

**METAL PARTITIONING IN THE DEPARTMENT OF ENERGY-OAK RIDGE
TSCA INCINERATOR**

Bryan Schoch
EET Corporation

ABSTRACT

An evaluation was conducted of trial burn, feed, and waste data from the Department of Energy-Oak Ridge Toxic Substances Control Act Incinerator (TSCAI) to determine if metal concentrations in the ash could be predicted from known feed data and operating conditions. The data suggest that even non-volatile metals may not partition to ash if solids are not a component of the waste feed. Ash partitioning coefficients were calculated for arsenic, cadmium, chromium, lead, mercury, and uranium for the time period September 1995 to September 1997. The amount of metal partitioning to ash was less than expected for arsenic, chromium, and uranium and more than expected for cadmium. The amount of lead and mercury partitioning to ash were approximately what was expected. Predictions of metal concentrations in the ash on a monthly basis were not possible due to the variability of the data.

INTRODUCTION

Hazardous waste residuals generated from the Department of Energy (DOE) Toxic Substances Control Act Incinerator (TSCAI) located in Oak Ridge, Tennessee include ash, sludge generated from the air pollution control system, and refractory lining the kiln. An associated waste stream is sludge generated from the water treatment plant receiving wastewaters from the incinerator (the Central Neutralization Facility, or CNF). Characterization of various populations of ash, sludge, and refractory generated between 1994 and 1997 has shown metal concentrations in the residuals which exceed the Resource Conservation and Recovery Act (RCRA) Universal Treatment Standards (UTS) values. Since these waste streams will now require treatment prior to disposal, it is desired to know whether the metal concentrations in the residuals can be predicted from known feed data and operating parameters.

The focus of this paper will be on ash residuals because ash has the largest body of associated analytical data, and can best be correlated to a specific feed burn period. The metal concentrations in the water leaving the incinerator and in the stack gas emissions have been measured too infrequently to perform reliable mass balance calculations on the incinerator over long periods of time. Focusing on ash will also allow the metal partitioning behavior in the TSCAI to be compared with published studies of other incinerators that may have different air pollution control systems or operate at different secondary combustion chamber temperatures. This paper will review typical operating conditions at the incinerator, provide an overview of the properties that influence metal partitioning, and evaluate existing trial burn, feed, and ash data to determine whether metal concentrations in the ash can be predicted. Based on their physical properties and concentrations in the feed and ash, six metals have been selected for review in this study: arsenic, cadmium, chromium, lead, mercury, and uranium.

The TSCA Incinerator, located at the East Tennessee Technology Park on the Department of Energy Oak Ridge Reservation, is a rotary-kiln incinerator designed to treat low-level radioactive TSCA and RCRA-regulated wastes. Key components of the incinerator include the rotary kiln, secondary combustion chamber (SCC), and off-gas treatment system. The off-gas treatment system consists of a quench chamber, a venturi scrubber, a packed bed scrubber, two ionizing wet scrubbers in series, an induced draft fan, and the stack. Other facility components include a wet ash handling system, and an aqueous effluent management system.

Wastes fed to the incinerator can be described in three categories: organic liquids, aqueous liquids, and solids. Available data reviewed for this study included detailed records of the total amount of metals and other constituents fed to the incinerator, three trial burn/metal partitioning studies conducted at the TSCAI, and ash data from multiple characterization projects.

PROPERTIES INFLUENCING METAL PARTITIONING

In order to provide a background of the expected partitioning behavior of metals during incineration, this section discusses the properties which most strongly influence how metals partition and summarizes the results of several published metal partitioning experiments. Based on these data, it will be possible to postulate how the metals selected for study will partition in the TSCAI.

Many studies on the fate of metals in combustion processes have shown that temperature is one of the most significant factors contributing to the behavior of metals. One property that can be used to provide qualitative predictions on the fate of metals during combustion is the volatility temperature. The volatility temperature of a metal is defined as the temperature at which the effective vapor pressure (the equilibrium vapor pressure of all species of a metal) is 0.10 Pa, which is the pressure at which a measurable amount of vaporization will occur. If the volatility temperature of a metal is much lower than the operating temperature in the kiln, the metal is predicted to vaporize, and therefore not be present in the ash. Metals with a volatility temperature much higher than the kiln operating temperature would not be expected to vaporize, and therefore be found to a large degree in the ash. Metals with volatility temperatures near the kiln operating temperature would be expected to exhibit intermediate behavior. Published volatility temperatures for the metals discussed in this paper are presented in Table I.

Table I. Volatility Temperatures of Selected Metals [1]

Metal	Volatility Temperature (°C, no chlorine in system)	Volatility Temperature (°C, 5% chlorine in system)
Arsenic	31.7	31.7
Cadmium	213.9	213.9
Chromium	1612.8	1610.6
Lead	626.7	-15.3
Mercury	13.9	13.9

Other factors which can impact metal partitioning behavior are the chlorine and sulfur content of the waste feed, and the feed matrix. The presence of chlorine is known to have a significant impact on the vapor pressure of some metals, increasing the vapor pressure with increasing chlorine content [2]. Increased chlorine will cause more of the metal to be converted to metal chloride, which is generally more volatile than the metal alone, resulting in less metal in the ash, and more in the air emissions and/or air pollution control (APC) residuals. This principle was demonstrated by Eddings [3] who noted that the presence of hydrochloric acid in the vapor phase will react with lead oxide to form a more volatile lead chloride. Experiments conducted by Carroll and Waterland [4] at the Environmental Protection Agency's (EPA) Incineration Research Facility in Jefferson, Arkansas suggested that chlorine had a much more significant effect on the partitioning of lead and cadmium at the temperatures studied (871.1 °C in the kiln, 1093.3 °C in the SCC) than did temperature. The volatility of other metals studied (arsenic, barium, bismuth, chromium, magnesium, and strontium) appeared relatively constant with respect to chlorine concentration.

The presence of sulfur in the waste stream has a similar effect on metal partitioning behavior as chlorine; however, the mechanism is more complex and has not been widely studied. In general, sulfur will increase the metal volatility if chlorine is also present, but the effect is less than that of chlorine alone [Tillman]. Experimental work performed by Eddings and Lighty concluded that lead sulfate would not exhibit the same volatile behavior as lead oxide in the presence of chlorine, due to its lower reactivity with hydrochloric acid [3]. The sulfur concentrations in TSCAI feed materials are typically low (less than 0.5%), therefore sulfur is not expected to have a large effect on metal partitioning in the TSCAI.

The matrix of the waste being burned can also have a significant effect on how metals partition. Examples of this are discussed in more detail below. Another matrix consideration is that if only liquids are being incinerated, there is reduced solid mass onto which a metal can bind, and less metal may end up in the ash residues.

Tables II and III show metal partitioning results obtained during three different metal partitioning experiments. Although slightly different incineration systems and test conditions were used, these values provide validation of the mechanisms previously discussed. The results of the metal partitioning experiments summarized in Tables II and III represent operating conditions slightly different than current normal operating conditions in the TSCAI. Typical operating conditions at the TSCAI are summarized in Table IV.

Table IV. TSCAI Typical operating conditions

Parameter	Value
Kiln temperature	1001.7 – 1010 °C
SCC temperature	1215.6 – 1221.1 °C
% Chlorine ^a	0.1 – 7.6 %
% Sulfur ^a	0.04 – 0.42 %

Based on the properties previously discussed and the metal partitioning data presented in Tables II and III, the expected behavior of arsenic, cadmium, chromium, lead, mercury, and uranium are summarized below.

