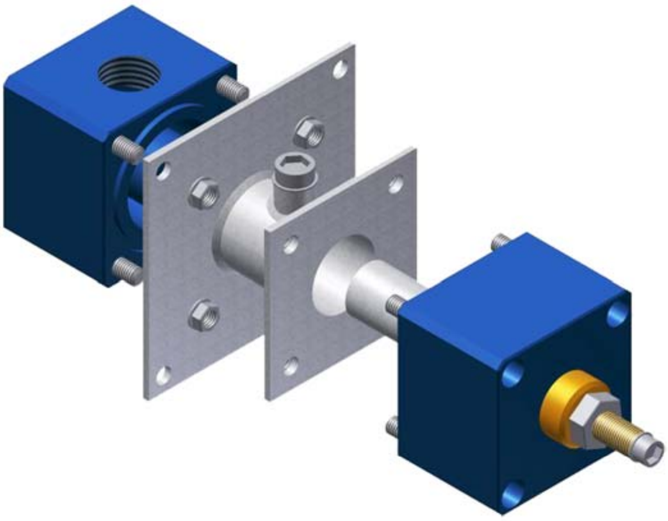
New techniques for treatment of water in Dansih swimming pools with focus on electrochemical oxidation and disinfection



Master thesis
Chemical Engineering
Jens Muff & Lars Bennedsen
AAUE, Spring 2007

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RAMBØLL

Title:	New techniques for treatment of water in Danish swimming pools with focus on electrochemical oxidation and disinfection
Specialisation:	Master of Science in Chemical Engineering
Profile:	Environmental Nanotechnology
Time period:	1. February - 8. June 2007
Place:	Esbjerg Institute of Technology, Aalborg University Rambøll A/S, Vejle
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CLASSIFIED!

Abstract

The present thesis considers two closely related topics. The first is contributions to a tender for an examination project called by the Danish EPA concerning tests of alternative techniques for treatment of swimming pool water. The tender was prepared by a consortium between Rambøll A/S and Scan Research A/S, and the project group has evaluated the applicability of a newly developed test trailer to conduct the required tests on swimming pools. The ozone as well as the electrochemical treatment system installed in the trailer were found to be applicable. A search for commercial applications on the Danish swimming pool market and an evaluation of the collected manufacturer experiences revealed that especially UV treatment of swimming pool water is well documented, and the treatment system installed in MarseillisborgCentrets Svømmebad was identified as very applicable as test installation.

The second topic is electrochemical treatment of swimming pool water, a technique widely used in Greece, but not implemented in Denmark. Laboratory investigations revealed the chlorine production rate to be $1.69 \cdot 10^{-4}\ {}^{mol}/_{min \cdot A}$ in a 0.9 % $NaCl$ electrolyte with a current efficiency of 55 % and energy efficiencies of 6-12 %. The efficiencies were enhanced by increasing $NaCl$ concentration. The cathodic production rate of hydrogen gas was determined to be $3.82 \cdot 10^{-4}\ {}^{mol}/_{min \cdot A}$, and the ratio of 2.3:1 to the chlorine production strongly indicates the formation of other oxidants. By the experimental method of bleaching p-nitroso-dimethylaniline (RNO), the formation of hydroxyl radicals was demonstrated. Ozone is another feasible oxidant expected to be identified in subsequent investigations. Through the bleaching tests, a synergetic effect was found by the presence of chloride in the electrolyte and the electrochemical treatment. In an electrochemical disinfection experiment, a linear logarithmic reduction of *E. coli* was found, and with a contact time of 0.33 s, a log-3 reduction was obtained at a current of 9 A in a 0.9 % $NaCl$ electrolyte. By model calculations, the disinfection caused by the produced chlorine was estimated to less be than 1 %. A full scale electrochemical treatment system for a 32 m^3 swimming pool was dimensioned, and the power consumption was estimated to 2.3 ${}^{kWh}/_{day}$. On the basis of the experimental work and the literature study, the project group considers the electrochemical technique as being very well suited for treatment of swimming pool water in Denmark.

Synopsis

Nærværende afgangsprojekt behandler to nært relaterede problemstillinger. Det første er bidrag til et tilbud på et undersøgelsesprojekt udbudt af Miljøstyrelsen, der omhandler tests af alternative renseteknikker til svømmebade. Tilbudet er udarbejdet af et konsortium bestående af Rambøll A/S og Scan Research A/S, og projektgruppen har evalueret muligheden af at anvende en nyligt udviklet test trailer i svømmebadstestene og dermed inddrage traileren i tilbudet. I den forbindelse blev trailerens ozonanlæg og elektrokemiske rensesystem vurderet til at være anvendelige. En undersøgelse af produkter på det danske marked for renseteknikker til svømmebade og en vurdering af dokumentationsmateriale indhentet fra producenter og distributører viste, at især rensning af svømmebadsvand med UV er en veldokumenteret teknik, som uden yderligere tests burde blive implementeret i standarderne for dansk svømmebadsbehandling. Ligeledes blev anlægget installeret i MarseillisborgCentrets Svømmebad identificeret som et særdeles anvendeligt testanlæg.

Det andet emne er elektrokemisk rensning af svømmebadsvand, en teknik som anvendes i Grækenland, men som endnu ikke er implementeret i dansk vandbehandling. Undersøgelser i laboratoriet viste en produktionshastighed af klor på $1.69 \cdot 10^{-4}\ ^{mol}/_{min \cdot A}$ i en 0,9 % *NaCl* elektrolyt med en strømeffektivitet på 55 % og en energieffektivitet på 6-12 %, som begge blev forbedrede ved stigende *NaCl* koncentrationer. Produktionshastigheden af brint ved katoden blev bestemt til $3.82 \cdot 10^{-4}\ ^{mol}/_{min \cdot A}$, og forholdet til klorproduktionen på 2,3:1 indikere kraftigt, at der bliver dannet andre oxidanter i den elektrokemiske proces. Dannelse af hydroxyl radikaler blev påvist ved afblegning af stoffet p-nitroso-dimethylanilin (RNO), og ozon er en anden oxidant, der forventes påvist ved kommende forsøg. Afblegningsforsøgene viste en synergieffekt imellem tilstedeværelsen af kloridioner i elektrolytten og den elektrokemiske proces. I et forsøg med desinficering af *E. coli* blev der påvist en linear logaritmisk reduktion, og ved en opholdstid på 0,33 s blev der i en 0,9 % *NaCl* elektrolyt opnået en log-3 reduktion ved en strømstyrke på 9 A. Modelberegninger viste, at mindre end 1 % af desinfektionseffekten kunne tilskrives klor. Et fuldskala elektrokemisk rensesystem til et 32 m^3 svømmebad er blevet dimensioneret og effektforbruget blev estimeret til 2.3 $^{kWh}/_{\text{døgn}}$. På baggrund af de udførte laboratorieforsøg og litteraturstudiet er det projektgruppens vurdering, at den elektrokemiske teknik er særdeles velegnet til rensning af vand i danske svømmebade.

Preface

The present master thesis concerns electrochemical treatment of swimming pool water and has been made as the final part of the study for Master of Science in Chemical Engineering at Esbjerg Institute of Technology, Aalborg University. The thesis was written in the specialization of Environmental Nanotechnology within the framework of the Chemical and Interface Chemistry (CIC) research group. In the preparation of the thesis, close co-operations with Rambøll A/S and Watersafe have resulted in a very exciting project, where a unique opportunity of transferring university knowledge to the commercial applications has served as valuable inspiration for the project group.

The target audience of the report is Watersafe A/S for an enhanced understanding of the chemical processes occurring in their electrochemical reactor, research groups interested in electrochemical water treatment, and consulting engineers interested in new applications and advanced water treatment. In addition, the report responds to the demands from the Danish EPA considering the lack of documentation material regarding the efficiency of the electrochemical treatment process in swimming pools. For a full understanding of the report, basic knowledge concerning oxidation and reduction reactions and electrochemistry is needed.

Tests and analyses were carried out at Aalborg University Esbjerg and at Aalborg University (SEM/EDS). In the preparation of the thesis, the project group went on an inspiring technical excursion to Greece.

All references are inserted as [author, year] and refer to literature found in the reference list, section 10. References are placed at the end of a section, unless referring directly to a number or fact. In such cases the reference is placed right after the given fact. Furthermore, all equations are numbered as (equation number).

The project group would like to thank Rambøll A/S for indispensable financial support allowing the opportunity of the technical excursion to Greece and providing the laboratory reactor, chlorine test kit, and spare parts to sensors. Thanks to Watersafe for financial support regarding the stay in Greece and for technical support concerning the work with the electrochemical reactor. Thanks to technical assistant Thomas Sørensen, Institute of Material Engineering, Aalborg University, for help with the SEM imaging and EDS analysis.

Lars Bennedsen & Jens Muff
June 2007

Contents

1 Introduction

This present project concerns two subjects related to treatment of swimming pool water. In February 2007, the Danish Environmental Protection Agency (EPA) called for tenders for an examination project comprising test and evaluation of different alternative techniques applied in treatment of swimming pool water [MST, 2007b]. Rambøll A/S decided to tender for the EPA examination project and the present master thesis was made in corporation with Rambøll A/S.

The first part of this thesis concerns a market search, investigating possibilities for practical test of alternative techniques in Denmark. The other main topic in this thesis is investigations of the chemical and operational principles in electrochemical treatment of swimming pools water. A combination of external factors and a close cooperation with Rambøll A/S and Watersafe resulted in changes of the content and structure of the report throughout the project. This section describes the way to the final content and layout of the present master thesis.

February 2007, the Danish EPA published a report concerning alternatives to chlorine as disinfecting agent in swimming pools [MST, 2007a]. Through a thorough review of the literature related to disinfection of swimming pool water, the EPA report provided a state of the art investigation of alternative disinfection techniques, the formation of disinfection by-products (DBPs) and the present common configuration of Danish swimming pool water treatment systems. Furthermore, relevant chemical and microbiological monitoring parameters were subject of debate and the statutory requirements in different countries in Europe were compared.

On the basis of this report, the Danish EPA invited for tenders concerning an examination project with the purpose of testing alternative disinfection techniques in practise, and thereby improves the basis of decision regarding implementation of the possibility to apply new disinfection techniques in the Danish legislation for swimming pool water treatment. The EPA examination project was divided into two phases [MST, 2007b]:

- Phase 1: selection of techniques and a swimming pool for practical testing
- Phase 2: actual testing of the selected techniques

The consultant engineering company Rambøll A/S decided to tender for the examination project in cooperation with the water treatment company Scan Research A/S.

This present master thesis was initiated in February, even though the fate of the tender was not scheduled to be clarified before ultimo Marts 2007. Despite promises given by the Danish EPA, the clarification of the winner was delayed several times, and by the end of the present project, the decision had not yet been announced. This extensive delay resulted in the preparation and content of the thesis to differ from the originally planned. During the first two month of the project period, the plan was to evaluate and optimise an analysis program developed for screening of the treatment techniques, which was part of the tender from the Rambøll and Scan Research consortium. Due to the lack of clarification from the Danish EPA, the project group decided to focus more extensively on electrochemical water treatment.

This present master thesis concerns two main topics, both derived from the EPA examination project. From the beginning, the project group was deeply involved in the preparation of the tender, and through this introductory work, the knowledge of the electrochemical oxidation and disinfection technique being applicable in swimming pool treatment was gained. A possibility of commencement of cooperation with Watersafe, a manufacturer of electrochemical reactors, turned up, and the project group decided to investigate this treatment technique in further detail through laboratory experiments. The Watersafe reactor is widely used in swimming pool treatment in Greece, but the Danish EPA report classified the technique as being in an early development phase, and the conclusion was that more systematic investigations are needed before implementation in Danish swimming pool treatment is advisable [MST, 2007a].

Based on the Greek experiences and literature studies, the project group found good opportunities in using the electrochemical technique in swimming pool treatment. The project group therefore decided to carry out laboratory test with the technique in order to respond to the demands from the Danish EPA. Subsequently, it was the plan to test the Watersafe reactor in a full scale swimming pool, but through the forces of circumstances considering the installation of the reactor, it was not possible within the duration of the project. The full scale installation in a public swimming pool in Århus is initiated during July 2007. Instead, the project group served as consultants and cooperated with the consultant engineering company Søren Jensen in the preparation of the project draft for the installation. Concurrently, the project group cooperated closely with Rambøll A/S and one of the aims of the present report was to serve as introductory works to both phase 1 and phase 2 of the EPA examination project.

Concurrent with the preparation of the tender, the project group has been involved in the development of a chemical test unit for treatment and remediation purposes of all kind of waste water, industrial process water, and polluted ground water, with the test unit being encased in a mobile trailer. The constructing contractor is Hans Friesesdahl A/S with Rambøll A/S as consultant and a number of external collaborators. Fortunately, the test trailer is equipped with some of the alternative treatment techniques, which are required to be tested in the EPA examination project, and another objective of the present project was to elucidate the chemical principles of the oxidation techniques towards swimming pool treatment, study their dissemination in Danish swimming pool treatment and evaluate the possibility of the test trailer to enter in the phase 1 screening of the tender.

The next chapter is intended to serve as a presentation of the background of the problem concerning water treatment in Danish swimming pools. The presentation includes a summation of the conclusion from the Danish EPA report prior to the tendered EPA examination project.

2 The issues in Danish swimming pool treatment

This section presents the current configuration of Danish swimming pool treatment based on chlorine disinfection, with the related problems of DBP formation. Likewise, the Danish legislation and regulation on the swimming pool area is presented and compared to the statutory requirements in our surrounding countries. The section is based on the conclusions from the Danish EPA report [MST, 2007a], but supporting references are included as well.

2.1 Legislation

In Denmark water treatment systems for swimming pool water are designed in order to meet the requirements given in executive order BEK no. 288 from 14/04/2005. The requirements are given in Table 1.

Table 1: Quality requirements for water in Danish indoor swimming pools. [1]swimming pools with a length above 25 m. [2]other swimming pools. [3]only if germ number was >500 in the previous inspection.

Parameter	Unit	Minimum	Recommended	Maximum
Temperature	°C		24-28	
pH		7.0	7.2-7.6	8.0
Free chlorine[1]	$^{mg}/_{l}$	0.5	0.5-2.0	3.0
Free chlorine[2]	$^{mg}/_{l}$	1.0	1.0-3.0	5.0
Combined chlorine	$^{mg}/_{l}$		< 0.5	1.0
COD	$^{mg\ KMnO4}/_{l}$			10 above feed water
THM[1]	$^{\mu g}/_{l}$		25	50
THM[2]	$^{\mu g}/_{l}$		50	100
Germs at 37 °C	pr. 100 ml		0-500	1000
Thermotolerant coli formed bacteria[3]	pr. 100 ml		< 1	< 10
Pseudomonas bacteria[3]	pr. 100 ml		< 1	< 10

Source: [BEK no. 288 from 14/034/2005]

The free chlorine parameter is a gathering term comprising the concentration of Cl_2, $HOCl$ and ClO^-, and will be frequently used in this report. According to the recommendation from WHO, the amount of free chlorine should not exceed 3.0 $^{mg}/_{l}$ and 5.0 $^{mg}/_{l}$ in swimming pools and hot tubs, respectively [WHO, 2006]. In Denmark, the US, the UK, and Australia among others, these guidelines are followed, whereas 0.3-0.6 $^{mg}/_{l}$ and 0.7-1.0 $^{mg}/_{l}$ are maintained in Germany even though alternatives to chlorine-based disinfectants are not yet permitted [Zweiner, 2007; DIN 19643, 1997]. In Germany the low levels of free chlorine are obtained by use of additional techniques e.g. ozone.

The legislation values for other parameters, such as the amount of combined chlorine (~chloramines), trihalomethanes (THM), and the pH, also vary between different European countries. The requirements for the general microbiological water quality (total germs, coli formed bacteria, *Pseudomonas aeruginosa*) are relatively similar in Europe, whereas no consistent regulation exists for other microorganisms such as *Legionella* and *Staphylococcus*. A comprehensive comparison of the different statutory requirements in Europe is found in MST, 2007a.

2.2 General design of treatment systems

In order to meet the requirements given in the executive order BEK no. 288 from 14/04/2005, swimming pools are designed to recirculate the water continuously through a treatment system consisting of filtration and disinfection. In the Danish Standard, DS 477 from 1996, recommended guidelines for the design are provided for different types of pools regarding materials, size, temperature etc.

An example of a typical treatment system for swimming pools is illustrated in Figure 1.

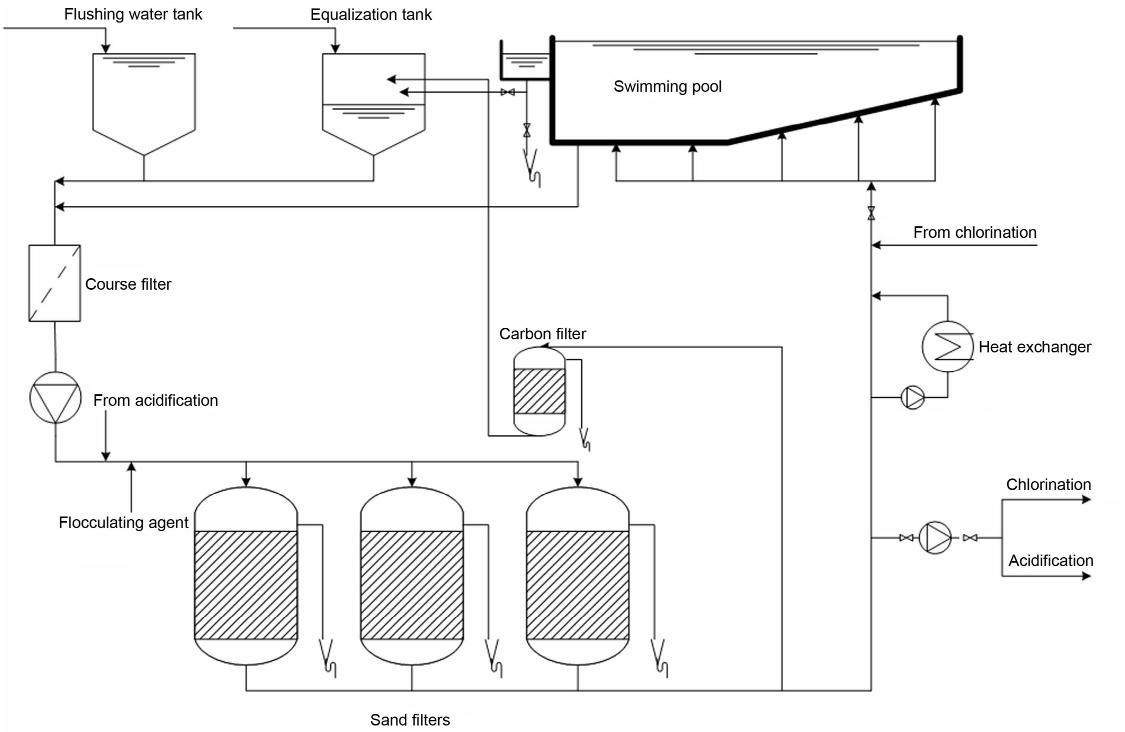

Figure 1: Example of a typical water treatment system in Danish swimming pools given in the Danish Standard DS 477, 1996. Modified from [MST, 2007a].

From the pool, the water is passed on to an equalization tank, and then through a course filter, where impurities (>1 mm) are removed. The next step is addition of acid (*HCl*) and a flocculating agent, with the object of precipitate and filter out particles and impurities (>25 µm) in the following sand filters. An active carbon filter is installed in a sub-stream in many swimming pools in order to reduce the concentration of chloramines. Before the water re-enters the swimming pool, a sub-stream is passed through a heat exchanger and chlorine is added.

2.3 Disinfection by chlorination

It is possible to use a range of disinfectants in swimming pools, but in Denmark only chlorine gas (Cl_2), and hypochlorite (normally *NaOCl*) are legal according to executive order BEK no. 288 from 14/04/2005. Both disinfectants form hypochlorous acid (*HOCl*), in contact with water according to the following reactions [White, 1972; Morris, 1946]:

$$NaOCl(s) + H_2O(l) \rightleftharpoons HOCl(aq) + Na^+(aq) + OH^-(aq) \qquad (1)$$

$$Cl_2(g) + H_2O(l) \rightleftharpoons HOCl(aq) + H^+(aq) + Cl^-(aq) \qquad (2)$$

The dissociation of hypohlorous acid into hypochlorite (ClO^-), is pH depending:

$$HOCl(aq) \rightleftharpoons H^{+}(aq) + ClO^{-}(aq) \tag{3}$$

The ionization constant of hypochlorous acid is $k_a = 3.7 \cdot 10^{-8}$ $^{mol}/_{l}$ (25 °C) and the hydrolysis constant of chlorine in water is $k_H = 4.47 \cdot 10^{4}$ $mol^2 \cdot l^{-2}$ (25 °C) [White, 1972; Morris, 1966]. On the basis of the given constant, the extent of the dissociation as a function of pH at 25 °C is seen from Figure 2.

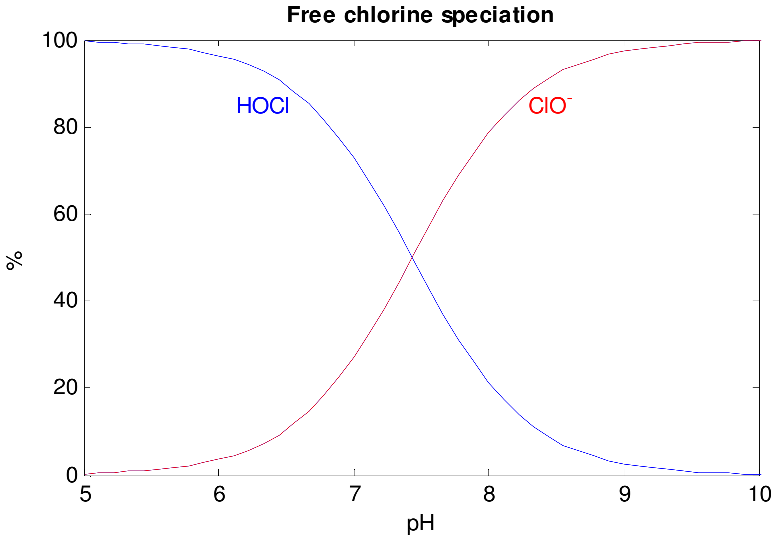

Figure 2: Dissociation of chlorine in water at 25 °C based on the constant provided by White, 1972. The MatLab script file and the equation for the figure are found in appendix 1.

At the recommended pH of 7.2-7.6, given in the executive order, hypochlorous acid comprises 40-63 % of the reactive free chlorine. At lower pH, the irritation of the eyes and risk of corrosion increases. At higher pH, the concentration of hypochlorous acid decreases, which is inappropriate, since it is 80 times more efficient as disinfecting agent compared to hypochlorite [Fair, 1948]. In order to maintain an optimal pH, it is necessary with adjustment using hydrochloric acid (HCl) or sodium hydroxide ($NaOH$) depending on the disinfectant used.

Of all chlorine compounds, hypochlorous acid is the most effective disinfectant. This is due to its small molecular size and lack of charge, which ease the penetration of the cell wall of the bacteria [White, 1972].

Several suggestions for explaining the bactericidal nature of chlorine solutions have been provided. Knox et al., 1948, proposed the idea that inhibition of glucose oxidation was the reason. Later Albrich et al., 1981, suggested the cause of death may be due to metabolic dysfunction caused by depletion of adenine nucleotides. Recently it has been proposed that inactivation of membrane proteins involved in DNA replication are the mechanism of action of *HOCl* [Rosen et al., 1990; Rosen et al., 1998].

2.4 Disinfection by-products

When chlorine is used for disinfection, it reacts with natural organic matter (NOM), which acts as precursor, and forms chlorinated DBPs. The precursors can be derived from a number of sources such as source water, bathers, and handling.

The main reason, causing the formation of DBPs, is the release of pollutants from bathers in the swimming pool. Nitrogen compounds that are extracted from bathers by the skin, sweat, and urine react with free chlorine and form several DBPs. In Table 2, the nitrogen-containing compounds in sweat and urine are showed.

Table 2: Nitrogen-containing compounds in sweat and urine.

	Sweat [$^{mg}/_{l}$]	Urine [$^{mg}/_{l}$]
Urea	640	10,240
Ammonia	180	560
Amino acids	45	280
Creatinine	7	640
Other compounds	80	500
Total nitrogen	992	12,220

Source: [WHO, 2006]

The average urine release into swimming pools has been estimated to 25-30 $^{ml}/_{bather}$ [Gunkel and Jessen, 1988], 50 $^{ml}/_{bather}$ [Judd and Black, 2000] and as high as 77.5 $^{ml}/_{bather}$ [Erdinger et al., 1997]. Judd and Black, 2000, also estimated the average release of sweet to be 200 $^{ml}/_{bather}$.

Although the major constituent in sweat and urine is urea, swimming pool water exhibits a considerable amount of ammonia-derived compounds. It therefore appears as if urea degrades through reactions with free chlorine [WHO, 2006].

In a recent report from the WHO, the predominant DBPs, formed in swimming pools using chlorine for disinfection, are listed [WHO, 2006]:

- Trihalomethanes (THMs)
- Haloacetic acid (HAA)
- Haloacetonitriles
- Haloketones
- Chloral hydrate (trichloroacetaldehyde)
- Chloropricin (trichloronitromethane)
- Cyanogen chloride
- Chlorate
- Chloramines

The two DBPs in swimming pools, currently considered as the key compounds, are chloramines and THMs, which both have been subject to considerable research over the years. Furthermore, they are the only DBPs included in the current statutory requirements. In the past few years, more DBPs and their health impact have been brought into focus.

There are three main routes for exposure to DBPs in swimming pools:

- Direct ingestion of water
- Inhalation of aerosols and volatile components
- Dermal contact and absorption through the skin

Several comprehensive studies concerning the health impact of different DBPs have been carried out through the years. These will not be reviewed in this report, but for more information concerning these studies please refer to [MST, 2006; WHO, 2004; WHO, 2006; Aggazzotti, 1998; Erdinger et al., 2004; Fantuzzi et al., 2001].

2.5 Microbiological parameters

In swimming pools, a variety of microorganisms can be found, which may be introduced in a number of ways. Bathers releases microorganisms through phlegm and spit ($1 \cdot 10^{6}\ ^{\text{bacteria}}/_{\text{ml}}$), from the skin ($6 \cdot 10^{8}\ ^{\text{bacteria}}/_{\text{person} \cdot 5\ \text{min}}$), and via faeces [MST, 1986]. These microorganisms represent a risk of illness or infection for bathers. A diagram showing the potential microbial hazards in swimming pools divided into faecally-derived and non-faecally-derived microorganisms is showed in Figure 3.

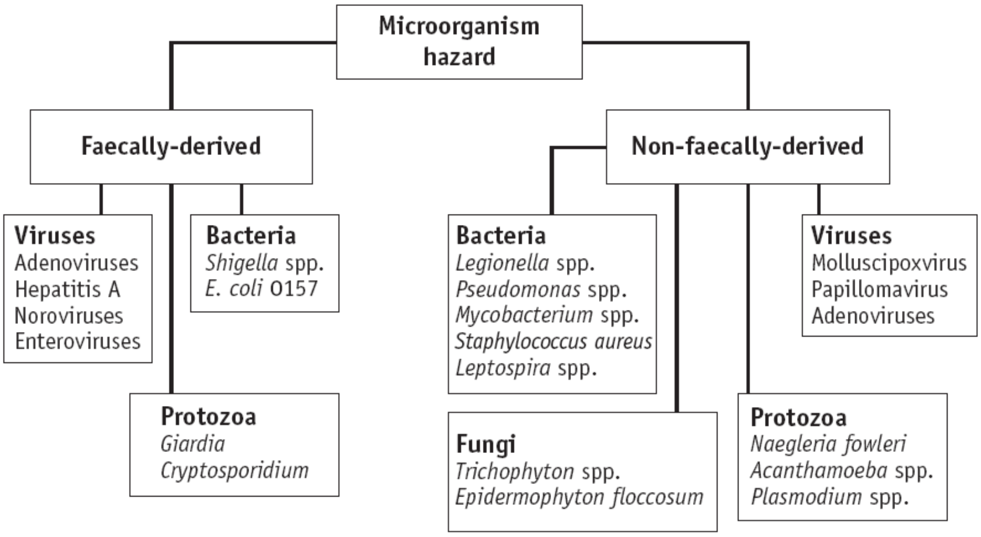

Figure 3: Potential microbial hazards in swimming pools [WHO, 2006].

WHO, 2006, has made a comprehensive literature study and gathered information concerning hazard identification, outbreaks in swimming pools, risk assessment, and risk management for every group of microorganisms provided in Figure 3.

In order to monitor the microbial quality of the water, it is possible to analyze for indicator organisms or specific pathogenic microorganisms. The indicator organism needs to have similar resistance to the disinfection as the pathogens, it is indicator for. However, in the literature there is no common agreement considering the use of indicator organisms. As regards test of new disinfection techniques in swimming pools, it is recommended by the Danish EPA to establish an analysis programme, which ensures a useful documentation of the efficiency of the technique [MST, 2007a]. The development of such an analysis programme was intended to be contained in the present project, but due to the delays from the EPA, it was left out.

Different microorganisms require different concentrations of disinfectants. For more information on this topic please refer to [EPA, 1999; MST, 1986; MST, 2007a].

2.6 Alternative techniques and the EPA examination project

According to MST, 2007a, it appears likely that chlorine also in the future will be used as the primary disinfectant in swimming pools, but it will be possible to reduce the concentration of free chlorine and DBPs. This can be accomplished by a combination of lowering the pH, which makes it possible to maintain an acceptable level of active hypochlorous acid, by a decrease in the free chlorine concentration, and by applying new technology, which directly degrades the DBPs or the DBP-precursors. Table 3 lists the technologies reviewed by MST, 2007a.

Table 3: List of technologies, status of development and effect towards chloramines, THM/AOX (Adsorbable organic halogens), and microorganisms. The project group has on the basis of MST, 2007a, rated the technologies concerning their applicability by the number of *. **** is the best, - means no effect.

	Sand filter	Active carbon filter	UV	Ozone	Membrane filtration	Advanced oxidation	Electrochemical oxidation	Stripping
Development status	****	***	***	***	**	*	*	-
Chloramines	-	***	***	***	**	**	**	**
THM/AOX	-	**	*	**	*	**	**	**
Microorganisms	-	-	***	***	***	***	***	-

Source: modified from [MST, 2007a]

As a general rule, the reviewed technologies, except for sand filtration and active carbon filtration, are new to Danish swimming pool treatment. By the Danish EPA they are considered to be insufficiently described in relation to swimming pools and have to be examined experimentally in order to establish documentation of the efficiency, design and economy [MST, 2007a].

From the project group's point of view, the effort from the Danish authorities, in order to improve the quality of the swimming pool water in Denmark, has been inadequate, especially when the technology level is compared to our surrounding countries. The above reviewed areas regarding swimming pool water treatment show the need for improvements, which presumable requires the implementation of one or more of the techniques listed in Table 3. The new techniques have in general showed promising results, and regarding the UV and ozone treatment, the efficiency is well documented.

The Danish EPA seems finally to have reached the same conclusion and by use of the considered report, MST, 2007a, as a starting point, they called for tenders, comprising an examination project with the purpose of testing alternative disinfection techniques in practise. The treatment techniques that are required to be tested in the screening are outlined in the draft for the examination project [MST, 2007b]:

- Membrane filtration
- UV treatment
- UV based advanced oxidation processes (AOPs)
- Ozone
- Stripping

The EPA examination project is expected to contain the following phases [MST, 2007b]:

- Phase 1: selection of techniques and a swimming pool for practical testing
- Phase 2: actual testing of the selected techniques

The consultant engineering company Rambøll A/S, by who the project group cooperated, decided to tender for the project with the deadline for delivery of the tender being 8th of March. The tender was, by the Danish EPA, required to comprise:

- Suggestions for test method, resources employed, and time schedule
- Finally determination of 2-3 techniques to be tested
- Suggestion to practical test procedure of the techniques

The main focus areas for the project group with regard to the preparation of the tender were the suggestions to practical test procedures and study of the chemical principles in the applied techniques. In addition, the electrochemical treatment technique was reviewed in the MST, 2007a, report, but was left out of the EPA examination project because of the insufficiently status of development. The project group was however aware of the Watersafe electrochemical reactor being applied in Greek swimming pool treatment, and, since a possibility for cooperation with Watersafe Denmark developed, the project group and Rambøll A/S found it very interesting to build up more knowledge concerning electrochemical treatment of swimming pool water, create some Danish references, and thereby draw attention towards this treatment technique.

3 Problem formulation

This present master thesis project concerns two main investigations, which are gathered in the following problem formulation:

“Which possibilities exist for practical tests of alternative swimming pool treatment techniques and what are the chemical principles and oxidation and disinfection efficiency of the Watersafe reactor in electrochemical swimming pool treatment?”

The project group has answered the question through literature studies and practical laboratory experiments. The project consists of two parts; identification of test possibilities for alternative swimming pool treatment techniques including a study of the chemical principles in ozone UV, and electrochemical water treatment, and a thorough laboratory investigation of the electrochemical Watersafe reactor. The laboratory investigations served as the fundamental work prior to the preparation of a project draft concerning a full scale installation.

The first part of the project contributed to the tender and acted as a part of the preliminary work to phase 1 and 2 of the EPA examination project. In the first part, the answers to the following sub-questions were elucidated:

- Is the newly developed chemical test trailer applicable to participate in the screening of the required disinfection techniques?
- Which alternative swimming pool treatment techniques are commercially available in Denmark?
- Which existing full scale treatment installations are applicable as test installations?
- What are the fundamental chemical treatment principles in the alternative techniques ozone, UV, and electrochemical treatment, and what are the experiences?

The answers are provided through a presentation and evaluation of the applicability of the developed chemical test trailer to enter in the tender as a test unit. The project group has searched the Danish swimming pool market for commercially available applications of the treatment techniques demanded by the Danish EPA to be tested. The market search was applied in order to survey the market, identify applicable full scale installations suitable for test purposes, and identify suitable collaborators to enter in the tender.

The second part of the project concerned electrochemical treatment of swimming pool water. The investigation was prepared on the basis of the following sub-questions, primary answered through laboratory investigations:

- What are the relationship between chlorine production, applied current, and $NaCl$ concentration?
- Which oxidizing agents are formed by the reactor?
- What is the bactericidal efficiency of the electrochemical treatment technique towards *Escherichia coli*?
- What is the composition of the surface of the anode in the Watersafe reactor?

- How is the full scale electrochemical reactor at the public swimming pool in Århus designed and installed?

Succeeding the laboratory investigations, the obtained results were used to prepare a suggestion for design and installation of a full scale electrochemical reactor, which is to be installed in July 2007 at the public swimming pool Spanien.

In the preparation of the project, limitations were needed in order to maintain focus on the primary subjects. Regarding the swimming pool chemistry, the free chlorine chemistry and the disinfection has been in focus, whereas the complex chemistry of DBP formation, evaporation etc. has not been considered. For more information of this topic the project group refers to the specified references. The thorough theory study only concerns the techniques installed in the test trailer, which also constitute the most developed and tested techniques. Hence, a study of the chemical principles in advanced oxidation processes, membrane filtration, and stripping are left out of the present report. In the laboratory investigation, the focus areas were the formation of oxidants and the disinfection. Hence, the oxidation of combined chlorine and the DBP precursors were left for future investigations. In the preparation of the project draft for the full scale installation of the Watersafe reactor in Spanien, the focus of the project group was on the chemistry in the treatment system and dimensioning of the reactor, and hence the dimensioning of the additional pipes, equipment and detailed technical drawings has not been considered. Comprehensive economic considerations have not been treated.

4 Identification of practical tests possibilities

In the identification of the possibilities for conducting tests of the techniques required to be included in the tender, the project group was aware of the necessity to keep down the cost of equipment investment. This could be obtained by a combination of two strategies; by using a newly developed chemical test trailer or by using existing full scale installations.

