

Demonstration plasma gasification/vitrification system for effective hazardous waste treatment

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Abstract

Plasma gasification/vitrification is a technologically advanced and environmentally friendly method of disposing of waste, converting it to commercially usable by-products. This process is a drastic non-incineration thermal process, which uses extremely high temperatures in an oxygen-starved environment to completely decompose input waste material into very simple molecules. The intense and versatile heat generation capabilities of plasma technology enable a plasma gasification/vitrification facility to treat a large number of waste streams in a safe and reliable manner. The by-products of the process are a combustible gas and an inert slag. Plasma gasification consistently exhibits much lower environmental levels for both air emissions and slag leachate toxicity than other thermal technologies.

In the framework of a LIFE-Environment project, financed by Directorate General Environment and Viotia Prefecture in Greece, a pilot plasma gasification/vitrification system was designed, constructed and installed in Viotia Region in order to examine the efficiency of this innovative technology in treating industrial hazardous waste. The pilot plant, which was designed to treat up to 50 kg waste/h, has two main sections: (i) the furnace and its related equipment and (ii) the off-gas treatment system, including the secondary combustion chamber, quench and scrubber.

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1. Introduction

According to the European Environmental policy and strategy, hazardous waste constitutes one of the waste streams that should be dealt with special priority due to its potential negative impact to the public health and the environment.

With respect to industrial hazardous waste in Greece, the problems it creates refer not only to the quantities generated, but also to the fact that inappropriate methods are applied for its management. However, a relative progress has been achieved in the domain of hazardous waste during the last several years. The total quantity of hazardous waste for the

year 2000 was 287,000 tonnes. That is 15.6% lower than in 1988 (340,000 tonnes). Hazardous waste is generated by 19 main industrial sectors as follows: refineries, oil pumping, production of other oil products, waste oils recovery, fertilizers, metal industries such as steel, aluminum, ferrous-nickel, cement and manganese, metal surface treatment, production of batteries and accumulators, recycling of Pb accumulators, tanneries, dyeing industries, chemical industries, synthetic wood industries, synthetic fibers and pesticides production. Twenty industrial units that fall into the sectors of chemical industries, fertilizers, pesticides and oil refineries are responsible for the 90% of the hazardous waste generated. A big number of small and medium sized units such as tanneries, metal plating and dyeing units generate 10% of the total hazardous waste. In addition, hazardous waste is

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generated at shipyards (8000 tonnes for the year 2000). The reduction of the quantities generated between 1988 and 2000 is attributed to the fact that many small and medium sized units have closed and also to the fact that some of the large industries have either applied cleaner or recycling/recovering technologies for the management of the generated waste [1].

In the Viotia Region, which is sited western of Athens, in close distance from Attica Region, there is an extensive industrial activity (more than 300 industrial units). These units are responsible for the generation of approximately 18,000 tonnes of hazardous industrial waste per year. The main industrial activities include: textile dyeing and finishing, paints and coating manufacturing, production and treatment of metals, manufacturing of plastic products, production of medicines, agrochemicals, organic and inorganic chemicals [2].

The majority of industries store the generated hazardous waste in private places. A small number of them transport waste to other EU countries (e.g. Finland, Germany, France) in order to be treated or for final disposal. It must be mentioned that the transportation cost is extremely high for small quantities of hazardous waste and, since most of the units located in the area of concern are of small or medium size, this solution is not economically feasible. In addition, the mini-mization of transboundary transportation constitutes a major national environmental policy all around Europe [1].

Landfilling and incineration can also entail dangers for human health and the environment as a whole. The main potential threat arising from sanitary landfill is due to leachates that can pollute groundwater, while a huge discussion about the role of incineration has begun all around Europe because of the existence of toxic substances in the flue gases.

As a result, the development of a demonstration unit for the treatment of hazardous waste generated in Viotia Region was a project of particular interest.

