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## POTENTIAL SURROGATE METALS FOR INCINERATOR TRIAL BURNS

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### ABSTRACT

New and renewing hazardous waste management permits for hazardous waste incinerators and other thermal destruction devices require that the emissions of hazardous constituent trace metals be controlled via established metals feedrate limits. Thus, the trial burn required to obtain a permit must include consideration of metals emissions. To preserve a high degree of operating flexibility within the ultimate permit conditions defined, incinerator operators generally spike a mixture of hazardous constituent trace metals into the waste burned during the trial burn to increase the metals feedrates tested in the trial burn. This exercise can significantly increase the cost of the trial burn, as some metal constituents are quite expensive. The question thus arises, can surrogate metals be used as substitutes for select hazardous constituent metals to decrease the cost of a trial burn.

Over the past 4 years, the research program at the Environmental Protection Agency's (EPA's) Incinerator Research Facility (IRF) has developed an extensive body of metals partitioning data from pilot-scale incineration tests using synthetic hazardous wastes, actual listed hazardous wastes, and contaminated materials from Superfund sites. From these data, augmented by bench-scale studies and some full-scale incinerator tests, it has become apparent that the same metals volatilization/condensation mechanisms, first used to explain metals enrichment in flyash from coal combustion 15 years ago, drive metals partitioning in incinerators. Further, metals partitioning can largely be explained using only vapor pressure/temperature relationships for metal species in thermodynamic equilibrium in the combustion zone.

Because metals volatility dominates partitioning, surrogates can be used and the choice of surrogates is simplified. This paper discusses the results of three extensive parametric test programs performed at the IRF using synthetic hazardous wastes containing both hazardous constituent and potential surrogate metals. These results show that surrogates partition in the same manner as selected hazardous constituent metals. Thus, the use of surrogates deserves consideration, if not in actual trial burns, then at least in scoping tests used to guide the formal trial burn.

### INTRODUCTION

In 1988, the EPA's Risk Reduction Engineering Laboratory initiated a research program at its Incineration Research Facility (IRF) in Jefferson, Arkansas, to investigate the fate of trace metals fed to a rotary kiln incinerator. Three parametric studies of the fate of five hazardous constituent trace metals (arsenic, barium, cadmium, chromium, and lead) and four nonhazardous constituent trace metals (bismuth, copper, magnesium, and strontium) have now been completed. In these tests each metal's partitioning to the incinerator's discharge streams (kiln ash, wet scrubber air pollution control system scrubber liquor, and flue gas) was measured, and the effects of kiln temperature, afterburner temperature, and feed chlorine content on metal partitioning were evaluated.

The first parametric study, completed in 1988, investigated a venturi scrubber, packed-column scrubber combination for particulate and acid gas control. A second parametric study, identical in scope to the first, was completed in 1989. The only difference between the first and second studies was the air pollution control system (APCS), which was a single-stage ionizing wet scrubber. Results of the studies were reported in detail in 1991 (1,2). A third parametric study was completed in 1991 (3). This study added mercury to the set of test metals and used a Calvert Flux-Force/Condensation scrubber system as the APCS. The use of surrogates in trial burns and scoping tests could significantly reduce permitting costs and improve incinerator operation. Therefore a major objective of the studies was to evaluate the four nonhazardous constituent metals as surrogates for the hazardous constituent

metals. This paper examines the trace metal partitioning and scrubber collection efficiency data in light of this objective.

### TEST PROGRAMS

#### Test Facility

All test programs discussed in this paper were performed in the IRF's rotary kiln incinerator system (RKS). A process schematic of the RKS is shown in Fig. 1. The IRF RKS consists of a primary combustion chamber, a transition section, and a fired afterburner chamber. After exiting the afterburner, flue gas flows through a quench section followed by a primary APCS. Two primary APCSs are available at the IRF for use on the unit. One consists of a venturi scrubber followed by a packed-column scrubber fabricated by Andersen 2000. The other is a single-stage ionizing wet scrubber fabricated by Air Plastics, Inc. Downstream of the primary APCS, a backup secondary APCS, comprised of a demister, an activated-carbon adsorber, and a high-efficiency particulate (HEPA) filter, is in place. This secondary APCS is designed to ensure the particulate and organic emissions from the system are acceptable even under upset conditions. The modular design of the APCS permits the installation of the other pilot-scale scrubber system, such as the Calvert Flux-Force/Condensation scrubber system used in the third parametric test series. A process schematic of the Calvert scrubber system is shown in Fig. 2.

