

Fate of trace elements in energy recovery from recycled paper sludge

J. JEFFERSON GREGG, AMY K. ZANDER, AND THOMAS L. THEIS

WASTE SLUDGE FROM PAPER production is a global disposal problem. In the United States, paper mills produce more than four billion dry kilograms of sludge each year. Paper mills around the world are searching for alternative methods of waste volume reduction and disposal. Although landfill disposal remains the most common disposal method, the large waste volume, increasing landfill tipping fees, and decreasing landfill space make this option increasingly unattractive. Combustion or incineration of dried paper sludge are possible options, but they entail meeting air quality regulations and ash disposal.

The manufacture of paper products from recycled paper has additional waste disposal concerns. Paper production from recycled paper produces approximately 440 kg of sludge per metric ton of finished paper. Virgin paper production produces approximately 190 kg per metric ton of finished paper (1). Recycled paper contains inks, clay fillers, brighteners, bleaching agents, and other contaminants not found in virgin materials that bear trace elements. Concern exists in combustion or incineration of sludge from a recycled paper manufacturing process about the fate of trace elemental species and the composition of the ashes produced.

The objective of this project was to determine the fate of trace metals for combustion in an institutional boiler of pelletized sludge from a paper plant using 100% recycled paper. Determination of technical feasibility includes establishing the fate of the trace

elemental species during combustion. The sludge pellets underwent co-combustion with wood chips following an order from the New York State Department of Environmental Conservation (NYSDEC). The concentration of trace elemental species was measured in the pellets and wood chips fed to the boiler, the air emissions from the boiler, and in the bottom and fly ashes produced. The fate of the trace elements was analyzed to determine compliance with applicable regulations.

MATERIALS AND METHODS

Sludge characteristics

The James River mill in Carthage, NY, produces two grades of paper resulting in two types of sludge—unbleached and semi-bleached. The unbleached sludge has brown color and consists of 30% clean clippings—20% each of corrugated cardboard, office wastepaper, and flyleaf and 10% mill ends. The semi-bleached sludge is not bleached at the plant but consists of some materials previously bleached. It is light gray and consists of 20% each of computer paper, colored register tape, office wastepaper, and bleached white newspaper, 10% mill ends, and the remainder foil paper and flyleaf (2). Following primary settling of paper making wastewater, the sludge underwent processing in a screw press to approximately 45% moisture content with delivery to Clarkson University in drums for processing into pellets.

Pelletization

A die-and-roller pelletizer (California Pellet Mill Co.) was retrofitted to process the sludge into pellets 6 mm in

SLUDGE BURNING

ABSTRACT

The authors tracked the fate of trace elements of concern in the energy recovery from sludges created by the processing of 100% recycled paper throughout sludge co-combustion with wood chips in an institutional boiler. Ash produced was not a characteristic hazardous waste. Air emissions were significantly below concentrations that would deem the source major under NE-SHAP. Trace elements in air emissions comprised less than 0.15% of the total trace element mass transported from the system.

Application:

Disposal of paper sludge is a serious concern in mill operations especially for sludge from recycled paper processing. This work investigates combustion in an institutional boiler as a method of volume reduction and energy recovery from the sludge.

diameter and 0.6–2.5 cm in length. The pellets were dried in a conveyor oven to approximately 17% moisture and stored in sacks until needed.

Combustion

Energy recovery used an institutional multi-fuel boiler (OptiMizer, Bethlehem Corp.) serving part of the Clarkson University campus. The boiler was installed in 1981. It has a rated capacity of 5000 kg/h saturated steam at 850 kPa. Under normal operating conditions, the boiler combusts wood chips obtained from various logging and saw mill operations. Exhaust gases from the boiler discharge to the atmosphere through a single stack approximately 21 m above grade. Before discharge, the exhaust gases pass through two multi-stage cyclones in series (Zurn, Inc., Birmingham, AL). Each cyclone has a design capacity of approximately 125 actual m³/min and a maximum operating temperature of 200°C.

