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Electrochemical Oxidation of Organics in Nuclear Waste Streams using a Boron - Doped Diamond (BDD) Electrode

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Abstract

It is important to remove organic substances, particularly organic complexing agents, from radioactive waste streams. The main aspect is that organics could act as carriers of radionuclides in the final repository of radioactive operational waste. Another reason is due to fouling of cleaning equipment such as filters, membranes and ion exchange resin.

The aim of this work was to perform a feasibility study of an electrochemical oxidation method with the use of a boron-doped diamond (BDD) anode in order to decompose and thus reduce the content of organics in nuclear wastewaters. Experiments have also been done with the purpose of evaluating the use of hydrogen peroxide in combination with electrochemical treatment. The study has been carried out at the nuclear power plant Ringhals by supervision from the division of Nuclear Chemistry at Chalmers University of Technology.

Complexing agents are extensively used in detergents in order to ensure an efficient washing. The effluent from the laundry where the protective clothing is cleaned from radioactive particles was especially studied in the work. Water analyses were done in order to monitor the reduction of chemical oxygen demand (COD) and total organic carbon (TOC) during the study. In addition, ion exchange experiments with activity measurements were carried out in order to specifically evaluate the destruction of complexing agents and not organic substances in general. The studied model solutions had an initial TOC content between 50 and 250 mg/l and initial COD between 160 and 525 mg/l.

Electrochemical oxidation using a BDD anode can successfully treat dissolved organic compounds with a high degree of destruction. Analyses have shown a decrease in TOC to non-detectable levels during several experiments under varying conditions.

The applied current density did not seem to have a significant influence on the oxidative degradation of organics in the studied interval, 125 - 312.5 mA/cm^2. However, small positive effects were observed at higher currents regarding the COD reduction rate at low values and the TOC reduction over a single passage at the start of experiments.

Within the studied superficial velocity range through the cell, 2.4 - 19.0 cm/s, the best possible reduction in TOC of a single passage was achieved at the lowest superficial velocity. This is probably due to that the residence time is longer resulting in a more efficient degradation of organics. Generally, the TOC reduction rate at the start of experiments was rather low. The unexpectedly low reduction rate at the start shows that the initial organic compounds are rather resistant to oxidation. A possible explanation of this behaviour is provided by assuming that the compounds turn into relatively stable intermediate molecules, which still have high carbon contents. These intermediate molecules can then be oxidized easier to carbon dioxide.

Experiments have shown that the current efficiency was consistently low. This behaviour is in line with the observations regarding a very powerful evolution of hydrogen and oxygen after cell passage. Accordingly, a very small fraction of the cell current was used for an organic compound removal. The current efficiency depends to a great extent on the cell configuration, mainly the inter-electrode spacing and is therefore not that alarming. This is owing to the used cell, which was not optimized for the aim of the study. It was desirable with a smaller gap between the anode and the cathode but this was not possible due to the construction of the cell.

It has not been possible to follow the destruction of organic complexing agents. An incomplete oxidative degradation of organics could result in the formation of new strong complexing agents, for example carboxylic acids. However, since the organic contents in whole decreased to the lower detection range limit, 3 mg/l during several experiments, it is reasonable to assume a significant reduction of organic complexing agents as well.

Furthermore, the use of hydrogen peroxide in combination with electrochemical treatment seems to increase the TOC reduction rate in the beginning of the treatment but does not shorten the total treatment time. In other words, the lower detection range limit was not reached more rapidly with the use of H_2O_2. Moreover, experiments have shown that the technology seems to effectively treat low organic loads with the same achieved organic reduction over a single passage as treatment of more concentrated streams.

Even though the feasibility study indicates a promising use of BDD electrodes, further research and investigations are required in order to develop a future large-scale treatment process.

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1 Introduction

Most energy production processes, effects the environment in different ways. Nuclear power production comes off well from the environmental point of view in comparison with other techniques for producing energy. A modern nuclear power plant does not, for example, release any greenhouse gases. However, due to radiation risks, environmental requirements from authorities are strict.

According to the environmental management systems EMAS[1] and ISO 14001[2], it is important with continuous work for reducing the environmental impact from nuclear power. Environmental work includes for example emissions of radioactive substances to air and water and the phase-out of chemical products classified as environmentally hazardous. In order to create opportunities for reducing emissions of radioactive substances to the environment it is important to remove organic matter from radioactive waste streams. This is due to problems with fouling of cleaning equipment such as filters, membranes and ion exchange resin. Another reason is that complexing agents have the ability to form neutral complexes with nuclides. This means that the ion exchange resin does not adsorb the complexes with the same effectiveness as if the nuclides were presented as ions. However, the most important aspect is that organic substances could act as carriers of radioactive nuclides in the final repository of radioactive operational waste.

The nuclear power plant Ringhals has realised the potential of a new electrochemical method for destruction of organics in water. This is since several studies have shown that the use of a boron-doped diamond (BDD) anode can be an effective method of wastewater treatment for industrial effluents. The need for an investigation of the effects of this method has resulted in this master's thesis. The study has been carried out at Ringhals by supervision from the division of Nuclear Chemistry[3] at Chalmers University of Technology.

1.1 Problem Background

In nuclear power production, neutrons are consumed in the fission process and together with fission fragments new neutrons are released forming a nuclear chain reacting system. The operating nuclear power plants in Sweden have light water moderated and cooled reactors. This means that water is used, both to produce thermal neutrons and to maintain a stable operating temperature in the reactor. Neutrons are slowed down (thermalised) since the probability to induce fission reactions increases with lower neutron energy. [Ref B.1]

Wastewater effluents within Ringhals contain a minor amount of radioactive elements when it is released to the surrounding sea. The radioactive substances originate from the fission and activation processes and it is of importance to treat nuclear waste streams from radioactivity before it is released to the sea.

[1] Eco Management & Audit Scheme
[2] International Organization for Standardization
[3] Nuclear Chemistry at Chalmers belongs to the Department of Chemical and Biological Engineering

For an efficient treatment with purification technology such as membrane filtration and ion exchange processes, it is an advantage to remove organic substances in advance, especially organic complexing agents. This is due to several reasons. First, membranes, filters and ion exchange resin tend to become deactivated or fouled by organics during use, which lowers the effectiveness and shortens the useful lifetime and capacity. This is a major problem, especially with charged organic substances.

Furthermore, complexing agents have the ability to form neutral complexes with nuclides and as a consequence, the ion exchange resin does not adsorb the complexes with the same effectiveness as if the nuclides were presented as ions. This may give rise to radiotoxic problems.

The Swedish nuclear fuel and waste management company, SKB[4], issues regulations regarding the storage of organic chemicals in the final deposit. Due to the future risk of leakages where organics could acts as carriers of long-lived radioactive nuclides, regulations from SKB force the nuclear industry in Sweden to find an applicable method to reduce the organic content in the final waste. It is of special interest to find a method suitable for destruction of organic complexing agents.

SFR[5] is a final disposal for radioactive operational waste, which has a low or intermediate level of radioactivity and a short half-life. SFR is situated near the nuclear power plant in Forsmark. Residual products from treatment of nuclear wastewaters at Ringhals will be stored here but strict regulations according to the contents of organic matter, especially organic complexing agents makes it necessary to decompose and reduce the contents before transportation to SFR.

In the final repository, pH will be high. Under these conditions, cellulose will degrade to isosaccarine acid, ISA, which is known to be a strong complexing agent. Organic complexing agents such as EDTA and NTA have similar properties as ISA and are widely used in detergents. The most common used organic complexing agent in Ringhals is trisodium nitrilotriacetate, abbreviated NTA. [Ref R.1]

Carboxylic acids as oxalic acid, citric acid, maleic acid and furmaric acid are also known to have complexing properties. Mainly oxalic acid and citric acid are found in nuclear waste streams at Ringhals. Appendix IX present the amount of organic complexing agents from detergents, stored in SFR-1 after use.

In the study, destruction of organics was investigated by anodic oxidation using a BDD electrode.

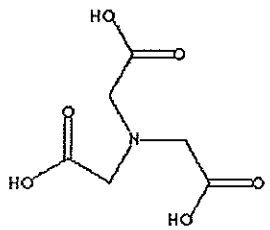

Fig 1.1. Picture of a NTA molecule

[4] Swedish: Svensk Kärnbränslehantering AB
[5] Swedish: Slutförvar av radioaktivt driftavfall

1.2 Purpose

The purpose of this master's thesis was to perform a feasibility study of the electrochemical oxidation method, with emphasis on decomposition and reduction of the content of organic substances in nuclear wastewaters. A study of the organic matter decomposition has been done using a pilot plant rig at Ringhals.

It was investigated whether it is possible to treat water streams directly due to low concentrations of organics and high flow rates or if it is necessary to concentrate streams through cross flow filtration, evaporation, electrical ion exchange or other processes before the electrochemical treatment.

This work should result in a recommendation whether the use of a BDD electrode is a suitable treatment method for Ringhals and if it is worth further investigations and research in order to plan for a future large-scale plant. Moreover, it should give guidance in the field of controversy surrounding the best choice of technology for destruction of organics in radioactive waste streams.

Experiments have also been done in order to evaluate the use of hydrogen peroxide in combination with electrochemical treatment.

1.3 Delimitations

To match the available amount of time with the fulfilment of the purpose stated above it has been necessary to make delimitations. The collection and interpretation of economical data have therefore not been focused on in this study.

Moreover, the oxidation mechanisms have not been studied in the work. This means that for example the production of new complexing agents not could be excluded. Optimization with respect to temperature has not been done and further investigations in regard to the limiting current density are recommended.

In addition, due to time limitations, no evaluation and detailed comparisons with currently applied water treatment techniques has been done. Though, a brief discussion of some of the existing technologies for wastewater treatment and their limitations are described.

As well, no experiments have been carried out in order to compare the reduction of organic substances with the use of different anode materials. The work was aimed at studying the decomposition of organics at a BDD surface. The option of using BDD as cathode has not been explored.

2 Characterisation of Wastewater Streams in Ringhals

Wastewaters from sinks, floor-drains, laboratories and decontamination facilities contain different kinds of organics. Another source of importance is the effluent from the laundry where the protective clothing is cleaned from radioactive particles. The organics originates mainly from washing agents but traces from lubricants, grease and oil also occur in streams. Organics from detergents can cause irreversible damage to membranes that are used in almost all membrane filtration techniques.

Complexing agents are extensively used in detergents in order to ensure an efficient washing. They are utilized to form stable water-soluble complexes with metal ions, and thus remove these metals. The complex is a chemical compound whose molecules consist of one or more metal atoms or charged ions joined to organic residues. Complexes may be non-ionic (neutral), anionic or cationic, depending on the charges carried by the central metal ion and the coordinated groups. The total number of points of attachment to the central element is termed the coordination number.

The most widely used organic complexing agent at Ringhals is NTA. The inorganic group of compounds, polyphosphates are also known to be very efficient complexing agents for many metal ions. Both NTA and polyphosphates are found in detergents used at Ringhals. Three waste streams have been studied: the effluent from the laundry, the effluent from the site of decontamination and the effluent from the clean-up at R1.[6]

The amount of washing agents and water used every year in the three streams are described in detail below, table 2.1 - 2.3. [Ref R.1] Model solutions, which should represent the annual mean composition and load of the effluents described in the tables were prepared and subsequently, total organic carbon (TOC), chemical oxygen demand (COD) and pH was measured. Results from the analyses are presented in the same tables. Information about the average NTA concentration is also shown. The prepared solutions did not contain possible organic species from the facilities itself such as oil, grease, lubricants and fibres from protecting clothing.

In chapter 2.4, water analyses of a real wastewater from the laundry are presented. A washing cycle (pre-wash, two main washes and two rinse phases) was analyzed with respect to COD, TOC and BOD-7[7]. The samples were removed from a washing machine the 29th August and originated from a washing set where protective clothing was cleaned. Values shown in brackets are analyzed after passage of a membrane filter with pore size 0.45 μm.

The composition of detergents used in the study is presented in Appendix VIII.

[6] R1 is a shortening for reactor 1.

[7] Biological oxygen demand represents the amount of biodegradable organic material present in a sample of water. BOD is expressed as the mass of oxygen consumed per litre of solution which microorganisms, principally bacteria, consume while degrading organic matter. The analysis is done over a certain time period, commonly seven days, notified BOD-7. TOC and COD are described in chapter 4.1 and 4.2 respectively.

2.1 Effluent from the Laundry

Table 2.1. Consumption of detergents and water at the laundry

Substance	Amount [dm^3/year]
Water	10000000
Clax Delta Free 1DL3	2200
Clax 200S free 2CL3	50
Clax Soft conc 5DL1	220
COD*	64.2 mg O_2 / l solution
TOC*	26.2 mg C / l solution
pH*	10
NTA content	-

* Analyses done on a synthetic model solution

2.2 Effluent from the Site of Decontamination

Table 2.2. Consumption of detergents and water at the site of decontamination

Substance	Amount [dm^3/year]
Water	950000
Jif Cream	144
Sumatox LPH-deko	90
Clax elegant free	75
Induren A	150
Biosafe	240
Detaljtvätt KS 101	250
COD*	262 mg O_2 / l solution
TOC*	124 mg C / l solution
pH*	9.2
NTA content	0.096 mM

* Analyses done on a synthetic model solution

2.3 Effluent from Floor Drains and Sinks at R1[8]

Table 2.3. Consumption of detergents and water at the clean-up at R1

Substance	Amount [dm^3/year]
Water	10000000
Induren A	545
Biosafe	60
Detaljtvätt KS 101**	63
COD*	38.3 mg O_2 / l solution
TOC*	23.2 mg C / l solution
pH*	8.5
NTA content	0.0096 mM

* Analyses done on a synthetic model solution
** Assumption: same amount used, R1 - R4

2.4 Wastewater Analyses from the Laundry

Table 2.4. Water analyses from a washing cycle, 29th August. Values shown in brackets are analyzed after passage of a membrane filter with pore size 0.45 µm.

Washing cycle phase	COD [mg/l]	TOC [mg/l]	BOD-7 [mg/l]
Pre-wash	2152 (1352)	147 (186)	251 (328)
First main wash	544 (272)	83 (70)	> 275 (88)
Second main wash	876 (448)	136 (104)	108 (123)
First rinse phase	314 (188)	55 (50)	83 (68)
Second rinse phase	64 (52)	20 (16)	17 (14)

[8] R1 is a shortening for reactor 1

3 Wastewater Treatment Technologies

3.1 Wastewater Treatment Technologies in General

The choice of wastewater treatment technology depends on the economical performance of the method as well as on the ease of control, reliability, and treatment efficiency.

Regulations from authorities regarding emissions of organics force Ringhals to reach low TOC values in conformity with environmental legislations. This is one reason to reduce the contents of organic matter by means of liquid waste treatment.

In order to create opportunities for an effective, safe final storage of nuclear operation waste in SFR, it is necessary to remove organic substances. This could be done in two fundamental different ways. If possible, it is favourable to remove organics before other treatments to protect filters, membranes and resin from organic contaminants. This requires a capacity to decompose low concentrations in high flow rates.

If the destruction technique cannot treat low concentrations of organics effectively, it is necessary to first concentrate waste streams and subsequently decompose organic substances. However, this would give rise to problems with fouling of purification equipments.

Major disadvantages with treatment technologies used historically are the use of harmful chemicals and the generation of secondary waste streams requiring further treatment or disposal. Indeed, a fundamental quality of a suitable future destruction technology is the lack of secondary waste.

An ideal wastewater treatment method would give rise to a complete degradation of organic contaminants or at least a high degree of destruction. Another important quality is the capability of treating a variety of wastes with varying constituents. Furthermore, the capital and operation costs are of importance.

Generally, it is not fully known or investigated whether what happens with radioactive nuclides in many wastewater treatment technologies. For example, in many incineration techniques such as plasma and supercritical water oxidation, it is likely that some radioactive nuclides would end up in gaseous phase and consequently require further purification treatment.