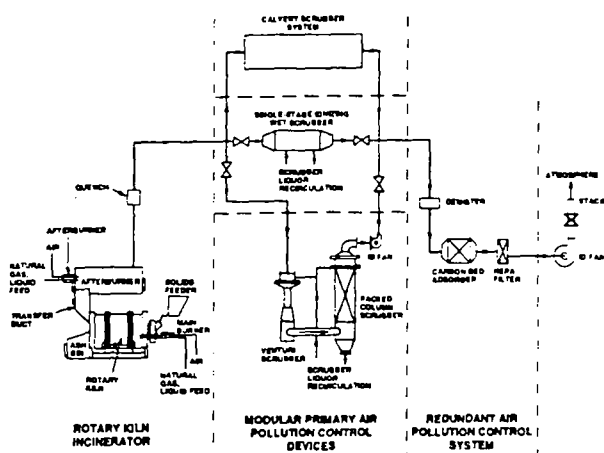


Fig. 1. Schematic of the IRF rotary kiln incineration system.

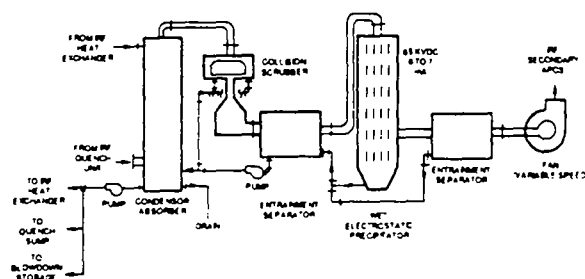


Fig. 2. Schematic of the Calvert Flux-Force/Condensation Scrubber System.

**Synthetic Waste Mixture**

The parametric tests were performed with a synthetic waste feed mixture prepared by adding a mixture of organic compounds (toluene, chlorobenzene, and tetrachloroethene) to a clay-based oil sorbent material. The clay/organic mixture contained nominally 25 percent by weight organic liquids, though it remained a free-flowing solid. The waste feed chlorine content was adjusted by varying the ratio of the three organics compounds.

Test trace metals were added to the clay/organic mixture by metering a concentrated aqueous metals solution onto the clay/organic mixture at the head of the screw feeder used to feed the synthetic waste to the kiln. All metals were added as soluble nitrates, with the exception of arsenic, which was added as As<sub>2</sub>O<sub>3</sub>. Table I summarizes the average metal concentrations in the integrated feed mixtures.

**Test Conditions**

The test matrix was the same for the first two test series. Table II summarizes the average achieved values for the three test variables. Each was varied over three levels, with the other variables held nominally constant. Target kiln exit temperatures were 816°, 871°, and 927°C (1,500°, 1,600°, and 1,700°F). Target afterburner exit temperatures were 982°, 1,083°, and 1,204°C (1,800°, 2,000°, and 2,200°F). Target concentrations for chlorine in the synthetic waste feed were 0, 4, and 8 percent).

Based on the observations from the first two test series, the test matrix for the third test series was slightly modified. The test variables were kiln exit temperature, waste feed chlorine content, and scrubber pressure drop. In the first two test series, metal partitioning and scrubber collection efficiencies were not affected by changes in afterburner exit temperature, so it was eliminated as a test variable and held constant at 1,094°C (2,000°F). In addition, the range of kiln exit temperatures was expanded downward to 538°C (1,000°F) and the

TABLE I  
Average Integrated Feed Metal Concentrations

Metal	Concentration, mg/kg		
	Venturi/packed-column scrubber test series	Single-stage ionizing wet scrubber test series	Calvert Scrubber test series
Arsenic	44	48	34
Barium	53	390	465
Bismuth	150	330	370
Cadmium	8	10	20
Chromium	87	40	280
Copper	470	380	350
Lead	52	45	74
Magnesium	17,200	18,800	34,500
Strontium	280	410	390

