Thermal Plasma: A Technology for Efficient Treatment of Industrial and Wastewater Sludge

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Abstract: Thermal plasma treatment technique is widely used in the treatment of domestic and industrial waste. The technique has the potential of converting organic portion of waste into synthetic gas that has energy value, while the inorganic portion is cemented into a vitreous slag which is stable to leaching of harmful heavy metals. This paper review looked at the application of the treatment technique to industrial and wastewater sludge. In the first part of the paper, description of thermal plasma technology; classification, characteristics and comparison of different types of plasma, is presented. The second part of the paper reviewed thermal plasma treatment processes, equipment specifications and process variables for different types of sludges (electroplating sludge, stormwater sludge, and tannery sewage sludge, a mixture of fly ash and wastewater sludge, paper sludge and ship oil sludge). The last part of the report compared the product analysis from different studies conducted at laboratory, pilot and industrial scale. In the light of this literature view, thermal plasma technology is considered as a highly attractive means of treating industrial and wastewater sludge. Synthetic gas obtained from the treatment processes meet the stringent environmental regulations and also can serves as source of energy for steam turbine and electric energy generations. Heavy metals in sludge are captured in a solid matrix of slag with none or insignificant leaching capabilities. The slag can be used for building and road construction purposes

Keywords - *Heavy metals, syngas, thermal plasma, vitreous slag, wastewater sludge*

I. Introduction

Thermal plasma technology has become a prominent waste treatment technique for a wide variety of waste because of the increasing problems associated with the traditional waste disposal methods. The new technology is credited with the advantage of producing less harmful by-products which can be used in building and road construction. Plasma treatment of industrial and wastewater sludge is gaining wider acceptance due to its ability to reduce the volume of sludge by about 90% and chemically detoxify the waste. The plasma gasification of the organic portion of sludge has attracted interest as a source of energy and spawned process developments for treatment of sludges from different sources. There are quite a number of plasma treatment approaches for different sludge types with variant characteristics and varying targets. This paper provide a general review on the application of the different equipment setups and specifications, treatment conditions and products characteristic derivable from different sludge types.

II. Plasma Technology

Plasma constitutes approximately 99% matter of the entire universe [13]. It is an electrified gas with a chemically reactive species such as electrons, ions, and neutrals [14]. Lightening is a natural occurring plasma whereas fluorescent light is a manmade plasma. A comparison of plasma regime with the other three state of mater is shown in Table 1. Plasma is distinguished into high temperature (50 000 – 10^{6} K) and low temperature ($\leq 50 000$ K) plasma, the low temperature plasma is further subdivided into thermal and non-thermal plasma. In high temperature (or high energy or fusion) plasma the species (i.e. electrons, ions and neutrals) are in a thermodynamic equilibrium. A segregation on the types of plasma and their examples is shown in Fig. 1.

Thermal plasmas is characterized by quasi-equilibrium between electrons, ions and neutrals. The temperature of activities is the same between all the three particles [15]. Laboratory or industrial generation of plasma is done with the aid of plasma torches (plasmatrons) or with microwave devices [16]. The plasma torches and the microwave devices produce plasma with high heat flux that are commonly utilized in material processing and waste treatment. Thermal plasma gasify organic waste to valuable fuel gas (synthetic gas), whereas inorganic waste is vitrify into ingot and slag [17-19]

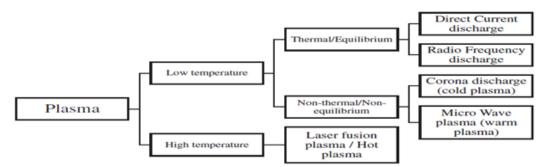


Fig. 1: Types of plasma and their examples [10]

Table 1: Comparison between	en plasma regimes and the other three states of matter
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Properties	Plasma	Gas	Liquid	Solid	
Mass, volume,	Stable mass, no	Stable mass, no definite	Stable mass and volume,	Stable mass, volume,	
density and shape	definite shape volume,	volume, density and	no definite density and	density and shape	
	density	shape	shape		
Relative position	Relatively far away	Relatively far away from	Free lowing, loosely	Fairly stationary,	
of particles	from each other	each other	packed	tightly packed	
Particle	Collective behavior	Two-particle collision,	Slides over each other	Vibrates in place	
interaction			and few collisions		
Independently	Different particles	Particles behave in the	Atoms/molecules behave	Atoms/molecules	
acting species	behave differently	same way in neutral gas	the same way	behave the same way	
Velocity	Often non-Maxwellian	Maxwellian vel.	Eddy and laminar	Vibrate about a fixed	
distribution		distribution	velocities	position	
Energy	Extremely high	High	Medium	low	
Electrical	Usually very high	Conductivity is very low	Conductivity is low	Very high in solid	
Conductivity	(infinite)			conductors	

In non-thermal plasma, the particles are not in thermodynamic equilibrium with each other; both ions and the neutrals are near room temperature whereas the electrons are at much higher temperature. This type of plasma is characterized with a strong thermodynamic non-equilibrium state, high selectivity, low gas temperature and presence of reactive chemical species. Non-thermal plasma is used in the treatment of polymers and bio-tissues and other heat sensitive materials [14]. Properties comparison between high-temperature plasma, low-temperature thermal plasma and low-temperature non-thermal plasma is shown in Table 2.

