Treatment of Stormwater Pond Sediment by Thermal Plasma Systems

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Abstract

This thesis focuses on the thermal plasma treatment of non-point source pollutants accumulating in stormwater ponds. Stormwater ponds are constructed as a part of urban non-point source pollution control systems. Pollutants from various sources are collected in the stormwater ponds as sediments. In this work, stormwater sediments were first separated by a filter with an opening of 208µm. The filtered sludge-water was subjected to pulsed arc electrohydraulic discharge (PAED) treatment while the solid part (i.e., wet sludge and dried PAED treated sludge) was subjected to thermal plasma treatment under non-DC transferred and partial transferred operation modes. The results from the PAED sludge-water treatment show that the reduction of TOC in sludge-water was approximately 80% and was greater than 90%, respectively, after 5 minutes and 2 hours of PAED treatment. The accumulated gaseous concentrations of C_xH_y, CO, CO_2, SO_2, H_2S and NO emission from sludge-water treatment were 8.2, 3.1, 1.9, 0.32, 0.29 and 0.07 mg/L, respectively, after 2 hours of PAED treatment. The concentrations of volatile elements in sediments such as S, Br, Cl and K decreased approximately 80, 90, 30 and 20% respectively. The solid-phase carbon was observed to be approximately completely removed after treatment. Based on the above results, it can be concluded that PAED successfully degraded organic compounds into CO_2, CO and C_xH_y, and converted sulfur and nitrate compounds into SO_2, H_2S and NO.

Thermal plasma wet-sludge treatments showed that a reduction of TOC was approximately 52% with argon plasma gas and air flow rates (in the reaction zone) of 24 and 2.4 L/min, respectively. Based on SEM images, wet sludge was melted under partial transferred mode. Thirteen elements with concentration relationships of O > Si > Al > Ca > S > Fe > K > Mg > Na > Cu > C > Ti > Cl were quantified by the X-ray energy dispersion technique. The elemental weight percentages of Si, K, Fe and O increased with increasing reaction zone air flow rate, while Ca and Cu decreased with increasing air flow rate. Thirty two elements were quantified by Neutron Activation Analyses (NAA) but only 27 elements were above the detection limits. Major elements (concentration > 1000 ppm) with relative concentrations of Ca > Al > Fe > K > Mg > Na > Ti > Cl; minor elements (100 - 1000 ppm) with relative concentrations of Mn > Ba > Sr > Zn; and trace elements (< 100 ppm) with relative concentration were Mo > V > Cr > Br > La > As > Sc > Th> As > Co > Dy > W > Sb > Eu; were determined. Concentrations of Zn, La and Co were enriched 90, 50 and 30% on average respectively, while concentrations of Br, W and As decreased by 80, 50 and 20% on average respectively. The chemical compositions in sludge were quite different after thermal plasma treatment. The average percentages of sand (SiO_2) and calcite ($CaCO_3$) decreased 35 and 10% respectively, while compounds such as $KAlSi_3O_8$, Fe_3O_4, NaCl and $CaSO_4$ were formed after thermal plasma treatment. Gaseous hydrocarbons, H_2S, CO and NO were emitted continuously during the thermal plasma treatment of sludge. Higher reduction of organics and sulfur compounds and suppression of NO_x formation were observed in the thermal plasma treatment of wet sludge. The integrated system consisting of PAED sludge-water treatment and thermal plasma wet sludge treatment under partial transferred mode may provide a potential for stormwater pond sediment treatment control.

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Table of Contents

List of Tables

List of Figures

Chapter 1: Introduction

1.1 Non-Point Source Pollution and Stormwater Sediment

1.1.1 Background

Non-point source pollution is the pollution caused by sediment, nutrients, organics and toxic substances originating from various land use activities or directly deposited from the atmosphere. As opposed to point sources of pollution, non-point sources of pollution have no single, localized sources. Common origins of urban non-point source pollution include non-localized industrial discharges, pet waste, lawn and garden fertilizers and pesticides, improperly disposed household chemicals, automobile fluids, road deicing/anti-icing chemicals, and vehicle emissions (USEPA, 2005). During rainfall events, these pollutants are transported to downstream water bodies, and eventually have a negative impact on the environment.

Urban stormwater management facilities, such as stormwater detention/retention ponds, are designed and constructed to partly treat urban stormwater runoff. Urban runoff is often accompanied with a variety of chemicals such as heavy metals, phosphorus, trace organic and hydrocarbons. Detention/Retention ponds are usually designed to trap and settle out solid materials carried by stormwater, and thus protecting downstream water bodies from harmful chemical and biological effects of the suspended solids. With an adequate design, these facilities can achieve removal efficiency as high as 90% (Marsalek et al., 1997). However, as the service time of these facilities increases, the sediment accumulating at the bottom of the pond also increase and the corresponding storage volume is progressively reduced over time. Figure 1.1 shows the types and sources of contaminants and the schematic of a stormwater pond. The sediment accumulation results in reduced settling time for the contaminants and potential erosion of bottom deposits (Marsalek et al., 1997; MOEE, 1994). Regular removal of sediment is required to ensure adequate storage capacity and to maintain treatment effectiveness. In other cases, sediment removal will be necessary if excessive pollutant concentrations have been reported for a specific stormwater facility. Therefore, in addition to regular maintenance, stormwater sediment needs to be removed or remediated if it poses a potential threat to downstream receiving water bodies.

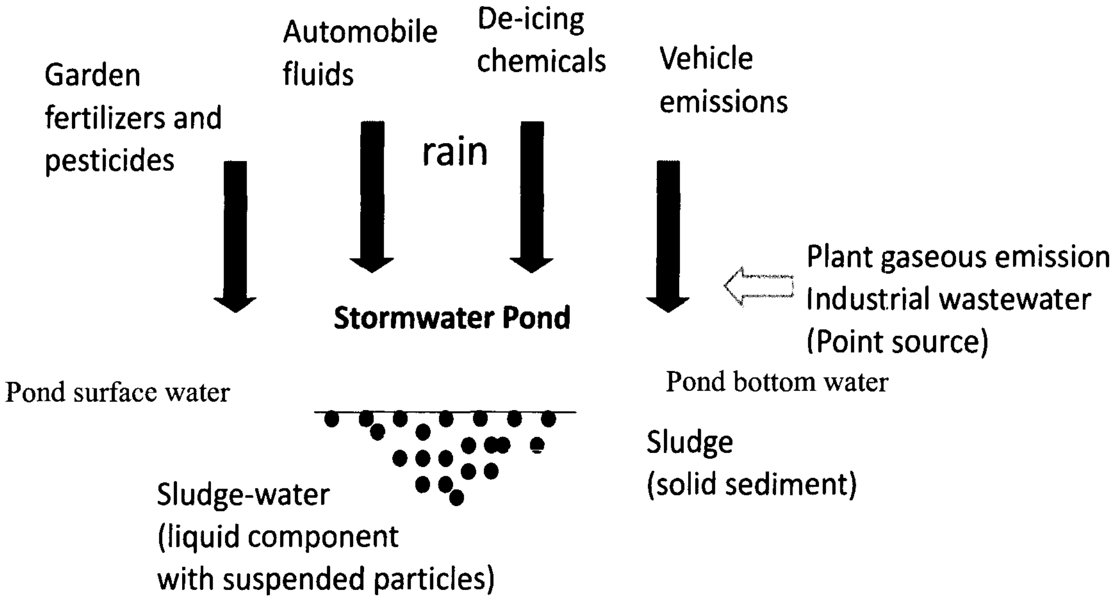


Figure 1. 1 Typical contaminant sources and the schematic of a storrmwater pond

The Ontario Ministry of the Environment (MOEE) established Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario (known as PSQG) to protect the aquatic environment by setting safe levels for metals, nutrients (substances which promote the growth of algae), oil and grease, and organic compounds (MOEE,1993). These guidelines provide assistance to environmental managers to determine the level of contamination of the sediment, based on the relative toxicities of metals, nutrients, pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and other parameters. PSQG regulation does not include for disinfection. More specifically, the Ontario guidelines establish the following three levels of effect:

(i) No Effect Level (NEL): This is the level at which the chemicals in the sediment do not affect fish or sediment-dwelling organisms. At this level, no transfer of chemicals through the food chain will occur and no effect is expected. Sediment that has a NEL rating is considered clean and no management decisions are required;

(ii) Lowest Effect Level (LEL): This indicates a level of contamination, which has no effect on the majority of the sediment-dwelling organisms. The sediment is clean to marginally-polluted. Contamination in sediment that exceeds the LEL may require further testing and a management plan. The exceeded concentrations of metals and organic contaminants could endanger the organisms that live or feed in the sediment; and

(iii) Severe Effect Level (SEL): At this level, the sediment is considered heavily polluted and would likely affect the health of sediment-dwelling organisms. If the level of contamination exceeds the SEL, testing is required to determine whether or not the sediment is acutely toxic. At the SEL, a management plan may be required. The plan may include control of the source of the contamination and removal of the sediment. The Provincial Sediment Quality Guidelines for metals, nutrients and organics in Ontario, Canada are shown in Table 1.1.

Table 1. 1 Ontario Provincial Guidelines for metal elements and total organic carbon (MOEE, 1993) (values in µg/g dry weight unless otherwise noted)

Elements	**LEL µg/g**	**SEL µg/g**
Chromium	26	110
Iron	20000	40000
Zinc	120	820
Arsenic	6	32
Cadmium	0.6	10
Copper	16	110
Lead	31	250
Nickel	16	75
Mercury	0.2	2
Iron (%)	2	4
Manganese	460	1100
Nutrients		
Total Organic Carbon (TOC) (%)	1	10
Total Kjeldahl Nitrogen (TKN)	550	4800
Total Phosphorus (TP)	600	2000

The quality of the stormwater pond sediment is dependent on the age of development, land uses of surrounding area, the upstream area and other factors. Source areas such as parking lots, rooftops, streets and landscaped areas have important effects on stormwater sediment properties (MOEE, 1993; MOEE, 1994;

Li et al., 2007). In past years, many studies have examined the quality of stormwater sediment in Ontario, Canada. For example, Rochfort et al. (2000) tested sediment toxicity and chemistry in a stormwater pond located in the residential areas of Richmond Hill, Ontario. The assessment of total metals in the pond sediment against the PSQG indicated a marginal-to-significant pollution by trace metals including As, Cu, Fe, Hg, Mn, Ni, Pb and Zn. Another study was conducted for chemical characteristics of bottom sediment in a Kingston, Ontario stormwater pond (Marsalek et al., 1997). The pond was constructed in 1982 for remediation of a nearby shopping plaza runoff. The assessment of the concentration of Cr indicated a gross pollution according to PSQG, while other regulated metal concentrations including Cd, Cu, Fe, Pb, Mn, Ni and Zn indicated a marginal-to-significant pollution. The sediment analysis also indicated that 40 - 90% of the retained metals were in potentially mobile forms.

Li et al. (2007) conducted a comparison of sediment chemistry for stormwater ponds located in different land-use areas. Four different stormwater ponds around the cities of Burlington and Hamilton, Ontario were sampled, of which two ponds are located in residential areas, one in highway/commercial areas and the other in commercial/light industrial areas. The concentration of Cr was above the SEL in the highway and commercial/light industrial areas, while the concentrations of As, Fe, Mn and Zn indicated a marginal-to-significant pollution in all areas. Other studies also showed the negative effect of highways, roads and adjacent lands on stormwater (Thomson et al., 1997). Marsalek et al.

(1997) sampled the stormwater runoff sediment from the skyway bridge in Burlington, Ontario and observed that the mean concentrations of Zn, Cu and Pb exceeded the SELs of PSQG. Sediment contamination is therefore expected for stormwater ponds located in highway areas.

Concerns regarding the availability and uptake of metals in the accumulated stormwater sediment by aquatic ecosystems have risen recently. In 1997 and 1998, Environment Canada conducted a study to evaluate the level of sediment contamination in different land-use types (Great lake Fact Sheet, 1997; Bishop et al., 2000). Six stormwater ponds in the Greater Toronto Area (GTA) and nine stormwater ponds in the city of Guelph were studied. Twelve ponds are located in residential areas. The remaining three ponds are located separately in commercial areas, commercial/light industrial areas and residential/commercial areas. Sediment from all ponds contained at least one contaminant that exceeded the LEL of PSQG. Sediment in one site (commercial/light industrial) were grossly polluted by Cr. For each sediment sample, the toxicity to aquatic animals was evaluated and it was concluded that stormwater ponds did not offer clean ecosystems for wildlife.

The relationship between stormwater sediment and aquatic ecosystems was also studied (Great Lakes Fact Sheet, 1999). In order to demonstrate the uptake of trace metals in sediment by aquatic biota, freshwater mussels were caged in various locations in several stormwater treatment facilities in southeastern Ontario. Some sediment were grossly polluted by Cu and Cr, while all concentrations of Cu, Pb and Cr in all stormwater facilities indicated a marginal-to-significant pollution among the three facilities. From the investigation of the trace metal impacts on freshwater mussels, it was suggested that the availability of Pb could be a possible concern in aquatic ecosystems.

Selected regulated metal elements were measured in three stormwater management facilities located in the Ottawa-Carleton area for ecotoxic risk (Vanloon et al., 2000). The study expressed concern of potential risk of stormwater sediment to the ecosystem. The facilities are all located in residential areas, with the first pond serving an exclusively residential area. The second pond serves five to ten agricultural areas and drainage from a roadside ditch in addition to residential areas. The results indicated a marginal-to-significant pollution according to PSQG for Cu, Zn, Cr and Ni; in particular, the concentrations of Cu and Znwere both substantially higher than the LEL in the pond serving an exclusively residential areas. These results show the existence of significant ecotoxic risks.

Other studies conducted in the United States also show potential contamination of stormwater sediment. Elevated concentrations of Cd, Cr, Cu, Ni, Pb, Zn and trichloroethylene (TCE) were observed in a stormwater retention pond located in the urban community of Hillcrest (Graney et al., 2004). The community is located in an urban area with local industrial activities including computer manufacturing, a coal-fired power plant, camera film processing and metal plating operations. The trace metal concentrations were compared to the New York State Department of Environmental Conservation (NYSDEC) guidelines. Similar to PSQG, the New York state guidelines set the LEL and SEL for regulated elements. As a general remark, both levels in the two guidelines (Ontario vs New York) are in the same order of magnitude. The concentrations of Zn and Pb in the sediment samples show a gross pollution, while Cu, Cd and As are at the marginal-to-significant pollution level. Atmospheric transport and deposition of pollutants from local and regional point sources were confirmed.

An intensive study has summarized stormwater sediment characteristics in fourteen cities around the United States (Cox et al., 1997). The study compared the level of pollutants in sediment and debris from 87 treatment systems and background samples of native soils collected by each participating entity. The results were compared to the Florida Sediment Quality Assessment Guidelines (SQAG's). The guidelines identified two levels, a threshold effects level (TEL) and a probable effects level (PEL), which have, respectively, low to high probabilities of adverse biological effects. Stormwater sediment are usually contaminated well beyond these levels with a wide variety of inorganic and organic pollutants compared to native soils. Pb, Cu, Zn and Cd were the most frequently detected inorganic pollutants in excess of SQAG. More problematic pollutants were identified to be organic compounds. Pesticide chlordane exceeded the PEL at most sites (82%), and several PAHs exceeded the same criteria at more than half of the sites. Levels of several metals and PAHs routinely exceed criteria established in sediment quality assessment guidelines; therefore, appropriate sediment disposal must be carried out for regular stormwater pond maintenance regardless of the upstream land use types. (Marsalek et al., 1997; MOEE, 1994).

1.1.2 Sediment Disposal Options

Sediment in other water bodies (e.g., harbors, estuaries, etc.) are subjected to chemical analysis prior to removal and disposal as well. Sediment chemistry analysis helps identify disposal options or treatment methods. Currently, disposal methods are determined by the USEPA Regulation 347 Leachate Test, or Guidelines for Use at contaminated sites in Ontario (GCSO) and PSQG in Ontario (MOEE, 1993; MOEE, 1996). Three common sediment disposal options are landfill disposal, land spreading and open water disposal (MOEE, 1993; Greenland International Inc., 1999). Details of which are as follows:

Landfill Disposal: 33 standard leachate contaminants including certain trace metals, organic compounds and nutrients are used to determine if the sediment will pose a potential threat to ground water resources. Depending on the level of contamination, the sediment will be disposed into either registered non-hazardous or hazardous waste disposal facilities.

Land Spreading: Depending on the analysis results and according to GCSO criteria, sediment may be disposed on agricultural land, residential land, commercial or industrial areas. The most stringent GCSO soil contamination criteria apply to agricultural lands and the least stringent criteria apply to commercial and industrial areas.

Open Water Disposal: Sediment might be safe for open water disposal if the sediment contaminant concentrations are below the LEL of PSQG.

Greenland International Consulting Inc. (1999) investigated eight case studies regarding stormwater sediment removal and disposal in Ontario. Table 1.2 shows the summary of sediment removal and disposal for the eight sites. The eight sediment removal projects included two ponds located in industrial areas and six others located in residential areas. None of the site sediment were qualified for open water disposal. The sediment from the industrial areas required disposal at a registered non-hazardous landfill facility, while the six residential area sediment were disposed of as land spreading. The total cost of landfill and upland disposal included dredging, transportation, tipping fees and dewatering costs. Solid waste landfill operators will not accept sediment in the form of slurries. For sediment that do not meet the slump test requirements by EPA Regulation 347, dewatering was applied to the sediment prior to disposal. The dewatering process and tipping fees vary for each case, and usually the tipping fee for a registered landfill is much higher than the cost of upland disposal.

Table 1. 2 Summary of sediment removal and disposal at eight sites (Greenland International Inc., 1999)

Site	**Waste Disposal Classification**	**Year Cleaned**	**Approved Disposal Method**	**Criteria Exceedences**	**Cost ($/m^3)**
Merivale, Garden Pond (Industrial)	Non-Hazardous, registered waste	1997	Registered Landfill	Above LEL: Total Cr, Pb, Ni, Zn Above SEL: Cu	124
Netley Pond, Nepean (Industrial)	Non-Hazardous, registered waste	1997	Registered Landfill	Above LEL: Total Cr, Pb, Ni, Zn Above SEL: Cu, Fe, Ni	669
Lake Aquitaine, Missisauga (Residential)	Non-Hazardous, registered waste	1994	Daily cover at the Sanitary Landfill Site	Above LEL: Cd, Total Cr, Cu, Pb, Ni, Zn	62
Toogood Pond , Markham (Residential)	Non-Hazardous, registered waste	1997	Used as backfill for the construction of a Toboggan hill	Data Unavailable	32
Bluffers Park Pond, Scarborough (Residential)	Non-Hazardous, registered waste	1995	Used as Back fill for several land Development projects	Above LEL: TKN, Total Cr, Pb, Ni, Zn	162
Lincoln Homes Pond, Uxbridge (Residential)	Non-Hazardous, registered waste	1994	Landfilled by the Town of Uxbridge	Data Unavailable	33
Victoria Lake, Kitchener (Residential)	Non-Hazardous, registered waste	1997	Disposed at a closed gravel pit located within the City of Kitchener	Above LEL: TKN, Total Cr, Cu, Pb, Ni, Zn	18
Silver Lake, Waterloo (Residential)	Non-Hazardous, register waste	1997	Spread on agricultural field	Above LEL: TKN, Total P, Total Cr, Cu, Pb, Ni, Zn	14

1.2 Conventional Sludge Treatment Technologies

As reviewed in Section 1.1, most of the stormwater sediment are contaminated. Sediment in ponds serving all land use types consistently exceeded the LEL criteria for different parameters including metals, total organic carbon (TOC), total kjeldahl nitrogen (TKN) and poly chlorinated Biphenyl (PCBs); some of the sediment even exceeded the SEL criteria for at least one parameter. With reference to the PSQG guidelines, these sediment cannot be reused in an urban area, nor disposed at municipal landfills.

Since the tipping fee of the registered landfill is site specific, the cost of disposal varies greatly. Also, the increasing pressure on the limited landfill sites in urban areas raises many public concerns. Attractive options other than disposal include reducing, destroying, immobilizing or decontamination of the stormwater sediment followed by beneficial reuse of the end products.

Development of treatment technologies for contaminated sediment is widely supported within Canada and the USA, especially for the restoration of the Great Lakes Basin (Zarull et al., 2001). The Water Quality Board of the International Joint Commission has submitted a detailed Remedial Action Plan (RAP) for environmental restoration in 42 Areas of Concern in and around the Great Lakes basin (Glouceter Harbor, 2002). One of the important issues in RAP is developing potential sediment decontamination technologies. Most techniques for treatment of sediment are in the early stages of development, and very few methods are currently commercially available. Treatments of contaminated sediment involve the application of the primary decontamination processes to reduce, destroy or immobilize the targeted contaminants (MOEE, 1996; Glouceter Harbor, 2002). Generally, the current post-removal treatment options fall into one of three different types, namely (1) biological; (2) chemical/immobilization; and (3) thermal processes.

1.2.1 Biological Treatment Technologies

Biological treatment uses micro-organisms to degrade organic contaminants with the addition of materials such as nitrate, sulfate, hydrogen, nutrients, etc., either under aerobic or anaerobic conditions. In the presence of oxygen, micro-organisms may ultimately convert toxic organic compounds to carbon dioxide, water, and microbial cell mass. In the absence of oxygen, the contaminants may be ultimately reduced to methane, carbon dioxide and trace amounts of hydrogen gas. These treatments include in-situ bio-remediation, fungal remediation, landfarming, composting, in-vessel bio-remediation and phyto-remediation. Typical biological sediment (also referred to as sludge) treatment technologies are summarized in Table 1.3. These treatments are typically ineffective for the treatment heavy metals and high-level of toxic organic contaminants.

Table 1. 3 A list of typical biological sludge treatment technologies

Biological Process	**Target Contamination**	**Treatment Method**	**Side Streams**	**References**
In-Situ Bioremediation	Organics: Petroleum hydrocarbons, pesticides	Microbial degradation of contaminants under aerobic and anaerobic conditions	N/A	[USEPA, 2002; Stern et al., 1998]
Fungal Remediation	Organics: PAHs, PCBs, Pesticides	Fungi degradation of contaminants	N/A	[Rock, 1998]
Slurry bioreactor	Organics: Chlorinated volatile organics, PAHs, PCBs, pesticides	Microbial degradation of slurry sediment in a temperature controlled vessel	Dewatering, off-gas	[USEPA, 2002]
Landfarming	Organics: Low molecular PAHs and non-chlorinated PCBs	Bioremediation of sediment in a large area, controlled pH, moisture, nutrient and oxygen concentration	N/A	[USEPA, 2002; Bogomaz et al., 1991]
Composting	Organics: Low molecular PAHs and non-chlorinated PCBs	Remediation by windrow and/or aerated static pile.	Off-gas, leachate	[USEPA, 2002]
In-vessel bio-remediation	Organics: Aliphatic halocarbons	Composting in bioreactors with leachate collection system and aeration equipment.	Off-gas Leachate	[USEPA, 2002, Stern et al., 1998]
Phyto-remediation	Organics: Low-to-medium PAHs, fertilizer or metals	On-site pollutant remediation for cleanup area with low-medium contamination	N/A	[Stern et al., 1998; Bogomaz et al., 1991]

1.2.2 Immobilization or Chemical Processes

Immobilization processes mainly convert the contaminants into a less bio-avaliable, less mobile or less toxic form by adding chemicals or other additives. However, presence of non-target compounds may also react with the additives and more toxic intermediate compounds might be produced. The processes are usually accompanied with waste streams containing excess chemicals. These processes mainly include solidification, stabilization, soil washing, solvent extraction, chemical reduction/oxidation and dehalogenation. A list of immobilization/chemical sludge treatment technologies are summarized in Table 1.4.

Table 1. 4 A list of typical immobilization/ chemical sludge treatment technologies

Immobili-zation Chemical Process	**Target Contamin a-tion**	**Treatment Method**	**Additives**	**Residuals and Side Stream**	**Ref.**
Soil Washing	Volatile organics Semi-volatile organics Metals	Physical separation of sediment into a reusable bulk fraction and a smaller fraction containing concentrated contaminants	Treatment of concentrated contaminants by different chemicals	bulk fraction of sand, the fine contaminated sediment. solvent , suspended fines	[USEPA, 2002; Hall et al., 1998]
Solidification/ Stabilization	Organics: PAHs	Mixing the solid or liquid reagents with the feed	asphalt, cement and lime	Stabilized blocks of sediment (mostly	[USEPA, 2002; Jones et al., 2001]

	Bacteria Inorganic Metals	sediment in a pug mill. Stabilized mass by physical bond (solidification) Reduce the mobility by chemical reactions (stabilization).		reusable as construction materials); air emission	
Chelation	Metals	Chemical stabilization process particular for metal immobilization.	Acetic acid	Treated sediment needs to pass TCLP for disposal option; Wastewater from the dewatering process	[USEPA, 2002]
Solvent Extraction	Organics: PCBs, PAHs, VOCs, petroleum hydrocarbons and chlorinated compounds	Extract the organic contaminants in sediment	Organic solvents	Treated sediment with traces of extraction solvent; Wastewater from dewatering, off-gas and spend solvent used during	[USEPA, 2002]
Chemical Reduction/ Oxidation[5]	Selected organics and inorganics	Convert contaminants into less toxic or immobile forms	Various form of chlorine, potassium permanganate, hydrogen peroxide, persulfate and ozone.	Treated sediment with excess chemical agents; Wastewater from dewatering	[USEPA, 2002; Ancheta, 1998]
Dehalogenation	Halogen	Destroying or removing	Sodium bicarbonate,	Dehalogenated sediment,	[USEPA, 2002;

	atoms	halogen atoms form halogenated aromatic compounds	polyethylene glycol	possible hazardous intermediate compounds; Steam vapor with volatile organic compounds, solution with soluble toxic compounds	Gloucester harbor, 2002,]

1.2.3 Thermal Processes

Thermal treatment processes use high temperatures to destroy chemical bonds of the contaminants or to vitrify contaminants and sediment into a solid mass. Treatment efficiency of organics by thermal processes normally exceeds 99% (MOEE, 1996; Rienks, 1998; USEPA, 2002; Santiago et al., 2001) However, potential air quality impact by the processes causes the public and environmental groups' discouragement of the development and implementation of this technology. Incineration, pyrolysis, thermal desorption, vitrification and thermal plasma are processes which fall into this category. Typical thermal treatments are summarized in Table 1.5 while thermal plasma sludge treatment will be discussed in detail in Chapter 3.

Table 1. 5 A list of typical thermal sludge treatment technologies

Thermal Process	**Target Contamination**	**Treatment Method**	**Residuals**	**Side Streams**	**Ref.**
Incineration	Wide range of organics	Destruction of contaminants in the presence of oxygen under high temperatures	Fly ashes with leachable heavy metals	Air emissions, waste water generated by the post-treatment of the air pollution	[USEPA, 2002; Jones et al., 2001]
Pyrolysis	Wide range of organics	Destruction of organic in the absence of oxygen under high temperature. Separation of organic fraction into gas and the inorganic fraction into salts, metals and particulates.	Fly ashes with leachable heavy metals	Air emissions	[USEPA, 2002; Anderson et al., 2004]
Thermal Desorption	Wide range of organics	Volatilize organic contaminants under high temperature. Some metals are volatilized with organic contaminants at high temperature process (320°C to 550°C)	Concentrated heavy metal residuals	Pre-treatment dewatering if moisture content is high	[USEPA, 2002; Hall et al., 1998]
Vitrification	Most of the organics,	Destruction of organic	Oxide glasses	Gaseous discharges,	[Rienks, 1998;

	inorganics and metals	contaminants, melts and converts the inorganic contaminants into oxide glasses in temperature above 1600°C.		wastewater from cooling molten products	USEPA, 2002; Santiago et al., 2001;Rienks, 2003]

1.2.4 Multiple Sediment Decontamination Treatment Processes

In-situ sludge treatment can be performed using not only one, but also multiple processes in series. A study has been conducted to examine the performance of thermal desorption followed by solidification/stabilization for dredged harbor sediment (Hall et al., 1998). Five US gallons (18.9L) of New York/New Jersey Harbor sediment were tested under the proposed treatment method. The dredged sediment were observed to have gross organic levels of organo-chlorinated pesticides, PCBs, PAHs and dioxins, and leachable Cd, Cu, Pb, Ni and Zn. Toxicity decreased in severity as the thermal treatment temperature increased from 350 to 550°C. Results indicated that PCBs in sediment were lowered from 6969 μg/kg to 1.8 ug/kg (dry basis) while the dioxins were lowered from 695 μg/g to 154 ng/kg. Selected additives were added to the sediment followed by thermal desorption. Stabilization process resulted in effective fixation of metals. All tested parameters, other than zinc, were not detectable in the toxicity characteristic leaching limit (TCPL). The thermally treated/stabilized sediment resulted in reductions of > 99.6%, > 90.0%, and > 93.7% for PCBs, pesticides and SVOCs, respectively. The end products were designed to be reused as construction materials. Cost estimation, including capital cost, futilities and labor, was $ 68 per m^3 of sediment.

1.2.5 Summary of Alternative Treatment Technologies' Practicability for Stormwater Sediment

Tabular summaries of the cost and performance of each technology acquired through literature reviews are shown in Tables 1.6 and 1.7, respectively. Applications of previously described in-situ treatment technology often indicate technical limitations on the effectiveness to treat sediment. Site-specific factors such as concentrations, types, forms of contaminants, and moisture or soil content of the sediment greatly affect treatment performance. For example, the high level of heavy metal contamination is not suitable for biological treatment, as heavy metals are toxic to most of the micro-organisms. In-situ treatments relying on injection of chemicals and additives require development of an effective delivery system, and sometimes including the recovery of the additives as well. Public and environmental groups raise concerns of potential air quality impact with the use of incineration and pyrolysis.

Table 1. 6 Advantages and disadvantages of potential sediment decontamination technologies

Technology	**Target Contamination**	**Removal Efficiency %**	**Advantages**	**Disadvantages**
Biological				
In-Situ Bioremediation	Organics: Petrolieum hydrocarbons, pesticides	>90	Relatively low cost, low technology	Inability to treat PAHs, limited temp. range
Fungal Remediation	Organics: PAHs, PCSs, Pesticides	50	Relatively low cost, low technology	Relatively low concentration of organics, Inability to treat metals
Slurry bioreactor	Organics: chlorinated volatile organics, PAHs, PCBs, pesticides	>90	Effective for most organics, optimize the process	Inability to treat metals, dewatering requirement after treatment
Landfarming	Organics: Low molecular PAHs and non-chlorinated PCBs	>90	Relative low cost, low technology	Inability to treat metals and PAH. Slow process, large land area requirement
Composting	Organics: Low molecular PAHs and non-chlorinated PCBs	>90	Relative low cost, low technology	Inability to treat metals and PAH. Slow process, large land requirement
In-vessel Bio-remediation	Organics: Aliphatic halocarbons	70-95	High efficiency, smaller area	Inability to treat metals. Not effective for inorganics and PAHs
Phyto-remediation	Organics: Low-to-medium PAHs, fertilizer or metals	N/A	Relative low cost, low technology	Inability to treat high level contaminants, large area
Chemical				

Soil Washing	Volatile organics Semi-volatile organics Metals	>90 40-90 70-95	Relative low cost, low technology	Particle size dependent. Not appropriate for fine particles (slit and clay) Dewatering after treatment
Solidification/ Stabilization	Organics: PAHs Bacteria Inorganic Metals	70-90	Reusable residuals	Not effective for some organics (VOC), increased volume after treatment
Chelation	Metals	75-90	Effective for metal treatment	Not effective for organics, side stream wastes
Solvent Extraction	Organics: PCBs, PAHs, VOCs, petroleum hydrocarbons and chlorinated compounds	>90	Effective for organics	Not effective for metals, dewatering requirement after treatment generation of potential toxic residuals
Chemical Reduction/ Oxidation	Selected organics and inorganics	90-95	Effective for organics and inorganics	Not effective for some metals and PAHs, generation of potential toxic residuals
Dehalogenation	Halogen atoms	N/A	Effective for PCBs and Chlorinated pesticides	Inability for metals and PAHs
Thermal				
Incineration	Wide range of organics	>99.99	High treatment efficiency, volume reduction	Inability to treat metals, public concerns, air emissions

Pyrolysis	Wide range of organics	>99.99	High treatment efficiency, volume reduction	Inability to treat metals, low moisture content, cost, air emissions
Thermal Desorption	Wide range of organics	>99	High treatment efficiency	Inability to treat metals, low moisture content, air emission
Vitrification	Most of the organics, inorganics and metals	>99.99	High treatment efficiency, volume reduction	Cost, air emission

Table 1. 7 Comparison of costs of sediment decontamination technologies (Data sources: [1]Cloucester harbor DMMP, 2002; [2] USEPA, 2002; [3] USEPA, 1997)

Technology	**Cost Range**	**Average Cost ($ per cubic yard)**	**Number of Technologies**
In-Situ Bioremediation	$6-$116 [1] $3-$152 [2]	$42 [1] $23 [2]	22 [1] 12 [2]
Fungal Remediation	$165-$264 [1]	$215 [1]	2 [1]
Slurry Bioreactor	$3-$264 [1] $97-$335 [2] $96-$268 [3]	$223 [1] $200 [2]	12 [1] 7 [2]
Landfarming	$44-$52 [1] $8-$183 [2]	$48 [1] $77 [2]	2 [1] 30 [2]
Composting	$25-$298 [1] $166-$465 [2] $187-310	$73 [1] $281 [2]	7 [1] 10 [2]
In-vessel bioremediation	$33-$220 [1]	$154 [1]	3 [1]
Phytoremediation	$9-$23 [2]	$16 [2]	2 [2]
Soil Washing	$20-$220 [1] $120-220 [3]	$89 [1]	19 [1]
Solidification/Stabilization	$48-$330 [1] $50-483 [3]	$99 [1]	1 [1]
Chelation	N/A	$83 [1]	1 [1]
Solvent Extraction	$21-$567 [1] $75-$400 [3]	$182 [1]	21 [1]
Chemical Reduction/Oxidation	$39-$2805 [1]	$232 [1]	8 [1]
Dehalogenation	$220-$330 [1]	$263 [1]	15 [1]
Incineration	$55-$880 [1] $140-$190 [3]	$243 [1]	8 [1]
Pyrolysis	$248-$275 [1]	$262 [1]	3 [1]
Thermal Desorption	$11-$908 [1] $100-$600 [3]	$177 [1]	52 [1]
Vitrification	$66-$1540 [1]	$462 [1]	17 [1]

1.3 Conventional Sludge-Water Treatment Technologies

Provincial water guideline USEPA regulates the quality of surface water discharge for aquatic life and recreation (USEPA, 2009). Effluent guidelines are national standards that, in this case, apply to storm water and wastewater discharges to surface waters. Elevated bacteria concentrations (E.coli, Cryptosporidium and Giardia) in runoff and during wet-weather flow conditions in stormwater pond were being reported (Clary et al., 2008; Slifko et al., 2007) . The disinfection of wastewater treatment plant effluents ensures that levels of disease-causing organisms do not contaminate the receiving water body (Hydromantis et al., 2003). The most widely used disinfectants are chlorine, ozone and ultraviolet light (WEF, 1996). In a typical wastewater treatment plant, screening is most often applied prior to any other treatment process. However, fine particles might pass through the screen and enter into downstream processes. Particles in water may inhibit disinfection processes. Studies have shown that the suspended solids interfere with UV disinfection by scattering or absorbing the light, or provide shading for the bacteria (Madge et al., 2002; Wu et al. 2005). Increasing the particle concentration and bacterium-particle attachment time prior to UV irradiation can effectively lower the degree of bacterial inactivation.

Chlorine is effective at inactivating bacteria and viruses with low capital and operating costs. The disinfection effect of chlorine is dependent on both the contact time and dosage applied. Depending on regulatory requirements, the contact time can range from 30 to 120 minutes (Metcalf and Eddy, 2003). However, a number of safety precautions are required for transportation and storage of the toxic gas. Chlorine residuals and disinfection byproducts (DBPs) might also cause toxic effects on aquatic life. Dechlorination is normally required prior to discharging treated water into surface water bodies.

Ozone gas is a chemical disinfectant used as an alternative to chlorine. It is highly effective on bacteria, viruses and protozoa. Oxidation reactions between ozone or hydroxyl radicals can effectively decompose toxic organic compounds as well. Similar to chlorine, the disinfection effect of ozone depends on both the contact time and the dosage delivered. Contact times for ozone disinfection (approximately 10 - 30 minutes) are shorter than chlorine disinfection (USEPA, 1999). The ozone gas is usually manufactured on-site, and the remaining ozone in the off-gas must be converted back to oxygen before being released to the atmosphere. The general performance, advantages and disadvantages of the three disinfectants in sludge-water treatment are summarized in Table 1.8.

Table 1. 8 General performance, advantages and disadvantages of conventional sludge-water treatments

	UV	Cl/ClO_2	O_3/H_2O_2	Ref
Efficiency against micro-organisms	Good	Relatively good	Good	[USEPA, 1999; USEPA, 2002]
Oxidation power	None	Relatively high	High	[USEPA, 2002]
Removal of inorganic pollutants	None	None	Partial	[USEPA, 2002; Metcalf and Eddy, 2003; Chang, 2001]
Destruction of algae	Yes (with high doses)	None	Yes	[USEPA, 2002; Metcalf and Eddy, 2003; Chang, 2001]

Destruction of urine components	None	Relatively good	Partial	[USEPA, 1999;USEPA, 2002; Chang, 2001]
Destruction of phenols	None	None	Yes	[USEPA, 1999;USEPA, 2002]
Advantages	Effective disinfectant of bacteria, viruses and protozoa Short treatment times compared to ozone and chlorine	Relatively low cost Effective disinfectant for bacteria and viruses	Effective disinfectant for bacteria, viruses, and protozoa. Improves wastewater quality in terms of colour, odour, turbidity and dissolved oxygen Residuals ozone reacts disappeared quickly	[USEPA, 1999;USEPA, 2002; Hydromantic Inc. and Stantec Consulting Ltd., 2003]
Disadvantages	UV disinfection affect by TSS and turbidity of wastewater Energy intensive	Residual chorine is toxic to aquatic life Dependent of pH of wastewater Possible formation of DBPs Relatively long contact time	Ozone must be generated and disposed of on-site Relatively expensive	[Hydromantis Inc. and Stantec Consulting Ltd., 2003; WEF, 1996; Wu et al., 2005]

1.4 Proposed Integrated System

Sediment with high-level contamination are not appropriate for bioremediation treatment, and the wide variety of organics and heavy metals associated with stormwater sediment also makes both conventional thermal and chemical extraction processes challenging. A feasible stormwater sediment decontamination technology must be able to remove a diverse range of inorganic chemical species and organic matters with widely varying concentrations. The proposed integrated treatment system for stormwater pond sediment has two main components: (1) pulsed arc electrohydraulic discharge (PAED) for sludge-water treatment and (2) thermal plasma decontamination of stormwater sludge. A detailed schematic of the integrated treatment system is shown in Figure 1.2. After dredging, the stormwater sludge will be spread on top of a filter. The solid component (sludge) will be transferred to a thermal plasma reactor while the filtered sludge-water will be subjected to PAED treatment.

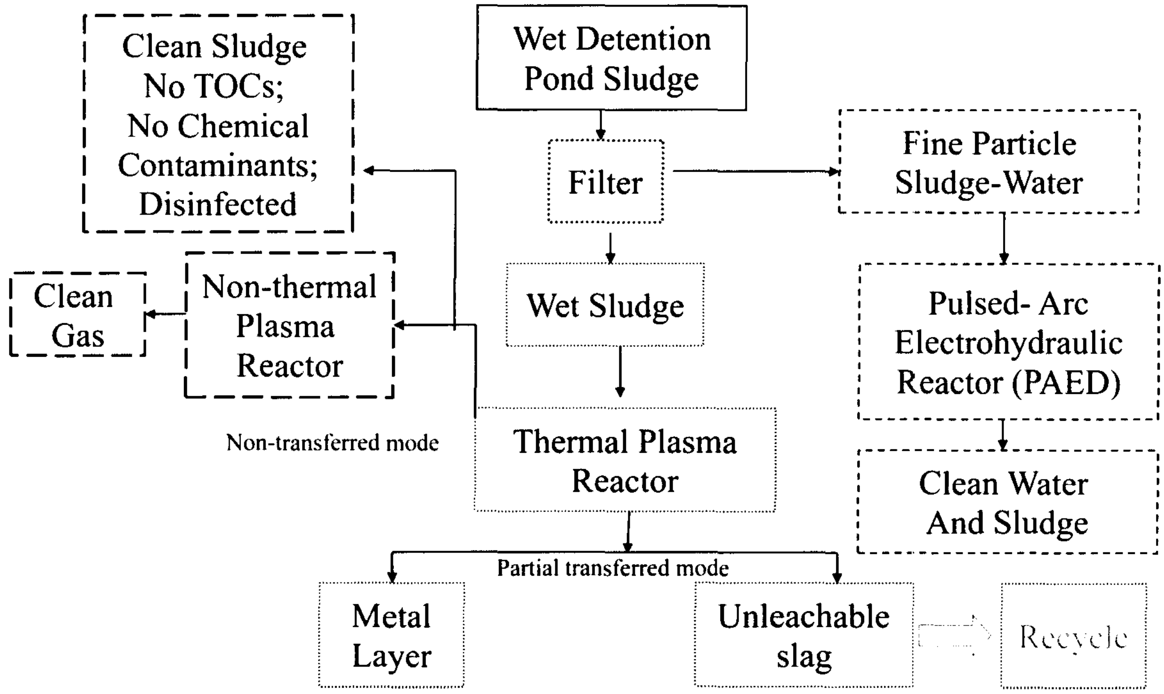


Figure 1. 2 Proposed thermal plasma stormwater sludge treatment system

(i) Sludge-Water Treatment

The filtered sludge-water will be subjected to Pulsed Arc Electroydraulic Discharge (PAED) treatment. The liquid-phase electrical discharge (electrohydraulic discharge) causes concurrent removal of chemical contaminant and inactivation of viruses and bacteria. Fundamental characteristics such as pressure, voltage, current and power etc., will be investigated for pond surface water, pond bottom water with various sediment concentrations and sludge-water. Radical generation and UV emissions will be observed during the treatment process. Generation of gaseous by-products during PAED treatment of sludge-water will be investigated. Solid analyses will also be conducted for the solid components before and after PAED treatment.

(ii) Wet Sludge Treatment

The solid part (wet sludge) will be placed in a thermal plasma treatment system. Two approaches will be examined for the sludge decontamination process: non-transferred DC (low heat transfer) and partial transferred system (high heat transfer). This study will compare these two approaches. Furthermore, wet sludge will be treated directly. Eliminating the dewatering/drying process can possibly decrease the total treatment time and cost. The decontamination processes will generate two different types of treated sludge: (1) with high temperature and heat transfer rate (partial transferred mode), the solid product will be melted into unleachable slag (with volume reduction), which can be recycled as construction materials; or (2) with low heat transfer rate (non-transferred mode), disinfected clean sludge can be safely disposed or reused as landfill materials.

1.5 Outline of Thesis

This study examines the feasibility of the proposed treatment system for storwmater pond sediment. Chapters 2 and 3 provide the essential background previous research finding related to the two thermal plasma techniques: Pulsed arc electrohydraulic discharge water treatment and thermal plasma sludge treatment. Chapter 4 focuses on the experimental apparatus and measurement techniques employed in this study; Chapters 5 and 6 present and discuss the experimental results. Chapter 7 concludes with a summary of findings, and Chapter 8 provides recommendations for further development and research.

Chapter 2: Pulsed Arc Electrohydraulic Discharge Technique for Water Treatment

2.1 Plasma Water Treatment

Plasma water treatment techniques can be divided into three categories: indirect plasma, remote plasma and direct plasma methods. Previous applications mostly focus on indirect plasma treatment (UV radiation) or remote plasma treatment (ozone). The focus of recent studies have also included direct energetic electron-induced plasma processes, electrohydraulic discharge and gas-phase non-thermal plasma applied above the water surface or in close contact with the liquid water phase. UV, radicals, ions, electrons and pressure waves are used for the destruction of pollutants in water in these systems. The target pollutants, applications, advantages and disadvantages of each treatment method are summarized in Table 2.1.

Table 2. 1 Summary of applications, advantages and disadvantages of plasma water treatment (Chang, 2001)

	Optical	**Electrohydraulic Discharge Plasma**				**Radiolysis**	
	UV-C	**GDE-dc**	**Barrier Discharge**	**Pulsed Corona**	**Pulsed Arc**	**Electron Beam**	**γ-Ray**
Efficiency against micro-organisms	Good	Less good	Less good	Good	Good	Less good	
Oxidation power	None	High	High	High	High	High	High
Removal of inorganic pollutants	None	Yes	Yes	Yes	Yes	Yes	Yes
Destruction of algae	Yes(relatively heavy doses)	No	No	Yes (relatively high power)	Yes	No	No
Destruction of urine Components (NH_3)	None	Partial	Partial	Good	Good	Good	Good
Destruction of phenols	None	Yes (partial)	Yes (partial)	Yes	Yes	Yes	Yes
Advantages	No modification of flavour, no bacteria resistant to it, relatively simple, cheap	Simple operation	Simple operation	Less power consumption	Purification of large volume water Less power consumption	Purification of large volume water	Purification of large volume allow for objects in water
Disadvantages	No oxidation or lasting effect; control difficult; efficiency dependent on amount of water pollution etc.	Reduce pressure operation, Control difficulty, Scale-up of reactor	Heat generations, Scale-up of reactor, Excess ozone generation	Excess ozone generations, Power supply, Power loss in matching, Scale-up of reactor	Power supply, Loss of electrode	Power supply, Radiation from window	Radiation protection, Radio isotope Costs, Control difficulty
Application	Drinking water (conditional); swimming pools[2]; Aquariums; cooling water; water supply spa water; brewery water; laboratory water	Industrial waste water	Industrial waste water	Industrial waste water, Water supply	Sewage water, Industrial waste water, Industrial water in take, Water supply	Industrial waste water	Sewage water, Water supply, Industrial waste water

2.2 Electrohydraulic Discharge Water Treatment

Liquid phase electrical discharge reactors have been recently studied in environmental applications (Locke et al., 2006). High voltage electrical discharges directly in water (electrohydraulic discharge) initiate both chemical and physical processes. Electrohydraulic discharge can be divided into three types based on the amount of energy deposited in the system: pulsed corona type system

(PCED) uses discharges around 1 J/pulse, while pulsed arc (PAED) and pulsed power (PPED) type systems uses discharges around 1 kJ/pulse and larger (Chang et al. 2007). The characteristics of the three different types of electrohydraulic discharges are compared in Table 2.2.

The pulsed corona system operates at 10^2 -10^3 Hz, with a charging voltage of 10^4 -10^6 V and a peak current at 10 -10^2 A. When the discharge occurs, a streamer-like corona is generated in water. Relatively weak pressure waves and UV radiation were observed. Radicals and reactive species form in the narrow region near the corona discharge electrodes. The pulsed arc system operates at a relatively low frequency (10^{-2} -10 Hz), with a charging voltage at 10^3 -10^4 V and a peak current at 10^3 -10^5 A. An arc channel generates strong shock waves within the cavitation zone, and the gas inside the bubbles is ionized. Strong UV emission and high radical density are observed to be short-lived inside the cavitation zone. The PPED system operates at a frequency of 10^{-3} -10^1 Hz with the peak current and a charging voltage in the range of 10^2 -10^5 A and 10^5 -10^7 V, respectively. The system generates strong shock waves and some moderate UV radiation.

During the electrohydraulic discharge process, hydrogen peroxide, molecular oxygen and hydrogen, hydroxyl, hydroperoxyl and other radicals are produced. UV and pressure waves might be formed depending on the solution conductivity and discharge energy. Potential applications of electrohydraulic discharge in environmental protection include degradation of a range of organic compounds, destruction and inactivation of viruses, yeast and bacteria.

Table 2. 2 Characteristics of two different types of electrohydraulic discharges (Chang et al., 2002)

Parameters	Pulsed corona	Pulsed arc	Pulsed power
Operating frequency	10^2 -10^3 Hz	10^{-2} -10 Hz	10^{-3} -10 Hz
Current (peak)	10 -10^2 A	10^3 -10^5 A	10^2 -10^5 A
Voltage (peak)	10^4 -10^6 V	10^3 -10^4 V	10^5 -10^7 V
Voltage rise	10^{-7} -10^{-9}s	10^{-5} -10^{-6}s	10^{-7} -10^{-9}s
Pressure wave generation	Weak to moderate	Strong	Strong
UV generation	Weak to moderate	Strong	Moderate

2.3 Pulsed Arc Electrohydraulic Discharge Water Treatment

The application of Pulsed Arc Electrohydraulic Discharge (PAED) has been investigated for several environmental applications in recent years, including drinking water and wastewater treatment. It injects energy directly into an aqueous solution through a plasma channel formed by a high-current/high voltage electrical discharge between two submersed electrodes (Chang et al., 2002). The process generates UV radiation, radical reactions, ionic and electronic reactions, thermal dissociation and strong pressure waves (Chang et al., 2002; Yamatake et al., 2007). A schematic of the proposed PAED water treatment is shown in Figure 2.3.1. The liquid-phase electrical discharge generates concurrent removal of chemical contaminant and inactivation of virus and bacteria (Sato et al. 1996; Chang et al., 2002; Lee et al., 2004; Zastawny et al., 2004; Vel Leitner et al., 2005; Angeloni et al., 2007; Locket et al., 2006, Boxman et al., 2007). This technology has also been used in dislodgement of mussels and removal and prevention of biofilms on cooling and water intake pipes (Lock et al., 2006; Chang et al., 1998).

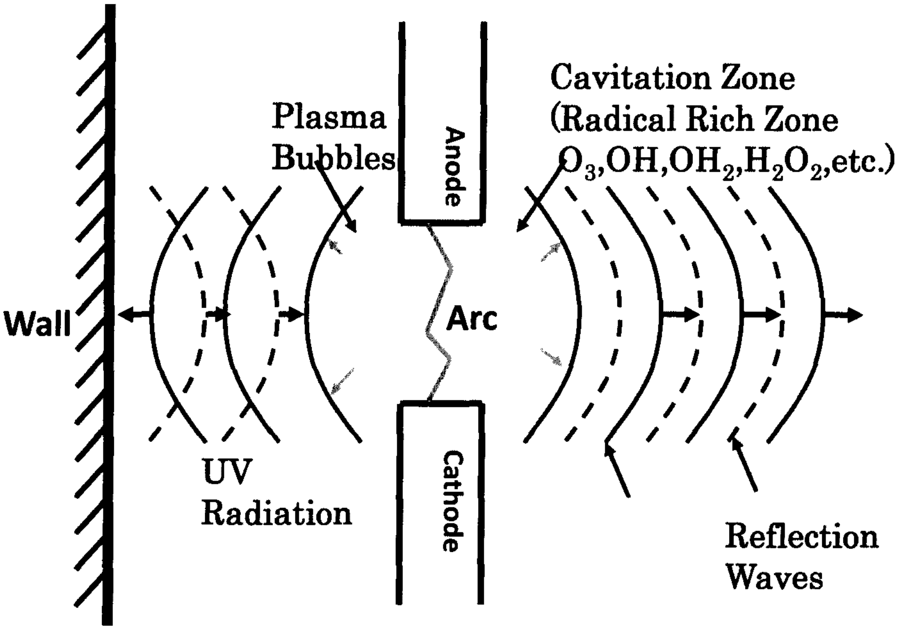


Figure 2.3. 1 Schematic of water treatment using PAED

The pulsed arc system operates at 10^{-2} to 10^{-3} Hz and the peak current is above 1 kA with a microsecond order voltage rise. The effects of the physical processes and the chemical reactions initiated by the discharge depends on the reactor and electrode configurations. Physical processes resulting from the discharge include the possible development of supercritical fluid conditions, and production of localized regions of high temperature and pressure, the formation of shock and pressure waves and emissions of UV light. The effects of UV radiation and shock waves generated by the high-energy electrohydraulic arc discharges reactors are effective for bacteria and virus inactivation. A 2-log reduction of *Escherichia coli* cells and *B.subtillis* with a charging voltage of 4 kV and arc gap distance of 0.5 mm within an hour was reported (Lee et al., 2009). Contaminants in liquid state can also be either degraded directly or indirectly by radicals generated by the discharge. Recent work has also demonstrated the destruction of organic compounds such as methyl tert-butyl ether (MTBE) (Angeloni et al., 2007) and atrazine by the electrohydraulic discharges (Vel Leitner et al., 2005).

The occurrence and strength of the physical and chemical processes are closely linked to various factors, including reactor design, electrode geometry, electrode materials, solution conductivity and compositions (Locket et al., 2006). For pulsed arc systems, a point-to-point electrode system has been used. Chang et al. (2002) conducted a preliminary test of water treatment using PAED. The discharges were generated by a spark gap type switch power supply (0.3kJ) with rod-to-rod type electrodes inside a cylindrical reactor filled with pure and tap water. The results showed a positive pressure wave (a shock wave) with a maximum of 500 - 600 kPa. Wall reflections keep generating oscillating pressure waveforms and the rise of the pressure wave was 5 to 10 x 10^{11} Pa/sec. This acoustic emission impulse was sufficient to cause mortality of most of the bacteria (Yelveron, 1981). Strong UV light and presence of OH and H radicals in the discharge arc zone were also observed by optical emission spectrum (Chang et al., 2002). The radicals also altered the pH of the solution. PAED treatment tests with trace ammonia compounds and phenol illustrated that the treated solution changed to acidic and alkaline pH values respectively; suggesting that pulsed-arc treatment could result in neutralized pH values.

A more detailed study of the UV emission generated by the electrohydraulic process was carried out by Chang et al. (2007). Optical spectrum was measured by an optical spectrometer accompanied by UV-A and UV-B dosemeters through an optical window placed below the location of the arc water gap. Results showed that H, OH and O radicals were evident, and the intensities of UV-A and UV-B emissions depended on both water gap and charging voltage. Generally, the UV intensity was higher with larger water arc, and UV-A intensity increased with increasing charging voltage while UV-B intensity decreased with increasing charging voltage. The emission of UV-C cannot be confirmed in the measurement locations, as it tends to attenuate in water.

