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THE RELATIVE EFFECTIVENESS OF MINERAL-BASED SORBENTS FOR METAL CAPTURE IN A BENCH-SCALE INCINERATOR

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INTRODUCTION

Given the concern over the emission of hazardous constituent trace metals from incinerators, there is currently considerable interest in the potential use of mineral-based sorbents for capturing and retaining those metals in the incinerator "ash" discharges (fly ash and bottom ash).

Most of the research completed to date has focussed on quantifying the effectiveness of various proposed sorbents for capturing vaporized metals from the flue gas. In such applications, it is theorized that vaporized metals will react with the sorbent particles at elevated incinerator temperatures or heterogeneously condense onto the sorbents as the flue gas cools. In the absence of available condensation sites, vaporized metals will primarily undergo homogeneous condensation, forming a fine fume. Thus, the goal with flue-gas sorbents is to make particles available with which the metals can react or upon which the metals can condense. Metals bound to larger sorbent particles will be more effectively collected by air pollution control systems (APCSs) than metals presented as a fine fume. Studies completed to date suggest that chemical reaction between the metal and the sorbent dominates over physical adsorption, offering the additional advantage of reduced potential for metal leaching from collected particulate.

Other researchers have studied the incorporation of sorbents into the solid feed. This approach seeks to capture and bind the metals in the incinerator bottom ash, preventing them from exiting with the combustion gases. Research completed to date suggests that for this approach to be effective, the metal should become volatile in the incinerator environment and chemically react with the sorbent material.

The subject test program was designed to further investigate this second approach by screening several minerals for their suitability as sorbent materials for capturing metals in the solid bed and preventing their release to the flue gas. In addition to capturing the metals, an ideal sorbent would retain them in the ash when disposed, so that extraction of the ash by the toxicity characteristic leaching procedure (TCLP) would yield a leachate with metals concentrations below respective regulatory levels. Accordingly, the objective of this screening program was to evaluate several candidate sorbents with respect to: [1] the degree to which they facilitate retention of trace metals in the ash/solid bed discharged from an incinerator; and [2] the degree to which they retain trace metals in the solid bed when subjected to TCLP extraction.(1)

METHODOLOGY

Test Equipment

The screening tests comprising this program were conducted in the bench-scale thermal

treatability unit (TTU) at the U.S. EPA Incineration Research Facility (IRF). The TTU is a small commercial pathological incinerator that has been modified to allow: continuous test material feed and treated material (e.g., ash) removal; variable treatment temperature control; and expanded process operation monitoring.

The combustor portion of the TTU consists of three chambers. The charge chamber is designed to accept the solid material feed stream and corresponds to the primary combustion chamber (or kiln portion) of a waste incinerator. The retention chamber, which directly follows the charge chamber, is designed to effect further organic constituent destruction and corresponds to the secondary combustion chamber (or afterburner) of a waste incinerator. The breaching chamber serves as a second-stage afterburner. Volumes of the charge chamber, retention chamber, and breaching chamber are 0.82 m^3 (29 ft^3), 0.67 m^3 (23.5 ft^3), and 0.10 m^3 (3.5 ft^3), respectively. Each of the three chambers is fired with natural-gas-fueled burners.

Test Program

The test program consisted of 50 tests, including two duplicates of one test condition. Test variables were sorbent material type, solid bed temperature, feed chlorine content, and metal form in the feed.

Six sorbents were evaluated. The first five (silica, diatomaceous earth, kaolinite, bauxite, and alumina) were selected based on the most promising results from other researchers and make up a sorbent-material spectrum ranging from pure silica to pure alumina. The attapulgite clay used in past IRF trace metals studies was tested as the sixth sorbent.

The approximate mineral content of diatomaceous earth, kaolinite, and bauxite are given in Table 1. Silica is presumed to be pure SiO_2; alumina is presumed to be pure Al_2O_3; and the attapulgite clay is a hydrated magnesium aluminum silicate $[(Mg,Al)_5Si_8O_{22}(OH)_4 \cdot 4H_2O]$ containing some dolomite $[Ca,Mg(CO_3)_2]$, calcite $[CaCO_3]$, and silica.

Three solid bed temperatures were tested: 540°C, 700°C, and 870°C (1000°F, 1300°F, and 1600°F). Two feed chlorine contents were tested: 0% and 4% by weight. Polyvinyl chloride powder was added to the mixtures as the chlorine source.

TABLE 1. APPROXIMATE SORBENT MINERAL COMPOSITION

	Diatomaceous earth	Kaolinite	Bauxite
SiO_2	90.4	52	11
Al_2O_3	6.5	45	84
Fe_2O_3	2.3	1	5
TiO_2	--	2	--
CaO	0.2	--	--
MgO	0.3	--	--
Other oxides	0.3	--	--

Sorbent impact on the retention of the following trace metals was evaluated in the program: arsenic, cadmium, chromium, lead, and nickel. Two forms of incorporating the metals into the feed mixtures were evaluated. Past trace metals tests at the IRF have used aqueous metal spike solutions containing soluble nitrate salts of the metals (with the exception of arsenic which has been added as

As_2O_3). For continuity, this form was one of the two used in the tests.

The second form of metal spiking was a metal compound "dispersion". The dispersion consisted of metal compound powders suspended in a liquid carrier analogous to pigments dispersed in paint or ink. Chromium, cadmium and lead were present as metal oxides in the dispersion, while arsenic and nickel were introduced as sulfides and carbonates, respectively. Because of a difficulty achieving homogenous feed mixtures with the metal compound dispersion, the discussion of results in this abstract is limited to the 36 tests in which the aqueous metal spike solution was used.