	Table 2. Characteristic of anterent types of plasma							
Properties	High temperature plasma	Thermal plasma	Non-thermal plasma					
Plasma state	$T_e \approx T_i \approx T_g$	$T_e \approx T_i \approx T_g$	$T_e \approx T_i \approx T_g$					
Plasma temperature (T _P)	$T_p = 10^6 - 10^8 K$	$T_P \le 2 \times 10^4 K$	$T_p = 300 - 10^3 K$					
Electron density (n _e)	$n_e \geq 10^{20} m^{-3}$	$n_e \ge 10^{20} m^{-3}$	$n_e \approx 10^{10} m^{-3}$					
Plasma pressure	Over a wide range	≈101 kPa	$\leq 10 \text{ kPa}$					
Examples [20]	Laser fusion plasma	Arc plasma, RF inductively couple discharge	Glow, corona,					
Typical applications [21]	Energy, military	Solid waste treatment, ceramic processing, cutting and welding	Air pollution control and polymer coating					

 Table 2: Characteristic of different types of plasma

 T_e = electron temperature, T_i = ion temperature, T_n = neutral temperature, T_P = plasma temperature, n_e = electron density and T_g = gas temperature

III. Generation of Artificial Plasma

Manmade plasmas are generated by the application of electric and/or magnetic fields through a neutral gas. The plasma generated can be categorized based on the following [22]:

- Power source used whether it is AC, DC, RF or microwave
- Operating pressure, whether it is vacuum, moderate pressure or atmospheric pressure
- Degree of ionization of the plasma, whether fully, partially or weakly ionized
- Particles temperature relation with that of plasma, i.e. thermal or non-thermal plasma
- Configuration of electrodes in the plasma generator, i.e. transferred or non-transferred
- Magnetization of particles, whether magnetized, partially magnetized or non-magnetized

Electric energy (AC or DC) is required to generate and sustain plasma. An electric field is created when electric potential is applied between two electrodes (a cathode and an anode), the gas molecules in the

inter-electrodes space are dissociated. An increase in the applied voltage will pull the nucleus and the electrons in the opposite direction until the gas reached its dielectric limit. Further increase in the applied voltage will result to electrical breakdown, where the gas is transform to a conductor as a result of molecular ionization. This is the Townsend Avalanche ionization shown in Fig. 2. The equipment used for plasma generation is called plasma torch. There are basically two types of plasma torches; the transferred arc torch and the non-transferred arc torch.

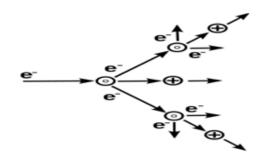


Fig. 2: Townsend Avalanche ionization [3]. 'e = Electrons, 'o' = neutral atoms, and '+' = cations

3.1 Transfer Arc Torch

In the transferred arc torch, the cathode is inside the torch while the anode is outside the torch [23]. The anode is usually the material to be treated, in case of a conducting material, or a conducting container that holds the material to be treated, if the material is a non-conductor. This electrodes arrangement allows the plasma to be generated outside the water-cooled torch thereby generating plasma with high heating efficiency [24]. Transfer arc torch is characterized with relatively large electrodes separation that ranges from a few centimeters up to a meter [25]. The cathode is either a consumable material, like graphite, or a water-cooled metal, while the anode is usually a metal with high thermal conductivity like copper or silver [26].

3.2 Non-transfer Arc Torch

The two electrodes in non-transferred arc torch are located within the water-cooled body of the torch [25]. High density and high temperature arc is generated in between the electrodes. The pressure of the flowing gas stream pushes the plasma out of the torch through the nozzle creating a plasma jet [16]. This type of torch has a lower power consumption and a lower electrode degradation [26], it produces less noise and less vibration resulting into more stable operation, it has low heating efficiency of between 50 and 75%. A schematic diagram of transferred arc and non-transferred arc torches are shown in Fig. 3, whereas a characteristic and performance comparison between the two torches is presented in Table 3.

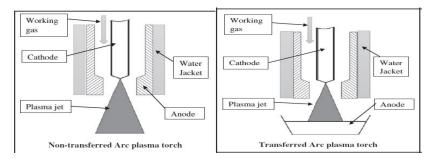
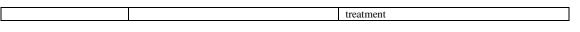


Fig. 3: Schematic diagrams of thermal plasma torches [10]

Table 3. C	Table 5. Comparison between transferred are toren and non-transferred are toren						
Property	Non-transferred torch	Transferred torch					
Location of the arc	Formed between the negative electrode and	Formed between negative electrode and work					
	water-cooled constricting nozzle	peace (positive electrode)					
Projection mechanism	Projected out of the nozzle as flame	Extended from electrode to work peace					
Relation with work piece	Work piece is independent of electric circuit	Work piece form part of electric circuit					
Electrode separation	Ranges from few millimeters up to 5cm	Ranges from few centimeter up to a meter					
Plasma peak temperature	Ranges between 10,000 to 14,000K	Ranges between 12,000 to 20,000K					
Energy density	Low	High					
Heating efficiency	Between 50 & 75%	Over 90%					
Application	Used in welding and ceramic metal plating	Used in welding, metal cutting and waste					

 Table 3: Comparison between transferred arc torch and non-transferred arc torch

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IV. Thermal Plasma Treatment of Sludge

Many scientific studies concerning high temperature plasma treatment of sludge were reported in the literature in the last few decades [10, 27-30]. The fundamental goal of the thermal plasma pyrolysis, gasification and vitrification processes is to render the waste sludge harmless and reduce its volume to a minimal size that can be handle efficiently and effectively. In the pyrolysis process, the organic matter is gasified into products with high fuel value while the inorganics and metal components are vitrified into stable slag and ingot respectively. A schematic of end products from thermal plasma waste process is shown in Fig. 4.