The project group has participated in the development of a mobile chemical test unit, a project started by Rambøll in September 2006. The purpose was to create an advanced mobile chemical oxidation unit, which was suitable equipped in order to test different chemical treatment and remediation possibilities of industrial waste water, all kind of process water, and polluted groundwater, and thereby quickly establish a diagnosis towards the most efficient combination of treatment techniques. When the EPA examination project came up in February 2007, some of the requested treatment techniques were already agreed to be installed in the trailer, and the task for the project group was to evaluate the applicability of the test trailer to participate in the screening of the swimming pool techniques, and hence be included in the tender. The evaluation had to be conducted by considering; the demands from the EPA examination project, the specific equipment which was agreed by the collaborators to be included in the trailer, and the practical possibilities of using the test trailer for swimming pool tests with regards to dimensions and capacities.

According to the second strategy, the project group was aware of the fact that some of the required techniques were already installed in Danish full scale swimming pool treatment system, and the objective was to identify these installations and evaluate their applicability to enter in the tender as test installations. By searching the Danish swimming pool treatment market, the primary market actors; manufactures and distributors of the techniques were identified. By the literature study of the Danish EPA, 2007b, only scientifically published results were considered, and the project group misses the full scale experiences obtained by the manufacturing and distributing companies. Hence, once identified, the market actors were contacted and asked for reference material. The market actors and the most relevant full scale treatment installation applicable for test purposes are presented with the collected documentation materials in section 4.2.

The next section provides a presentation of the test trailer, from the development phase, through the construction phase to a presentation of the installed techniques and their application possibilities. Succeeding the presentation, the evaluation of the applicability of the test trailer to enter in the testing of the swimming pool treatment techniques is performed. Then the market search is presented, and a conclusion is drawn of the test possibilities.

4.1 Presentation of the test trailer

In the past two years, Rambøll A/S has developed and constructed two test trailers; one for physical in-situ tests and one for biological on-site tests, mainly intended for remediation tests with polluted soil and groundwater, see Figure 4. In the late summer 2006 Rambøll A/S got the idea of developing a third test trailer for chemical tests. This section describes the different phases of the process, in which the project group was involved from the beginning and through several meetings served as adviser regarding the chemical issues. In the end of the section, the final result is presented.

Figure 4: The two existing test trailers for biological and physical test.

4.1.1 Development phase

The objective in the development phase was to design a versatile trailer, which was able to provide the possibility of conducting a fast screening of several chemical oxidation techniques on different types of water comprising waste water, groundwater, swimming pool water, drinking water etc. In this way, it is possible to achieve technical documentation for treatment of a specific water matrix with different techniques or combinations of techniques, and thereby provide a stronger basis for decision, on which kind of full scale treatment system to install afterwards.

Through discussions, it was decided to include the following techniques in the new test trailer:

- Chemical oxidation (permanganate, persulphate, hydrogen peroxide, Fenton)
- Ozone
- UV
- Electrochemistry
- Advanced oxidation processes (AOPs)

The term Advanced oxidation processes mainly refers to combinations of different chemical oxidation techniques where UV is often included and also includes photocatalytic processes. The market for the above mentioned techniques was investigated, and it was chosen to enter into agreements with external collaborators, who possess the technology and the knowledge. In this way, some of the equipment in the test trailer was partly sponsored by the different individual collaborators, which in return entered into an agreement concerning the use of the test trailer and the resulting projects. The collaborators and the provided equipment are seen from Table 4. Buch and Holm is the Danish distributor of the Infors HT fermentor, and hence both of the companies entered as collaborators regarding the fermentor.

Table 4: Collaborators and the provided equipment.

Technique	Collaborator	Provided equipment
Ozone	Air Liquide	Ozone generator and safety equipment
UV	Aqua System A/S	UV-unit for disinfection
Electrochemistry	Watersafe	Electrochemical treatment system
-	Buch & Holm	Fermentor and lab equipment
-	Infors HT	Fermentor

The whole development process of the test trailer was carried out in close collaboration with the construction contractor, Hans Frisesdahl A/S. Besides the closely work with the CIC (Colloid and Interface Chemistry) Research Group at Esbjerg Institute of Technology, Aalborg University, in which framework the present master thesis has been conducted, a number of universities; DTU, Vitus Bering, and SDU were at the level of interest included in the collaboration.

4.1.2 Construction phase

The construction of the trailer was initiated ultimo February 2007 at Hans Frisesdahl A/S, Vejen. The applied trailer was a special designed 6x2 m Humbaur closed trailer. A standard version is seen from Figure 5.

Figure 5: Standard Humbaur trailer 6x2 m.

For security reasons, the trailer was divided into three separated compartments with extraction ventilation through active carbon filters in the two small rooms at the ends, see Figure 6. Ozone was situated in one of the closed rooms and the tanks for mixing of liquid oxidants in the other. Concentrated chemicals are placed in a small compartment outside at the front of the trailer.

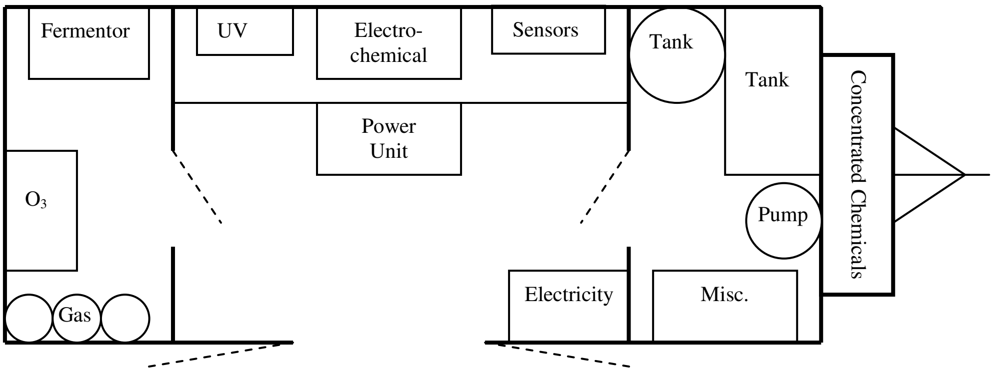

Figure 6: Design of the test trailer at the beginning of the construction phase.

Throughout the construction phase, the test trailer was inspected several times and new ideas, improvement, and problems were discussed and initiated on location.

4.1.3 Techniques

The test trailer, called "Environmental Innovation Unit", was presented for the public April 20th and the result is seen from Figure 7 and Figure 8. The trailer configuration presented is only the first version, and the intention is that the configuration is continuously developed and that the trailer is equipped dependent on the types of future projects.

Figure 7: The completed test trailer with logos and exhaust ventilation.

Figure 8: Photos from the inside, showing the final configuration of the test trailer.

In order to obtain maximum versatility, the inside walls of the trailer are covered with perforated plates, whereupon hoses, measuring instruments, reactors, peristaltic pumps etc. can be placed. The combination of this flexible system, the different treatment techniques and that all flow of water is lead through hoses, which easily can be switched from one unit to another, makes it possible to treat a wide variety of water and use the techniques in sequential treatment processes.

For treatment purposes, the test trailer is equipped with a fermentor, an ozone generator, an UV system, an electrochemical reactor, and tanks and dosage pumps for mixing and addition of liquid oxidants. A brief description of the possibilities with the specific treatment equipment and the auxiliary equipment is provided.

Fermentor

The fermentor installed is a Terrafors from Infors HT. Among other things, it can be used for studying bioremediation and solid state fermentation. It allows the creation of a controlled environment, which can be used for treatment of solid and semi-solid waste and contaminated soils. The Terrafors fermentor is seen from Figure 9.

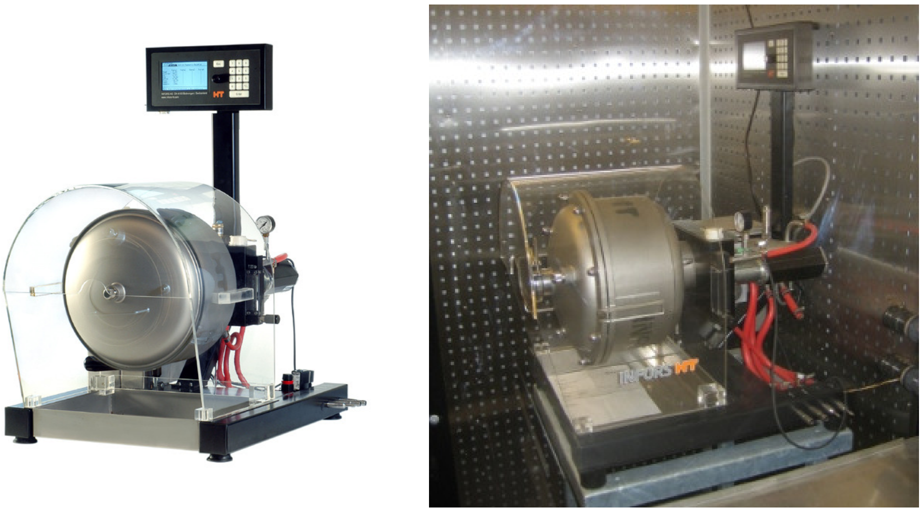

Figure 9: The Terrafors fermentor from Infors HT [Infors, 2007].

The base unit consists of a supporting frame for the 15 l stainless steel vessel with a water circulation system, gas supply rotameter and drive motor. Ports are provided in the lid for e.g. liquid sampling. The whole unit is controlled by a flexible software system with potential for expansion and addition of external sensor systems and the possibility of data logging.

Ozonia trailer configuration

The test trailer is equipped with an ozone generator, OZAT CFS-2G, from Ozonia. The Unit is placed in a sealed compartment in the test trailer with oxygen cylinders, exhaust ventilation, and ozone gas detectors for safety. A ML210-10 manual gas central is installed for regulation of the inlet pressure (max 3-10 bar) and flow (<10 Nm^3/h) of oxygen to the ozone generator. Photos of the generator and the installation in the test trailer are seen from Figure 10, and technical data can be found in Table 5.

Figure 10: OZAT CFS-2G ozone generator from Ozonia and the installation in the test trailer.

Table 5: Technical data for OZAT CFS-2G ozone generator from Ozonia.

Parameter	Value	Unit
General technical data		
Cooling water	0.09	m^3/h
Mains power	0.76	kW
Dimensions (LxWxH)	720x370x800	mm
Weight	50	kg
Ambient temperature	5-40	ºC
Oxygen feedgas (10 wt-% ozone)		
Ozone production	55	g/h
Outlet pressure	0.7	barg
Oxygen requirement	0.39	Nm^3/h
Dry air feedgas (3 wt-% ozone)		
Ozone production	37	g/h
Outlet pressure	2.0	barg
Dry air requirement	0.95	Nm^3/h

Source: [Ozonia, 2007]

From Table 5 it is seen that the ozone generator is capable of producing 37-55 g O_3/h dependent on the composition of the feed gas. For oxidation investigations, the produced ozone can be lead through different reactors installed in the test trailer or directly to larger systems outside the trailer.

UV system

The cooperative partner Aqua System A/S has delivered an UV system for installation in the test trailer. The received GENO-UV 60 S system is equipped with low pressure UV lamps and is intended for disinfection of water and not oxidation. Hence, its main working area is not swimming pool treatment, but is more directed towards disinfection of industrial waste water, drinking water and other types of process water. The installation of the UV system is seen in Figure 11.

Figure 11: The installation of the UV disinfection system in the test trailer.

Electrochemical treatment system

The electrochemical treatment system is delivered by Watersafe and consists of a reactor and an auxiliary power unit. A photo of the installation is seen in Figure 12, the operation parameters of the electrochemical system are seen in Table 19.

Figure 12: The electrochemical water treatment system consisting of reactor and power unit.

Table 6: Dimension of the reactor and operational parameters of the power unit. *Cylindrical volume between anode and cathode.

Total height:	800 m
Width:	170 m
Depth:	170 m
Anode diameter:	30 mm
Anode surface:	471 cm^2
Active volume*:	3 L
Capacity:	36 m^3/h
Max. voltage:	50 V
Max. current:	500 A
Weight:	600 kg

The installed electrochemical system is very powerful and is capable of treating several kinds of contaminated waters by direct or indirect treatment. In direct treatment, the contaminated water is passed through the reactor, and in indirect treatment, a brine solution is electrolysed in the reactor forming a range of oxidants and subsequently mixed with the contaminated water. The electrochemical processes are investigated in section 5.3. The capacity of the system is much higher than the pump in the trailer is capable of delivering, and the weight of the power unit provides a problem regarding the total weight of the trailer. However, the system is operational at all parameters below the maximum values.

Chemical oxidation

The test trailer contains two tanks with stirrers and feed pumps in a separated compartment. The feed is pumped from smaller tanks situated in a small compartment outside the trailer. This design provides the opportunity of mixing strong oxidants, e.g. permanganate, persulphate, hydrogen peroxide, and Fenton's reagent under safe conditions. The oxidants can furthermore be combined with other techniques such as UV in order to carry out advanced oxidation processes (AOP). The installation is seen in Figure 13.

Figure 13: The dosing system, and the tanks for addition and mixing of liquid oxidants.

Subsequently to the mixing, the oxidants can be lead to small reactors in the test trailer through peristaltic pumps and a versatile system of rubber hoses. In this way, continuous addition of oxidant to larger systems outside the trailer is also possible.

Miscellaneous

In order to operate the trailer and conduct the tests, the auxiliary equipment comprises:

- Refrigerator for sample storage
- On-line pH, ORP, oxygen, conductivity and temperature sensors (WTW)
- Peristaltic pumps
- Circulation pump (5.8 m^3/h)
- Safety equipment (shower, eye rinser, gloves, glasses etc.)
- Different lab equipment (glassware, stirrer, pipettes etc.)

The test trailer was presented for the public April 20th and caused a lot of attention in the media. April 22nd, two articles in a national newspaper [JV, 2007a and 2007b] and a 2 min TV feature [TV-Syd, 2007] were brought. The engineering newspaper "Ingeniøren" also brought an article about the trailer May 4th [Ing, 2007a]. The main themes in all the media were the idea of a broad cooperation between universities, consultants and technology suppliers and the use of the electrochemical reactor for remediation of contaminated soil and groundwater at Kærgård Plantation, one of the biggest contaminated sites in Denmark.

4.1.4 Evaluation

The developed test trailer, reviewed in the above section, is a versatile unit with several potential areas of application. This section evaluates its applicability towards chemical tests on swimming pool water, with special focus on fulfilling the specifications given in the EPA examination project. The techniques available in the test trailer are reviewed one at a time.

Electrochemical treatment system

Even though the EPA examination project does not mention the use of electrochemical oxidation and disinfection as one of the possible alternatives to traditional chlorination, the technique is found highly relevant by the project group. The unit installed in the test trailer has a maximal capacity of 36 m^3/h and a maximal operating temperature of 55 ºC. These specifications make the test trailer able to treat full scale swimming pools. Additional pump capacity needs to be installed.

UV treatment

The UV-unit from Aqua System A/S installed in the trailer is only for disinfection of mainly process and waste water. Several other UV-systems are specially designed for treatment of swimming pool water both for disinfection and oxidation, which makes the UV-unit currently installed in the test trailer uninteresting regarding test on swimming pool water. One of the products of Aqua System is however an UV reactor designed for reduction of chloramines, and an agreement of the installation of this type of UV reactor might be possible to enter at a reduced cost.

Chemical oxidation

Not relevant for treatment of swimming pool water.

Fermentor

Not relevant for treatment of swimming pool water.

Ozone treatment

The capacity of the ozone generator (37-55 g O_3/h) installed in the test trailer makes it possible to continuously treat 25-75 m^3/h of swimming pool water according to the German standard [DIN 19643, 1997]. This makes it possible to treat a small swimming pool or as a sub-stream in a larger pool. Additional pump capacity needs to be installed.

Sub-conclusion

As it is seen from the above review of the techniques in the test trailer, only the electrochemical reactor and the ozone generator were found useful for test on swimming pool water. Since the electrochemical method is not mentioned in the EPA examination project, more techniques, besides ozone, have to be localised for implementation in the tender. However, the test trailer with its present configuration is found applicable to enter into the tender with regards to the conduction of the ozone treatment test. It is then possible to offer the electrochemical test as an additional service for low cost.

The next section identifies the available Danish full scale techniques and the possibilities for including cooperative partners in the project.

4.2 *Identification of available full scale techniques*

The second strategy, in order to keep down the cost of treatment equipment, was to identify available full scale swimming pool installations based on the techniques required to be contained in the tender. These treatment systems have been installed by different distributors of swimming pool treatment devices in Denmark, and the analysis results from these installations have not yet been scientifically published, but they provide valuable experiences, which are not included in MST, 2007a. In order to identify these installations, the project group searched the market and pointed out Danish distributors of the alternative treatment techniques mentioned in MST, 2007a. Likewise, a practical overview of the market was needed in order to point out possible cooperative partners, whose treatment installations are applicable as test applications.

The result of the market search is seen in Table 7. There are a lot of other small companies, who distribute treatment systems for private and public pools, but their equipment is from the same manufacturers as the ones included in Table 7, and hence they were left out of the table. Each manufacturer and associated distributor(s) were contacted and asked for documentation material from full scale installations, primary in Denmark, but material from treatment systems installed in other countries was found to be relevant as well. The collected documentation material representing the manufacturer’s experiences are presented in section 5, where the chemical principles in UV, ozone, and electrochemical treatment techniques are studied.

Table 7: Important distributors and manufacturers on the Danish swimming pool treatment market providing alternative disinfection techniques. The brackets provide the country codes.

Technique	Manufacturer	Distributor	Pool experience
UV	Grünbeck (de) / Aqua System (dk)	Aqua System (dk)	(de) (dk)
	Wedeco (uk)	Krüger Aquacare (dk)	(uk)
		Silhorko (dk)	
	Hanovia (uk)	Axflow (dk)	(uk)
	Berson (nl)	HOH (dk)	(no)
	Wallace and Tiernan (de)	Løewener (dk)	(de)
	Triogen (uk)	Aquatec (dk)	(uk)
	Scan Research (dk)	Aquamaticsverige (se)	(dk)
Ozone	Triogen (uk)	Aquatec (dk)	(uk) (de) (fi)
	Ozonia (uk)	Air Liquide (dk)	-
Membrane	Scan Research A/S (dk)	Aquamaticsverige (se)	(dk)
	Ultraaqua (dk)	Aquahouse A/S (dk)	(soon dk)
Electrochemical	Watersafe (gr)	Watersafe (dk)	(gr) (dk)
	Adamant Technologies (ch)	-	(ch)
AOP (UV/O_3)	Triogen (uk)	Aquatec (dk)	(soon dk)
AOP (UV/TiO_2)	Wallenius (se)	Bluetec (dk)	(dk) (se)
		Swimtec (se)	
AOP (UV/ TiO_2)	Scan Research A/S (dk)	Aquamaticsverige (se)	(soon dk)
Metal disinfection	ECOsmarte (us)	Makri Pool (dk)	(us)

UV disinfection of water is an old well-known technique, which is reflected in the fact that several applications from many different manufacturers are available on the Danish swimming pool market. UV is not only disinfection, but is also used for oxidation of combined chlorine as well, and all of the included manufacturers provide applications capable of both disinfection and combined chlorine oxidation especially designed for the swimming pool market. Aqua System A/S and Scan Research A/S are Danish companies with Danish full scale references, and regarding the test trailer Aqua system

A/S has contracted as a cooperative partner. At the present time, the UV system delivered from Aqua System A/S for the test trailer is only for disinfection purposes and not combined chlorine oxidation, and is not relevant for swimming pool treatment. However, Aqua System A/S is responsible for several Danish installations, where combined chlorine UV systems are installed and are applicable for test purposes. Scan Research A/S has a similar UV system for combined chlorine oxidation and is as well in possession of suitable Danish full scale test installation that can be included in the tender.

Ozone is not used in swimming pool treatment in Denmark, but in United Kingdom, Germany, and Finland this treatment technique has been used for several years. Air Liquide has contracted as a cooperative partner regarding the test trailer with an ozone generator, which can be used for swimming pool treatment. No applicable Danish test installations were found during the market search.

Membrane filtration is mentioned in MST, 2007a, as a very interesting technique applied in cooperation with other treatment techniques such as UV. There are several companies in Denmark, who provide membrane filtration units for industrial purposes, but with regards to swimming pool treatment, Scan Research and Ultraaqua were the only companies with specific swimming pool units pointed out by the project group. A membrane filtration unit from Scan Research is installed in the same swimming pool installation as the UV systems for combined chlorine reduction. In cooperation with Aalborg University and Vandpartnerskabet, Ultraaqua is installing a membrane treatment system for test purposes in Bernstorffsminde Efterskole. The treatment installation is scheduled to be ready for operation at the 1st of September 2007 [Ing, 2007b].

Electrochemical treatment of swimming pool water is a technique, defined by the Danish EPA as still being in the early development phase. However, two individual companies with up and running applications in swimming pool treatment were pointed out during the market search. Adamant Technologies is a spin-off company from Centre Suisse d'electronique et de Microtechnique (CSEM) from Switzerland, and currently there is no Danish distributor of their products. The cooperation partner Watersafe provides an electrochemical reactor, which is widely used in swimming pool treatment in Greece, and the Danish distributor has contracted as a cooperative partner regarding installation in the test trailer. The Watersafe electrochemical treatment is not yet applied in Denmark, but at least one Watersafe treatment system is about to be installed for the treatment of a Danish swimming pool during July 2007. In addition, the main part of the present project concerns preparation of documentation material for the use of the electrochemical treatment technique in Danish swimming pool treatment. Test of the electrochemical technique is not demanded by MST, 2007a, but the conduction of preliminary test with the Watersafe unit by the project group was included in the tender.

AOPs are very interesting, and several combinations and techniques have shown promising results in the laboratories. However, a search for ready to use AOP commercial applications with Danish distributors revealed a more narrow range of techniques. Aquatec offers an UV/ozone combined technique from Triogen (Ozonia), where the first application is about to be installed in a Danish swimming pool during summer 2007 (Vejlefjord). The photocatalytic degradation technique applied in swimming pool treatment is very interesting as well, and the project group found a commercial application by the Swedish company Wallenius, distributed by Bluetec in Denmark. The unit has been evaluated by Technological Institute (TI) and is at present installed in four Danish swimming pool treatment systems with more coming up [Feilberg, 2006; Bluetech, 2007]. One of these installations could be applicable as test installation. The Danish company Scan Research A/S has recently developed an UV based AOP technique based on the combination of UV and TiO_2, photocatalytic oxidation. This unit from Scan Research A/S has not yet been installed in the treatment of a Danish swimming pool, but the preliminary work, in order to test it in the same installation as the UV and membrane techniques, has been conducted.

The last commercial alternative technique, found by the project group, available from Danish distributors in swimming pool treatment, is the ECOsmarte, which is based on electrolytic cupper release. ECOsmarte makes use of the strong bactericidal effect of cupper in the disinfection of microorganisms and posses no oxidative effect. Still no Danish references with the ECOsmarte technique are available. The cupper release disinfection principle is by the Danish EPA considered only to be applicable in association with chlorine disinfection, and further well documented full scale tests are needed before the use of the technique is advisable [MST, 2007a]. Test of the technique is not demanded in the called tenders, it is not considered interesting by the project group, and is not comprised in the tender.

4.3 Sub-conclusion

The search of the Danish market for swimming pool treatment equipment pointed out the main manufacturers and distributors. In the distribution of UV systems, several different applications are available, and Aqua System has several Danish installations suitable as test installations. During the search, Scan Research A/S was identified as being in possession of very interesting technologies, such as UV techniques, membrane filtration and photocatalytic treatment, which is one of the AOP required from the Danish EPA to be included in the tender. Furthermore, the techniques are all installed in treatment of the same swimming pool, which indeed optimises the possibility of successful comparisons. The possibility of including this installation, identified by the project group, in the tender as a test installation, made Rambøll A/S and Scan Research A/S form a consortium with respect to the tender.

The treatment installation, which was agreed to be included in the tender as a test installation, was installed in MarselisborgCentrets Svømmebad, Århus, and consists of:

- Vacuum membrane filtration; three membrane units with 0.05 µm ultra filtration membranes with a total filtrations area of 1,000 m^2. The membrane units can be operated in single, pairs or series mode, and both sub-stream and full stream treatment is possible. Injection of air beneath the membranes makes it possible to test the stripping effect on e.g. THM.
- An advanced photo oxidation process (APOP, same as AOP with UV) unit for combined chlorine oxidation.
- Possibility for installation of photocatalytic reactor, which is applicable for full scale test in both sub- and full stream operation.

Furthermore, an optimization of the existing traditional treatment system at Hørsholm swimming pool and an upgrade with an APROP-system (AOP with UV and TiO_2) was recommended.

By including these installations in the tender, the main part of the techniques required in the EPA examination project was covered, and the expenses for equipment investment in order to fulfil the requirements were highly reduced.

In the next section, the fundamental chemical principles in the treatment techniques required by the Danish EPA are studied; the ozone and UV treatment techniques. In addition, the fundamental chemical principles in the electrochemical treatment technique are studied, in order to constitute the basis for the laboratory experiments and the full scale project draft.

5 Theory and experience

In order to be sufficient prepared for the tests of the treatment techniques required by the Danish EPA, the project group found it necessary thoroughly to study their fundamental chemical principles. Especially treatment with ozone and UV radiation are well known and well tested techniques, and a review of the laboratory and full scale experiences, obtained through the research done in this area, is essential to gain the knowledge, which is necessary to provide the fundament for the evaluation of the tests of the techniques. The actual tests of the techniques, contained in the tender, are at the earliest scheduled to be initiated in July 2007, after the present project period has ended. However, one of the aims with this project was to provide adequate introductory works to both phase 1 and phase 2 of the EPA examination project and in the case that the Rambøll and Scan Research consortium wins the project, the project group is going to be deeply involved in the actual examination project as well. Likewise, the reference material obtained from the manufacturers and distributors from Table 7 are presented in this section of the report.

In order to constitute the basis for the laboratory experiments with the electrochemical Watersafe reactor, the fundamental chemical principles of this treatment technique is studied, and the results from existing research relevant for swimming pool treatment are presented. In establishing the cooperation with Watersafe Denmark, the project group and supervisors visited the production facilities in Greece and inspected swimming pool treatment installations, where the Watersafe reactor takes care of the treatment. Highlights from the technical excursion are found in section 5.3.3.

5.1 Ozone water treatment

Ozone, which is a powerful oxidant, has been used for disinfection and chemical oxidation of organic substances for decades. Ozone treatment was first applied in swimming pools in the 1960s, and has mainly been examined in Germany since the early 1970s. Tests in laboratory and full scale have demonstrated the efficiency of the technique towards oxidation of chloramines, DBP pre-cursors, and organic substances in general.

This section studies the theory of ozone disinfection and oxidation with principal focus on the use of ozone in swimming pools. Research in other water treatment areas, mainly drinking water, will also be included to supplement the theory and statements given in the literature concerning swimming pools. Besides describing the theory, references related to practical experience will be presented and reviewed.

5.1.1 Theory and laboratory investigations

Ozone is an unstable gas, decaying to ordinary diatomic oxygen.

$$2O_3(g) \rightarrow 3O_2(g) \tag{4}$$

Due to this decay, ozone has to be generated on site with an ozone generator.

Ozone stability in water

As in the case with ozone gas, ozone dissolved in water is also unstable and decays through various reactions. Depending on the water quality, the half-life of ozone ranges from seconds to hours. The stability of ozone in water mainly depends on the water matrix, especially its pH, the type and content of NOM, and its alkalinity [Hoigné and Bader, 1983]. The mechanisms and the kinetics involved in ozone decomposition have been investigated in numerous of studies [Gunten, 2003a]. The pH is of importance since hydroxide ions initiate the decomposition of ozone according to the following system of reactions [Gunten, 2003a]:

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \tag{5}$$

$$O_3 + HO_2^- \rightarrow OH^{\bullet} + O_2^{\bullet -} + O_2 \tag{6}$$

$$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2 \tag{7}$$

For pH below ~8:

$$O_3^{\bullet -} + H^+ \rightleftharpoons HO_3^{\bullet} \tag{8}$$

$$HO_3^{\bullet} \rightarrow OH^{\bullet} + O_2 \tag{9}$$

For pH above ~8:

$$O_3^{\bullet -} \rightleftharpoons O^{\bullet -} + O_2 \tag{10}$$

$$O^{\bullet -} + H_2O \rightarrow OH^{\bullet} + OH^- \tag{11}$$

Reaction 12 proceeds very fast and is important for waters with a low concentration of scavengers, i.e. low dissolved organic carbon (DOC) or low alkalinity, and results in consumption of ozone and hydroxyl radicals, which lowers the oxidation capacity of the water [Gunten, 2003a]:

$$OH^{\bullet} + O_3 \rightarrow HO_2^{\bullet} + O_2 \tag{12}$$

From reaction 5-12, it is seen that decomposition of ozone results in formation of hydroxyl radicals, and hence the ozonation processes always involves reaction by both ozone and hydroxyl radicals. The two species are of different importance; disinfection mainly occurs through ozone, while oxidation processes may occur through both ozone and hydroxyl radicals [Hoigné, 1998; Facile el al., 2000]. However, there is a frequent debate on the role of hydroxyl radicals for disinfection processes. While some authors state that ozone is the main disinfectant, others suggest that hydroxyl radicals may play an important role for disinfection [Gunten, 2003b].

Oxidation by ozone

Ozone is a very selective oxidant, while hydroxyl radicals react fast with many dissolved organic compounds. To assess the ozonation processes, the concentration or exposure to both oxidants have to be known. Ozone can easily be measured by electrochemical, optical or colorimetric methods, while the hydroxyl radicals are very complicated to measure due to their high reactivity towards the water matrix. In steady-state situations during ozonation, this results in very low concentrations of hydroxyl radicals, typically below 10^{-12} M [Gunten, 2003a].

The oxidation of organic compounds, S, typically follows second order kinetics [Gunten, 2003a]:

$$-\frac{d[S]}{dt} = k \cdot [S] \cdot [O_3] \tag{13}$$

where k is the second order rate constant. The activation energy for ozone reactions usually lie in the range of 35-50 $^{kJ}/_{mol}$ [Hoigné and Bader, 1983].

Tests in laboratory have shown that ozone was able to degrade urea and chloramines and reduce the concentration of chlorinated organic substances. However, the reactions occurred slowly [Eichelsdörfer and Harpe, 1970; Eichelsdörfer and Jandik, 1979]. If contact times of 15-20 minutes were used, concentrations of the main contaminants could be efficiently reduced at an ozone flow of 1 g O_3/m^3 [Eichelsdörfer and Jandik, 1985]. Another laboratory test carried out in a 1.4 l stirred reactor showed a reduction in the THM formation potential of 76 % at an addition of 1.1 g O_3/m^3 [Kleiser and Frimmel, 2000].

Pilot scale ozonation of swimming pools have shown that ozone was capable of reducing the content of organic matter by 99 %, and maintain the concentration of THM below 10 $^{\mu g}/_{l}$ at free chlorine concentrations of 0.2-0.5 $^{mg}/_{l}$ [Rice, 1989]. Another pilot test showed a reduction of 32 % of the THM formation potential with 2 minutes of contact time and 3 g O_3/m^3 [Vahala et al., 1999].

Disinfection by ozone

Ozone can only be used as a primary disinfectant, since it cannot maintain a residual disinfection effect in the swimming pool. Thus, ozone disinfection must be coupled with a secondary disinfectant such as chlorine.

Ozone is an excellent disinfectant and is capable of inactivating even more resistant microorganisms compared to conventional disinfectants such as chlorine. The disinfectant exposure (ct), which is a product of the disinfectant concentration and the contact time, can be estimated from the Chick-Watson equation [Phelps, 1911]:

$$\log(N / N_0) = -k \cdot c^n \cdot t \tag{14}$$

where N_0 is the number of microorganisms at time t = 0, N is the number of vital microorganisms at t, k is the rate constant for the inactivation, c is the concentration of disinfectant, n is the fitting parameter (in many cases, n is equal to 1, resulting in a first order inactivation process). Typically, the assessment of disinfection is based on published ct-values. Not much kinetic data exists on inactivation of microorganisms, since the rate constants only have been measured in recent years [Gunten, 2003b].

Table 8 and Table 9 show the kinetics of the inactivation of different microorganisms with ozone determined in lab and pilot studies.

Table 8: Kinetics of the inactivation of microorganisms with ozone at pH 7.

Microorganism	$k_{O_3}\,[{}^{1}\!/_{mg\cdot min}]$	$k_{O_3}\,[{}^{1}\!/_{mol\cdot s}]$	T [ºC]
E. coli	130	$1.04\cdot 10^{5}$	20
B. subtilis spores	2.9	$2.3\cdot 10^{3}$	20
Rotavirus	76	$6\cdot 10^{4}$	20
Giardia lamblia cysts	29	$2.3\cdot 10^{4}$	25
	12	$9.5\cdot 10^{3}$	22
Giardia muris cysts	15.4	$1.2\cdot 10^{4}$	25
Cryptosporidium p. oocysts	0.84	$6.7\cdot 10^{2}$	20

Source: modified from [Gunten, 2003b]

Table 9: ct-values for different microorganisms for both ozone and free chlorine.

Microorganism	Removal	T	pH	ct_{O_3}	ct_{Cl_2}
	[%]	[ºC]		$[{}^{mg\cdot min}\!/_{l}]$	$[{}^{mg\cdot min}\!/_{l}]$
Giardia muris	99	25	7	0.3	26-45
Giardia sp. Human	99	25	7	0.2	<15
Cryptosporidium p.	99.9	22	7	3-15	-
	99	22	7	2-8	-
	99	25	7	-	7200
Virus	99.9	10	6-9	0.8	4

Source: modified from [MST, 2007a]

The rate constants provided in Table 8 exemplify the problems associated with the use of *E. coli* as indicator organism to assess the efficiency of disinfection processes, since it is far easier to inactivate, compared to the other microorganisms reviewed. The temperature dependence of the inactivation differs for the microorganisms. The general trend for *B. subtilis* shows a less efficient inactivation for increasing temperatures, whereas the opposite is the case for *C. parvum* [Pinkernell and Gunten, 2000]. From Table 9 it is also seen that ozone is a much more effective disinfectant compared to chlorine.

Driedger et al., 2000 and 2001, investigated the inactivation of *B. subtilis* and *C. parvum* with ozone and $HOCl$ in combination with varying temperature, pH, and concentration and found a synergetic effect between ozone and $HOCl$.

Generally it is believed that the effect of hydroxyl radicals in disinfection processes in ozonation can be neglected, since the main target of inactivation is the cell core DNA and the hydroxyl radicals would be scavenged in the cell wall [Gunten, 2003b]. Another argument is the difference in the significant concentration ratio between hydroxyl radicals and ozone (OH/O_3), which is in the order 10^{-6}-10^{-9} [Gunten, 2003a]. However, in electrochemical studies, the presence of hydroxyl radicals is believed to results in comprehensive damage on the cell wall of the bacteria [Li et al., 2004]. As it is seen, there is disagreement concerning the role of the hydroxyl radicals in the disinfection processes, and it is subject to frequent debate.

Disinfection by-products

In conjunction with the beneficial effects regarding oxidation and disinfection, ozonation also results in formation of numerous undesired by-products from the reactions of ozone and hydroxyl radicals with compounds in the water matrix. A review of the literature concerning DBPs from ozonation shows that the formation of bromate, which is considered carcinogenic, is the most studied DBP.

Ozone has been shown to oxidize bromide to hypobromite and bromate, and hypochlorite to chlorate. Ozonation of swimming pool water may result in the formation of [WHO, 2006]:

- Bromate
- Aldehydes
- Ketones
- Ketoacids
- Carboxylic acids
- Bromoform
- Brominated acetic acids

For a comprehensive review of DBPs related to ozonation, the project group refers to [WHO, 2004a; WHO, 2006; Gunten, 2003b].

The oxidation of chlorination-derived DBPs by ozone is very slow because of their high degree of halogenation, which leads to a low electron density at the carbon centre. Therefore ozonation is not suitable for removal of DBP [Gunten, 2003a; Hoigné and Baden, 1983]. The rate constants for oxidation of halogenated DBPs at an ozone concentration of 1 $^{mg}/_{l}$ and pH 7 are shown in Table 10.

