Plasma Gasification and Vitrification of Ash – Conversion of Ash into Glass-like Products and Syngas

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ABSTACT

The Plasma Gasification and Vitrification of Ash (PGVA) system is a patented process that uses energy generated by plasma arcs along with the controlled addition of small amounts of air and steam to convert the organic portion of ash into a synthesis gas (gasification) and the inorganic portion into a glassy rock (vitrification).

The vitrification of the ash's inorganic portion significantly reduces its volume (five to ten times), prevents heavy metals from leaching out (TCLP results are typically several orders of magnitude below regulatory levels), and allows the ash to be used as construction material (e.g. aggregate).

In addition to vitrifying the ash, the PGVA process recovers the energy present in the ash by gasifying the organics into a synthesis gas (syngas). The energy released by the gasification of the organics provides some of the energy required for vitrification and, more importantly, the resulting syngas (mainly carbon monoxide and hydrogen) can be fed back to the main combustion unit for use as a fuel. In addition, since the PGVA system only requires a simple and compact gas cleaning system, capital investments are greatly reduced compared to stand alone ash vitrification systems.

Pilot plant results for the treatment of pulp and paper boiler ash as well as MSW combustor ash, at feed rates between 50 and 100 kg/h, are presented, including experimental results for TCLP, and syngas composition. Case studies, including material and energy balances, are given for various types of ash, including ash from coal.

INTRODUCTION

Plasma[1] and arc furnace technologies[2] have been under development for many years for the vitrification of combustion residues such as ash, in particular for municipal solid waste incinerator residues. High temperature Vitrification of ash offers several advantages: volume reduction, destruction of organic contaminants such as dioxins and furans and inertization of heavy metals in an inert, non leachable, silica matrix.

The patented plasma gasification and vitrification of ash (PGVA) process uses graphite electrodes to produce the plasma energy. The energy produced by the gasification of unburned organics to carbon monoxide (CO) and hydrogen (H_2) by dissociation of water is used to heat up the ash and synthesis gas to about 800°C. The plasma arc energy is used to melt the ash to a slag and to increase the temperature to approximately 1,500°C. Since the ash is treated hot, on site, as it comes out of the boiler, some of the latent heat from the boiler is recuperated thereby reducing the energy requirement of the plasma arc furnace. The synthesis gas can be returned directly to the boiler with minimal treatment, increasing the energy efficiency of the overall plant.

PROCESS DESCRIPTION

Plasma is a gas that conducts electricity. In order for a gas like air to conduct electricity, it must be subjected to a large differential in electrical potential. This is done between two electrodes which are separated by a gas. When this potential is large enough, electrons can be pulled from the normally neutral molecules in the gas. These electrons then move with the electric field and impact other molecules, releasing more free electrons at an exponential rate. This phenomenon is called an electron cascade and once enough electrons are moving with the electric field, an arc is created between the electrodes. All of this happens within a fraction of a second.

In terms of the electrical circuit, the gap where the arc is created can be seen as a resistance. While going through this resistance, the electrical current releases large amounts of heat. Several technologies have been developed to use this source of heat which can reach temperatures from 5,000 to 10,000ºC.

With plasma, it is possible to treat waste with a high concentration of inorganic material with a very low heating value, such as ash, since most of the heat necessary for the gasification comes from the plasma and not from the oxidation of the waste. Moreover, since electricity is used as a source of heat, the impact on the gas volume generated is negligible, as compared to a combustion process using fossil fuel.

The PGVA process is illustrated schematically if Figure 1.

