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Project Summary

Analysis and Assessment of Incinerated Municipal Sludge Ashes and Leachates

Thomas L. Theis, Margaret McKiernan, and Lawrence E. Padgett

Research was conducted to analyze the physical and chemical properties of ashes from incinerated municipal sludge and of corresponding dewatered sludge. Samples were gathered from 10 wastewater treatment plants ranging in size from 0.22 to 27.1 m^3/sec. These samples were subjected to a series of physical, chemical, and biological tests, including batch and chemical extractions and the Ames *Salmonella* assay.

Results showed that the addition of supplemental chemicals during wastewater or sludge treatment strongly influenced the leachate properties and composition of both dewatered sludge and ash samples. Both iron(III) and aluminum salts acted to concentrate trace metals, which were then readily leached from the sludge ashes. The addition of lime during treatment elevated the ash and sludge pH values, which determine the availability of metals to the environment. In the absence of inorganic chemical addition, incineration acted generally to decrease trace metal availability.

The behavior of arsenic during the various leaching tests was the opposite of that for metal cations with respect to pH. Low pH values resulted in the release of larger numbers of cations, but arsenic release was usually greatest at high pH values.

Incinerated sludges demonstrated weak mutagenic activity in the Ames assay. Four of the 10 ash samples gave positive results, generally in the presence of activating mammalian enzymes. In addition, one dewatered sludge sample also gave positive results. Both frameshift and base-pair mutagens were implicated.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In the United States, slightly more than 4.5 million metric tons (5 million tons) of municipal wastewater sludge solids are produced yearly. This figure is expected to increase to 6 million metric tons (6.6 million tons) per year by 1985. Presently, some 30 percent of these solids are thermally reduced in volume by incineration methods, the most popular of which are the multiple-hearth and fluidized-bed types. An average figure of 75 percent for the volatile fraction of municipal sludge yields about 338,000 metric tons (373,000 tons) of ash residue that must be disposed of yearly. The most common disposal methods are landfilling and lagooning. Because of the initial cost and complex operation of sludge incinerators, their use is confined mostly to wastewater treatment plants with capacities exceeding 0.044 m^3/sec (1 MGD), most being greater than 0.22 m^3/sec (5 MGD). Thus, though the total quantities of ash generated are not as great as other types of combustion wastes, their disposal can be a sizable operation on a local basis.

Handling the ash from both of the commonly used incineration methods often involves contact with water. In the fluidized-bed system, the ash is removed from the exit stream by a scrubber. For the multiple hearth system, ash handling can be either wet (for slurry pipelines) or dry. But even for dry handling, the ash is usually conditioned for disposal with water.

The purpose of this research was to investigate the physical and chemical properties of the ashes from a number of incinerated municipal sludges and of the corresponding dewatered sludges. Characteristics that define the release of inorganics were determined using single-reagent leachate tests, and the effects of organics were assessed through application of the Ames *Salmonella* assay.

Experimental Methods

Representative samples of dewatered sludge and incinerated sludge ash were obtained from 10 municipalities. Analyses for pH, moisture content (for dewatered sludge only), and volatile matter were made according to established methods. Bulk composition for major and trace elements was achieved through an HF-aqua regia digestion procedure followed by analysis with flame or flameless atomic absorption spectrophotometry (AAS). The method of additions was used with deuterium arc background correction. Dewatered sludge samples were further treated with hydrogen peroxide (final concentration 2 percent) to eliminate interferences from organic matter. Analyses for arsenic and selenium were made by flameless AAS using the nickel complexation method.

Three single reagent extraction tests were used in this research: ASTM Method A water shake extraction procedure (ASTM-A), U.S. Environmental Protection Agency (EPA) extraction procedure (EP), and the International Atomic Energy Agency (IAEA) leaching test.

Ames assays were performed on a number of inorganic and organic extraction procedures (Table 1). In tabulating results, revertants were taken from the linear portion of the dose-response curve and were reported at the highest concentration that was not toxic to the bacteria. Ratios of diluted-to-original samples ranged from 1:10 to 1:10,000.

