methods employed were sound. Attached below is the summary of the report.

The key findings were that gasification of poultry litter for direct thermal energy usage or for electrical power generation for the Roberta facility were technically feasible but not economically viable. For firing in the calciner, a gasification unit for 20,000 lb/hr (9,072 kg/hr) broiler litter will provide 76 MMBtu/hr (80 GJ/hr), satisfying 12 % of the kiln heat demand. The capital cost was estimated to be $11,500,000 and the rate of return (even with favorable costs for poultry litter) lass than 4%. A key technical feature is that there is not adequate space to locate the gasifier in close proximity to the firing location, thus a lot of heat is lost from the syngas as it is transported between the gasifier outlet and the injection point.

Error! Reference source not found.EXECUTIVE SUMMARY FROM PRIMENERGY STUDY

As part of a Department of Energy grant, Auburn University is developing a feasibility study to evaluate the technical and economic feasibility of using gasification of biomass (primarily poultry litter) to provide a portion of the energy needs for the cement production process at the Lafarge North America Roberta Cement Plant.

To this end, Primenergy has evaluated two methods of energy production for the Roberta facility. Those methods are 1) biomass gasification with direct syngas injection into the cement kiln and 2) biomass gasification with syngas firing into a steam boiler for electrical generation.

Both methods have been determined to be technically feasible, although direct firing of the syngas into the kiln presents some technical challenges. Although the kiln operates at a negative pressure, it is not sufficiently negative for adequate control of the gasification process. Therefore, in order to prevent excessive energy loss from the syngas, a hot gas fan, operating at temperatures to 1600°F (871°C) will be used to provide the motive force to pull the syngas from the gasification process and deliver it into the kiln. Large diameter (approx. 1 meter), fairly tight shutoff valves are also required to and from the kiln when changing from startup to normal operation or normal operation to shutdown. Vendors specializing in design and supply of high temperature equipment have been contacted, and we trust that these issues have been properly addressed.

The proposed single R-24 gasification system for kiln firing would consume 20,000 lb/hr (9,072 kg/hr) of broiler litter, and it would satisfy approximately 12 % of the kiln heat load. The proposed electrical power generation system is the same size unit, and it would also consume 20,000 lb/hr (9,072 kg/hr) of broiler litter to produce approximately 18 % of the cement plant’s power requirement.

The economic feasibility of either method is questionable. Neither project shows outstanding economics, especially electrical generation. Direct firing into the kiln has the potential to be economical, depending on the financial assumptions made. The economics presented in this written study are based on assumptions made by Primenergy, which may not be the ones preferred by Auburn and Lafarge. The financial spreadsheets are provided with the software package for Auburn and Lafarge to manipulate as they desire.

Task H: Continuation of Phase 2 Analysis and Initiation of Long-term Concrete Testing

Concrete mixtures were made from the cement collected from the switchgrass and woodchips test burns. The concrete properties will be compared to determine if the use of various alternative fuels have impacted some of these properties. Additional isothermal calorimeter tests will be performed to evaluate the behavior of the cements with various chemical admixtures. Calorimetry tests are being performed to determine the interaction (if any) of chemical admixtures with the cements produced with alternative fuels.

Test results will be presented for the following test burns:

1. **Coal (C) Burn:** Coal is the conventional fuel used at the cement plant and was therefore considered the baseline for comparison purposes.
2. **Coal and Tires (CT1) Burn:** This trial burn used both coal and scrap tires as fuel.
3. **Coal, Tires, and Plastics (CTP) Burn:** Coal, scrap tires, and waste plastics were used during this trial burn.
4. **Coal, Tires, and Broiler Litter (CTB) Burn**: Coal, scrap tires, and broiler litter were used as fuel for this trial burn.
5. **Coal, Tires, and Woodchips (CTW) Burn** : Coal, scrap tires, and woodchips were used as fuel for this trial burn.
6. **Coal, Tires, and Switchgrass (CTS) Burn**: Coal, scrap tires, and switchgrass were used as fuel for this trial burn.
7. **Coal, Tires, Plastics, & Woodchips (CTPW) Burn** : Coal, scrap tires, and waste plastics and woodchips were used as fuel for this trial burn.

For each burn period, cement was sampled and used to make concrete to evaluate the effect of using alternative fuels to produce portland cement. The clinker produced from each trial burn had to be isolated in emptied silos to ensure that the portland cement produced from grinding the clinker was truly from each specific trial burn. All the cement from the burns was collected by making a composite specimen over the entire burn period using 5-gallon (18.9-liter) samples collected at each of the discrete sampling times.

Two concrete mixture designs were made and tested at Auburn University. These concrete mixtures were made from the cement collected from each trial burn. The primary mixture design, referred to as Mix A, had a water-to-cement ratio of 0.44, and used No. 57 crushed limestone and a natural river sand as aggregate. The secondary mixture design, referred to as Mix B, had a water-to-cement ratio in of 0.37, and used No. 78 crushed limestone and a natural river sand as aggregate. In an attempt to eliminate the variability due to differences in aggregates, enough of each aggregate type was collected on the same day to make all the concrete for all burns. Mix A was also produced by the cement plant’s specialty laboratory. The aggregate used by the cement plant’s concrete laboratory for Mix A was collected and provided by personnel at Auburn University. Long term results for these two mixtures are shown in Figures H-1 through H-5.

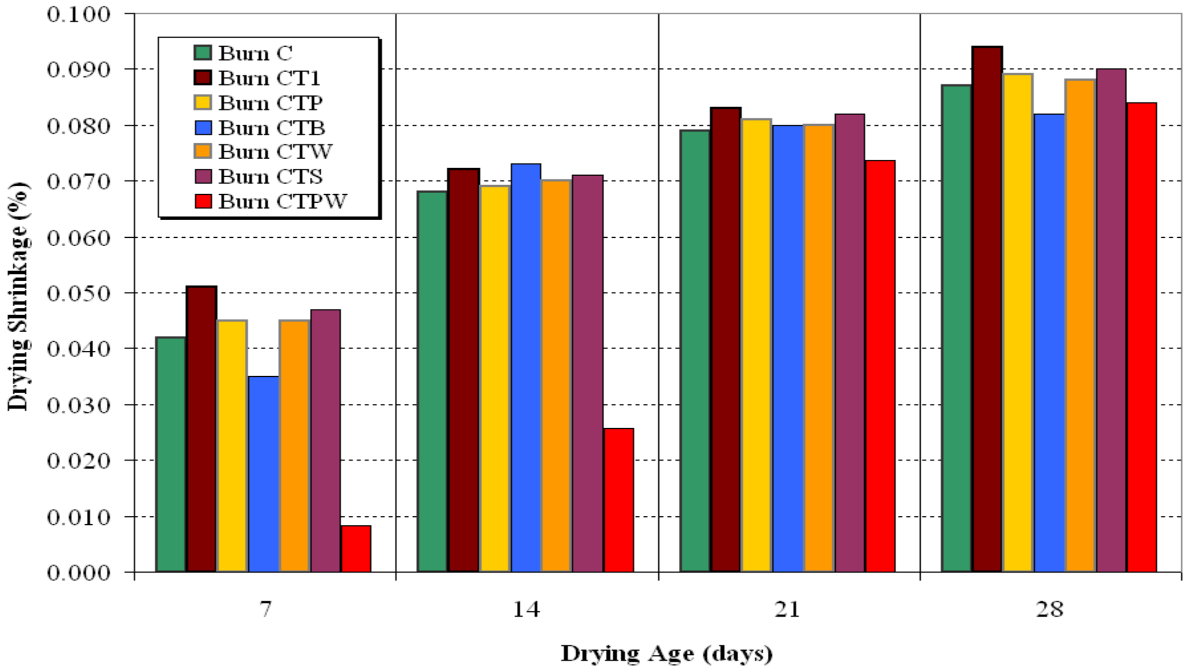


Figure H-1: Drying shrinkage results for paste samples made from cement sampled from each of the trial burns

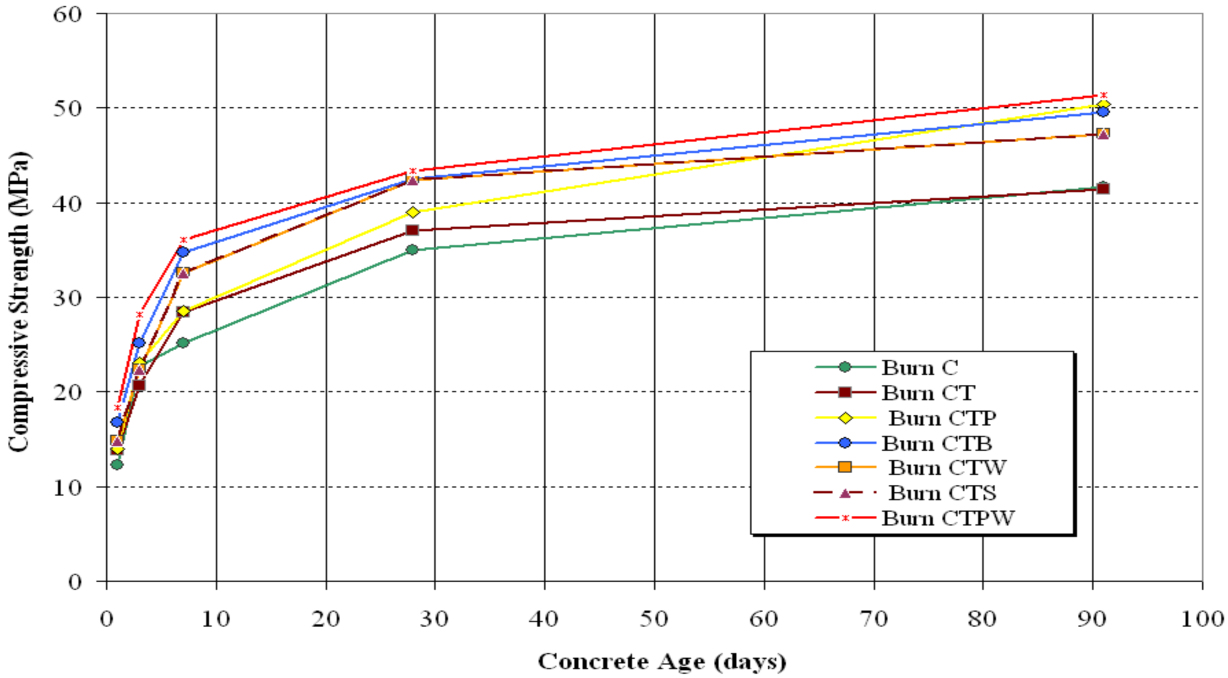


Figure H-2: Compressive strength development for the w/c = 0.44 concrete samples made from cement sampled from each of the trial burns

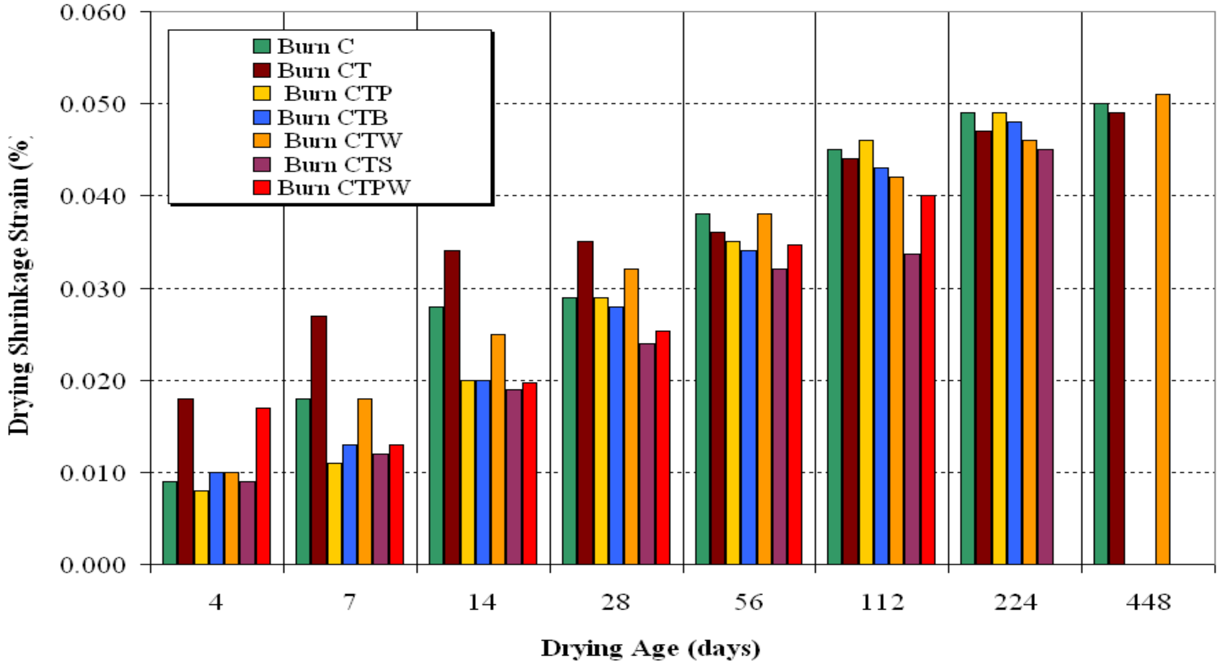


Figure H-3: Drying shrinkage development for the w/c = 0.44 concrete samples made from cement sampled from each of the trial burns

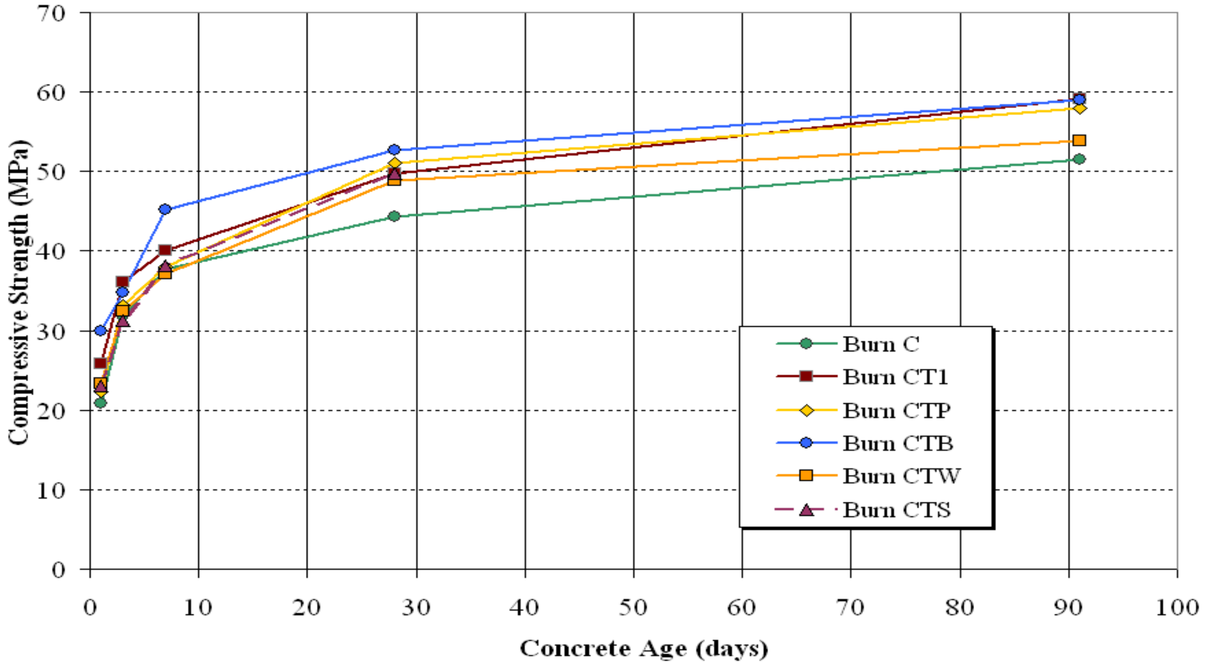


Figure H-4: Compressive strength development for the w/c = 0.37 concrete samples made from cement sampled from each of the trial burns

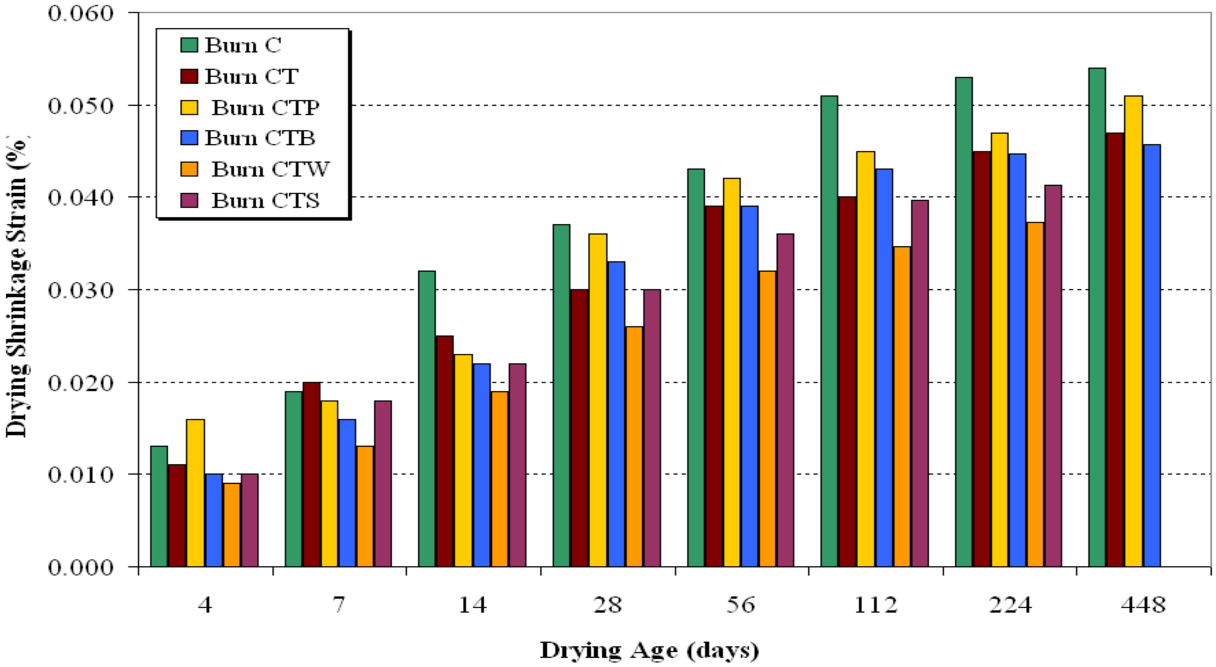


Figure H-5: Drying shrinkage development for the w/c = 0.37 concrete samples made from cement sampled from each of the trial burns

An admixture study was initiated during this phase of the study to examine the effects of chemical admixtures on hydration, flow, and setting time properties of the cement produced from alternative fuels. Three cement pastes were prepared from each cement: one control paste containing no admixture, one containing an accelerating admixture, and one containing a retarding admixture. The five burns periods are listed below, in addition to the fuels utilized during each.

- **FT –** Trial burn utilizing coal, petroleum coke (coke), tires, plastic, and forest trimmings (FT),
- **B-CCTP –** Baseline burn utilizing coal (C), coke (C), tires (T), and plastics (P),
- **B-CCP –** Baseline burn utilizing coal (C), coke (C), and plastics (P),
- **RR –** Trial burn utilizing coal, coke, plastics, and railway ties (RR), and
- **GL** – Trial burn utilizing coal, coke, plastics, and liquid glycerin (GL)

A summary of the flow and setting time results from each paste mixture are provided in Table H-1. Also shown is the percent difference relative to the control mixture (containing no admixture). The percent differences for flow and setting times are also plotted in Figures H-6 and H-7, respectively. Note that the flow was increased significantly for all pastes mixed with the retarder. This change in flow was greatest for GL and least for FT. The accelerator had seemingly little effect on flow.

The results on Figure H-7 are as expected. For all pastes, the accelerator decreased setting times, and the retarder increased setting times. Note that these are final setting times as initial set was not recorded. The accelerator seems to have the greatest effect on GL and least on FT. The retarder seems to have the greatest effect on RR and the least on GL.