Arsenic

Based on the volatility temperatures presented in Table I, arsenic is expected to be the second-most volatile of the metals considered here. In practice, however, data from published experiments have shown that most of the arsenic (63 – 94%) remains in the ash. In his experiments with incineration of arsenic-containing soils, Barton postulated that this effect may be due to the arsenic tightly binding to the clay matrix being incinerated [2]. Another potential explanation that has been presented is that a less volatile arsenic compound is being formed in parts of the incinerator system (e.g. As_2O_5 vs. As_2O_3). An additional matrix effect that can influence the behavior of arsenic in ash is the presence of calcium. When calcium oxide (lime) is present in the system, arsenic will react with it to form a stable orthoarsenate compound. This is most prevalent at lower temperatures; at temperatures above 871.1 °C, little arsenic has been found to volatilize, regardless of the presence of calcium. **Based on these data, the majority of the arsenic fed to the TSCAI is expected to be present in the ash.**

Cadmium

Based on its volatility temperature of 213.9 °C, the majority of cadmium fed to the TSCAI is not predicted to be present in the ash. The experiments summarized in Table II support this prediction, with ash partitioning values ranging from 9.2% to 26.4%. The effect of chlorine on cadmium partitioning is substantial; a series of eight test runs conducted by Carroll and Waterland [4] showed that increasing the

chlorine concentration in the waste feed from 0 to 8.3% decreased the fraction of cadmium partitioning to the ash from 29% to 9%. Based on these data and TSCAI's higher kiln operating temperature of 1001.7 – 1010 °C, **less than 30% of the cadmium fed to the incinerator is expected to be present in the ash.**

Chromium

The amount of chromium that partitions to ash is expected to be large, based on its volatility temperature of approximately 1612.8 °C. In addition, experiments have shown that the presence of chlorine has little effect on the volatility of chromium at temperatures greater than 537.8 °C [1]. **The average percentage of chromium found in the ash for the experiments and conditions summarized in Table II ranged from 92.5% to 95.8%, this is expected to be similar for the TSCAI.**

Lead

The volatility temperature of lead with no chlorine in the feed suggests that lead will be volatile at waste incineration temperatures. This is particularly true if chlorine is in the system, as evidenced by the large drop in volatility temperature. The effect of chlorine on lead volatility is significant within a relatively narrow temperature range, as shown in Figure 1. This was demonstrated experimentally in a series of eight test runs conducted by Carroll and Waterland [4] in which increasing the chlorine concentration in the waste feed from 0 to 8.3% decreased the fraction of lead partitioning to the ash from 84% to 6%. The average values summarized in Table II are for chlorine concentrations of approximately 4%. At these conditions, the amount of lead partitioning to ash was found to vary from 11.9% to 36.7%. Because the chlorine content of TSCAI feed appears to be highly variable, it is difficult to make anything other than general statements on the expected partitioning behavior of lead. **During periods when feed chlorine concentrations are high, it is likely that less than 25% of the lead fed to the incinerator will be present in the ash. During periods when the feed chlorine concentrations are low, more lead should be expected to be present in the ash.**

Mercury

At approximately 13.9 °C, mercury has the lowest volatility temperature of the metals considered here, **and is therefore expected to partition mainly to the stack gas and/or APC residuals.** This expected behavior is confirmed by the data in Table II (mercury in the ash was present below analytical method detection limits) and by published data from a municipal waste combustion facility showing that only 4% of the mercury fed partitions to ash [5].

Uranium

A review of the metal partitioning literature suggests that little research has been published on the fate of uranium in combustion systems. Based on vapor pressure relations developed by Rand and Kubaschewski [6], the volatility temperature of uranium metal is approximately 1,704 °C. **Based on this, uranium is not expected to be volatile in the incinerator, and most of the uranium is expected to partition to ash.**

The following sections discuss the trial burns that have been conducted at the TSCAI and the waste burn data. These data will be compared to the information previously presented to evaluate if metals in the TSCAI partition as expected and will allow correlations to be made between the feed and ash data.

Table II. Summary of Metal Partitioning Behavior in Three Experiments [1,4,7]

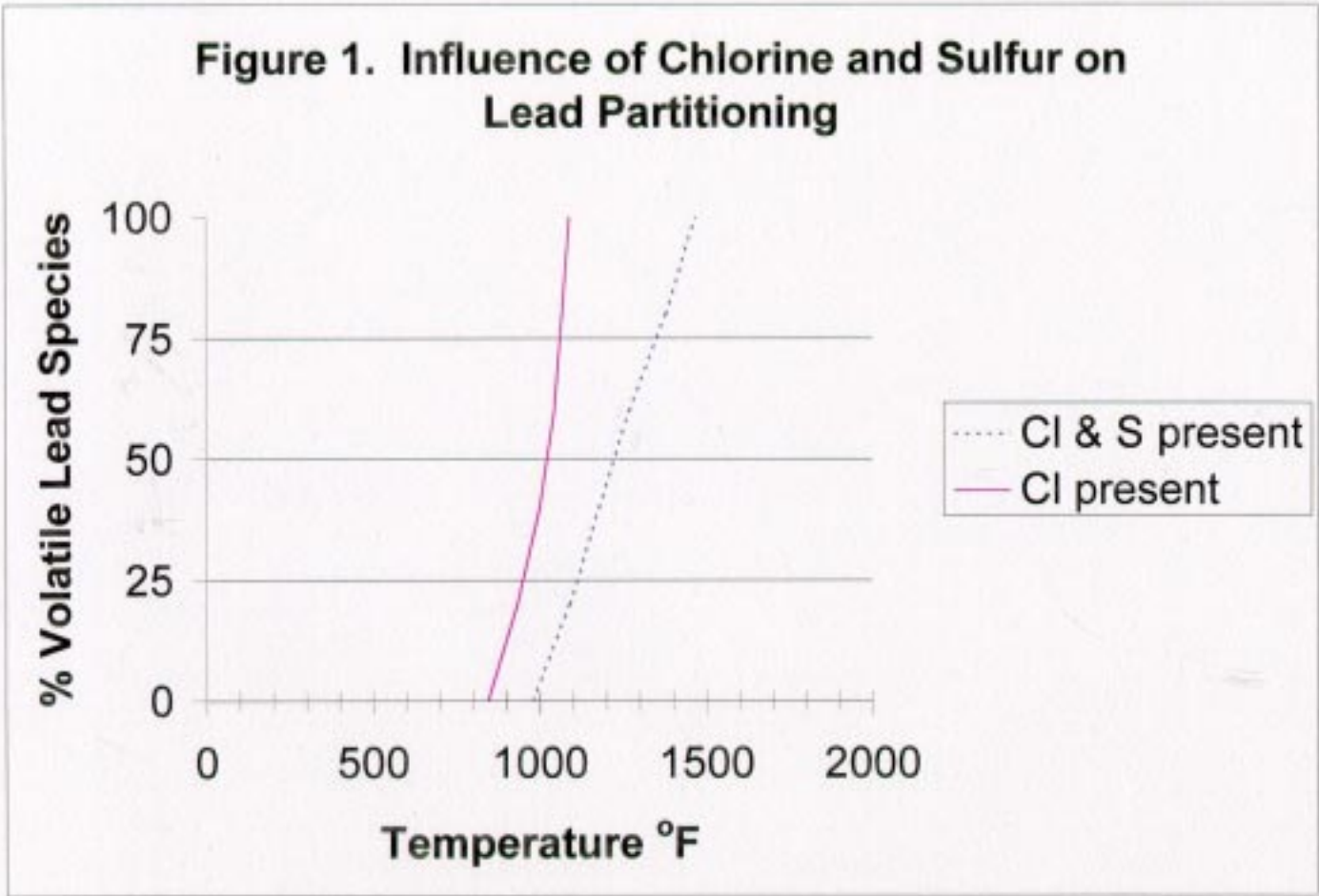
Metal	Fraction of Metal Found in Kiln Ash*		
	Carroll/Waterland	Thurnau	Tillman
Arsenic	90.3%	62.6%	94%
Cadmium	<12.9%	N/A	17.8% (9.2% – 26.4%)
Chromium	92.5%	N/A	95.8%
Lead	11.9%	N/A	25.9% (15.2% – 36.7%)
Mercury	N/A	N/A	~0%