2. The applied plasma technology

Plasma chemistry is in the forefront of modern environmental analyses. The unique characteristics of plasmas should result in much broader applications in environmental mitigation and are increasingly becoming valuable environmental tools in future research of environmental areas. Existing plasma technologies currently applied in the steel industry may be adapted to solve environmental problems ranging from analyzing solid surfaces in glow discharges to analysis of wastewater in ICPs, utilizing microwave plasma cleaning in the semiconductor industry and applying onsite aerosol measurements [3]. Some commercial applications include metal and ceramic powder production, smelting and metal cutting and welding. This paper focuses on plasma technology as an innovative thermal waste treatment technique, which is very effective and presents great prospects especially in hazardous waste management.

Plasma refers to every gas of which at least a percentage of its atoms or molecules is partially or totally ionized. In a plasma state of matter, the free electrons occur at reasonably high concentrations and the charges of electrons are balanced by positive ions. As a result, plasma is quasi-neutral. It is generated from electric discharges, e.g. from the passage of current (continuous, alternate or high frequency) through the gas and from the use of the dissipation of resistive energy in order to make the gas sufficiently hot. Plasma is characterized as the fourth state of matter and differs from the ideal gases, because it is characterized by 'collective phenomena'. 'Collective phenomena' originate from the wide range of Coulomb forces. As a result, the charged particles do not interact only with neighboring particles through collisions, but they also bear the influence of an average electromagnetic field, which is generated by the rest charges. In a large number of phenomena, collisions do not play important role, as 'collective phenomena' take place much faster than the characteristic collision time [4].

Thermal plasmas have the potential to play an important role in a variety of chemical processes. They are characterized by high electron density and low electron energy. Compared to most gases even at elevated temperatures and pressures, the chemical reactivity and quenching rates that are characteristic of these plasmas is far greater. Plasma technology is very drastic due to the presence of highly reactive atomic and ionic species and the achievement of higher temperatures in comparison with other thermal methods. In fact, the extremely high temperatures (several thousands degrees in Celsius scale) occur only in the core of the plasma, while the temperature decreases substantially in the marginal zones.

Waste treatment applications exploit the plasma's ability to rapidly initiate a variety of chemical reactions including decomposition, evaporation, pyrolysis and oxidation. Inorganic materials can be heated to high temperatures where they melt and are transformed into molten slag and metal phases.

A typical processing unit includes a feeding system, a gasification/vitrification furnace, one or more plasma torches with their associated power supplies and controls, pollution abatement and monitoring hardware, plus assorted gas and slag handling equipment. The entire system is controlled from a central operator's console [5].

Waste is fed to the electric arc furnace from a feed hopper. In the plasma gasification/vitrification process, shown in Fig. 1, waste is fed into a plasma arc furnace from the top and falls onto a layer of molten slag. A layer of untreated waste is maintained on top of the molten slag, where the gasification reactions occur. Metered amounts of air and steam are introduced at that level. This layer of untreated waste, called a "cold top", also acts as a filter to heavy metals and reduces entrainment of waste from the furnace.

Gasification reactions are complex reactions, still under investigation, consisting of a combination of gas–solid and gas phase reactions, as demonstrated in Tables 1 and 2. The product gases, mainly consisted of synthesis gas (mixture of CO and H₂) are fed to the secondary combustion chamber,

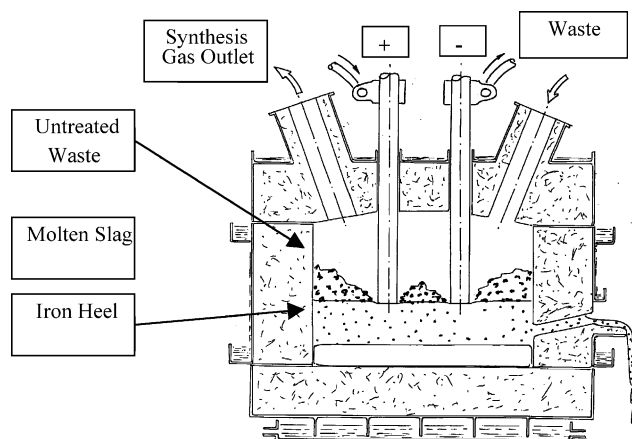


Fig. 1. Plasma gasification/vitrification process.