There is a large quantity of different destruction technologies and the purpose of this chapter is to review some of the existing technologies for wastewater treatment and presenting their limitations and some technical, environmental and economic aspects.

3.2 Chemical Treatment

Chemical oxidation could be used to destroy dissolved organic contaminants. A variety of organics are very reactive with chemical oxidizing agents and a complete degradation, or at least their decomposition into harmless or biodegradable products could be efficiently managed with ozone or hydrogen peroxide. The main drawback of utilising chemicals is that very few agents can be applied in continuous mode, which makes the treatment of larger fluxes complicated. In addition, it might be difficult to reach a high conversion solely with the use of chemicals. This is due to the lack of a very powerful oxidizing capability.

3.3 Advanced Oxidation Processes

An improved removal of dissolved organic carbon can be achieved by means of so called advances oxidation processes. [Ref R.1] All these processes aim at the formation of highly reactive radicals, particularly hydroxyl radicals, which subsequently oxidize organic compounds, independently of their biodegradability.

A radical is a cluster of atoms one of which contains an unpaired electron in its outermost shell. This is an extremely unstable configuration, and radicals quickly react with other molecules or radicals to achieve a more stable configuration.

One example of a technology of interest within this category is a process where one uses ultraviolet radiation in combination with hydrogen peroxide. H_2O_2 is added to the contaminated water and the mixture is fed into one or more chambers where each chamber contains a UV-lamp. UV light ($h\nu$) serves to catalyze the dissociation of hydrogen peroxide to produce hydroxyl radicals.

$$H_2O_2 + h\nu \rightarrow 2\,OH\cdot \qquad \text{[Reaction 3.1]}$$

Radicals react with organic matter, ideally producing carbon dioxide equivalent of total decomposition. Furthermore, many contaminants absorb UV light and undergo a change in their chemical structure. As a result of this, the compounds become more reactive to oxidizing agents. [Ref R.1]

However, using UV radiation in combination with hydrogen peroxide is not a spread or common used technology for wastewater treatment due to several limitations. The key reason is due to requirements of cleaning the lamps periodically because of formation of dirt that decreases the process efficiency.

The Fenton process is another advanced oxidation technology where iron ions are used in combination with hydrogen peroxide. A disadvantage is the formation of sludge. Another interesting example is the Perozon process, which is a combined application of ozone and hydrogen peroxide. The reaction for formation of hydroxyl radicals is then given by

$$2O_3 + H_2O_2 \rightarrow 2OH\cdot + 3O_2 \qquad \text{[Reaction 3.2]}$$

Advanced oxidation processes produce ideally carbon dioxide and water and consequently no hazardous by-products or air pollutions are formed. However, a major drawback is the

continuous demand of chemicals. It is important to mention that advanced oxidation processes are used successfully world wide for wastewater treatment in order to reach results below the environmental reject levels.

3.4 Wet Combustion & Supercritical Water Oxidation

Wet combustion is an oxidation process in liquid phase. Normally, a high temperature and a high pressure are used to initiate a spontaneous combustion of organic compounds. At temperatures higher than 390 °C and pressures more than 22.1 MPa, wet combustion is usually termed supercritical water oxidation. Oxygen is in both cases used as oxidizing agent and the reaction usually takes place in a tube reactor. It is also possible to add an acid to the water sample in order to decompose organics in liquid phase. $HClO_4$ is sometime used in combination with HNO_3.

When water becomes supercritical, the physical properties change dramatically. Organics and oxygen becomes completely soluble, eliminating mass transfer constrains. This means that the reaction rate is extremely fast compared to the slower rate in conventional wet combustion.

3.5 Plasma Incineration

Plasma incineration is a promising water treatment technology. The basic technique is to create a plasma, which means that gaseous molecules become ionized and consequently very reactive to oxygen molecules. Plasma is in other words a gaseous material having free ions and free electrons and could for instance be created by radio frequency wave energy.

The main drawbacks of this technology are that it is not suitable to treat waste streams with a low organic concentration and the production of harmful gases and consequently the need of further gas treatment.

3.6 Electrochemical Organic Oxidation

An electrolytic cell uses electrical energy to produce chemical changes. In other words, electrical work causes an otherwise nonspontaneous chemical reaction to occur. The electrochemical process involves electron transfer and often it is useful to break the redox reaction into half-reactions, one involving oxidation and one involving reduction. The oxidation occurs at the anode and the reduction at the cathode.

The destruction of soluble organics in a variety of waste streams can be achieved electrochemically. Electrolytic technologies have some definite advantages over the traditionally used treatment processes. The primary benefit is that chemical change in an electrochemical process is caused by the ability to add or remove electrons, a non-polluting agent from organic matter. This eliminates the use of redox agents to carry out oxidations or reductions and also eliminates the need for treatment of redox streams.

In general, organic pollutants can be destroyed by a direct anodic oxidation involving simple electron transfer or by an indirect oxidation process. The latter involves the electrochemically generation of powerful oxidants, such as hydroxyl radicals.

The use of electrochemical oxidation of organic pollutants involves high operating costs. [Ref A.4] This is due to the high energy consumption associated with the technology and that the electricity price in many areas is discouraging. Large numbers of electrons are needed to completely oxidize organics to carbon dioxide. However, a nuclear power plant producing electricity can reasonable calculate with a lower electricity prize than the general industry resulting in a more economically attractive cost estimate.

Another aspect on the operation costs are given by the fact that electrochemical reactors normally do not require moving parts, and are thus mechanically simple and of relatively low maintenance. In addition, the lack of required chemicals and catalysts are economical favourable. Moreover, contrary to other techniques or processes like incineration and wet oxidation, electrochemical treatment does not require high temperatures and pressures.

The electrode material is an important parameter since the mechanism and the products of several anodic reactions are known to depend on the anode material. Common used electrodes are for example RuO_2, PbO_2, TiO_2, IrO_2 and platinum. Comparative studies with different electrode materials have been done, which have shown promising results using a BDD electrode. [Ref A.8, A.11] This is due to specific properties of boron doped diamond electrodes.

Ideally, electrochemical oxidation of organic pollutants should result in zero values of TOC.

3.6.1 Properties of BDD Electrodes

Unique electrochemical properties of BDD electrodes are mainly due to the fact that it is a "nonactive" electrode material, which means that it is not oxidizable. Comninellis *et.al.* [Ref A.1, A.2, A.9] have suggested that such electrodes may promote formation of hydroxyl radicals at the electrode surface in a larger extent than active electrodes. Active electrode material can only oxidize organics by direct electron transfer and do not generate a significant amount of hydroxyl radicals, which are non-selective, very powerful oxidizing agents. The generation of hydroxyl radicals results in a more rapid and efficient destruction of pollutants and are generally thought of as a suitable procedure to decompose organic contaminants.

In many cases, direct electrochemical oxidation of organic species using conventional electrodes, such as simple metal or graphite carbon is not possible. This is due to the high potentials required and instead, water is directly split into hydrogen and oxygen. However, BDD electrodes exhibit a wide potential window of water stability, about 3V [Ref I.3] whereby ozone or hydroxyl radicals maybe formed instead of the generation of hydrogen at the cathode and oxygen at the anode. Diamond has the highest overpotential for the generation of oxygen at the anode, considerably higher than for example the one of platinum, where water decomposition occurs at potentials more than 1.5 V. [Ref I.3]

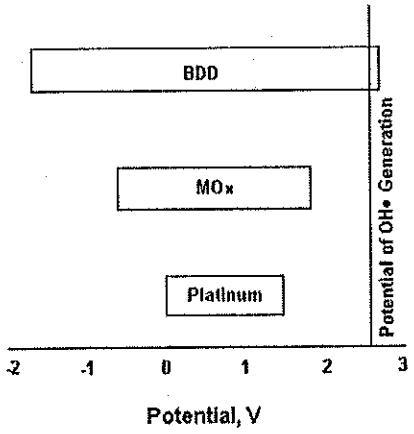

Fig 3.1. Working potential windows of different electrode materials. [Ref I.3]

Hydroxyl radicals are formed by electrochemical oxidation of water at the BDD anode surface.

$$H_2O \rightarrow OH\cdot + H^+ + e^- \qquad \text{[Reaction 3.3]}$$

This reaction together with the direct oxidation is desirable reactions while the oxygen evolution at the anode is undesirable.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{[Reaction 3.4]}$$

Additionally, small amounts of H_2O_2 and O_3 are also known to be produced from water oxidation at BDD anodes

The cathodic reaction is primarily water electrolysis:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \text{[Reaction 3.5]}$$

Electrochemical oxidation using a BDD anode is an environmentally compatible treatment method. Oxidizing species are generated at the anode surface in an electrochemical cell. The oxidizers then attack any organic compound, convert most of them to carbon dioxide, water and inorganic ions at ambient temperature. The destruction method is safe, easy to control and handle, does not require any additional chemicals and due to the conversion of organics to "harmless" gases, the method is promising for future large-scale industrial use.

BDD electrodes present some other useful properties including high resistance to corrosion, high thermal stability and they have also shown a favourable chemical and electrochemical stability during long term operation. [Ref A.7] These unique properties suggest diamond as an excellent electrode material for the anodic oxidation of organics in industrial wastewaters.

4 Analysis Methods

4.1 Total Organic Carbon (TOC)

Generally, total organic carbon analyzers employ the same basic technique. Initially, a liquid sample is introduced to an inorganic carbon removal stage, where acid, often hydrogen chloride is added to the sample in order to oxidize inorganic carbon to CO_2. For example do carbonate ions react with acids. Usually, a shaker removes the produced carbon dioxide.

The remaining inorganic carbon-free sample is then oxidized in a second step and the carbon dioxide generated from the oxidation process is directly related to the TOC in the sample. The oxidation could be initiated in different ways. One way is to use ozone or persulfate in combination with heat, which oxidizes the remaining carbon compounds to carbon dioxide. Another way is to combust the compounds in an oxygen-rich environment. CO_2 produces together with a reagent a specific coloured reaction. The colour change is measured with a spectrophotometer and depends on the concentration of the substance to be determined. The TOC value is expressed as the mass of carbon per litre of solution.

4.2 Chemical Oxygen Demand (COD)

The COD value represents the oxygen requirement of a sample that is susceptible to oxidation by a strong chemical oxidant, in this case, potassium dichromate. Oxidation of most organic compounds is 95-100 % of the theoretical value due to that potassium dichromate is a strong oxidizing agent under acidic conditions. The COD value is expressed as the mass of oxygen consumed per litre of solution.

The generalized reaction of potassium dichromate with organic compounds is given by [Ref B.5]

$$CH_2 + Cr_2O_7^{2-} + 8H^+ \rightarrow CO_2 + 2Cr^{3+} + 5H_2O \qquad \text{[Reaction 4.1]}$$

The oxidation with oxygen is given by:

$$2CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O \qquad \text{[Reaction 4.2]}$$

Consequently, 1 mole of $Cr_2O_7^{2-}$ is equivalent to 1.5 moles of O_2.

Silver sulphate was used as a catalyst and added mercury serve to remove chlorides, which can react with potassium dichromate and generate a too high COD value. Potassium dichromate was reduced forming, Cr^{3+} which has a green colour. The colour change is measured by a spectrophotometer.

4.3 Ion Exchange with Activity Measurements

4.3.1 Theory

In order to evaluate the electrochemical oxidation method, with emphasis on decomposition and thus reducing the content of organic complexing agents in nuclear wastewaters, the uses of ion exchange with activity measurements might be a suitable method as a complement to COD and TOC.

If a radioactive nuclide is mixed with the model solution, an appropriate analyze experiment could be constructed as illustrated in Fig 4.1, with activity measurements in point 1,2,3 and 4. The high level of complexing agents in point 1 would reasonably result in a high activity level after passage of a column filled with ion exchange resin.

If the electrolytic degradation of complexing agents works well, there should be a significant smaller amount of complexing agents in point 3 resulting in a lower activity level in point 4. In other words, the difference in activity between point 3 and 4 would reasonably be larger compared to the difference between point 1 and 2, if the degradation of complexing agents is efficient. The activity level in point 1 and 3 should reasonably be the same.

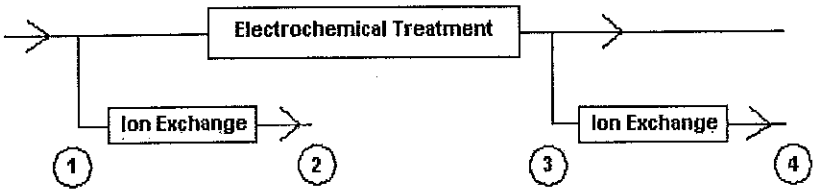

Fig 4.1. Schematic description of an ion exchange experiment with activity measurements.

4.3.2 Preliminary Work

In order to investigate whether the ion exchange experiments work well enough, preliminary work was carried out with model solutions. The analysis of data gathered in the experiment made it possible to come to the decision that it is suitable to use ion exchange with activity measurements as an analyzing tool in this work.

4.3.2.1 Analysis Procedure

Ion exchange experiments were done in two steps. First, 250 ml of a radioactive solution was fed under acidic conditions through a micro filtration system in order to selectively remove non-ion radioactive particles. The solution was fed through a membrane filter with pore size 0.45 μm and after that, a filter with 0.1 μm pore size. Afterwards, pH was adjusted by adding an appropriate amount of 2 M NaOH until pH = 9,3 was reached.

pH has a major impact on properties of complexing agents due to the fact that under acidic conditions, the coordination sites are occupied by H^+ ions, which means that there are no possibilities for other counter ions, i.e. nuclides to form stable complexes with complexing agents. This was the reason why sodium hydroxide was added as described above. Unfortunately, a high pH give rise to sorption effects and hydrolysis of many metals. Hydrolysis means that metal hydroxide or metal oxide are formed and because of that, may precipitate from an aqueous solution.

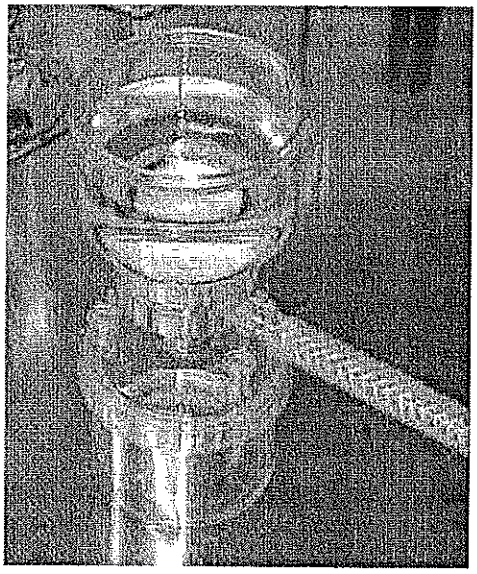

Fig 4.2. Picture of the micro filtration system and the tube connected to a vacuum pump

After the filtration, the solution was split in two equal parts. Chemicals containing complexing agents were added to one half of the solution and the other part remained untouched.

The filtrated solutions were passed through two identical ion exchange columns filled with mixed-bed resin.[9] Five samples were taken to activity measurement, the untouched radioactive solution, the filtrated solution, the filter and the two different samples obtained from passage through the columns.

[9] Mixed-bed resin has the ability to remove both cationic and anionic substances.