Table 10: Rate constants and half-lifes for oxidation of halogenated DBPs at an ozone concentration of 1 $^{mg}/_{l}$ and pH 7.

Substance	$k_{O_3}\,[^{1}/_{mol \cdot s}]$	$t_{½}$	Reference
Chloroform	<< 0.1	>> 100 h	[Hoigné and Baden, 1983]
Bromoform	<< 0.2	>> 50 h	[Hoigné and Baden, 1983]
Iodoform	< 2.0	> 5 h	[Bichsel, 2000]

5.1.2 Bench and full scale experience in swimming pools

Many swimming pools use ozone for treatment of the water, but still, not many results and test concerning ozone in swimming pools have been scientifically published. In Germany, 1057 ozone treatment systems were installed in swimming pools between 1954 and 1983 [Eichelsdörfer and Jandik, 1988]. Some of the most thorough laboratory and full scale test carried out concerning ozonation of swimming pool water have been performed in Germany since the early 1970s. Based on these experiments and tests, DIN 19643, 1997, describes the application of ozone for treatment of swimming pool water. The recommended ozone concentrations are showed in Table 11.

Table 11: Recommended ozone concentrations for treatment of swimming pool water as a function of temperature.

Temperature	Ozone feed
≤ 28ºC	0.8 g O_3/m^3
>28 ºC, ≤ 32 ºC	1.0 g O_3/m^3
>32 ºC, ≤ 35 ºC	1.2 g O_3/m^3
>35 ºC	1.5 g O_3/m^3

Source: [DIN 19643, 1997]

DIN 19643, 1997, recommends a contact time of 3-15 min and a sufficient concentration of free chlorine of 0.2-0.5 $^{mg}/_{l}$. It is also recommended to use an ozone generator, which produces more than 20 g O_3/m^3 in order to obtain an acceptable efficiency of the absorption process.

Based on results obtained from the laboratory [Eichelsdörfer and Harpe, 1970; Eichelsdörfer and Jandik, 1979], a full scale test in a swimming pool was conducted over 5 days [Eichelsdörfer and Quentin, 1982]. The test showed that longer contact time (15 min) resulted in an effective reduction of organic matter regardless of the bathing load. This also ensured a reduction in THM formation potential of 60 % and a following concentration of THM of 3-7 $^{\mu g}/_{l}$. The combined chlorine content was also brought down to 0.22 $^{mg}/_{l}$ from 0.35 $^{mg}/_{l}$. No problem in maintaining the microbiological requirements given in DIN 19643 was encountered.

Glauner et al., 2005b, has investigated the use of ozone in swimming pools and compared it with ozone based AOPs; O_3/UV and O_3/H_2O_2. The combination of AOPs and ozone showed an increased elimination efficiency regarding TOC (Total Organic Carbon), AOX (Adsorbable Organic halogen compounds), and AOX formation potential. Glauner et al., 2005b, also showed that membrane filtration and AOPs resulted in 10-90 % elimination of DBPs and their precursors.

In the next section, the fundamental principles in UV treatment of swimming pool are studied.

5.2 UV water treatment

UV light has been known for its bactericidal effect since the start of the 1900s century, and since the beginning of the 1980s the possibilities of UV light for oxidation in swimming pool treatment has been investigated as well. At the present state, the UV techniques are widely used in the treatment of swimming pools, and many different commercially available applications have been thoroughly tested and documented by the manufactures. This section presents the theory of UV radiation used in disinfection and in the photochemical oxidation of the combined chlorine species.

A lot of documentation material was received from some of the contacted manufactures, and an overview of the results is presented in section 5.2.2.

5.2.1 Theory and laboratory investigations

UV light is electromagnetic radiation with a wavelength in the range of 100 to 400 nm. According to International Commission of Light (CIE), UV is classified in four classes; vacuum UV (100-200 nm), UV-C (200-280 nm), UV-B (280-315 nm), and UV-A (315-400 nm). Traditionally, the bactericidal effect is provided by the UV-C radiation, especially at the wavelength of 253.7 nm, while the oxidative effect towards combined chlorine and other pollutants are obtained at wavelength in the range of 245-340 nm [Kalisvaart, 2001; Wallace and Tiernan, 2004c].

Disinfection by UV

In traditional disinfection by UV radiation, the microorganisms are inactivated by destruction of cell core DNA and RNA destroying the ability of microorganisms to reproduce. According to Sonntag, 1986, the absorption curve of DNA shows maximum absorption at 200 nm, with an additional peak at around 260-265 nm. Traditionally, the wavelength of 253.7 nm is applied in disinfection, which is generated in low pressure UV mercury lamps, and it has been assumed that this wavelength was the most efficient in the killing of microorganisms, despite that maximum absorption does not occur at 253.7 nm [Kalisvaart, 2001]. The 253.7 nm radiation has proved its efficiency towards a wide range of waterborne pathogens, in the inactivating of living cells, oocysts and spores from bacteria, and viruses [Hijnen et al., 2006]. One of the major advantages of UV disinfection in swimming pool treatment is its efficiency towards *Cryptosporidium parvum*, which is not affected in traditional chlorine disinfection.

However, microorganisms are able to recover from the exposure to the 253.7 nm UV radiation using available active enzymes, but is has not been shown that UV damage caused by higher intensity radiation can be repaired, and repair processes in other biomolecules than DNA has not been identified [Kalisvaart, 2001]. Hence, the second generation of UV lamps for disinfection purposes was medium pressure UV lamps, which produce a wider range of UV wavelength, allowing them to affect biomolecules other than DNA. The third generation of UV lamps developed for disinfection, which were introduced in the late 1990s, combines the high UV efficiency of the low pressure lamps with the multiple germicidal effects of the wide-band output from medium pressure lamps. The second and third generations of lamps are however not as widely applied in disinfection systems yet, and a lack of published results by these lamps exists. Hence the results presented in Table 12 only cover studies obtained by the traditional low pressure UV lamps.

Different types of microorganisms require different dosages of UV light in order to obtain a specified reduction level. The dose of UV is correctly specified by the UV fluence, *D*, calculated by equation 15 [EPA, 1999]:

$$D\,[{}^{mJ}\!/\!{}_{cm^2}] = I\,[{}^{mW}\!/\!{}_{cm^2}]\cdot t\,[s] \tag{15}$$

I is the intensity and *t* is the time of exposure. By use of the UV fluence, the inactivation of microorganisms by UV can according to Hijnen et al., 2006, be described with first order kinetics, but no inactivation at low fluences and/or no increased inactivation at higher fluences were observed for some microorganisms. Inactivation results are in the literature most commonly presented as the obtained logarithmic inactivation of a given bacteria concentration provided by certain fluences. Inactivation results by UV radiation selected from the review paper by Hijnen et al., 2006, for microorganisms relevant in swimming pool water are presented in Table 12.

Table 12: Selected results from inactivation studies of different microorganisms. The rate constants are provided by first-order models concerning the fluence.

Microorganism	Fluence $[{}^{mJ}\!/\!{}_{cm^2}]$	Rate constant, k $[{}^{cm^2}\!/\!{}_{mJ}]$	Inactivation
E. coli	1-15	0.506	log-6
Legionella pn.	1-12	0.400	log-4.4
Streptococcus fa.	2.5-16	0.312	log-4.6
MS2-phages	5-139	0.055	log-4.9
Cryptosporidium p.	0.9-13.1	0.225	log-3

Source: [Hijnen et al., 2006]

The required radiation intensity, in order to obtain the required fluence, is however dependent on the quality of the treated water, since particles and UV absorbing substances will reduce the penetration of the radiation [EPA, 1999].

Oxidation by UV

Photochemical oxidation by UV light is performed by the use of medium pressure UV lamps that emit energy at wavelengths from 200 to 600 nm [Cassan et al., 2006]. The first step in photooxidation is UV induced electronic excitation of the organic substrate, reaction 16 [Legrini et al., 1993]:

$$C \xrightarrow{h\nu} C^* \tag{16}$$

The excited substance in most cases transfer an electron to ground state molecular oxygen, reaction 17, which is succeed by either recombination or hydrolysis of the radical cation [Legrini et al., 1993]:

$$C^* + O_2 \rightarrow C^{\bullet +} + O_2^{\bullet -} \tag{17}$$

Homolysis is a possibility as well, reaction 18, where radicals are generated by UV induced breakage of atomic bonds, succeeded by subsequent reaction with molecular oxygen, reaction 19 [Legrine et al., 1993].

$$R - X \xrightarrow{h\nu} R^{\bullet} + X^{\bullet} \tag{18}$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \tag{19}$$

Oxidation with pure UV is primarily applied in the reduction of combined chlorine represented by the chloramines. According to Dreyer and Lyngkilde, 1983, the superior reaction schemes for chloramine reduction are as follow; monochloamine, reaction 20, dichloramine, reaction 21-24, and trichloramine, reaction 25.

$$2NH_2Cl + HOCl \xrightarrow{hv} N_2 + 3H^+ + 3Cl^- + H_2O \tag{20}$$

$$NHCl_2 + OH^- \xrightarrow{hv} Cl_2N^- + H_2O \tag{21}$$

$$Cl_2N^- + NHCl_2 \rightarrow Cl_2N - NHCl + Cl^- \tag{22}$$

$$Cl_2N - NHCl_2 \rightarrow Cl - N = N - Cl + H^+ + Cl^- \tag{23}$$

$$Cl - N = N - Cl + H^+ + Cl^- \rightarrow Cl_2 + N_2 + H^+ + Cl^- \tag{24}$$

$$2NCl_3 + 3H_2O \xrightarrow{hv} N_2 + 3HOCl + H^+ + Cl^- \tag{25}$$

In the literature study, the project group found that the wavelength required for optimum reduction of chloramines was specified by the manufactures to the ones shown in Table 13.

Table 13: Wavelength for optimum chloramine reduction.

Substances	Wavelength [nm]	UV fluence [$^{mJ}/_{cm^2}$]
Monochloramine	245	25-50
Dichloramine	297	25-50
Trichloramine	260 and 340	25-50

Source: [Wallace and Tiernan, 2004b]

A further detailed discussion concerning why these respective wavelength apply has not been found despite a comprehensive and intensive literature search. According to the project group, the energies gained by the chloramines from the respective wavelength are expected to correspond to the bonding energies in the molecule and the energies required for exciting the chloramines. In Cooper et al., 2007, a wavelength of 245 nm was specified as absorption maximum of monochloramine in the UV/VIS spectrum, and this promote the thought that similarities apply for the wavelength connected to the di- and trichloramine. The absorption maximum indicates the energy needed to induce the electronic transitions in the respective chloramine. Through computational chemistry consideration performed with the Gaussian v.03 software, the project group investigated the theoretically excitation energies for the chloramines, but due to a lack of experience with the use of this research tool, the obtained results was to no avail. However, the obtained excitation energies indicated the same tendency as showed in Table 13; that the lowest energy is needed for excitation of trichloramine. The computational investigation is seen in appendix 2.

In a recent study by Cassan et al., 2006, investigating the effects of radiation from medium-pressure UV lamps on water quality in a chlorinated indoor swimming pool, it was concluded that the UV radiation led to an increase in the concentration of active free chlorine by photolysis of the combined chlorine. Therefore, it was possible to reduce the addition of chlorine to the water and the water renewal volume, while maintaining the bacteriological quality of water within the allowable limits. The combined chlorine level was significant decreased ($P<0.001$) from 0.6 $^{mg}/_{l}$ to 0.2 $^{mg}/_{l}$. It was also concluded that the medium-pressure UV lamps induced a TOC removal.

One of the major questions in applying medium pressure UV lamps for chloramine reduction is the subsequent formation of THMs. Beyer et al., 2004, observed, in a report conducted for the manufacturer Wallace and Tiernan, a reduction on 30 % in the THM level by the use of the medium-pressure UV lamps, but the study by Cassan et al., 2006, found a significant increase ($P<0.001$) in the level of total THMs, particularly $CHCl_3$ and $CHBrCl_2$, and further studies are indeed needed to verify this question.

5.2.2 Bench and full scale experiences in swimming pools

UV treatment of swimming pool water with medium pressure UV lamps are widely used in Northern Europe, and even though not a great amount of results have been scientifically published, the technique has showed its efficiency in a great number of full scale installations. The use of low pressure UV lamps exclusively for disinfection purposes is not commonly used in swimming pools.

In this section, the results from the collected reference material obtained from the manufacturers and distributors are presented, but not all of the contacted manufacturers and distributors from Table 7 in section 4.2 returned with their reference material. The quality of the analysis results is unknown. The level of combined chlorine is very dependent on the number of guest pr. day, but in most of the presented reference material this has been taken into account. The result is seen in Table 14.

Table 14: Collected references by the reduction of combined chlorine by the use of medium-pressure UV lamps.

Location	Pool temp. [°C]	Combined chlorine [$^{mg}/_{l}$] Before	After	Reduction	Reference
Berlin (de)	-	0.3	0.14	40 %	[Wallace and Tiernan, 2004(b)]
Bench sc. (nl)	-	0.3	0.17	43 %	[Wallace and Tiernan, 2004(c)]
Langnau (de)	-	-	-	33 %	[Wallace and Tiernan, 2005(a)]
Burgess (uk)	-	1.22	0.26	78 %	[Wallace and Tiernan, 2005(b)]
Birmingham (uk)	30	1.0	0.2	80 %	[Aqua System, 2006(a)]
Clithroe (ir)	32	1.2	0.2	83 %	[Aqua Sytem, 2006 (b)]
Dundee (ir)	34	1.0	0.2	80 %	[Aqua System, 2006(c)]
Tralee (ir)	29	0.8	0.4	50 %	[Aqua System, 2006(d)]
Århus (dk)	34	0.6	0.25	58 %	[Aqua System, 2003]
Skive (dk)	34	0.6	0.31	50 %	[Aqua System, 2003]
Køge (dk)	28	0.74	0.46	37 %	[Aqua System, 2003]
Køge (dk)	33	0.5	0.23	54 %	[Aqua System, 2003]
Fredrikshavn	33	0.61	0.29	52 %	[Aqua System, 2003]
Kalundborg (dk)	27	0.59	0.11	81 %	[Aqua System, 2003]
Kalundborg (dk)	33	0.7	0.19	72 %	[Aqua System, 2003]
Islinge (dk)	28	0.55	0.28	49 %	[Aqua System, 2003]
Nakskov (dk)	28	0.95	0.42	56 %	[Aqua System, 2003]
Blåvandshuk (dk)	32	0.56	0.23	50 %	[Aqua System, 2003]
Helsinki (fl)	32	-	0.2	-	[Aqua System, 2003]
Center Parcs (de)	-	0.35	0.15	57 %	[Hanovia, 2006(a)]
Kerfi (ice)	-	0.5	0.2	60 %	[Hanovia, 2006(b)]

Each company has its own UV application for combined chlorine reduction, but all of the results are obtained with medium pressure UV lamps. Most of the results are from leisure pools, but also hot tubs and sports basins are represented as well. Likewise, some of the installations are full stream, while sub-stream treatment is sufficient in other cases. Finally, the UV treatment only operates part time in some of the installations. It is seen that independently on manufacturer application, a minimum of 50 % reduction is obtained in the majority of the presented references, where the start level of combined chlorine was above 0.5 $^{mg}/_{l}$. The use of UV in chloramine reduction often prompts a reduction in the consumption of fresh water for renewal, and hence reduces cost. The references presented in Table 14 is of course selected by the manufacturer and can not be considered representative, but they show that commercially available applications exists and can perform the oxidation of the unwanted chloramines to below the applicable limits.

In the next section, the chemical and operational principles in the electrochemical treatment of swimming pool water are studied.

5.3 Electrochemical water treatment

Electrochemical treatment of water has shown to be efficient for disinfection of a range of different pathogens as well as capable of oxidising DBPs and the DBP precursors. In general, electrochemical disinfection and oxidation occur by use of electrodes, between which a voltage is applied, creating an electrolytic system with direct exchange of electrons between the electrodes and the water constituents. The degree of electron exchange is dependent on the size of the applied voltage, which to a certain extent makes the chemical reactions controllable.

This section studies the theory in electrochemical disinfection and oxidation, which are highly related, since produced oxidants act as the disinfecting agents towards the pathogens. The focus will be on swimming pool water treatment, but the main part of the world wide research has been performed in the drinking water research area. However, the issue with chlorine currently being the main disinfectant exists in this area as well and the provided results are believed to be transferable to swimming pool water treatment. Electrochemical disinfection has been studied related to waste water issues, and some research results from this area will be included as well.

The project group has investigated the use of laboratory, bench scale, and full scale electrochemical treatment of swimming pool water. The collected references will be presented.

5.3.1 Theory and laboratory investigations

An electrochemical process requires the presence of a current between an anode and a cathode which generates a potential. The size of the potential depends on the applied voltage and hence the resulting current. Applying a simplified consideration, at least three reaction zones with different conditions exist in the electrochemical reactor [Bergmann and Koparal, 2005]:

- The contact plane and vicinity of the anode with acidic pH due to the main reaction of oxygen formation, reaction 26:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{26}$$

- The contact plane and vicinity of the cathode with increased basic pH due to the main reaction of molecular hydrogen formation, reaction 27:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{27}$$

- The bulk zone of the electrolyte

In swimming pool water treatment the reactions in the oxidation zone is generally of most interest. In order to create the conditions needed for a certain reaction to occur, the system has to be applied an excess voltage as related to the equilibrium potential of the reaction. In Table 15, some selected reaction potentials related to swimming pool water treatment are presented.

Table 15: Standard reduction potentials at 25 ºC and 1 atm.

Reaction	E^0 [V]	Reaction	E^0 [V]
$HOCl + H^+ + e^- \rightarrow ½Cl_2 + H_2O$	1.611	$OCl^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	0.81
$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.482	$ClO_2^- + 2H_2O + 4e^- \rightleftharpoons Cl^- + 4OH^-$	0.76
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	1.358	$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.695
$ClO_2 + H^+ + e^- \rightleftharpoons HClO_2$	1.277	$ClO_2^- + H_2O + 2e^- \rightleftharpoons ClO^- + 2OH^-$	0.66
$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$	1.229	$CHCl_3 + 3H^+ + 6e^- \rightleftharpoons CH_4 + 3Cl^-$	0.340
$ClO_2(aq) + e^- \rightleftharpoons ClO_2^-$	0.954	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.828

Source: [Linde, 1996]

From natural water constituents, powerful oxidants can be formed during electrolysis, but in swimming pool treatment a further addition of $NaCl$ to a concentration in the order of 1 % is often needed. The primary oxidants are chlorine components, but in theory and to a certain extent in practise, the formation of a range of other more powerful oxidants such as free hydroxyl radicals, ozone, persulfate and hydrogen peroxide are feasible as well [Patermarakis and Fountoukidis, 1990]. In this section the fundamental research in the formation of electrochemical oxidants is reviewed followed by the results from investigations of electrochemical disinfection and oxidation applied on bacteria and DBPs related to swimming pool treatment.

Formation of chlorine species by electrolysis

The electrolysis of chlorine occurs at the anode, where chloride is oxidised to chlorine, reaction 28 [Patermarakis and Fountoukidis, 1990; Stoner and Cahen, 1982].

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (28)$$

Chlorine reacts with water and forms hypochlorous and hydrochloric acids, reaction 29, and hypochlorous acid dissociates as a function of pH, reaction 30. The reactions are similar to the ones presented in section 2.3.

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \qquad (29)$$

$$HOCl \rightleftharpoons H^+ + ClO^- \qquad (30)$$

The disinfecting agents from this process are Cl_2, $HOCl$ and ClO^-, the free chlorine species as described in section 2.3, and the action of the free chlorine takes place in the entire volume of water and is primarily responsible for the residual disinfection capacity. The concentration of the free available chlorine in the water is dependent on the applied current [Bergmann and Koparal, 2005].

Electrochemical treatment with $NaCl$ addition results in the formation of several chlorine components, which makes the composition of the electrolyte a complex chemical system. It has been investigated towards the formation of chlorine dioxide, one of the by-products and a poisonous gas that can be explosive at partial pressures higher than 300 mmHg (~0.4 atm) [Bergmann and Koparal, 2005]. From thermodynamic considerations, chlorine dioxide may be formed electrocatalytic by reaction 31 and 32:

$$Cl^- + 2H_2O \rightarrow ClO_2 + 4H^+ + 5e^- \tag{31}$$

$$Cl_2 + 4H_2O \rightarrow 2ClO_2 + 8H^+ + 8e^- \tag{32}$$

The dissolution reaction of chlorine dioxide leads to the formation of chlorate and chlorite according to reaction 33, preferably in alkaline solution:

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O \tag{33}$$

According to Adam et al., 1992, ClO_2^- is also a short-living product of chlorine production in the medium pH region. In the acidic pH range, ClO_2^- and free chlorine react to form an intermediate species, Cl_2O_2, reaction 34 [Gordon et al., 2002]:

$$Cl_2 + ClO_2^- \rightarrow Cl_2O_2 + Cl^- \tag{34}$$

The role of the intermediate is important, since the pH of the electrolyte in the vicinity of the anode typically is acidic and in the presence of free chlorine, the intermediate forms ClO_3^-, reaction 35 and 36 [Gordon et al., 2002]:

$$Cl_2O_2 + H_2O \rightarrow ClO_3^- + Cl^- + 2H^+ \tag{35}$$

$$Cl_2O_2 + HOCl \rightarrow ClO_3^- + Cl_2 + H^+ \tag{36}$$

$HClO_2$ may be formed electrochemically as described in reaction 37,

$$HClO + H_2O \rightarrow HClO_2 + 2H^+ + 2e^- \tag{37}$$

and contribute to the chlorine dioxide formation via reaction 38 [Bergmann and Koparal, 2005].

$$HClO_2 \rightarrow ClO_2 + H^+ + e^- \tag{38}$$

However, the chlorine dioxide formation was showed to be proportional to the chloride concentration and the main contributor of chlorine dioxide was ascribed the reaction between hypochlorous acid and chlorite, reaction 39 [Bergmann and Koparal, 2005]:

$$HOCl + 2ClO_2^- \rightarrow 2ClO_2 + Cl^- + OH^- \tag{39}$$

The concentrations measured in the study corresponded to about 10 % of the concentration of free chlorine [Bergmann and Koparal, 2005]. According to Bergmann and Koparal 2005, the electrochemical formation of chlorine dioxide in electrochemical treatment of drinking and swimming pool water has to be further investigated, and the technical electrochemical cells have to be better controlled in order to exclude any health risk.

The formation of free chlorine by the electrolysis of a salt solution is postulated to result in the same formation of DBPs as in the ordinary disinfection with sodium hypochlorite [Kerwick et al. 2005], but the in-situ free chlorine formation together with the other possible oxidants makes it feasible to run the treatment process with a residual free chlorine concentration in the 0.2-0.7 $^{mg}/_{l}$ range [Häenni et al. 2002].

The formation of other oxidants

The presence and role of other feasible oxidants in electrochemical water treatment processes have been the subject in numerous papers [Patermarakis and Fountoukidis, 1990; Gordon et al., 2002; Gordon, 1998; Li et al., 2004; Feng et al., 2004; Tanaka et al., 2004 etc.]. The oxidants are typically very difficult to measure due to very fast reaction rates, and hence a lack of direct evidence of their presence exists. This is especially applicable for the free radicals, while the presence of electrochemical generated ozone and hydroperoxide is more widely accepted. Investigations with indirect methods, reviewed in section 6.4.1, have however provided evidence for the existence of hydroxyl radicals.

Patermarakis and Fountoukidis, 1990, present the most evident oxidative species:

- Active oxygen atoms produced at the anode by hydroxide ions:

$$2OH^- \rightarrow H_2O + [O] + 2e^- \quad (40)$$
$$2[O] \rightarrow O_2 \quad (41)$$

- The formation of ozone, which is supported by Kleiser and Frimmel, 2000, Rennecker et al., 1999, among others. The formation is expected to occur via a reaction between atomic and molecular oxygen:

$$[O] + O_2 \rightarrow O_3 \quad (42)$$

- The formation of radicals. The produced ozone is expected to participate in reactions generating free radicals, including hydroxyl radicals:

$$O_3 + H_2O \rightarrow HO_3^+ + OH^- \quad (43)$$
$$HO_3^+ + OH^- \rightarrow 2HO_2^{\bullet} \quad (44)$$
$$O_3 + HO_2^{\bullet} \rightarrow 2O_2 + OH^{\bullet} \quad (45)$$

The free radicals are very powerful oxidants and as discussed in section 5.1.1, the free radicals are by some authors believed to be efficient disinfecting agents, but their presence in electrochemical treatment is questionable. Comninellis, 1994, revealed that by applying p-nitroso-dimethylaniline (RNO) as a spin trap, hydroxyl radical accumulation were detected at the surface of a SnO_2 anode, but not detected at Pt and IrO_2 anodes, and hence the electrochemical radical production is highly dependent on the applied anode material. The RNO spin trap method for indirect hydroxyl radical detection is more thoroughly reviewed in section 6.4.

Comninellis, 1994, proposed a mechanism in which the oxide anode (MO_x) produces adsorbed hydroxyl radicals according to reaction 46, in acidic solution from H_2O and in alkali solution from OH^-.

$$MO_x + H_2O \rightarrow MO_x(OH^\bullet) + H^+ + e^- \tag{46}$$

In the second step, the adsorbed hydroxyl radicals may interact with the oxygen already present in the oxide anode with possible transition of oxygen from the adsorbed hydroxyl radical to the lattice of the oxide anode forming a so-called higher oxide MO_{x+1}, see reaction 47.

$$MO_x(OH^\bullet) \rightarrow MO_{x+1} + H^+ + e^- \tag{47}$$

Thus, two states of active oxygen can be present at the surface; physisorbed active oxygen (the adsorbed hydroxyl radicals, $OH^\bullet$) and chemisorbed active oxygen (oxygen in the oxide lattice, MO_{x+1}). In the absence of oxidizable compounds, molecular oxygen is produced according to reaction 48 and 49.

$$MO_x(OH^\bullet) \rightarrow MO_x + ½O_2 + H^+ + e^- \tag{48}$$

$$MO_{x+1} \rightarrow MO_x + ½O_2 \tag{49}$$

Evidence for the oxygen production at a PtO_x anode has been provided by Rosenthal, 1956, and the presence of hydroxyl radicals in electrochemical treatment has among other been verified by Feng et al., 2003, by the RNO method. A more detailed discussion of the results obtained by the RNO experimental method is provided in section 6.4.

At the cathode, lethal species can be produced by reduction of molecular oxygen [Patermarakis and Fountoukidis, 1990; Porta and Kulhanek, 1986; Drogui et al., 2001a; Drogui et al., 2001b]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{50}$$

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \tag{51}$$

The hydroperoxide and the hydroperoxide ions are very active disinfecting agents and a controlled electrochemical production of hydroperoxide was achieved by Drogui et al. 2001a without addition of chemicals.

Oturan, 2000, developed an electrochemical system based on a carbon electrode, where Fenton's reagent was generated in-situ in the reactor by electrochemical reduction of dissolved molecular oxygen, which reacted with added ferric ions. The molecular oxygen was reduced to hydroperoxide at the cathode and reacted with *Fe(II)* according to reaction 52.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{52}$$

In this system, a controlled production of hydroxyl radicals was achieved, which was applied in the destruction of different organic pollutants. The production of hydroxyl radicals was believed mainly to depend on the amount of ferric ion and not on the anode material. Li et al., 2004, and Li et al., 2002, provide indirect evidence of the presence of powerful oxidative species in electrochemical disinfection of artificial waste water contaminated with *E. coli*, by a comparison of bacteria cells, treated by different disinfecting agents, in scanning electron microscopy. They conclude that electrochemical treatment generates chemical products with oxidising and germicidal power similar to that of ozone and much stronger than that of chlorine, and the investigation supports the theory that the major killing mechanism is due to free radicals. They state that electrochlorination only contribute with 10 % of the overall disinfection determined for the electrochemical process. Electrochlorination could cause a partial disinfecting effect, but cannot explain all of the bactericidal action observed for the electrochemical treatment [Li et al., 2004].

Analytical interference by free chlorine

However, Gordon et al., 2002, and Gordon et al., 1998, object against the presence of multiple oxidants in an electrolysed salt brine solution. In the term multiple oxidants, they include chlorine dioxide and ozone. According to the argumentation, free available chlorine is unambiguously the primary oxidant, and they account for the continuing confusion to be the misapplication of the widely used DPD analytical method for measuring free and combined chlorine [DS/EN ISO 7393-2, 2002]. The DPD method is based on the reaction between free chlorine and N,N-diethyl-p-phenylenediamine (DPD), which forms a red/pink coloured complex, and the absorbance of the coloured solution is measured spectrophotometrically. More about the DPD method is found in section 6.2.1. The DPD method is often used to measure chlorine dioxide, but the use of insufficient masking agents to completely remove free available chlorine before its reaction with DPD provides a false-positive measurement. Just as well, changes in ionic strength can result in spectral changes not attributable to equilibrium shifts [Silverman and Gordon, 1980]. Gordon et al., 2002, provides evidence that gas diffusion flow injection analysis (GDFIA) is more reliable in the analysis of chlorine dioxide and ozone in the presence of free available chlorine, such as in salt brines and swimming pool water.

Results from oxidation studies

A wide range of literature has been published in the study of electrochemical oxidation of waste water and groundwater. The reported results mainly concerns oxidation of specific pollutants such as halogenated aromatic compounds, but the electrochemical effect on COD has also been investigated [Wikoff and Suciu, 1994; Gotsi et al., 2005; Chantzisymion et al., 2006 etc.]. Regarding electrochemical oxidation of the substances that cause problems in swimming pool water, the DBPs and the DBP precursors, only a very small amount of published scientific material was found by the project group.

Sonoyama et al., 1999, showed that by using a silver impregnated carbon fibre electrode, the concentration of the main trihalomethane, chloroform, was decreased from 0.25 $^{\mathrm{mmol}}/_{\mathrm{l}}$ to below the detection limit of the applied analysis system (1 ppm). The experiment was performed with current densities of 1-10 mA/cm^2 in a 0.5 M K_2SO_4 electrolyte. The main cathode product of the electrochemical process was methane, but at higher current densities molecular hydrogen production began to occur. In succeeding studies, Sonoyama et al., 2001 and Sonoyama et al., 2003 investigated ppm and ppb level decomposition of trihalomethane in tap water by different cell constructions. The effect on the decomposition depended on the initial concentration, but in experiments with initial concentrations related to swimming pool water (25-50 $^{\mu g}/_{l}$), the concentration of the main trihalomethane, chloroform, was decreased to below 6 ppb at an applied voltage of -1.2 V vs. the *Ag/AgCl* reference electrode.

Simka et al., 2007, has in a most recent study investigated the influence of anode material on electrochemical decomposition of urea, one of the important DBP precursors. Urea is known to be electrochemical anodic oxidised into CO_2, N_2, and H_2, but different conditions of the treatment have showed to results in different products of urea decomposition [Simka et al., 2007]. At potentials over 1.7 V vs. SCE (Standard Calomel Electrode) in an acidic environment, urea was decomposed by a direct oxidation at the electrode surface, primarily to CO_2 and N_2, while at lower potential, urea reacted with hydroxyl radicals, and the decomposition products remained in solution as CNO^-, NO_3^-, NO_2^-, $[N_2O_2]^-$, N_2O, NO_2, $NH_2CONH_2^{\cdot+}$. The anode of titanium coated with Pt-Ir at a molar ratio of 70:30 ($Ti/(Pt\text{-}Ir)_{70:30}$) was found to be most stable, and the optimum process parameters were a current density of 8 A/dm^2 and a $NaCl$ electrolyte concentration of 5 $^g/_l$.

Results from disinfection studies

Electrochemical disinfection can be separated into two categories; direct electrolysis and mixed oxidant generation. Direct electrolysis interfere directly with contaminated water, whilst the mixed oxidant method uses a concentrated brine solution to generate "anolyte", a mixture of strong oxidising species as the ones presented in the previous section [Kerwick et al., 2005].

Several electrochemical cell configurations and electrode materials have been investigated for disinfection against a variety of microorganisms in laboratory scale, and direct electrochemical treatment, which is the most applicable technique in swimming pool water treatment [Häenni, 2002], has showed its efficiency in most investigations. The important parameters in an electrochemical reactor are the oxidising capacity of the materials at the surface of the electrodes, the provided current from the applied voltage, and the conductivity of the electrolyte provided by the distance between the electrodes and concentration of salts.

Escherichia coli

E. coli is the most used model microorganism in electrochemical disinfection studies, and in the review of the published literature many papers with electrochemical disinfection were found. The project group has determined to present a selection of the found results, but to provide a full overview of the investigations is beyond the objective of this project.

Li et al., 2002, found a killing efficiency of 99.9 % on total coliform bacteria in the direct electrochemical treatment of secondary effluent from saline waste water with contact time less than 10 s and a power consumption of 0.01 kWh/m^3. In a succeeding study, Li et al., 2004, found that the efficiency generally increased with increasing current density, contact time and chloride concentration. In an electrolyte with a chloride concentration of 0.01 M (~0.06 %), a log-3 reduction was achieved at a current density of 5 mA/cm^2 with a contact time of 6 s. By increasing the chloride concentration to 0.025 M, a contact time of 3 s was sufficient in order to obtain a 99.9 % kill at a current density of 3.5 mA/cm^2.

Stoner and Cahen, 1982, found a log-3 reduction with a current density of 7.5 mA/cm^2 and a salinity of 0.85 %. The disinfection efficiency was independent of temperature changes, but was very dependent on pH. Okochi et al. 1999 showed a survival ratio below 5 % at a potential of 0.4 V by addition of a 0.5 mM ferrocenemonocarboxylic acid (FCA).

By using a carbon-cloth electrochemical reactor, Matsunaga et al., 1992, demonstrated that 10^2 *E. coli* cells pr. cm^3 were killed at 0.7 V at a dilution rate of <0.6 h^{-1}, which equals a retention time of >10 min. In order to be electrochemically killed, the cells had to be attached to the microelectrode, but this fact was suggested to be due to the oxidising efficiency of the anode material. The killing mechanism was ascribed to be directly oxidation of intracellular CoA, which led to decreased respiration and consequent cell death [Matsunaga et al., 1992], a mechanism which was earlier developed by Matsunaga et al., 1984. By applying a *TiN* electrode similar results under similar conditions were later achieved [Matsunaga et al., 2000].

A kinetic model was developed by Patermarakis and Fountoukidis, 1990, in the electrochemical disinfection of *E. coli* at different conditions:

$$\alpha = k \cdot i^2 \cdot t \tag{53}$$

α is a disinfecting factor, which is proportional to the residence time and the square of the current density. k is a characteristic constant of the system dependent on several factors such as material and surface of the electrodes, the volume of water to be treated, the stirring rate and consequently the diffusion rate of lethal species, the killing mechanism etc.

One of the recent studies by Kerwick et al., 2005, showed that a log-7 inactivation of *E. coli* was achieved in 60 min by a current density of 4 mA/cm^2 and a chloride concentration of 0.01 M. The study revealed that disinfection was possible without the presence of chloride, but less efficient with a comparable log-4 inactivation.

Disinfection of other microorganisms

A very limited number of papers have been found, investigating the electrochemical disinfection of *Legionella*. In a high-voltage pulsed electric field study, which is difficult to compare with the common electrochemical treatment, Feng et al., 2004, achieved a decrease in the cell concentration from initial $3.4 \cdot 10^2$ $^{CFU}/_{100\ ml}$ to 1.7 $^{CFU}/_{100\ ml}$ after 30 min at 1.0 kV, but further improvements was not detected at 1.5 kV. In a more comparable study, inactivation of 90 % *Legionella* was reached after 60 min contact time at 150 mA/cm^2 in a 0.19 $^{mg}/_{l}$ free chlorine concentration by a DiaCell reactor [Pupunat and Rychen, 2002].

Drogui et al., 2001b, applied electrochemical produced hydroperoxide in disinfection of *Pseudomonas aeruginosa*. By indirectly disinfection with the produced hydroperoxide solution, a log-2 reduction was showed compared to no treatment, and by direct electrolysis a log-6 reduction appeared.

