

TRANSITION METALS AS CATALYSTS FOR PYROLYSIS AND GASIFICATION OF BIOMASS

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INTRODUCTION

We envision a two stage process for the conversion of lignocellulosic waste (such as sawdust or newsprint) into useful chemicals and simple gases. In the first stage, vacuum pyrolysis at relative low temperatures produces a charcoal, a condensible organic liquid (pyrolysis tar) and a noncondensable low Btu fuel gas. In the second stage, the charcoal which contains a major portion of the energy content of the feedstock is either pyrolyzed at high temperatures, or gasified to produce simple gases. The gasification is free from tar forming reactions, with the energy balance and product gas composition dependent on the composition of the reactant gas.^{1,2}

The production of LG from vacuum pyrolysis of pure cellulose and wood has frequently been reported.(*e.g.*^{3,4}) Higher yields of LG from wood pyrolysis were obtained by prior removal by acid washing of the indigenous metal ions bound to the hemicellulose in the wood. We have recently⁵ studied the effect of individual metal ions (ion exchanged into wood) on gaseous products from pyrolysis of wood using coupled TG/FTIR. These studies showed that K but not Ca, acts as a catalyst in pyrolysis reactions resulting in formation of CO₂, CO, and formic acid (especially from polysaccharides), acetic acid (from hemicellulose), and methanol (from lignin). This type of study has now been extended to include a wider range of metal ions, and to embrace newsprint as well as wood. Since the major motivation in this work lies in the thermochemical utilization of lignocellulosic waste, we have especially included metal ions which are known to increase char yield and to act as catalysts in char gasification.

In this paper we are specifically concerned with air gasification of the chars doped with metal ions that result from LG producing pyrolyses (*i.e.* Fe and Cu-doped chars). Several studies have been made of the catalytic effects of copper and its salts in accelerating the oxidation of graphite.⁶⁻⁹ In fact, copper is reported to be the most effective catalyst of the carbon-air reaction (for Spanish lignite char) of the first transition series of elements.^{10,11} The same authors report (for air gasification of Cu-doped lignite char) a dramatic jump from a region of low reactivity and high apparent activation energy to a region of high reactivity and low apparent activation energy for a 5 °C temperature increase.¹²

This laboratory has also observed this jump phenomenon for copper catalysis¹³ and for iron catalysis¹⁴ in the air gasification of cellulosic chars. For this study we utilized carboxymethylcellulose (CMC) for incorporation of ion exchanged cations and cellulose fibers (CF-11) for incorporation of salts by sorption from aqueous solution. The doped cellulosic fibers were then pyrolyzed to chars for gasification studies. We were able to report "jump temperatures" (T_j , defined by Moreno-Castilla *et al.*¹² as the lowest temperature of the high reactivity region) for ion-exchanged Cu CMC and sorbed Cu salt CF-11 samples.

Part of this paper reports our continued study of this jump phenomenon. We use the approach described above (*viz.* copper doped CMC and CF-11 samples) since we are able to achieve particularly exact control of the distribution of the metal species in the cellulosic substrates and hence in the char.

EXPERIMENTAL

The ion-exchanged wood (milled cottonwood sapwood, *Populus trichocarpa*) and carboxymethylcellulose (CMC) and salt-sorbed samples were prepared as described earlier.¹⁵ Newsprint samples were prepared from the Wall Street Journal, macerated with deionized water (or salt solutions for salt-sorbed newsprint) in a Waring blender, filtered and air-dried to a mat ca. 2 mm thick. The mats were cut into cubic pellets (ca. 2 mm³) before pyrolysis. Metal ion contents were measured by inductively coupled argon plasma spectrometry (see Tables 1 to 4).

Pyrolyses were carried out at 2 Torr under flowing nitrogen as described previously¹⁷ with tars condensed at room temperature and "distillate" condensed at -50°C. LG contents of tars were determined by GLC of tri-O-methylsilyl ethers¹⁷ and the compounds in the second condensate (other than water) were determined by ¹H NMR.¹⁸ The yield of levoglucosone (LGO) in the second distillate was determined by relating the integrated signal for the C-1 hydrogen (5.31 ppm, s, 1H)¹⁹ to the internal standard (2-methyl-2-propanol; 1.21 ppm, s, 9H).

The thermogravimetry system used to measure gasification rates has been described.¹³ The samples were first pyrolyzed at a heat treatment temperature (HTT) for 15 min in nitrogen *in situ* (80 mL min⁻¹), and subsequently gasified (gasification temperature = GT) in air (80 mL min⁻¹, 22% O₂). The TG balance was purged with helium (20 mL min⁻¹). The temperature program and weight loss curve of a typical gasification experiment are shown in Figure 1.

The apparatus for measuring differences in sample and furnace temperatures is described elsewhere.²⁰ Essentially, a thermocouple was placed in the furnace near to the sample (similar to TG temperature measurement) and a second thermocouple embedded in the sample. The temperature program and gas flow control was similar to a typical gasification, and during the course of the experiment the two thermocouple readings were compared.

RESULTS AND DISCUSSION

Pyrolysis of Ion-exchanged Wood

The yields of char, tar, and distillate from the pyrolysis of ion-exchanged wood are shown in Table 1. The alkali metal and calcium wood samples showed increased char formation, low tar and high distillate yield compared to acid-washed wood. All other ion-exchanged wood samples showed char and tar yields similar to acid-washed wood, with the transition metals especially favoring tar formation. The analysis of the tar for LG shown in Table 1 indicates that the tars from Li, K and Ca wood samples were not only obtained in reduced yield, but also contained a lower proportion of LG than tar from acid-washed wood. All other metal ions produced yields of LG above 10.5% compared with 5.4% from acid-washed wood. In other words, wood samples ion-exchanged with transition metals gave higher yields of a cleaner tar.

The best yield of LG observed was 15.8% from the ferrous wood sample. Assuming that LG is derived only from cellulose and that the latter represents 50% of the wood,²¹ then the conversion of cellulose to LG was 31.6%. This yield may be compared with 41.5% obtained from pure cellulose (CF-11 cellulose).

The mechanism whereby the yield of LG is increased by the presence of these metal ions is not known. However, since cupric acetate sorbed in pure cellulose does not catalyze the formation of LG, we tentatively conclude that catalysis of LG formation in wood may involve some interaction with lignin. The low yield of LG from original wood (0.4%) is probably associated with two inhibiting factors, viz. indigenous metal ions (especially K and Ca) and lignin. When the metal ions are removed by acid washing, the LG yield increases to 5.4% (*i.e.* 10.8% based on cellulose), but the lignin effect presumably holds the LG yield well below that from cellulose (41.5%). The presence of some metal ions, especially the transition metals, may decrease the interference by lignin in the conversion of cellulose to LG.

Pyrolysis of Wood Sorbed with Salts

Since the improved yields of LG from wood pyrolysis induced by the presence of added metal ions are of considerable interest (in connection with thermochemical utilization of biomass), this study was extended to determine whether it is necessary to remove the indigenous cations in the wood, and whether the "beneficial" metal ion can be added more simply and economically as salts by sorption rather than by ion-exchange. This study concentrated on cuprous and ferrous salts because these ions were most effective in increasing LG and charcoal yields when ion-exchanged, and also because the chars from such pyrolyses are likely to contain elemental Cu or active Fe species which are known to be catalysts of gasification reactions.¹³

The products of pyrolysis of wood sorbed with cupric acetate, ferrous acetate and ferrous sulfate are shown in *Table 2*. The addition of cupric ion by sorption of the acetate salt in acid-washed wood (to 0.45% Cu) is effective in increasing LG yield to 11.2%; higher concentrations of copper did not significantly improve the LG yield. When the indigenous ions (predominantly K and Ca) are not removed by acid washing before addition of the cupric acetate, the improvement in LG yield is much less marked. The indigenous cations negate some of the catalytic influence of the Cu. The results with sorbed ferrous acetate were similar, although the LG yield with the salt sorbed in the acid-washed wood (7.5%) was considerably less than for the corresponding ion-exchanged wood (15.8%).

The pyrolysis of wood sorbed with ferrous sulfate was studied as an example of an anion likely to remain in the pyrolyzing solid and to generate acid conditions (acetate ions are lost from the solid at the pyrolysis temperature). Acid-washed wood containing ferrous sulfate yielded 6.1% LG and an additional 3.0% levoglucosenone (1,6-anhydro-3,4-dideoxy- β -D-glycero-hex-3-enopyranos-2-ulose, LGO), which was found in the distillate. LGO is a known product of acid-catalyzed cellulose pyrolysis²² and its formation was observed only in the presence of the sulfate anion.

Application to Newsprint

Newsprint comprises about one-third of the solid municipal waste in developed countries, it is likely soon to be excluded from landfill disposal and there is a limit to the proportion which can be recycled into paper. Thermochemical processes have the potential to account for the utilization of large amounts of waste newsprint. Our sample contained 24% lignin.²³ It was therefore expected, on the basis of the above experiments with wood, to be similarly amenable to the "beneficial" effects of ferrous sulfate in terms of increased LG and LGO yields.

Table 3 shows the influence of sorbed ferrous sulfate on products of pyrolysis in nitrogen at 400°C for 30 min. In the absence of added ferrous sulfate, pyrolysis of newsprint yielded 3.2% LG, but no LGO. Sorption of ferrous sulfate (to 2.08% FeSO₄) before pyrolysis increased the yield of LG to 16.6%, and also yielded 4.2% LGO. Char yield also increased from 15% for newsprint to 20% for FeSO₄ sorbed newsprint. Thus we have a procedure to generate chemical

feedstocks (LG and LGO) from pyrolysis of newsprint, while simultaneously forming in increased yield a char which already contains an efficient gasification catalyst.

Gasification of Cu and Fe ion-exchanged CMC chars

We have previously reported the effect of HTT and mode of addition of metal ions on the T_j of Cu-doped chars.¹⁶ Jump temperatures were determined in a series of gasification experiments where GT was successively lowered 5°C until the low reactivity region was reached. The T_j for Fe-doped CMC char (HTT 400°C, [Fe] 2.47% d.a.f.), determined by the same method, was 295°C. Figures 2 and 3 show rate-time plots for the gasification in air of Cu- and Fe-doped cellulose chars (HTT 400°C) at and below the jump temperature (T_j = 255°C for Cu and 295°C for Fe). Copper appears to be a superior catalyst over iron; the T_j of Cu is lower and the rate maximum (R_g(max)) is higher. In the case of Cu-doped chars, the initial rate of gasification increases ca. 160-fold for a 5°C temperature increase at T_j.

In a series of experiments to determine the effect of Cu concentration on T_j we gasified Cu-doped CMC chars in a temperature program (HTT 400°C, GT 200°C + 5°/min). Table 4 shows the effect of Cu concentration on the apparent T_j. Increasing Cu concentration in the range shown in Table 4 effected a decrease in the apparent T_j but did not change R_g(max). We expected to measure T_j as the temperature at which the rate suddenly increased, and that the T_j of our CuCMC-1 sample would be as previously determined (i.e. 255°C). However, the T_j of CuCMC-1 determined by this method was significantly different. We conclude that this jump in reactivity is also affected by the thermal history of the char.

Effect of oxygen chemisorption on sample temperature in the furnace

It seemed likely, based on the observation of small spikes in the TG thermocouple reading on the introduction of air into the furnace (see Figure 1), that the TG apparatus may not be recording the true temperature of the sample during rapid gasification. In fact, when a ca. 20 mg CuCMC-1 char (HTT 400°C) was gasified (GT 260°C) with a thermocouple in contact with the char, the temperature of the char ran ahead of the furnace temperature soon after air was admitted (see Figure 4).

We have reported²⁰ that for calcium-doped chars prepared at relatively low temperatures (e.g. HTT 400°C), the initial rate of gasification in air (R_g(max) from TG) is extremely high for a short time. This effect was shown to be due to "run away" temperature increase associated with exothermic oxygen chemisorption. In this case the effect can be avoided by pre-sorption of oxygen below the gasification temperature. However, unlike calcium-doped chars, in the copper-catalyzed gasification the initial high R_g(max) peak at GT 260°C could not be eliminated by pre-sorption of oxygen at 200°C (see Figure 5). We conclude that exothermic oxygen chemisorption contributes to, but does not fully account for the jump phenomenon in copper catalysis of gasification.

It seems likely that this jump in reactivity is associated with the mobility of the metal species acquired at the Tammann temperature,¹² and that jumps in reactivity below the Tammann temperature can be explained by the thermal history of the sample and its heat capacity, and by the heat generated by oxygen chemisorption.