Table H-1: Summary results for flow and final setting time for all burns

Parameter	Paste	Control	Accelerator	% Diff.[1]	Retarder	% Diff.[1]
Flow (%)	**FT**	242	234	-3.27	372	53.7
	B-CCTP	238	238	-0.294	370	55.2
	B-CCP	237	238	0.253	367	54.7
	RR	236	240	1.65	387	63.9
	GL	246	243	-0.9	406	65.3
Final Set (min.)	**FT**	353	242	-31.4	512	45.0
	B-CCTP	355	200	-43.7	557	56.9
	B-CCP	354	215	-39.3	534	50.8
	RR	356	209	-41.3	567	59.3
	GL	427	227	-46.8	540	26.5

Notes: [1] **Relative to Control Paste**

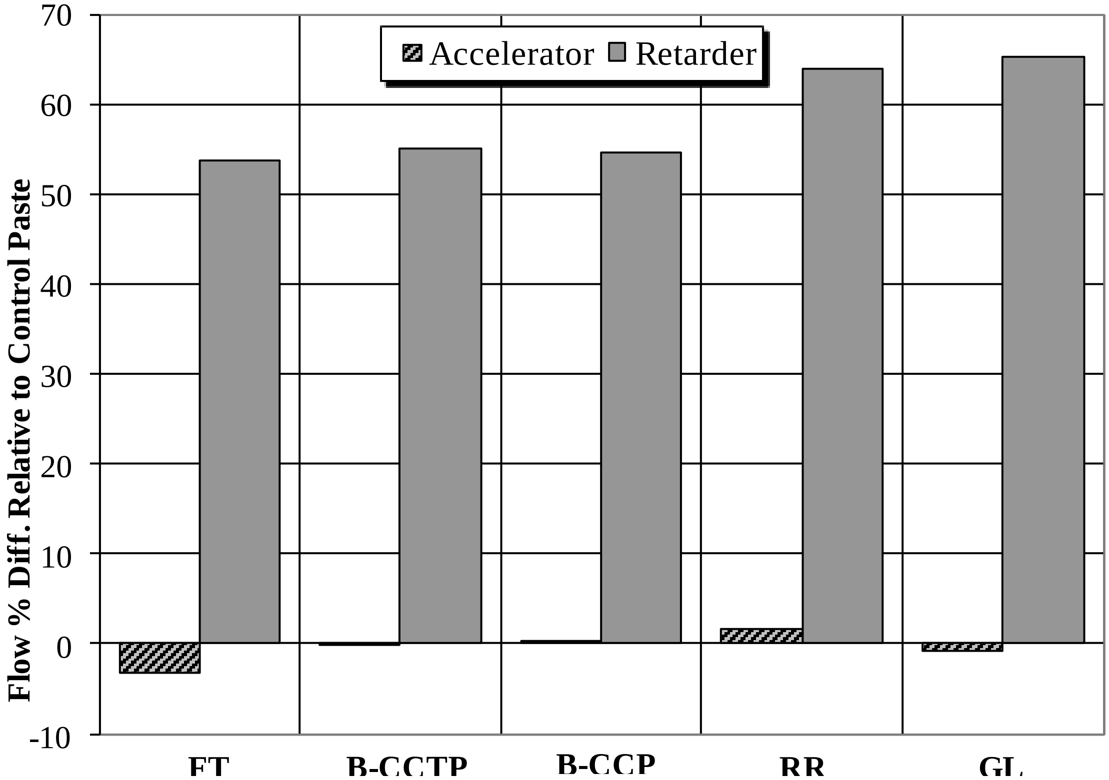


Figure H-6: Percent difference in flow relative to control paste

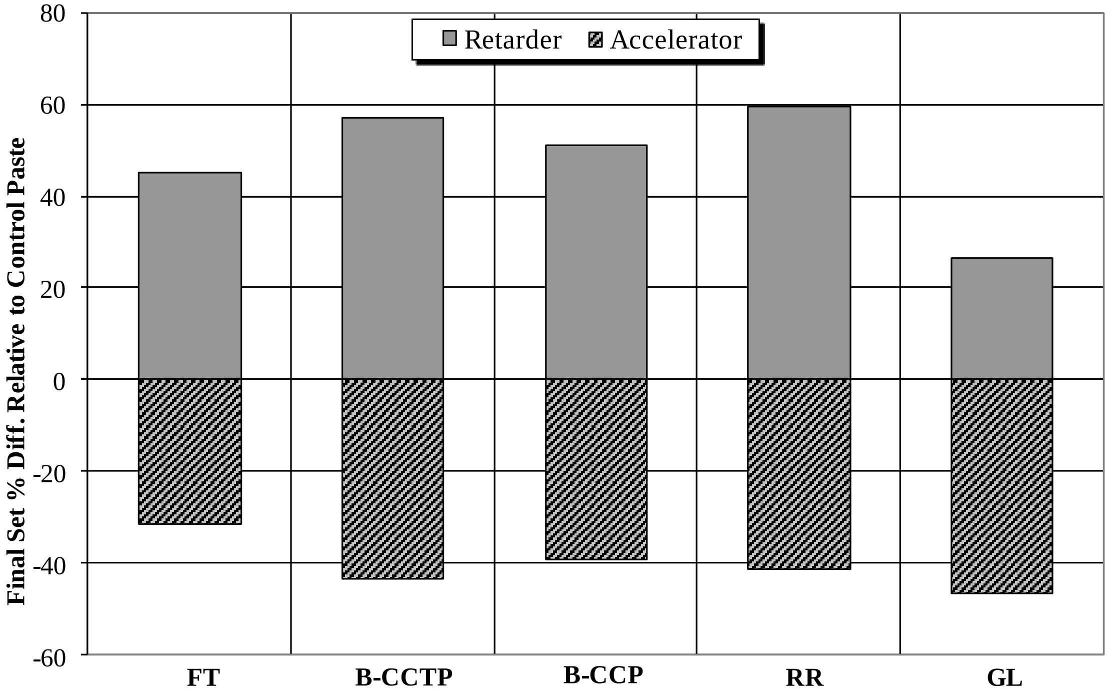


Figure H-7: Percent difference in final setting time relative to control paste

The percent difference in flow and setting times for each of the trial burns with respect to their corresponding baseline burn is shown in Table H-2. The pastes made with cement from the trial burns are seen to be fairly consistent with their baseline. The greatest difference is seen in the final set for the FT paste mixed with the accelerating admixture, which set 21% later than the B-CCTP paste. This indicates that this dosage of accelerator was not as effective with the FT cement as it was with its baseline cement. The final set for GL cement's control paste increased significantly relative to B-CCP. This was also seen in the cement paste physical properties for this burn.

The hydration processes of each paste mixture with and without chemical admixtures were also monitored using a TAM Air isothermal calorimeter. It took approximately ten minutes from mixing to initiate the test, so the initial C_3A hydration peak was not captured. Each paste was monitored for forty-eight hours, but emphasis is placed on the first twenty-four hours of hydration. Heat flow was recorded in fifteen-minute intervals to produce a hydration curve for each paste mixture. An example of these results are shown in Figure H-8.

Table H-2: Percent difference in flow and final setting time relative to baseline

Test	Mixture	FT	RR	GL
		% Diff.[1]	**% Diff.[2]**	**% Diff.[2]**
Flow	Control	1.51	-0.548	3.46
	Accelerator	-1.52	0.841	2.23
	Retarder	0.541	5.36	10.5
Final Set	Control	-0.563	0.565	20.6
	Accelerator	21.0	-2.79	5.58
	Retarder	-8.08	6.18	1.12

Notes: [1] **Relative to B-CCTP**

[2] **Relative to B-CCP**

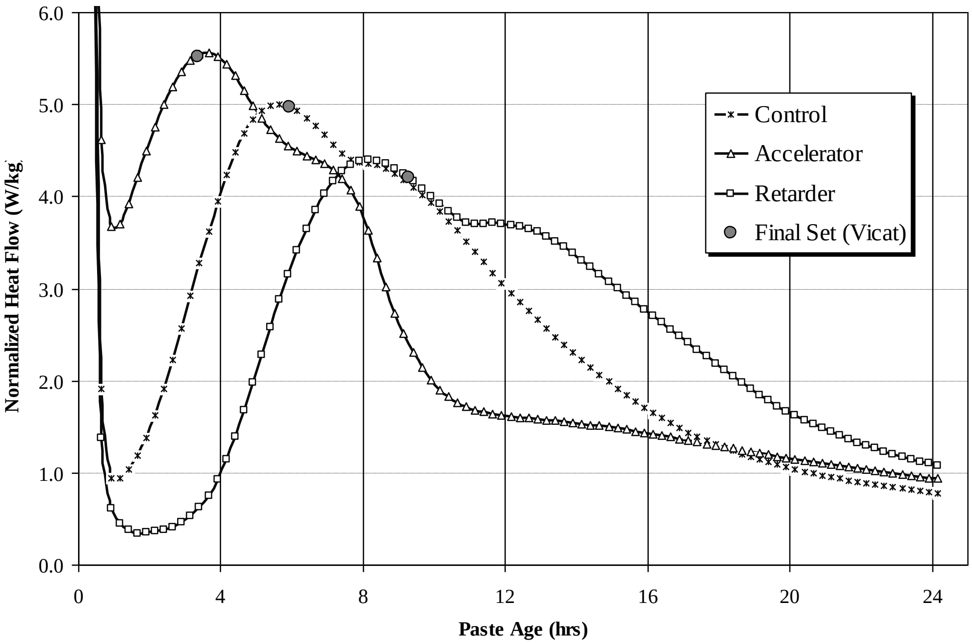


Figure H-8: Hydration curves and final setting times for B-CCTP paste

Task I: Assessing the Burn Characteristics of Alternative Fuels with Burn Simulator

Three component color images were obtained for particles undergoing combustion in the drop tube. The images were obtained with a scientific grade camera. The spectral response curves for the camera were determined for each of the three color components. Personnel were trained to use Matlab and preliminary image processing algorithms and procedures has been initiated. Figures I-1, I-2, and I-3 shows images that were obtained for 100 micrometer diameter particles of coal, wood, and switch grass in the clear drop tube just below the water cooled nozzle. These images were obtained with the monochrome Cohu inspection grade CCD camera and the Questar high magnification lens. The images display the resolution and focus capabilities of the imaging system, as well as the ability to stop motion blur with high shutter speed. The resolution for this optical set up is 0.32 pixels/micrometer (determined from a USAF 1951 resolution target).

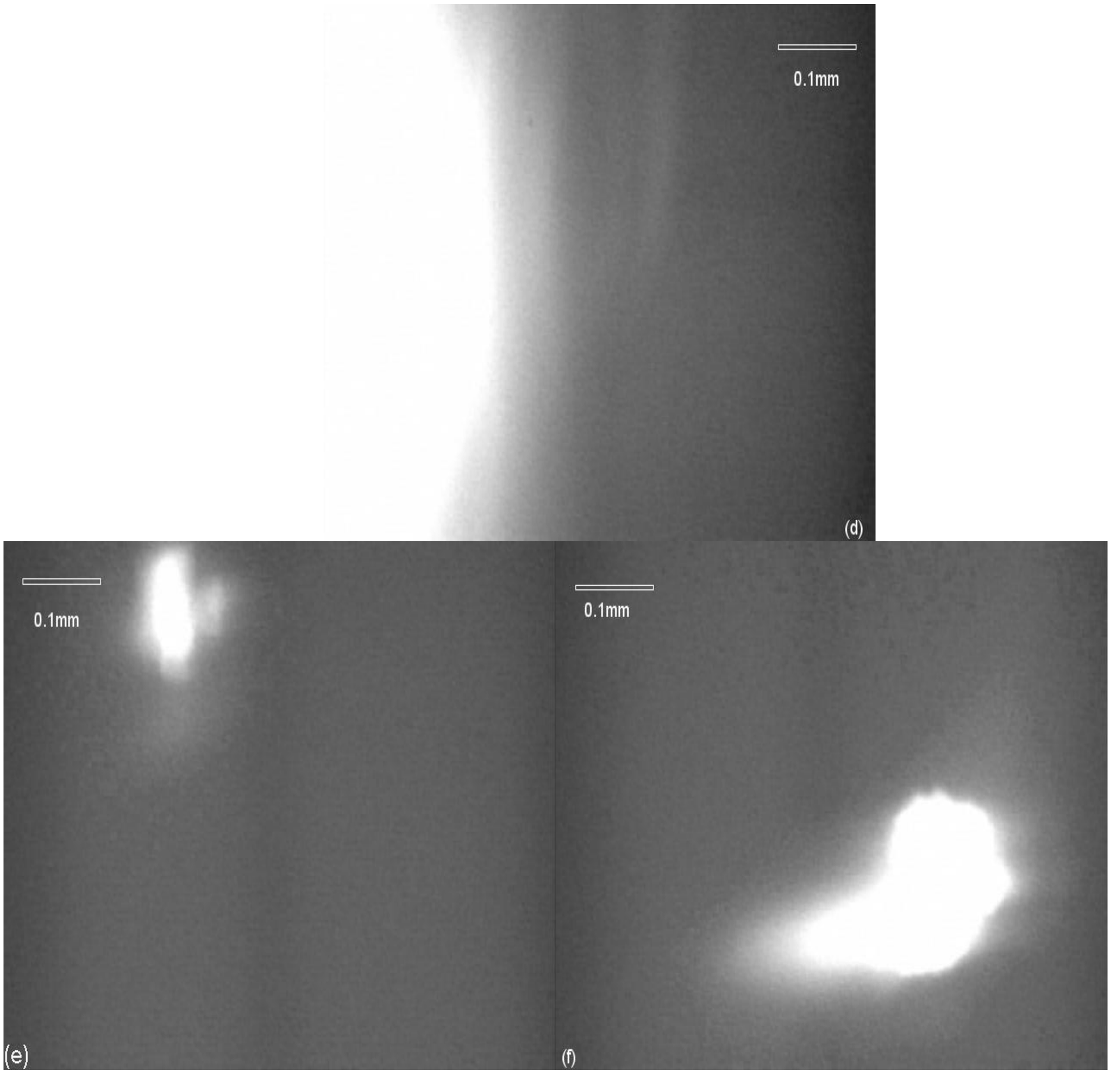


Figure I-1: Coal particles in air at 856 °C.

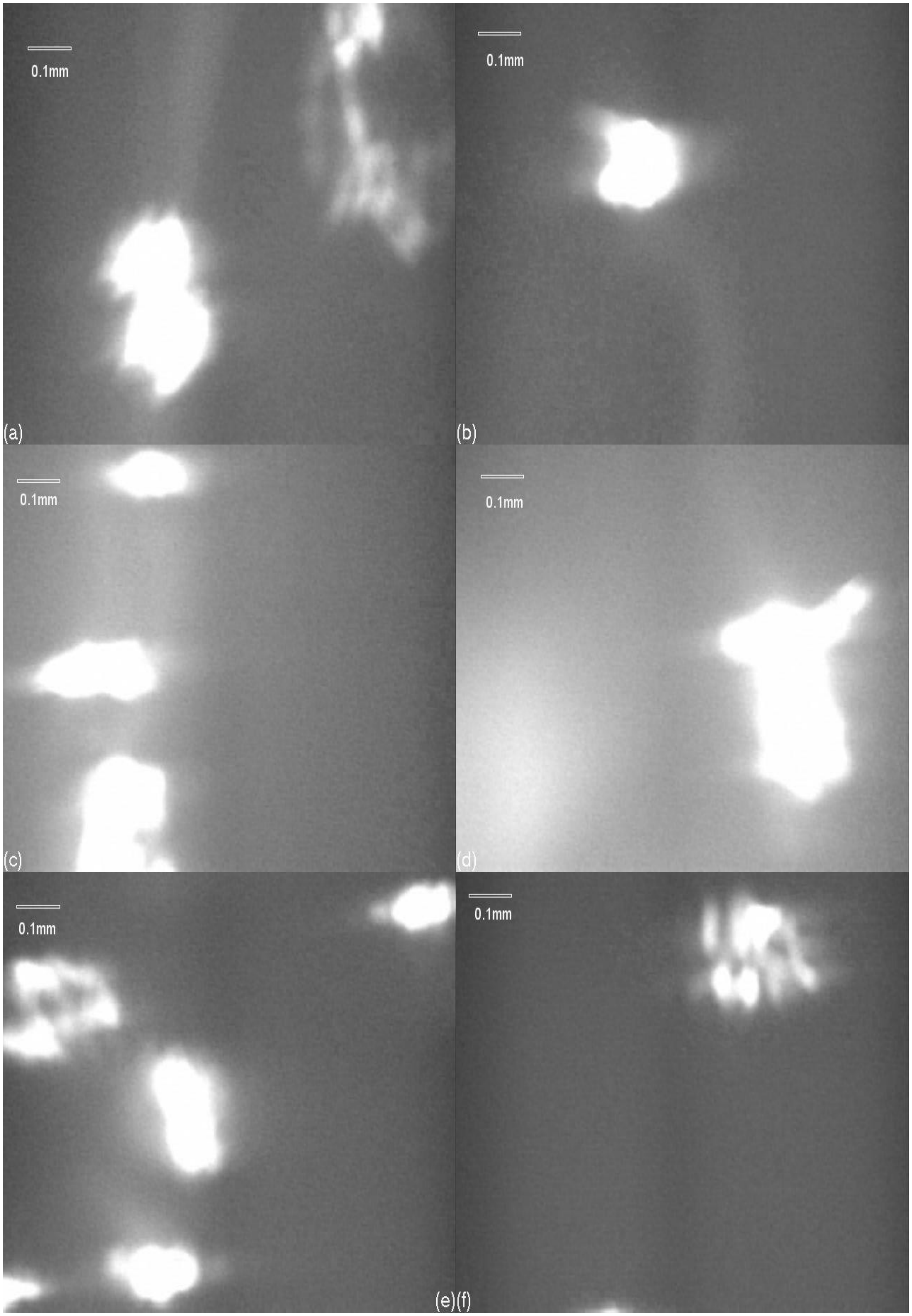


Figure I-2: Switch grass particles in air at 856 ^{o}C

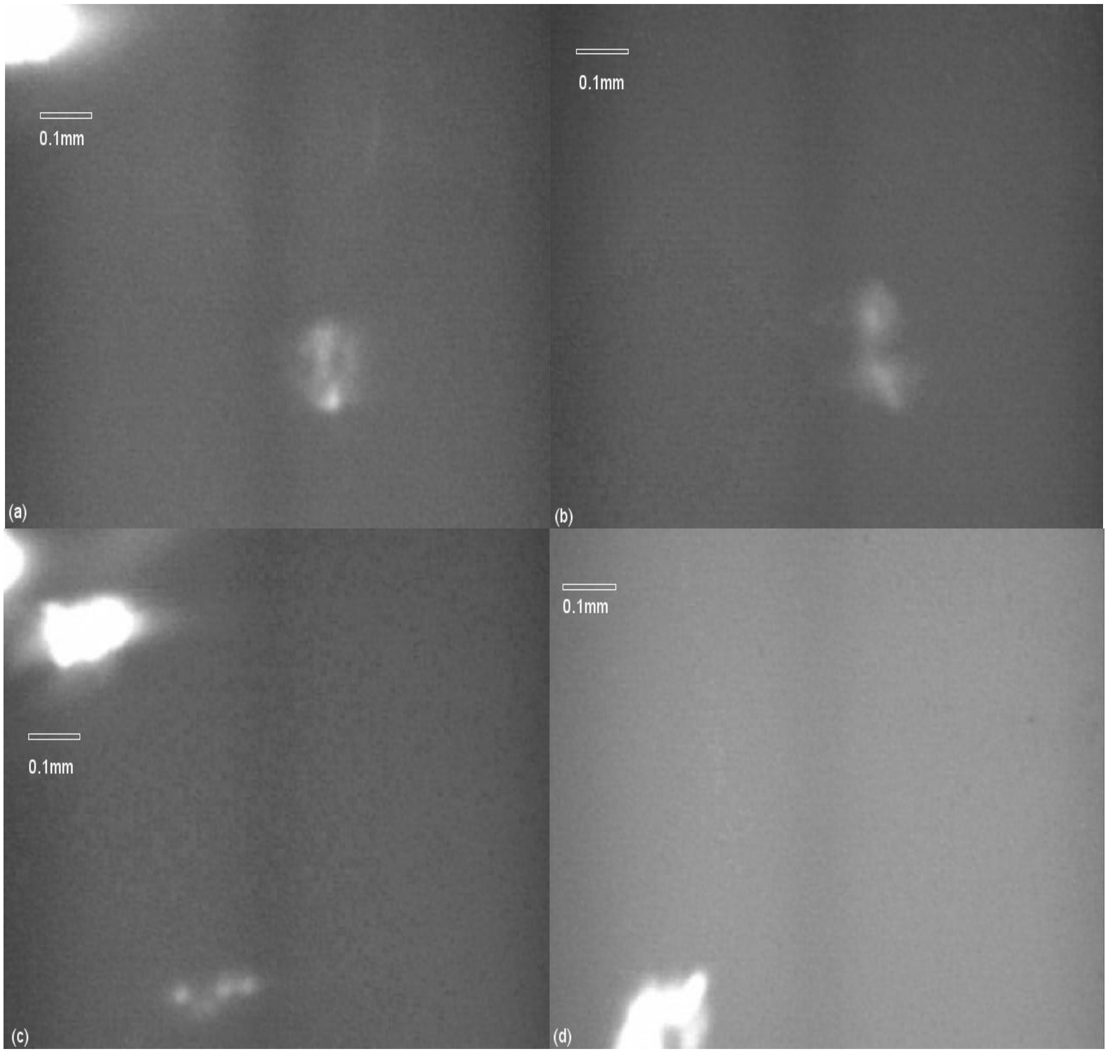


Figure I-3: Wood particles in air at 856 °C.