* normalized data

Table III. Test Conditions for Data Summarized in Table II. [1,4,7]

Experiment	Incinerator Design	Matrix	Kiln Temperature	SCC Temperature	Chlorine Content	# Test runs summarized above	Mass Balance Closure
Carroll/Waterland	Rotary kiln with ionizing wet scrubber	Clay absorbent	815.6 °C to 926.7 °C	1093.3 °C to 1204.4 °C	4%	8	Not reported
Thurnau	Rotary kiln with packed bed scrubber	Soil	815.6 °C to 926.7 °C	1093.3 °C	~0%	5	37% - 84%
Tillman	Transportable rotary kiln with wet scrubber and cyclone between kiln and SCC	Sludge	929.4 °C	1152.8 °C	Not reported**	2	90% – 110%

** Although not reported, the chlorine content was likely between 0% - 4%, based on comparisons to the Carroll and Waterland data.



EVALUATION OF TRIAL BURNS CONDUCTED AT THE TSCAI

In June of 1990 and in June and July of 1995, the TSCAI conducted air performance tests to demonstrate that the emissions of certain metals were within permitted limits. The 1990 Air Test examined lead and beryllium emissions, while the 1995 Air Test evaluated lead, beryllium, and mercury. This discussion will focus only on the lead and mercury partitioning results.

The 1990 Air Test consisted of three runs, with approximately six hours of operating time per run. The feed materials were similar to those used during normal treatment operations: organic liquids, aqueous liquids, and solids (soil). The 1995 Air Test consisted of three runs during which only liquids were fed, and three runs during which a combination of solids and liquids were fed. The runs during the 1995 Air Test where liquid feeds only were fed were noted to generate very little ash, as a result, no ash data were collected and the following discussion applies only to the solid/liquid combination feed runs.

Incinerator operating conditions during the 1995 Air Test were similar to those used for the 1990 Air Test, with the exceptions that the SCC was operated at a higher temperature and less chlorine was present in the system than during the 1990 Air Test. Incinerator operating conditions were maintained at relatively constant levels for all test runs; a summary of the operating conditions during both tests is presented in Table V.

Table V. Operating Conditions for the 1990 and 1995 Air Tests [8,9]

Parameter	1990 Value	1995 Value
Kiln temperature	870.6 °C	874.4 °C
SCC temperature	1038.9 °C	1214.4 °C
% Chlorine*	3.8%	1.1%
Lead feed rate	122.6 g/hr	52.3 g/hr
Mercury feed rate	N/A	0.726 g/hr
Average run time	6 hours	4.2 hours

* 1990 chlorine content calculated from June 1990 feed data; 1995 chlorine content calculated from ash and chlorine concentrations in 1995 Air Test report

Based on the lead feed rates and operating times presented in the Air Test reports, the total mass of lead feed for each test run was calculated. These values were then compared to the mass of lead calculated to be present in the ash. Because the Air Test reports did not list the mass of ash generated, the ash mass values were obtained by reviewing waste generation records and obtaining the mass generated on each of the test days. For mercury, the partitioning evaluation was made by comparing the feed rates to the stack exhaust gas emission rates. A summary of the resulting values is presented in Tables VI through VIII.

Table VI. Lead Partitioning Results for the the 1990 Air Test [8]

Test Run #	Lead mass fed (g)	Lead concentration in ash (ppm)	Lead mass in ash (g)	Percent lead partitioning to ash
1	762.7	340	780.9	102.4%
2	735.5	133	276.9	37.7%
3	708.2	141	544.8	76.9%
Average	735.5	205	535.7	71.8%

Table VII. Lead Partitioning Results for the 1995 Air Test [9]

Test Run #	Lead mass fed (g)	Lead concentration in ash (ppm)	Lead mass in ash (g)	Percent lead partitioning to ash
1	237.4	107	133.6	56.3%
2	232.6	103	131.0	56.3%
3	239.5	90	102.1	42.6%
Average	236.5	100	122.3	51.7%

Table VIII. Mercury Partitioning Results for the 1995 Air Test [9]

Test Run #	Mercury feed rate (g/hr)	Mercury stack gas emissions (g/hr)	Mercury concentration in ash (ppm)	Percent mercury partitioning to stack gas	Percent mercury partitioning to ash
1	0.817	0.817	0	100%	0%
2	0.636	0.817	0	129%	0%
3	0.726	0.772	0	106%	0%
Average	0.726	0.812	0	100%	0%

Because the feed and burn conditions for each respective test were held relatively constant, the trial runs for each test have been averaged. Based on the lead partitioning values calculated above, and the air pollution control efficiencies provided in the Air Test Reports, the amounts of lead partitioning to ash, sludge, and the stack gas are shown in Table IX.

The measured mercury stack gas emission rates were all equal to or greater than the mercury feed rates, showing that **100% of the mercury partitions to the stack gas**. Values of greater than 100% partitioning to the stack gas are reportedly due to the precision and accuracy of the analytical procedures used for measuring mercury in the waste feed and exhaust gases.

Table IX. Comparison of Lead Partitioning in 1990 and 1995 Air Tests

	1990 Air Test	1995 Air Test
Ash	71.8%	51.7%
Sludge	27.4%	46.8%
Stack Gas	0.8%	1.5%

During the 1990 Air Test, the average amount of lead partitioning to ash was 71.8%, during the 1995 Air Test, the average was 51.7%. The main difference between the two tests, with respect to lead partitioning, is the higher chlorine content in the 1990 Air Test feed material. The results, however, do not correspond to the behavior expected by theory and observed in other incineration systems: all other factors being equal, the higher chlorine content during the 1990 Air Test would be expected to yield a lower fraction of lead partitioning to ash. The reason for this discrepancy is unclear; however, two possible explanations include:

- Analytical variation of the ash may have skewed the results. This is of particular concern in the 1990 Air Test, when one ash value was reported at 340 ppm, compared to values of 133 ppm and 141 ppm for similar lead feed rates.

WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

- Because the mass of ash generated during each test run was not measured, the masses were obtained from waste generation records. Review of the records showed minor discrepancies between waste descriptions and generation dates, which may contribute to calculation errors.

