

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

LUT School of Engineering Science

Master's Degree Program in Chemical & Process Engineering

*Adnan Munir*

**Oxidation of Aqueous Thiosulfate Solutions by Pulsed Corona Discharge**

Examiner: Professor Marjatta Louhi-Kultanen

Supervisor: M.Sc. (Tech) Alexander Sokolov

## **ABSTRACT**

Lappeenranta University of Technology

LUT School of Engineering Science

Master's Degree Program in Chemical & Process Engineering

Adnan Munir

### **Oxidation of Aqueous Thiosulfate Solutions by Pulsed Corona Discharge**

Master's thesis

2015

Examiners: Professor Marjatta Louhi-Kultanen

D.Sc. (Tech) Alexander Sokolov

**Keywords:** Pulsed Corona Discharge (PCD), Advanced Oxidation Process (AOP), sodium thiosulfate ( $S_2O_3$ ), cyanide, water treatment, electric discharge,  $\cdot OH$  radicals, ozone, energy efficiency, sulfates.

The aim of this Master's thesis focused on the oxidation of sodium thiosulfate using non thermal plasma technology as an advance oxidation process (AOP). By using this technology we can degrade certain toxic chemical compounds present in mining wastewaters as pollutants. Different concentrations of thiosulfate and pulse frequencies were used in the PCD experiments and the results in terms of various delivered energies ( $kWh/m^3$ ) and degradation kinetics were compared.

Pulsed corona discharge is an energy efficient process compared to other oxidation processes using for the treatment of waste water pollutants. Due to its simplicity and low energy costs make it attractive in the field of waste water treatment processes. This technology of wastewater treatment has been tested mainly on pilot scale level and in future the attempts are to be focus on PCD investigations on larger process scale. In this research work of oxidation of thiosulfate using pulsed corona discharge, the main aim of this research was to study degradation of a studied toxic and not environmental friendly chemical compound.

The focus of this research was to study the waste waters coming from the gold mines containing leachate compound thiosulfate. Literature review contained also gold leaching process when cyanide is used as the leachate. Another objective of this work was to compare PCD process with other processes based on their energy efficiencies.

In the experimental part two concentrations of sodium thiosulfate, 1000ppm and 400ppm, were used. Two pulse generator frequencies of 833 and 200 pulses per second (pps) were used. The chemical analyses of the samples taken during semi-batch PCD oxidation process were analyzed by ion chromatographic (IC). It is observed after the analyses that among different frequencies and concentrations, the most suitable ones for the process is 200pps and 1000ppm respectively because the pollutants present in the waste water has more time to react with the OH radicals which are the oxidants and the process is energy efficient compared to other frequencies.

## **ACKNOWLEDGEMENTS**

First of all, I am really thankful to Almighty Allah for establishing me to complete this Master's thesis and tasks of this research study. I owe my debt gratitude to Professor Marjatta Louhi-Kultanen in charge of chemical separation technology at Lappeenranta University of technology who gave me this opportunity to work on that through her support, advice and guidance to achieve this task.

I would like to express my sincere gratitude to Alexander Sokolov for his help not only being a supervisor but also as a colleague. I am really grateful for his support and instructions during the Master's thesis. I am also grateful to Mrs. Jaana Ruokonen for carrying out the chemical analyses and her contributions are highly appreciated.

I would also like to express my gratitude to my brothers Rehan Munir, Irfan Munir and Imran Munir for all their financial help and support in completing my master's studies.

Finally my gratitude also goes to my parents for their prayers, support and understanding, Throughout my life, they have always sacrificed to ensure that I had the best opportunity and they have constantly believed in me and encouraged me to do my tasks not only educational but also in other prospective of life too.

I dedicated to this thesis work to my late father Mr. Muhammad Munir Ahmed who is not any more in this world and I cannot put into words what their love and support has meant to me over the years.

ADNAN MUNIR

February, 2016 Lappeenranta, Finland

## Contents

1. Introduction.....	7
1.1 Background .....	7
1.2 Uses and Sources of Thiosulfate .....	8
1.3 Uses and Sources of Cyanide .....	8
1.4 Aims and Objectives .....	9
1.5 Structure of the research study .....	10
2. Cyanide as a Leachate of Gold .....	12
2.1 Introduction .....	12
2.2 Properties of Cyanide .....	14
2.2.1PHYSICAL PROPERTIES .....	14
2.2.2CHEMICAL PROPERTIES .....	15
2.3 Cyanide Treatment.....	15
2.3.1 Catalytic Oxidation .....	15
2.3.2 Chlorine Treatment and Chlorine Oxidation.....	16
2.3.3 Ozone Oxidation .....	16
2.3.4 INCO or Sulphur Dioxide (SO <sub>2</sub> )/Air process .....	17
2.3.5 Hydrogen Peroxide.....	17
3. Thiosulfate .....	18
3.1 Introduction .....	18
3.2 Chemistry of Thiosulfate.....	20
3.3 Uses of Thiosulfate .....	20
4. Advanced Oxidation Process Technology .....	21
4.1 Classification of Advanced Oxidation Processes.....	22
4.1.1 Oxidants .....	23
4.1.2 Advanced Oxidation Process Methods .....	26
5. EXPERIMENTAL PART .....	32
5.1 PCD Reactor.....	32
5.2 Pulse Generator .....	33
5.3 Water Circulation System .....	34
5.4 Solution Preparation.....	35
5.5 Experiment procedure .....	35

5.5.1 Analytical method .....	36
6. RESULTS AND DISCUSSION.....	36
7. Conclusion.....	42
Bibliography .....	44
Appendix.....	48

Figure 1. Use of cyanide in different process (Oraby, 2009) .....	9
<b>Figure 2. Waste water treatment in gold mine.....</b>	<b>10</b>
Figure 3. Structure of the research study. ....	12
Figure 4. Classification of cyanide on the basis of waste water content (Anon., 2003).....	14
Figure 5. Chemical structure of the thiosulfate ion. ( Stone, 1962) .....	20
Figure 6. Uses of thiosulfate in different industries ( Bean, 1996) .....	21
Figure 7. Classification of Advanced Oxidation Processes (Intec, 2015) .....	22
Figure 8. Electric discharge water treatment (Jahivolt, n.d.).....	30
Figure 9. Systematic diagram of pulsed discharge corona (sokolov, 2015).....	31
Figure 10. Image of pulsed corona discharge ( Jahivolt, n.d.) .....	32
Figure 11. Pulse Generator of 100W .....	33
Figure 12. Water Circulation System .....	34
Figure 13. Relation of pH and time. ....	37
Figure 14. Concentration of thiosulfate over time.....	38
Figure 15 . Logarithmic concentration ratio over time (first-order reaction). ....	39
Figure 16. 1/c over time (second-order reaction). ....	39
Figure 17. Concentration ratio versus delivered energy kWh/m <sup>3</sup> .....	40
Figure 18. Concentration increase of transformation product sulfate over PCD oxidation treatment time. ....	40

# 1. Introduction

## 1.1 Background

The gold mining industry has been using cyanidation process in its production processes since 1887. Thus, the environmental and public concerns on cyanide usage have been actual during last 130 years. Cyanide has been used for decades and it is still widely used chemical that is very essential part of the modern world and especially for the mining and recovery of gold. A lot of attentions has to be paid regarding the use of cyanide in the mining process, since it is very toxic compound and the problems arisen due to the lack of understanding of toxicity and handling of this toxic compound and one of the major problem with this compound is the transportation because most of the people were not aware of its toxicity that how dangerous it is for the health and environment. (Karen Hagelstein 1999.)

This research work focuses on the new oxidation method based on non-thermal plasma technology known as Advance Oxidation Process which can be used to degrade the toxic compounds known as Pulsed Corona discharge to remove or degrade the cyanide (CN) and thiosulfate ( $S_2O_3^{2-}$ ) in the gold mining industry. Thiosulfate is a compound which can be used to replace of cyanide since cyanide is toxic and it has some public and environmental concerns. Actually the thiosulfate is less toxic and cheaper than cyanide and its handling is easier compared to cyanide and it can stabilize gold in the aqueous solution. (Arima1 and Yen1 2009)

Thiosulfate oxidation can be considered as a non-poisonous methodology because this is the alternate of cyanide in the gold mine industry used as a lixiviate, it has less toxicity than cyanide and its handling is very easy compared to cyanide as well. It has its own advantages and disadvantages which have been discussed in this work. The theme of this work is the destruction or removal of thiosulfate using the Advanced Oxidation Process based on Pulsed Corona Discharge method.

## **1.2 Uses and Sources of Thiosulfate**

## **1.3 Uses and Sources of Cyanide**

In the literature part of the present work cyanide was one of the studied model pollutants. Many attempts have been made to find the replacement of cyanide. This compound is still the choice in the precious metal industry as a lixiviate due to many factors like effectiveness, low cost, availability and its ability to use under the minimal controlled conditions. (Mudde et al. 2001).

The most widely type of cyanide is sodium cyanide (NaCN) for precious metal industry. Calcium cyanide and potassium cyanide are also used.

More than 90% of the gold is produced by cyanide because of its availability and effectiveness according to Mudder (2001). Hydrogen cyanide (HCN) is produced about 1.4 million ton annually out of which 13% of the amount is converted into sodium cyanide (NaCN) and it is used in the extraction of gold and silver. Remaining 87% of the hydrogen cyanide (HCN) is consumed in the production of different products, such as computer electronics, adhesives, dyes, nylons, nitrides, paints and cosmetics. According to the figure 1. 13% Cyanide is used in the mining industry while the rest of cyanide is used in other industries.

Cyanide is also naturally occurring in bacteria, algae, fungi plants and in some insects too.

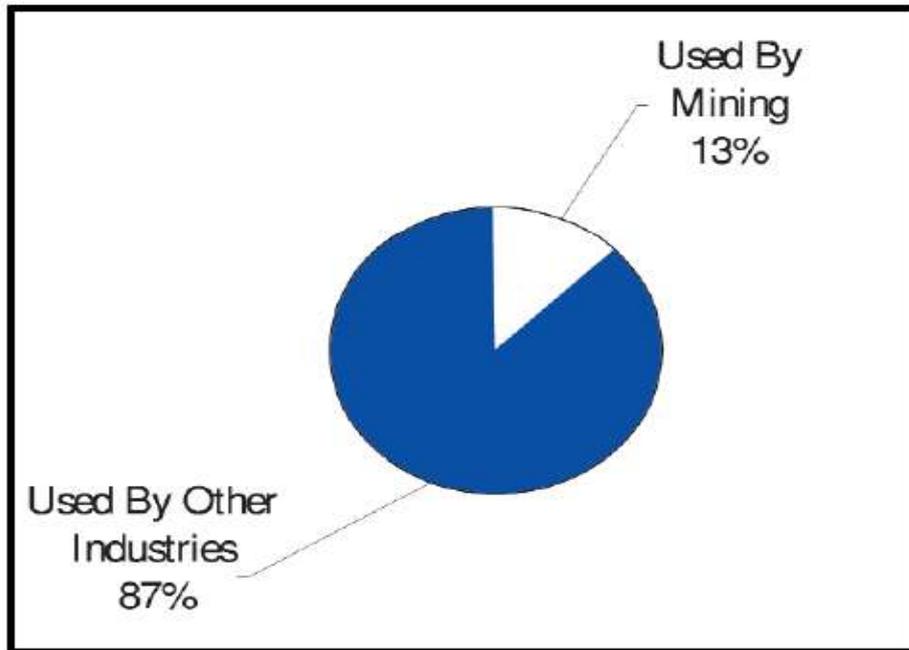


Figure 1. Use of cyanide in different process (Oraby, 2009)

#### 1.4 Aims and Objectives

The main aims and objectives of the present work are as follows:

- Oxidation of thiosulfate using the Advance oxidation process known as Pulsed Corona Discharge.
- This technology allows the degradation of the toxic chemical compounds present in mining wastewater as pollutants.
- Using different concentration of these compounds and get the result in comparison of energy (kWh) used during the process and the amount of chemical used.
- Pulsed Corona Discharge is an energy efficient process compared to other oxidation processes for the treatment of waste waters.

In this research work the main aim is to investigate oxidation of waters containing gold leachate by Pulsed Corona Discharge. The focus of this research is to purify the water coming from the gold mines and the waste waters contain thiosulfate. Another objective of this work is to compare PCD process with other processes based on their energy efficiencies. Furthermore, the subject is to determine what is the energy required to decompose the compound to reach the certain reduction level.