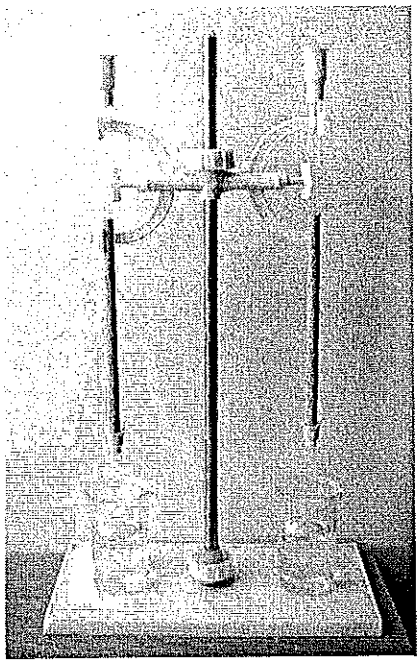

Fig 4.3. Picture of the ion exchange columns

4.3.2.2 Model Solutions

The radioactive model solution used in the preparing work as well as all other radioactive experiments during the study had the composition as follows. *(June 29th)*

Table 4.1. Radioactive test solution

Nuclides	Half-life [days]	Activity, [Bq/kg]
Co-58	70.8	$2.89 \cdot 10^4 \pm 0.01 \cdot 10^4$
Co-60	1924	$1.89 \cdot 10^4 \pm 0.01 \cdot 10^4$
Nb-95	35.2	$4.39 \cdot 10^3 \pm 0.07 \cdot 10^3$
Zr-95	64.4	$8.55 \cdot 10^2 \pm 0.84 \cdot 10^2$
Ag-110m	250	$1.11 \cdot 10^4 \pm 0.02 \cdot 10^4$
Sb-124	60.2	$2.78 \cdot 10^4 \pm 0.02 \cdot 10^4$

As described above, after the filtration, chemicals were added to one half of the solution. This was done in a way that the chemical load and content should represent the annual mean value of the effluent from the site of decontamination. The composition is illustrated in Table 4.2.

Table 4.2. Test solution representing the annual mean composition and load of the site of decontamination. The composition of the used detergents is presented in Appendix VIII.

Substance	Amount [ml]
Jiff Cream	0.02
Sumatox LpH-deko	0.01
Clax elegant free	0.01
Induren A	0.02
Biosafe	0.03
Detaljtvätt KS101	0.03
Filtrated radioactive test solution	112.5
2 M NaOH	15

4.3.2.3 Results and Discussion

Complexing agents presented in the added washing chemicals were primarily NTA and polyphosphates.

Results from the procedure described above are presented in Table 4.3. All activity measurements are expressed in Bq/kg. The standard deviations are not presented but are in each case less than 5 %.

Table 4.3 Results from ion exchange preliminary work

Nuclides	Radioactive solution	After filtration	Filter	AIE*	AIE-CA**
Co-58	$2.89 \cdot 10^4$	$2.51 \cdot 10^4$	$8.59 \cdot 10^3$	$2.75 \cdot 10^2$	$2.25 \cdot 10^3$
Co-60	$1.89 \cdot 10^4$	$1.58 \cdot 10^4$	$5.55 \cdot 10^3$	$1.33 \cdot 10^3$	$2.58 \cdot 10^3$
Nb-95	$4.39 \cdot 10^3$	non detectable	$4.92 \cdot 10^3$	non detectable	non detectable
Zr-95	$8.55 \cdot 10^2$	non detectable	$2.70 \cdot 10^3$	non detectable	non detectable
Ag-110m	$1.11 \cdot 10^4$	$5.91 \cdot 10^3$	$5.41 \cdot 10^4$	$3.47 \cdot 10^2$	$1.64 \cdot 10^3$
Sb-124	$2.78 \cdot 10^4$	$2.50 \cdot 10^4$	$9.47 \cdot 10^2$	non detectable	non detectable
$\sum$	$0.92 \cdot 10^5$	$0.72 \cdot 10^5$	$0.77 \cdot 10^5$	1605***	4830***

* After ion exchange
** After ion exchange, chemicals added
*** Only nuclides mainly presented as ions summarized: Co-58, Co-60 & Sb-124.

The high detected values on the used filter are due to geometric detection effects. This results in a wrong overall activity balance, which means that the activity in the radioactive solution must be the same as the filter and the filtrated solution together. However, a reasonable assumption is that the activity of Zr-95 and Nb-95 must be the same in the filter as in the radioactive solution due to the total lack of activity in the filtrated solution. This means that the detected activity in the filter is 2.14 times too high calculated as an average between the two radionuclides. A correction makes the overall activity balance more correct. For instance, the activity of Co-58 in the radioactive solution is $2.89 \cdot 10^4$ Bq/kg and in the filtrate and filter together $2.91 \cdot 10^4$ Bq/kg, revised as described above. A similar calculation for Co-60 ends up in $1.89 \cdot 10^4$ Bq/kg compared to $1.84 \cdot 10^4$ Bq/kg

It can clearly be stated that Co-58, Co-60 and Sb-124 are presented mainly as ions due to the small removal efficiency of the filter: 13 %, 16% and 10 % respectively. Zr-95 and Nb-95 was due to the high pH, totally hydrolyzed. A fraction of Ag-110m did pass the filter but about 50 % was removed, probably due to sorption effects.

The ion exchange experiments work as expected. The measured activity after the columns is very low indicating a promising effectiveness of the resin. However, the very low activity level after the ion exchange column in the case where strong complexing agents were added is somewhat unexpected.

For Co-58, Co-60 and Sb-124, which are presented mainly as ions, the overall activity level was reduced with 97.6 % when the filtrated solution was fed through the column filled with mixed bed resin while the overall activity level only was reduced with 92.7% for the sample where complexing agents among other compounds were added.

It could be concluded that the smaller reduction in activity probably is connected with the ability of complexing agents to form neutral complexes with nuclides. The complexes are not adsorbed by the resin with the same effectiveness as if the nuclides were presented as ions. The significant difference between the two samples makes it possible to use this experimental method as an analyzing tool in the evaluation of the effectiveness of the BDD technique in order to decompose organic complexing agents.

5 Oxidation using Hydrogen Peroxide

5.1 Theory

Hydrogen peroxide is a very powerful oxidizing agent, which could be used to decompose dissolved organics.

The use of hydrogen peroxide in combination with electrochemical treatment might be interesting due to the formation of radicals. The hydrogen peroxide molecule contains one extra oxygen atom, compared to the more stable water molecule. The bond between the two oxygen atoms, the so-called peroxide bond may broke while two hydroxyl radicals are formed. This is illustrated in reaction 5.1.

$$H_2O_2 \rightarrow 2\,HO\cdot \qquad \text{[Reaction 5.1]}$$

Radicals quickly react with other substances, while new radicals are formed and a chain reaction takes place. It is also reasonable to assume the formation of highly reactive peroxide radicals ($HOO\cdot$) when hydrogen peroxide is present during an electrochemical treatment.

5.2 Preliminary Work

In order to investigate the oxidizing capability of hydrogen peroxide, preliminary work was done. Two concentrations of H_2O_2 were studied, 0.01 M and 0.1 M respectively. The concentrations correspond to a hydrogen peroxide content of 0.03 % and 0.3 % respectively.

5.2.1 Analysis Procedure

500 ml of model solution A was used for each experiment. The test solution represents the effluent from the laundry but with a ten times higher concentration of chemicals compared to the annual mean value. (Appendix II) The solution was synthetic, did not contain possible organic species from the laundry itself such as oil, grease, lubricants and fibres from the protecting clothing.

H_2O_2 was added from a 30 % solution until the desired concentrations were reached. (Appendix VI for calculations)

The beakers containing the model solution and the added hydrogen peroxide were stirred for 5 minutes and subsequently TOCs were measured. TOC in the model solution was measured as a reference.

5.2.2 Results and Discussion

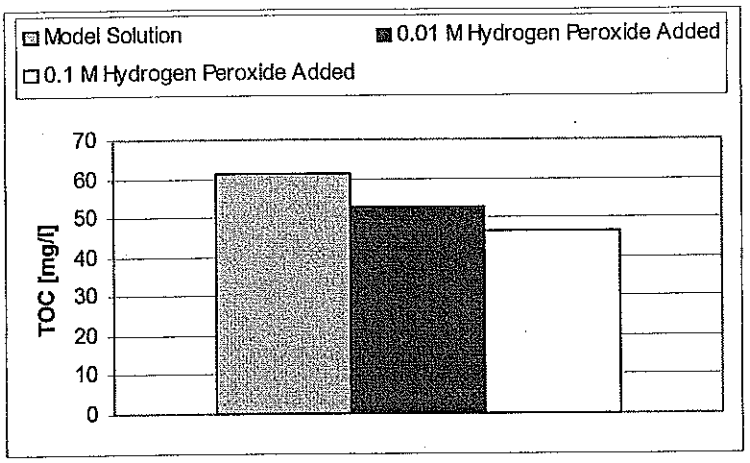

Fig 5.1. TOC measured in three solutions used in preliminary work

The added amounts of hydrogen peroxide influence the TOC values in the expected direction. A reduction of 14% was obtained at the low H_2O_2 concentration and 24% reduction was obtained at the higher concentration. 0.1 M H_2O_2 is a rather high concentration and due to economical aspects it is not reasonable to further increase the concentration in a future large-scale plant.

6 Current Efficiency

Comninellis *et.al.* have suggested that the instantaneous current efficiency, ICE of the anodic oxidation could be calculated by means of the relation [Ref A.1, A.2, A.9]

$$ICE = \frac{(COD)_t - (COD)_{t+\Delta t}}{8 \cdot I \cdot \Delta t} \cdot F \cdot V \qquad \text{[Equation 6.1]}$$

where $(COD)_t$ and $(COD)_{t+\Delta t}$ are the CODs at times t and $t + \Delta t$ expressed in the unit g O_2 per dm^3 solution. I is the current (A), F is the Faraday constant (96487 C mol^{-1}), V is the volume electrolyte (dm^3) and 8 is the equivalent mass of oxygen (g eq^{-1}). The theoretical model that permits the prediction of the ICE is valid during galvanostatic conditions in a batch recirculation system.

An average value of the current efficiency can be determined using: [Ref A.1, A.2, A.9]

$$\bar{\eta} = \frac{\int_0^{\tau} ICE\,dt}{\tau} \qquad \text{[Equation 6.2]}$$

where τ is the duration of the electrochemical treatment.

Equation 6.1 is not a precise measure of the current efficiency but gives a good overall estimation. It is not possible to calculate a totally correct current efficiency with the use of Faraday's law due to the very complex composition of the model solutions used in the work.

7 Statistical Quality Control

There is always some uncertainty in experimental science since experiments cannot be designed for every conceivable contingency. Hence, statistical methods are designed to allow the assessment of the degree of uncertainty presented in data. Decisions are made based on the analyses of data gathered in carefully designed experiments.

The numeric value of distribution parameters gives a quick insight into the nature of the variables.

Three such parameters were considered: the mean $\bar{x}$, the variance σ^2, and the standard deviation, σ. The variance σ^2 is a parameter that reflects the level of consistency. A large positive value is obtained if the random variable fluctuates in the sense that it often assumes values far from its mean.

The variance of a random variable reported alone is not very informative. To overcome this problem, a second measure of variability was employed, the square root of the variance. It is called the standard deviation, σ and has the advantage of having the same unit as the original data. σ and σ^2 are estimated by s and s^2. [Ref B.3]

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \qquad \text{[Equation 7.1]}$$

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n}\left(\bar{x} - x_i\right)^2 \qquad \text{[Equation 7.2]}$$

$$s = \sqrt{s^2} \qquad \text{[Equation 7.3]}$$

7.1 Flow Rate Measurements

Online flow rate measurements were carried out in connection to the electrochemical pilot plant rig. To confirm that the flow rate was recorded correctly, 5 samples were taken when the monitor showed 5.5 l/min. An arbitrary volume was collected and the time was measured. The distribution parameters were calculated resulting in the flow rate 5.52 ± 0.19 l/min, which prove the accuracy of the monitor. Experimental statistical data are presented in Appendix I.

7.2 Total Organic Carbon (TOC)

In order to confirm that the total organic carbon was analyzed with a repeating accuracy and to demonstrate the validity of the used results in the master's thesis, five samples were analyzed and the distribution parameters were calculated. The sample treated during two and a half hour from experiment 1 was used resulting in a TOC value of 9.15 ± 0.15 mg/l. The small standard deviation guarantees repeating accuracy. Experimental statistical data are presented in Appendix I.

7.3 Chemical Oxygen Demand (COD)

The same procedure was carried out with the COD analyzer as described above with TOC measurements. The sample treated during five hours from experiment 1 was used resulting in a COD value of 13.22 ± 0.19 mg/l. The small standard deviation guarantees repeating accuracy. Experimental statistical data are presented in Appendix I.

7.4 Activity Measurements

Activity measurements were performed by HPGe-detectors. A computer program generated nuclide identification reports and the measured activities were presented together with the connected standard deviations. It was assumed that the standard deviations were correctly presented and no values higher than 5 % were used in the report. However, geometric detection effects influence the results. (Chapter 4.3.2.3 for details.)

8 Experimental Details

8.1 Model Solutions

The use of a BDD anode in order to reduce the content of organics was evaluated by experiments with different model solutions with varying organic composition and load.

In general, the destruction of organics could either be done by treating wastewater before any other treatment or by treating concentrated streams obtained through for example, evaporation. The first way to deal with the organic contents problem requires a capacity to decompose low concentrations in high flow rates and the latter involves a capacity to decompose high concentrations of organics, other species and chemicals in low flow rates. The model solutions reflect these possible alternatives by the different organic load and contents.

The studied model solutions had an initial TOC content between 50 and 250 mg/l and initial COD between 160 and 525 mg/l. A real wastewater sample was studied with an initial organic content less than the used model solutions.

Test solution A has the same composition as the effluent from the laundry but a ten times higher concentration of chemicals than the annual mean value. Appendix II describes the composition in detail.

Test solution B represents the effluent from the site of decontamination and has the same composition and load as the annual mean value. Appendix II describes the composition in detail.

Solution A and B were prepared using tap water because this is the water type used at the laundry and the site of decontamination. Using tap water instead of Milli-Q[10] also enhances the conductivity, which is favourable in order to reach high current densities.

Both model solutions were synthetic, did not contain possible organic species from the facilities itself such as oil, grease, lubricants and fibres from protecting clothing.

[10] Milli-Q is a water standard "free" from ions

8.2 Electrode Materials and Cell Design

The anode consists of a metallic base material, in this case Ti with a surface area of 400 cm^2. The electrode has been passed through a chemical vapour deposition (CVD) process where it was coated with a polycrystalline diamond layer doped with boron atoms. The boron atoms substitute for carbon in the diamond lattice at parts per million levels, and serve to increase the electrical conductivity of the diamond film. The diamond layer thickness is up to 5 μm and follows the contours of the base material. The anode was purchased from Condias. [Ref I.4]

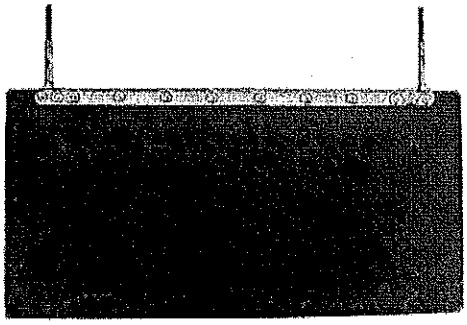

Fig 8.1. Picture of an electrode, possible to use in the electrochemical cell. The electrode has a surface area of 400 cm^2.

The cathode was made of nickel with the same area as the anode. The inter-electrode spacing between the anode and the cathode was approximately 5 mm and both electrodes had a rectangular geometry. It was desirable to use a smaller gap between the anode and the cathode in order to achieve a thinner liquid film but this was not possible due to the construction of the electrochemical cell.

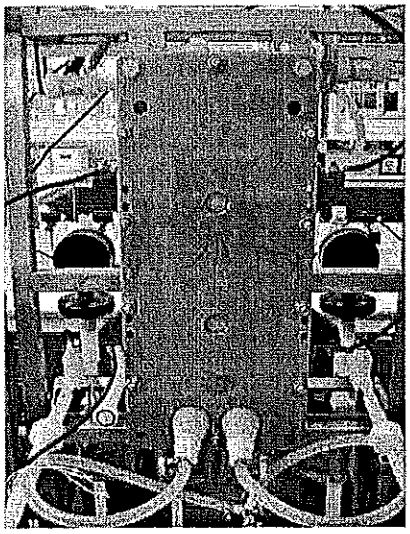

Fig 8.2. Picture of the electrochemical cell, containing two electrodes.