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Table 1. Vacuum pyrolysis of ion-exchanged wood

Sample	Metal ion (% d.a.f.) ^a	char (% d.a.f.)	Tar (% d.a.f.)	Distillate (% d.a.f.)	LG (% d.a.f.)
Acid-Washed Wood	---- ^b	19	43	16	5.4
Li	----	19	25	44	0.7
Mg	0.08	16	45	29	10.5
K	0.20	22	21	40	0.4
Ca	0.14	20	32	27	4.1
Mn[III]	0.19	15	44	29	10.6
Fe[II]	0.37	15	50	30	15.8
Co[III]	0.20	15	49	29	12.4
Ni[II]	----	14	56	25	13.0
Cu[II]	0.19	17	54	26	13.5
Zn	0.26	16	45	31	11.4
CF-11 cellulose	----	13	67	14	41.5
CuAc ₂ /CF-11 ^c	----	24	51	14	31.0

a % weight based on dry ash free wood. Pyrolysis at 350°C/30 min.

b Not determined

c Cupric acetate sorbed on CF-11 (not ion-exchanged)

Table 2. Vacuum pyrolysis of wood sorbed with salt solution

Sample	Metal ion (% d.a.f.) ^a	char (% d.a.f.)	Tar (% d.a.f.)	Distillate (% d.a.f.)	LG (% d.a.f.)
Original wood		15	25	24	0.4
Acid-Washed (AW)		19	43	16	5.4
AW/CuAc ₂	0.45	29	38	--- ^b	11.2
AW/CuAc ₂	0.74	30	40	---	11.2
AW/CuAc ₂	1.10	20	42	---	12.5
CuAc ₂	0.43	15	43	21	5.9
AW/FeAc ₂	3.34	22	24	26	7.5
FeAc ₂	3.18	28	19	28	5.2
AW/FeSO ₄ ^c	1.43	38	18	25	6.1

a % weight based on dry ash free wood. Pyrolysis at 350°C/30 min.

b Not determined

c Pyrolysis at 300°C/60 min

Table 3. Vacuum pyrolysis products from newsprint (NP)^a

Sample	char	Tar	Distillate	LG	LGO
Original NP	15	44	32	3.3	ND
NP + 2.08% FeSO ₄	20	43	37	16.6	4.2

a % weight based on dry ash free wood. Pyrolysis at 400°C/30 min.
 ND not detected

Table 4. The Effect of Copper Concentration on the Apparent Jump Temperature^a

Sample	Cu in char (% d.a.f.)	T _J (°C)	R _g (max) (min ⁻¹)
CuCMC-1	2.82	312	1.6
CuCMC-2	1.54	320	1.8
CuCMC-3	0.67	340	1.8

a For HTT 400°C, GT 200°C + 5°/min

Figure 1. CuCMC-1 Gasification in air
 HTT 400°C, GT 255°C

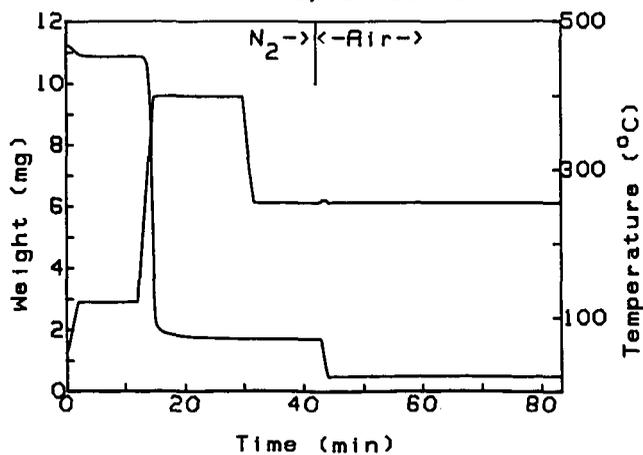


Figure 2. DTG Curves for Fe and Cu CMC at T_j

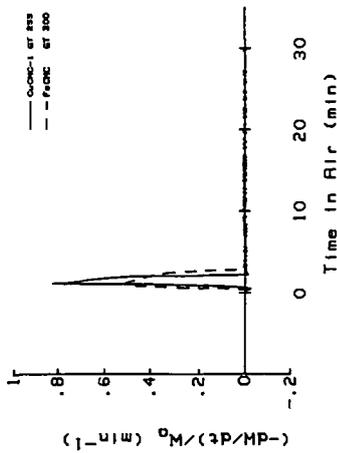


Figure 3. DTG Curves for Fe and Cu CMC Below T_j

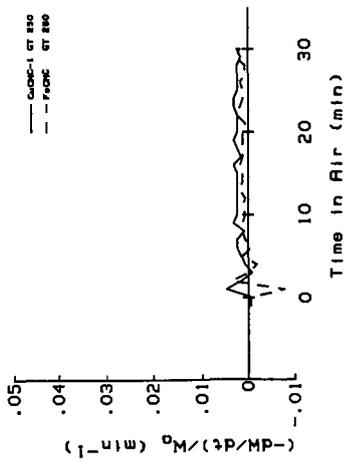


Figure 4. CuCMC-1 Gasification in Air (HTT 400)

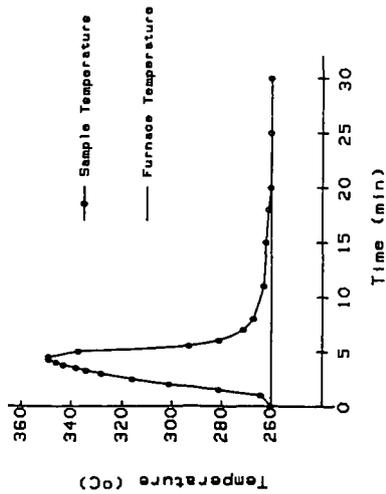
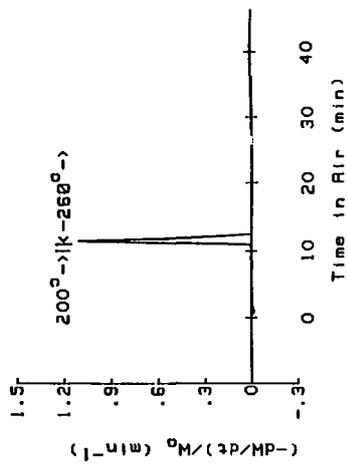


Figure 5. CuCMC-1 Gasification with Pre-sorption at 200°C



Metals Emissions Control Technologies For Waste Incineration

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INTRODUCTION

A major issue facing industrialized nations is the environmentally sound disposal of municipal solid wastes and industrial hazardous wastes. The amounts of these wastes generated has shown an annual growth rate over the past several decades ⁽¹⁾ and improper disposal has resulted in numerous environmental problems. Incineration in properly designed combustion systems has been demonstrated as a method of achieving a very high degree of destruction and control for these wastes and is often combined with heat recovery systems to simultaneously recover energy in the form of steam or electricity. A wide variety of incinerator types as well as boiler and industrial furnaces are used for destroying these wastes.

Incineration of municipal and hazardous waste has the potential for increasing air pollution due to emissions of constituents contained in these waste streams and products of their combustion. Municipal and hazardous wastes are likely to contain sulfur and chlorine compounds as well as a wide number of toxic heavy metals (e.g. arsenic, beryllium, cadmium, chromium, lead, mercury, and silver). During combustion sulfur and chlorine compounds are converted to the acid gases SO₂ and HCl. Heavy metals are converted to their oxide or chloride forms. The high combustion temperature employed in modern incinerators will cause many of the metal compounds present to volatilize and be carried out of the incinerator device with the hot flue gases. These compounds then condense out as fine particulate matter or in some instances can leave the system still in the vapor form.

The increase in waste incineration has been accompanied by increased public concerns over air pollution and an increase in local, state, and federal regulations. The USEPA has recently revised federal regulations to further limit incinerator emissions. This increased regulatory climate has resulted in an increase in the complexity and efficiency of air pollution controls employed for emissions controls.

This paper presents a review of the current U.S. regulations covering incinerator emissions and describes technologies used for their control. Typical emission levels and control efficiencies achievable are presented.

AIR POLLUTION REGULATIONS

Air pollution regulations applied to incinerator flue gas emissions vary widely in the compounds controlled, emissions levels, removal efficiencies required, averaging times and testing requirements. On the national level, municipal waste incinerators are regulated under Clean Air Act provisions whereas hazardous waste incinerators are regulated under the Resource Conservation and Recovery Act (RCA). In addition to national regulations, local or state permitting agencies may require more stringent emissions controls or control of additional pollutants as a part of a facility's operating permit. The EPA has recently been active in setting standards for municipal waste incinerators, hazardous waste incinerators and boilers and industrial furnaces which burn hazardous wastes.

Municipal Waste Incinerators

EPA promulgated "New Source Performance Standards and Emissions Guidelines for Existing Facilities" for Municipal Waste Combustors in February 1991. These standards are summarized in Table 1.

In setting these standards, EPA recognized differences in facility size, type of incineration (mass burn fired versus refuse derived fuel fired) and new sources versus existing sources. The facility capacity refers to the total burn rate for all refuse combustors at a single site. EPA selected total particulate matter emission limits as the way of controlling trace heavy metal emission limits. EPA will add emission limits based on applying Maximum Achievable Control Technology (MACT) for mercury, cadmium and lead emissions in the coming year. EPA has until late 1992 to establish comparable emission standards for smaller combustors, those less than or equal to 250 tons per day per train.

Emissions limits are established for total emissions of poly-chlorinated dibenzyl-dioxins (PCDD) plus polychlorinated dibenzyl-furans (PCDF). These compounds were selected as surrogates for organic emissions because of their potential adverse health effects. In addition, EPA has established carbon monoxide (CO) emission limits as a measure of "good combustion practices" which limit the formation of PCDD, PCDF and their key precursors. CO emission limits vary from 50 to 150 ppm (1 at 7% O₂ dry gas conditions) depending on the type of combustion.

Acid gas emission limits (HCl and SO₂) are based on either a percent reduction or a maximum stack emission level whichever is the least stringent. Nitrogen Oxides (NO_x) emissions levels are proposed only for large new sources.

Hazardous Waste Incinerators

In April 1990, the EPA published a proposed rule and requests for comments in the Federal Register for Standards for Owners and Operators of Hazardous Waste Incinerators and Burning of Hazardous Wastes in Boilers and Industrial Furnaces.⁽³⁾ The final rules for "Burning Hazardous Wastes in Boilers and Industrial Furnaces" was published in the Federal Register in February 1991.⁽⁴⁾ Key provisions of these regulations are presented in Table 2.

EPA proposed extending current emissions limits covering Destruction and Removal Efficiencies for organic constituents and for particulate matter. EPA proposed to establish risk-based emission limits for individual toxic metals, hydrogen chloride, and organic emissions. EPA added limits for chlorine when they published their final rule for Boilers and Industrial Furnaces.⁽⁴⁾ Reference Air Concentration (RAC's) were proposed for maximum modeled annual average ground concentrations of these pollutants. The RAC's for the carcinogenic metals were set at levels which would result in an increased cancer risk for a Maximum Exposed Individual of less than 1 in 100,000. The RAC's for the non-carcinogenic metals, and chlorine were set at 25 percent of the reference dose (RfD) with the exception of lead which was set at ten percent of the National Ambient Air Quality level. The RAC for HCl is based directly on inhalation studies. RfD's are estimates of a maximum daily exposure (via injection) for the human population that is not likely to cause deleterious effects.

In setting these standards, EPA established a three tiered approach for demonstrating compliance. The tiers are arranged from the easiest to demonstrate and most conservative to the more complex and less conservative. Compliance with any tier is considered to prove compliance with these regulations.

Tier I EPA established conservative maximum feed rates (lb/hr) for each constituent as a function of effective stack height, terrain and land use. In setting these limits, EPA assumed no partitioning in the incinerator, no removal in an air pollution control system, and reasonable worst case dispersion. Demonstration of compliance is through monitoring of feed composition. Two examples of Tier I screening limits are 2.4×10^{-4} to 4.1×10^{-3} pounds per hour for arsenic and 9.4×10^{-3} to 1.6 pounds per hour for lead, depending on stack weight, terrain and land use.

Tier II EPA established conservative emission rate limits for each constituent as a function of effective stack height, terrain, land use and assumed reasonable worst case dispersion. Demonstration of compliance is through periodic stack emission testing and continuous emission monitoring of carbon monoxide, hydrocarbons and oxygen. Two examples of Tier II screening limits are 3.1×10^{-3} to 5.3×10^{-3} grams per second for arsenic and 1.2×10^{-3} to 2.0×10^{-3} grams per second for lead.

Tier III EPA established RAC's which must be met for each component. Demonstration of compliance is through periodic emissions testing and site specific dispersion modeling to demonstrate actual (measured) emissions do not exceed the RAC's. For the carcinogenic metals, the ratios of each metal's measured value to its RAC's are added to give a cumulative value which must be below ONE (a risk of 1 in 100,000). Tier III RAC's for all metals are shown in Table 2.

The standards will be implemented through limits on specific incinerator and air pollution control system operating parameters. In addition, emissions testing of all dioxin/furan tetra-octa congeners, calculation of toxic equivalents, dispersion modeling and health risk assessments will be required for incinerators equipped with a dry particulate control device (electrostatic precipitator or fabric filter operating at an inlet temperature between 450 and 750°), or if hydrocarbon emission levels exceed 20 ppmv (d).⁽⁹⁾

AIR POLLUTION CONTROLS

Heavy metals emissions from municipal and hazardous waste incinerators are controlled primarily through the use of particulate collection devices (electrostatic precipitators, fabric filters, wet scrubbers) or acid gas control systems (dry injection, spray dryer absorption, wet scrubbing). The major fraction of heavy toxic metals in the flue gas exists as fine particulates and is effectively controlled by properly sized electrostatic precipitators or fabric filters. Additional control of vaporized toxic metals is achieved in spray dryer absorption system or wet scrubbers.

Spray dryer absorption (SDA) has been widely applied for municipal waste incinerator emissions control and has demonstrated high collection efficiencies for most heavy toxic metals present in the flue gas. SDA has been specified as Best Available Control Technology (BACT) in a number of municipal waste incinerator air permits. Typical control efficiencies and emission levels achieved using SDA are presented in Table 3.

Figure 1 shows simplified process flow diagram for the SDA process. The SDA system is comprised of a spray dryer, absorber, a dust collector and a reagent preparation system. Incinerator flue gas enters the spray dryer where it is contacted by a cloud of finely atomized droplets of reagent (typically hydrated lime slurry). The flue gas temperature is decreased and the flue gas humidity is increased as the reagent slurry simultaneously reacts with acid gases present and evaporates to dryness. In some systems a portion of the dried product is removed from the bottom of the spray dryer, while in others it is carried over to the dust collector. Collected reaction products are sometimes recycled to the feed system to reduce reagent consumption.

Several different spray dryer design concepts have been employed for incinerator SDA applications. These include single rotary, multiple rotary and multiple dual fluid nozzle atomization; downflow, upflow and upflow with a cyclone pre-collector spray dryers; and single and multiple gas inlets. Flue gas retention times range from 10 to 18 seconds and flue gas temperatures leaving the spray dryers range from 230°F up to 300°F.

Heavy toxic metals removal in the downstream dust collector is enhanced through cooling of the incoming flue gas (from 450°-500°F) as it passes through the spray dryer with the subsequent condensation of some vaporized metal forms, and through impaction and agglomeration of fine particulate matter with the very high number of lime droplets produced by the atomization devices.

Generally, the lower the spray dryer outlet temperature, the more efficient acid gas absorption and vaporized toxic metals removal. The minimum reliable operating outlet temperature is a function of the spray dryer and dust collector design and the composition of the dry fly ash reaction product mixture. The spray dryer outlet temperature must be maintained high enough to ensure complete reagent evaporation and the production of a free flowing product. Low outlet temperature operation requires efficient reagent atomization, good gas dispersion and mixing, adequate residence time for drying and design of the dust collector to minimize heat loss and air in-leakage.

The dust collector downstream of the spray dryer may be an electrostatic precipitator, a reverse-air baghouse or a pulse-jet type baghouse. The selection of a specific type of dust collector is dependent on site specific factors such as particulate emission limits, overall acid gas removal requirements and project economics. Each of these dust collection devices offers process advantages and disadvantages that are evaluated on a site specific basis. Generally where high acid gas control is required, (95+ % HCl, 85+ % SO₂), a baghouse is utilized as it functions as a better chemical reactor than an electrostatic precipitator. Heavy toxic metals control efficiencies achievable with a SDA system are quite high (99+%) except for the relatively highly volatile mercury. Mercury emissions however, can be controlled at greater than 90 percent efficiency through the use of additives such as sodium sulfide or activated carbon. ^(4,7)

SDA has also been shown to be an effective method of controlling heavy toxic metals emissions from hazardous waste incinerators ^(6,38), however, wet scrubbing systems have been most commonly applied for overall emissions control. Wet scrubbing has been applied either alone or after a dust collection device to achieve acid gas control or to act as a polishing step for particulate and heavy toxic metals control. In some instances, wet scrubbers have been installed downstream of SDA systems with evaporation of the scrubber blowdown in the spray dryer to eliminate a liquid effluent stream. Figure 2 shows a typical emissions control system process flow scheme for hazardous waste incinerators.