The removal of MTBE was investigated in an experiment carried out by Angeloni et al. (2007) using a similar electrohydraulic discharge system as used in Chang et al. (2007). Over 99% removal was achieved when cumulative input energy exceeds 12 kWh/m^3, where the highest percentage of removal (60%) appeared at a cumulative input energy between 1.4 - 1.7 kWh/m^3. The removal efficacies were improved with increasing detention time and decreasing arc electrode gaps. Generation of radicals was observed after MTBE treatments. The same experimental setup was used to investigate microbial inactivation of *E.coli* and *B.subtillis* by the PAED treatment process (Lee et al., 2004). That research showed a 2-log reduction (99%) of both micro-organisms with a charging voltage of 4 kV and arc gap distance of 0.5 mm within an hour.

The generation of active entities and removal of atrazine was investigated by Vel Leitner et al. (2005). Maleic and furnaric acids were used to estimate the impact of UV photolysis. Conversions of approximately 35% of maleate and furnarate ions gave evidence of UV radiations during the PAED process. The conversion of nitrates to nitrites and hydroquinone to paraquinone confirmed the reductive and oxidative reactions respectively. In the second part, the above chemical processes (photolysis, oxidation and reduction) generated by PAED resulted in successful degradation of atrazine. The formation of Deetylatrazine (DEA), a by-product formed from atrazine decomposition, also confirmed the generation of OH radicals during the discharge process. Despite the small overall energy efficiency in removal of atrazine by PAED, the formation of DEA (a toxic compound) was much lower compared to the other existing advanced oxidation technologies. Also, the energy efficiency could be increased sharply (30%) by increasing the arc electrode gap distance. Both Chang et al. (2002) and Vel Leitner et al. (2005) have illustrated the degradation of phenol, ammonia and atrazine in PAED systems. The studies suggested that PAED first degraded the toxic organic compounds into organic acids, and the intermediates were further decomposed into CO_2. Hence, it is suggested that the mechanisms induced by PAED can mineralize various organic compounds.

Other studies have demonstrated the degradation of atrazine by PAED in combination of ferrous salts (Mededovic et al. 2007). Fenton reaction enhanced the degradation of organic compounds by acting as an additional source of OH radicals to supplement OH radicals from the discharge. In the electrical discharge treatment process with ferrous sulfate as electrolyte, atrazine was degraded firstly by Fenton's reaction followed by the hydroxyl radicals degradation generated by the discharge. It was shown that 90% of atrazine was degraded in 1 hour, and the degradation combining the PAED and Fenton reaction achieved the same removal efficiency within 10 minutes.

A combination of photo-catalytic reactions and UV irradiation arising from the discharge can result in further effective reduction of organic compounds. Ikeda et al. (2007) investigated the generation of potential photo-catalysts by employing Fe and Ti electrodes in PAED. Parts of the metal electrodes were vaporized and these species contributed to the active entities. Gravity filtration and cellulose filter paper were used to collect the fine particles after a treatment time of 30 minutes. When using iron electrodes, no iron oxide particles were observed from the process. The composition of the particles might be in the form of $Fe(OH_3)$. When using Ti electrodes, the particles generated by the PAED process had 170 nm of mean size and consisted of Titanium (II) oxide, TiO_2.

Anatase structured TiO_2 (which can act as photo-catalyst) was not observed at the current experimental condition.

The fundamental characteristics of the PAED system operated for the treatment of lake-water have been experimentally investigated by Li et al. (2010). The PAED discharge created pulsed arc plasma channels directly between two electrodes submerged inside water, and leads to the formations of intense UV irradiations, rich active radical chemical reactions and strong pressure waves for the concurrent removal of chemical contaminants, pathogens, bacteria and zooplanktons. In that work, preliminary PAED polluted lake water treatment is experimentally investigated and the mechanism of treatment are investigated. The results show that BOD and COD of the lake water were significantly improved.

Chang et al. (2009) reported that the maximum plasma density and electron temperature in a PAED pulse are in the order of 10^{19} to 10^{21} m^{-3} and 0.5 to 1.3 eV for lake water, respectively. Maximum plasma density and electron temperature increase with increasing charging voltage and conductivity. The magnitude of pressure intensity is in the order of 10^6 - 10^8 MPa/sec. The acoustic emission impulses range from 0.5 to 1.5 Pa•sec. The ionization fraction in plasma channels is estimated to be around 0.1 % and the temperature reaches around 10^4 K during the arc pulse discharge.

Experiments were also conducted to study the effect of PAED discharge for the mortality of *Daphnia* (Yantsis et al., 2008). The results show that exposure of zooplankton *Daphnia* to 10-minute PAED treatment resulted in 84.7% mortality (mean of 10 trials) immediately after treatment, and 96.9 to 100 % after an additional 24 to 48 hours. Treatments with a single pulse or 1 minute treatment yielded lower mortalities of around 90 % after 48-hour period, however, the energy cost is negligible (0.5 kJ per pulse per 3 L water) for a single pulse treatments.

PAED has the advantages of giving a multiple, concurrent treatment for micro-organisms, inorganic and organic pollutants. In addition, the process does not require other injection equipment (e.g. UV, Ozone). Also, previous research found that the energy requirement for PAED is approximately 50% less than other plasma technologies for equivalent treatment results (Lee et al., 2009).

Chapter 3: Thermal Plasma Treatment of Solid Wastes

The thermal plasma decontamination technology offers near-quantitative destruction of toxic organic and microbiological contaminants, immobilization of heavy metals, and vitrifies the noncombustible counter parts into glassy slags with a very low leaching rate (Chang et al., 1996; Chang et al., 2003; Chang et al., 2005; Chang et al., 2008; Copsey, 1009; Funfschilling et al., 1990; Haugsten et al., 2000; Kostic et al., 2000; Donaldson et al., 2001; Tzeng et al., 1998; Li, 2006; Jones et al., 2001; Jimbo et al., 1997; Ramachandran et al., 2002). The process might be able to provide treatment of the stormwater sediment with a wide variety of contaminants.

Research has been conducted to use thermal plasma in treating municipal waste (Chang et al., 2003), incineration fly ash (Chang et al., 2003; Chang et al., 2005; Haugsten et al., 2000; Jimbo et al., 1997), toxic medical waste (Kostic et al., 2000), radioactive waste (Donaldson et al., 1991; Tzeng et al., 1998), used tires (Chang et al., 1996), industrial waste (Copsey, 1990; Funfschillin et al., 1990; Ramachandran et al., 2002), electroplating sludge (Ramachandran et al., 2002), harbor sediment (Jones et al., 2001) and dried stormwater sediment (Chang et al., 2008; Li, 2006).

3.1 Thermal Plasma Decontamination of Ashes and Other Solid Wastes

In the past, thermal plasma treatment of municipal solid waste (MSW) achieved a large volume reduction and decontamination of the waste, and the production of reusable materials. The combustible materials in MSW (around 50%) are converted into a low calorific value fuel gas, and the non-combustible solids are melted down to unleachable slag. In the year of 1990, Resorption Canada Ltd. operated a thermal plasma treatment pilot plant in Gloucester for MSW treatment (Chang et al., 1997). The MSW were successfully converted into product gas and slag, and the volume reduction of wet MSW to slag was 183.5 : 1.

Ebara Infilco Company and the Tohoku University in Japan conducted a study the on treatment of MSW-incinerated residues with a 240 kW plasma torch (Jimbo et al., 1997). The solid by-product was separated into a slag layer and metallic components. The total power consumption was 700 kWh/tons with a feed rate of 180 kg/h of residuals. Swedish Company ScanArc Plasma Technologies AB also developed a thermal treatment process for municipal waste incineration fly ashes under different conditions, including pH, oxidation/reduction conditions, and granulation methods (Haugsten et al., 2000). Large variation in the composition of the slag was observed, with the main compositions consisting of SiO_2 and CaO. The leaching results of all slag satisfied the Dutch regulation for building materials with the exception of Sb, of which the concentration varied around the limit value. The leaching of Sb was within the limit with the addition of iron ore.

The plasma conversion process of Nuform Ltd. in Australia used a 150 kW blown arc torch to treat chlorophenolic waste at 5000 K. The waste was pyrolized and produced CO, H_2, HCl, H_2O and argon as gaseous products. Post-treatment methods for the hot gases included conversions of gaseous HCl to NaCl in a scrubber, flaring H_2 to produce H_2O, and complete combustion of CO to CO_2.

Another study compared the solid product detoxicity characteristics for two different thermal plasma processes for incinerator-plasma ash treatment (Chang et al., 2005). The treatment employed a 0.5 MW DC plasma torch and a 2 MW three-phase submerged arc type ash melting system with feed rates of 12 tons/day and 45 tons/day of fly ash, respectively. Although both systems achieved a volume reduction of one tenth of the waste and generated unleachable slag, the comparison indicated that plasma torch system produced less leachable slag with better iron confinement and has a higher efficiency. However, NO_x generation was a major disadvantage of the system.

High temperature profile in thermal plasma can completely decompose many hazardous and radioactive wastes. Indaho National Engineering Laboratory (INEL) has researched the efficacy of thermal plasma treatment for mixed and radioactive wastes in their early years (Donaldson et al., 1991). Immobilization of beta and gamma emitting radionuclides in low-level transuranic (TRU) showed promising results for the thermal plasma technology.

3.2 Thermal Plasma Decontamination of Sludge

Management of solid wastes dredged materials has encouraged the application of a decontamination technology followed by creation of a product suitable for beneficial uses (Jones et al., 2001) which can partially or completely defray the cost of decontamination and obviate the need for waste disposal (McLauglin, 1999). Westinghouse Plasma Vitrification Ltd. has successfully decontaminated dredged material and altered the final product from a good quality glass into a highly valued product (Jones et al., 2001). The project started from bench testing to the construction of a demonstration plant (75357 m^3/yr). A summary of the different phases of study are as follows:

Phase I bench testing characterized the dredged sediment from New York/New Jersey Harbor and converted them into a good quality glass. The harbor sediment consisted of a wide variety of contaminants, including heavy metals and toxic organic compounds from urban runoff. The treatment process provided nearly-complete destruction of organics and microbiological contaminants, immobilization of heavy metals, and converts the sediment into high quality glass materials. The addition of fluxing agents into harbor sediment controlled the viscosity and eased the formation of the fully vitreous product in

1250°C. The final product passed the Toxicity Characteristic Leaching Procedure (TCLP) for heavy metals by several orders of magnitude.

Phase II pilot plant study included pretreatment processes such as screening, dewatering and blending in addition to the plasma melting process. Off gas treatment consisted of removal of sulfur oxides and acid gases. Wastewater included dewatering from the sediment and rinse water in screening. Gaseous and wastewater emissions were characterized and both met the discharge requirements. In one of the tests, a total of 3980 kg of harbor sediment was converted to glass over 7.7 hours at an average rate of 533 kg/hr. Preliminary costs ranged from $ 0.09 to $ 0.12/kg for the integrated sediment treatment process without the consideration of the re-sale value of the end products.

Phase III testing converted the vitrified sediment to highly valued commercial architectural tile. Westinghouse collaborated with Futuristic Tile (a company currently producing vitreous tile from waste materials), and converted 1000 kg of sediment glass into 2200 kg of tiles. The resale value of this commercial product is much higher compared to other plasma decontamination end-products, including road aggregate or other building materials.

Although thermal plasma technology provides successful volume reduction, decontamination of a wide variety of waste and production of salable end-products, the gaseous emission and fly ashes generated from the treatment are still problematic. Relatively significant amounts of NO_x and HCl were reported in previous studies (Chang et al., 2008). Plasma torch operates under an air environment can thermally dissociate N_2 and O_2 into NO_x. For argon plasma treatment, previous study (Ara et al., 2005) indicated the generation of CO, NO, NO_2 increased with increasing plasma torch power, plasma density and operating temperature. Other toxic gaseous by-products such as HCl are produced when chlorinated compounds exist in the feed. Gaseous control devises for the post-treatment stream might be necessary.

Thermal plasma has been applied to the electroplating of sludge with high concentrations of heavy metals. Ramachandran et al. (2002) has focused on using plasma treatment to eliminate the heavy metal contents and to convert sludge into inert slag. DC transferred and non-transferred arc plasmas were used with various power inputs and plasma gas environments. The final products included slag with low leachability and fine metal-bearing particles that were refinable in a conventional metallurgical plant. The DC plasma demonstrated the best heavy metal elimination rate with an oxidation environment (N_2-O_2). However, the production of NO_x, SO_x and CO_2 were identified in this environment as well. The approaches, advantages and disadvantages of each thermal plasma treatment method mentioned above are summarized in Table 3.1.

Table 3. 1The approaches, advantages and disadvantages of thermal plasma treatments

Project	**Type of Solid/Sludge waste**	**Approaches**	**Advantage and disadvantage**	**Reference**
Resorption Canada Ltd. and Nuform Ltd.	MSW	Gasification/ Pyrolysis	Advantage: large volume reduction, Production of small amount of syngas Disadvantage: Production of CO and H_2	[Chang et al., 1996; Chang et al., 1997]
Ebara Infilca And Incineration ash melting system	MSW-incinerated residues	Volume reduction	Advantages: Melted material can be recycled as building material. Higher efficiency if using air plasma Disadvantage: Generate NOx, HCl and Hg if uses air as plasma gas	[Chang et al., 2005; Funfschilling et al., 1990]
ScanArc Plasma and Plasmox reactor	MSW incineration fly ashes	Oxidizing environment	Advantage: Slag can recycled as building materials Disadvantage: NOx generation	[Haugsten et al., 2000]

			by air plasma	
WestingHouse	Harbor sludge	Oxidizing and melting	Advantages: Production of high saleable tiles, which might possible cover the process cost Disadvantages: Feasibility of tile production is highly depended on specific sediment quality.	[McLaughlin, 1999]
McMaster University	Dried stormwater sediment	Oxidizing /reducing environment	Advantages: Less energy input for detoxification of sediment Disadvantage: No melting and formation of slag Production of NO_x, H_2S and SO_2 in air environment	[Chang et al., 2008; Li, 2006]

3.3 Thermal Plasma Treatment of Stormwater Sludge in Non-Transferred Mode

Chang et al. (2008) conducted a preliminary study of thermal plasma decontamination of stormwater sediment under non-transferred mode. Dried stormwater sludge was placed into a 99.8% pure alumina-made ceramic container, and the weights of each sludge sample were mostly in-between 20 to 30 g. Pure argon gas was used in the plasma torch, and air was injected through the anode in order to produce an oxidation environment. The mean weight percentage removal by argon plasma treatment using pure argon flow rate of 17.5 L/min and combined with 2 L/min of air flow rate mixture were approximately 3 and 4%, respectively. The treatment time period varied from 30 minutes to 2 hours. The maximum weight removal of 5.87% was achieved with air mixture and two hours of treatment time. After the treatment, the two-phase structure in the stormwater sludge was crystallized and only one structure (inorganic) was left in the sediment. The total organic carbon (TOC) percentage in the sample decreased with longer treatment time.

Eight gas compounds including CO, CO_2, NO, NO_2, NO_x, SO_2, H_2S and C_xH_y were emitted during the treatment process. Concentrations of NO, NO_2 and NO_x might be generated by nitrogen-compounds in the sample. The concentrations of CO, NO, NO_2, SO_2, CO_2 and C_xH_y were much higher in an oxidizing environment. The increased oxygen concentration in the chamber had a direct effect on the CO concentration (Ara et al., 2005). Most of the CO is formed by dissociation of CO_2 via negative ions or electrons. The increase in concentration of CO might be caused by the increased availability of CO_2 from the increased air flow rates (Chang et al., 1997; Beuthe et al., 1997).

The comparison of major (concentrations > 10000 ppm), minor (concentrations between 100 and 10000 ppm) and trace (concentrations < 100 ppm) compositions between treated and original sediment samples shows that the presence of major elements is similar to that of sediment prior to the treatment, but in different concentrations and enrichment. For major compositions, the concentrations of Mg, Cl and Na for the treatments with air flow rates of 2 and 0 L/min increased by 174 and 88%, 105 and 133%, and 83 and 61%, respectively; while the concentrations of K and Ca under the two different air flow rates decreased by 23 and 35%, and 12 and 2%, respectively. For minor compositions, the concentrations of Cr, Sr, Ba and Mn fluctuate between 10 - 50% while Zn decreases by 25 and 29% respectively with the presence and absence of air. Enrichments of trace elements are observed after the treatment, with the exception of As and Nd. A deviation between main concentrations of elements does occur under oxidizing and reducing environments. This can be explained by the fact that in the presence of oxygen the formation of binary or tertiary oxides greatly decreases the volatilization of metals (Reich, 2003). Two of the volatile metals, Zn and K, decreased in concentration after the treatment. Conversely, Na and Cl, also characterize as volatile elements, increased in concentration instead. According to the study, thermal plasma decontamination achieved the removal of TOC, and hence, the chemical and biological contaminants as well as volatile organics. However, gaseous by-products generated during the process require treatment before emission to the atmosphere.

Chapter 4: Sampling Procedures, Experimental Apparatus and Measurement Techniques

Basic information of the stormwater pond and sediment sampling procedures will be presented in Section 4.1, while Sections 4.2 and 4.3 will focus on the detailed experimental apparatus and procedures used in pulsed arc electrohydraulic discharge (PAED) sludge-water treatment and thermal plasma sludge treatment, respectively. Sections 4.4 through 4.6 give information on the measurement techniques employed in the two types of treatment experiments.

4.1 Sample Collection and Preparation

The sludge samples were collected from the Dartnell stormwater pond, located at the Dartnell Road Interchange of the Lincoln Alexander Parkway in the city of Hamilton, Ontario in June, 2006. In addition to portions of the highway, the pond services mainly commercial areas and the average imperviousness of the upstream area was estimated to be approximately 0.36. The surficial pond water was sampled by two 20 L plastic containers. Sediment samples from five different locations in the detention pond were obtained with the assistant of the West Central Region of the Ontario Ministry of Environment. Their field personnel (Mr. Brian Thorburn) did the sampling and their field procedures were followed. Surficial sediment (top 10 -15 cm) were collected with a steel scoop. The equipment was first washed with hexane in order to elute possible contaminants.

Five samples were taken at different locations within the pond. The samples were sealed in a 10 L plastic container and were kept at 10 - 15 °C before analyses.

The sample preparation for PAED and thermal plasma treatments is shown in Figure 4.1. Sediment was dredged at the bottom of the stormwater pond, thus the samples contained both pond bottom water and solid sediment. The solid and liquid portions were separated by sedimentation, where the solid portion is referred to as **sediment** (particle size ranges from 0.1 to 1000 μm) and the liquid portion is referred to as **pond bottom water**. The sediment was further separated by screening using a filter with 208 μm opening. The filtrate is referred to as **sludge-water** (with particle size < 208 μm) and the residue is referred to as **sludge** (with particle size > 208 μm). Surficial pond water is referred to as **pond surface water**. PAED experimental works were carried out for pond surface water, pond bottom water with various additions of sediment (0 – 266 g/L) and sludge-water. After the PAED treatment of sludge-water, the solid part (referred as **PAED treated sludge**) was separated by sedimentation and dried. Thermal plasma treatment was carried out for wet sludge (original sludge from stormwater pond) and PAED treated sludge.

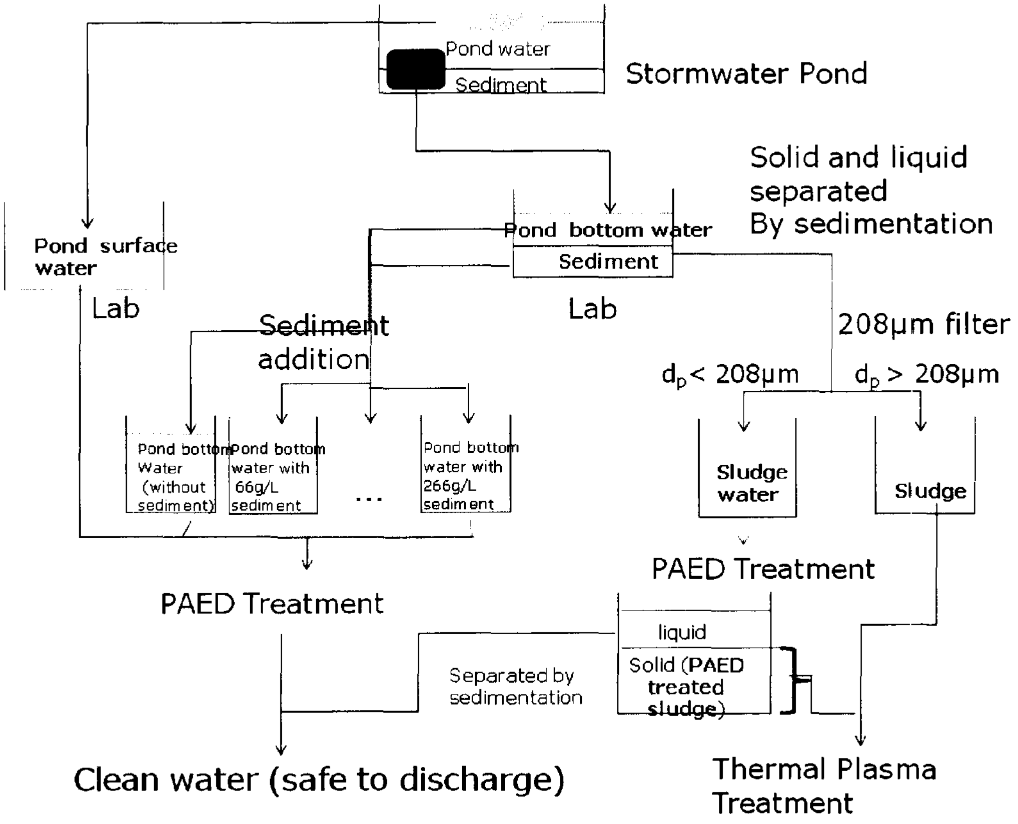


Figure 4. 1 Preparation of solid and water samples from samples collected in the field

4.2 Pulsed Arc Electrohydraulic Discharge Experimental Apparatus and Procedures

The PAED system consisted of a spark-gap switch type power supply (0.5 kJ) (Chang et al. 2002) and a 3L stainless steel reactor with eccentrically configured 5mm o.d. rod-to-rod titanium electrodes. The sample water was injected from the top of the PAED reactor and filled to the top. Then, the water gap distance was adjusted by a micro-meter with an electrical insulation elastic holder. The charging voltage was controlled by the air gap distance in pulsed power supply, and the current and voltage waveforms were measured directly from the current shunt in pulsed power supply and by secondary side voltage output via high voltage probe respectively. The corresponding pressure waveforms were taken simultaneously by a four-channel oscilloscope. The reactor was supported by an electrical insulating wood stand, and it was covered fully with an electrically insulating plastic chamber during operations. The schematic of the experimental set-up and reactor layout are shown in Figures 4.2.1 and 4.2.2, respectively. Quartz windows located vertically above the discharge were used during the measurement of UV-dosage and optical emissions. UV-A and UV-B dosages were averaged from 10-20 discharges for each charging voltage and water gap distance. Water was sampled for water quality analysis via a liquid sampling pipe. A 1 L glass sampling chamber was attached to the top of the reactor and used to collect the gaseous by-products during PAED treatment. The sampling valve was opened during gaseous by-product analyses.

Fundamental characteristics (voltage, current, pressure) were recorded by a digital oscilloscope (Tektronix, TDS 3014B) for each liquid solution for various sediment concentrations. Pressure waveforms were observed at 2 different reactor inner wall locations (Pb and Ps) simultaneously using Piezo-electric pressure transducers (Columbia Research Laboratories, Model 4103). Generations of UV-A,UV-B and radicals by the discharge in each sludge-water condition were observed by UV-A and UV-B dosimeters (Cole-Parmer Instrument Co., Series 9811), and optical emission spectrum, respectively. An optical fiber/PC computer-based optical spectrometer (Ocean Optics Inst. Co. 200-800nm) was used to measure the optical emission spectrum time dependant emission for specific wavelength (strip chart mode) through the Quartz window. For each optical emission spectrum and strip chart analysis, the corresponding voltage and current waveforms were recorded. Water quality including pH, total dissolved solids (TDS), dissolved oxygen (DO), salinity, conductivity and temperature were recorded by a multi-parameter water quality monitoring device (Horiba U-21 ex) and the TOC was measured by digestion method (Hach Co., TOC reagent set, middle range) . Gaseous by-products were collected by a 1 L glass sampling chamber above the PAED reactor and were measured by the combustion gas analyzer (Eurotron Greenline 8000, O_2, CO, CO_2, NO, NO_2, H_2S, SO_2 and C_xH_y concentrations). Table 4.1 shows the detection limit and accuracy of the various measurement techniques.

Table 4.1 Detection limit and accuracy of water quality and gaseous emission measurements

Parameters	Detection range	accuracy
pH	0 – 14	±0.1
Conductivity (mS/m)	0 – 100	±3%
Turbidity (NTU)	0 – 800	±5%
Dissolved oxygen mg/L	0 - 19.9	±0.2
Salinity %	0 – 4	±0.3
Total Dissolved Solid g/L	0 -99	±0.5
T°C	0 - 50	±1
TOC mg/L	15 -500	±6
CO ppm	0 - 20000	±10
CO_2%	0 – 20	±0.3
NO ppm	0 - 4000	±5
NO_2 ppm	0 – 1000	±5
SO_2 ppm	0 – 4000	±5
H_2S ppm	0 – 1000	±5
C_xH_y ppm	0 – 2000	±4
O_2%	0 - 25	±0.1

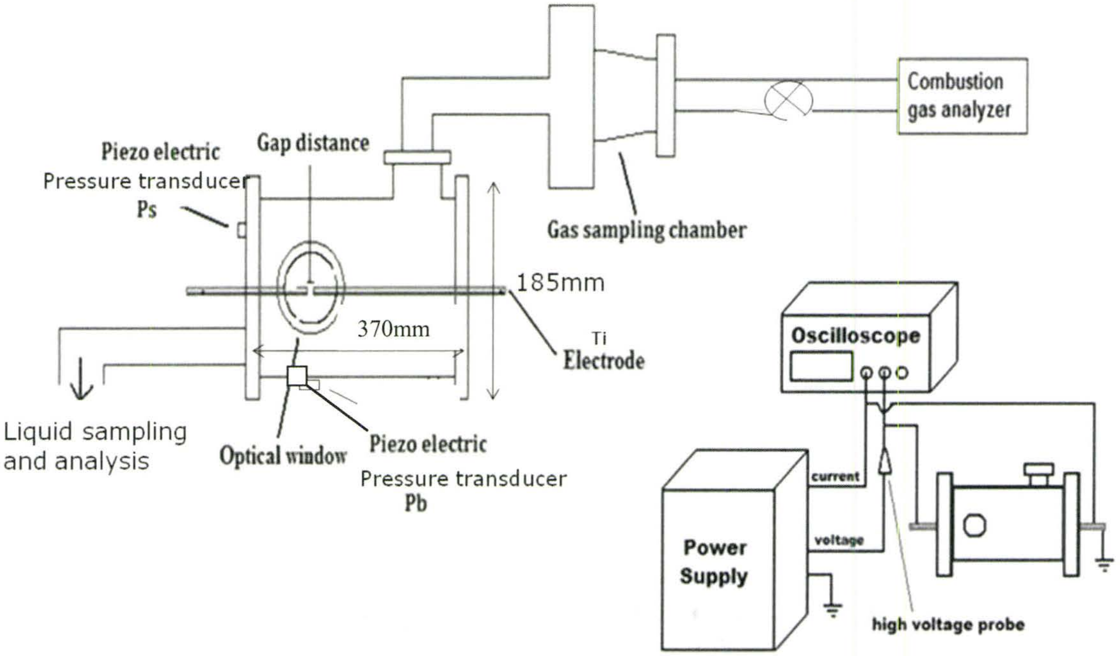


Figure 4.2. 1 Schematic of PAED experimental set-up

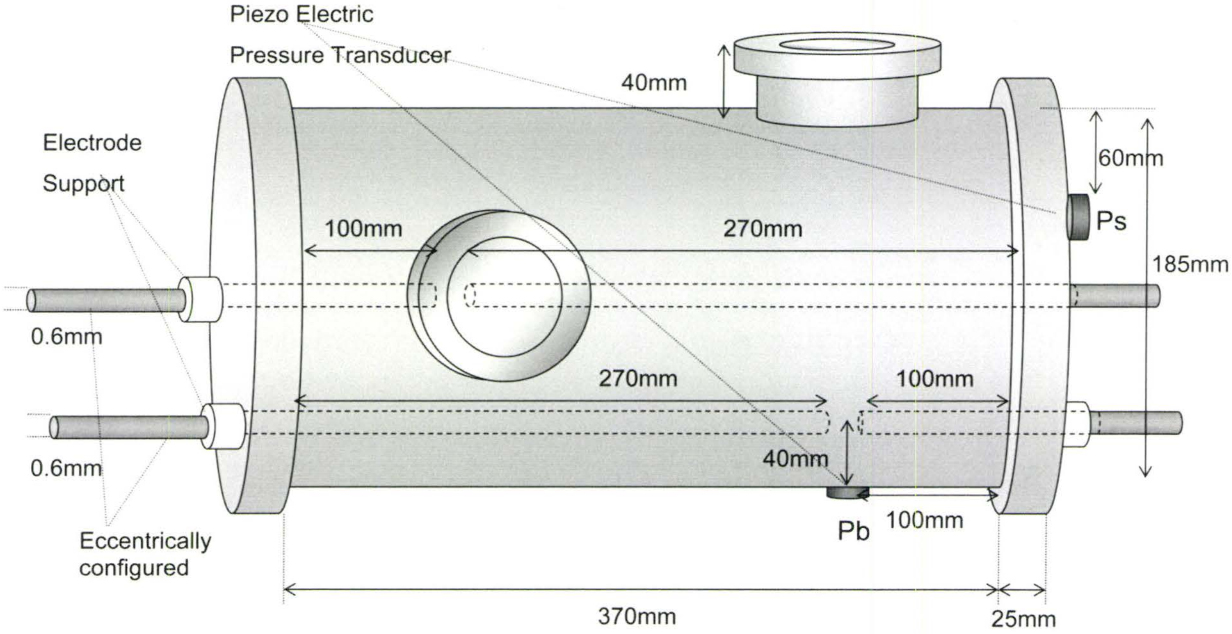


Figure 4.2. 2 Details of the PAED reactor

4.3 Thermal Plasma Experimental Apparatus and Measurement Techniques

A schematic of the plasma torch type sludge treatment system under partial transferred mode is shown in Figure 4.3.1. Figures 4.3.2(a) and (b) show the ceramic made plasma reactor used for non-transferred and partial transferred operation modes, respectively. Both reactors were composed of 99.8% pure alumina with 11.5 cm i.d.. The depths of non-transferred and partial transferred mode reactors are 2.5 and 12 cm respectively. The partial transferred plasma reactor is attached to a ground electrode at the reactor's bottom. This electrode arrangement enhances the heat transfer from the plasma to sludge. Wet stormwater sludge was placed inside the reactor and was treated in both oxidization and reduction atmospheres. A DC 10 kW plasma torch was placed vertically above the ceramic reactor and the environmental chamber (Beuthe et al., 1997). Pure argon gas (99.995%) was used as the plasma gas, and air was injected through environmental chamber (close to the exit of plasma torch) in order to produce an oxidation environment. A constant-voltage power supply, in series with a resistor bank, was used to control the power to the plasma torch. The efficiency of the treatment varied with argon flow rate, air flow rate, power input and the distance between the plasma torch and the ceramic reactor. A k-type thermocouple was placed on the top right hand corner of the ceramic reactor (approximately 2 cm away vertically, and 3 cm away horizontally, of the exit of the plasma torch) to measure the near reactor gas temperature.

Blank test studies of thermal plasma treatment (without sludge treatment) were conducted before sludge decontamination experiments. Stable thermal plasma operation was obtained with argon flow rate between 24 - 35 L/min, where an optimum near reactor gas temperature was observed with an argon flow rate of 24 L/min. A fixed voltage of 120 V was applied to the plasma torch. Current was controlled by a resistor bank and adjusted between 0 – 86 A (Appendix 3). In partial transferred mode, small parts of current (2 - 5 A) flowed through the ground electrode via sludge. Air flow rates to the environmental chamber were adjusted to 0 - 20 % of the fixed argon flow rate of 24 L/min, which was correspondingly 0 - 4.8 L/min. Wet stormwater sludge of 30 - 40 grams and dried PAED treated sludge of 10 grams were treated by thermal plasmas.

A non-thermal plasma reactor was proposed as a post treatment for gaseous pollution control. However, this technology was not investigated in this study, as it has been thoroughly studied elsewhere already (Kanazawa et al., 1997; Urashima et al., 1998; Urashima and Chang, 2000). A zeolite pellet packed bed toxic gas adsorption system was used as a safety device of flue gases before exhaust.

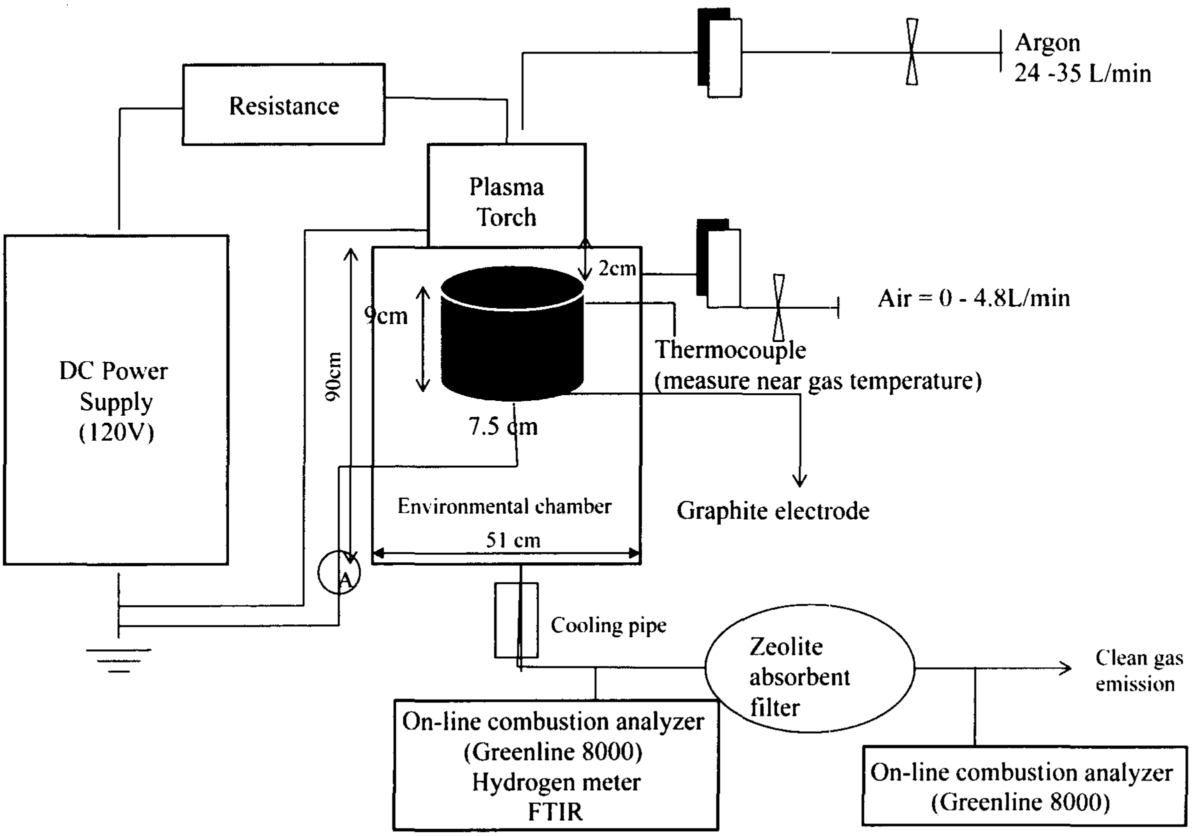


Figure 4.3. 1 Schematic of thermal plasma sludge treatment

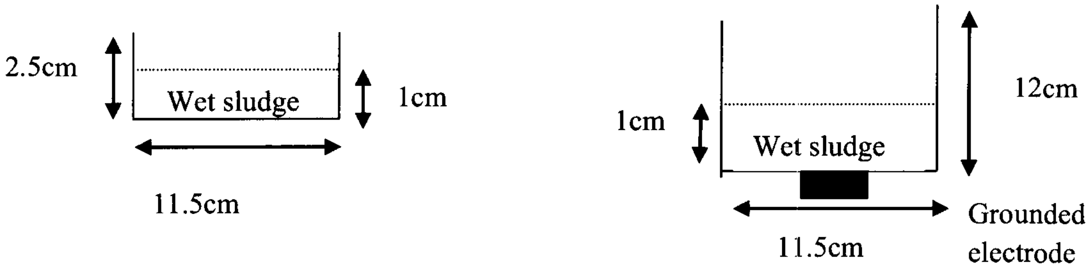


Figure 4.3. 2 (a) Ceramic plasma reactor for non-transferred mode placed 2cm away from the torch, and (b) Ceramic plasma reactor with graphite electrode at the bottom for transferred mode and placed 2cm away from the torch

4.4 Gaseous By-Products Analyses

In the gaseous by-product analyses, the generated gases were measured on-line by a combustion gas analyzer (Eurotron Inc., GreenLine 8000), hydrogen meter (Beacon 200) and by a Fourier transfer infra-red (FTIR) after gas sampling. Concentrations of O_2, CO, NO, NO_2, SO_2, C_xH_y and H_2S were measured by electrochemical sensors, while concentrations of CO_2 and C_xH_y were measured by an infra-red sensor in the Greenline 8000 combustion gas analyzer. Chemical bonds and chemical structures of the gaseous by-products were determined by FTIR. Another combustion gas analyzer (Greenline 6000) was used to ensure clean gas emission after the zeolite absorption chamber.

4.5 Solid Product Analyses

For the solid products, their weights and TOC percentages were measured by the weight difference and TOC percentage difference between sediment loaded and the treated residue, respectively. Neutron activation analysis (NAA) and X-ray energy dispersion microanalysis were carried out on the original and treated sludge for elemental compositions. X-ray diffraction (XRD) was used to detect crystalline structures in the original and treated sludge. Scanning electron microscope (SEM) images were taken to analyze the nature of the original sludge, and structural changes in sludge after plasma treatment.

4.5.1 Neutron Activation Analysis

Sludge was naturally dried at room temperature under a fume hood and stored in a 10 g container for NAA analysis. The samples were irradiated in the core of the nuclear reactor. Figure 4.5.1 shows the principle of NAA. Neutrons are injected into a sample and interact with a target nucleus by a non-elastic collision, a compound nuclei are formed in a highly excited state. The excited nuclei emit nuclear particles or prompt gamma rays and undergo a rapid de-excitation to a more stable configuration, typically within 10 - 14 seconds. The new nuclei are radioactive and will further de-excite by emitting decay gamma rays with a specific energy depending upon each composition and element. The NAA relies on the measurement of either the characteristic prompt or decay gamma rays for identifying elements and determining their amounts present in samples. The technique is flexible with respect to decay time for different nuclei. Elements can be separated into two categories: long-lived and short-lived. Nuclei that take more than 10 hours to decay are called long-lived elements and the given reaction time would be longer. Nuclei that take shorter than a few hours to half decay are called short-lived. Long-lived nuclides are difficult to excite, therefore the irradiation time should be long enough. The delay time of long-lived elements is approximately one week. On the other hand, easily excited nuclides have a short half-life and therefore the cooling and counting times are less.

The standard reference material (SRM) was used for the calibration of intensity and the evaluation of techniques employed in the analysis of coal and similar materials. The standards for the sludge are SRM 1632b and 1633b. SRM 1632b consists of a 50 g bottle of bituminous coal with a nominal sulfur content of 1.9%. A unit of SRM 1633b consists of 75 g of the same powdered material. The total error in each standard was calculated to be slightly less than 1 percent at the 95% confidence level. Elements measured as below the detection limit indicate their existence but with unknown concentrations. The expected major components of the sludge that could not be measured by present NAA system are Si, C, N, O, Cu, Pb and H. Most of these elements are difficult to be excited by nuclei. Special techniques and handling combined with current NAA system are necessary for measuring these elements. A list of detection limit of NAA is shown in Appendix G.

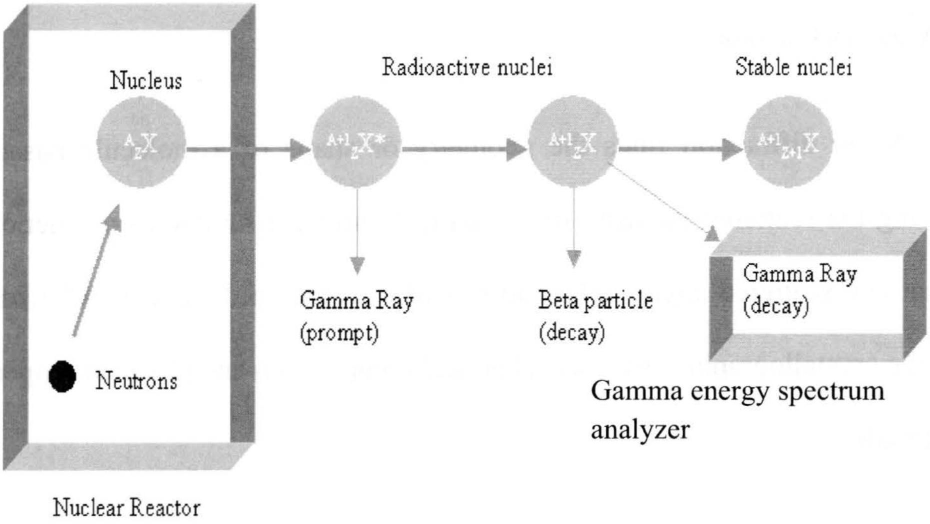


Figure 4.5. 1 Principle of Neutron Activation Analysis

4.5.2 X-ray Energy Dispersion Microanalysis

The process of X-ray energy dispersion microanalysis is shown schematically in Figure 4.5.2. Electron from the scanning electron microscope ejects an electron from an inner shell of a sample atom. The resulting vacancy is filled by an electron from a higher-energy shell in the atom. Energy is emitted in the form of electromagnetic radiation when electron dropped to a lower energy state. Since the energy difference is fairly large for inner shells, the radiation appears as X-rays. This energy is exactly equal to the energy difference between the two electronic levels involved.

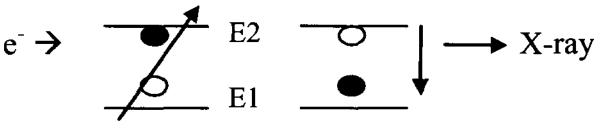


Figure 4.5. 2 Schematic of X-ray microanalysis

4.5.3 X-ray Diffraction

X-ray diffraction finds the geometry or shape of a molecule based on observing the scattered intensity of an X-ray beam by a sample as a function of incident and scattered angle, polarization and wavelength. It reveals information about the crystallographic structure, chemical composition and physical properties of materials.

4.5.4 Scanning Electron Microscope

The Scanning Electron Microscope (SEM) is a microscope that uses electrons to form an image. Based on the conductivity of the sample, it produces images of high resolution and high magnification of the sample. The electron source is located at the top. The electron beam comes from a filament, made of various types of materials. When the electron beam hits the sample, it produces secondary electrons. These electrons are collected by a backscatter detector, then converted to a voltage and amplified. For standard SEM imaging, the back-scattered electrons (BSE) and secondary electrons are detected, and the resulting signal is processed to yield a pixel in an image. Progressively, as the entire sample is scanned, an image of the sample is formed. The resulting image can be saved and reprocessed in the same way that a grey scale image is modified by image analysis.

4.6 Water Quality Analyses

Transient TOC in stormwater were recorded as a function of treatment time (from 0 to 120 min). The TOC was measured by the digestion method (Walkley, 1947). The digestion method involves the oxidation of carbon to carbon dioxide by persulfate. Carbon dioxide dissolves into a colored pH indicator solution and converts to carbonic acid. The resulting color change is directly proportional to the carbon concentration. Water quality including pH, total dissolved solids (TDS), dissolved oxygen (DO), salinity, conductivity and temperature were measured by a multi-parameter water quality monitoring device during the PAED treatment.

Chapter 5: Pulsed Arc Electrohydraulic Discharge Treatment of Sludge-Water

5.1 Pulsed Arc Electrohydraulic Discharge Water for Inactivation and Mortality

Preliminary laboratory work with similar experimental set-up as used by Yamatake et al. (2007) and Ikeda et al. (2007) has been conducted for PAED treatment of sludge-water. An initial study of the fundamental characteristics was done as a part of this preliminary work and the results showed that the PAED system can operate in a wide range of sludge-water concentrations (Li et al., 2007). In that initial study, the stormwater sludge was injected to the reactor filled with tap water with increasing sludge concentrations from 0 to133.3 g/L. The pH and conductivity of tap water used for the test range were between 6.6 and 7.1, and between 230 and 400 µs/cm, respectively. The discharge waveforms observed were similar to the waveforms obtained with pure tap water (sludge = 0 g/L) treatment (Yamatake et al., 2007). When charging high voltage was applied to the arc electrode by the power supply, the conduction current was relatively small (0.4 - 0.8 kA), and the discharging voltage decreased very slightly. Applied voltage reduced to approximately 0 when pulsed current was initiated around 250 µsec. An arc was initiated after the discharge channel was boiled and formed gas phase bubbles. The arc discharge ended within several hundreds of microseconds. The maximum current for various sludge-water concentrations was relatively similar; however, the maximum power in tap water was slightly higher. Both the maximum current and power increase with increasing charging voltage (V_{ch}) and decreasing electrode gap distance (d). The net resistance became larger with wider electrode gaps, and might result in a smaller maximum current.

All maximum pressures measured at different locations increase with increasing charging voltages. The locations of PT_1, PT_2 and PT_3 are placed below eccentric arc gap wall, in the reactor side flange and the opposite side of the reactor, respectively. As PT_1 located the closest to the discharge arc, without reflections it is expected to have the largest pressure. PT_2 is located at the side flange and farthest to the discharge arc, the measured pressure was several times smaller than at PT_1 and PT_3 due to propagation attenuation and wall reflections. The pressure wave's attenuation time was around 1000 μsec. The sharp change of pressure waves is efficient to inactivate bacteria, pathogen and viruses (Yelverton, 1981; Lee et al., 2009).

Yantsis et al. (2008) used the same experimental set-up of the current PAED study for zooplankton mortality in water. The zooplankton species used was Daphnia magna (1.5 to 2.5 mm; mean length of 1.81 mm). Experiments were conducted with pulse charging voltages from 2.3 to 3.8 kV, PAED electrode gap distances from 0.5 to 1.5 mm, and plankton concentrations from 10 to 100 animals/L. Exposure of zooplankton to 10-minute PAED treatment resulted in 84.7% mortality (mean of 10 trials) immediately after treatment, and 96.9 to 100 % after waiting for an additional 24 to 48 hours. Treatments with a single pulse or 1 minute PAED yielded lower mortalities. It is observed that the current PAED system achieved a maximum pressure magnitude and pressure rise of 3 MPa and 0.3 Pa·sec respectively. Yelverton (1981) shows that the mortality of plankton was related to body mass (g) and pressure impulse (Pa·sec). The PAED system provided effective pressure impulse for Daphnia mortality with body masses below a few mg (Yantsis et al., 2008).

5.2 Discharge Characteristics and Plasma Parameters for Pond Water

The fundamental characteristics including voltage, current, power and pressure waveforms were measured during the discharge period for the treatment of pond surface water, pond bottom water with various sediment additions (0 to 266 g/L) and sludge-water. The waveforms were fundamentally similar between pond bottom water and sludge-water, but were different from pond surface water. For pond surface water, the conductivity (22 mS/m) is one order of magnitude smaller than pond bottom water (237 mS/m) and sludge-water (637 mS/m). The voltage current and power waveforms in pond bottom water with sediment additions (with conductivity ranging from 237 to 254 mS/m) were similar to sludge-water as well. Figures 5.2.1 and 5.2.2 show the typical voltage, current and power waveforms of sludge-water and pond surface water, respectively. For sludge-water with relatively higher conductivity, a double arc discharges were generated in sludge-water. In stage I, Joule heating started and small conducting current was flowing between electrodes. When the Joule heated water formed a gas-phase from nucleate boiling, the micro-gap spark discharge was initiated at the edge of both electrodes to gas-liquid interface in stage II. Since the sludge-water has a relatively higher conductivity, the conductive liquid solution acting as a liquid electrode, and a partial arc discharge was initiated. After the discharge is terminated, however, the charging voltage continued since the void is not bridged. Joule heating and conducting current further expanded void and initiated another discharge after the void was bridged in stage III. The spark discharge was initiated again in stage IV, and with the external heating source and plasma bubbles from the previous discharges. These rapid expansion of void and discharge generated heat and pressure waves. The main arc discharge formed successfully in stage V while the charging voltage dropped to zero as all the electrical energy were transferred to the sludge-water. The discharge ended when both the current and voltage dropped to zero completely in stage VI and finally generating condensation shock waves when void is collapse suddenly (Chang et al., 2009; Li et al., 2009).

For pond surface water with lower conductivity, only one main discharge was generated as shown in figure 5.2.2. Joule heating started and small conducting current was flowing between electrodes in stage I_a. When the Joule heated water formed a gas-phase after nucleate boiling, the spark discharge was initiated at the edge of both electrodes and void (micro-gap) in stage II_a, and further developed into arc discharge in stage III_a. The charging voltage dropped to zero gradually in stage II_a, and the discharge ended when the current also dropped to zero in stage IV_a. This discharge waveform is very similar to the waveform observed in tap water with similar conductivity (Li et al., 2007). The results imply that the discharge waveform is highly dependent on the solution conductivity.

The power waveforms are calculated based on the multiple of current and voltage. The waveforms were thus different between sludge-water and pond surface water. The maximum current and power in sludge-water and pond surface water were 59 kA and 52 MW, and 45 kA and 54 MW respectively. It should be noted that the charging voltages in sludge-water (0.6 to 1 kV) were smaller compared to pond surface water (2 to 3 kV). Due to the low conductivity, a charging voltage below 1.7 kV in pond surface water was unable to initiate a discharge. The maximum current and power of pond surface water were in similar orders of magnitude of sludge-water with lower charging voltage. Longer discharge duration was observed in sludge-water as compared to pond surface water. The discharge ended at 400 and 300 μs in sludge-water and pond surface water respectively. Despite a longer discharge duration which occurred in sludge-water, the self-organized pulse discharge repetitions rate was slightly higher as compared to pond surface water. The self-organized pulse discharge repetition rate was 0.25 and 0.17 Hz in sludge-water and pond surface water respectively for above condition, and it increases with increasing charging voltage. The relatively high conductivity in sludge-water might act as the conductive liquid solution and enhances the discharge process.

The order of magnitude of time and discharge channel averaged plasma parameters such as electric field, electron temperature and plasma density can be estimated from discharge current-voltage characteristics. The transient discharge-channel averaged plasma density is evaluated by $Ne = I/(e\mu E_Z A)$, where Ne, I, e, μ, E_Z and A are plasma density [ions / m^3], current [A], elementary charge [C], mobility of electron [m^2/ v.s], electric field [V / m] and surface area [m^2], respectively (Chang et al., 2008). Based on the optical emission spectrum, a significant amount of hydrogen gas was generated in the plasma channel. Thus, the mobility of electrons data of hydrogen gas (obtained by Swarm parameter, (Huxley and Crompton, 1994) were used to calculate the averaged plasma density in the above equation. The approximation of electron temperature based on Einstein correlation $kT_e/e = \mu/D_e$ can be determined by Swarm parameter as well (Kawn & Chang, 1999, Chang et al., 2008), where k, T_e, e, μ, D_e are Boltzmann constant, electron temperature [eV], elementary charge [C], mobility of electron [m^2/ v.s] and diffusion coefficient [m^2/ s]. The discharge channel averaged maximum plasma density and electron temperature were in the order of 10^{21} to 10^{23} ions per m^3 and 0.3 to 3 eV, respectively, for various solutions with 1 to 2 kV charging voltages.

The maximum plasma density and electron temperature increased with increasing charging voltage and sludge fraction, as shown in Figures 5.2.3 and 5.2.4 respectively. The conductivity slightly increased with increasing sediment fractions in pond bottom water. As shown in Figure 5.2.5, the two parameters were also highly dependent on the conductivity of the liquid solution. Maximum plasma density and electron temperature slightly increased in relatively low range of conductivities (20 to 200 mS/m), but increased one order of magnitude when conductivity rises to 600 mS/m. The input energy density for power supply in PAED treatment with 0.2 Hz reputation rate and a 0.5 kJ pulsed power is 0.12 kWh/m^3. The power supply efficiency needed detail analyses of power waveform in the future.