Kerwick et al., 2005, studied the electrochemical treatment against viruses, where the bacteriophage *MS2* was applied as a model virus. Significant inactivation of the *MS2* was observed after 30 min in a 0.03 M sodium sulphate electrolyte with a current density of 24 mA/cm^2. A log-6 inactivation was shown after 75 min of treatment at an energy consumption of 7.8 kWh/m^3. When comparing with the similar inactivation of *E. coli*, the *MS2* was more susceptible to the electrochemical disinfection. This was however in contrast to results published by Dress et al, 2003, who found the electrochemical inactivation rate of *E. coli* at 5 V and 5 mA to be 2.1-4.3 times greater than *MS2*.

In indirectly treatment of waste water by addition of 10-13 $^{mg}/_{l}$ oxidant generated from salt brine, a log-3 reduction of *Cryptosporidium parvum* oocysts after 90 min was obtained [Casteel et al., 2000]. The oxidant was made from a 10 $^{mg}/_{l}$ $NaCl$ solution exposed to 7.5-7.6 A at a flow rate of 20-25 $^{l}/_{h}$.

In addition, electrochemical disinfection has been investigated against marine bacteria, such as *Vibrio alginolyticus* [Okochi et al., 2000; Nakayama et al., 1998] revealing that electrochemical disinfection of these bacteria was possible as well.

Killing mechanism

Li et al., 2004, found increasing disinfection efficiency with an increasing chloride concentration up to 0.025 M. According to a hypothesis proposed by Saran et al., 1999, chloride ions in the solution can further enhance the disinfective action of free radicals. The participation of hydroxyl radicals in cell killing has been taken for insignificant due to the short free pathlenght of this species, but according to Saran et al., 1999, it should once again be taken into consideration.

The theory suggest a catalytic role of chloride ions in the chain reactions of a cyclic process that involve hydroxyl radicals, a process which is driven by excess Cl^- in the direction to extend the lifetime of hydroxyl radicals by an order of magnitude, making the radicals many times more effective for cell destruction. The mechanism is proposed in order to explain the killing of cells by phagocytes and involves the participation of different enzymes, but the main idea in the hypothesis may be transferable to electrochemical disinfection. The mechanism describes the chemistry in the cleft between the phagocyte and the bacterium. A schematic overview of the mechanism is seen in Figure 14.

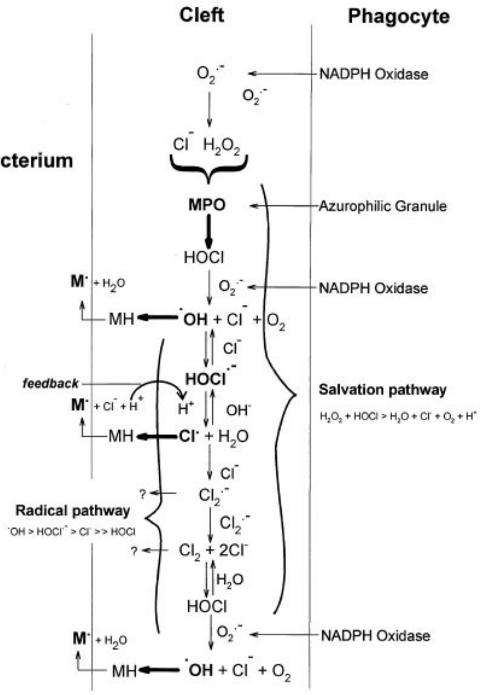

Figure 14: Proposed chloride dependent radical chemistry in the killing of cells [Saran et al., 1999].

The chloride dependent radical chemistry occurs in the cleft between the bacterium and the phagocyte. $O_2^{\cdot}$ and the enzyme myeloperoxidase (MPO), discharged by the phagocyte into the cleft, starts to produce $HOCl$ from hydroperoxide and chloride. By a reaction with $O_2^{\cdot -}$, $HOCl$ may produce hydroxyl radicals, see reaction 54.

$$HOCl + O_2^{\bullet -} \rightarrow OH^{\bullet} + Cl^{-} + O_2 \qquad (54)$$

Due to a high concentration of Cl^-, a substantial part of the hydroxyl radicals runs into equilibrium with $HOCl^{\cdot -}$ according to reaction 55.

$$OH^{\bullet} + Cl^{-} \rightleftharpoons HOCl^{\bullet -} \qquad (55)$$

Reaction 55 is kinetically fast, but since it is an equilibrium reaction, the hydroxyl radicals may readily leave to react with any suitable substrate. The chloride ions slow down the reactions of hydroxyl radicals by stabilising it for a few nanoseconds in the form of $HOCl^{\cdot -}$. The authors propose that chloride extends the lifetime of the hydroxyl radicals by a factor of 10 and thus makes them tenfold more useful for destructive purposes. Equilibrium 55 may either set hydroxyl radicals free again or react with protons via chain reaction 56-59 proceeding via the transient radicals $Cl^{\cdot}$ and $Cl_2^{\cdot -}$ to finally generate Cl_2 and $HOCl$.

$$HOCl^{\bullet -} + H^{+} \rightleftharpoons Cl^{\bullet} + H_2O \qquad (56)$$

$$Cl^{\bullet} + Cl^{-} \rightarrow Cl_2^{\bullet -} \qquad (57)$$

$$Cl_2^{\bullet -} + Cl_2^{\bullet -} \rightarrow Cl_2 + 2Cl^{-} \ (several\ reaction\ steps) \qquad (58)$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^{+} + Cl^{-} \qquad (59)$$

The whole chain, which would redeliver $HOCl$ for another round of the radical pathway only runs effectively at acidic pH. However, the first reaction steps producing $Cl^{\cdot}$ are under positive feedback control by protons and lead to continuous acidification of the microenvironment. The chlorine and hydroxyl radicals will attack biomolecules and react with hydrogen atoms by reaction 60 and 61.

$$MH + Cl^{\cdot} \rightarrow M^{\cdot} + H^{+} + Cl^{-} \tag{60}$$
$$MH + OH^{\cdot} \rightarrow M^{\cdot} + H_2O \tag{61}$$

In case the source of $O_2^{\cdot -}$ is turned off, the remaining H_2O_2 and $HOCl$ will disappear within seconds via the termination pathway, reaction 62.

$$HOCl + H_2O_2 \rightarrow H_2O + O_2 + Cl^{-} + H^{+} \tag{62}$$

The mechanism provides a possible explanation to the observed correlation between disinfection efficiency and chloride concentration, especially through reaction 55. For a further and thorough review of the mechanism, the project group refers to Saran et al., 1999.

Summary

In electrochemical oxidation and disinfection, a range of oxidative species is produced. Free chlorine is according to some papers the primary disinfectant, but also chlorine dioxide, ozone, hydroperoxide, and much more powerful oxidants such as free radicals has been observed and is believed to contribute to the strong oxidising efficiency of electrochemical oxidation. Some papers only assign 10 % of the disinfection to the produced free chlorine.

Only a small number of studies have been reported in the electrochemical oxidation of swimming pool related compounds. THMs, represented mainly by chloroform, have been showed efficiently to be decomposed at initial concentrations in the lower ppb level comparable to swimming pool water. Likewise, important DBP precursors like urea have been showed efficiently to be oxidised in a $NaCl$ electrolyte.

The efficiency of the electrochemical disinfection has revealed itself in a number of investigations, where *E. coli* is the most widely used model bacteria. The efficiency has turned out to be dependent on the current, the retention time, and the presence of chloride ions in the electrolyte. In order to summarize, the presented results are showed in Table 16.

Table 16: Results of selected electrochemical disinfection studies. The presented results are only intended to serve as examples, and do not provide a full overview of the research done in this area. * High-voltage electrical field study. ** Indirect treatment.

Micoorganism	Anode	Current density	NaCl	Reduction	Reference
E. coli	*Pt/Nb*	4 mA/cm^2	0.058 %	log-7	[Kerwick et al., 2005]
E. coli	Ti/RuO_2 Ti/TiO_2	5 mA/cm^2	0.058 %	log-3	[Li et al., 2004]
E. coli	Ti/RuO_2 Ti/TiO_2	8 mA/cm^2	0.008 %	log-3	[Li et al., 2002]
E. coli	*Graphite*	7.5 mA/cm^2	0.85 %	log-3	[Stoner and Cahen, 1982]
Legionella*	Ti/RuO_2	-	0.1 %	log-3	[Feng et al., 2004]
Legionella	*B- doped diamond*	150 mA/cm^2	0.7 %	log-1	[Pupunat and Rychen, 2002]
Pseudomonas au.	Ti/RuO_2	20 mA/cm^2	-	log-6	[Drogui et al., 2001b]
MS2	*Pt/Nb*	24 mA/cm^2	-	log-6	[Kerwick et al.,2005]
Cryptosporidium p.**	-	-	0.001 %	log-3	[Casteel et al., 2000]

A complicating issue is that the studies reviewed above have been performed using different kind of electrochemical reactors based on different electrochemical techniques and electrode materials, and hence they are difficult to imply in a direct comparison. However, they all show that electrochemical disinfection is efficient towards a range of different microorganisms, but a further comparison, taken the electrode material into account, is desired. This task is however outside the aims of the present project, but it shows the necessity of initial fundamental investigations concerning formation of disinfectants and disinfection efficiency, when the Watersafe electrochemical reactor is about to be implemented in Danish swimming pool water treatment.

A bacteria killing mechanism has been proposed, where hydroxyl radicals are stabilised by chloride, which hence extends the lifetime of the hydroxyl radicals by a factor of 10, making them more useful in the oxidation of the biomolecules.

5.3.2 Bench and full scale experiences in swimming pools

The use of electrochemical treatment in disinfection of swimming pools is not widely used despite the extensive laboratory research. Only one bench scale study has been published, performed by a research group in Switzerland. However, the Watersafe reactor has been used in swimming pool water disinfection in Greece for the last 6 years without any documentation has been published, and similar cases might be found in other parts of the world. A great advantage of the Watersafe reactor is that it is a final product already on the market, whereas the other studies reviewed in section 5.3.1, except the DiaCell reactor, were conducted with laboratory equipment.

In this section, the results published by Häenni et al., 2002, will be reviewed and documentation for the quality of the swimming pool water disinfected by the Watersafe unit will be presented.

Bench scale swimming pool test using the DiaCell disinfection unit

Häenni et al., 2002, has published results from a bench scale study using a commercial electrochemical disinfection unit for swimming pool water disinfection. The DiaCell unit is equipped with a boron-doped diamond electrode. The study was carried out on a 60 m^3 pool with a recirculation of water of 15 m^3/h. The DiaCell was installed in a sub-stream with a flow of 1 m^3/h through the unit. The concentration of free chlorine was maintained in the range of 0.2-0.4 $^{mg}/_{l}$ by loop-controlled chlorine production with a free chlorine sensor assisted by a microprocessor. In order to maintain the level of free chlorine, an amount of 0.1 % $NaCl$ had to be added initially. The pH value was kept constant at 7.2 by addition of $NaHSO_4$.

Preliminary laboratory test showed that an initial level of $1 \cdot 10^6$ $^{CFU}/_{ml}$, *E. coli* was inactivated in 20 min by electrochemical disinfection with a loop-controlled chlorine production of 0.35 $^{g}/_{h}$. This was compared with traditional $NaOCl$ disinfection where 60 min was needed with total amount of free chlorine of 0.45 $^{g}/_{h}$.

The bench scale test showed that the pool water quality could be maintained in the test period with a level of living bacteria below 5 $^{CFU}/_{ml}$ with a constant free chlorine concentration of 0.2-0.3 $^{mg}/_{l}$. All the basic pool water components maintained unchanged through the test period. All introduced organic matter, sun protection oils, urea etc., could be destroyed by the electrochemical oxidation. No limestone deposition on the electrodes was observed through the experimental run of 6 month. The current density did not exceed 200 mA/cm^2 and by a cell potential of maximum 48 V an average energy consumption of 8 $^{kWh}/_{day}$ was registered. [Häenni et al., 2002]

Documentation for full scale application of the Watersafe reactor

The Watersafe electrochemical reactor is used in swimming pool water treatment in a number of full scale swimming pools in Greece and has been in action since 2001. The electrochemical reactor treats the swimming pool water according to the outline presented in Figure 15.

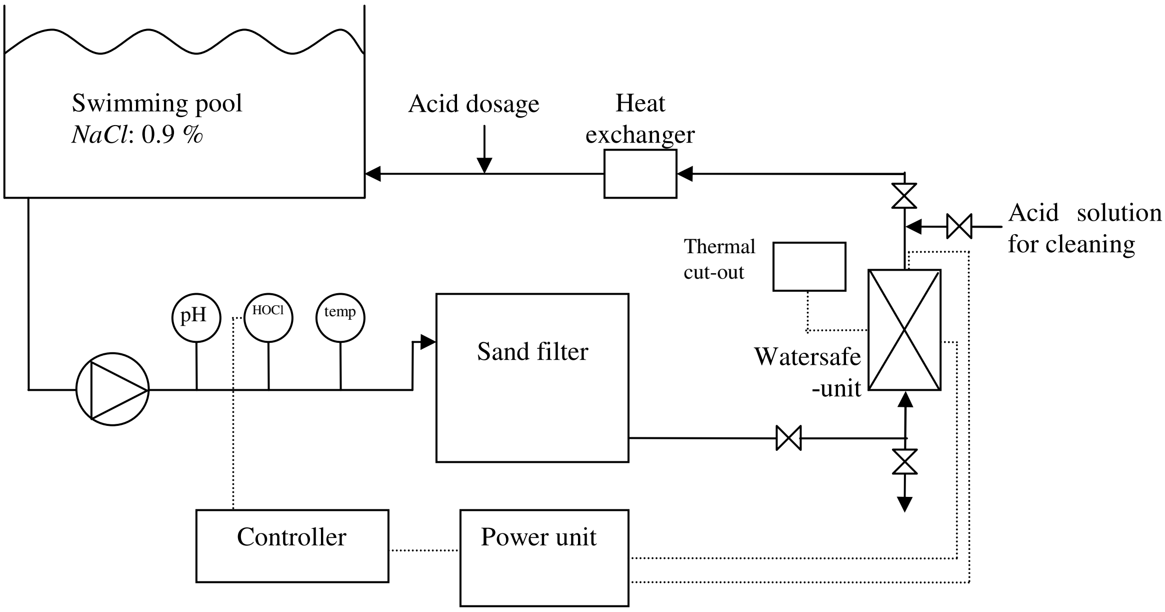

Figure 15: Outline of the Watersafe reactor used in swimming pool treatment.

With appropriate sensors, pH, free chlorine, and temperature are measured prior to the sand filter. The pH measurements control the dosage of acid, the pH is kept at 7.2-7.3, and the temperature measurements control the heat exchanger. By on/off regulation, the concentration of free chlorine controls the power to the power unit, which feds the electrochemical reactor. When the level of free chlorine falls to 0.5 $^{mg}/_{l}$, the power is turned on and the electrochemical reactor is operating, producing oxidants. When the free chlorine level reaches 0.7 $^{mg}/_{l}$, the power is turned off. In order to maintain a sufficient free chlorine production, a *NaCl* concentration of 0.9 % is needed in the swimming pool water. The set-point of the free chlorine is adjustable and the 0.5 $^{mg}/_{l}$ set-point is chosen on behalf of the Greek regulations.

The Watersafe reactor has on these premises been working in the treatment of several swimming pools in Greece, mainly on Crete, but installations are found in Athens as well. It has turned out to be a prolonged procedure to get in hand of documentation material for the maintenance of the water quality in the pools, where the Watersafe reactor is installed, and the project group is only in possession of very few certified analysis results. It is however believed by the project group that this does not have something to do with an intention of hiding inappropriate results; it is only a derivative of the general Greek mentality. The documentation material received from Watersafe Greece only considered microbiological parameters and is seen in Table 17.

Table 17: Documentation material received from Greece. *Grand Bretagne, 13.10.2003. **06.02.2006. ***06.02.2006.****03.05.2006. *****03.052006.

Microorganism	Unit	GB* Athens	Iraklio** Crete	Iraklio*** Crete	Iraklio**** Crete	Iraklio***** Crete
Heterotrophics	$^{CFU}/_{ml}$	0	0	0	0	0
Tot. Bacteroid	$^{CFU}/_{100\ ml}$	0	0	0	0	0
Bacteria	$^{CFU}/_{100\ ml}$	0	-	-	-	-
Enterococcus	$^{CFU}/_{100\ ml}$	0	-	-	-	-
Pseudomonas au.	$^{CFU}/_{100\ ml}$	0	0	0	0	0
Escherichia coli	$^{CFU}/_{100\ ml}$	-	-	-	-	-
Streptococcus	$^{CFU}/_{100\ ml}$	-	0	0	0	0
Staphylococcus	$^{CFU}/_{100\ ml}$	-	0	0	0	0

As it is seen from Table 17, no living bacteria were found in the swimming pool water. The material is however very limited, and it can not be considered representative for all installation. The project group is still trying to get in possession of further analysis results.

5.3.3 Technical excursion

Watersafe joined in as a cooperative partner regarding the developed test trailer, and agreed to contribute with a full scale electrochemical reactor. In addition, an electrochemical Watersafe reactor in laboratory size was purchased for investigations at Esbjerg Institute of Technology, Aalborg University. The electrochemical oxidation and disinfection technique has its applicability in the treatment and remediation of a wide range of polluted waters. Since the use of this technique is in an early phase in swimming pool water treatment in Denmark, the project group and supervisors went on a field trip to explore the Watersafe installations in action in Greece and in order to gain inspiration for other uses. At the same time, the production facilities were presented and the use of the electrochemical reactor in the treatment of different kind of waste water was demonstrated.

Three swimming pool treatment systems were showed, all based on the same outline as presented in Figure 15. In Figure 16, some photos of the installations are seen.

Figure 16: Photos from three different Watersafe swimming pool installations in Crete and 8 parallel operated Watersafe reactors from a waste water treatment plant.

The dimensions of the reactor are depended on the water flow. The production facilities were a regular small size engineering work shop, where versatile conversion of the production according to the specific orders has high priority. The power units were purchased by a subcontractor. Photos from the production facility and the Watersafe reactor at different stages of the production line are seen in Figure 17.

Figure 17: Photos from the Watersafe productions facilities.

The technical excursion to Greece resulted in much more insight in the range of application of the electrochemical reactor and how the reactors were installed and operated in practice. Furthermore, a meeting with Mr. Nicolas Kalegorakis, a professor at the University of Crete, who has been involved in several research studies with the electrochemical reactors from Watersafe regarding waste water treatment, resulted in a useful collaboration, if further support is needed.

5.4 Sub-conclusion

The study of the ozone and UV treatment techniques and there applicability in swimming pool treatment, revealed that enough documentation is available in order to consider them well tested full scale techniques. The next step in implementing ozone and UV in Danish swimming pool treatment is full scale tests, in order to provide the Danish documentation material requested by the Danish EPA even though the project group considers the demanded need for further tests unnecessary. The ozone test should be performed on the basis of DIN 19643, 1997. The same recommendation is given in MST, 2007a. From the project groups point of view, the planned tests concerning ozone seem unnecessary, since experiences from especially Germany is considered sufficient in order to ensure a applicable implementation. The ozone and UV treatment will not be treated further in the present report.

The electrochemical technique has only showed its potential towards treatment of swimming pool water in a few laboratory studies and undocumented full scale systems in Greece. This clearly indicated the need for more knowledge about this technique and the relevance of performing more scientific documented test, which will be the objective in the following chapters and the main objective of this project report.

6 Laboratory investigations

The literature study concerning electrochemical treatment of swimming pool water showed that only one published investigation was available, Haenni et al, 2002, although the technique is widely use in Greece. The study also revealed that several different designs of electrochemical reactors exist, with a varying efficiency mainly determined by the composition of the anode material. Since no scientific published investigations about the Watersafe unit concerning swimming pool water treatment exist, it was necessary to conduct fundamental laboratory experiments in order to investigate the efficiency and the principles of operation, before the unit is installed in a full scale swimming pool treatment system. Based on the results of the laboratory test, the project group made a project draft to a full scale installation in a public swimming pool in Århus. This work is presented in section 7.

For a thorough investigation of the Watersafe unit, the laboratory investigation was divided into five separate types of experiments with the purposes of determine the:

1. Chlorine production
2. Gas production
3. Identification of oxidizing agents
4. Inactivation of *Escherichia coli*
5. Composition of the anode material

In electrochemical treatment of saline waters, the oxidation of chloride is the main chemical process occurring in the reactor, and the first task was to estimate the chlorine production rate with respect to applied voltage, current, and concentration of $NaCl$. Concurrent to the oxidative processes in the electrochemical reactor at or near the anode, reductive processes occur at the cathode. It was expected that the main reductive process was reduction of water to molecular hydrogen that escapes to the gas phase, and in order to prevent explosive mixtures, knowledge about the gas production rate was important. It was also important to investigate the composition of the gas phase, since the presence of undissolved chlorine gas, oxygen and ozone was feasible.

According to the literature study, strong oxidizing agents such as ozone and hydroxyl radicals are believed to be generated in the electrochemical process, and the third task was to identify the species and provide documentation for their existence, concentrations, and stability. The literature study revealed that a possible experimental method was bleaching of p-nitroso-dimethylaniline (RNO), which is believed selectively to reacts with hydroxyl radicals. The last test with the laboratory set-up was an investigation of the efficiency of the Watersafe reactor regarding electrochemical disinfection of the microorganism *Escherichia coli*.

Finally, the composition of the anode material was investigated with a scanning electron microscope (SEM) with energy dispersive x-ray spectroscopy (EDS).

During the laboratory experiments, the impacts caused by change in the variables salinity, voltage, and current were the main subjects of interest. The investigation resulted in a range of experiments, which are listed in Table 18. More detailed information about the operating conditions of the experiments is found in the respective sections.

Table 18: The experiments conducted in the laboratory.

No.	Name	$NaCl$ [%]	Voltage [V]	Current [A]	Comments
1	Chlorine production 1	0.9	10	10.9-12.9	Introductive test
2	Chlorine production 2	0.9	10	13.5-15.1	Introductive test
3	Chlorine production 3	0.9	15	25.3-33.1	-
4	Chlorine production 4	0.9	5	3.9	-
5	Chlorine production 5	0.9	20	35.6-51.2	-
6	Chlorine production 6	0.9	10	13.2-14.8	-
7	Chlorine production 7	4.0	10	45.3-53.0	-
8	Chlorine production 8	2.0	10	27.0-30.2	-
9	RNO 1	0.9	6	5.0	-
10	RNO 2	0.9	20.2	30.6-38.4	Demonstration test
11	RNO 3	0.9	3.4-3.6	1.0	-
12	RNO 4	0.9	8.0-8.8	10.0	-
13	RNO 5	0.9	-	-	Add. of liq. $NaOCl$
14	RNO 6	0.9	-	-	Add. of liq. $NaOCl$
15	RNO 7	0.0	-	-	Add. of liq. $NaOCl$
16	RNO 8	0.0	20.2	0.2	-
17	RNO 9	0.9	3.5	1.0	Start/stop test
18	RNO 10	0.0	3.5-15.0	1.0-20.0	KNO_3 0.9 %
19	Gas production	0.9-3.6	3.8-16.8	5.0-30.0	-
20	Gas composition	0.9-4.0	-	30.0	-
21	Disinfection *E. coli* 1	0.9	0.02-8.3	1.0-20.0	-
22	Disinfection *E. coli* 2	0.9	-	1.0-5.0	-
23	Disinfection *E. coli* 3	0.9	2-30	-	-
24	Test trailer	0.65	44.7-48.0	100	-
25	Hydrogen concentration	0.9	-	10.0-20.0	-
26	Anode material	-	-	-	SEM and EDS

The first four types of tests were with minor adjustments conducted in a basic laboratory set-up, which is described in the following section.

6.1 General experimental design

The reactor used in the experiments was purchased from Watersafe Greece. The model was by request custom made for laboratory use, but the reactor design is apart from the dimensions similar to the models used in full scale swimming pool treatment. Sketches of the used laboratory reactor are seen in Figure 18.

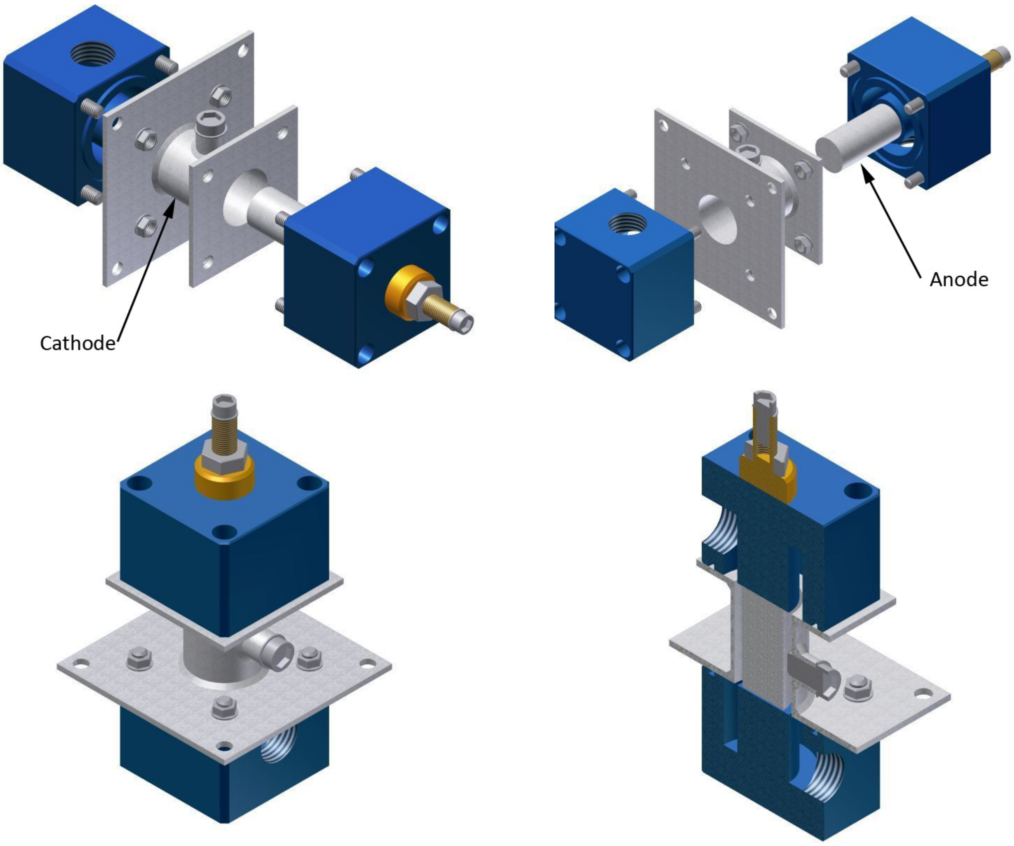

Figure 18: Sketches of the applied laboratory Watersafe reactor made with Autodesk Inventor.

The reactor is based on an AISI 316 steel pipe with an inner diameter of 42 mm, which act as the cathode. For improved corrosion properties, 1 % titanium doped steel was applied. The inner anode is rod shaped with a diameter of 30 mm and is secured to the outlet top part by a chamfered nut. The anode rests on a plateau in the bottom inlet part of the reactor. The flow trough the reactor has in the experiments been operated up-streams in order to secure that the reactor was filled with water. The inlet and outlet parts are made of hard plastic. The dimensions of the reactor are seen in Table 19.

Table 19: Dimension of the reactor. *Cylindrical volume between anode and cathode.

Total height:	243 mm
Width:	138 mm
Depth:	138 mm
Anode diameter	30 mm
Anode length	64 mm
Anode surface:	60.3 cm^2
Inner cathode diameter	42 mm
Active volume*:	38.7 cm^3

Since the electrical processes occur in the space between the anode and the cathode, the active volume of electrical exposure is calculated as the volume between the anode and the inner wall of the steel pipe. Photos of the laboratory reactor are seen in Figure 19.

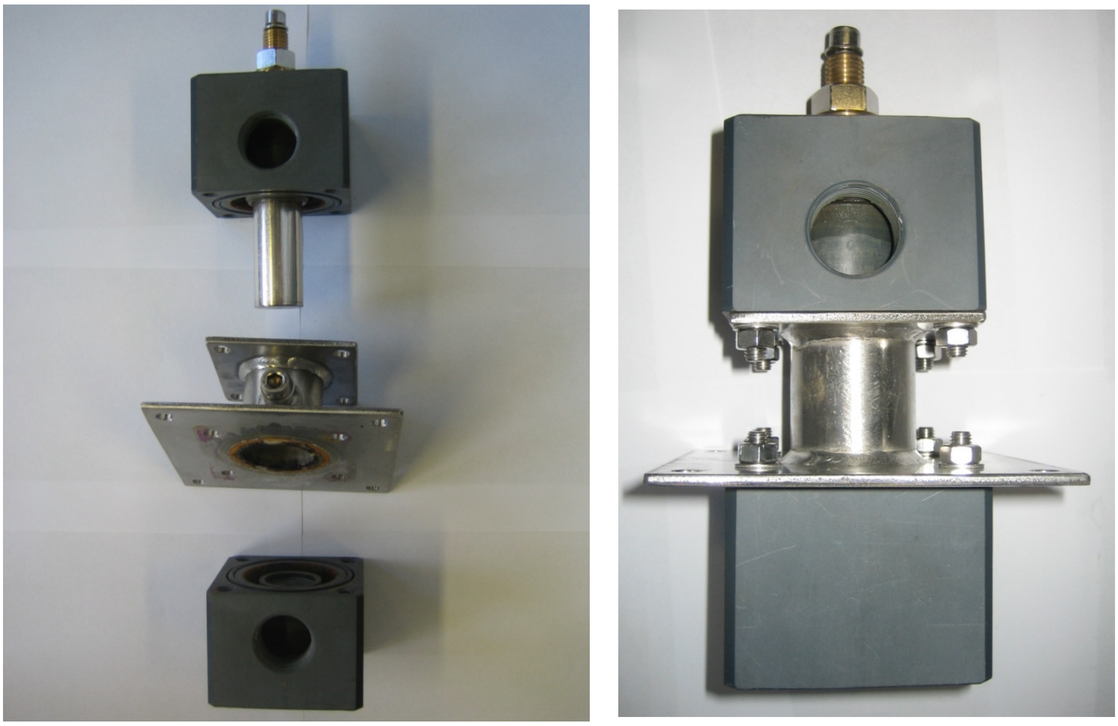

Figure 19: Photos of the reactor.

The positive terminal from the power unit is connected to the anode in the top part and the negative pole to the cathode. The operating parameters for the power unit are seen in Table 20.

Table 20: Operating parameters for the power unit.

Input voltage:	220 V
Output voltage:	0-20 V
Output current:	0-70 A
Max. temp.:	65 °C

The rod shaped anode can according to the patent consists of a solid core of *Ti* or a *Ti/Pd* alloy with or without an enclosed bar of *Al* or *Cu* [Ninolakis, 2002]. The anode is then coated by two metals films. The outer film, which constitutes the surface and hence is important for the oxidation efficiency, is for the used laboratory reactor specified as an alloy of platinum and iridium in the ratio of 90 % and 10 % respectively. The anode material is investigated with SEM/EDS in section 6.6.

In the laboratory, the standard experimental set-up was based on a recirculation system. The set-up is seen in Figure 20 and Figure 21.

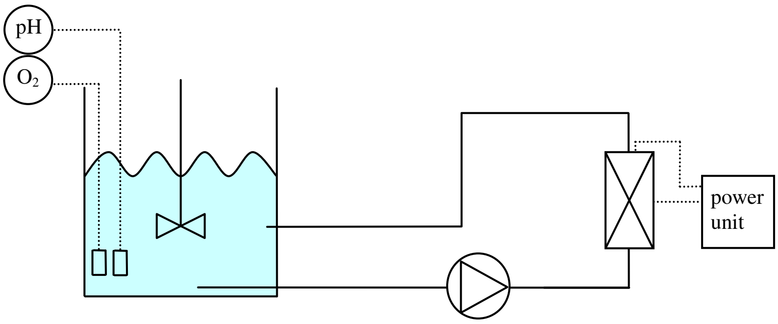

Figure 20: Outline of the experimental set-up.

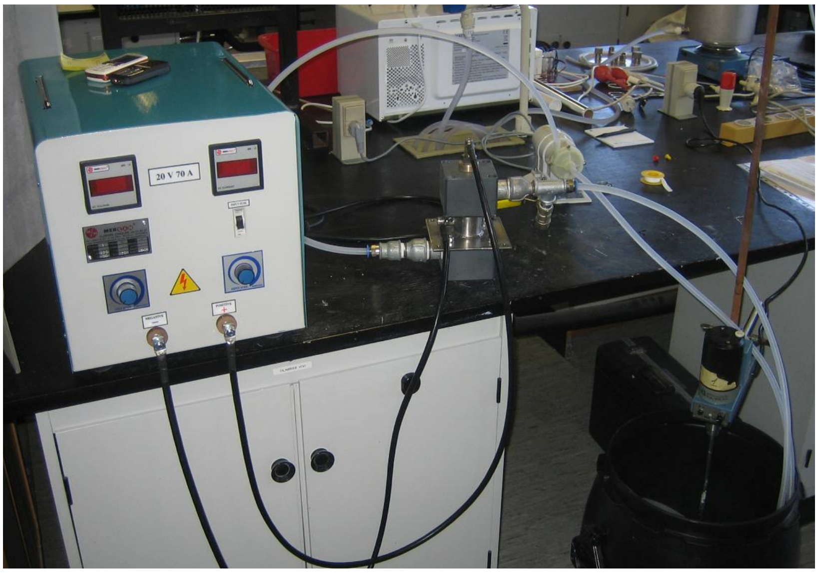

Figure 21: The experimental set-up.

Water was pumped up-streams through the Watersafe reactor by a SIEBEC M7 N° 33271 pump with a pump house of plastic in order to prevent corrosion and contamination with metal ions. Maximum delivery height was 4 m and the maximum flow was specified to 0.8 m^3/h. Measurements done by the project group revealed the flow through the system to 0.424 m^3/h. The units in the set-up are connected through ø 12 mm plastic hoses.

The water tank was equipped with a mechanical stirrer and pH and dissolved oxygen (DO) electrodes. Temperature measurements were included in the DO electrode. Conductivity and oxidation and reduction potential (ORP) were measured in extracted samples. The specific applied electrode models and measurement ranges are seen in Table 21.

Table 21: Electrodes used in the laboratory experiments.

Electrodes	Model	Range
pH	Radiometer PHC2401-8	0-14
DO	WTW CellOx 325	0-50 mg/l
ORP	SenTix ORP 103 648	-2000 - +2000 mV
Conductivity	Radiometer CDC566T	0-55 ms/cm
Ozone	Prominent Dulcotest ozone	0-2 ppm
Hydrogen peroxide	Prominent Dulcotest Perox	0-2000 ppm
Hydrogen	Unisense (needle sensor)	0-1 atm pH_2

Sampling for chemical and bacteriological analysis was manually conducted from the water tank with beakers or pipettes. Prior to every experiment, the recirculation system was flushed several times with tap water or demineralised water. Ahead of the first experiment, the applied fittings were cleaned in hydrochloric acid.

The next sections present the procedures and results from the conducted experiments, divided in the five types of tests, and provide a detailed discussion of the obtained results and tendencies. All results from the tests are found in appendix 3 to 6.

6.2 Test 1 – Chlorine production

The Watersafe unit is capable of producing free chlorine by electrolysis of the chloride content in the water, which makes the addition of chlorine unneeded in swimming pools. As described in section 5.3.2, the Watersafe unit is in its present configuration on/off-regulated and controlled by free chlorine measurements, when used in swimming pool treatment. This regulation strategy makes it very interesting to investigate the electrochemical production of free chlorine at various currents and $NaCl$ concentrations. The next sections describe in details how the test was performed.