TABLE II  
Incinerator Operating Conditions

Test Series	Test	Feed mixture Cl content, %	Average kiln exit temperature, °C (°F)	Average afterburner exit temperature, °C (°F)
Venturi/packed-column scrubber	1	0	874 (1,606)	1,093 (1,999)
	2	3.7	825 (1,517)	1,071 (1,959)
	3	4.2	928 (1,702)	1,092 (1,989)
	4	3.8	878 (1,612)	1,088 (1,991)
	5	3.6	871 (1,599)	1,196 (2,184)
	6	3.4	875 (1,607)	983 (1,803)
	7 <sup>a</sup>	4.6	873 (1,603)	1,094 (2,000)
	8	8.3	870 (1,599)	1,092 (1,998)
Single-stage ionizing wet scrubber	1	0	900 (1,652)	1,088 (1,990)
	2	3.5	819 (1,507)	1,096 (2,002)
	3	3.5	929 (1,704)	1,092 (1,998)
	4	3.5	877 (1,610)	1,096 (2,006)
	5	3.7	885 (1,625)	1,163 (2,125)
	6	3.6	887 (1,629)	1,017 (1,863)
	7 <sup>b</sup>	3.6	881 (1,618)	1,103 (2,018)
	8 <sup>b</sup>	3.8	879 (1,615)	1,098 (2,008)
	9	6.9	881 (1,617)	1,087 (1,988)
				<b>Scrubber pressure drop, kPa (in WC)</b>
Calvert scrubber	1	0	541 (1,006)	12.9 (52)
	2	0	819 (1,507)	12.4 (50)
	3	0	909 (1,669)	12.4 (50)
	4	0.6	555 (1,031)	12.4 (50)
	5	0.6	842 (1,547)	12.4 (50)
	6	0.8	919 (1,686)	12.4 (50)
	7	3.6	543 (1,010)	12.4 (50)
	8	3.4	817 (1,502)	12.4 (50)
	9	3.1	944 (1,731)	12.2 (49)
	10	2.3	829 (1,524)	8.2 (33)
	11	3.4	827 (1,521)	16.9 (68)

<sup>a</sup>Test point 7 is a duplicate of test point 4.

<sup>b</sup>Test points 7 and 8 are replicates of test point 4.

target concentrations for chlorine in the waste feed were adjusted to 0.1, and 4 percent.

All tests were conducted under excess air conditions. Oxygen concentrations were nominally 12 to 14 and 8 to 10 percent in the kiln and afterburner exit flue gas, respectively. Solids residence time in the kiln was approximately 1 hour.

### TEST RESULTS

The measured feed and discharge stream metal concentrations can be combined with measured feed and discharge flowrates, and the fraction of the metals fed accounted for in the respective discharges can be calculated. The sum of these discharge fractions represents the mass balance closure for each metal in each test. Ideally, near 100 percent trace metal mass balance closure would be desirable. However, past experience in tests to determine the distribution of trace metals from combustion sources has shown that typical good results are in the 30 to 200 percent range. The ranges and averages for the metal mass balance closures for three parametric test series are summarized in Table III.

Given that variable and less than perfect mass balance closure is invariably experienced, it is difficult to draw conclusions regarding the affect of incinerator operation or feed characteristics on metal partitioning using only percent-of-feed fractional distributions. However, a clearer picture of the variation in relative metal distributions is possible when percent-of-feed fractional distributions are normalized by the total mass balance closure achieved. These normalized, or percent-of-measured fractions represent fractions that would have resulted had mass balance closure in each case been 100 percent. Use of distribution fractions normalized in this manner allows clearer data interpretation, because variable mass balance closure is removed as a source of test-to-test data variability. The use of normalized distributions repre-

sents a best attempt to quantify metal partitioning phenomena, given variable and less than perfect mass balance closure.

When subjected to incineration conditions, metals are expected to vaporize to varying degrees, depending on their relative volatilities. To characterize a metal's volatility, equilibrium analyses can be performed to identify the metal's volatility temperature for a given set of incinerator conditions. The volatility temperature is defined to be the temperature at which the effective vapor pressure of a metal is  $10^{-6}$  atm. The effective vapor pressure is the combined equilibrium vapor pressures of all species containing the metal, reflecting the quantity of metal that would vaporize under a given set of conditions. A vapor pressure of  $10^{-6}$  atm is selected because it represents a measurable amount of vaporization. The lower the volatility temperature, the more volatile the metal is expected to be.

Because the volatility temperature is based on vapor pressure/temperature relationships for metal species in thermodynamic equilibrium it provides a useful parameter for comparing relative partitioning behavior. Table III also notes the volatility temperature for each metal, based on its elemental and oxide forms (4).