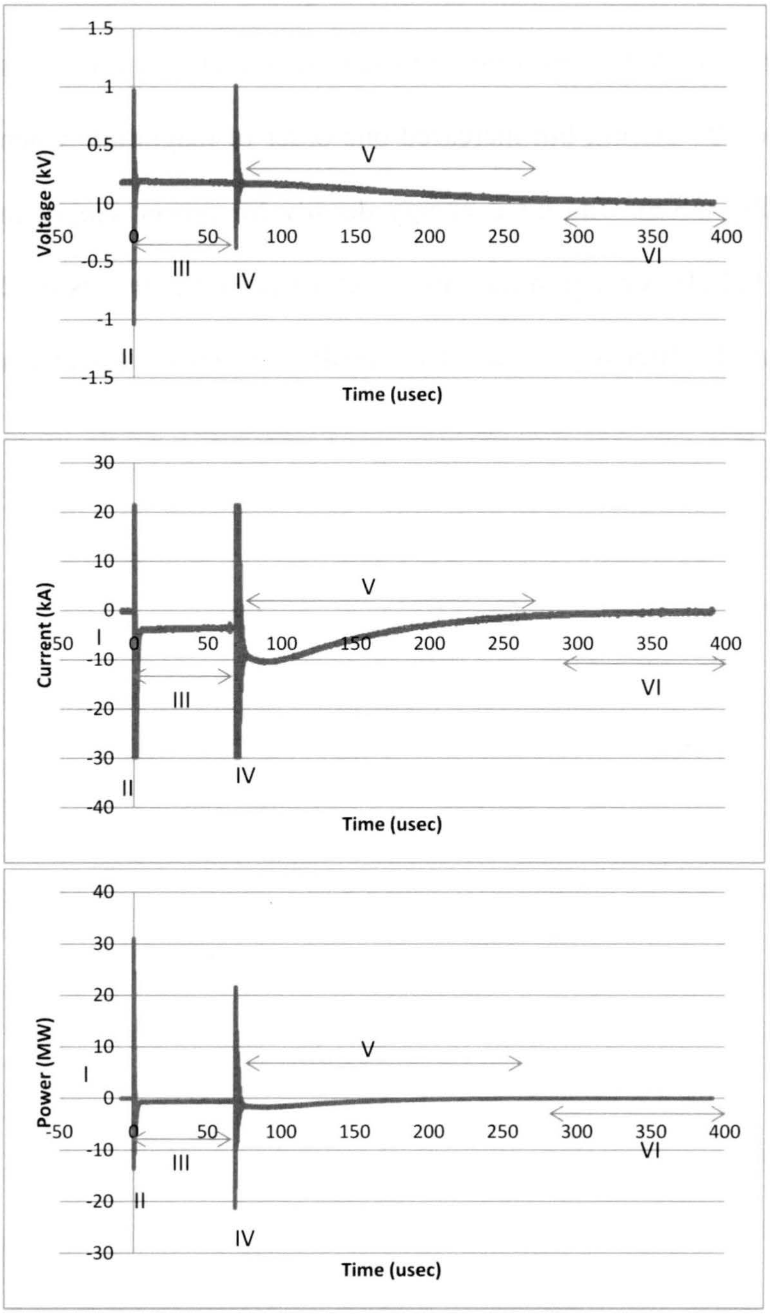


Figure 5.2. 1 Typical voltage, current and power waveforms for sludge-water (V_{ch} = 1 kV and d = 0.5 mm)

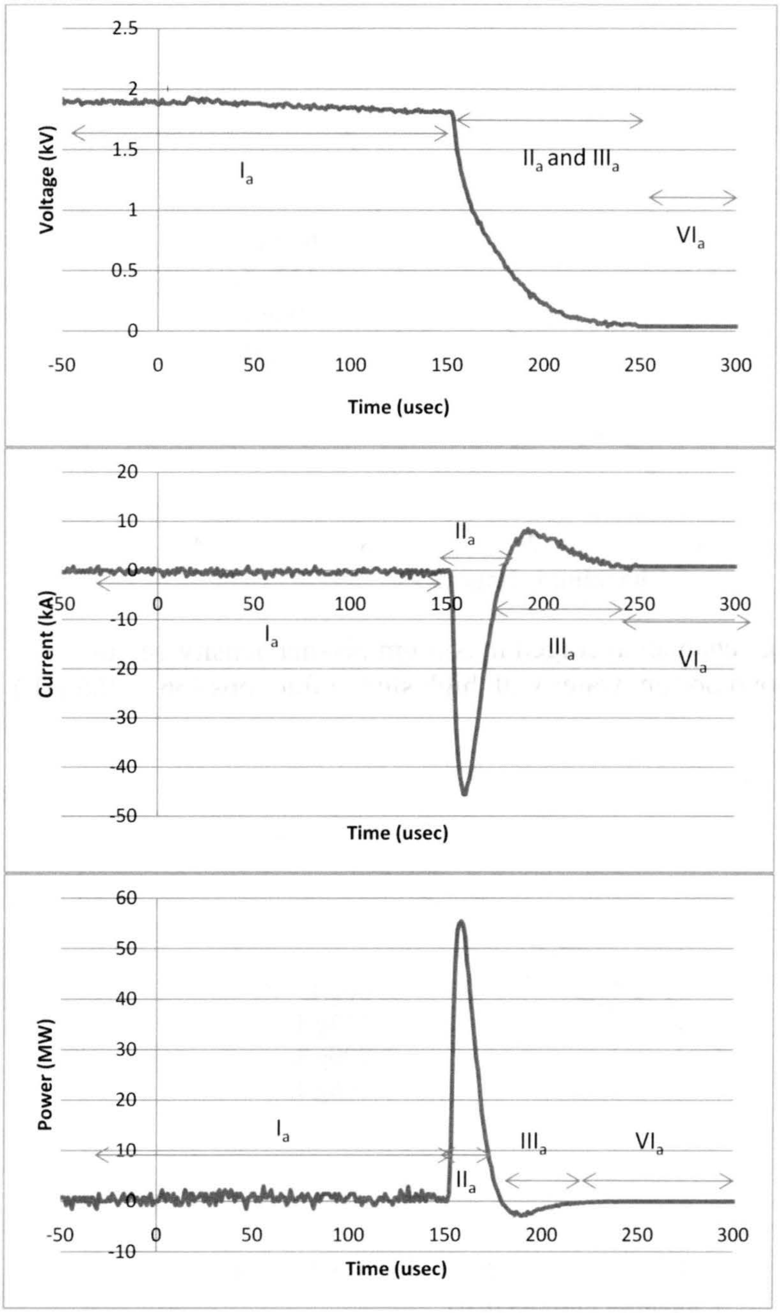


Figure 5.2. 2 Typical voltage, current and power waveforms for pond surface water ($V_{ch} = 2kV$ and d = 0.5mm)

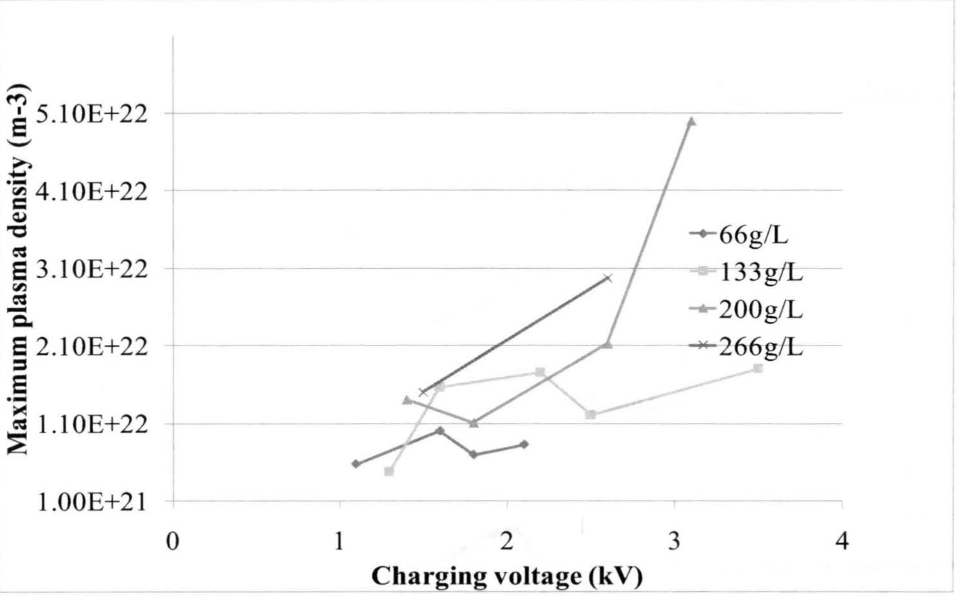


Figure 5.2. 3 Discharge channel averaged maximum plasma density versus charging voltage in pond bottom water with high sludge fractions (66 - 266 g/L)

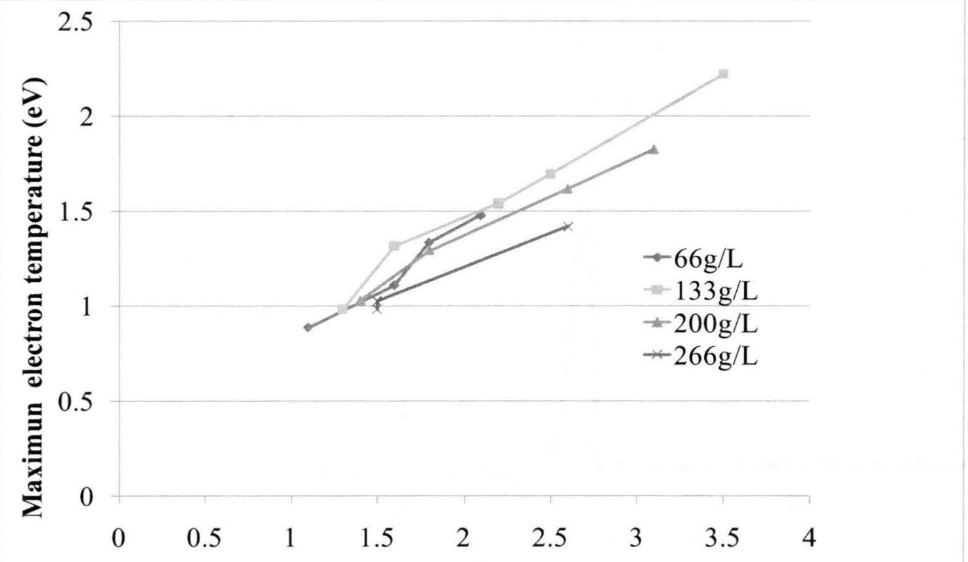


Figure 5.2. 4 Discharge channel averaged maximum electron temperature versus charging voltage in pond bottom water with high sludge fractions (66 - 266 g/L)

Typical pressure waveforms for sludge-water and pond surface water are shown in Figures 5.2.6 and 5.2.7 respectively. Despite differences in discharge waveforms, the pressure waveforms showed similarity in both waveforms and magnitude in all experiments. Figure 5.2.7 illustrates a detailed analysis of a typical pressure waveform observed at 4 cm (Pb) and 13 cm (Ps) from water arc gap corresponding to a charging voltage of 0.6 kV in sludge-water. During the first discharge initiated at t = 0 μsec, an electromagnetic pulse (EMP) with a magnitude of 4 MPa and 0.1 MPa in Pb and Ps were generated due to a sudden rise of large pulse current during the short pulse operation, i.e. $P_{EMP} = \underline{D}\bullet\underline{E} + \underline{B}\bullet\underline{H}$, where $\underline{D}$, $\underline{E}$, $\underline{B}$ and $\underline{H}$ are dielectric flux density, electric field, magnetic field and magnetic flux density respectively (Yamatake et al., 2007, Li et al., 2008). Small fluctuation of pressure was observed after the 1st discharge. The result indicates that the discharge did not fully transfer to a main arc, and the void was still growing after the boiling of the gas phase (as discussed in V and I waveform). A second EMP occurred during the second discharge at 97 μsec, and following a positive pressure wave P_s (shock wave) and then the negative pressure wave P_e (expansion wave). The magnitude of second EMP in Pb and Ps were 0.4 and 0.1 MPa respectively, and was slightly lower than the first EMP. A shock wave with a 1 and 0.1 MPa maximum were observed at Pb and Ps after the pressure wave reached sensors at 121 and 202 μsec respectively. The corresponding travel time of pressure wave generated by the expansion of arc channel in the gas-phase during the discharge period for Pb and Ps (4 and 13 cm away from the discharge) were approximately 20 and 90 μsec respectively, and the calculated propagation values based on sound velocity agreed with the experimental results. The expansion wave with 100 and 10 kPa in magnitude following the shock wave after 7 to 10 μsec in Pb and Ps respectively. The rise of pressure wave in Pb and Ps were 0.5 - 1.5 × 10^8 and 1 - 2.5 × 10^6 MPa/sec respectively. The magnitude of acoustic emission impulses in Pb and Ps were 1.5 and 0.5 Pa•sec respectively, and are both high enough to inactivate bacteria based on experimental correlation of Yelverton (1981).

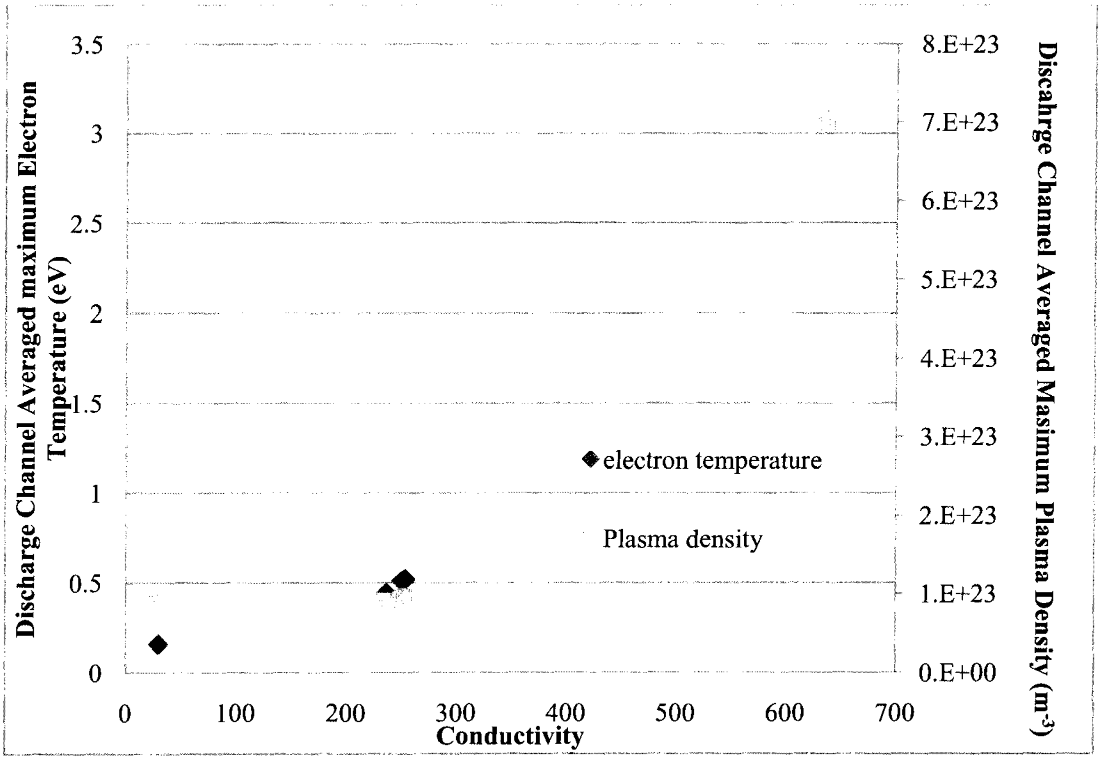


Figure 5.2. 5 Discharge channel averaged maximum plasma density and electron temperature versus various conductivities

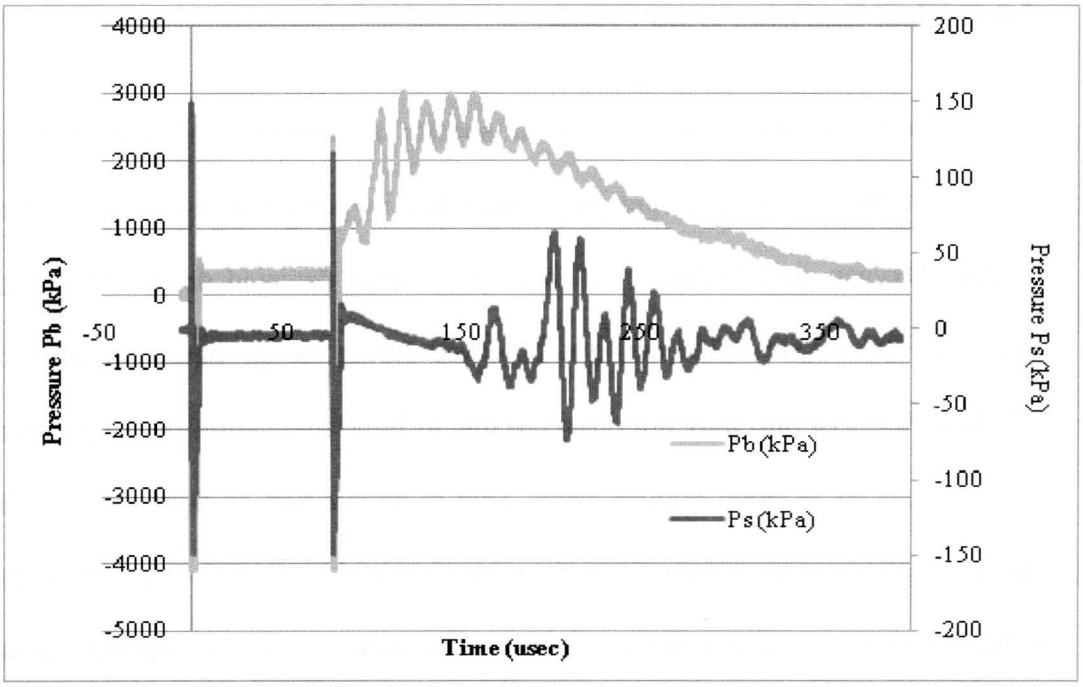


Figure 5.2. 6 Typical pressure waveform for pond surface water

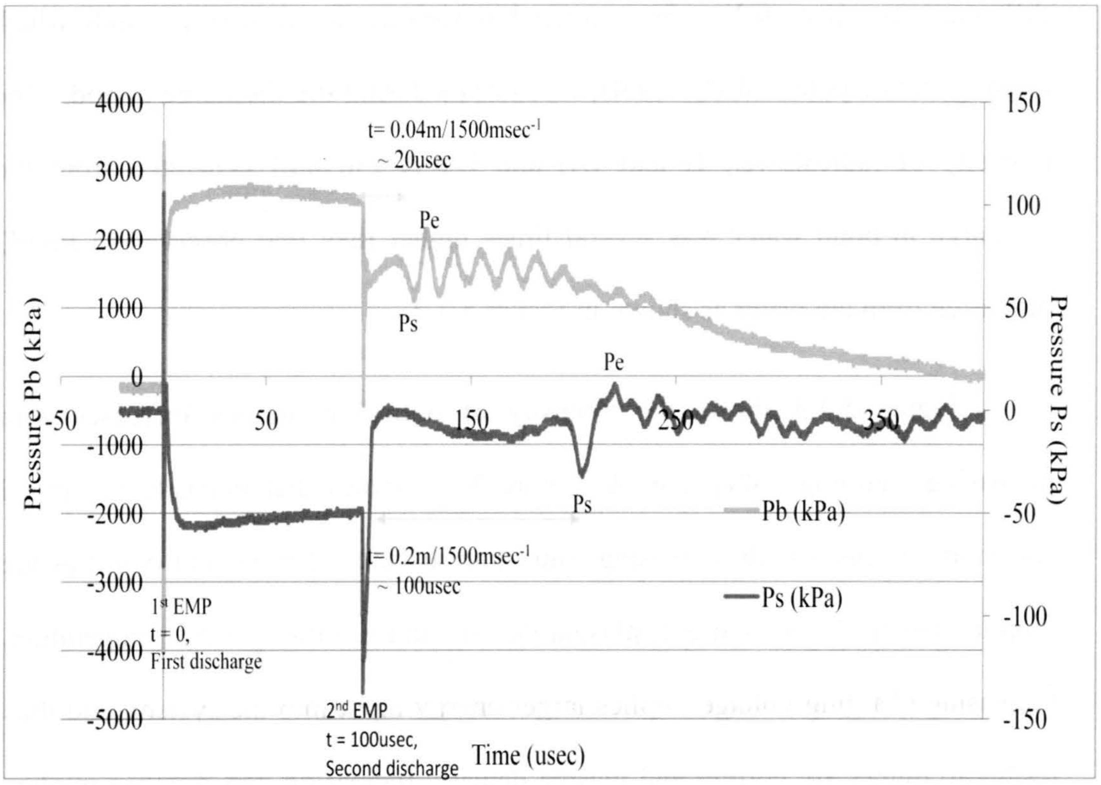


Figure 5.2. 7 Typical pressure waveform for sludge-water

5.3 Optical Emission from PAED

Based on the optical emission spectra as shown in Figure 5.3.1, a significant amount of hydrogen was generated in pond bottom water without sludge. Oxygen and hydroxyl radicals were also detected from the optical emission. UV-A (315 – 400 nm) was observed during the discharge period while UV-B (280 – 315 nm) may not observed due to light attenuation by the presence of fine particles in pond bottom water. Due to attenuation of light emission by particle scattering, no emission spectra were observed by PAED discharge in the pond bottom water with sediment addition. The optical emission spectrum in tap water is quite different from the one obtained in stormwater. It might be due to the difference in water quality. Stormwater has various chemical compounds which might generate potential O, H, OH, O_3 radicals during the discharge period. The intensity of radicals (O, H and O_3) and UV-A (365nm) generated from the discharge in pond water was several times higher than that observed in PAED discharge from tap water as shown in Figure 5.3.2.

Figure 5.3.3 shows the intensity of optical emissions increases with increasing charging voltage, while Figure 5.3.4 shows that intensity of optical emission decreases with increasing water gap distance. The radical densities are proportional to the arc current, plasma density and electron/plasma temperature. Increasing charging voltage implies larger energy input into the system, and thus results in higher arc current and plasma density. Increasing gap distance implies larger resistance in the discharge channel, resulting in a lower arc current and plasma density.

UV-A and UV-B dosages were also measured by UV dosimeters during PAED treatment in pond bottom water without sediment. Figure 5.3.5 shows that UV-A dose increases with increasing charging voltage. UV-A dose reached up to 0.45 mW/cm^2 with a charging voltage at 3 kV and a water gap distance of 0.5 mm. UV-B dosimeter shows dosages ranging between 0.001 and 0.014 mW/cm^2 during the PAED discharge period. UV-B was only observed occasionally since it is easily absorbed by the thick water layer and by scattering of moving gas-liquid interfaces. All UV-A and UV-B dosage values observed outside optical window were not corrected to attenuation due to window materials and fine particles exist between arc electrode gap and window inner wall.

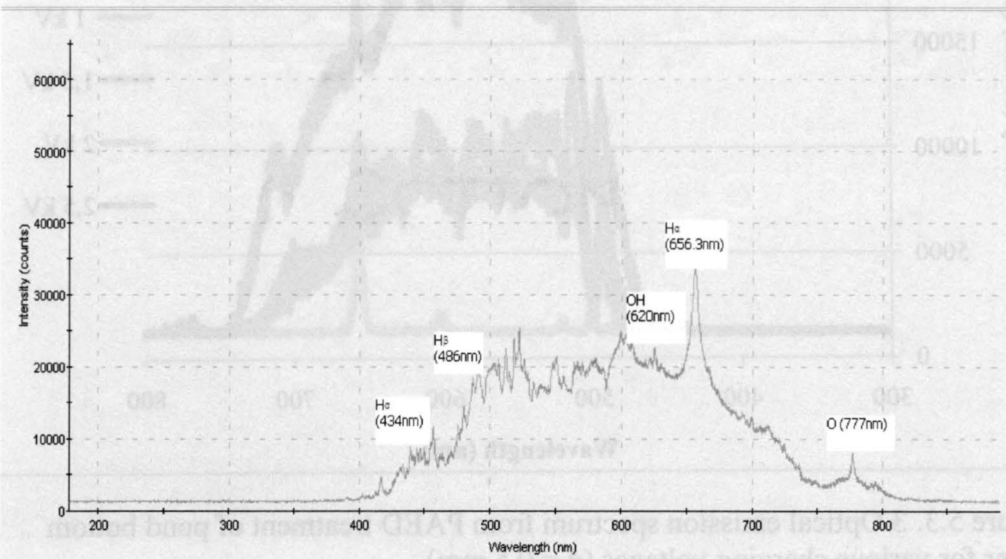


Figure 5.3. 1 Typical optical emission spectrum from PAED treatment of pond bottom water without addition of sludge (V_{ch} =2 kV, d = 0.5 mm)

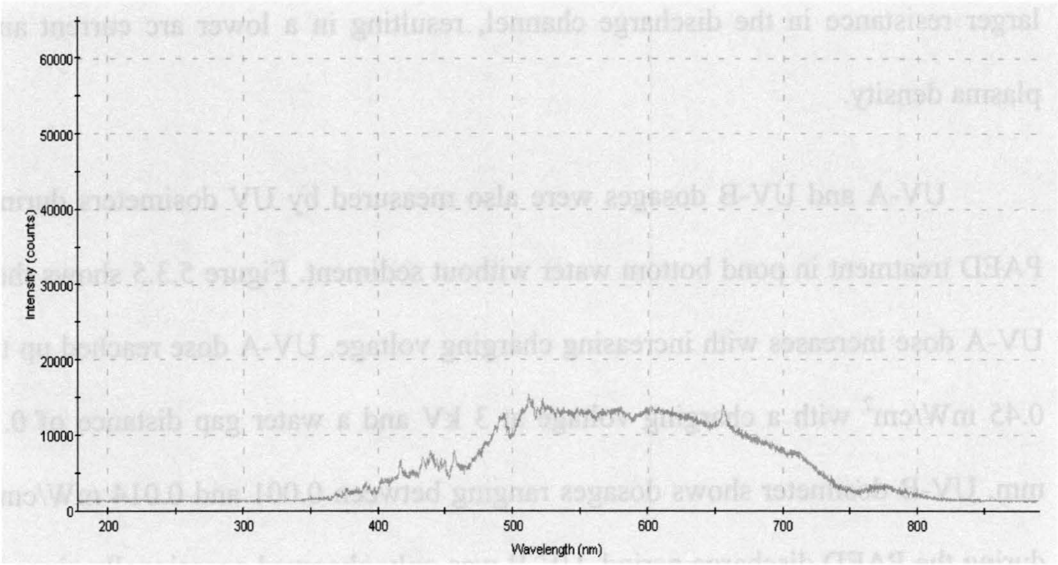


Figure 5.3. 2 Typical optical emission spectrum from PAED treatment of tap water (V_{ch} =2 kV, d = 0.5 mm)

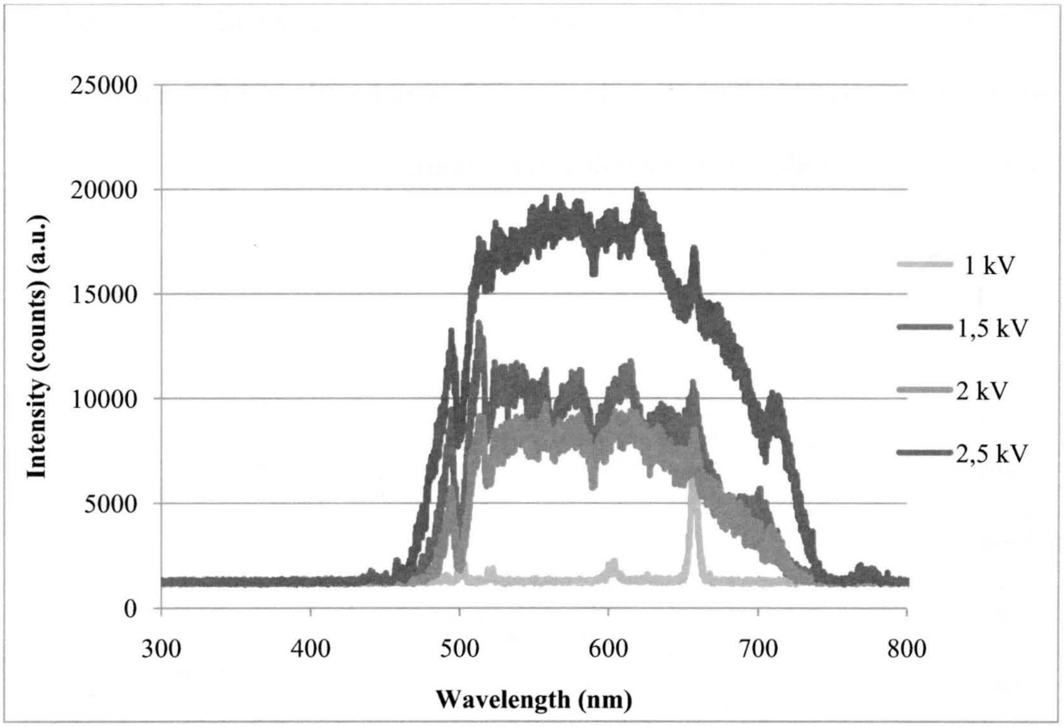


Figure 5.3. 3 Optical emission spectrum from PAED treatment of pond bottom water for various charging voltages (d = 0.5 mm)

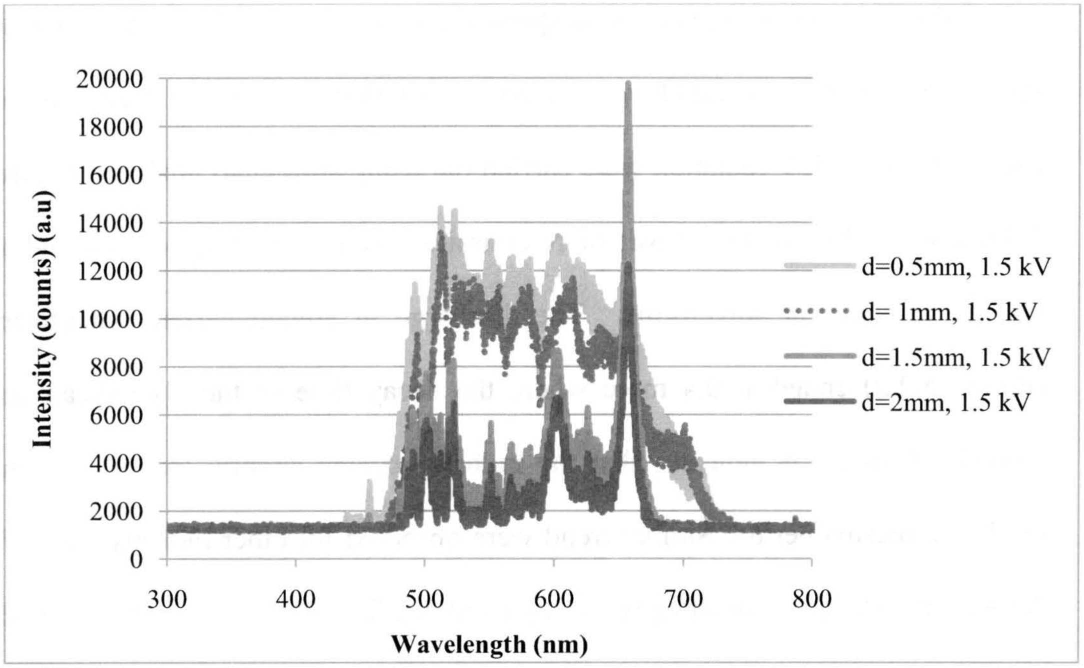


Figure 5.3. 4 Optical emission spectrum from PAED treatment of pond bottom water for various water gap distances (V_{ch} = 1.5 kV)

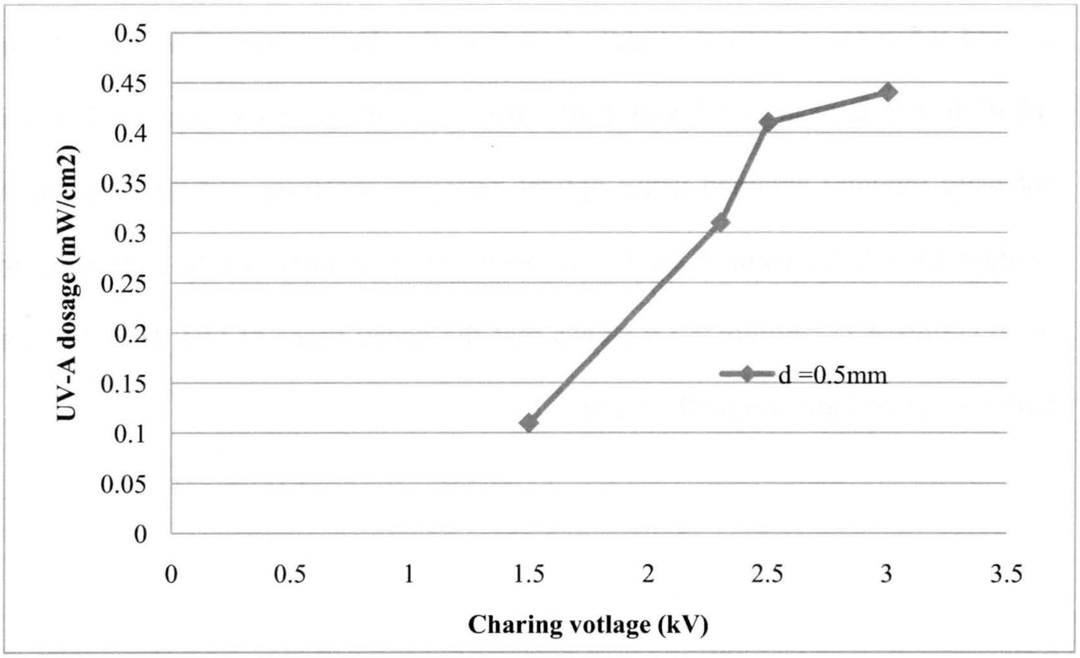


Figure 5.3. 5 UV-A dosage as a function of charging voltage in pond bottom water (without sludge) (d = 0.5 mm)

Based on the optical emission spectrum in Figure 5.3.1, UV-A and radicals such as N_2, O_3, OH, H and O were observed. Detailed study of the decay time of each radical and UV radiation were carried out using strip chart analysis. Figures 5.3.6 and 5.3.7 show the transit of N emission intensity and the corresponding voltage and current waveforms. The discharge in voltage-current waveforms (Figure 5.2.2) ended at 0.4 msec where the decay time of the N_2 radicals are around 0.6 msec. It indicates that the radicals existed slightly longer than the discharge plasma period. Similar trend were observed for other radicals and UV-A (365nm). The corresponding wavelengths of N_2, O_3, OH, H and O are 337, 606, 620, 656 and 777 nm, respectively. Figure 5.3.8 shows the transients of N_2, UV-A (365nm) and O_3 after discharge. The decay times of UV-A (365nm) and O_3 are around 0.5 msec, which is slightly less than the decay time of N_2 radicals. In addition, the intensity of UV-A (365 nm) by dosimeter were compared to the intensity (counts) obtained using optical emission spectrum and time transit. A reading of 0.45 mW/cm^2 from UV-A dosimeter is approximately equivalent to 5000 counts/A.U. Figure 5.3.9 shows that the decay times of OH, H and O are very similar and are around 0.5 msec.

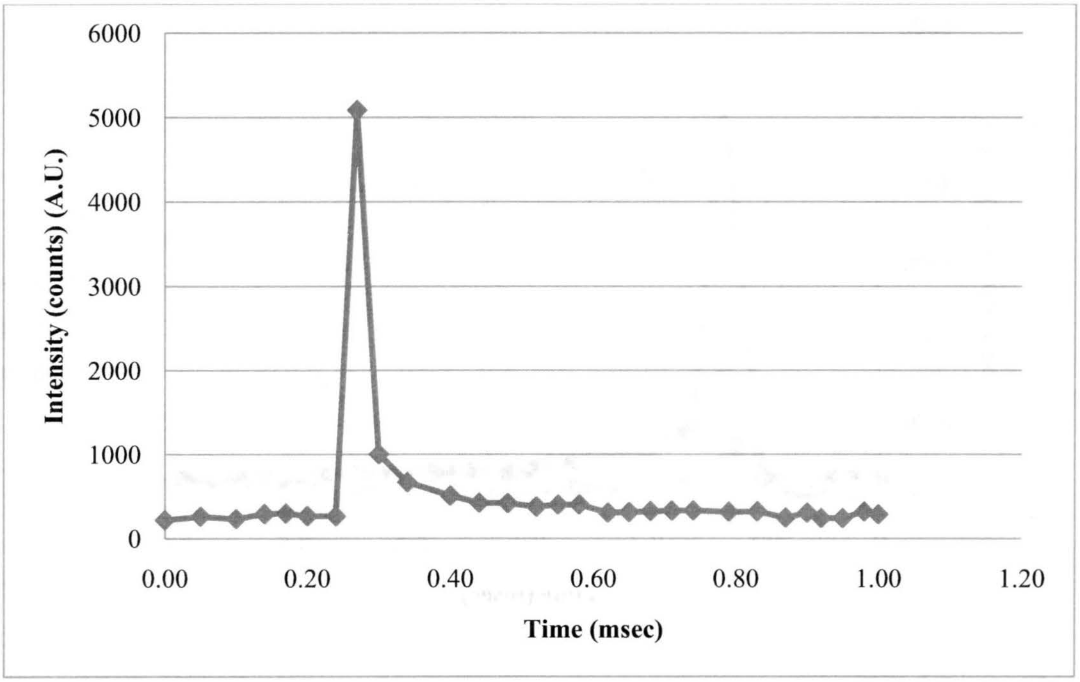


Figure 5.3. 6 Typical N_2 radical transit (wavelength of 337nm) observed during single PAED discharge (V_{ch} = 1.5 kV, d = 0.5 mm)

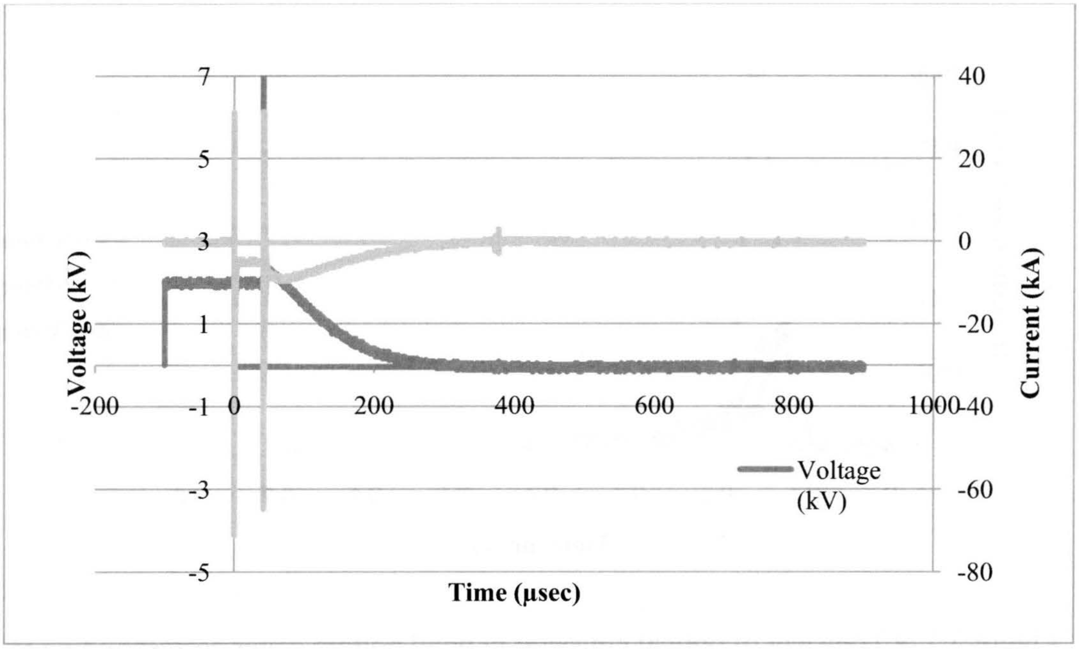


Figure 5.3. 7 Voltage and current waveforms corresponding to N_2 radicals transit as shown in Figure 5.3.6

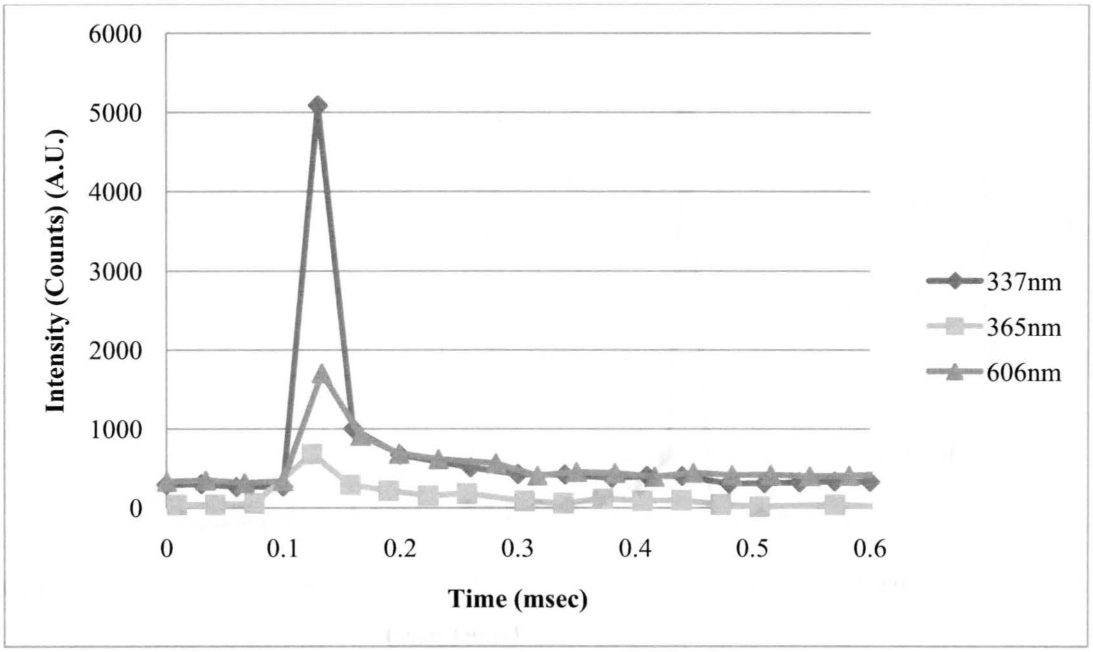


Figure 5.3. 8 Transient of optical emission in pond bottom water corresponding to wavelengths of 337, 365 and 606 nm (V_{ch} = 2 kV and d = 0.5 mm)

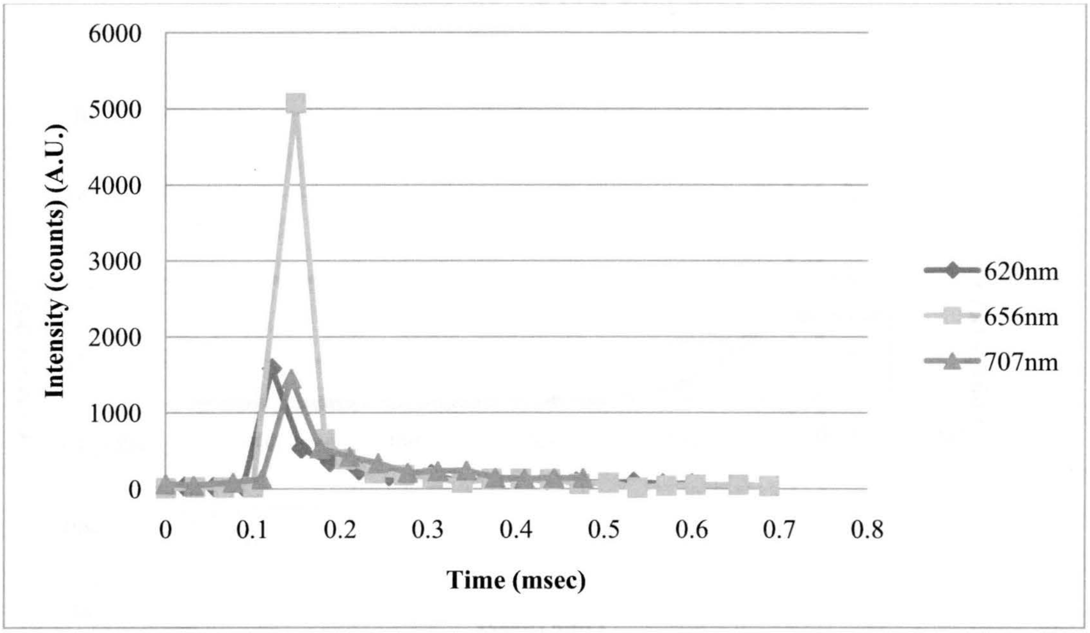


Figure 5.3. 9 Transient of optical emission in pond bottom water corresponding to wavelengths of 620, 656 and 777 nm (V_{ch} = 2kV and d = 0.5 mm)

5.4 Water Quality Parameters

Water quality was analyzed by a multi-function water quality monitor, and the data are shown in Table 5.1, where DO is dissolved oxygen, TDS is the total dissolved solids and Sal is the salinity. Differences in water quality were observed even between pond surface water and pond bottom water. Higher conductivity, DO, TDS and TOC were observed in pond bottom water. The pH, total organic carbon (TOC) and conductivity slightly increase with increasing sediment fractions in pond bottom water. It may due to the fact that pollutants accumulated in sediment might partly diffuse into the liquid phase (pond bottom water). The DO, in contrast, decreased with increasing sediment fractions.

The water quality of sludge-water is also significantly different than the pond surface and bottom water. The TOC and the conductivity in sludge-water are two orders of magnitude higher than the pond surface water, while total dissolved solids (TDS) in sludge-water are several times higher than pond surface and bottom water. The data may indicate that higher concentrations of pollutants are dissolved in sludge-water. Water quality were measured at 5, 15, 30, 60, 90 and 120 minutes during the two-hour PAED treatments (V_{ch} = 2 kV and d = 0.5 mm). The TDS and salinity stayed relatively constant after PAED treatment. Other water quality data, on the other hand, were influenced by the discharge treatment. Figures 5.4.1, 5.4.2, 5.4.3 and 5.4.4 show that pH, conductivity, dissolved oxygen and temperature change over the course of treatment in all cases. The accuracy of each parameter is shown in Table 4.1. The temperature increases 10 °C in average after two hours of treatment. The pH values increase with increasing treatment time for all samples. Based on spectroscopic observation in Section 5.3 and the reading of UV-A dosimeter, the present pulsed-arc system generates radicals such as $H^{\cdot}$, $O^{\cdot}$ and $OH^{\cdot}$, etc., and strong UV radiation. This is an evidence of the effect of radical generation on pH alterations. As shown in Figures 5.4.5 and 5.4.6, the pH and DO are stabilized after 1 and 5 minutes respectively. The results indicate that the active species in water were only present for less than 5 minutes. In general, pH increases after two hours of PAED treatment. The conductivities increased 6, 2 and 3%, respectively, for PAED treatment of pond bottom water with sediment of 0, 33, 100 g/L. Formation of ions in liquid during discharge might increase the conductivity. The increment of conductivity decreases with increasing sediment fraction since free ions in sediment are less available. The conductivity of the sludge-water, however, decreased 1% at the end of the PAED treatment.