6.2.1 Theory

Theoretically, the conversion of two moles of chloride to chlorine requires two faradays, since two electrons have to be removed from the chloride. The value of one faraday, F, is given by:

$$F = N_a \cdot e = 6.022 \cdot 10^{23}\ {}^{1}\!/_{mol} \cdot 1.602 \cdot 10^{-19} C = 96,472\ {}^{A\cdot s}\!/_{mol} \tag{63}$$

where N_a is Avogadro's number and e is the elementary charge. Hence, the oxidation resulting in one mole of chloride requires about $1.93 \cdot 10^5$ A·s. The theoretical chlorine production is hence proportional to the applied current and is given by:

$$Chlorine\ production\ rate = 3.1097 \cdot 10^{-4}\ {}^{mol}\!/_{A \cdot min} \tag{64}$$

In practice, 100 % current efficiency is not reached because of competing reactions and a reduction of $HOCl$ at the cathode.

6.2.2 Materials and methods

Free chlorine concentrations were measured by a colorimetric method as described in DS/EN ISO 7393-2. This method of chlorine measurements is widely used for both industrial and laboratory purposes. The principle of measuring with the method is the reaction between free chlorine and N,N-diethyl-p-phenylenediamine (DPD), which forms a red/pink coloured substance:

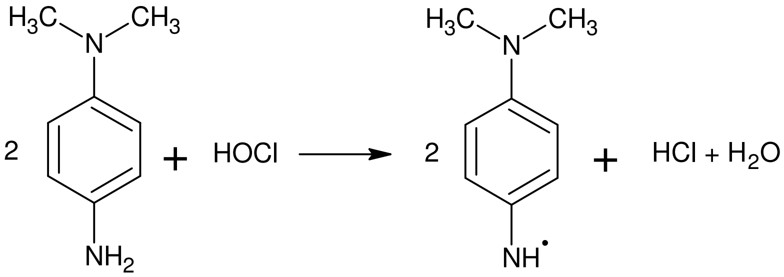

Figure 22: DPD reaction with $HOCl$ [Reckhow, 2006].

The absorbance of the coloured solution is measured spectrophotometrically. In the present project, a test kit from Lovibond was used with a specified measuring range of 0.01-2 ${}^{mg}\!/_{l}$. A buffer powder (pH 6.5) including DPD is added to a sample in order to have the free chlorine at $HOCl$ form. The absorbance was then measured at 528 nm for determination of the free chlorine concentration. At concentrations exceeding the measuring range, the samples were diluted with tap water.

The chlorine production test was performed with the set-up described in section 6.1 and was repeated six times with different voltages and concentrations of *NaCl*. The tested combinations of parameters are provided in Table 22. Test no. 1 and 2 served as an introduction and the results are left out of the present report.

Table 22: Test conducted for investigating the free chlorine production.

Test no.	Voltage [V]	Current [A]	Time [min]	*NaCl* [%]	Volume [l]
3	15	25.3-33.1	60	0.9	25
4	5	3.9	60	0.9	25
5	20	35.6-51.2	50	0.9	25
6	10	13.2-14.8	60	0.9	25
7	10	45.3-53.0	30	4.0	25
8	10	27.0-30.2	30	2.0	25
24	44.7-48.0	100	32	0.65	750

6.2.3 Results and discussion

The first tests (3-6) were performed in order to investigate the production of free chlorine as a function of voltage. The results from the chlorine analysis in these tests are presented in Figure 23.

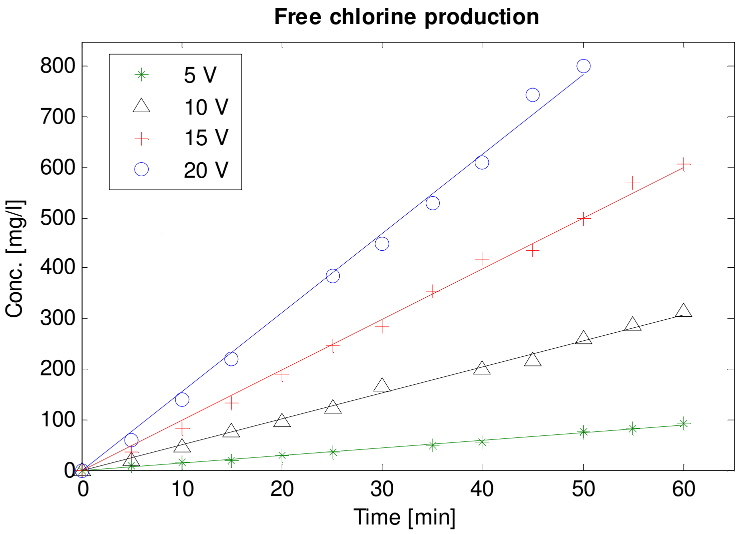

Figure 23: Production of free chlorine as a function of voltage and time (test 3-6).

It is clearly seen from Figure 23 that the production of chlorine follows a zero order reaction, and hence is linear in time for the four different voltages applied with the fastest production at 20 V and the slowest at 5 V. The linear production rates for the different voltages are provided in Table 23.

Table 23: Rates, given by the slopes from Figure 23 with a volume of 25 l (test 3-6).

Voltage [V]	Rate [$^{mg}/_{min \cdot l}$]	Rate [$^{mg}/_{min}$]	R^2
20	15.673	392	0.9947
15	10.014	250	0.9953
10	5.1338	128	0.9956
5	1.4656	36.6	0.9938

From the theory presented in section 6.2.1, it was showed that the production of chlorine was proportional to the applied current. However, the voltage was kept constant during the test, whereas the current increased with time, which is apparent from Figure 24. This increase in current ought to result in a non-linear behaviour of the chlorine production with higher production rates with time. As shown in Figure 23, this is however not the case in this study. This might be due to uncertainties, an increased release of chlorine gas to the atmosphere at increased chlorine concentrations and temperatures, or because more free chlorine is reduced at the cathode at higher concentrations. These factors could have balanced out the theoretical increase.

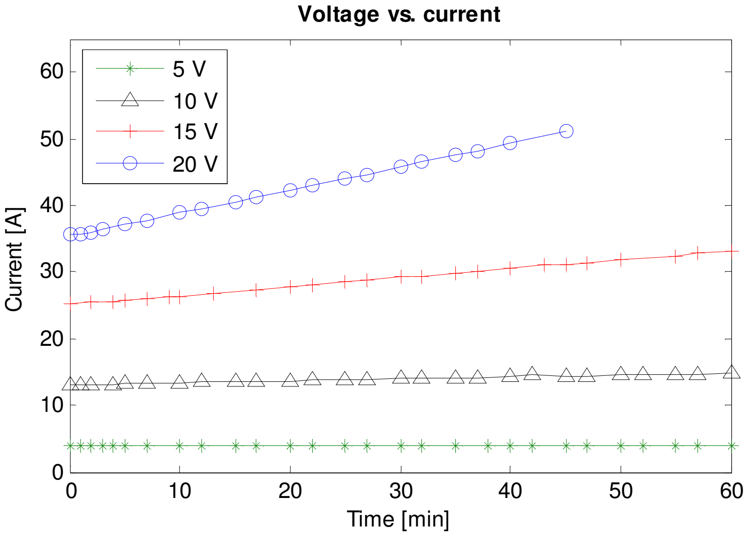

Figure 24: The increase in current with time at different voltages (test 3-6).

The increase in current with time can be explained by Ohm's law and the measured temperature increase, since the electrical resistance, R [Ω] of the water decreases with increased temperature, T [°C]. From Ohm's law it is seen that the current, I [A], will change as a function of temperature at a constant voltage, U [V]:

$$U = R(T) \cdot I \tag{65}$$

The resistivity, ρ [Ω·m], or the conductivity, κ [$\Omega^{-1} \cdot m^{-1}$] given in expression 66 can be incorporated into expression 65 in order to obtain expression 67:

$$\rho(T) = R(T) \cdot \frac{A}{l} \quad and \quad \kappa(T) = \frac{1}{\rho(T)} \tag{66}$$

$$U = \frac{l \cdot I}{A \cdot \kappa(T)} \tag{67}$$

Since the cross-sectional area, A [m^2], and the length l [m], and the applied voltage were constant in the reactor, the current can only vary as a function of conductivity. The electrical conductivity and temperature relation of water is generally nonlinear. However, the degree of nonlinearity is relatively small at room temperature, and a linear equation is commonly used to represent the relation [Hayashi, 2004]:

$$\kappa_T = \kappa_{25°C}[1 + \alpha(T - 25°C)] \tag{68}$$

where α [ºC^{-1}] is a temperature compensation factor. Several values for α have been reported; 0.0191, 0.02, and 0.025 [Hayashi, 2004]. These values are equivalent to an increase in electrical conductivity of about 2 $^{\%}/_{°C}$ and are furthermore dependent on the geochemistry of the water.

Since the temperature dependency of the conductivity can be approximated as being directly proportional over a limited temperature range, a straight line will appear, when the current is plotted as a function of temperature, see Figure 25.

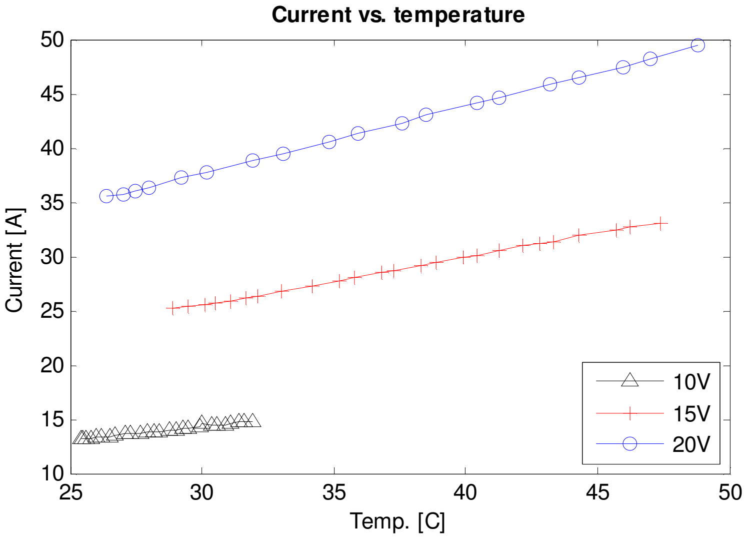

Figure 25: Current as a function of temperature at a constant voltage (test 3, 5, 6).

The measured increases in current in the test were 1.86, 1.66, and 1.73 $^{\%}/_{°C}$ for 10, 15, and 20 V respectively, which fits the expected increase of about 2 $^{\%}/_{°C}$. Based on these results, it can be concluded that the observed increase in current at constant voltage was caused by a linear increase in conductivity, which again can be approximated to be a linear function of the temperature.

Since the increase in current during the test and the chlorine production rate were linear, it was acceptable to use the average current for plotting the free chlorine production rate as a function of current. The result from this is seen in Figure 26.

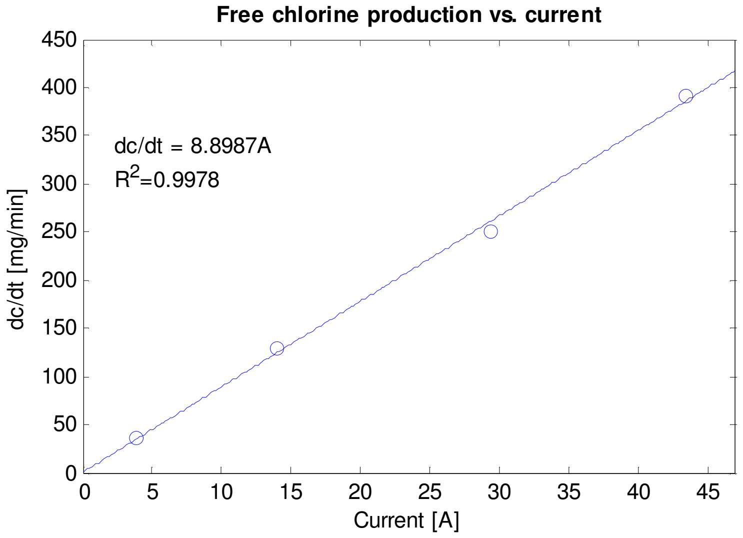

Figure 26: Free chlorine production rate as a function of current (test 3-6).

The linear regression provided in Figure 26 shows the expected linear relationship between free chlorine production and applied current. The rate obtained in the laboratory tests was 8.90 $^{mg}/_{A\cdot min}$ at 0.9 % $NaCl$. Converted to a molar production based on $HOCl$ the practical rate is:

$$Chlorine\ production\ rate = 1.69 \cdot 10^{-4}\ {}^{mol}/_{A\cdot min} \tag{69}$$

Compared to the theoretical production provided by expression 64, the current efficiency of the Watersafe unit regarding chloride electrolysis was 55 %. This indicated that only 55 % of the current was used for chlorine production, while the remaining current (electrons) was used in other oxidation reactions including formation of more aggressive oxidants. For typical commercially available electrolysis units, current efficiencies of 97 % may be obtained along with energy efficiencies of 58 % [Downs and Adams, 1973].

In order to investigate the influence of the concentration of $NaCl$ in the electrolyte, the chlorine production rate was measured at three different $NaCl$ concentrations (0.9 %, 2.0 %, 4.0 %) at a constant voltage of 10 V and a volume of 25 l. The results from the experiments are seen from Figure 27.

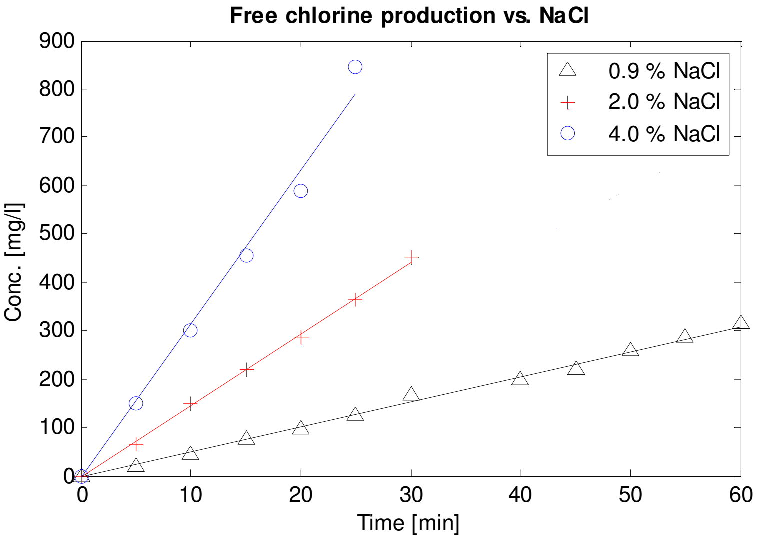

Figure 27: Free chlorine production rate as a function of $NaCl$ concentration at 10 V (test 6-8).

From Figure 27 it is seen that an increased $NaCl$ concentration resulted in an increased free chlorine production, which was also expected, since the conductivity, and hence the current, increases linearly with the $NaCl$ concentration. In order to determine if the efficiency of the chlorine production increased, the found production rates were divided by the applied current, see Table 24.

Table 24: Free chlorine production rates and current efficiencies for different $NaCl$ concentrations (test 6-8).

$NaCl$	Rate [$^{mg}/_{min}$]	R^2	Rate [$^{mg}/_{min\cdot A}$]	Current efficiency
0.9 %	128	0.9956	9.1	55 %
2.0 %	369	0.9979	12.9	79 %
4.0 %	791	0.9883	16.1	98 %

The test showed that it was possible to increase the current efficiency from 55 % to 98 % by increasing the concentration of *NaCl* from 0.9 % to 4.0 %. In swimming pools this means that power can be saved by increasing the *NaCl* concentration of the water. The efficiency is plotted in Figure 28.

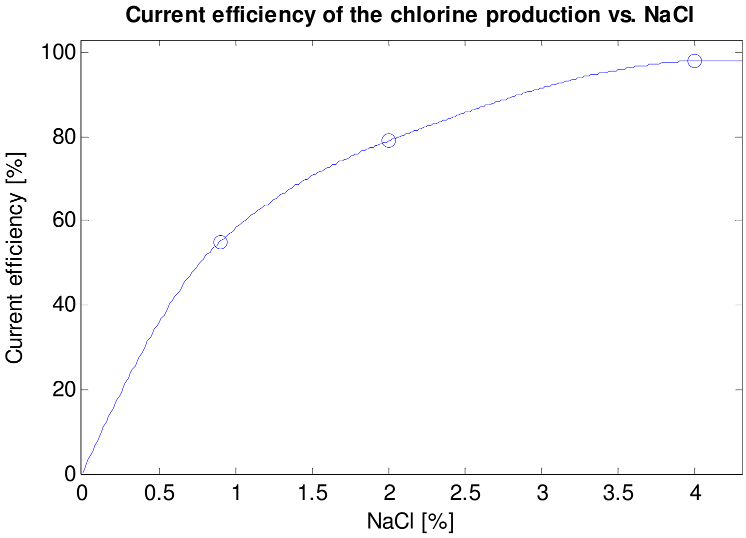

Figure 28: Measured current efficiency as a function of the *NaCl* concentration (test 6-8).

Besides the chlorine concentration the pH, DO, and temperature were monitored during the tests. The results from these measurements are given in Figure 29, Figure 30, and Figure 31 respectively.

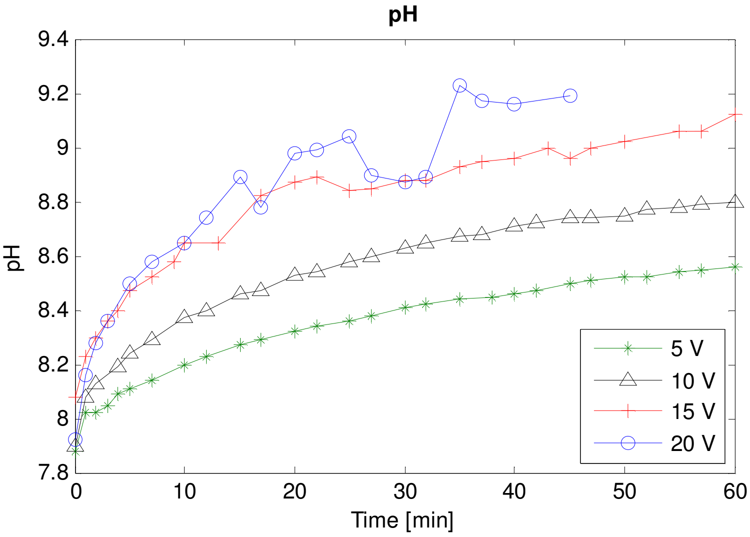

Figure 29: The observed increase in pH during the tests (test 3-6).

The pH increased with time with the largest increase at 20 V and the lowest at 5 V as expected, see Figure 29. The increase in hydroxide concentration was caused by reduction of water to molecular hydrogen at the cathode. The overall reactions are seen in 70-71 of chloride:

$$2Cl^- + 2H_2O \rightarrow Cl_2 + H_2 + 2OH^- \tag{70}$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{71}$$

Even though the chlorine production, reaction 70, occurred at constant rate, the decrease in H^+ concentration was non-linear. One of the reactions causing this non-linearity was the dissociation of hypochlorous acid into hypochlorite (pK_a = 7.54 [Andersen et al., 1994]):

$$HOCl \rightleftharpoons H^+ + ClO^- \qquad (72)$$

At increasing pH and free chlorine concentrations, the dissociation, reaction 72, will shift towards right and suppress the increase in pH. Furthermore, the oxidation of water into molecular oxygen and the production of ozone, hydroxyl radicals, and active oxygen, among others, will results in consumption of hydroxide and therefore a lowering of the pH. A model only considering the production of free chlorine as the anode reaction was developed by the project group in an attempt of describing the pH during the tests. However, the model provided pH values higher than the ones experimentally measured, which was ascribed to the complexity of the electrochemical system with formation of ozone, radicals, and other oxidants at the anode.

The DO measurements during the chlorine production tests are showed in Figure 30.

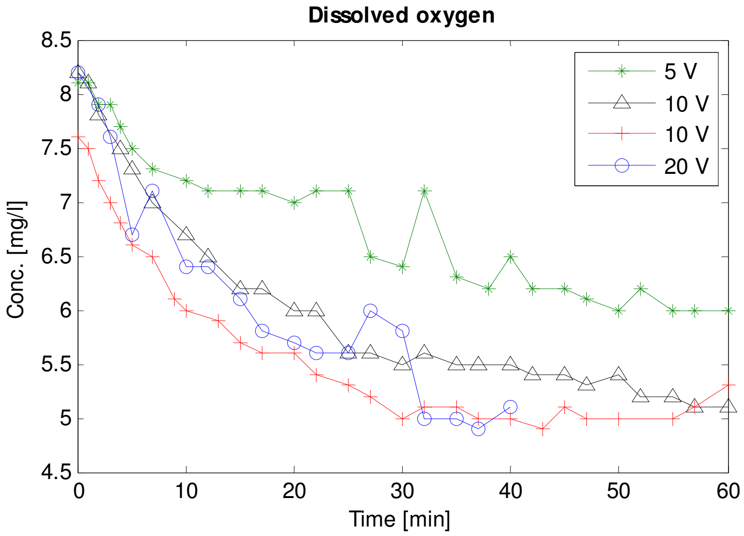

Figure 30: The observed decrease in DO during the tests (test 3-6).

From Figure 30 it is seen that oxygen was consumed in the electrochemical process. As expected, an increase in applied current resulted in higher oxygen consumption. An important notice is that the saturation of the water (temperature and salt variations included) never exceeded 100 % (8.2 $^{mg}/_{l}$ at 25 ºC, 6.4 $^{mg}/_{l}$ at 40 ºC). This showed that the decrease in DO was not caused by the temperature increase shown in Figure 31. Instead, the observed decrease indicated the formation of other oxygen containing oxidants such as ozone, peroxides etc. It also indicated that the oxidation of water to molecular oxygen at the anode was insignificant. Another reason for the decrease in DO could be the presumed molecular hydrogen formation. If large amounts of molecular hydrogen is produced and bubbled through the water, it might result in a lowering of the oxygen concentration caused by stripping. This second hypothesis is further investigated in section 6.3.

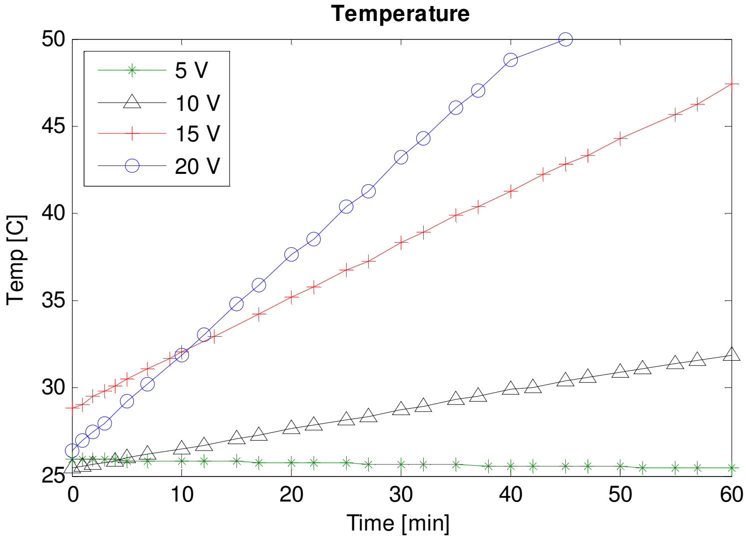

Figure 31: The observed temperature changes during the tests (test 3-6).

The electrochemical reactor generated heat during the tests, which was reflected by the measured temperature increase of the recirculated water. In Figure 31 it is showed that the temperature increase was linear in the temperature interval investigated in the tests. The linear expressions for the temperature trends are found in Table 25.

Table 25: Temperature expressions (test 3-6)

Voltage [V]	Temp. expression	R^2
5	-0.0089·t+25.89	0.9679
10	0.1094·t+25.44	0.9994
15	0.3071·t+28.97	0.9997
20	0.5586·t+26.37	0.9999

The effects used in order to obtain the increases in water temperature found in the tests were calculated by multiplying the slope of the temperature expression with the specific heat capacity of water ($c_p = 4.1855\ ^{J}/_{g\cdot K}$ at 25 ºC [Andersen et al., 1994]). During this procedure, it was assumed that the expression was linear, an assumption which was considered a good approximation. Also the contribution from the pump and the heat of reactions were left out of the calculation. An example of the calculation for the 10 V test assuming no release of heat to the surroundings is given by equation 73 and 74:

$$0.00183\,{}^{K}\!/_{s} \cdot 4.1855\,{}^{W\cdot s}\!/_{g\cdot K} = 0.00763\,{}^{W}\!/_{g} \tag{73}$$

$$0.00763\,{}^{W}\!/_{g} \cdot 25{,}000\,g = 191\,W \tag{74}$$

Effect used for heating the water and the total effect of the system at different voltages is given in Table 26.

Table 26: Heating effect vs. total effect from the reactor (test 3, 5, 6).

Voltage [V]	Heating effect [W]	Effect from reactor [W]
10	191	140
15	535	438
20	974	868

From Table 26 it is seen that the heating effect calculated from the increase of temperature in the water is higher than the total effect delivered from the power supply. The difference is ascribed uncertainties in the volume of water, heat from the stirrer, heat from the pump, side reactions and the fact that c_p for salt water is slightly lower than for pure water.

The overall reaction in the chlorine production is:

$$Cl^- + 3H_2O \rightarrow H_2 + 2OH^- + HOCl + H^+ \ , \quad \Delta H = +443 \, {}^{kJ}\!/_{mol} \tag{75}$$

The process is endothermic and based on the chlorine production rate, the chlorine oxidation at 10, 15, and 20 V takes account of 17, 36, and 54 W respectively. The calculation for the 10 V is seen in equation 76.

$$\frac{1.69 \cdot 10^{-4} \, {}^{mol}\!/_{A \cdot min} \cdot 14A \cdot 443{,}000 \, {}^{J}\!/_{mol}}{60 \, {}^{s}\!/_{min}} = 17W \tag{76}$$

This results in lower temperature increases, since potential chemical energy is stored in the chemical compounds formed. The reaction makes it even harder to explain the high temperature increase. From these energy considerations, the energy efficiency of the Watersafe reactor can be calculated to be 12, 8, and 6 % for 10, 15, and 20 V, and hence, the reactor is most efficient at low voltages. Commercially available electrolysis systems for chlorine production reach energy efficiencies of 58 % [Downs and Adams, 1973].

Full scale test

In order to investigate the scale up of the chlorine production process, a short test (test no. 24) was conducted with the electrochemical reactor installed in the chemical test trailer, see section 4.1. A tank filled with 750 l tap water and a concentration of 0.65 % *NaCl* was recirculated at a flow rate of 3.70 m^3/h through the entire system in the trailer including flowmeter, reactor, and in-line measuring cells (conductivity, ORP, pH, DO) placed immediately after the reactor. The free chlorine analyses were conducted on water samples from the tank. The tank was not equipped with a stirrer and contained substantial amounts of suspended material that might reduce the produced chlorine. Only half an hour was at disposal for the test, and the accuracy of the measurements was therefore not as good as in the laboratory. The set-up of the electrochemical reactor and auxiliary equipment in the trailer is seen from Figure 32.

Figure 32: Electrochemical reactor placed above the installed power supply. The inline measuring cells for conductivity, ORP, pH, and DO are placed to the right.

The results obtained during the 32 minutes of test are presented in Figure 33.

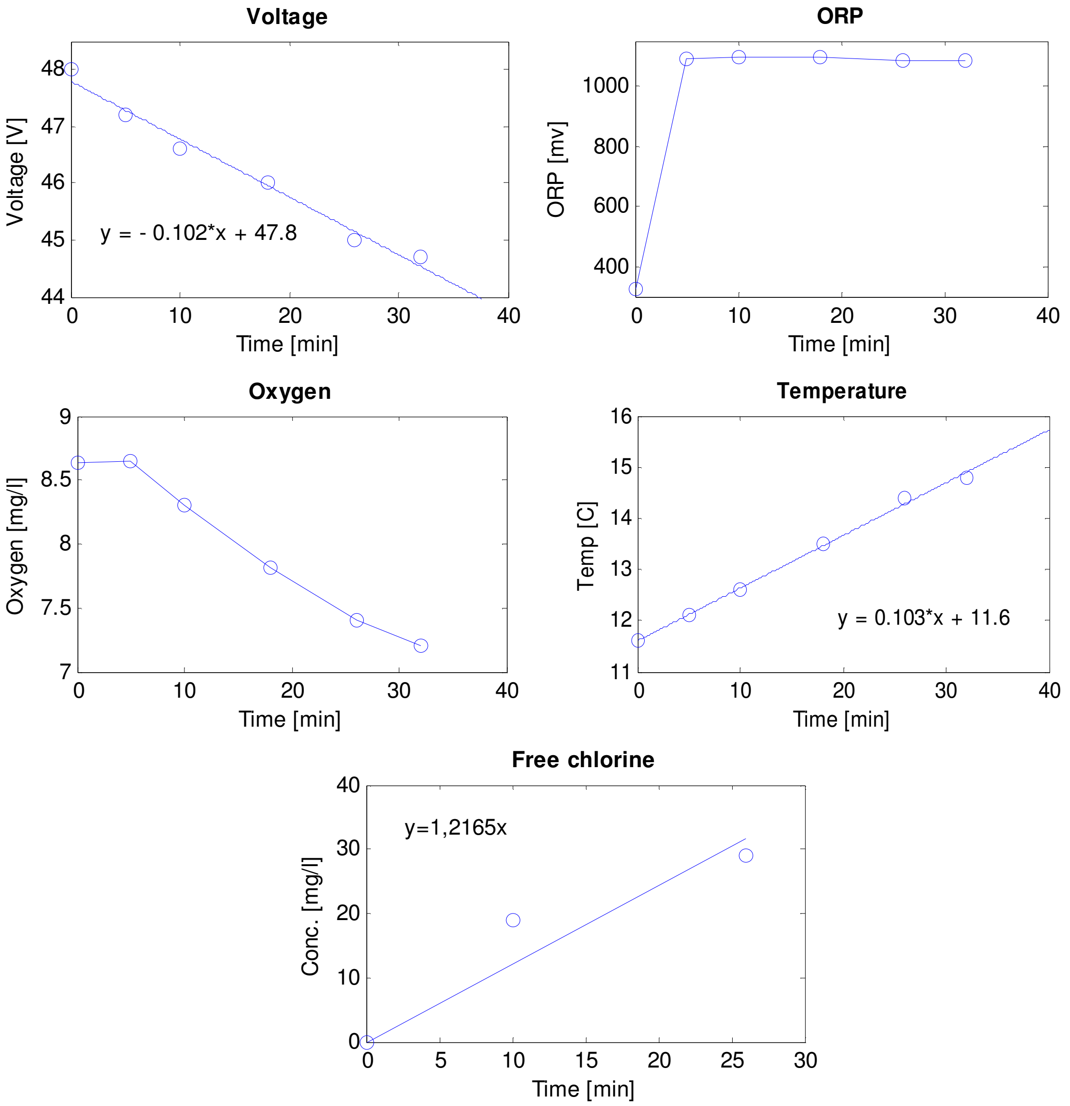

Figure 33: Voltage, ORP, oxygen, temperature, and free chlorine measured during the test conducted in the chemical test trailer (test 24).

The trends regarding all the measured parameters were consistent with the results obtained in the laboratory tests. ORP in this test was far more trustworthy than the results measured by the laboratory sensor, and indicated a constant oxidation potential of about +1100 mV in the water outlet from the reactor. This was the same level as measured in the full scale industrial installations visited in Greece, and it proved the high oxidation potential of the produced water. The free chlorine analyses contained a high degree of uncertainty, due to the low-tech sampling procedure and the content of suspended organic material in the water, which most likely reacted with the produced chlorine. Converted to a molar production the following was obtained:

$$\frac{1.2165\, {}^{mg}\!/_{l\cdot min} \cdot 750l}{100A \cdot 52{,}500\, {}^{mg}\!/_{mol}} = 1.74 \cdot 10^{-4}\, {}^{mol}\!/_{A\cdot min} \tag{77}$$

Compared to the production rate obtained in the laboratory test, $1.69 \cdot 10^{-4}\, {}^{\mathrm{mol}}/_{\mathrm{A\cdot min}}$, it can be concluded that the process most likely is linear scaleable for the production of free chlorine in the two reactors and probably also the remaining parameters such as pH, ozone, radicals etc. It also shows that only the applied current, and not the size of anode surface and hence the current density, significantly influences the efficiency of the chlorine oxidation process.

6.3 Test 2 – Gas production

During the investigation of the electrolysis of chlorine, a significant production of gas was observed. According to the theory in section 5.3.1, this gas was most likely molecular hydrogen formed, when water was reduced at the cathode in the reactor. The objective of the experiments presented in this section was to examine the qualitative composition of the gas. Furthermore, the rate, at which it was produced, was investigated as a function of current and *NaCl* concentration and the concentration of dissolved hydrogen was measured.

6.3.1 Materials and methods

The test was performed with the basis laboratory set-up as described in section 6.1. Additional equipment was added to the set-up in order to measure the gas production. At first, the gas production rate was measured with the set-up shown in Figure 34. In this set-up, produced gas was collected in a water filled inverted measuring glass.

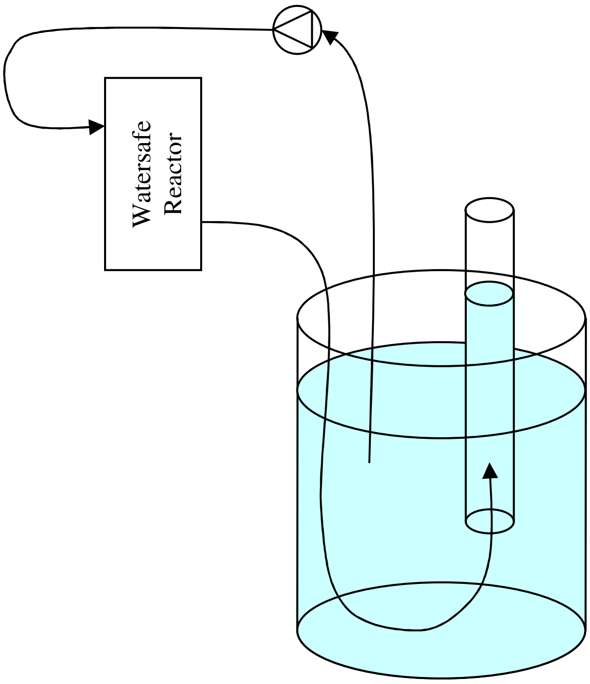

Figure 34: Test set-up for measurements of the gas production rate (test 19).

A qualitative experiment was conducted in order to determine the presence of chlorine in the produced gas. This was done by bubble a large amount of the produced gas through 20 ml of demineralised water. The set-up for this test was similar to the one shown in Figure 34; only the cylindrical measuring glass was changed to a 2 l Erlenmeyer flask. A rubber hose was placed in the headspace of the flask and directed to a measuring glass, where the produced gas was bubbled through demineralised water as showed in Figure 35.

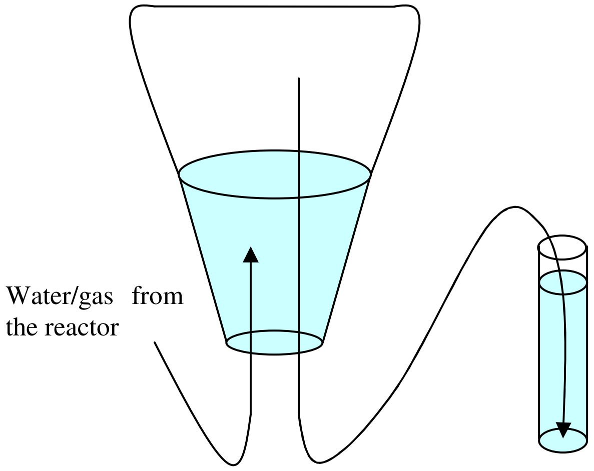

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Figure 35: Test set-up for the qualitative determination of chlorine gas (test 20).

After a while (7-15 min), the demineralised water was analysed for free chlorine as described in section 6.2.2. All tests were repeated several times at different currents (5-30 A) and *NaCl* concentrations (0.9-3.6 %).

In order to investigate the content of dissolved hydrogen in the water over time, measurements were conducted with a hydrogen sensor from Unisense connected to a pico ampere meter, see Figure 36.

Figure 36: Pictures of the Unisense hydrogen sensor with the protection cap, the used pico ampere meter, and the set-up for calibrating the sensor in hydrogen saturated salt water.