Flue gases at approximately 2200°F are ducted from the incinerator to a quench tower (or a high temperature spray dryer) where they are cooled to 300-450°F. The cooled flue gas then enters a fabric filter (or electrostatic precipitator) where the majority of particulate matter and heavy toxic metals are removed. From the dust collection device, the flue gas enters a saturator venturi where the flue gas is further cooled to 160-200°F. Here HCl and some additional particulate matter as well as heavy toxic metals are removed. The flue gas then enters a packed tower where it is contacted with a caustic scrubbing solution for removal of SO₂.

The flue gas may then enter the induced draft fan or may pass through a secondary scrubber for additional fine particulate and heavy toxic metal removal. This secondary scrubber is typically a charged droplet or condensation type designed for light inlet particulate loading and fine particulate control.

Table 4 presents hazardous waste incinerator particulate and heavy toxic metals emissions levels achievable with these types of emissions control systems. The first column indicates conservative estimated removal efficiencies used by EPA in establishing Tier II screening levels for the ten heavy toxic metals of concern. These values are based on using a spray dryer absorption system incorporating a fabric filter as the dust collector or a system consisting of a four-field electrostatic precipitator followed by a wet scrubber as the control device. The next column presents data believed to be more representative of control efficiencies achieved in trial burns where these types of air pollution controls are employed. The final column presents typical ranges of emission rates for particulate matter and the toxic heavy metals. These values are obtained from our in-house emission data base compiled from a wide range of sources. These values are used to estimate incinerator metals emissions in permit support activities.

CONCLUSIONS

The increased use of incineration for control and destruction of municipal and hazardous wastes has led to increasingly stringent air pollution control regulations. EPA has recently promulgated New Source

Performance Standards for municipal waste combustors which require health risk based emissions limits for specific metals to be established within the next year. EPA has proposed hazardous waste incinerator emissions limits which include risk based emissions limits for ten toxic heavy metals.

Spray dryer absorption is considered to represent BACT for many municipal waste incinerator application and is capable of achieving high collection efficiencies for the metals of concern. Spray dryer absorption is also used for emissions control from hazardous waste incinerator. Dust collectors followed by wet scrubbers or also often used to control metals emissions from hazardous waste incinerators. Both types of systems have demonstrated the ability to achieve high collection efficiencies for the ten toxic heavy metals proposed for regulation. Emission rates from medium to large incinerators equipped with properly designed air pollution control systems are capable of achieving the required emission levels.

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Table 1. USEPA Municipal Waste Combustion Emission Standards. ⁽²⁾

	New Source Performance Standards	Emission Guidelines For Existing Facilities	
		Unit	Facility
Capacity-Tons/day	Unit >250	Unit >250 ≤ 1100	Facility >1100
Particulate Matter-(gr/dscf)	0.015	0.030	0.015
Opacity-%	10	10	10
Organic Emissions-ng/dscm Total Chlorinated PCDD Plus PCDF			
-Mass burn units	30	125	60
-RDF fired units	30	250	60
Acid Gas Control % Reduction or Emissions-(ppm)			
HCl	95 (25)	50 (25)	90 (25)
SO ₂	80 (30)	50 (30)	70 (30)
NO _x	(180)	None	None
Carbon Monoxide, ppm	50-150*	50-250*	50-250*

All emissions limits are referenced to dry gas conditions at 7% oxygen concentration.
Range of values reflect differing types of MWC's

Table 2. USEPA Proposed Hazardous Waste Incineration Standards ⁽³⁾

Destruction and Removal Efficiency (DRE)	99.9999% Dioxin - Listed Wastes 99.99% All Other Wastes		
Particulate Matter	0.08 gr/dscf	@ 7% O ₂	
Carbon Monoxide (Tier I)	100 ppmv (d)	@ 7% O ₂	
Hydrocarbons (Tier II)	20 ppmv (d)	@ 7% O ₂	
Continuous Emissions Monitoring	CO, O ₂ , HC		
<u>Tier III Reference Air Concentrations</u> (annual limits, $\mu\text{g}/\text{m}^3$)			
Hydrogen Chloride	0.7	Free Chlorine	0.4
<u>Carcinogenic Metals</u>		<u>Non Carcinogenic Metals</u>	
Arsenic	2.3×10^{-3}	Antimony	0.3
Beryllium	4.1×10^{-3}	Barium	50
Cadmium	5.5×10^{-3}	Lead	0.09
Chromium	8.3×10^{-4}	Mercury	0.3
		Silver	3
		Thallium	0.3

Table 3. Typical Refuse Incinerator Uncontrolled and Controlled Emissions.

Pollutant	Uncontrolled Emissions	Controlled Emissions	Percent Reduction
Particulate Matter, gr/dscf	0.5-4.0	0.002-0.015	99.5+
Acid Gases ppm _v			
HCl	400-100	10-50	90-99+
SO ₂	150-600	5-50	65-90+
HF	10-0	1-2	90-95+
NO _x	150-300	60-180	30-65*
Heavy Metals mg/nm ³			
Arsenic	<0.1-1	<0.01-0.1	90-99+
Cadmium	1-5	<0.01-0.5	90-99+
Lead	20-100	<0.1-1	90-99+
Mercury	<0.1-1	<0.1-0.7	10-90+
Total PCDD/PCDF ng/nm ³	20-500	<1-10	80-99

Reference conditions - Dry Gas @ 12%CO₂

Table 4. Hazardous Waste Incinerator Emissions Estimates

	EPA * Conservative Estimated Efficiencies	Typical Actual Control Efficiencies	Typical Range of Emissions Rates µg/Nm ³
Particulate Matter	99+	99.9+	0.005-0.02 gr/dscf
Arsenic	95	99.9+	1-5
Beryllium	99	99.9	<0.01-0.1
Cadmium	95	99.7	0.1-5
Chromium	99	99.5	2-10
Antimony	95	99.5	20-50
Barium	99	99.9	10-25
Lead	95	99.8	10-100
Mercury	85-90	40-90+	10-200
Silver	99	99.9+	1-10
Thallium	95	99+	10-100

*Based on spray dryer fabric filter system or 4 field electrostatic precipitator followed by a wet scrubber (3)

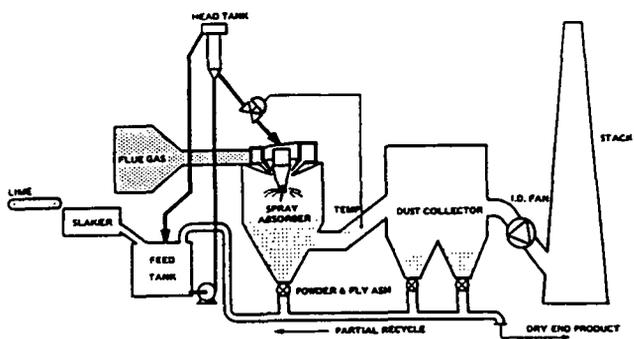


Figure 1. Spray Dryer Absorption Process
(Courtesy of Niro Atomizer)

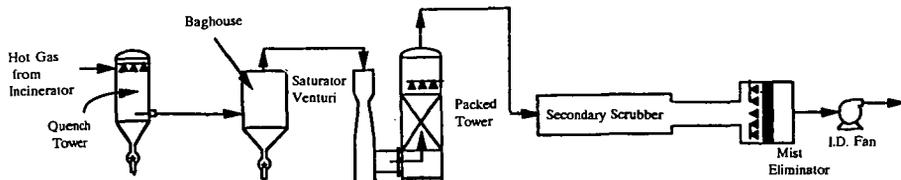


Figure 2. Hazardous Waste Incinerator - Emissions Control Scheme

CHARACTERIZATION AND CONTROL
OF CADMIUM, LEAD, AND MERCURY FROM RDF
MUNICIPAL WASTE COMBUSTORS

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INTRODUCTION AND SUMMARY

Title III of the 1990 Clean Air Amendments mandates EPA to propose maximum achievable control technology (MACT) standards for cadmium, lead and mercury air emissions from municipal waste combustors (MWC's) by November 1991. There is growing concern in this country and in Europe regarding environmental levels of lead and mercury, and a fear exists that MWC's may be a major contributor to these levels. Finally, Congress will soon be debating amendments to RCRA, the Solid Waste Act, which will likely consider disposal and reuse requirements for ash from MWC's where questions of leachability of trace metals, particularly cadmium (Cd), lead (Pb), and mercury (Hg) will be of concern.

Because of these important factors, this paper will primarily focus on air and ash emissions for these three trace metals from refuse derived fuel (RDF) type MWC's. Secondly, the paper will attempt to point out what emission controls are being, and could be, imposed, and what future trends are likely to occur to reduce these emissions. Thirdly, the paper will put into perspective the contribution that Hg emissions from MWC's have to the global emissions of Hg.

Most of the data that will be presented comes from the Mid-Connecticut RDF facility located in Hartford, Connecticut. That facility is a 2,000 ton/day facility owned by the Connecticut Resources Recovery Authority and designed and constructed by ABB Resource Recovery Systems (ABB/RRS). The facility contains a waste processing facility that produces RDF which is operated by the Metropolitan District Commission. Slides will be presented which illustrate how this facility produces RDF (see Figure 1). Slides will also be presented showing how pre-processing MSW to produce RDF can reduce levels of Cd, Pb and Hg by 33% - 90% prior to combustion.

Next, the paper will describe the power block facility (see Figure 2) which is operated by ABB/RRS. Slides will be presented which describe the boiler, the combustion controls, the dry scrubber, and the reverse air fabric filter from this facility. Slides will also be presented which summarize the uncontrolled levels of Cd, Pb and Hg in the flue gas before the scrubber as well as the controlled levels of these same pollutants after the baghouse. These levels will be compared for different steam loads, combustion conditions and scrubber settings. Finally, data will be presented showing the high removal efficiencies for these trace metals in the flue gas (i.e. 97.6 - 100%) and the impact that varying the calcium to sulfur stoichiometric ratio has on removal efficiency.

Next, the paper will describe the facility ash handling system. Slides will be presented showing both the concentration (ug/g) and quantity rates (kg/hr) of Cd, Pb, and Hg in the RDF and the various ash fractions. These slides will illustrate the concentration buildup of these trace metals in fly ash. Slides

will also be presented which show results of leachability studies on the ash using sequential batch extraction and TCLP leach tests.

Finally, the paper will conclude with general observations on trends in control of Cd, Pb, and Hg from all types of MWC's, and what EPA may be considering in the new air regulations that must be promulgated soon. The paper will discuss general confusion that currently exists about the magnitude that MWC's may play in contributing to environmental levels of Hg. The paper will put Hg emissions from MWC's into perspective and compare them to emissions from other sources.