Metal discharge distributions have been summarized for each test program and presented in Figures 3, 4, and 5. These figures show the amounts of metal found in each discharge stream normalized as a fraction of the total found in the three discharge streams — kiln ash, scrubber exit flue gas and scrubber liquor. In these figures, the bar for each metal represents the range in the fraction accounted for by each discharge stream over all tests of the respective test series. The average fraction for that test series is noted by the midrange tick mark. Metal discharge distribution data are plotted versus volatility temperature. For all three test series these figures indicate a correlation between the observed metal volatility and the calculated volatility temperatures. With increasing volatility temperature there is a gradual increase in average

TABLE III  
Summary of Metal Mass Balance Closure Around the Kiln Ash and Scrubber Discharges

Metal	Volatility temperature, °C	Mass balance closure, % of metal fed								
		Venturi/packed column scrubber series		Single-stage ionizing wet scrubber series		Calvert scrubber series				
		Range	Average	Range	Average	Range	Average			
Arsenic	700	39	77	60	47	95	66	70	128	94
Barium	849	57	147	86	17	60	27	60	106	77
Bismuth	621	36	74	53	35	63	50	38	86	58
Cadmium	214	37	120	96	36	68	50	26	98	60
Chromium	1,613	61	94	73	77	204	154	34	171	96
Copper	1,116	46	79	63	30	81	50	67	103	83
Lead	627	8	96	70	47	177	110	54	118	77
Magnesium	1,549	70	134	92	63	123	99	71	105	87
Strontium	1,454	28	71	48	15	60	28	59	99	74

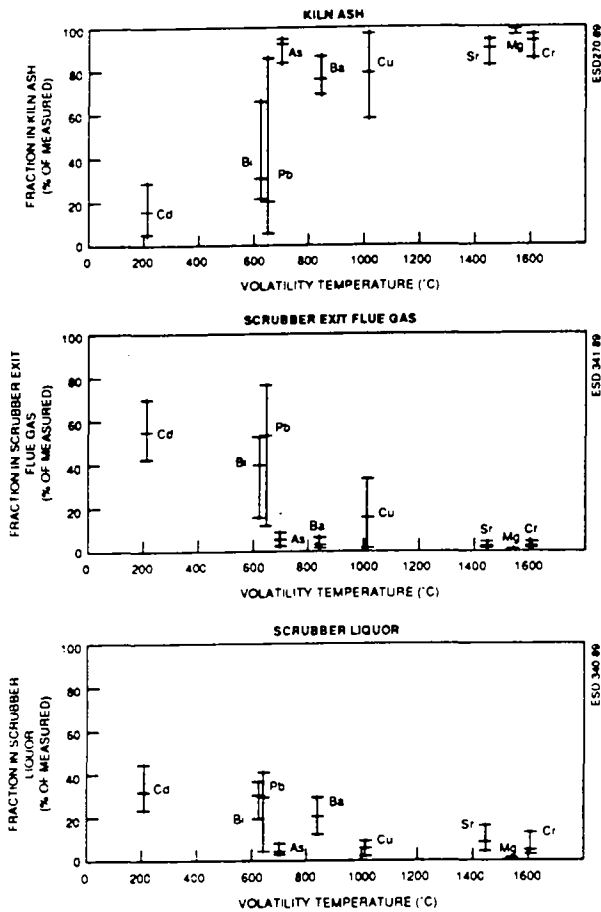


Fig. 3. Normalized distribution of metals in the RKS discharge streams in the venturi/packed-column scrubber tests. Bar indicates range observed over all eight tests. Average is noted by midrange tick mark.

kiln ash fraction and decrease in average scrubber exit flue gas and liquor fractions. This is as expected. The less volatile a metal is, as reflected in its higher volatility temperature, the less likely it will volatilize in the kiln and be carried out of the kiln in the vapor phase in the combustion flue gas.

The relationships between metal partitioning and the calculated volatility temperature is particularly useful because it suggests that surrogates can be selected to represent particular hazardous constituent metals of interest based on relative volatilities. To further defend the use of the nonhazardous metals as surrogates, it is necessary to compare the partitioning data on a test by test basis. This task can be simplified by noting that strontium, magnesium, and chromium were highly refractory for each test. Because the partitioning of these metals did not vary with any of the test variables, little can be gained by looking at their partitioning on a test by test basis. These figures do clearly indicate, however, that strontium, and perhaps magnesium, accurately represent the partitioning behavior of chromium. Test by test comparisons of metal partitioning for the remaining six metals can also be simplified to partitioning to the kiln ash and APCS collection efficiency.

Figures 6 through 11 show the partitioning of cadmium, bismuth, lead, arsenic, barium, and copper to the kiln ash as a function of the test variables kiln exit temperature and waste feed chlorine content for the three parametric test series.