If the aims will be achieved and objectives of this research will be successful during the experimental part, the aim is to provide appropriate suggestions and recommendations based on the obtained findings for the studied application. Also if the studies will be successful then a deeper understanding will be gained on the oxidation of thiosulfate by Pulsed Corona Discharge. PCD is a new waste water treatment method and it is not yet employed widely in industrial applications. However, the pilot scale studies give the bases for the development of larger scales processes. Moreover, there is a great chance to get new data for knowledge, information and knowhow on PCD oxidation of the studied application.

### 1.5 Structure of the research study

The present work comprises of three main tasks. The first task of this research work is literature part of the topic. Literature part starts with the introduction part containing the background, aims and objectives and structure of the research study were briefly discussed.

In figure 2. Waste water treatment process for a gold mine is shown, first the leaching gold takes place with thiosulfate which acts as a lixiviate then the waste water from the gold mine contained thiosulfate as a pollutant which causes some environmental concerns. Treatment of waste waters with pulse corona discharge takes place afterwards which removal of thiosulfate is done by oxidation to sulfate. Sulfate can then easily be disposed to soil and it's not harmful for the marine life as well.



Figure 2. Waste water treatment in gold mine.

The motivation of the present work is to decompose the pollutants from the water coming from the mining and to make the water pure from these toxic compounds because these chemical compounds are toxic and harmful for environment, human life and also for the aquatic life. By using Advanced Oxidation Processes it is easy to remove these pollutants and this process is energy efficient and cost effective also. In the experimental part thiosulfate as a leaching chemical of gold from its ore is used.

Different oxidations methods used in the gold mining are also discussed in the literature part. The study of this topic is very important because many chemical compounds discharge during the gold process. Some of them are very toxic as well and not easily removed in wastewater treatment. Therefore, there is a need to develop energy efficient and environmental friendly method for the decomposition and removal of these toxic compounds.

Advanced oxidation process has recently emerged as an important class of technology for accelerating the oxidation and destruction of wide range of pollutants and toxic compounds. Advance oxidation process when applied gives a good opportunity to reduce the contaminant concentration from several hundred of ppm to less than 5ppb. For this reason it is known as the process for 21<sup>st</sup> century.

The experimental part of the research work describes the procedure used in the research work in order to achieve the desired goals. The obtained experimental results are discussed in the experimental part which includes also the suggestions and remarks observed during the experimental work and procedures and conclusions after the completion of the results.

Figure 3 shows the aims and objectives and structure of the research study.

## Theoretical part (literature)

- oxidation of cyanide and thiosulfate by Pulsed corona discharge
- decompose or degrade toxic compounds by using corona discharge
- energy efficient process no harmful and sludge products will form after treatment.
- cyanide oxidation
- chemistry of thiosulfates
- Advance oxidation process

## Experimental part

- experimental setup and procedure
- results and discussion
- conclusion

Figure 3. Structure of the research study.

## 2. Cyanide as a Leachate of Gold

### 2.1 Introduction

Cyanide is a compound made up of carbon and nitrogen and it is referred as  $-C-N$ . It can be inorganic or organic compound. Inorganic compounds are simple like (HCN) and (KCN) or they may be complexes, such as  $CU [CN]^{2-}$  (Rajesh Roshan Dasha, 2008). It is also occurring in nature and it is produced by the plants and the organisms. Cyanide reacts with the hydrogen to form hydrogen cyanide, and process of metal dissolution is called leaching. The total content of cyanide in process waste waters consists of five different forms of cyanide (Bernd G, 2005).

Cyanide is a toxic compound found in many industrial effluents produced by metallurgical operations. Strong affinity with the metals makes the cyanide as a favourable agent for treatment and as a lixiviate for leaching of metals, especially gold.

The technologies for the remediation of cyanide are environmentally sound but they require safety to prevent any spill accident contaminating from soil and with the surface or ground waters. (Jordan, 104-107)

Cyanide reacts with the hydrogen to form hydrogen cyanide



Furthermore hydrogen cyanide reacts with the sodium hydroxide to form sodium cyanide,



The process of metal dissolution is called leaching. The total content of cyanide in process waste water consists of five different forms of cyanide (Bernd G, 2005). It is explained by the following diagram.

Cyanide can be classified into four types, as shown in figure 4:

1. Total cyanide (these are the complexes of Iron (II), Iron (III) and cobalt).
2. WAD term as Weak Acid Dissociable (complexes with the metals, like cadmium, copper nickel and zinc)
3. SAD term as Strong Acid Dissociable (complex with the metals Cobalt, Gold, Iron and Silver)
4. Free Cyanide CN and H
5. CN (NaCN, KCN).

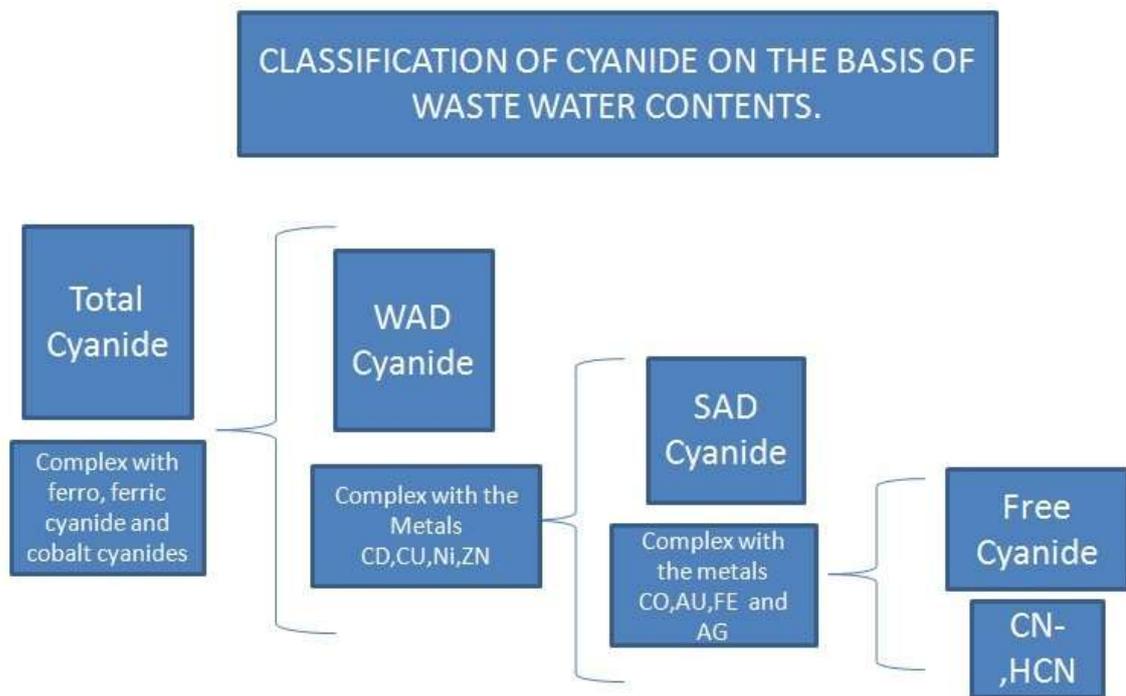


Figure 4. Classification of cyanide on the basis of waste water content (Anon., 2003)

## 2.2 Properties of Cyanide

- a- compound detail: Name: cyanide (inorganic) compounds
- b- CASR No. 57-12-5
- c- Molecular Formula: CN-
- d- Other names: cyanide, iso-cyanide, cyanide ion, cyanide anion. (Cluness, 1993)

### 2.2.1 PHYSICAL PROPERTIES

Hydrogen cyanide (HCN) exists in colourless or pale blue gas or liquid with the range of 1-5 ppm detected with bitter almond odour.

Sodium cyanide, calcium cyanide and potassium cyanide are examples of free cyanides salts available as white solid salts. These white solids dissolved in water and the smell is like a bitter almond. (Cluness, 1993)

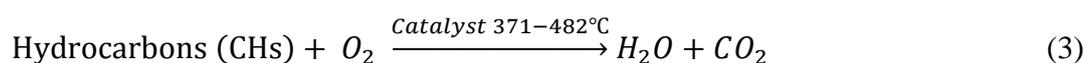
## 2.2.2 CHEMICAL PROPERTIES

Cyanide is a special chemical with the combination of carbon and nitrogen, when cyanide combines with the chemicals from the metals group it forms salts which are known as simple salts like CaCN, NaCN and KCN and it liberates HCN (hydrogen cyanide) gas soluble in water and it also smells like bitter almond in acidic water. (Anon., 1995)

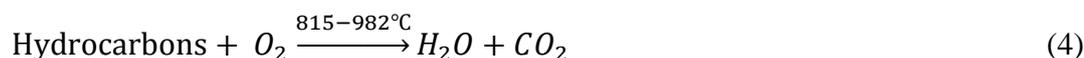
## 2.3 Cyanide Treatment

### 2.3.1 Catalytic Oxidation

A catalyst is used in catalytic oxidation processes. In this oxidation the hydrocarbons and oxygen reacts in the presence of catalyst at specific temperature normally at high temperatures to yield carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O). (Anon., 1995).



In the absence of catalyst the required temperature is high and this type of oxidation is known as thermal oxidation, as the below equation shows the reaction without catalyst.



### Drawbacks of the Catalytic Oxidation

There are many drawbacks of the catalytic oxidation including decrease in the performance of the system and the deactivation of the process and system too. These problems are not accumulated gradually and they took long period of time in a system or process called aging. Contamination on the surface of catalysts is also another problem it affects the performance of the catalyst and different measures have been taken to restore the performance of the catalyst.

Catalysts are attacked by some external substances this results the alternation of the composition of the catalyst and they affect their performance as well. Now the scientists have already made new generation high technology catalysts to resist against the poisoning. (Anon., 1995)

### 2.3.2 Chlorine Treatment and Chlorine Oxidation

Using of chlorine takes place in an alkaline atmosphere; in this oxidation method chlorine is used for degrading the cyanide. Chlorination is one of the most commonly and effective processes used to decompose cyanide. It is operating in either batch or continuous mode of processing. (Wang & Tse, 2009)

It is an effective process but it is not that much effective for the slurries. It was the most effective process for the destruction of cyanide when the cyanidation process was used. (Jordan, 1995). This oxidation process is carried out in two steps: in the first step the cyanide is converted into cyanogen chloride (CNCl) and in the second step cyanogen chloride is hydrolysed to give cyanate



In the second step cyanogen chloride is hydrolysed to give cyanate which is less toxic than cyanide.



In the presence of excess of chlorine the cyanate is further hydrolysed to yield ammonia in the presence of catalyst. (Pargaa, et al., 2002)

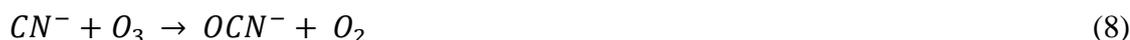


The reaction is carried out at the greater pH value about 10.0 or greater in order to hydrolyse cyanogen chloride completely because this gas is very toxic and in this reaction copper is not used as a catalyst like H<sub>2</sub>O<sub>2</sub> and Inco processes. (Baghalha, 2006, p. 1)

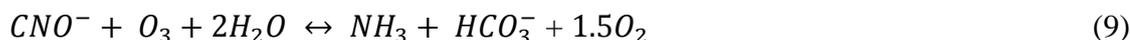
Normally the solutions made from this process are permitted to discharge. (Botz, 1999)

### 2.3.3 Ozone Oxidation

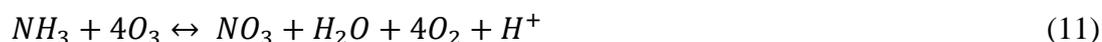
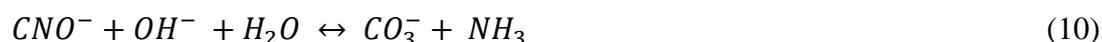
Ozonation is the most effective process in order to decompose the strong complexes, such as iron, nickel and cobalt cyanide. Ozone is a powerful oxidizing agent and it may offer none or a little by transformation products upon treatment of wastewater containing cyanide. The concentration of ozone depends upon the ozone generator parameters like air flow generator and power etc. The reduction efficiency of ozone is high (+2.07) in acidic solutions.



If ozone is used in excess, cyanate is oxidized to nitrogen and carbonates or bi-carbonates depending on the pH.



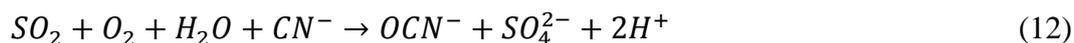
Cyanate is hydrolysed under the basic conditions to give ammonia, which is oxidized by ozone mixture.



