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DOE MIXED WASTE METALS PARTITION IN A ROTARY KILN WET OFF-GAS SYSTEM (U)

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DOE Mixed Waste Metals Partition in a Rotary Kiln Wet Off-Gas System

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ABSTRACT

In 1996, the Savannah River Site plans to begin operation of the Consolidated Incineration Facility (CIF) to treat solid and liquid RCRA hazardous and mixed wastes. The Savannah River Technology Center (SRTC) leads an extensive technical support program designed to obtain incinerator and air pollution control equipment performance data to support facility start-up and operation. Test burns were conducted at Energy and Environmental Research Corporation's Solid Waste Incineration Test Facility, using surrogate CIF wastes spiked with hazardous metals and organics. The partition of metals between the kiln bottom ash, scrubber blowdown solution, and stack gas was measured as a function of kiln temperature, waste chloride content, and waste form (liquid or solid).

Three waste simulants were used in these tests, a high and low chloride solid waste mix (paper, plastic, latex, PVC), and a liquid waste mix (benzene and chlorobenzene). An aqueous solution containing: antimony, arsenic, barium, cadmium, chromium, lead, mercury, nickel, silver, and thallium was added to the waste to determine metals fate under various combustion conditions. Test results were used to divide the metals into three general groups, volatile, semi-volatile, and non-volatile metals. Mercury was the only volatile metal. No mercury remained in the kiln bottom ash under any incineration condition. Lead, cadmium, thallium, and silver exhibited semi-volatile behavior. The partition between the kiln ash, blowdown, and stack gas depended on incineration conditions. Chromium, nickel, barium, antimony, and arsenic exhibited nonvolatile behavior, with greater than 90 wt% of the metal remaining in the kiln bottom ash. Incineration temperature had a significant effect on the partition of volatile and semi-volatile metals, and no effect on nonvolatile metal partition. As incineration temperatures were increased, the fraction of metal leaving the kiln increased. Three metals, lead, cadmium, and mercury showed a relationship between chloride concentration in the waste and metals partition. Increasing the concentration of chlorides in the waste or burning liquid waste versus solid waste resulted in a larger fraction of metal exiting the kiln.

INTRODUCTION

The Savannah River Site plans to begin operation of the Consolidated Incineration Facility (CIF) in 1996 for treatment of solid and liquid RCRA hazardous and mixed wastes. The CIF will utilize a 13 million Btu rotary kiln incinerator and 5 million Btu secondary combustion chamber (SCC) to treat both solid and liquid combustible waste. The air pollution control system (APCS) consists of a liquid recirculating quench and steam-atomized scrubber for offgas cooling/cleaning, a cyclone separator and mist eliminator for liquid/gas separation, and final HEPA filtration prior to atmospheric discharge through the facility stack.