Table 1. *Extraction Procedures*

Extraction Type	*Reagent*	*Solution (ml) Solid (g) Ratio*	*Contact Time*	*Comments*
Inorganic (ASTM Method A. neutral)	*Double-distilled water*	*4:1*	*48 hours*	*Collects water-soluble materials from the ash.*
Inorganic (acidic)	*1.0 N nitric acid*	*5:1*	*24 hours*	*Collects strong acid-soluble materials.*
Inorganic (acidic)	*0.1 M hydroxylamine hydrochloride in 0.01 M* HNO_3	*50:1*	*30 min.*	*Dissolves Mn oxides.*
Inorganic (near-neutral)	*0.05 M calcium chloride*	*10:1*	*16 hours*	*Releases easily-exchangeable species.*
Inorganic (basic)	*0.01 M sodium hydroxide*	*10:1*	*16 hours*	*Dissolves Al oxides.*
Inorganic (basic)	*0.1 M sodium pyrophosphate*	*10:1*	*16 hours*	*Dissolves Al oxides.*
Inorganic (acidic)	*0.2 M oxalic acid/ 0.4 M ammonium oxalate*	*10:1*	*1 hour*	*Dissolves oxides of Fe and Al.*
Inorganic (IAEA method, neutral)	*Double-distilled water*	*12:1*	*1 week*	*Collects water-soluble materials.*
Organic (acidic)	*0.5 M acetic acid*	*5:1*	*24 hours*	*Collects weak acid-soluble organics.*
Organic (strong solvent)	*Dimethyl sulfoxide*	*10:1*	*24 hours and 1 week*	*Collects organics.*
Organic (Soxhlet)	*95% Ethanol*	*20:1*	*12 hours*	*Collects organics.*
Organic (Soxhlet)	*Benzene*	*20:1*	*12 hours*	*Collects organics.*
Organic	*Acetone*	*4:1*	*1 week*	*Collects organics.*
Inorganic/organic (resin column)	*Water/eluted with acetone*	*4:1*	*48 hours*	*Collects and concentrates organics.*

Results

Pertinent information and basic data characterizing the sludge ash and dewatered sludge samples appear in Tables 2 and 3, respectively.

Except for sample number 10, each ash sample produced an alkaline reaction in distilled water. Samples 5,6, and 8, to which lime was added at the treatment facility, also displayed the highest pH values. The pH of the dewatered sludge is, without exception, lower than that of the corresponding sludge ash. But this result is to be expected since acidic volatiles such as hydrogen sulfide and carbon dioxide are driven off during incineration.

Values for bulk elemental concentrations of the ashes and dewatered sludges are given in Tables 4 and 5, respectively. Elevated values of iron, aluminum, and calcium are evident in those locations where ferric chloride, aluminum sulfate, or lime were added. Though comparisons of absolute mass conservation in Tables 4 and 5 are not valid since the samples were gathered at different locations and times in their respective treatment schemes, the ash and dewatered sludge concentrations do, nonetheless, correspond generally on the basis of fixed solids.

Analyses for the elements arsenic, cadmium, chromium, nickel, lead, and ıble 2. *General Characterization for Sludge Ash Samples*

Sample	Type of Incinerator	Highest Operating Temperature (°C)	Disposal Method	Physical Characteristics	pH	% Volatile Matter	Chemical Addition	Purpose of Chemical Addition	Fe(III) & Al Added-mg as $FeCl_3$/g Dry Sludge[a]
1	Multiple hearth	925	Landfill	Brown, variable	7.71	0.28	Polymer, pickel liquor	Sludge conditioning phosphorus removal	
2	Multiple hearth	760	Landfill	Light brown, very fine	8.81	0.59	$FeCl_3$, Alum	Phosphorus removal	93.3
3	Fluidized bed	760	Lagoon to landfill	Gray, very fine	7.94	0.89	Polymer	Sludge conditioning	
4	Multiple hearth	980	Lagoon to landfill	Brown, fine	8.15	0.20	Polymer	Sludge conditioning	
5	Multiple hearth	840	Landfill	Brownish-gray intermixed with fibrous material	9.81	5.85	$FeCl_3$, lime	Sludge conditioning	158.6
6	Multiple hearth	870	Lagoon	Dark brown, very fine	12.20	0.49	$FeCl_3$, lime, polymer	Sludge conditioning, phosphorus removal	97.5
7	Multiple hearth	925	Lagoon	Reddish-brown variable	8.79	0.04	Polymer	Sludge conditioning	
8	Multiple hearth	760	Landfill, lagoon occasion-ally	Brown, fine	11.72	0.16	$FeCl_3$ lime polymer	Sludge conditioning phosphorus removal	240.0
9	Fluidized bed	730	Landfill	Black and brown, fine	8.02	1.35	Alum, polymer	Sludge conditioning phosphorus removal	46.2
10	Fluidized bed	790	Landfill	Light brown, fine	5.89	0.53	Polymer	Sludge conditioning	

Chemical dosage normalized to a weight per weight basis of dried sludge solids, regardless of the manner.