The oxidation of cyanide depends on the addition of ozone. The oxidation of cyanate by ozone is slow compared to cyanide so that cyanate accumulates and cyanide is almost completely oxidized. (Pargaa, et al., 2002).

### 2.3.4 INCO or Sulphur Dioxide (SO<sub>2</sub>)/Air process

The INCO process was developed by Inco in 1980. In this process sulphur dioxide (SO<sub>2</sub>) and air are utilized in the presence of soluble catalyst to oxidize cyanide to a less toxic compound cyanate.

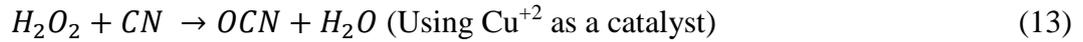


This process is appropriate for treatment of tailing slurries but this is also used for the process treatment solutions. (Akcil, 2003)

If cyanide level is very high, then the costs of reagents and the electrical power will also be high. During this process cyanide cannot not fully recovered and significant amount of sulfates may form during the solution treatment. (Smith, 1991)

### 2.3.5 Hydrogen Peroxide

Hydrogen peroxide is commonly used oxidant and also used for oxidation of cyanide. The chemical formula is H<sub>2</sub>O<sub>2</sub>. The process chemistry of hydrogen peroxide is very similar to that of Inco process. The only difference is that in this process H<sub>2</sub>O<sub>2</sub> is used instead of SO<sub>2</sub> and air. Soluble copper (Cu) is used as a catalyst and the resultant product will be cyanate.



The advantage of this process is this that oxidation method can be used mainly for treatment of solutions, but not slurries. The treatment of slurries with would require high H<sub>2</sub>O<sub>2</sub> consumption. This process is typically suitable to achieve cyanide effluent level which is suitable for discharge. It is a simpler process than any other process and allows operating at wide range of pH (Akcil, 2003)

Although all the processes discussed above are widely used in the industry, they have some drawbacks, such as low energy efficiency, high reagent consumptions, generation of problematic by-products and needs to develop these methods more. The aim of this literature review was to collect the most commonly technologies used to remove or degrade cyanide. Non-thermal plasma technology based on Pulsed Discharge Corona is a new oxidation process and it has potential to be used also for treatment of waste waters containing cyanide. The method is discussed in section 5.

### 3. Thiosulfate

#### 3.1 Introduction

The chemical formula of thiosulfate ion is S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. It is less toxic compound than cyanide and maximum amount of thiosulfate for humans is 12g per day. Furthermore, it has no side effects on health. (Lewis, 1997)

It is generally recognized as safe and it is used as a fertilizer. (Carnahan, 1992). In gold leaching processes thiosulfate is used as a reagent to replace cyanide because of its handling, toxicity and water contamination. Therefore, gold leaching with thiosulfate is more attractive alternative process than cyanidation. (Muir, 2001).

Thiosulfate is considered to be less toxic than cyanide and it is more environment friendly and it has an ability to leach gold faster than cyanide. The only disadvantage of leaching with thiosulfate is high reagent consumption during the process. Oxidation of metal gold Au to the aurous Au<sup>+</sup> ion in ammonical thiosulfate solution in the presence of Cu (II) can be expressed by the following equation. (Aylmore, 2004)

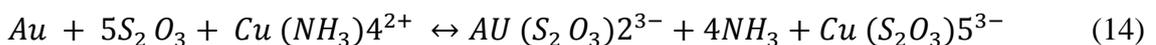


Table 1 shows some toxicity data for selected lixiviates depending on their dosage, concentration and their contamination with the water.

**Table 1 Toxicity data for selected Lixiviates (Gos & Rubo, 2000).**

Reagent	emission	Toxicity Handling		Exotoxicity /transport spillages	
		LD50/LC50	TLV	Water contaminated	Lethal conc.(LC50/EC50
Thiourea	NH <sub>3</sub> ,H <sub>2</sub> S	LD50 1750 mg/kg	none	2	LC50 100mg/L
Thiosulfate (Sodium)	H <sub>2</sub> S	LD50 4000 mg/kg		0	LC50 1000mg/L
Thiosulfate (Ammonium)	NH <sub>3</sub> , H <sub>2</sub> S	LD50 2890 mg/kg		1	Consider Ammonia or Ammonium
Thiocyanate (Sodium)		764 mg/kg		1	EC50 100mg/L
Thiocyanate (Ammonium)		LD50 15g		1	consider Ammonia or Ammonium 280-300ppm/1h killed sunfish
Ammonia		LD50 350 mg/kg	14mg/m <sup>3</sup>	2	LC50 0.53mg/L
Chlorine		LD50 293ppm/1h	1.45mg/m <sup>3</sup>	2	LC50 0.05mg/L
bromine		LD50 1750 mg/kg	0.6mg/m <sup>4</sup>	3	LC50 10mg/L
Iodine		LD50 1750 mg/kg	1.1mg/m <sup>5</sup>	1	LC50 0.083mg/L
cyanide (sodium)		LD50 6.4 mg/kg	5mg/m <sup>6</sup>	3	LC50 0.16mg/L
cyanide (hydrogen)		LD50 3.7 mg/kg	5mg/m <sup>7</sup>	3	LC50 2.29mg/L

TLV=Threshold limit value LD50=Lethal dosage LC50=Lethal concentration EC50=Exotoxicity concentration	WGK= It is the indicator used for Water contamination IF, WGK=0 (No water contamination) WGK=1 (Slightly water contamination) WGK=2(Water is contaminated) WGK=3(strong water contaminated)
--	---

Table 1 shows toxicity data based on a German standard used for the testing of water contamination normally applied for the treatment of lixiviates. Sodium and ammonium thiosulfate are two main commercial sources of thiosulfates and both are main and common thiosulfate salts which are used in research and leaching of gold with thiosulfate. Thiosulfate is considered to be non-hazardous and biodegradable by work place and it is known to be the generally recognized as safe. (Haddad, 2003).

### 3.2 Chemistry of Thiosulfate

Thiosulfate and its salts have been studied long time, as they have been used in the different industries for more than two centuries. (Schmidt, 1962).

The chemical formula of the thiosulfate is  $S_2O_3$  and the thiosulfate anion is denoted as follows:

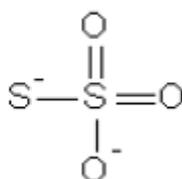
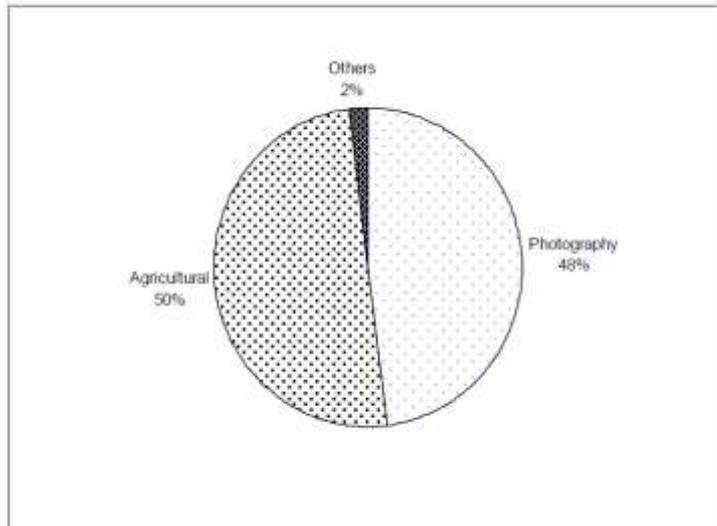


Figure 5. Chemical structure of the thiosulfate ion. (Stone, 1962)

It is tetrahedral in shape and it is derived by replacing one of the oxygen atom by a sulphur atom in a sulfate anion. The distance between the S-S represents the single bond and it shows the sulphur bears a significant negative charge and the S-O interactions have been more double bond character and it is concluded that it is natural sulphur donor.

### 3.3 Uses of Thiosulfate

The great proportion of ammonium thiosulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_3$ ) is used in the agriculture sector as a fertilizer, since the contents present in it both sulphur and ammonium are important nutrients for plants. Figure 6 below shows the amount of thiosulfate by percentage of usage in different industries, agriculture industry uses about 50% of overall amount. (Bean, 1996) Another alternative application of thiosulfate is to use it for dissolving of gold instead of cyanide in extraction of gold. It is also used in a flue gas desulfurization and as a chemical reagent. Many of the lixiviates are toxic and thiosulfate can replace these lixiviates.



**Figure 6. Uses of thiosulfate in different industries ( (Bean, 1996)**

#### **4. Advanced Oxidation Process Technology**

During the last few years new technologies have been developed for the purification of waters. With the aid of development of the Advanced Oxidation Process technology (Gogate, 2004), these technologies have been launched more for waste water treatment of industrial wastewaters and waste waters from other sources. Figure 7 explains the Advance oxidation processes and their classifications based on different techniques like ozonation, Fenton, peroxide photo catalysis, heterogeneous photo catalysis and electrochemically mediated which are known as (EOPS).

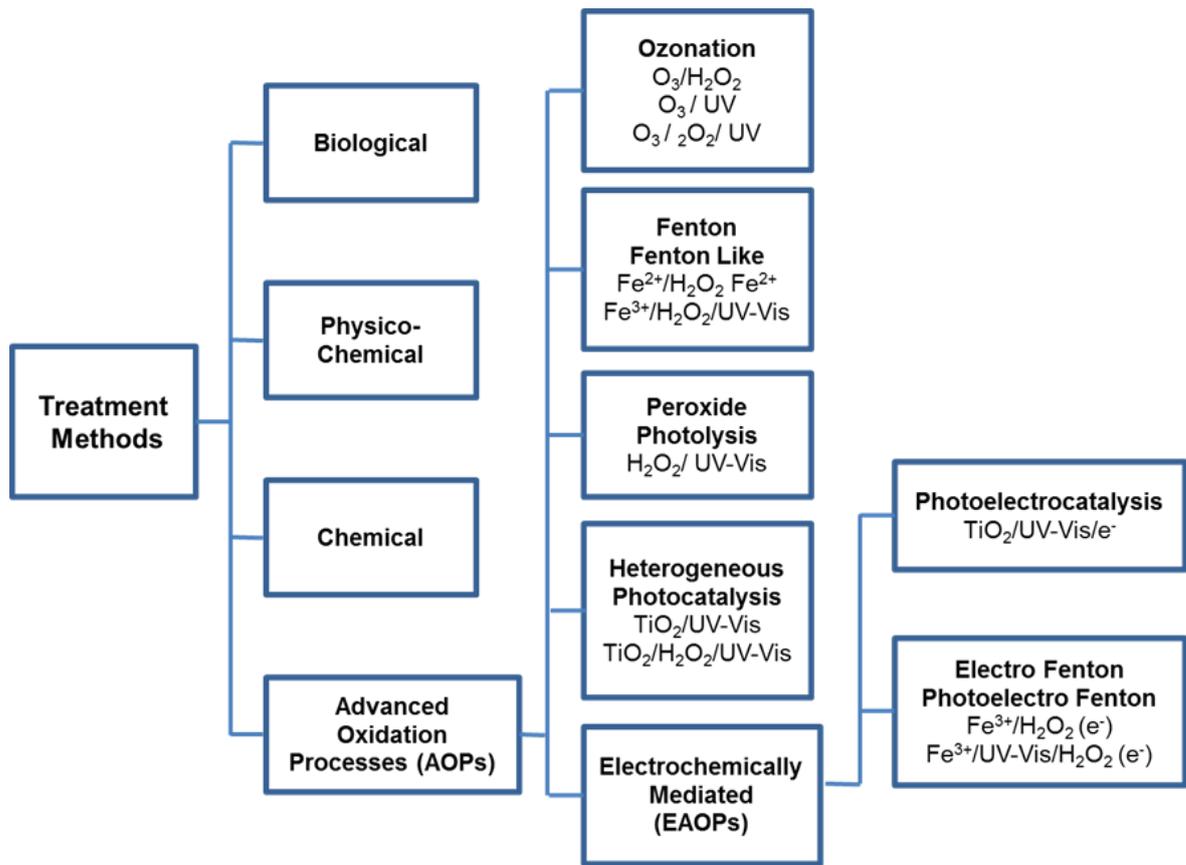


Figure 7. Classification of Advanced Oxidation Processes (Intec, 2015)

#### 4.1 Classification of Advanced Oxidation Processes

Advanced oxidation processes (AOP) have received the great attention as a new technology for the water treatment and the concept of this technology is established by Glaze et al (1987). Advanced Oxidation Process is defined as the oxidation process which generates OH radicals in sufficient quantity in order to produce effective treatment of water. Most of the systems are lie under the broad definition of Advanced Oxidation Process. Most of them consists of the combination of strong oxidants, like ozone ( $O_3$ ), hydrogen peroxide ( $H_2O_2$ ), catalytic, photo catalytic and irradiation, e.g. ultra violet (UV), ultra sound (US) and electron beam. (Gogate, 2004)

All the Advanced Oxidation Processes are characterized by their production of highly reactive and non-selectivity of OH radicals and theses radicals are the strongest in the aqueous medium. (Stahelin, 1995).