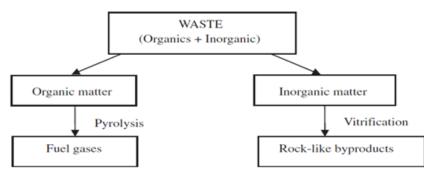


Fig. 4: Schematic showing end products in the plasma process [12]

4.1 Plasma Gasification of Sludge

Thermal plasma gasification of sludge has been demonstrated in recent studies as one of the most effective and environmentally friendly methods for sludge treatment and energy generation [31, 32]. Sludge gasification is a combination of complex gas—solid and gas phase reactions involving organic compounds and oxygen as shown in the reactions 1 through 6. The oxygen is supplied by partial molecular dissociation of water in sludge and also from air supply to the reaction chamber [6, 33]. The basic reactions are:-

Combustion of carbon: $C + O_2 \leftrightarrow CO_2$ (exothermic)
Water gas reaction: $C + H_2 0 \leftrightarrow C0 + H_2$ (endothermic)2
Boudouard reaction: $C + CO_2 \leftrightarrow 2CO$ (endothermic)3
Water gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$ (exothermic)4
Methane gasification: $CH_4 + H_2 0 \leftrightarrow CO + 3H_2$ (endothermic)5
Molecular dissociation of water: $H_2 0 \leftrightarrow H_2 + \frac{1}{2}O_2$ (endothermic)6

4.2 Plasma Vitrification of Sludge

Thermal plasma provides an efficient means of vitrifying sludge and confined heavy metals within a vitreous slag that is stable to leaching. The process also reduced the volume of sludge to about 10% of its original volume. A study was carried out by Kim and Park [2] to evaluate the reduction in volume and detoxification of mixture of wastewater sludge and fly ash using thermal plasma process. Result of the leaching test conducted revealed that leaching of heavy metals from vitrified slag is well below the regulatory limits. A model developed by Leal-Quiros [3] relating mass of slag (M_L) produce from plasma vitrification to the plasma torch energy (P) is given in equation 7

$$M_L(kg) = 0.35P(kWh)$$

V. Overview of Approaches for Plasma Treatment of Sludges

Thermal plasma systems have been developed and utilized in the treatment of electroplating sludge, stormwater sludge, tannery sewage sludge and wastewater sludge. Design specifications and conversion achievable are unique due to differences in the characteristics of sludge as well as the variety sludge sources. Subsequent sections presents a description of the process equipment employed in documented studies on thermal plasma treatment of sludge.

5.1 Electroplating Sludge

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Treatment of industrial sludge using thermal plasma energy can be dated back to late 1990s, when a plasma group at Instituto de Pesquisas Tecnologicas de Sao Paulo (IPT) patented a process based on the use of transferred arc torch to recover metals from electroplating sludge [7, 34]. An earlier laboratory investigation prompted the team to develop the pilot-scale reactor described by Szente, et al. [7]. The reactor has a capacity of 150kg/h of dried sludge, and the inside wall is lined with chrome-magnesia bricks to prevent chemical attack. The transferred arc with a maximum power output of 300 kW used argon at flowrate of 20 L/min as plasma gas. With the application of 300 V and input current of 500 A the team was able to achieve a temperature of 1700 °C. A schematic diagram of the plasma process is shown in Fig. 5.

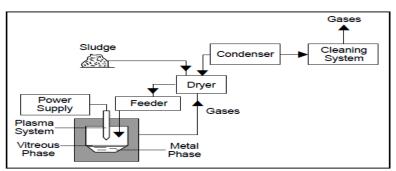


Fig. 5: Schematic diagram of plasma process for treating electroplating sludge [7]

Treatment of electroplating sludge in thermal plasma arc was also investigated by Ramachandran and Kikukawa [1] and [35] and Cubas, et al. [36]. Both the Japanese and Brazilian research teams used a batch setup to study the effect of both transferred and non-transferred arc plasma on elimination efficiency of heavy metals from sludge and the conversion of the residual to slag. The Japanese setup, shown in Fig. 6, consist of a graphite crucible for holding the sample placed inside a reaction chamber. A power input of 7 to 16 kW and different plasma gas regime (Ar, H_2 , N_2 and mixture of two at a time), were used.