ılenium in the ASTM-A shake test were niformly low (frequently at or near the ɜtection limit), and they are not summarized ere. This test is buffered by protolysis ɪactions that occur at the surface of the ɔlid material. Thus, the pH during the ɪst remains close to those values given ı Tables 2 and 3—that is, in the neutral to lkaline range. In addition, the ionic rength is generally low (though uncon-·olled). Neither of these conditions romotes the release of surface-bound ıetal species.

Results for both ash and sludge amples in the EP test appear in Table 6. ;omparison of Table 6 with Tables 2 and reveals that the leachability of all lements studied in the EPA-EP appears ɔ depend strongly on the earlier addition ıf iron(III) and/or aluminum salts to the ıastewater during treatment or to the sludge for conditioning. Table 7 summarizes the important trends in terms of average values extracted for both ashes and sludges. The correlation with iron(III) and aluminum addition and the amount of metal cations released is a direct one. For arsenic, which has an anionic aqueous chemistry, an inverse relationship exists. At pH 5, the most common forms of iron and aluminum oxides possess positively charged surfaces, implying that the proton can successfully compete for surface sites against trace metal cations. Under these conditions, however, arsenic (existing most probably as arsenate or arsenite) will be electrostatically attracted to the surface. Attractive chemical forces may also exist. An additional feature of the data is that (except for cadmium) incineration acts to increase the leachability of cation elements if iron(III) and/or aluminum(III) salts have been added. For arsenic and cadmium, incineration decreases their leachability. If these salts are not added, cationic elements are generally less leachable in the ash than the sludge.

A summary of the IAEA leaching test results appears in Table 8. This test was performed on six ash samples only. The data show a trend toward greater metal release for those ashes obtained from treatment facilities that use iron or aluminum salts (samples 5, 8, 9). Again, an inverse relationship exists for arsenic, which has an anionic aqueous chemistry.

The amount of a given metal released was found to change as the test proceeded, revealing some interesting trends. Figure 1 shows detailed IAEA release data for ash Sample No. 1. Changes in concentration for the indicated metals are shown

Table 3. *General Characteristics for Dewatered Sludge Samples*

Sample	Flow to Treatment Plant (MGD)	Dry Sludge Produced (Metric Tons Per Day)	Color	% Solids	% Volatile Content	pH
1	615	435	Black	18.2	54.6	4.95
2[a]	36	24	Dark brown	37.8	68.4	5.43
3	6	6.1	Dark brown	35.1	60.0	5.73
4	163	136	Dark brown	33.1	30.1[d]	5.79
5[b]	53	27	Gray	24.1	62.5	7.17
6[b]	18	18	Black	21.1	43.2	6.53
7	8	4.4	Black	15.8	69.1	5.38
8[b]	18	16	Dark brown	29.2	30.8[e]	7.23
9[c]	9	9.3	Black	16.0	52.2	5.91
10	5	3.2	Black	17.0	75.6	5.24

[a] $FeCl_3$, alum added.
[b] $FeCl_3$, lime added.
[c] Alum added.
[d] Portion of ash is recycled as a dewatering aid.
[e] Anaerobically digested.

along with pH, which rises sharply during the test (probably because of the exposure to solution of a base deposit). Though the metal cations chromium and cadmium show gradual declines with increasing pH, arsenic release rises. As suggested earlier, such behavior would be expected as the surface assumes a negative charge at the high pH. Trends similar to those of Figure 1 were also found for other ash samples. Such changes during the IAEA test suggest a rather nonuniform distribution of major and minor elements, both on the surface and as a function of depth in the ash.

In the Ames test, the extraction procedures that resulted in the greatest number of positives were those designed to extract nonpolar organic compounds, or to concentrate them, or both. Table 9 summarizes these results. Four of the ten ashes gave positive results using the Ames criteria of induced reversions greater than two times the spontaneous reversion rate, with one or more extractants. In addition, one dewatered sludge (Number 5) was tested and also gave positive results. Most positives were found in the presence of the activating mammalian enzymes, suggesting that the compounds responsible for the positive results are in a promutagenic form. In addition, strain responsiveness verifies the increased sensitivity of the R factor strains TA 98 and TA 100 over the original strains TA 1538 and TA 1535. These two strains produce the greatest number of positives, indicating that mutagens in the samples can induce both base pair and frameshift mutations.