Table 5. 1 Typical water quality data for various water samples; DO (dissolved water), TDS (total dissolved solid), Sal (salinity) and TOC (total organic carbon)

	pH	Conductivity (mS/m)	DO (mg/L)	TDS (g/L)	Sal (%)	TOC (mg/L)
Pond Surface Water	7.58	22	9.1	0	0.14	3
Pond Bottom Water	7.03	237	3.5	1.6	0.1	10
Pond Bottom Water with 33g/L Sludge	7.03	251	2.4	1.6	0.1	10.5
Pond Bottom Water with 100g/L Sludge	7.09	254	1.7	1.6	0.1	14.5
Sludge-Water	7.49	637	1.8	4	0.3	310

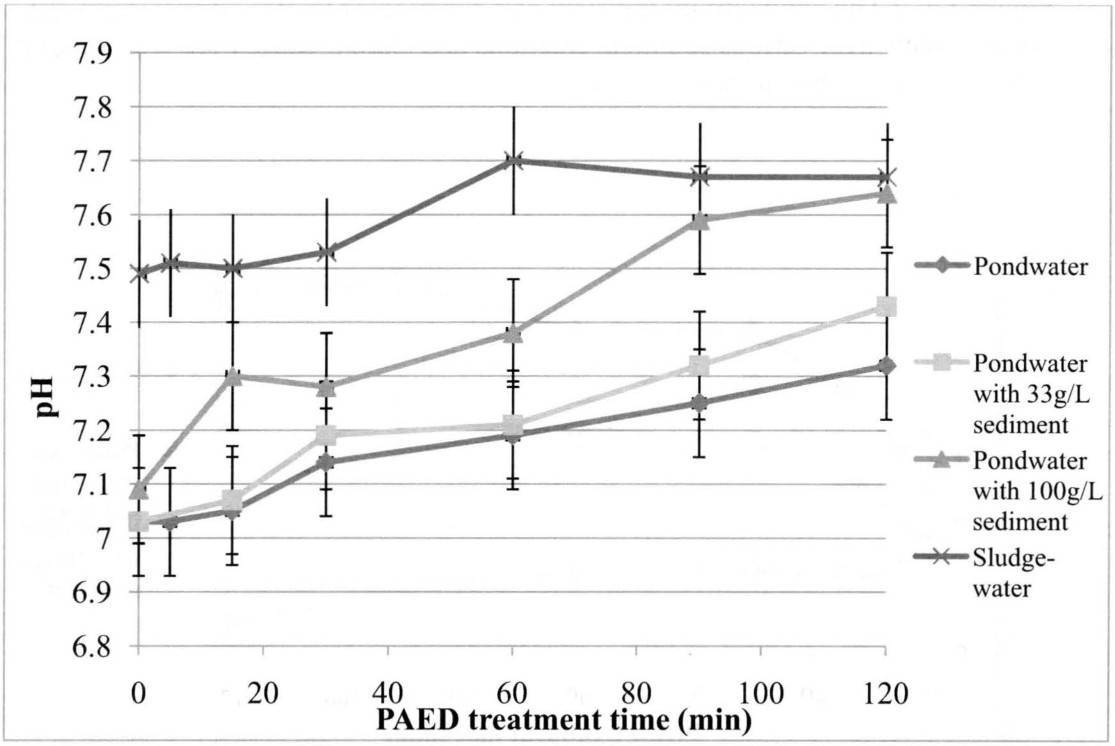


Figure 5.4. 1 The pH transient as a function of treatment time for pond bottom water with various sludge fractions and sludge-water (V_{ch} = 2kV and d = 0.5mm, experimental error = 0.1 pH)

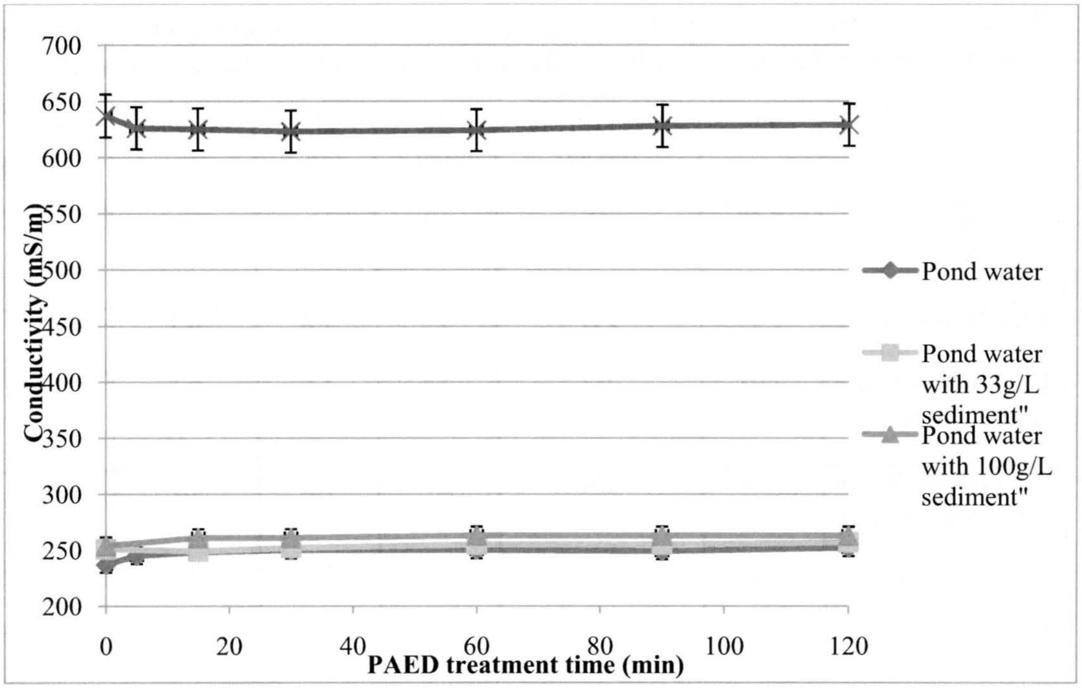


Figure 5.4. 2 The conductivity transient as a function of treatment time for pond bottom water with various sediment fractions and sludge-water (V_{ch} = 2kV and d = 0.5mm, experimental error = 3 %)

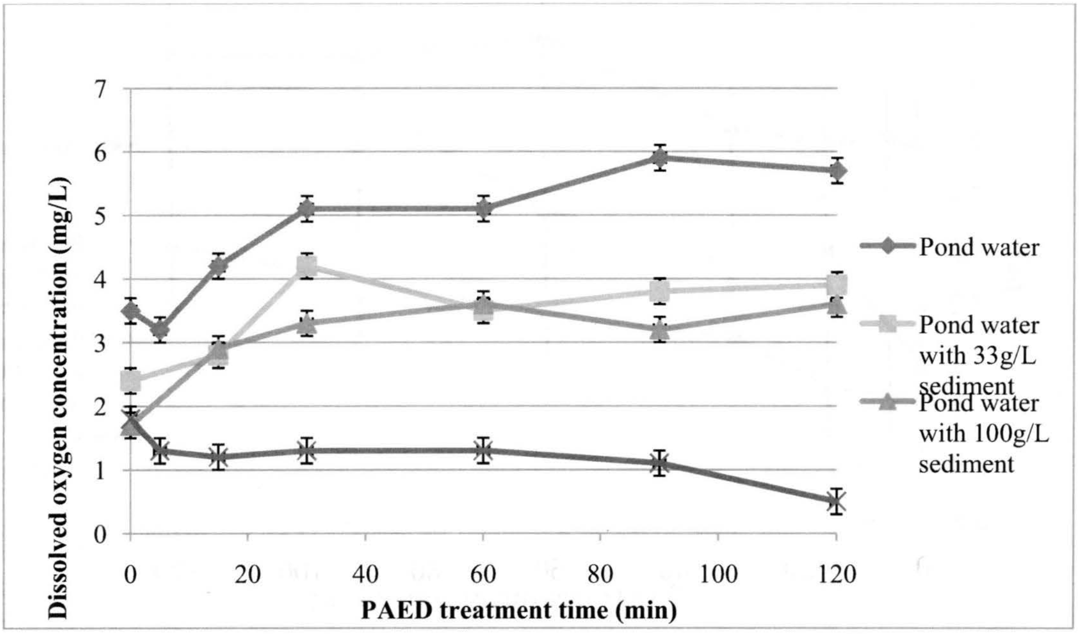


Figure 5.4. 3 The DO transient as a function of treatment time for pond bottom water with various sediment additions and sludge-water (V_{ch} = 2kV and d = 0.5mm, experimental error = 0.2 mg/L)

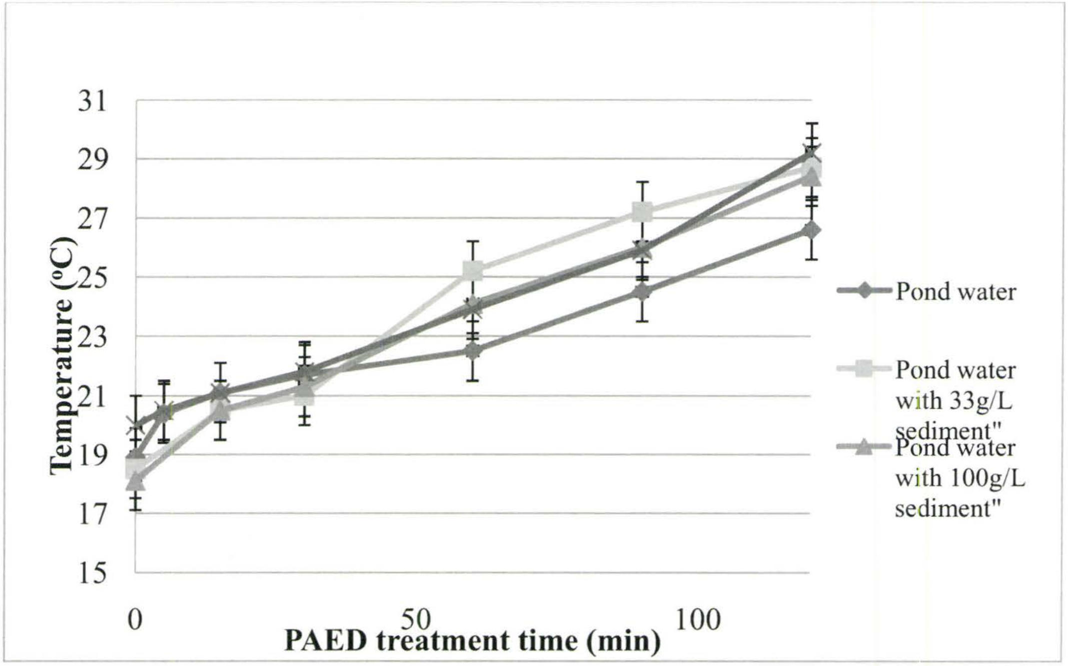


Figure 5.4. 4 The water temperature transient as a function of treatment time for pond bottom water with various sediment additions and sludge-water (V_{ch} = 2kV and d = 0.5mm, experimental error = 1°C)

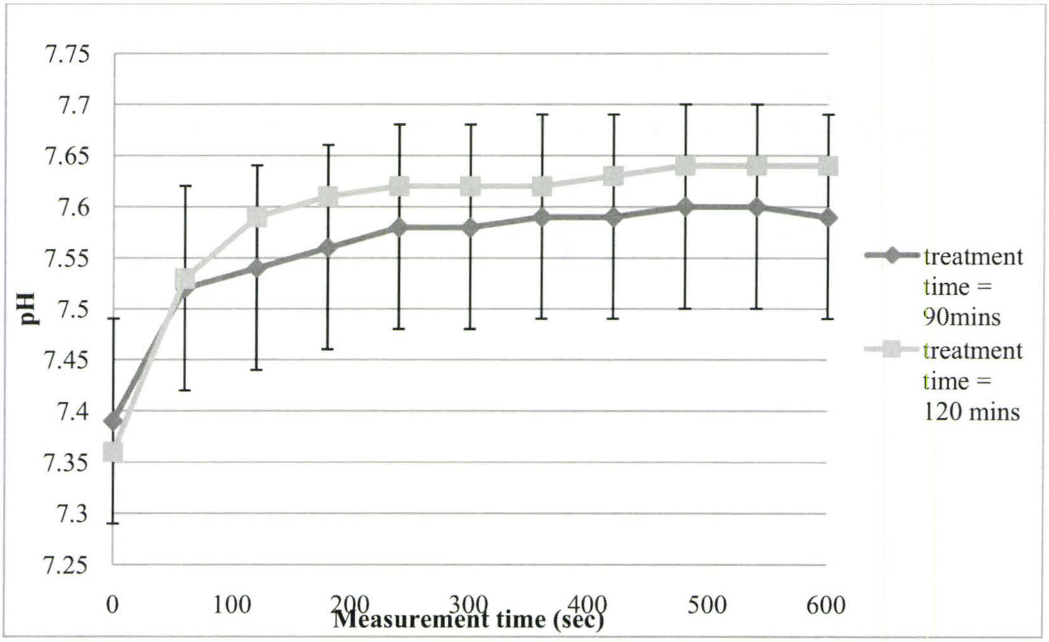


Figure 5.4. 5 Change of pH with measurement time for pond bottom water with 33g/L sediment addition (V_{ch} = 2kV and d = 0.5mm, experimental error = 0.1 pH)

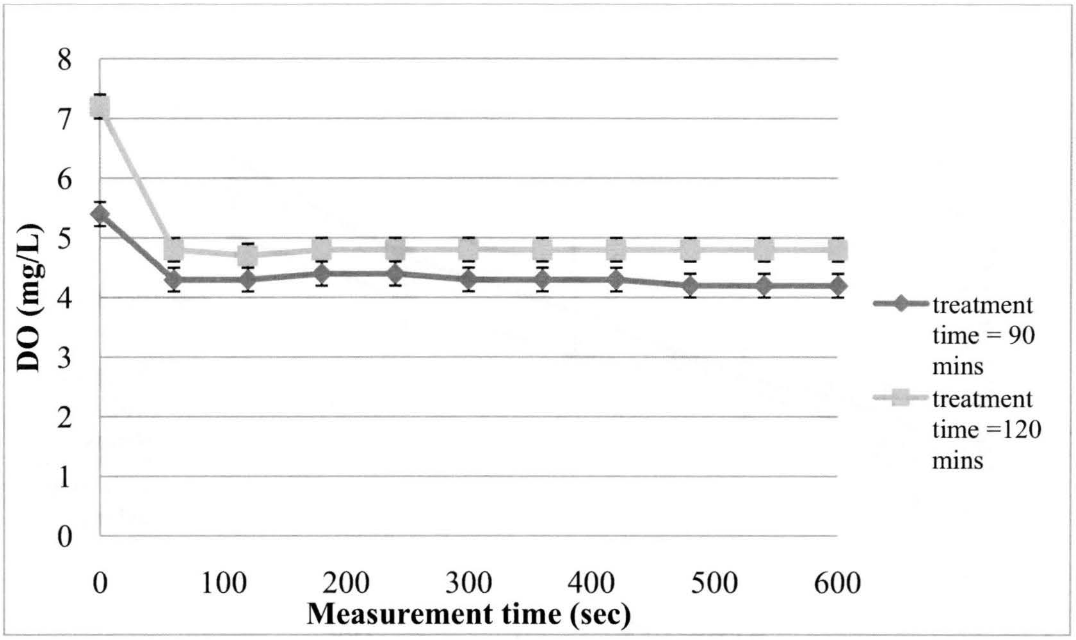


Figure 5.4. 6 Change of DO with measurement time for pond bottom water with 33g/L sediment addition (V_{ch} = 2kV and d = 0.5mm, experimental error = 0.2 mg/L)

In Figure 5.4.3, DO concentrations increase more than 60% in pond bottom water with various sediment concentrations. The increase of DO after PAED treatment of pond bottom water can be explained by the formation of $O^{\cdot}$ and $O_3^{\cdot}$ radicals during liquid discharges. In addition, the formation of oxide compounds was confirmed by XRF in Section 5.5. The concentration of DO in sludge-water, on the other hand, decreased 50% after two hours of PAED treatment. In Figure 5.4.7, the reduction of TOC in sludge-water reaches 80% and is even greater than 90%, respectively after 5 minutes and 1 hour of PAED treatment. The decreases of TOC concentration are not obvious in pond surface and bottom water due to the fact that the original TOC concentrations are below the detection limit of the measurement technique. As shown in Figure 5.4.8, the percentage of DO decreases by 20 and 40%, respectively, at a measurement time of 60 seconds in pond bottom water (with addition of 33g/L sediment) and in sludge-water. The result indicates that more reactions were carried out with O· and O_3· radicals in sludge-water. It may suggested that PAED first degrade the toxic organic compounds into organic acids, and the inter-mediates may further decomposed into CO_2 (Chang et al., 2002; Yong and Jiang, 2005) The generations of CO_2, CO and C_xH_y will be discussed in Section 5.5.

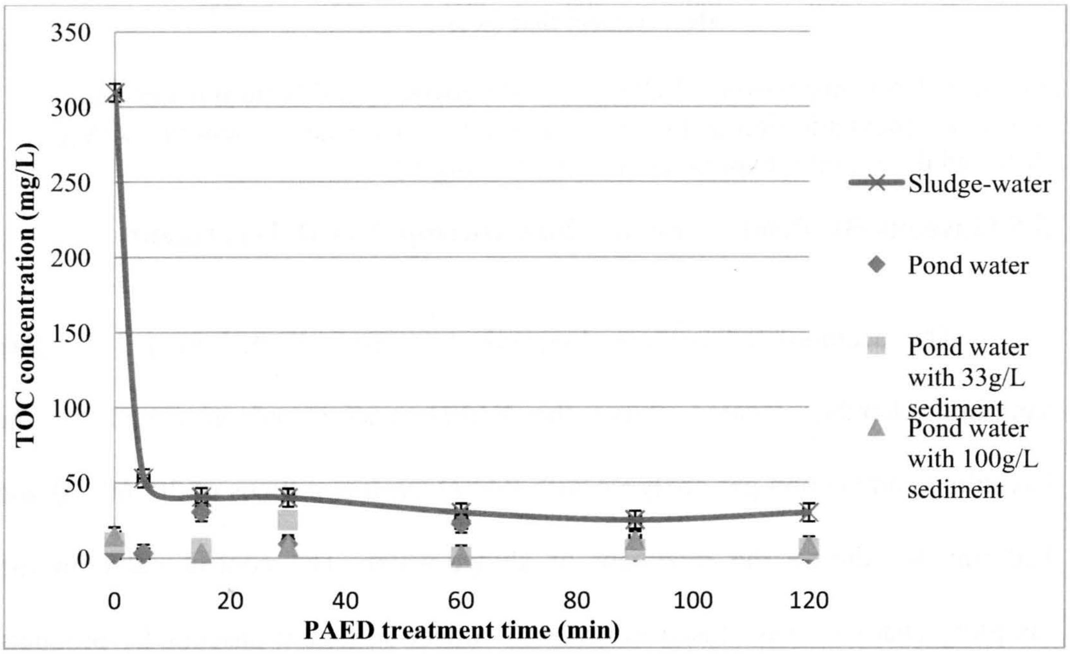


Figure 5.4. 7 TOC reduction in sludge-water and pond bottom water with various sediment additions (V_{ch} =2kV and d =0.5mm, experimental error: 6mg/L)

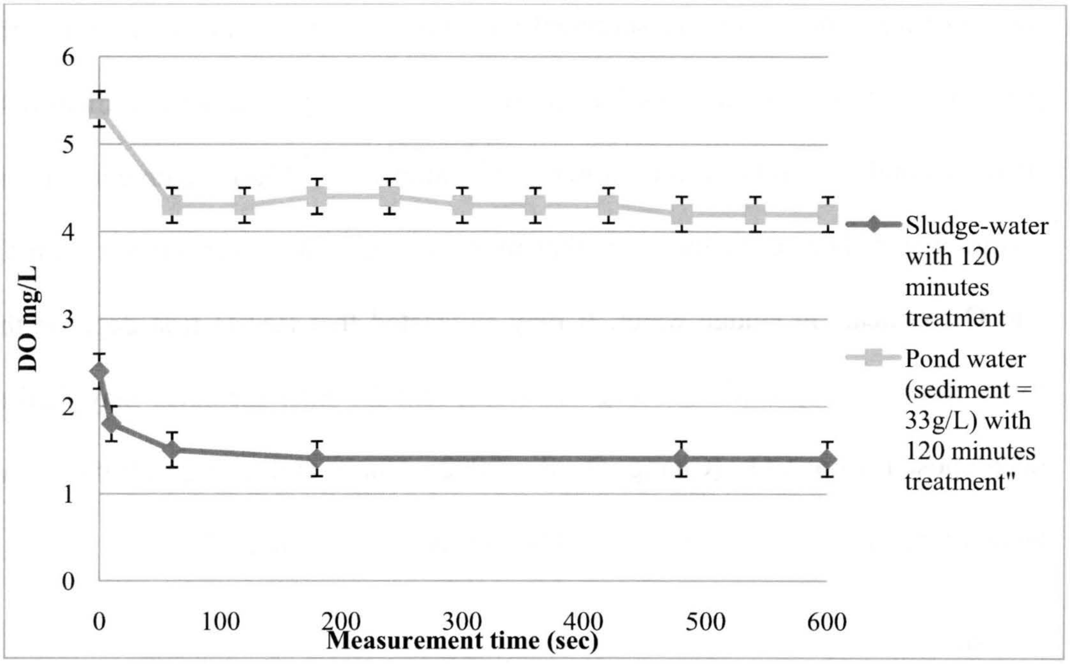


Figure 5.4. 8 Comparisons of DO transient between pond bottom water with 33g/L sediment addition and sludge-water at various measurement times (V_{ch} = 2kV and d = 0.5mm, experimental error: 0.1 mg/L)

5.5 Gaseous By-Product Formations During PAED Treatment

The accumulated gaseous by-products were collected in a 1 L glass sampling chamber located above the PAED reactor and measured by the Greenline combustion gas analyzer with PAED treatment times of 30, 60, 90 and 120 minutes during the treatment of sludge-water. The control valve in the sampling chamber was closed in order to collect sufficient gaseous by-products generated during PAED treatment. The combustion gas analyzer started gas analyses when the treatment was temporarily stopped and the valve of the sampling chamber was opened at each time interval. Each transient measurement ranged from 25 to 30 minutes. The transients of all gaseous by-products from

PAED treatment with treatment times of 30, 60, 90 and 120 minutes are shown in Figures 5.5.1, 5.5.2, 5.5.3 and 5.5.4.

In figures 5.5.1 through 5.5.4, the generation of smaller gaseous hydrocarbons likely C_xH_y with $x \leq 3$ and $y \leq 8$was observed continuously throughout the sampling time, while CO_2 formed occasionally. Other gaseous by-products such as CO, H_2S and SO_2 reached their maximum at a transient time of 3 minutes. The trend was quite similar for different PAED treatment times. After the stored gaseous compounds in the sampling chamber were pumped out by the combustion gas analyzer, some of the dissolved CO, H_2S and SO_2 might shift from liquid phase to gaseous phase occasionally due to de-pressurization of sampling chamber.

The accumulated concentrations of CO, CO_2 and C_xH_y, NO and NO_2, and SO_2 and H_2S, are shown in Figures 5.5.5, 5.5.6 and 5.5.7 respectively. Since the reactor was in batch operation mode, the generations of C_xH_y and CO were continuous and more selective than CO_2. The generation of CO was terminated after one hour of PAED treatment while the generation of NO was observed after 60 minutes of PAED treatment. Both SO_2 and H_2S were formed continuously throughout the course of treatment time. The accumulated concentrations of C_xH_y > CO > CO_2 > SO_2 > H_2S > NO were 8.2, 3.1, 1.9, 0.32, 0.29 and 0.07 mg/L, respectively.

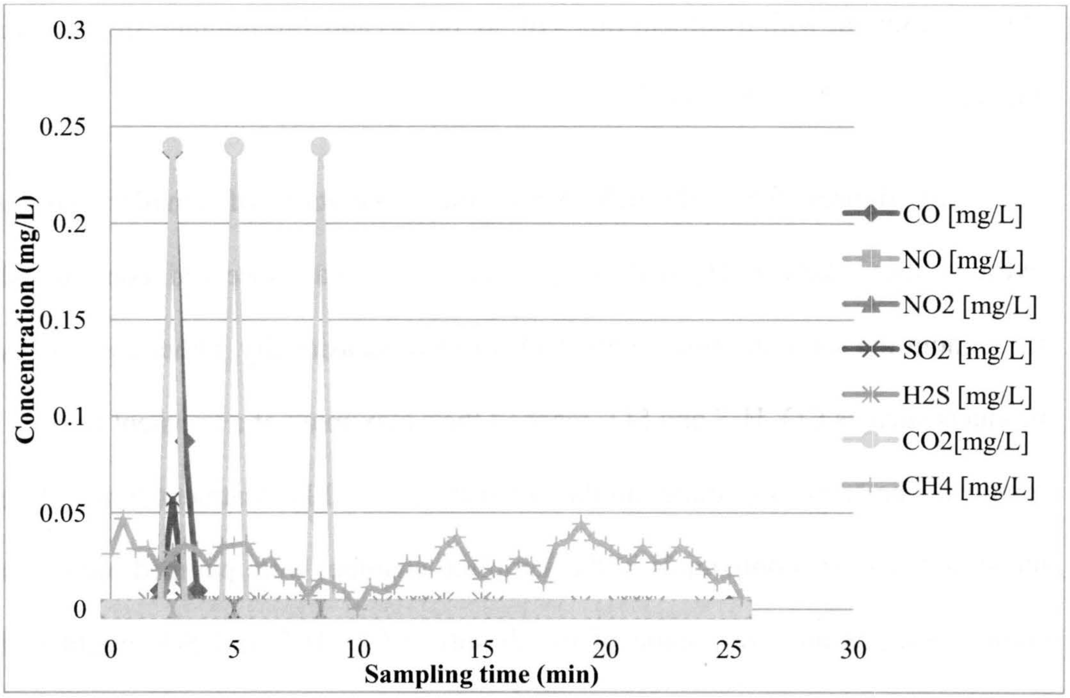


Figure 5.5. 1 Transient of all gaseous by-products with a PAED treatment time of 30 minutes (V_{ch} = 2 kV and d = 0.5mm)

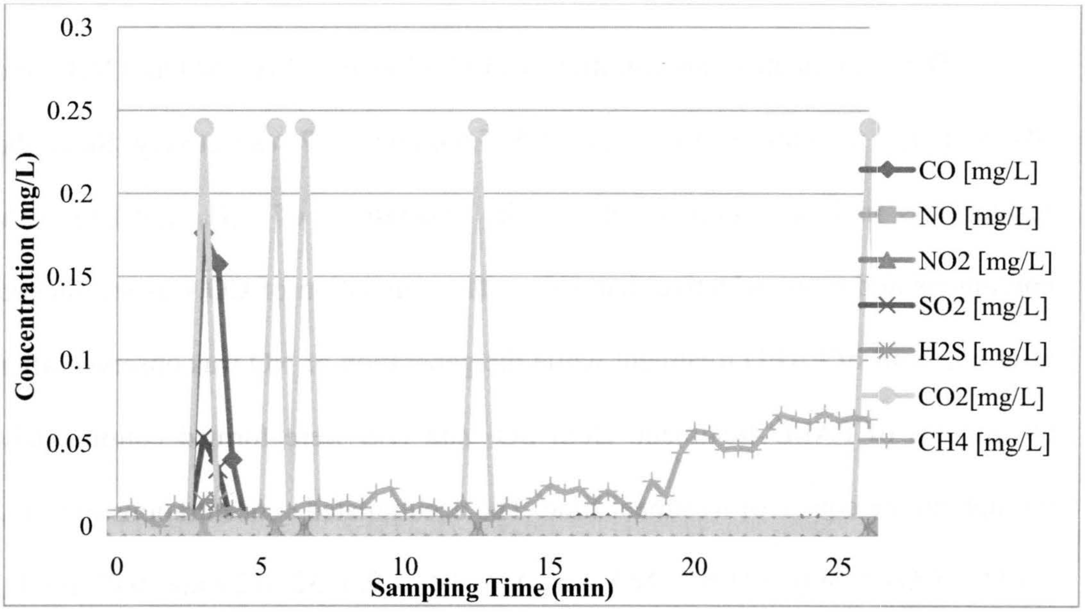


Figure 5.5. 2 Transient of all gaseous by-products with a PAED treatment time of 60 minutes (V_{ch} = 2kV and d = 0.5mm)

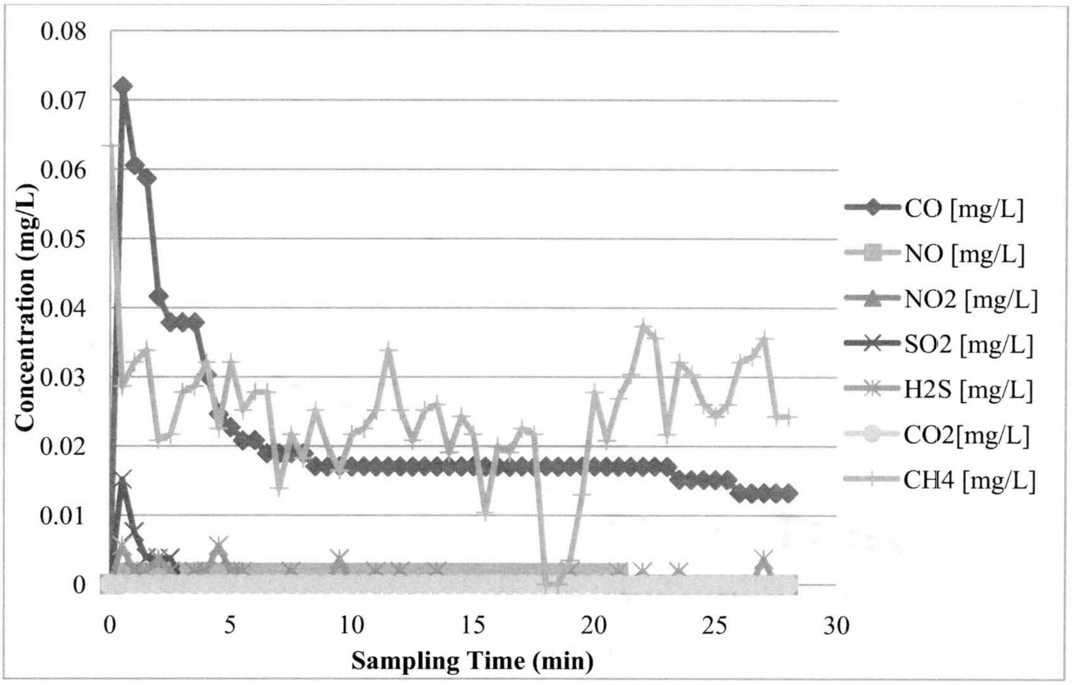


Figure 5.5. 3 Transient of all gaseous by-products with a PAED treatment time of 90 minutes (V_{ch} = 2kV and d = 0.5mm)

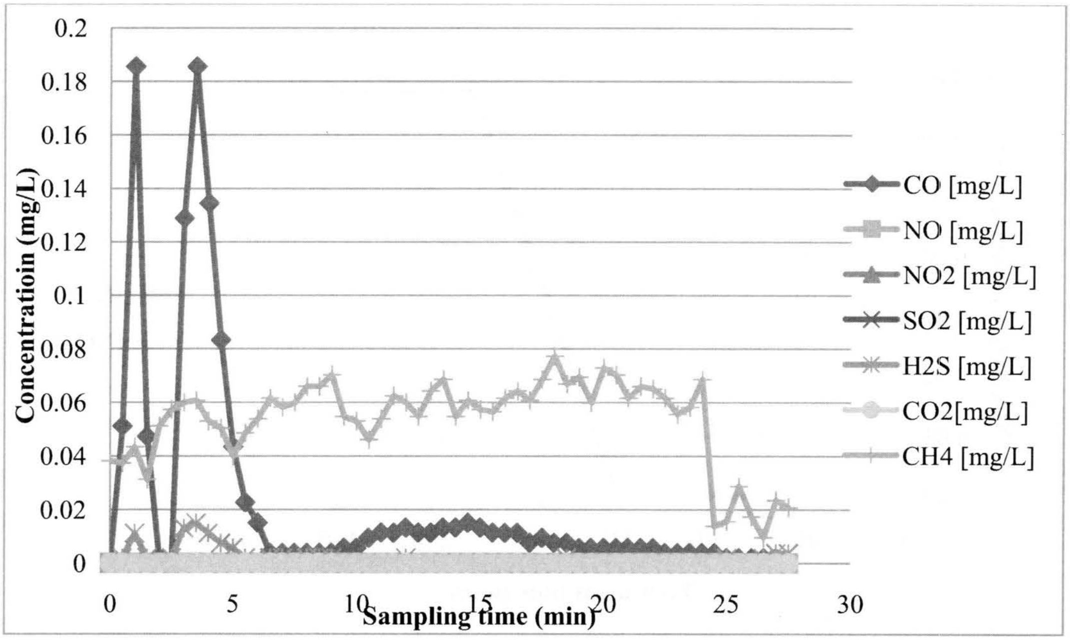


Figure 5.5. 4 Transient of all gaseous by-products with a PAED treatment time of 120 minutes (V_{ch} = 2kV and d = 0.5 mm)

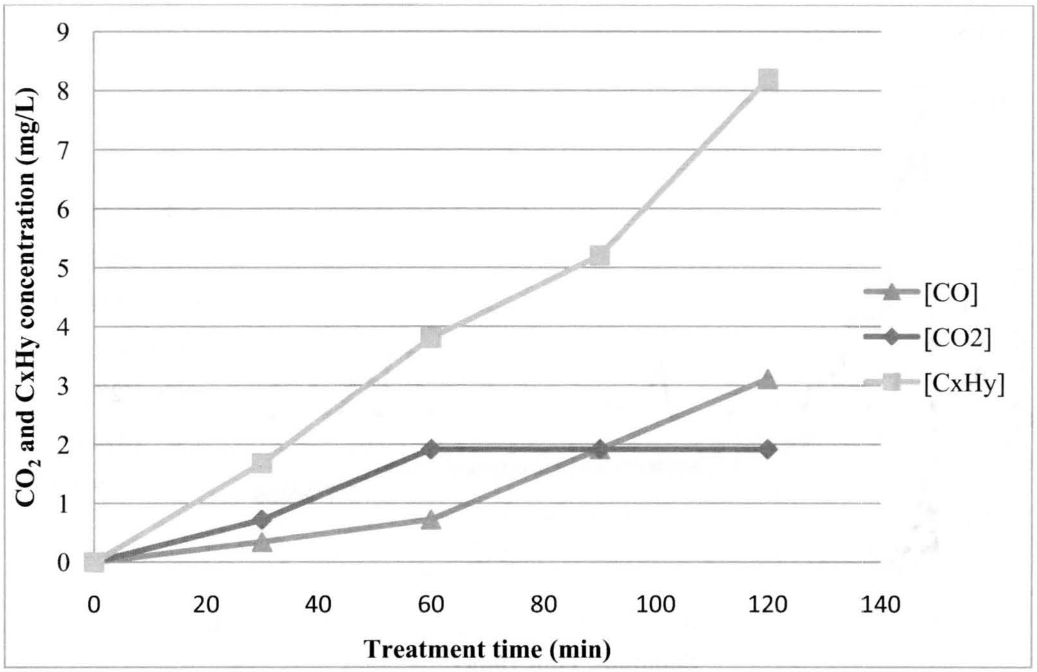


Figure 5.5. 5 Accumulated concentrations of CO, CO_2 and C_xH_y during PAED treatment (V_{ch} = 2kV and d = 0.5mm)

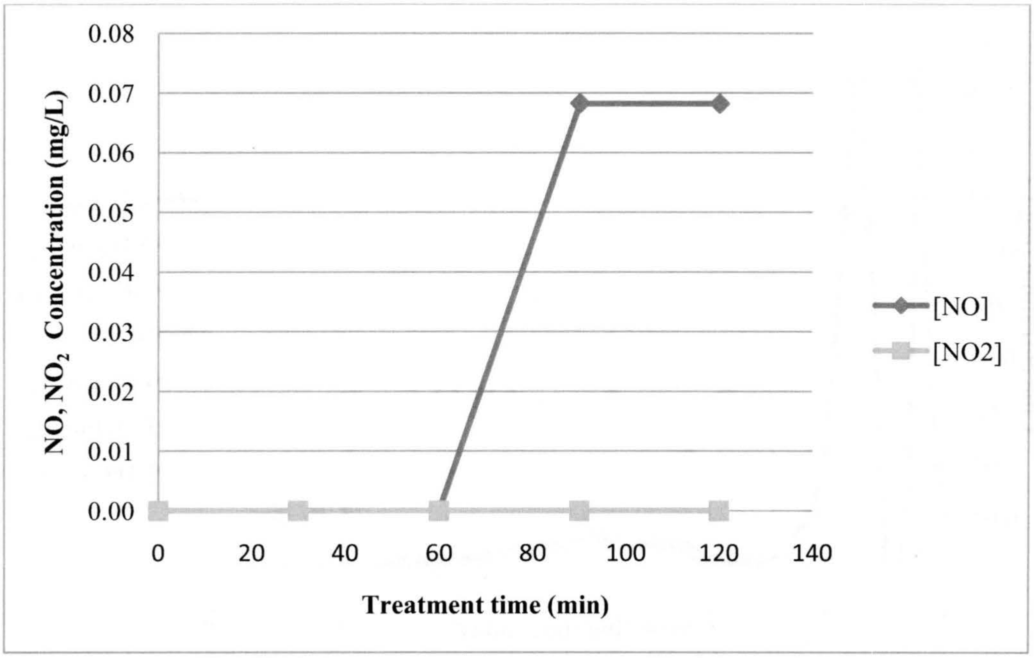


Figure 5.5. 6 Accumulated concentrations of NO and NO_2 during PAED treatment (V_{ch} = 2kV and d = 0.5mm)

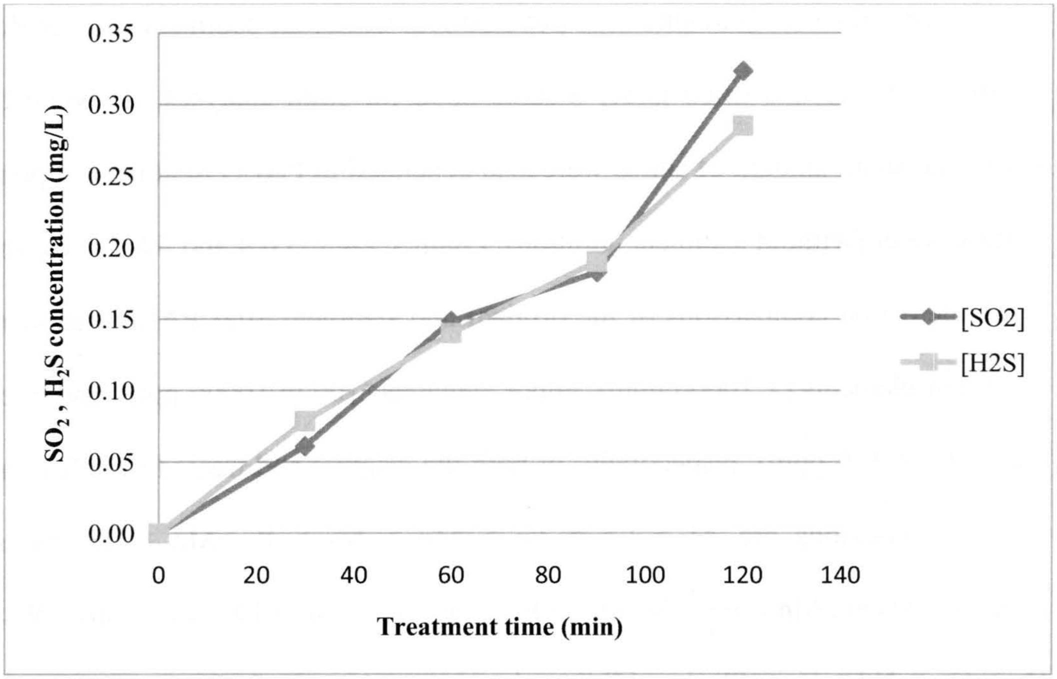


Figure 5.5. 7 Accumulated concentrations of SO_2 and H_2S during PAED treatment (V_{ch} = 2kV and d = 0.5mm)

5.6 Solid Analyses of PAED Treated Sludge

The sludge-water and stormwater sediment particle size distributions are shown in Figure 5.6.1. Overall, the particle size ranges from 0.3 to 1000 μm. Sludge-water has a peak particle size around 10 μm, while the stormwater sediment is bimodal and have peaks particle size around 10 and 700 μm. With the scanning electron microscope (SEM) image analysis, two different types of particles appeared in the image as shown in Figure 5.6.2. One was irregular in shape and the other was long and cylindrical. They may correspond to, respectively, inorganic and organic fractions (Li et al., 2007).

After the PAED treatment of pond bottom water, the sediment were settled down by gravity and dried under a fume hood for solid analyses. It should be noted that small amount of solids were also generated in PAED treatment of pond bottom water (without sediment addition). Figures 5.6.3, 5.6.4 and 5.6.5 show the NAA elemental comparisons of the original and sediment after PAED treatment for major elements (> 10000 ppm), minor elements (100 to 10000 ppm) and trace elements (< 100 ppm), respectively. In both the original and treated samples, the main compositions are Al > Ca > Fe > Mg > Na > K >Mn > Ti, minor compositions are Mn > Ba > Sr > Cr > Br > Zn > As > Sc > Th > Co > Sm > W > Dy > Co > Nd > Eu > Sb. In addition, elements such as C, O, Si, Cu and S were determined by XRF, as shown in Figure 5.6.6.

Combining the results from both NAA and XRF, it is shown that the abundant elements in the samples are O and Si, followed by Al, Ca and Fe (which can be observed in NAA). Based on this observation, most of the elements may present in their oxide form. This can also be confirmed by XRD, which detects the crystalline structures and compound compositions in dried sediment. The XRD shows that the four main compositions are Quartz (SiO_2), Calcite ($CaCO_3$), Anorthite ($CaAl_2Si_2O_8$) and Dolomite ($CaMg(CO_3)_2$), which commonly exist in soil. Some toxic components including Zn, Fe, Cr, Cl, etc., might have been accumulated from stormwater runoff. The figures show that the concentrations of volatile elements such as Br, Cl, S and K decreased more than 50% after two hours of PAED treatment. Two of the most abundant elements, Al and Ca, decreased 1 and 2.5% in mass respectively. Some more volatile metals including Zn and Na, however, increased after PAED treatment. As these two elements usually are present as oxide or chloride, the boiling points of the compounds are usually higher than those of their elemental forms.

Sedimentation was observed after the PAED treatment of sludge-water. The dried solid PAED (referred as **PAED treated sludge**) was settled down by gravity and were dried under a fume hood for solid analyses. The major, minor and trace elements between original sediment and the PAED treated sludge are shown in Figures 5.6.7, 5.6.8 and 5.6.9 respectively. The concentrations of volatile elements such as Br, Cl and K decreased 90, 30 and 20% respectively. Figure 5.6.10 shows that the concentration of O increased more than 5% after treatment. Since the discharge in liquid solution generates oxygen and hydroxyl radicals, these radicals might react with various compounds and convert to oxide forms. The variation of element concentrations within samples should be considered as well. Two duplicate samples of solid by-product from each treatment were analyzed for all solid analyses. In general, element concentrations in both sediment and PAED treated sludge decrease after two hours of PAED treatment.

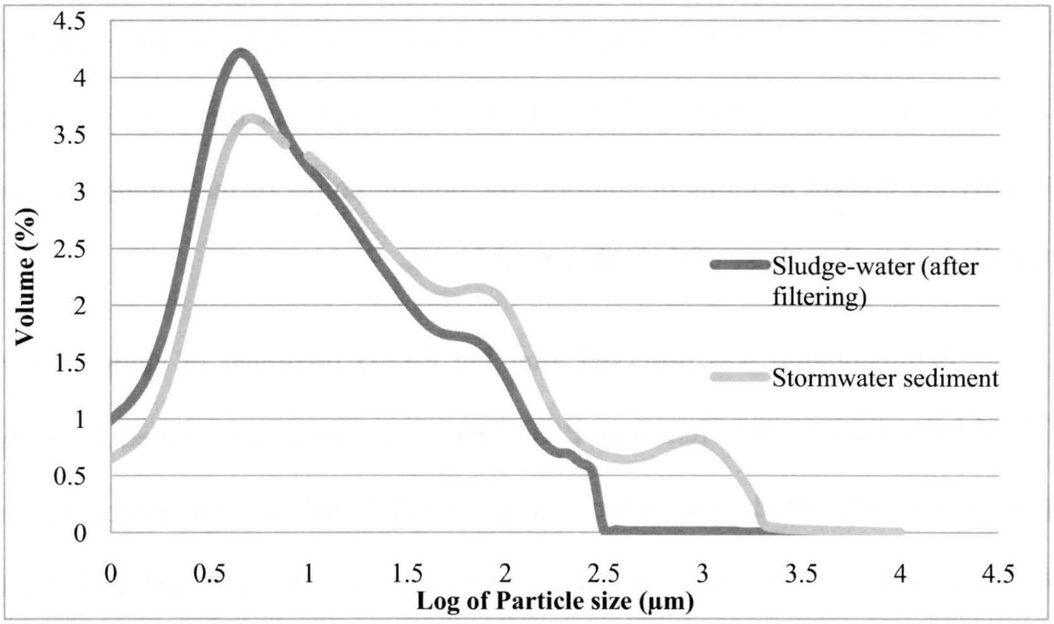


Figure 5.6. 1 Particle size distribution of sludge-water and stormwater sediment.

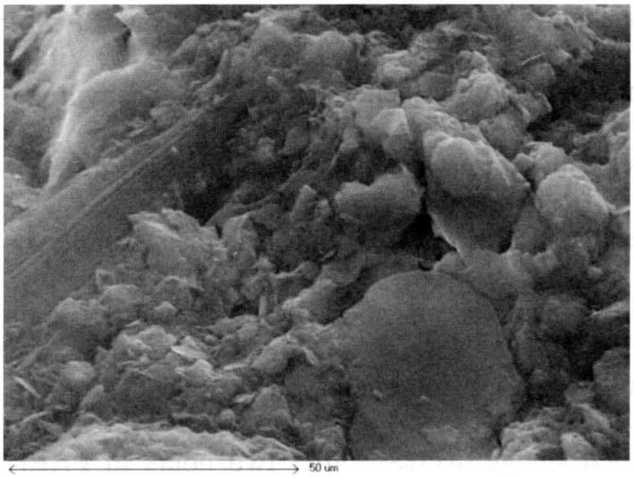


Figure 5.6. 2 Particle image of untreated sediment under SEM with magnification of 4200 times.

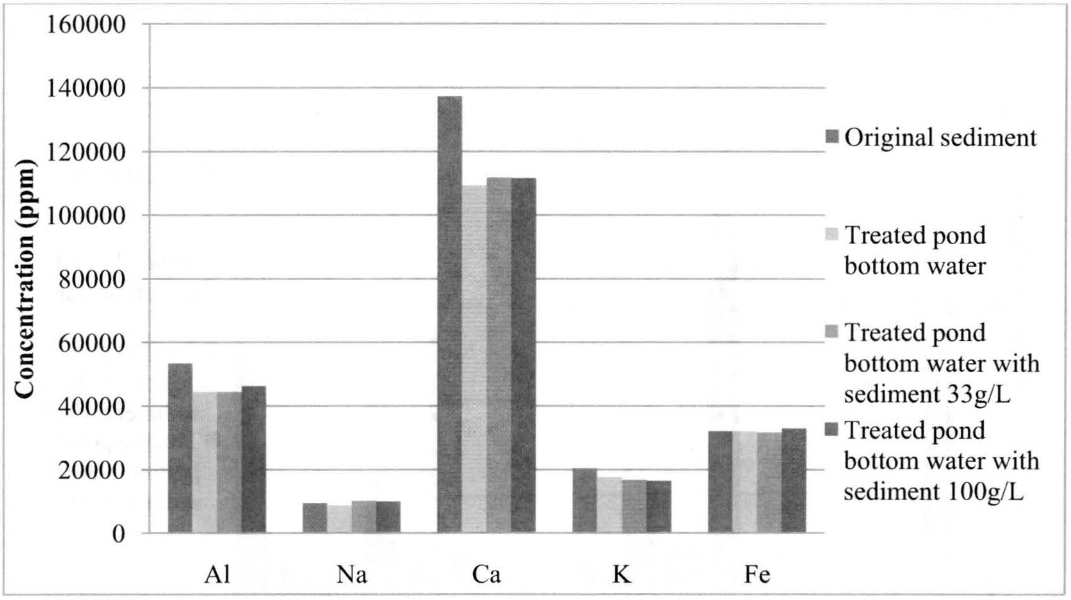


Figure 5.6. 3 Comparison of major elements between original sediment and PAED treated pond bottom water with various sediment additions observed by NAA (d = 0.5 mm, V_{ch}= 2 kV, Treatment time = 2 hrs)

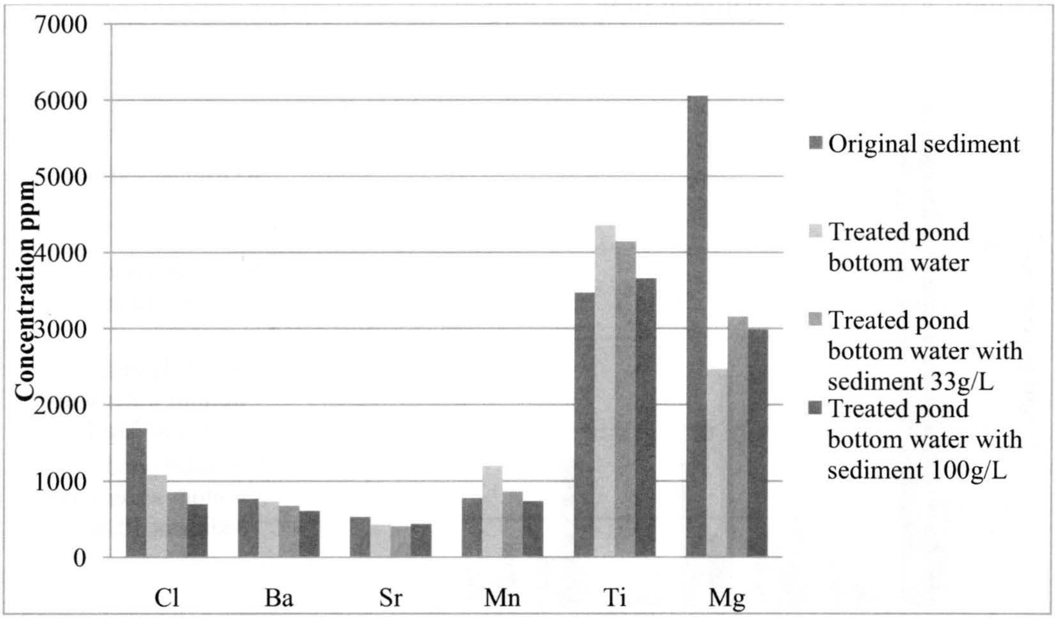


Figure 5.6. 4 Comparison of minor elements between original sediment and PAED treated pond bottom water with various sediment additions observed by NAA (d = 0.5 mm, V_{ch}= 2 kV, Treatment time = 2 hrs)

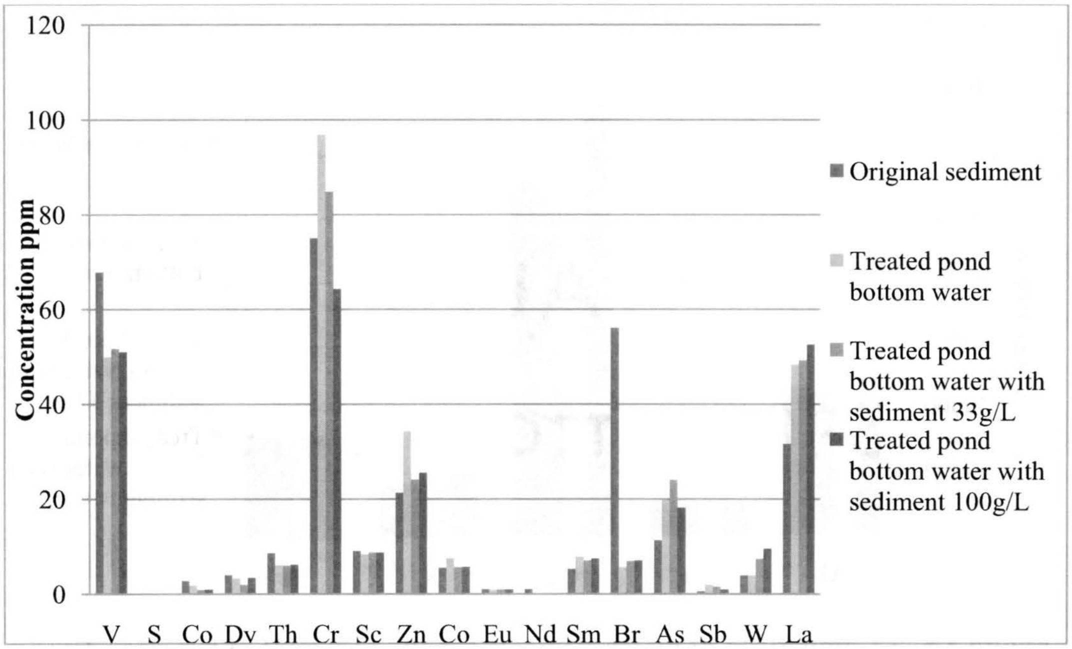


Figure 5.6. 5 Comparison of trace elements between original sediment and PAED treated pond bottom water with various sediment additions observed by NAA (d = 0.5 mm, V_{ch}= 2 kV, Treatment time = 2 hrs)

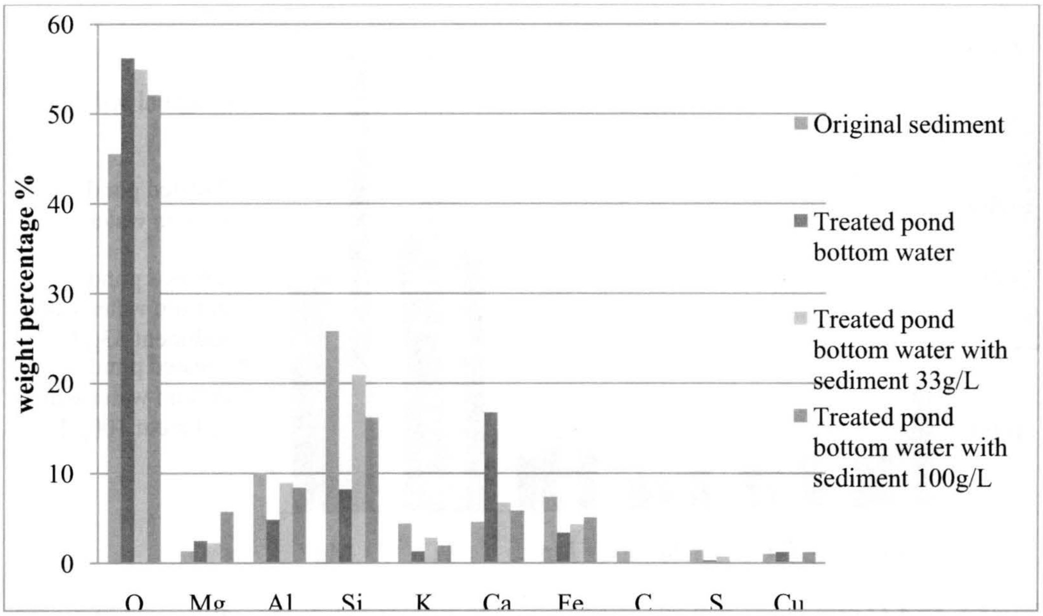


Figure 5.6. 6 Comparison of element weight percentages between original sediment and PAED treated pond bottom water with various sediment additions observed by NAA (d = 0.5 mm, V_{ch}= 2 kV, Treatment time = 2 hrs)

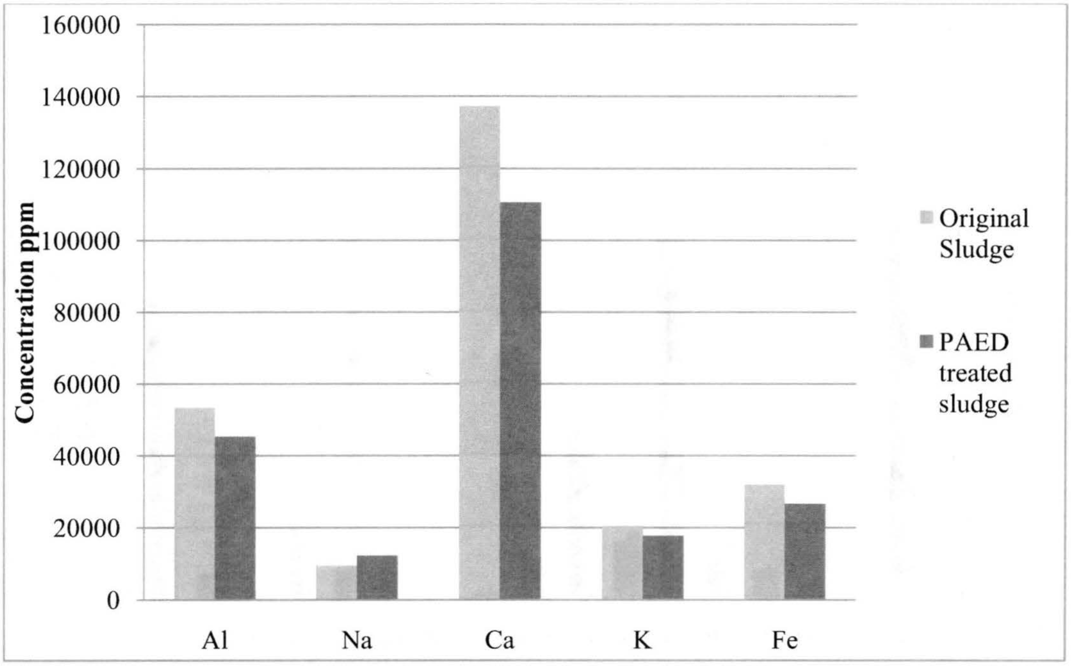


Figure 5.6. 7 Comparison of major elements between original sediment and PAED treated sludge-water observed by NAA (d = 0.5 mm, V_{ch}= 2 kV, Treatment time = 2 hrs)

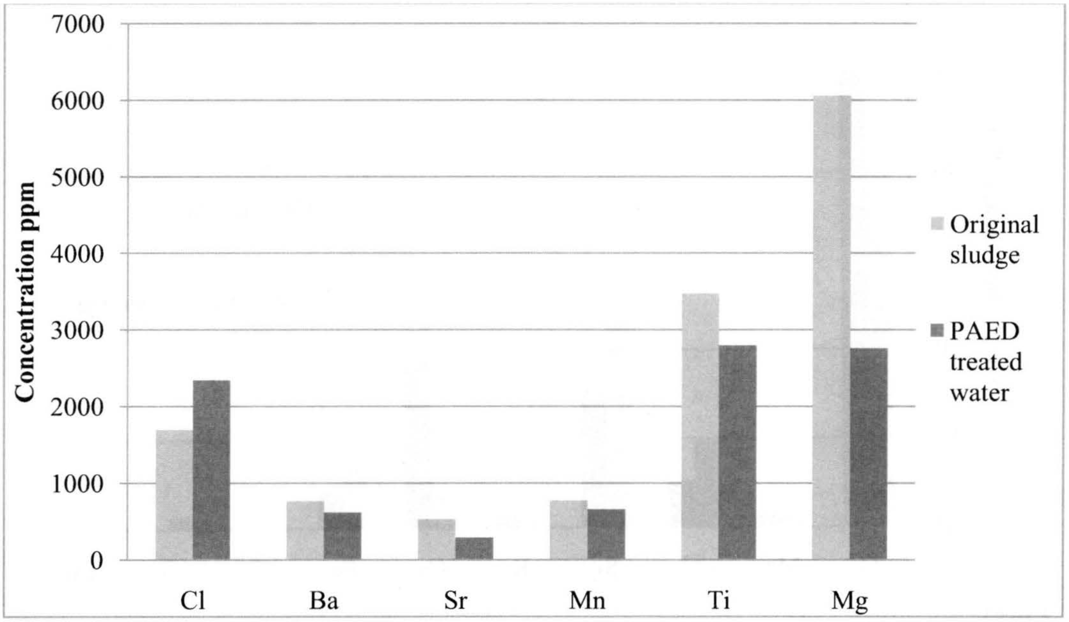


Figure 5.6. 8 Comparison of minor elements between original sediment and PAED treated sludge-water observed by NAA (d = 0.5 mm, V_{ch}= 2 kV, Treatment time = 2 hrs)

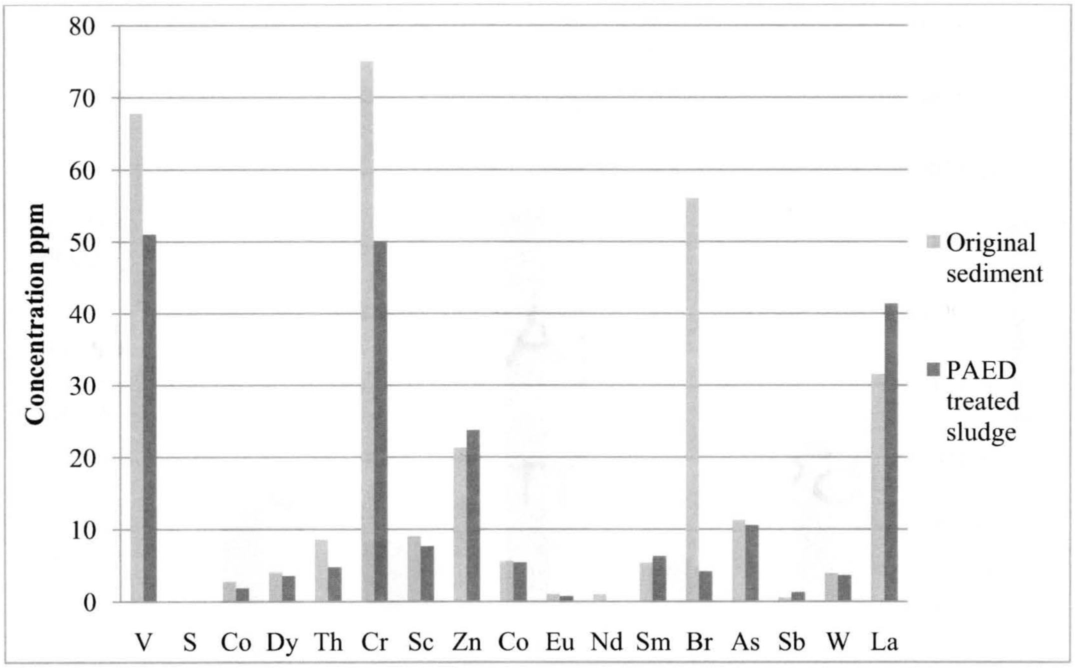


Figure 5.6. 9 Comparison of trace elements between original sediment and PAED treated sludge-water observed by NAA (d = 0.5 mm, V_{ch}= 2 kV, Treatment time = 2 hrs)

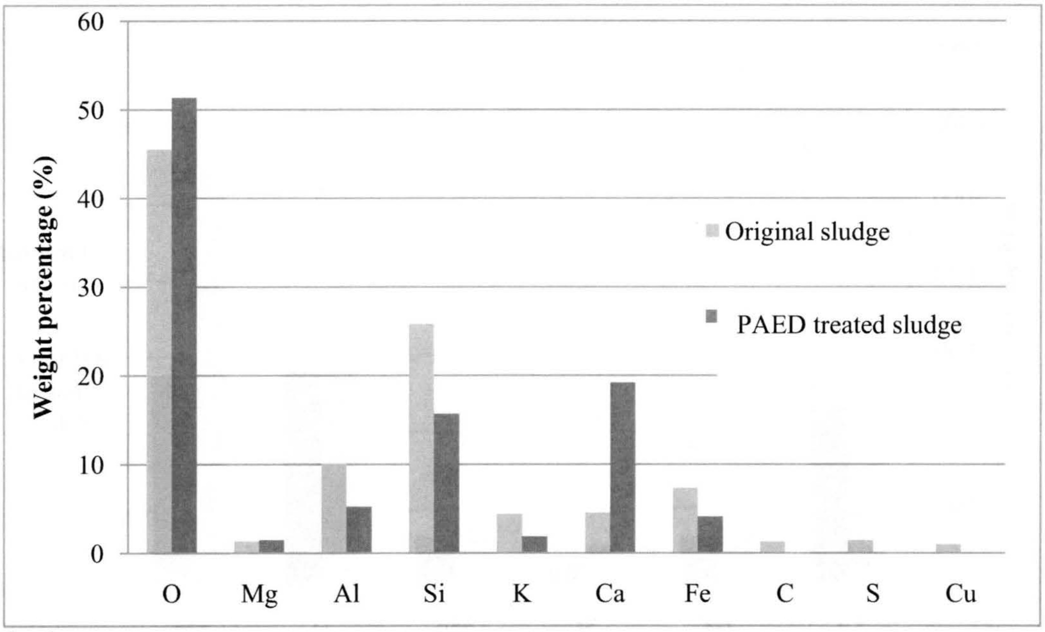


Figure 5.6. 10 Comparison of element weight percentages between original sediment and PAED treated sludge-water observed by XRF (d = 0.5 mm, V_{ch}= 2 kV, Treatment time = 2 hrs)

Chapter 6: Thermal Plasma Treatment of Stormwater Sludge

Two different operation modes were applied to thermal plasma sludge treatment: non-transferred and partial transferred modes. Seven sets of experiments conducted for thermal plasma treatment of stormwater sludge will be used for discussion. A fixed voltage of 120 V was applied to the plasma torch. Current was controlled by a resistor bank and adjusted between 70 and 86 A. Small part of current (2 - 5 A) flowed through the ground electrode via sludge under the partial transferred mode. Based on the blank test (without sludge) of the thermal plasma torch, stable operation with optimum temperature was achieved under an argon flow rate of 24 L/min. Air flow rates to the environmental chamber were adjusted to 0 - 20 % of the argon flow rate of 24 L/min, which is correspondingly about 0 - 4.8 L/min. The environmental chamber was being purged by argon gas prior to the treatment. In addition, air flow rate was introduced into the system after plasma torch operated in stable condition (around 5 minutes after turning on the torch). Wet stormwater sludge of 30 - 40 grams and dried PAED treated sludge of 10 grams were treated by thermal plasmas. The experimental treatment matrix discussed in this Chapter is summarized in Table 6.1, where only one experiment was conducted for non-transferred mode as a reference since comprehensive non-transferred mode experiments were already conducted by Li (2006) using the same experimental set-up.