Hydroxyl radicals can oxidize nearly all organic compounds to water, carbon dioxide and mineral salts, which is known as the mineralization process. (Chen, 2000). Technologies that can be classified as AOP fall under two categories, one uses ultra violet light as a source with other chemicals like UV/H<sub>2</sub>O<sub>2</sub>: UV/O<sub>3</sub>: UV/TiO<sub>2</sub>: UV/Fenton while the other category is when UV source is not used, the process is known as the Dark oxidative process e.g. ozonation, Fenton Reagent and ultra sound. (Gilmour, 2012).

Many chemicals and toxic compounds are discharged in waste waters containing cyanide and many toxic compounds in gold mining industry. Therefore, these compounds are needed to be removed in waste water treatment and there is a need to develop energy efficient methods for the removal or degradation of these toxic compounds. Advanced Oxidation Process is recently emerged technology which provides higher oxidation rates and destructs a wide range of pollutants in water and air.

In a certain applications AOP can lead to reduction of the concentrations of contaminated solutions from hundreds of ppm to less than 5ppb. Therefore, it is known as the process of 21<sup>st</sup> Century. (GOI 2005).

The main advantages of these methods are small equipment sizes and high rates of pollutants oxidation flexibility concerning water quality. The only drawback of these processes is highly treatment cost and special safety requirement because of use of very reactive chemicals like (ozone and H<sub>2</sub>O<sub>2</sub>) and highly energy sources like UV lamps, electron beams and radioactive sources. Some of the small pilot plants are still working to make these processes more developed some of the process technologies already registered like ULTROX, WEDECO, UVOX, ECOCLEAR and BIOQUINT (Kochany, 1992)

#### **4.1.1 Oxidants**

There are many oxidants that tend to counter with other chemical compounds by eliminating one or more electrons. Therefore, the transformations of the required compounds may lead to new chemicals and it may reduce its toxicity or increase its biodegradability.

There are more available oxidants nowadays, but quite a few of them are widely used in the field of environmental technology and Advanced Oxidation Processes. Some of the oxidants and their oxidation potential is shown in table 2. In waste water treatment systems these values shows the ability of potential of waste water to permit the rate of specific Oxi-

reduction reactions. The high values of oxidants shows the high oxidizing capabilities of the oxidants.

Table 2: Relative oxidation power of some Oxidation species ( (Ullmanns, 1991)

Oxidation species	Oxidation potential, eV
Fluorine	3.06
Hypochlorous Acid	1.49
Chlorine	1.36
Hydrogen peroxide	1.77
Ozone	2.07
Perhydroxyl radical	1.70
Hydroxyl radical	2.80
Nascent oxygen	2.42

Following common reactions show the removal of hydrogen atom to initiate a radical chain oxidation.



Nitrogen in organic compound is usually oxidized to nitrate or to free N<sub>2</sub>. Sulphur is oxidized to sulfate and the cyanide is oxidized to cyanate, which can be further oxidized to CO<sub>2</sub> and NO<sub>3</sub> or perhaps N<sub>2</sub>.

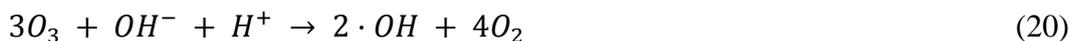
The rule of thumb suggests that contaminant's decomposition rate is proportional to rate constant of contaminant comprises of OH radical. Oxidation of inorganic contaminants including cyanide, sulphide and nitrite can also be done by AOPs.

The present study focuses on the hydroxyl radical and ozone oxidant oxidants that will be produced by an electric discharge at atmospheric pressure.

## Ozone

Ozone was found and named by Christian Friedrich Schönbein in 1839 for its strong odour (Greek word ózein). It is one of the strongest oxidant and very responsive gas inferable from its electronic arrangement as a half and half of our sub-atomic reverberation structures. As an atom, it can respond specifically with the objective compound. Inorganic constituents like arsenic, manganese and iron are capable of oxidizing into insoluble oxides which are the main target compounds in this study to remove inorganic constituents. (von Gunten, 2003)

Following reaction is the grouping of the sequence reactions from beginning to an end, displaying that in order to yield two ·OH radicals it is essential to introduce three molecules of ozone.



The reaction shows that more molecules of ozone are needed to produce ·OH radicals. Above The decomposition of ozone is faster at pH ranges from 5-7 and dominance of OH radicals become more prominent. The process of decomposition of ozone to form OH radicals can be enhanced by treating with active carbon, UV light, metallic ions of various valence catalysts and H<sub>2</sub>O<sub>2</sub>, (Böhme, 1999)

## Hydroxyl radicals

The production of hydroxyl radical which is neutral type of hydroxide ion can be achieved from dissociation of H<sub>2</sub>O<sub>2</sub>, ozone, or by reaction of atomic oxygen with water. Depending on the intermediates, numerous ways have been studied for producing hydroxyl radicals and they are normally collected as ozone based UV-based, photo catalysis, and Fenton reactions (von Gunten, 2003).

But irrespective of oxidizing abilities of these mentioned reagents, these reagents show complex behavior in wastewater and primarily they are affected by properties of solution which are pH, temperature, conductivity and concentration.

### 4.1.2 Advanced Oxidation Process Methods

There are several processes available for generating OH radicals. These processes are categorized as non-photochemical and photochemical methods. Some processes are discussed below:

- 1- Ozonation at elevated pH (8.5)
- 2- Ozonation + hydrogen per oxide ( $O_3/H_2O_2$ )
- 3- Fenton system ( $H_2O_2/Fe$ )
- 4- Photo- Fenton/ Fenton-like systems
- 5- Photo catalytic oxidation (UV/ $TiO_2$ )
- 6-  $O_3/UV$
- 7-  $O_3/H_2O_2/UV$  (Kogelschatz, 1988)

#### Ozonation

Ozone is one of the most important oxidants in the waste water treatment process and it is also one of the most influential oxidants having oxidation potential 2.07V. Under the acidic conditions the ozone undergoes the selective electrophilic attack and will result into the complex agent with the higher electronic density. While on the other hand in alkaline conditions ozone is catalysed by OH under basic conditions to intermediate compounds such as superoxide OH radicals and highly reactive radicals of  $HO_2$ .

Following reactions are taking place in the ozonation process. (Sillanpää, 2011)



Application of ozone offers many advantages in the waste water treatment. Its life time in the solution is short, less than one minute. Ozonation consumes a lot of energy for reducing the chemical pollutants present in the waste water.

The performance of the ozone is based on the following operating parameters (Qu, 2009).

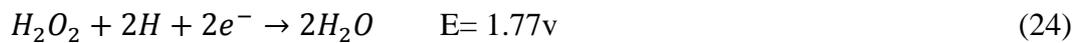
- 1- Operational pH

- 2- Ozone partial pressure
- 3- Interfacial area and Contact time
- 4- Very low reaction rate. (Qu, 2009)

### Hydrogen peroxide

Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is another strong oxidant and it is known as more environment friendly oxidant which can oxidise the organic pollutants efficiently and economically as well. It is a strong oxidant both in acidic and basic media with a standard potential of 1.77 v and 0.88v (Busca G, 2008).

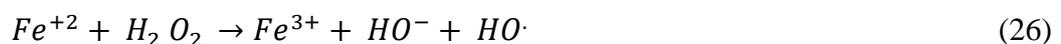
It has very low decomposition rate in the drinking water treatment but it can oxidize many organic contaminants directly in the waste water treatment. It has mild operation pressure and temperature that ensure its longer disinfection. Because it's low decomposition rate it can be used as dechlorinating agent and therefore it is ideal oxidant and disinfectant for drinking water.



However, in wastewater the reactivity of peroxide to remove organic compounds is generally low and mainly incomplete due to the reaction kinetics especially in the acidic media.

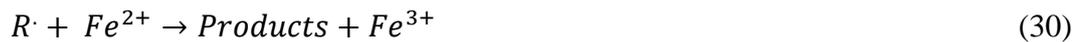
### Fenton

The Fenton's process was discovered in 1894 and efficiency of water treatment was enhanced significantly by Fenton process. In Fenton's process ferrous ion ( $Fe^{+2}$ ) promotes strongly the hydrogen peroxide oxidation of tartaric acid. But complexity of Fenton's process is high in terms of reaction mechanism and it consists of tens of equations for its explanation. It can be clarified by the following steps. Hydroxyl radicals are generated by mixture of H<sub>2</sub>O<sub>2</sub> and ferrous ion in acidic solution for further reaction with the organic pollutants present in the solution. (Herney- Ramirezj, 2010)



The main reaction mechanism of Fenton's reaction is that the most outer electron from the sphere transfer from  $Fe^{+2}$  to  $H_2 O_2$  and it will generate hydroxyl radicals and anions.

Hydroxyl radicals are one of the most powerful species and its oxidation potential is very high. The range of its oxidation potential varies from +2.8 and +2.0V at pH 0 and 14, respectively. Since the OH radicals have high reactivity that ensures it will attack a wide range of pollutants and organic compounds. Fenton's reactions yield the CO<sub>2</sub> and from oxygenated species such as NO<sub>x</sub>, SO<sub>x</sub> and PO<sub>x</sub> generates heteroatoms. This means that the carbon and heteroatoms of the organic substrates are converted into inorganic species. Following equations illustrates the chemistry of Fenton's reactions. (Gracia, 2010)



Following parameters will assist in highlighting performance of Fenton's oxidation in wastewater treatment:

- 1- Operational pH
- 2- Quantity of ferrous ion
- 3- Concentration of H<sub>2</sub>O<sub>2</sub>
- 4- Initial concentration of the pollutant
- 5- Functional temperature.

### **Electric discharges**

Electric discharge portrays the entrance of an electric charge in a material which non-conductive to electricity. Gas could be dielectric medium, fluid, or solid. Electric release is frequently gone with the arrangement of plasma which is an electrically unbiased ionized gas. Maybe the most widely recognized events of plasma in nature are lightning and auroras.

Short duration pulses at atmospheric pressures can generate non-thermal plasma, while the surrounding gas is at room temperature to avoid electrons heating up. The plasma is caused by ionization of the medium gases, however radicals are also produced in the process due to which this process is continuously being improved. (Busca G, 2008)

The non-thermal plasma technology operating usually at non-equilibrium conditions is based on the small duration pulsed power to a gaseous phase at the atmospheric pressure. The phenomena taking place in plasma technology are based on the electron generation and its influence on the ionization, excitation of molecules and the production of the radicals. Radical generation is the main topic in the present work. (Busca G, 2008)

One of the most important applications of this technology is that the plasma is generated at an atmospheric pressure and no low pressure chambers are required, that is why this technology is developing in the field of waste water treatment.

The electric discharges produced by high voltage have been confirmed to degrade the pollutants from the wastewater. In non-thermal plasma induced by high voltage in water for producing ozone and  $\cdot\text{OH}$  radicals from water and oxygen temperature is not playing a vital role. This means that it is a temperature independent process so the energy inputs will be small.

Oxidation reaction produces the following strong oxidants.



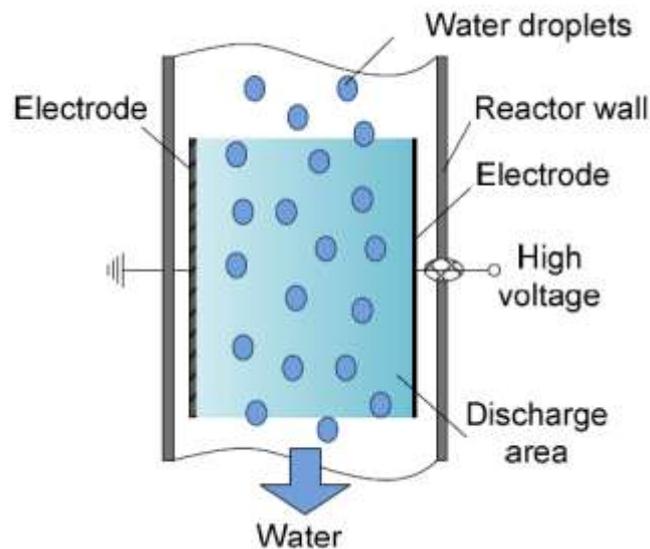
Ozone is dissolved in water and it can decompose and converted to form  $\cdot\text{OH}$  radicals to react straight with the pollutants present in the wastewater.