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Table 4. *Bulk Concentration of Metals in Sludge Ash (µg/g dry wt.)*

Sample	Al	As	Ca	Cd	Cr	Cu	Fe	Hg	K	Mn	Na	Ni	Pb	Se	Zn
1	34800	3.7	74000	270	6560	4700	305000	8.4	6600	2000	10900	3900	1190	<4.0	10700
2[a]	35600	1.2	146000	21	2200	3200	82000	8.8	6600	5500	24600	840	760	<4.0	4400
3	64000	1.7	68000	900	810	3300	50000	3.1	8800	2500	25800	880	1070	<4.0	6000
4	75000	3.7	102500	190	4800	6000	62000	5.0	6500	1000	19400	1230	2080	<4.0	15100
5[b]	38000	8.1	118000	9	1670	4900	101000	7.0	3800	800	29900	1200	1620	<4.0	9000
6[b]	9200	20.1	380000	4	350	1500	171700	4.5	800	500	16100	690	90	<4.0	900
7	38000	2.7	90000	7	2060	5500	82500	9.2	7400	5000	28000	670	230	<4.0	6400
8[b]	29200	20.8	245500	5	1150	3600	179000	9.0	2700	4300	8700	1700	1650	<4.0	8000
9[c]	108000	1.3	58500	14	870	7000	41300	5.8	23000	1800	265000	980	1600	<4.0	23800
10	22800	1.8	80000	45	350	4500	40700	2.0	3900	5000	13500	270	910	<4.0	4000

[a] $FeCl_3$, alum added.
[b] $FeCl_3$, lime added.
[c] Alum added.

Table 5. *Bulk Concentration of Metals in Dewatered Sludge Samples µg/g dry wt.*

Sample	As	Cd	Cr	Fe	Ni	Pb	Se
1	0.5	120	2230	168,500	950	430	<4.0
2[a]	0.4	7	820	21,200	140	240	<4.0
3	0.5	250	440	19,200	190	480	<4.0
4	0.8	90	3500	47,300	840	1040	<4.0
5[b]	1.6	4	340	44,000	230	530	<4.0
6[b]	4.1	1	80	78,900	130	20	<4.0
7	0.5	3	420	21,200	140	70	<4.0
8[b]	2.0	2	560	131,000	930	1090	<4.0
9[c]	0.4	5	380	21,100	210	420	<4.0
10	0.4	18	90	9,500	80	240	<4.0

[a] $FeCl_3$, alum added.
[b] $FeCl_3$, lime added.
[c] Alum added.

Table 6. *Percentage of Elemental Extractions in the EPA EP Test*[d]

	Ash					Dewatered Sludge				
Sample	As	Cd	Cr	Ni	Pb	As	Cd	Cr	Ni	Pb
1	17.5	.4	0.1	0.4	.3	15.7	3.9	1.13	13.7	.4
2[a]	1.7	2.4	.4	85.6	.2	10.0	4.7	.05	15.1	.6
3	14.5	1.0	.1	0.8	.2	4.0	1.8	.8	3.7	.2
4	13.5	1.1	.01	0.3	.2	20.0	2.1	.2	27.3	.04
5[b]	1.6	13.8	.9	79.0	.2	5.2	33.8	.3	78.1	.04
6[b]	2.3	17.5	6.4	59.1	4.5	.5	51.0	1.9	30.0	.7
7	15.0	5.0	.03	51.5	0.8	9.8	6.7	.1	15.5	1.0
8[b]	3.9	5.0	1.3	12.1	.1	1.5	26.5	2.8	44.9	.1
9[c]	1.5	2.5	.1	80.2	.1	5.0	6.4	.3	54.0	.2
10	2.8	0.6	.01	1.6	.1	7.5	2.1	.1	51.6	.3

$FeCl_3$, alum added.
$FeCl_3$, lime added.
Alum added.
Computed as a percentage of total concentration.

Table 7. *Average Percent Removed in EPA-EP Test for Ash and Sludge*

	Ash		Sludge	
Element	Fe(III)/Al Added	Fe(III)/Al Not Added	Fe(III)/Al Added	Fe(III)/Al Not Added
As	2.2	12.6	4.4	11.5
Cd	8.2	1.6	24.5	3.3
Cr	2.0	0.03	0.8	0.3
Ni	63.2	10.9	43.6	21.2
Pb	1.0	0.3	0.3	0.4

Table 8. *IAEA Leaching Test Results for Sludge Ash Samples (Total Percent Extracted)*

Sample	As	Cd	Cr	Ni	Pb
1	60.2	0.08	0.01	0.01	-
3	54.0	0.01	0.03	-	0.02
4	24.0	0.04	-	-	0.02
5	5.0	0.7	0.2	0.03	0.02
8	2.8	0.2	0.1	-	0.02
9	17.5	0.8	0.07	0.03	0.02