There were eight test burns: two with wood chips alone, two with un-

Trace element	Unbleached pellets, mg/kg	CV	Semi-bleached, mg/kg	CV	Wood chips, mg/kg	CV
Antimony	< 0.16	-	< 0.16	-	< 0.16	-
Arsenic	0.61 ± 1.2	1.9	0.67 ± 1.4	2.1	< 0.08	-
Barium	< 20	-	20 ± 14	0.7	< 20	-
Beryllium	< 0.03	-	< 0.03	-	< 0.03	-
Cadmium	0.20 ± 0.11	0.55	0.12 ± 0.05	0.41	0.36 ± 5.9	15
Chromium	7.50 ± 3.5	0.47	6.6 ± 1.7	0.25	0.70 ± 0.16	0.22
Cobalt	0.64 ± 0.17	0.26	0.47 ± 0.12	0.25	< 0.03	-
Copper	35 ± 11	0.31	41 ± 22	0.53	1.1 ± 0.69	0.63
Lead	6.4 ± 2.3	0.35	5.1 ± 1.3	0.25	< 0.1	-
Manganese	3.8 ± 6.6	1.7	14 ± 4.4	0.31	78 ± 31	0.39
Nickel	8.5 ± 7.2	0.84	5.2 ± 2.3	0.44	< 0.09	-
Selenium	0.62 ± 0.03	0.05	0.56 ± 0.05	0.09	0.62 ± 0.05	0.08
Thallium	< 0.13	-	< 0.13	-	< 0.13	-
Vanadium	5.4 ± 1.3	0.24	6.5 ± 2.9	0.44	0.57 ± 0.33	0.57
Zinc	180 ± 42	0.23	140 ± 50	0.35	9.0 ± 3.8	0.42

I. Trace element concentration in each fuel

Trace wood element	% in pellets	% in wood chips	Trace element	% in pellets	% in chips
Antimony	12	88	Lead	100	0
Arsenic	99	10	Manganese	2	98
Barium	9	91	Nickel	88	12
Beryllium	11	89	Selenium	11	89
Cadmium	4	96	Thallium	11	89
Chromium	55	45	Vanadium	60	40
Cobalt	55	45	Zinc	68	32
Copper	83	17			

II. Average mass percentage contribution of each fuel to input of each trace element

bleached pellets co-fired with wood chips in an 8:1 wood chip to pellet ratio by mass, and four with semi-bleached pellets co-fired with wood chips in the same ratio. NYSDEC set the ratio due to the unknown nature of the emissions in this project. This system used normal combustion temperatures of 500–650°C. These are much lower than typical incineration temperatures of approximately 1000°C and below wastewater sludge incineration temperatures of 750–850°C.

Sampling and analysis

Representative samples of wood chips, semi-bleached pellets, unbleached pellets, and bottom and fly ashes from each test burn were collected according to ASTM method E 725-86 (3,4). Samples were digested by U.S.

Environmental Protection Agency (USEPA) method 3050 and the digestate tested for antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, selenium, thallium, vanadium, and zinc. Except barium, zinc, and higher concentrations of manganese, all trace element analyses used electrothermal atomic absorption spectrophotometry (Perkin Elmer Zeeman 5000 Atomic Absorption Spectrophotometer (AAS) with a HGA-400 furnace and an AS40 autosampler) according to method 3113B. Analyses for zinc and manganese used direct air-acetylene flame atomic absorption of method 3111B and for barium used direct nitrous oxide-acetylene flame atomic absorption of method 3111D.

Ash was removed from the boiler and cyclones manually following each test burn. The ash was weighed, and the ash generation rate determined by dividing the total mass of ash in each category by the time of the test burn.

Air emissions were monitored for the semi-bleached pellet test burns according to USEPA method 29. The sampling and analyses were performed in triplicate by Galson Corporation (East Syracuse, NY). Trace elements analyzed in air emissions were specified by NYSDEC and consisted of antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, nickel, selenium, thallium, and zinc.

Ash composition was examined using electron microscopy (Jeol JSM-6300 Scanning Microscope, Tokyo) with energy dispersive X-ray spectroscopy (Noran Instruments Voyager, Middleton, WI) and by powdered X-ray diffraction (Siemens D500, Germany).