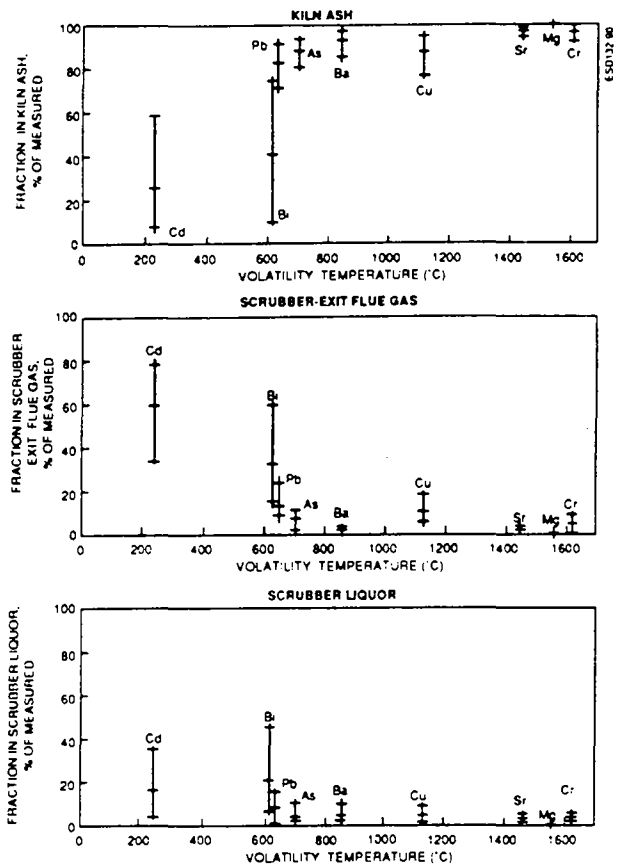


Fig. 4. Normalized distribution of metals in the RKS discharge streams in the single-stage ionizing wet scrubber tests. Bar indicates range observed over all nine tests. Average is noted by midrange tick mark.

Cadmium is not included in Figures 6 and 7 because it was not found in any kiln ash sample above detection limits, although calculated partitioning fractions to the kiln ash using sample concentrations set to the analytical detection limit were less than 25 percent.

For the first two parametric test series, Figs. 6 through 9 show that bismuth and cadmium were relatively volatile, with a maximum kiln ash fraction of about 75 percent and an average partitioning fraction to the kiln ash of less than 40 percent. Figures 10 and 11 show that all of the metals were less volatile in the third test series, although cadmium and bismuth were more volatile than the other metals. Lead volatility behavior differed between the three test series. For the venturi/packed-column test series, the average fraction of lead recovered in the kiln ash was 20 percent. For the single-stage ionizing wet scrubber test series, the average fraction of lead recovered in the kiln ash was 82 percent. For the Calvert scrubber test series, the average kiln ash fraction was 94 percent.

These figures show that of the nonhazardous constituent metals tested, bismuth best represented cadmium on a test by test basis for partitioning to the kiln ash. It was somewhat less volatile than cadmium, but was similarly affected by changes in the test variables. Figures 8 through 11 show that copper partitioning to the kiln ash was more typical of lead, arsenic,

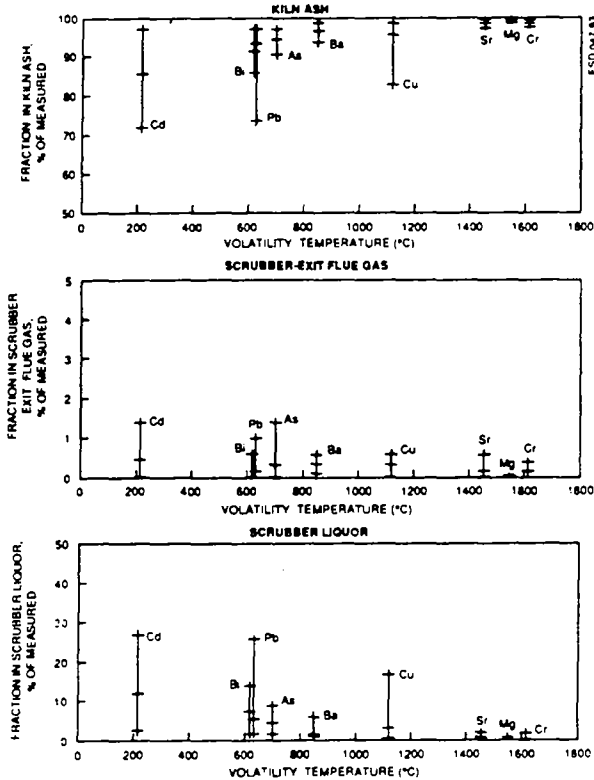


Fig. 5. Normalized distribution of metals in the RKS discharge streams in the Calvert scrubber tests. Bar indicates range observed over all 11 tests. Average is noted by midrange tick mark.