Table 1
Solid gas reactions

Reaction	Heat of reaction (kJ/kmol)	Reaction name
$C + O_2 \rightarrow CO_2$	+393,790	Combustion
$C + 2H_2 \rightarrow CH_4$	+74,900	Hydrogasification
$C + H_2O \rightarrow CO + H_2$	-177,440	Steam-carbon
$C + CO_2 \rightarrow 2CO$	-172,580	Boudouard

where they are combusted with air to form carbon dioxide and water. The combustion gases leaving the secondary combustion chamber are cooled down rapidly in the quench vessel by atomized water. The combustion gases are passed through a packed bed scrubber where the acid components of gas (such as HCl and SO₂) are neutralized by a caustic soda solution. Part of the water being re-circulated in the scrubber is sent to drain after filtration through a bag filter. The gases through the whole system are pulled through an induced draft blower, which maintains all equipment under a negative pressure.

In the meantime, once gasification is completed, the inorganic portion of waste melts by contact with a pool of molten slag. The layer of molten slag is maintained in the liquid state by a current flowing through two graphite electrodes. Electrodes are positioned slightly above the surface of the bath, creating two electric arcs. The current also flows through the molten bath. Thus, both resistive and arc mode heating are used. Below the surface of the slag, a layer of molten iron (or iron heel) is maintained, improving the flow of the current through the slag [6].

The following figure (Fig. 2) illustrates a brief schematic description of the gasification/vitrification process.

Table 2
Gas phase reactions

Reaction	Heat of reaction (kJ/kmol)	Reaction name
$CO + H_2O \rightarrow H_2 + CO_2$	+2,853	Water-gas shift
$CO + 3H_2 \rightarrow CH_4 + H_2O$	+250,340	Methanation

3. Plasma unit

The plasma gasification technology has been applied by the National Technical University of Athens, which set the relevant specifications for the development of the relevant pilot unit, trying to explore its potential in waste management. The developed plasma gasification/vitrification unit consisted of the following parts.

3.1. Waste feed systems

The primary waste feeding system consists of a hopper intended for feed of solid material having maximum moisture content of 50% and a maximum particle size of 2.5 cm. The screw conveyor solid feeder has a maximum capacity of about 85 kg/h of waste and the feeding capacity varies depending on the feed waste bulk density. The feed rate is adjustable by varying the speed of the screw conveyor. Waste is manually loaded into the hopper connected to the screw conveyor. The feed rate is continuous and very steady, compared to a hydraulic feeder.

3.2. Plasma torch and controls

It converts electrical to thermal energy and constitutes the heart of the treatment of hazardous waste where the plasma is generated and checked from other auxiliary systems. Two graphite electrodes are used to supply an electrical arc to the furnace. The current flows from the anode (+) to the molten bath and from the bath to the cathode (-). The cathode is grounded at zero (0) potential.

Graphite electrodes with male/female threads are used. The electrode dimensions were 7.6 cm in diameter and 106.7 in length. Electrodes are installed with the female end down, in order to avoid dust accumulation in the threads. Two electrodes were screwed together on each side (anode and cathode) and are mounted on flexible joints, which allow them to be moved over the slag pool and improve mixing. The mechanism also permits the electrodes' extension into the furnace to be adjusted during operation.

The dc power supply for the electrodes has a maximum power output of 200 kW (Plasma arc power supply, input: 600 VAC-3 ϕ -60 Hz, 3 \times 200 A fuses).