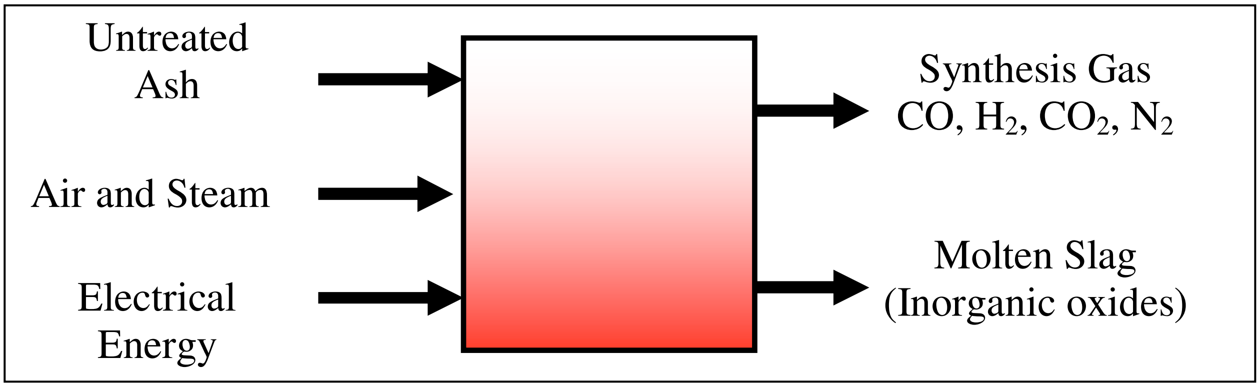

Figure 1. PGVA Process Schematic

In the PGVA furnace, the unburned carbon reacts with the oxygen in air and steam to form a synthesis consisting mainly of carbon monoxide (CO) and hydrogen (H_2). The following reactions are the main gasification reactions that occur within the furnace:

$C + O_2 <-> CO_2$ (exothermic)
$C + H_2O <-> CO + H_2$ (endothermic)
$C + CO_2 <-> 2 CO$ (endothermic)
$CO + H_2O <-> CO_2 + H_2$ (exothermic)

Electrical energy is used to melt the inorganic compounds present in the ash. Depending on the silicon based material content of the ash, the process may require the use of additives. The carbon content of the ash also has an impact on the process. With higher carbon content (such as in the case of bark boiler ashes), some of the energy for the process will be provided by the energy released by gasification.

The PGVA furnace is a direct current (DC) graphite arc plasma furnace (Figure 2). It uses the energy available in the electrical arc by transferring it directly to the material that will be destroyed. A high current (that can range from a few hundred amps to several thousands of amps) is directed through long cylindrical graphite electrodes into a furnace, lined with refractory material. The electrical energy typically jumps from one electrode (the cathode) to the slag (which is electrically conductive in the liquid state), then passes through the slag, resistively heating it by the Joule effect and then jumps to the second electrode (the anode), completing the circuit. This mode of operation is often referred to as the “transferred” mode, as the electrical energy is directly transferred into the waste. The arcing generates a tremendous of heat which serves to heat the waste.