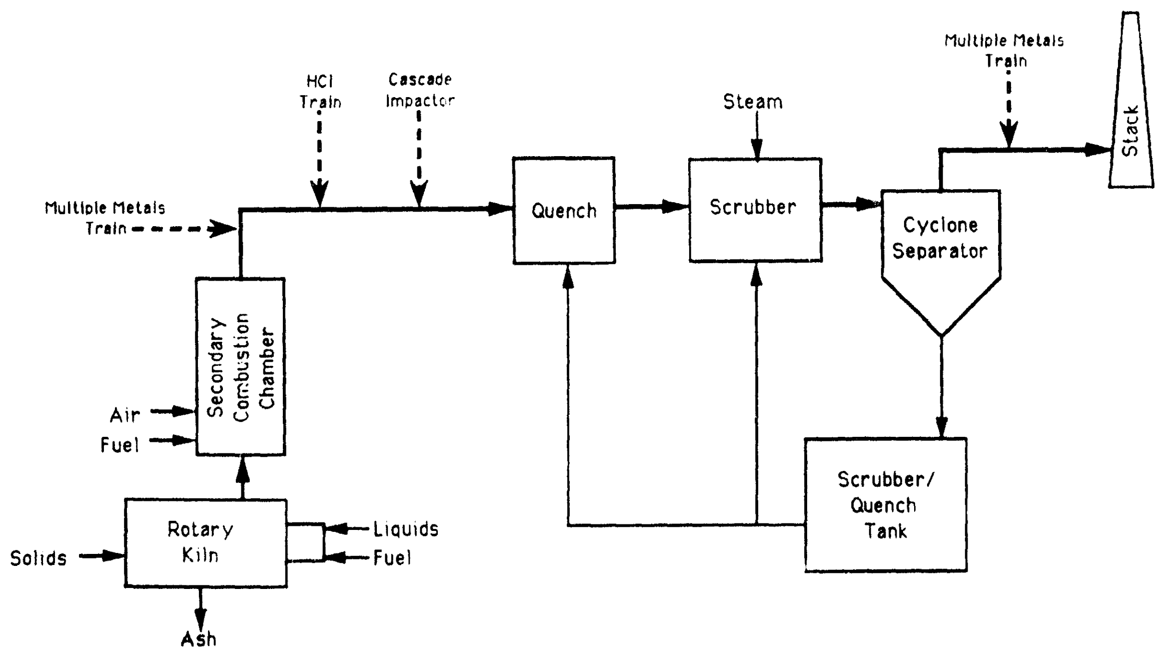
The CIF will treat wastes that contain hazardous heavy metals regulated by the Resource Conservation and Recovery Act (RCRA). Thus, all secondary wastes (kiln ash and scrubber blowdown) must comply with RCRA disposal requirements. Of specific interest is the waste feed metals partition to the three facility output streams, kiln bottom ash, scrubber blowdown, and the stack gas. Metals concentrations in the bottom ash and blowdown must be known to insure successful secondary waste treatment prior to final disposal. Kiln bottom ash will be solidified in portland cement and placed in onsite mixed waste burial vaults. This wasteform must pass strict leaching tests (Toxicity Characteristic Leaching Procedure, TCLP) before placement in the burial vaults. Typical and worst case ash compositions must be known to determine formulations that will pass TCLP. The scrubber blowdown must also be treated for permanent disposal. Blowdown treatment process development is ongoing, and accurate waste compositions are required.

To provide the required information for successful secondary waste treatment, test burns were conducted in a pilot scale rotary kiln incinerator equipped with a wet offgas scrubber. The primary test objective was to characterize the partition of metals between the kiln bottom ash, scrubber blowdown, and stack gas.

TEST PROGRAM

All testing was conducted at Energy and Environmental Research's (EER) Solid Waste Incineration Test Facility (SWIFT) pilot-scale Rotary Kiln incinerator System (RKS). A SRTC pilot-scale scrubber, prototypic of the CIF offgas scrubber, was added to the RKS to simulate the CIF APCS. A schematic of the RKS, with sampling locations, is presented in Figure 1.

Figure 1
EER Rotary Kiln Incinerator System



Simulated Waste

All tests were conducted using three CIF simulated waste mixes. The three waste compositions are presented in Table I. Two waste types, E and F, represent typical SRS combustible solid wastes. Waste type F, containing no PVC, was used to determine the impact of reduced chlorine concentration on metals emissions. Type G waste simulated typical high Btu liquid organic waste.

TABLE I

Simulated Waste Compositions (Wt %)

Component	Solid Waste Mix Waste Type E	No PVC Solid Waste Waste Type F	Liquid Waste Waste Type G
Paper [$C_6H_{10}O_2$]	45	55	0
Polyethylene [C_2H_2]	25	25	0
Latex [$(C_5H_8)_{23}S$]	20	20	0
PVC [C_2H_3Cl]	10	0	0
Benzene [C_6H_6]	0	0	95
Chlorobenzene [C_6H_5Cl]	0	0	5

To simulate the hazardous constituents in SRS waste, toxic metals and organics were spiked into the simulated waste feed. Metals spiking solutions were prepared by mixing soluble, nonchlorinated metal salts with deionized water. Metals spiking solution preparation was complicated by precipitate forming interactions between some metal compounds. These precipitates were acceptable (though not desirable) only for use in spiking the solid wastes (Types E and F). Antimony, arsenic, and barium had to be eliminated from the metals spike for the liquid waste tests (Type G) to prevent precipitation. The metals solution was added directly to the solid waste. For the liquid waste tests, the metals solution was injected into the kiln flame zone through an atomizing nozzle. The average metals concentrations for both solid and liquid waste are presented in Table II.