The toxicity characteristic leaching procedure (TCLP) was performed on ash samples as outlined in 40 CFR 261, appendix II. As prescribed by the procedure, acidic extraction fluid no. 2 was used due to the alkaline nature of the ashes. Leachate analysis was performed by atomic absorption spectroscopy (AAS) as shown above.

Trace element	Fly ash from unbleached pellets co-fired with wood chips, mg/kg	CV	Fly ash from semi-bleached pellets co-fired with wood chips, mg/kg	CV	Fly ash from wood chips, mg/kg	CV
Antimony	0.42 ± 0.11	0.26	0.53 ± 0.23	0.43	< 0.34	-
Arsenic	< 0.08	-	< 0.08	-	2.5 ± 0.62	0.25
Barium	1300 ± 120	0.09	990 ± 460	0.46	3000 ± 410	0.14
Beryllium	0.16 ± 0.08	0.5	0.85 ± 0.22	0.25	< 0.17	-
Cadmium	19 ± 0.01	0.01	18 ± 3.5	0.19	21 ± 0.45	0.02
Chromium	21 ± 2.9	0.13	30 ± 8.2	0.27	5.6 ± 0.71	0.13
Cobalt	3.0 ± 0.12	0.04	3.3 ± 0.27	0.08	1.8 ± 0.57	0.32
Copper	150 ± 6.0	0.04	140 ± 47	0.33	82 ± 0.49	0.01
Lead	34 ± 2.4	0.07	22 ± 2.4	0.11	7.8 ± 3.3	0.42
Manganese	3400 ± 130	0.04	3200 ± 310	0.09	2400 ± 500	0.20
Nickel	41 ± 2.8	0.07	28 ± 1.5	0.05	13 ± 2.4	0.18
Selenium	< 0.41	-	< 0.41	-	< 0.41	-
Thallium	< 0.68	-	< 0.68	-	< 0.68	-
Vanadium	28 ± 0.99	0.04	42 ± 7.4	0.17	6.4 ± 0.42	0.06
Zinc	530 ± 33	0.06	500 ± 35	0.07	510 ± 70	0.14

III. Mean trace element concentrations in fly ashes

RESULTS AND DISCUSSION

Trace elements in fuels

Table I shows trace element concentrations in mg/kg dry mass for each of the fuel sources to the institutional boiler. The values represent the mean ($\pm$ the standard deviation) of four to eight replicate analyses of each fuel type. The coefficient of variation (CV) that is equal to the ratio of the standard deviation to the mean is given for each set of replicates. As **Table I** shows, the concentration of trace elemental species in the pellets is similar to those in wood chips for antimony, barium, beryllium, selenium, and thallium. Trace elements for which a higher concentration could be measured in the pelletized sludge than in wood chips are arsenic, chromium, cobalt, copper, lead, nickel, vanadium, and zinc. Except vanadium, all these trace elements are present in printing inks or recycled paper (6,7). Other possible sources of these elements include minor impurities in fillers and additives and makeup water for the repulping and papermaking processes.

Table II presents the average mass percentage of the total trace element loading to the system provided by semi-bleached pellets as compared to

wood chips. The eight to one wood chip to pellet ratio imposed upon the test burns resulted in wood contributing 88% by mass of the inputs and pellets contributing 12%. A contribution greater than 12% by the pellets means a given trace element is enriched in the semi-bleached pellets over wood. This is the case for each of the previously listed trace elements.

Ash production

Much greater quantities of ash were produced in the test burns of the pellets co-fired with wood chips than for wood chips alone. The average rate of ash production for wood chips was 1.2 kg/h of fly ash and 1.0 kg/h of bottom ash. One can contrast this with burns of wood chips plus unbleached sludge pellets in which fly ash was produced at the rate of 3.1 kg/h and bottom ash at the rate of 2.2 kg/h and wood chips plus semi-bleached pellets that averaged 3.3 ± 1.2 kg/h of fly ash and 9.0 ± 2.9 kg/h of bottom ash. This copious rate of bottom ash production for the semi-bleached sludge pellet combustion is likely due to clay fillers used in bleached papers.