Figures I-4, I-5, and I-6 show char particles that were collected for combustion experiments in the furnace. The char particles were collected on glass filter pads in a stainless steel effluent filter holder that was described in the previous quarterly report. The images are simple high magnification microscope images of the particles shown to display the particle size and char morphology. These represent particles that were in the high temperature tube at 870 °C for approximately a half a second.

.

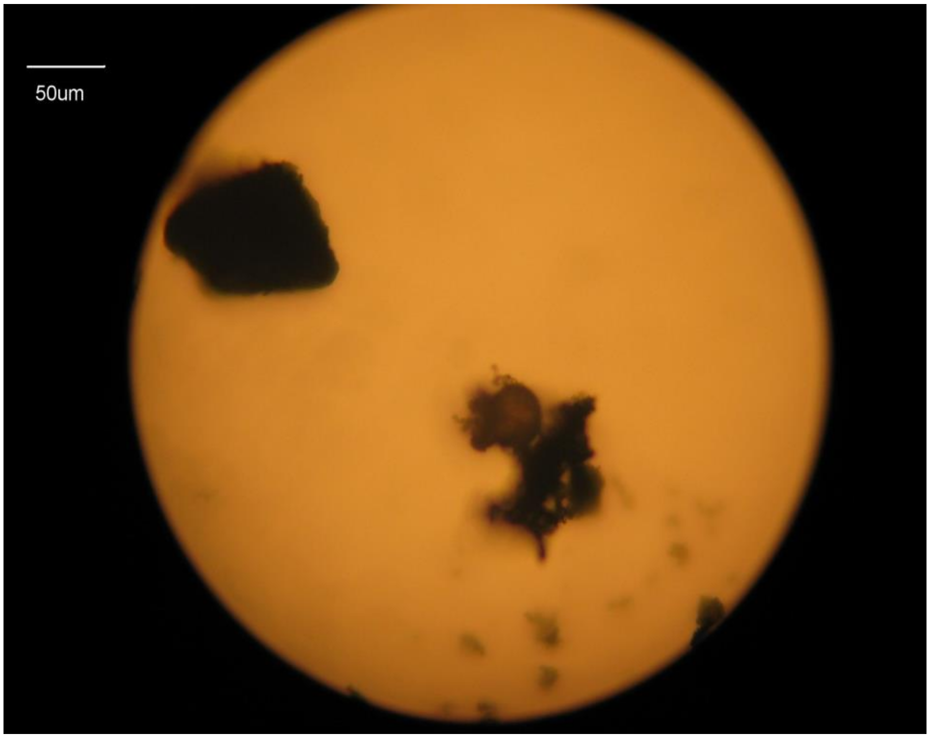


Figure I-4: Microscope image of chars of pulverized coal (720X)

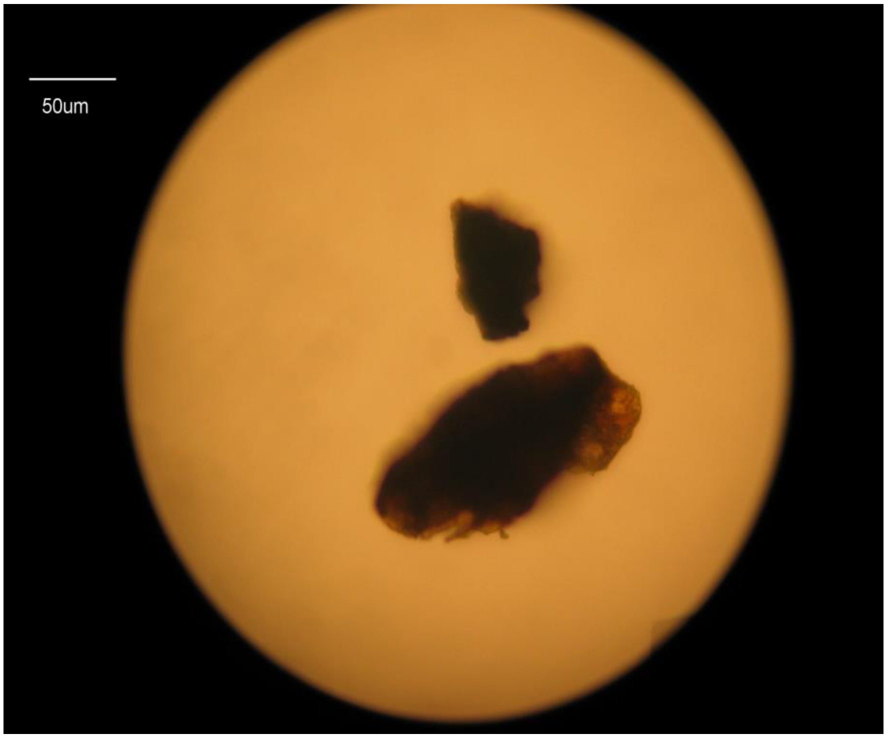


Figure I-5: Microscope image of chars of wood particles (720X)

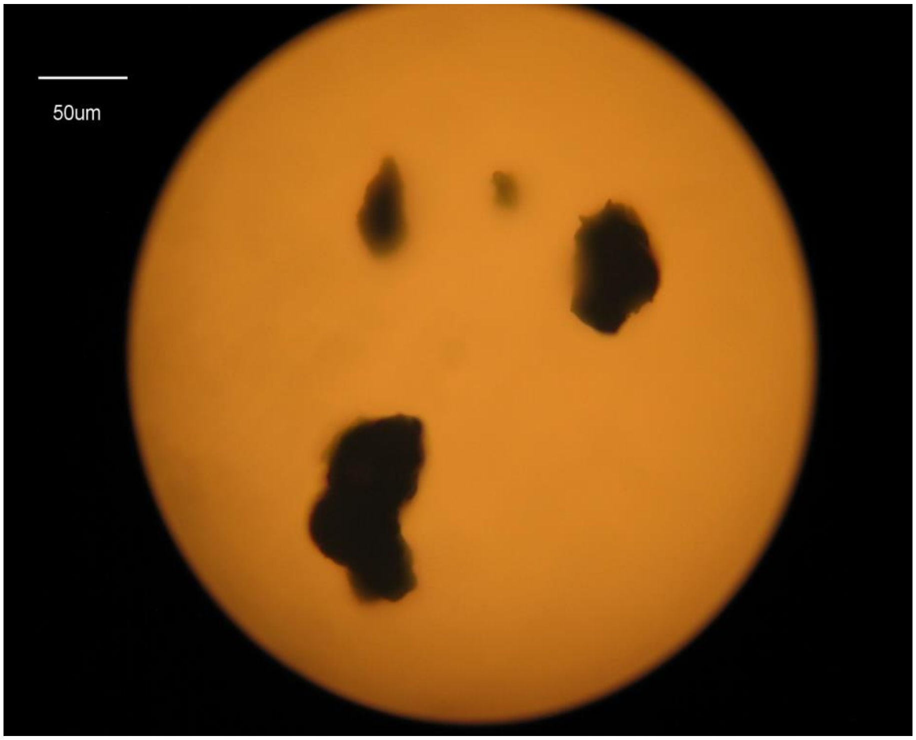


Figure I-6: Microscope image of chars of switch grass particles (720X)

The images of the particles undergoing combustion that were obtained with the monochrome camera demonstrated that combustion was occurring in the drop tube and that instantaneous high resolution images could be obtained. However, three component color images are needed to determine temperature distributions on the particle surface. Figures I-7 and I-8 show preliminary images for coal and switch grass obtained using the AVT Guppy F-033c and a Nikon Micro 60 mm lens. The resolution and magnification for this optical set up has not been measured yet, but the particles are approximately 60 micrometers in diameter and the switch grass particle is 100 micrometers in its shortest dimension. These images show the anticipated color spectrum and intensity for the particles undergoing combustion. We are now in the process of refining the optical focus and using these images to develop the image processing needed for surface temperature estimation.

Experiments were conducted in the furnace at 900°C and at gas compositions of 100% N_2 and 100% CO_2; the particles fell through the drop tube without burning as anticipated. We have begun experiments with O_2 concentrations lower than 21%: our target is 1 to 3% O_2 to match the combustion gas composition in the cement manufacturing plant at the point in the process where the alternative fuels are introduced. We have ordered and received two oxygen analyzers (from Nuvair) for the effluent gas stream and are in the process of installing them for in-line measurement. We installed a thermocouple system to measure temperature at several locations in the supply and effluent gas streams; these are used in conjunction with the flow meters and the vacuum educator described in a previous quarterly report to obtain a specific flow, composition, and temperature in the furnace drop tube. The establishment of the system flow rates and compositions allowed selection and specification of the effluent gas analysis system.

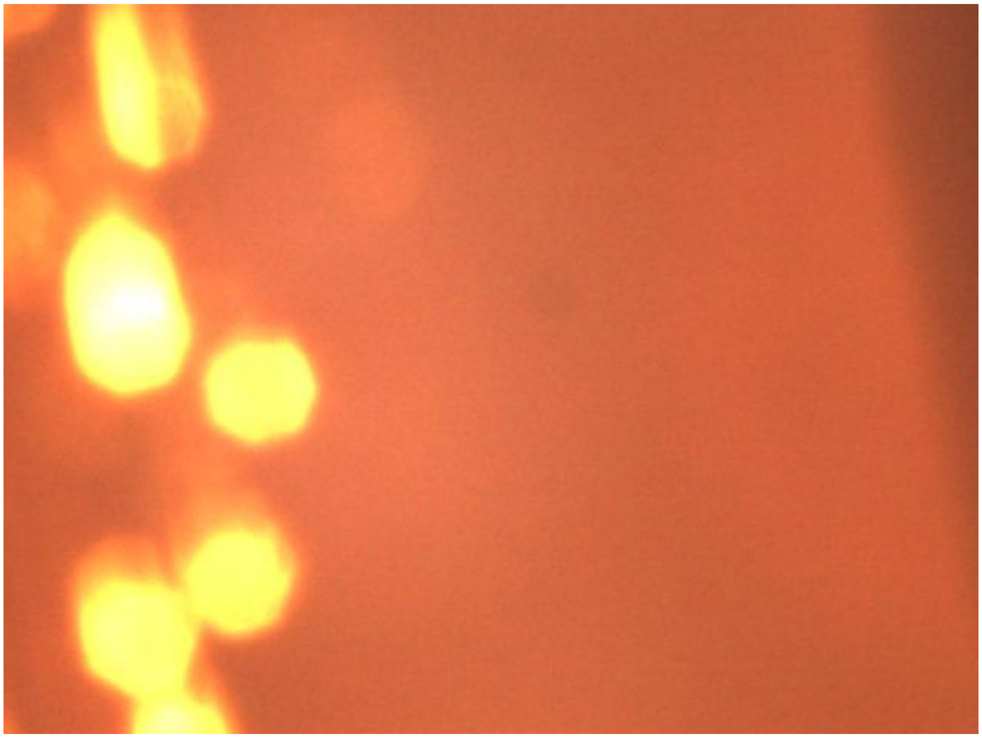


Figure I-7. Coal particles in air at 870 ^{o}C.

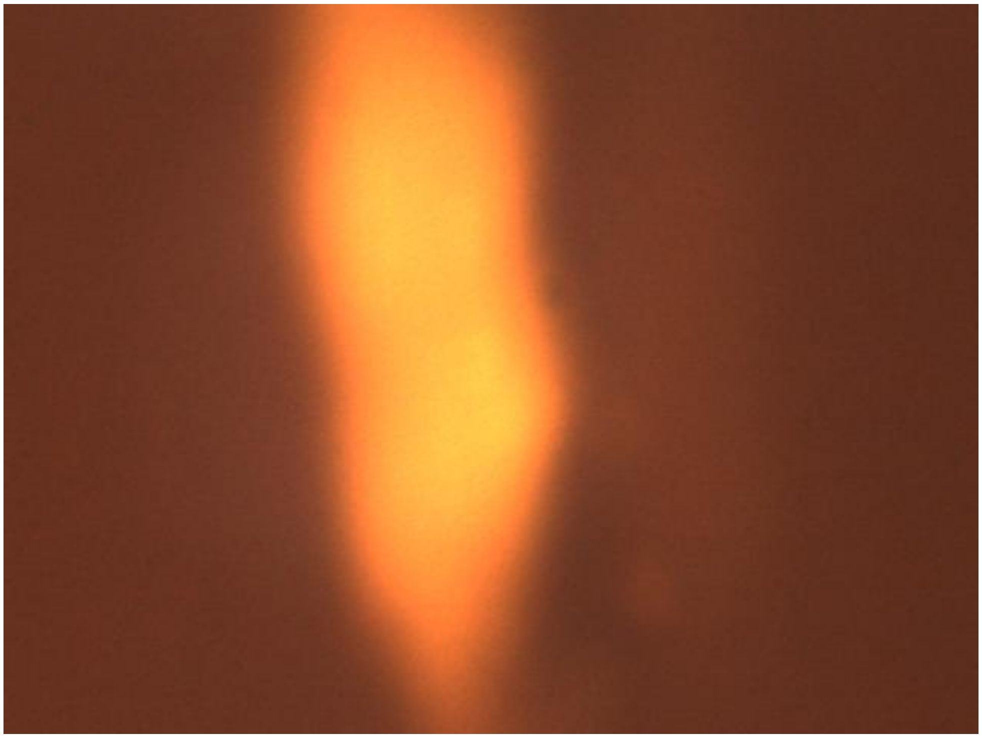


Figure I-8. Switchgrass particle in air at 870 ^{o}C.

The images and subsequent image analysis and processing revealed that the lenses used in our laboratory and the furnace view windows and the glass retort (drop tube) provided spatial resolution to the extent that the camera would allow. Video obtained with the existing high speed monochrome camera (Kodak Motion Corder, 1000 frames per second) revealed that the high frame rates were useful for capturing combustion images for the moving (falling) particles. Images with the Guppy color camera (F-033, 30 frames per second) and subsequent image processing and analysis on these revealed that the three color image provided pixel by pixel variation of each of the three color components that would be consistent with anticipated variation related to surface temperature variations. Successful image acquisition with the high speed monochrome camera and with the color sensor from the standard speed camera confirmed our selection of a color high speed and high spatial resolution camera, and so we are proceeding with the specification and purchase of the color camera system.

We have completed an image processing system that includes algorithms and Matlab code to separate out the three color components from color images from the Guppy camera, and it has been made general to handle color images from other cameras. We have developed expertise on use of the Matlab image processing capabilities. We are continuing development of methods to determine temperature at each pixel in a color image. We are evaluating and testing methods found in our literature review. We are particularly interested in the pyrometry methods developed in “Particle surface temperature measurements with multicolor band pyrometry” by Lu, Hong; Ip, Leong-Teng; Mackrory, Andrew; Werrett, Luke; Scott, Justin; Tree, Dale; and Baxter, Larry in *AIChE Journal*, v 55, n 1, p 243-255, January 2009. They provide a Plank’s law based determination of surface temperature by relating the digital number of the red, green, and blue signals from a color digital image to the spectral responsivity or the camera and the radiance of the hot surface of a particle. We have developed a Matlab code to repeat their pixel by pixel calculations, and have successfully applied these to images in the literature and we are in the process of applying these to our own images. The pixel by pixel calculations are computationally intensive (taking more than 30 hours for a single standard color image); we have developed block filters to shorten calculation time.

We have begun development of a system for generating fluid droplets for injection of alternative liquid fuels into the burn simulator furnace. The drop apparatus consists of a syringe pump, syringe, tubing, and a medical grade stainless steel flat-tip needle. The syringe pump is a KD Scientific model 210 which allows specific rate and volume control (generally 0.1 mL/min). Luer-lok syringes are used and attached to 1/8” tubing; a series of size adapters and a check valve is employed and a final luer-lok fitting is attached. The needles of various gauges are attached to the luer-lok fitting. Figure I-9 shows the apparatus and a water drop that is produced. The preliminary system was developed using water as the fluid. Tests with more viscous fluids are underway to determine drop diameter ranges and rates as a function of fluid properties and needle tip sizes.

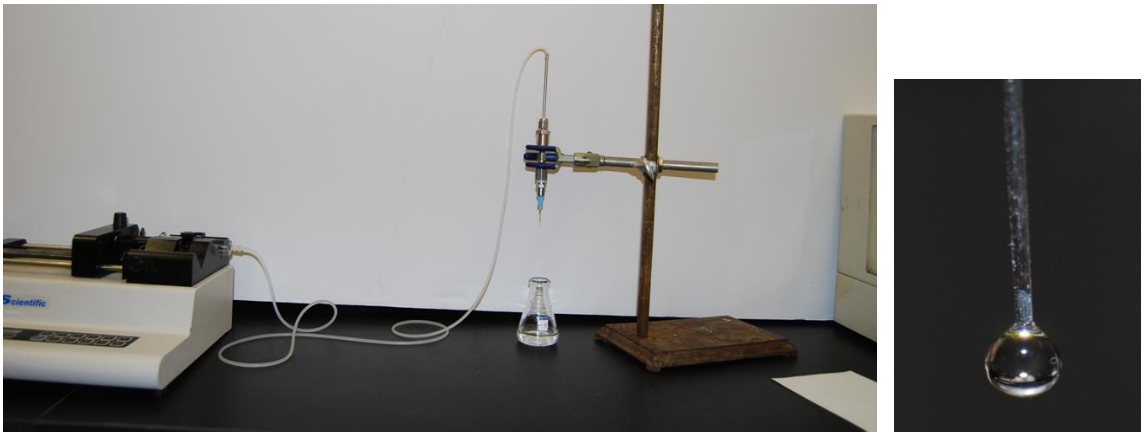


Figure I-9 – Preliminary Liquid Drop Apparatus

We are continuing development of methods to determine temperature at each pixel in a color image by furthering development of Matlab codes. As was mentioned in the previous quarterly report, we are adapting and evaluating methods found in our literature review, with a lead case being the pyrometry methods developed in “Particle surface temperature measurements with multicolor band pyrometry” by Lu, Hong; Ip, Leong-Teng; Mackrory, Andrew; Werrett, Luke; Scott, Justin; Tree, Dale; and Baxter, Larry in *AIChE Journal*, v 55(1),p243-255,2009. They provide a Plank’s law based determination of surface temperature by relating the digital number of the red, green, and blue signals from a color digital image to the spectral responsivity of the camera and the radiance of the hot surface of a particle. The pixel by pixel calculations are computationally intensive (taking more than 10 hours for a single standard color image). Figure I-10 shows a switch grass particle undergoing combustion in the drop tube furnace. Figure I-11 shows the color components for this image for the blue and green signals (intensity resolution); the red signal is not shown.