Non-thermal plasma technology is a feasible innovation for vast scale modern application. By delivering exceedingly responsive species, the procedure can degrade contaminants non-specifically, without requiring high temperatures. The most known wastewater treatment systems permitting processes at NTP circumstances are dielectric barrier release (DBD) and pulsed corona discharge (PCD). (Busca G, 2008)

### **Pulsed discharge corona**

Pulsed corona electric discharge is a method for water/wastewater treatment, in which the discharge of environmental friendly oxidants takes place (atomic oxygen, hydroxyl radical, ozone etc.). It can be classified as an Advanced Oxidation Process (AOP) technology because of the energy efficiency, the existing methods are very expensive and the by-products made are not desirable. (Mohammad Kebriaei, 2015)

The discharge takes place in air or oxygen atmosphere which is at atmospheric pressure and on ambient conditions. In the NTP (non-thermal plasma technology) technology operation takes place close to ambient temperature. In the reactor water droplets or film type water flows through the discharge zone consisting of multiple streamers, which propagate the water stream in the inter electrode volume as shown in figure 8 below. Short-duration high-voltage pulses are provided to the electrodes for avoiding transition of corona glow to spark. (Chang, 1991)



**Figure 8. Electric discharge water treatment (Jahivolt, n.d.).**

Pulsed corona discharge is an important source of producing strong radicals like  $\cdot\text{OH}$  hydroxyl, atomic oxygen ( $\text{O}$ ) and ozone  $\text{O}_3$ . These radicals can react with the pollutants present on the surface of the water. Oxidation with the pulsed corona discharge (PCD) results in the degradation of the organic and inorganic substances. PCD can cause complete mineralization to water and  $\text{CO}_2$  or transform them into less toxic biodegradable compounds.

Concerning inorganic substances it is also a useful technique and energy efficient process. Moreover, PCD is powerful in the disinfection of water as well. (Chang, 1991)

Oxygen based oxidants are environmental friendly even after the decomposition they do not form toxic by-products. Therefore, using these oxidants in this process will reduce the human health and environmental concerns.

Following is a systematic diagram of the Pulsed discharge corona:

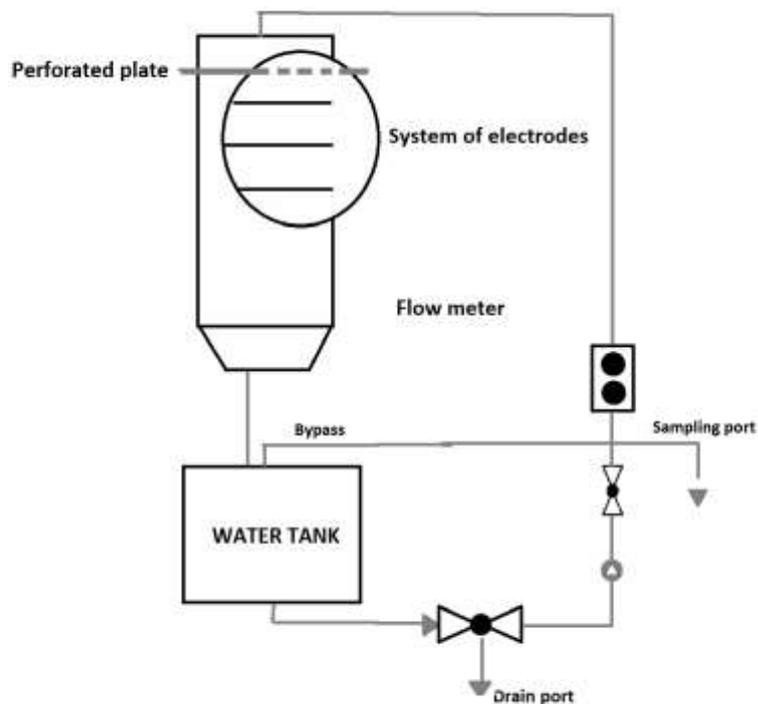


Figure 9. Systematic diagram of pulsed discharge corona (sokolov, 2015)

The construction of the PCD is very simple as can be seen from fig 8. It consists of the three main parts which are water tank reservoir, electric pulse generator and PCD reactor equipped with the perforated plate, electrodes and circulation pump.

The main benefit of the PCD system is the simplicity of the system in design and its process; the other advantages are easy maintenance and optimal system for the oxidation process.

The design of the system permits scattering of treated solution from top of the reactor. The discharge takes place in air or oxygen atmosphere in which water is dispersed in order to form droplets, jets, films and streams and then it passes through the electrodes where it reacts with the oxidants being produced in plasma zone. OH radicals and atomic oxygen form directly on the surface of the water permitting the reaction with contaminations in the water.

## 5. EXPERIMENTAL PART

### 5.1 PCD Reactor

In the present work PCD oxidation was studied. Multiple low energy channels propagates in the interelectrode volume in order to avoid transition of corona glow to spark, short duration of high voltage pulses are provided to the electrodes. Pulsed corona discharge is an effectual source of active oxidant species like atomic oxygen (O), hydroxyl radicals (OH) and ozone (O<sub>3</sub>) known as highly influential oxidizers.

Atomic oxygen (O) and hydroxyl radicals (OH) are formed at the surface of the water droplets and it will react with the impurities.

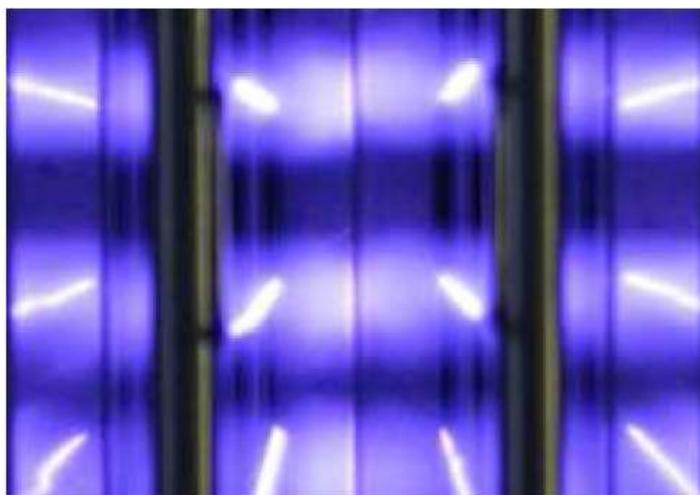


Figure 10. Image of pulsed corona discharge ( (Jahivolt, n.d.)

The overall configuration of the Pulsed corona discharge equipment is illustrated in figure 8. The system consists of mainly pulsed corona discharge reactor and high voltage pulse generator.

The experimental setup for the Pulse corona Discharge consists of four main units:

- 1- Pulse generator with minimum frequency of 50 pps and maximum 833 pps
- 2- PCD reactor
- 3- Solution tank is also located at the middle above

- 4- Pumping unit with flow and sampling valve
- 5- Water reservoir with a volume of 10L

The PCD reactor is made of with the acrylic chamber comprising of two grounded perpendicular plate electrodes placed into a dielectric or grounded metal compartment. The treated water is fed on the top of the electrode system and the down flow streams passes between the electrodes where it will treated by active oxidants species produced by the discharge.

Fig 11 shows the interelectrode area with the frequency of 833 pps and 100 W.

## 5.2 Pulse Generator



Figure 11. Pulse Generator of 100W

Table 3. Pulsed generator parameters (Alexander Sokolov)

Parameter values used the PCD experiments with the 100W pulse generator		
Time per pulse (ms)	Frequency (pps)	Generator power (W)
20	50	6
5	200	24
3.3	300	36
2	500	60
1.5	667	80
1.2	833	100

The maximum power output is 100W and six different pulse frequencies between 50 to 833 pps can be used the generator shown in figure 11. The delivered energy and the pulse frequency were defined with an oscilloscope as presented in table 3.

The maximum power output of the pulse generator is 100W and the energy of a single pulse obtained from the oscillogram derivation is 0.12J at 22kV.

### 5.3 Water Circulation System

The pump used in the PCD system with a capacity of 10L/min was used to circulate the solution in the system. A flow meter equipped with a manually adjustable valve was used to control the flow rate to the reactor. The maximum flow rate measurable with the flow meter is 3.5L/min.



Figure 12. Water Circulation System

## **5.4 Solution Preparation**

The thiosulfate solutions were prepared for the PCD experiments with concentrations of 1000 ppm and 400 ppm. All the solutions were made using Millipore water and the solution flask was 10 liter in volume.

Firstly before going to the laboratory all the safety equipment, like laboratory coat, gloves and glasses, were put on. The sodium thiosulfate solution was made in the bottle in which the sodium thiosulfate powder dosed with a spoon was dissolved. Dilutions of sodium thiosulfate solution samples were made with the flasks and pipettes.

A hand basket was used in order to carry samples and glassware safely to the other laboratory. As discussed above, two solution concentrations, 1000ppm and 400ppm, were prepared for the experiments. A small beaker was placed on an electrical balance which was firstly tared to reach its zero value. Then 10g of sodium thiosulfate was added to the beaker slowly in order to prevent any mistakes in dosing.

The beaker and the 1000ml flask were carried to the other laboratory where the Millipore water is available. The flask was rinsed with Millipore water for some time in order to prevent any contamination. A certain amount of water was added to the sodium thiosulfate beaker and then the flask was shaken. The dissolved sodium thiosulfate solution was poured to the 1000ml flask, which was filled with Millipore water. The flask was shaken 2 to 3 times and after that it was mixed with the magnetic stirrer.

After that the PCD device was cleaned with Millipore water, which was circulated inside the PCD device to avoid any contamination with the other material or other solutions used in previous PCD experiments. The samples were collected to the bottles on which the concentration, time and date were written visibly and placed them in the PCD room.

8.8 liters of Millipore water was taken in order to make the total solution of 10 liter. Weighing was done with a bigger electrical scale. The small flask was rinsed with 200ml of additional Millipore water to recover all the sodium thiosulfate from the 1000ml flask. Thus, the final solution is prepared for the experiment.

## **5.5 Experiment procedure**

Sodium thiosulfate is a compound whose degradation requires higher oxidation efficiencies. The duration of the experiments were relatively long being about 2 to 4 hours with the frequencies of 833 and 200 pps, respectively. The research topic was to investigate oxidation of sodium thiosulfate by PCD and formation of transformation sulfate products during the PCD oxidation. Sampling was conducted with time interval of every 20 to 25 minutes. Zero sample for every experiment was taken after the solution circulated within the system of about 7 minutes and pH of every sample were measured with a pH meter and electric conductivity was also measured with a conductivity meter.

Firstly, the frequency level was adjusted and then after taking zero samples the PCD was switched on immediately and this process was repeated again to provide an indication of repeatability.

6 to 7 samples were collected and placed in sample bottles. The bottles were filled to the half of the total bottle volume and they were marked with the date, frequency, and concentration.

After that the samples were carried to the ion chromatography room for the analysis. The PCD device was cleaned with tap water in order to prevent any ozone generation inside the water reservoir and after that the PCD device was cleaned by circulating Millipore water the Millipore water for about 10 minutes. Finally, the pulse generator and pump were switched off.

### **5.5.1 Analytical method**

Ion chromatography (IC) was first developed in the mid-1970s by Small et al. (1975). This is physio-chemical technique that gives a quantitative analysis of inorganic or organic ions from complex mixture. Ion chromatographic method is used for the convenience and accuracy for the results. Anion column is used for the analysis of the thiosulfate concentration. For the mobile phase 4.5 mM Na<sub>2</sub>CO<sub>3</sub> and 9.1 mM NaHCO<sub>3</sub> was used.

## **6. RESULTS AND DISCUSSION**

Color changes could be visually observed during the thiosulfate treatment. In the beginning the solution had slightly a pale yellow color. It is found that when more energy was delivered, color changed to opaque. PH was not adjusted when the initial solution was prepared. PH of the samples collected during the experimental run was measured. The pH results of the experiments shown in fig. 13. During the experiment, it was observed that pH decreases and the solutions becomes more acidic. In PCD oxidations pH typically decreases.

The forming transformation products are mainly sulfates. Which are together dependent on delivered energy and pulse frequency. It is also observed during the experiment that the pH is lower, decreasing with respect to time very slowly.