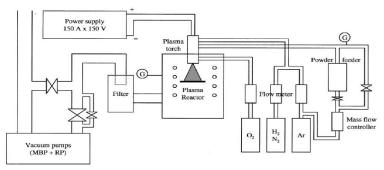


Fig. 6: Block diagram for Thermal plasma treatment of electroplating sludge [1]

Two separate setups where used by the Brazilian team for the study in transferred and non-transferred mode respectively. The two setups obtained from Cubas, et al. [36] are shown in Fig. 7. A crucible furnace (3 cm diameter and 3 cm depth) sculpted in a brick of Magnesite ($20 \text{ cm} \times 10 \text{ cm}$) was used for the non-transferred mode. The torch comprised a copper tube (the cathode) refrigerated in water and a tungsten electrode (the anode) in the center. In the case of transferred arc plasma the reactor is constructed with a tungsten cathode and the crucible furnace serves as the anode. A power supply of 180ADC and argon flowrate of 25 L/min were supplied to generate the plasma.

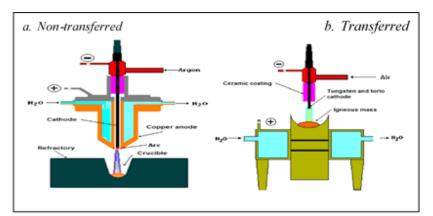


Figure 7: Thermal plasma reactors employed by Cubas et al. (2014)

5.2 Stormwater Sludge

A typical plasma reactor system for treatment of stormwater sludge as described by Chang, et al. [5] and Li, et al. [37], [11] and [9] consists of a plasma torch, a crucible placed inside a reaction chamber, a DC power supply, an argon gas supply, a gas supply and a product gas analyzer. Chang, et al. [5] used alumina crucible (7.6cm ID and 5.1cm depth) placed 5cm below a non-transferred plasma torch to investigate the effect of residence time on the treatment efficiency of stormwater detention pond sludge. A power of 1.5 kW and argon flowrate of 17.5 L/min were supplied to treat 20 -30g of the dried sludge for a period of 60, 90 and 120min respectively. The experimental setup is shown in Fig. 8.

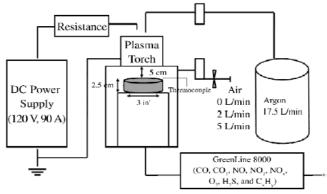


Fig. 8: experimental setup for the treatment of stormwater detention pond sludge [5]

A collaboration research team from Japan and Canada used a similar setup employed by Chang, et al. [5] to studied a number of variables and effects on the treatment of stormwater sludge. In one of their studies, a detoxification characteristics of wet stormwater sludge was investigated. In another experiment, a two-component integrated system was used to treat and detoxify stormwater sludge. The two systems are the pulsed arc electrohydraulic discharge (PAED) system used for aqueous phase treatment and the thermal plasma decontamination system used for solid-phase treatment. A performance study comparing non-transferred arc plasma and transferred arc plasma was also carried out by the same research group. Experimental setup used in the three separate investigations are shown in Fig 9 and 10.

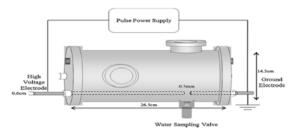


Fig. 9: Schematic of pulsed arc electrohydraulic (PAED) treatment for aqueous phase of sludge water [11]

5.3 Tannery Sewage Sludge

Few investigations on the application of thermal plasma in the treatment of tannery sewage sludge were reported by Polish research groups [38-40]. A research team in the Institute of Environmental Engineering, Czestochowa University of Technology, Poland did an evaluation study on the effect of additives, such as waste molding sands and dolomite flotation waste, on heavy metal immobilization during plasma vitrification of tannery sewage sludge. A 350 cm³ capacity graphite pot placed in furnace was used as the plasma reactor. 150 cm³ of substrate was treated for 10 min using argon at 20 dm³/min as plasma gas.

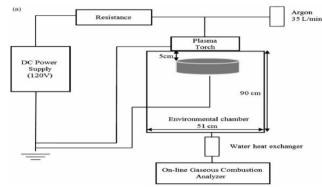


Fig. 10: Schematic of thermal plasma treatment for solid phases of sludge water [9]

The research group at the Institute of Environmental Engineering carried out another study to determine the mixing ratio of tannery sewage sludge and materials of waste character that will produce a vitrified product with the lowest possible heavy metal leaching levels and highest hardness rating. Eight different formulation, as shown in Table 4, where vitrified in the 350 cm³ capacity graphite furnace used in their earlier investigation. The treatment time was 10 min, and argon at 20 dm³/min was used to generate the plasma.

Another Polish research team at the Lodz University of Technology carried out a study on the mixing ratio of hazardous waste, fly ash and chromium-rich sludge, on the chemical stability of vitreous slag obtained from thermal plasma vitrification [39]. A Little Jet-arc system was developed and used by the research team. The system consist of a 20 kW arc furnace placed inside a stainless steel reaction chamber connected to a vacuum pump. The arc furnace is a graphite crucible, which holds the sewage sludge, and is placed below a graphite electrode. A power of 1.4 kJ was supplied for 5 min. An optical temperature recorder Minolta/Land-Cyclops 152 and off-gas analyzer Madur GA-40 T were used for measurement.