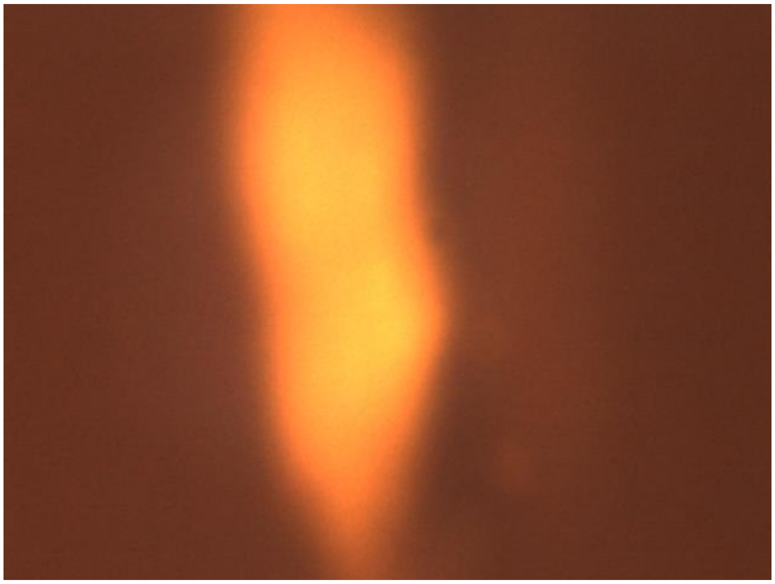


Figure I-10. Switch grass particle in the drop tube furnace in air at 900°C

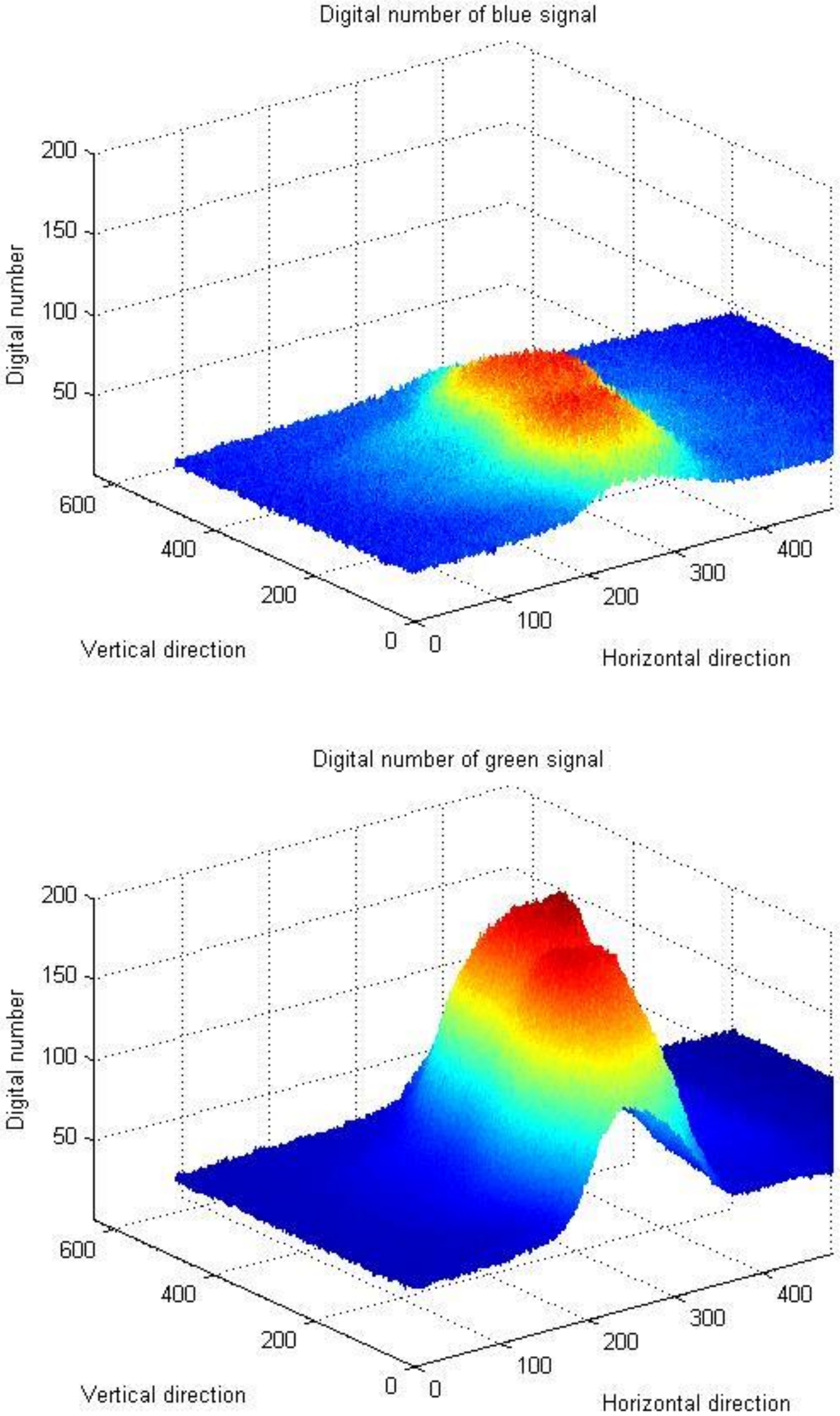


Figure I-11. Digital signals for the blue and green components of the image shown in Figure I-10..

The ration of these signals at each pixel in the image is used to determine the temperature at each pixel through an integration method that seeks to find the temperature in the object plane that would result in the particular ratio of blue to green signals, taking into account the camera sensitivity response curve over a full range of wavelengths. We will describe the mathematics in the final report. We are still developing and validating our methods and calculations, however Figure I-12 displays our preliminary temperature representation for image I-10.

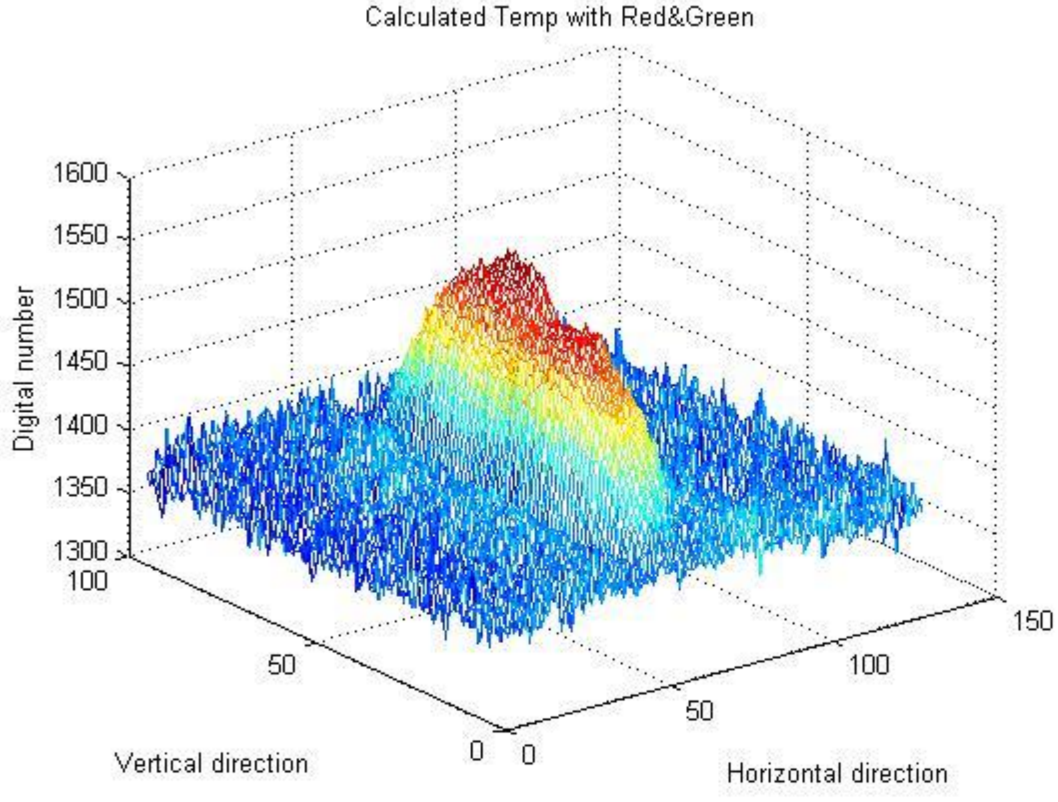


Figure I-12. Temperature (Digital number) from preliminary calculations. Values shown represent relative temperatures. Spatial corrections for particle shape are being developed and were not applied to this image.

We completed development of a system for generating fluid droplets for injection of alternative liquid fuels into the burn simulator furnace. The drop apparatus uses a KD Scientific model 210 syringe pump to feed fluid at a controlled rate to stainless steel tubing leading to Luer-lok needles with stainless steel tips of varying diameters. We have worked with several fluids of differing viscosities and surface tensions (water, soy oil, isopropyl alcohol). We obtained glycerin from VWR Scientific and have begun working with it in the drop injector. Figure I-13 shows a glycerin drop and as anticipated its size is larger than drops that would be anticipated from a spray nozzle type injection.

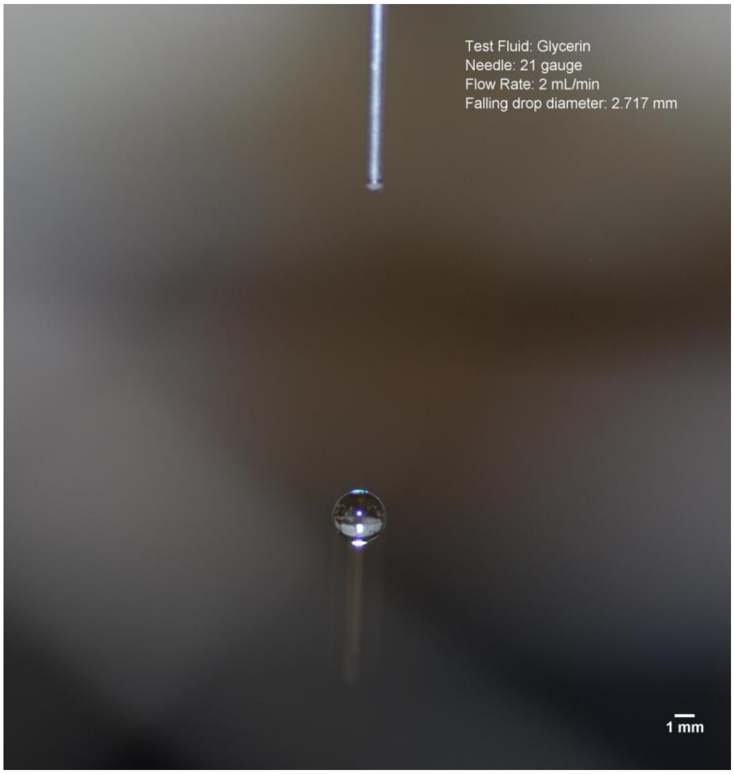


Figure I-13. Glycerin drop from the liquid fuel drop apparatus.

Drop diameters of about 2 mm are the smallest we can obtain from this apparatus. We are pursuing other means of creating smaller drop sizes, but at the same time we are modifying the water-cooled drop tube furnace injection nozzle to allow injection of the 2 mm drops to allow us to obtain visualizations of the drops undergoing combustion.

Task J: Continuation of Phase 2 Feasibility Analysis of Commercially Available Gasification Technologies for using Alternate Fuels to Produce Clean Burning Fuels for Cement Production

Discussions were held during two teleconferences and a face-to-face meeting and it was agreed that the findings from the Primenergy study were sound and that use of gasification of broiler litter at the Roberta facility had unfavorable economics. The project team did not think that additional feasibility or process simulation studies related to gasification were warranted until additional data is determined from the laboratory and pilot scale gasification studies. The funds to support Task J should be used to support other tasks for this project.

Task K: Trials with Small-Scale Gasifier to use of Alternative Fuels to Produce Syn Gas Suitable for Cement Production

Three solid biofuels (poultry litter, railroad ties, and switchgrass) were selected and tested in a Community Power Corporation 25kWe downdraft gasifier to determine the feasibility of the process in regards to syngas production for cement kiln usage. The producer gas was sampled and analyzed, and the gasifier performance was monitored during all experiments to determine the effectiveness of the three fuels. Chipped railroad ties and pelletized switchgrass were found to be suitable fuels as is, but the poultry litter pellets would require special considerations if used in this application. However, because of the distinct economic and environmental advantages that poultry litter usage presents, gasification of this fuel should be further explored. The gasification trial with pelletized switchgrass was conducted upon receipt of pellets from Agrecol in Wisconsin. The test was conducted on May 19th and 200 lbs were run for 3 hours. The pellets fed well, as expected, and produced an exceptionally high quality syngas (average HHV ~5.6 MJ/m³, Figure K-1).

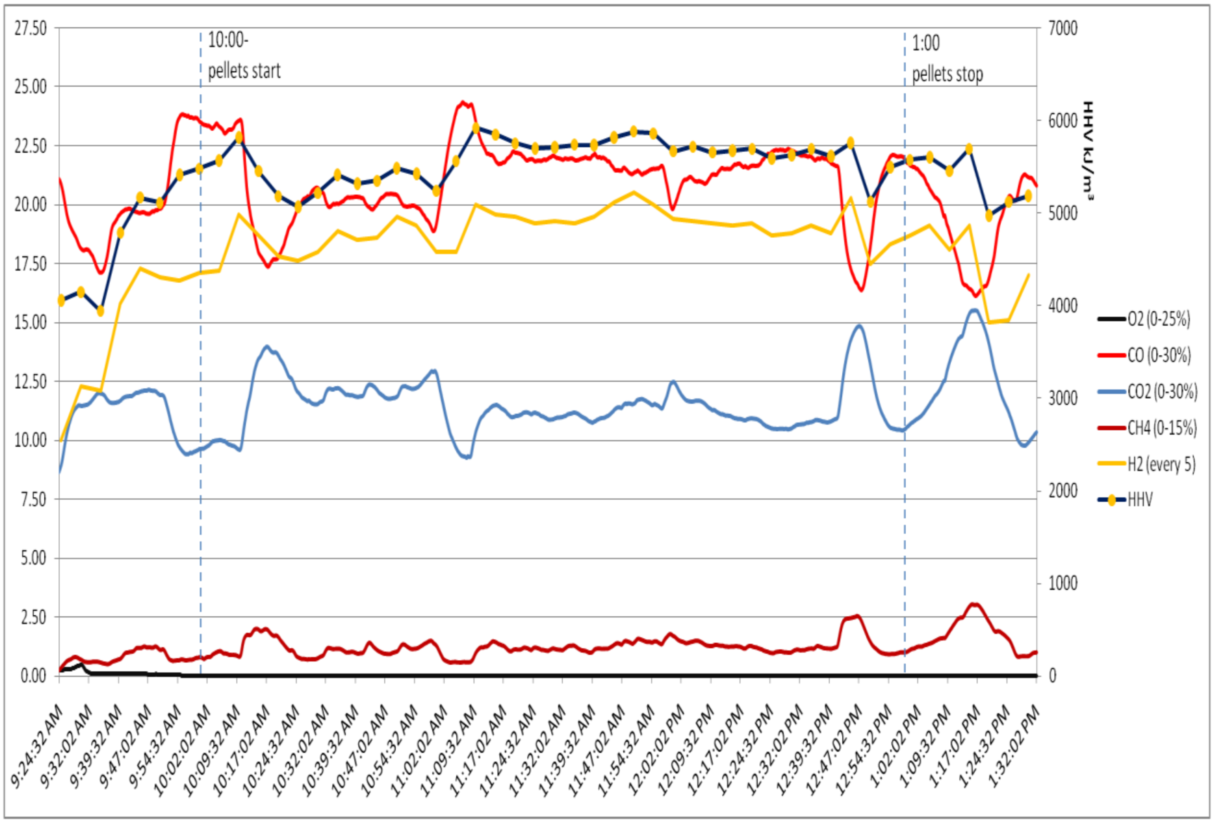


Figure K-1: Gas composition and HHV of syngas over entire run

However, because of the dry nature of the switchgrass pellets, the flame front tended to advance rapidly and occasionally penetrated the top of the gasifier. This is a very minor issue, though, and if anticipated can be easily remedied.

Upon inspection of the ash, a few tiny clinkers (Figure K-2) had been formed during the gasification process, but the adhesion was very minimal and infrequent, so bridging or any clogging of the gasifier should be negligible. Overall, switchgrass pellets were the best performing feedstock tested.

Figure K-2: Few, small switchgrass pellet clinkers

On the project for test alternate fuel using a gasifier vehicle, different feedstock mixtures were tested in a small biomass gasifier mounted on a Dodge Dakota pickup. Wood was used as the primary feedstock, then tested with mixtures containing 80% wood and 20% of broiler litter, switchgrass and plastic on an as-is weight basis. Gasoline was used as a reference point. The following steps were taken for each feedstock combination:

- Modifications were made to the pickup so that the gas tank could be drained completely dry, and to the gasifier so samples of the syngas could be easily drawn for analysis.
- Prior to the gasifier tests, the pickup was driven on 2 gallons of gasoline to provide a point of reference. The gas tank was completely drained to be sure that the 2 gallons of gasoline were accurately measured
- Feedstocks were accurately weighed on a medical scale and loaded into the gasifier, being sure the mixture was spread as evenly as possible
- Feedstocks were sub-sampled for composition analysis, including ultimate and proximate analyses, and ash fusion temperature, at the Alabama Power Analytical Lab, Calera, AL.
- Performance of each feedstock combination was determined by driving the pickup on the NCAT test track at 50-55 mph till the fuel was completely used up. Exact time and distance and weather conditions were recorded.
- Every thirty minutes after starting the performance test for each gasifier feedstock, the pickup was stopped to measure composition of the synthesis gas (% hydrogen, carbon monoxide, methane, carbon dioxide and oxygen; being produced, with a gas analyzer, resulted in 4 readings per feedstock.

- Efficiency for each feedstock was calculated by determining the distance traveled per unit of energy.

Results of the tests: Feedstock test data, including time of test, syngas composition and distance traveled, are presented in Table K-1, and weather data are presented in Table K-2. Of particular interest, is that the tests with gasoline and wood + plastic were conducted in cloudy weather with no rain, but the other feedstocks were tested under extended severe thunderstorm conditions with almost constant extremely heavy rain. This, together with the fact that no stops were made with the gasoline test, as opposed to 4 stops with each gasifier feedstock, resulted in the gasifier tests incurring a disadvantage relative to gasoline.

Table K-1. Syngas, Mileage and Weather Records May 29, 2010

1) Gasoline: 2 gal – 41.9 miles Time 9:00 – 10:00

2) 50 lb of wood Time: 10:00 – 12:00

Reading	**Miles**	**H%**	**CO%**	**CO2%**	**CH4%**	**O%**
1	9.0	14.7	20.99	7.09	0.74	0.76
2	27.5	20.0	18.82	8.50	1.56	1.30
3	39.6	22.2	19.38	9.30	1.74	1.03
4	50.0	20.5	18.92	9.80	1.74	0.82
Total/mean	65.0					

3) 40 lb of wood, 10 lb switchgrass Time: 12:00 – 14:00

Reading	**Miles**	**H%**	**CO%**	**CO2%**	**CH4%**	**O%**
1	10.3	18.4	22.41	6.20	0.71	1.01
2	27.5	18.9	14.46	9.10	1.47	1.58
3	39.6	22.9	15.89	11.4	3.14	0.74
4	48.4	18.2	15.51	9.20	1.13	1.04
Total	58.0					

4) 40 lb wood, 10 lb broiler litter Time: 14:00 – 16:00

Reading	**Miles**	**H%**	**CO%**	**CO2%**	**CH4%**	**O%**
1	10.4	19.3	14.30	9.81	3.09	0.92
2	27.6	24.6	22.90	7.33	2.52	0.89
3	39.7	22.2	16.04	10.2	1.92	0.79
4	50.2	5.83	22.36	4.82	0.06	0.70
Total	50.2					

5) 40 lb wood, 10 lb plastic Time:16:00 – 18:00

Reading	**Miles**	**H%**	**CO%**	**CO2%**	**CH4%**	**O%**
1	10.4	13.3	13.21	9.50	5.15	1.44
2	27.6	17.9	17.02	6.53	2.72	2.82
3	39.7	15.9	17.00	4.84	2.61	4.43
4	50.1	14.5	15.43	4.64	1.66	4.85
Total	69.9					

Table K-2. Hourly Weather Data for Opelika obtained from the Weather Channel

Time	Description	Temp ^{0}F	Dew pt ^{0}F	Humidity%	Pressure	Wind
09:30	Cloudy	74	68	82	29.87	E 7mph
10:30	Cloudy	75	69	80	29.87	ESE 5mph
11:30	Cloudy	78	70	76	29.88	ESE 7 mph
12:30	Thunder Heavy Rain	81	70	70	29.87	SE 8 mph
13:30	Thunder Heavy Rain	78	70	70	29.86	E 8 mph
14:30	Thunder Heavy Rain	75	69	82	29.85	NE 8 mph
15:30	Light Rain	68	68	100	29.86	WNW 7 mph
16:30	Cloudy	69	67	95	29.85	NE 6 mph

Based on Alabama Power Lab analyses (except for moisture content, which was not representative of these samples, and which was therefore determined separately at Auburn University) data presented in Table K-3 was generated. In conclusion, it is concluded fro these results that the falsifier was more efficient than gasoline, and within the gasifier feedstock mixtures, efficiency appeared to increase with moisture content.