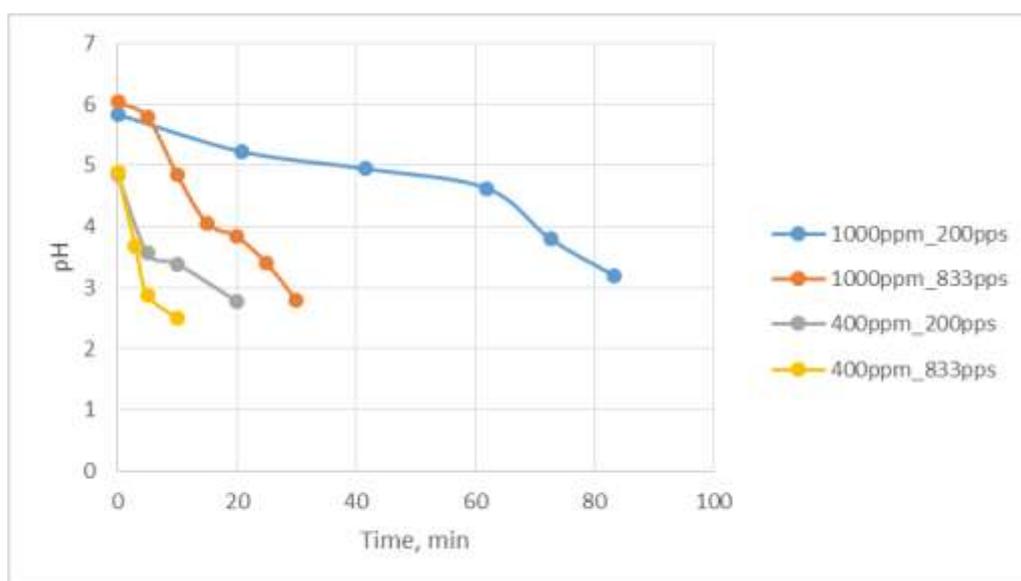


Figure 13. Relation of pH and time.

Flow rate of 4L/min was used in every experiment. It can be so that volume flow rate of solution circulated by the pump was not necessarily all the time constant.

The samples were collected after time T and pH was measured after getting each sample. The degradation of sodium thiosulfate was observed more energy efficient with the lower pulse repetition rate, because the compound had more time to degrade with the less frequency.

With the longest time of 1.38 hours for the frequency of 200 pps (lower level) the degradation degree of thiosulfate was 90 percent. This corresponds the energy consumption of 3.33 kWh/m<sup>3</sup>. On the other side with 1000 ppm and 833 pps (higher level) corresponding to the energy consumption was 5 kWh/m<sup>3</sup> in just 0.5 hours.

It was also found that the level of energy delivered was lower at 200 pps than the 833pps. The experiment was repeated with the concentration of 400 ppm and results showed the same trend: the lower energy repetition frequency is much better than high energy repetition frequency of 833pps.

The energy delivered with 400 ppm and 200 pps at 10 minutes was 0.4 kWh/m<sup>3</sup>. On the other hand, the energy delivered on 400 ppm and 833 pps at 10 minutes was 1.66 kWh/m<sup>3</sup>. This shows that the process is more efficient if the frequency is lower. The process will be energy efficient and it requires less energy to degrade the toxic compound compared to high frequency repetition pulses. All the experiments were carried out with different concentration and different repetition pulses and they all are successful for removing the desired compound.

The obtained results of reaction kinetics and as a function of delivered energy are presented in figures 14, 15, 16. At the beginning stage of the reaction the pattern of thiosulfate

degradation was followed a linear pattern and it was observed almost linear with every experiment and with different concentrations and with different repetition pulse frequency.

The exact explanation of chemical kinetics is difficult due to the presence and formation ·OH radicals but from the graph it is clear that the reaction rate is of zeroth order because of the linearity of the lines in fig. 14.

The zero-order (eq. 38), first-order (eq. 39) and the second-order (eq. 40) reaction kinetics can be expressed by following equations ( Burton., 2003).

$$\frac{dc}{dt} = -K_0 \quad \text{Zero-order} \quad (38)$$

$$\frac{dc}{dt} = K_1 \times c \quad \text{First-order} \quad (39)$$

$$\frac{dc}{dt} = K_2 \times c^2 \text{ or } \frac{dc}{dt} = K_3 c_A c_B \quad \text{Second-order} \quad (40)$$

Where  $c$  is the concentration over time  $t$  and  $K_0$ ,  $K_1$ ,  $K_2$  and  $K_3$  are the reaction rate coefficients, respectively. The slope values and  $R^2$  values are shown in figures 14, 15 and 16 are shown below.

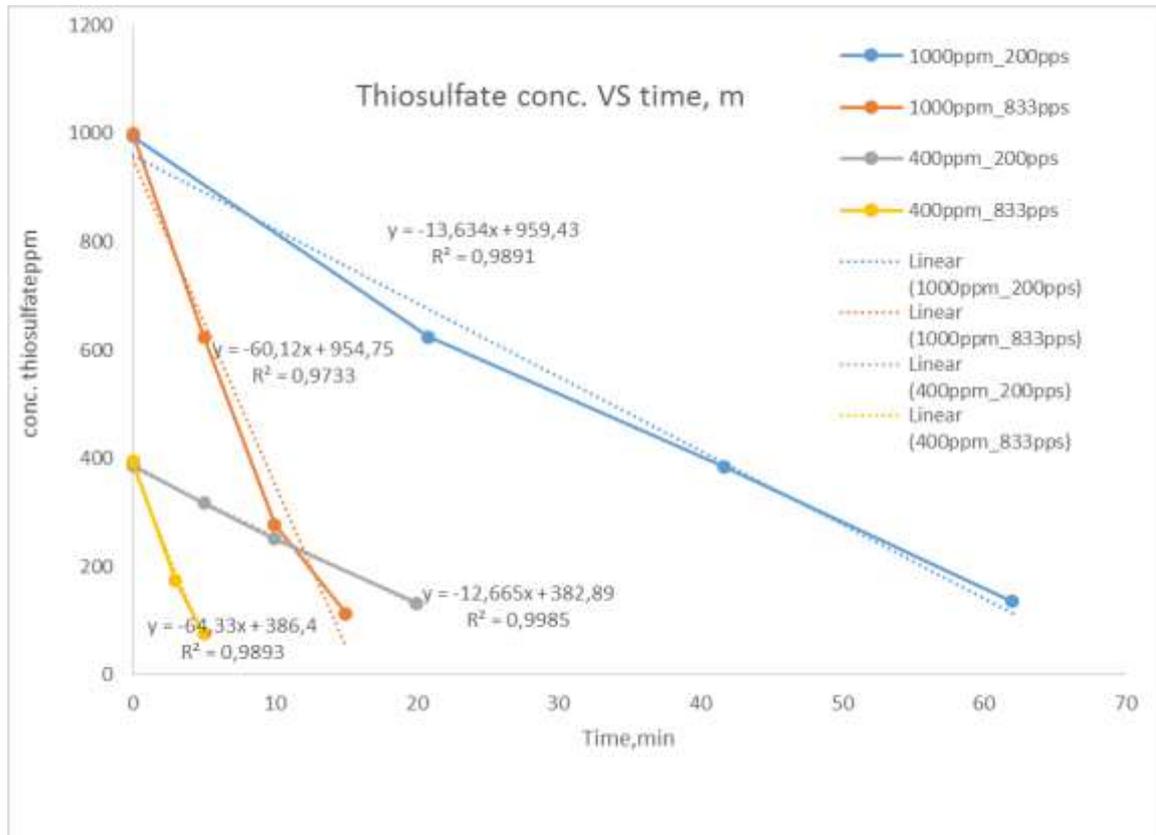


Figure 14. Concentration of thiosulfate over time.

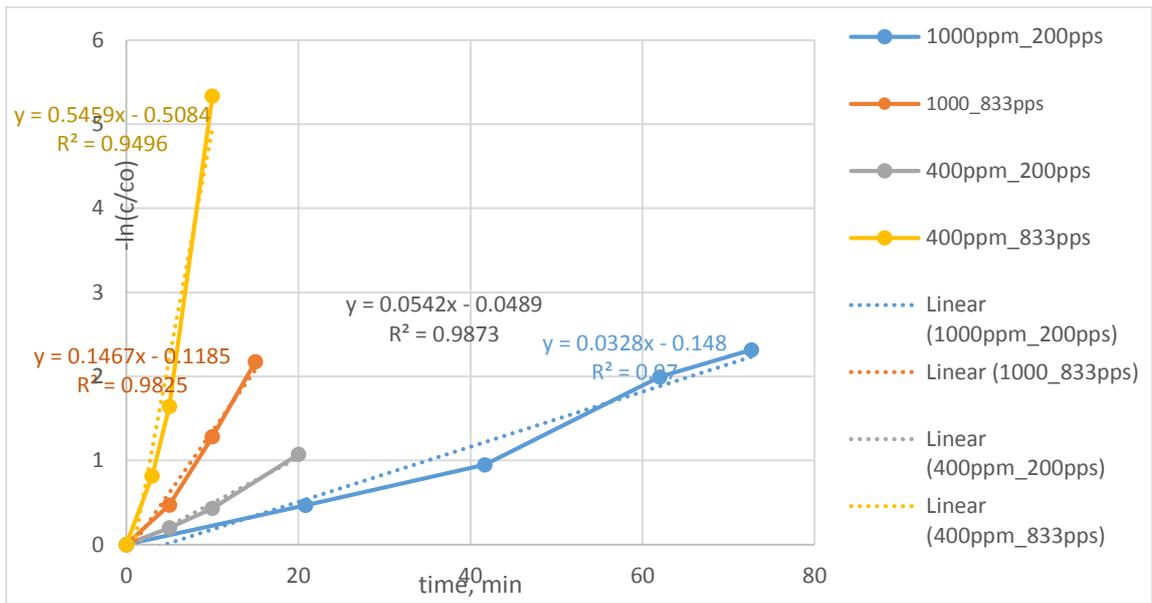


Figure 15 . Logarithmic concentration ratio over time (first-order reaction).

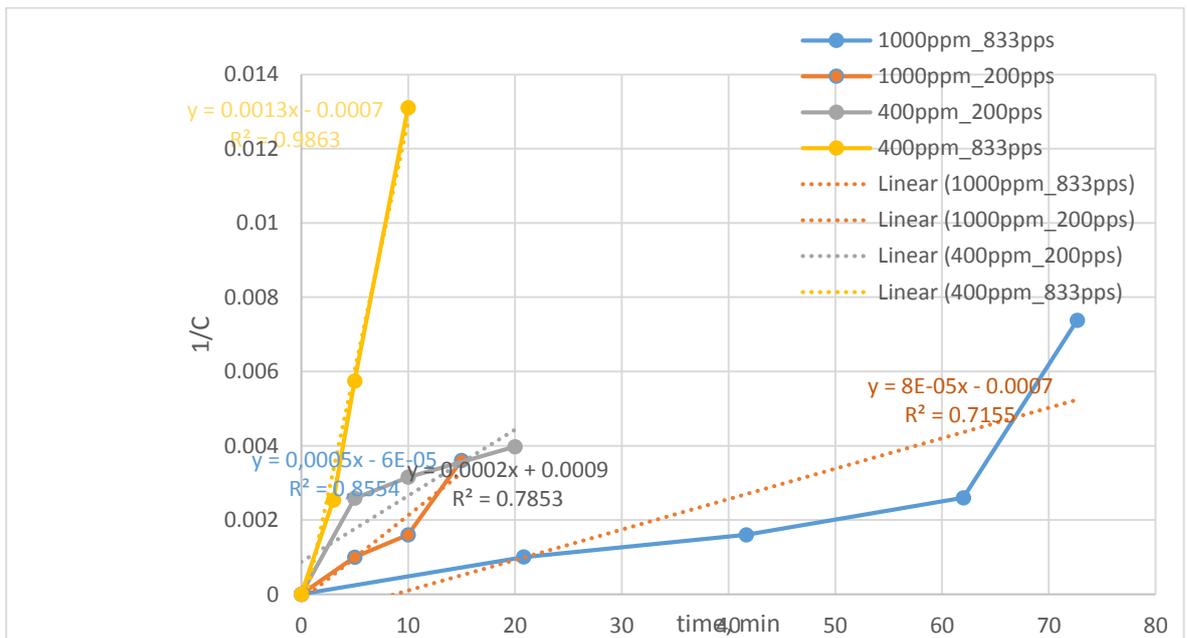


Figure 16. 1/c over time (second-order reaction).