Ash composition

Several mineral species were identified in the ash formed in the test burns by

X-ray diffraction. These include calcium carbonate, calcium oxide, titanium dioxide, and an aluminosilicate that is most likely kaolinite. Calcium carbonate and kaolin clays are common brighteners in papermaking (8). Titanium dioxide is less common due to its expense. Calcium oxide is likely present from decomposition of calcium carbonate in localized high temperature regions in the boiler.

X-ray microanalysis of the spherical ash particles revealed their most common elements. These were aluminum, silica, calcium, potassium, oxygen, magnesium, titanium, and carbon. Notably absent from this list is iron found in abundance in coal, municipal solid waste, and wastewater treatment sludge ashes (9,10). With this exception, the ashes produced in this study were similar in major elemental composition to other types of ashes.

Trace elements in fly and bottom ash

Table III gives the concentration of measured trace elemental species in fly ashes from the test burns. The table presents concentrations in the fly ash from combustion of unbleached pellets mixed with wood chips, semi-bleached pellets mixed with wood

Trace element	Bottom ash from unbleached pellets co-fired with wood chips, mg/kg	CV	Bottom ash from semi-bleached pellets co-fired with wood chips, mg/kg	CV	Bottom ash from wood chips, mg/kg	CV
Antimony	0.90 ± 0.08	0.09	0.92 ± 0.47	0.51	< 0.34	-
Arsenic	< 0.08	-	< 0.08	-	3.5 ± 0.09	0.03
Barium	870 ± 120	0.13	420 ± 110	0.26	2300 ± 120	0.05
Beryllium	0.14 ± 0.11	0.78	1.2 ± 0.38	0.32	< 0.17	-
Cadmium	11 ± 2.0	0.18	7.1 ± 2.3	0.32	15 ± 2.3	0.15
Chromium	21 ± 0.4	0.02	35 ± 5.8	0.16	5.6 ± 0.71	0.04
Cobalt	3.2 ± 0.01	0.01	4.2 ± 0.22	0.05	2.7 ± 0.10	0.04
Copper	160 ± 18	0.11	120 ± 21	0.18	240 ± 31	0.12
Lead	25 ± 5.1	0.21	15 ± 1.6	0.11	19 ± 13	0.68
Manganese	3500 ± 860	0.25	4200 ± 390	0.09	3100 ± 16	0.01
Nickel	68 ± 3.8	0.05	38 ± 11	0.29	15 ± 1.1	0.07
Selenium	< 0.41	-	< 0.41	-	< 0.41	-
Thallium	< 0.68	-	< 0.68	-	< 0.68	-
Vanadium	43 ± 0.06	0.01	58 ± 4.1	0.07	14 ± 1.3	0.09
Zinc	420 ± 35	0.08	380 ± 12	0.03	640 ± 21	0.03

IV. Mean trace element concentrations in bottom ashes

Trace element	Emission rate, SHAP kg/h	CV	NE-
Antimony	<1.72 × 10<+>-5<+>	-	x
Arsenic	<3.75 × 10<+>-5<+>	-	x
Barium	3.8 × 10<+>-3<+> ± 0.2 × 10<+>-3<+>	0.05	
Beryllium	<3.2 × 10<+>-5<+>	-	x
Cadmium	2.7 × 10<+>-4<+> ± 0.5 × 10<+>-4<+>	0.18	x
Chromium	<7.6 × 10<+>-5<+>	-	x
Cobalt	<4.5 × 10<+>-5<+>	-	x
Copper	5.5 × 10<+>-4<+> ± 1.5 × 10<+>-4<+>	0.27	
Lead	2.2 × 10<+>-4<+> ± 0.3 × 10<+>-4<+>	0.12	x
Nickel	<8.9 × 10<+>-5<+>	-	x
Selenium	3.9 × 10<+>-5<+> ± 0.9 × 10<+>-5<+>	0.23	x
Silver	<3.3 × 10<+>-5<+>	-	
Thallium	<2.4 × 10<+>-5<+>	-	
Zinc	6.2 × 10<+>-3<+> ± 0.7 × 10<+>-3<+>	0.12	