The sensor was calibrated in hydrogen free salt water (4 pA) and in hydrogen saturated salt water (1760 pA) and according to the manufacturer the calibration is linear from 0-100 % saturation.

6.3.2 Results and discussion

Quantitative measurements of the gas production were repeated 25 times at different currents and *NaCl* concentrations. The results from these tests are shown in Figure 37.

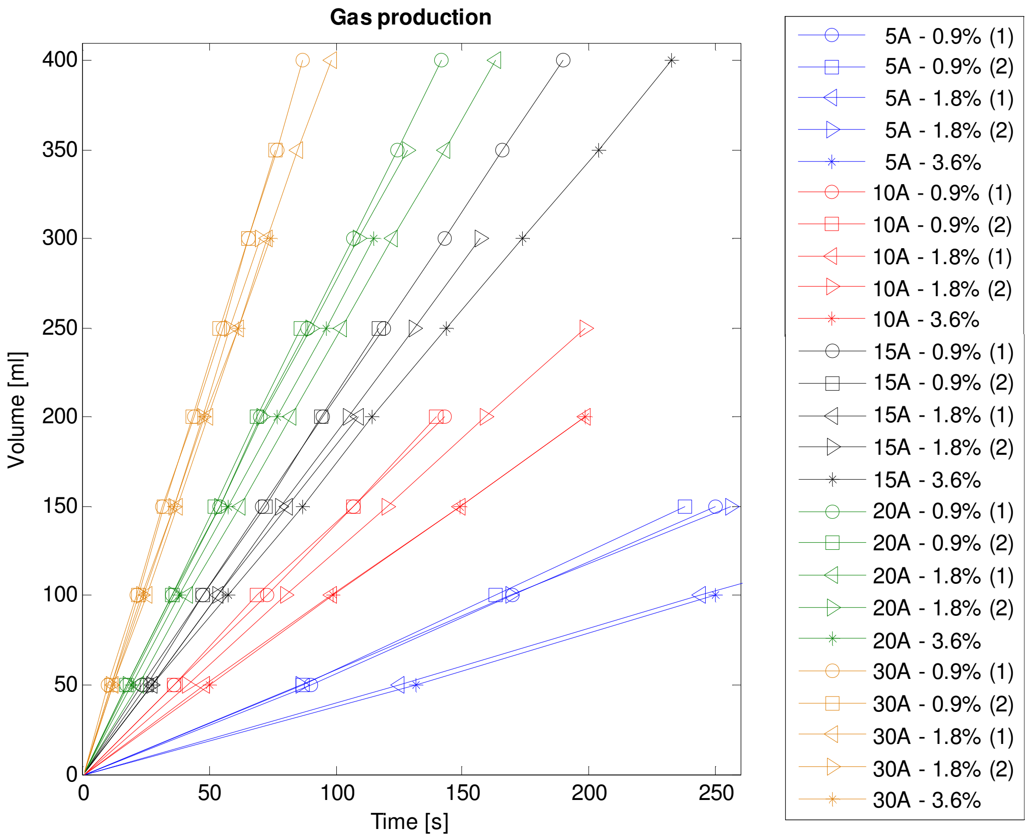

Figure 37: Gas production as a function of current and *NaCl* concentration (test 19).

As it is seen from Figure 37, the electrochemical gas production increased with the applied current, an observation which fitted the expectations.

One method of calculating the solubility of molecular hydrogen in water is with Henry’s law:

$$p = k \cdot c \tag{78}$$

where p [atm] is the partial pressure of molecular hydrogen, k (1282.1 $^{\mathrm{l \cdot atm}}/_{\mathrm{mol}}$ at 25 ºC [Andersen et al., 1994]) is the Henry’s law constant for molecular hydrogen, and c [$^{\mathrm{mol}}/_{\mathrm{l}}$] is the concentration of molecular hydrogen in the solution. For a partial pressure of 1 atm, the solubility is 18.7 ml molecular hydrogen per litre of water [Linde, 1996]. The partial pressure of molecular hydrogen in the atmosphere is $5 \cdot 10^{-7}$ atm [Andersen et al., 1994]. The saturated concentration of molecular hydrogen in water can be found from Henry’s law and converted to volume concentration by multiplying the molar concentration with the density of the molecular hydrogen (ideal gas):

$$p = k \cdot c \Leftrightarrow c = \frac{5 \cdot 10^{-7}\, atm}{1281.1\, ^{l \cdot atm}\!/_{mol}} = 3.90 \cdot 10^{-10}\; ^{mol}\!/_{l} \tag{79}$$

$$vol_{H_2} / vol_{H_2O} = 3.90 \cdot 10^{-10} \,{}^{mol_{H_2}}\!/_{l_{H_2O}} \cdot 24000 \,{}^{ml_{H_2}}\!/_{mol_{H_2}} = 9.36 \cdot 10^{-6} \,{}^{ml_{H_2}}\!/_{l_{H_2O}} \quad (80)$$

According to this calculation, the 10 l of water used in the experiment can only contain an insignificant amount of hydrogen compared to the gas production. However, it is expected that this equilibrium concentration will be exceeded, when the produced hydrogen is bubbled through the solution. The hydrogen concentration in the electrochemical system was measured over time at two different currents; 10 and 20 A. The measurements converted from pA to saturation based on a 1 atm partial pressure of hydrogen are seen from Figure 38.

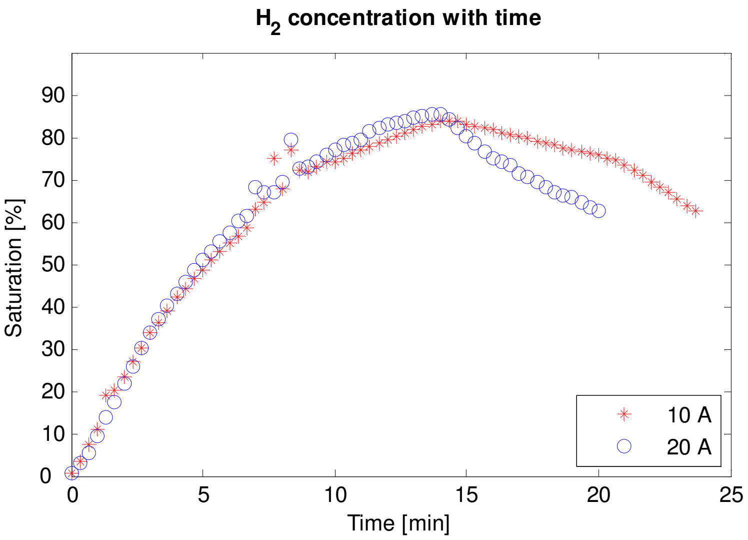

Figure 38: The hydrogen saturation at different applied currents as a function of time (test 25). The current was switched on a t = 0 and turned off at t = 14 min. The stirring was increased for the 10 A test at t = 20 min.

The concentration of hydrogen in the water reached about 85 % saturation within 14 minutes and the results were almost equal for 10 and 20 A. These measurements prove that the produced gas contains a large amount of hydrogen and show that the dissolution of hydrogen in the water is at a maximal rate for the applied set-up, since the change in concentration is equal for 10 and 20 A. When the current was turned off after 14 minutes, the hydrogen concentration slowly decreased with time. This rate was significantly influenced by the rotation speed of the stirrer. Also, the sensor had a very fast response time and the signal changed from 1100 to 30 pA within a few seconds, when it was remove from the electrochemical system and put into hydrogen free tap water. This ensures that the graphs in Figure 38 described the actual behaviour of the concentration changes and is not caused by en slow response time. The specified response time (90 %) is <5 s [Unisense, 2007].

It was expected that the concentration of $NaCl$ in the electrolyte did not have any influence on the rate of the gas production, if the current was keeps constant. However, some variation was seen from Figure 37. In all tests, the linear correlation was very high and all the calculated gas production rates are showed in Table 27.

Table 27: Gas production rates in $^{ml}/_{s}$ for different currents and *NaCl* concentrations (test 19).

	0.9 % (1)	0,9 % (2)	1.8 % (1)	1.8 % (2)	3.6 %	Average
5 A	0.59	0.62	0.41	0.59	0.40	0.52
10 A	1.40	1.42	1.01	1.25	1.01	1.22
15 A	2.11	2.12	1.85	1.91	1.72	1.94
20 A	2.82	2.90	2.45	2.76	2.61	2.71
30 A	4.59	4.62	4.09	4.28	4.10	4.34

A visual overview of the gas production rates as functions of *NaCl* concentrations and the applied current are shown in Figure 39 and Figure 40.

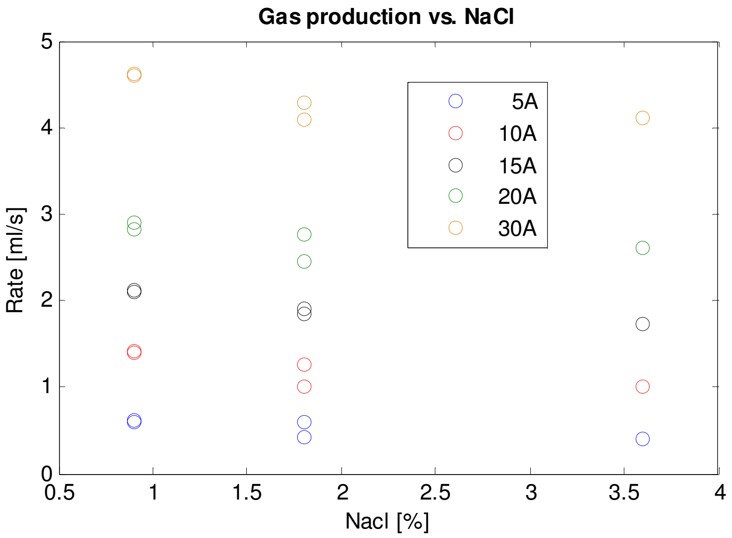

Figure 39: Gas production rate as a function of *NaCl* concentration at different currents (test 19).

Table 27 and Figure 39 indicate that higher *NaCl* concentrations result in lower gas production rates, but from these data it was not possible to observe a significant correlation because of the uncertainties.

The salt concentration was not expected to influence the gas production rate, but the observed deviation might be due to sodium covering the cathode in competion with the molecular hydrogen. At higher concentrations of *NaCl* in the electrolyte, Na^+-ions surrounds the cathode and are reduced to metallic *Na*. It rapidly reacts with water in order to return to ion state and produce H_2, but the reaction competes with the reduction of H_2O to H_2. Theoretically this would result in lower production rates in the beginning of the experiments, but after a while, when equilibrium is obtained, the rate will be at a maximum. This also explains why the difference in rates as a function of *NaCl* concentration at higher currents is not as distinct as with the lower currents, since equilibrium is reached faster at higher currents.

Another more likely reason for the decreased gas production at higher *NaCl* concentrations can be explained by the increased current efficiency at increasing *NaCl* concentrations as showed in section 6.2.3. When the efficiency increased, more chlorine is produced per ampere and fewer electrons are used for oxidation of other compounds such as water, and hence less oxygen is produced. This will result in a lower gas production and a more pure hydrogen gas at higher *NaCl* concentrations.

At higher *NaCl* concentrations, less voltage is needed to maintain a constant current and hence constant chlorine production. This results in lower power consumption at higher *NaCl* concentrations, which shows that the electrolysis is more efficient at higher *NaCl* concentrations. If the rate is plotted as a function of the applied current, a linear relationship between rate and current is found, se Figure 40 and Table 28.

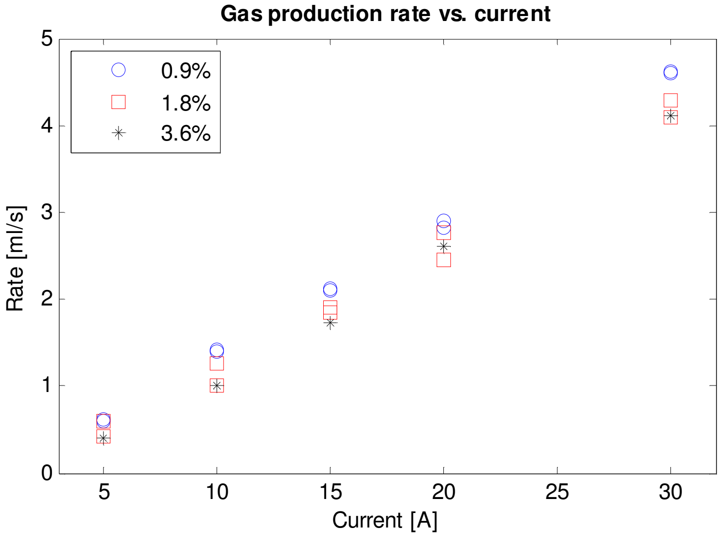

Figure 40: Gas production rate as a function of current at different *NaCl* concentrations (test 19).

Table 28: Current vs. gas production rate (test 19).

NaCl	Linear expression	R^2
0.9 %	0.1586·I-0.2188	0.9978
1.8 %	0.1483·I-0.3131	0.9916
3.6 %	0.1507·I-0.4437	0.9975
Average	0.1529·I-0.3015	0.9824

If the constant term from the expressions in Table 28 was left out, and the average gas production rate was converted to a molar rate (1 ml H_2 = $4.167 \cdot 10^{-5}$ mol at 1 atm, 25 ºC), the expression will be:

$$0.1529 \, {}^{ml}\!/_{s \cdot A} \cdot 4.167 \cdot 10^{-5} \, {}^{mol}\!/_{ml} = 6.371 \cdot 10^{-6} \, {}^{mol}\!/_{s \cdot A} \tag{81}$$

Production of one mole of free chlorine will result in one mole of molecular hydrogen according to the following overall reaction:

$$2Cl^- + 2H_2O \rightarrow Cl_2 + H_2 + 2OH^- \tag{82}$$

In section 6.2.3, the chlorine production rate was found to be $2.82 \cdot 10^{-6}$ ${}^{mol}/_{s \cdot A}$. The stoichiometric relationship between the formation of molecular hydrogen and chlorine was therefore 2.3:1, and hence 130 % more hydrogen was produced compared to reaction 82. This showed that more water was reduced at the cathode compared to the oxidation of chloride at the anode, and hence other oxidants were produced including molecular oxygen, or that some of the produced chlorine evaporated as a gas and entered the measured gas production. If the last assumption was correct, the collected gas would contain chlorine and not pure molecular hydrogen. This was investigated by two different methods; bubble the gas trough demineralised water and measure the chlorine concentration afterwards and by ignition of the collected gas in order to examine the sound.

In the bubble test, the produced gas was diluted and bubbled through 20 ml of demineralised water in order to produce a measurable concentration of $HOCl$ in the water. From these data it was possible to calculate the volume of Cl_2 produced pr. second, if it was assumed that all the chlorine from the gas was dissolved in the demineralised water. The results from the tests are shown in Table 29.

Table 29: Results from the qualitative investigation of chlorine gas production (test 20). *calculated

Current	$NaCl$	Time	$HOCl_{water}$	Gas produced*	Dilution	Cl_2 rate*
30A	0.9 %	7 min	0.07 $^{mg}/_{l}$	1800 ml	1.8	$3.4 \cdot 10^{-6}$ $^{ml}/_{s}$
30A	4.0 %	15 min	0.08 $^{mg}/_{l}$	3900 ml	1.4	$3.0 \cdot 10^{-6}$ $^{ml}/_{s}$

The calculations in Table 29 were done with very large uncertainties, and the results were only applicable to conclude that the electrochemical produced gas contained very small amounts of free chlorine (~0.00007 %), and that the measured volume of gas was only attributable to the molecular hydrogen production.

This conclusion was further supported by the ignition test. This test showed that ignition of the collected gas resulted in a sound only made by pure molecular hydrogen and not a squeal, which would have been an indication of an impure hydrogen gas. It can however not be excluded that the gas includes a small amount of oxygen.

These two small qualitative experiments showed that the gas produced can be considered as almost pure hydrogen and maybe a small amount of oxygen, and therefore oxidation of other substances besides chloride to chlorine occurred at the anode. This was the only explanation of the stoichiometric relationship between molecular hydrogen and chlorine not being 1:1. Formation of oxygen, ozone, peroxides, hydroxyl radicals, chlorine dioxide, chlorate, chlorite, and other oxidants might have caused the increased molecular hydrogen production.

Safety issues

Since molecular hydrogen forms explosive mixtures with air, if the lower explosion limit, LEL, is exceeded, special caution has to be taken, when working with the electrochemical reactor. Table 30 shows some of the important data for hydrogen gas concerning safety.

Table 30: Important data for hydrogen gas concerning safety.

Flammability limits in air:	4 % to 77 %.
Auto ignition temperature:	500 ºC
Specific gravity at 0 ºC and 1 atm (air = 1):	0.07

Source: [Kemikalieberedskab, 2007]

When working in closed rooms, there is a risk of exceeding the LEL, if hydrogen leeks into the trailer. If all the hydrogen produced at 200 A (~138 $^{l}/_{h}$) is released in the trailer (~37 m^3), it would take about 11 hours to reach the LEL. Because of the very low specific gravity of molecular hydrogen, it is important not to allow the hydrogen gas to accumulate in elevated locations. However, hydrogen gas possesses a high diffusivity, which makes ventilation a very effective method to avoid exceeding LEL.

6.4 Test 3 – Identification of oxidizing agents

In order to investigate if the disinfection and oxidation by the Watersafe unit is caused entirely by the chlorine species produced in the chlorine electrolysis, the electrochemical processes occurring in the reactor were examined in greater detail. In the study of the electrochemical theory in section 5.3.1, it came apparent that some electrochemical reactors produce more powerful short-living oxidants that strongly increase the reactors performance in the degradation of unwanted water contaminants. The extent of oxidant formation in the Watersafe reactor has not former been clarified, and the project group was therefore keen on identifying the possible oxidants contributing to the oxidation potential of the reactor.

Experimental methods in order to investigate the production and role of oxygen radicals have been of great interest in several research fields, especially within biochemistry, photochemistry, and photobiology [Bors et al., 1978; Kraljic & Trumbore, 1965]. One of the methods, adapted to the electrochemical research field for the detection of hydroxyl radicals, is the bleaching of p-nitroso-dimethylaniline (RNO). RNO is applied as a selective scavenger towards hydroxyl radicals, since it has been shown that the compound, which posses a strong yellow colour in aqueous solution, does not react with other oxygen radicals as singlet oxygen ($^1O_2$) or peroxo compounds as $HOO^\cdot$ and H_2O_2 [Bors et al., 1978; Kraljic and Mohsni, 1978]. It has been shown that relatively high concentrations of hydroxyl radicals were obtained at lead dioxide anodes, but only in trace amounts at platinum anodes [Wabner and Grambow, 1985]. Also boron-doped diamond electrodes have shown to be able of producing hydroxyl radicals [Holt et al., 2003]. The alloy, which constitutes the surface of the anode in the Watersafe reactor, has never undergone such investigations, which makes this examination very relevant.

In the next sections, the theory concerning RNO bleaching is explained, and the conduction of the experiments and experimental parameters are presented. The obtained results are presented, and on this basis a thorough discussion of the occurring electrochemical processes is provided.

6.4.1 Theory

In the search for hydroxyl radicals, direct detection is possible by Electron Spin Resonance (ESR), but only if the radicals are produced in high concentrations [Comninellis, 1994]. At low concentrations, hydroxyl radicals can be detected by the indirect method of bleaching of RNO, which involves trapping of the hydroxyl radicals by an addition reaction (spin trap) in order to produce a more stable radical (spin adduct):

$$OH^\bullet + spin\ \ trap \rightarrow spin\ \ adduct \qquad (83)$$

RNO, see Figure 41, is acting as a spin trap for indirect detection of hydroxyl radicals formed at anode surfaces.

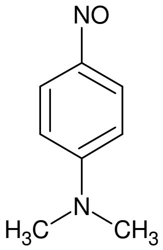

Figure 41: p-nitroso-dimethylaniline (RNO)

Another possibility is to use α-(4-pyridyl-1-oxide)-N-tert-butyl-nitrone (4-POBN) as a spin trap. The radical ads to this unsaturated spin trap to form a new radical adduct of longer lifetime that can be detected using ESR. [Chen et al., 1999]

As mentioned above, RNO in neutral and basic solution is shown to react selectively with hydroxyl radicals and not with singlet oxygen or other peroxo compounds. This has been shown by adding ethanol to the solution, since ethanol is a very efficient scavenger for hydroxyl radicals [Wabner and Grambow, 1985]. An example is provided in Figure 42.

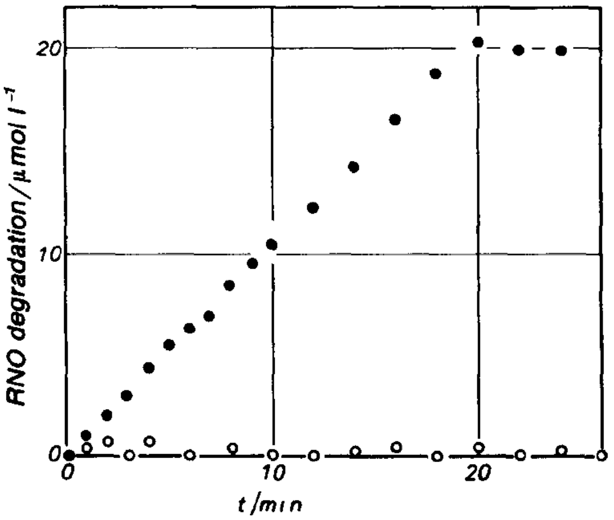

Figure 42: Degradation of RNO in an electrochemical reactor with (white marks) and without (black marks) 10 % ethanol, showing that RNO is not degraded in the absence of hydroxyl radicals, since ethanol is a very efficient scavenger for hydroxyl radicals [Wabner and Grambow, 1985].

Experiments performed by Wabner and Grambow, 1985, also showed that ozone caused a significant bleach of the RNO solution. Even though ethanol was added in excessively concentrations, it did not result in a complete suppression of the ozone induced RNO bleaching.

RNO is sensitive even at very low radical concentrations, since the rate of the reaction between hydroxyl radicals and RNO is extremely rapid ($k = 1.2\cdot10^{10}\ {}^{1}/_{\mathrm{mol\cdot s}}$) [Comninellis, 1994; Bors et al., 1978]. The bleaching involves the reactions presented in Figure 43:

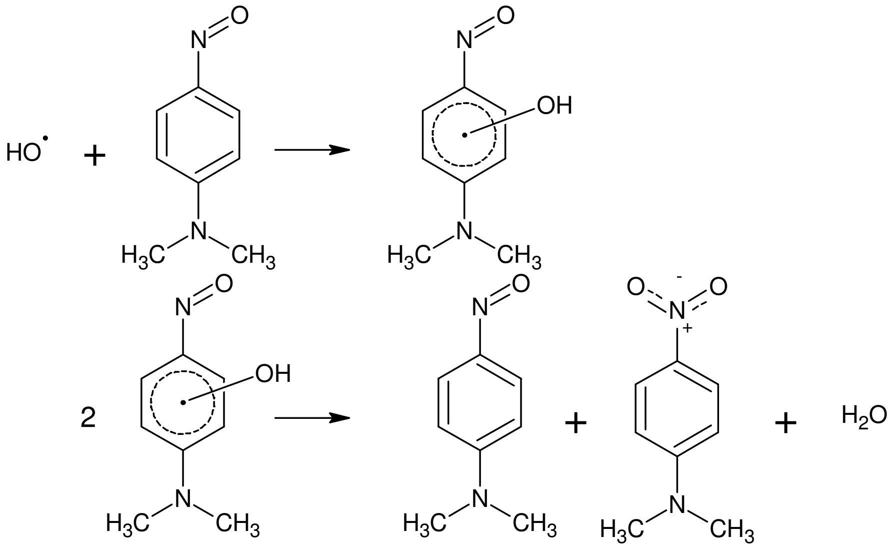

Figure 43: Bleaching of RNO by hydroxyl radicals [Bors et al., 1979; Baxendale & Kahn, 1969].

RNO dissolved in demineralised water generates a yellow coloured aqueous solution, which is bleached during reaction with hydroxyl radicals. Hence, the production of hydroxyl radicals are indirectly measured spectrophotometric with a UV/VIS spectrophotometer at the strong adsorption band at 440 nm [Wabner and Grambow, 1985; Holt et al., 2003]. The reaction mechanism has not been clarified, but the commonly applied suggestion is showed in Figure 43. The chromophoric group of the RNO molecule is the nitroso group. During reaction with hydroxyl radicals, the delocalized π-orbital of the aromatic is attacked, and the intermediate spin adducts subsequently reacts in the oxidation of the nitroso to a nitro group.

In Cyclic voltametry, which is an electroanalytical technique, the potential of an electrode immersed in an unstirred solution is linearly cycled while measuring the resulting current. The obtained voltammograms have shown that RNO is electrochemically inactive at Pt, IrO_2, PbO_2 and SnO_2 anodes [Comninellis, 1994].

Detection of other oxygen radicals are also possible with RNO by an analytical method described by Kraljic and El Mohsni, 1978, and Kraljic and Trumbore, 1965. ${}^1O_2$ does not react directly with RNO, but reaction with histidine is possible, where it forms endoperoxides, which in turns are able to bleach RNO. Bors et al., 1978, used RNO for detection of peroxo compounds, $HOO^{\cdot}$ and H_2O_2, by adding $Fe(II)$ ions to the RNO solution, which converted the peroxo compounds to hydroxyl radicals according to reaction 84 and 85:

$$HOO^{\bullet} + Fe^{2+} + H^{+} \rightarrow Fe^{3+} + H_2O_2 \qquad (84)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \qquad (85)$$

For this purpose, the solution should contain no more than 100 $^{\mu mol}/_{l}$ $Fe(II)$. Excessively $Fe(II)$ ions would serve as hydroxyl radical scavengers [Wabner and Grambow, 1985].

The research papers found by the project group, where bleaching of RNO has been applied as a method for hydroxyl radical detection in electrochemical experiments, have mainly been conducted in minor (3-150 ml) batch reactors in laboratory set-ups. The results from existing laboratory studies are gathered in Table 31.

Table 31: Results from four different electrochemical researches using RNO for indirect detection of hydroxyl radicals. The effect column indicates if hydroxyl radicals were formed. + high concentrations, - almost zero radicals formed. *in presence of Cl^-.

Anode material	[RNO]	Current density	Effect	Reference
Boron/diamond	$2\cdot10^{-5}$ M	1-20 mA/cm^2	+	[Holt et al, 2003]
PbO_2	$5\cdot10^{-5}$ M	5 mA/cm^2	+	[Wabner and Grambow, 1985]
Pt	$5\cdot10^{-5}$ M	5 mA/cm^2	-	[Wabner and Grambow, 1985]
Pt	$2\cdot10^{-5}$ M	20 mA/cm^2	-	[Comninellis, 1994]
Ti/IrO_2	$2\cdot10^{-5}$ M	20 mA/cm^2	-	[Comninellis, 1994]
Ti/SnO_2	$2\cdot10^{-5}$ M	20 mA/cm^2	+	[Comninellis, 1994]
Pt^*	$3\cdot10^{-6}$ M	32 mA/cm^2	+	[Fukatsu and Kokot, 2001]

The spectrophotometric measurements in the reference researches from Table 31 was all carried out in build-in cuvettes in the small batch reactors for direct spectrophotometric observations of the bleaching at the anode.

In recent years, an increasing interest in applying electrochemical oxidation and disinfection in treatment of industrial waste water has developed, and the project group has found three published papers, where the RNO bleaching method has been applied in the investigation of hydroxyl radical formation in electrochemical treatment of saline waste water [Fukatsu and Kokot, 2001; Feng et al., 2003; Tanaka et al., 2004]. Only one of the experimental set-ups was based on a recirculation system. The obtained results indicated that the hypochlorite formed by the chlorine electrolysis entailed bleaching of the RNO solution as well. Fukatsu and Kokot, 2001, suggested that hypochlorite generates hydroxyl radicals, which carries the responsibility for the bleach, reaction 86-88, a suggestion supported by studies of bleaching mechanisms in general [Holst, 1954; Epstein et al., 1962]:

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{86}$$

$$HOCl \rightarrow OH^\bullet + Cl^\bullet \tag{87}$$

$$Cl^\bullet + HOCl \rightarrow OH^\bullet + Cl_2 \tag{88}$$

The mechanism is supported by Tanaka et al., 2004, who investigated bleaching of RNO by a liquid hypochlorite solution. By addition of the hydroxyl radical scavenger NO_2^- to the solution, the bleaching was significantly reduced and almost inhibited compared to the control experiment without NO_2^-. This strongly suggests that electrochemical bleaching is likely to be caused by the same mechanism as chemical bleaching using $NaOCl$ [Tanaka et al., 2004]. According to Ferro et al., 2000, the oxidation of chloride is caused by the formation of chlorine radicals, reaction 89-90, which then are capable of hydroxyl radical formation according to reaction 88.

$$Cl^- \rightarrow Cl^\bullet + e^- \tag{89}$$

$$2Cl^\bullet \rightleftharpoons Cl_2 \tag{90}$$

The fact that RNO apparently is bleached by ozone and to a certain extent by free chlorine as well as the hydroxyl radicals may constitute some difficulties in the interpretation of the results obtained in the RNO experiments. However, the bleaching of RNO is very useful in the evaluation of the oxidative potential of the Watersafe reactor at different parameter settings, and the amount of published data material is small, and confirmation or rejection of suggested mechanisms are of highest interest. It is also very interesting to evaluate the possibility of applying the RNO bleaching method in the, in the present project, applied larger electrochemical recirculation system compared to the referred studies.

6.4.2 Materials and methods

The RNO bleaching experiments were conducted with the experimental set-up described in section 6.1. The concentration of the electrolyte was controlled by conductivity measurements. Approximately 10.0 $^{mg}/_{l}$ RNO ($6.67 \cdot 10^{-5}$ M) served as the initiating concentration in all of the conducted experiments, and the volumes of the solutions differed from 1-25 l. Full dissolution of the added RNO powder in demineralised water was obtained after 2 hours of stirring. Measurements of the absorbance at 440 nm were conducted by manually sampling of 25 ml solution with pipette into a glass beaker, and the solution was analysed by a Philips PYE UNICAM PU 8600 UV/VIS spectrophotometer at 440 nm. All RNO measurements were duplicate analysis on the same sample. The standard deviations were calculated, but due to the small values of the deviations, they were intentionally left out of the graphs. The duration between sampling and analysis was approximately 30 s. The conducted RNO experiments are seen in Table 32.

Table 32: The experiments conducted in the investigation of RNO bleaching.

No.	Name	Electrolyte [%]	Voltage [V]	Current [A]	Volume [L]	Start conc. [$^{mg}/_{l}$]	Calib.
9	RNO 1	*NaCl*: 0.9 %	6	5.0	10	9.55	1
10	RNO 2	*NaCl*: 0.9 %	20.2	30.6-38.4	5	-	-
11	RNO 3	*NaCl*: 0.9 %	3.4-3.6	1.0	10	10.3	1
12	RNO 4	*NaCl*: 0.9 %	8.0-8.8	10.0	10	10.2	1
13	RNO 5	*NaCl*: 0.9 %	0	0	1	9.3	2
14	RNO 6	*NaCl*: 0.9 %	0	0	1	14.1	3
15	RNO 7	*NaCl*: 0.9 %	0	0	1	10.0	4
16	RNO 8	*NaCl*: 0.0 %	20.2	0.2	10	10.1	4
17	RNO 9	*NaCl*: 0.9 %	3.5	1.0	10	10.2	4
18	RNO 10	KNO_3: 0.9 %	3.5-15.0	1.0-20.0	10	10.2	4

The experiments no. 9-12 concerned the bleaching of RNO at different constant currents. The applied currents are equivalent to current densities between 16.6-335 mA/cm^2. Experiment no. 10 was a demonstration test recorded on video. In experiment 13-15 liquid *NaOCl* was added to RNO solutions in order to investigate the bleaching caused by hypochlorite without influence by the electrochemical processes. In experiment 16, bleaching in a pure demineralised water solution with very low conductivity was investigated. In experiment 17, the power unit was stepwise turned on and off in order to investigate the controllability of the bleaching reaction and the bleaching caused by free chlorine contra the other electrochemically generated oxidants. Experiment 18 investigated the bleaching in a potassium nitrate electrolyte, where the influence from free chlorine could be ignored.

The different volumes applied in the experiments were for practical purposes only. The numbers provided in the calib. column of Table 32 reflect that a calibration curve was prepared each day, the experiments were conducted and refer to the calibration curves found in appendix 4.

6.4.3 Results and discussion

The first investigation conducted by the RNO bleaching method concerned the effect of the current on the oxidation potential. Three different currents from 1-10 A were applied and the concentration of RNO was followed for 60 min in each experiment. All experiments were carried out at an electrolyte concentration of 0.9 % *NaCl*. Prior to the start of the first experiment, the RNO solution was recirculated through the turned off reactor, in order to investigate any contribution to the bleach caused by reactions on the anode surface due to the alloy composition. The concentration of RNO remained unchanged for 10 min. The results of the main tests are seen in Figure 44.

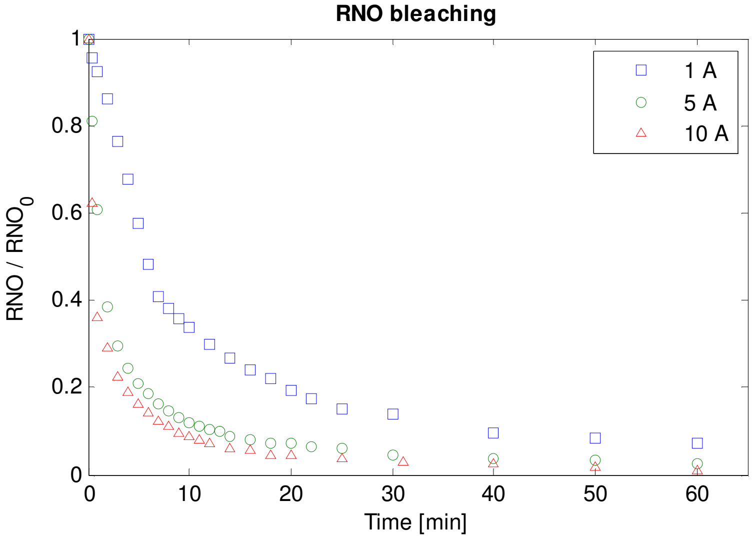

Figure 44: Electrochemical bleaching of RNO in a 0.9 % *NaCl* electrolyte. (Test 9, 11, and 12)

It is seen from Figure 44 that the efficiency of the electrochemical process in the bleaching of RNO is high even at a constant current of 1 A. A sharp decrease in RNO absorbance occurred within 10 minutes of the electrochemical treatment, but if the bleach was caused solely due to the chlorine production or due to direct formation of hydroxyl radicals and ozone was at the present state of the investigation not evident. The reactions, by which the bleaching of RNO occurred, resulted in an immediately change of the colour of the solution to dark green, which slowly faded out to yellow-brown. However, the solution was as expected found bright yellow after 60 min. Photos of the RNO solution during the electrochemical treatment are found in Figure 45.


t = 0 min t = 5 min t = 40 min

Figure 45: Photos of the RNO solution during electrochemical treatment.

The appearance of the dark green colour was not mentioned in any of the reference papers, but it might be due to the formation of the intermediate spin adduct. The applied spectrophotometer only allowed absorbance readings at a specific wavelength, but in further investigations it would be interesting to measure the whole UV/VIS absorbance spectrum in order to investigate the development of the green colour. Also the green colour made it impossible to observe the bleach of the yellow RNO by the naked eye. The rate of the bleaching reaction was clearly dependent on the concentration of RNO, which indicates a first or higher order degree of reaction. This matches the published results where saline waste water was the electrolyte [Tanaka et al., 2004; Fukatsu and Kokot, 2001; Feng et al., 2003], but in the investigations without a high conductive electrolyte, the rate of the bleaching was found constant [Wabner and Grambov, 1985; Bors et al., 1978]. The degradation of organic compounds by electrochemically processes is however mainly found to follow first order reactions [Baun et al., 2004]. In Figure 46, the electrochemical bleaching of RNO by the Watersafe reactor should reveal a straight line in order to represent a first order model.