8.3 Electrolytic System

Electrochemical experiments were performed in a one compartment electrochemical cell. The solution was fed into the cell using a centrifugal pump. Electrolysis experiments were carried out at constant currents and no external heating or cooling was used.

The centrifugal pump flow was divided into two streams. One stream going through the cell and one used for internal circulation. This was done in order to supply the centrifugal pump with enough water. It was possible to vary the flow rate through the cell by regulating the ratio between the two streams. The electrolyte was stored in a 20 l tank, stirred with the internal circulation stream and with the returning treated water.

In an early phase of the work, an unknown concentration of hydrogen was present in the chamber, presenting a significant fire and explosion risk. A gas monitor, with a built-in alarm made an audible indication for a highly explosive mixture. Due to this, the pilot plant rig was provided with an off gas chamber and an evacuation system for removal of gases. The gas monitor was purchased from Dräger. (Pac Ex 2) A picture of the gas monitor is presented in Fig 8.3.

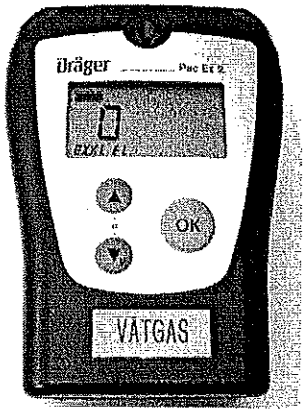

Fig 8.3. Picture of the gas monitor, "Pac Ex 2" from Dräger used for detection of explosive gas mixtures during the experiments.

A schematic drawing of the electrolytic system used in this study is depicted in Fig 8.4. A real photo of the system and its components are shown in Fig 8.5.

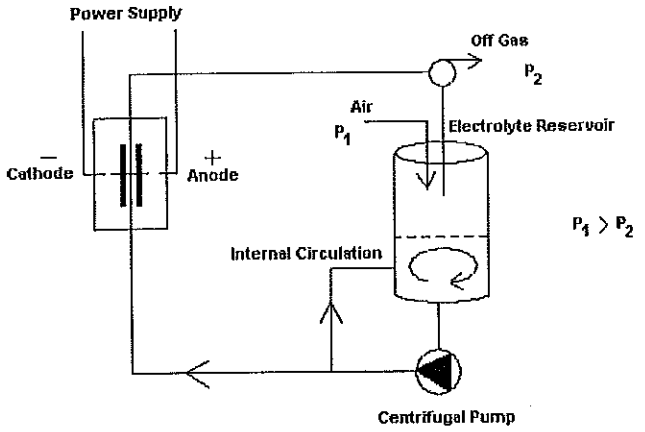

Fig 8.4. Schematic layout of the electrochemical pilot rig used in the study.

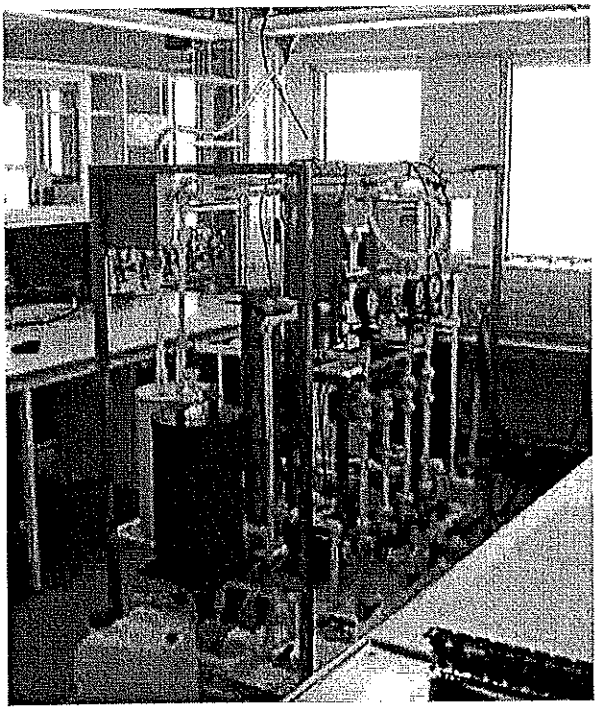

Fig 8.5. Picture of the electrochemical pilot plant rig used in the study.

It should me mentioned that the cell voltage did decrease by time as the electrolysis was advancing, even though the current was constant. This is probably due to formation of protons and hydroxyl ions, which could be seen in reaction 3.3, 3.4 and 3.5. The formation of ions enhances the conductivity. Furthermore, the decreased cell voltage was partially due to the increasing temperature.

It was possible to analyze samples from three different places in the electrolytic system. First, a sample could easily been poured out from the bottom of the electrolyte reservoir. Furthermore, single pass experiments have been carried out by a direct withdrawal of samples before and after the cell passage.

A volume of approximately 40 ml of each sample was used for analysis and consequently removed from the electrolytic system in the experiments.

8.4 Flow Rate versus Linear Velocity

The degradation of organics was studied at different flow rates in the interval 1 l/min - 8 l/min. However, the flow rate is connected to the used cell/cell configuration and is consequently an unsuitable parameter to use. This is because it is not possible to direct translate the investigated flow rate into other cell equipments. Hence, linear velocity is a better parameter to use. Fig 8.6, or Equation 8.1 could be used to translate flow rate into the more general parameter, linear velocity. Appendix VI describes the calculation procedure.

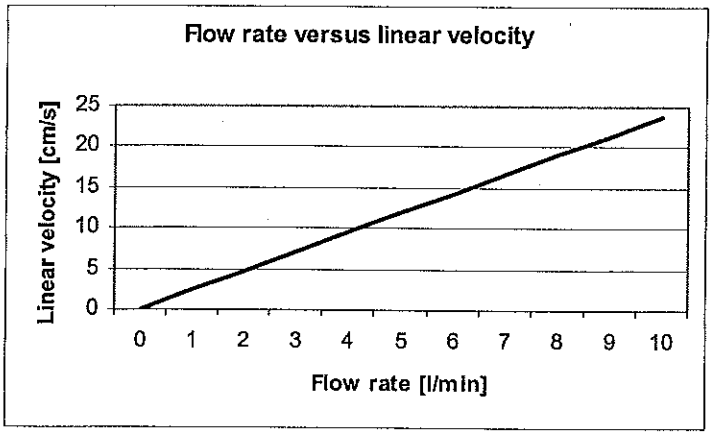

Fig 8.6. Flow rate versus linear velocity

$$Linear\ velocity, [cm/s] = Flow\ rate, [l/\min] \cdot 2.381 \qquad \text{[Equation 8.1]}$$

8.5 Apparatus

Electrochemical measurements were carried out with a rectifier, switch-kraft 15/100 from Kraftelektronik AB, Surte, Sweden. At currents higher than 100 A, another rectifier was used in parallel mode. This rectifier (Power Supply B32-30R, number 1639, Oltronix) gave additionally 35 A.

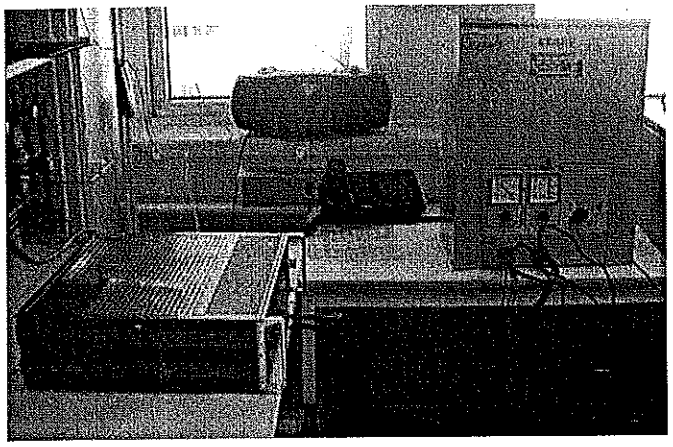

Fig 8.7. Picture of the rectifiers used in the study

The solution pH was measured with a PHM 240 pH-meter from Radiometer Copenhagen. Conductivity measurements were carried out with a conductivity-meter from Kemotron.

The pH-meter and the conductivity apparatus have been calibrated according to specifications from Radiometer and Kemotron.

8.6 Activity Measurements

Activity measurements were done by four different HPGe-detectors with ID-numbers: ORT 36-TP21091 B, PGT DI 291, PGT DI 608 and Canberra BP7103, from Harshaw Chemie BV, Canberra and Princeton Gamma Tech (PGT). The computer program, "Procount ECP", generated nuclide identification reports.

8.7 Spectrophotometric Water Analyses

Spectrophotometric water analyses were done to monitor reduction of chemical oxygen demand (COD) and total organic carbon (TOC) during the study.

Analyses were performed by the Dr. Lange analysis system, which is a complete system with ready-to-use cuvettes. The system consist of two components, the cuvette which contains an accurately amount of a reagent, and a spectrophotometer. The reagent reacts with the water sample, producing a specific colour reaction. The colour change is measured by a spectrophotometer, which was of type, XION 500.

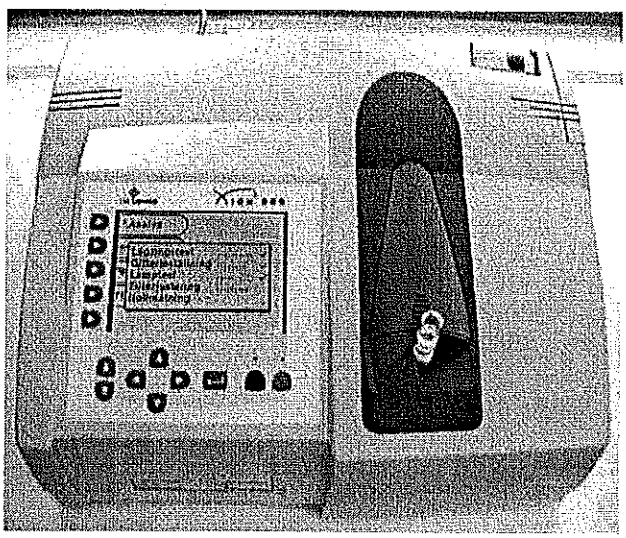

Fig 8.8. Picture of the spectrophotometer

Two types of ready-to-use cuvettes were used for COD analysis. LCK 414 with the defined concentration range: 5 - 60 mg/l O_2 and LCK 614 with the defined concentration range: 50 - 300 mg/l O_2. COD was determined by the dichromate method. Thus, a volume of 2 cm^3 of sample was mixed with the required amount of reagent. The mixture was heated for two hours at 148 °C, and then the absorbance was checked with a spectrophotometer. For TOC analysis, LCK 385 was used in the range 3 -30 mg/l and LCK 386 in the range: 30 - 300 mg/l.

Fig 8.9. Pictures of used TOC and COD cuvettes

To achieve the specified temperatures in the TOC and COD analyses respectively, a heating/cooling apparatus of type HT 200S was used. HT 200S was equipped with a built in timer.

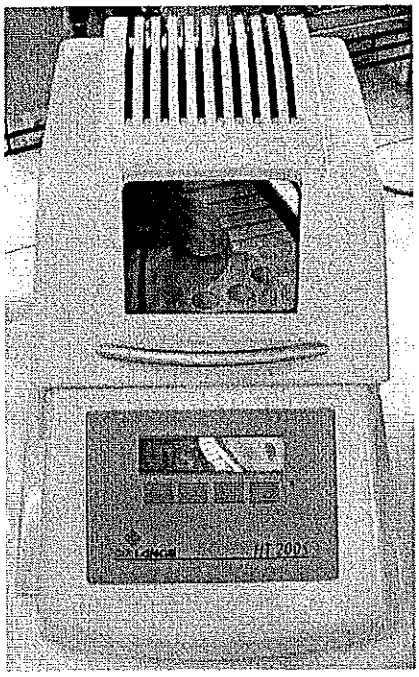

Fig 8.10. Picture of the heating/cooling apparatus.

As described in chapter 4.1, a shaker was used to remove the carbon dioxide in the inorganic carbon removal step in TOC analyses. The type, TOC-X5 was used, depicted in Fig 8.11.

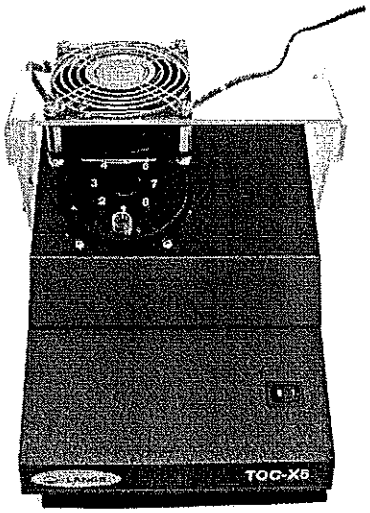

Fig 8.11. Picture of the shaker, TOC-X5

It was possible to obtain result above and below the defined ranges but due to the uncertainty and the lack of reliability, those results were not used in this thesis with a few exceptions. However, this is very clearly pointed out in the presentation of results.

8.8 Ion Exchange Experiments

Ion exchange experiments were carried out with a mixed-bed resin from Ideco Group. (SUPREX - SBMR 72. Code: 120201, Lot No.: 5470502, N'file: 1862)

Membrane filters were purchased from Microfiltration Systems. The diameter was 47 mm and the pore size 0,45 μm and 0,1 μm respectively. The 0,1 μm filter had Lot No.: C24BD and Cat. No.: A010A047A. The 0,45 μm filter had Lot No.: C44HI and Cat. No.: A045J047A.

9 Experimental Problems

Experiments performed with the same model solution should ideally have the same TOC and COD level at t_0 independently of the experimental conditions. However, this was not the case, which makes the evaluation of the decomposition of organics more difficult. The variation of organic load at t_0 when the same solution was used in repeating experiments could reasonably depend on at least three factors.

Firstly, in experiments where different current intensities were used, different amounts of supporting electrolyte were added. At higher currents, more sodium hydroxide was used resulting in a small dilution effect, which consequently should gave rise to lower COD and TOC values.

Secondly, few detergents used in the model solutions were non-water soluble. When the prepared 20 l solution was used in repeating experiments of smaller volumes the different parts could then achieve a slightly different organic load due to mixing problems between water and non-water soluble compounds.

Finally, the pilot plant rig consists of many tubes, pipes and circuits. It is therefore likely that a significant volume of liquid will remain in the rig after the water has been poured out from a previous experiment. It seems reasonable to assume that those memory effects will have an impact on the organic load at t_0.

Due to the evolution of oxygen and hydrogen during electrolysis, it was necessary with good ventilation because of safety aspects. This was done with an off gas chamber and an evacuation system described in chapter 8.3. Despite this, high concentrations were measured above the electrolytic reservoir because of the problem that rising gases from the reservoir should pass the falling treated water. This could be seen in Fig 8.4. Probably, the falling water forced down the rising gases. However, this was easily managed by switching off the centrifugal pump a few seconds during experiments resulting in a very fast removal of gases.

It is noteworthy that the water level in the electrolyte reservoir remained notably constant during all experiments. In other words, no lowering could be observed due to the evolution and removal of gases, particularly oxygen and hydrogen produced from water electrolysis.

At higher flow rates, foam was continuously produced in the electrolytic reservoir. This was only a problem in experiment 8, where the decomposition of organics was studied at a flow rate of 8 l/min. The foam production is also a security problem since foam with high hydrogen content could be explosive.

No external heating or cooling was used during experiments. Though, the electrolysis generates heat itself resulting in problems with condensate in the off gas tube during long treatment periods. TOC and COD analyses were not performed until the samples had reached ambient temperature.

Moreover, in the start of the study, leakages in connection to the cell were a problem. However, this was fixed with gaskets.