ABB Resource Recovery Systems

Municipal Solid Waste Processing - Single Line

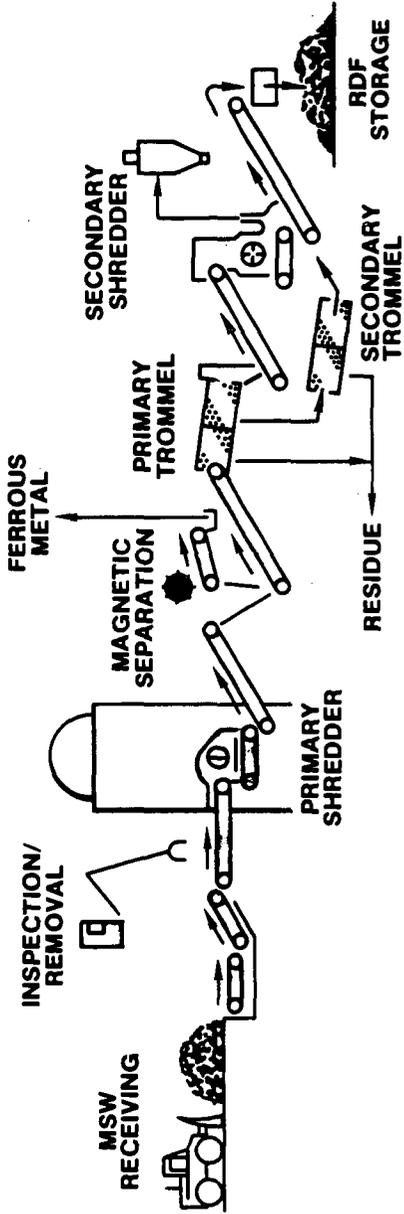


FIGURE 1

ABB Resource Recovery Systems

Prepared Fuel Steam Generation System

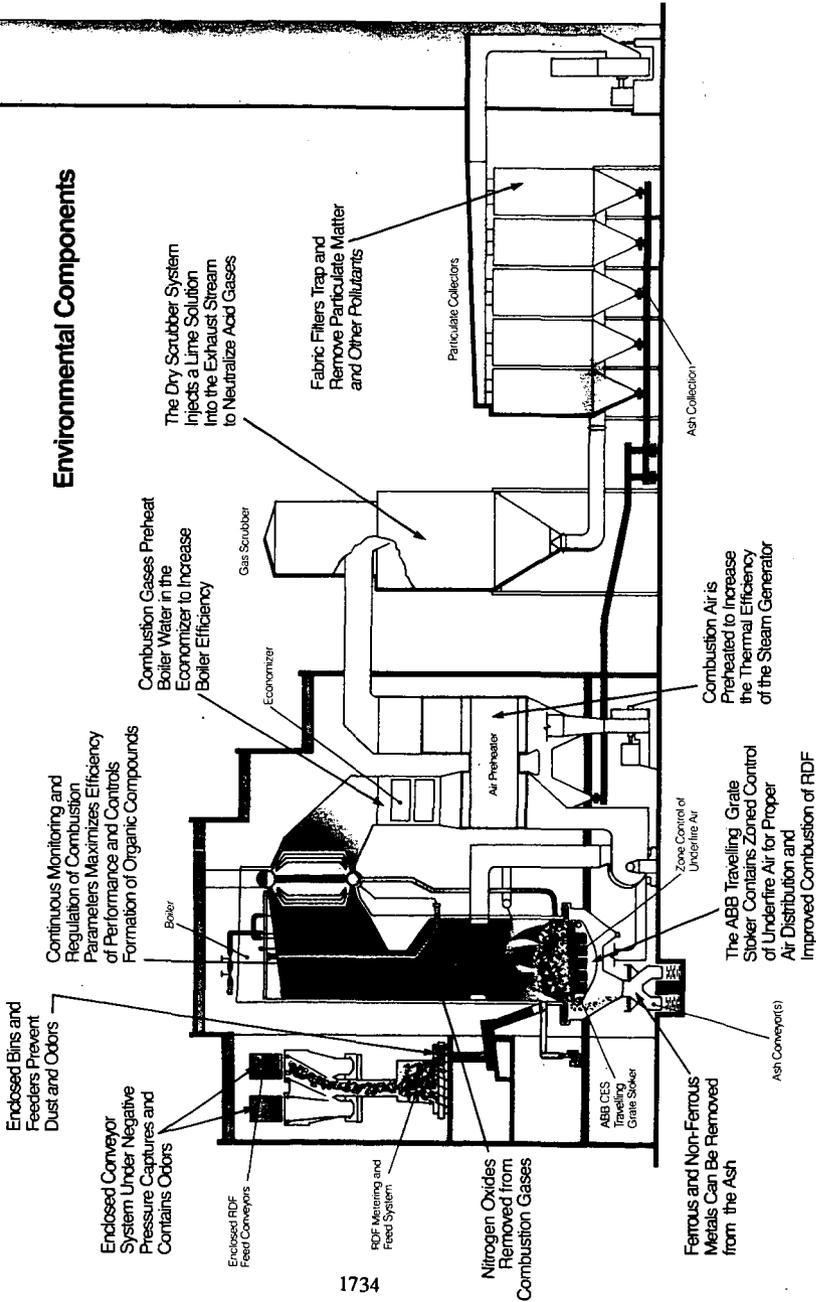


FIGURE 2

METALS BEHAVIOR DURING MEDICAL WASTE INCINERATION

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ABSTRACT

Medical waste contains toxic metals such as lead, cadmium, and mercury. Consequently, the incineration of medical waste may result in the emissions of trace metals into the environment, if incinerators are not properly designed and operated. EPA's Risk Reduction Engineering Laboratory initiated a study in 1988 to document what is known about medical waste treatment, particularly in the area of medical waste incineration. This paper is to summarize the findings from this study regarding the behavior of metals in incineration processes. Highlights of these findings are as follows:

- Lead and cadmium are the two most-often-found metals in medical waste.
- Metals can partition into different phases (gas, liquid or solid) but cannot be destroyed during incineration.
- There are several potential pathways that metals follow to reach the environment. They exit incinerators with sifting, bottom ash, fly ash, scrubber waste, and flue gas.
- Data on the capture efficiency of metals by air pollution control equipment used at medical waste incinerators is very limited.
- Wet scrubbers generally capture cadmium moderately well but normally perform poorly in removing chromium and lead. Fabric filter systems efficiently capture all metals.

INTRODUCTION

It has been well known that medical waste contains toxic metals such as lead, cadmium, and mercury. These metals will only change forms (chemical and physical states) but will not be destroyed during incineration. They can be emitted from incinerators on small particles capable of penetrating deep into human lungs. Thus, the emission of trace amounts of heavy metals from medical waste incinerators is one of the major concerns to those who are involved in medical waste management. A clear understanding of metals behavior in medical waste incinerators is critically needed.

EPA's Risk Reduction Engineering Laboratory initiated a study in 1988 to document what is known about medical waste treatment, particularly in the area of medical waste incineration. Potential toxic metal emissions from medical waste incineration was one of main subjects studied. This paper is to summarize the findings of that study.

METAL SOURCES

Researchers at the University of California at Davis conducted a study to identify the sources of toxic metals in medical wastes (Hickman, 1987). The research effort focused on lead and cadmium because they were the two most-often-found metals in medical waste. They concluded that plastics in the waste contributed most to the presence of these two metals. Cadmium is a component in common dyes and thermo- and photo-stabilizers used in plastics. Lead was found in many materials including plastics, paper, inks, and electrical cable insulation. However, the primary source of lead appeared to be plastics. Like cadmium, lead is used to make dyes and stabilizers which protect plastics from thermal and photo-degradation. It is ironic to note that the dyes made from lead and cadmium are used to color plastic bags. Thus, part of the lead and cadmium emissions could be due simply to the "red bags" that infectious waste is placed in.

Under the hazardous waste program of the Resource Conservation and Recovery Act of 1976, EPA has identified ten (10) metals of most concern from 40 CFR 261 Appendix VIII. Four of the ten metals are classified as carcinogenic and the other six metals are considered to be toxic. The EPA's Carcinogen Assessment Group has estimated the carcinogenic potency for humans exposed to low levels of carcinogens. An assigned "Unit Risk" indicates the relative health threat of the metals. Unit Risk (UR) is the incremental risk of developing cancer to an individual exposed for a lifetime to ambient air containing one microgram of the compound per cubic meter of air. Inhalation is the only exposure pathway considered in determining UR.

Toxicity data are used to define concentrations for the six toxic metals below which they are not considered dangerous. Ambient concentrations should not exceed this concentration. The EPA has defined the maximum toxic concentration, or Reference Air Concentration (RAC), for each metal. If ground level concentrations of any of these metals exceeds its RAC, adverse health effects are likely. The Unit Risk of the four carcinogenic metals and the RAC of the six toxic metals are listed in Tables 1 and 2 (EPA, 4/91).

EMISSION PATHWAYS

A majority of metal emissions is in the form of solid particulate matter and a minority is in vapor form. It was generally concluded that particulate emissions from the incineration of medical wastes are determined by three major factors:

- (1) Suspension of noncombustible inorganic materials;
- (2) Incomplete combustion of combustible materials (these materials can be organic or inorganic matter); and
- (3) Condensation of vaporous materials (these materials are mostly inorganic matter).

The ash content of the waste feed materials is a measure of the noncombustible portion of the waste feed and represents those materials which do not burn under any condition in an incinerator. Emissions of noncombustible materials

result from the suspension or entrainment of ash by the combustion air added to the primary chamber of an incinerator. The more air added, the more likely that noncombustibles become entrained. Particulate emissions from incomplete combustion of combustible materials result from improper combustion control of the incinerator. Condensation of vaporous materials results from noncombustible substances that volatilize at primary combustion chamber temperatures with subsequent cooling in the flue gas. These materials usually condense on the surface of other fine particles.

Figure 1 shows the transformation of mineral matter during combustion of metals-containing waste. The Figure is self-explanatory. There are several potential pathways to the environment that metals may follow. Most metals remain in the bottom ash. A small fraction of the ash (on a weight basis) is entrained by the combustion gases and carried out of the primary chamber as fly ash. Volatile metals may vaporize in the primary combustion chamber and leave the bottom ash. These metals recondense to form very small particles as the combustion gases cool. Some of the entrained ash and condensed metals are captured in the air pollution control equipment (APCE). The rest enters the atmosphere. Four key variables affecting the vaporization of metals are (EPA, 4/91):

- Chlorine concentration in the waste;
- Temperature profiles in the incinerator;
- Metal species concentration in the waste; and
- Local oxygen concentration.

CURRENT CONTROL PRACTICE

Two strategies are used to minimize metals emissions: (1) The primary chamber is operated at conditions which do not promote vaporization or entrainment of metals; and (2) Any metals which do escape can be captured in the APCE, if present. The parameters usually used to control the escape of metals from the primary chamber are the primary chamber temperature and gas velocity. The key APCE parameters used are specific to the device which is utilized.

- (1) Combustion control: Most operating medical waste incinerators are simple single-chamber units with an afterburner located in the stack. The ability of batch incinerators to control metals emissions is limited because only the temperature in the stack is usually monitored.

Most new incinerators are starved-air units. The primary chamber is designed to operate at low temperatures and low gas flow rates. This minimizes the amount of materials entrained or vaporized.

To ensure that metal emissions are minimized, operators must maintain the primary chamber at the temperatures and gas flow rates for which it was designed. Usually the only parameter that system operators

can directly control is feed rate. High feed rates can lead to high temperatures and high gas velocities. Thus, many operators carefully control the feed rate. The feed rate is reduced when primary temperatures increase.

- (2) APCE control: When metals reach the APCE, they are present in one of three forms. Non-volatile metals are on large entrained particles. Metals which have vaporized and recondensed are usually present on fly ash particles with diameters less than 1 micron. Extremely volatile metals are present as vapors. Table 3 summarizes the ability of common APCE to control these different metal forms. The Table is based on data and worst case predictions. Wet scrubbers are often used to minimize the temperature of the flue gases. Use of low temperatures ensure that all metal vapors have condensed. As indicated in Table 3, vapors are much more difficult to capture than particles (EPA, 4/91).

EMISSION DATA

Figure 2 compares the concentration of arsenic (chosen merely for illustrative purposes) in flue gases before any APCE, and in emitted gases for a variety of incinerators. As shown, a wide variety of flue gas cleaning equipment is used. The Figure indicates the effectiveness of the various types of APCE. Arsenic is predicted to be relatively volatile, compared to other metals. Significant amounts of arsenic are therefore expected to vaporize in an incinerator (EPA, 4/91).

CONCLUSION

Some metals and metal species found in waste materials are volatile and will vaporize at the conditions found in incinerators. The vapors are carried away from the waste by the exhaust gas and they recondense as the gas cools. The vapors condense both homogeneously to form new particles and heterogeneously on the surfaces of existing fly ash particles. To control metal emissions, metals which are of a highly volatile nature are of main concern in terms of installing the proper APCE. Because there are many APCE sizes and types, it is very important to fully understand metal emissions characteristics, combustion control and operating possibilities, and expected APCE performance so that metal emissions can be minimized.

REFERENCES

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(Hickman, 1987), "Cadmium and Lead in Bio-Medical Waste Incinerators," Master of Science Thesis, University of California, Davis, 1987.

TABLE 1. UNIT RISK (UR) VALUES FOR FOUR CARCINOGENIC METALS	
Metals species	Unit risk
Arsenic (As)	0.0043
Beryllium (Be)	0.0025
Cadmium (Cd)	0.0017
Chromium (Cr ⁺⁶)	0.012
UR: incremental lifetime cancer risk from exposure to 1 $\mu\text{g}/\text{cubic meter}$	

TABLE 2. REFERENCE AIR CONCENTRATIONS (RACs) FOR SIX TOXIC METALS	
Metals species	RAC ($\mu\text{g}/\text{m}^3$)
Antimony (Sb)	0.025
Barium (Ba)	50.00
Lead (Pb)	0.09
Mercury (Hg)	1.70
Silver (Ag)	5.00
Thallium (Tl)	500.00

TABLE 3. TYPICAL APCE CONTROL EFFICIENCIES			
APCE	Control Efficiency(%)		
	Particulate	Fume	Vapor
Venturi scrubber 20" pressure drop	90	85	60
Venturi scrubber 60" pressure drop	98	97	90
Fabric filter	95	90	50
Spray drier/fabric filter	99	95	90

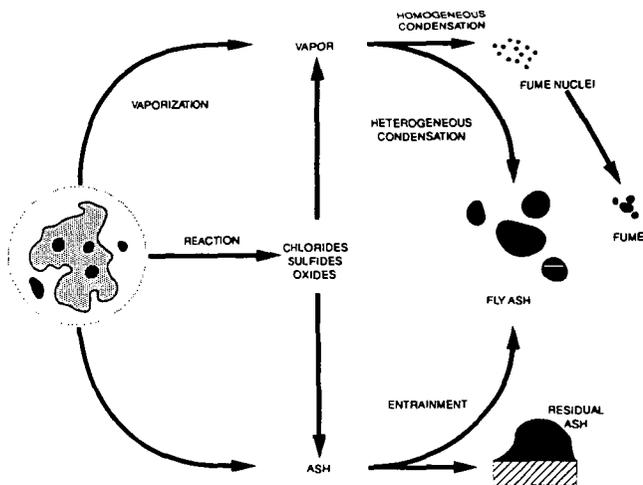


FIGURE 1. METAL TRANSFORMATION DURING INCINERATION (EPA, 4/91)

Arsenic

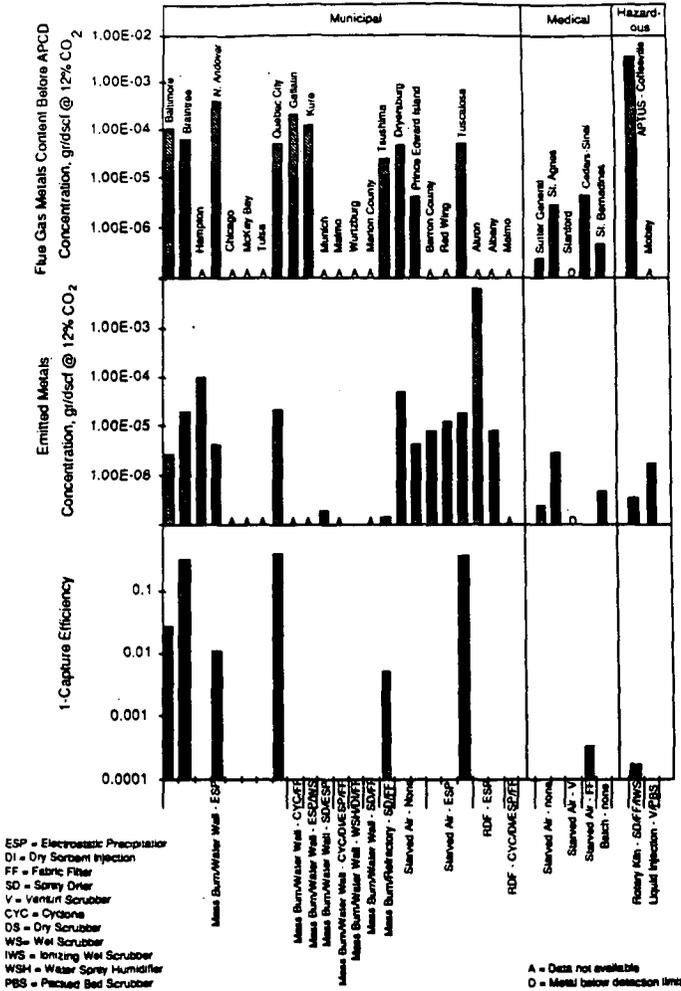


FIGURE 2. ARSENIC EMISSIONS (EPA, 4/91)

FUNDAMENTALS OF HEAVY METAL REMOVAL BY DRY SORBENTS

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Abstract

Emission of toxic metal compounds is a major problem in many combustors and incinerators. In the present work, using cadmium chloride as a model compound, the use of solid sorbents for removal of toxic metal compounds from high temperature flue gases is investigated. The sorbents tested were silica, alumina, kaolinite, emahlite and lime. Compounds containing aluminum oxide show high cadmium removal efficiency. In particular, bauxite has the highest rate and capacity for cadmium capture. The overall sorption process is not just physical adsorption, but rather a complex combination of adsorption and chemical reaction.