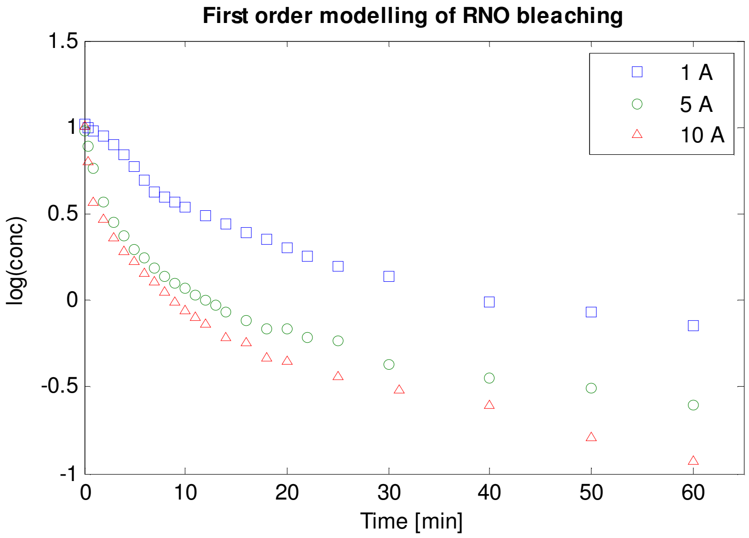

Figure 46: Fit of the results to a first order model. (test 9, 11, and 12)

The first order model does not match the obtained results, and hence a second order model is investigated, see Figure 47.

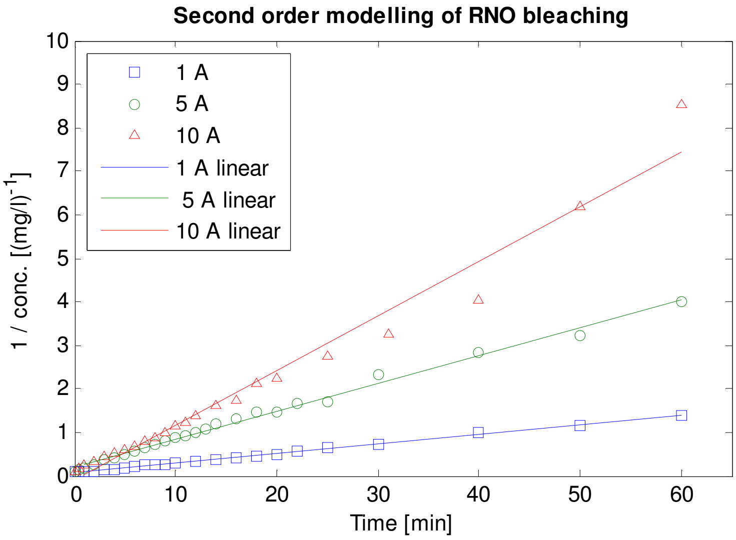

Figure 47: Fit of the results to a second order model (test 9, 11, and 12).

The second order model nicely governs the obtained results at the low currents, see Figure 47. At 10 A, the rate of the reaction seems to increase, but in the last RNO measurements (40, 50, 60 min), the absorbance was close to the detection limit, and hence the uncertainty was considerable. The second order model provided an applicable description of the overall observed bleaching reaction. This discovery was important in order to evaluate the overall oxidation potential of the electrochemical process, but information about the elementary reactions contributing to the second order dependence was limited. It could be due to the mechanism showed in Figure 43, where two RNO molecules are involved in the reaction.

According to Tanaka et al., 2004, direct reduction and oxidation of RNO occur at the electrodes according to reaction 91-93.

Cathode:

$$RNO + 2e^- + 2H^+ \rightarrow RNHOH \tag{91}$$

Anode:

$$2RNO + 2H_2O \rightarrow 2RNOOH + H_2 + 2e^- \tag{92}$$

$$RNOOH \rightarrow RNO_2^- + H^+ \tag{93}$$

According to the electrochemical theory presented in section 5.3.1, a constant formation of hydroxyl radicals most likely occurs at the anode surface, when the current is kept constant. The produced radicals stay at the surface or desorbs to the solution. In both cases an instantly reaction with RNO or other substances occurs. If hydroxyl radicals are formed at the anode, they surely do not result in a zero order bleaching of RNO as seen from Figure 44. Therefore they have to be included in the rate constant. The formation of ozone will also result in a bleaching of RNO. However, it is not possible to tell, if ozone is produced, if the ozone concentration is constant or ozone accumulates in the solution. The Prominent ozone sensor, which was intended to be applied in the investigation, was updated with new spare parts, but it never became operational, and hence no knowledge was gained concerning the ozone production in the Watersafe system. Simultaneously, RNO might be bleached by hydroxyl radicals generated from the free chlorine, equation 86-89. The fact that at least three oxidizing species might be produced during the electrochemical process, and that all three are contributing to the bleaching, showed the complexity of the chemical processes. The observed rate constant, k_{obs}, which was specified by the slope of the linear fits, might consist of contributions from all three reactions:

$$\frac{d[RNO]}{dt} = k \cdot [OH^\bullet]^a \cdot [O_3]^b \cdot [HOCl]^c \cdot [RNO]^d \tag{94}$$

A kinetic model, taking account of all the oxidative species, was attempted to be developed by the project group, but the development revealed too many unknowns due to little knowledge about the elementary reactions. A simpler model only including *HOCl* and RNO concentrations indicated that *HOCl* did not significantly influence the bleaching process. Therefore, the best model is still the second order overall rate equation obtained from Figure 47:

$$\frac{d[RNO]}{dt} = k_{obs} \cdot [RNO]^2 \tag{95}$$

$$\frac{1}{[RNO]} = k_{obs} \cdot t + \frac{1}{[RNO]_0} \tag{96}$$

This model assumes a constant, if any, concentration of hydroxyl radicals and ozone, and it excludes the contribution from *HOCl*. If this approximation is reasonably, regarding the role of *HOCl*, is investigated experimentally later in this section. The value of the rate constants and the half-lifes at the investigated currents are provided in Table 33.

Table 33: Rate constants and half-lifes of the RNO bleaching (test 9, 11, 12).

Current [A]	k_{obs} [$^1/_{mg \cdot min}$]	k_{obs} [$^1/_{mol \cdot s}$]	$t_{½}$ [min]
1	0.022	55	4.37
5	0.064	160	1.63
10	0.125	313	0.77

Since the rate constant for the reaction between hydroxyl radicals and RNO is $1.2 \cdot 10^{10}$ $^1/_{mol \cdot s}$ [Comninellis, 1994], the reaction proceeds almost immediately. Therefore the production of hydroxyl radicals is expected to be the limiting step in the process of bleaching of RNO. It is also expected that the formation of hydroxyl radicals is constant (zero order) at a constant current. The value of the rate constants increased by increasing current, and this increase was most likely due to an increased production of hydroxyl radicals at higher currents. Figure 48 revealed a proportional relationship between reaction rate and applied current.

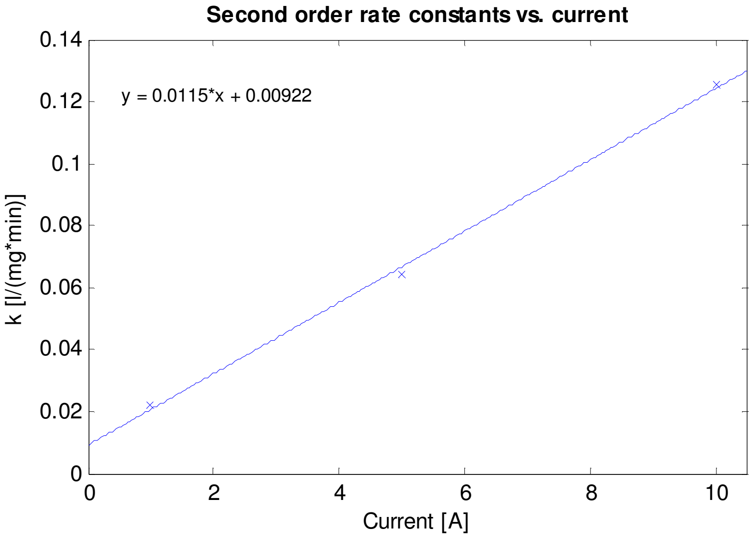

Figure 48: The linear relationship between the rate constants and the current (test 9, 11, and 12).

Expression 95 then becomes a pseudo second order rate expression at constant currents, since the concentration of hydroxyl radicals is determined by the applied current. When the expression for the relationship is inserted in equation 96, the theoretical bleaching of RNO at different currents, *I*, can be calculated from expression 97:

$$\frac{1}{[RNO]} = (0.0115 \cdot I + 0.00922) \cdot t + \frac{1}{[RNO]_0} \tag{97}$$

The model is seen in Figure 49, where the graphs for the respective currents were compared to the experimental results obtained. It is important to notice that the model only applies for an electrolyte composition of 0.9 % *NaCl*.

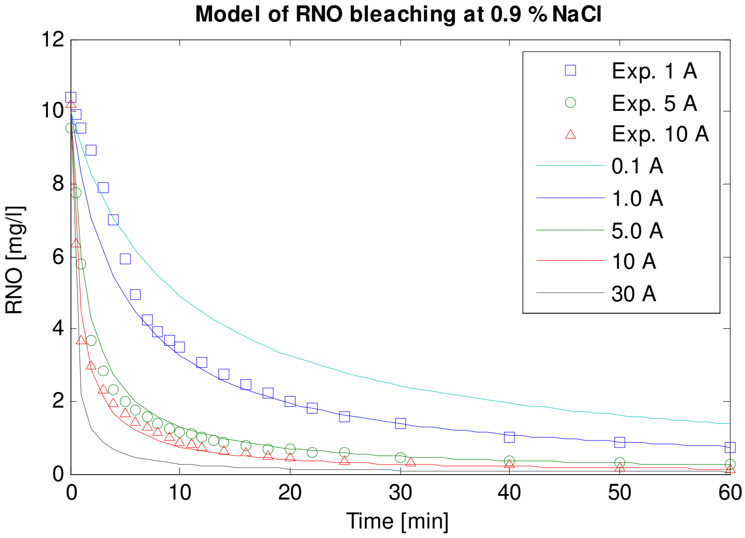

Figure 49: Developed model for electrochemical bleaching of RNO in the Watersafe reactor in a 0.9 % *NaCl* electrolyte.

In order to investigate the effect of the free chlorine in the electrochemical bleaching of RNO, experiments no. 13-15 with bleaching by addition of liquid sodium hypochlorite were conducted. The experiments were conducted in a smaller scale in volumetric flasks, where water containing RNO was mixed with a sodium hypochlorite solution according to the three mixtures described in Table 34.

Table 34: The three mixtures used for determine the influence of $HOCl$ of RNO bleaching.

Blank	300 ml demineralised water (1.8 % $NaCl$, 10 $^{mg}/_{l}$ RNO) + 300 ml demineralised water
Solution 1	300 ml demineralised water (1.8 % $NaCl$, 10 $^{mg}/_{l}$ RNO) + 300 ml of a 655 $^{mg}/_{l}$ $HOCl$ solution
Solution 2	300 ml demineralised water (1.8 % $NaCl$, 10 $^{mg}/_{l}$ RNO) + 300 ml of a 1310 $^{mg}/_{l}$ $HOCl$ solution

The solutions were magnetically stirred, and the concentrations of free chlorine prior to the addition were determined by the DPD method described in section 6.2.2. A photo of the experimental set-up is seen in Figure 50.

Figure 50: The experimental set-up in the investigation of chemical bleaching of RNO. To the left: Solution 2, in the middle: Solution 1, to the right: Blank (test 14).

The performance of the chemical bleaching experiments caused some troubles, and hence experiment no. 13 served as introductory work, and the results obtained in experiment 15 were by the project group considered as failures. However, experiment no. 14 generated results considered believable and to a certain extent comparable to results obtained by Tanaka et al., 2004. The obtained results from the chemical bleaching by free chlorine are seen in Figure 51.

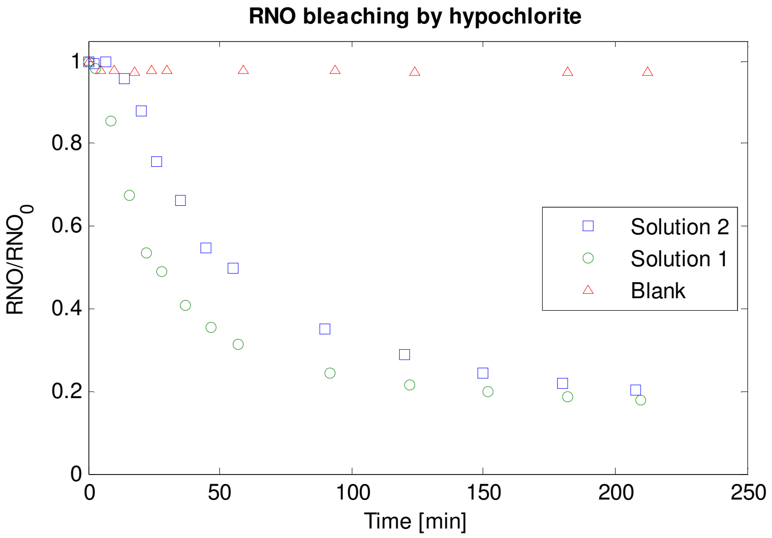

Figure 51: Chemical bleaching of RNO by addition of *NaOCl* (test 14).

The experiment showed that no bleaching of the blank occurred, and hence any photochemical bleaching caused by daylight can be ignored in the following discussion. The bleaching was dependent on the concentration of RNO in the solution, but compared to the electrochemical bleaching in Figure 44, the rate of the bleaching was much slower. An observation, which constituted a great surprise to the project group, was the fact that solution 1 possessed the fastest reaction rate compared solution 2. This result was roughly confirmed by experiment 15. The explanation is for the project group not evident. The pH in the two solutions can be calculated to be about 9.57 and 9.72 and from equation A-4 in appendix 1, it can be calculated that about 0.73 % and 0.52 % is present as *HOCl* for solution 1 and 2 respectively. This is not enough to account for the inverse relationship. It is however expected that the difference in pH is the main reason for the unexpected behaviour

The results from test 14 were modelled to first and second order models in order to investigate the dependency of the concentration of RNO on the bleaching, see Figure 52.

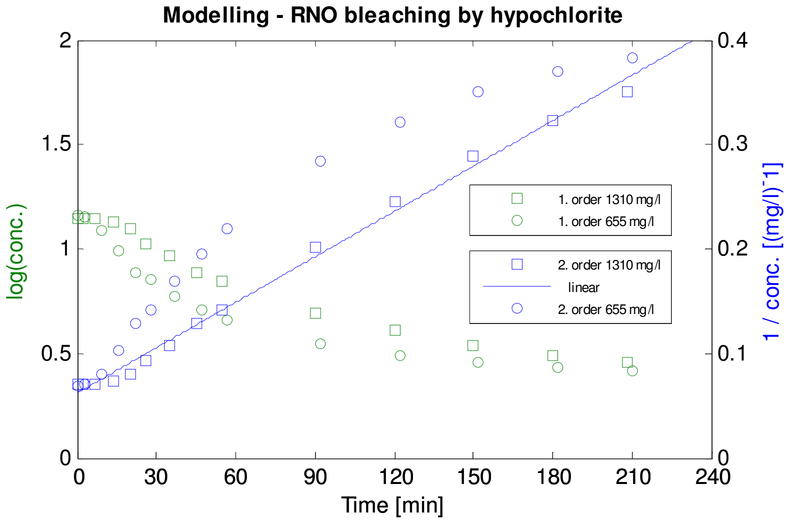

Figure 52: Modelling of the chemical bleaching results to first and second order models (test 14).

The modelling in Figure 52 showed that neither the first nor the second order model were capable of providing a fully acceptable explanation for the chemical bleaching. In both cases solution 2 was closest to be fitted to a straight line, and the fit to the second order model showed in Figure 52 revealed a rate constant of 0.00145 $^{1}/_{mg \cdot min}$. This is 15-86 times as slow as the electrochemical bleaching, but the direct comparison is inconvenient, since ongoing chlorine production occurs in the reactor, which does not leave a constant chlorine concentration. Solution 2 was much higher than the one produced in the electrochemical bleaching of RNO, where the 10 A current according to Figure 23 resulted in a concentration of approximately 300 $^{mg}/_{l}$ after 60 min, without considering the consumption of $HOCl$ during the oxidation of RNO. Hence, the bleaching rate caused by the free chlorine in the electrochemical experiment is likely to be considered even more slowly. However, the unexplained inverse relationship revealed between the free chlorine concentration and the chemical bleaching rate may interfere with this statement.

The experiments conducted leaved no doubt about the very fast initial reaction rates observed in the electrochemical bleaching experiments were caused by the generation of strong oxidative species other than $HOCl$. At this time in the experiment, the concentration of free chlorine was very low and did not contribute significantly to the initiated bleach of the RNO. If the bleaching occur due to direct oxidation or reduction at the electrodes according to reaction 91-93, or if the main contribution is due to a hydroxyl radical generation at the anode according to the reaction schemes presented in section 5.3.1, which subsequently oxidise RNO according to reaction 86-89, has not been clarified. Another possible contributor to the bleaching is the generation of ozone, as it is observed by others [Wabner and Grambov, 1985]. Ozone is also known to generate hydroxyl radicals through equation 43-45.

In order to completely exclude the bleaching effects caused by free chlorine, the bleaching of RNO was investigated with another composition of the electrolyte. At first, the electrochemical bleaching was investigated in low-conductive demineralised water with conductivity of 7.77 $^{\mu S}/_{cm}$, experiment 16, but at maximum applied voltage of 20.2 V, the current in the reactor was only 0.2 A and no bleaching was observed during 10 min of treatment. In experiment 18, potassium nitrate was added as electrolyte to a 0.9 % solution in order to provide conductivity (~11 $^{mS}/_{cm}$) and secure that the wanted currents could be obtained. The investigated chemical system was totally different compared to the other bleaching experiments, since no chlorine electrolysis could occur, and it was very exciting to investigate the bleaching of RNO, which then had to be caused by direct oxidation, hydroxyl radical formation, or ozone production. The results of the experiment are seen in Figure 53.

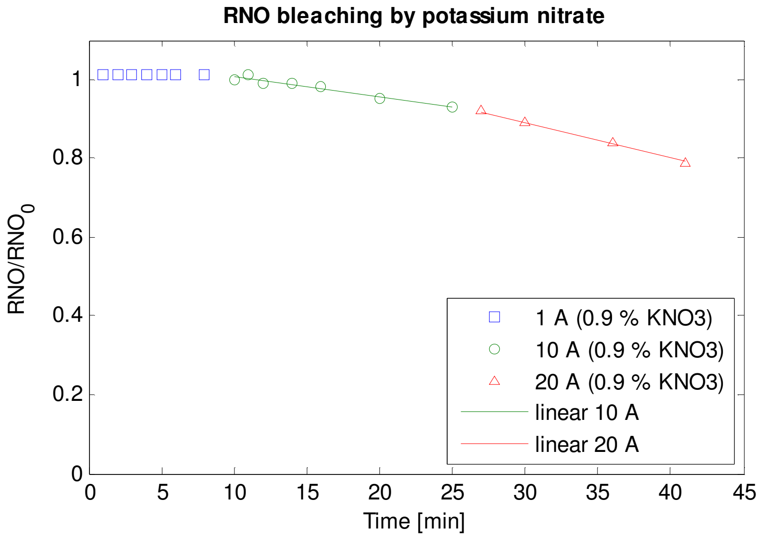

Figure 53: Electrochemical bleaching of RNO in a 0.9 % KNO_3 electrolyte at a stepwise increase of current (test 18).

By a current of 1 A, no bleaching was observed within the first 10 minutes of the experiment after which the current was increased to 10 A. At 10 A, a slow bleaching of the RNO occurred, but the bleaching rate increased, when the current was increased to 20 A. The bleaching rate showed a linear relationship indicating a zero order reaction rate. The rate constants for 10 and 20 A were $5.15 \cdot 10^{-3}$ and $9.15 \cdot 10^{-3}$ $^{mg}/_{l \cdot min}$ respectively. The constant zero order reaction rate was equivalent to results obtained by Tanaka et al., 2004, where similar results were obtained by a Na_2SO_4 electrolyte. The zero order reaction rates were caused by direct oxidation or reduction at the electrode surfaces as well as the zero order formation of hydroxyl radicals from the anode surface. However, the low rate constants obtained with KNO_3 could not account for the very fast initiating RNO bleaching observed in tests with *NaCl*.

The formation of hydroxyl radicals seemed by this experiment to be of minor importance, when potassium nitrate constituted the electrolyte. The investigated chemical system is different compared to the *NaCl* electrolytic systems prior investigated. This was also showed by the fact that molecular oxygen was produced and not consumed as in the chlorine electrolysis. This became evident by measurements of the dissolved oxygen and pH during the experiment, results which are showed in Figure 54.

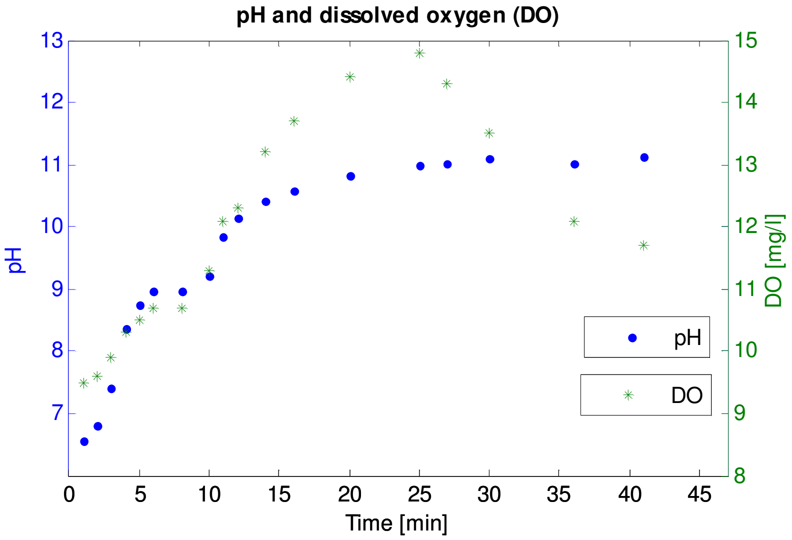

Figure 54: Measurements of dissolved oxygen and pH during the electrochemical bleaching of RNO in a 0.9 % KNO_3 electrolyte (test 18).

During the first 25 minutes of the experiment, the RNO solution became supersaturated with dissolved oxygen (13 $^{mg}/_{l}$). Then the concentration started to decrease at the same time as the current was increased to 20 A and an enhanced bleaching of RNO was observed. It was not possible to explain this tendency change in DO. No minor change was observed at 10 A.

The pH of the solution rapidly increased and stabilised around 11. The fact that oxygen was not consumed caused doubt about the extent of ozone production, a factor which could provide some explanation to the poor bleaching obtained. The increase in oxygen is caused by oxidation of water, which is expected to be preferred compared to oxidation of nitrate to pernitrate.

The bleaching experiment with potassium nitrate revealed that this electrochemical system did not favour hydroxyl radical formation or ozone production. The experiment did not reveal the wanted information about the main contributor to the very fast electrochemical bleaching of RNO observed in the initiating part of the electrochemical experiment, where the free chlorine concentration was very low. The contribution to the electrochemical RNO bleaching rate caused by chemical bleaching added with the rate for bleaching without chlorine production was not sufficient to describe the obtained electrochemical bleaching rate in a *NaCl* solution:

$$rate_{el.bleach,Cl^-} > rate_{el.bleach,KNO_3} + rate_{chem.bleach} \tag{98}$$

At the present state of knowledge, gained through the experiments, it seems like a synergetic effect exists between the hydroxyl radical formation and the chloride content in combination with the chlorine production. The effect could be explained by the extension of the hydroxyl radical life-time proposed by Saran et al., 1999, in combination with the electrochemical induced formation of hydroxyl radicals from the free chlorine [Fukatsu & Kokot, 2001; Ferro et al., 2000].

As a final experiment in the investigation of RNO bleaching, a start/stop experiment was conducted. The experimental settings were 1 A and initial concentrations of 10.2

$^{mg}/_{l}$ RNO and 0.9 % *NaCl*. The power to the electrochemical reactor was turned on at t = 0 and the bleaching was followed. At t = 6 the power was turned off while continuous measurements of the absorbance were conducted. At t = 12 the power was turned on, and this pattern was followed for 30 min. The result is seen in Figure 55.

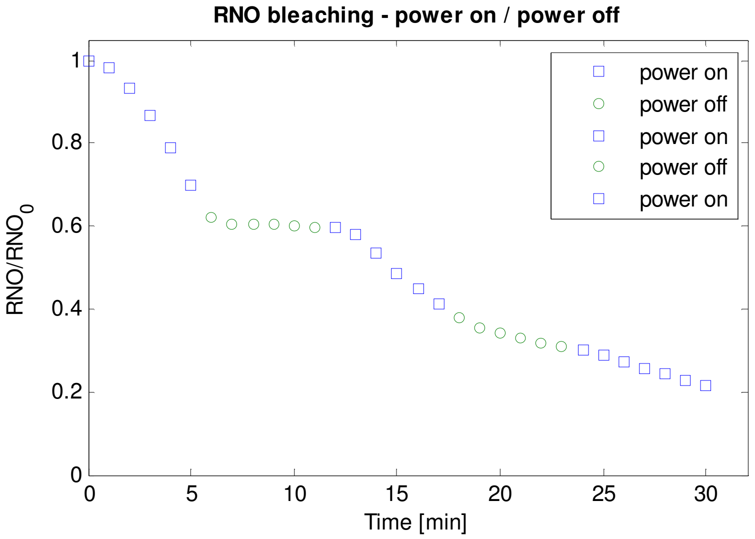

Figure 55: Stepwise electrochemical bleaching of RNO in a 0.9 % *NaCl* electrolyte (test 17).

The experiment strongly clarifies that bleaching in the initiating part of the experiment was not caused by free chlorine. When the reactor was turned off the first time, the bleaching stopped, even though the concentration of free chlorine still was sufficient to cause an observable bleaching: By applying 8.90 $^{mg}/_{A\cdot min}$, found in section 6.2.3, as the chlorine production rate and divide with the volume of 10 l, a calculated concentration of 5.34 $^{mg}/_{l}$ free chlorine was present in the solution at the first stop, without considering the reactions with RNO. If it is assumed that all the free chlorine, produced the first 6 min, reacted with RNO, on a 1:1 molar basis, only about 25 % of the chlorine would have been consumed and enough would be present to bleach RNO after the 6 min. Hence, the main bleaching is not caused by free chlorine.

When the power was turned back on at t = 12 min, the bleaching continued unaffected. At the second stop, the bleaching continued, which might be caused by accumulated ozone from the second power on-period. The proposed ozone accumulation might be due to the less bleaching of RNO compared to the first power on-period.

At the last power on-period, the rate decreased due to the second order dependency of the RNO concentration. The rates of the bleaching in the different periods of the experiment are showed in Figure 56.

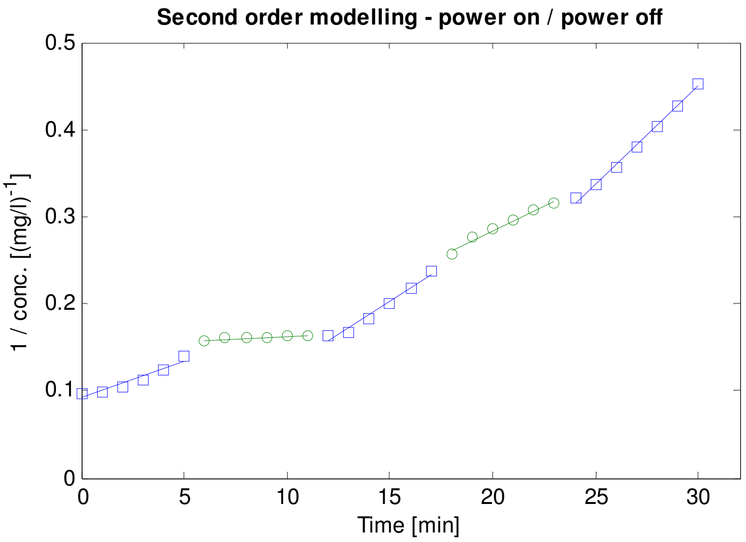

Figure 56: Second order modelling of the step-wise electrochemical bleaching of RNO (test 17).

Theoretically, the slopes of the blue lines should match, but the rate constants in the three power on-period showed an increasing tendency, which is showed in Table 35. The last rate constant is identical to the rate constant obtained at 1 A in test 11. Test 11 was identical to this test 17 aside from the power stops.

Table 35: Rate constants from the power on / power off experiment.

Step	k_{obs} [$^1/_{mg \cdot min}$]
Power on (1)	0.0083
Power off (1)	0.0011
Power on (2)	0.0152
Power off (2)	0.0112
Power on (3)	0.0222

This increase subsequent to an off-period was an interesting observation, but hard to explain. A suggestion is that *HOCl* might be adsorbed on the surface sites of the anode in the power off periods and when the power is turned on, the adsorbed *HOCl* induce a formation of hydroxyl radicals.

The power on/off experiment definitely established that other strong oxidants besides free chlorine are produced in the electrochemical processes in the Watersafe reactor. When the rate constant of the initiating step is considered, where influence by the free chlorine is showed to be insignificant, it is apparent that it is much faster than the one obtained in the KNO_3 electrolytic experiment. It was also another order of rate reaction (zero order), indicating that fundamental different bleaching mechanisms occur in the two systems. This experiment also supports the idea of a synergetic effect, where the chlorine production, or at least the chloride ions, favours the hydroxyl radical formation.

6.5 Test 4 – Inactivation of *E. coli*

The literature study revealed that the electrochemical treatment technique in general has proven to be efficient for disinfection of different microorganisms. The fact that the electrochemical technique possesses this disinfecting effect is very important, when the Watersafe reactor is installed in Danish swimming pools. Despite the swimming pool water analysis conducted in Greece in monitoring of the water quality, see Table 17, the actual disinfection efficiency of the Watersafe reactor has never been directly investigated in laboratory experiments, and the knowledge about the needed current in order to kill swimming pool microorganisms is very important in order to determine the most effective settings for operation.

In the investigation *Escherichia coli* was applied as a model microorganism, since it is a common indicator microorganism and applied in most of the researches referred to in Table 12. This makes it easier to compare it to other electrochemical studies. The following sections will in detail present the applied materials and methods, while the theory concerning electrochemical disinfection is found in section 5.3.1.

6.5.1 Materials and methods

Each disinfection tests demanded a prolonged and thorough preparation. At first, 1 ml of *E. coli* stock culture was propagated for 24 hours at 37 °C in a proper growth medium. Then the medium was transferred to centrifuge flasks and centrifuged for ten minutes at 3000 rpm. The water from the stock solution was removed, and the bacteria were then washed and centrifuged in sterilized isotonic salt water. This procedure resulted in final stock solutions of approximately 220, 450 and 400 ml with *E. coli* concentrations around $1 \cdot 10^9\ {}^{\text{cells}}/_{\text{l}}$, which was estimated by optical density (OD) measurements conducted with a Philips PYE UNICAM PU 8600 UV/VIS spectrophotometer at 450 nm. The operating parameters for the three conducted disinfection experiments are seen in Table 36.

Table 36: Operating parameters used in the disinfection experiments.

No.	Stock OD	*NaCl* [%]	Current [A]	Volume [L]	Analysis method
21	5.90	0.9	1.0 - 20.0	20	Membrane filtration
22	5.65	0.9	1.0 - 5.0	40	Direct plating
23	5.15	0.9	2.0 - 30.0	40	Direct plating

The disinfection experiments were carried out in the experimental set-up showed in Figure 57.

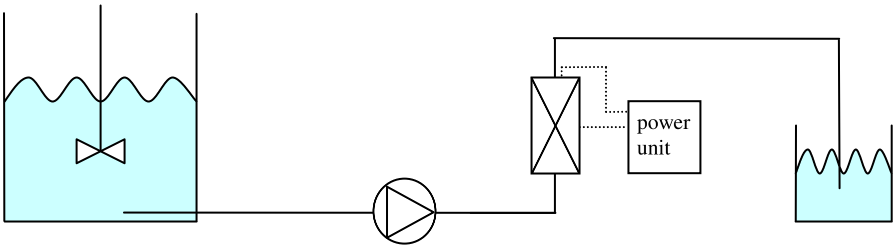

Figure 57: Experimental set-up applied in the disinfection experiments.

The set-up was based on one time through flow. The prepared stock solution was added to the tap water with 0.9 % *NaCl*. In experiment no. 21, a total volume of 20 l electrolyte was used, but in experiments no. 22 and 23 the volume of stock solution was twice the amount, and a volume of 40 l electrolyte was possible to apply. After recirculation for 10 minutes, the pump was stopped and sampling was conducted in the tank in order to determine the initial concentration of bacteria.

In the first disinfection experiment, no. 21, the membrane filtration analysis method was applied for cell enumeration in accordance with the standard method described in DS 2217, 1999. In the membrane method, 0.1 ml of sample was diluted in approximately 20 ml of sterilized water and filtered through a 0.45 μm sterilized membrane, which then was placed in a Petri dish containing a blood agar nutrient medium. The membrane was placed such that the upper side of the membrane faced away from the nutrient. Colonies were counted after 24 hours of incubation at 37 °C, and the results were provided in colony forming units (CFU) per 100 ml. Experiment no. 21 served as an introductory test, and the membrane method turned out to be easily contaminated under the conditions, in which the experiment was conducted. This prompted the shift to a more simple analysis method, where direct plating of 0.1 ml samples on the blood agar plates was chosen. Incubation for 24 hours was needed for this analysis method as well, and the CFU was determined by manual enumeration. In experiment 22 and 23, free chlorine was neutralised with $Na_2S_2O_3$ immediately after sampling, reaction 99, in order to avoid further killing subsequent to the sampling caused by the residual chlorine content.

$$HOCl(aq) + 2S_2O_3^{2-}(aq) \rightarrow Cl^-(aq) + S_4O_6^{2-}(aq) + OH^-(aq) \qquad (99)$$

Approximately 0.4 g of $Na_2S_2O_3$ was added to each sample, and due to the stoichiometric ratio of 1:1 the added amount was sufficient to neutralise 132 mg hypochlorous acid, and hence in great excess.

The experiments were conducted by the following procedure:

1. The pump was stopped
2. The outflow hose was transferred to an empty tank
3. The Watersafe reactor was turned on, and the current was adjusted
4. The pump was started
5. Sampling was conducted in a beaker from the outflow hose after 30 s of flow
6. The pump and power was switched off after 60 s of flow
7. The analysis procedure was initiated
8. After analysis, the procedure was repeated from step 3 with a different current

By this experimental method, it was possible to investigate the disinfection at four or five different currents with the same batch of *E. coli*. At the constant flow of 424 $^{l}/h$, the contact time in the electrochemical reactor was about 0.33 s. Between each current investigation in the single experiments, the inflow hose was closed with a stopper in order to avoid siphon effect.

6.5.2 Results and discussion

The conduction of the disinfection experiments was challenging, and the experiments no. 21 and 22 showed contradictory results and hence served as introductory tests. In the first disinfection experiment, no. 21, a broad range of currents (1.0-20.0 A) were investigated, and it seemed like the disinfection by the electrochemical process was very efficient even at the low currents. However, there was no relation between the different dilutions of the same sample, and the Petri dishes were highly contaminated, which complicated the enumeration. In addition, the content of free chlorine was not neutralised. In experiment 22, currents of 0.5-5.0 A were investigated with triple determination in order to enhance the quality of the results. Based on the experience from experiment no. 21 it was decided only the conduct plating of the non-diluted samples and the factor 10 diluted samples. However, too many colonies were grown in all the Petri dishes, and enumeration was not possible.

Taught by the gained experience, the broad current investigation was repeated in experiment no. 23, with neutralisation of the samples by $Na_2S_2O_3$ and plating of five different dilutions each with double determination. The results achieved in the experiment are seen in Table 37.