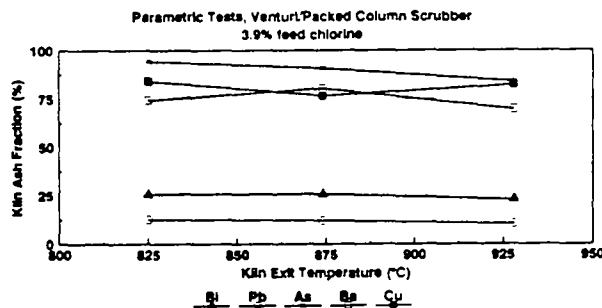


Fig. 6. Metal partitioning to the kiln ash versus kiln exit temperature at constant waste feed chlorine content for the parametric test series using the venturi/packed-column scrubber.

partitioning to the kiln ash was more typical of lead, arsenic, and barium behavior. Lead was much more volatile in the first test series. The reason for this behavior is not clear as the test were conducted over the same range of operating conditions as the later parametric tests.

Figures 12 and 13 show the apparent scrubber collection efficiency for each of the test metals as a function of the kiln exit temperature and waste feed chlorine content, respectively. The apparent scrubber collection efficiencies are calculated by assuming that the sum of the amount of metal measured in the two scrubber discharges (the scrubber liquor and the scrubber exit flue gas) was the amount of metal

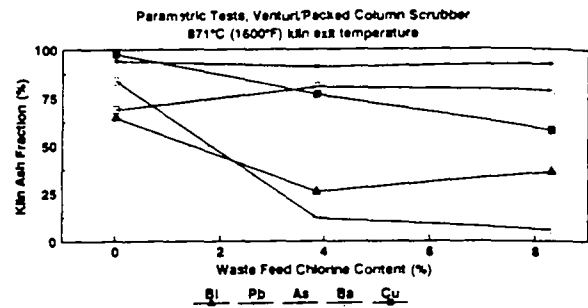


Fig. 7. Metal partitioning to the kiln ash versus waste feed chlorine content at constant kiln exit temperature for the parametric test series using the venturi/packed-column scrubber.

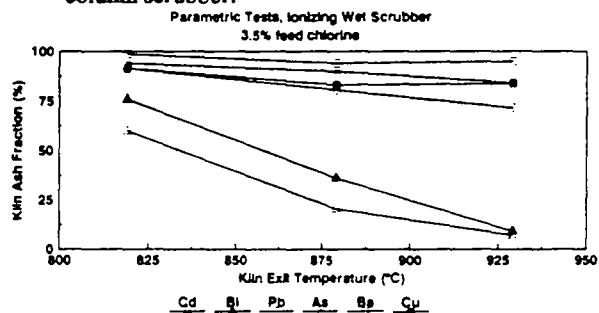


Fig. 8. Metal partitioning to the kiln ash versus kiln exit temperature at constant waste feed chlorine content for the parametric test series using the single-stage ionizing wet scrubber.

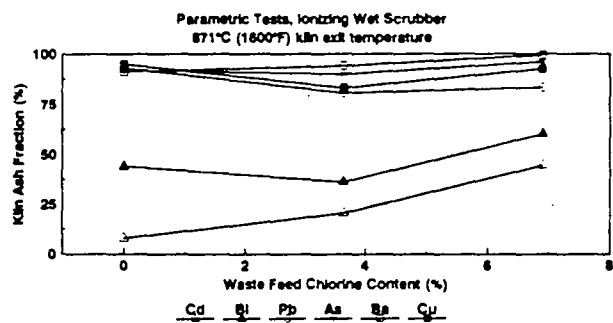


Fig. 9. Metal partitioning to the kiln ash versus waste feed chlorine content at constant kiln exit temperature for the parametric test series using the single-stage ionizing wet scrubber.

present in the scrubber inlet flue gas. This allows the apparent scrubber collection efficiency to be calculated as: (scrubber liquor fraction)/(scrubber liquor fraction + scrubber exit flue gas fraction).

Figure 12 shows the apparent scrubber collection efficiency for each of the test metals as a function of the kiln exit temperature at constant waste feed chlorine content for the three scrubber systems tested. Figure 13 similarly shows the apparent scrubber collection efficiencies as a function of the waste feed chlorine content at constant kiln exit temperature for two of the three scrubber systems tested. These figures show that magnesium behavior approximates barium behavior, while copper and bismuth behavior is similar to that of arsenic, cadmium, and lead.