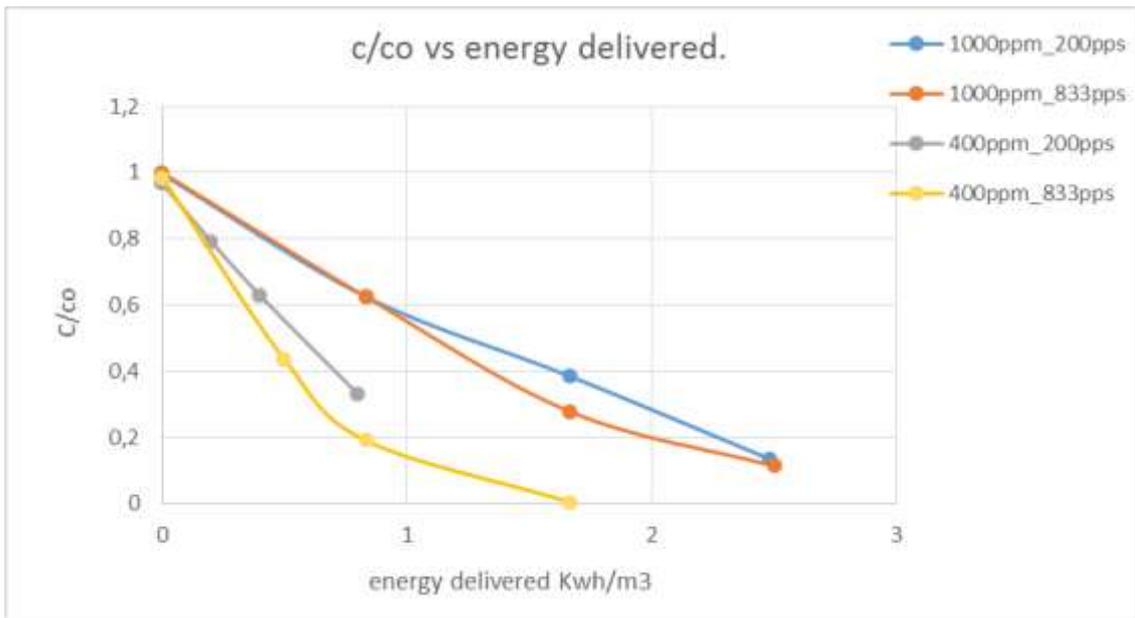


Figure 17. Concentration ratio versus delivered energy  $\text{kWh/m}^3$ .

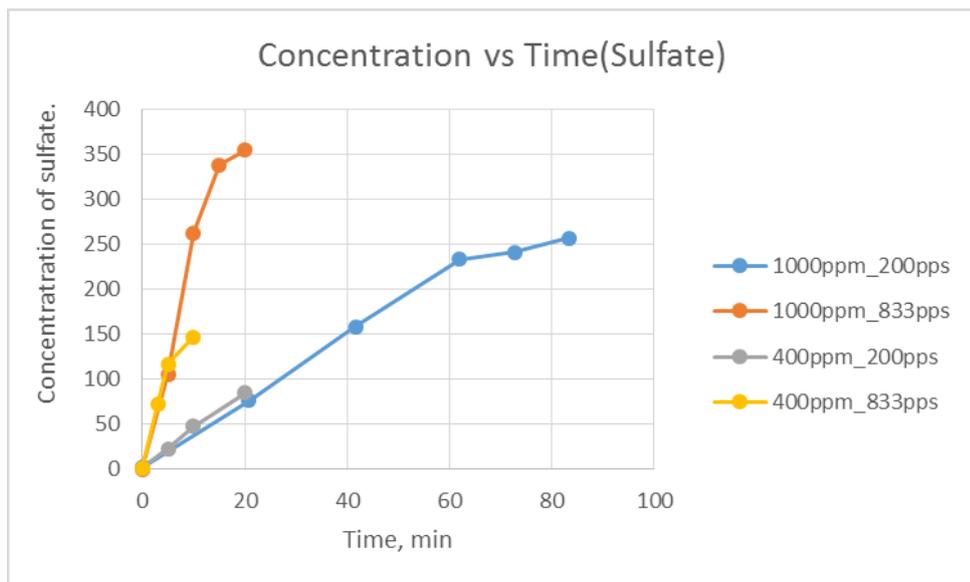


Figure 18. Concentration increase of transformation product sulfate over PCD oxidation treatment time.

Sodium thiosulfate concentration decreases linearly with elapsed time as shown in fig. 14. When comparing results obtained with studied two concentrations and two pulse frequencies the concentrations decrease quite linearly. The lower frequency curve shows the probability of oxidant and the pollutant collusion. Apart from that concentration of sulfate, we get better results from the higher concentration 1000ppm and lower frequency 200 pps, because oxidation rate is low and energy efficiency is high as compared to high frequency. With the time, the amount of the main transformation product, i.e. sulfate increases, as shown in fig. 18.

## 7. Conclusion

Degradation of sodium thiosulfate was observed from the waste water by pulsed corona discharge. It was found that rate of oxidation of thiosulfate is higher with higher frequency but the process was not energy efficient when compared to the low frequency oxidation of thiosulfate. Complete removal of thiosulfate was achieved during the experiments.

The concentration of thiosulfate decreased linearly in every experiment but with the first case that is 1000ppm and 200pps it was more linear as shown in the figure 14 and figure 17. Because the pollutants have more time to react while with the other case 1000ppm and 833pps the oxidation rate was maximum but the energy value was high. It was concluded from the results that if the frequency is high than the time to degrade sodium thiosulfate will be less because of the energy delivered is high and if the frequency is small than the more time required to degrade the sodium thiosulfate vary with the amount of concentration used during the experiment. It was also shown in the appendix below.

The overall kinetics of the oxidation reaction in our case is zero order kinetics. Concerning the oxidation of sodium thiosulfate by pulsed corona discharge the obtained results are promising.

The effectiveness of the process boosts with the reduced pulse frequency, and the oxidants have enough time to react with the pollutants. The oxidants oxidise them and convert them to a beneficial product which is sulfate and it can easily be dispose to a soil or to the water it has no harmful effect on the marine life as well. With high frequency pulse repetition the oxidation rates are significantly increased since the influence of hydroxyl radical oxidants is greater and the chemical reactions of hydroxyl radicals are fast.

The energy efficiency is achieved in PCD oxidation compared to other Advanced Oxidation Processes. This makes the process suitable for several waste water treatments because of its simple configuration. The benefit of PCD equipment is in terms of oxygen usage which means the amount of oxygen used during the experiment. It is an energy cost and more environmentally friendly technology than others available in the market because there is no formation of sludge and no usage of chemicals in the process everything is happening inside the pulsed corona reaction chamber and this process is also very cheap because of the simplicity of the equipment.

More methodology development has to be made to apply PCD method in industrial processes. To date, it is not yet suitable for large scale waste water treatment processes. Further development is required to make it more efficient for industrial applications. The studied PCD system was a pilot scale device. This scale PCD process could be used for small scale applications, such as pharmaceutical and textile industry where the waste water volumes are moderate.

## **Bibliography**

Akcil, A., 2003. Destruction of cyanide in gold mill effluents: Research review paper on cyanide, Biomin Group Turkey Volume 21, Issue 6 pp. 501-502.

Akcil, A., 2003. Destruction of cyanide in gold mill effluents: Destruction of cyanide in gold mill effluents: Research review paper on cyanide, Biomin Group Turkey Volume 21, Issue 6 pp. 503.

Arimal, H. & Yen, T., 2009. Gold Recovery from Nickel Catalysed Ammonium Thiosulfate Solution by Strongly Basic Anion Exchange Resin. *Materials Transactions*, Vol. 44, No. 10 (2003) pp. 2099 to 2107, pp. 1-2.

Aylmore, M. 2004. Thiosulfate as an alternative to cyanide for gold-processing issues and impediments. *Mineral Processing and Extractive Metallurgy*, Vol. 113, pp. 113, 2-12.

Baghalha, M., 2006. Leaching of an oxide gold ore with chloride/hypochlorite solutions. *International Journal of Mineral Processing* Volume. 82 Department of Chemical and Petroleum Engineering, Sharif University of Technology, Azadi St., Tehran, 11365, Iran, p. 1.

Bean, 1996. *Encyclopaedia of chemical technology* Fourth edition VOL 24. New York: Wiley - Interscience Publication.

Bennett, G. (1994). Industrial and hazardous waste treatment. *Journal of Hazardous Materials*, 37(2), p.378.

Bernd G, L., 2007. *Mine Wastes. Characterization treatment and Environment impact.* Townsville Queensland Australia: Third Edition 2007. Berlin: Springer.

Bessegato, G., Guaraldo, T. and Zanoni, M. (2014). Enhancement of Photo electro catalysis Efficiency by Using Nanostructured Electrodes. *Modern Electrochemical Methods in Nano, Surface and Corrosion Science*.

Böhme, A., 1999. *Ozone technology of German industrial enterprises*) Vol. 21. *Ozone: Science & Engineering* Koln Germany, p. 163-176 Botz, M., 1999. Overview of cyanide treatment methods, originally published as a booklet by The Gold Institute in August 1999, Washington, D.C, p 1-11

Burton, F. and Tchobanoglous, G (1991). *Wastewater engineering*. New York: McGraw-Hill.

Busca, G., Berardinelli, S., Resini, C. and Arrighi, L. (2008). Technologies for the removal of phenol from fluid streams: A short review of recent developments. *Journal of Hazardous Materials*, 160(2-3), pp.265-288.

- Carnahan, L, 1992. Copper-catalysed thiosulfate leaching of low-grade gold ores. *Hydrometallurgy*, Reno Research Centre, U.S. Bureau of Mines, Reno, NV, USA Vol 29, pp. 191-203.
- Chang, J. S., 1991. Corona discharge processes. *IEEE Transactions on Plasma*, Volume.19 pp. 1152 - 1166
- Chen, D., Sivakumar, M. and Ray, A. (2008). Heterogeneous Photo catalysis in Environmental Remediation. *Dev. Chem. Eng. Mineral Process.* 8(5-6), pp.505-550.
- Cluness, M., Turner, P., Clements, E., Brown, D. and O'Reilly, C. (1993). Purification and properties of cyanide hydratase from *Fusarium lateritium* and analysis of the corresponding *chl1* gene. *Journal of General Microbiology*, 139(8), pp.1807-1815.
- Dash, R., Gaur, A. and Balomajumder, C., 2009. Cyanide in industrial wastewaters and its removal: A review on bio treatment. *Journal of Hazardous Materials*, 163(1), pp.1-11.
- Gilmour, C. 2012. Water treatment using advanced oxidation processes: application perspectives, Ontario, Canada: The School of Graduate and Postdoctoral Studies, The University of Western Ontario London, Dissertation Repository. Paper 836.
- Gogate, P. P., 2004. Review of imperative technologies for wastewater treatment oxidation technologies at ambient conditions. : *Advances in Environmental Research*, vol 8, Chemical Engineering Section, Matunga, Mumbai 400019, India
- Goi, A., 2005. Advanced oxidation processes for water purification and soil remediation, Dissertation, Department of Chemical Engineering, Tallinn University of Technology.
- Blanco, M., Martinez, A., Marcaide, A., Aranzabe, E., Aranzabe, A., 2010. Heterogeneous Fenton catalyst based on clay silica and zeolite. Issue 2010, pp. 1-26.
- Haddad, G., 2003. Leaching and recovery of gold using ammoniacal thiosulfate leach liquors. *Hydrometallurgy*, Vol 69, pp. 69, 1-21.
- Herney-Ramirez, J., Vicente, M. and Madeira, L. (2010). Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review. *Applied Catalysis B: Environmental*, 98(1-2), pp.10-26.
- Jahivolt, Pulse electric discharge for potable and waste water treatment, Tomsk, Russia: Laboratory No.12 Institute of high technology physics.
- T.S, Jordan. And C.A., Young. (1995). Cyanide remediation: current and past Technologies. *Proceedings of the 10th Annual Conference on Hazardous Waste Research*. Montana: Department of Metallurgical Engineering, Butte, MT 59701, pp. 1-26

Kochany, J. B. J., 1992. Mechanism of photo degradation of aqueous organic pollutants. 2. Measurement of the primary rate constants for reaction of •OH radicals. *Environmental Science and Technology*, pp. 262-265.

Kogelschatz, U., Eliasson, B. and Hirth, M., 1988. Ozone Generation from Oxygen and Air: Discharge Physics and Reaction Mechanisms. *Ozone: Science & Engineering*, 10(4), pp. 367-377.

Levec, J. and Pintar, A., 1995. Catalytic oxidation of aqueous solutions of organics. An effective method for removal of toxic pollutants from waste waters. *Catalysis Today*, 24(1-2), pp.51-58.