The lead partitioning values obtained from the trial burns are considerably higher than those reported by the experiments previously discussed. One possible explanation for this is that the chlorine data reported for the 1990 Air Test are inaccurate. The experiments conducted by Carroll and Waterland [4] show that significantly more lead (~ 84%) partitions to ash when there is no chlorine in the system and that there is a significant difference in partitioning with no chlorine and 4% chlorine. The TSCAI data for the 1990 Air Test suggest that the chlorine content was much lower than 3.8% [8]. This is a distinct possibility: since the chlorine content was not reported in the trial burn report, the value was calculated from monthly feed data and may not be applicable to this particular test.

A study was also conducted at the TSCAI in December, 1993 to evaluate how strontium and cesium partitioned in the incinerator [10]. In addition to strontium and cesium, six other metals (beryllium, chromium, lead, molybdenum, silver, and uranium) were analyzed in order to expand the database on how metals would partition in the TSCAI. Feed streams used for the study consisted of aqueous and organic liquid spiked with strontium and cesium chlorides; no solid materials were fed. As during the portion of the 1995 Air Test where only liquid feeds were utilized, no significant amounts of kiln ash were produced and an ash sample could not be collected for analysis. The study reported that the majority of the strontium (75%) and chromium (95%) partitioned to the scrubber effluent, based on the concentrations measured in the feed materials. **This is significant because it shows that even non-volatile metals may not partition to ash if a solid matrix is not a component of the feed.** This suggests that an evaluation of metal partitioning behavior in the TSCAI before the introduction of solid feed materials on a regular basis will be difficult, because of the long times required to generate ash when only liquids were being treated. The remainder of this discussion will therefore concentrate on the time period from September 1995 to September 1997, when solids were a significant portion of the incinerator feed. Review of the data shows that these dates correspond to the period where the majority of problems with the residuals have occurred.

SUMMARY OF LAND DISPOSAL RESTRICTIONS (LDR) REQUIREMENTS

In order to evaluate the magnitude and extent of the metal problems in the residuals, it is necessary to understand the regulatory requirements for the disposal of hazardous waste. Ash generated at the TSCAI is managed as a RCRA hazardous waste based on the "derived-from" rule. According to the LDR regulations, any residues generated from treatment of wastes that have concentration-based treatment standards must also meet the concentration-based treatment standards. For metals, these values are based on the concentrations in the leachate, as measured by the Toxicity Characteristic Leaching Procedure (TCLP). In May 1998, the EPA promulgated revised treatment standards for metal wastes destined for land disposal. Although the rule provided a two-year exemption for radioactively contaminated waste, the disposal facility used by the DOE did not allow the exemption until 1999. For this reason, wastes evaluated for disposal were compared to the lowest values published in either the standards promulgated in May 1998 (Phase IV LDR standards found in 40 CFR 268) or the previous (Phase III) LDR standards. These values are summarized in Table X.

Table X. RCRA Universal Treatment Standards for Metals

Metal	Previous (Phase III) Treatment Standard (mg/L TCLP)	Current (Phase IV) Treatment Standard (mg/L TCLP)
Arsenic	5.0	5.0
Cadmium	0.19	0.11
Chromium	0.86	0.6
Lead	0.37	0.75
Mercury	0.025	0.025
Uranium	Not regulated by RCRA	

EVALUATION OF WASTE BURN DATA

In order to provide the best assessment of how metals partition in the TSCAI, it is necessary to review data from waste burns. As comparison between Tables IV and V show, conditions during waste burns are slightly different than were used during the TSCAI trial burns, or in tests conducted at other incinerators, namely that TSCAI operates at a higher kiln temperature (1001.7 – 1010 °C.)

The total amount of metals fed to the incinerator are calculated based on waste characterization data. For this assessment, a period of one month was selected because of the manner in which the ash is generated. Ash generated from the incinerator continuously falls into a mix chamber where it cools. Periodic operation of a conveyor removes the ash from the chamber, mixing it in the process. Because the conveyor is not operated continuously, a drum of ash is not always generated the same day as the waste being burned. A one month comparison period was believed to be the optimum to provide a good correlation between metals in the feed and metal concentrations in the ash.

Monthly metals feed data are available for the TSCAI from 1988 to August 1998. The amount of lead fed to the incinerator during this time period is shown in Figure 2. Months during which a data point is not plotted represent dates when the incinerator was not operating. Also plotted on Figure 2 are the ash analytical data and a dashed line showing the LDR regulatory limit. It should be noted that the dashed lines do not necessarily represent the specific date that the LDR regulatory limits changed, but rather, the values that applied to different groups of ash depending on when they would be disposed.

The ash analytical data were generated as a result of characterizing the ash for land disposal. In general, the ash was grouped into characterization populations based on generation dates. Because the population sizes could include 200 or more drums, containers were statistically selected to be sampled. This typically resulted in 12 to 22 containers sampled per population. A summary of the ash populations characterized for disposal is presented in Table XI.

Although there are a total of 123 TCLP metal data points, there are only 25 to 38 data points plotted for the metals listed in Figure 2. The reason for this is that the statistical selection often resulted in more than one container being analyzed for ash generated in a particular month. The values plotted for arsenic, cadmium, chromium, lead, and mercury represent the maximum value observed in any sample generated during a particular month. For uranium, an average, rather than a maximum was utilized. The reasons for this and a brief discussion of the feed and ash results are presented below.

Table XI. Ash Population Dates and Available Data Summary

Burn Type	Ash Generation Dates	Number of samples analyzed for TCLP metals
Solid / Liquid Waste Burns	October 1996 – December 1997	21
Solid / Liquid Waste Burns	December 1995 – October 1996	12
Solid / Liquid Waste Burns	November 1994 – December 1995	22
Liquid Burns	January 1992 – March 1992	13
Liquid Burns	October 1988 – July 1991	12
Solids trial burn	May 1990 - June 1990	22
Liquids / Solids trial burn	May 1989 – October 1989	16
Trial Burns / Liquid waste Burns	May 1988 – June 1988	1
Trial Burns / Liquid waste Burns	June 1987 – May 1988	4
Total:		123

Arsenic

The arsenic loading in the TSCAI has usually been less than 5,000 grams per month, with only eight exceptions. The period of maximum loading occurred in February and March of 1994 with 16,591 and 20,170 grams fed, respectively. A total of 38 data points were collected for arsenic in ash; most of these results were reported to be less than the laboratory's detection limit and none of the results have come close to exceeding the UTS limit of 5.0 mg/L. The effect of the February and March 1994 high loading rates on the ash can not be evaluated because no ash samples were collected during this time. Of the 38 ash data points, 14 (representing 27 individual analyses) occurred after the introduction of solids to TSCAI in September 1995. The fact that only one ash sample generated after September 1995 (October 1996; 0.13 mg/L) had a reported value greater than the laboratory detection limit suggests that either the arsenic is not partitioning to the ash or the arsenic is not leachable.

Cadmium

The mass of cadmium fed to the incinerator has generally been less than 2,000 grams per month; however, large spikes of over 14,000 grams per month (August 1996) have been seen since the introduction of solids at the end of 1995. A total of 38 data points for cadmium in ash were reviewed, with most of the results below the method detection limit. Fourteen (14) of these data points (representing 27 samples) represent ash generated after September 1995. Two ash samples have exceeded the current UTS limit of 0.11 mg/L cadmium. These samples were generated in February (0.296 mg/L) and March of 1997 (0.266 mg/L). These two samples were generated only two operating months after a period of relatively high cadmium feed (the incinerator was not operated in November and December of 1996, due to its annual maintenance outage). However, during the outage, all ash should have been removed from the incinerator, eliminating the possibility that ash with high concentrations of cadmium could be generated later. This suggests at least three possibilities: 1) that the relatively low cadmium feed rates from January to March 1997 were sufficient to cause the ash to exceed the UTS; 2) that the ash generation dates were improperly recorded, or 3) that characterization data failed to identify "hot-spots" of cadmium in the waste feed.

WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

It should also be noted that comparison of the high cadmium feed rates shows that the high cadmium concentrations observed in the TSCAI sludge and CNF sludge included waste generated during the period of high cadmium feed.

Chromium

With the exception of February to May 1991, when extremely high chromium feed levels were noted (~58,000 grams to 212,000 grams), similar behavior to that of cadmium was observed, with increased levels of chromium feed observed after September 1995. A total of 37 data points for chromium in ash were evaluated; most of these results were less than the laboratory method detection limit. Thirteen of these data points (representing 27 individual samples) represent ash generated in September 1995 or later. Despite the expected preference for chromium to partition mainly to ash, there have been no UTS failures for chromium, including two samples generated during and shortly after the February to May 1991 period of high chromium loading. As with arsenic, the data suggest that either the chromium is not partitioning to the ash or that the chromium is not leachable.

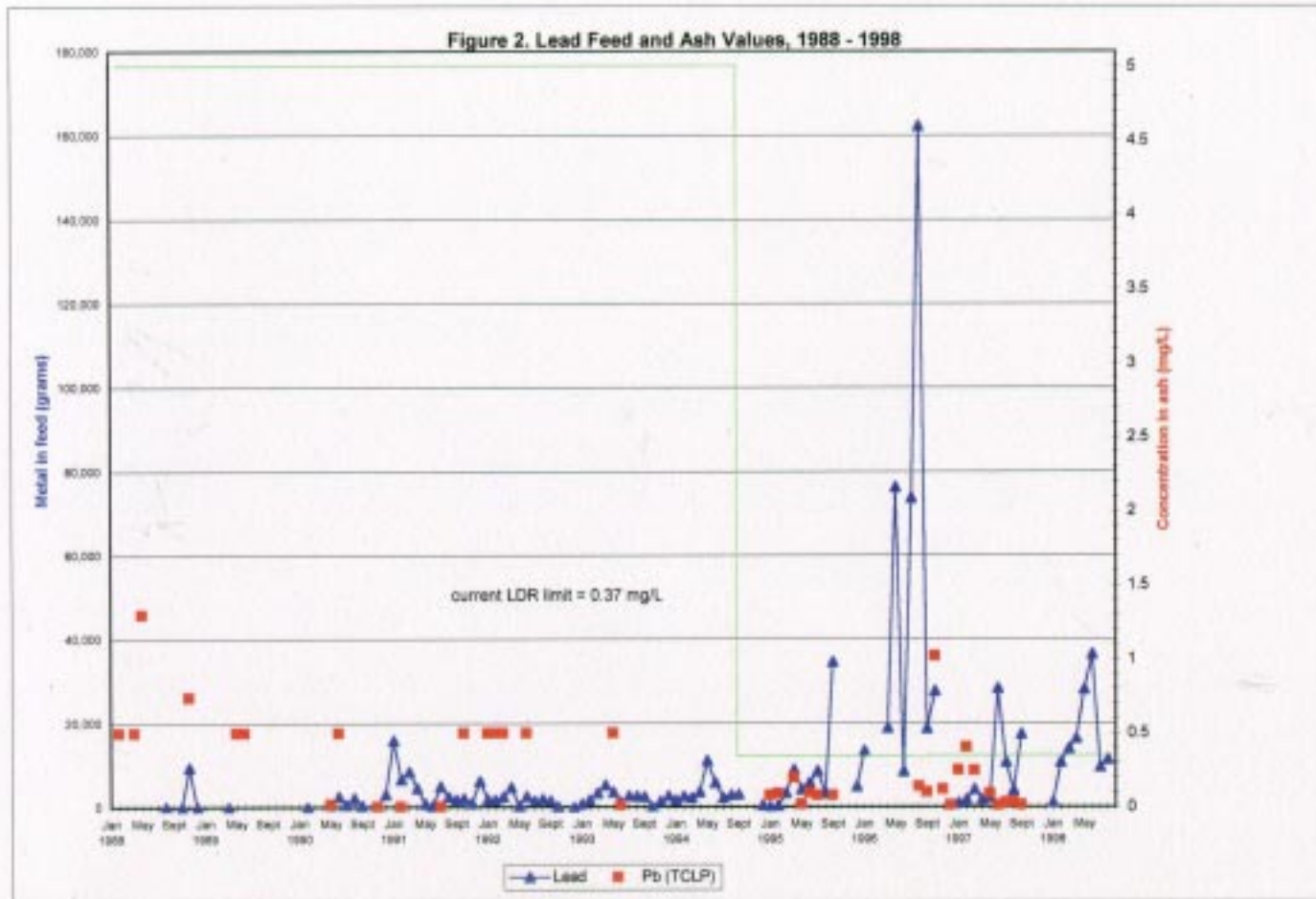
Lead

Figure 2 shows that the mass of lead fed to the incinerator generally mirrors that of cadmium, with sharp increases noted after September 1995 with the introduction of solid waste feeds. A total of 38 data points for lead in the ash are plotted, and again most of the results were below the method detection limit. Fourteen of these data points (representing 27 samples) were collected from ash generated after September 1995. The two samples which exceeded the UTS value of 0.37 mg/L for lead occurred in October 1996 (1.02 mg/L) and February 1997 (0.406 mg/L). The failure in the ash generated October 1996 corresponds well with the period of maximum feed, which occurred in August 1996 (~162,000 grams). The high level in the February 1997 drum raises the same questions previously discussed for the high cadmium results. In the case of lead, at least, the loading rates during January and February of 1997 were one to two orders of magnitude greater than cadmium, but still relatively low compared to the lead loading in previous months.

As was the case with cadmium, the period of higher lead loading to the TSCAI corresponds with the high lead concentrations observed in the TSCAI sludge and CNF sludge.

Mercury

The amount of mercury fed to the TSCAI has been relatively variable, but over a much smaller range than other metals. Only once has the mass of mercury in the feed exceeded 1,000 grams per month. Of the 39 samples which have been analyzed for TCLP mercury, only three samples had mercury present above the laboratory method detection limit, and none of these values exceeded the UTS limit of 0.025 mg/L. These results appear to confirm the expectation that mercury is not partitioning to the ash.



Uranium

Because there is no UTS limit for uranium, the ash data used in calculations represent total, rather than the leachable values plotted for the other metals. Unfortunately, the lack of an UTS limit for uranium has resulted in fewer individual ash samples being analyzed. There are only 25 data points available for the time period 1988 to 1998, compared to 37 to 39 for the other metals discussed. Of these 25 data points, only 11 were collected after the introduction of solid feeds, all in 1996 and 1997. As previously mentioned, the data represent an average of all analyzed samples of ash that were generated in a particular month. An average has been selected because the concentrations reported are usually real values, rather than non-detects and these values can be directly compared to the feed values, unlike the leachable results for the other metals. This comparison is possible because the total mass of ash generated during each month is known.