Formulation	Flotation sewage	Precipitation	Waste molding	Floatation waste from	Floatation waste
	sludge (v/v %)	sewage sludge (v/v %)	sand (v/v %)	copper industry (v/v %)	from lead-zinc industry (v/v %)
А	50	0	40	10	0
В	50	0	40	0	10
С	50	0	30	0	20
D	35	0	40	0	25
Е	0	70	25	5	0
F	0	70	25	0	5
G	0	50	45	0	5
Н	0	50	40	0	10

Table 4: Formulations used in the plasma vitrification [40]

5.4 Wastewater Sludge and Fly-ash

A stabilization of leachable chromium contain in incineration fly ash was carried out in a thermal plasma melting chamber [4]. The 125 kg/h capacity melting chamber was built at An-Nan campus of the National Cheng Kung University, Taiwan. Two torches worked alternatively to provide a high temperature regime at about 1,773 K and ensure continuous operation. A diagram of the plasma melting chamber used by the Taiwan research team is shown in Fig. 11.

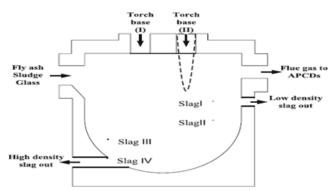


Fig. 11: Diagram of plasma melting chamber [4]

Another study on vitrification of wastewater sludge/fly ash was conducted by Kim and Park [2]. In the study, the authors evaluated the volume reduction and detoxification efficiency of fly ash and wastewater sludge in a thermal plasma reactor. The equipment setup employed by the group consists of a non-transferred water-cooled plasma torch, a water-cooled stainless-steel reaction chamber, and an off-gas system. The torch has a tungsten cathode and a copper anode. A cupper crucible placed 3cm below the plasma torch hold the sample to be treated. An output power of 6 - 9 kW was supplied to vitrified the sludge in 10 - 15 minutes residence time. The experimental setup is shown in Fig. 12.

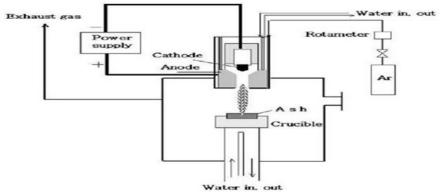


Fig. 12: Schematic diagram of the experimental setup employed by Kim and Park [2]

Sewage sludge from wastewater treatment plant was also treated in thermal plasma reactor by Mountouris, et al. [31]. The authors considered sewage sludge from the main wastewater treatment plant of Athens at Psittalia Island. The Psittalia treatment unit treat municipal wastewater mixed with industrial wastes, to produce about 250 ton per day of sludge. The research team used double transferred arc with two graphite electrodes as cathodes and a conducting receiver as the anode. The sludge and subsequently the slag was contained in the conducting receiver in the furnace bottom. Air was used as the plasma gas.

5.5 Paper Sludge

A feasibility and operational performance study of thermal plasma treatment of paper sludge and wood waste blend was done by Shie, et al. [8]. The study was conducted in a 10 kW plasma torch pilot-scale reactor to investigate the effects of batch feeding on product yield, gas composition and treatment performance. The pilot scale apparatus, shown in Fig. 13, consist of a crucible of one-liter capacity placed directly under a plasma torch in a reaction chamber. The reactor was insulated with a double layer refractory with inner and outer layers of 5 and 10 cm thick. A power of 2 - 6 kW and 10 L/min nitrogen gas were respectively supplied from power chopper and nitrogen gas cylinder to generate the arc. Sample were introduced in to the reactor through a primary sample feeding system consists of a closed cylinder hopper with upper and lower covers. The hopper has a maximum size of 45 mm diameter and 55 mm length.

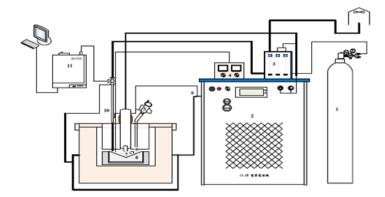


Fig. 13: Schematic diagram of plasma reactor system for treatment of paper sludge [8]. (1)Nitrogen cylinder, (2) power supply chopper & cooling system, (3) gas flowrate control (4) thermos-detector (5) sample input apparatus (6) sample (7) torch plasma & reactor (8) crucible (9) circulating water pipe (10) outlet line (11) gas detector & analytical instruments

5.6 Ship Oil Sludge

A plasma system, Plasma Arc Waste Destruction system (PAWDS), was developed under the support of the US Navy to gasify solid waste on board ships. The PAWDS was modified to treat sludge oil waste from ship's hull [6]. A PAWDS prototype used as a demonstration unit consists of three basic sub-systems; waste preparation, thermal destruction and off-gas treatment. As shown in a 3-D layout drawing in Fig. 14a, a plasma torch with two electrodes (a cathode and an anode) is used to generate plasma arc. Air is used as the plasma gas. Pre-heated sludge oil is introduced directly into the central element of PAWDS, the patented plasma-fired eductor shown in Fig. 14b

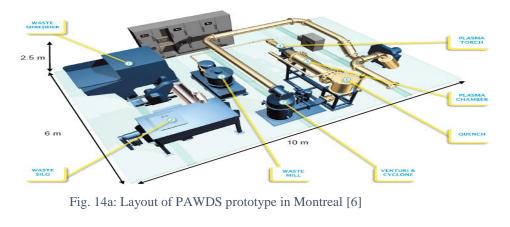




Fig. 14b: Schematic of Plasma-Fired Eductor [6]