10 Experiments and Results

10.1 Experimental Overview

Experiments 1 - 4 were done in order to evaluate the influence of the current. The experiments were done with 50, 70, 90 and 125 A. The experimental conditions were the same except the variation in current.

The degradation of organics was studied in single pass experiments at different flow rates. This was done in experiments 5 - 8.

Experiment 9 was done in order to specifically study the degradation of organic complexing agents and the analysis procedure described in chapter 4.3.2.1 was used.

Experiments 10 -12 were done in order to study the influence of added hydrogen peroxide in combination with electrochemical treatment. Experiment 10 was performed with an electrochemical treatment solely. Experiment 11 was done in the same way as experiment 10 but with an added amount of hydrogen peroxide. Experiment 12 was done for the sake of comparison, under the same experimental conditions but without electrochemical treatment.

All experiments done in the master's thesis were based on model solutions representing appropriate effluents within Ringhals. However, the test solutions only represented the chemical load and contents regarding the detergents and not temporarily, varying contaminations as for example, lubricants, grease, oil and fibres from clothes. However, as a final experiment a real sample was analyzed from the effluent of the laundry and the conditions as well as results are presented in chapter 10.6, experiment 13.

10.2 Experiment 1 - 4

7 litres of test solution A was used for treatment over a 7 h period and the flow rates were between 4.5 - 5 l/min. Five samples were analyzed at different time intervals: 0 min, 30 min, 150 min, 300 min and 420 min. The samples were removed from the bottom of the electrolytic reservoir. 2 M NaOH was added as supporting electrolyte until the conductivity was sufficient to reach the desired current intensities.

The solutions were electrolyzed at a constant current of 50 A, corresponding to 125 mA/cm^2, 70 A, corresponding to 175 mA/cm^2, 90 A, corresponding to 225 mA/cm^2 and in the fourth experiment, the solution was electrolyzed at a constant current of 125 A, corresponding to 312.5 mA/cm^2.

The added amount supporting electrolyte was 250 ml, 350 ml, 400 ml and 700 ml 2 M NaOH in experiment 1, 2, 3 and 4 respectively.

The initial cell voltage for all four experiments was at the start approximately 15 V and by time as the electrolysis was advancing, it decreased to a final value of approximately 10 V.

CODs and TOCs are plotted as a function of specific charge for each experiment. This is shown in Fig 10.1, 10.3, 10.5 and 10.7. ICE's have been calculated and are shown in Fig 10.2, 10.4, 10.6 and 10.8 as a function of specific charge.

Data are presented in detail in Appendix III.

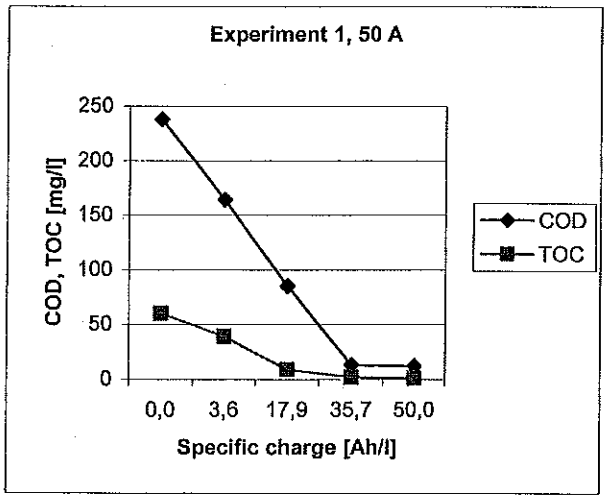

Fig 10.1. Experiment 1. COD, TOC as a function of specific charge

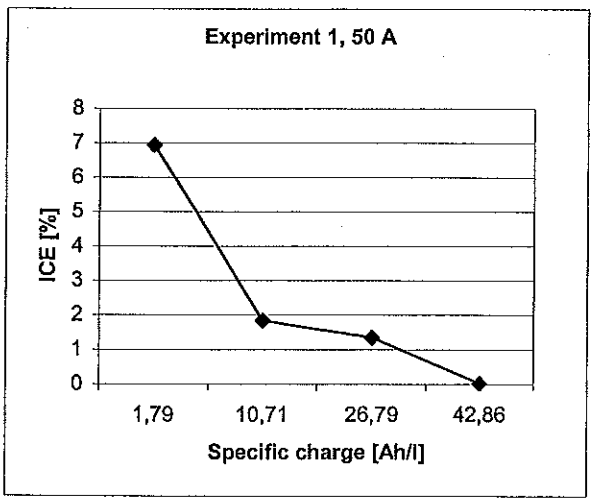

Fig 10.2. Experiment 1. ICE as a function of specific charge

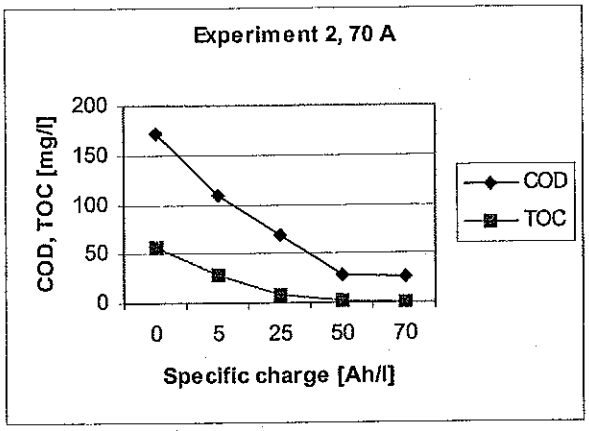

Fig 10.3. Experiment 2. COD, TOC as a function of specific charge

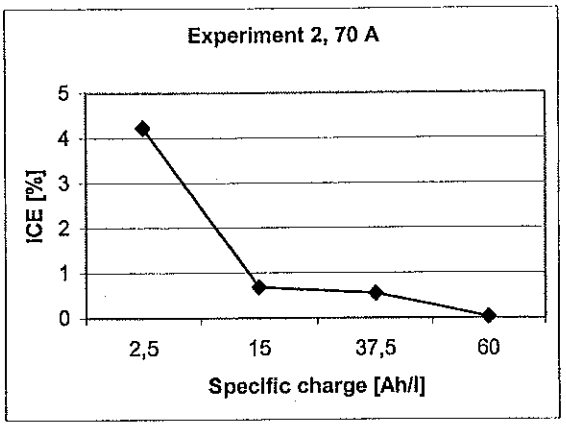

Fig 10.4. Experiment 2. ICE as a function of specific charge

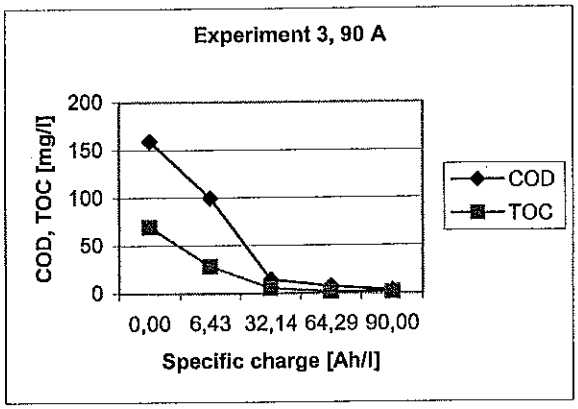

Fig 10.5. Experiment 3. COD, TOC as a function of specific charge

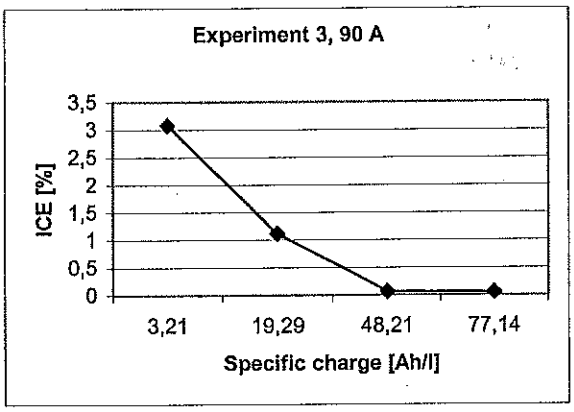

Fig 10.6. Experiment 3. ICE as a function of specific charge

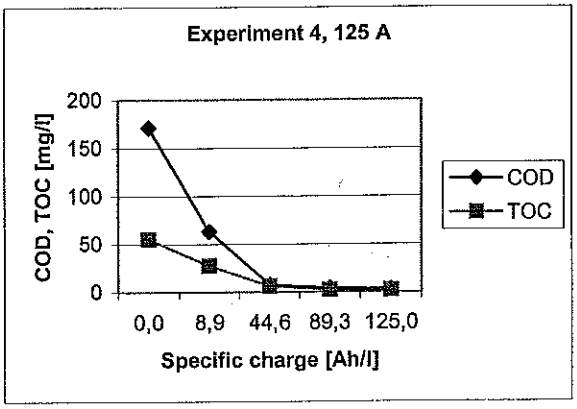

Fig 10.7. Experiment 4. COD, TOC as a function of specific charge

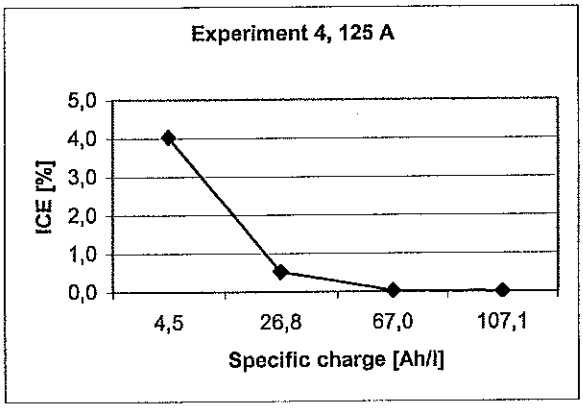

Fig 10.8. Experiment 4. ICE as a function of specific charge

Chemical oxygen demand (COD) offers organic contamination information. However, total organic carbon (TOC) provides a more direct expression of the organic chemical content of water compared to COD. This is because of that the strong oxidizing agent used in COD analyses not is selective to organic matter.

In Fig 10.9, TOC from experiment 1, 2, 3 and 4 are shown as a function of treatment time.

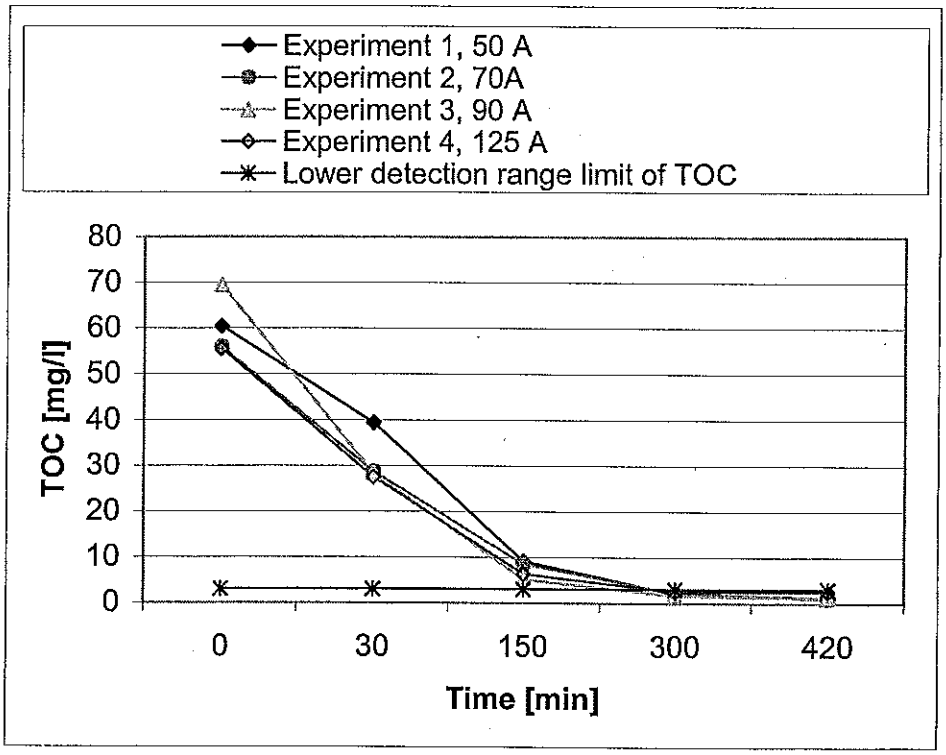

Fig 10.9. TOC from experiment 1, 2 and 3 as a function of treatment time

During the first 150 minutes of treatment, a TOC level below 10 mg/l was reached regardless of the operating conditions. The rate of decomposition is reasonably linear during this time period and with the help of *Microsoft Office Excel*, a trend line shows a TOC reduction rate as shown in Table 10.1:

Table 10.1. TOC reduction rate during 150 minuets of treatment.

Current [A]	TOC reduction rate [mg/l,min]
50	0.33
70	0.31
90	0.43
125	0.32

For the same time period, a trend line shows a COD reduction rate as shown in Table 10.2.

Table 10.2. COD reduction rate during 150 minuets of treatment.

Current [A]	COD reduction rate [mg/l,min]
50	1.0
70	0.7
90	1.0
125	1.1

For all experiments, it is important to emphasize that the last two TOC values representing the samples analyzed after 5h treatment and 7 h treatment respectively are not valid due to the fact that they are below the lower measuring range limit. Though, it could be concluded that they are below 3 mg/l. This could clearly be seen in Fig 10.9.

Table 10.3 summarizes the average values of the current efficiencies calculated on the basis of five hours treatment. The average value of the current efficiency was calculated according to Equation 6.2

Table 10.3. Average value of the current efficiency for experiment 1, 2, 3 and 4

Current [A]	Average current efficiency [%]
50	2.1
70	0.97
90	0.79
125	0.63

10.3 Experiment 5 - 8

7 litres of test solution A was used for treatment over a 4 h period. The effects of a single passage were investigated within the flow rate range 1 l/min - 8 l/min. 400 ml 2 M NaOH was added as supporting electrolyte. The solution was electrolyzed at galvanostatic conditions with a current of 90 A corresponding to the current density, 225 mA/cm^2.

The initial cell voltage for all four experiments was at the start approximately 15 V and by time as the electrolysis was advancing, it decreased to a final value of approximately 10 V.

Eight samples were analyzed for each experiment regarding TOC at four different time intervals: 0 min, 30 min, 120 min and 240 min. Samples were removed just before and just after the electrochemical cell in order to study the oxidation of a single passage.

Values of TOCs are plotted as a function of the duration of the experiments in Fig 10.10 - Fig 10.13. The dark blue line represents the TOCs before the cell (high TOC values) and the purple line the TOCs after the cell passage (low TOC values). The horizontal orange line represents the lower detection range limit of TOC, 3 mg/l. The written equations in the plots are connected to the dashed lines, which are trend lines for the TOC reduction based on the values before the cell.

Data are in detail presented in Appendix IV.