3.3. Gasification/vitrification furnace

The furnace is comprised of a crucible, with approximately 130 l capacity. The internal dimensions of the crucible are 0.44 m wide by 0.87 m long. A 3.8 cm layer of ram lined the outer steel shell. It also includes a start-up natural gas burner for preheating and idle operation, a port for gasification air injection, a water-cooling mechanism for the graphite electrodes, an external surface water-cooling for the furnace walls and a tapping hole for periodical or continuous slag removal. During the operation of the plasma unit, the bottom part of the furnace contains the molten slag, while the upper

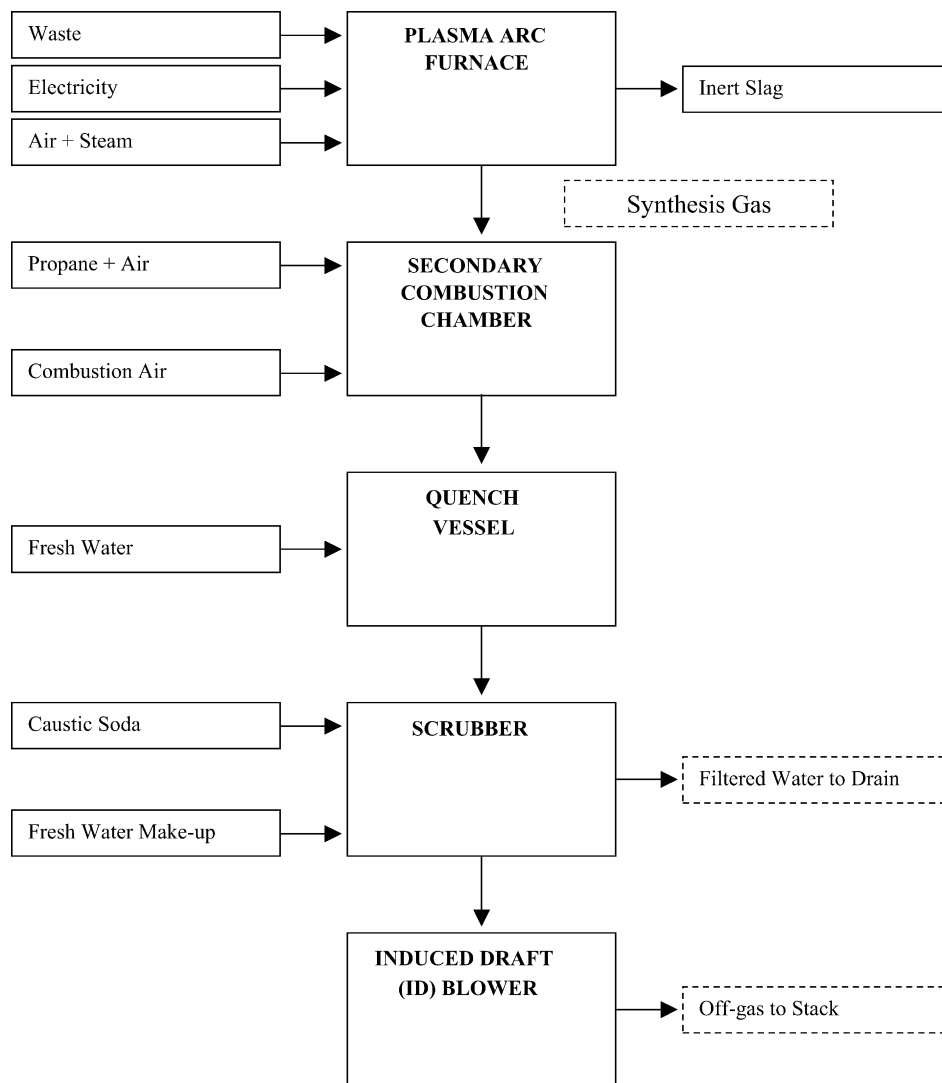


Fig. 2. Plasma gasification/vitrification of hazardous waste: process diagram.

section of it contains the process gases and is lined with a suitable high-temperature refractory. The required gasification air fed to the furnace is supplied by a compressed air system. Adjusting the valves on the compressed air line can control the flow rate.

The slag could be tapped out periodically from the tap hole located on the front side of the crucible, close to the bottom of the furnace. The slag was either poured in a slag mold to form ingots (Fig. 3) or quenched in a water tank to produce granulated slag (Fig. 4).