The average weight reduction of wet stormwater sludge and dried PAED treated sludge after thermal plasma treatment was 33 and 1.3% as shown in Table 6.2. The moisture percentage in the original wet sludge was approximately 30%. Water and organic contents were evaporated after treatment, hence the weight reduction in wet sludge was corresponded to the water and TOC reduction. In dried PAED treated sludge, the weight reduction is approximately equal to solely the reduction of TOC. In the following, Sections 6.1 and 6.2 focus on thermal plasma treatment of wet stormwater sludge under the non-transferred and partial transferred modes respectively. In Section 6.3, the results of thermal plasma treatment of dried PAED treated sludge under the partial transferred mode are discussed first, and then the results from a single thermal plasma treatment and those from the combined treatment by both PAED and thermal plasma are compared. Section 6.4 presents comparisons of the treatment results under different modes, and Section 6.5 presents discussions about the effect of argon and air flow rates, respectively, on gaseous by-product generations and the solid products.

Table 6. 1 Experimental treatment matrix

Experiment	Type of Sludge	Operation mode	Argon (L/min)	Air (L/min)	Treatment Time (hr)	Power (MW)
1	wet sludge	Non-Transferred	35	0	1	2.4
2	wet sludge	Partial Transferred	35	0	1	1.7
3	wet sludge	Partial Transferred	24	0	2.5	1.9
4	wet sludge	Partial Transferred	24	2.4	4	2.1
5	wet sludge	Partial Transferred	24	4.8	2	1.9
6	Dried PAED treated sludge	Partial Transferred	24	0 - 4.8	2	2.1

Note: Approximately 240W transferred to reactor's ground electrode in the partial transferred mode

Table 6. 2 Weight loss after thermal plasma treatment

Experiment	Weight before thermal plasma treatment (g)	Weight after thermal plasma treatment (g)	lost in weight (%)
1	33.53	21.79	35.01
2	40.29	27.74	31.15
3	41.81	27.27	34.78
4	41.23	27.19	34.05
5	41.58	27.89	32.92
6	11.17	11.03	1.25

6.1 Plasma Reactor Operation Under Non-Transferred Mode

6.1.1 Gaseous Emission Analyses During Plasma Treatment

A thermal plasma treatment of stormwater wet sludge was carried-out in anoxic (no air injection) environment under non-transferred mode as a reference. Figure 6.1.1.1 shows the gaseous emission during the thermal plasma treatment. NO and SO_2 were generated at the first 10 minutes; CO was generated between 10 and 30 minutes; H_2S and C_xH_y were generated continuously. This trend might be closely related to the near reactor gas temperature (also referred as gas temperature) transient as shown in Figure 6.1.1.2, where the near reactor gas temperature is proportional to the volume averaged plasma temperature (1500 - 2000 °C) (Khalaf et al., 2008: Appendix D). The gas temperature increased sharply in the first 10 minutes, and gradually became stable at 303°C when treatment time reached 30 minutes. Oxygen and hydrogen were dissociated from H_2O in wet sludge at the beginning, and provided for the formation of NO, SO_2 and C_xH_y. In addition, oxygen was also provided by oxide compounds in the sludge for oxidation. Reduction occurred after all oxidation was completed after the first 30 minutes. Organic contents were mostly converted into hydrocarbons in the anoxic environment, which was observed by Li (2006) for dry sludge treatment under non-transferred plasma mode. The accumulated concentrations of CO, NO, SO_2, H_2S and C_xH_y after one hour of treatment were 149, 31, 510, 38 and 3067 mg/m^3 respectively.

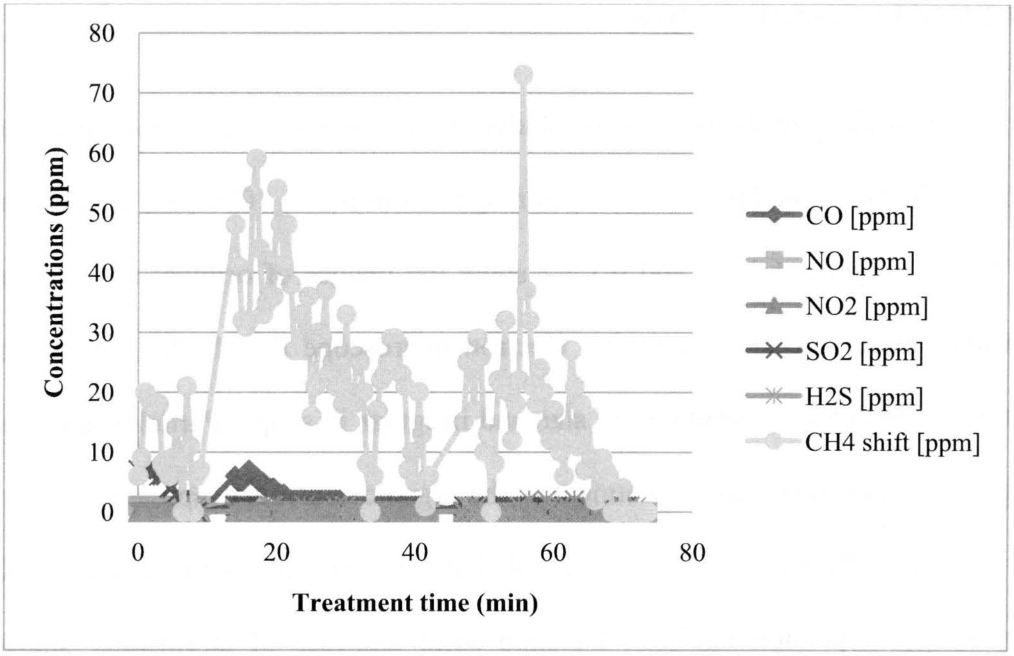


Figure 6.1.1. 1 Gaseous emission during thermal plasma treatment of wet sludge under non-transferred mode at argon = 35 L/min (Power (P) = 2.4 kW, treatment time = 1 hr)

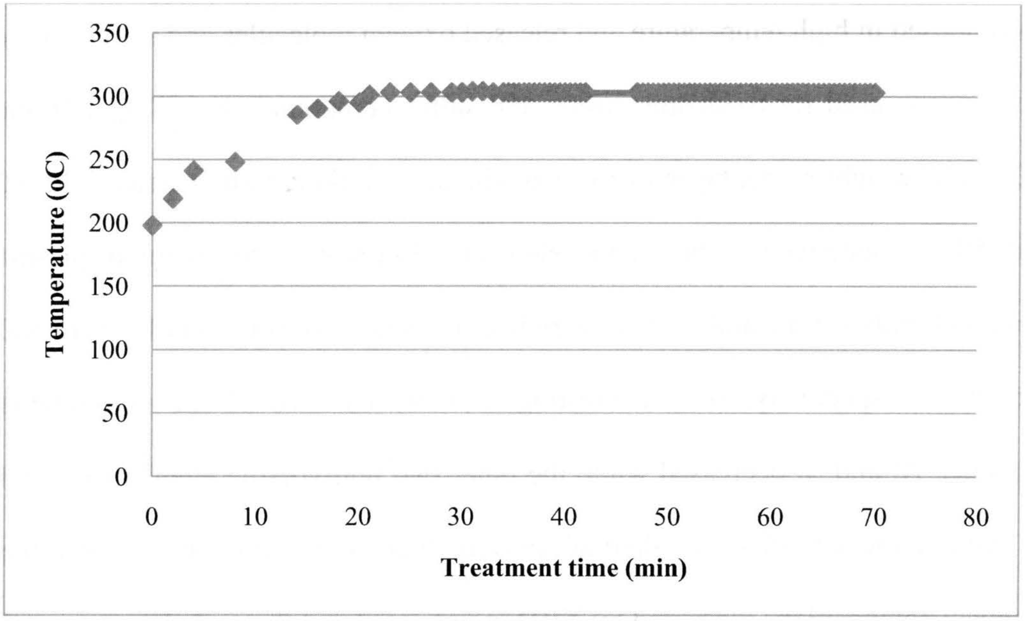


Figure 6.1.1. 2 Near reactor gas temperature transient during thermal plasma treatment under non-transferred mode (argon flow rate = 35 L/min, P = 2.4 kW)

6.1.2 Solid By-Products Analyses

Particle size distribution of sludge before treatment is shown in Figure 5.6.1 of Section 5.6. The particle sizes ranged from 0.3 to 1000 μm, with a peak of 10 μm. Figures 6.1.2.1 and 6.1.2.2 show the images of original and thermal plasma treated sludge by scanning electron microscope (SEM). In general, the untreated particles are scattered in size and irregular in shape. Particles appeared slightly smaller in size after treatment as the organic contents evaporated. Figure 6.1.2.3 shows the solid analysis results of sludge before and after treatment by X-ray energy dispersion analysis. Detailed solid analyses of stormwater sludge (untreated) were discussed in Section 5.6. After thermal plasma treatment, carbon and sulfur from the solid were converted into gaseous by-products. Oxides were decomposed in high temperature and released oxygen molecules and atoms. Some oxygen was used for oxidizing carbon and sulfur compounds into CO_2, CO and SO_2. The weight percentages of oxygen, silicon and aluminum decreased 40, 30 and 50% respectively. The major elements decreased after thermal plasma treatment, only Ca, Fe and Cl were enriched. Enrichments of Ca and Fe were 500 and 20%, respectively. It is interesting to note that two of the non-volatile elements, Al and Si decreased while the other two non-volatile elements Ca and Fe were enriched after the thermal plasma treatment. Table 6.3 shows the chemical compositions measured by XRD in untreated and thermal plasma treated sludge. Major compositions of original stormwater sludge were sand (SiO_2) and calcite ($CaCO_3$). The results corresponded well to the observation by X-ray energy dispersion in untreated sludge. The chemical compositions in sludge were quite different after thermal plasma treatment under non-transferred mode. The percentages of sand and calcite decreased 35 and 10% respectively. Other compositions such as $KAlSi_3O_8$, Fe_3O_4, NaCl and $CaSO_4$ were formed after treatment. It can be concluded that chemical compounds were decomposed and re-combined under thermal plasma treatment.

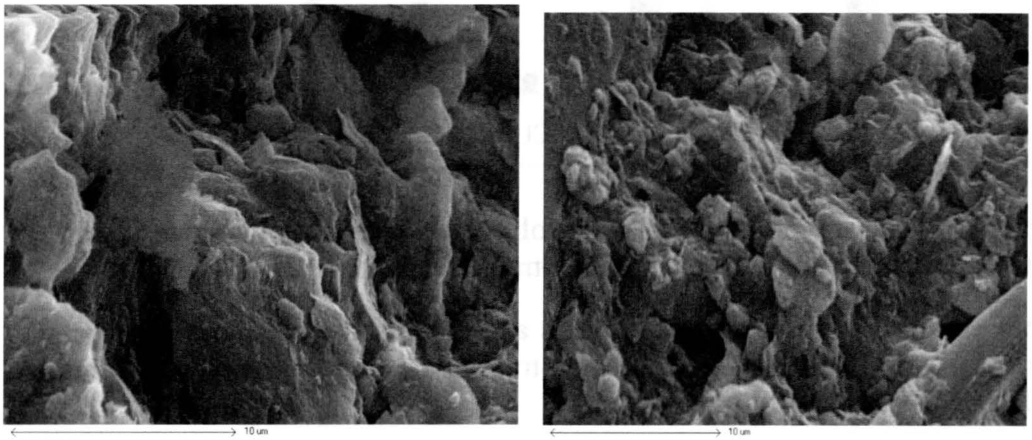


Figure 6.1.2. 1 SEM image of original untreated dried sludge (magnification of 4020) and Figure 6.1.2. 2 SEM image of treated sludge by thermal plasma treatment under non-transferred mode with argon flow rate of 35 L/min in one hour, P = 2.4 kW (magnification of 4300)

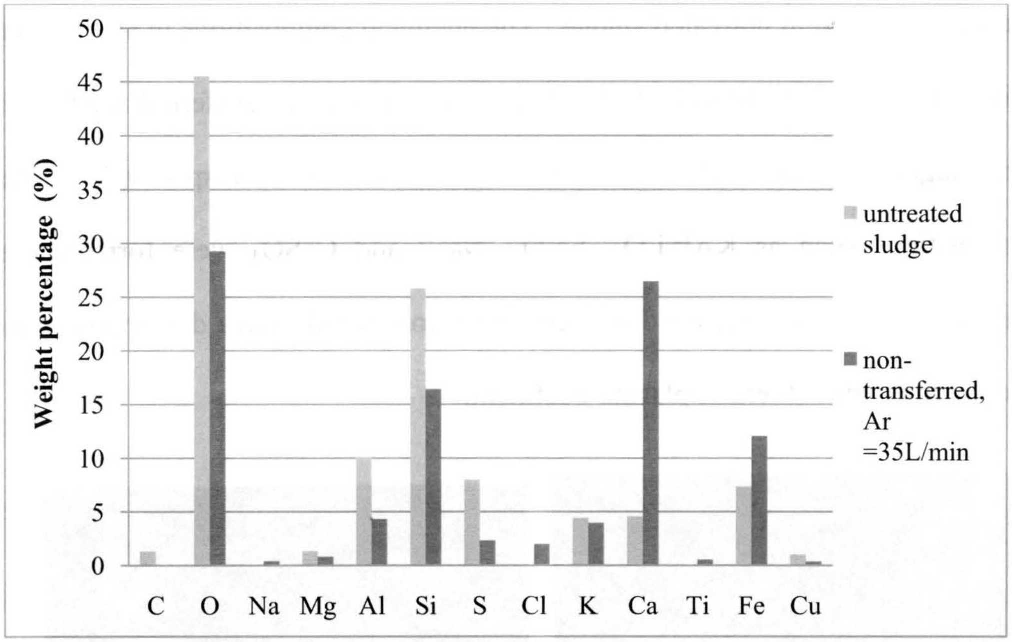


Figure 6.1.2. 3 X-ray energy dispersion solid analysis results of untreated and thermal plasma treated sludge under non-transferred mode (P = 2.4 kW)

Table 6. 3 XRD Chemical compositions analysis results for dried untreated and thermal plasma treated sludge under non-transferred mode with argon flow rate of 35 L/min (P = 2.4 kW)

Compounds	Dried untreated sludge	Treated under non-transferred mode
Quartz/sand	33%	21%
Calcite	20%	17%
Anorthite and albite/feldspars	9%	10%
Microcline $KAlSi_3O_8$		3%
Magnetite Fe_3O_4		4%
Chamosite/chlorite/(clay)	6%	7%
Amphibole	2%	2%
Biotite/micas/illite clay	6%	7%
Montmorillonite/clay	6%	8%
Halite NaCl		2%
Anhydrite CaSO4		2%
Bassanite,$CaSO_4 \cdot 0.5H_2O$		2%

Dolomite	8%	7%
Kaolinite/clay $Al_2Si_2O_5(OH)_4$	6%	1%
Rutile TiO_2		1%
Amorphous, ect.	4%	6%

6.2 Plasma Reactor Operation Under Partial Transferred Mode

6.2.1 Gaseous Emission Analyses During Thermal Plasma Treatment

The gaseous emissions during thermal plasma treatment of wet sludge under partial transferred operation mode with argon flow rate of 35 and 24 L/min are shown, respectively, in Figures 6.2.1.1 and 6.2.1.2. Hydrocarbons, H_2S, CO and NO were emitted continuously while SO_2 was formed in a certain period. CO_2 and NO_2 were not generated in the anoxic environment. The emission profile was correlated to the near reactor gas temperature profile as shown in Figure 6.2.1.3. The gas temperature increased gradually in the treatment with argon flow rate of 35 L/min, and reached 380°C at 55 minutes. Generation of C_xH_y, CO, H_2S and NO reached maximum, and SO_2 was formed within the sharp increase of gas temperature between 350 and 380 °C. Most of the organic contents and sulfur compounds were converted into gaseous by-products in treatment times between 50 and 60 minutes. The accumulated concentrations of C_xH_y, CO, NO, H_2S and SO_2 were 8172, 22748, 196, 53 and 373 mg/m^3 respectively.

The gas temperature with an argon flow rate of 24 L/min reached 450 °C and was stable after 40 minutes. Higher gas temperature was observed with lower argon flow rate and higher power. C_xH_y, H_2S, CO and NO were emitted continuously while SO_2 was formed in a certain period. Generation of NO reached a maximum in the first 10 minutes when the gas temperature increased from 200 to 250 °C. Nitrates and moisture in the wet sludge decomposed and recombined to form gaseous NO at the beginning. Other major gaseous compounds such as C_xH_y, H_2S and CO were generated at the highest during the treatment time of 30 minutes. In the temperature range of 350 – 430 °C, most of the organics were converted into gaseous hydrocarbons and CO. Oxide compounds in the sludge were decomposed and released oxygen to form CO and SO_2. The generation of C_xH_y and CO decreased after 40 minutes when the gas temperature was stable at 450 °C. Minimum concentrations of CO and NO were generated after a treatment time of 100 minutes, while no hydrocarbons were formed after a treatment time of 130 minutes. It can be surmised that the surface organic compounds in wet sludge were all evaporated. The accumulated concentrations of C_xH_y, CO, NO, H_2S and SO_2 were 14700, 8700, 1590, 350 and 590 mg/m^3 respectively.

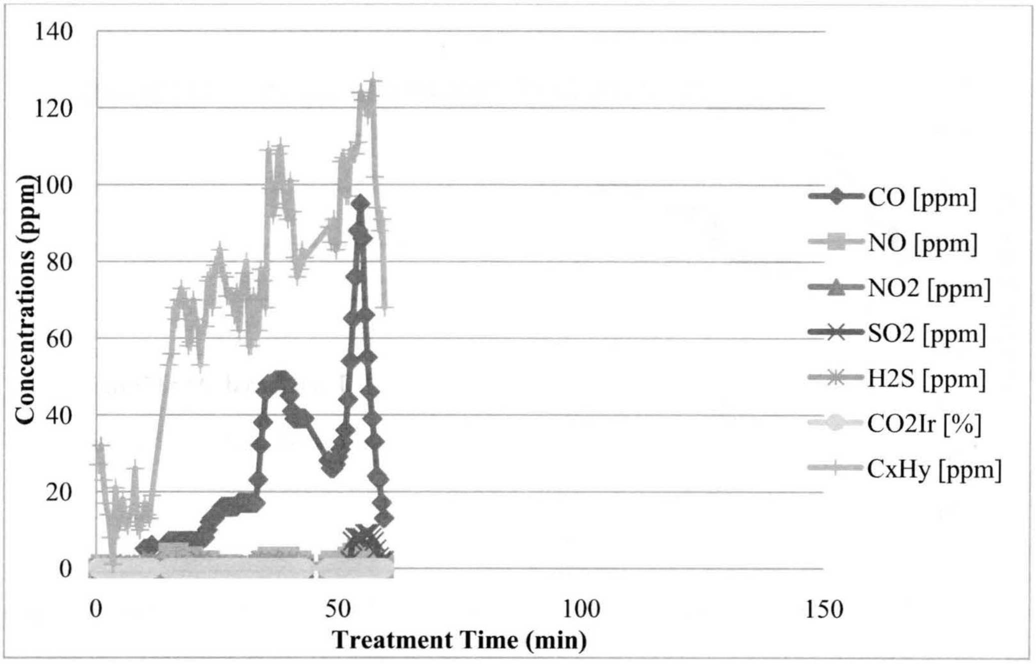


Figure 6.2.1. 1 Gaseous emission during thermal plasma treatment of wet sludge under partial transferred operation mode with argon flow rate of 35 L/min (treatment time = 1 hour, P = 1.7 kW)

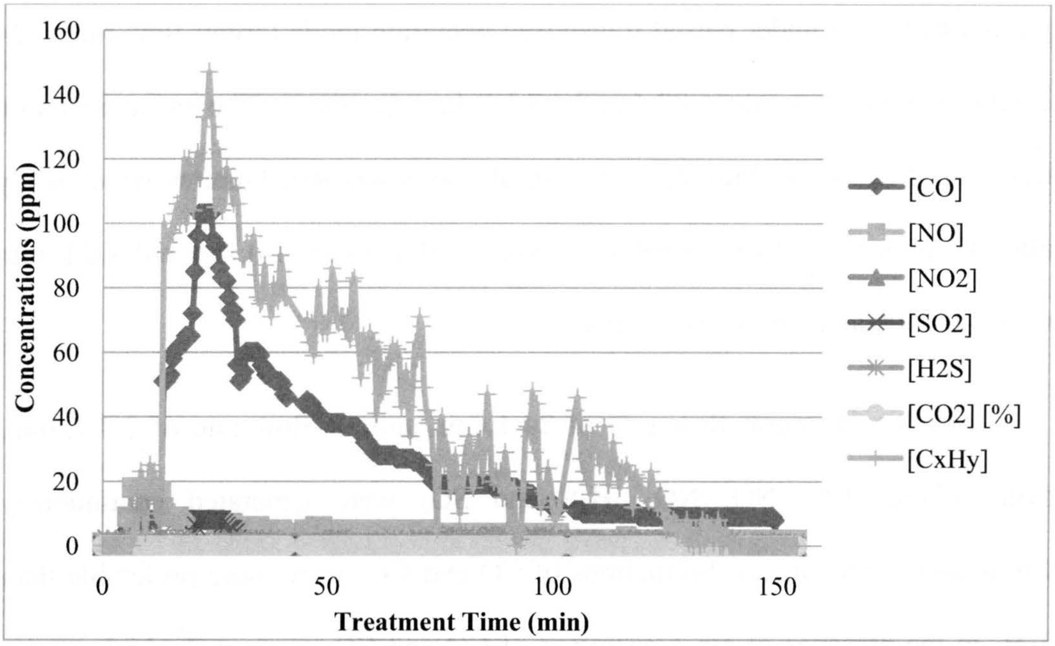


Figure 6.2.1. 2 Gaseous emission during thermal plasma treatment of wet sludge under partial transferred operation mode with argon flow rate of 24 L/min (treatment time = 2.5 hours, P = 1.9 kW)

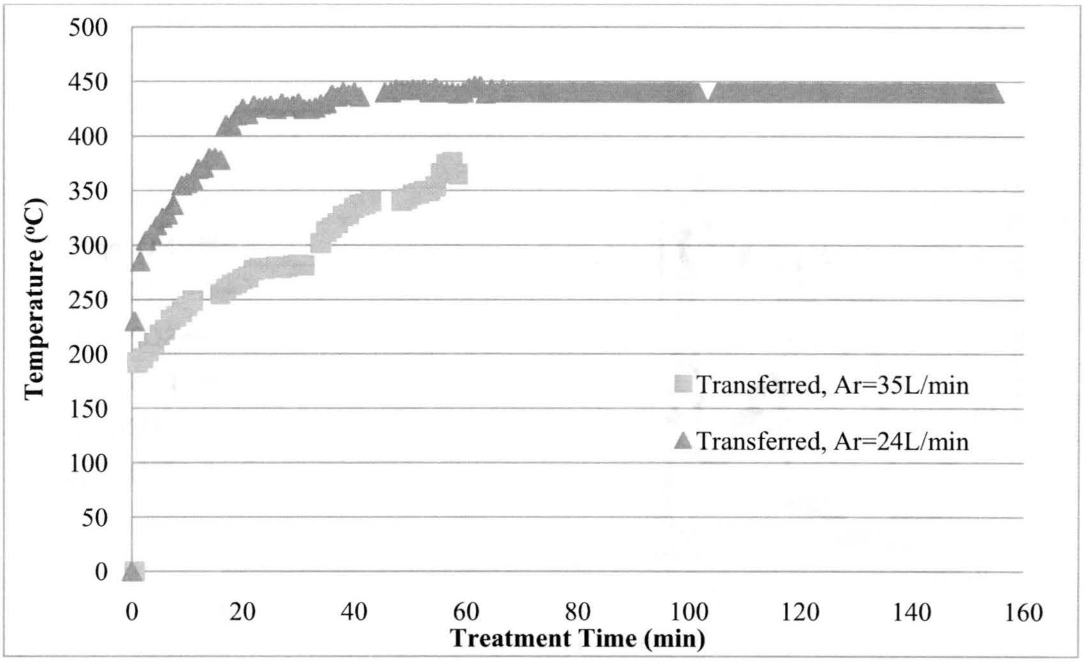


Figure 6.2.1. 3 Near reactor gas temperature transient with argon flow rates of 24 and 35 L/min (P = 1.7 - 1.9 kW)

Figures 6.1.2.4 and 6.1.2.5 show the gaseous emission during thermal plasma treatment under partial transferred operation mode (argon flow rate = 24 L/min) with air flow rates of 2.4 and 4.8 L/min respectively. The gas temperature transient is shown in Figure 6.1.2.6. In all cases gas temperatures were steady after 40 minutes. The gas temperature with air flow rates of 0, 2.4 and 4.8 L/min were 440, 500 and 450 °C, respectively.

Under the argon flow rate of 24 L/min and air flow rate of 2.4 L/min, hydrocarbons, CO, NO, NO_2, H_2S and SO_2 were generated continuously throughout the treatment. Formations of CO and CO_2 were more preferable than C_xH_y in the presence of air. Generation of CO and CO_2 were at the highest at a treatment time of 15 minutes. Concentrations of CO and CO_2 decreased sharply after reaching the maximum value, while NO stayed at a constant concentration.

The generation of CO also became steady after 90 minutes. Oxidation of surface organic contents in sludge was completed after 90 minutes. Further treatment of organics located at the bottom of sludge was observed at longer treatment times. A sudden increase of C_xH_y and CO_2 concentrations was detected between 170 - 190 minutes. It can be concluded that the additional gaseous by-products were generated when organic contents slowly diffused onto the surface. Close to the end of the experiment, the current was adjusted from 82 to 50 A between 200 and 210 minutes. The fluctuations of CO and NO concentrations can be correlated to the sudden decrease of current, which also corresponded to a sharp decrease in operating temperature. It can be concluded that the concentrations of CO and NO were depending on the power and operating temperature of the thermal plasma in the argon-air environment. The accumulated concentrations of C_xH_y, CO, CO_2, NO, NO_2, H_2S and SO_2 with 4-hour treatment were 13500, 22900, 14400, 28200, 640, 110 and 314 mg/m^3 respectively. Generation of CO was higher than C_xH_y and CO_2 with limited oxygen supply.

The gas temperature was stable at 400 °C after 30 minutes in thermal plasma treatment of sludge with argon and air flow rates of 24 and 4.8 L/min respectively. The system was first operated with argon flow alone in order to create a stable plasma environment. The air flow rate was adjusted to 4.8 L/min after 10 minutes. Generations of CO, CO_2, NO and NO_2 started when air flow was applied to the system. Hydrocarbons, CO, NO, H_2S and SO_2 were generated continuously. The concentrations of CO and CO_2 reached maximum at 20 and 30 minutes of treatment times respectively. Concentrations of NO and NO_2 became constant after 18 minutes. The accumulated concentrations of C_xH_y, CO, CO_2, NO, NO_2, H_2S and SO_2 after two hours of treatment were 11000, 5040, 38000, 3900, 390, 190 and 710 mg/m^3 respectively. Generation of CO_2 was higher than CO and C_xH_y with sufficient oxygen supply. In addition, sulfur compounds were more preferably being converted into gaseous SO_2.

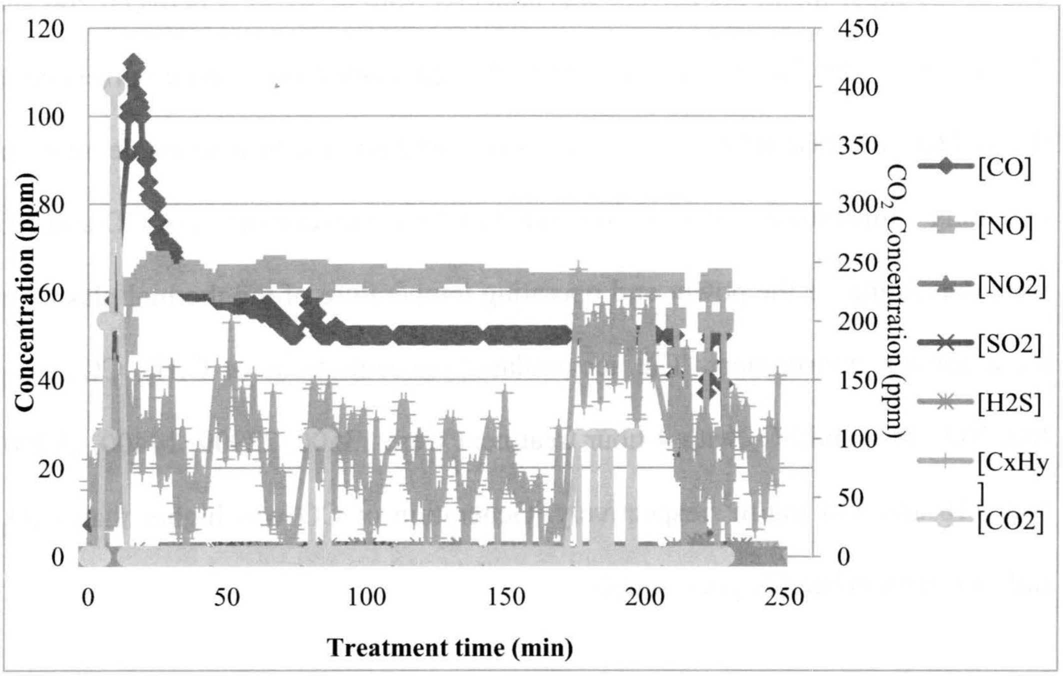


Figure 6.2.1. 4 Gaseous emission during thermal plasma treatment of wet sludge under partial transferred mode with argon flow rate of 24 L/min and air flow rate of 2.4 L/min (treatment time = 4 hours, P = 2.1 kW)

Figure 6.2.1. 5 Gaseous emission during thermal plasma treatment of wet sludge under partial transferred mode with argon flow rate of 24 L/min and air flow rate of 4.8 L/min (treatment time = 2 hours, P = 1.9 kW)

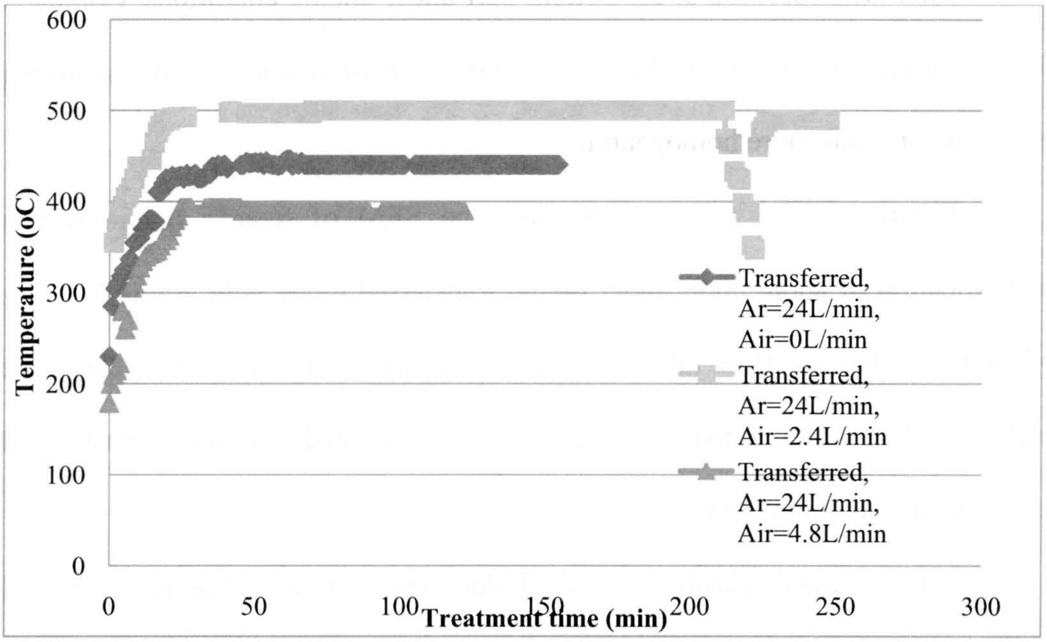


Figure 6.2.1. 6 Temperature profile for thermal plasma wet sludge treatment under partial transferred mode with argon flow rate of 24 L/min and various air flow rates (P = 1.9 - 2.1 kW)

6.2.2 Solid By-Products Analyses

Figures 6.2.2.1 and 6.2.2.2 show the images of treated sludge by thermal plasma treatment under partial transferred mode with argon flow rate of 24 L/min and air flow rate of 0 and 2.4 L/min respectively. Small holes were made at the beginning of treatment in order to increase the amount of current pass through (plasma) to the ground electrode via the wet sludge. Significant sludge color difference was observed in the images of treated sludge. The sludge appeared dark brown/black in color under anoxic environments and light brown under oxidizing environments. In addition, sludge was less homogenously treated under anoxic environments. A dark brown color was apparent in the upper part while a light brown color was observed at the bottom part under anoxic conditions. Compared to the anoxic environments, the thermal plasma treated sludge under oxidizing environments was more homogenous.

Figures 6.2.2.3 and 6.2.2.4 show the SEM of treated sludge with a magnification of about 5000 under partial transferred mode with argon flow rate of 24 L/min and air flow rates of 0 and 2.4 L/min respectively. Particles were melted under partial transferred mode, which indicated that the formation of unleachable slag might be possible.

Since thermal plasma treated sludge was not homogenous in partial transferred mode, the solid analysis by X-ray energy dispersion were carried out for both the darker and lighter parts of the treated sludge. Figures 6.2.2.5, 6.2.2.6, 6.2.2.7 and 6.2.2.8 show the solid analysis results of thermal plasma treated sludge by argon flow rate of 35 L/min, argon flow rate of 24 L/min, argon and air flow rate of 24 and 2.4 L/min, and argon and air flow rate of 24 and 4.8 L/min, respectively. In general, major elements except Ca and Fe decrease in weight percentage after thermal plasma treatments. Carbon and sulfur were mostly reduced to zero in oxidizing environments. On the other hand, reduction of sulfur was only 10 - 30% in anoxic environments. The result shows that removal of sulfur compounds in wet sludge can be enhanced by oxidation. In anoxic environments, oxygen decreased 30 - 60 % due to decomposition of oxide compounds during thermal plasma treatment. Weight percentages of Si, Al and Mg decreased 40, 50 and 30% where Ca and Fe enriched 500 and 60% on average after treatments.

Difference in elemental weight percentages was observed between the darker and lighter parts after treatment under anoxic environments. Higher weight percentages of Ca, Fe, S and Cl were observed in darker particles, while higher weight percentages of Al and Si were observed in lighter particles. For thermal plasma treatment under oxidizing environments, elemental percentages were quite similar between darker and lighter parts.

Detailed solid analysis of TOC and chemical compositions of thermal plasma treated sludge was obtained by XRD, as shown in Table 6.4. Despite the extremely high temperature in plasma, TOC were not totally vaporized after the treatment. It may be due to the fact that gaseous hydrocarbon quenched during the treatment process. Also, soot particles were observed around the environmental chamber. Effect of argon and air flow rate on TOC reduction of the thermal plasma treatment will be discussed in detail in Section 6.5.2. Under anoxic environments, lighter parts were found to be more similar to original sludge in chemical compositions. Compared to the lighter part, formations of NaCl, $CaSO_4$ and Fe_3O_4 are higher in darker parts. In addition, the darker parts were also slightly magnetic. The observation agrees with the results of NAA and X-ray energy dispersion, where concentrations of Na, Cl, Ca and Fe were higher in the darker parts as well. Recovery of Fe might be possible in this condition.

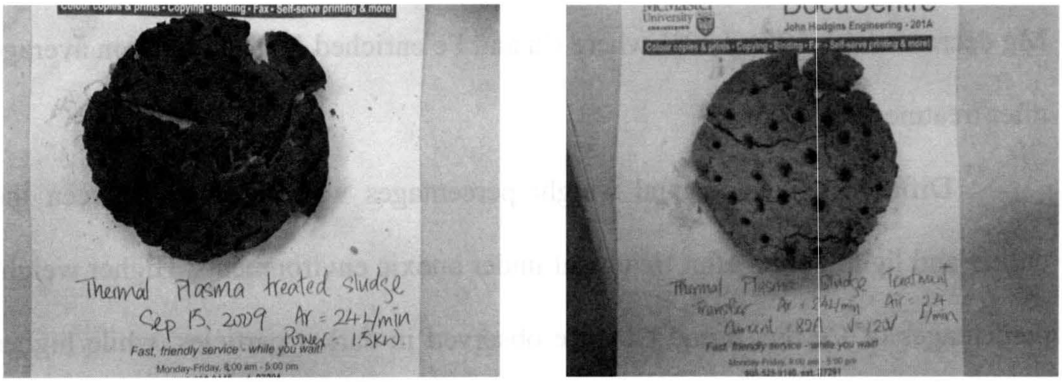


Figure 6.2.2. 1 X-ray energy dispersion solid analysis results of thermal plasma treated sludge under partial transferred mode (P = 1.7 kW) with argon flow rate of 35 L/min after one hour of treatment and Figure 6.2.2. 2 X-ray energy dispersion solid analysis results of darker and lighters part of thermal plasma treated sludge under partial transferred mode (P = 1.9 kW) with argon flow rate of 24 L/min after 2 hours of treatment

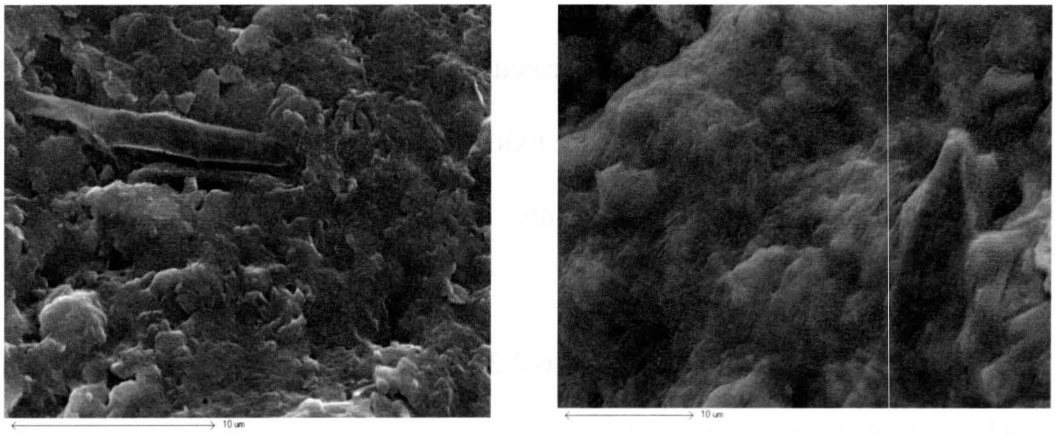


Figure 6.2.2. 3 X-ray energy dispersion solid analysis results of thermal plasma treated sludge under partial transferred mode (P = 2.1 kW) with argon and air flow rates of 24 and 2.4 L/min, respectively, after 4 hours of treatment and Figure 6.2.2. 4 X-ray energy dispersion solid analysis results of thermal plasma treated sludge under partial transferred mode (P = 1.9 kW) with argon and air flow rates of 24 and 4.8 L/min, respectively, after 2 hour of treatment

Since the elemental percentages in lighter and darker parts of treated sludge under oxidizing environments were similar (as shown in Figures 6.2.2.7 and 6.2.2.8), the solid analysis by XRD was only focused on the average chemical composition of treated sludge (hence the analyses were not carried out for darker and lighter parts separately). The most abundant elements in treated sludge under oxidizing environments were O, Ca, Si and Fe. Sand (SiO_2) and kaolinite decreased around 33 and 80% on average respectively while $CaSO_4$, $KAlSi_3O_8$, NaCl and Fe_3O_4 were formed after thermal plasma treatment.

A detailed analysis of elemental concentration by NAA was conducted on two thermal plasma treated sludge under partial transferred mode: with argon flow rate of 24 L/min in anoxic environment and in oxidizing environment (air flow rate = 2.4 L/min). In this Section, discussions of NAA results are only carried out for the lighter and darker parts of treated sludge under anoxic environment. The NAA results of treated sludge under oxidizing environment will be discussed, as well as compared to the NAA results obtained under anoxic environment in Section 6.5.2.

Figures 6.2.2.9, 6.2.2.10 and 6.2.2.11 show respectively the major, minor and trace elements of treated sludge under anoxic environments. Thirty-two elements were detected where 27 elements were above detection limits. Major elements (> 10000ppm) were Ca > Al > Fe > K > Mg > Na > Ti > Cl; minor elements (100-10000ppm) were Mn > Ba > Sr > Zn; and trace elements (<100ppm) were Mo > V > Cr > Br > La > As > Sc > Th> As > Co > Dy > W > Sb > Eu. The two most abundant elements, O and Si, cannot be detected by NAA, but other major elements were consistent with the results from X-ray energy dispersion. Unlike the results obtained from X-ray energy dispersion, enrichment of Ca in concentration was not observed in NAA. Enrichment of Ca in weight percentage might correspond to the formation of several new calcium compounds, as observed in XRD analysis in Table 6.4. Most elements were similar in concentration after thermal plasma treatment, with the exception of Zn, La, Co, Br and As. Concentrations of Zn, La and Co enriched 1500, 50 and 30% on average respectively, while Br, W and As decreased 80, 50 and 20% on average respectively. Volatile bromide compounds vaporized after thermal plasma treatments. Difference in concentrations between darker and lighter parts were mostly within 20%, with the exception of Cl. Lower concentrations of Al, Ca, Ba, Sr and Mn were observed in the darker part, while lower concentrations of Cl, Na, Fe and Zn were observed in the lighter part.