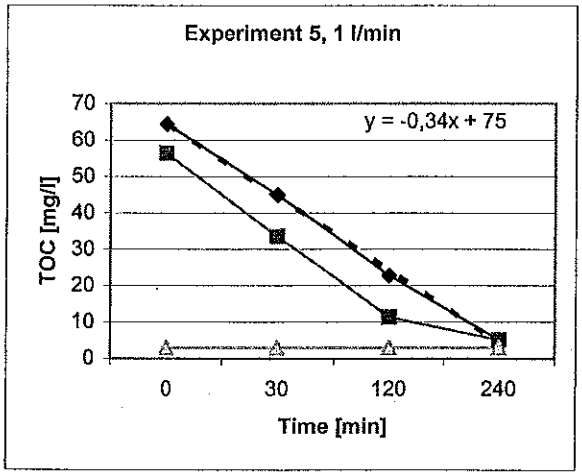

Fig 10.10. Experiment 5. TOC as a function of treatment time. Flow rate: 1 l/min

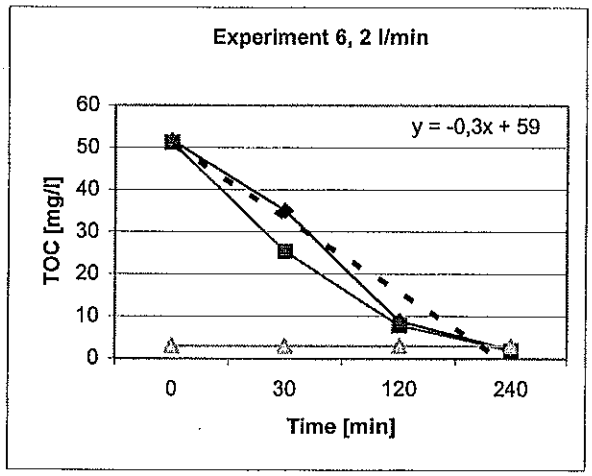

Fig 10.11. Experiment 6. TOC as a function of treatment time. Flow rate: 2 l/min

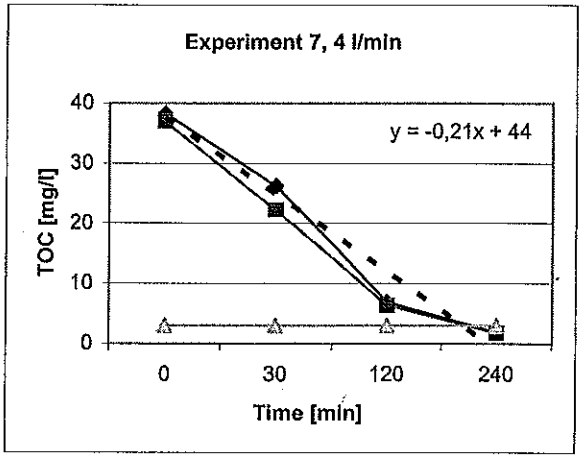

Fig 10.12. Experiment 7. TOC as a function of treatment time. Flow rate: 4 l/min

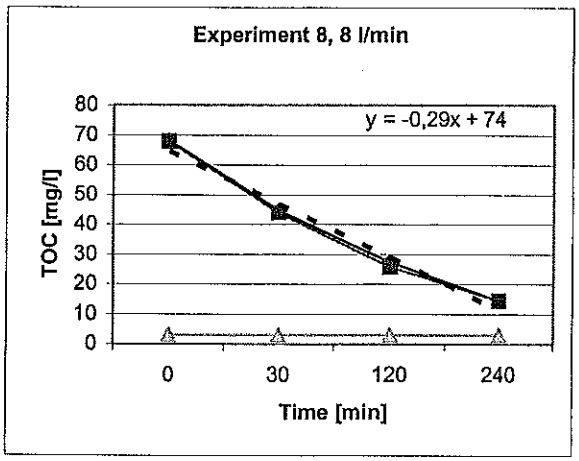

Fig 10.13. Experiment 8. TOC as a function of treatment time. Flow rate: 8 l/min

Trend lines show a TOC reduction rate as follows:

Table 10.4. TOC reduction rate during 240 minuets of treatment.

Flow rate [l/min]	TOC reduction rate [mg/l,min]
1	0.34
2	0.30
4	0.21
8	0.29

Fig 10.14 show the difference in TOC calculated as percentage over a single passage within the flow rate range 1l/min - 8 l/min.

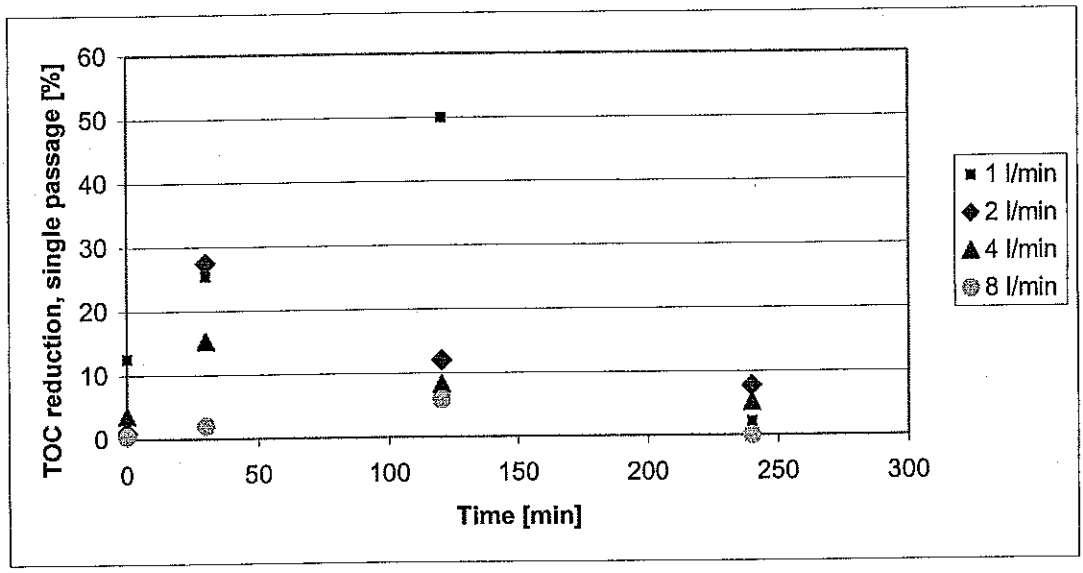

Fig 10.14. Results from single passage experiments. TOC reduction calculated as percentage as a function of time.

10.4 Experiment 9

Experiment 9 was done according to the analyze procedure described in chapter 4.3.2.1.

6.5 litres of test solution B was used for treatment over a 5 h period. The flow rate was approximately 1 l/min and 400 ml 2 M NaOH was added as supporting electrolyte. 500 ml radioactive solution was added with the nuclide content described in Table 4.1. The solution was electrolyzed at a constant current of 90 A, corresponding to 225 mA/cm^2. The initial cell voltage was at the start approximately 15 V and by time as the electrolysis was advancing, it decreased to a final value of approximately 10 V.

20 ml Sumatox LpH was added in order to achieve a high content of complexing agents. Sumatox LpH contains 5 - 15 % of the organic complexing agent, NTA and less than 5 % of the inorganic group of complexing agents, phosphates. The concentration of NTA in the model solution was 1.1 mM which is 11.5 times higher than the annual mean value at the site of decontamination.

Samples were analyzed at t_0 and after 5 hours treatment regarding COD and TOC. The samples were poured out from the bottom of the tank. Ion exchange with activity measurements were done according to the procedure described in chapter 4.3.2.1. A slightly larger sample volume than usual was removed from the electrolytic system due to the use of ion exchange as an analyzing tool.

Table 10.5 show TOC and COD before and after the electrochemical treatment.

Table 10.6 - 10.7 present the activity in points 1, 2, 3 and 4 for Co-58 and Co-60 respectively. (See Fig 4.1). Point (1) and (2) were analyzed at t_0 and point (3) and (4) were analyzed after 5 hours treatment.

Table 10.5. TOC and COD from experiment 9

Time [hours]	COD [mg/l]	TOC [mg/l]
0	525	244
5	20.2	9.22

Table 10.6.

Nuclide	Activity [Bq/kg]
Co-58 (1)	1400
Co-58 (2)	21.7
Co-58 (3)	511.3
Co-58 (4)	2.1

Table 10.7.

Nuclide	Activity [Bq/kg]
Co-60 (1)	1069
Co-60 (2)	43.7
Co-60 (3)	492.7
Co-60 (4)	3.1

Table 10.8 shows the reduction of activity before and after the electrochemical treatment.

Table 10.8. Reduction of activity before and after the treatment

Nuclide	ΔA, point 1 → point 2	ΔA, point 3 → point 4
Co-58	98.5 %	99.6 %
Co-60	95.9 %	99.4 %

10.5 Experiment 10 - 12

Experiment 10, 11 and 12 were done in order to study the decomposition of organic substances with help of hydrogen peroxide in combination with electrochemical treatment.

In experiment 10, 7 litres of model solution A was used for treatment over a 4 h period. The flow rate was approximately 1 l/min and 700 ml 2 M NaOH was added as supporting electrolyte. The solution was electrolyzed at a constant current of 125 ampere corresponding to 312.5 mA/cm^2 and no hydrogen peroxide was added. Four samples were analyzed at different time intervals: 0 min, 30 min, 120 min and 240 min, before and after the cell passage respectively.

Exactly the same experimental conditions were used in experiment 11 except that 23.6 ml 30 w/o H_2O_2 was added, corresponding to 0.03 M (0.09 %).

The initial cell voltage for experiment 10 and 11 was at the start approximately 15 V and by time as the electrolysis was advancing, it decreased to a final value of approximately 10 V.

Experiment 12 was done for the sake of comparison, under same experimental conditions but without an electrochemical treatment. In practise, this experiment was performed in a way that 50 ml solution was poured out from experiment 11 before the electricity was turned on. The solution was stirred in a beaker in four hours and subsequently, TOC was measured.

TOCs in experiment 10 and 11 are plotted as a function of treatment time in Fig 10.15, before and after the cell passage. The lower detection range limit of TOC is also depicted even thought it never was reached during the rather short treatment period. Data are in detail presented in Appendix V.

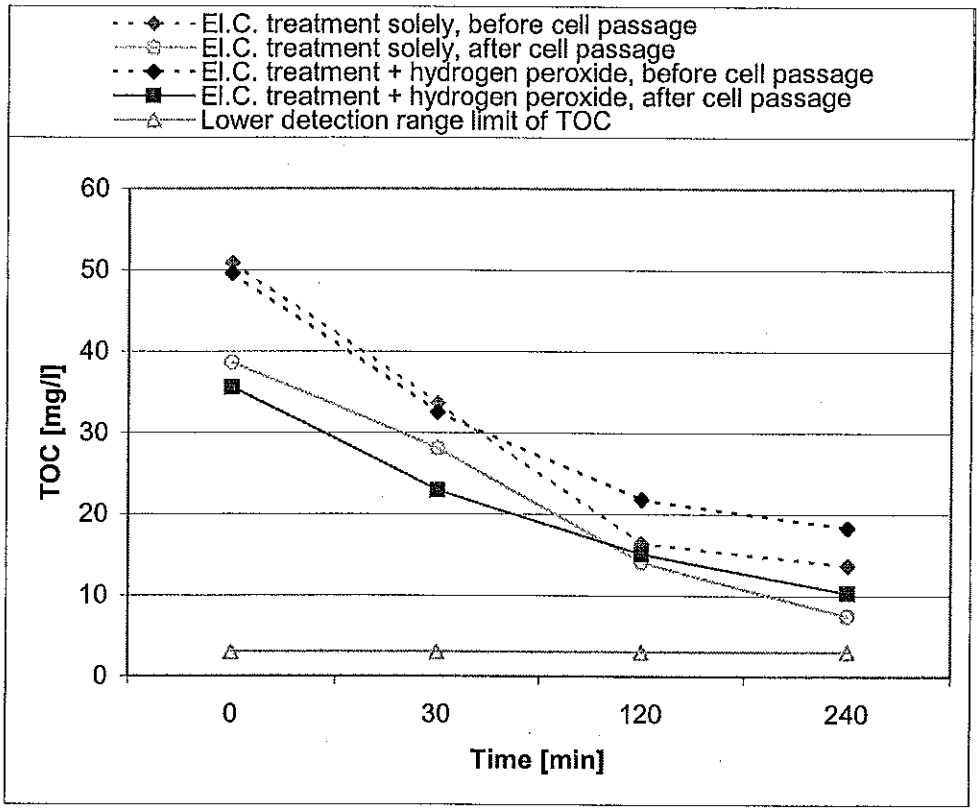

Fig 10.15. TOC reduction as a function of time in experiment 10 and 11.

It is noteworthy that the TOC measured at t_0 in experiment 11 and 12 before the cell passage is without added hydrogen peroxide. TOC analyzed at t_0 after the cell passage in experiment 11 is poured out a very short time after the current was turned on and the hydrogen peroxide was added in the electrolytic reservoir.

In Table 10.9, TOC at the start of experiment 12 and after four hours treatment are shown. No electrochemical treatment was performed.

Table 10.9. Experiment 12, TOC measured at t_0 and after 4 hours treatment.

Time [min]	TOC [mg/l]
0	49.6
240	48.7

Figure 10.16 show the difference in TOC calculated as a percentage over a single passage of experiment 10 and 11.

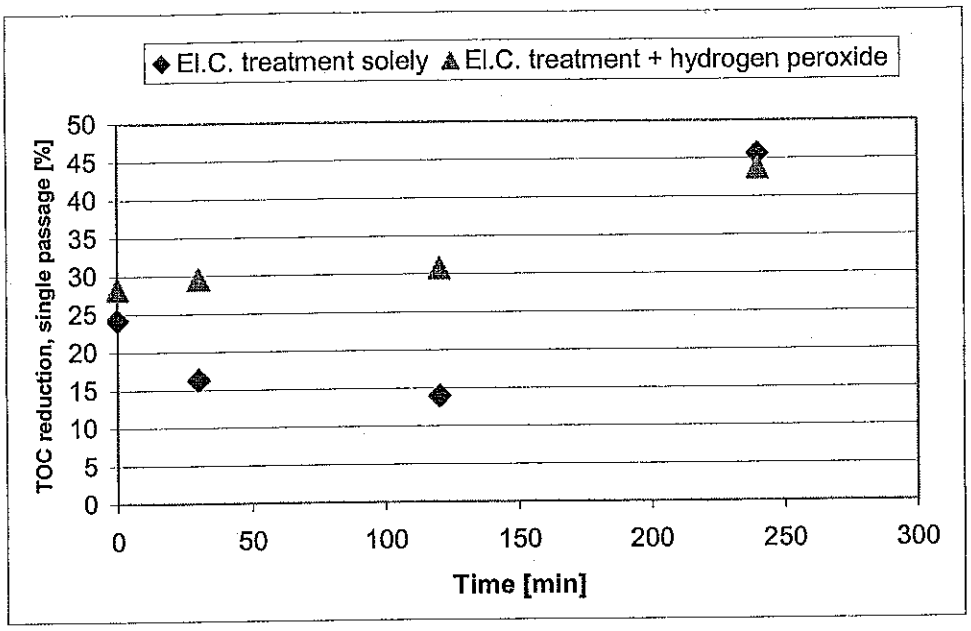

Fig 10.16. TOC reduction calculated as percentage as a function of time.

10.6 Experiment 13

7 litres of a real wastewater was studied in experiment 13. The sample was removed from the effluent of a washing machine the 22nd August. Protective clothing used during the revision of R4[11] was cleaned during the washing set. The water sample consisted of water from a main wash and two rinse phases.

The flow rate was approximately 1 l/min and the total electrolytic treatment was for 2.5 hours. A more concentrated NaOH than usual was used as supporting electrolyte due to unwanted dilution effects. 200 ml 8 M sodium hydroxide was added. The solution was electrolyzed at galvanostatic conditions with a current of 125 A, corresponding to the current density 312.5 mA/cm^2. The initial cell voltage was at the start approximately 15 V and by time as the electrolysis was advancing, it decreased to a final value of approximately 10 V.

Three samples were analyzed at different time intervals: 0 min, 30 min and 150 min, before and after the cell passage respectively.

TOCs are plotted as a function of treatment time, shown in Fig 10.17. Figure 10.18 show the difference in TOC calculated as percentage over a single passage.