Table K-3. Energy efficiency of different fuels based on distance traveled per unit of energy

Fuel	Total Btu Fuel	Total Mileage	Moisture %	Miles/gal gas equivalent	Miles/MMBtu
Gasoline	248,524	41.9	---	20.95	168.6
Wood	280,600	65.0	15.60	28.78	231.6
Wood + Broiler Litter	272,038	50.2	14.28	22.93	184.5
Wood + Switchgrass	298,050	58.0	14.56	24.18	194.6
Wood + Plastic	383,317	69.9	12.80	22.65	182.4

Task L: Testing of Burn Characteristics of Alternate Solid Fuels

Based on local availability and cost, forest trimmings was selected as fuel for the first trial. This trial was completed over the following period January 13-17, 2009. This trial burn was successfully completed. Photographs of the stockpiles of the actual forest trimmings and waste plastics used for this trial burn are shown in Figures L-1 and L-2.

Figure L-1: Stockpile of forest trimmings at the plant

Figure L-2: Stockpile of waste plastics (automotive trim) at the plant

A new control burn was conducted with plastics, scrap tires, coal, and coke as fuel from March 3-8, 2009. This trial burn when well and all the necessary samples were collected. The chemical composition of the cement samples collected for the two trial burns are shown in Figure L-3. Note that the results for the main cement compounds are very similar. The average primary plant emissions for the two trial burns are summarized in Figure L-4.

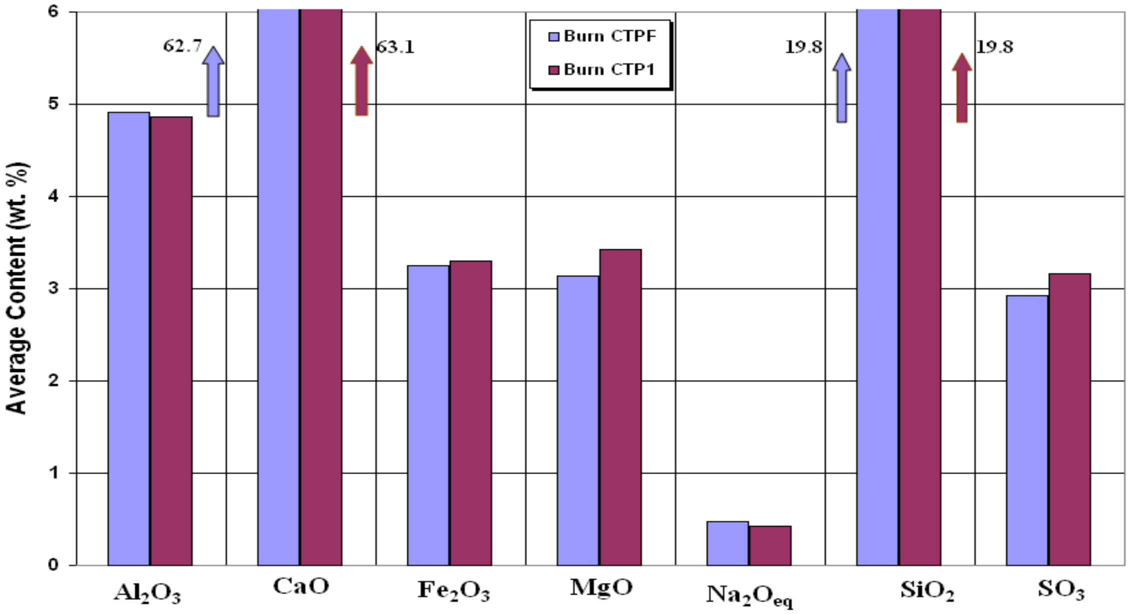


Figure L-3: Chemical composition of the cement samples collected for the two trial burns

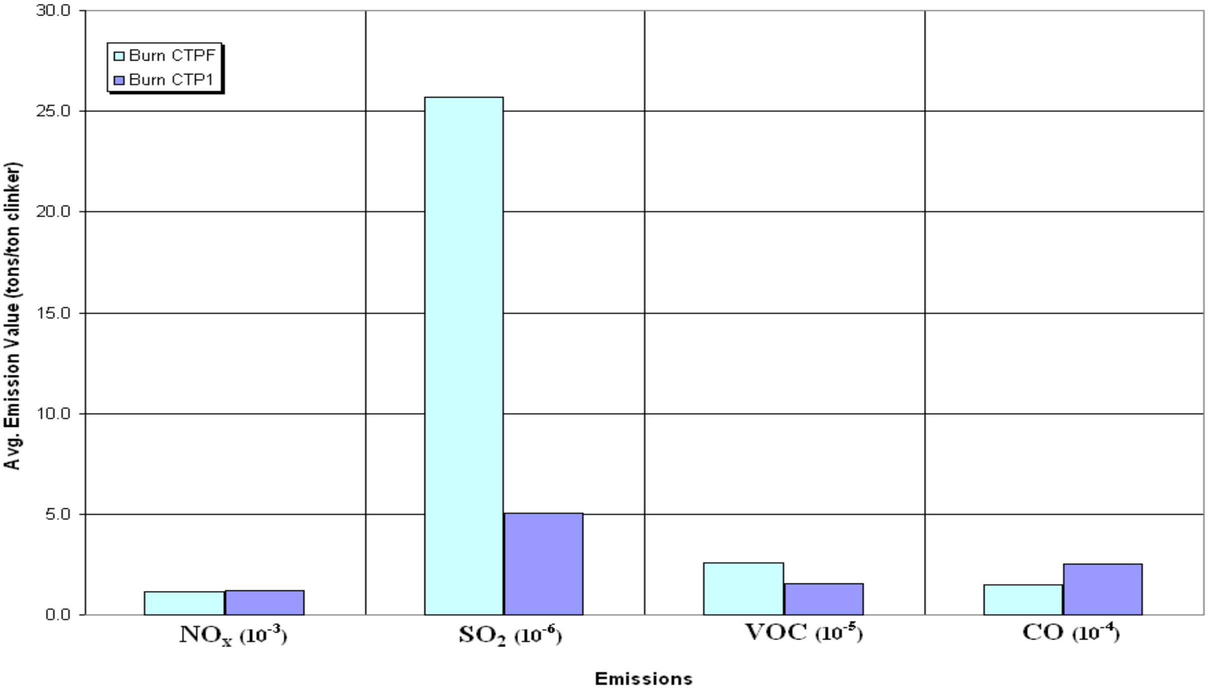


Figure L-4: Plant emissions for the two trial burns

The shredded railway tie burn was also completed from July 8, 2009 to July 12, 2009. Photographs of the stockpiles of the actual shredded railway tie material are shown in Figure L-5. The data collected for this burn are presented in Attachment A.

Figure L-5: Stockpile of shredded railway ties at the plant

The range of as-received energy outputs for each of the fuels utilized during this study were as follows:

- Coal: 10,730 to 11,500, with an average of 11,170 BTU/lb,
- Petroleum Coke: 11,683 to 13,756, with an average of 13,120 BTU/lb,
- Waste Tires: 13,710 to 14,540, with an average of 14,130 BTU/lb,
- Waste Plastics: 6,850 to 9,530, with an average of 8,720 BTU/lb,
- Forest Trimmings: 3,491 to 4,959, with an average of 4,140 BTU/lb, and
- Railway Ties: 5,641 to 6,774, with an average of 6,140 BTU/lb.

Plant emissions were closely monitored during each trial burn. The Continuous Emissions Monitoring System (CEMS) results were obtained by the cement plant in five-minute intervals. Emissions were reported in terms of tons per hour released; however, these were normalized to account for variation in production rates between the burns. Results are therefore expressed as tons per ton of clinker produced. The summary statistics for these emissions data are shown in Table L-1.

Emissions limitations were defined by the Alabama Department of Environmental Management (ADEM). Limitations were originally expressed in allowable tons per 30-

day period, which were converted to allowable tons per ton of clinker produced using production data from each burn. Therefore, each burn had its own limitation for the primary emission components, as shown in Table L-1. Each burn was evaluated individually and satisfied all ADEM limitations. The VOC emissions were significantly increased for all burns that used alternative fuels.

Table L-1: CPR – Summary statistics of normalized plant emissions for all burns

Emissions		**FT**	**B-CCTP**	**B-CCP**	**RR**	**GL**
NO$_x$ (tons/ton clinker)	**Average (10^{-4})**	11.4	11.8	7.03	7.12	9.59
	Coefficient of Variation (%)	15.4	16.1	26.5	13.6	23.0
	P-Value[2]	> 0.250	< 0.005[1]	0.083[1]	> 0.250	> 0.250
SO$_2$ (tons/ton clinker)	**Average (10^{-6})**	25.1	5.07	5.88	12.2	2.50
	Coefficient of Variation (%)	25.1	59.8	44.2	47.8	53.8
	P-Value[2]	0.077[1]	< 0.005[1]	< 0.005[1]	0.023[1]	0.006[1]
VOC (tons/ton clinker)	**Average (10^{-6})**	26.3	15.5	12.9	17.0	27.5
	Coefficient of Variation (%)	53.7	36.1	20.8	29.0	19.0
	P-Value[2]	0.008[1]	< 0.005[1]	> 0.250	< 0.005[1]	> 0.250
CO (tons/ton clinker)	**Average (10^{-5})**	15.2	25.2	15.3	15.4	43.9
	Coefficient of Variation (%)	18.9	20.7	24.4	14.4	11.1
	P-Value[2]	0.179	> 0.250	0.215	> 0.250	0.037[1]

Notes:
[1] Not Normally Distributed
[2] Anderson-Darling Statistics
[3] ADEM (2007)

We have also contracted Carbon Solutions Inc to conduct a carbon inventory study on the use of alternate fuels for cement processing to replace coal. Carbon Solutions has conducted the study and the report includes the development of a Fuel Switch Analysis Calculator which is a dynamic tool that allows the user to determine the emission reductions of a specific fuel mix based on variable factors and inputs. To allow for a common point of comparison, each feedstock will be examined in this report assuming a 90/10 co-fire with coal based on energy content.

Each fuel mix is evaluated against a 100% coal baseline. The baseline incorporates the coal combustion emissions (202,200 tCO2e), the plant process electricity (162,240 tCO2e), and the coal transportation to the plant (6,090 tCO2e) for a total of 370,530 tCO2e.

According to the plant, the amount of energy used annually is approximately 1,119,880 MMBtu for the production of clinker. Therefore, the tonnage of each alternative fuel will vary based on the energy content needed to comprise 239,967 MMBtu annually. Each 90/10 fuel mix considers combustion emissions, plant process electricity consumption, feedstock transportation, feedstock cultivation, and methane avoidance.

Using a 90/10 co-fire on an energy basis, the seven alternative feedstocks below are arranged in order of the amount of Emission Reductions against a 100% Coal Baseline:

	90/10 Co-Fire Fuel Mix		
Feedstock	Emission Reduction (tCO_2e/year)	Price per Ton	Cost per tCO_2 Avoided
Poultry Litter	41,161.05	$35.00	$8.06
MSW Pellets	28,722.75	$40.00	$13.45
Wood Chips	18,164.11	$32.00	$24.26
Railroad Ties	14,180.64	$70.00	$63.42
Tires	10,287.01	$25.00	-$20.31
Switchgrass	7,192.38	$70.00	$223.11
Plastic	-12,561.16	$45.00	N/A

Task M: Testing of Burn Characteristics of Alternate Liquid Fuels

The plant created access to the main burner to enable the addition of fluids to the kiln. The addition location used for the glycerin trial burn is shown in Figure M-1. Based on local availability and cost, a glycerin trial burn was conducted. This trial burn was successfully completed over November 5-7, 2009.

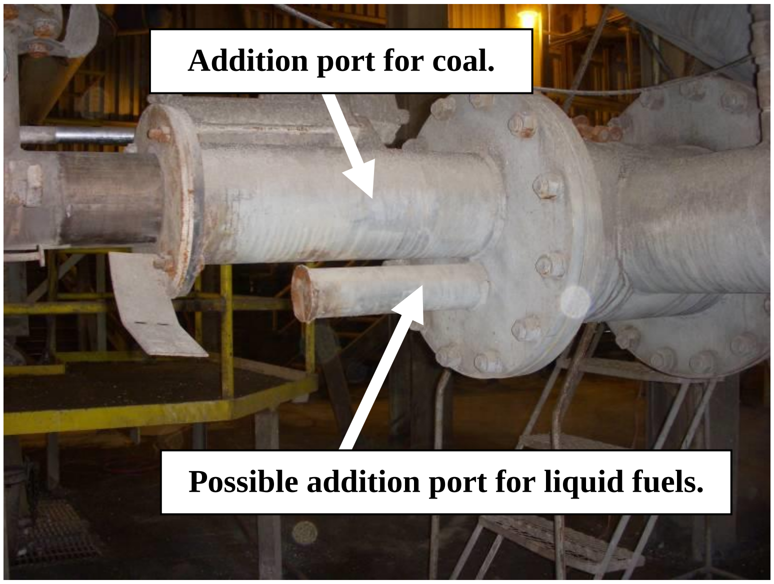


Figure M-1: Stockpile of shredded railway ties at the plant

Due to the limited supply of bio-diesel, waste-oil was used as the second liquid fuel for a trial burn. This burn was initially scheduled for March 2-4, 2010; however, due to changes in the plant's schedule this burn was conducted on April 20-23, 2010. A summary of the plant conditions during all trial burns is shown in Table M-1.

Table M-1: Summary of plant conditions during each burn

Burn	**FT**	**B-CCTP**	**B-CCP**	**RR**	**GL**
Period	Jan. 2009	Mar. 2009	Jul. 2009	Jul. 2009	Nov. 2009
Kiln Feed Rate (mtph)	170-315	205-281	203-306	230-307	252-297
Clinker Production Rate (mtph)	113-191	173-266	258-39	262-331	160-196
Coal Feed Rate (mtph)	8.8-21.5	5.4-18.4	3.7-12.4	6.1-14.9	4.9-13.4
Pet Coke Feed Rate (mtph)	0-6.1	0-6.3	4.0-7.5	3.2-7.8	5.4-7.4
Tire Feed Rate (mtph)	0-57.2	0-36.5	-	-	-
Plastic Feed Rate (mtph)	2.3-4.8	3.2-6.2	5.0-8.2	4.0-5.3	6.6-7.6
Alternative Fuel Feed Rate (mtph)	1.7-3.6	-	-	2.8-3.7	0-20.4
Alternative Fuel Replacement Rate (%)[a]	0.8-5.8	-	-	6.7-9.3	0-38.4

Note: **[a] Reported on an as-received, energy replacement basis**

The range of as-received energy output for the liquid glycerin was 4,307 to 16,684, with an average of 7,730 BTU/lb. The emissions associated with the GL burn are summarize in Table M-1.

The cube strength results from the cement plant are plotted in Figure M-1. The cements from the FT and RR burns have similar early-age and long-term strengths as compared to their control burns. The only result that is of practical significance is a reduction in early-age compressive strengths for the GL burn. This may be partially due to the increased P_2O_5 content seen in the liquid glycerin. During the GL burn, the P_2O_5 was 25% higher than burn B-CCP (0.059 compared to 0.047 percent by weight). The increase in cement P_2O_5 content could be linked to the liquid glycerin fuel which had an increase in P_2O_5, which was nearly fifty times greater than the amounts found in coal and petroleum coke.

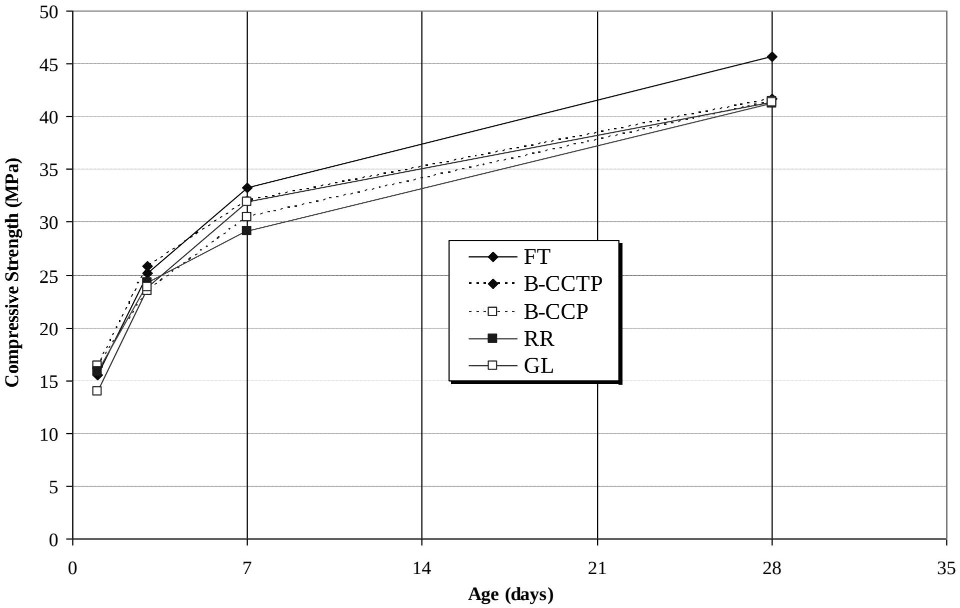


Figure M-1: Compressive strength of mortar cubes for all burns (CPR)

Although coal and coke provided the majority of the energy used during production, a substantial amount of these nonrenewable fossil fuels were replaced by the combination of waste tires and plastics with the alterative. A considerable amount of waste was diverted from landfills, while incineration needs were reduced, leading to less excess pollutants released into the atmosphere.

ATTACHMENT A:

Summary of Data Collected for the Coal, Coke, and Plastics, and Railway Ties Trial Burn: 07/08/2009 through 07/12/2009Burn

1. General comments

- Coal, petroleum coke, waste plastics, and railway ties were the fuels utilized in this trial burn. The raw data collected from the trial burn is presented in this document. Analysis of the data is not included.
- Burn B-CCP is the baseline for this trial burn. B-CCTP is the baseline for the FT trial burn (see Section 2 below).
- The trial began 8:00 AM on 7/8/2009 and ended 8:00 AM on 7/12/2009. This was a continuous trial burn. A total of 96 hours of data was used for analysis.