Introduction

Cadmium compounds are considered to be among the most toxic trace elements emitted into the environment during fuels combustion and waste incineration. Cadmium and cadmium compounds are primarily used in the fabrication of corrosion resistant metals. Cadmium is also used as a stabilizer in poly-vinyl chlorides, as electrodes in batteries and other electrochemical cells, and for numerous applications in the semiconductor industry (1). Due to this wide range of applications, cadmium is present in many municipal and industrial wastes. Cadmium is also present in coal in trace quantities (2). Consequently, emission of cadmium compounds is a problem in many waste incinerators and coal combustors. The chemical form and concentration of these compounds depend on a number of factors including feed composition and operating conditions (3).

The increased use and disposal of cadmium compounds, combined with their persistence in the environment and relatively rapid uptake and accumulation in the living organisms contribute to their serious environmental hazards. The present technology is inadequate to meet the expected cadmium emission standards. Therefore, new and effective methods need to be developed and investigated for controlling the emission of cadmium and other toxic metals in combustors and incinerators.

A promising technique for the removal of metal vapors from high temperature gases is through the use of solid sorbents to capture and immobilize the metal compounds by a combination of adsorption and chemical reactions. The sorbent can be

used in two ways:

- a. It could be injected as a powder (similar to lime injection) for in-situ removal of cadmium compounds.
- b. The cadmium containing flue gas could be passed through a fixed or fluidized bed of sorbent. The sorbent could be used in the form of pellets, beads, or monoliths (for high dust applications).

Previous studies by us and other investigators indicate that solid sorbents can be very effective in removing alkali and lead vapors from hot flue gases (4-7). In the present work, a number of potential sorbents were screened and compared for their effectiveness in removing cadmium compounds from hot flue gases. Details of the sorption mechanism were investigated for the selected sorbents.

Experimental

Materials

In the first part of this study, several model compounds and naturally available materials were evaluated as potential sorbents for removal of gaseous cadmium compounds from hot flue gases. The model compounds included silica (MCB grade 12 silica gel) and alpha alumina (Du Pont Baymal colloidal alumina, technical grade). The naturally available materials included kaolinite (52% SiO₂, 45% Al₂O₃, 2.2% TiO₂, 0.8% Fe₂O₃), bauxite (11% SiO₂, 84% Al₂O₃, 5% Fe₂O₃), emahlite (73% SiO₂, 14% Al₂O₃, 5% CaO, 2.6% MgO, 3.4% Fe₂O₃, 1.2% K₂O) and lime (97% CaO). Cadmium chloride was used as the cadmium source. For the screening experiments, the sorbents were used in the form of particles, 60 - 80 mesh in size. For the kinetic and mechanistic study the sorbents were used in the form of thin flakes (disks). The flake geometry is easy to model and characterize using analytical techniques. All the sorbents were calcined at 900°C for two hours and stored under vacuum until used. All the experiments were conducted in a simulated flue gas atmosphere containing 15% CO₂, 3% O₂, 80% N₂ and 2% H₂O.

Equipment and Procedures

Screening Experiments: The main components of the experimental system were a Cahn recording microbalance, a quartz reactor, a movable furnace and analyzers for determining the composition of the gaseous products. This system has been previously used for screening of sorbents for removal of lead compounds. Therefore, only the salient features of the system are described here. Details can be found in a previous publication⁸. The cadmium source was suspended by a platinum wire from the microbalance, which monitored the weight change during the experiments. A fixed bed of the sorbent particles was made by placing 100 mg of the sorbent particles on a 100 mesh stainless-steel screen in a quartz insert. All experiments in this study were performed with the source at 560°C and the sorbent at 800°C. This method ensured that the concentration of cadmium vapors around the sorbent was much below saturation, thereby preventing any physical condensation on the outer surface of the sorbent.

Heating of the cadmium source resulted in vaporization of CdCl_2 which was carried by the flue gas through the sorbent fixed bed. The percentage of cadmium adsorbed was determined from the amount of cadmium delivered (microbalance measurement) and the cadmium content of the sorbent at the end of the experiment. The cadmium content of the sorbent was determined by dissolving the samples in a $\text{H}_2\text{O}/\text{HF}/\text{HNO}_3$ (2/1/1 proportion by volume) mixture and subsequently analyzing the solution by atomic absorption spectroscopy. Separate water leaching experiments were performed to determine the water soluble fraction of adsorbed cadmium. The leaching of cadmium was conducted at 40°C in an ultrasonic bath for two hours. The cadmium content of the solution was subsequently determined by atomic absorption spectroscopy.

Study of Sorption Details: A microbalance reactor system was used for studying the sorption details. The sorbent flakes were suspended by a platinum wire from the microbalance. The weight of the sorbent was continuously monitored during the experiments by the microbalance. The cadmium source was placed in the horizontal arm of the reactor. The simulated flue gas from the gas preparation section was split in two parts. One part entered the reactor from the inlet below the balance and the remaining gas entered through the horizontal arm in which the cadmium source was placed. The cadmium source was heated by a heating tape and a furnace heated the sorbent flakes. All experiments were conducted with the source temperature of 560°C and the sorbent temperature of 800°C . When steady flow rates and cadmium concentrations were achieved, the sorbent was exposed to the cadmium containing flue gas. The sorbent weight was continuously recorded as it captured the cadmium vapors. The microbalance was continuously purged with ultra high purity nitrogen gas.

Results and Discussion

Screening Experiments

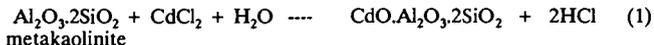
The results obtained from the screening experiments are given in Figure 2. Multiple experiments were conducted for most of the sorbents and good reproducibility was obtained. Since all experimental parameters except the sorbent type were kept constant, the amount of cadmium adsorbed is a good indication of the sorbent effectiveness (rate) for cadmium removal from hot flue gases. The most obvious feature of these results is the difference in the ability of the sorbents to capture cadmium from the flue gas passing through them. Alumina and bauxite had the highest cadmium capturing efficiencies. A large fraction of the cadmium captured by these two sorbent was water insoluble. Silica and kaolinite were not effective for removal of cadmium. Since cadmium chloride has a high water solubility, the formation of water insoluble compounds on sorption by alumina and bauxite leads to the conclusion that chemical reaction is the dominant mechanism of cadmium capture by these sorbents. Lime, a sorbent used for removal of sulfur compounds, did not have a high cadmium capturing efficiency. Since most of the cadmium captured by lime was water soluble, physical condensation is the dominant mechanism of cadmium capture for lime. From the screening experiments, it seems that compounds containing aluminum oxide have a

high cadmium capturing efficiency. Bauxite was therefore further studied to determine the mechanism of cadmium capture. Since previous studies have indicated that kaolinite is a good sorbent for removal of lead and alkali compounds, it was also included in the mechanistic study.

Details of the Sorption Process:

In the first part of this study, the cadmium sorption capacity of kaolinite and bauxite was investigated at 800°C. In these experiments the sorbent flakes were exposed to cadmium vapors until no further mass change was observed. The profiles for sorption for both kaolinite and bauxite are shown in Figure 3. The rate of sorption decreases with time and a final limit is achieved beyond which no further cadmium sorption takes place. The observed initial rate for cadmium capture by kaolinite was much slower than that for bauxite. This is consistent with the results from the screening experiments, where kaolinite captured much less cadmium compared to bauxite. Also, the final saturation limit for kaolinite (18%) was found to be lower than that for bauxite (30%) (Figure 3). When the concentration of cadmium in the flue gas was reduced to zero, no desorption from either sorbent was observed indicating that reversible physical adsorption was not the dominant sorption mechanism.

X-ray diffraction (XRD) analysis was used to identify the final products formed by sorption of cadmium chloride on kaolinite and bauxite. Analysis of kaolinite flakes exposed to cadmium vapors indicated the formation of a cadmium aluminum silicate compound, $\text{CdAl}_2\text{Si}_2\text{O}_8$, which is water insoluble. Based on XRD results, the following reaction scheme is proposed for capture of cadmium :



where metakaolinite is the dehydration product of kaolinite. Holland et al. (8) also observed the formation of this compound when a solid mixture of cadmium carbonate and kaolinite was heated to 800°C for twenty hours. Based on the stoichiometry of the overall reaction, 1 kg of kaolinite can capture 0.51 kg of cadmium, forming a product which is water insoluble and therefore safely disposable. The maximum weight gain postulated from this reaction (58% by weight) is much higher than that obtained experimentally in the microbalance reactor setup (18 wt%).

To further understand the reasons for low sorbent utilization, a kaolinite flake which had captured cadmium to its maximum capacity was mounted in epoxy and analyzed by SEM and EDX analysis. A cadmium map of the flake shows that cadmium is concentrated on the kaolinite edge (Figure 3). An EDX line scan on the flake surface indicated that the concentration of cadmium varied from 49 wt% at the edge to 2 wt% at the center. The concentration of cadmium at the edge (49%) is close to the value calculated from the postulated reaction mechanism assuming complete conversion (51%). This indicates that the surface of kaolinite was completely converted by reaction to form a cadmium aluminosilicate. Silicon and aluminum maps on the kaolinite surface indicate complete uniformity of distribution of these elements on the kaolinite surface. Since this flake had captured cadmium to its maximum capacity (microbalance data, Figure 3), the non-uniform distribution of cadmium indicates incomplete sorbent

utilization. Since the volume of the cadmium aluminosilicate phase is higher than that of the aluminum silicate phase, the formation of cadmium aluminum silicate at the outer surface probably blocks the sorbent pores, resulting in incomplete sorbent utilization.

XRD analysis of bauxite particles exposed to cadmium vapors indicated the formation of two crystalline compounds: a cadmium aluminum silicate and a cadmium aluminate. Since the cadmium aluminate has a higher water solubility compared to that of the aluminosilicate, bauxite has a larger fraction of water soluble cadmium in the screening experiments. The amount of SiO_2 present in bauxite is not enough to combine with all Al_2O_3 to form an aluminosilicate compound. Based on the stoichiometry of Reaction 1 and the amount of SiO_2 present, 1 kg of bauxite can capture 0.10 kg of cadmium to form a cadmium aluminosilicate. Based on the remaining alumina, 1 kg of bauxite can capture 0.94 kg of cadmium oxide forming a cadmium aluminate according to the following reaction mechanism:



If all the alumina and silica reacted with kaolinite to form cadmium aluminum silicate and cadmium aluminate (Reactions 1 and 2), the maximum weight gain possible is 1.06 kg per kg of bauxite. This is higher than the value obtained in the microbalance experiments conducted to completion (0.30 kg/kg bauxite).

To further understand the sorption mechanism, a bauxite flake exposed to cadmium vapors to the point of "no further weight change" was mounted in epoxy and analyzed by SEM and EDX analysis. The cadmium map on the bauxite surface indicated a non-uniform cadmium distribution (Figure 4). Comparison of the cadmium map with the aluminum and silicon maps on the flake surface indicated that regions high in both alumina and silica have high concentrations of cadmium. As confirmed by the XRD analysis, the cadmium present in the alumina phase reacts to form a cadmium aluminate. Regions rich in both alumina and silica combine with cadmium to form a cadmium aluminum silicate. EDX analysis of regions high in both aluminum and silicon indicated that the cadmium concentration was 26 wt%. EDX analysis of regions high in alumina indicated that the cadmium concentration in this phase (11 wt%) was much lower than that postulated by Reaction 2. This indicates that the alumina phase does not completely react with cadmium to form a cadmium aluminate. This could be due to the alumina phase having low porosity thereby preventing complete sorbent utilization. Also, formation of a higher volume product on the outer surface could inhibit further capture of cadmium.

From the mechanistic study it is clear that the sorption process under present experimental conditions is influenced by diffusional resistances. In practical systems, the rate of sorption can be increased by optimization of the sorbent pore structure to facilitate intraphase transport of cadmium vapors into the sorbent. The interphase mass transport limitations can also be reduced to increase the overall sorption rate. For in-situ applications, the efficiency of the sorbent can be increased by decreasing the particle size.

Conclusions

1. Bauxite and, to a lower degree, kaolinite are effective sorbents for removal of cadmium in combustors and incinerators.
2. The sorption mechanism and the nature of final products formed have important implications in the way each sorbent may be used. Compared to kaolinite, bauxite has a higher sorption rate and capacity; however, the products of sorption in bauxite are more water soluble. Therefore, kaolinite is more suitable when no leaching from the spent sorbent can be permitted.
3. The overall sorption process is a complex combination of adsorption, condensation, diffusion and chemical reactions.
4. In adsorbing cadmium chloride, chlorine is not retained by either kaolinite or bauxite. Additional cleanup steps may be needed in systems where the presence of chlorine in the flue gas cannot be tolerated.

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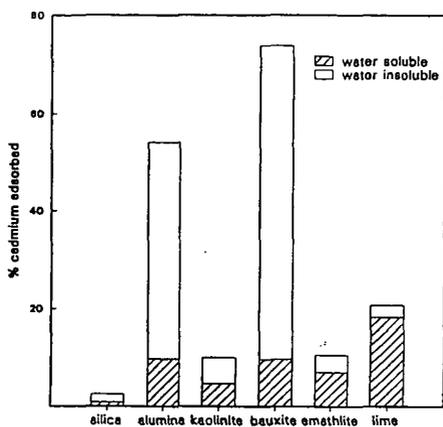


Figure 1: Cadmium removal efficiencies of various sorbents. Mass of sorbent used = 100 mg. $T=800^{\circ}\text{C}$. Amount of cadmium vaporized in each experiment = 6.5 mg.