5.7 Moist Paste from Spent Batteries

Inertization of moist paste from spent batteries in thermal arc plasma is consider under this review owing to its peculiarity. The moist paste was removed manually from spent batteries and pyrolyzed in a thermal plasma furnace (Cubas et al., 2015). The furnace is comprised of a graphite cathode with a central opening for plasma gas entrance and a graphite sheet serving as the anode and sample support. The anode was positioned 4 cm below the graphite cathode both located within a furnace as shown in Fig. 15a and b. Argon at a flowrate of 5 L/min was used as a plasma gas and also as coolant for the cathode. A tungsten-inert-gas plasma-welding

generator was used to supply a continuous current of 200A, a voltage of 12 V, and an equivalent power of 2.4kW for 5 minutes of treatment.

A summary of the equipment and their specifications used in previous investigations on the application of thermal plasma technology in the treatment of industrial and wastewater sludges is shown in Table 5 while operating conditions used are summarized in Table 6

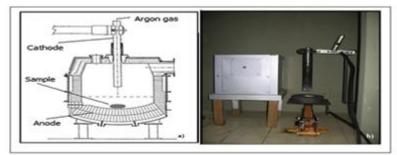


Figure 15: Thermal plasma reactor for sludge treatment; (a) schematic diagram and (b) photo showing the reaction chamber and the torch (Cubas et al., 2015)

Table 5: A review of equipment specification for previous study on thermal plasma treatment of sludge	Table 5: A review of equipment	t specification for p	previous study on	thermal plasma	treatment of sludge
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Type of sludge	Torch rating (kW)	Torch type	Plant scale	Reactor type	Reactor capacity	Operational mode	Reference
Sewage sludge	NA	Two transferred torches	Industrial	An integrated reactor	250 T/day	Continuous	[31]
Ship oil sludge	NA	Plasma eductor	Industrial	PAWDS	200 L/hour	Continuous	[6]
Paper sludge	10	Non-transferred	Pilot scale	Crucible	1 liter	Batch	[8]
Stormwater sludge	10	Non-transferred	Laboratory scale	Alumina crucible	7.6 cm ID & 5.1 cm depth	Batch	[5]
Fly ash and wastewater sludge	NA	Double torches	Industrial	Plasma melting chamber	125 kg/hour	Continuous	[4]
Stormwater sludge	10	Transferred	Laboratory	Alumina crucible	11.5cm ID & 12 cm depth	Batch	[37]
Stormwater sludge	10	Transferred	Laboratory	Alumina crucible	7.5 cm ID & 9 cm depth	Batch	[11]
Stormwater sludge	10	Transferred	Laboratory	Alumina crucible	11.5cm ID & 7.5 cm depth	Batch	[9]
NA	200 kVA	Two transferred torches	Pilot scale	Furnace crucible	44cm wide & 87cm long	Continuous	[41]
Fly ash and sludge	NA	Non-transferred	Laboratory	Copper crucible	NA	Batch	[2]
Tannery sewage sludge	NA	NA	Laboratory	Graphite put	350 cm ³	Batch	[38]
Electroplating sludge	50	Transferred	Laboratory	Alumina refractory	NA	Semi-batch	[7]
Electroplating sludge	300	Transferred	Pilot scale	Alumina refractory	NA	Continuous	[34]
Fly ash and chromium-rich sewage sludge	20	Transferred	Laboratory	Graphite crucible	NA	Batch	[39]
Electroplating	NA	Transferred	Laboratory	Brass crucible	3cm ID, 3cm depth	Batch	[36]
sludge		Non-transferred		Magnesite crucible	1 -		
Paste from spent batteries	NA	Non-transferred	Laboratory	Graphite crucible	NA	Batch	[42]
Chromium-rich tannery sewage sludge	NA	NA	Laboratory	Graphite crucible	350 cm ³	Batch	[40]
Electroplating sludge	150A, 150V	Non-transferred	Laboratory	Crucible	NA	Semi batch	[1]
Electroplating sludge	NA	Transferred & Non- transferred	Laboratory	Crucible	NA	Semi batch]

NA = not available, ID = internal diameter

Table 6: Operating conditions for previous works on thermal plasma treatment of sludge