2. Notation

AUR – Auburn University Results
CPR – Cement Plant Results
ELR – External Lab Results
SLR – Specialty Lab Results
NC – Not Collected
NA – Not Applicable
CIP – Collection in Progress
ASF – Alternative Solid Fuels
FT – Forest Trimmings trial burn
B-CCTP (Baseline) – Coal, Petroleum Coke, Tires, Plastics
B-CCP (Baseline) – Coal, Petroleum Coke, Plastics
RR –Railway ties trial burn

3. Fuel utilization

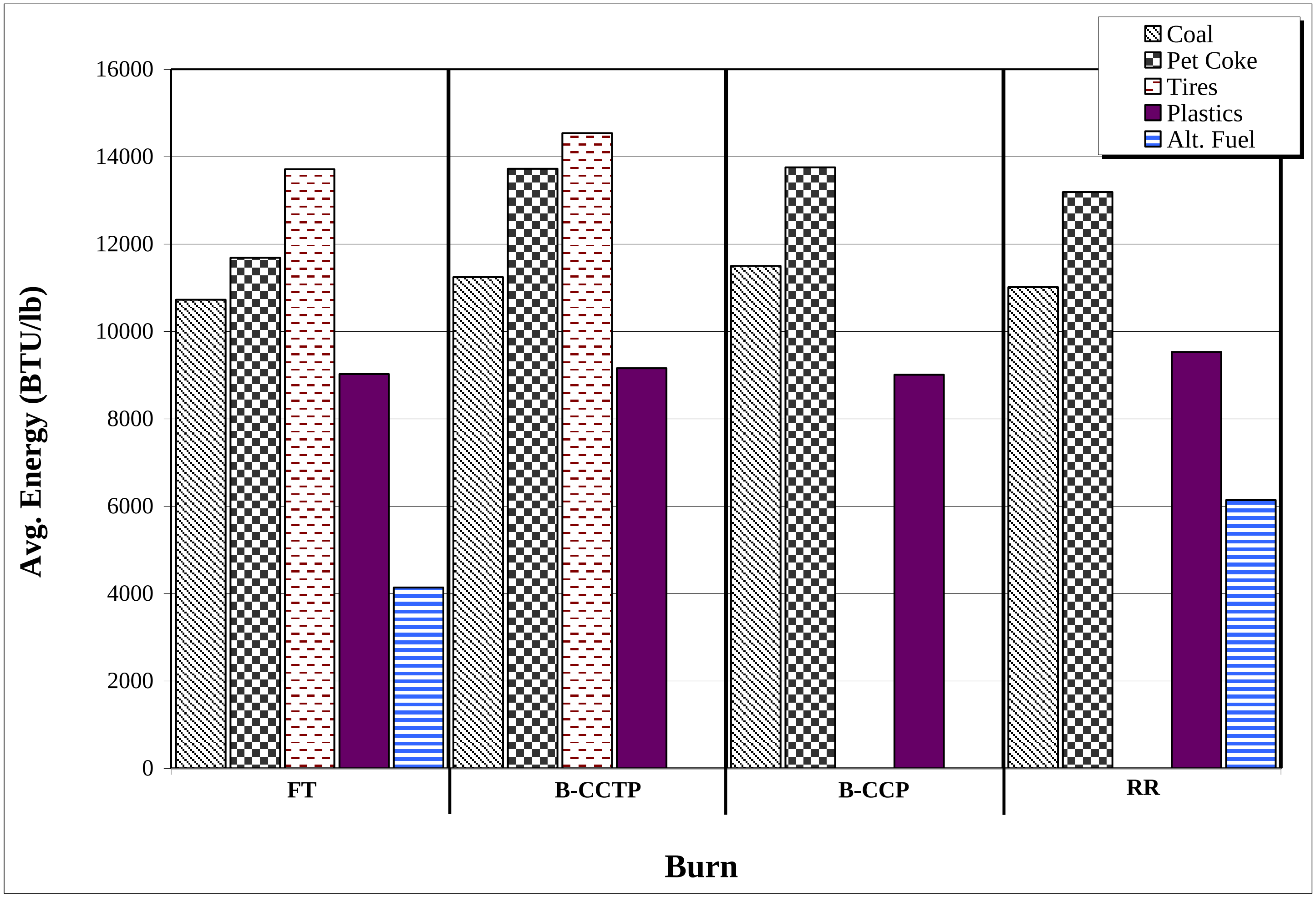


Figure 3.1: Fuel Percentages (energy basis)

4. Chemical composition of alternative fuels

Table 4.1: ELR – Proximate and ultimate analysis of ASF blend

Test	Parameter	Avg. Value (wt. %)	C.V. (%)
Proximate Analysis	**Ash**	9.01	39.9
	Fixed Carbon	12.46	24.7
	Moisture [1]	21.61	47.0
	Volatile Matter	78.53	4.6
Ultimate Analysis	**Carbon**	53.09	6.6
	Hydrogen	5.66	12.6
	Nitrogen	1.13	39.6
	Oxygen	30.91	17.1
	Sulfur	0.21	63.6
Heat Value [2] **(BTU/lb)**		9,767	9.5

Notes: [1] As received [2] Dry basis

Table 4.2: ELR – Chemical properties of ASF blend

Parameter	Avg. Value	C.V. (%)
Al_2O_3 (wt. %)	13.69	86.9
CaO (wt. %)	33.16	30.3
Fe_2O_3 (wt. %)	10.91	54.7
K_2O (wt. %)	0.79	27.6
MgO (wt. %)	3.23	43.4
Na_2O (wt. %)	1.85	67.3
P_2O_5 (wt. %)	0.37	71.1
SiO_2 (wt. %)	28.46	31.8
SO_3 (wt. %)	2.97	34.9
TiO_2 (wt. %)	1.73	76.7
As , ppm	-59.93	-375.3
Ba , ppm	NC	NC
Cd , ppm	< 6	NA
Cl , ppm	883.20	216.4
Co , ppm	284.94	90.6
Cr , ppm	3444.83	193.7
Cu , ppm	2137.80	80.0
Hg , ppm	0.41	29.2
Mn , ppm	NC	NC
Mo , ppm	214.91	105.2
Ni , ppm	1024.56	107.2
Pb , ppm	424.98	99.9
Sb , ppm	NC	NC
Se , ppm	< 2	NA
Sr , ppm	NC	NC
V , ppm	148.22	38.7
Zn , ppm	14797.68	49.3

Table 4.3: ELR – Proximate and ultimate analysis of plastics

Test	Parameter	Avg. Value (wt. %)	C.V. (%)
Proximate Analysis	**Ash**	8.57	34.2
	Fixed Carbon	7.63	37.9
	Moisture [1]	1.74	41.1
	Volatile Matter	83.80	4.3
Ultimate Analysis	**Carbon**	52.63	9.5
	Hydrogen	5.71	23.6
	Nitrogen	1.21	20.0
	Oxygen	31.67	15.7
	Sulfur	0.21	28.2
Heat Value [2] **(BTU/lb)**		9,725	10.6

Notes: [1] As received [2] Dry basis

Table 4.4: ELR – Chemical properties of plastics

Parameter	**Avg. Value (ppm)**	**C.V. (%)**
Al_2O_3 (wt. %)	23.94	55.3
CaO (wt. %)	39.04	47.8
Fe_2O_3 (wt. %)	4.38	76.6
K_2O (wt. %)	0.32	50.2
MgO (wt. %)	2.21	48.6
Na_2O (wt. %)	2.21	66.3
P_2O_5 (wt. %)	0.26	53.6
SiO_2 (wt. %)	21.04	45.5
SO_3 (wt. %)	2.01	64.9
TiO_2 (wt. %)	2.35	54.9
As , ppm	38.23	99.7
Ba , ppm	NC	NA
Cd , ppm	< 6	NA
Cl , ppm	333.68	73.0
Co , ppm	106.52	56.5
Cr , ppm	2970.24	100.9
Cu , ppm	1134.79	213.3
Hg , ppm	0.27	22.3
Mn , ppm	NC	NA
Mo , ppm	429.21	122.5
Ni , ppm	1575.85	110.6
Pb , ppm	198.45	113.0
Sb , ppm	NC	NA
Se , ppm	<2	NA
Sr , ppm	NC	NA
V , ppm	160.15	37.0
Zn , ppm	1227.86	132.0

Table 4.5: ELR – Proximate and ultimate analysis of RR ties

Test	Parameter	Avg. Value (wt. %)	C.V. (%)
Proximate Analysis	**Ash**	7.49	53.8
	Fixed Carbon	14.19	27.7
	Moisture [1]	28.41	15.3
	Volatile Matter	78.32	4.0
Ultimate Analysis	**Carbon**	50.26	2.4
	Hydrogen	4.99	4.7
	Nitrogen	0.88	17.4
	Oxygen	36.22	9.7
	Sulfur	0.16	92.2
Heat Value [2] **(BTU/lb)**		8,572	2.9

Notes: [1] As received [2] Dry basis

Table 4.6: ELR – Chemical properties of RR ties

Parameter	Avg. Value (ppm)	C.V. (%)
Al_2O_3 (wt. %)	6.13	39.9
CaO (wt. %)	43.10	28.2
Fe_2O_3 (wt. %)	7.75	27.3
K_2O (wt. %)	0.80	30.9
MgO (wt. %)	5.52	48.4
Na_2O (wt. %)	0.52	42.5
P_2O_5 (wt. %)	0.22	16.9
SiO_2 (wt. %)	28.37	25.6
SO_3 (wt. %)	4.38	37.7
TiO_2 (wt. %)	0.54	46.4
As , ppm	28.78	49.5
Ba , ppm	NC	NA
Cd , ppm	< 6	NA
Cl , ppm	321.10	156.6
Co , ppm	215.58	64.8
Cr , ppm	388.23	48.0
Cu , ppm	1374.22	52.2
Hg , ppm	0.18	75.6
Mn , ppm	NC	NA
Mo , ppm	889.27	144.5
Ni , ppm	266.35	49.7
Pb , ppm	105.02	53.0
Sb , ppm	NC	NA
Se , ppm	< 2	NA
Sr , ppm	NC	NA
V , ppm	126.59	106.3
Zn , ppm	15648.23	72.2

5. Chemical composition of coal

Table 5.1: ELR – Proximate and ultimate analysis of coal

Test	Parameter	Value (wt. %)	C.V. (%)
Proximate Analysis	**Ash**	24.70	3.12
	Fixed Carbon	50.58	2.40
	Moisture [1]	1.67	17.25
	Volatile Matter	24.73	2.10
Ultimate Analysis	**Carbon**	64.75	0.30
	Hydrogen	2.99	1.75
	Nitrogen	0.98	8.07
	Oxygen	4.44	16.79
	Sulfur	2.14	14.79
Heat Value [2] **(BTU/lb)**		11,199	1.36

Notes: [1] As received [2] Dry basis

Table 5.2: ELR – Chemical properties of coal

Property	Value	C.V. (%)
Al_2O_3 (wt. %)	21.70	4.65
CaO (wt. %)	10.14	4.55
Fe_2O_3 (wt. %)	8.76	6.67
K_2O (wt. %)	2.53	3.61
MgO (wt. %)	1.24	3.48
Na_2O (wt. %)	0.27	23.66
P_2O_5 (wt. %)	0.16	2.68
SiO_2 (wt. %)	49.45	4.97
SO_3 (wt. %)	4.51	89.46
TiO_2 (wt. %)	1.02	5.11
As (ppm)	130.29	25.81
Ba (ppm)	NC	NA
Cd (ppm)	< 6	NA
Cl (ppm)	114.00	5.16
Co (ppm)	37.65	7.78
Cr (ppm)	306.10	14.35
Cu (ppm)	577.12	58.26
Hg (ppm)	1.01	1.40
Mn (ppm)	NC	NC
Mo (ppm)	38.20	13.57
Ni (ppm)	174.89	17.59
Pb (ppm)	32.03	31.06
Sb (ppm)	NC	NC
Se (ppm)	< 2	NA
Sr (ppm)	NC	NA
V (ppm)	658.97	21.23
Zn (ppm)	91.44	50.23

6. Chemical composition of petroleum coke

Table 6.1: ELR – Proximate and ultimate analysis of petroleum coke

Test	Parameter	Value (wt. %)	C.V. (%)
Proximate Analysis	**Ash**	12.33	3.91
	Fixed Carbon	71.07	0.89
	Moisture [1]	0.68	11.10
	Volatile Matter	16.59	1.98
Ultimate Analysis	**Carbon**	76.35	0.49
	Hydrogen	2.76	0.21
	Nitrogen	1.07	4.67
	Oxygen	0.22	84.29
	Sulfur	7.26	2.89
Heat Value [2] **(BTU/lb)**		13,281	0.66

Notes: [1] As received [2] Dry basis

Table 6.2: ELR – Chemical properties of petroleum coke

Property	Value	C.V. (%)
Al_2O_3 (wt. %)	11.92	3.85
CaO (wt. %)	22.29	4.60
Fe_2O_3 (wt. %)	5.27	5.02
K_2O (wt. %)	1.37	4.88
MgO (wt. %)	1.15	1.61
Na_2O (wt. %)	0.18	15.13
P_2O_5 (wt. %)	0.12	5.90
SiO_2 (wt. %)	27.83	5.24
SO_3 (wt. %)	27.33	4.31
TiO_2 (wt. %)	0.55	3.69
As (ppm)	116.11	12.28
Ba (ppm)	NC	NA
Cd (ppm)	< 6	NA
Cl (ppm)	124.00	4.03
Co (ppm)	36.11	5.90
Cr (ppm)	106.81	73.69
Cu (ppm)	543.53	49.01
Hg (ppm)	0.90	2.22
Mn (ppm)	NC	NA
Mo (ppm)	209.62	14.58
Ni (ppm)	1434.65	12.11
Pb (ppm)	68.39	6.71
Sb (ppm)	NC	NA
Se (ppm)	< 2	NA
Sr (ppm)	NC	NA
V (ppm)	5918.81	12.87
Zn (ppm)	174.51	19.09

7. Chemical composition of kiln feed

Table 7.1: CPR - Chemical composition of kiln feed

Property (wt. %)	Average	C. V. (%)
Al_2O_3	3.21	0.9
CaO	43.02	0.6
Fe_2O_3	2.19	1.9
K_2O	0.37	3.1
MgO	2.00	2.3
Na_2O	0.06	9.3
Na_2O_{eq}	0.31	4.3
P_2O_5	0.05	0.00
SiO_2	13.60	1.0
SO_3	0.17	13.9

Table 7.2: ELR - Chemical composition of kiln feed

Property	**Average**
Al_2O_3 (wt. %)	3.12
CaO (wt. %)	43.11
Fe_2O_3 (wt. %)	2.24
K_2O (wt. %)	0.34
MgO (wt. %)	2.14
Na_2O (wt. %)	0.05
P_2O_5 (wt. %)	0.03
SiO_2 (wt. %)	13.69
SO_3 (wt. %)	0.14
TiO_2 (wt. %)	0.12
Moisture (wt. %)	0.12
LOI (wt. %)	34.83
As (ppm)	26
Ba (ppm)	NC
Cd (ppm)	< 5
Cl (ppm)	48
Co (ppm)	19
Cr (ppm)	544
Cu (ppm)	339
Hg (ppm)	3.00
Mn (ppm)	NC
Mo (ppm)	4
Ni (ppm)	29
Pb (ppm)	17
Sb (ppm)	NC
Se (ppm)	< 2
Sr (ppm)	NC
V (ppm)	58
Zn (ppm)	131

8. Chemical composition of cement kiln dust

Table 8.1: CPR - Chemical composition of cement kiln dust

Property	Average (wt. %)	C. V. (%)
Al_2O_3	3.64	10.61
CaO	46.79	6.46
Fe_2O_3	1.79	11.33
K_2O	0.44	9.39
MgO	1.74	18.26
Na_2O	0.07	15.06
SiO_2	11.48	9.19
SO_3	0.69	86.24

Table 8.2: ELR - Chemical composition of cement kiln dust

Property	**Average**	**C.V. (%)**
Al_2O_3 (wt. %)	3.64	3.79
CaO (wt. %)	48.11	5.39
Fe_2O_3 (wt. %)	1.80	5.66
K_2O (wt. %)	0.41	18.43
MgO (wt. %)	1.70	11.36
Na_2O (wt. %)	0.08	7.59
P_2O_5 (wt. %)	0.04	10.65
SiO_2 (wt. %)	10.61	4.97
SO_3 (wt. %)	0.62	43.45
TiO_2 (wt. %)	0.14	5.85
Moisture (wt. %)	0.18	43.17
LOI (wt. %)	32.70	9.74
As (ppm)	36.00	25.48
Ba (ppm)	NA	NA
Cd (ppm)	< 5	NA
Cl (ppm)	176.67	61.02
Co (ppm)	16.50	19.32
Cr (ppm)	421.17	18.92
Cu (ppm)	422.33	32.18
Hg (ppm)	0.10	74.54
Mn (ppm)	NC	NA
Mo (ppm)	3.17	29.48
Ni (ppm)	22.17	13.13
Pb (ppm)	20.80	89.38
Sb (ppm)	NC	NA
Se (ppm)	4.00	NA
Sr (ppm)	NC	NA
V (ppm)	58.33	9.74
Zn (ppm)	127.17	19.45

9. Chemical composition of clinker

Table 9.1: CPR - Chemical composition of clinker

Property (wt. %)	Average (wt %)	C.V. (%)
Al_2O_3	5.14	6.1
CaO	63.32	4.1
Fe_2O_3	3.38	4.7
K_2O	0.59	8.9
MgO	3.02	7.3
Na_2O	0.12	14.8
Na_2O_{eq}	0.50	9.0
SiO_2	20.94	4.5
SO_3	1.24	31.1
F CaO	1.27	64.6
C_3S	59.28	6.7
C_2S	15.31	25.4
C_3A	7.90	7.3
C_4AF	10.29	4.7

Table 9.2: ELR - Chemical composition of clinker

Property	Average	C.V. (%)
Al_2O_3 (wt. %)	5.04	6.09
CaO (wt. %)	64.61	0.39
Fe_2O_3 (wt. %)	3.41	6.42
K_2O (wt. %)	0.56	10.15
MgO (wt. %)	3.41	2.34
Na_2O (wt. %)	0.07	19.39
P_2O_5 (wt. %)	0.06	8.56
SiO_2 (wt. %)	20.96	1.18
SO_3 (wt. %)	1.40	16.94
TiO_2 (wt. %)	0.18	12.60
Moisture (wt. %)	0.05	11.77
LOI (wt. %)	0.04	499.94
As (ppm)	29.00	5.63
Ba (ppm)	NC	NA
Cd (ppm)	< 5	NA
Cl (ppm)	175.00	35.27
Co (ppm)	18.00	13.61
Cr (ppm)	458.00	9.17
Cu (ppm)	87.00	259.58
Hg (ppm)	0.01	0.00
Mn (ppm)	NC	NA
Mo (ppm)	10.00	20.62
Ni (ppm)	31.00	23.70
Pb (ppm)	17.00	38.27
Sb (ppm)	NC	NA
Se (ppm)	< 2	NA
Sr (ppm)	NC	NA
V (ppm)	95.00	27.72
Zn (ppm)	119.00	27.22

Table 9.3: SLR – Rietveld analysis of clinker

Property	Value (wt. %)	C.V. (%)
Alite (C_3S)	56.49	6.07
Belite (C_2S)	24.72	9.91
Aluminate (C_3A)	3.36	12.82
Ferrite (C_4AF)	11.27	2.33

10. Chemical composition of cement

Table 10.1: CPR - Chemical Composition of Cement

Property	Average (wt. %)	C. V. (%)
Al_2O_3	4.80	2.5
CaO	63.11	0.5
CO_2	1.30	0.0
Fe_2O_3	3.23	1.8
K_2O	0.53	4.4
MgO	2.78	2.8
Na_2O	0.11	5.1
Na_2O_{eq}	0.46	3.8
SiO_2	20.16	0.7
SO_3	3.20	7.8
F CaO	1.08	38.2
LOI	2.17	7.0
C_3S	50.99	5.4
C_2S	19.32	12.2
C_3A	7.27	3.1
C_4AF	9.83	1.8
Blaine SSA (m^2/kg)	386	3.2

Table 10.2: ELR – Chemical composition of cement

Property	Average	C.V. (%)
Al_2O_3 (wt. %)	4.82	0.9
CaO (wt. %)	64.05	0.7
Fe_2O_3 (wt. %)	3.30	2.9
K_2O (wt. %)	0.46	5.5
MgO (wt. %)	3.17	1.7
Na_2O (wt. %)	0.10	25.7
P_2O_5 (wt. %)	0.05	1.4
SiO_2 (wt. %)	20.01	1.4
SO_3 (wt. %)	3.01	7.9
TiO_2 (wt. %)	0.17	9.9
Moisture (wt. %)	0.00	0.0
LOI (wt. %)	0.60	21.9
C_3S (wt. %)	56.24	8.2
C_2S (wt. %)	14.94	28.7
C_3A (wt. %)	7.20	2.8
C_4AF (wt. %)	10.04	2.9
TOC (wt. %)	0.35	12.4
As (ppm)	21.7	18.7
Ba (ppm)	NC	NA
Cd (ppm)	< 5	NA
Cl (ppm)	NC	NA
Co (ppm)	16.3	12.7
Cr (ppm)	485.0	10.4
Cu (ppm)	237.3	97.6
Hg (ppm)	NC	NA
Mn (ppm)	NC	NA
Mo (ppm)	NC	NA
Ni (ppm)	30.7	5.0
Pb (ppm)	15.3	39.8
Sb (ppm)	NC	NA
Se (ppm)	< 2	NA
Sr (ppm)	NC	NA
V (ppm)	94.0	6.4
Zn (ppm)	148.0	12.3

Table 10.3: SLR – Rietveld analysis of cement

Property	**Value (wt. %)**	**C.V. (%)**
Alite (C_3S)	52.91	2.27
Belite (C_2S)	23.49	4.83
Aluminate (C_3A)	3.34	5.63
Ferrite (C_4AF)	10.83	3.19