Calculation of the uranium partitioning values for the months in 1996 and 1997 for which ash data are available results in values ranging from 1 to 114% of the uranium partitioning to ash (see Table XII). This wide range of values may be partly due to slight lags in the ash generation dates: a certain amount of ash may exist as slag inside the kiln which is not "generated" until the kiln refractory is replaced at the end of each year. Calculation of uranium partitioning over the entire 1996-1997 timeframe results in **an average value of 30% of the uranium partitioning to the ash**. This is lower than expected, based on the calculated volatility temperature of uranium. Based on this value, it is probable that other species of uranium, with lower volatility temperatures are being formed in the incinerator, resulting in the majority of the uranium partitioning to the TSCAI sludge. For additional comparison, the uranium partitioning value was calculated for the May-June 1990 trial burn, since mostly solid wastes were burned during this period. The calculated partitioning value for the trial burn was 14%.

Table XII. Uranium Partitioning in TSCAI Ash

Date	Net kg ash	Average uranium concentration in ash (ug/g)	Total uranium in feed (g)	Grams uranium in ash	% Uranium partitioning to ash
October 1996	10,562	74.2	14,299	784	5.5
January 1997	3,130	1,070	2,934	3,350	114
February 1997	6,893	798	6,216	5,499	88.5
March 1997	6,234	31.5	14,842	196	1.3
April 1997	4,297	70.2	29,879	302	1.0
June 1997	3,716	1,450	21,568	5,388	25.0
July 1997	7,743	5,150	49,214	39,876	81.0
August 1997	5,796	815	9,908	4,721	47.7
September 1997	4,062	1,386	34,741	5,630	16.2
October 1996 – September 1997	58,496	1,043	206,208	61,027	30

Calculation of the partitioning values of the other metals discussed in this study is more difficult because the majority of the analytical data are based on leachable metals, which are the LDR regulated values. Review of existing ash analytical data showed 39 samples for which both leachable and total metals were analyzed. These data were evaluated to determine if typical total metal to leachable metal ratios could be developed for the TSCAI ash. Comparison of these data shows one concern with using such a ratio as a comparison tool: the ratios are often significantly effected by the analytical method detection limit. This is particularly evident for the total metals analyses, which were often reported as not detected, but at a

WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

relatively high detection limit (e.g. < 100 ug/g). In such a case, if the total metal were actually present at 10 ug/g, the total to leachable ratio would change by a factor of 10. Because of this limitation, the worst case condition of the highest ratio obtained was used to calculate partitioning coefficients. The total to leachable metal ratios used were:

- Arsenic 31.2:1
- Cadmium 6,800:1
- Chromium 12,000:1
- Lead 8,000:1
- Mercury 330:1

Because of concerns with the high variability observed in the uranium partitioning coefficients calculated on a monthly basis, average partitioning values were developed over the time period September 1995 to September 1997. The calculated values, compared to the partitioning values calculated during trial burns and the experimental data reported by Carroll and Waterland^b (refer to Tables II and III) are shown in Figure 3. The partitioning values listed in Figure 3 were calculated using the maximum ash data previously discussed and should therefore be biased toward partitioning to ash. Results of the data summarized in Figure 3 are discussed below.

Arsenic

The calculated amount of arsenic partitioning to ash was 0.6%, compared to approximately 90% observed in the experiments performed by Carroll and Waterland. This much lower value may be due to matrix effects. The experiments performed by Thurnau and Carroll and Waterland used a clay-based matrix for the feed. Greater than 90% of the solid feed mass fed to the TSCAI has consisted of spent activated carbon and combustible materials such as cloth, paper, and plastic. These wastes may not provide a suitable matrix to which arsenic can bind. If this is the case, the partitioning of arsenic becomes mainly a function of temperature. With a volatility temperature of 31.7 °C, little partitioning to ash would be expected. The effect of the presence of calcium on arsenic partitioning can not be evaluated at the present time because the calcium feed rates to the TSCAI are not recorded. The lower than expected partitioning value is consistent with the observation made based on review of the data that arsenic does not appear to be partitioning to the ash.

Cadmium

The calculated amount of cadmium partitioning to TSCAI ash was 54%, which is higher than expected based on published experiments. Some of this difference may be attributable to the lower chlorine content in the TSCAI feed: an average value of 2.9% chlorine was fed during the time period September 1995 to September 1997. The higher than expected cadmium partitioning value is consistent with the previous observation that even relatively low cadmium feed rates could be sufficient to cause the ash to exceed the UTS.

Chromium

The amount of chromium calculated to partition to TSCAI ash was 59%, considerably lower than the expected value of greater than 90%. The reasons for this apparent discrepancy are not known, but one possible explanation is that the analytical detection limits failed to provide a worst case total to leachable metals ratio. The lower than expected calculated value supports the previous observation that either less chromium was partitioning to ash than expected or that the chromium is present in the ash in a leach-resistant form.

Lead

The amount of lead partitioning to ash was calculated to be 23%. This is higher than the 12% value obtained by Carroll and Waterland, but lower than the 52% value calculated from the 1995 Trial Burn. These differences can be explained by the chlorine concentrations in the feed. During the 1995 Air Test, the chlorine concentration was 1.1%, whereas an average value of 2.9% chlorine was fed during September 1995 to September 1997. The additional chlorine fed during the waste burns could be sufficient to account for the decreased amount of lead in the ash. The chlorine feed concentrations and the lead partitioning coefficients reported by Carroll and Waterland and calculated for the 1995 Air Test and the waste burn data are summarized in Table XIII.