[11] R4 is a shortening for reactor 4

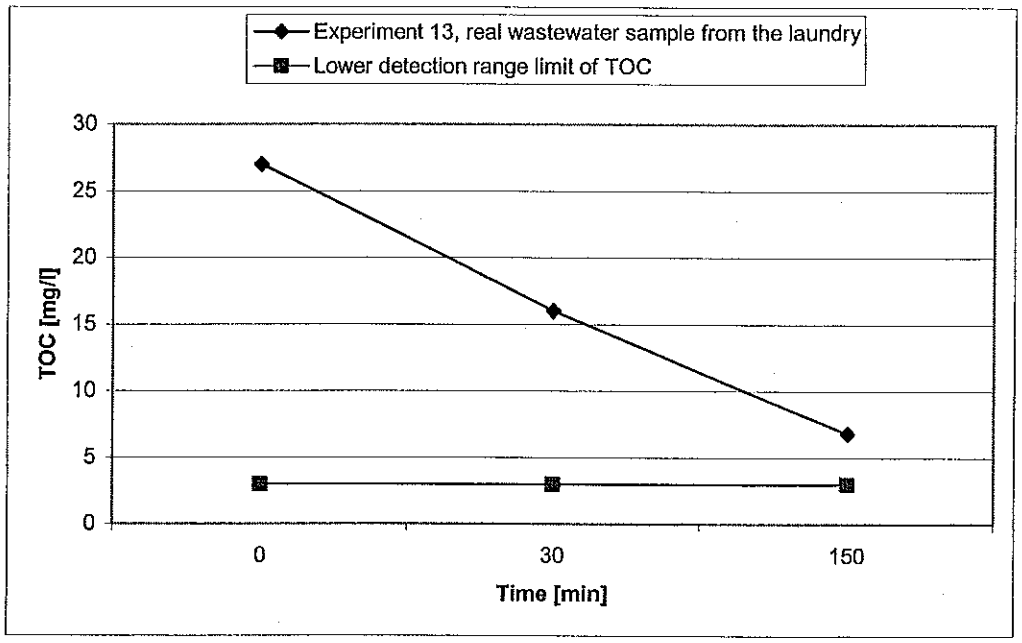

Fig 10.17. TOC reduction as a function of time.

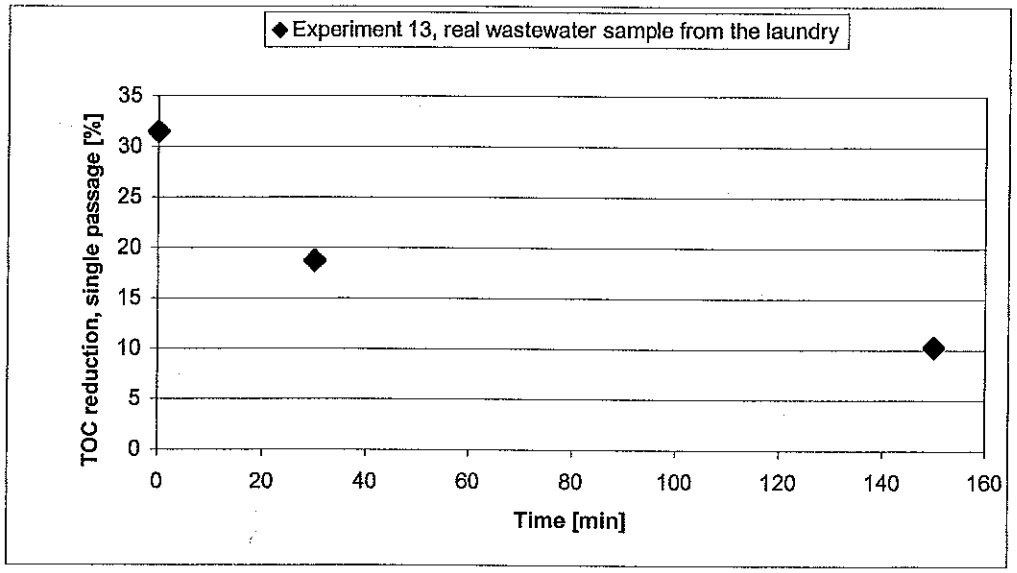

Fig 10.18. Experiment 13, TOC reduction over a single passage as a function of time.

The rate of decomposition is reasonable linear during the 150 minuets of treatment. With help of *Microsoft Office Excel*, a trend lines shows a TOC reduction rate as shown below.

$$TOC: \quad 0.13 \frac{mg}{l \cdot \min}$$

11 Discussion

11.1 Current Influence

The removal off organic pollutants from a simulated wastewater was examined in experiment 1 - 4 with different applied current densities.

When the applied current density was studied in the interval 125 - 312.5 mA/cm^2, the degradation of organics was not significantly influenced by different applied current intensities within the studied range.

The overall TOC reduction rate varies in a very small interval between 0.31 - 0.43 mg/l,min with the best result obtained from experiment 3, where 90 A was applied corresponding to 225 mA/cm^2. However, the slightly better result from experiment 3 is probably due to the somewhat higher initial organic content. Regarding the COD reduction rate, the variation was between 0.7 - 1.1 mg/l,min with the highest value obtained from experiment 4 where 125 ampere was applied. Nevertheless, no significant increased reduction rate regarding TOC and COD could be observed at higher applied currents.

The organic content decreases almost linearly with the specific electrical charge passed until the lower detection range limit of TOC was reached, 3 mg/l. For all experiments, this limit was reached after about the same treatment time, approximately four hours. Hence, in accordance with these experimental facts, present results clearly indicate that the BDD electrode destroyed almost all of the organic matter, independently of the studied experimental conditions.

A different situation was obtained regarding COD. The lower detection range limit of COD is 5 mg/l. This limit was not reached when 50 and 70 A was applied because when CODs of 13 mg/l and 27 mg/l respectively were reached, almost no further reduction in chemical oxygen demand seems to appear. The discontinuing in COD reduction above the lower detection range limit is probably due to that inorganic compounds are present that not could be further oxidized electrochemically under these experimental conditions but anyway gives a contribution to COD. However, when experiments were performed using 90 and 125 A, the lower detection range limit was reached confirming the more powerful oxidizing capability of a higher current density.

11.2 Flow Rate Influence

In a future large-scale plant, it is probably necessary to operate the treatment in a continuous mode due to large fluxes. (5-10 m^3/h) This was the reason why single pass experiments were carried out.

Within the flow rate range 1 l/min - 8 l/min, the best possible reduction in total organic carbon of a single passage was achieved at the lowest flow rate. At 1 l/min, the TOC decreased from 22.8 to 11.4 mg/l in a single passage after two hours treatment, corresponding to 50 %, which is remarkable. It should be noted that further increase of the flow rate did result in a lower reduction percentage. It can be seen that at 8 l/min, the reduction was not at any times more than 6 % over a single passage. In Fig 10.8 - 10.11, this behaviour is clearly demonstrated by the larger distance between the two lines in experiment 5 and 6 compared with experiment 7 and 8.

A possible interpretation of this behaviour is provided by the fact that at lower flow rates, the residence time is longer resulting in a more efficient conversion of organics.

In addition, it seems reasonable to assume that the flow pattern is dependent on the flow rate. However, the cell is developed for multi purpose use and it is difficult to have an idea about the way that the flow rate influences the flow pattern. Generally, higher fluxes cause turbulence, which use to be favourable for the prevention of stagnant zones. Turbulence is even favourable in order to get a good contact between organic compounds and the electrodes.

It is noteworthy that the TOC reduction rate at the start of each experiment is rather low, independently of the flow rate. By time as the electrolysis is advancing, the reduction rate increases the first two hours. The unexpectedly low reduction rate at the start shows that the initial organic compounds are rather resistant to oxidation. A possible explanation for this behaviour is provided by assuming that the compounds turn into relatively stable intermediate molecules, which still have high carbon contents. These intermediate molecules then can be oxidized easier to carbon dioxide.

Due to the fact that the knowledge about the characteristics of the organics is scarce, it is impossible to make a fair judgement about the oxidation mechanism and the rate determining step. However, according to the results, the first oxidation step is probably rate determining.

The overall TOC reduction rates presented as dashed trend lines in Fig 10.10 - 10.13 are in line with the behaviour of the more effective reduction at lower flow rates. The overall reduction rate varies in a very limited interval even though the flow rate doubles for each experiment. It is remarkable that an eight times higher flow rate (8 l/min compared with 1 l/min) in a batch circulation system did result in a smaller overall TOC reduction rate.

On the basis of these results, it is apparent that the anodic oxidation should be performed at a lower flow rate if possible. Another positive aspect related to a lower flow rate is the fact that foam continuously was produced in the electrolytic reservoir at higher flow rates. This is a problem due to operating and security reasons.

The very low TOC reduction rate at the start of each experiment independent of the flow rate is alarming. An operation in continuous mode might be complicated due to this.

11.3 Current Efficiency

Optimizing an electrochemical treatment process requires minimizing unwanted side reactions that decrease the current efficiency. The current efficiency is defined as the fraction of the overall cell current going toward the desired reaction, in this case, an organic compound removal. The formula used in this work for calculation of the ICE, is not a precise measure of the current efficiency but gives a good overall estimation.

It can be seen, in experiment 1, 2, 3 and 4 that the current efficiency was consistently low. This behaviour is in line with the observations regarding a very powerful evolution of hydrogen and oxygen after the cell passage. However, the very low current efficiency is not that alarming due to the fact that it depends to a great extent on the cell configuration. In a future large-scale plant, the overall current efficiency could be improved by means of for example the inter-electrode spacing. Probably a "zero gap" would be positive in the sense of a better current efficiency because this would reasonably result in a thinner liquid film.

The flow pattern is very important and could be managed with the flow rate and the cell configuration. It is desirable to have a liquid film as thin as possible between the electrodes in order to get a good contact between organics and the anode. It is highly probably that the current efficiency could be improved significantly by studying oxidative mechanisms, perform further process optimizations and change the cell configuration to a smaller inter-electrode gap.

It is noteworthy that the treatment results in a gradual decrease of the current efficiency with time. This is not surprising and it seems reasonable to assume that in the beginning of each treatment, more easily decomposable organics results in the highest current efficiency during the first time period in each experiment. More difficultly decomposable organics together with lower concentrations results in a very low current efficiency at longer treatment times.

The average value of the current efficiency defined in *'Equation 6.2'* is highly dependent of the total duration of the electrochemical treatment. Generally, for the same period of electrolysis, the average efficiency decreases with a more positive applied cell current. Although, the conversion efficiency might be higher resulting in a shorter treatment time to reach the desired degree of conversion. In other words, it could be very attractive with a highly positive value on the cell current even with respect to the current efficiency.

The calculated current efficiencies should not be used to give an indication of the operation costs according to the discussion above.

11.4 Decomposition of Complexing Agents

The decomposition of complexing agents was studied in experiment 9.

It has not been possible to prove the destruction of complexing agents from the obtained results. The difference calculated as percentage between the measured activities over the ion exchange column before and after the treatment is basically too small even if it is in the right direction, both regarding Co-58 and Co-60.

It has consistently trough the study been difficult to obtain high activity levels after passage of an ion exchange column even when a high content of complexing agents with strong complexing power were present. The used resin seems to effectively remove the complexes. This was shown in the preliminary work but was even clearer in experiment 9. However, the need to destroy the complexing agents is than even more important due to that these should not be stored together with the used resin containing radionuclides in the final deposit at SFR.

It should be noted that the activity measured in point 1 and point 3 not is the same. This is probably due to the fact that the nuclides have adsorbed to surfaces in the pilot plant rig during the 7 hours treatment.

Since the organic contents in whole decreased to the lower detection range limit, 3 mg/l during several experiments, it is reasonable to assume a significant reduction of organic complexing agents as well. However, it is important to mention that the oxidative degradation of organics could result in the formation of new strong complexing agents, for example carboxylic acids. Though, the production of new complexing agents probably act as intermediate molecules which become further oxidized to carbon dioxide by time as the electrolysis advancing. However, an organic reduction of 50 % of a single passage does not necessary mean a reduction of organic complexing agents.

Furthermore, in spite of the difficulties in obtain evidence for a destruction of complexing agents, it is reasonable to assume that the initial organic complexing agents decompose in line with the loss of TOC. This is due to several reasons.

First, NTA has a similar structure as the more known molecule EDTA that has been used as a complexing agent for more than 50 years. It has been shown that EDTA does not persist in the environment and that it is slowly biodegradable which indicates that the molecule is not that resistant to oxidation. [Ref I.6]

Moreover, the uses of a BDD anode generate radicals and the indirect oxidation is likely to be important. Radicals quickly react non-selectively with other molecules to achieve a more stable configuration. Due to their powerful oxidation capability, it is highly probable that NTA decompose in line with the loss of TOC.

Further investigations are necessary to get evidence for a destruction of organic complexing agents and not organic matter in general. It is important to perform ion exchange experiments with activity measurements under carefully designed experiments where only individual organic complexing agents are present and not a mixture of many compounds presented in detergents. Moreover, phosphates are inorganic complexing agents that probably not could be

further oxidized electrochemically. It is therefore important that phosphates not are present in the investigation of the decomposition of organic complexing agents.

11.5 Hydrogen Peroxide Influence

The use of hydrogen peroxide seems to increase the TOC reduction rate in the beginning of the treatment. The reduction over a single passage calculated as percentage is significantly higher in experiment 11 than 10 the first 120 minuets of treatment. This could clearly be seen in Fig 10.16. The slopes connected to experiment 11 are also slightly steeper the first 30 minuets compared with experiment 10 which are in line with these results. This could be seen in Fig 10.15.

However, something unexpected seems to happen between 30 and 120 minutes treatment where the experiment without added hydrogen peroxide seems to show better results. This is the case both regarding the samples analyzed before and after the cell passage. This can easily be seen in Fig 10.15 where the dashed lines crosses each other after 30 minuets treatment and the continuous lines crosses each other just before 120 minuets treatment. During the entire treatment, the TOC had decreased to 14.6 % of its initial value in experiment 10 and for experiment 11, the achieved value was only 20.8 % of its initial value.

This is surprising results, because it can be seen in Fig 10.16 that during the entire treatment, the reduction is higher in experiment 11 compared to experiment 10 over a single passage independently of the time of treatment except in the last analyzed samples where the reduction calculated as percentage is about the same.

Experiment 12 show that the reduction in total organic carbon is 1.8 % when hydrogen peroxide was used solely. This is a very small reduction which not is in line with the results obtained in the preliminary work described in chapter 5.2. A possible interpretation of this behaviour is provided by the fact that the sample that was poured out and used in experiment 12 not was representative because of insufficient mixing. The hydrogen peroxide was added to the electrolytic reservoir and the sample was removed a short time after, before the cell passage. Because of the very low flow rate, 1 l/min, the sample that was removed from the electrolytic system probably had a too low hydrogen peroxide content. It is therefore more reasonable to assume that the used model solutions are rather easy to oxidize with the help of H_2O_2 which was confirmed in the preliminary work. However, this is a short-time effect and in the long run, electrolysis is necessary to reach low TOC levels and the use of hydrogen peroxide does not shorten the total treatment time.

Nevertheless, it could be concluded that the use of hydrogen peroxide gives desirable results at the start of the treatment, which is very important when a potential large-scale process probably will be constructed in a continuous mode.

The use of H_2O_2 is an efficient way to overcome the problem with a very low TOC reduction rate at the start of each experiment. Additionally, a higher current seems to be positive for the same reason. This is discussed below.

An interesting comparison could be done between experiment 5, 10 and 11 regarding the decomposition of organic substances in a single passage at the start of each treatment, t_0. In the three experiments, the same model solution and flow rate, 1 l/min was used. In experiment 5, 90 ampere was applied resulting in a reduction of TOC from 64.4 mg/l to 56.3 mg/l, equal to 12.6 %. This was a rather low reduction and the reason of this was discussed in chapter 11.2. In experiment 10, exactly the same experimental conditions were used except that the current was increased to 125 ampere. This resulted in a TOC reduction from 50.9 mg/l to 38.6 mg/l, equal to 24.2 %, which is a considerably better situation. In experiment 11, the conditions were the same as in experiment 10 except that 0.03 M hydrogen peroxide was added. This resulted in a TOC reduction from 49.6 mg/l to 35.6 mg/l, equal to 35.6 % which is a drastically improvement from 12.6 % obtained in experiment 5. A high current density in combination with added H_2O_2 is shown to be important and probably necessary if a large-scale continuous process should be constructed in the future.