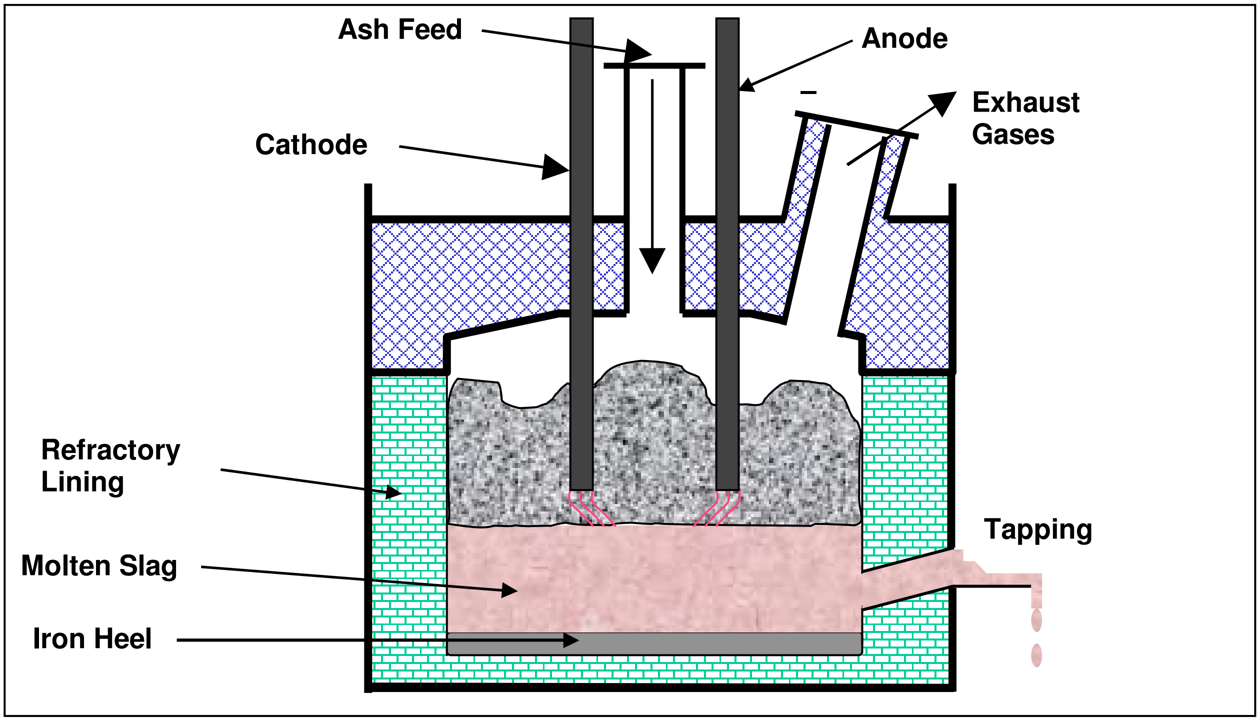

Figure 2. PGVA Furnace Schematic

The temperature the furnace can attain 1,500ºC. At this temperature, the ash is vitrified (turned to a dense, glassy substance called slag). The molten pool of slag at the bottom of the furnace also serves as a hot mass of energy, allowing waste to be processed at high feed rates.

The furnace is operated with a “cold top”, meaning that a large column of ash is maintained on top of the molten slag and is continually sinking into it. This allows the formation of temperature zones which the waste goes through gradually, permitting evaporation of water, reduction and oxidation reactions to occur. This has been recognized as one of the most important conditions to achieve good gasifier operation. In addition, the cold top protects the furnace wall from potential damage resulting from plasma arc jets. Finally, the cold top operation improves the energy efficiency of the process, by keeping the slag pool insulated from the surroundings.

Depending on the inorganic content of the waste, it is necessary to tap out the molten slag, either periodically (for smaller furnaces) or continuously (for larger furnaces), in order to maintain an optimal level in the furnace. The slag can be tapped directly into a cold water bath, where it very quickly solidifies and granulates into fine gravel sized pieces. The slag can also be tapped into a mold to make shapes such as tiles or blocks (Figure 3). The key to obtaining a good quality slag with very low leaching characteristics is to cool the molten liquid as quickly as possible. When cooled quickly, the result is an amorphous structure, where a matrix of silicate molecules traps contaminants such as arsenic and lead at the molecular level. If the slag is not cooled quickly enough, it will form a crystalline structure, which does not possess the same resistance to leaching.

Figure 3. Sample Products from Slag

The chemical composition of the inorganic slag depends heavily on the composition of the waste treated. The presence of silica (SiO_2) is crucial to obtain a vitrified product and if the source of waste being treated does not contain sufficient amounts, some additives are required. Ideally, these additives should be readily available, and low cost. Waste outputs from other industries could be used for that purpose. For example, contaminated crushed glass not easily suited for recycling (glass cullet) or spent foundry sand would be an ideal source of silica.

PILOT PLANT

A flexible pilot plant using the PGVA is installed at PyroGenesis' facility in Montreal, Quebec, Canada (Figure 4). The unit can process up to 100 kg/h of ash and other inorganic wastes. The pilot plant can also treat organic waste, but at reduced capacities. The pilot plant includes a PGVA furnace, cyclone for collecting ash entrained with the gas, a plasma eductor gasifier, a complete gas cleaning system, capable of treating gases produced by the treatment of a wide variety of waste types, as well as an afterburner, used to combust the syngas. This system is designed to accept both solid and liquid feeds of various types, including, in addition to ash, highly organic waste, such as municipal solid waste (MSW), oils, solvents, and plastics[3].

Figure 4. Pilot PGVA Furnace

RESULTS

The slag produced from the vitrification of ash has been tested extensively to ensure that it is resistant to leaching of toxic elements. The TCLP analysis (Toxicity Characteristic Leaching Procedure) is used to simulate long term exposure to conditions that could be found in landfills. It determines how mobile the toxic elements are in the slag and how likely they are to contaminate surrounding ground and water.

Fly ash samples were obtained from an MSW incinerator in April 2003. The physical properties of the ash are reported in Table 1. The estimated composition of fly ash from SEM-EDS analysis are shown in Table 2.The chlorine content of the fly ash was cross-checked with a measurement by dissolution of the ash in water and measurement of the dissolved chlorine with test strips. The chlorine content from this method was measured to be 2.7%, which is lower than the EDS result. This expected as some of the chloride in the ash could be in non soluble compound form.