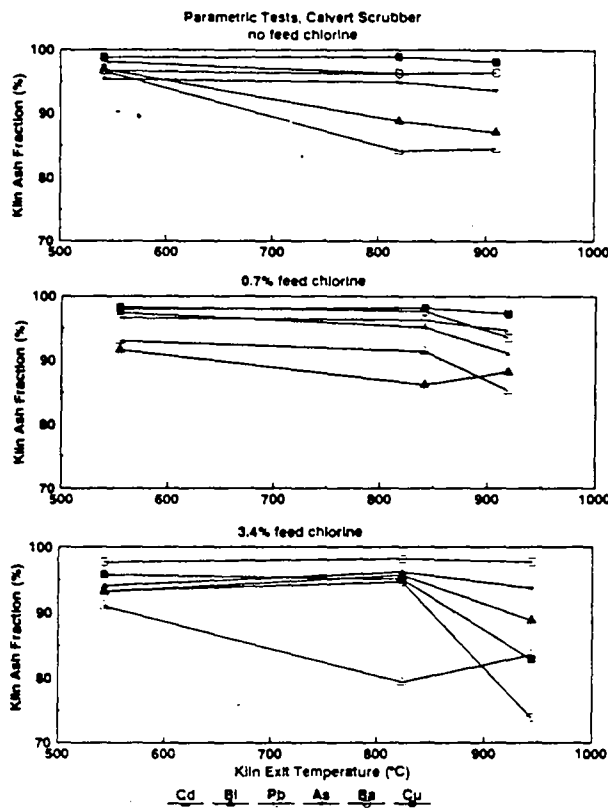


Fig. 10. Metal partitioning to the kiln ash versus kiln exit temperature at waste feed chlorine concentrations of 0, 0.7, and 3.4 percent for the parametric test series using the Calvert Flux-Force/Condensation scrubber system.

CONCLUSIONS

Data from three sets of parametric trace metal partitioning tests performed at the IRF show that metal partitioning among incinerator system discharges can largely be explained using only vapor pressure/temperature relationships for metal species in thermodynamic equilibrium. Given this, the data from the parametric tests performed to date suggest that bismuth behavior in an incineration process is quite similar to that of cadmium, magnesium or strontium behavior is similar to that of chromium, and copper behavior is similar to that of arsenic, barium, and lead. With respect to APCS collection efficiency, magnesium behavior is similar to that of barium, and bismuth and copper behavior is similar to that of arsenic, cadmium, and lead. Use of these nonhazardous constituent metals as surrogates for the corresponding hazardous constituent metals warrants consideration for use in scoping tests used to guide trial burn planning. Other potential surrogates can be similarly identified based on equilibrium vapor pressure/temperature calculations.

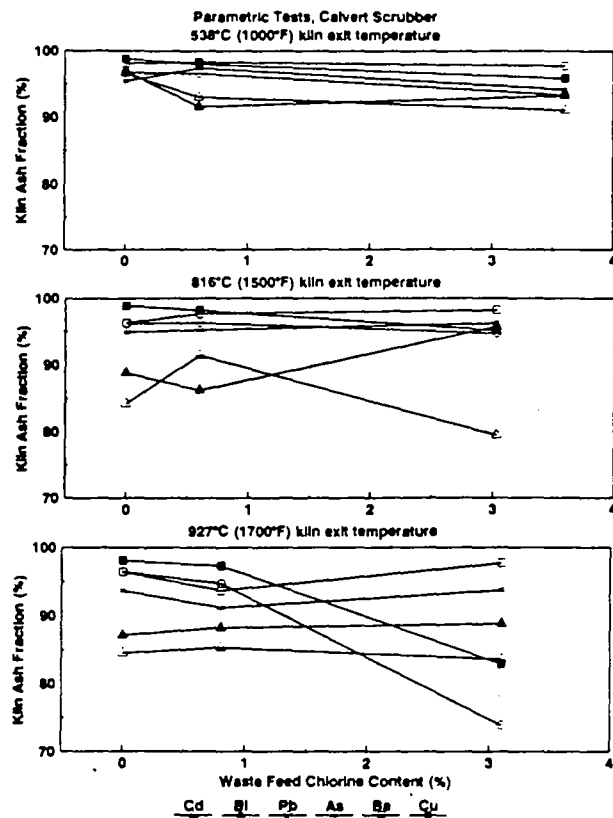


Fig. 11. Metal partitioning to the kiln ash versus waste feed chlorine content at constant kiln exit temperature of 538°, 816°, and 927°C (1,000, 1,500, and 1,700°F) for the parametric test series using the Calvert Flux-Force/Condensation scrubber system.