11.6 Treatment of High versus Low Organic Loads

In experiment 13, a real wastewater from the laundry was studied with an initial TOC content of 27 mg/l. This is the lowest studied initial organic load in the work, about 2 - 3 times less than most other experiments where model solution A was used representing a simulated high-concentrated wastewater from the laundry.

It could be seen in Fig 10.18 that electrochemical oxidation using a BDD anode can treat waste streams with a low organic load with the same effectiveness as more concentrated streams regarding a once through system. Experiment 10 was done under about the same experimental conditions as experiment 13 with the only difference in initial organic load. The initial TOC value of the electrolyte used in experiment 10 was 50.9 mg/l, which is almost twice the load of experiment 13. The TOC reduction calculated as percentage over a single passage at t_0 was 31.5 % with the low organic load compared to 24.2 % when the solution with a higher organic load was treated. In other words, the relative reduction was accordingly higher when a low organic concentration was treated. The case was the same even after 30 minuets treatment. The reduction was than 18.8 % compared to 16.4 % in a single passage.

It should me mentioned that the organic content probably not was the same in the two experiments described above because the real wastewater contained chemical substances and other species from the laundry itself why this not was the case in experiment 10. Furthermore, the reduction in a single passage is highly dependent on the flow rate which fluctuates during electrolysis. Consequently, the flow rate was probably not exactly the same in the two experiments. However, it could definitely be concluded that treatment of low organic concentrations don't seems to significantly differ in effectiveness compared to higher organic loads.

12 Conclusions & Future Aspects

In this work, galvanostatic oxidation experiments were performed to study the removal of organics from aqueous solutions. The studied model solutions had initial TOC contents between 50 and 250 mg/l and initial CODs between 160 and 525 mg/l. The following conclusions can be drawn:

Electrochemical oxidation using a BDD anode can successfully treat dissolved organic compounds with a high degree of destruction. Analyses have shown a decrease in TOC to non-detectable levels during several experiments under varying conditions. The maximum TOC reduction rate was achieved in experiment 9 where TOC decreased from an initial value of 244 mg/l to 9.22 mg/l during five hours treatment. This corresponds to a reduction rate of 0.78 mg/l,min. The COD reduction rate in the same experiment was 1.68 mg/l,min.

The current density did not seem to have a significant influence on the oxidative degradation of organics in the studied interval, 125 - 312.5 mA/cm^2. TOC decreased almost linearly with the specific electrical charge passed until the lower detection range limit was reached, 3 mg/l. This was the case for all experiments independently of the applied current. However, small positive effects were observed at higher currents regarding the COD reduction at lower values and the TOC reduction over a single passage at the start of experiments.

The single passage reduction is highly dependent on the flow rate but the overall reduction rate varies in a very limited interval at different flow rates. The best possible reduction in total organic carbon of a single passage was achieved at the lowest investigated flow rate, 1 l/min. A reduction of 50 % was the best obtained result.

TOC reduction rates at the start of experiments were rather low, independently of the flow rate. This shows that the initial organic compounds are rather resistant to oxidation. However, it is possible to overcome the problem by means of a high current density and even better if hydrogen peroxide is used in combination with a high current density. Generally, the use of hydrogen peroxide seems to increase the TOC reduction rate in the beginning of the treatment but it is a short-time effect and in the long run, electrolysis is necessary to reach low TOC levels. The use of hydrogen peroxide does not shorten the total treatment time.

Experiments have shown that the current efficiency was consistently low. This behaviour is in line with the observations regarding the very powerful evolution of hydrogen and oxygen after the cell passage. The current efficiency depends to a great extent on the cell configuration, mainly the inter-electrode spacing.

It has not been possible to prove or follow the destruction of organic complexing agents. However, since the organic contents in whole decreased to the lower detection range limit of TOC, 3 mg/l during several experiments, it is reasonable to assume a significant reduction of organic complexing agents as well. An incomplete oxidative degradation of organics could result in the formation of new strong complexing agents, for example carboxylic acids.

Due to problems where membranes, filters and ion exchange resin tend to become deactivated or fouled by organics during use it is a major advantage to treat wastewaters in advance if possible. Experiments have shown that electrochemical treatment with a BDD anode seems to

effectively could handle low organic loads with the same achieved organic reduction in a single passage as treatment of more concentrated streams.

Hydrogen is a dangerous, inflammable and explosive gas when it is mixed with air or oxygen. Due to the evolution of hydrogen during electrolysis it is necessary to ensure extensive safety procedures in a future large-scale plant. A gas monitor with inbuilt alarm should be purchased and installed to continuously monitor both hydrogen and oxygen concentrations in the chamber, and provide visible and audible indication of any problems. All users should be fully trained in the use of the equipment, and should be fully conversant with the potential hazards and how to manage associated risks.

Even thought the feasibility study indicates promising use of BDD electrodes, further research and investigations are required in order to develop a future large-scale treatment process. Both electrochemistry and safety issues should be studied. For example may hydrogen evolution be lower with the use of BDD cathodes.

First, it is necessary to study oxidation mechanisms of individual organic compounds under controlled conditions in order to bring improvements to the process in whole. It is important to understand the limiting mechanisms for the organic degradation. For instance, when the dissolved organics are being consumed at the electrode, the concentrations near the surface are diminished and a concentration gradient will form. This could result in a reduced reduction rate because the current might become limited by rate at which the reactants arrive to the electrode by diffusion. Those mechanisms need to be studied.

In addition, further investigations of the influence of hydrogen peroxide are required. It is important to clarify whether the organic oxidation originates mainly from a direct contact with H_2O_2 or the indirect way by formation of radicals. Those investigations are necessary to perform in order to answer the question if hydrogen peroxide is required and economically favourable to use in the process.

Moreover, the influence of the temperature has not been studied in this work. This is essential to carry out together with further process optimizations. It is highly reasonable to assume that the optimizations together with the investigations described above results in a significantly improved process. This will hopefully result in shorter times of treatment and a higher current efficiency ending up in a single treatment process that will economically treat nuclear wastewaters from different sources.

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Appendix I

Experimental data for calculation of distribution parameters checking the rightness of the flow rate monitor.

Sample Number	Time [s]	Volume [ml]	Flow Rate [l/min]
1	10.8	960	5.3
2	11.5	1080	5.6
3	10.2	940	5.5
4	10.8	980	5.4
5	10.4	1000	5.8

Distribution parameters:

$\bar{x} = 5.52$ $\sigma^2 = 0.04$ $\sigma = 0.19$ $n = 5$

Experimental data for calculation of distribution parameters checking the repeating accuracy and the validity of the COD analyzer.

Sample Number	COD [mg/l]
1	13.2
2	13.3
3	13.3
4	12.9
5	13.4

Distribution parameters:

$\bar{x} = 13.22$ $\sigma^2 = 0.04$ $\sigma = 0.19$ $n = 5$

Experimental data for calculation of distribution parameters checking the repeating accuracy and the validity of the TOC analyzer.

Sample Number	TOC [mg/l]
1	9.00
2	9.09
3	9.39
4	9.08
5	9.19

Distribution parameters:

$\bar{x} = 9.15$ $\sigma^2 = 0.02$ $\sigma = 0.15$ $n = 5$

Appendix II

Model solution A

20 l solution representing the effluent from the laundry but with a ten times higher concentration of chemicals than the annual mean value.

Washing Agent	Amount (ml)
Clax Delta Free 1DL3	44
Clax 200S free 2CL3	1
Clax Soft conc 5DL1	4
Tap Water	20000

The main complexing agents used at the laundry are polyphosphates.

Model solution B

20 l solution representing the effluent from the site of decontamination. The solution contains the same load and content of chemicals as the annual mean value.

Washing Agent	Amount (ml)
Jif Cream	3
Sumatox LpH-deko	1,9
Clax elegant free	1,6
Induren A	3,2
Biosafe	5,1
Detaljtvätt KS101	5,5
Tap Water	20000

The main complexing agents used at the site of decontamination are NTA and polyphosphates.

Appendix III

Data from experiment 1

Time [min]	COD [mg/l]	TOC [mg/l]
0	238	60.4
30	164	39.4
150	30.2	9.19
300	13.2	2.06*
420	12.3	1.11*

* Outside defined concentration range

Time [min]	ICE [%]
15	6.94
90	1.84
225	1.35
360	0.02

Conductivity at $t_0 = 8.78\ mS/cm$

Data from experiment 2

Time [min]	COD [mg/l]	TOC [mg/l]
0	172	55.9
30	109	28.8
150	68.1	8.53
300	27.3	2.17*
420	25.6	0.97*

* Outside defined concentration range

Time [min]	ICE [%]
15	4.22
90	0.69
225	0.55
360	0.03

Conductivity at $t_0 = 11.02\ mS/cm$

Data from experiment 3

Time [min]	COD [mg/l]	TOC [mg/l]
0	159	69.4
30	99.8	28.4
150	14.2	5.20
300	7.4	1.61*
420	2.84*	1.22*

* Outside defined concentration range

Time [min]	ICE [%]
15	3.09
90	1.12
225	0.07
360	0.06

Conductivity at $t_0 = 11.29\ mS/cm$

Data from experiment 4.

Time [min]	COD [mg/l]	TOC [mg/l]
0	171	55.5
30	63.4	27.6
150	7.67	6.38
300	4.39*	2.48*
420	3.39*	2.48*

* Outside defined concentration range

Time [min]	ICE [%]
15	4.04
90	0.52
225	0.03
360	0.01

Conductivity at $t_0 = 11.05\,mS/cm$

Appendix IV

Data from experiment 5 - 8.

Experiment 5, 1 l/min			Experiment 6, 2 l/min		
Time [min]	TOC, before [mg/l]	TOC, after [mg/l]	Time [min]	TOC, before [mg/l]	TOC, after [mg/l]
0	64.4	56.3	0	51.6	51.1
30	44.9	33.5	30	35	25.4
120	22.8	11.4	120	8.9	7.83
240	5.16	5.05	240	2.05*	1.89*

* Outside defined concentration range

Experiment 7, 4 l/min			Experiment 8, 8 l/min		
Time [min]	TOC, before [mg/l]	TOC, after [mg/l]	Time [min]	TOC, before [mg/l]	TOC, after [mg/l]
0	38.3	36.9	0	68.1	67.8
30	26.2	22.2	30	44.7	43.8
120	6.89	6.32	120	27.4	25.8
240	1.92*	1.82*	240	14.4	14.4

* Outside defined concentration range

Appendix V

Data from Experiment 10 - 12

Experiment 10

Time [min]	TOC, before [mg/l]	TOC, after [mg/l]
0	50.9	38.6
30	33.6	28.1
120	16.4	14.1
240	13.7	7.45

Experiment 11

Time [min]	TOC, before [mg/l]	TOC, after [mg/l]
0	49.6	35.6
30	32.5	22.9
120	21.8	15.1
240	18.3	10.3

Experiment 12

Sample	TOC [mg/l]
Before added hydrogen peroxide	49.6
After 4 hours mixing	48.7

Appendix VI

Calculation for preparation of 0.01 M H_2O_2 solution. (~ 0.03 %)

Goal: 0.01 M H_2O_2 ↔ 0.34 g H_2O_2 / litre solution {M(H_2O_2) = 34 g/mol}

The weight of 1000 ml 30 w/o H_2O_2 solution is 1110 g.

This means that 0.34/2 g H_2O_2 is obtained from 0.511 ml 30 w/o H_2O_2.

Calculation for preparation of 0.1 M H_2O_2 solution. (~ 0.3 %)

Goal: 0.1 M H_2O_2 ↔ 3.4 g H_2O_2 / litre solution {M(H_2O_2) = 34 g/mol}

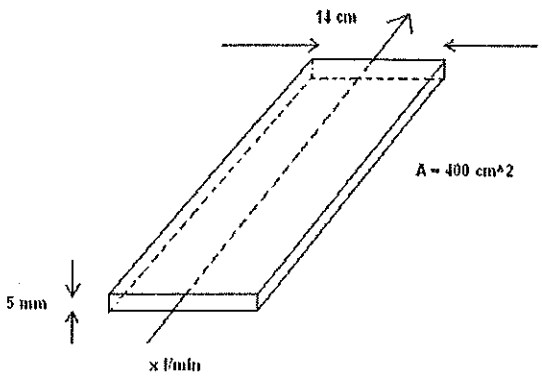
The weight of 1000 ml 30 w/o H_2O_2 solution is 1110 g.

This means that 3.4/2 g H_2O_2 is obtained from 5.11 ml 30 w/o H_2O_2.

Calculation for translation of flow rate into linear velocity

The surface area of each electrode is 400 cm^2. The flux passes between the two electrodes. Hence, the linear velocity is the flow rate, expressed in cm^3/s divided by the cross section area (0.5 cm * 14 cm), shown in the picture below.

Flow rate [l/min]	Linear velocity [cm/s]
0	0.0
1	2.4
2	4.8
3	7.1
4	9.5
5	11.9
6	14.3
7	16.7
8	19.0
9	21.4
10	23.8



Appendix VII

Data from Experiment 13

Experiment 13

Time, [min]	TOC before, [mg/l]	TOC after, [mg/l]
0	27	18.5
30	16	13
150	6.8	6.1

Appendix VIII

Composition of detergents used in the study. [Ref R.1]
The composition is incomplete due to scarce information.

Clax Delta free 1DL3
Sodium/Potassium metasilicate, 15-30 % (CAS nr: 6834-92-0 and 1312-76-1)
Potassium hydroxide, 1-5 % (CAS nr: 1310-58-3)
Sodium triphosphate, 5-15 %
Phosphonic acid, 0.2-1 %

Clax 200S free 2CL3
Nonionic surfactant (CAS nr: 68131-39-5)

Clax Soft conc 5DL1
Hydroxyethylmonium methosulfate, 5-15 % (CAS nr: 91995-81-2)
Isopropyl alcohol, < 5 % (CAS nr: 67-63-0)

Jif Cream
Sodium carbonate, 2-5 % (CAS nr: 497-19-18)
Anionic surfactant, 2-5 % (CAS nr: 1886-81-3)
Nonionic surfactant, 0.2-1 % (CAS nr: 68131-39-5)
Soap/different polymers, 0.2-1 %

Sumatox LPH-deko
NTA, 5-15 % (CAS nr: 5064-31-3)
Phosphate, 5-15 % (CAS nr: 13845-36-8)
Potassium carbonate, 2-5 %

Clax elegant free
Anionic surfactant, 5-15 % (CAS nr: 68585-47-7)
Nonionic surfactant, 15-30 % (CAS nr: 68002-97-1)
Polycarboxylate

Induren A
Sodium metasilicate, 2-3 % (CAS nr: 6834-92-0)
NTA, 3-5 % (CAS nr: 5064-31-3)
Potassium monodecyl phosphate ester, 2-3 % (CAS nr: 68427-32-7)
Ethoxylated alcohols, C9/C11, 3-5 % (CAS nr: 68439-46-3)

Biosafe
Paraffinic hydrocarbons, 50-100 % (CAS nr: 64771-72-8)

Detaljtvätt KS 101
Sodium metasilicate, 3-5 % (CAS nr: 6834-92-0)
NTA, < 5 % (CAS nr: 5064-31-3)
Phosphates, < 5 %
Nonionic surfactant, < 5 %

Appendix IX

Organic complexing agents presented in detergents, stored in SFR-1 after use. The amounts are from a single year (1998) and originate from all Swedish nuclear power plants. [Ref R.2]

Substance	Amount [kg]
EDTA	0.02
NTA	16.8
Citric acid	39.3
Oxalic acid	12.0

SKI[12] issues rough regulations regarding the total amount of cellulose in SFR-1. Approximately 1100000 kg cellulose will be stored in SFR-1. [Ref R.2]

[12] Swedish: Statens kärnkraftsinspektion