Table 6. 4 TOC and chemical compositions of original sludge, treated sludge with argon flow rate of 24 L/min and various air flow rates (0 - 4.8 L/min) under partial transferred mode in weight percentage (P =1.7 -2.1 kW)

	Dried untreated sludge	Transferred, Ar = 24 L/min (Darker)	Transferred, Ar = 24 L/min (Lighter)	Transferred, Ar = 24 L/min, air =2.4 L/min	Transferred, Ar = 24 L/min, air = 4.8 L/min
TOC	8%	5.3%	3.9%	2.6%	3.7%
Quartz/sand	33%	17%	22%	23%	22%
Calcite	20%	14%	19%	19%	18%
Anorthite and albite/feldspars $CaAlSi_2O_8$	9%	8%	10%	10%	10%
Microcline $KAlSi_3O_8$		2%	4%	3%	3%
Magnetite Fe_3O_4		6%	4%	4%	4%
Chamosite/chlorite	6%	6%	7%	7%	7%
Amphibole	2%	2%	2%	2%	2%
Biotite/micas/ clay	6%	6%	7%	7%	7%
Montmorillonite/clay	6%	7%	8%	8%	8%
Halite NaCl		7%	0%	0%	0%
Anhydrite CaSO4		9%	2%	2%	3%
Bassanite $CaSO_4 \cdot 0.5H_2O$		2%	2%	2%	3%
Dolomite $CaMg(CO_3)_2$	8%	7%	7%	7%	7%
Kaolinite/clay $Al_2Si_2O_5(OH)_4$	6%	2%	1%	1%	1%
Rutile TiO_2		1%	1%	1%	1%
Amorphous, ect.	4%	4%	4%	4%	4%

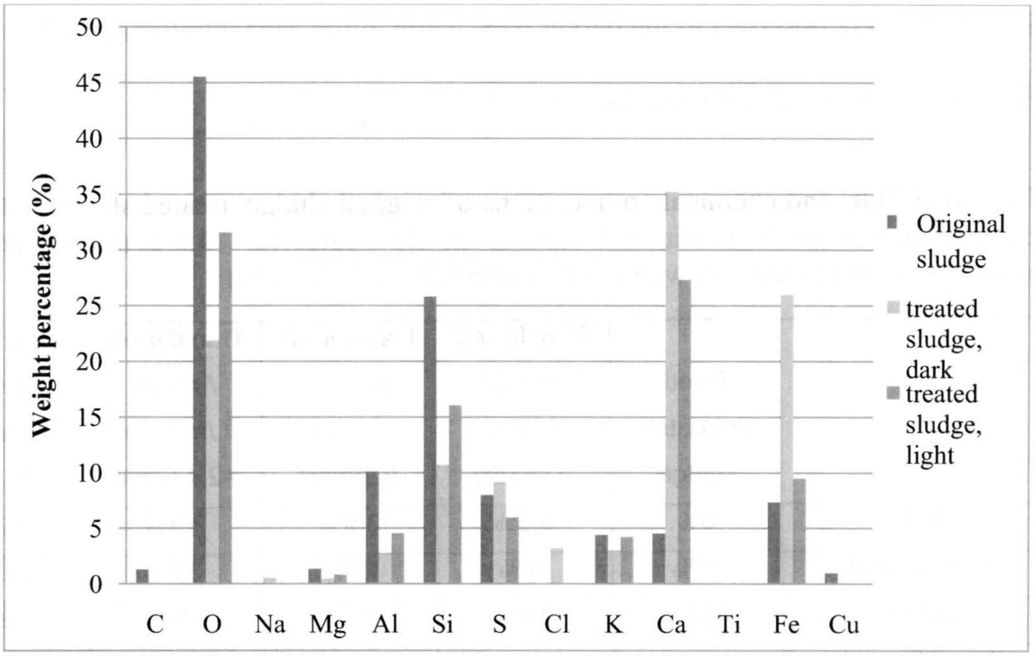


Figure 6.2.2. 1 X-ray energy dispersion solid analysis results of thermal plasma treated sludge under partial transferred mode (P = 1.7 kW) with argon flow rate of 35 L/min after one hour of treatment

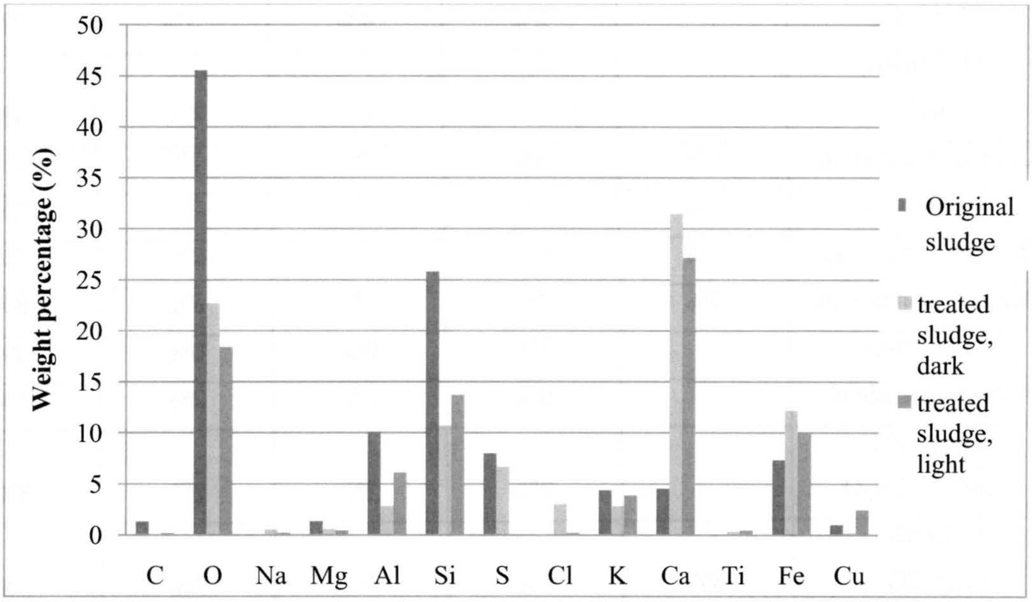


Figure 6.2.2. 2 X-ray energy dispersion solid analysis results of darker and lighter parts of thermal plasma treated sludge under partial transferred mode (P = 1.9 kW) with argon flow rate of 24 L/min after 2 hours of treatment

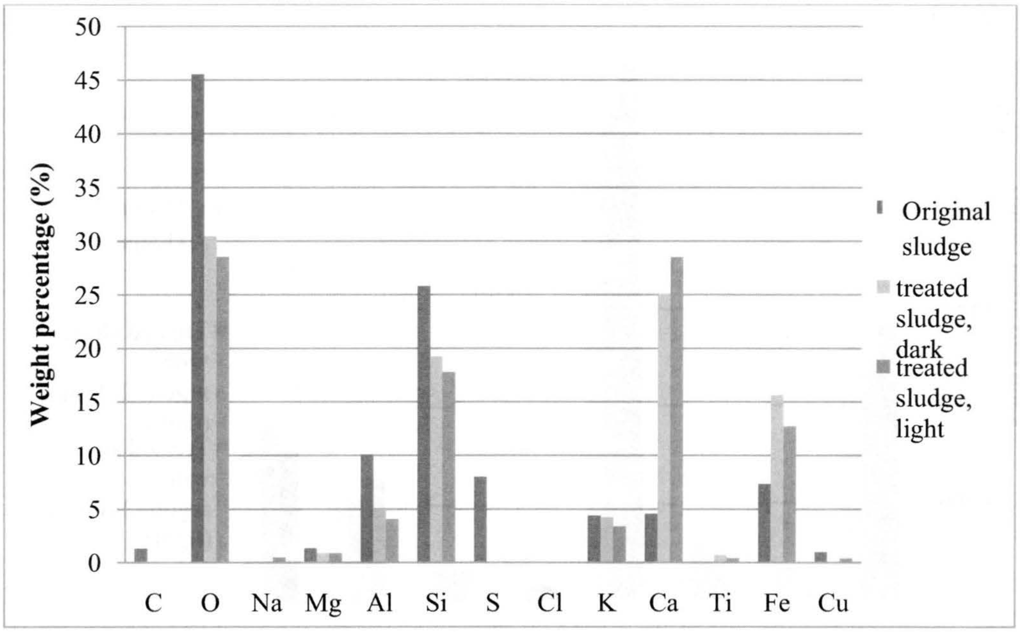


Figure 6.2.2. 3 X-ray energy dispersion solid analysis results of thermal plasma treated sludge under partial transferred mode (P = 2.1 kW) with argon and air flow rates of 24 and 2.4 L/min, respectively, after 4 hours of treatment

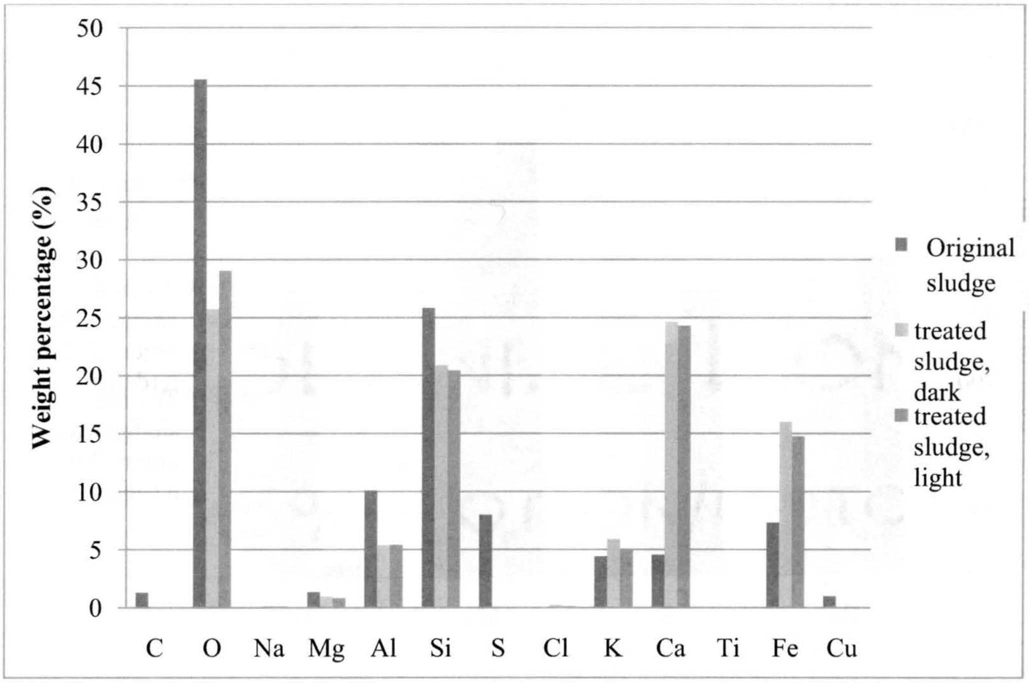


Figure 6.2.2. 4 X-ray energy dispersion solid analysis results of thermal plasma treated sludge under partial transferred mode (P = 1.9 kW) with argon and air flow rates of 24 and 4.8 L/min, respectively, after 2 hours of treatment

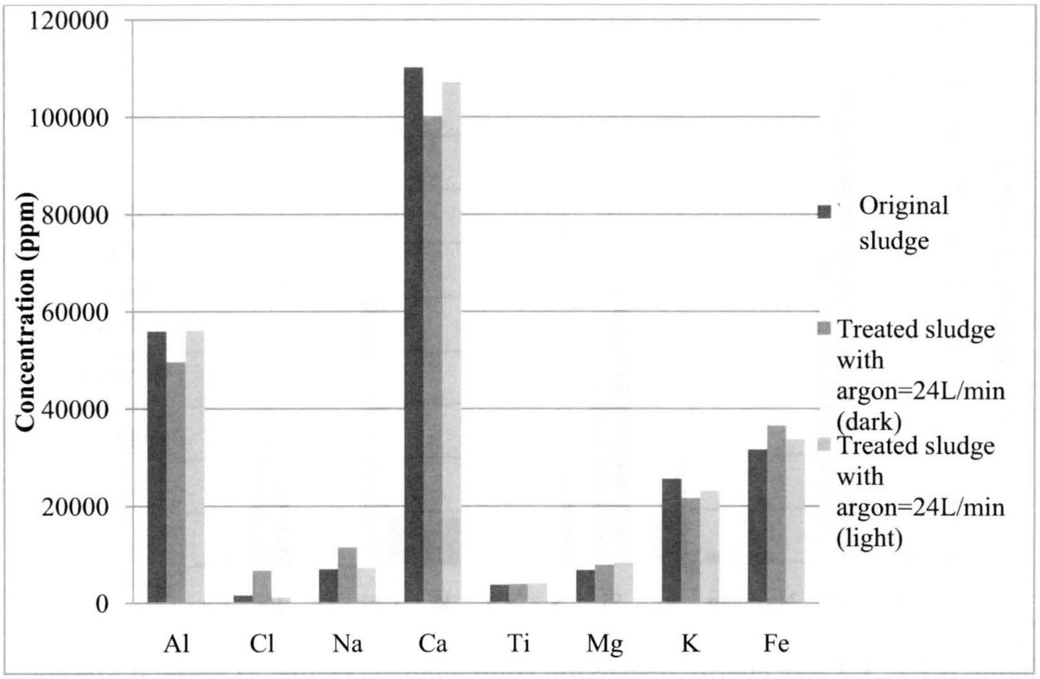


Figure 6.2.2. 5 Major elements of thermal plasma treated sludge under partial transferred mode (P = 1.9 kW) with argon flow rate of 24 L/min after 2.5 hours of treatment (NAA)

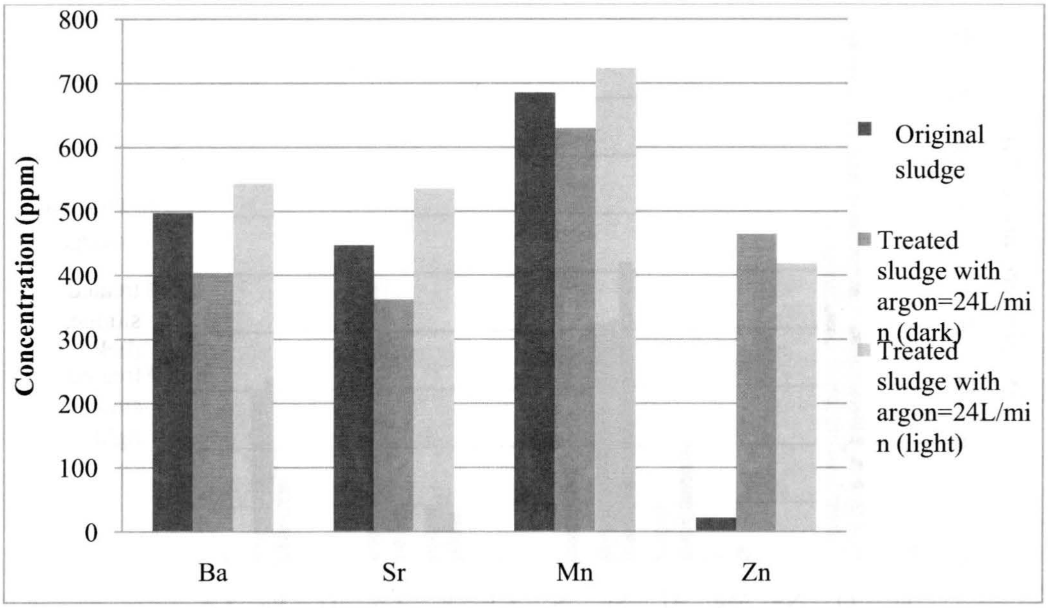


Figure 6.2.2. 6 Minor elements of thermal plasma treated sludge under partial transferred mode (P = 1.9 kW) with argon flow rate of 24 L/min after 2.5 hours of treatment (NAA)

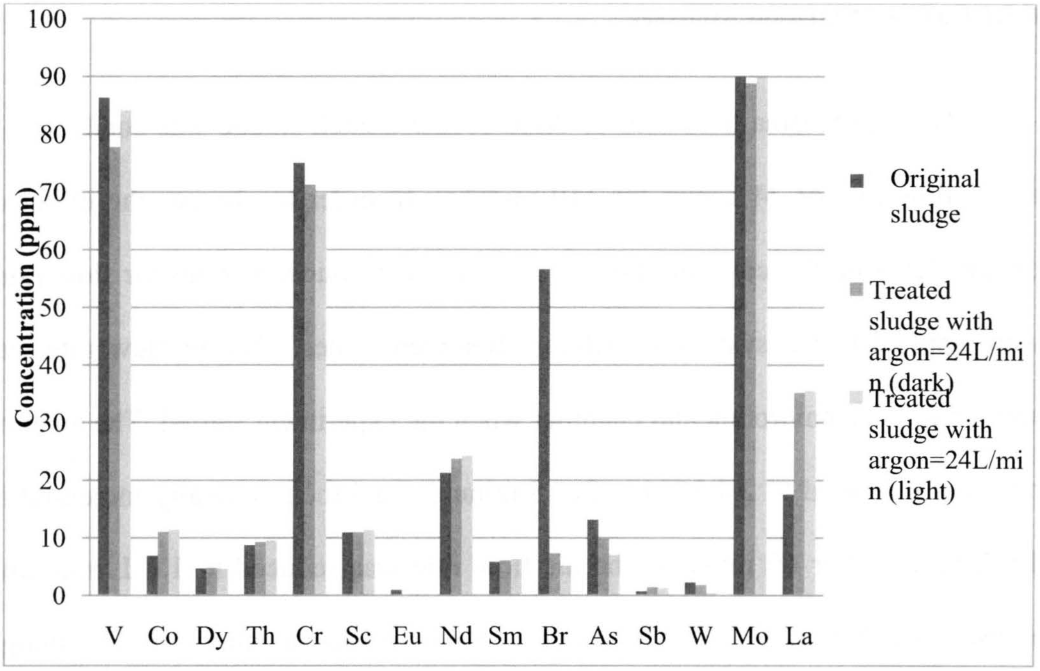


Figure 6.2.2. 7 Trace elements of thermal plasma treated sludge under partial transferred mode (P = 1.9 kW) with argon flow rate of 24 L/min after 2.5 hours of treatment (NAA)

6.3 Thermal Plasma Treatment of Dried PAED Treated Sludge Under Partial Transferred Mode

The PAED treated sludge was obtained by the sedimentation of sludge-water after PAED treatment. For comparison to the thermal plasma treatment of wet sludge, PAED treated sludge was dried under a fume hood first and then put into the thermal plasma treatment. The discussion of gaseous emission analysis in Section 6.3.1 focuses on the generation of gaseous by-products in the treatment of dried PAED treated sludge while the discussion of solid analysis results in Section 6.3.2 emphases the comparison of treated sludge by a single thermal plasma treatment and a combined treatment of PAED and thermal plasma.

6.3.1 Gaseous Emission Analyses

Thermal plasma treatment of dried PAED treated sludge was conducted at argon flow rate of 24 L/min for 110 minutes. In order to observe the effect of oxygen level on the concentration of gaseous by-products, various air flow rates were applied to the system at different treatment times. No air flow rate was applied into the environmental chamber when the experiment started. The air flow rate was increased to 2.4 L/min after 5 minutes, and then gradually increased to 4.8 L/min. After 60 minutes, the air flow rate was reduced to 1.2 L/min, and adjusted to 0 L/min after 90 minutes. Since intensive study of dry sludge treatment was carried out by Li (2006), only one representative experiment is carried out in this study. Figures 6.3.1.1, 6.3.1.2 and 6.3.1.3 show the emissions of carbon, nitrogen and sulfur compounds with respect to oxygen concentration during thermal plasma treatment of dried PAED treated sludge.

Figure 6.3.1.1 shows that emission of hydrocarbons was quite constant and continuous throughout the treatment. The concentrations of C_xH_y slightly increased when the CO concentration started to decrease. CO and CO_2 were at maximum at a treatment time of 5 minutes. CO decreased slowly after it reached the peak level, and reached a constant of 50 ppm after 60 minutes. The concentration of CO decreased to 7 ppm when the oxygen level was reduced to zero after 90 minutes. It may be concluded that the organic compounds decomposed and formed CO within one hour of treatment, and constant CO concentration was generated by thermal plasma operation, regardless of whether or not the organic and nitrate compounds are present in sludge. Some organics formed CO_2 when the oxygen level increased to 4% at a treatment time of 15 minutes. However, the generation of CO was more preferable due to limited supply of oxygen. Oxidation and combustion of organics were mostly completed at the treatment time of 90 minutes.

Figure 6.3.1.2 shows that the generations of NO and NO_2 were dependent on the oxygen levels as expected. Formation of NO was continuous, while NO_2 was generated in small amounts when oxygen level reached 4%. This result agrees with previous observation of NO and NO_2 production in argon thermal plasma under air environment by Ara et al. (2005). With the same oxygen level of 2%, the concentration of NO at the beginning was higher than the concentration at 60 minutes. It is believed that the concentration of NO was generated by nitrate compounds in sludge at the first 10 minutes, and the concentration of NO at 60 minutes was only produced by thermal plasma in the argon-air environment. Figure 6.3.1.3 shows that SO_2 was mostly generated in higher oxygen levels and H_2S was produced under oxygen depletion conditions. Since the generation of H_2S was still continuous in small amounts (between 1-3ppm) after 100 minutes, it suggests that decomposition of sulfur compounds in sludge need longer time as compared to organic and nitrate compounds. The accumulated concentrations of C_xH_y, CO, CO_2, NO, NO_2, H_2S and SO_2 with two-hour treatment were 7500, 11500, 11200, 11900, 260, 56 and 106 mg/m^3 respectively. Figure 6.3.1.4 shows the temperature transient with respect to various oxygen levels. The system temperature became stable at 490 °C after 30 minutes with an air flow rate of 4.8 L/min (oxygen level of 4%), and slightly increased to 520 °C in 90 minutes when the air flow rate was reduced to 0 L/min (oxygen level of 0.1%). It seems that air flow provided a slight cooling effect on the system.

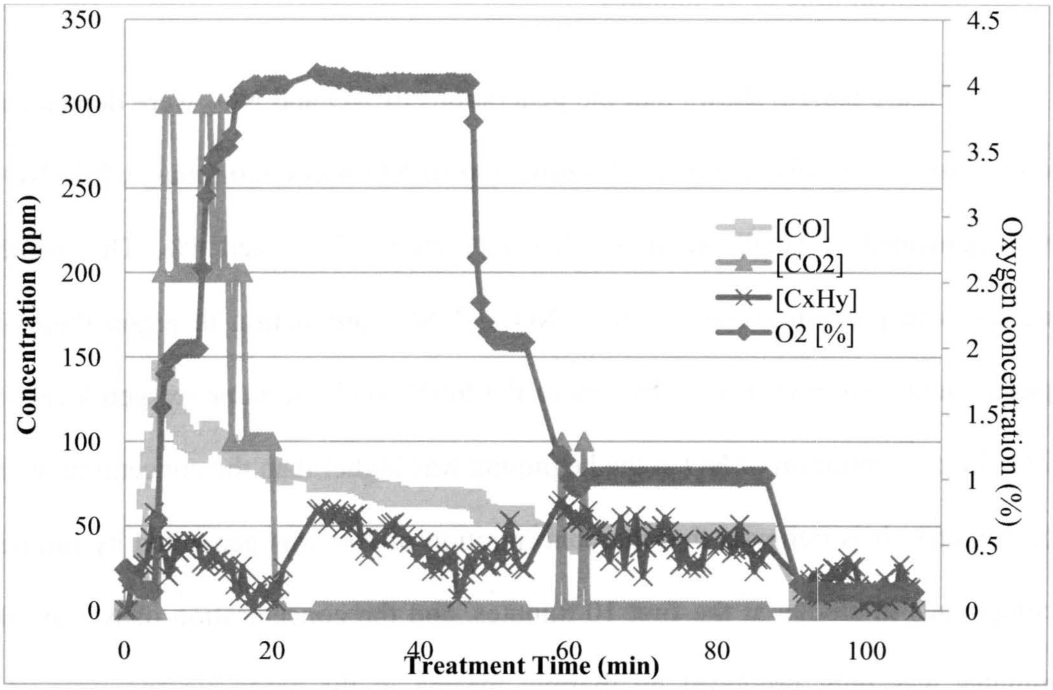


Figure 6.3.1. 1 Transient of CO, CO_2, C_xH_y and O_2 generation under thermal plasma treatments of dried PAED treated sludge with argon flow rate of 24 L/min and various air flow rates (P = 2.1 kW)

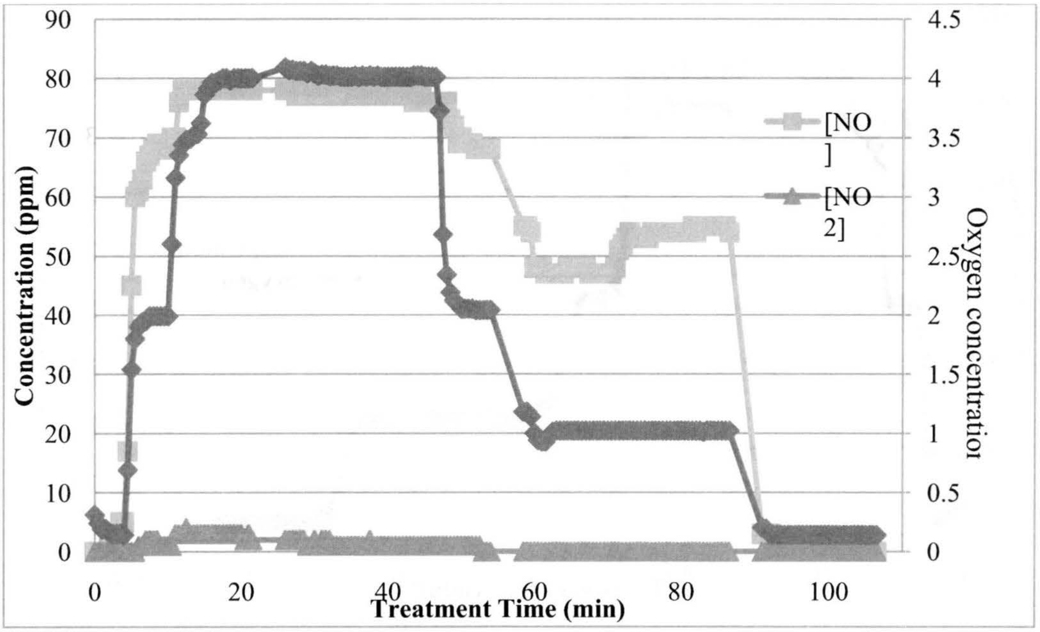


Figure 6.3.1. 2Transient of NO, NO_2 and O_2 generation under thermal plasma treatments of dried PAED treated sludge with argon flow rate of 24 L/min and various air flow rates (P =2.1 kW)

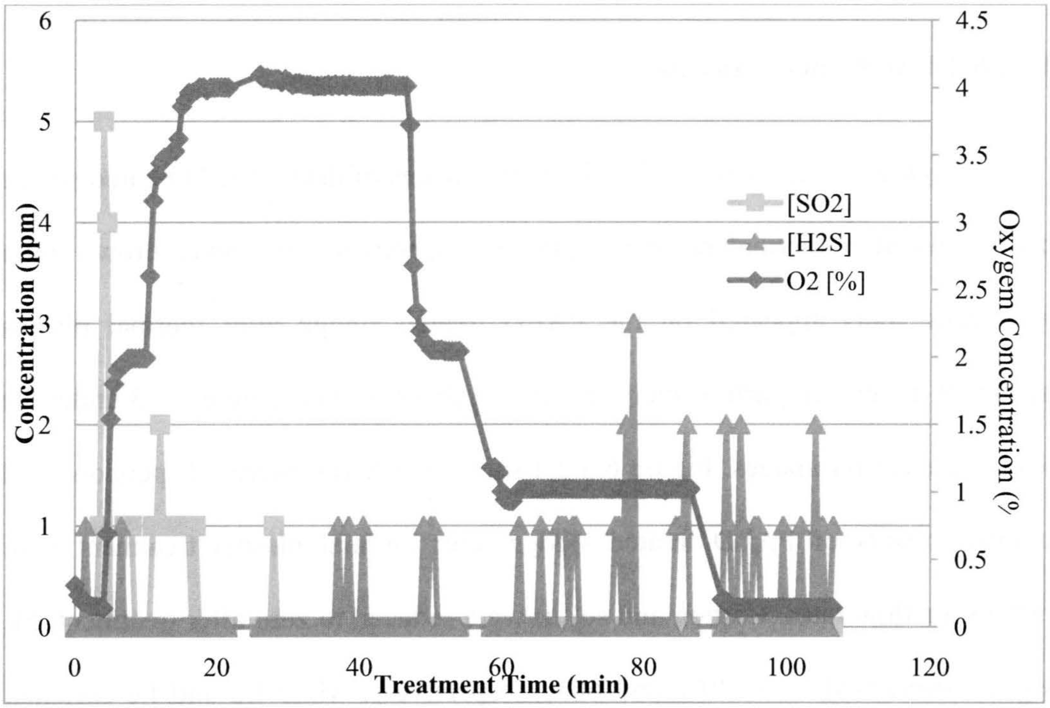


Figure 6.3.1. 3 Generation of SO_2, H_2S and O_2 under thermal plasma treatments of dried PAED treated sludge with argon flow rate of 24 L/min and various air flow rates (P = 2.1 kW)

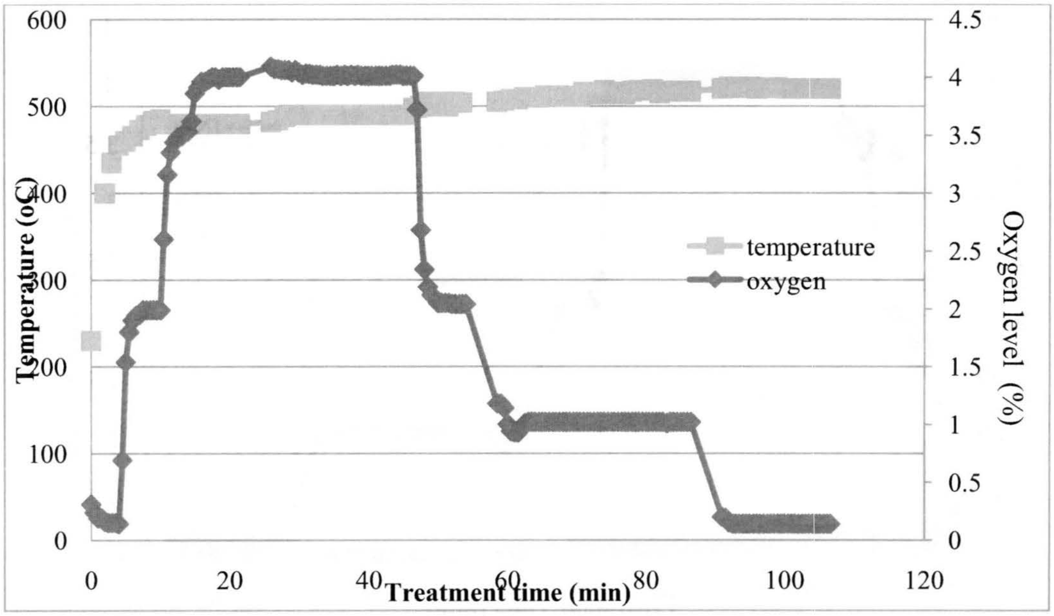
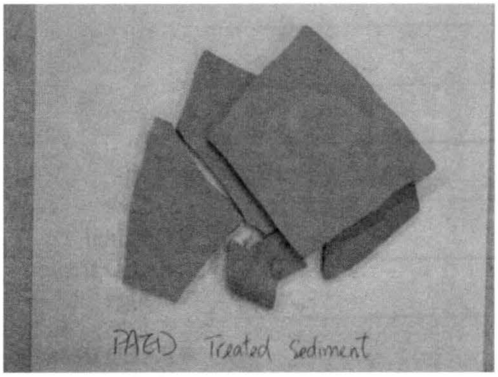


Figure 6.3.1. 4 Temperature transient and oxygen level under thermal plasma treatments of dried PAED treated sludge with argon flow rate of 24 L/min and various air flow rates (P = 2.1 kW)

6.3.2 Solid By-Products Analyses

Figures 6.3.2.1 and 6.3.2.2 show the images of dried PAED treated sludge before and after thermal plasma treatment respectively. A deeper brown color with dark spots appeared on the PAED treated sludge after thermal plasma treatment. However, particle melting was not observed in Figure 6.3.2.3 under the scanning electron images. Figure 6.3.2.4 shows the X-ray energy dispersion solid analysis results of PAED treated sludge after thermal plasma treatment with various air flow rates. Carbon and sulfur were reduced to zero after treatment; Si, Mg, Al decreased 25%, 30% and 60%, respectively, while Ca and Fe enriched 400% and 25%, respectively.



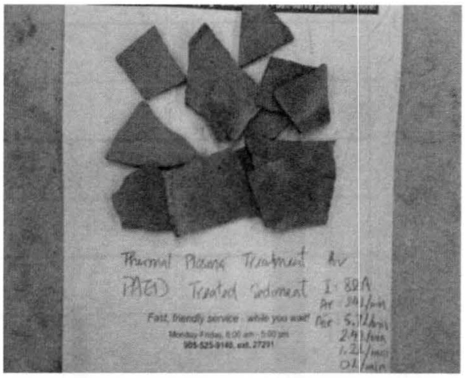


Figure 6.3.2. 1 Image of PAED treated sludge before thermal plasma treatment and Figure 6.3.2. 2 Image of PAED treated sludge after thermal plasma treatment under partial transferred operation mode (P = 2.1 kW) at argon flow rate of 24 L/min with varying air flow rates

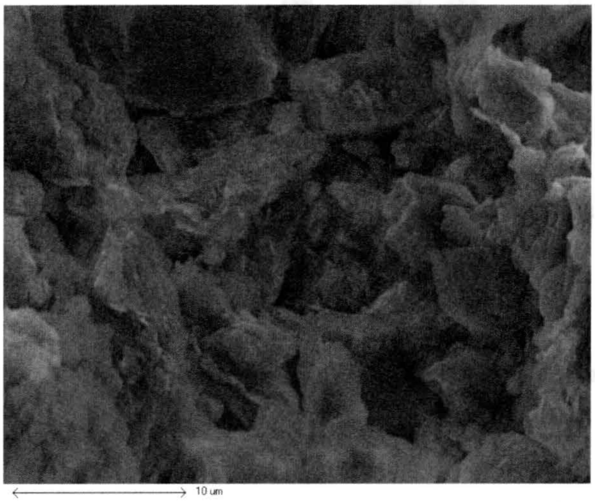


Figure 6.3.2. 3 SEM images of PAED treated sludge after thermal plasma treatments under partial transferred mode (P = 2.1 kW) at argon flow rate of 24 L/min with varying air flow rates (Magnification of 4800)

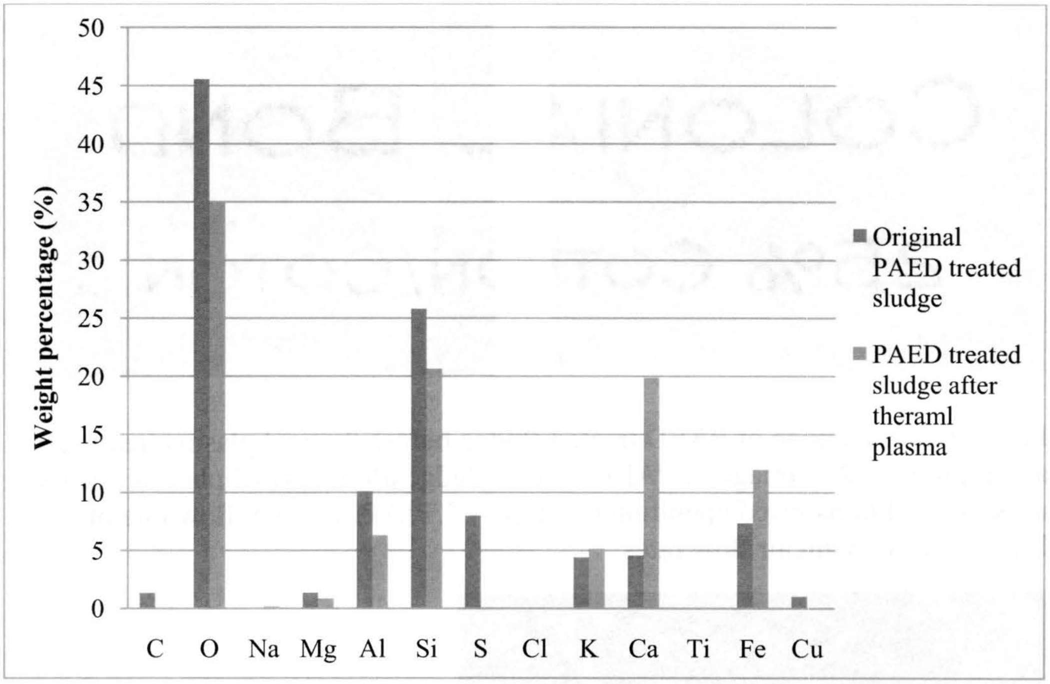


Figure 6.3.2. 4 X-ray energy dispersion solid analysis results of PAED treated sludge before and after thermal plasma treatment under transferred mode (P = 2.1 kW) with argon flow rate of 24 L/min and varying air flow rates between 0 - 4.8 L/min after 2 hours of treatment

6.3.3 Comparison of the Thermal Plasma Treatment of Wet Sludge and Dried PAED Treated Sludge

A comparison between thermal plasma treatment under partial transferred mode of dried PAED treated sludge and wet sludge is presented in this Section. Since the treatment of dried PAED sludge was carried out with varying air flow rates, the results used for wet sludge were averaged from the data of air flow rates of 0 to 4.8 L/min with 2-hour treatment time. Figures 6.3.3.1, 6.3.3.2, 6.3.3.3 and 6.3.3.4 show the accumulated concentrations of C_xH_y, CO and CO_2, NO and NO_2, H_2S and SO_2, as well as H_2, respectively. In general, thermal plasma treatment of wet sludge generates more gaseous by-products with the exceptions of CO and NO. The accumulated concentrations of C_xH_y and CO_2 in wet sludge were twice the amount of dried PAED treated sludge. Total generations of H_2S and SO_2 from wet sludge were 11 and 6 times more than those from dried PAED treated sludge. Higher conversion of organics and sulfur compounds into gaseous compounds was observed in wet sludge. On the other hand, the accumulated concentration of NO from treating dried PAED treated sludge was 3 times higher than that from wet sludge. Khalaf et al., (2008) explained the suppression of NO_x formation by the presence of H_2O during thermal plasma treatment. Gaseous NO and nitrates are more preferable for conversion into HNO_3 under wet conditions.

Figure 6.3.3.4 compares the TOC percentages under thermal plasma treatment with similar conditions for wet and dried PAED treated sludge. The percentage of TOC slightly decreased from 8% to 7.5% after PAED treatment and was further reduced to 5.3% on average after a thermal plasma treatment of 2 hours. The reductions of TOC were 45% and 30% in wet and dried PAED treated sludge respectively.

Figure 6.3.3.5 compares the weight percentages of major elements measured by X-ray energy dispersion of the wet and PAED treated sludge before and after thermal plasma treatments. The gas temperature in both experiments were approximately 480 °C. In general, some deviations in weight percentages are observed between the treatments. Weight percentages of Mg, Al, Si, K, Ti and Cu in dried sludges were 40, 40, 20, 50, 500 and 40% higher than in wet sludge.

Deposition of Ti particles was observed after PAED treatment, and that resulted in larger enrichment of Ti in dried sludge. Weight percentages of O and Fe in PAED treated sludge were 35 and 20% lower than in wet sludge. Table 6.5 shows the results of chemical composition analysis by XRD between wet and PAED treated sludge after thermal plasma treatment. Weight percentages of sand (SiO_2), calcite ($CaCO_3$) and rutile (TiO_2) were higher in PAED treated sludge, while weight percentages of $CaCO_4$ and NaCl were higher in wet sludge. The elemental and composition weight percentages in wet sludge were more deviated from the untreated sludge. In addition, melting of sludge was only observed in wet sludge.

In principle, the concurrent treatment by PAED and thermal plasma results in higher treatment efficiency as compared to a single thermal plasma treatment. The results, however, show that higher treatment efficiency can be achieved under wet conditions in thermal plasma treatment with similar power and gas temperature. This may due to the fact that the water content in wet sludge increased the heat transfer rate by increasing conductivity, and provided elemental hydrogen and oxygen for reactions.

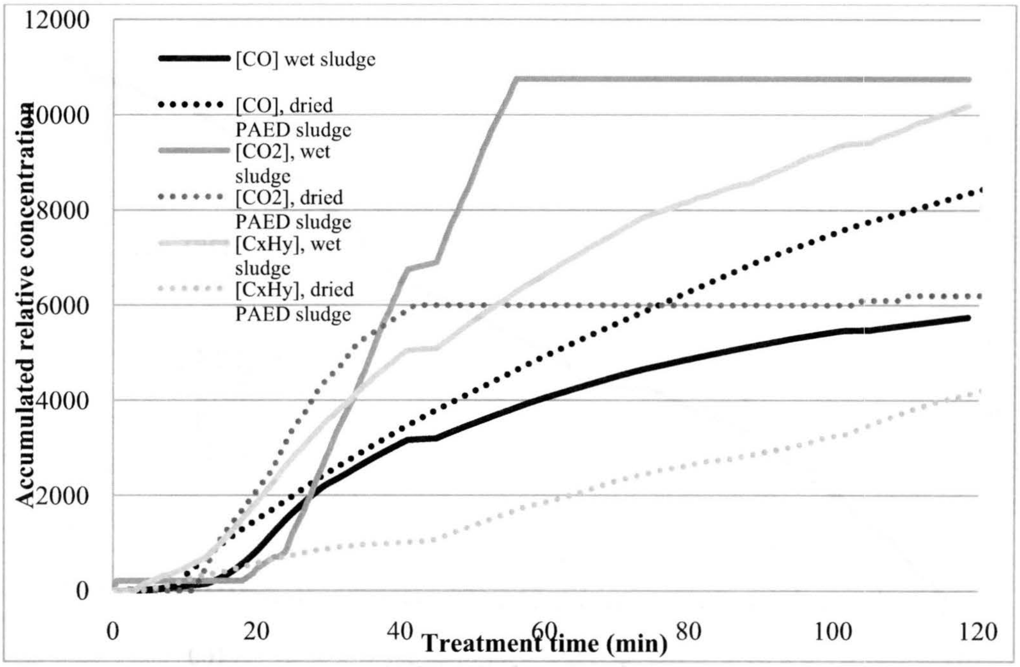


Figure 6.3.3. 1 Accumulated CO, CO_2 and C_xH_y generated by thermal plasma treatments (P = 2.1 kW) of wet sludge and PAED treated sludge with argon flow rate of 24 L/min and various air flow rates under partial transferred mode

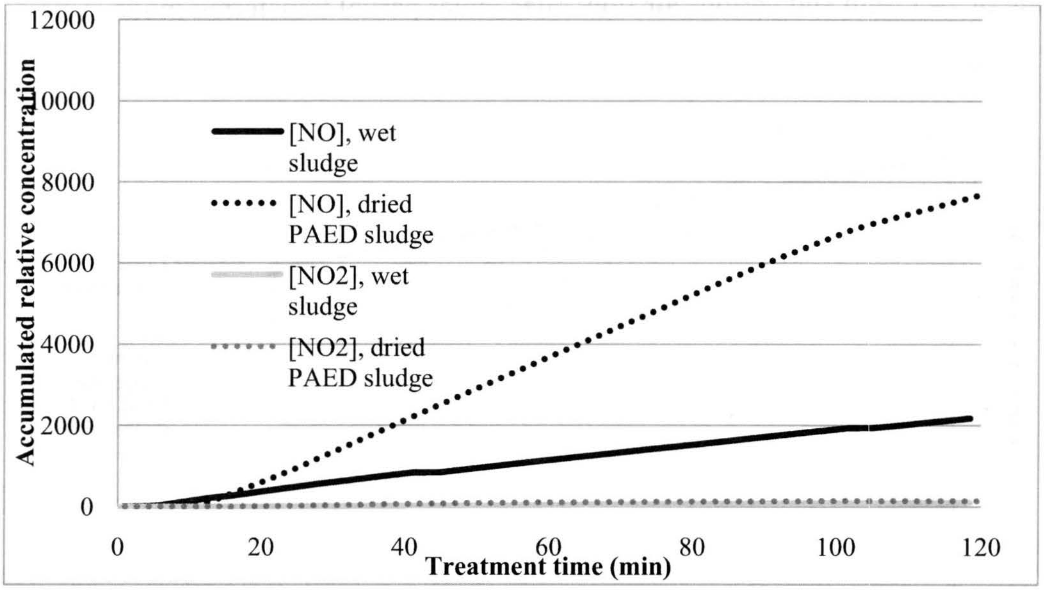


Figure 6.3.3. 2 Accumulated NO and NO_2 generated by thermal plasma treatments (P = 2.1 kW) of wet sludge and PAED treated sludge with argon flow rate of 24 L/min and various air flow rates under partial transferred mode

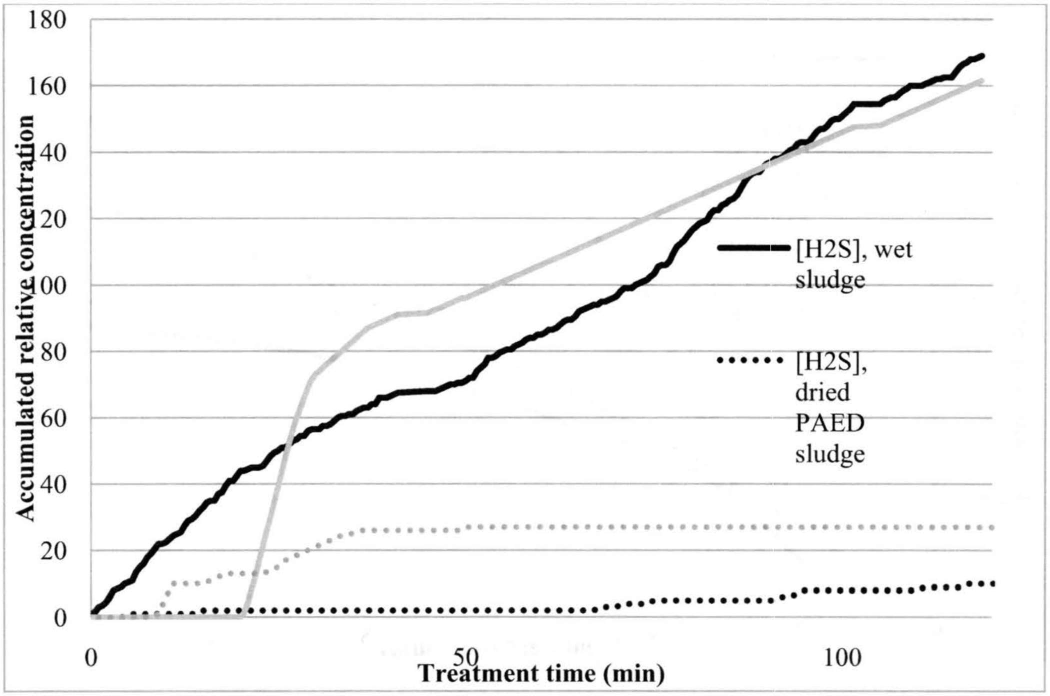


Figure 6.3.3. 3 Accumulated H_2 S and SO_2 generated by thermal plasma treatments (P = 2.1 kW) of wet sludge and PAED treated sludge with argon flow rate of 24 L/min and various air flow rates under partial transferred mode

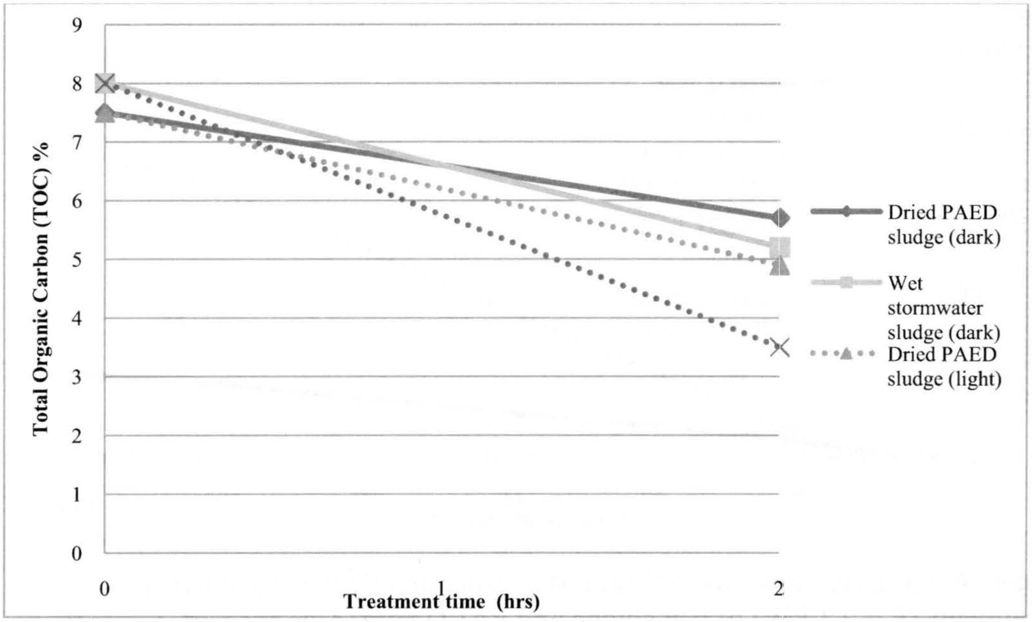


Figure 6.3.3. 4 Percentage of TOC with respect to thermal plasma treatment time (P = 2.1 kW) with argon flow rate of 24 L/min and air flow rates of 0 - 4.8 L/min in wet sludge and PAED treated sludge

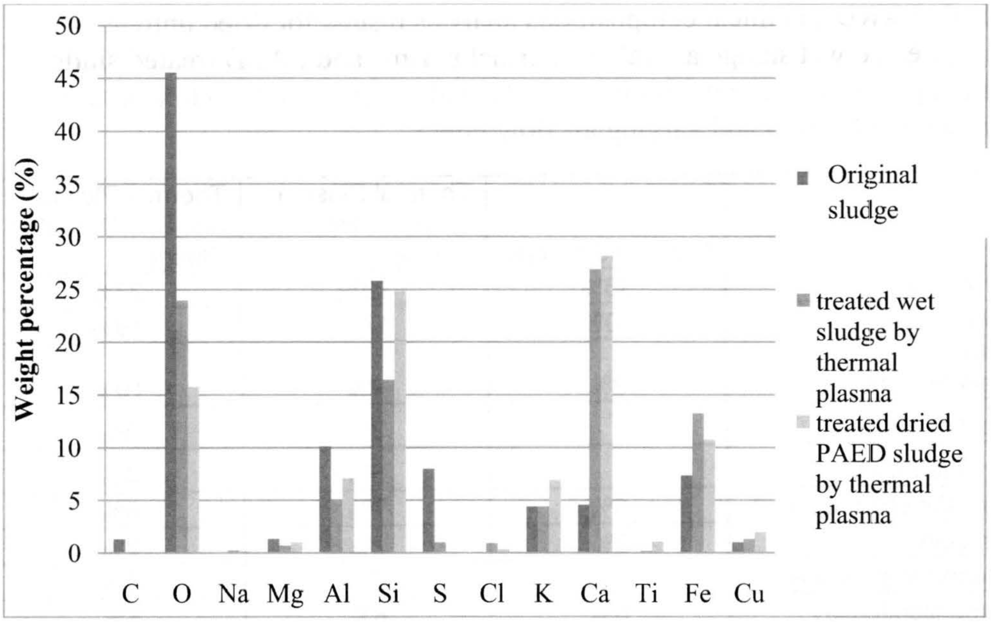


Figure 6.3.3. 5 X-ray energy dispersion solid analysis results of wet sludge and PAED treated sludge by thermal plasma treatment (P = 2.1kW) under partial transferred mode with argon flow rate of 24 L/min and varying air flow rates

Table 6. 5 XRD Chemical compositions analysis results for dried untreated sludge, treated wet sludge as well as thermal plasma and PAED treated sludge (thermal plasma treatment with P = 2.1 kW under transferred mode with argon flow rate of 24 L/min and varying air flow rates)

	Untreated Sludge	Thermal Plasma Treated Wet Sludge	Thermal Plasma and PAED treated Sludge
Quartz/sand	33%	20%	23%
Calcite	20%	17%	19%
Anorthite and albite/feldspars	9%	9%	10%
Microcline $KAlSi_3O_8$		3%	3%
Magnetite Fe_3O_4		5%	4%
Chamosite/chlorite/(clay)	6%	7%	6%
Amphibole	2%	2%	2%
Biotite/micas/illite clay	6%	7%	7%
Montmorillonite/clay	6%	8%	8%
Halite NaCl		2%	1%
Anhydrite $CaSO_4$		5%	2%
Bassanite,$CaSO_4 \cdot 0.5H_2O$		2%	2%
Dolomite	8%	7%	6%
Kaolinite/clay	6%	1%	1%
Rutile TiO_2		1%	2%
Amorphous, ect.	4%	4%	4%

6.4 Comparison of Results Between Reactor Operation Under Non-Transferred and Partial Transferred Modes

The results of gaseous by-products and solid analysis will be compared between thermal plasma treatment of wet sludge under non-transferred and partial transferred modes. In the gaseous by-product analyses, the focus is on the accumulated relative concentrations of CO, CO_2, NO, NO_2, SO_2, H_2S and C_xH_y in different operation modes. Solid analyses will include comparison of TOC and concentrations of major elements.

6.4.1 Gaseous Emission Analyses during Thermal Plasma Treatment under Non-transferred and Partial Transferred Modes

Figures 6.4.1.1, 6.4.1.2 and 6.4.1.3 show the comparison of carbon, nitrogen and sulfur gaseous by-products under non-transferred and partial transferred thermal plasma treatment modes respectively. The argon flow rate was fixed at 35 L/min in anoxic environments. A stable gas temperature of 300 and 380 °C were observed in non-transferred and partial transferred modes respectively. The temperature in partial transferred mode was higher than non-transferred mode even with less power input. Higher heat transfer rates were observed in partial transferred mode. The accumulated C_xH_y, CO, NO and H_2S were higher in partial transferred mode than non-transferred mode. This result agrees with the higher reduction of TOC from partial transferred mode as shown as in Section 6.5.2. The concentrations of C_xH_y and CO were saturated after 60 minutes in non-transferred mode while both gaseous compounds were still increasing in concentration in partial transferred mode. Decomposition of organics could not go further in non-transferred mode due to the relatively low gas temperature. Concentration of NO saturated at 15 minutes in non-transferred mode but kept increasing in partial transferred mode. This illustrates that higher gas temperature creates NO in thermal plasma. No CO_2 and NO_2 were formed in the anoxic environments. Generation of H_2S was continuous while formation of SO_2 was occasional in both operation modes. Sulfur compounds were usually converted into H_2S in oxygen deficient environments, however, when the oxide compounds were decomposed and released oxygen, sulfur compounds were converted into SO_2.

Figure 6.4.1.4 shows the concentration of H_2 with respect to treatment time. Hydrogen gas was generated from moisture and volatile organic compounds (VOC) in sludge during thermal plasma treatment in both operation modes. Since the hydrogen meter reached saturation of 4000 ppm within 5 minutes, the total accumulated concentration of H_2 could not be measured. The hydrogen gas was not produced after 20 minutes when the water contents and VOC were completely evaporated.

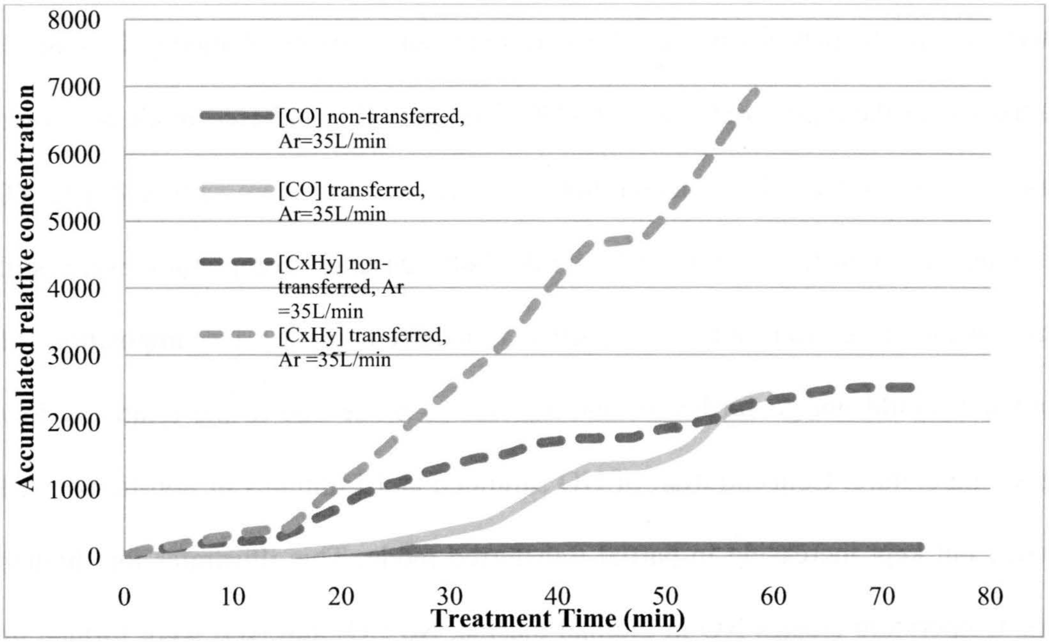


Figure 6.4.1. 1 Accumulated CO and C_xH_y generated by thermal plasma treatments with argon flow rate of 35 L/min under non-transferred (P = 2.4 kW) and partial transferred modes (P = 1.7 kW)

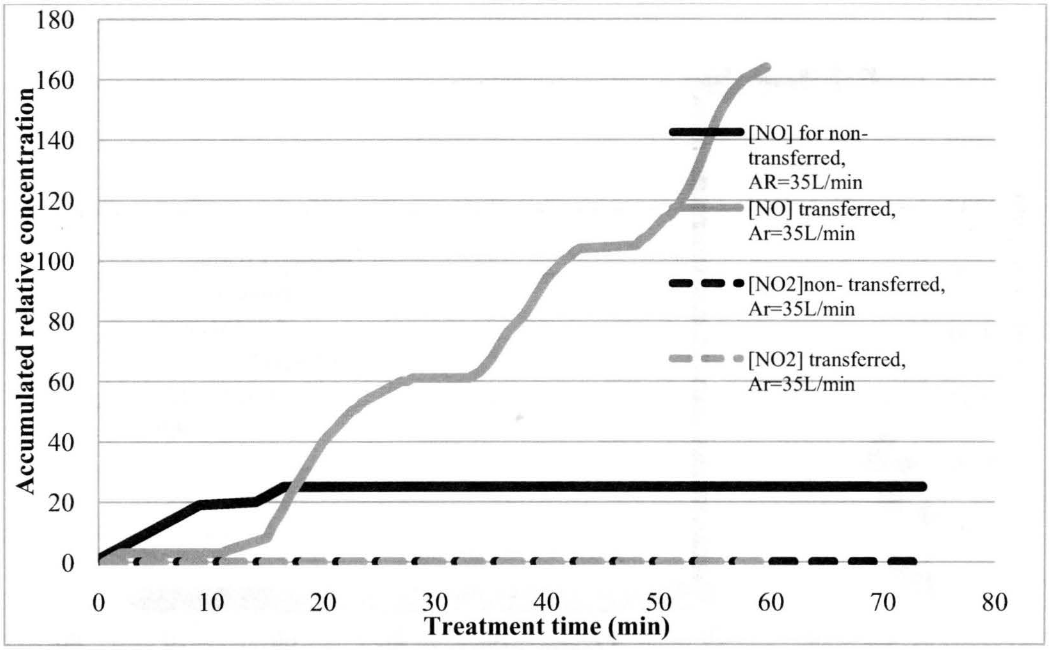


Figure 6.4.1. 2 Accumulated NO and NO_2 generated by thermal plasma treatments with argon flow rate of 35 L/min under non-transferred (P = 2.4 kW) and partial transferred modes (P = 1.7 kW)

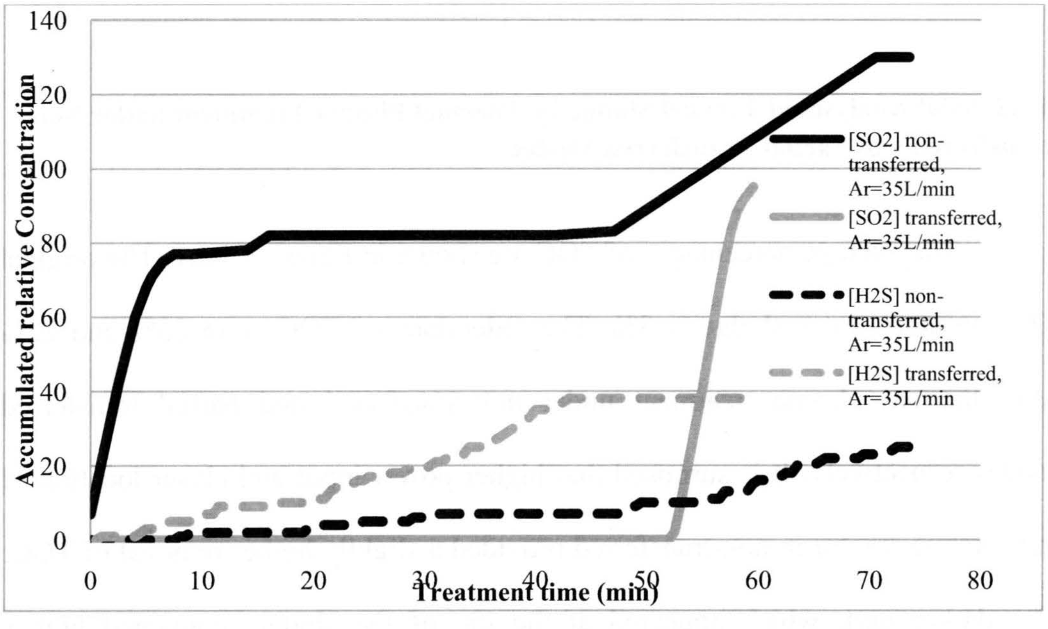


Figure 6.4.1. 3 Accumulated SO_2 and H_2S generated by thermal plasma treatments with argon flow rate of 35 L/min under non-transferred (P = 2.4 kW) and partial transferred modes (P=1.7 kW)

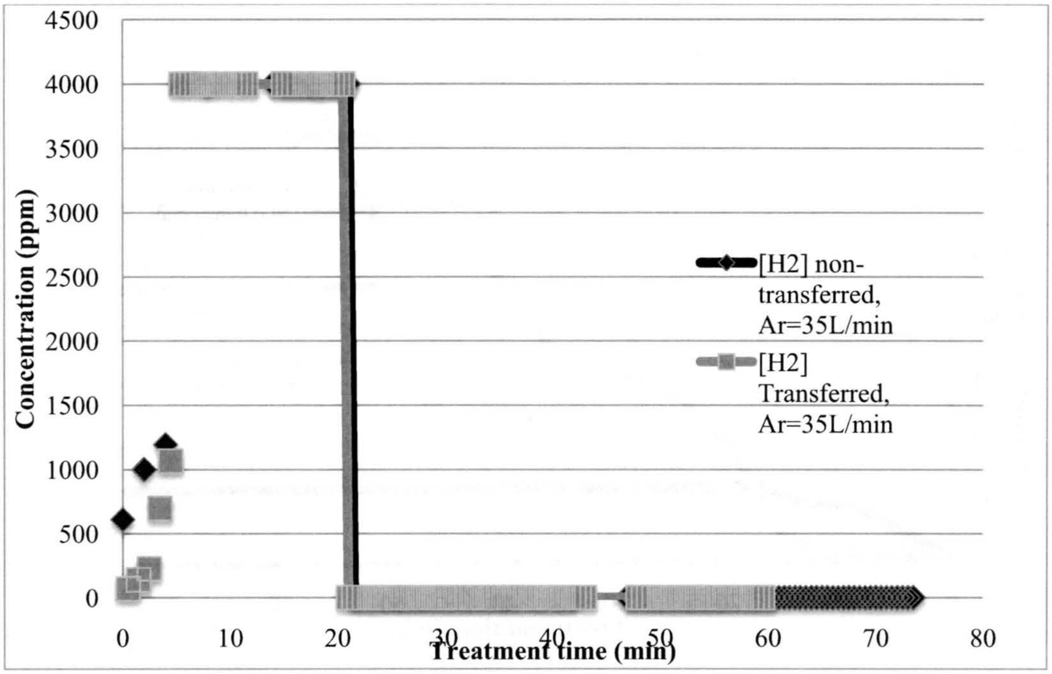


Figure 6.4.1. 4 Hydrogen gas transient in thermal plasma treatments with argon flow rate of 35 L/min under non-transferred (P = 2.4 kW) and partial transferred mode (P = 1.7 kW)

6.4.2. Solid Analyses of Treated Sludge by Thermal Plasma Treatment under Non-transferred and Partial Transferred Modes

The average percentages of TOC are shown in Figure 6.4.2.1. The original TOC in stormwater sludge is 8%. The reductions of TOC were 25% and 22% after thermal plasma treatment under non-transferred and partial transferred modes respectively. It is surmised that higher power input and closer location of the ceramic reactor in non-transferred provided a slightly higher removal of TOC. The darker part, which appeared at the top of the sludge, contained higher percentage of TOC. Gaseous hydrocarbons might be condensed and deposited on the top when the temperature decreased sharply after the system was turned off.