TABLE II

Average Metals Concentrations in Waste Feed
(mg metal/kg waste feed)

Metal Compound	Solid Waste (Type E & F)	Liquid Waste (Type G)
Antimony, $C_4H_4KO_7Sb$	538	0
Arsenic, $Na_2HAsO_4 \cdot 7H_2O$	38	0
Barium, $Ba(C_2H_3O_2)_2 \cdot H_2O$	85,741	0
Cadmium, $Cd(NO_3)_2 \cdot 4H_2O$	9	10
Chromium, $Cr(NO_3) \cdot 9H_2O$	1,860	2,267
Lead, $Pb(NO_3)_2$	7,426	9,114
Mercury, $Hg(NO_3)_2 \cdot H_2O$	446	542
Nickel, $Ni(NO_3) \cdot 6H_2O$	7,297	8,963

Silver, $AgNO_3$	5,435	6,663
Thallium, $TlC_2H_3O_2$	545	663

Test Conditions

The test variables included kiln temperature, SCC temperature, waste chloride content, and scrubber/ quench water chloride content. The test plan is shown in Table III. Kiln temperature was varied from 760°C to 1000°C and the secondary chamber temperature varied from 870°C to 1100°C. The waste chloride content varied from 1.5 wt% (Waste Type F) to 6 wt% (Waste Type E). Both temperature and waste chloride concentration have been shown to influence the partition of heavy metals in waste incinerators. The remaining variable in the test matrix is NaCl concentration in the scrubber water. This variable was included in the test matrix to determine if NaCl in the scrubber water impacted metal scrubbing efficiency.

TABLE III
Test Plan

Run	Waste Type	Kiln Temperature (°C)	Afterburner Temperature (°C)	Salt in Scrubber Water
1	E	1000	1100	Y
2	E	1000	1100	Y
3	E	1000	1100	N
4	F	1000	1100	N
5	E	870	980	Y
6	F	870	980	Y
7	G	1000	1100	Y
8	G	870	980	Y
9	E	760	870	Y

TEST RESULTS

When subjected to incineration conditions, metal compounds in the waste feed can either remain in the kiln ash or vaporize, depending on the metal volatility. The metal volatility temperature has been defined as the temperature at which the effective equilibrium vapor pressure of all species containing the metal is 10^{-6} atmospheres. This vapor pressure was selected because it represents a measurable amount of vaporization. The lower the volatility temperature, the more volatile the metal. Volatility temperatures have been successfully used to predict general trends in metals partitioning.[1] Table IV presents the calculated volatility temperatures for the metals used in this study.

TABLE IV
Metal Volatility Temperature[2]

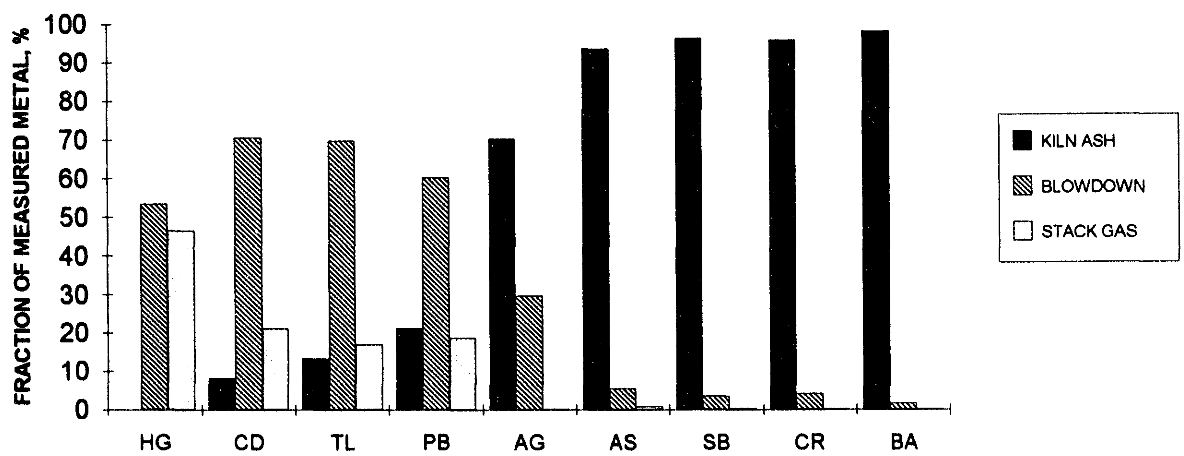
Metal	Volatility Temp (°C)	Volatility Temp (°C) with chlorides present
Chromium	1613	1610
Nickel	1210	693
Silver	904	627
Barium	849	904
Thallium	721	138
Arsenic	700	700
Antimony	660	660
Lead	627	15
Cadmium	214	214
Mercury	14	14