x = considered hazardous under NESHAP

V. Trace elemental air emissions from test burns of semi-bleached pellets with wood chips

chips, and wood chips combusted alone with the coefficients of variation obtained from four samples each of un-

bleached pellet burns and wood chip burns, sixteen samples of semi-bleached pellet burns and wood chip burns, and sixteen samples of semi-bleached pellet burns. **Table IV** shows similar data for bottom ashes. With few exceptions, measured trace elemental concentrations in the fly and bottom ashes from this study were below or within the lower end of a range of concentrations for coal combustion, mu-

nicipal solid waste incineration, and wastewater sludge incineration (10). Barium, cadmium, and manganese were present in the ashes from this study at concentrations greater than in ashes from coal combustion but within the range for ashes from municipal solid waste and wastewater sludge incineration. The enrichment of these species over coal ashes is likely due to the contribution of wood ash to the system.

Trace elemental air emissions

The emission rates of several trace elemental species were measured in triplicate during the test burns of semi-bleached pellets co-combusted with wood chips. NYSDEC determined the species tested. Some are regulated by New York state and some also considered hazardous by the USEPA under the National Emission Standards for Hazardous Air Pollutants (NESHAP) as outlined in section 112 of the Clean Air Act Amendments of 1990. **Table V** lists the emission rates of trace elemental species measured and their coefficients of variation. It also indicates the species considered hazardous under NESHAP. Mercury and manganese are also considered hazardous by the USEPA, but their emissions were not

KEYWORDS

Ash content, combustion, energy conservation, fuels, metals, printing ink, reclaimed fibers, recovery, recycling, sludge disposal, trace elements.

monitored in this study as they were not specified by NYSDEC.

Cadmium, lead, and selenium were the only measurable trace elemental emissions considered hazardous under NESHAP. The sum of their contributions to the air emission load would be less than 5 kg/y if a boiler operating similarly to this test boiler operated 24 h/day for 365 days/year. This emission rate is well below 23,000 kg/year—the sum of NESHAP emissions required to be considered a major source under that provision (11,12).