11. Physical properties of cement

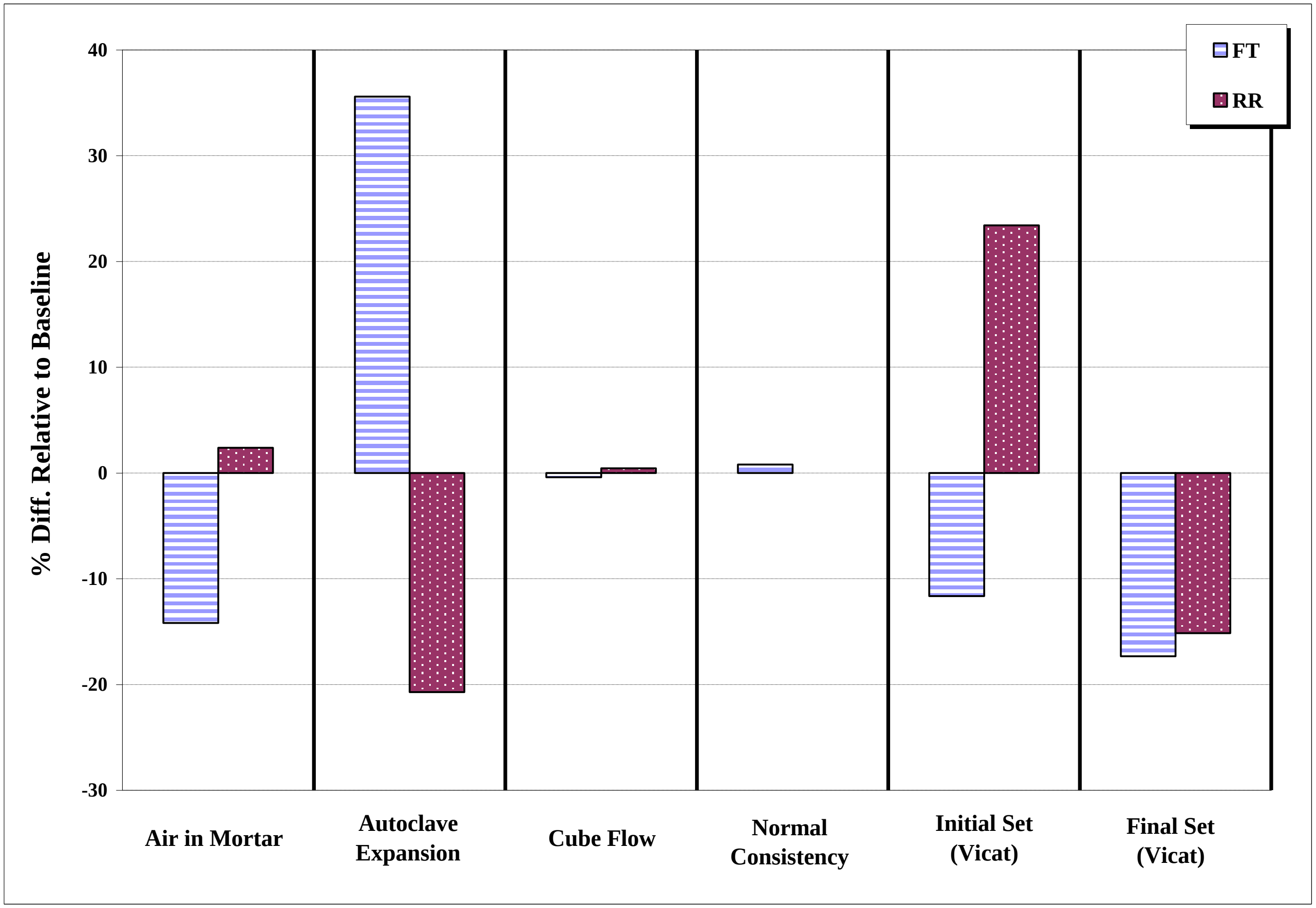


Figure 11.1: CPR – Physical properties of cement

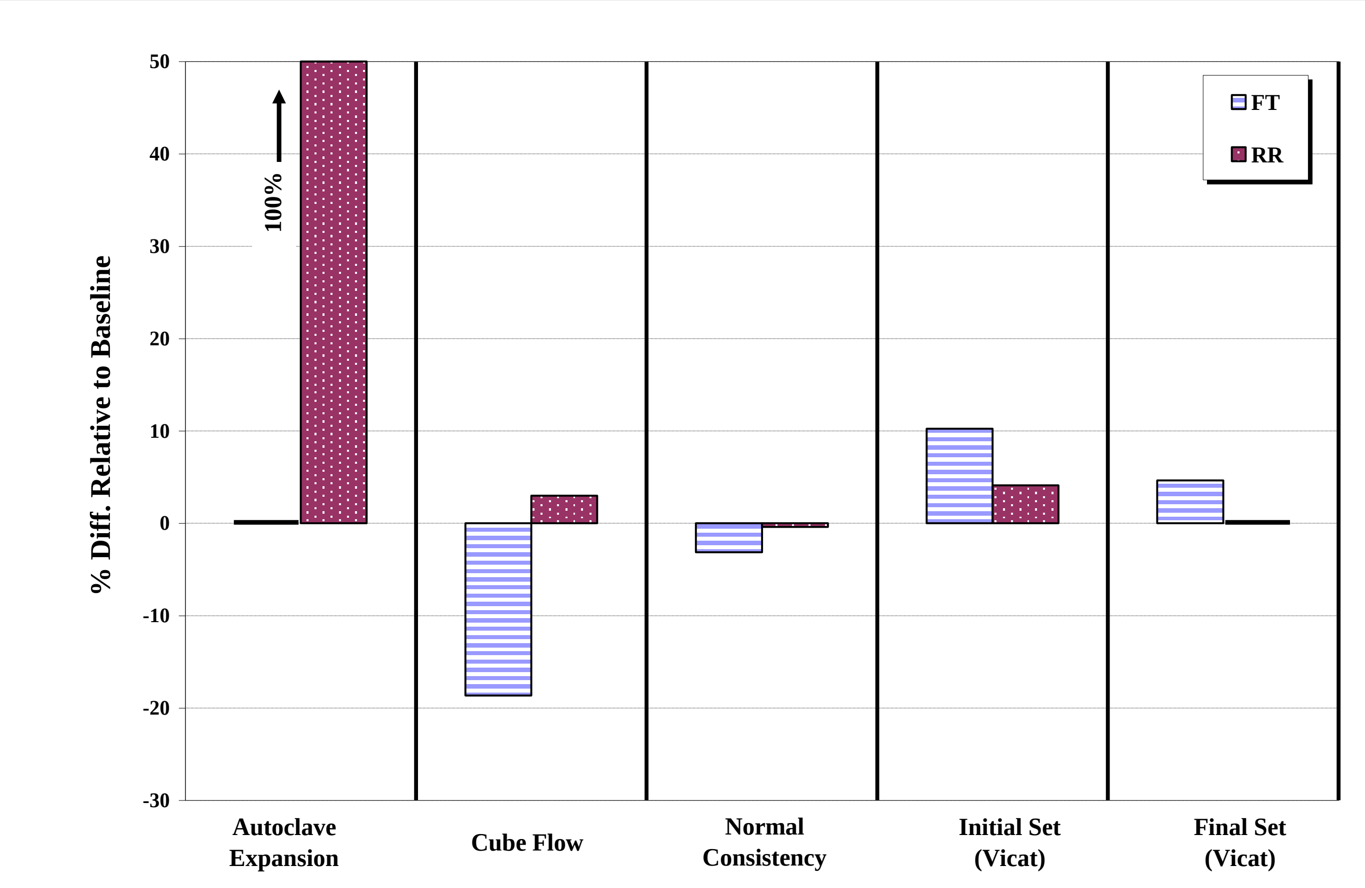


Figure 11.2: AUR – Physical properties of cement

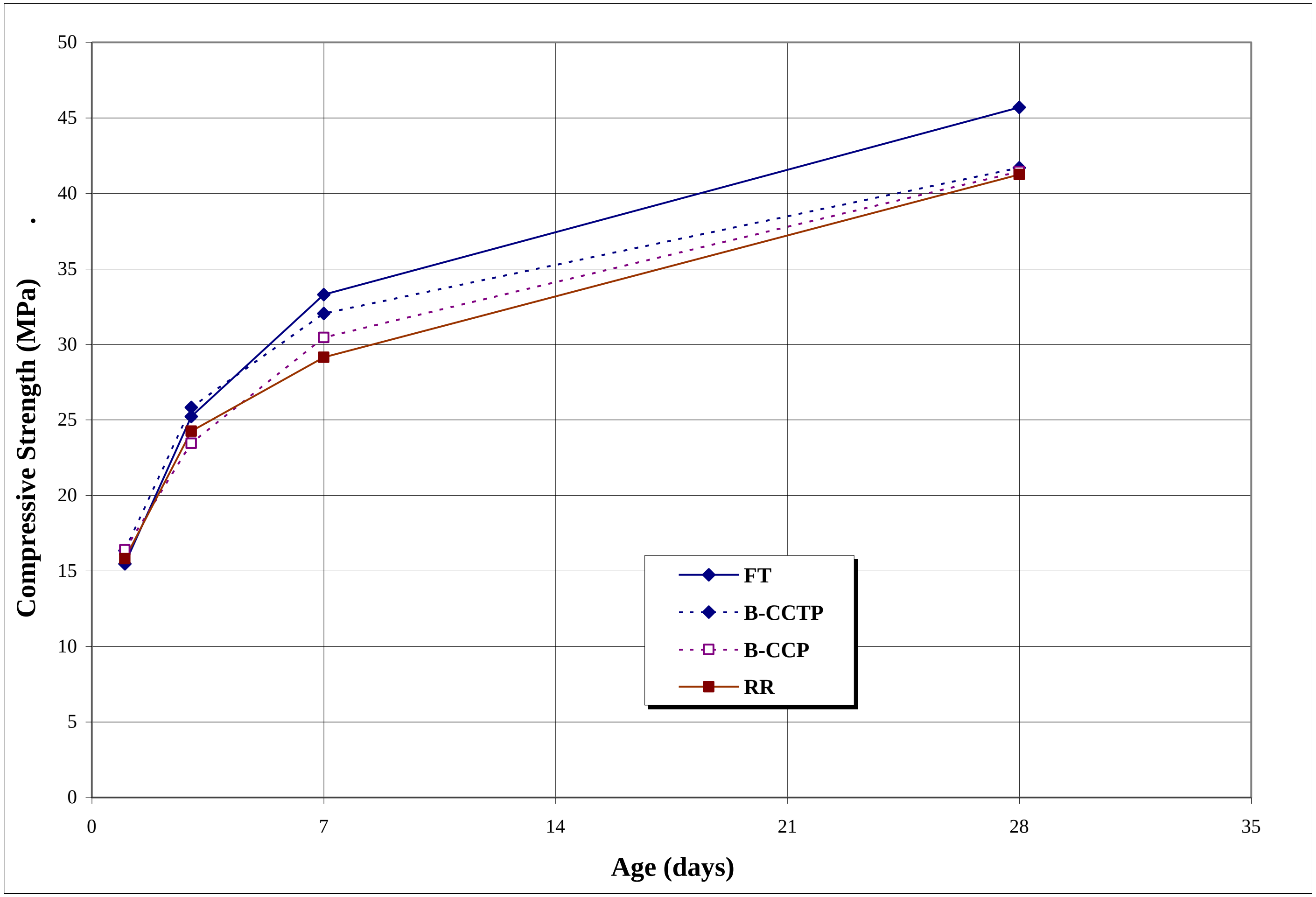


Figure 11.3: CPR – Cement mortar compressive strength

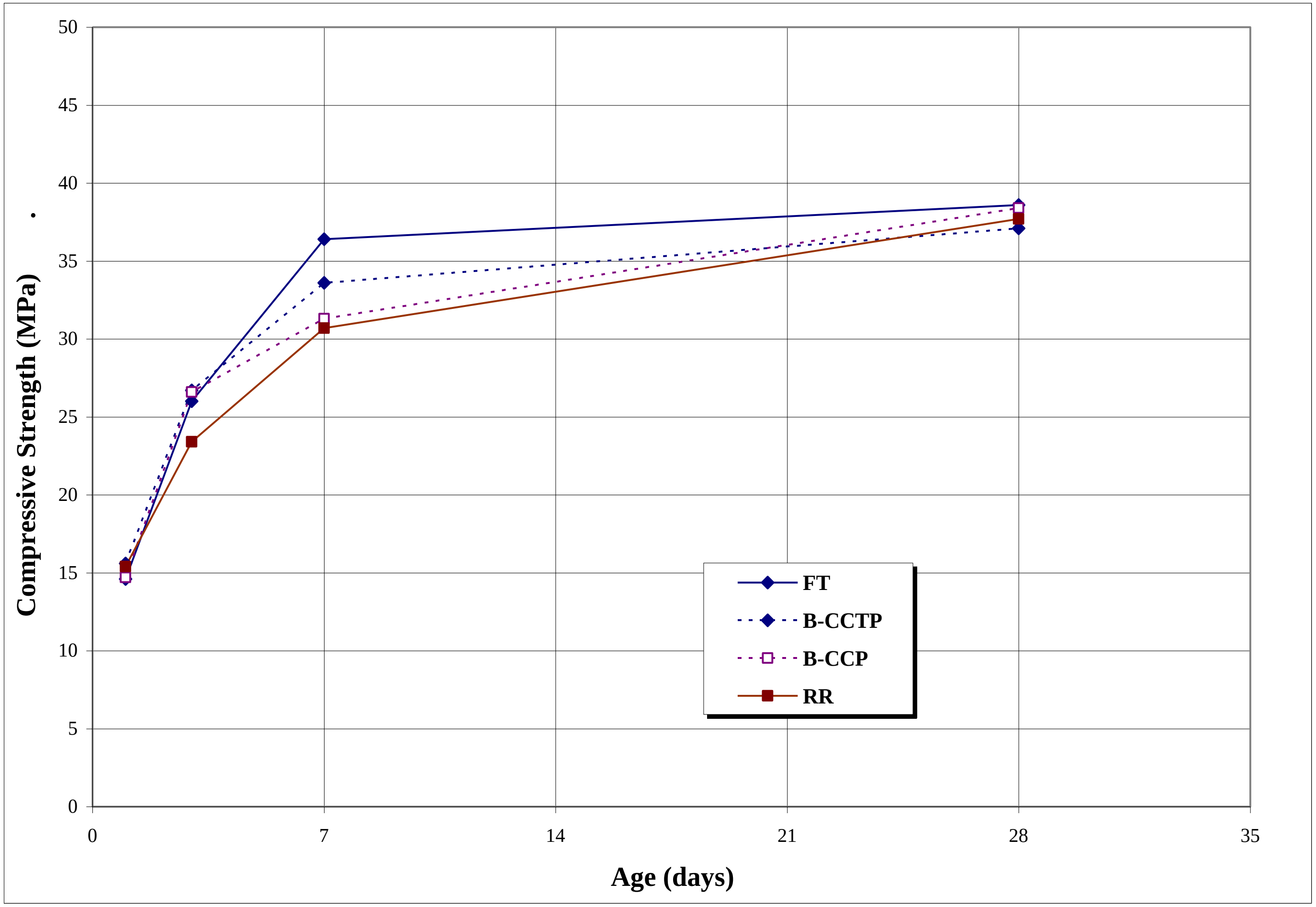


Figure 11.4: AUR – Cement mortar compressive strength

12. Physical properties of concrete

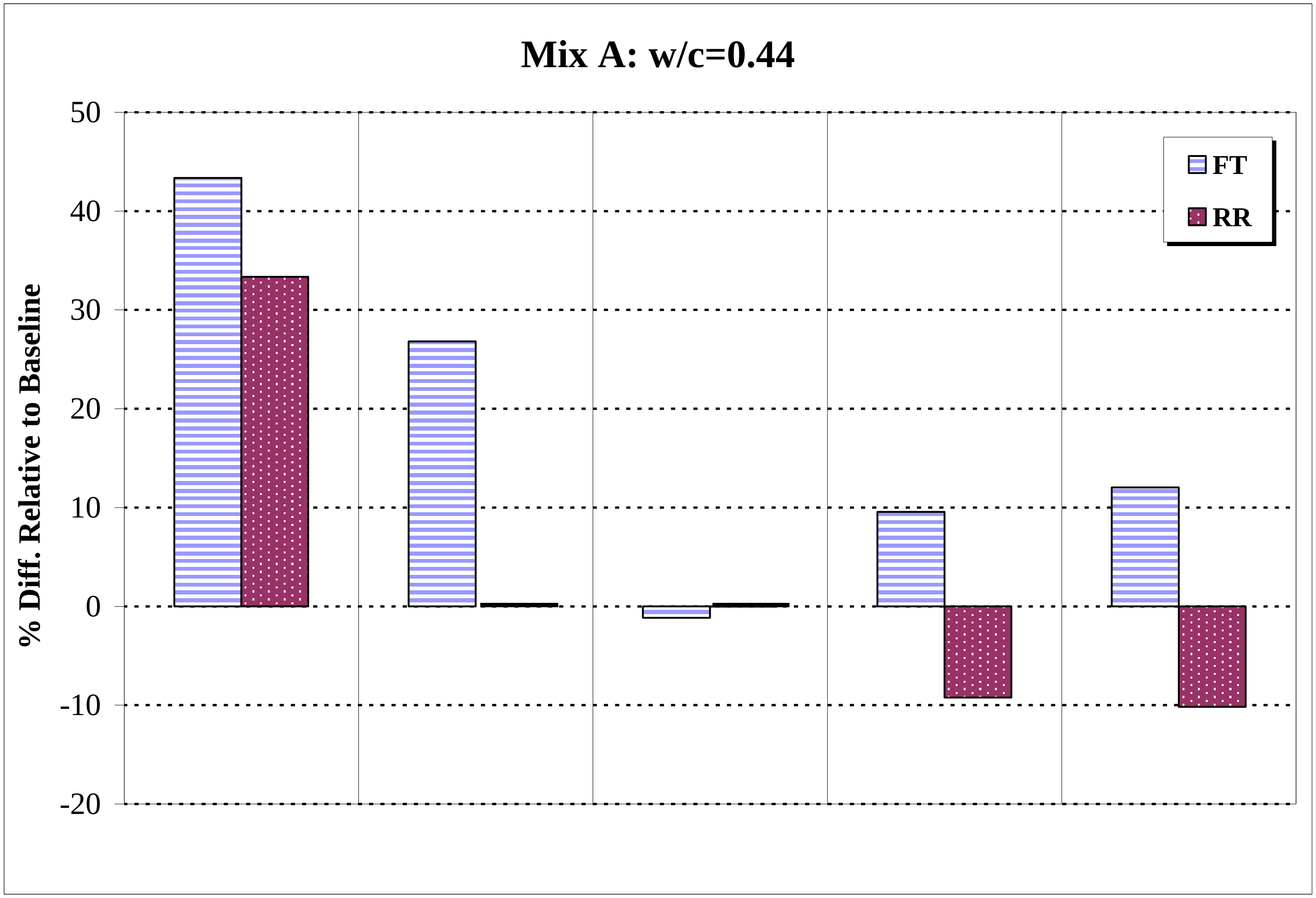


Figure 12.1: AUR – Physical properties of concrete (Mix A: w/c=0.44)

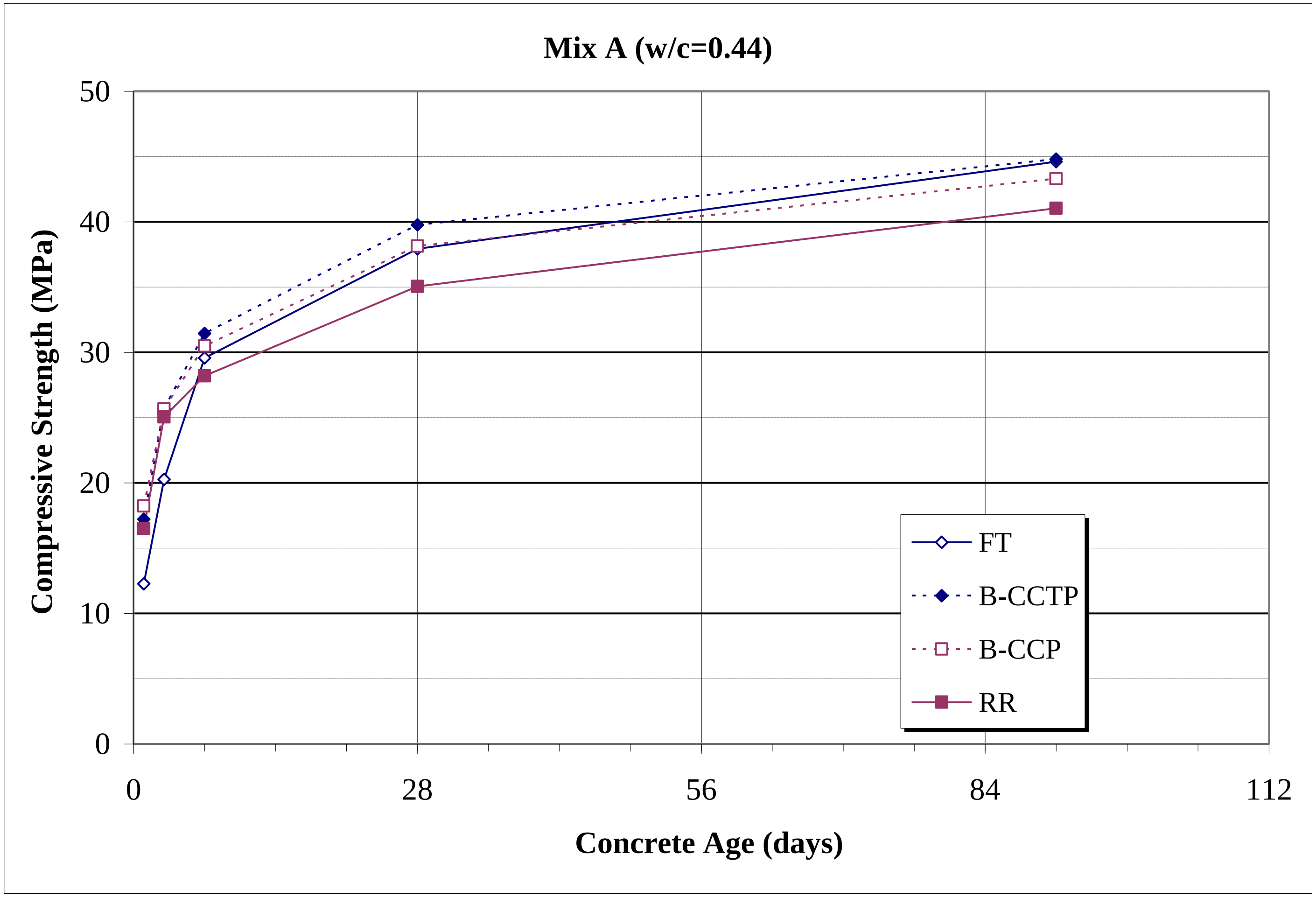


Figure 12.2: AUR – Compressive strength of concrete (Mix A: w/c=0.44)