Partition factors were determined by measuring metal concentration in the kiln bottom ash, scrubber blowdown, and stack gas generated during each test run. Since equipment configuration prevented recovery of all kiln bottom ash, a theoretical ash wt%, based on waste feed analyses, was used to calculate total metal recovered in the kiln bottom ash. Since no solid waste was burned in runs 8 and 9, partition for these runs is limited to the offgas blowdown and stack gas.

All metals partition data was normalized by the total mass balance closure achieved. The run to run variation in metals mass balance closure was removed from the data by normalizing with the total closure achieved. Therefore, data is presented as percent of total metal measured in the outlet streams (ash, blowdown, and stack), instead of percent of metal in the waste feed. Use of normalized distributions is the best method to quantify metal partition, given the variable and less than perfect metals mass balance closure.

Figure 2 shows the partition of heavy metals at CIF design operating conditions (Runs 1 and 2).

Figure 2
Metals Partition at CIF Design Operating Conditions



The following general observations can be made from Figure 2. The metals divide into three general groups. The first group contains volatile metals. These metals completely volatilize from the kiln and enter the APC system. A fraction is removed by the APC equipment, and a fraction remains in the stack gas. Mercury was the only metal falling into this group with a volatility temperature less than 100°F. As expected, no mercury remained in the kiln bottom ash. All mercury vaporized, exited the kiln, passed through the APCS, and a fraction exited with the stack gas which has been observed in other studies.[3] The partition factors are shown in Figure 2.

The second general group contains semi-volatile metals. Depending on incineration conditions, a fraction of the metal remains in the kiln bottom ash, while the remainder enters the APC system and is either captured by the scrubber or emitted with the stack gas. Lead, cadmium, thallium, and silver fall into this group. The metals volatility temperatures in the presence of chlorides range from 15 to 627°C. Since all runs contained chloride, either in the PVC or the organic POHC spiked in the waste, the volatility temperature with chlorides present must be used. The test data indicates that lead was not as volatile as the theoretical volatility temperature would have predicted.

The third group contains nonvolatile metals. The metals volatility at incineration temperatures is so low, metals concentration in the vapor phase is negligible, and all metal remains in the kiln ash. A small metal fraction can be found in the blowdown due to particulate entrainment to the APCS. Chromium, nickel, barium, antimony, and arsenic are in this group. These metals calculated volatility temperatures are higher than the semi-volatile metals. Other studies have documented their relative nonvolatile in the incineration environment.[4,5]

Each test variable effect on metals partition is discussed below.