Table 1. Physical Properties of Fly Ash Collected April 2003

Moisture Content	0.1%
Loss on Ignition (L.O.I.)	2.3%
Bulk Density	0.6 g/cc
Base density	1.6 g/cc

Table 2. Fly Ash Chemical Composition Estimate from SEM-EDS Analysis for the Sample Collected April 2003

Compound	**Mass (%)**
Na_2O	6.9
MgO	2.4
Al_2O_3	15.8
SiO_2	23.9
P_2O_5	5.6
S	3.7
Cl	3.1
K_2O	3.1
CaO	25.4
TiO_2	2.9
Fe_2O_3	5.1
ZnO	2.1
TOTAL	100

Fly ash was melted in a laboratory furnace and sent out to an independent certified laboratory for TCLP analysis MA-100-LIX2.0 EPA 1311-1. Local Canadian measurement methods and regulations were used as a basis for the analysis. Results are shown in Table 3. For all parameters measured, the vitrified ash was below the detection limit, except for lead, which was 15 times below the regulation.

TCLP Results for MSW Fly Ash (Lab Furnace Test)

METAL	Units	Sample 1	Sample 2	Sample 3	Regulation*
Arsenic (As)	mg/L	ND	ND	ND	5.0
Baryum (Ba)	mg/L	ND	ND	ND	100
Boron (B)	mg/L	ND	ND	ND	500
Cadmium (Cd)	mg/L	ND	ND	ND	0.5
Chromium (Cr)	mg/L	ND	ND	ND	5.0
Lead (Pb)	mg/L	0.34	0.29	0.36	5.0
Selenium (Se)	mg/L	ND	ND	ND	1.0

ND = Not detected

** Province of Quebec Hazardous Material Regulation (RMD), c. Q-2, r.15.2, ch. 1, §. 3.*

A pilot test was carried out with fly ash obtained from the same MSW incinerator as the samples obtained in 2003. This sample was obtained during the spring of 2006. Physical properties of the fly ash sampled are given in Table 3. Table 4 show the ash chemical analysis based on SEM-EDS data.

Table 3. Physical Properties of Fly Ash Collected May 2006

Moisture Content (after wetting)	10.0%
Loss on Ignition (L.O.I.)	8.8%
Bulk Density	0.4 g/cc
Base density	1.0 g/cc

Table 4. Fly Ash Chemical Composition Estimate from SEM-EDS Analysis for the Sample Collected May 2006

Compound	Mass (%)
Na_2O	10.5
MgO	2.0
Al_2O_3	13.3
SiO_2	18.1
P_2O_5	3.1
S	3.9
Cl	8.5
K_2O	3.8
CaO	26.6
MnO	3.0
Cr_2O_3	0.2
Fe_2O_3	3.0
ZnO	4.0
TOTAL	100

For the pilot test, one drum containing 95 kg (200 lbs) of fly ash was fed to the PyroGenesis pilot furnace along with 14 kg (30 lbs) of glass. The dry fly ash obtained from the local incinerator was wetted with 10% water prior to feeding, in order to limit carryover through the gas treatment system and to provide a source of hydrogen to hydrolyze the chlorine and sulphur salts in the fly ash into HCl and H_2S and hence prevent the formation of salt layers and mattes inside the furnace. The mass balance is shown in Table 5.

Table 5. Mass balance for the pilot trial

Inputs:	
Fly Ash:	95 kg
Glass Cullet:	14 kg
Total Inputs	109 kg
Outputs	
Slag tapped	52 kg
Slag recovered in the furnace crucible	27 kg
Moisture in ash fed – 10.0 %	9.5 kg
Volatiles in ash – 8.8% of dry ash	7.5 kg
Total Outputs	96 kg
Inputs - Outputs	13 kg
Mass balance error	13/109 = 12%

The TCLP results are shown in Table 6. The pilot results were comparable to those of the laboratory furnace results with most measured TCLP results below the detection limit.

Table 6. TCLP Results for MSW Fly Ash (Pilot Furnace Test)

METAL	Units	Result	Regulation*
Arsenic (As)	mg/L	ND	5.0
Baryum (Ba)	mg/L	ND	100
Boron (B)	mg/L	ND	500
Cadmium (Cd)	mg/L	ND	0.5
Chromium (Cr)	mg/L	ND	5.0
Lead (Pb)	mg/L	0.2	5.0
Selenium (Se)	mg/L	ND	1.0

ND = Not detected

** Province of Quebec Hazardous Material Regulation (RMD), c. Q-2, r.15.2, ch. 1, §. 3.*

VOLUME REDUCTION

The net volume reduction of MSW fly ash can be estimated by measuring the bulk density of the slag of 1.4 g/cc. The net volume reduction for the dry fly ash can be estimated as:

$$\frac{1.4\text{ g/cc (bulk density of the slag)}}{0.4\text{ g/cc (bulk density of the fly ash)} \times 90\%\text{ inorganic content}}$$

This is a net volume reduction of approximately 4 times.