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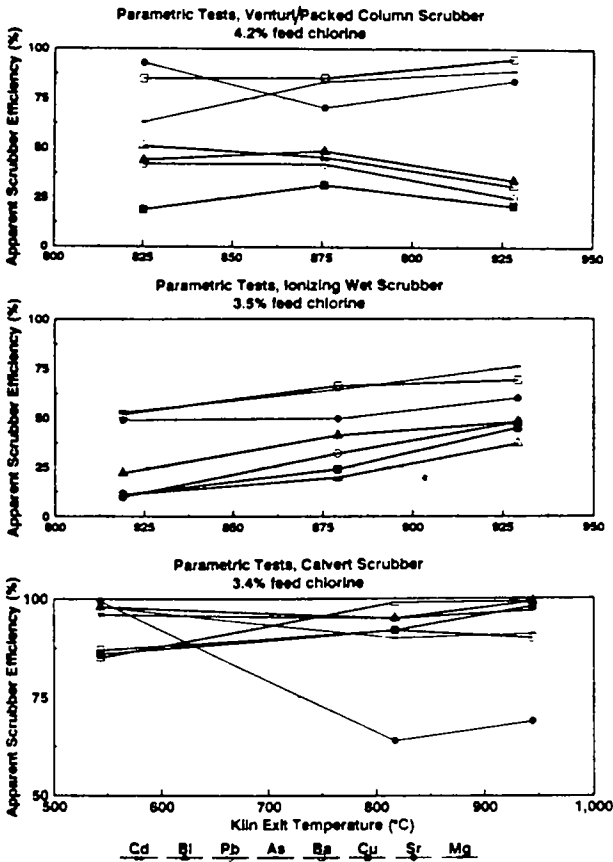


Fig. 12. Apparent scrubber collection efficiency versus kiln exit temperature for the three scrubber systems.

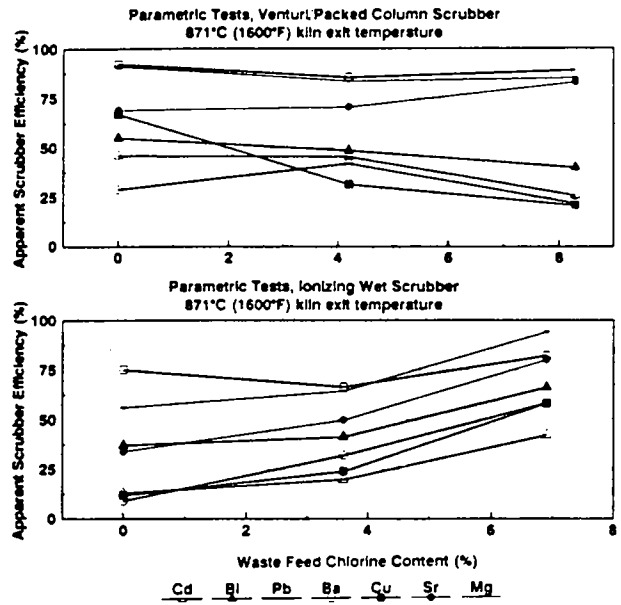


Fig. 13. Apparent scrubber collection efficiency versus waste feed chlorine content for the two scrubber systems.

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16. ABSTRACT Over the past 4 years, the research program at the Environmental Protection Agency's (EPA's) Incinerator Research Facility (IRF) has developed an extensive body of metals partitioning data from pilot-scale incineration tests using synthetic hazardous wastes, actual listed hazardous wastes, and contaminated materials from Superfund sites. From these data, augmented by bench-scale studies and some full-scale incinerator tests, it has become apparent that the same metals volatilization/condensation mechanisms, first used to explain metals enrichment in flyash from coal combustion 15 years ago, drive metals partitioning in incinerators. Further metals partitioning can largely be explained using only vapor pressure/temperature relationships for metal species in thermodynamic equilibrium in the combustion zone.  Because metals volatility dominates partitioning, surrogates can be used and the choice of surrogates is simplified. This paper discusses the results of three extensive parametric test programs performed at the IRF using synthetic hazardous wastes containing both hazardous constituent and potential surrogate metals. These results show that surrogates partition in the same manner as selected hazardous constituent metals. Thus, the use of surrogates deserves consideration, if not in actual trial burns, then at least in scoping tests used to guide the formal trial burn.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
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