The tapping hole was plugged with a carbon-based paste during the operation of the furnace. Two methods of tapping were investigated. First, the use of an oxygen lance, normally used for metal cutting, was investigated. The lance was efficient at drilling through slag, but it was inefficient at piercing the carbon-based paste used for plugging the tap hole. A second method was tried, a standard, heavy-duty impact drill was used to drill the tap hole paste. Then, a pointed steel rod was used to break the thin layer of frozen slag at the inside



Fig. 3. Slag ingot in pouring mold.



Fig. 4. Slag granules.

surface of the tap hole. This technique was found to be more effective at tapping the hole.

The slag tapping in the pilot facility was conducted periodically. A clean system requires the addition of around 100 kg of ash to reach the tapping hole. After this level is achieved, slag tapping could be performed every 50 kg of waste addition to the system (Fig. 5).

3.4. Hot cyclone

The hot cyclone was designed to remove dust in the synthesis gas. The hot cyclone is refractory-lined and equipped with a self-cleaning system using a pulsed nitrogen jet and operated from the central control room. The dust is collected at the bottom of the cyclone and should be removed during and/or after each test. The produced gases while entering the cyclone are put in circular movement and the centrifugal force makes particulate matter contained in the gases to be removed to a high degree.



Fig. 5. Tapping inert slag.

3.5. Secondary combustion chamber

The result of its operation is the oxidation of the components of the furnace gases. The secondary combustion chamber was designed to combust hydrogen (H_2) and carbon monoxide (CO) in the synthesis gas. In order to combust CO and H_2 into CO_2 and H_2O , air is added into the secondary combustion chamber. Propane burners are used to maintain the chamber temperature at $1100\text{ }^\circ\text{C}$. The operator can check local regulations to determine the required temperature in secondary combustion chamber. This temperature is required to fully combust CO and H_2 in a region where no hazardous by-products are created. In normal operation, the gas residence time in the secondary combustion chamber is about 2 s. The secondary combustion chamber is a refractory-lined vessel with exterior dimensions of 3.56 m high by 0.81 m in diameter. Interior dimensions are 3.00 m long and 0.48 m diameter. The refractory is comprised of a 2.54 cm layer of insulation and a 10.2 cm thick layer of high alumina working refractory. The outer shell is water-cooled with a double wall cooling system. A single blower provides the combustion air for the burners and the combustion air for the synthesis gas.

3.6. Water quench

It is located at the outlet of the secondary combustion chamber. Its role is to cool the combustion gases quickly to approximately $75\text{ }^\circ\text{C}$ so as to minimize any production of dioxins, furans or other organic compounds. The shock-like cooling avoids the formation of the aforementioned compounds from elementary molecules in the synthesis gas due to the de novo synthesis back reactions [7]. These reactions are known to occur in waste heat boilers where a slow cooling in the range from 400 to $250\text{ }^\circ\text{C}$ of flue gases with chlorine compounds, non combusted organic molecules and catalysts such as dust will result in dioxin formation. The quench vessel uses two atomizing nozzles to quench the gas from the secondary combustion chamber. These nozzles are capable of providing 2 l/min of flow. Regulating the amount of the quenching water can control the gas temperature exiting the vessel.

3.7. Venturi/damper

The Venturi/damper is located at the exit of the quench and its opening can be manually adjusted. The Venturi was designed to remove particulate from the gas stream. There are two water nozzles in the Venturi/damper, and water is injected during the tests to capture particulate in the water stream.

3.8. Scrubber

It removes water-soluble components of the off-gas including hydrochloric acid and most oxides of sulphur, prior to discharge. Since the synthesis gas may contain acid gases

(such as HCl or SO₂), a packed tower type wet scrubber uses caustic soda to neutralize the acid gas from the quench vessel. The pH of the scrubbing solution is controlled at 9.0. The scrubber liquor is re-circulated through a wet bag filter in order to remove suspended particles. The bag house is a cartridge unit having series of cylindrical filters that are cleaned periodically by an automatic sequence using pulses of compressed gas.

4. Results

The large number of the trial runs of the demonstration plasma gasification/vitrification unit showed that the prospective of the technology under investigation is significant for industrial hazardous waste treatment. During the testing period, a large number of waste streams generated by the industrial units located in Viotia Region were treated in the demonstration plasma unit.