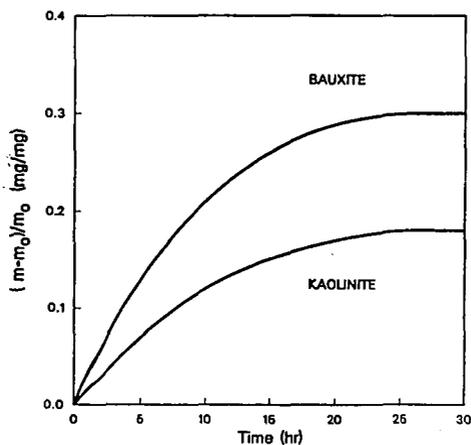


Figure 2: Temporal profiles of cadmium sorption on kaolinite and bauxite. $T=800^{\circ}\text{C}$. Flow rate = 200 cc/min. Mass of flake = 15.1 mg (bauxite); 20.4 mg (kaolinite). Flake thickness = 0.71 mm (bauxite); 1.1 mm (kaolinite)



Figure 3: Cadmium concentration map on kaolinite flake surface

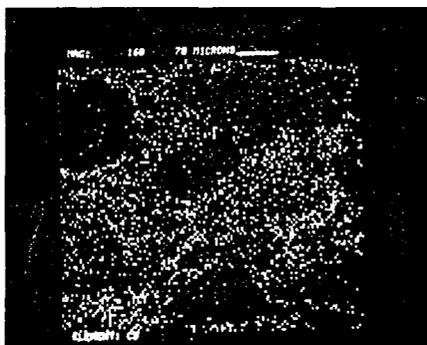


Figure 4: Cadmium concentration map on bauxite flake surface.

CELLS ON FIBERS FOR WASTE CLEAN UP

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Keywords: Coal, Metals, Paper

INTRODUCTION: Fibers have a large surface area so many cells can be immobilized. Sulfur can be taken out of coal, metals removed from wastewater, pulp mill effluent decolorized, and a non-corrosive road deicer made.

At a recent conference in Boston (1) uses and methods of making CMA (calcium magnesium acetate) were discussed. Beer told how (2) calcium acetate could be sprayed into burning coal to remove 70% of the sulfur in the stack gas. Acid rain causes much damage to trees and lakes. Yang (3) described methods of making CMA from lactose (cheese whey) with organisms on cotton. Chapter 16 of a new book (4) teaches producing CMA from glucose with cells on rotating fibers, covered in Clyde's patent 4,407,954. CMA is also a non corrosive road deicer. Salt causes millions of dollars damage to bridges, cars and plant life. Using woody biomass or old newspapers as a raw material would reduce the cost.

Patent 4,530,763 describes removing uranium and other metals from wastewater. Recently it has been found that when a strip of Tyvek[®] fiber with *Zymomonas mobilis* on it was put into lead and six valent chromium, the metals got not only on the section immersed, but climbed right up the fiber and got on the fingers of the holder, all in a couple seconds. The EPA will soon lower the limits on lead in drinking water, and Cr6 is also very toxic.

Thousands of lawsuits have been filed against paper mills for putting deadly dioxin into rivers. It also gets in milk cartons, fish, tea bags, and diapers. The fungus *Phanerochaete chrysosporium* grows on fibers and high area Celite entrapped in fibers, to decolorize pulp mill effluent. When an RBC (rotary biological contactor) is run half full and a light shone in the top, the light hits a thin moving film. UV light destroys dioxin. In most photo reactors, colored solution blocks the light.

Methanol can be made from coal (5) and dissociated to clean burning CO and H₂, with 20% increase in energy (because waste heat from the exhaust is utilized) as in patent 4,420,462.

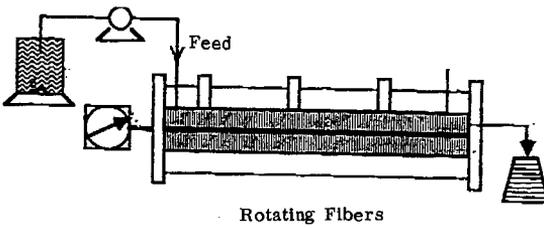
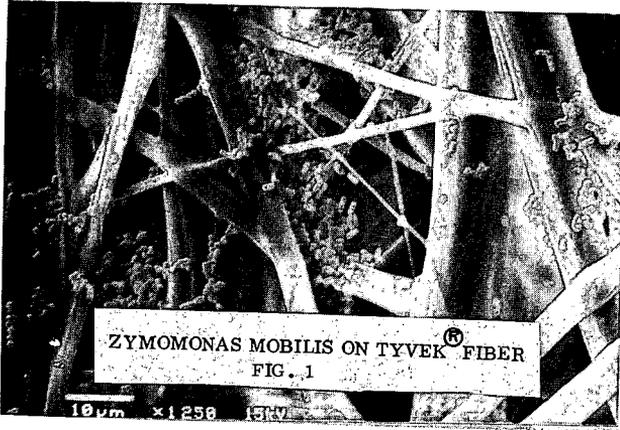
Wayman (6) confirms that sugar can be fermented to alcohol for gasohol in 15 minutes. Dale (7) reports that when yeast is immobilized on fiber, high rates of mass transfer are achievable even at low agitator speeds.

Old cars and trucks that use leaded gasoline put the lead into air and rain washes it into drinking water supplies. If gasohol were used this would not be a problem. Sugar can be converted to alcohol as follows:

A few spoons of Celite[®] (from Manville Company, Denver, CO) are slurried in water and poured into a fermenter with rotating fibers (Reemay 2033 from Reemay Co. Old Hickory, Tenn.) of polyester. The unit is sterilized and *Zymomonas mobilis* (NRRL 14023, US Department of Agriculture, Peoria, Il.) is added. It takes about 30 hours for the cells to grow and attach to the fibers, and then the fermenter is flushed with four times its volume of nutrient which is 10% glucose, 10g/l yeast extract (from Difco) and 1 g/l of three salts (NH₄)₂SO₄, MgSO₄, and KH₂PO₄. If the pH is lower than 6, K₂HPO₄ is used instead of KH₂PO₄. After flushing, aliquotes are taken and in 10 minutes 4% ethanol is measured by HPLC. This is an 80% yield, since one mol of glucose is fermented to two of ethanol and two of CO₂, and the molecular weights of these are about the same (46 and 44) so the theoretical yield is 51 g/l. The unit can then be run for several weeks with residence times of 10 minutes. Some alcohol can be stripped off and sugar recycled. If 96% yield is desired, it can be run with a 15 minute residence time as Wayman did. We believe that this reactor design is so efficient because nutrients have intimate contact with cells, and the same thing should apply to other applications. Membranes are expensive but Tyvek[®] fiber from DuPont is not (only 75¢/sq.yd) and it has small pores and many fibers so we plan on using Tyvek[®] in place of Reemay. *Zymomonas* on Tyvek is shown in Fig. 1.

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UTILIZATION OF COAL GASIFICATION SLAG: AN OVERVIEW

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Keywords: Coal gasification slag, solid waste utilization, slag lightweight aggregate

ABSTRACT

Coal gasification generates solid waste materials in relatively large quantities, and their disposal can represent a significant expense. For example, a 100-MW power plant based on IGCC technology using 1000 tons of 10% ash coal per day may generate over 110 tons/day of solid waste or slag, consisting of vitrified mineral matter and unburned carbon. As coal gasification technologies, considered clean and efficient methods of utilizing coal, find increasing applications for power generation, it becomes imperative that slag utilization methods be developed, tested, and commercialized in order to address the costly problems associated with its disposal as solid waste. This paper presents an overview of the experimental work that has been conducted to characterize samples of slag from various gasifiers and to identify and test a number of commercial applications for their utilization, and discusses various issues with regard to slag utilization. In the course of examining various utilization applications for a number of coal gasification slags that parallel those developed for fly ash, a better understanding of slag as a construction material has been achieved. The applications tested include the use of slag as an aggregate for road construction, cement concrete and asphalt concrete, and production of lightweight aggregate from slag.

HISTORICAL PERSPECTIVE ON COAL WASTE UTILIZATION

In the past decade, fly ash, bottom ash, and boiler slag have increasingly been utilized in construction and other applications. In 1984, 51 million tons of fly ash was generated nationwide, of which 10 million tons, or 19.6%, was utilized in a number of applications. In Europe and Japan combustion solid wastes are utilized to a greater extent; this is attributed to the demand for construction aggregate and fill materials, the shortage of space for waste disposal, and environmental and economic factors.

The search for utilization applications for coal gasification slag parallels that of fly ash, which has been tested successfully for a variety of applications including aggregate stabilization in airport, highway, and dam construction, engineered backfill, soil amendment, cement additive, and lightweight aggregate production. A number of similar applications for gasification slag have been studied by Praxis Engineers, Inc. under a series of contracts funded primarily by the Electric Power Research Institute (EPRI) with additional support from Texaco, Inc. and Southern California Edison.

DEVELOPMENT OF SLAG UTILIZATION TECHNOLOGY

Using fly ash utilization as a model, Praxis started work in 1986 to develop the utilization of gasification slag. The steps involved in this approach can be summarized as follows:

- o Measurement of physical and chemical properties expected to affect the utilization of slag,
- o Screening of conventional industrial and construction materials and products for potential slag utilization applications,

- o Comparison of the properties of gasification slag with the specifications established for other materials to identify possible slag substitution,
- o Testing of promising applications at the bench scale,
- o Enhancement of the properties deemed significant from the utilization viewpoint by simple, low-cost preparation techniques, and
- o Selection of successful applications for further testing at the pilot or demonstration level.

Initial testing was performed using slag samples from the Cool Water Demonstration Plant (CWDP) to demonstrate this methodology. The Cool Water plant was based on the Texaco gasification process. Sixteen potential applications for the utilization of gasification slag were initially identified based on a comparison of the preliminary characteristics of CWDP slag with those of ash by-products. The most promising of these applications included use of slag as a soil conditioner, abrasive grit, roofing granules, ingredient in cement and concrete manufacture, road construction aggregate, and lightweight aggregate. The results of this work were summarized in a paper¹ and presented in an EPRI report².

Once successful utilization concepts had been identified for this slag, samples of another slag generated at CWDP from a different coal feedstock and three other slags generated from different gasifiers were also evaluated³. The three additional gasifier technologies were the Shell Coal Gasification Process, the British Gas Corporation/Lurgi Slagging Gasifier, and the Dow Entrained-Flow Gasification Process, using single-stage operation.

In a parallel study, use of slag for the production of synthetic lightweight aggregate was investigated. The findings of this study were presented in an EPRI report⁴. In a follow-on project, the production of lightweight aggregate from slag was successfully advanced to the pilot scale.

COAL GASIFICATION SLAG PROPERTIES

The physical and chemical properties of coal gasification slags were found to be related to the composition of the coal feedstock, the method of recovering the molten ash from the gasifier, and the proportion of devolatilized carbon particles (char) discharged with the slag. The rapid water-quench method of cooling the molten slag inhibits recrystallization, and results in the formation of a granular, amorphous material. Some of the differences in the properties of the slag samples that were characterized may be attributed to the specific design and operating conditions prevailing in the gasifiers. For instance, the British Gas/Lurgi gasifier produced a slag with a distinct iron-rich phase in addition to the silicate phase, and the Texaco gasifier generated slag containing a higher proportion of discrete char particles.

In general, slag is nominally in the 5-mm x 0.3-mm size range, which is equivalent to the classification for fine aggregates used in cement concrete and asphalt concrete. The apparent specific gravity of slag ranges between 2.64 and 2.81, and its dry compacted unit weight is between 70.1 and 104.9 lb/ft³. The water absorption capacity of slag varies from 2 to 16% and increases with its char content.

The elemental composition of the slag samples with respect to both major and trace elements is similar to that of the gasifier feed coal ash, as shown in Table 1. The major constituents of most coal ashes are silica, alumina, calcium, and iron. Slag fluxing agents, when used to control molten ash viscosity inside the gasifier, can result in an enrichment of calcium in the slag.

The Cool Water slag was classified as nonhazardous under the RCRA regulations. EP toxicity and ASTM extraction tests were run on a number of slags to evaluate their leachability. The slags appear to be nonleachable with respect to RCRA-listed metals. Tests for eight common anions were run, with only sulfate anions being detected at significant concentrations (25 to 200 mg/l).

EVALUATION OF POTENTIAL UTILIZATION CONCEPTS

Selection of applications to utilize gasification slag must take into account the fact that it is in competition with conventionally used materials whose acceptability has been established over long periods. In this effort, the emphasis was placed on evaluating the functional requirements of various applications (such as compressive strength in the case of cement concrete) in order that existing specifications--written for natural materials--do not rule out slag utilization. Ultimately, if slag is found to satisfy the functional requirements of an application, suitable standards can be established for its use in particular cases. A precedent for this procedure is the creation of a standard such as ASTM C 989-87a which was adopted for utilization of ground blast-furnace slag as cement.

Selection of the specific utilization concepts was guided by the following criteria:

- o Similarity between the properties of slag and those of the material it replaces, and
- o Achievement of comparable final products meeting the necessary functional requirements.

Based on these criteria, a number of utilization concepts were identified. These include:

Agriculture:	Soil conditioner, lime substitute, low analysis fertilizer, carrier for insecticides
Industrial material:	Abrasive grit, catalyst and adsorbent, roofing granules, industrial filler, mineral (slag) wool production, filter media
Cement and concrete:	Concrete aggregate, mortar/grouting material, pozzolanic admixture, raw material for portland cement production, masonry unit production
Road construction and maintenance:	De-icing grit, fine aggregate for bituminous pavement, base aggregate, subbase aggregate, seal-coat aggregate
Synthetic aggregate:	Lightweight construction aggregate, landscaping material, sand substitute
Landfill and soil stabilization:	Soil conditioner to improve stability, structural fill, embankment material
Resource recovery:	Source of carbon, magnetite, iron, aluminum, and other metals

Of these, a number of high-volume applications were tested at the laboratory scale and found to be suitable. For example, the potential for using slag as a fine aggregate for base, subbase, and

backfill applications is suggested by the slag size gradation. Shear strength, permeability, and compaction test data also indicate that slag would perform well as an aggregate fill material. While these applications would consume large quantities of slag they provide few economic incentives to the industry to replace cheap and abundant conventional materials with slag at this stage. However, as concern about the environment increases and recycling of waste products becomes a priority, this situation could change rapidly.

USE OF SLAG IN ROAD CONSTRUCTION

The use of slag in road construction was studied by testing various asphalt mix designs incorporating slag. By itself, the slag was not found to be suitable for surface pavement applications due to the lack of coarse particles and the tendency to degrade when abraded. However, its use as a subbase and base material in road construction is quite feasible as it meets a number of requirements for resistance values, e.g., the California Department of Transportation standards for Class 1, Class 2, and Class 3 subbases, and Class 2 aggregate base. To compensate for the high proportion of fine material in the slag, it may need to be mixed with a coarser material for use in specification base material and as an asphalt concrete aggregate.

Asphalt concrete hot mixes containing varying concentrations of asphalt and 30-50% slag by weight as the fine aggregate were tested for their strength (S-values) in a laboratory. A mix in which 30% slag was combined with 6% asphalt yielded an S-value of 50, which is much higher than the minimum value of 30-37 required for various grades of asphalt concrete. This mix, which had good workability, compares favorably with the standard test mix containing 5% asphalt, with an S-value of 58.