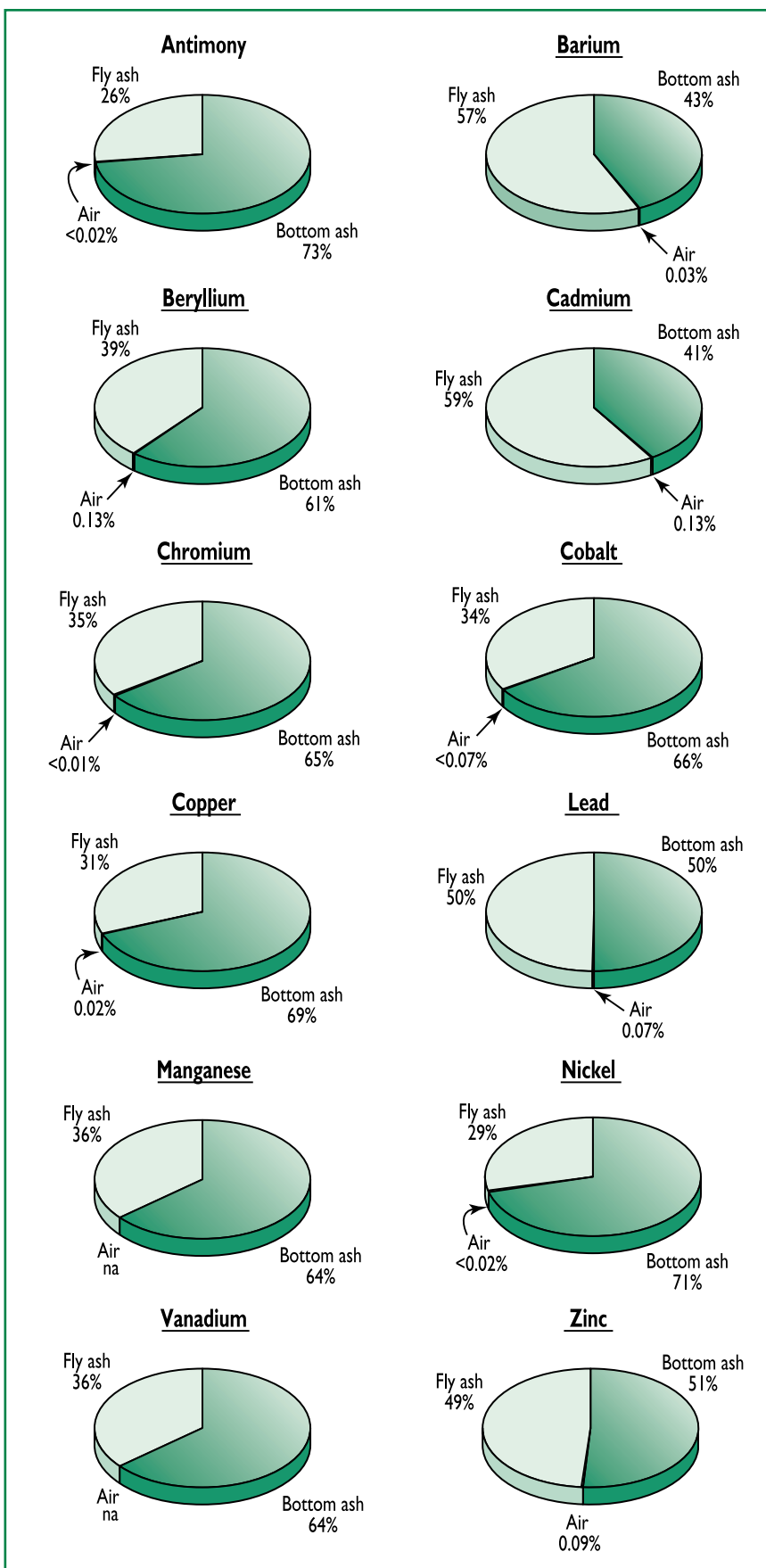
Mass balances

The measured mass of each trace element in the input to the boiler was compared with the measured mass exiting the system in the bottom ash, fly ash, and air emissions where possible. Sometimes, data were below the analytical detection limit. For these elements, the detection limit itself was used in the mass balance. A mass balance was considered attained for those trace elemental species for which the inputs and the outputs agreed within one standard deviation. Using this criterion, a mass balance was attained for all but five of the trace elements tested. This verifies the validity of the measurements.

No balance was possible for antimony, selenium, or thallium because the method detection limits appear to have greatly overestimated the inputs to the system. For thallium, all measurements were below detection making a balance meaningless. Although all measured concentrations for chromium and zinc were above the detection limits, the inputs and outputs of these trace elements did not balance. In each case, the measured inputs to the system were greater than the outputs. Consequently, data for these two trace elements may be suspect.

Comparison of fate of trace elements

The fate of measured trace elemental species in the output from the system was compared for each trace element. Figure 1 displays the percentage by mass of each element in each output phase (air, bottom ash, and fly ash). Arsenic, selenium, and thallium do not



1. Mass percentage of each trace element transported from the system by fly ash, bottom ash, and air emissions in test burns of semi-bleached pellets co-fired with wood chips

Trace element	Fly ash leachate concentration, mg/L	Bottom ash leachate concentration, mg/L	Maximum TCLP concentration, mg/L
Arsenic	nd	nd	5.0
Barium	17.6	4.6	100.0
Cadmium	<0.0001	0.018	1.0
Chromium	<0.003	0.033	5.0
Lead	<0.001	<0.001	5.0
Selenium	0.008	0.0047	1.0

nd = not detected; MDL not established

VI. Toxicity characteristic leaching procedure concentrations

appear in the figure because all concentrations in the outputs were below method detection limits.

As Fig. 1 shows, the percentage by mass of each element exiting the system in air emissions is very small—always less than 0.15% of the total trace element mass. Most of the trace elements were found partitioned to the ashes. One would expect this due to condensation of the vapors and deposition of aerosols onto ash particles as the particles leave the boiler and retention within the bottom ashes of elemental fractions not volatilized during combustion.