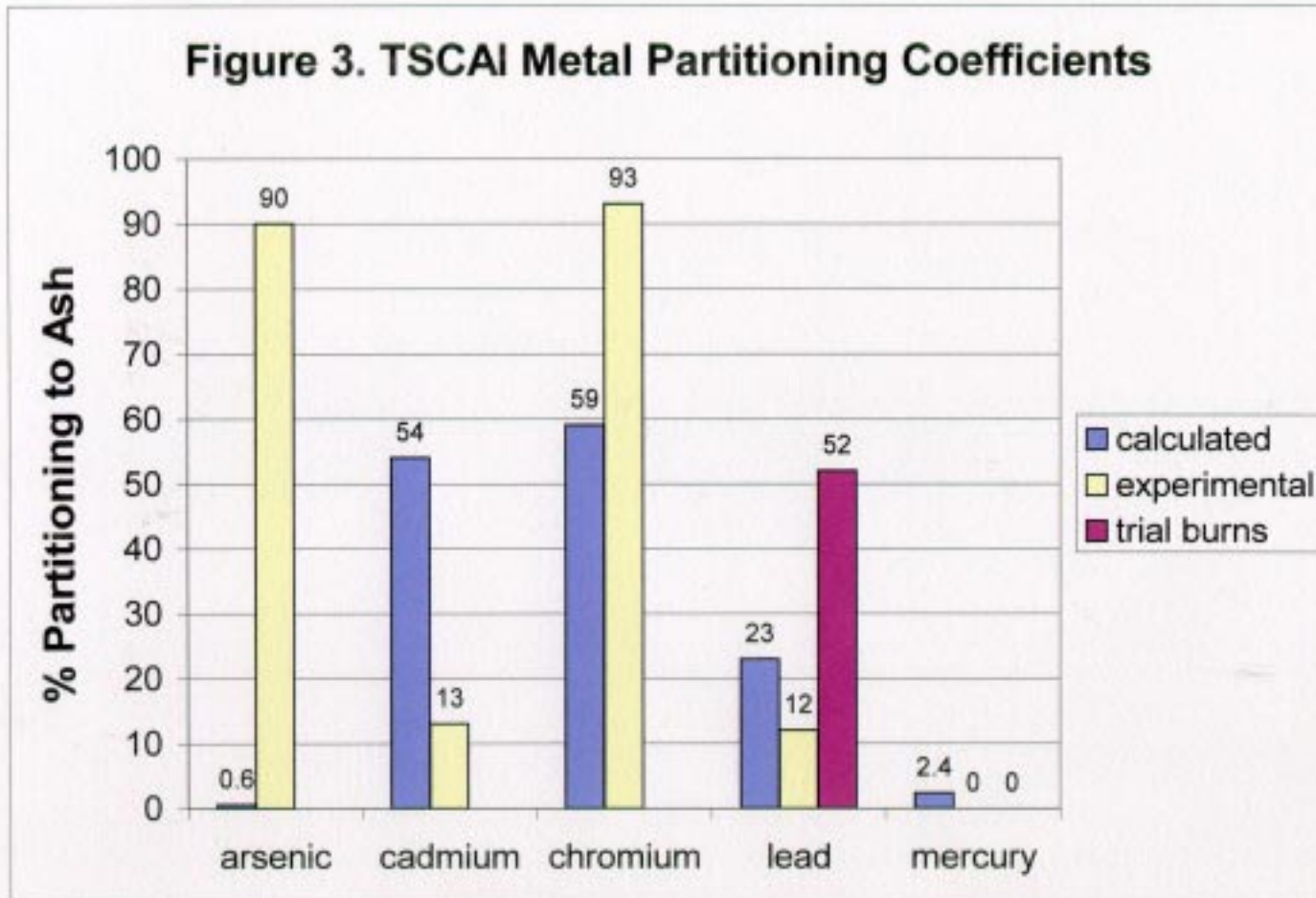
Table XIII. Lead Partitioning Coefficients at Various Chlorine Feed Concentrations

Data Source	Chlorine Content	Lead Partitioning Coefficient
Carroll and Waterland	0%	84%
1995 Air Test	1.1%	52%
1995 to 1997 Waste Burn Data	2.9%	23%
Carroll and Waterland	4%	12%
Carroll and Waterland	8.3%	6%

Mercury

The calculated partitioning of mercury to TSCAI ash was 2.4%, which is higher than expected based on the trial burn results. It is likely that this result has been effected by analytical method detection limits and that virtually all of the mercury in the feed is emitted from the stack.

Figure 3. TSCAI Metal Partitioning Coefficients



PREDICTION OF METAL LEVELS IN ASH

The ash partitioning values calculated in the previous section could be used to establish a maximum amount of metal that can be in the feed without causing the ash to exceed the UTS, if the amount of ash to be produced can be approximated. The formula to calculate this is given by:

$$(M_f * P_c) / M_a < UTS * M_r \quad [Equation 1]$$

where:

M_f = mass of metal in feed;

P_c = partitioning coefficient of metal;

M_a = mass of ash generated;

UTS = Universal Treatment Standard concentration of metal (mg/L);

M_r = Total to leachable metals ratio;

(units of UTS * M_r are in ug/g)

In practice, the use of this formula as an aid in determining metal loading should be used with caution. Although the amount of ash to be generated from each waste feed stream is calculated from characterization data, comparison of these values with the actual ash mass generated shows some large discrepancies on a month-to-month basis, as shown in Table XIV. The reason for the discrepancy may result from applying a uniform moisture correction factor to the expected ash value; in reality, the ash moisture may vary significantly. Based on the data presented in Table XIV, accurate and timely quantitative predictions can not presently be made of the amount of feed metals that will result in ash exceeding the treatment standards.

Although quantitative predictions may not be possible, some qualitative predictions can be made for the next group of ash to be characterized for disposal (ash generated from January 1998 through October 1998). Based on the metal loading rates during this time and the calculated partitioning coefficients, arsenic, chromium, and mercury in the ash are not expected to exceed the Universal Treatment Standards. Because cadmium and lead partitioning can be significantly influenced by the chlorine in the feed, it is helpful to see how the loading of these metals corresponded to the percentage of chlorine in the feed. These data for cadmium and lead (refer to Figure 4 for lead) are discussed below.