USE OF SLAG IN CEMENT AND CONCRETE

The composition of the slag and its natural pozzolanic properties are similar to the raw material used to make portland cement clinker. In this application, the slag carbon (char) content may be beneficial and may provide some of the fuel needed to make the clinker. The slag could also be added to cement clinker and ground with it.

The carbon content of some of the slags is far higher than the 1% limit placed on aggregate. This makes it necessary to recover the unburnt carbon from the slag, both in order to meet the standard for aggregate and to improve the process economics. Char removal was accomplished by means of simple specific gravity devices. The recovered char is a usable by-product.

Several batches of concrete were prepared using slag to replace varying quantities of the sand in the mix. Specimens in which 50% and 75% of the sand was replaced by slag had compression strengths of 2786 and 2483 psi respectively, over a 28-day curing period. This compared well with the control sample containing no slag, which had a compression strength of 3407 psi. These results indicate that slag could be used to replace a large proportion of the fine aggregate in making light-duty nonstructural concrete.

Tests to replace some of the fine aggregate used to make concrete with slag were performed by substituting 50% of the sand by slag. The test specimens achieved satisfactory results, with compressive strengths ranging from 3000 to 3500 psi, compared with a control strength of 3900 psi at the same cement content. These results satisfy typical compressive strength requirements of 2000 psi for concrete pads for sidewalks, driveways, and similar applications.

Another series of tests involved using slag ground to a fine powder as a cement replacement. Cement additive requirements have been established for blended cements in ASTM C 595 which covers five classes of blended hydraulic cements made from conventional materials for both general and specific applications. Following initial exploratory tests, it was concluded that it was necessary

to process the slag samples to remove potentially deleterious substances. The lighter char fraction was removed from one of the slags by density separation, and an iron phase was recovered from another slag by magnetic separation. The percentages of cement replaced by slag in these tests was 15% and 25% respectively. The use of processed slags resulted in a more successful replacement of cement by slag. All of the 15% slag-cement blend samples exceeded the 3-, 7-, and 28-day strength requirements of 1800, 2800, and 3500 psi respectively, and one of the four slags tested exceeded these requirements at the 25% replacement level. The other three 25% replacement level slag samples achieved the required 28-day strength but did not satisfy the 3- and 7-day requirements. The average 28-day strength for the 15% blend was 5600 psi, and that of the 25% blend was 4900 psi.

The success of the prepared slag-cement blends in achieving long-term compressive strength suggested that the ground slag would also qualify as a pozzolanic mineral admixture. A pozzolan is a finely ground siliceous material which can react with calcium ions, in the presence of water and at room temperature, to form strength-producing calcium silicate minerals in a manner similar to cement reactions. A 35% replacement of cement by slag was evaluated in accordance with the procedures outlined in ASTM C 311. The success of a pozzolanic test is measured by the Pozzolanic Index, which indicates the ratio of the sample's compressive strength to that of an ordinary portland cement control sample. All of the concrete samples thus produced exceeded the Pozzolanic Index requirement of 75%, with index values ranging between 90 and 118%.

SLAG LIGHTWEIGHT AGGREGATE

Lightweight aggregates (LWA) have unit weights that are approximately 40-60% those of standard aggregates. Annual consumption of LWA in the United States for various applications is approximately 15 million tons. Major applications of LWA are in the production of lightweight structural concrete used in highrise buildings and lightweight precast products such as roofing tiles, masonry blocks, utility vaults, cement concrete pipes, etc. Conventional LWAs are produced by pyroprocessing of naturally occurring expandable shales or clays at temperatures ranging between 1880 and 2200°F after pulverizing, working into a paste, and extruding them to produce pellets of the desired size. The strength requirements for lightweight concretes made from LWA are given in Table 2.

Slag-based lightweight aggregates (SLA) were produced by duplicating the processing methods used for commercial LWA manufacture. These steps included grinding the slag, mixing it with a clay binder and water, and extruding it to form long strands that were cut to the desired sizes. These wet green pellets were then dried and fired in a laboratory muffle furnace at 1800°F for 4 minutes. A unit weight of 45 lb/ft³ was measured for the SLA, which is below the minimum coarse LWA specification of 55 lb/ft³. Concrete made from the SLA had a 28-day compressive strength of 3100 psi and a unit weight of 105 psi, which exceeds the ASTM requirements shown in Table 2.

Further tests have confirmed that the density of the SLA can be controlled as a function of the firing temperature, as shown in Figure 1. This indicates that SLA products can be produced to meet specific density requirements such as those for cement concrete LWA, lightweight concrete masonry units, or ultra-lightweight material used in insulating concrete.

Tests on discrete 2-mm particles of each slag showed that they also expand to form a lightweight material when fired at 1600-1900°F. Further tests on all particles larger than 0.3 mm, without pelletization, confirmed this phenomenon. The materials resulting from these tests had unit weight values of 15-25 lb/ft³. The concrete produced from one of the expanded slag samples had a unit weight of 33 lb/ft³, which qualifies it to be classified as an insulating concrete. However, it had a compressive strength of only 125 psi which is somewhat lower than the strength of commercially available insulating concretes at 200-250 psi. It is expected that the strength can be considerably

increased with minor adjustments to aggregate gradation and the cement proportions used to formulate these test samples.

The experimental work on slag utilization has been developed to the continuous pilot scale for the production of SLA from slag. The results from this test program have been very encouraging and have confirmed the bench-scale test results. During the tests, engineering information on energy requirements, scale-up information, and off-gas analysis was obtained, and the mechanism of slag expansion was investigated. The energy requirements for SLA production are considerably lower than those for conventional LWA production due to the lower kiln temperatures required for slag. Samples of the SLA generated during the pilot tests are undergoing extensive testing.

CONCLUSIONS

Gasification slag has been determined to be an environmentally nonhazardous material, whose unique properties may be attributed to the composition of the mineral matter in the coal feedstock and the method of quench-cooling applied in the gasifier. Bench-scale test data have shown that there are a number of promising applications for the utilization of gasification slags. In particular, the utilization of slag in applications such as road and construction aggregates, cement additives, and lightweight aggregates has been demonstrated. Production of slag-based LWA (or SLA) is feasible and should be established as a priority. The high unit price of LWAs will permit SLA to be transported for greater distances while remaining economically competitive, thus rendering slag utilization less sensitive to the location of the gasifier.

FUTURE OF SLAG UTILIZATION

Currently, in most utilization scenarios, gasification slag would be used as a replacement for materials that have a relatively low unit cost, such as road aggregates. Unless potential commercial users of slag are provided with extensive characterization and utilization data, the economic incentives alone are unlikely to be sufficient to cause them to incorporate slag into their production scenarios. The initial resistance to the use of new materials that may be encountered in the construction materials manufacturing industry can be addressed in two ways. First, the slag producer can supply complete engineering data on slag utilization to the prospective end user, who would then be responsible for any processing steps that might be required for a particular application. An alternative, more comprehensive approach would be for the slag producer to deliver the slag to the end user in a form that meets the user's specifications; these specifications could vary depending on the market demand in the vicinity of the gasifier. If recent legislation in California can be used to gain an insight into coming regulatory trends, at least 50% of the slag produced in the state will be required to be utilized in the coming decade, thereby creating additional incentives for producers and prospective end users to work together to realize its utilization potential.

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Table 1

COMPARATIVE COMPOSITION OF TYPICAL BLAST-FURNACE SLAG, COOL WATER FEED (UTAH) COAL ASH, AND COOL WATER SLAG

<u>Mineral</u>	<u>Blast Furnace Slag</u>	<u>Cool Water (Utah)</u>	
		<u>Coal Ash</u>	<u>Cool Water Slag</u>
SiO ₂	32-42	48.0	40-55
Al ₂ O ₃	7-16	11.5	10-15
CaO	32-45	25.0	10-15
MgO	5-15	4.0	2-5
Fe ₂ O ₃	0.1-1.5	7.0	5-10
MnO	0.2-1.0	NA	NA
S	1.0-2.0	NA	<1

Table 2

UNIT WEIGHT, MINIMUM COMPRESSIVE STRENGTH, AND TENSILE STRENGTH (28-Day Requirements for Structural Concrete, ASTM C 330)

<u>100% LWA mix</u>		<u>Sand/LWA Mix</u>	
<u>Unit Weight</u> <u>lb/ft³</u>	<u>Compressive</u> <u>Strength, psi</u>	<u>Unit Weight</u> <u>lb/ft³</u>	<u>Compressive</u> <u>Strength, psi</u>
115	--	115	4000
110	4000	110	3000
105	3000	105	2500
100	2500	100	--

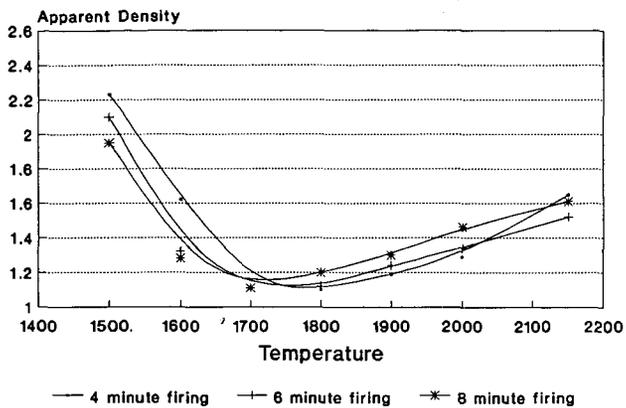


Figure 1. Time/Temperature/Density Relationship for Expansion of Slag Pellets

ASH UTILIZATION AND DISPOSAL
by

CARL A. HOLLEY
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ABSTRACT

There are many changes taking place in the utilization and disposal of ash and related materials and each day it seems that there are more restrictions on the disposal of ash. In one project, mass burn ash has been screened to remove the plus one inch pieces and then combined with the fly ash and portland cement to produce a pellet that is non-leaching with all of the heavy metals "fixed".

In the northeastern United States, the ash from circulating fluidized bed combustors needs to be pelletized so it can be transported back to the mine for easy disposal. The ash can also be blended with digested municipal sewage sludge to form a soil additive which contains lime and nutrients.

The new clean air standards are making it necessary for utilities to install sulfur dioxide scrubbers which produce gypsum. This gypsum filter cake can be pelletized so that the pellet produced can be utilized in the final grind of Portland cement or can be disposed of in a non-leaching pile.

We have taken the lead in producing these agglomeration techniques and many more processes which we will describe and show the detailed process flow diagram for each of these methods.

INTRODUCTION

The utilization and disposal of fly ash in a legal and environmentally safe manner is becoming a major engineering challenge because of rapidly changing government laws and regulations.

There are many changes taking place in ash management based on the fact that pellets can be produced which are non-leaching. Pellets can be moved with conventional bulk material handling equipment without producing a dusty environment. The pellets can be disposed of in any type site and do not need to be placed in a lined landfill. In addition, slight modifications to the pelletizing process can produce usable products such as lightweight aggregate or aggregate to be utilized in asphalt.

We see that each situation or plant needs to be treated as a separate problem and a process developed to solve that particular problem. The two key pieces of equipment required to process fly ash are the Ferro-Tech-Turbulator" (Figure 1) and the Ferro-Tech Disc Pelletizer (Figure 2). The Ferro-Tech-Turbulator" is a proprietary, intense, highly efficient, agitative agglomeration device. The unit has maximum efficiency because it operates by fluidizing the material and atomizing the injected liquid. Each whirling dust particle is uniformly coated with a very thin layer of water or other binder. These coated dust

particles, moving at a high velocity in suspension, collide and impact with great force with the other coated, spinning particles within the turbulent wake created behind the pins, forming a very uniformly sized and dense particulate or microgranule. The thick, resilient polymer liner in the Turbulator™ combined with critical close pin tip tolerance causes the pins to fully sweep or wipe the liner, eliminating product build-up on the inner casing of the Turbulator™ body. Because of the intensity of the Turbulator™, it can efficiently pre-blend, de-dust, blend, condition, densify, hydrate and micropelletize all types of fine powders, dust, fume and hard-to-wet particulates. The fly ash particles are uniformly coated with water in the Turbulator™ before they are discharged to be pelletized in the disc pelletizer. The conditioning step in the Ferro-Tech-Turbulator™ compensates for the variation in particle size and surface area which is an inherent quality of fly ash, due to changes in combustor operations and variation in fuel.

CIRCULATING FLUIDIZED BED COMBUSTOR ASH AGGLOMERATION

Most of the new cogeneration plants are utilizing a circulating fluidized bed combustor principle which burns coal having reasonable levels of sulfur (up to 3%). The ash from these combustors consists of two fractions, bed drain or bottom ash and fly ash. The bed drain ash is approximately 25 to 30% of the total ash. The best ash systems keep the two ash fractions separated so they can be blended uniformly together for agglomeration. The fly ash can be agglomerated alone, but the bed drain ash must be blended with at least 50% fly ash before quality pellets can be produced.

The basic process flow diagram for producing a 1/4" x 1/2" pellet is shown in Figure 3. This system includes two (2) surge bins with feeders feeding the ash into a Ferro-Tech-Turbulator™ where most of the water required for pelletizing is added. The conditioned ash from the Turbulator™ discharges directly into the disc pelletizer where pellets are formed. This disc pelletizer is designed for this specific agglomeration application. The pellets or green balls from the disc pelletizer have a modest amount of strength so that they can withstand the treatment of the material handling system to the pellet curing area. The pellets require some curing if they are to be moved by normal material handling methods. After curing, a typical 1/2" diameter pellet may require a force of 300 pounds to crush it. These pellets can easily be utilized as road bed material or as aggregate in concrete.

CIRCULATING FLUIDIZED BED COMBUSTOR ASH AGGLOMERATION (High Sulfur Coal)

When a high sulfur coal (above 3%) is burned in a circulating fluidized bed combustor, this fly ash acts very differently. When water is added to the fly ash in a Ferro-Tech-Turbulator™, the ash very quickly (5 to 10 minutes) gains temperature. A typical temperature is shown in Figure 4 where the temperature rose to 290° F in seven minutes. If enough water has been added to produce pellets, the pellets will quickly heat up and will completely disintegrate becoming an even finer dust than it was in the beginning.

The process flow diagram necessary to produce pellets from this fly ash on which Ferro-Tech holds a patent is shown in Figure 5. The conditioned fly ash from Turbulator™ No. 1 is discharged directly into a conditioning bin where the fly ash hydrates and the temperature increases to as much as 300° F. The conditioned material from Turbulator™ No. 1 is retained in the conditioning bin until all of the water which was added in Turbulator™ No. 1 has chemically reacted and the fly ash is completely dry. During the hydration phase, the chemical reaction will produce much finer particles with a lower bulk density than the original fly ash. The material from the conditioning bin is fed into Turbulator™ No. 2 where most of the water for pelletizing is added. Again, the material from the Turbulator™ is discharged directly into a disc pelletizer where pellets are formed. The pellets are placed in a curing area where they cure and gain strength.