The gross volume reduction can also be estimated by comparing the bulk density of the ash compared to the base density of the slag, In that case, the slag would be recovered in the form of solid ingots. Example volume reduction is shown in Table 7.

Table 7 – Example Volume Reduction for Pulp and Paper Bark Boiler

Ash type	Ash Bulk Density	Slag Base Density	Volume Reduction*
Fly Ash	0.320 g/cc	2.77	11:1
Grate Ash	0.485 g/cc	3.06	7:1

*Taking into account volatile content

SYNGAS COMPOSITION

An example of syngas composition obtained from the gasification of pulp and paper bark boiler fly ash is shown in Table 8. This composition corresponds to a gas heating value of 5.8 MJ/Nm^3.

Table 8 – Example syngas composition from the gasification of bark boiler ash

Compound	Syngas composition (% vol.)
Carbon monoxide – CO	34.8%
Carbon dioxide CO2	7.0%
H2	10.8%
N2 (by difference)	47.4%

MASS AND ENERGY BALANCE EXAMPLES

An example mass and energy balance for bark boiler ashes containing 27% carbon is shown in Table 9 and Table 10. All calculations are based on 1 metric tonne of ash (1000 kg). In this case, the amount of energy available in the syngas will be almost five times the amount of electrical energy used by the system. Even considering the power plant's efficiency factor, there will be an net energy gain from using the PGVA process.

Table 9 – Example mass balance for bark boiler ash

INPUTS	Ash	1000	kg
	Gasification Air	1512	kg
	Gasification Steam	61	kg
	TOTAL INPUTS	2573	kg
OUTPUTS	Slag	730	kg
	Syngas	1843	kg
	TOTAL OUTPUTS	2573	kg

Table 10 – Example energy balance for bark boiler ash[4]

INPUTS	Ash (200℃)	Heating Value	2455	kWh
		Sensible Heat	55	kWh
	Gasification Air (200℃)		75	kWh
	Gasification Steam (200℃)		51	kWh
	Plasma Energy (Electricity)		367	kWh
	TOTAL INPUTS		3004	kWh
OUTPUTS	Slag (1500℃)		482	kWh
	Syngas (800℃)	Heating Value	1785	kWh
		Sensible Heat	487	kW
	Heat losses		250	kW
	TOTAL OUTPUTS		3004	kW

A second example mass and energy balance for lower carbon content ash (5% carbon) typical, for example, of the fly ash from more efficient coal fired power boilers and MW incinerators is shown in Table 11 and Table 12. All calculations are based on 1 metric tonne of ash (1000 kg). In this case, the amount of energy available in the syngas will only be about one half of the electrical energy required by the process. In this case, the main benefit from PGVA will be from volume reduction and immobilization of heavy metals.

Table 11 – Example mass balance for ash containing 5% carbon

INPUTS	Ash	1000	kg
	Gasification Air	280	kg
	Gasification Steam	11	kg
	TOTAL INPUTS	1291	kg
OUTPUTS	Slag	950	kg
	Syngas	341	kg
	TOTAL OUTPUTS	1291	kg

Table 12 – Example energy balance for ash containing 5% carbon

INPUTS	Ash (200℃)	Heating Value	455	kWh
		Sensible Heat	54	kWh
	Gasification Air (200℃)		14	kWh
	Gasification Steam (200℃)		9	kWh
	Plasma Energy (Electricity)		766	kWh
	TOTAL INPUTS		1298	kWh
OUTPUTS	Slag (1500℃)		627	kWh
	Syngas (800℃)		331	kWh
			90	kWh
	Heat losses		250	kWh
	TOTAL OUTPUTS		1298	kWh

CONCLUSION

The Plasma Gasification and Vitrification of Ash (PGVA) allows to convert different types of ash, including MSW fly ash, into non leachable slag (TCLP results are typically several orders of magnitude below regulatory levels) and combustible fuel gas. The vitrified products could be used as construction material (e.g. aggregate).

In addition to vitrifying the ash, the PGVA process recovers the energy present in the ash by gasifying the organics into a synthesis gas (syngas). The energy released by the gasification of the organics provides some of the energy required for vitrification and, more importantly, the resulting syngas (mainly carbon monoxide and hydrogen) can be fed back to the main combustion unit for use as a fuel. For high carbon content ash from wood bark boilers and less efficient coal power plants, the PGVA provides the ability to recover more energy than what is required for operating the plasma arcs.

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