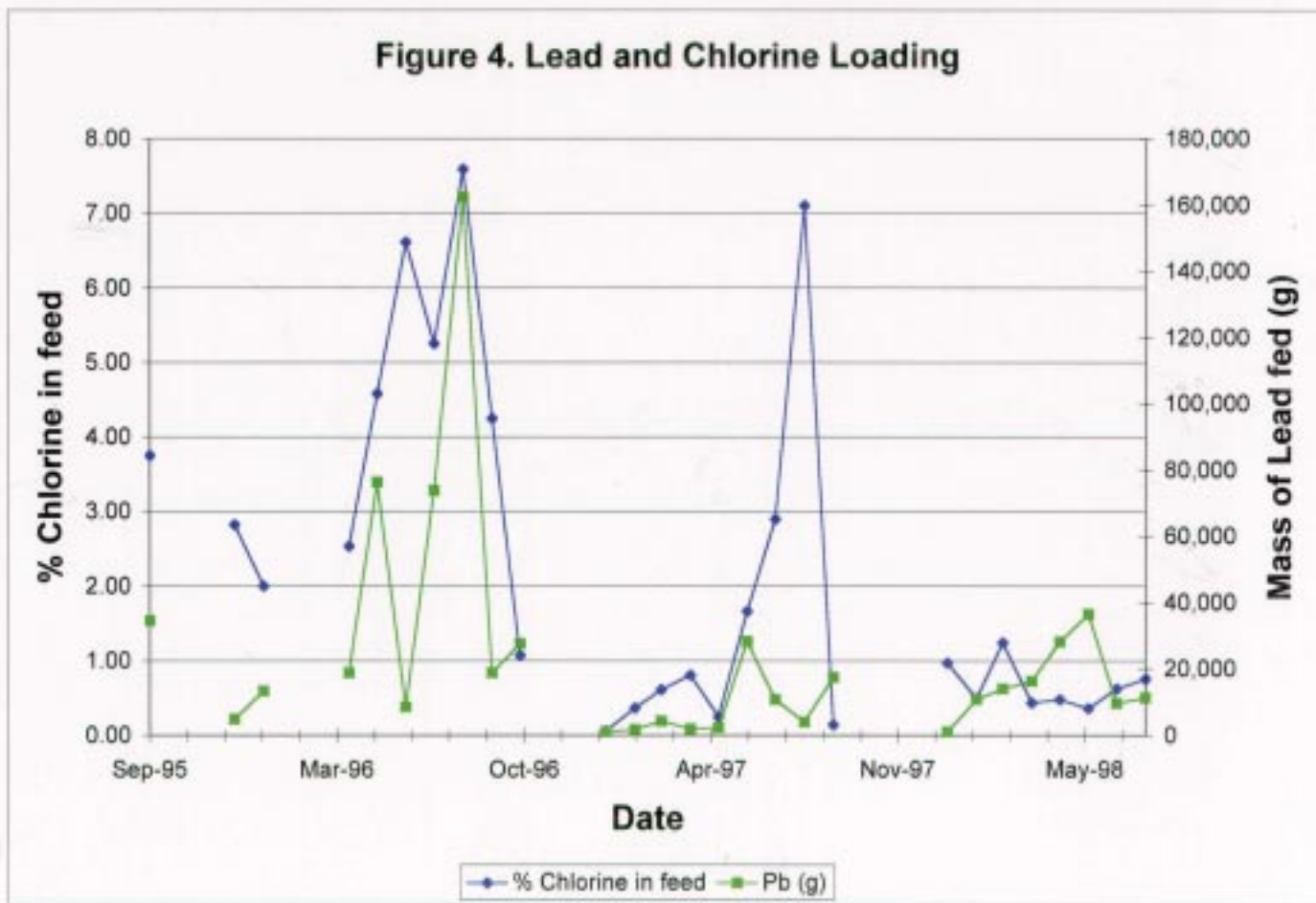
Cadmium

The ash samples which previously exceeded the UTS for cadmium were generated during a time of relatively low cadmium (<200 grams per month) and chlorine (< 0.7%) loading. The period during 1996, which had no cadmium failures, had relatively high loading rates but correspondingly high chlorine loading. The ash generated from January through October 1998 has relatively low cadmium and chlorine loading. Based on the conditions existing for the early 1997 samples which failed, it is possible that the 1998 ash will exceed the UTS for cadmium.

WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

Table XIV. Comparison of Actual vs. Predicted Ash Masses

Date	kg ash actual	kg ash expected	kg ash expected, corrected for moisture	% difference
Sep-95	3652	3238	4048	-10.8
Oct-95	0	0	0	N/A
Dec-95	500	417	521	-4.2
Jan-96	1427	2102	2628	-84.1
Feb-96	0	0	0	N/A
Mar-96	0	0	0	N/A
Apr-96	1049	2475	3094	-194
May-96	2854	5223	6529	-129
Jun-96	1446	950	1188	17.9
Jul-96	1834	2172	2715	-48.0
Aug-96	5733	6868	8585	-49.7
Sep-96	3865	5511	6889	-78.2
Oct-96	10562	8176	10219	3.2
Nov-96	0	0	0	N/A
Dec-96	0	0	0	N/A
Jan-97	3130	1008	1260	59.7
Feb-97	6893	1023	1279	81.4
Mar-97	6234	3949	4936	20.8
Apr-97	4297	1297	1621	62.3
May-97	6063	2412	3015	50.3
Jun-97	3716	2995	3744	-0.74
Jul-97	7743	4381	5477	29.3
Aug-97	5796	5934	7418	-28.0
Sep-97	4062	8112	10140	-149
Oct-97	0	0	0	N/A
Jan-98	197	626	783	-297
Feb-98	5814	6077	7596	-30.6
Mar-98	4519	3815	4768	-5.5
Apr-98	7699	7314	9143	-18.8
May-98	6304	4348	5435	13.8
Jun-98	6769	2930	3663	45.9
Jul-98	6285	5355	6694	-6.5
Aug-98	2937	2698	3372	-14.8



Lead

Figure 4 shows that at the latter part of 1998, the lead loading exceeded the loading during the time the previous samples exceeded the treatment standards, while the chlorine loading is lower, leading to the conclusion that more lead will be present in the 1998 ash. Based on these data, it is likely that the 1998 ash will exceed the UTS for lead.

CONCLUSIONS AND RECOMMENDATIONS

The waste feed to the incinerator has a significant effect on metal partitioning behavior in the TSCAI. The lack of solid materials in the feed will apparently cause even metals with high volatility temperatures to partition away from the ash. Preliminary ash partitioning values were calculated for arsenic (0.6%), cadmium (54%), chromium (59%), lead (23%), mercury (2.4%), and uranium (30%). These values were derived from data obtained from September 1995 through September 1997, when solids were a significant fraction of the waste feed.

The partitioning coefficients of arsenic, chromium, and uranium were less than expected based on published experimental data and thermodynamic properties, while the partitioning coefficient of cadmium was nearly twice as high as expected. The lower than expected arsenic partitioning value is likely due to matrix effects, while the reason for the high cadmium partitioning value is only partially explained by the chlorine concentration in the feed. The partitioning coefficients of lead and mercury corresponded well with their expected behavior.

The fraction of metals not partitioning to the ash appear to be partitioning to the sump sludge, or in the case of mercury, to the stack gas. This is supported by the fact that high metal loading rates during the period September 1995 to September 1997 correspond with dates that metals (i.e. cadmium and lead) in the TSCAI sludge and CNF sludge have exceeded the Universal Treatment Standards.

The use of a monthly time period for comparing feed and ash data appears to be too short to enable quantitative predictions to be made regarding residual concentrations in the ash. This is especially true for periods when solids were not a significant portion of the waste feed. The calculated partitioning values are based upon a limited number of data points and may be subject to error due to the use of the total to leachable metal ratio, which is significantly influenced by the analytical method detection limits. Additional experimentation is needed to refine the preliminary partitioning estimates cited in this paper. Future trial burns should attempt to incorporate the measurement of the ash produced each day to more readily allow ash partitioning calculations to be made.

FOOTNOTES

^a Calculated from September 1995 to September 1998 feed data

^b Data reported by Tillman [1] have been utilized in the case of mercury.

REFERENCES

1. Tillman, David A. (1994) *Trace Metals in Combustion Systems*. Academic Press, Inc. San Diego, USA.
2. Barton, Robert G., Clark, W.D., and Seeker, W.R. (1990) Fate of Metals in Waste Combustion Systems. *Combustion Science and Technology*. **74**, 327-341.
3. Eddings, Eric G. and Lighty, Joann S. (1991) Fundamental Studies of Metal Behavior During Solids Incineration. *Combustion Science and Technology*. **85**, 375-389.

WM'00 Conference, February 27 - March 2, 2000, Tucson, AZ

4. Carroll, Gregory J., Waterland, Larry R., et al. (1989) The Partitioning of Metals in Rotary Kiln Incineration. *International Conference on New Frontiers in Hazardous Waste Management (3rd)*, San Diego, CA. EPA/600/D-89/208.
4. Waterland, L.R., Fournier, D.J., Lee, J.W., and Carroll, G.J. (1991) Trace Metal Fate in a Rotary Kiln Incinerator with an Ionizing Wet Scrubber. *Waste Management*. **11**, 103-109.
5. Pershing, D.W., Heap, M.P, et al. (1993) Solid Waste Incineration in Rotary Kilns. *Combustion Science and Technology*. **93**, 245-276.
6. Rand, M.H. and Kubaschewski, O. (1963) *The Thermochemical Properties of Uranium Compounds*. Interscience Publishers, New York.
7. Thurnau, Robert C., and Fournier, Donald Jr. (1992) The Behavior of Arsenic in a Rotary Kiln Incinerator. *Journal of the Air and Waste Management Association*. **42**, 179-184.
8. Beryllium and Lead Emissions Performance Test. (1990) Martin Marietta Energy Systems.
9. TSCA Incinerator Division. (1995) Air Performance Test Report for the Oak Ridge Toxic Substances Control Act Incinerator. Lockheed Martin Energy Systems. K/TSCA-SCS-RPT-3002.
10. Gibson, L.V. et al. (1994) Partitioning of Strontium and Cesium in the TSCA Incinerator. *International Incineration Conference Proceedings*, Houston Texas. K/ASD-033.