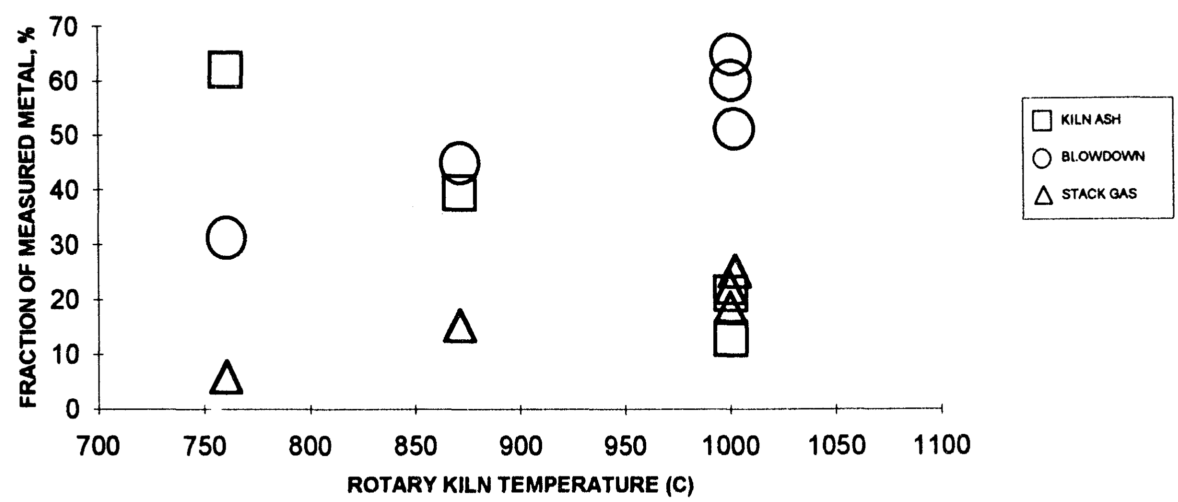
Incineration Temperature

As expected, incineration temperature did have a significant effect on the partition of several metals. These tests did not investigate the PCC and SCC temperature effects separately, because previous studies demonstrated SCC temperature had minimal impact on metals partition.[4,5] The PCC temperature effect was expected to be most pronounced for metals with a volatilization temperature near the kiln operating temperature. Increasing kiln temperatures is expected to increase volatile metals concentration in the kiln offgas. And metals concentrations in the kiln offgas would be unchanged for metals with volatilization temperatures significantly above tested kiln temperatures.

As expected, the semi-volatile metals partition was dependent on kiln temperature. Silver and lead (Figure 3) showed the most significant relationship between kiln temperature and metal partition for solid waste. Increasing the kiln temperature decreased the metal fraction in the kiln ash. Mercury, cadmium, and thallium also exhibited a noticeable kiln temperature effect. Although the metal partition to the kiln ash remained relatively constant (and very low) as the kiln temperature increased, the metal fraction out the stack increased and the metal captured by the scrubber decreased. The increased stack emissions at higher PCC temperatures for all these metals is most likely due to increased submicron particle generation at higher PCC temperatures. Volatilized metals condense on offgas particulate in the APC system which are then removed by the offgas scrubber. However, the scrubber has a lower collection efficiency for submicron particles. Thus, an increase in the fraction of submicron particles would be expected to cause an increase in metals stack emissions.