FLY ASH LIGHTWEIGHT AGGREGATE

One of the better uses for Class F and Class C fly ash from pulverized coal power plants is to produce lightweight aggregate. This aggregate can be utilized to produce lightweight concrete block and other masonry forms. The basic process flow diagram for the process is shown in Figure 6. The aggregate seems to have many advantages over other lightweight aggregates including its spherical shape. The aggregate produced by this process bonds to the mortar with both a mechanical bond and a chemical bond instead of just a mechanical bond as is true of other non-reactive aggregates.

The bulk density of the aggregate is approximately 45 to 50 lbs./cu.ft. The typical sieve analysis (ASTM C136) of the aggregate for concrete block is:

<u>Sieve Size</u>	<u>Product Percent Passing</u>	<u>Specification Percent Passing</u>
1/2"	100	100
3/8"	99	90 - 100
4 mesh	83	65 - 90
8 mesh	49	35 - 65
16 mesh	31	---
50 mesh	19	10 - 25
100 mesh	15	5 - 15

SYNTHETIC GYPSUM & FLY ASH PELLETIZING

One of the major problems at pulverized coal power plants burning high sulfur coal which have a wet line scrubber is how to dispose of the synthetic gypsum slurry. One very simple solution is to produce a pellet by blending dry fly ash with the gypsum filter cake or even with the gypsum slurry. Figure 7 shows the basic process flow diagram for the required system. In this system, the filter cake is metered into the Ferro-Tech-Turbulator™ at a constant rate. The feed rate of the fly ash is controlled by a Ferro-Tech patented moisture control system on the disc pelletizer. This system adjusts the feed rate to maintain a constant surface moisture on the pellets which are about to discharge from the disc pelletizer.

The pellets from the disc pelletizer are placed in a curing pile where they gain strength before being placed in a landfill. The pellets increase in strength quickly and can then be transported in standard material handling equipment.

MASS BURN ASH AGGLOMERATION

The processing of mass burn ash is in a state of change since there is obviously a need to produce a product that has all of the heavy metals "fixed" so they do not leach from a landfill. The requirement is to process both the bottom ash and the fly ash. Processing the bottom ash alone is very difficult because of the extreme variation in the size of the pieces and in the high moisture of the material. A finger screen can be utilized to separate the plus one inch particles from the minus one inch pieces even though the moisture may be as high as 20 to 25% as shown in Figure 7.

Once the oversized pieces are removed, the available fly ash is added uniformly along with 15 to 20% Portland cement. These are all fed directly into a disc pelletizer which is equipped with a reroll ring. Moisture is added to the disc pelletizer through spray nozzles until pellets are produced. It normally requires a total of 16 to 20% moisture to produce pellets.

The completed pellets are discharged from the disc pelletizer pan into the reroll ring where 1 to 3% Portland cement is added to coat the pellets. The coating of the pellets with Portland cement serves two purposes. The first purpose is to seal the surface of the pellets which will assist in eliminating any leaching, the second purpose is to keep the pellets from sticking together as they cure in the tote bin.

After approximately seven days of curing, the heavy metals in the ash are fixed to the point that they will pass the T.C.L.P. leaching test. The pellets will have strength enough to be easily handled and should not crush under normal handling.

CONCLUSION

Essentially any fly ash can be agglomerated into non-dusting and non-leaching agglomerates. The requirements for the agglomerates keep changing and become more restrictive as the regulators try to make the environment safer. Our goal is to assist the customer in developing the best process to fulfill the regulators present and future demands. Many of the processes appear to be simple, but there has been much experience involved in the development. We feel that the simplest process is the best process if it meets all of the customer's goals. We know that each situation is unique and a process must be adapted to the special ash from a specific plant. It is advisable to cooperate with a supplier who has the most experience so you can have confidence in their recommendations.

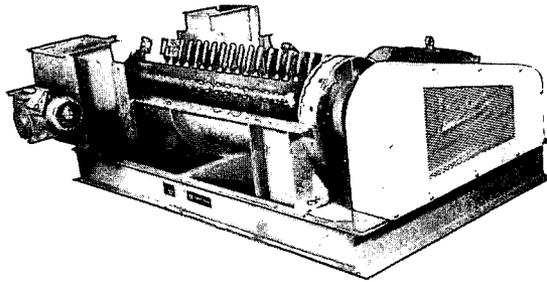


FIGURE 1
FERRO-TECH-TURBULATOR™

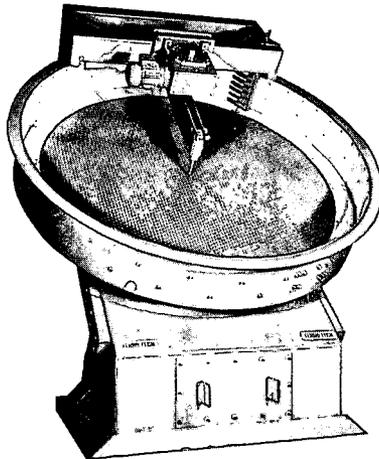
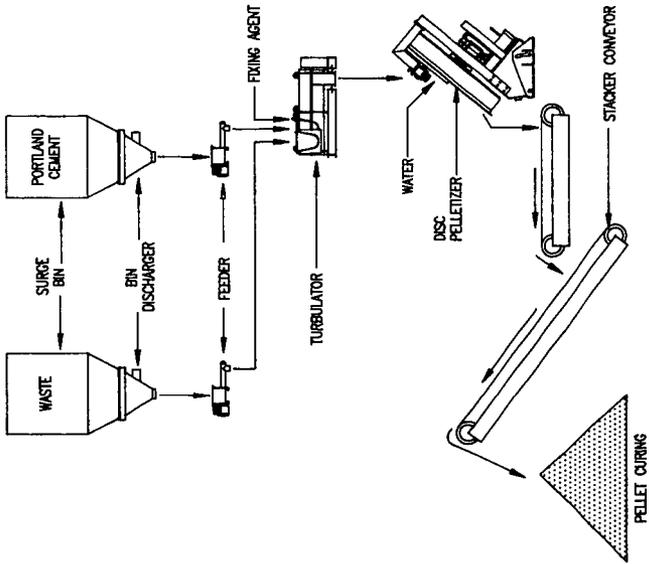


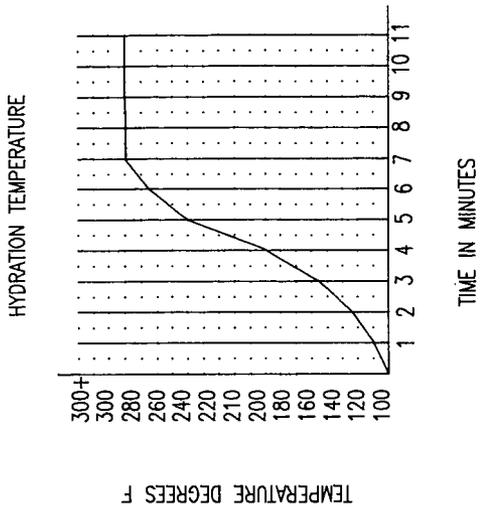
FIGURE 2
DISC PELLETTIZER



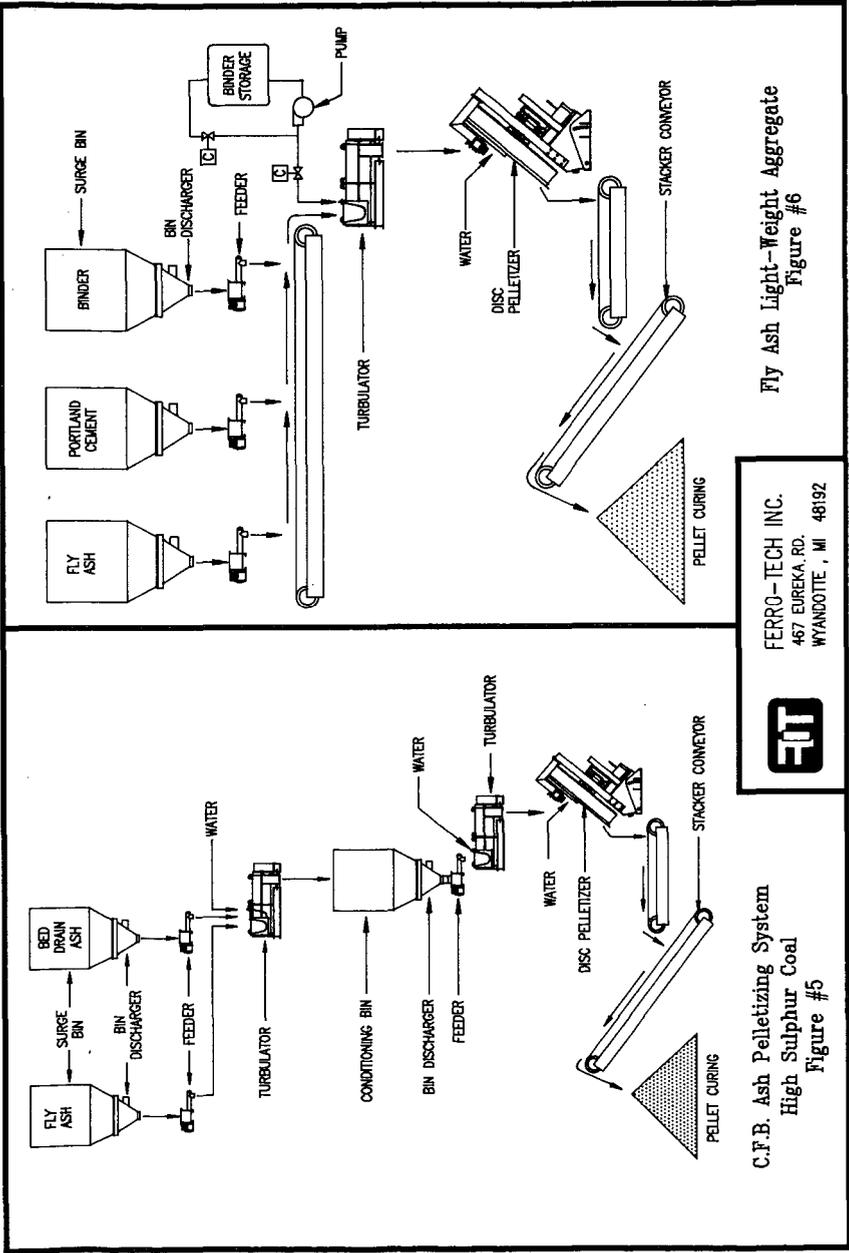
C.F.B. Ash Pelletizing System
Figure #3



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Temperature Curve
Figure #4

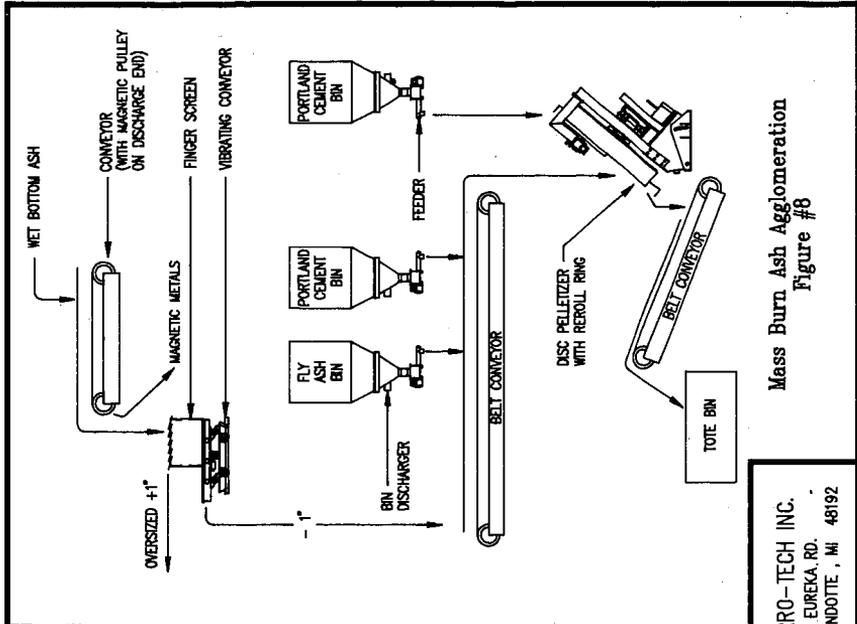


Fly Ash Light-Weight Aggregate
Figure #6

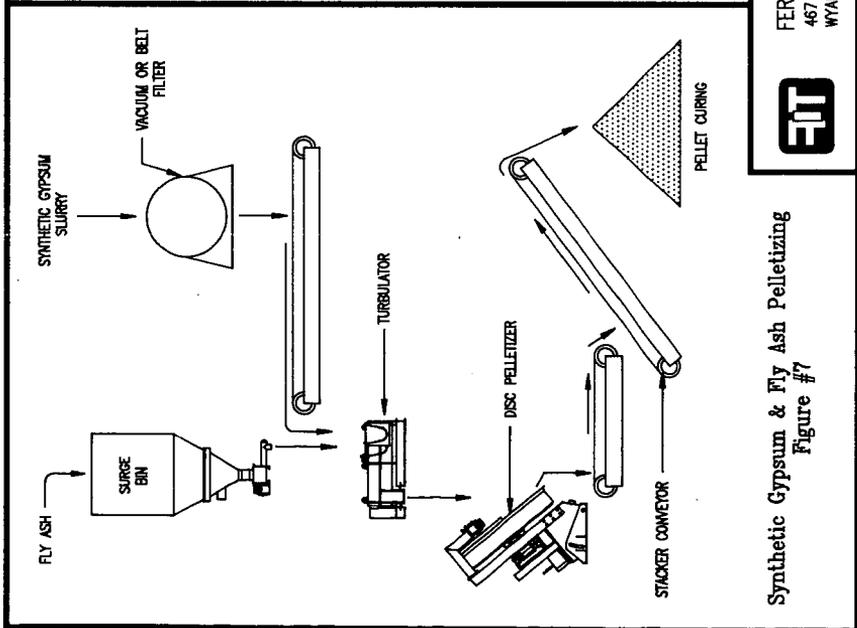
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C.F.B. Ash Pelletizing System
High Sulphur Coal
Figure #5



Mass Burn Ash Agglomeration
Figure #6



Synthetic Gypsum & Fly Ash Pelletizing
Figure #7

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