Lewis, R. (1997). *Hazardous chemicals desk reference*. New York: John Wiley & Sons.

Li, D. and Qu, J. (2009). The progress of catalytic technologies in water purification: A review. *Journal of Environmental Sciences*, 21(6), pp.713-719.

Review of: "The Management of Cyanide in Gold Extraction". Mark J. Logsdon, Karen Hagelstein and Terry I. Mudder: *International Council of Metals and the Environment*. (2000). *International Journal of Surface Mining, Reclamation and Environment*, 14(4).

Kebriaei M, Ketabi A, Halvaei A., 2015. Pulsed Corona Discharge, a New and Effective Technique for Water and Air treatment. *Biological Forum – An International Journal*. Vol 7, p 1687-1692

Mudde, T. I., Botz, M. M. & Smith, P. A., 2001. *Chemistry and Treatment of Cyanidation Wastes*, Mining Journal Books Ltd., USA, p. 333

Muir, A., 2001. Treatment of a refractory gold-copper sulfide concentrate by copper ammoniacal thiosulfate leaching. *Minerals Engineering*, pp. 615-637

Oraby, E., 2009. *Gold Leaching in Thiosulfate Solutions and Its Environmental Effects Compared With Cyanide*. PhD. Curtin University of Technology, Australia.

Pargaa, J. R., Shuklab, S. & Carrillo-pedrozac, F. R., 2002. Destruction of cyanide waste solutions using chlorine dioxide. *Waste Management* Vol 23, pp. 184-190.

Parga, J., Shukla, S. and Carrillo-Pedroza, F. (2003). Destruction of cyanide waste solutions using chlorine dioxide, ozone and titania sol., *Waste Management*, Vol 23, Iss 2, pp.183-191.

Rubin, G. (2000). Comparative Genomics of the Eukaryotes. *Science*, Vol 287(5461), pp.2204-2215.

Schmidt, 1962. *Sulfur polymer, Inorganic polymers*. New York: Academic Press.

Sillanpää, M., Kurniawan, T. and Lo, W. 2011. Degradation of chelating agents in aqueous solution using advanced oxidation process (AOP). *Chemosphere*, Vol 83(11), pp.1443-1460.

Sokolov, A., 2015. Energy calculations of PCD, Lappeenranta, oral communication.

Staehelin, J. and Hoigne, J., 1985. Decomposition of ozone in water in the presence of organic solutes acting as promoters and inhibitors of radical chain reactions. *Environmental Science & Technology*, Vol 19(12), pp.1206-1213.

Stone, F., Graham. W., 1962. Sulphur polymer, inorganic polymers, NY: Academic press.

Tomizawa S, Tezuka. M., 2007. Kinetics and mechanism of the organic degradation in aqueous solutions with gaseous plasma. *Plasma chemistry and plasma processing*, Volume 27, Issue 4, pp. 486-495.

Ullmanns, 1991. *Encyclopaedia of industrial chemistry*, Germany: VCH Verlagsgesellschaft.

Von Gunten, U., 2003. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Research*. Volume 37, Issue 7, pp. 1443–1467

Wang, L., Shamas, N. and Hung, Y. (2009). *Advances in hazardous industrial waste treatment*. Boca Raton, FL: CRC Press. 0th Edition

## Appendix

Table 3 Analysis 7.05.2015. The first PCD run. 1000 pp, 833 pps

No.	Name	Time min	Area n.a.	Rel.Area %	Height n.a.	Rel.Height %	Amount ppm
Sulfaatti	Sulfaatti	Sulfaatti ECD_1	Sulfaatti ECD_1	Sulfaatti ECD_1	Sulfaatti ECD_1	Sulfaatti ECD_1	Sulfaatti ECD_1
1	10 x eluent	6.797	0.0676	4.75	0.14	2.26	0.6494
2	MQ	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Std1	7.180	0.0939	74.31	0.18	81.14	0.9096
4	Std2	7.154	0.5190	61.84	1.16	77.78	5.0259
5	Std3	7.121	1.0823	62.01	2.78	78.56	10.2689
6	Std4	7.107	1.5907	61.90	4.37	78.39	14.8149
7	Std5	7.094	2.1800	62.43	6.25	78.70	19.8893
8	Std6	7.080	2.8080	62.65	8.29	79.21	25.0908
9	Std6	7.081	2.8051	62.68	8.28	79.07	25.0676
10	0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11	5min	7.141	0.2907	21.80	0.62	31.35	113.3514
12	10min	7.124	0.6266	55.89	1.41	68.07	241.8072
13	15min	7.107	0.8097	79.65	2.02	85.36	310.4213
14	std6	7.057	2.8044	62.45	8.47	79.09	25.0614
15	20min	7.047	3.9103	89.97	11.64	90.52	337.7440
16	20min	6.997	41.1774	92.95	103.03	89.13	211.0861
17	std3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
18	10x eluent	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
19	10 x eluent	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
20	MQ	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	<b>Sum:</b>	99.087	60.766	855.264	158.640	998.638	1341.188
	<b>Average:</b>	7.078	4.340	61.090	11.331	71.331	95.799
	<b>Rel.Std.Dev:</b>	1.316 %	245.877 %	38.320 %	235.219 %	34.203 %	129.622 %

Table 4 Analysis 7.05.2015. The first PCD run. 1000 pp, 833 pps

No.	Name	Time min	Area n.a.	Rel.Area %	Height n.a.	Rel.Height %	Amount ppm
Tiosulfaatti	Tiosulfaatti	Tiosulfaatti ECD_1					
1	10 x eluent	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	MQ	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Std1	15.004	0.0325	25.69	0.04	18.86	0.8645
4	Std2	14.901	0.3202	38.16	0.33	22.22	5.1266
5	Std3	14.854	0.6630	37.99	0.76	21.44	10.1996
6	Std4	14.804	0.9793	38.10	1.20	21.61	14.8766
7	Std5	14.764	1.3120	37.57	1.69	21.30	19.7923
8	Std6	14.724	1.6743	37.35	2.18	20.79	25.1405
9	Std6	14.724	1.6702	37.32	2.19	20.93	25.0792
10	0	14.731	1.5547	100.00	2.04	100.00	934.9810
11	5min	14.751	1.0296	77.20	1.30	66.08	624.7922
12	10min	14.801	0.4653	41.50	0.55	26.54	290.9674
13	15min	14.834	0.1636	16.10	0.18	7.78	112.3191
14	std6	14.667	1.6865	37.55	2.24	20.91	25.3190
15	20min	14.771	0.1485	3.42	0.17	1.32	25.8419
16	20min	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
17	std3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
18	10x eluent	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
19	10 x eluent	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
20	MQ	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	<b>Sum:</b>	192.326	11.700	527.950	14.883	369.772	2115.300
	<b>Average:</b>	14.794	0.900	40.612	1.145	28.444	162.715
	<b>Rel.Std.Dev:</b>	0.598 %	70.812 %	60.035 %	74.546 %	91.636 %	179.260 %

Table 5 Analysis 01.05.2015 The 6th and 7th PCD runs (01.06.2015): paramiters : 1000 ppm, 833 pps and 200 pps

No.	Name	Time min	Area µS*min	Rel.Area %	Height µS	Rel.Height %	Amount ppm
Sulfaatti	Sulfaatti	Sulfaatti ECD_1	Sulfaatti ECD_1	Sulfaatti ECD_1	Sulfaatti ECD_1	Sulfaatti ECD_1	Sulfaatti ECD_1
1	10 x eluent	6.314	0.1247	9.61	0.22	3.82	0.8035
2	MQ	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Std1	6.004	0.1262	100.00	0.28	100.00	0.8187
4	Std2	5.954	0.5833	75.29	1.44	86.31	5.1726
5	Std3	5.941	1.1342	66.05	3.14	79.63	10.2336
6	Std4	5.924	1.6550	64.80	4.86	79.34	14.8479
7	Std5	5.907	2.2306	63.88	6.79	78.24	19.7765
8	Std6	5.894	2.8810	65.00	8.86	79.34	25.1497
9	Std4	5.917	1.6527	64.31	4.83	78.91	14.8284
10	0 1000ppm 200 pps	6.027	0.0228	1.45	0.04	1.91	n.a.
11	00:20:50	5.974	0.2637	21.29	0.62	30.35	85.7452
12	00:41:40	5.940	1.0317	45.01	2.74	58.03	186.1371
13	01:02:00	5.894	2.9744	74.45	8.98	82.62	259.0577
14	01:12:40	5.864	6.6988	79.89	20.24	84.85	267.2167
15	01:12:40	5.824	34.9955	66.21	83.09	71.85	192.2265
16	01:23:20	5.817	40.0263	80.22	91.01	79.90	210.9361
17	std 4	5.881	1.6646	60.04	5.01	78.16	14.9321
18	0 min 1000ppm 833 pps	5.954	0.0272	1.56	0.05	2.00	n.a.
19	5 min	5.937	0.3166	15.86	0.82	29.51	106.0236
20	10 min	5.934	0.7331	66.49	1.97	77.75	262.7429
21	15 min	5.897	1.8963	84.39	5.53	88.29	338.7059
22	20 min	5.847	9.4057	93.41	27.40	91.81	355.1749
23	25 min	5.807	59.1153	93.20	106.37	85.86	274.0106
24	30 min	5.801	67.6635	92.22	116.40	82.99	299.2207
25	std 4	5.867	1.6852	64.46	5.07	78.60	15.1116
26	10x eluent	6.351	0.1185	3.00	0.20	2.89	0.7436
27	10 x eluent	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28	MQ	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	<b>Sum :</b>	148.469	239.027	1452.092	505.977	1612.969	2959.616
	<b>Average :</b>	5.939	9.561	58.084	20.239	64.519	128.679
	<b>Rel.Std.Dev:</b>	2.223 %	200.139 %	53.445 %	178.518 %	49.260 %	100.636 %

Table 6 Analysis 01.05.2015 The 6th and 7th PCD runs (01.06.2015): paramiters : 1000 ppm, 833 pps and 200 pps

No.	Name	Time min	Area µS*min	Rel.Area %	Height µS	Rel.Height %	Amount ppm
Tiosulfaatti	Tiosulfaatti	Tiosulfaatti ECD_1	Tiosulfaatti ECD_1	Tiosulfaatti ECD_1	Tiosulfaatti ECD_1	Tiosulfaatti ECD_1	Tiosulfaatti ECD_1
1	10 x eluent	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	MQ	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Std1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
4	Std2	11.387	0.1914	24.71	0.23	13.69	4.9510
5	Std3	11.344	0.5831	33.95	0.80	20.37	10.1992
6	Std4	11.304	0.8991	35.20	1.27	20.66	14.6973
7	Std5	11.251	1.2614	36.12	1.89	21.76	20.2062
8	Std6	11.214	1.5513	35.00	2.31	20.66	24.9475
9	Std4	11.287	0.9172	35.69	1.29	21.09	14.9636
10	0 1000ppm 200 pps	11.217	1.5475	98.55	2.29	98.09	995.3192
11	00:20:50	11.291	0.9612	77.63	1.38	67.23	624.5200
12	00:41:40	11.257	1.2001	52.36	1.75	36.91	384.9073
13	01:02:00	11.287	0.8205	20.54	1.11	10.26	135.5385
14	01:12:40	11.234	1.2245	14.60	1.78	7.44	98.1300
15	01:12:40	10.904	15.3739	29.09	22.02	19.04	n.a.
16	01:23:20	10.971	6.9546	13.94	10.36	9.10	n.a.
17	std 4	11.117	0.9117	32.88	1.35	21.03	14.8818
18	0 min 1000ppm 800 pps	11.044	1.5944	91.13	2.55	94.84	1027.2760
19	5 min	11.117	1.6656	83.44	1.90	68.61	1076.5396
20	10 min	11.287	0.3427	31.09	0.45	17.77	277.6014
21	15 min	11.274	0.2470	10.99	0.34	5.35	113.5393
22	20 min	11.307	0.0988	0.98	0.13	0.43	18.7846
23	25 min	11.291	0.1835	0.29	0.25	0.20	4.8490
24	30 min	11.294	0.0725	0.10	0.13	0.09	3.4206
25	std 4	11.087	0.9291	35.54	1.38	21.40	15.1383
26	10x eluent	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
27	10 x eluent	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28	MQ	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	<b>Sum:</b>	246.765	39.531	793.814	56.931	595.995	4880.410
	<b>Average:</b>	11.217	1.797	36.082	2.588	27.091	244.021
	<b>Rel.Std.Dev:</b>	1.107 %	185.727 %	78.894 %	185.977 %	105.897 %	153.695 %