Operating power (kW)	Operating voltage (V)	Operating current (A)	Plasma gas (PG)	PG flowrate (L/min)	Carrier gas (CG)	CG flowrate (L/min)	Arc length (cm)	Treatment period (min)	Mass of sample	Reference
NA	NA	NA	Air	NA	NA	NA	NA	NA	250 T/day	[31]
NA	NA	NA	Air	NA	NA	NA	NA	NA	200 L/h	[6]
2-6	NA	NA	Nitrogen	10	Helium	30	NA	5	10g	[8]
1.5	120	90	Argon	17.5	Air	0 - 5	5	120	20 - 30g	[5]
NA	NA	NA	NA	NA	NA	NA	NA	NA	125 kg/h	[4]
1.9	NA	NA	Argon	24 & 35	Air	2.4	5	150	10g	[37]
NA	NA	NA	Argon	24	Air	0 - 4.8	5	120	10g	[11]
NA	120	0 - 86	Argon	35	NA	NA	5	70	10g	[9]
NA	NA	NA	NA	NA	Air and steam	NA	NA	NA	50 kg/h	[41]
6 - 9	40	NA	Argon	15	NA	NA	3	10 - 15	25g	[2]
NA	NA	NA	Argon	20	NA	NA	NA	10	150 cm ³	[38]
50	60	150	Argon	10	NA	NA	NA	60	5 kg/h	[7]
250	280	350	Argon	20	NA	NA	NA	90	150 kg/h	[34]
1.40 kJ	NA	NA	Argon	NA	NA	NA	NA	5	NA	[39]
(T)	NA	180	Argon	10	NA	NA	2	7	2.5g	[36]
(NT)	NA	180	Argon	25	NA	NA	2	12	2.5g	
2.4	12	200	Argon	5	NA	NA	4	5	21.4g, 32.1g	[42]
NA	NA	NA	Argon	20	NA	NA	NA	10	150 cm ³	[40]
7 - 16	NA	NA	Argon, H ₂ & N ₂	25	Argon	8.3 x10-5 kg/s	15	NA	3.3-15 x10-6 kg/s	[1]
7 – 16 (NT)	NA	NA	Ar, H ₂ , & N ₂	40 - 80	Argon	NA	14	NA	0.2-0.9 g/min	[35]
9.5 – 12 (T)	NA	NA	Argon	25	Argon	NA	5.5		0.5g/m	

NA = Not available, (NT) = Non-thermal arc plasma, (T) = thermal arc plasma

VI. Thermal Plasma Pyrolysis of Sludge

Thermal plasma pyrolysis of sludge is accomplished via two processes; (1) plasma gasification of organic portion producing synthetic gas of energy value and (2) plasma vitrification of inorganics and heavy metals into molten slag and ingot, the molten slag turns to rocklike solid upon cooling. The characteristics and leachability of the slag formed varied depending on the chemical constituents of inorganic materials in the parent sludge, the treatment approach and the method adopted for cooling the molten slag.

Results from laboratory and pilot scale investigation on electroplating sludge confirmed a high level of heavy metals such as Fe, Zn, Cr, Cd and Ni in sludge sample. Two separate slags, one with high percentage of metal element and the other the residual of the sludge, were obtained by Bender, et al. [34] and Szente, et al. [7]. The metal slag (ingot) can be recycled and used in metal industry. However the residual slag was stable to leaching of heavy metals and therefore can be used in building and road construction. Similar findings was observed by the Japanese research team, Ramachandran and Kikukawa [1] and [35]. The electroplating sludge considered by the Japanese team contained large percentage of Nickel, Chromium and Zinc. Heavy metals (Cr, Ni, Cu and Zn) present in the sludge were separated into a metal ingot while the resulting slag was found to be inert to leaching test. Ramachandran and Kikukawa [35] obtained the highest metal elimination rate with N₂-O₂ plasma. A comparison study of performance efficiency of Inertization of metals between a transferred arc and non-transferred arc plasma conducted by a Brazilian research team, Cubas, et al. [36], showed that DC transferred arc plasma is the most efficient reactor for inertizing metals in sludge. Their investigation revealed that addition of quartzite to the sludge enhances the inertization of metals present. Chromium, zinc and iron were the metals with the highest inertization efficiencies of 100%, 99% and 100% respectively.

Stormwater from industrial and urban cities is often accompanied with a variety of pollution materials such as heavy metals, phosphorus, trace organic and hydrocarbons. Thermal plasma technology proffers a high decontamination rate of a wide range of toxic compound and immobilization of heavy metals. Treatment of stormwater detention pond sludge in thermal plasma system bears similarities in outcome among the various researches documented in literature. There is a general reduction in TOC in the plasma treated sludge as compared to the untreated sludge. The organic compounds are likely converted into valuable gaseous compounds which can be recycled as an energy source. Li, et al. [37] observed a TOC reduction of 22% after plasma treatment. A more efficient reduction was obtained with argon and air flowrate of 24 and 2.4 L/min. Li, et al. [9] observed a much higher reduction of TOC and accumulated concentration of CxHy, CO, NO and H₂S with transferred DC plasma arc as against non-transferred arc. Chang, et al. [5] observed a decrease in TOC concentration with increase in treatment time.