For each test, weighed amounts of the appropriate mixtures of sorbent, PVC (for tests with chlorine-containing feed), and metal spiking formulations were added to a TTU quartz tray. Charge depth was held constant at nominally 2 cm, corresponding to a charge volume in the tray of approximately 300 cm^3. Target feed metal concentrations were also constant as follows: arsenic (200 mg/kg); cadmium (50 mg/kg); chromium (150 mg/kg); lead (250 mg/kg); and nickel (150 mg/kg). Charge mass ranged from 50 g to 320 g, depending on sorbent bulk density.

Tray residence time in the TTU was approximately 20 minutes at the target solid bed temperature. Based on the results of other research, no further reaction between the sorbent and metals was expected after the first 10 minutes at target temperature.

Sampling and Analysis

For each test, TTU gas temperatures and solid bed temperatures were measured. Samples of unspiked sorbent, metal spiking solution, TTU feed, and TTU discharge were collected for metal analyses. Additionally, one TTU feed sample from each of the sorbent/metal formulation combinations and TTU discharge samples from every test were subjected to TCLP extraction, and the resulting leachates analyzed for trace metals.(2) Quality assurance samples were prepared as well.

Aqueous liquid samples were digested using EPA Method 3010.(3) Solid samples were digested using a microwave-assisted HNO_3/HF procedure.(4) Analyses of each of the latter digestates for arsenic were by Method 7060 [GFAA].(3) All other digestates analyses were by Method 6010 [ICAP].(3)

RESULTS

Feed Samples

Despite the use of a rigorous digestion method, analyses of feed samples often yielded concentrations below those expected (based on prepared metal spike solutions). Of the five metals, cadmium and lead exhibited the largest difference between target and measured concentrations. On average, metal concentrations in the attapulgite clay and kaolinite were below target more so than the other matrices.

Since the same preparation and analysis methods were applied to both the feed and treated material samples, it is assumed that any sampling or analysis bias should manifest itself in both sample types (i.e., the feed and treated material associated with a particular sorbent). Therefore, comparisons between the feed samples and treated material were based on measured (as opposed to prepared) feed concentrations.

Retention of Metals in Ash

Metal volatility was judged by examining treated material (ash) concentrations relative to feed concentrations (adjusted for loss of mass during treatment); the greater the reduction in concentration, the greater the volatility. On average, there was little difference among the sorbents for limiting the volatility for chromium and nickel. With no chlorine in the feed, there was also little difference between the sorbents for cadmium. With 4% chlorine present in the feed, cadmium appeared to be less volatile from kaolinite, relative to the other sorbents. Finally, for the tests both with and without chlorine in the feed, arsenic appeared to be less volatile from the attapulgite clay and lead less volatile from kaolinite, compared to the other sorbents.

In addition to the overall differences noted above, changes in temperature affected the retention of metals in several of the sorbents when chlorine was present in the feed. Arsenic volatility in the silica, diatomaceous earth, and alumina matrices increased with increasing temperature, while the reverse occurred in the attapulgite clay. Cadmium volatility in diatomaceous earth, alumina, and bauxite increased with increasing temperature. Chromium volatility was relatively constant across the temperature range. Lead volatility increased with increasing temperature for the alumina and bauxite matrices. Nickel volatility in the attapulgite clay decreased with temperature.

In cases where chromium appeared to impact metal behavior (independent of temperature), it consistently increased the volatility of the metal. Such increases were seen for arsenic in bauxite; cadmium in silica and attapulgite clay; and lead in silica. Chromium and nickel volatility did not appear to be impacted by chlorine in any of the matrices.

Resistance to Leaching by TCLP

"Fractional leachability" represents the ratio of the TCLP-extracted metal to the total metal measured in the sample. In nearly every case, leachabilities from treated samples were less than the corresponding feed samples. Attapulgite clay, bauxite, kaolinite, and alumina were better for limiting arsenic leachability during tests with and without chlorine in the feed. With no chlorine in the feed, all of the sorbents had similar leachabilities for cadmium and lead. With feed chlorine, attapulgite clay, kaolinite, and diatomaceous earth were better for limiting cadmium and lead leachability, as was bauxite for cadmium leachability. With one exception, all of the sorbents had similar chromium leachability; chromium was very easily leached from the treated attapulgite clay samples. Nickel leachability did not differ significantly among the sorbents for the tests with chlorine in the feed. With no chlorine in the feed, alumina, attapulgite clay, bauxite, and kaolinite were better at limiting nickel leachability.

Increases in temperature consistently led to decreased leachability of cadmium from each of the sorbents and of arsenic, chromium, lead, and nickel from diatomaceous earth. Arsenic leachability from the other sorbents was not affected by temperature. When chlorine was not present in the feed, chromium leachability from silica and alumina decreased with increasing temperature, as did lead leachability from kaolinite and nickel leachability from silica. With chlorine in the feed, lead leachability from silica, and nickel leachability from silica, alumina and bauxite decreased as temperature rose.(5)

CONCLUSIONS

Given the screening nature of these tests, and considering the analytical problems encountered with many of the feed samples, the results of the tests should be used with caution. Nevertheless, a number of preliminary conclusions may be made. Combining the two sorbent criteria of limited metal volatilization and reduced leaching by TCLP, kaolinite and attapulgite clay appear to be the most promising sorbents for arsenic; kaolinite for cadmium; kaolinite, diatomaceous earth, and attapulgite clay for lead. With few exceptions, the sorbents showed comparable performance for the other matrix/metal combinations; chromium leachability appeared to increase in the attapulgite clay matrix with increased temperature.(5)

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FOR MORE INFORMATION

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