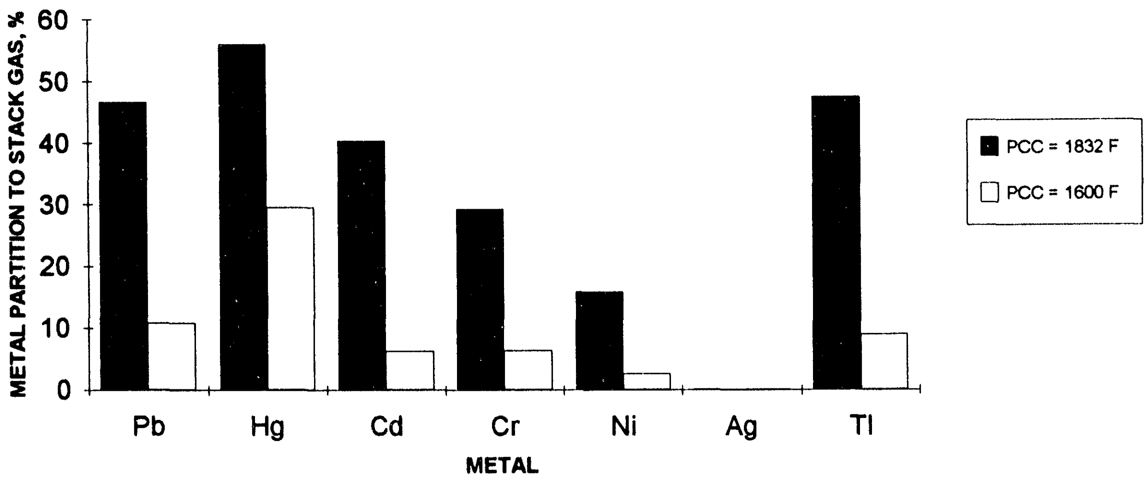
Figure 3

Lead Partition as Function of Incineration Temperature



The temperature effect was even more pronounced for liquid waste. Since no kiln bottom ash was recovered during liquid waste incineration, all metals partitioned between the scrubber blowdown and the stack gas. For every metal (except silver with 100% partition to the blowdown), the metal fraction in the stack gas increased 2X to 5X at higher kiln temperatures. This behavior is likely due to the increase in offgas submicron particulate at higher kiln temperatures (70% submicron at 1000°C and 54% submicron at 870°C). Figure 4 illustrates the increase of metals partition to the stack gas for liquid waste incineration at different kiln temperatures.

Figure 4
Liquid Waste Stack Gas Partition vs. Kiln Temperature



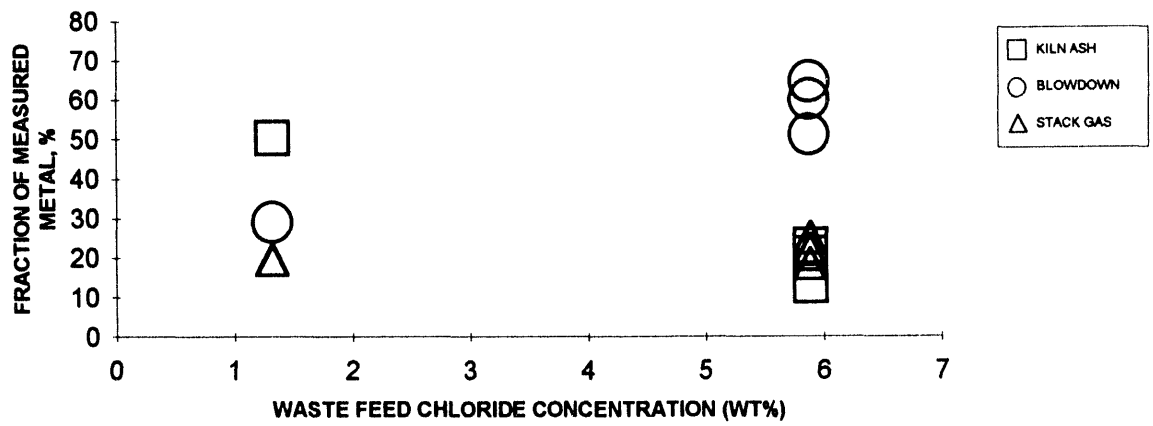
Waste Chloride Concentration

To investigate the impact waste chloride concentration has on metal partition, two types of solid wastes were burned. One type contained 6 wt% chloride (Waste Type E), the other contained 1.5 wt% chloride (Waste Type F). Incinerating metals bearing waste with chlorides can result in the formation of metal salt compounds, which usually have a lower volatilization temperature than the metal oxide or hydroxide. Table IV compares metal volatilization temperatures both with and without chlorides. Metals with lower volatilization temperatures in the presence of chlorides would be expected to have a greater partition to the APCS.

Test data clearly shows a chloride effect on metal partition for three spiked metals (lead, mercury, and cadmium). Four metals, nickel, silver, thallium, and lead have lower calculated volatility temperatures in the presence of chlorides. Thus, increasing waste chloride concentration should increase the metals fraction in the kiln offgas. Of these four, only lead had a significant chloride effect (Figure 5). The chloride effect for silver and thallium was not clearly discernible due to data scatter. The large drop in volatility temperature for thallium in the presence of chlorides would have predicted a significant dependence between chloride concentration and thallium partition. Yet, the data shows chlorides had little effect on thallium partition. The reason a chloride effect was not observed for nickel is the volatility temperature in the presence of chloride is still too high to allow measurable quantities of nickel to enter the offgas.