Volatile metal concentration might be reduced in the solid by-product being enriched in the gas phase. This was observed by Li, et al. [9]. Chang, et al. [5] observed that introduction of air into the treatment chamber affect the removal efficiency of metal from stormwater sludge. They obtained removal efficiency of 2.78 and 3.85% respectively for none air and 2 L/min air flowrate. A much higher removal efficiency of 5.87% was observed with 2 L/min air flowrate and 2 hours treatment period. There was a change of structure from the twophase structure of the stormwater sludge to a single crystallized structure in the slag. X-ray energy dispersion solid analysis of product slag obtained by Li, et al. [11] showed complete removal of carbon and sulfur, whereas Si, Mg, and Al decreased by 25, 30, and 60%, respectively. Calcium and iron were enriched during the thermal process by 400 and 25%, respectively. It was inferred that chemical compounds were decomposed and recombined under thermal plasma treatment. Li, et al. [37] observed a decrease in the concentrations of sand (SiO₂) and calcite (CaCO₃) and a formation of new compounds like KAlSi₃O₈, Fe₃O₄, NaCl and CaSO₄ after plasma treatment. Similar observation was reported by Li, et al. [9] where concentrations of calcium and iron in the solid product were enriched by 500% and 40%, respectively. Also formation of new chemical compounds such as KAlSi₃O₈, Fe₃O₄, NaCl and CaSO₄ in partially DC transferred arc were reported. Eight gas compounds, CO, CO₂, NO, NO₂, NOx, SO₂, H₂S, and CxHy were measured and observed during the treatment process conducted by Chang, et al. [5]. Similarly, Li, et al. [37] obtained an accumulated concentrations of 6100, 10000, 6200, 9700, 140, 40 and 27 ppm, respectively for CxHy, CO, CO₂, NO, NO₂, H₂S and SO₂ after a two hour treatment. Gaseous emission from thermal plasma treatment of stormwater sludge was demonstrated by Li, et al. [11] to be possible energy source for heating and electric energy generation. Li, et al. [9] observed a higher emission of CxHy, CO, NO and H₂S in partially transferred arc as compared to non-transferred arc.

Tannery sewage sludge is rich in chromium, cadmium and zinc, its disposal poses potential threat to both soil and water environments. Biological treatment is not sufficient to eliminate the hazardous effect of chromium and other heavy metals present, its landfilling is equally not recommended. The need for more efficient treatment method is therefore being sought. Vitrification of the sludge with the addition of mineral waste provide an alternative solution. A number of investigations on detoxification of tannery sewage sludge using thermal plasma technology were reported. Sobiecka and Szymanski [39] applied plasma vitrification process to transform a mixture of fly ash and chromium-rich-sludge into a chemically stable glassy products. Celary and Sobik-Szołtysek [40] looked into the feasibility for using plasma vitrification process to treatment and management of chromium-rich sewage sludge from the tannery industry. Bień, et al. [38] evaluated the effect of some additives on heavy metal immobilization during thermal plasma vitrification of tannery sewage sludge. According to Sobiecka and Szymanski [39] the nature of vitrificate obtained from plasma treatment depends on the chemical composition of the parent materials, in this case, fly ash and chromium-rich sludge. Result from leaching and hardness test on the obtained solid product fall within the environmental regulatory limit, which confirmed the safe usability of the glassy product. Similar observation was reported by Celary and Sobik-Szołtysek [40]. The later added a waste material of mineral character to the chromium-rich sludge and obtained a glass-hard, vitreous and homogenous product which is safe to soil and water environments. Waste molding sands and carbonate flotation waste were used by Celary and Sobik-Szołtysek [40]. As observed by Bień, et al. [38] an increase in the content of waste molding sands in the mixture with chromium-rich sludge may cause a higher immobilization of heavy metals in the silica matrix. However, there was no any noticeable effect of addition of dolomite flotation waste on the immobilization of heavy metals.

The concentration of inorganic material in wastewater sludge from wastewater treatment plant may not enough to cause vitrification of the sludge. Fly ash with silica content is added to sludge to enhance its vitrification. The feasibility of vitrifying a mixture of fly ash and wastewater sludge in thermal plasma reactor, and the effect of cooling method on the stability of slag formed from the vitrification process were investigated by Kim and Park [2]. Their findings revealed that sludge with low content of mineral matter may not vitrified on its own but require the addition of other waste with material high content of inorganic matter, like fly ash, to achieve the vitrification. They also saw that slag cooled in water are more stable to leaching than that cooled by natural convection. Leachable chromium in the incineration fly ash and wastewater sludge has also been thermally stabilized by plasma melting process. During thermal plasma vitrification treatments, toxic chromium compounds, CrO_3 , in the fly ash and the chromium in sludge are respectively reduced and decomposed to Cr_2O_3 and Cr. Slags with much less leachable chromium concentration were obtained by Tuan, et al. [4] at a melting temperature of 1,773 K. varying the melting temperature between 1,100 and 1,700 K does not show any effect on the Cr_2O_3 phase of the slag. Thus, the concentration of more-soluble chromium in the slags can be reduced by decreasing the residence time of the melting process.

VII. Conclusion

This paper provides a comprehensive review of pyrolysis and detoxification of plasma treatment of industrial and wastewater sludge. A description of plasma technology, classification, characteristics as well as comparison of the different types was presented. Thermal plasma treatment processes, equipment specifications and process variables for different types of sludges (electroplating sludge, stormwater sludge, and tannery sewage sludge, a mixture of fly ash and wastewater sludge, paper sludge and ship oil sludge) were highlighted. Product analysis from different studies were compared. In the light of this literature view, thermal plasma technology is considered as a highly attractive means for treating industrial and wastewater sludge. Synthetic gas obtained from the treatment processes meet the stringent environmental regulations and also can serves as source of energy for steam turbine and electric energy generations. Heavy metals in sludge are captured in a solid matrix of slag with none or insignificant leaching capabilities. However, additives may be required to improve the silica content of sludge to enhance its vitrification. The main conclusion from the findings demonstrated by many authors in this review is that the final product obtained from thermal plasma vitrification process poses no ecotoxicological risk. Vitrificates in form of glassy material or slag can be re-used in buildings and road construction.

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