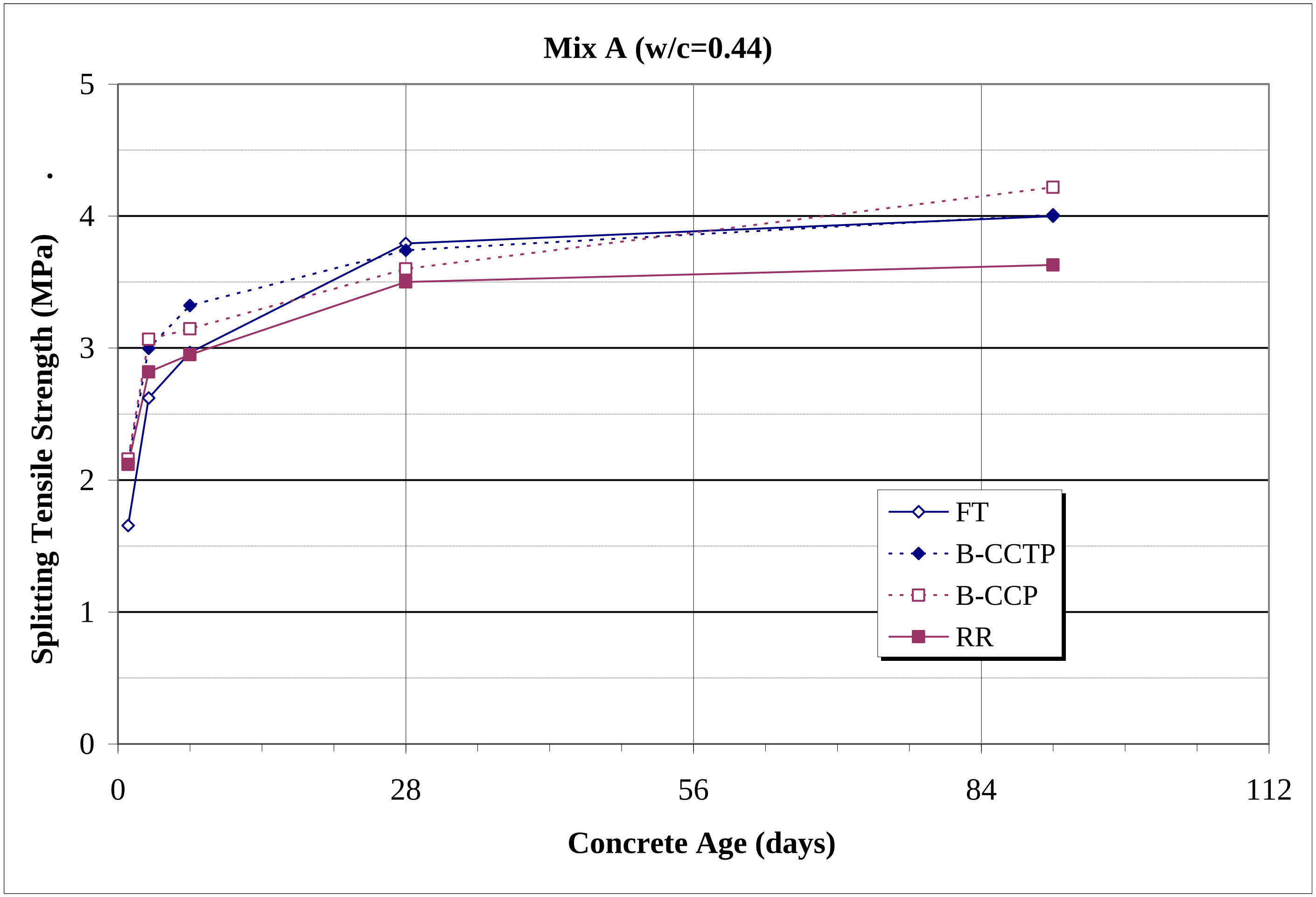


Figure 12.3: AUR – Splitting tensile strength of concrete (Mix A: w/c=0.44)

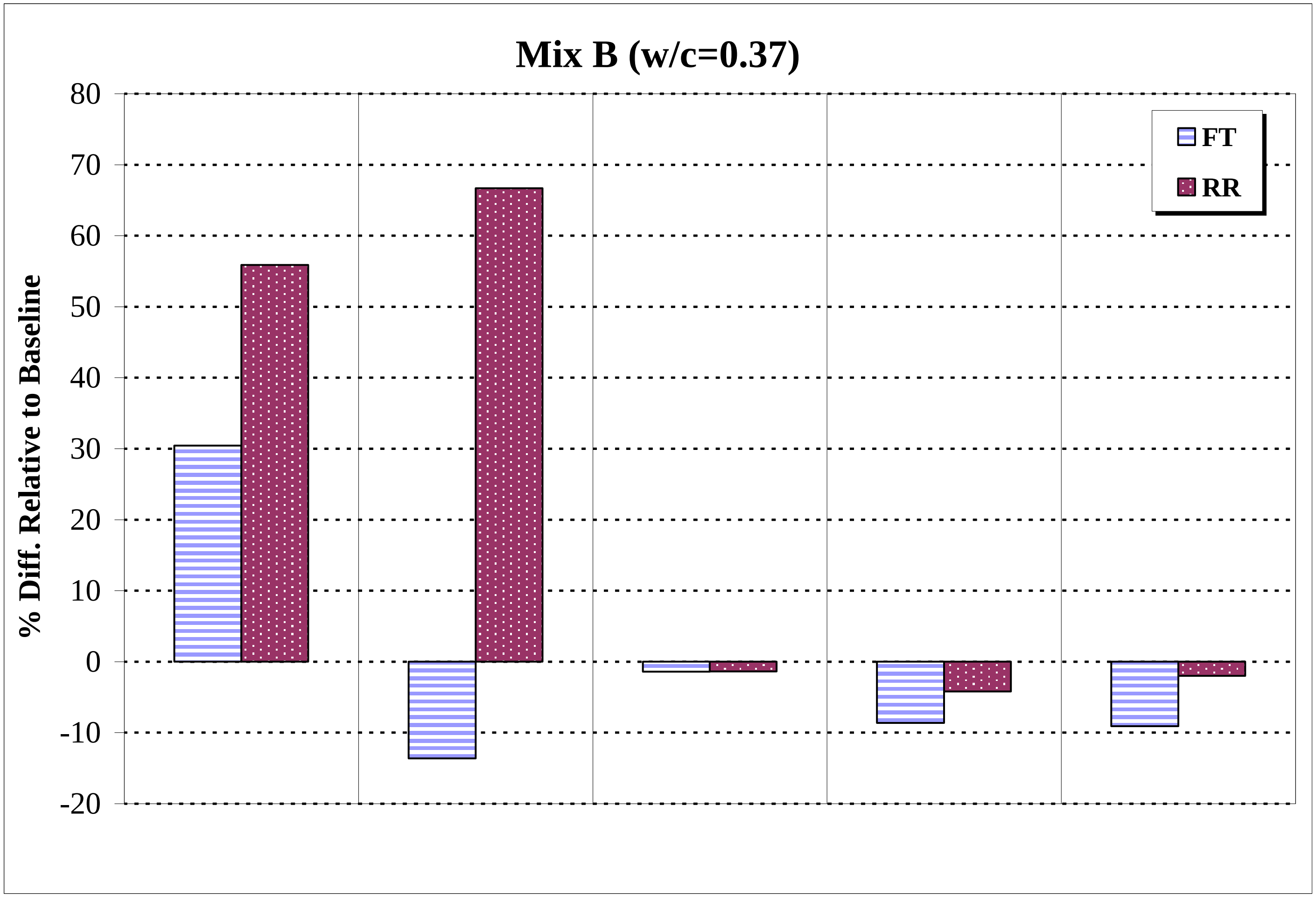


Figure 12.4: AUR – Physical properties of concrete (Mix B: w/c=0.37)

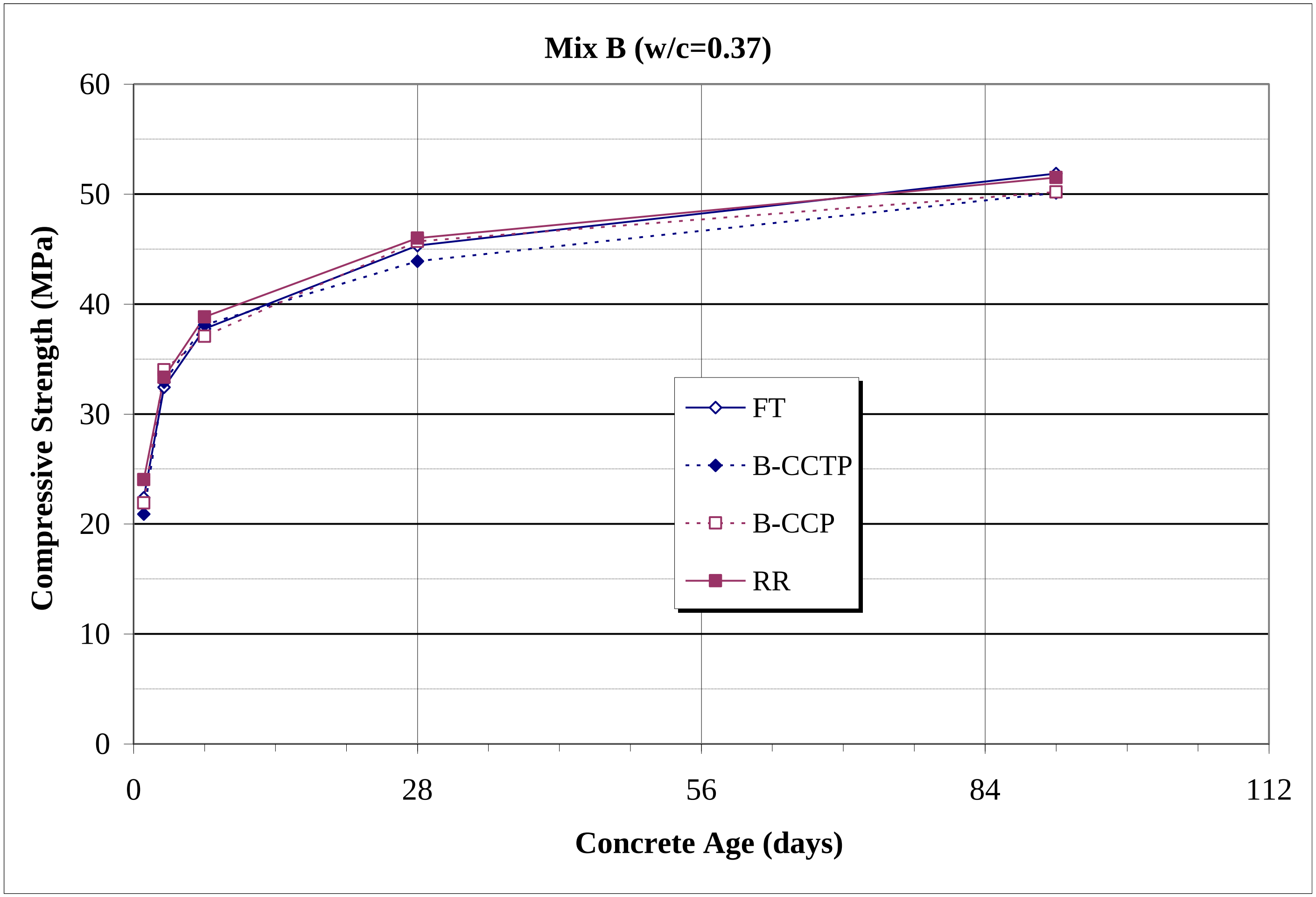


Figure 12.5: AUR – Compressive strength of concrete (Mix B: w/c=0.37)

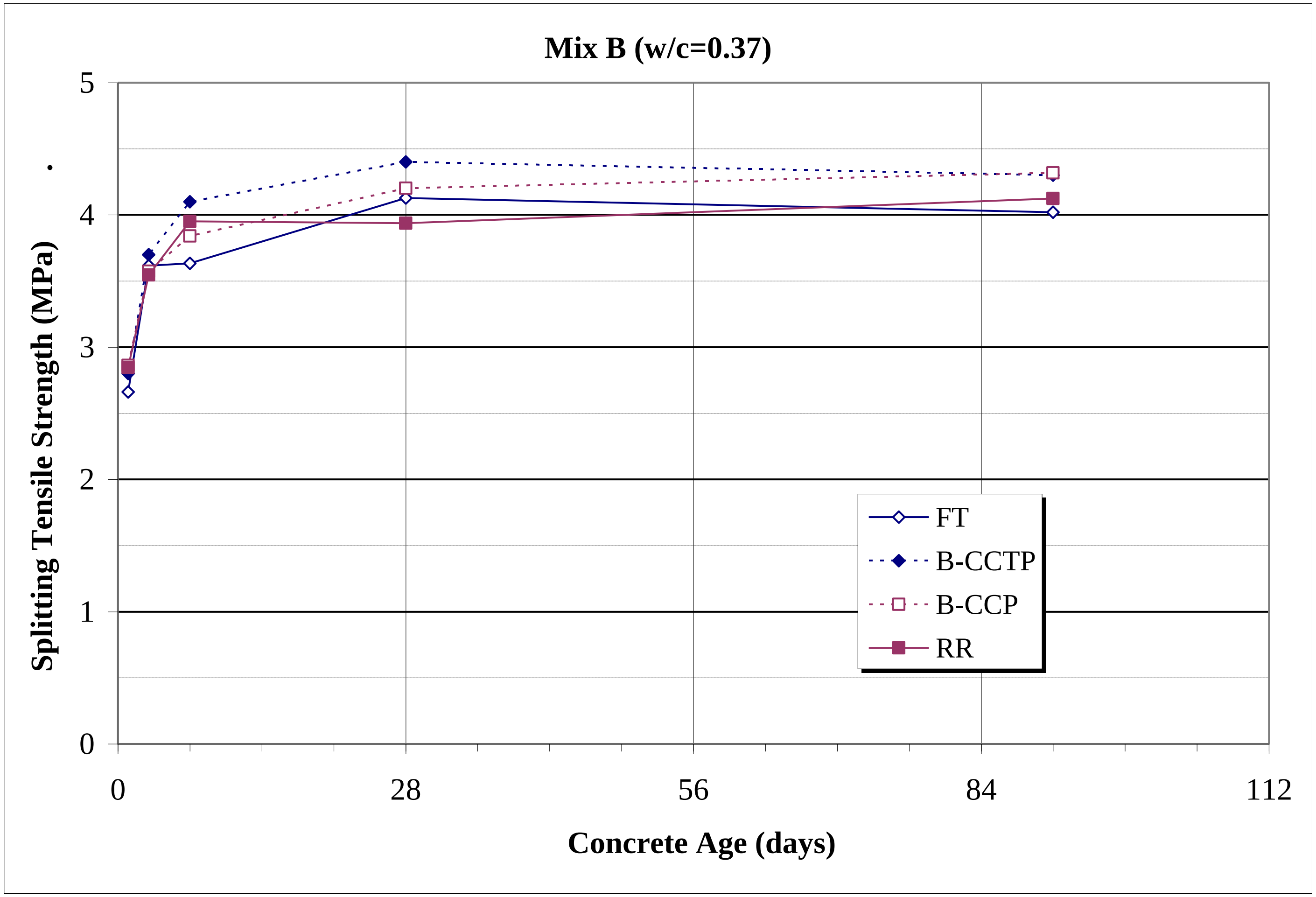


Figure 12.6: AUR – Splitting tensile strength of concrete (Mix B: w/c=0.37)

13. Plant emissions

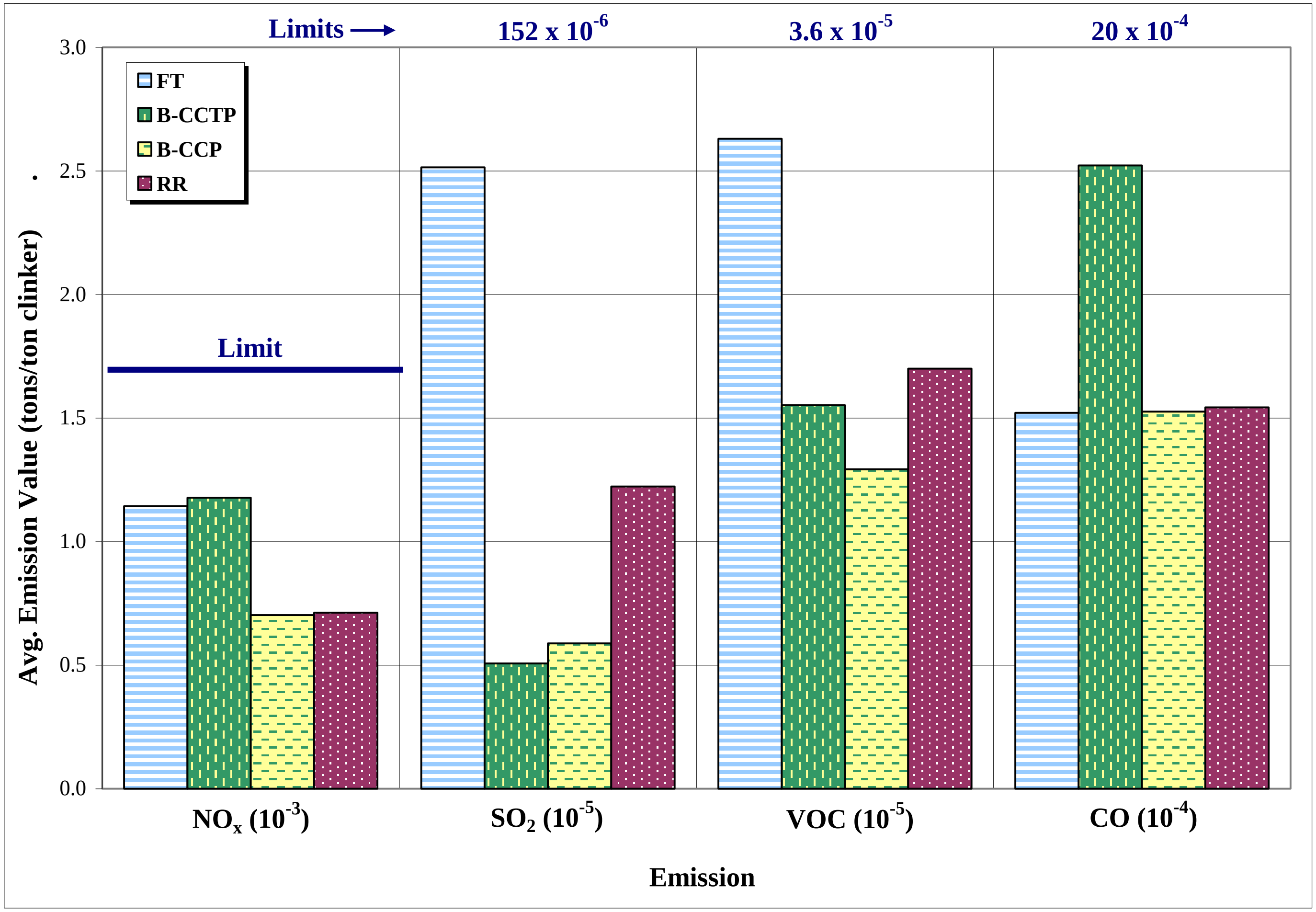


Figure 13.1: CPR – Comparison of average emission values