For every test carried out, several measurements and analyses took place, including TCLP tests regarding the produced slag, determination of the polluting parameters of the small amount of the generated wastewater and determination of the qualitative and quantitative composition of the produced synthesis gas and the final air emissions (discussed in detail in coming publications). The results were then compared with the limits set by the European legislation framework. In general, it can be said that the environmental performance of this method using hazardous waste is far more satisfactory than other thermal treatment techniques.

The amount of electrical power required for the gasification of a certain amount of waste depends directly upon the chemical composition of the waste. Only as much oxygen is necessary is added for the transformation of all the carbon into the gas phase. The hydrogen is found in molecular form and in hydrogen chloride. The products of the gasification are not completely burned, but are cooled down and cleaned. The benefit arising from the gasification process is that the transformation, for instance, of halogens takes place in a reducing atmosphere ensuring a complete transformation into hydrogen halogenide—particularly hydrogen chloride. At temperatures less than 2000 K in a reducing atmosphere both hydrogen and chlorine exist almost only in the form of hydrogen chloride. Above 2500 K atomic hydrogen and chlorine as well as molecular hydrogen are present in the equilibrium.

5. Conclusions and discussion

The consistently low environmental emission characteristics exhibited by plasma gasification indicate that it can be used as a waste treatment as alternative to other technologies, with substantial environmental emission level improvements for both air emissions and slag leachate toxicity.

Actinides and oxidized heavy metals migrate to the slag phase. Following rapid final cooling and solidification of this

material results in vitrified (non-crystalline) fine-grained, by-product consisting predominately of quartz and feldspar, with minute quantities of biotite and amphibole. Physically, it is similar to naturally occurring obsidian and extrusive, igneous rock, which has very high structural integrity.

Generally, the properties of the slag depend on the waste input and the operation mode. If the waste does not contain silica, some suitable slag formers (e.g. glass or silica sand) may be used in order to adjust the slag properties. The effect of silica is that it affects the acidity of the slag and may, thus, result in a more glassy and non-leaching slag. Experience shows that if the slag turns alkaline, the leaching resistance will suffer [8]. The right properties of the produced slag make it suitable material for further uses, such as construction material.

The product gas contains substantial sensible heat, which is amenable for heat recovery to improve the efficiency of the electricity generation subsystem. A typical composition of this gas is 24–43% (v/v) H₂, 25–44% (v/v) CO, 10–26% (v/v) CO₂ and N₂, depending mainly on the waste input composition. In fact, the purified synthesis gas can have multiple end uses in a large-scale plant, such as hydrocarbon production (petrol), hydrogen (fuel cells, gas engines), ammonia production (fertilizers), methanol manufacture (chemical industry) and electricity. This is of vital importance, since the use of electric energy as energetic force can substantially raise the operating cost of the plasma unit.

In addition, the torch water-cooling and scrubber water subsystems also contain sensible heat. This means that this technology allows the convention of a high percentage of the waste into usable products.

In conclusion, a large number of good points can be achieved by the implementation of the gasification/vitrification process for waste treatment after the optimization of the operating parameters for every different waste stream [9,10].

More specifically:

- Plasma technology is characterized by elevated energy density that allows the treatment of the same quantity of waste in plants of smaller dimensions, in comparison with plants of other conventional thermal methods.
- The elevated heating speed allows reaching the regime conditions quickly. The energy flux is also high.
- The elevated temperature allows the treatment of work in only a process, eliminating the need of separate stages.
- The reaction velocities are very high and, therefore, a high reduction in the contact times is obtained.
- The use of electric energy, as energy source, allows the operation of the plasma unit in oxidising, reducing or inert atmosphere in function of the waste type. Furthermore, the use of electric energy reduces the need of gaseous flow and offers a better control on the chemical processes including the possibility of generation of marketable co-products.
- Traditional combustion processes demand high air quantity. Regarding plasma technology, the reduction of the air

needed involves a notable reduction of the volumes of the exhausted fumes.

- These plants are typically 30–50% lower in investment costs than incinerators of the same capacity.

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