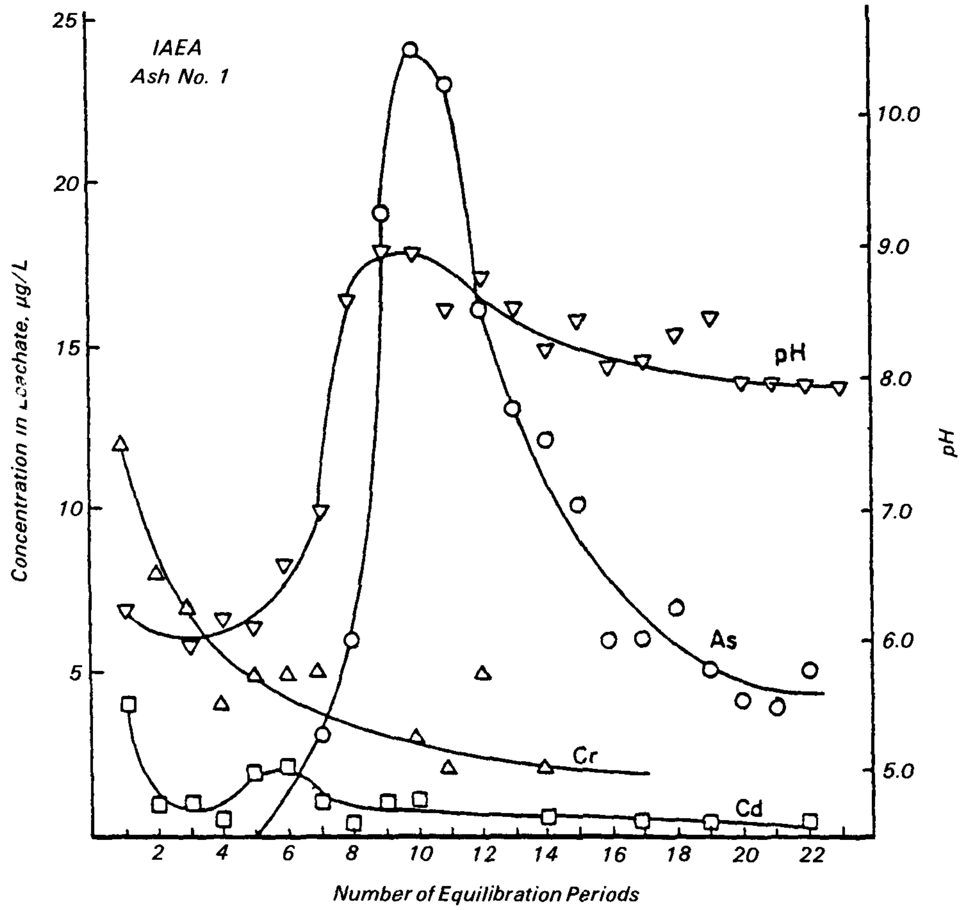

Figure 1. *IAEA leaching test for sludge ash Sample No. 1.*

'able 9. Positive Results of Test Extractions Using the Ames Positive Determination Method

'ample Source	Extraction	Strain	Activation (+/-)
Valdwick ash	DMSO	98	+
		1535	+
'ort Huron sh	Ammonium oxalate	1537	+
	Acetone$_2$ (50 g ash)	100	+
		1535	+
	Soxhlet benzene	1537	+
	Resin column	1537	-
ıdianapolis sh	Resin column	1537	-
ersey City sh	DMSO	100	-
		1535	+
	$CaCl_2$	1535	+
	H_2O (IAEA)	1537	+
	Ammonium oxalate	98	-
	Soxhlet benzene	98	+
		1537	+
		1538	+
	Acetone$_1$ (25 g ash)	98	+
	Acetone$_2$ (50 g ash)	98	+
	Resin column	98	+
		100	-
		1537	+
		1538	+
ersey City udge	Acetone$_1$ (25 g sludge)	98	+
	Acetone$_2$ (50 g sludge)	98	+ -
		1535	+
		1538	+
	Resin column	98	+ -
		100	+ -
		1535	+
		1537	+
		1538	+

Thomas L. Theis, Margaret McKiernan, and Lawrence E. Padgett are with the University of Notre Dame, Notre Dame, IN 46556.
***A. E. Eralp** is the EPA Project Officer (see below).*
The complete report, entitled "Analysis and Assessment of Incinerated Municipal Sludge Ashes and Leachates," (Order No. PB 84-155 563; Cost: $13.00, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
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Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
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