One could also expect that the concentration of trace elements would be higher on the smaller size particles due to a greater specific surface area on these particles (10). A higher concentration of trace elements by mass therefore would be expected on fly ash particles compared to bottom ash. Since the mass of fly ash leaving the system is approximately 27% of the

total mass of ashes, any trace element for which more than 27% by mass is transported from the system in the fly ash would be considered enhanced on the fly ash particles. This is the case for all trace elements measured with the exception of antimony and nickel. These two trace elements are evenly distributed between the bottom and fly ashes. Barium and cadmium preferred the fly ash and show distinct concentration effects in the fly ash.

Although the concentration of trace elements is generally greater on fly ash, Fig. 1 also shows that the greatest mass of trace element is transported from the system in the bottom ash due to its greater production rate. Only barium and cadmium are transported from the system to a greater extent in the fly ash.

Toxicity characteristic leaching procedure

TCLP analysis performed on the fly and bottom ashes revealed the ashes are not considered characteristic haz-

ardous wastes as Table VI shows. All measured concentrations of regulated trace elements were well below the regulatory standards. Although arsenic was not detected in the leachate, analytical difficulties prevented the determination of a specific method detection limit (MDL). The MDL is probably two or more orders of magnitude below the regulatory level for arsenic like the other trace elements tested.

CONCLUSIONS

The fate of trace elements was tracked as inputs to and outputs from an institutional boiler. Trace element constituents of concern included those commonly found in printing inks. Acceptable mass balances were achieved for most elements. Ash produced in the test burns was determined not to be a characteristic hazardous waste. Trace elements in air emissions comprised less than 0.15% of the total mass transported from the system. **TJ**

Gregg, Zander*, and Theis are graduate student, associate professor and professor, respectively, at Clarkson University, Department of Civil and Environmental Engineering, William J. Rowley Laboratories, Box 5710, Potsdam, NY 13699.

This work was performed under Grant No. 3095-EEED-IA-94 from the New York State Energy Research and Development Authority with co-sponsorship by the James River Corp. Carthage Mill, P.M. Earth, Inc., and Clarkson University.

Received for review Aug. 25, 1996.

Accepted March 28, 1997.

*Corresponding author

LITERATURE CITED

1. Anon., *Beneficial Uses of Paper Mill Residuals for New York State's Recycled Paper Mills*, BES Technologies, Watertown, 1995, pp. 1-4.
2. Haverstock, L., personal communication.
3. ASTM E 725-86, "Sampling granular carriers and granular pesticides."
4. Gregg, J. J., "Pelletization and Combustion of Kraft Process Pulp and Paper Sludge: Operational Feasibility and Inorganic Chemical Mass Balance," Masters thesis, Clarkson University, Potsdam, NY, 1996.
5. Anon., *Standard Methods for the Examination of Water and Wastewater*, 18th edn., APHA Washington, 1992, pp. 3-28.
6. Donvito, T. N., Turan, T. S., and Wilson, J. R., *Tappi J.* 75(4): 163(1992).
7. Praskievicz, R. W. and Subt, S. S. Y., *Proceedings 1976 TAPPI-CPPA Fall Graphic Arts Conference*, CPPA, Montreal, p. 23.
8. Kline, J. E., *Paper and Paperboard: Manufacturing and Converting Fundamentals*, 2nd edn., Miller Freeman, New York, 1991, pp. 142-143.
9. Kaufherr, N., and Lichtman, D., *Environmental Science and Technology* 187: 544(1984).
10. Theis, T. L. and Gardner, K. H., *Critical Reviews in Environmental Control* 20(1): 21(1990).
11. Brownell, F. W., in *Environmental Law Handbook* (J. G. Arbuckle, Ed.), 12th edn., Government Institutes, Rockville 1993, pp. 120-150.
12. Majumdar, S. B., *Regulatory Requirements for Hazardous Materials*, McGraw-Hill, New York, 1993, pp. 101-125.