Two metals, cadmium and mercury, had significant chloride effects at high PCC temperatures, although chlorides did not change the calculated volatility temperature. This data indicates that more volatile metal chloride compounds appear to be forming that are not included in the equilibrium code used to calculate metal volatility temperature. At the lower PCC test temperature, the chloride effect was significantly reduced. Previous tests have demonstrated increased cadmium and lead volatility in the presence of chlorides and no chloride effect for chromium, arsenic, and barium.[6]

Figure 5
Lead Partition vs. Waste Chloride Concentration



Waste Form (Solid or Liquid)

To determine the effect waste form has on metal partition, both liquid and solid simulated wastes were burned. The waste form effect on metal partition was found to differ for the volatile/semi-volatile metals, and non-volatile metals. For both volatile and semi-volatile metals, the metal fraction in the stack gas increased when liquid waste was burned. The fraction changed from 20-30% metal in the stack gas to approximately 50% when burning liquid waste. The remainder of the metal was found in the scrubber blowdown since no ash remained in the kiln after liquid waste incineration. This behavior is likely due to the increase in offgas submicron particulate while burning liquid versus solid waste (70% submicron for liquid waste and 50% submicron with solid waste).

Nickel and chromium were the only non-volatile metals in the simulated liquid waste. Greater than 90% of the metal remained in the kiln bottom ash when solid waste was burned, yet 70-80% of the metal was found in the scrubber blowdown when liquid waste was burned. The remaining metal exited the stack.

Chloride Concentration in the Scrubber Water

The CIF will use a steam-atomized scrubber to remove particulates, acid gases, and metals from the kiln offgas. Scrubbed acid gas (primarily HCl) accumulation will cause the recirculating scrubber solution pH to decrease. Sodium hydroxide will be added to the scrubber liquid to maintain a neutral pH. The neutralization reaction will cause salt (NaCl) to buildup in the solution. The average NaCl concentration in the scrubber will be approximately 2 wt%. Several runs were conducted with 2 wt% NaCl in the scrubber solution. Two runs, 3 and 4, were conducted with no NaCl in the scrubber solution to determine if salt in the scrubber or quench solutions impacts metals partition.

The test data did not reveal any relationship between scrubber or quench solution salt concentration and metal partition. For every spiked metal, there was no significant difference in metals partition or metals removal efficiency when the salt concentration was 0 or 2 wt%.

CONCLUSIONS

The primary test objective was characterizing the metals partition between the kiln bottom ash, scrubber blowdown, and stack gas. Three simulated waste mixes spiked with metals and organics were burned at three incineration temperatures. Metals partition was determined from analysis of ash and blowdown samples and stack gas metals sampling.

The metals were categorized into three groups based on partition behavior; volatile, semi-volatile, and nonvolatile. Only mercury showed volatile behavior with all the mercury escaping the kiln ash in every run. The mercury split between the blowdown and stack gas was dependent upon incineration conditions. Lead, cadmium, thallium, and silver exhibited semi-volatile behavior. These metals would divide between the kiln ash, blowdown, and stack gas with ratios dependent upon incineration conditions. Chromium, nickel, barium, antimony, and arsenic exhibited nonvolatile behavior at incineration temperatures. The metal concentration in the vapor phase at incineration temperatures was negligible, resulting in greater than 90 wt% of the metal remaining in the kiln bottom ash.

The effect of several incineration operating parameters on metals partition was evaluated. As expected, incineration temperature had a significant effect on volatile and semi-volatile metals partition, and minimal effect on nonvolatile metals partition. As incineration temperatures were increased, the fraction of metal leaving the kiln ash increased. For mercury, the fraction of metal in the stack gas increased with increasing incineration temperature. Three metals tested, lead, cadmium, and mercury showed a relationship between chloride concentration in the waste and metals partition. Increasing the concentration of chlorides in the waste resulted in a larger fraction of metal exiting the kiln and stack. Feeding the metals to the kiln in liquid waste versus solid waste resulted in an increase in metals partition to both the blowdown and stack gas for all metals. One reason for this behavior is that no kiln bottom ash was recovered for the liquid waste runs. Chloride concentration in the scrubber water did not show a significant effect on metals partition.

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