Figure 6.4.2.2 and Table 6.6 show solid analysis results of elemental and chemical compositions by X-ray energy dispersion and XRD respectively. The major elements were O > Si> Al> Fe > Ca in the original sludge, and changed to Ca > O > Si > Fe > Al after thermal plasma treatment. Ca and Fe enriched 500% and 20%, while O, Al, Mg and S decreased by 30%, 50%, 50% and 10-20% respectively. Percentages of sand, calcite and clay decreased 30-40%, 15-20% and 70-80% respectively. Formations of $CaSO_4$, $KAlSi_3O_8$, NaCl and Fe_3O_4 were observed and reached 2-4%.

The elemental and chemical compositions were different in the darker part of thermal plasma treated sludge under partial transferred mode. It may be due to the fact that the treatment of sludge under partial transferred mode is not homogenous. The darker part of the treated sludge is located at the top, and might have experienced higher heat transfer rate and more surface reaction in thermal plasma treatment compared to the bottom part of the sludge.

Table 6. 6 Chemical compositions of untreated sludge, treated sludge with argon flow rate of 35 L/min under non-transferred (P = 2.4 kW) and partial transferred mode (P = 1.7 kW)

Compounds	Dried untreated sludge	Non-transferred	Partial transferred, Ar =35 L/min (Darker)	Partial transferred, Ar =35 L/min (Lighter)
Quartz/sand	33%	21%	17%	23%
Calcite	20%	17%	14%	18%
Anorthite and albite/feldspars	9%	10%	9%	10%
Microcline $KAlSi_3O_8$		3%	3%	3%
Magnetite Fe_3O_4		4%	4%	4%
Chamosite/chlorite/(clay)	6%	7%	6%	7%
Amphibole	2%	2%	2%	2%
Biotite/micas/illite clay	6%	7%	6%	7%
Montmorillonite/clay	6%	8%	8%	8%
Halite NaCl		2%	5%	1%
Anhydrite CaSO4		2%	9%	2%
Bassanite,$CaSO_4\cdot 0.5H_2O$		2%	2%	2%
Dolomite	8%	7%	7%	7%
Kaolinite/clay	6%	1%	2%	1%
Rutile TiO_2		1%	1%	1%
Amorphous, ect.	4%	6%	5%	4%

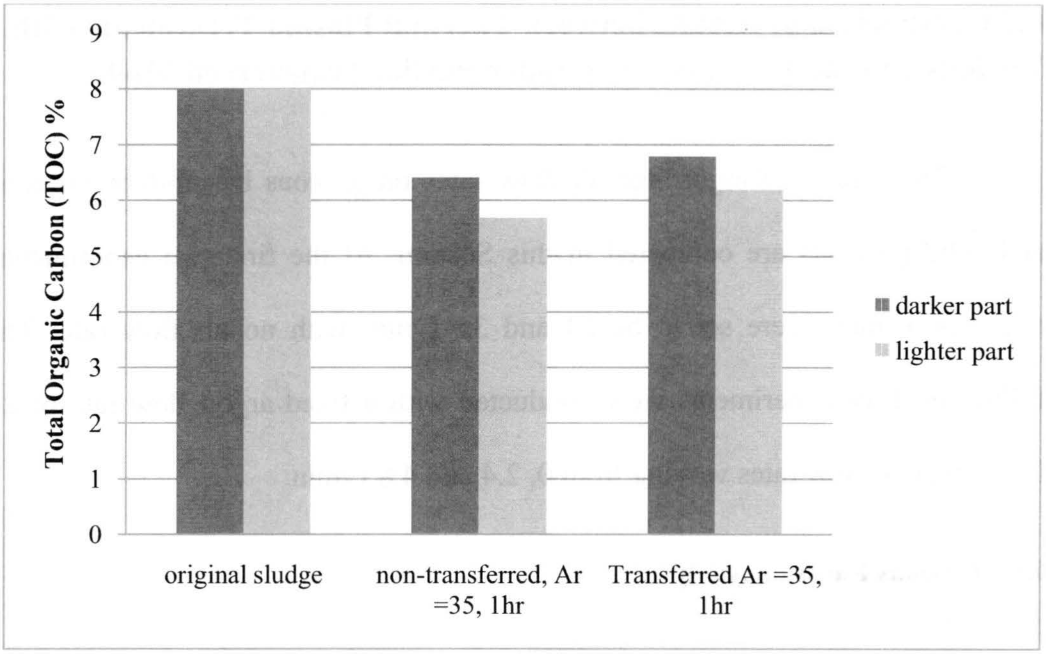


Figure 6.4.2. 1 Percentages of TOC in sludge before and after thermal plasma treatment with argon flow rate of 35 L/min under non-transferred (P = 2.4 kW) and partial transferred modes (P = 1.7 kW) (treatment time = 1 hr)

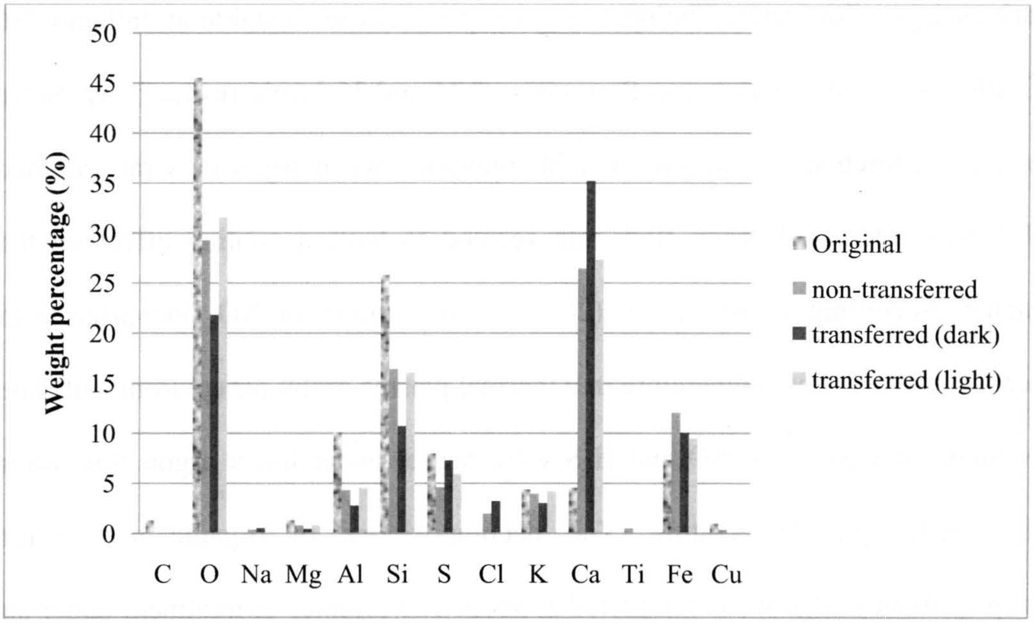


Figure 6.4.2. 2 X-ray energy dispersion solid analysis results of wet sludge by thermal plasma treatments with argon flow rate of 35 L/min under non-transferred (P = 2.4 kW) and partial transferred mode (P = 1.7 kW) modes (treatment time = 1 hr)

6.5 Comparison of Results between Thermal Plasma Treatments with Various Operating Parameters under Partial Transferred Mode

The effects of argon and air flow rates on gaseous by-product emission and solid products are compared in this Section. At the first two experiments, argon flow rates were set to be 24 and 35 L/min with no air flow rate. The following three experiments were conducted with a fixed argon flow rate of 24 L/min and air flow rates varying from 0, 2.4 and 4.8 L/min.

6.5.1 Gaseous Emission Analyses

Figures 6.5.1.1, 6.5.1.2 and 6.5.1.3 show the accumulated concentrations of, respectively, carbon, nitrogen and sulfur gaseous by-products with respect to various argon flow rates. The operating temperatures were stable at 480 and 380 °C after 30 minutes with argon flow rates of 24 and 35 L/min respectively. Since the plasma torch started to have a stable operation when argon flow rate reached 24 L/min, additional argon flow rate seemed to have a cooling effect on the reactor. According to Ara et al. (2005), concentration of NO_x increased with increasing power and temperature in a thermal plasma argon-air environment. The accumulated C_xH_y, CO, NO and H_2S were higher under lower argon flow rates with higher gas temperature. The decompositions of organic and sulfur compounds in sludge were completed at about 100 minutes of treatment under an argon flow rate of 24 L/min. No CO_2 and NO_2 were formed in the anoxic environment.

Figures 6.5.1.4, 6.5.1.5, 6.5.1.6, 6.5.1.7 and 6.5.1.8 show the accumulated relative concentrations of, respectively, CO and C_xH_y, CO_2, NO, NO_2, H_2S and SO_2 with respect to various air flow rates. Figure 6.5.1.9 shows the transient of hydrogen gas. Figure 6.1.2.6 in Section 6.1.2 reported that the optimum gas temperature was reached with an air flow rate of 2.4 L/min. It is surmised that the combustion process facilitated by the essential oxygen input might increase the gas temperature. However, additional air flow might create a slightly cooling effect. Thus the gas temperature under an air flow rate of 4.8 L/min was the lowest. In an anoxic environment, organic compounds were majorly converted into hydrocarbons. Generations of CO was most favorable with an air flow rate of 2.4 L/min and formation of CO_2 was most preferable with an air flow rate of 4.8 L/min. An increase of hydrocarbons was observed when operating temperatures rised from 350 to 450°C. Accumulated NO and NO_2 were at the highest with air flow rates of 2.4 and 4.8 L/min, respectively. Constant generation of nitrogen gaseous compounds was observed during thermal plasma treatment, and the least at the air flow rate of 0 L/min. More gaseous H_2S was produced in oxygen deficient environments. Optimum gas temperature for the formation of H_2S and SO_2 might be between 350 and 450 °C. H_2 was produced in the first 5 to 20 minutes. The time for the generation of hydrogen gas was shorter under higher air flow rates.

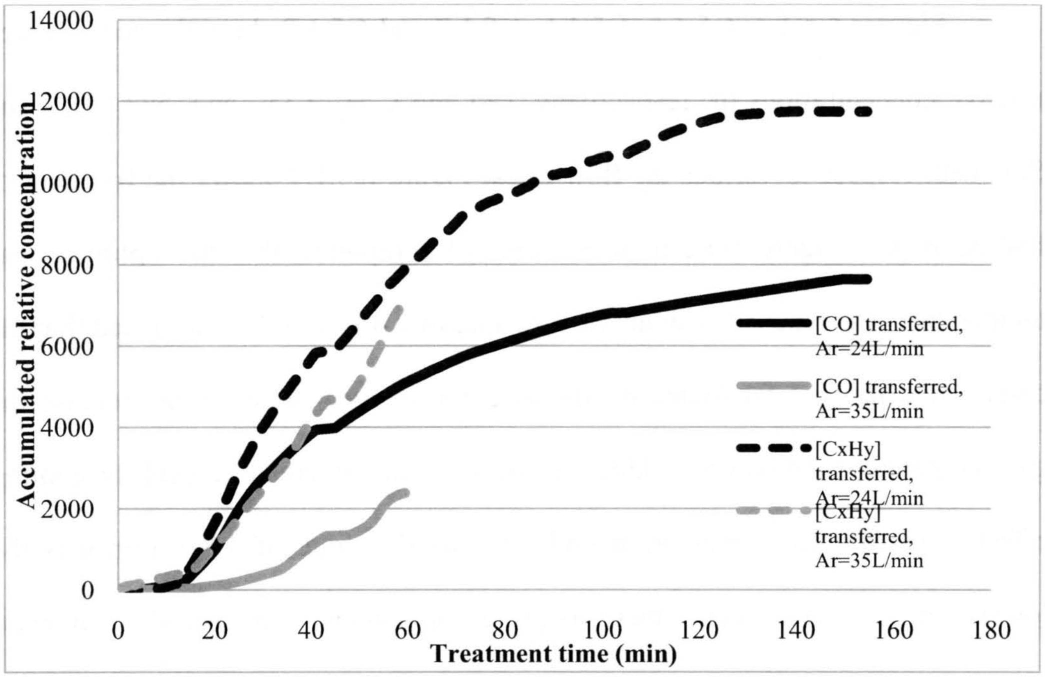


Figure 6.5.1. 1 Accumulated CO and C_xH_y generated by thermal plasma treatments with argon flow rates of 24 and 35 L/min under partial transferred mode

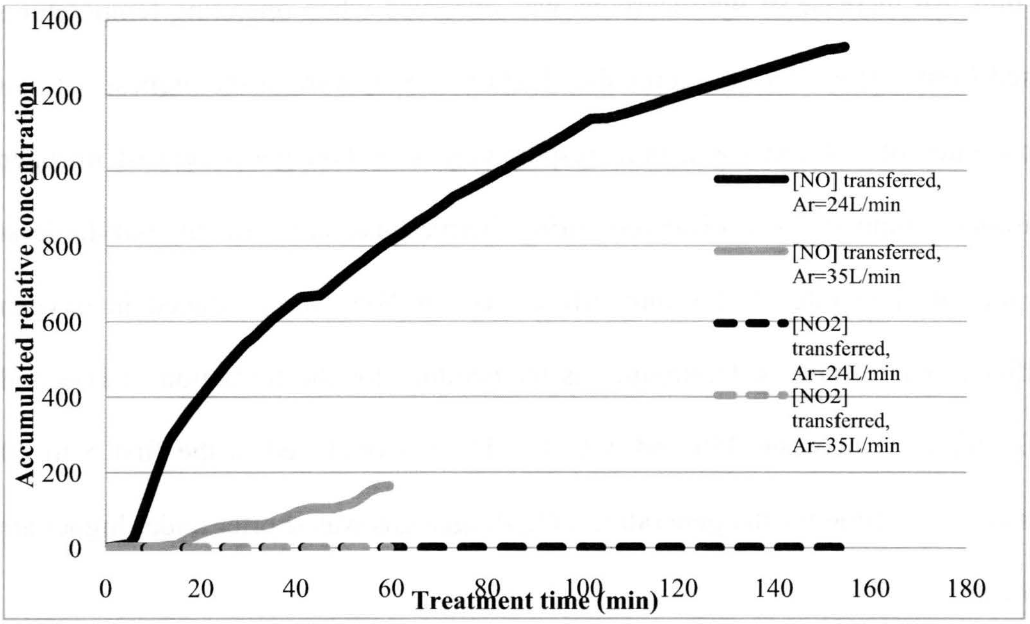


Figure 6.5.1. 2 Accumulated NO and NO_2 generated by thermal plasma treatments with argon flow rates of 24 and 35 L/min under partial transferred mode

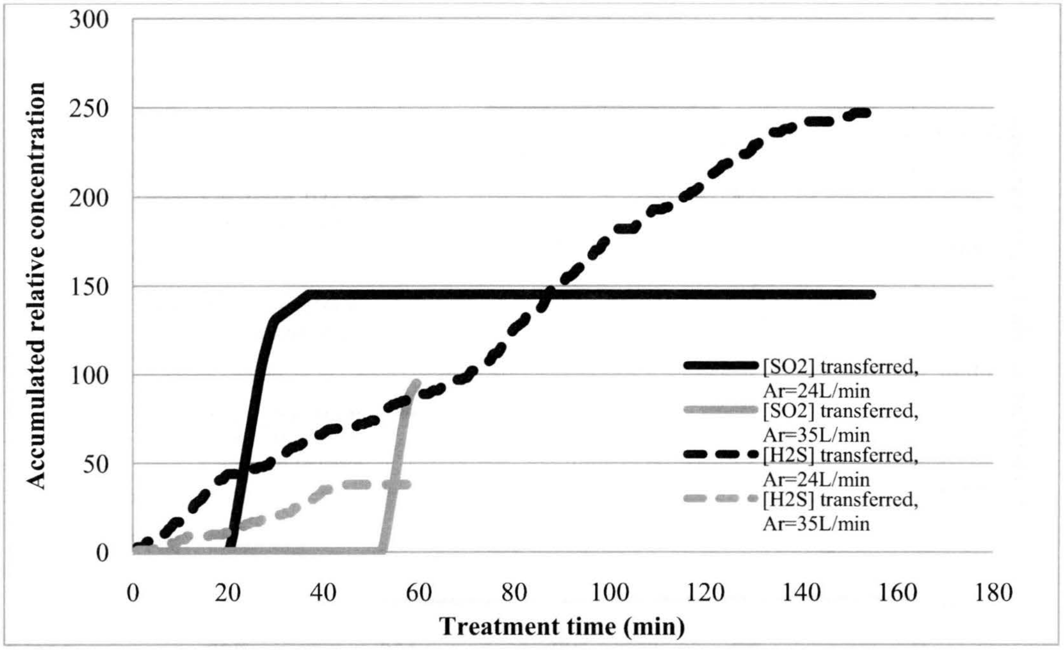


Figure 6.5.1. 3 Accumulated H_2S and SO_2 generated by thermal plasma treatments with argon flow rates of 24 and 35 L/min under partial transferred mode

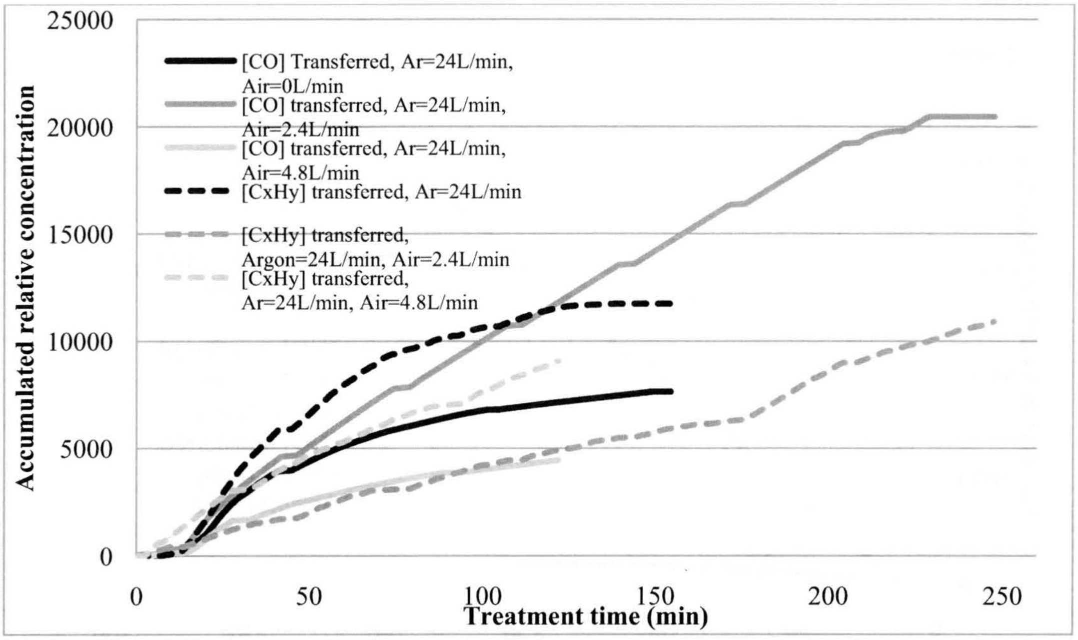


Figure 6.5.1. 4 Accumulated CO and C_xH_y generated by thermal plasma treatments with argon flow rate of 24 L/min and various air flow rates under partial transferred mode

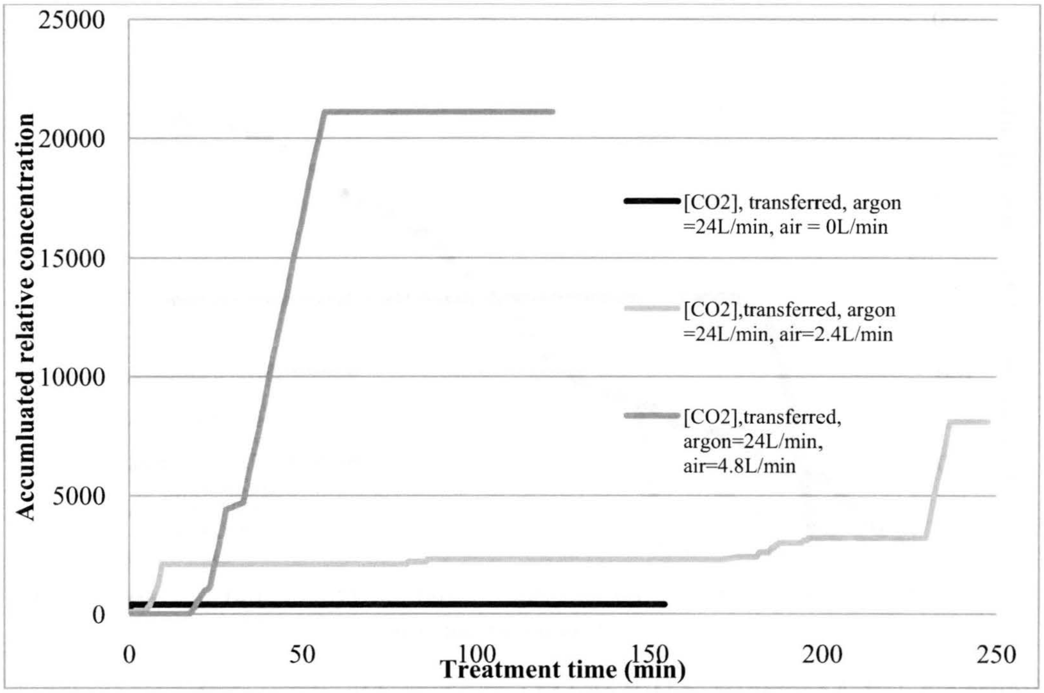


Figure 6.5.1. 5 Accumulated CO_2 generated by thermal plasma treatments with argon flow rate of 24 L/min and various air flow rates under partial transferred mode

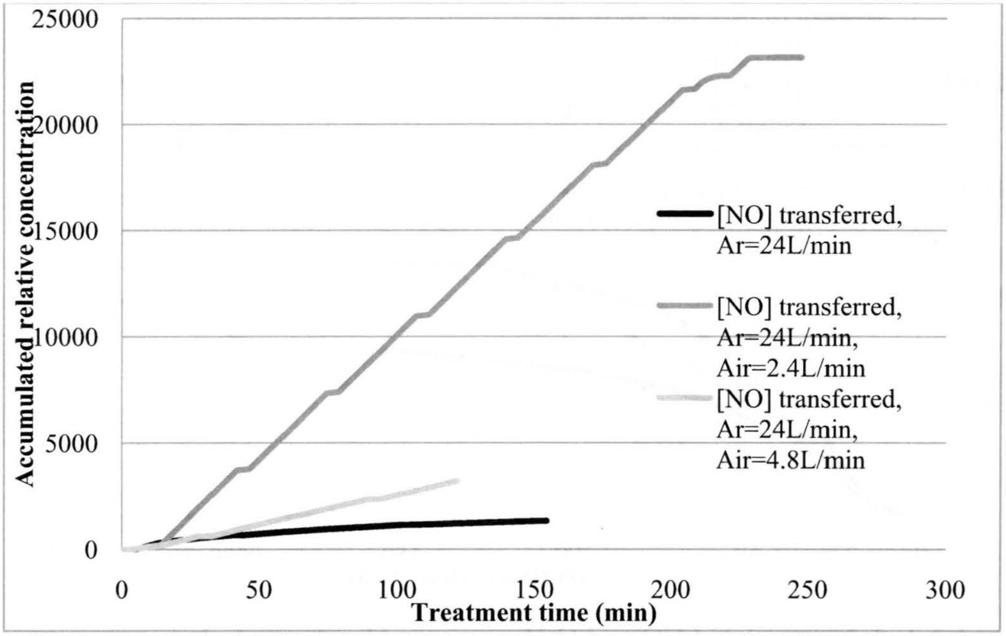


Figure 6.5.1. 6 Accumulated NO generated by thermal plasma treatments with argon flow rate of 24 L/min and various air flow rates under partial transferred mode

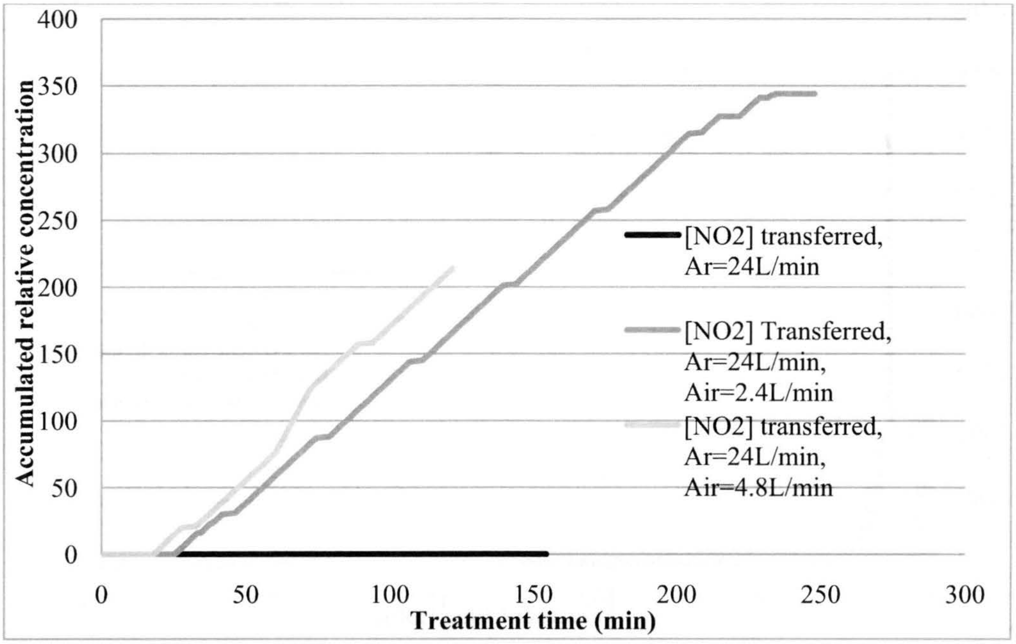


Figure 6.5.1. 7 Accumulated NO_2 generated by thermal plasma treatments with argon flow rate of 24 L/min and various air flow rates under partial transferred mode

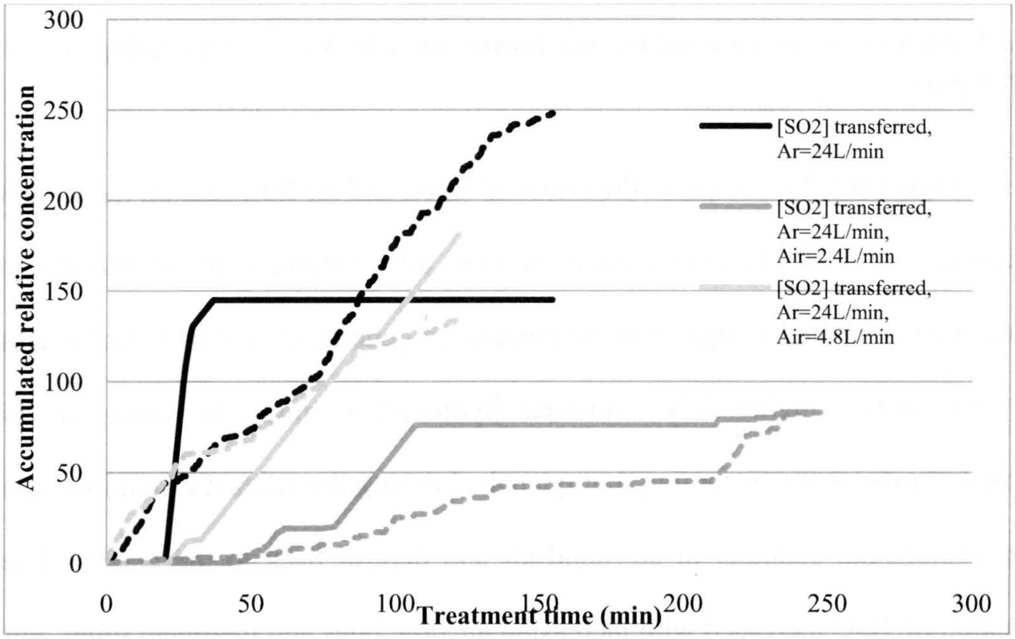


Figure 6.5.1. 8 Accumulated H_2S and SO_2 generated by thermal plasma treatments with argon flow rate of 24 L/min and various air flow rates under partial transferred mode

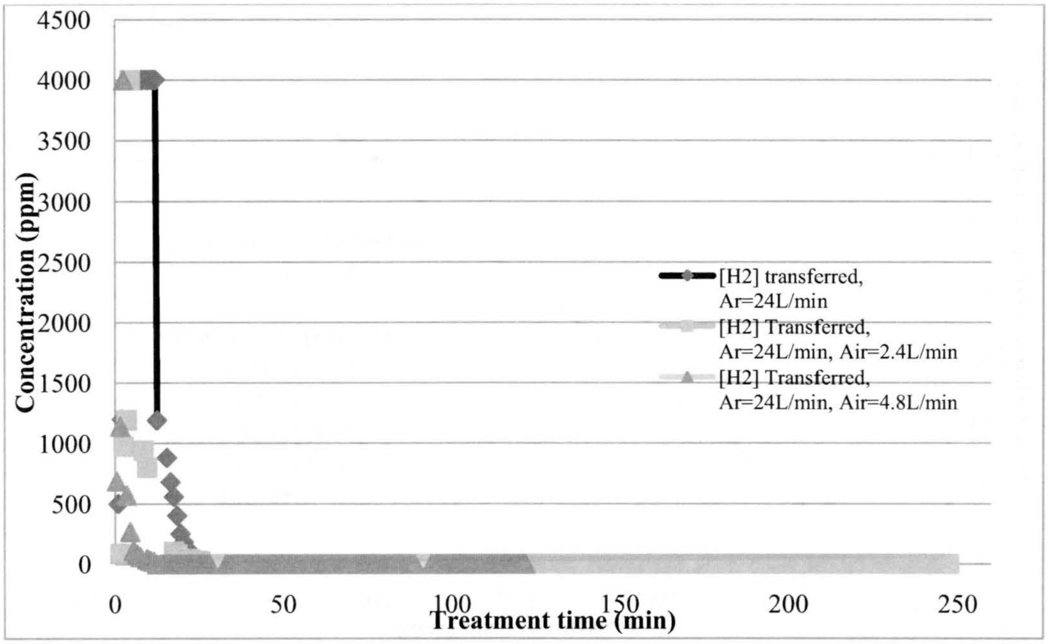


Figure 6.5.1. 9 H_2 gas transient during thermal plasma treatments with argon flow rate of 24 L/min and various air flow rates under partial transferred mode

6.5.2 Solid Analyses of Thermal Plasma Treatments with Various Operating Parameters

Figure 6.5.2.1 compares the effect of argon and air flow rate on the weight percentages of TOC. The percentages of TOC were measured in the darker and lighter part of treated sludge in all treatments. In general, darker parts (located at the top) contain higher TOC. Gaseous hydrocarbon might be vaporized by thermal plasma at the beginning, but quenched during the contact of cold surface of environmental chamber or surround air and deposit back to the reactor. The reduction of TOC increased with increasing air flow rates and treatment times, but stayed rather constant with decreasing argon flow rates. Since increasing air flow rate limits the formation of hydrocarbon (organics are more selectively converted into CO and CO_2), thus less hydrocarbons are quenched during the treatment.

Figures 6.5.2.2 and 6.5.2.3 compare the effect of argon and air flow rates, respectively, on the weight percentage of major elements measured by X-ray energy dispersion. Averaged weight percentages of darker and lighter parts were used for the comparison. The percentages of O and S were lower with smaller argon flow rates. The gas temperatures were 380 and 430 °C with argon flow rates of 24 and 35 L/min in anoxic environments respectively. In addition, the treatment time under an argon flow rate of 24 L/min was one hour longer than the treatment time under an argon flow rate of 35 L/min. Higher gas temperature with longer treatment time increases the reduction of sulfur and organic compounds into gaseous by-products. The weight percentages of Si, K, Fe and O increase with increasing air flow rates, while Ca and Cu decreased with increasing air flow rates. Weight percentages of other major elements deviated within 10 percent with increasing argon flow rates.

In general, elemental weight percentages of treated sludge under oxidizing environment are more similar to each other. Enrichment of Ca and Fe were 60 and 600%, 100 and 550%, and 110 and 500% under air flow rates of 0, 2.4 and 4.8 L/min respectively. The reduction of Si and O were higher in reducing environments. The weight percentages of Si and O decreased 55 and 50%, 33 and 25% and 30 and 20% under air flow rates of 0, 2.4 and 4.8 L/min respectively. Figure 6.2.2 also shows that the percentages of sand (SiO_2) and calcite ($CaCO_3$)

were at the lowest in anoxic environments. It may be concluded that oxygen released from oxides were partly used for the oxidation processes to generate gaseous by-products.

Detailed elemental analysis on treated sludge with various air flow rates was carried out by NAA. Figures 6.5.2.4, 6.5.2.5 and 6.5.2.6 show the major, minor and trace elements of treated sludge with air flow rates of 0 and 2.4 L/min respectively. Concentrations of Mg and Fe enriched slightly with increasing air flow rates, while concentrations of other major elements were quite constant with increasing air flow rates. The deviation of major element concentrations is within 10 percent between reducing and oxidizing environments. The concentrations of minor and trace elements were quite consistent with increasing air flow rates except Ba, Co and Nd. The results differ from those of the solid analysis by X-ray energy dispersion since quite significant difference in weight percentages was observed in Figure 6.5.2.3. It may suggest that chemicals in sludge were firstly decomposed by thermal plasma and then recombined. During the decomposition process, volatile elements/compounds and organics were converted into gaseous by-products while non-volatile and volatile condensable elements remained for recombination. This assumption may supported by the chemical composition analysis results presented in Table 6.5. Valuable metals (Fe, Zn and etc) are enriched in the treated sludge and might be recycled as salable products.

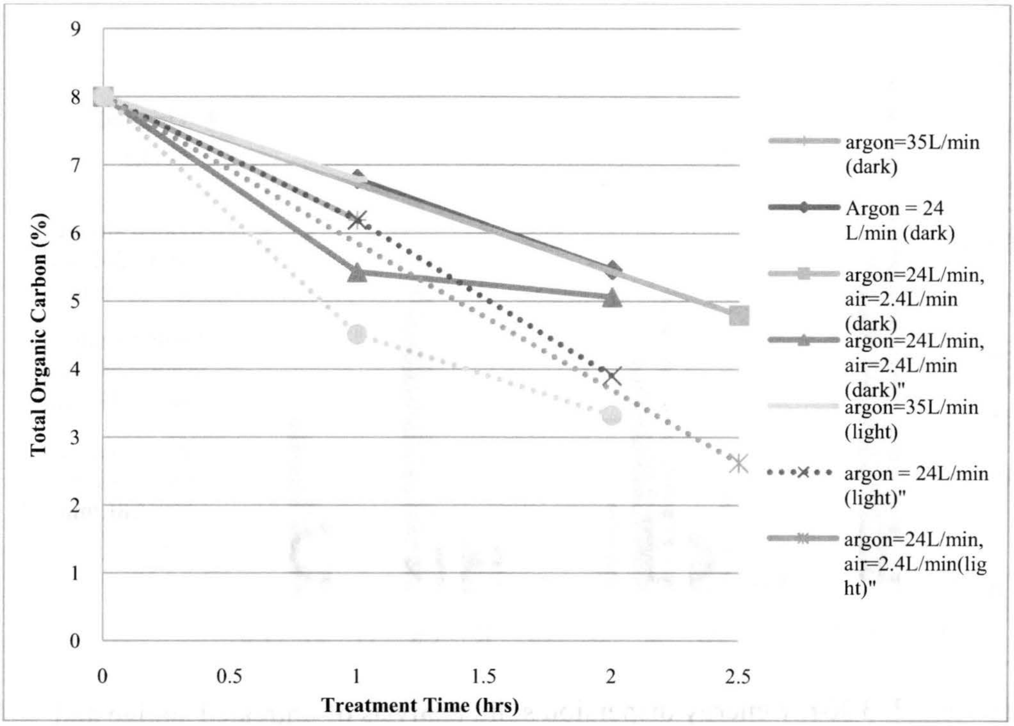


Figure 6.5.2. 1 Percentages of TOC in sludge with respect to thermal plasma treatments under various argon and air flow rates

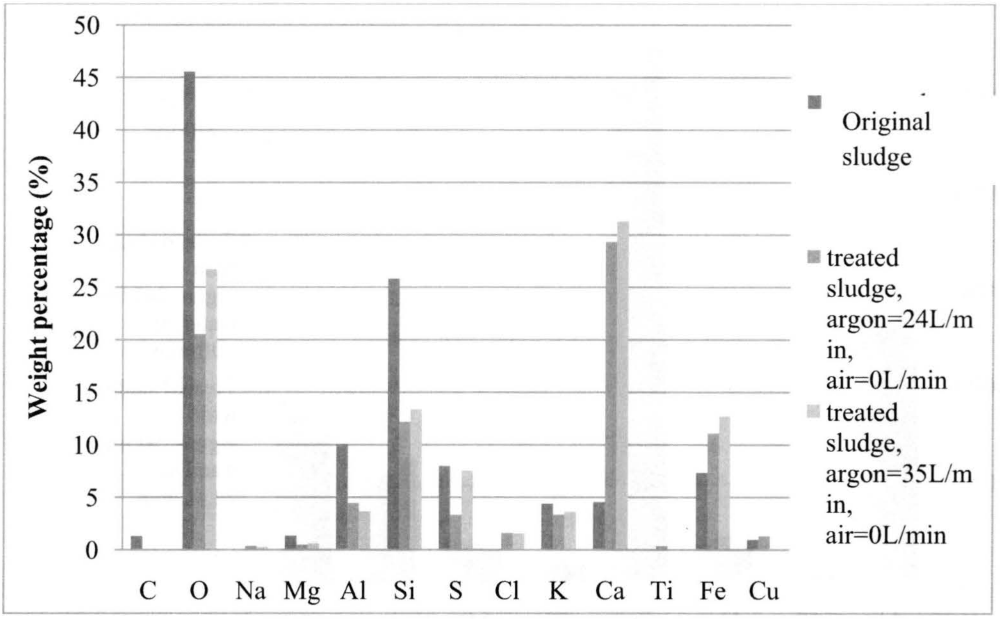


Figure 6.5.2. 2 X-ray energy dispersion solid analysis of untreated sludge and treated sludge by thermal plasma under partial transferred mode with argon flow rates of 24 and 35 L/min

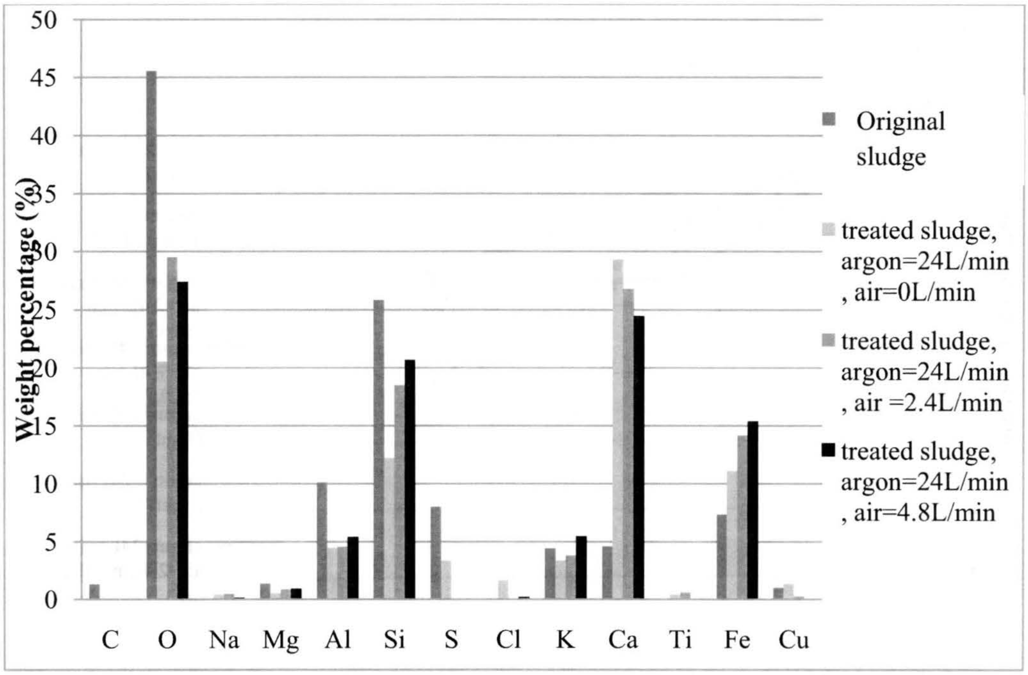


Figure 6.5.2. 3 X-ray energy dispersion solid analysis of untreated sludge and treated sludge by thermal plasma under partial transferred mode with argon flow rate of 24 L/min and varying air flow rates

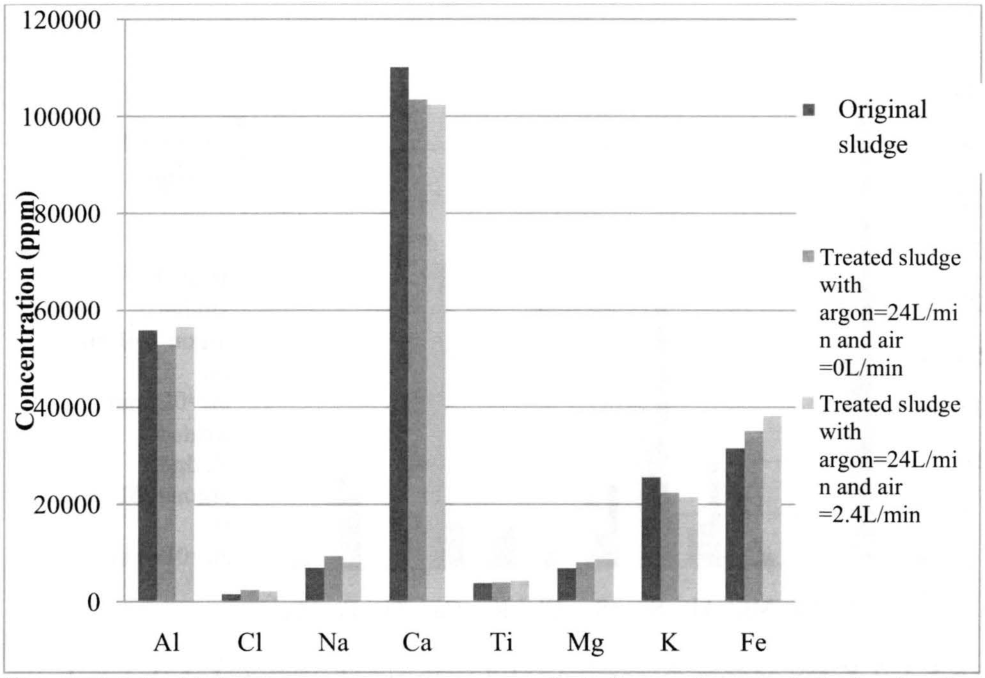


Figure 6.5.2. 4 Major elements of untreated sludge and treated sludge by thermal plasma under partial transferred mode with argon flow rate of 24 L/min and varying air flow rates (by NAA)

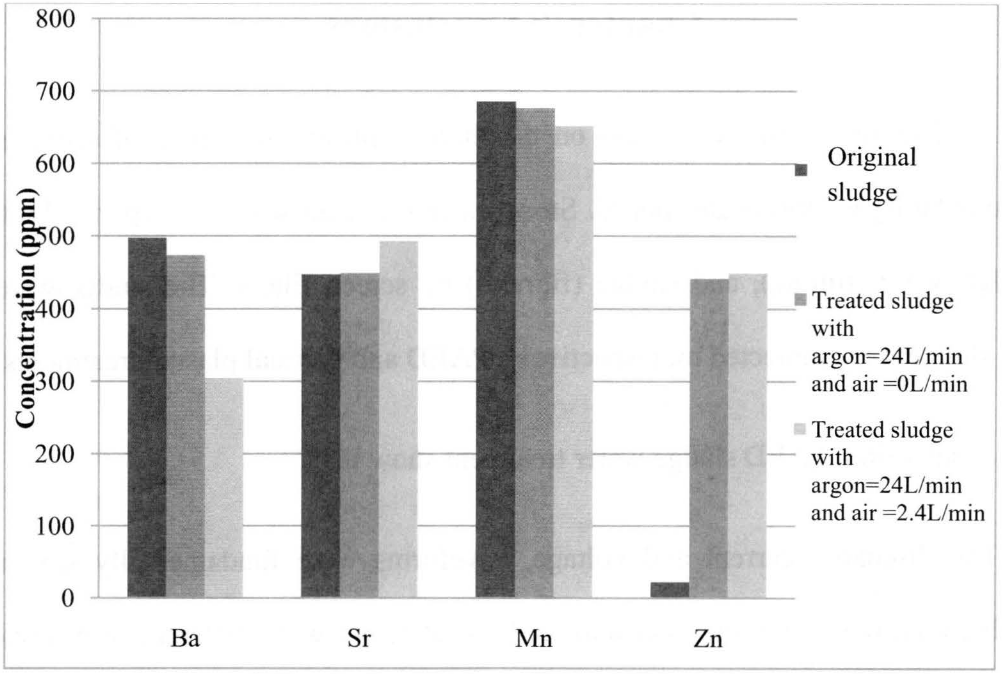


Figure 6.5.2. 5 Minor elements of untreated sludge and treated sludge by thermal plasma under partial transferred mode with argon flow rate of 24 L/min and varying air flow rates (by NAA)

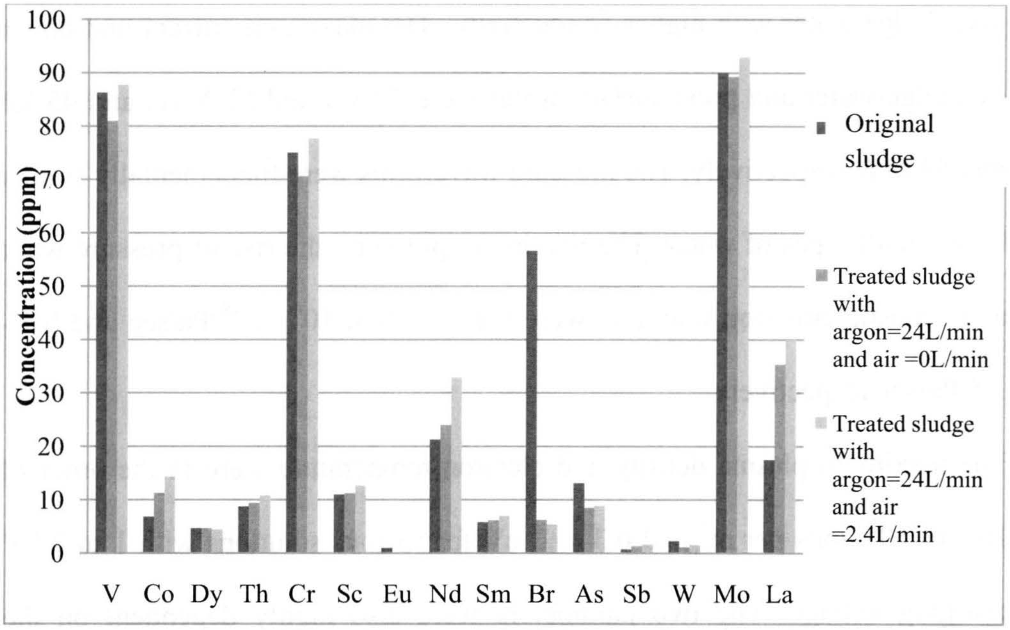


Figure 6.5.2. 6 Trace elements of untreated sludge and treated sludge by thermal plasma under partial transferred mode with argon flow rate of 24 L/min and varying air flow rates (by NAA)

Chapter 7: Conclusions

The aim of this work was on the thermal plasma treatment of sediment accumulating in stormwater ponds. Stormwater sediment was first separated into sludge-water (filtrate), and sludge (filtrand) by screen filters. The sludge-water and sludge were subjected to, respectively, PAED and thermal plasma treatments.

The results from PAED sludge water treatment show that:

(1) The discharge current and voltage waveforms were fundamentally similar between pond bottom water and sludge-water, but were different from pond surface water. Single discharge was observed in pond surface water with lower conductivity, while double discharges occurred in pond bottom water and sludge-water with higher conductivity. The maximum current and power in sludge-water and pond surface water were 59 kA and 52 MW, and 45 kA and 54 MW respectively. The pressure waveforms were fundamentally similar between all types of water. The maximum pressure, the rise of pressure wave and acoustic emission impulses were 0.1 - 1 MPa, 10^6 - 10^8 Pa/sec and 0.5 - 1.5 Pa•sec respectively.

(2) The maximum plasma density and electron temperature were in the order of 10^{21} to 10^{23} ions per m^3 and 0.3 to 3 eV for various solutions with 1 to 2 kV charging voltage. The two parameters were also highly dependent on the conductivity of the solutions. Maximum plasma density and electron temperature increased slightly with relatively low range of conductivity (20 to

200 mS/m), but increased one order of magnitude when conductivity raised from 200 to 600 mS/m.

(3) UV-A and radicals such as N_2, O_3, OH, H and O were detected from optical emission. Intensity of optical emissions and UV-A increased with increasing charging voltage but decreased with increasing gap distance. UV-A and UV-B dosimeters showed that the dosages of UV-A and UV-B ranged between 0.18 and 0.45 mW/cm^2, and between 0.001 and 0.014 mW/cm^2, respectively. In strip chart analyses, the decay time of the UV-A, N_2, OH, H and O radicals were around 0.4 to 0.6 msec. The results indicate that the radicals existed slightly longer than the discharge period.

(4) Reduction of TOC in sludge-water reached 80% and was greater than 90% after 5 minutes and 2 hours of PAED treatments, respectively. The pH, conductivity, dissolved oxygen and temperature changed over the course of treatment. pH values increased with increasing treatment time for all samples, while conductivity and dissolved oxygen (DO) increased in pond bottom water but decreased in sludge-water after 2 hours of PAED treatment. During the measurement time in water quality analysis, pH and DO were stabilized after 1 and 5 minutes respectively.

(5) The accumulated gaseous concentrations of C_xH_y, CO, CO_2, SO_2, H_2S and NO were 8.2, 3.1, 1.9, 0.32, 0.29 and 0.07 mg/L, respectively, after two hours of PAED treatment. The generations of C_xH_y and CO were continuous and more

favorable than CO_2. Formations of SO_2 and H_2S were continuous. The generation of NO started after 60 minutes of PAED treatment.

(6) The main elements of PAED treated sludge were O > Si > Al > Ca > Fe > Mg > Na > K >Mn > Ti, minor elements were Mn > Ba > Sr > Cr > Br > Zn > As > Sc > Th > Co > Sm > W > Dy > Co > Nd > Eu > Sb. The concentrations of volatile elements in sediment such as C, S, Br, Cl and K decreased approximately 100, 80, 90, 30 and 20% respectively. Two of the most abundant elements, Al and Ca, decreased 1 and 2.5% in mass respectively. The concentration of O increased more than 5% in all samples after PAED treatment.

Thermal plasma wet sludge treatments were applied under two different plasma operating modes: non-transferred and partial transferred modes. The results show that:

(1) Treatment by thermal plasma under partial transferred mode was not homogeneous, especially under anoxic environments. The upper part of the treated sludge appeared darker in color. Under SEM images, wet sludge was melted in partial transferred mode. The formation of unleachable slag might be possible.

(2) The average reductions of total organic carbon (TOC) were 25 and 22% by thermal plasma treatments at an argon flow rate of 35 L/min under non-transferred and partial transferred modes, respectively. In general, the darker part contains higher TOC percentages. The average reductions of TOC were

40%, 52% and 48% by thermal plasma treatments at an argon flow rate of 24 L/min under partial transferred mode with air flow rates of 0, 2.4 and 4.8 L/min, respectively. The reduction of TOC was most efficient with thermal plasma wet sludge treatment under partial transferred mode, and reached its maximum with argon and air flow rates at 24 and 2.4 L/min, respectively.

(3) Thirteen elements were detected by X-ray energy dispersion. The elements in the untreated sludge were O > Si > Al > Ca > S > Fe > K > Mg > Na > Cu > C > Ti > Cl. After thermal plasma treatment, the average weight percentages of O, Si and Al decreased 40, 30 and 50%, respectively; while Ca and Fe enriched 500 and 40%, respectively. No significant differences in elemental concentrations were observed in thermal plasma treatment operated with different modes. The elemental concentrations were also similar with increasing argon flow rates. Variation of elemental concentrations was apparent between the darker and lighter parts of sludge in anoxic environments. Reduction of sulfur was only 10 - 30% in anoxic environments, while carbon and sulfur were mostly reduced to zero in oxidizing environments. The weight percentages of Si, K, Fe and O increased with increasing air flow rates, while Ca and Cu decreased with increasing air flow rates. Weight percentages of other major elements deviated within 10% with increasing argon flow rates.

(4) Thirty two elements were detected by NAA where 27 elements were above detection limits. Major elements (> 10000ppm) were Ca > Al > Fe > K > Mg

> Na > Ti > Cl; minor elements (100 - 10000ppm) were Mn > Ba > Sr > Zn; and trace elements (< 100ppm) were Mo > V > Cr > Br > La > As > Sc > Th> As > Co > Dy > W > Sb > Eu. Most elements were similar in concentration after thermal plasma treatments, with the exception of Zn, La, Co, Br and As. Concentrations of Zn, La and Co enriched 90, 50 and 30% on average respectively, while Br, W and As decreased by 80, 50 and 20% on average, respectively. Concentrations of Mg and Fe enriched slightly with increasing air flow rates, while concentrations of other major elements were quite constant with increasing air flow rates. The difference of major element concentrations is within 10% between anoxic and oxidizing environments. The concentrations of minor and trace elements remained quite consistent with increasing air flow rates except for a few elements. Enrichments of La, Co and Nd were higher in oxidizing environments, while the concentration of Ba was higher in anoxic environments.

(5) The major compositions of the original stormwater sludge were sand (SiO_2) and calcite ($CaCO_3$). The chemical compositions in sludge were quite different after thermal plasma treatment. The average percentages of sand and calcite decreased by 35 and 10% respectively, and weight percentages of both compounds were at the lowest in anoxic environments. Other compositions such as $KAlSi_3O_8$, Fe_3O_4, NaCl and $CaSO_4$ were formed after treatment. It is surmised that chemical compounds were decomposed and re-combined under thermal plasma treatments.

(6) In anoxic environments, variation of elemental concentrations was apparent between the darker and lighter parts of sludge. Darker particles consisted of more NaCl, $CaSO_4$ and Fe_3O_4. In addition, the darker particles were slightly magnetic. The percentages of sand (SiO_2) and calcite ($CaCO_3$) were at the lowest in anoxic environments, where similar percentages were found for other compositions with increasing argon and air flow rates.

(7) Hydrocarbons, H_2S, CO and NO were emitted continuously during thermal plasma treatments. It was observed that the minimum CO, NO and NO_2 were formed by thermal plasma in the argon-air environment, regardless of the existence of organic and nitrate compounds in the sludge. The accumulated C_xH_y, CO, NO and H_2S were higher in partial transferred mode than those in non-transferred mode. In anoxic environments, organic compounds were mainly converted hydrocarbons. Generation of CO was most favorable under an air flow rate of 2.4 L/min and the formation of CO_2 was most preferable under an air flow rate of 4.8 L/min. Accumulated NO and NO_2 were at the highest with air flow rates of 2.4 and 4.8 L/min, respectively. Accumulated H_2S and SO_2 were generated at the highest amount in anoxic environments, and the least at an air flow rate of 2.4 L/min. Hydrogen gas was generated from moisture and volatile organic compounds in sludge at the first 20 minutes of treatment.

Thermal plasma treatment of dried PAED treated sludge under partial transferred mode shows that:

(1) From the examination of SEM images, dried PAED treated sludge was not melted in partial transferred mode. The percentage of TOC slightly decreased from 8 to 7.5% after PAED treatment and was further reduced to 5.3% on average after a thermal plasma treatment of two hours. The reduction of TOC in wet sludge was 15% higher than that in dried PAED treated sludge with the same argon and air flow rates.

(2) The accumulated concentrations of C_xH_y, CO, CO_2, NO, NO_2, H_2S and SO_2 after a two-hour treatment were 6100, 10000, 6200, 9700, 140, 40 and 27 ppm, respectively. Thermal plasma treatments of wet sludge generated more gaseous by-products than those from dried PAED treated sludge with the exceptions of CO and NO. Higher conversion of organics and sulfur compounds and suppression of NO_x formation into gaseous compounds were observed in wet sludge. Formations of NO and CO were continuous, while NO_2 was generated in small amounts when the oxygen level reached 4%. The generations of CO, NO and NO_2 by thermal plasma were dependent on oxygen levels.

(3) X-ray energy dispersion solid analyses show that elemental weight percentages of Mg, Al, Si, K, Ti and Cu in dried PAED treated sludge were higher than in wet sludge after thermal plasma treatment. In addition, carbon and sulfur in PAED treated sludge were reduced. Concentrations of Si, Mg, Al

decreased by 25, 30 and 60%, respectively; while Ca and Fe enriched by 400 and 25%, respectively. It is observed that elemental weight percentages in dried PAED treated sludge were less deviated before and after thermal plasma treatments.

(4) Weight percentages of sand (SiO_2), calcite ($CaCO_3$) and rutile (TiO_2) were higher in dried PAED treated sludge, while weight percentages of $CaCO_4$ and NaCl were higher in wet sludge. Both weight percentages and compositions in dried PAED treated sludge were less deviated before and after thermal plasma treatments.

Based on the above results and observations, it is concluded that PAED discharges in pond bottom water and sludge-water ionized liquid molecules and resulted in high electron temperatures and plasma densities. Generation of UV-A and radicals such as N_2, O_3, OH, H and O were observed during the discharge period. The system degraded organic compounds into CO_2, CO and C_xH_y, and converted sulfur and nitrate compounds into SO_2, H_2S and NO. Volatile elements such as Br and Cl decreased after treatment as well. Thus, contaminated sludge-water and pond bottom water are safe to be discharged to receiving water bodies after PAED treatments.

The reduction of TOC was highest and melting of particles was observed in thermal plasma wet sludge treatments under partial transferred mode. Concentrations of C and S were reduced to almost zero in oxidizing environments. Minimum productions of CO, CO_2 and NO_x were observed in anoxic environments. The wet sludge was therefore decontaminated from harmful chemicals. In addition, new chemical compositions such as $KAlSi_3O_8$, Fe_3O_4, NaCl and $CaSO_4$ were formed after treatment. Enrichment of valuable metals such as Zn and Fe was observed and thus recovery of these metals might be possible. This is a result of chemical compound decomposition and re-combination under thermal plasma treatments. As such thermal plasma sludge treatment can reduce TOC and degrade harmful organic compounds. It is therefore recommended that sludge-water be first subjected to PAED treatment, while the liquid portion is safe to be discharged into receiving water bodies, the remaining solid portion can then be subjected to (without drying) thermal plasma treatment under partial transferred mode for further decontamination.

Chapter 8: Recommendations for Future Study

This work has shown that, for PAED sludge-water treatment, TOC in the liquid portion was almost completely removed after 10 minutes of treatment. A previous study also showed that 99% inactivation of bacteria was achieved with PAED treatments of 10 minutes (Yantis et al., 2008). Based on these results, the decontamination of sludge-water can be achieved within 10 minutes of PAED treatment. Sedimentation of sludge particles was observed after PAED treatment. The resulting solid components (PAED treated sludge) can be separated and subjected to thermal plasma treatment for further decontamination. This may be studied in the future.

Modifications of the ceramic plasma reactor for thermal plasma treatment should be considered in future studies as well. The experiment results showed that the melting of sludge only appeared near the surface area. Due to the low conductivity of the sludge, limited current was transferred into the ground graphite electrode. The treatment efficiency may highly increase by improving the heat transfer and current transfer within the ceramic reactor. Although melting of particles was observed after thermal plasma treatment, leaching test following the toxicity characteristic leaching procedure (TCLP) should be conducted on the thermal plasma-treated sludge. Depending on the leachability and material strength, the treated sludge can be either recycled as building material or landfilled (Legret and Pagotto, 2006).

Enrichments of Zn and Fe were observed after thermal plasma treatment. In anoxic environments, darker part was slightly magnetic. Solid analysis by XRD also confirmed the formation of magnetite (Fe_3O_4). Thus, recovery of heavy metals in stormwater sludge is another potentially feasible idea to reduce the cost of treatment (Legret and Pagotto, 2006; Haugsten and Gustavson, 2000; Izaumikawa, 1996). It is expected that greater adsorption of heavy metals is on finer particles (Allan, 1986). This is in agreement with the observation of substantially higher metal concentrations in the fine particle fractions of sediment (< 45 μm) in stormwater ponds (Marsalek et al., 1997). It is suggested that stormwater sludge may be separated by mechanical sieving with an opening of 45 μm. After PAED sludge-water treatment, the solid components can be subjected to thermal plasma treatment in anoxic environment for higher metal recovery and low gaseous by-product emissions. The thermal plasma treated sludge can be crushed into powders, and the magnetic portion can be separated out by magnets. The magnetic part may be further treated for metal recovery while the non-magnetic part may be recycled as building materials or landfilled. As the organic compounds in stormwater sludge are not sufficient to self-generate the power needed for treatment, mixing of sludge with other high organic content solid wastes is recommended. The mixed sludge can be subjected to thermal plasma treatment in oxidizing environments for higher reduction of TOC and higher emission of flue gases such as hydrocarbons, CO and CO_2.

The emission of toxic gases during the treatment is another major concern. Significant amount of N, Cl and S components in stormwater sediment may be converted to NO_x, HCl and SO_x in the treatment process. Conversion of CO to harmless CO_2 should be included in the PAED and thermal plasma treatment designs. Some gas control systems should be introduced at the exit. Selective Catalytic Reduction (SCR) can be used to treat NO_x and SO_x and calcium injection can be used to eliminate HCl (Chang et al., 2005). High efficiency particulate air (HEPA) filters can be inserted in the exit to capture volatile and semi-volatile materials in the off-gas stream. Hydrocarbon in flue gas and hydrogen gas can be used as a part of energy sources for power supply in the treatment system.

References

Allan, R.J., 1986. The role of particulate matter in the fate of contaminants in aquatic ecosystems, *Sci. Series* No.**142,** Burlington, Ontario.

Ancheta, C., 1998. Remediation Strategies and Options for Contaminated Sediment. *Proceeding of National conference on management and treatment of contaminated sediment.* pp. 85 – 89

Anderson, B.C., T. Bell, P. Hodson, J. Marsalek, W.E. Watt, 2004. Accumulation of trace metals in freshwater invertebrates in stormwater management facilities. *Water Quality Research Journal of Canada* (39) 362

Angeloni, D.M., S.E. Dickson, M.B. Emelko, J.S. Chang, 2007. Removal of Methyl-tert-butyl Ether from Water by a Pulsed Arc Electrohydraulic Discharge System. *Japanese Journal of Applied Physics.* **45** 8290

Anpilov, A.M., E.M. Barkhudarov, N. Christofi, V.A. Kop'ev, I.A. Kossyi, M.I. Taktakishvili, Y.V. Zadiraka, 2004. The Effectiveness of a Multi-spark Electric Discharge System in the Destruction of Microorganisms in Domestic and Industrial Wastewaters. *Journal of Water and Health* **2(4)** 267

Ara, M., N. Debacher, J.S. Chang, 2005. Formation of Toxic Gases by Argon Plasma Torch Operation in Air Environment. Proceeding of *International Symposium on the Basic and Application of Plasma Technology* pp. 4 – 10

Barrett, M.E., Jr. L.B Irish, Jr. J.F Malinia, R.J. Charbenuea, 1998. Characterization of highway runoff in Austin, Texas, Area. *J. Environ. Eng., ASCE* **124** 131

Bogomaz, A.A., V.L. Goryachev, A.S. Remennyi, F.G. Rutberg. 1991. Efficiency of Pulsed Electric Discharge in Water Disinfection. *Lett. J. Theor. Phys.* **17** 65

Boxman, R.L., N. Parkansky, H. Mamane, M. Meirovitz, Y. Orkabi, T. Halperin, D. Cohen, N.Orr, E. Gidalevich, B. Alterkop, S. Cheskis, 2007. *Proc. Of NATO Advanced Study Institute on Plasma Assistd Decontamination of Biological and Chemical Agents.* pp. 41-50

Beuthe, T.G. and J.S. Chang, 1997. Chemical Kinetic Modelling of Non-Equilibrium Ar-CO_2 thermal Plasmas. *Japanese Journal of Applied Physics.* **36** 4997

Bishop, C.A., J. Struger, L.J. Shirose, L. Dunn, G.D. Gampbell, 2000. Contamination and Wildlife Communities in Stromwater Detention Ponds in Guelph and the Great Toronto Area, Ontario, 1997 and 1998, *Water Quality Research Journal of Canada,* **35(3)** 313

Chang, J.S., B.W. Gu, F.Y. Chu, C.J. Simpson, 1996. Thermal plasma pyrolysis of used old tires for production of syngas *J. Env. Sci. & Health,* **A31** 1781

Chang, J.S., Y. Takakura, S. Jamal, S. Ono, S. Teii, 1996. Thermal Plasma Dissociation of CO_2. *Plasma Society, Japan.* Pp. 61-66 EP-96-29

Chang, J.S., H. Jimbo, T. Kikuchi, T. Amemiya, 1997. Fly ash particles generated by a plasma municipal waste incinerator ash volume reduction system *J. Aerosol. Sci.* **28(S1)** S551

Chang, J.S., P.C. Looy, K. Urashima, 1998. *Proc. 1998 Advanced Oxidation Technologies: Innovations and Commercial Applications* pp.148 -154

Chang, J.S., 2001. Recent development of plasma pollution control technology: a critical review *Sci. Technol. Adv. Mater* **2** 571

Chang, J.S., K. Urashima, Y. Uchida, 2002. "Characteristics of Pulsed Arc Electrohydraulic Discharges and Their Application to Water Treatment. *Res. Rep. Tokyo Denki Daigaku* **50** 1

Chang, J.S., K. Urashima, M. Iriyama, Y. Naka, T. Usui, 2003. Slag Detoxicity Analysis of Swirl Flow Municipal Incineration Ashes and Sludge Melting Systems. *Proc. 8th Int. Conf. Solid Waste Technology and Management.* pp. 286 -295

Chang, J.S., M. Ara, K. Urashima, H. Jimbo, K. Oniuma, 2005. Comparison of Solid By-Products Generated from Thermal Plasma Incineration Ash Melting Systems by Palsma Torch and Three-Phase Submerged Arc Process *J. Adv. Oxid. Tech* **8** 59

Chang, J.S., S. Ono, H. Ukai, T.C. Huang, W.Y. Chang, P. Shou, M.Sato, S. Teii, C. Liu, K.Ting, 2007. UV and Optical Emissions Generated by the Pulsed Arc Electrohydraulic Discharge. *International J. of Plasma Environmental Sci. Tech* **1(2)** 130

Chang, J.S., O.L. Li, Y. Guo, 2008. Thermal Plasma Treatment of Stormwater Detention Pond Sludges *Journal of Pure and Applied Chemistry.* **80(9)** 1993

Chang, J.S., S. Dickson, Y. Guo, K. Urashima, M.B. Emelko, 2008. Electrohydraulic Discharge Direct Plasma Water Treatment Processes, Chapter 24 of Advanced Plasma Technology, R.d'Augestino et al Eds., Wiley-VCH Verlag, GmbH & Co., Weinheim, pp.421-433

Chang, J.S., O.L. Li, Y. Guo, 2009. Plasma Parameters in a Pulsed Arc Electrohydraulic Discharge. *The Institute of Electrical Engineers of Japan - Plasma Tech. Meeting.* pp. 9-14 PST-09-105

Clary. J., J.E. Jones, B.R Urbonas, M.M. Quigley, E. Strecker, T. Wagner. 2008. Can stormwater BMPs remove bacteria. *The Journal for Surface Water Quality Professionals. pp 4-7*

Copsey, M.J., 1990. Plasma technology for the destruction of. hazardous wastes. *Proc. Conf. Plasma for Industry and Environment, Oxford, U.K.,*Sep.

Cox J.H. and E.H. Livingston, 1997. Stormwater Sediment: Hazardous Waste or Dirty-Dirt- An Update. *Proc. Biennial stormwater research conference.* **5** pp.11 - 19

Donaldson, A.D., R.O. Aoa, T.L. Eddy, J. Eflinn, 1991. A review of plasma destruction of hazardous mixed waste. *Heat transfer in thermal plasma processing. ASME Press New York.* **41** pp. 194-202

Funfschilling, M.R., W. Bernhard, H. Bretscher, H. Felix, C.M. Rippestein, 1990. A New Plasma Technology for Hazardous Waste Destruction and Nuclear Waste Consolidation. *Proc. Conf. Plasma for Industry and Environment, Oxford,* U.K., Sep. 1990

Gloucester harbor DMMP DEIR, 2002. Dredged Material Management Plan Technical Reports, Section 4. *The Commonwealth of Massachusetts.* Massachusetts Office of Coastal Zone Management, Boston, U.S

Graney, J.R. and T.M. Eriksen, 2004. Metals in Pond Sediment as Archives of Anthropogenic Activities: A Study in Response to Health Concerns. *Applied Geochemistry.* **19** 1177

Great Lakes Fact Sheet, 1999. Stormwater detention ponds of Southern Ontario: Are they a risk to wildlife. *Minster of Environment,* Minister of Public Works and Government Services Canada

Greenland International Consulting Inc., 1999. The Storm Water Management Facility Sediment Maintenance Guide. *Storm water management facility;* Greenland International Consulting Inc.

Hall, M., E. Alperin, S. Shealy, K. Jones, 1998. Treatment of Dredged Harbor Sediment by Thermal Desorption. *Proc. U.S. EPA National conference on management and treatment of contaminated sediment.* pp.112 – 114 (EPA/625/R-98/001)

Hartig, J.A., G. Krantzberg, M.A. Zarull, 2000. Contaminated Sediment Remediation in the Laurentian Great Lakes: an Overview. *Water Quality Journal of Canada* **36(3)** 347

Haugsten, E.K and B. Gustavson, 2000. Environmental Properties of Vitrified Fly Ash from Hazardous and Municipal Waste Incineration *Waste Management* **20** 167

Huxleh L.G and R.W. Crompton. 1994. The Difussion and Drift of Electrons in Gases, John Wiley and Sons, New York.

Hydromantis Inc. and Stantec Consulting Ltd, 2003. Final Report on Ultraviolet disinfection technology for municipal wastewater treatemtn plant applications in Canada. Hydromantis, Inc and Stantec Consulting Ltd.

Ikeda, T., H. O. Li, K. Teii, J. S. Chang, 2007. Analysis of Fine Particle Formations by Pulsed Arc Electrohydraulic Discharges in Water with Fe and Ti Electrodes *Proc. ISPC* **18** (CD)

Izumikawa, C., 1996. Metal Recovery from Fly ash Generated form Vitrification Process for MSW ash. *Waste Management.* **16** 501

Jones, K.W., H. Feng, E.A. Stern, J. Lodge and N.L. Clesceri,. 2001. Dredged material decontamination demonstration for the port of New York / New Jersey. *Journal of Hazardous Materials.* **85(1-2)** 127

Jimbo, H., T. Kikuchi, T. Amemiya, J.S. Chang, 1997. *Proc.* By-Product Detoxicity Characteristics of Thermal Plasma Municipal Incinerator Ash Volume

Reduction System. *Proceedings of the First Asia-Pacific International Symposium on the Basic and Application of Plasma Technology* pp175-182

Kanazawa, S., J.S. Chang, G.F. Round, G. Sheng, T. Ohkubo, Y. Nomoto, T. Adachi, 1997. Removal of NOx from Flue Gas by Corona Discharge Activated Methane Radical Showers", *J. Electrostatics*, **40** 651

Khalaf, P.I., N.A. Debacher, M. Ara, J.S. Chang, 2008. Gaseous By-Products from Argon Thermal Plasma-Air-Water System. *Proc of 17th International Conference on Gas Discharges and Their Applications* pp. 365-368.

Klein D.H., A.W. Andren, J.A Carter, J.F. Emery, C.Feldman, W. Fulkerson, W.S Lyon, J.C. Olge, Y. Talmi, R. I. Can Hook, and N. Bolton, 1975. Pathways of Thirty-seven Trace Elements Through Coal-Fired Power Plant. *Enviro Sci and Tech.* **9(10)** 973

Knoll, G.F., 1989. Radiation Detection and Measurement. John Wiley & Sons, New York.

Kostic, Z.G., P.L. Stefanovic, P.B. Pavlovic, 2000. Comparative Analysis of Polychlorinated Biphenyl Decomposition Processes in Air or Argon (+oxygen) Thermal Plasma. *Journal of Hazardous Materials.* **75(1)** 75

Legret, M, C. and Pagotto, 2006. Heavy Metal Deposition and Soil Pollution along Two Major Rural Highways. *Environmental Technology.* **27(8)** 247

Lee, L., A.J. Arnold, C.A. Santillan, M.B. Emelko, S. Dickson, and J.S. Chang, 2008. Bench-scale Bacteria and Viruses by Pulsed Arc Electrodraulic Discharge Disinfection. *Water Quality Res. J. Canada* **43** 77

Li, O.L., 2006. Novel Physical and Chemical Characterization of Stormwater Sediment. Master Thesis. Dept. Civil Eng., McMaster University

Li, O.L., J. S. Chang, Z.Zhang , H.Ukai , S.Ono, Y.C.Hang , C.Y.Liao, P.W.Peng, C.Liu, K.Ting and S.Teii, 2007. Discharge Characteristics of Pulsed Arc Electrohydraulic Discharge System in a Sludge Water Treatment *Proc. International Symposium on the Basic and Application of Plasma Technology* **5** pp. 4 – 8

Li, O.L., Y. Guo and J.S. Chang, 2008. Characterization Comparisons of Sediment from Four Stormwater Ponds in Ontario *Reliable Modeling of Urban Water System* **16**, published by CHI, Guelph, Ontario, Canada. pp.229-248

Li, O.L., Y. Guo and J.S. Chang, 2009. Pulsed Arc Electrohydraulic Discharge Characteristics and Plasma Parameters of Sludge-Water *Annual Report of Conference on Electrical Insulation and Dielectric Phenomena, IEEE (CEIDP)* pp. 331-334

Li, O.L., Y. Guo and J.S. Chang, 2009. Treatment of Contaminated Sludge and Pond Water in Stormwater Pond by Pulsed Arc Electrohydraulic Discharge Reactor. *Proc. to Asia-Pacific International Symposium on the Basics and Applications of Plasma Technology 6 (APSPT-6).* pp. 104-107

Li, O.L., Y. Guo and J.S. Chang, 2010. Solid and Gaseous By-Products from Thermal Plasma Treatment of Stormwater Pond Sediment under Non-Transferred and Partial Transferred Operating Modes. *Proc. To International Conference on Gas Discharges and Their Applications (GD 10) (In press)*

Li, O.L., Y. Guo, J.S. Chang, Z. He, 2010. Gaseous By-products from Pulsed Arc Electrohydraulic Discharge in Treatment of Contaminated Stormwater Detention Pond. *Proc. To International Symposium on Non-Thermal/Thermal Plasma Pollution Control Technology & Sustainable Energy (ISNTP-7)* (In press)

Li O.L., J.S. Chang, Y. Guo, Z. He, 2010. Discharge, Pressure Propagation and Optical Characteristics of Polluted Lake Water Pulsed Arc Electrohydraulic Discharges. *Proc. of French Society of Electrostatics (SFE) (In press)*

Li, O.L., J.S. Chang, F. Jaquemier, Y. Guo, 2010. Pulsed Arc Electrohydraulic Discharge Plasma Treatment of Polluted Lake Water. *Proc. of 4th International Engineering Research Conference (IERC).* pp.4-7

Lenihan, J.M.A., S.J. Thomson, V.P. Guinn, 1971. Advances in Activation Analysis, London; New York: Academic Press, Volume1.

Lieben. J., 2001; Heavy Metal Contamination of Sediment in Stormwater Management Systems: the Effect of Land Use, Particle Size, and Age. *Environmental Geology* **41** 341

Locke, B.R., M. Sato, P. Sunka, M.R. Hoffmann, J.S. Chang, 2006. Electrohydraulic Discharge and Nonthermal Plasma for Water Treatment. *Industrial and Engineering Chemistry Research* **45** 882

Madge B.A and J.N. Jensen, 2002. Disinfection of Wastewater Using 20 kHz Ultrasound *Water Environment Research.* **78** 294

Marsalek J. and P.M. Marsalek, 1997. Characteristics of Sediment from a Stormwater Management Pond. *Water Science and Technology* **36(8-9)** 117

Marsalek J., W.E. Watt, B.C. Anderson, C. Jaskot, 1997. Physical and Chemical Characteristics of Sediment from a Stormwater Management Pond *Water Quality Research Journal of Canada.* **32** 89

Marsalek, J., B. Brownlee, T. Mayer, S. Lawal, G.A. Larkin, 1997. Heavy Metals and PAHs in Stormwater Runoff from the Skyway Bridge, Burlington, Ontario. *Water Quality Research Journal of Canada* **32** 815

McLaughlin, D., 1999. Evidence in Virgo for the Universal Dark Matter Halo. *Astrophysical Journal* **512** 9

Mededovic, S. and B.R. Locke, 2007. Side-chain degradation of atrazine by pulsed electrical discharge in water. *Ind. Eng. Chem. Res.* **46** 2702

Megy, S., C. Vandensteendam, P. Roumilhac, J.M. Baronnet, 1997. Plasma Arc Vitrification of Fly Ashes from Municipal Waste Incineration Plant *Proc. 4th Int. Therm. Plasma Processes Conf.,* pp.463-475

Metcalf and Eddy, 2003. Wastewater engineering - treatment and reuse. 4th edition. Mcgraw-Hill higher education, New York

Ministry of the Environment, Ontario, 1993. Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario. ISBN 0-7729-9248-7

Ministry of Environment, Ontario, 1994. Stormwater management practices planning and design manual. Ontario, MOEE

Ministry of the Environment, Ontario, 1996. An Integrated Approach to the Evaluation and Management of Contaminated Sediment. ISBN 0-7778-3845-1, Ontario, MOEE

Ministry of the Environment, Ontario, 2001. The influence of urban runoff on sediment quality and benthos in Toronto harbor. Ontario, MOEE

Ministry of the Environment, Ontario, 2004. Guideline A-7 Combustion and Air Pollution Requirements for New Municipal Waste Incinerators. 1746e Ontario, MOEE

Quann R.J, M. Neville, M. Janghorbani, C.A. Mlms and A.G. Saroflm. 1982. Mineral matter and Trace-Element Vaporization in a laboratory-Pulverized Coal Combustion System. *Enviro. Sci. Techno.* **16** 776

Ramachandran, K and N. Kikukawa, 2002. Thermal Plasma In-flight Treatment of Electroplating Sludge. *IEEE Transactions on Plasma Science* **30(1)** 310

Rienks, J., 1998. Comparison of Results for Chemical and Thermal Treatment of Contaminated Dredged Sediment. *Water Science and Technology.* **37** 355

Reich, J., 2003. Slag from Hazardous Waste Incineration: Reduction of Heavy Metal Leaching. *Waste Management and Research.* **21(2)** 110

Rochfort, Q., L. Grapentine, J. Marsalek, B. Bownlee, T. Reynoldson, S. Thompson, D. Milani, C. Logan, 2000. Using Benthic Assessment Techniques to Determine Combined Sewer Overflow and Stormwater Impacts in the Auqatic Ecosystem. *Water Quality Research Journal of Canada.* **35(3)** 365

Rock, S.A., 1998. Potential for phytoremediation of contaminated sediment. *Proc. National Conference on Management and Treatment of Contaminated Sediment.* pp. 101 -110

Santiago R. and J.P. Pelletier, 2001. Contaminated Sediment Management: the Canadian Experience. *Water Quality Research Journal of Canada* **36** 395

Sato, M., T. Ohgiyama, J.S. Clements, 1996. Formation of Chemical Species and Their Effects on Microorganisms Using a Pulsed High-Voltage Discharge in Water. *IEEE Trans. Ind. Appl.* **32** pp.106-112

Sawell, S.E., T.R. Bridle, T.W Constable, 1988. Heavy metal Leachability from Solid Waste Incinerator Ashes. *Waste Mamagement and Research* **8** 227

Slifko, T., O. County and N. Shaber. 2007. Occurrence of Cryptosporidium, Giardia, and metals in Florida stormwater ponds and assessment as alternative water supplies for irrigation. *9th Watershed Conference pp.78-89*

Soete, D., D. De Gijbels, R. Renaat, J. Hoste, 1972. Nuclear Activation Analysis, Chemical Analysis. 34, London, New York: Wiley-Interscience.

Stern, E.A., K.R. Donato, N.L. Clesceri and K.W. Jones, 1998. Integrated Sediment Decontamination for the New York/New Jersey Harbor. *Proc. National Conference on Management and Treatment of Contaminated Sediment.* pp.71-74

Thomson, N.R., E.A. McBean, W. Snodgrass, I.B. Monstrenko, 1997. Highway Stormwater Runoff Quality: Development of surrogate parameter relationships *Water, Air and Soil Pollution.* **94(3-4)** 307

Tzeng, C.C., Y.Y. Kuo, Y. Huang; D.L Lin, Y.J .Yu, 1998. Treatment of radioactive wastes by plasma incineration and vitrification for final disposal. *Journal of Hazardous Materials.* **58** 207

USEPA, 1999. Wastewater technology fact sheet: Ozone disinfection. EPA 832-F-99-063

USEPA, 2002. Application, performance and costs of biotreatment technologies for contaminated soils. EPA/600/R-03/037

USEPA, 2005. National Management Measures to Control Nonpoint Source Pollution from Urban Area, PA 841-B-05-004

Urashima, K., J.S. Chang, J.Y. Park, D.C. Lee, A. Chakrabarti and T. Ito, 1998. Reduction of NOx from Natural Gas Combustion Flue Gases by Corona Discharge Radical Injection Techniques. *Trans. IEEE Industry Appli. Soc.* **34** 934

Urashima, K and J.S. Chang, 2000. Removal of volatile organic compounds from airstreams and industrial flue gases by non-thermal plasma technology. *IEEE Transactions on Dielectrics and ElectricalIinsulation.* **7(5)** 602

Urashima, K., J.S. Chang, and Y. Uchida, 2004. Comparisons of UV and Pulsed Arc Electrohydraulic Discharge Treatment of Ammonia Compounds in Water with and without Phtocatalyst", *Proc. of The fourth International Symposium on Non-Thermal Plasma Technology (ISNTP-4)*, pp.93-97

Vanloon, G., B.C. Anderson, W.E. Watt, J. Marsalek, 2000. Characterizing Stormwater Sediment for Ecotoxic Risk. *Water Quality Research Journal of Canada,* **35** 341

Vel Leitner, N.K.V., G. Syoen, H. Romat, K. Urashima, J.S. Chang, 2005. Generation of active entities by the pulsed arc electrohydraulic discharge system and application to removal of atrazine. *Water Research* **39** 4705

WEF Water Environment Federation, 1996. Wastwater Disinfetion. Manual of Practive FD-10, Alexandria VA

Wu, Y,. T. Clevenger and B. Deng. 2005. Impacts of Goethite Particles on UV Disinfection of Drinking Water. *Applied and Environmental Microbiology.* **7** 4140

Yamatake, A., D.N. Angeloni, S. Dickson, M.B. Emelko, K. Yasuoke and J.S. Chang, 2007. Pulsed Electrohydraulic Discharge Characteristics in an Eccentric Electrode Cylindrical Reactor using Phosphate-Buffered Saline water. *Japanese Journal of Applied Physics* **45** 8298

Yantsis, S.N., P. Chow-Fraser, O.L. Li, Y. Guo, J.S. Chang and S. Terui, K. Watanabe, M. Itoh, 2008. Zooplankton Mortality in Lake Water Treated by Pulsed Arc Electrohydraulic Discharge plasma *International Journal of Plasma Environmental Science and Technology* **2(2)** 128

Yelverton E., 1981. *Nature* **294** 275

Yong, J.L and X.Z Jiang, 2005. Phenol degradation by a nonpulsed diaphragm glow discharge in an aqueous solution. *Environ. Sci. Technol.* **35** 8512

Zarull, M.A., J.H. Hartig and G. Krantzerg, 2001. Sediment Management: Ecological and Ecotoxicological Effects Must Direct Actions. *Water Quality Research Journal of Canada* **36** 351

Zastawny, H.Z., H. Romat, N. Karpel, V. Leitner, J.S. Chang, 2004. Pulsed Arc Discharges for Water Treatment and Disinfection. *Electrostatics 2004,* No.137, pp.325-330. IOP Publishers: Bristol, U.K

Appendix A: Table of Element Toxicities

Table A- 1 Element Toxicities (Ara et al., 2005)

Element	**Abbreviation**	**Toxicity**
Aluminum	Al	Low
Arsenic	As	High
Barium	Ba	High
Bromine	Br	Medium
Calcium	Ca	Low
Chlorine	Cl	Medium-High
Cobalt	Co	Medium-High
Chromium	Cr	High
Dysprosium	Cy	Medium
Iron	Fe	Low
Potassium	K	Low
Lanthanum	La	Low-Medium
Magnesium	Mg	Low
Manganese	Mn	Low
Molybdenum	Mo	Low
Sodium	Na	Low
Neodymium	Nd	Medium
Rubidium	Rb	Low-Medium
Sulphur	S	Medium-High
Antimony	Sb	High
Scandium	Sc	Low
Samarium	Sm	Low-Medium
Strontium	Sr	Low
Thorium	Th	High
Titanium	Ti	Low
Vanadium	V	Medium-High
Tungsten	W	Mediuim
Zinc	Zn	Medium-High

Appendix B: Table of Element Volatility

Table B- 1 Element volatilities (Klein et al., 1975; Quann et al., 1982)

Class	Characteristics	Boiling Point (including oxides) °C	Elements
1	Non-Volatile	> 1500	Al, Ca, Co, Cr, Cs, Eu, Fe, K, La, Mg, Na, Rb, Sc, Sm, Sr, Tn, Si, Ti
2a	Volatile Condensable:	> 1200	As, Cd, Pb, Sb, Ti, Zn
b	Volatile Condensable: more volatile than 2a, enrichment in particulates		Ba, Cu, Ge, Mo, Mn, Ni, P, Rb, Sr, U, V, W
3	Volatile, emitted in gas phase	Very low	B, Br, Cl, F, Hg, I, Se, S

Appendix C: Plasma Torch Current – Voltage Characteristics

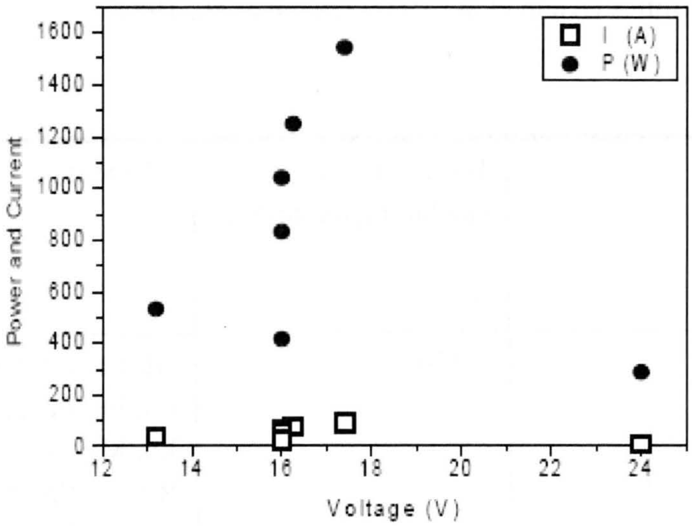


Figure C- 1 Plasma torch current-voltage characteristics (Khalaf et al. 2008)

Appendix D: Axial Averaged Argon Plasma Temperature in Plasma Torch

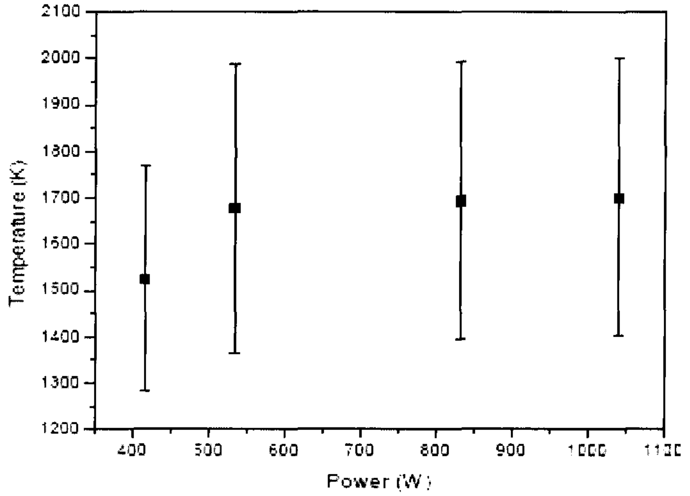


Figure D- 1 Axial Averaged argon plasma temperature observed by optical emission with Boltzmann methods (Khalaf et al. 2008)

Appendix E: Images of Treated Sludge

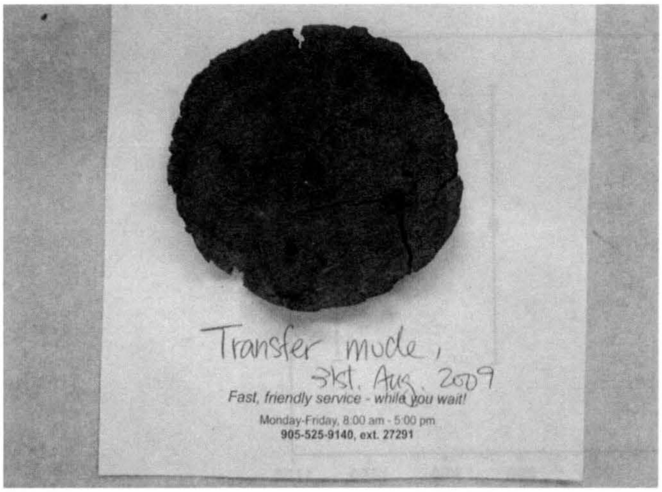


Figure E- 1Treated sludge by thermal plasma treatment under partial transferred operation mode at argon flow rate of 35 L/min after two hours of treatment (P = 1.7kW)

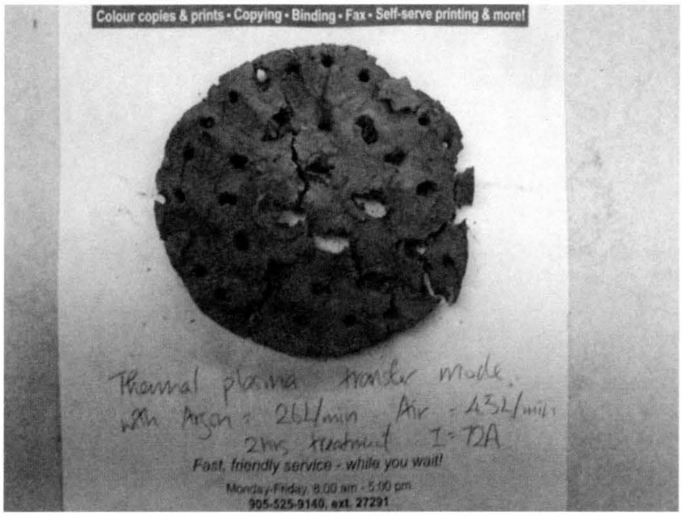


Figure E- 2 Treated sludge by thermal plasma treatment under partial transferred operation mode at argon flow rate of 35 L/min, air = 4.8 L/min, after one hour treatment (P=1.9kW)

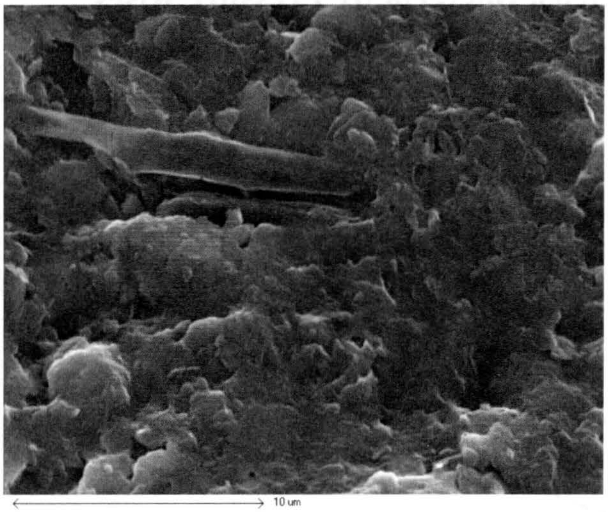


Figure E- 3 SEM image of treated sludge by thermal plasma treatment under partial transferred operation mode at argon flow rate of 35 L/min after two hours of treatment (P = 1.7kW, Magnification = 5000)

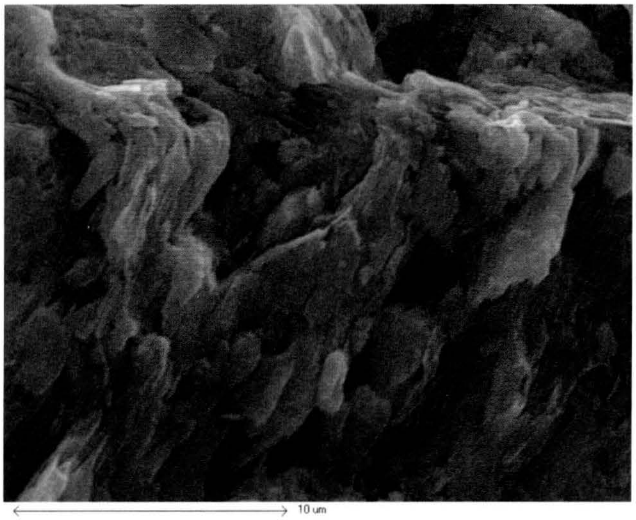


Figure E- 4 Treated sludge by thermal plasma treatment under partial transferred operation mode at argon flow rate of 35 L/min, air = 4.8 L/min, after one hour treatment (P = 1.9kW, Magnification = 5000)

Appendix F: Mortality of Virus, Bacteria by Pressure Rises

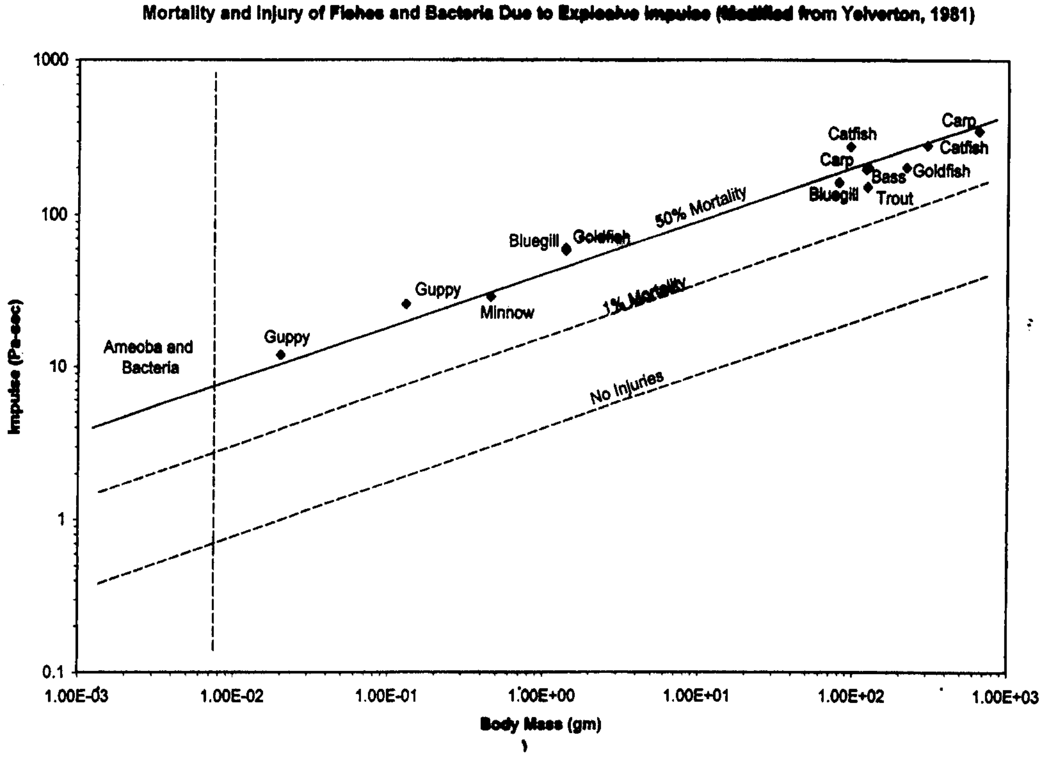


Figure F- 1 Mortality and injury of fishes and bacteria due to explosive impulses (Yelverton, 1981)

Appendix G: Detection Limits for Neutron Activation Analysis (NAA)

Table G-1: Detection limit for NAA

Element	**Detection Limit**
Al	**10**
As	**0.5**
B	**3**
Ba	**40**
Br	**2**
Ca	**1000**
Cd	**1**
Cl	**10**
Co	**1**
Cr	**1**
Dy	**0.3**
Eu	**0.5**
Fe	**1000**
Ga	**10**
Gd	**1**
I	**10**
K	**1000**
La	**0.1**
Mg	**300**
Mn	**1**
Mo	**5**
Na	**10**
Nd	**1**
S	**5000**
Sb	**0.1**
Sc	**0.1**
Sm	**0.1**
Ti	**200**
Th	**0.3**
V	**0.5**
W	**1**
Zn	**100**

Appendix H: List of Publications Related to the Present Work

Journal Publications:

1. **O.L. Li**, J.S. Chang and Y. Guo. 2010. "Pulsed Arc Electrohydraulic Discharge Characteristics, Plasma Parameters and optical emission of Sludge-Water." IEEE Electrical Insulation (EI) Magazine (invited, submitted in May, 2010)
2. **O.L. Li**, J.S. Chang and Y. Guo. 2009. "Toxic Element Analyses of Summer and Winter Stormwater Sediment by Neutron Activation Analyses." Journal of Environmental Science and Technology (submitted Dec, 2009)
3. J.S. Chang, **O.L. Li** and Y. Guo. 2008. "Thermal Plasma Treatment of Stormwater Detention Pond Sludges" Journal of Pure and Applied Chemistry. 80(9) 1993
4. S.N. Yantsis, P. Chow-Fraser, **O.L. Li**, Y. Guo, J.S Chang and S. Terui, K.Watanabe, M.Itoh. 2008. "Zooplankton Mortality in Lake Water Treated by Pulsed Arc Electrohydraulic Discharge plasma." International Journal of Plasma Environmental Science and Technology. 2(2) 128

Referred Conference Proceedings in Full Text:

1. **O.L. Li**, J.S. Chang, Y. Guo, Z. He. 2010. Proc. of French Society of Electrostatics (SFE). "Discharge, Pressure Propagation and Optical Characteristics of Polluted Lake Water Pulsed Arc Electrohydraulic Discharges"
2. **O.L. Li**, Y. Guo and J.S. Chang. 2010. Proc. of International Symposium on Non-Thermal/Thermal Plasma Pollution Control Technology & Sustainable Energy (ISNTP-7). "Gaseous By-products from Pulsed Arc Electrohydraulic Discharge in Treatment of Contaminated Stormwater Detention Pond." (accepted Feb, 2010)
3. **O.L. Li**, Y. Guo and J.S Chang. 2010. Proc. To Gas Discharge 10 (GD-10) "Solid and Gaseous By-Products from Thermal Plasma Treatment of Stormwater Pond Sediment under Non-Transferred and Partial Transferred Operating Modes." (submitted on Jan, 2010)
4. **O.L. Li** , J.S. Chang, F. Jaquemier, Y. Guo. 2010. Proc. of 4th International Engineering Research Conference (IERC). "Pulsed Arc Electrohydraulic Discharge Plasma Treatment of Polluted Lake Water." pp.4-7
5. **O.L. Li**, Y. Guo and J.S. Chang, 2009. Proc. to Asia-Pacific International Symposium on the Basics and Applications of Plasma Technology 6 (APSPT-6). "Treatment of Contaminated Sludge and Pond Water in Stormwater Pond by Pulsed Arc Electrohydraulic Discharge Reactor." pp. 104-107
6. **O.L. Li**, Y. Guo and J.S. Chang, 2009. Annual Report of Conference on Electrical Insulation and Dielectric Phenomena, IEEE (CEIDP). "Pulsed Arc

Electrohydraulic Discharge Characteristics and Plasma Parameters of Sludge-Water." pp. 331-334

7. J.S. Chang, **O.L. Li** and Y. Guo, 2009. Proc. Of The Institute of Electrical Engineers of Japan - Plasma Tech. Meeting. IEEE Japan Press, Tokyo PST-09-105. "Plasma Parameters in a Pulsed Arc Electrohydraulic Discharge." pp.9-14
8. **O.L. Li**, Y. Guo and J.S. Chang, 2008. "Characterization Comparisons of Sediment from Four Stormwater Ponds in Ontario" Reliable Modeling of Urban Water System, Monograph 16, CHI press, Guelph. pp.229-248
9. T. Ikeda, **O.L. Li**, K. Teii, J.S. Chang, 2008. International Symposium on Plasma Chemistry, in Aug 2007, Japan. "Analysis of Fine Particle Formations by Pulsed Arc Electrohydraulic Discharges in Water with Fe and Ti Electrodes." In CD
10. **O.L. Li**, J.S. Chang, Z. Zhang, H. Ukai, S. Ono, Y.C. Hang , C.Y. Liao, P.W. Peng, C. Liu, K. Ting and S. Teii. 2007. "Discharge Characteristics of Pulsed Arc Electrohydraulic Discharge System in a Sludge Water Treatment." Proc. of Asia-Pacific International Symposium on the Basics and Applications of Plasma Technology 5 (APSPT-5). pp.58-61

Conference Abstract:

1. J.S. Chang, **O.L. Li**, K. Urashima, N. Kunimoto and T. Inaba. 2010. Proc. To Thermal Plasma Sysmposium. "Waste Cell Phone Thermal Plasma Recycling Techniques: Solid By-Products Anlaysis." (submitted Feb, 2010)
2. F. Jacquemier and **O.L. Li**. 2009. Student Conference on High Voltage Engineering and Applied Electrostatics (CAGE), Canada. "Gaseous By-Products Analysis from Pulsed-Arc Electrohydraulic Discharge Lake Water Treatment."
3. **O.L. Li**, S.N. Yantsis, P. Chow-Fraser, Y. Guo, J.S. Chang and S. Terui, K. Watanabe, M. Itoh, 2008. The 3rd International School of Advance Plasma Technology, Italy. "Potential Ballast Water Treatment by Pulsed Arc Electrohydraulic Discharge Reactor."
4. **O.L. Li**, S.N. Yantsis, P. Chow-Fraser, Y. Guo, J.S. Chang and S. Terui, K. Watanabe, M.Itoh, 2008. Student Conference on High Voltage Engineering and Applied Electrostatics (CAGE), in, Canada. "Potential Ballast Water Treatment by Pulsed Arc Electrohydraulic Discharge Reactor."
5. J.S. Chang, **O.L. Li**, T. Ikeda, K. Teii. 2008. European Electromagnetics (EUROEM), Switzerland. "Electromagnetic Pulse Generated by Pulsed Arc Electrohydraulic Discharge Water Treatment Reactors."
6. T. Ikeda, **H.O.L. Li**, K.Teii and J.S. Chang. 2007. Proc. To Asian-European International Conference on Plasma Surface Engineering (AEPSE). "Discharge Characteristics of Titanium Electrode Eccentric Pulsed Arc Electrohydraulic Discharge Reactor."

7. **O.L. Li**, J.S. Chang, Y. Guo. 2007. Student Conference on High Voltage Engineering and Applied Electrostatics (CAGE), Canada. "Pulsed Arc Electrohydraulic Discharge Characteristics (PAED) in Sludge-Water."
8. **O.L. Li**, J.S. Chang, S. Dickson, M. Emelko. 2007. Ontario Centres of Excellence, Canada. "Pulsed Arc Electrohydraulic Discharge for the Concurrent Treatment of Chemical and Microbial Compounds in Drinking Water."
9. **O.L. Li**, J.S. Chang, Y. Guo. 2006. Student Conference on High Voltage Engineering and Applied Electrostatics (CAGE), Canada. "Advanced Characterization of Stormwater Sediment."
10. O.L. Li, J.S. Chang, Y. Guo. 2005. Student Conference on High Voltage Engineering and Applied Electrostatics (CAGE), Canada. "Characterization of Stormwater Sludge for the Design of the Thermal Plasma Sludge Volume Reduction/Verification System."