Table 37: The results obtained in the disinfection experiment no. 23.

Current [A]	N [$^{CFU}/_{100\ ml}$]	Std. dev. [$^{CFU}/_{100\ ml}$]	Killing ratio [%]
0.0 (Start)	$8.83 \cdot 10^8$	$3.79 \cdot 10^7$	-
2.0	$2.15 \cdot 10^8$	$6.36 \cdot 10^8$	68.54
5.0	$1.55 \cdot 10^7$	$1.55 \cdot 10^7$	97.73
10.0	$2.90 \cdot 10^5$	$2.83 \cdot 10^4$	99.96
20.0	0	0	100
30.0	0	0	100

The results from Table 37 are visualised in Figure 58.

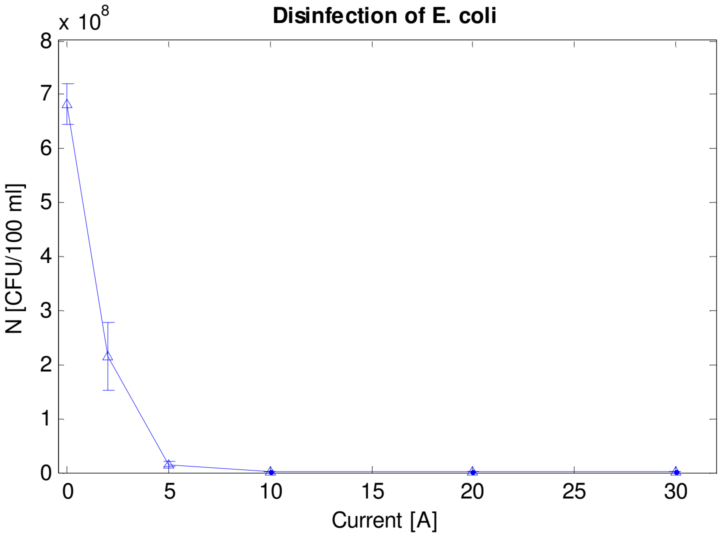

Figure 58: The disinfection of *E. coli* in a 0.9 % *NaCl* electrolyte and a contact time of 0.33 s (test 23).

As seen in Figure 58, the experiment showed that the concentration of surviving *E. coli* cells rapidly decreased as a function of the applied current. At the investigated currents of 20.0 and 30.0 A, no living germs were found in the Petri dishes, and 100 % disinfection was obtained. In Figure 59, the logarithmic reduction and the survival ratio of *E. coli* as a function of current are showed.

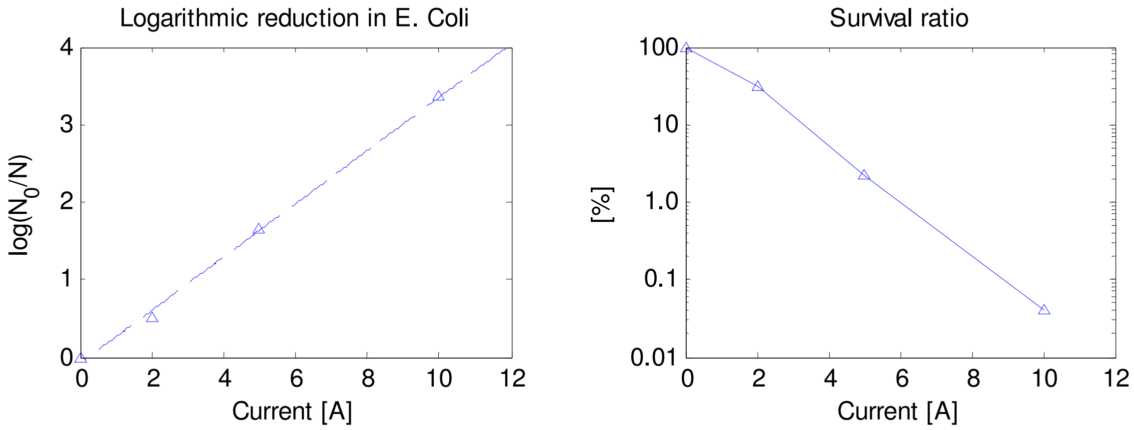

Figure 59: The reduction of the concentration of *E. coli* as a function of current (test 23).

At the investigated contact time of 0.33 s in the 0.9 % *NaCl* electrolyte, the logarithmic reduction of *E. coli* showed a linearly tendency with $R^2 = 0.9974$. In order to achieve a log-3 reduction (99.9 % killing ratio), a current of 9 A was needed, which is equivalent to a current density of 149 mA/cm^2. A direct comparison with the referred disinfection studies presented in section 5.3.1 is complicated, since the contact time in the present experiment is much shorter, and the current densities applied in this experiment generally were higher than the other studies, found by the project group. An example is Li et al. 2004, which in a ~0.6 % *NaCl* electrolyte found a log-3 reduction at a current density of 5 mA/cm^2, but with a contact time of 3.1 s. In general, the literature states that the efficiency of electrochemical disinfection is enhanced with increased contact time and current density, which seems obvious. However, the proportionality between the killing ratio and the square of the current density found by Patermarakis and Fountoukidis 1990, showed in expression 53 in section 5.3.1, was not found in the present disinfection experiment.

In order to evaluate the role of the chlorine production in the electrochemical disinfection compared to the formation of other oxidizing agents, the Selleck-Collins model, for disinfection efficiency of coliform bacteria in domestic waste water effluent by chlorinination, was applied. The model is seen in equation 100 [Li et al., 2002; Selleck et al., 1978]:

$$\frac{N}{N_0} = (1 + 0.23 \cdot C \cdot t)^{-3} \tag{100}$$

N_0 is the initial concentration, N is the concentration after chlorination, C [$^{mg}/_{l}$] is the concentration of residual chlorine, and t [min] is the contact time. When the time needed for the water to pass through the hose from the outlet of the reactor until the sample was neutralised in the test tube, is added to the contact time in the reactor, the total time for chlorination was 2.2 s (260 cm^3). The concentration of free chlorine obtained in one passage at 9 A becomes:

$$\frac{8.8725\,{}^{mg}/_{A\cdot\text{min}} \cdot 9A}{7.07\,{}^{l}/_{\text{min}}} = 11.3\,{}^{mg}/_{l} \tag{101}$$

From the Selleck-Collins model it was calculated that the contact time should be 207 s in order to obtain a log-3 reduction from a free chlorine concentration of 11.3 $^{mg}/_{l}$. Hence, less than 1 % of the disinfection can be ascribed the chlorine content, and the chlorine content could only have reduced the bacteria with 24 % and not 99.9 %. The remaining is caused by the electrochemical processes in the reactor, and most likely hydroxyl radicals and other short-lived and high-energy intermediates play an important role in the disinfection as described by Li et al., 2004. Also ozone could have caused the inactivation. According to Chick-Watson, expression 14, 0.6 $^{mg}/_{l}$ of ozone was needed to obtain the log-3 reduction in 2.2 s:

$$\log\left(\frac{0.001}{1}\right) = -130\ {}^{l}\!/_{mg\cdot\min}\cdot c\cdot 0.0367\,\min \Leftrightarrow c = 0.63\ {}^{mg}\!/_{l} \qquad (102)$$

Since the ozone production in the Watersafe reactor is unknown, it is not possible to tell, if the inactivation is caused by hydroxyl radicals, ozone, or a combination. However, it can be concluded that the electrochemical disinfection by direct treatment is far more efficient compared to ordinary chlorination by hypochlorite.

6.6 Test 5 – Anode material

The anode used in Watersafe reactors is protected by a patent [Ninolakis, 2002]. This patent describes the used materials, and how the anode is constructed. According to the patent, the main difference and advantage of the Watersafe anode compared to conventional technology is that it is capable of supporting intense flows of electric currents (380 V - 1000 A) for a long period of time without disintegration of the anode.

The anode consists of a bulk metal coated with two metal films each of a thickness of 0.015-0.5 mm. The different elements used for the anode is given in Table 38.

Table 38: Elements used for the anode.

Bulk	*Ti*, *Ti/Pd* alloy. Both with or without an enclosed bar of *Al* or *Cu*
Inner layer	*Ta*, *Nb*, *Hf*, *Zr* or alloys of these
Outer layer	*Pt*, *Rh*, *Ir*, *Ru*, *Pd*, *Zr* or alloys of these

Watersafe Greece specified the outer film of the used laboratory anode to consist of 90 % platinum and 10 % iridium. It was not possible to investigate the used laboratory anode without damaging it. Instead, a piece of a 3 years old anode was cut off and investigated with scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS). In this way, it was possible to conduct EDS analyses at the surface, in order to determine the elemental composition of the outer film and the bulk material. The results are reviewed in the following sections.

The Watersafe reactor is further patented for use in 5 different set-ups for disinfection and oxidation [Ninolakis, 2000, 2003a, 2003b, 2006a, 2006b]. These patents covers the use of the Watersafe reactor in treatment of waste water from fish slaughtering, sterilizing sea ballast water, and some oxidation methods applied in remediation of soils.

6.6.1 Materials and methods

The SEM and EDS analyses were carried out at Institute for Materials Engineering, Aalborg University, at a LEO Scanning Electron Microscope including the Røntec Elements' Analyzer, see Figure 60.

Figure 60: The used scanning electron Microscope at Aalborg University.

Subsequent to the cutting, polishing of the bulk material of the anode was tried. However, this showed not to be possible because of the hardness of the material, and several grinding wheels were torn apart. Before the metal was placed in the microscope, it was cleaned in a 0.01 M *HCl* solution. The results of the investigation are found in the next section.

6.6.2 Results and discussion

The obtained SEM images of the anode surface at different magnifications are seen from Figure 61.

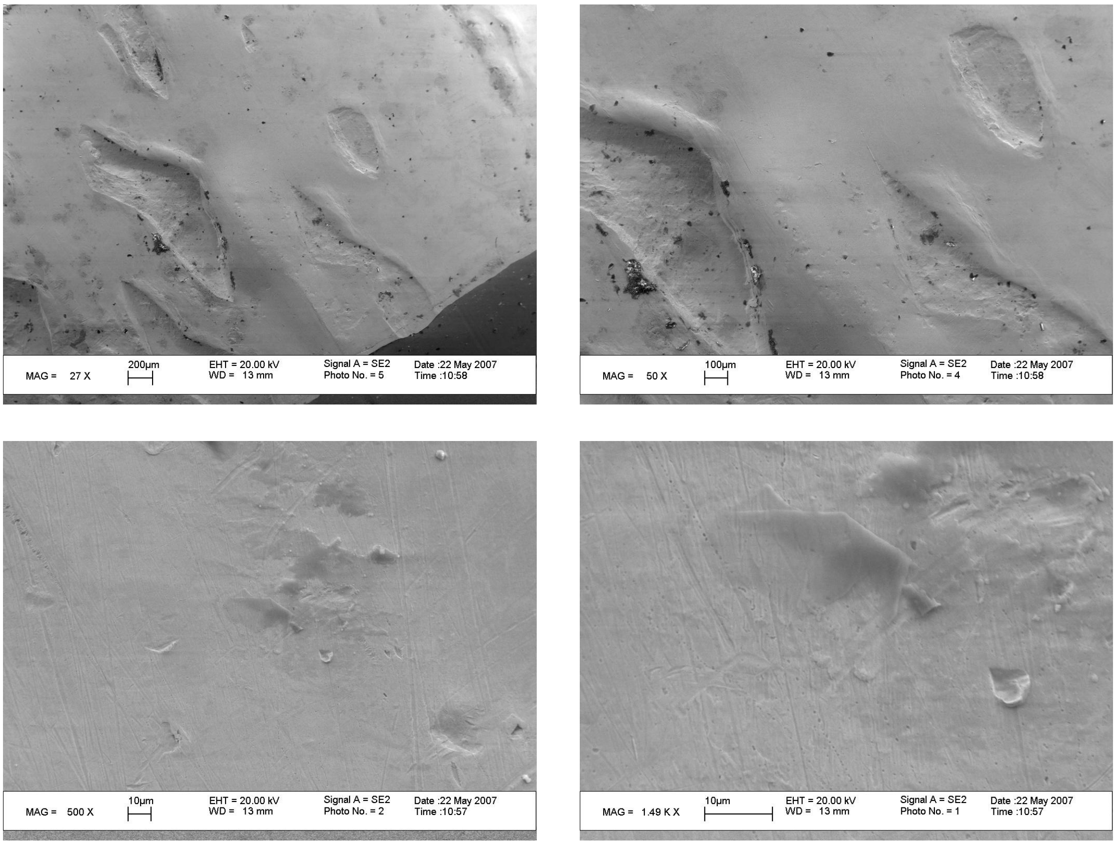

Figure 61: SEM images of the anode at magnifications from 27x - 1490x.

From the SEM images it is seen that the surface of the anode is very smooth. A larger surface area could be obtained, if the surface was made rougher, which most likely will result in a more efficient anode, because of the larger surface area and more turbulence in order to obtain a better diffusion to the surface. However, this would most likely result in lack of durability.

In order to investigate the elemental composition, EDS analyses of the anode surface and the anode bulk were performed. The analyses were all made over relatively large areas, and the composition is therefore considered an average of the investigated area. The results are found in Table 39.

Table 39: EDS analyses four different places on the anode.

Element	Surface 1	Surface 2	Surface 3	Bulk
Pt	79.14 ±18.48	81.83 ±26.22	94.12 ± 21.36	-
C	11.92 ± 2.33	10.34 ± 2.22	0.01 ± 0.13	-
Se	1.96 ± 3.49	-	-	-
O	6.79 ± 1.50	5.10 ± 1.24	5.27 ± 1.19	-
Rh	0.19 ± 0.51	-	0.59 ± 1.02	-
Cu	-	1.73 ± 1.14	-	-
Fe	-	1.01 ± 1.05	-	-
Ti	-	-	-	98.71 ± 13.18
V	-	-	-	1.24 ± 0.87
Al	-	-	-	0.07 ± 0.27

From the results it is seen that the surface of the anode mainly consists of platinum (~94 %) and oxygen (~5 %). In two of the analyses carbon was found at the surface. This is by the project group considered as contamination. Also the elements *Se*, *Rh*, *Cu*, and *Fe* were found, but not in all the samples and the confidence interval contained zero in all cases. Iridium was not found in any of the analyses, and it can be concluded that the investigated anode only consisted of platinum and some platinum oxides. According to Watersafe Greece the material composition used for the anodes have changed during the years, which is considered to explain the absent of iridium.

The bulk of the anode was shown to consist of titanium and might include a small amount of vanadium, which is commonly alloyed with titanium.

6.7 Sub-conclusion

In order to provide an overview of the experimental part of the present report, the most important results obtained in the laboratory experiments are outlined below.

Test 1 – Chlorine production

- Zero order production of chlorine as a function of current: $1.69 \cdot 10^{-4}\ {}^{mol}/_{min \cdot A}$.
- Linear increase in current with time at constant voltage caused by an approximate linear increase in conductivity, which again is ascribed a linear increase in temperature.
- 55 % current efficiency at 0.9 % *NaCl*. Increased to 98 % at 4.0 % *NaCl*.
- 6-12 % energy efficiency at 0.9 % *NaCl*.
- pH increases with time as *HOCl* is formed.
- DO decreases because of formation of other oxidants than chlorine or due to oxygen being stripped out by cathodic production of molecular hydrogen.

Test 2 – Gas production

- Zero order production of hydrogen as a function of current: $3.82 \cdot 10^{-4}\ {}^{mol}/_{min \cdot A}$.
- More water is reduced at the cathode than chloride oxidized at the cathode indicating formation of other oxidants.
- No Cl_2 in the produced gas in the outlet of the reactor.
- Almost pure hydrogen in the produced gas.
- Cautions should be made at full scale installations because of the hydrogen gas production and risk of explosive mixtures.

Test 3 – Identification of oxidizing species

- Second order bleaching of RNO with k_{obs} being a linear function of the applied current in a *NaCl* solution (14 ${}^{mS}/_{cm}$).
- Manual addition of a sodium hypochlorite solution resulted in bleaching of RNO. However, the chemical bleaching was much slower than the electrochemical bleaching even though the concentration of *HOCl* in the electrochemical bleaching was much lower.
- The very fast initial bleaching of RNO was caused by other oxidants than *HOCl*.
- No bleaching occurred in demineralised water (7.77 ${}^{\mu S}/_{cm}$).
- Slow zero order bleaching in a potassium nitrate solution (11 ${}^{mS}/_{cm}$), which increased with increasing current.
- It was concluded that a synergetic effect exists between the hydroxyl radical formation and the chloride content or chlorine production.

Test 4 – Inactivation of *E. coli*

- A linear logarithmic reduction of *E. coli* as a function of the applied current was obtained.
- At a contact time of about 0.33 s, a flow of 424 ${}^{l}/_{h}$, and 0.9 % *NaCl* only 9 A was needed in order to obtain a log-3 reduction (99.9 % killing).
- At 20 A all the bacteria were killed.
- The produced chlorine could only account for less than 1 % of the killing and hence, 99 % of the killing was presumed to be caused by more aggressive oxidants such as hydroxyl radicals and ozone.

- The electrochemical disinfection is far more efficient than ordinary disinfection with hypochlorite.

Test 5 – Anode material

- The investigated old anode consisted of a solid titanium core with an outer layer of platinum with a small amount of oxide.

7 Full scale installation

During the review of the electrochemical treatment of swimming pool water only very few published results were found. Based on the lack of knowledge, the laboratory experiments in the previous section were conducted in order to understand the processes and efficiency of the Watersafe reactor. The next step was to investigate a full scale installation based on the laboratory tests.

No full scale systems are currently installed in Denmark, but during the work of the present report, an opportunity to participate in the design and test of a full scale installation turned up. The project group provided consultancy to the engineering consultant company, Søren Jensen, which was hired to rebuild a municipal swimming pool in Århus called Spanien. The rebuilding is planned to be initiated 9th of July 2007 and hence, only the design phase can be reviewed in this present project report. However, the project group is most likely going to be involved in the subsequent monitoring and evaluation of the installation as well.

The following sections describe the available technical documentation, on which the dimensioning and design of the electrochemical system are to be made. Finally, a suggestion for the design, installation, run-in, and monitoring are given.

7.1 Basis for design

The Watersafe reactor is going to be installed in the treatment of the children's pool in the municipal swimming pool Spanien in Århus during July 2007. The existing water treatment system is a traditional treatment system as described in section 2.2 with an additional possibility for UV treatment for the reduction of combined chlorine. The UV system is purchased from Aqua system, and is only used at maximum load, since the traditional treatment normally performs very well. Technical data for the pool are found in Table 40.

Table 40: Technical data for the swimming pool (7th of May 2007).

Volume of pool	25 m^3
Volume of pool and treatment system	32 m^3
Temperature	34 ºC
Free chlorine	1.1-1.6 $^{mg}/_{l}$
Combined chlorine	0.1-0.3 $^{mg}/_{l}$
pH	7.3
ORP	752 mV

The main pipe with the treated water divides into six inlets to the pool as shown from Figure 62. A schematic diagram, including the final steps in the water treatment after the filtration at Spanien, is seen from Figure 63.

Figure 62: The main pipe with the treated water is divided into 6 separate inlets in the swimming pool. The photo is taken from underneath the pool.

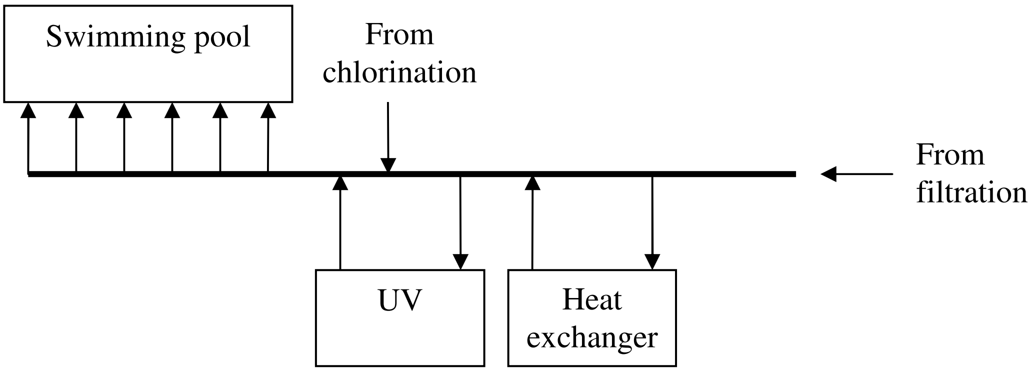

Figure 63: The final steps in the water treatment in Spanien, before the water re-enters the swimming pool through six inlets.

The Danish executive order BEK no. 288 from 14/034/2005 gives a maximal turnover time of 0.5 hours for this type of swimming pool. With a total volume of 32 m^3, the water treatment system is operating at a flow rate of 64 m^3/h.

The existing addition of chlorine occurs from an electrolysis system, where a strong chlorine solution is produced in a closed circuit, and it was not possible to get in hand of any information about the present chlorine consumption or the number of visitors in the swimming pool. This was very unfortunate, since the chlorine consumption and the load level are primary parameters concerning the dimensioning of the reactor.

From the above review of the current installation, a suggestion for the installation of a Watersafe reactor is given in the following sections.

7.2 Design and installation

7.2.1 Full or sub-stream?

The first choice to make was to decide, if the reactor was going to treat a sub-stream or the full stream. All Watersafe installations inspected in Greece were full stream. However, the study published by Häenni et al., 2002, with the DiaCell electrochemical system, showed that it was possible to obtain an efficient treatment in a sub-stream comprising only 1 m^3/h of the total flow of 15 m^3/h in a 60 m^3 pool. MST, 2007a, suggests installation of the electrochemical reactor in a sub-stream, where the treated sub-stream is returned to the equalizing tank, in a similar way as traditionally active carbon filters are installed.

The project group finds it most relevant to install the reactor in the full-stream in order to utilize the full potential of the short-living aggressive oxidants. In a sub-stream these oxidants might not be as useful, if not enough organic material is present in the water, since the electrochemical degradation in most cases follows first order degradation regarding the content of organic material [Baun et al., 2004]. Furthermore, the direct oxidation will be more powerful in a full-stream, due to the higher amount of organic matter passing the reactor. One of the advantages of the sub-stream installation, where the water is returned to the equalizing tank, is that the tank then acts as a reaction tank and release of ozone and other strong oxidants to the swimming pool is avoided.

However, the consequence of installing the reactor in full-stream will be a more expensive reactor because of the larger size. Furthermore, the costs of operation will increase, because higher voltage is needed in order to produce the same amount of chlorine, when the distance between the anode and the cathode is increased in a larger reactor. Parallel installation of two smaller reactors in full stream might be a possibility to reduce the costs of operation. Optimization of the effects contra the price of installation and operation has to be conducted.

Since the installation of the Watersafe reactor in Spanien is the first in Denmark, the project group suggests the full stream installation of the reactor, even though this results in a more expensive solution. The advantage will be a more effective system, which more easily is modelled, evaluated, operated, and controlled, and the project group is more certain about an uncomplicated maintenance of the water quality by the full stream solution. In future installations, the sub-stream solution most likely will be considered, when the experiences from Spanien are gained.

7.2.2 Location

In the treatment system, the reactor should be installed after the sand filtration in order to avoid mechanical wear of the anode by suspended particles in the water. In Greece, the reactor was placed before the heat exchanger, but in order to avoid unnecessary corrosion, the reactor might as well be placed after the heat exchanger as showed in Figure 64.

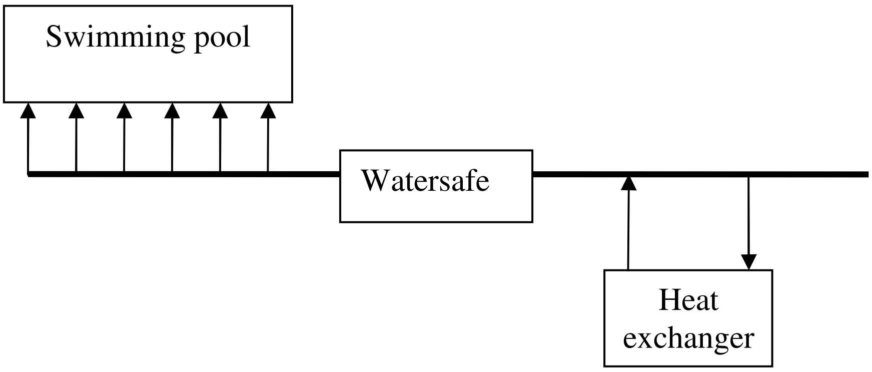

Figure 64: Suggested location for the Watersafe reactor in the swimming pool.

The inspection of the technique room underneath the swimming pool showed that only about 1.5 m of the main pipe is present after the heat exchanger, before the pipe splits up into six smaller inlets to the swimming pool as showed in Figure 62. The last meter of the main pipe and the in- and outlet to the heat exchanger are shown in Figure 65.

Figure 65: Left: the last meter of the main pipe before it splits up into smaller pipes. Right: the in- and outlets to UV, chlorination, and heat exchanger placed on the main pipe just before the pipe splits up.

Besides the small length of the pipe, where it is possible to install the reactor, the installation is further complicated due to the location of the pipe 4-5 m above the ground. It is however considered possible to make the installation.

7.2.3 Dimensioning

The cost for the chlorine production increases linearly with the distance between the anode and the cathode, due to the linear relationship between distance and resistance. The optimal reactor should therefore hold the minimal distance between the anode and cathode without increasing the flow rate to a level causing mechanical wear of the anode. The project group is not in possession of production and sale prices for different sizes of the reactor, and hence optimization concerning the price of the installation can not be made.

The specifications of the reactor recommended to be installed in Spanien, according to Watersafe Greece, are given in Table 41.

Table 41: Technical specification for the recommended reactor.

Anode length	150 mm
Anode diameter	25 mm
Cathode diameter	42 mm
Power supply	50 A

Source: [Watersafe Greece, 2007]

The power supply is recommended to work at a maximum of 60 % of its capacity in order to be most cost effective, and Watersafe Greece therefore suggest to operate it at 24 A. This gives a chlorine production of:

$$\frac{24A \cdot 1.69 \cdot 10^{-4}\ {}^{mol}\!/_{A \cdot min} \cdot 60\ {}^{min}\!/_{h}}{64\ {}^{m^3}\!/_{h}} = 0.0038\ {}^{mol}\!/_{m^3} \tag{103}$$

Compared to the recommendations provided in the German DIN 19643-1 regarding the capacity of chlorination systems, which recommends a minimum capacity of 0.0282 mol/m^3 treated water (2 g Cl_2/m^3), the maximal production capacity of the Watersafe system is very low. However, Watersafe Greece states that it is sufficient to maintain the wanted concentration of free chlorine. The project group believes that the low capacity will result in problems, if the system has to be used for chock chlorination of the swimming pool water, where concentrations of 10-15 $^{mg}/_{l}$ free chlorine are normally used. For this purpose, it would take about 38 hours to reach a concentration of 15 $^{mg}/_{l}$ by the electrochemical chlorine production:

$$\frac{32{,}000l \cdot 15\ {}^{mg}\!/_{l}}{1.69 \cdot 10^{-4}\ {}^{mol}\!/_{A \cdot min} \cdot 24A \cdot 52{,}500\ {}^{mg}\!/_{mol} \cdot 60\ {}^{min}\!/_{h}} = 38h \tag{104}$$

If the recommendation in the German standard is followed, it will only take about 5 hours to reach the same concentration. Based on these calculations, it is recommended to use an additional chlorine source for chock chlorination, e.g. a strong hypochlorite solution.

In order to calculate the power consumption, the operating voltage has to be calculated. This is done by combining equation 67 and 68 from section 6.2.3, in order to obtain an expression for the needed voltage:

$$U = \frac{l \cdot I}{A \cdot \kappa_{25°C}[1 + \alpha(T - 25°C)]} \tag{105}$$

where l [m] is the length between the anode and the cathode, I [A] is the wanted current, $\kappa_{25°C}$ [$\Omega^{-1} \cdot m^{-1}$] is the measured conductivity at 25 ºC, α [0.02 ºC^{-1}] is a temperature compensation factor, T [ºC] is the temperature, and A [m^2] is the cross-sectional area. A is calculated as a logarithmic mean area between the anode and the cathode surface according to equation 106. The length l is defined as r_2-r_1, where r_1 and r_2 are the radii of the anode and the cathode respectively, see Figure 66.

$$A = \frac{A_2 - A_1}{\ln\left(A_2 / A_1 \right)} \tag{106}$$

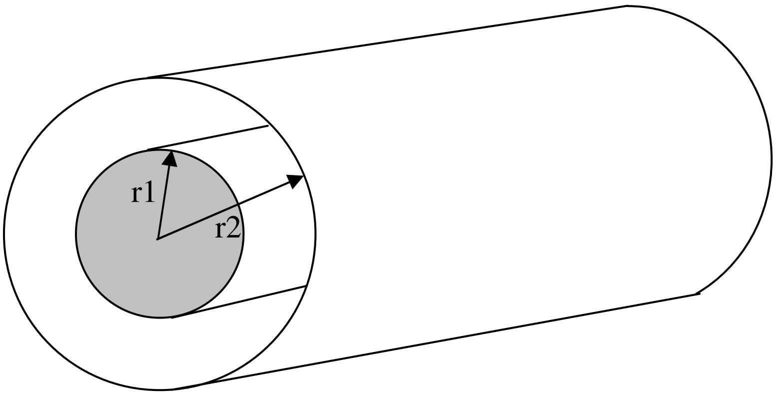

Figure 66: Sketch of the anode placed in the cylindrical cathode.

In the model it is assumed that the conductivity of the wires and the metals are very high compared to the water, and hence negligible. In order to validate the model, results from the used laboratory reactor was inserted in equation 105. The results are seen in Table 42. Measured currents, conductivities, and temperatures from the earlier tests were used. Equation 107 is an example for the small laboratory reactor, the same calculation have also been carried out for the large reactor in the chemical test trailer.

$$U = \frac{0.6cm \cdot I}{\frac{84.4cm^2 - 60.3cm^2}{\ln\left(84.4cm^2 / 60.3cm^2 \right)} \cdot \kappa_{25°C}[1 + 0.02°C^{-1}(T - 25°C)]} \tag{107}$$

Table 42: Validation of the model for the operating voltage, equation 107.

Test no.	Current [A]	Temperature [°C]	Conductivity $[^{mS}/_{cm}]$	Voltage $[V]_{calculated}$	Voltage $[V]_{displayed}$	Difference [%]
3	25.3	28.9	14.98	13.1	15.0	-13
3	30.5	41.3	14.98	12.8	15.0	-15
4	3.9	25.4	13.90	2.3	5.0	-54
5	35.6	26.4	14	20.7	20	+4
5	45.9	43.2	14	20.1	20	+1
6	13.2	25.4	14.47	7.5	10	-25
6	14.8	31.9	14.47	7.5	10	-25
7	45.3	24.4	55	7.0	10	-30
7	53.0	35	55	6.7	10	-33
8	27.0	25.6	30.57	7.3	10	-27
9	5.0	20	14	3.3	5	-34
10	30.6	20	14	20.3	20.2	0
11	1.0	20	14	0.6	3.4	-88
12	10.0	20	14	6.6	8.8	-25
17	1.0	25	14.29	0.6	3.4	-88
18	1.0	20	10.38	0.9	3.4	-74
18	10.0	20	10.38	9.0	10.9	-17
18	20.0	20	10.38	17.9	17.0	+5
24	100	11.6	11.41	31.5	48	-34
24	100	14.4	11.01	32.7	44,7	-27

As it is seen from Table 42, the model is not capable of describing the low voltages, when 1-5 A is applied, but it is found applicable for currents ranging from 10-100A. However, the uncertainties are high. The project group is unable to explain the lack of accuracy at low currents theoretically. It could by explained by uncertainties of the displayed currents at the power supply, but this has been investigated and rejected by manual measurements. The model is however applied in the further dimensioning of the reactor going to be installed in Spanien.

The calculated voltage, needed to deliver a current of 24 A in the system in Spanien, is:

$$U = \frac{0.85cm \cdot 24A}{\dfrac{198cm^2 - 118cm^2}{\ln\left(198cm^2 / 118cm^2\right)} \cdot 0.014\, {}^{S}/_{cm}[1 + 0.02°C^{-1}(34°C - 25°C)]} = 8.0V \qquad (108)$$

From this calculation, the operating conditions are specified to 24A/8V and the power supply therefore most likely will be 50A/20V in order to have an efficient cost of operation and the possibility to increase the current in periods with peak load. The operating power then becomes 192 W, and, if the operating time is 12 $^{h}/_{day}$, it corresponds to a power consumption of 2.30 $^{kWh}/_{day}$.

According to Watersafe Greece, mechanical wear of the anode is not a problem and no maximum allowed velocity in the reactor exists. The velocity, *v*, of the water in the reactor will however influence the pressure drop in the treatment system. With the required flow rate in Spanien of 64 m^3/h, the velocity between the anode and the cathode becomes:

$$v = \frac{1000 \, {}^{cm^2}\!/_{m^2} \cdot 64 \, {}^{m^3}\!/_{h}}{[\pi(2.1cm)^2 - \pi(1.25cm)^2] \cdot 3600 \, {}^{s}\!/_{h}} = 2.0 \, {}^{m}\!/_{s} \tag{109}$$

Regarding the concentration of salt, it was chosen to operate with a concentration of 0.9 % *NaCl* in the pool. Since the total amount of chloride in the pool at 0.9 % *NaCl* is $4.93 \cdot 10^5$ mol and the maximal rate of electrochemical consumption at 24A/8V is 5.84 ${}^{mol}/_{day}$, addition of *NaCl* is only very seldom necessary. Hence, the primary reason for *NaCl* addition is because of the renewal of the water in the swimming pool. The optimal solution would be installation of an automatic dosage system, but regular manual addition ought to be sufficient. In both cases, the dosage should be controlled by the measured conductivity of the water (~15 ${}^{mS}/_{cm}$ = 0.9 % *NaCl*).

The last part of the installation to be considered is a system, which makes it possible to clean the reactor with a hydrochloric acid solution, as sketched in Figure 67.

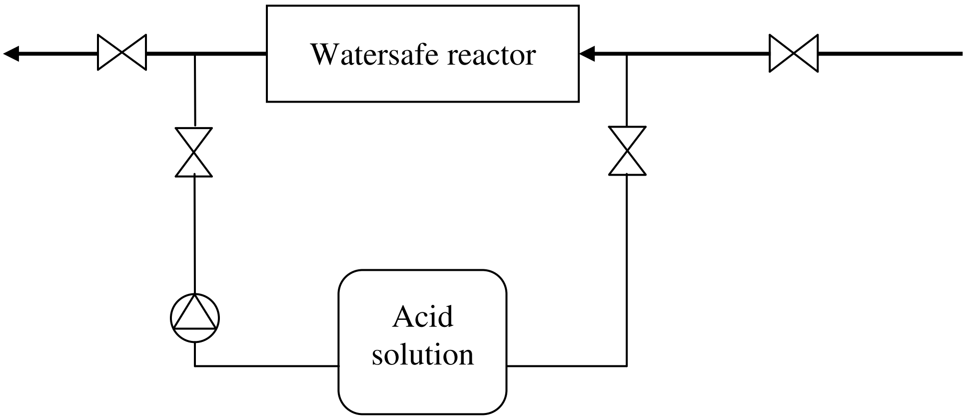

Figure 67: Schematic diagram of the acid cleaning system.

The acid cleaning system can be made with a 20 l tank filled with a 2-3 % *HCl* solution. Estimated upon experiences, it is expected that the reactor needs cleaning about 4 times a year [Watersafe Greece, 2007].

7.2.4 Parameters and settings

In order to obtain a better effect of the content of free chlorine, the project group suggests lowering the pH to 7.0, which is the minimum allowed value in Denmark. Later, the value can be lowered to 6.5-7.0 as suggested by MST, 2007a. The existing system for pH measurement and acid addition in Spanien can be used and requires no modification besides changing the set-point.

Regarding the concentration of free chlorine, the project group suggests lowering the concentration to 1.0 ${}^{mg}/_{l}$ at a start, since no dispensation from the Danish authorities is needed for this. Later, when the treatment system is running satisfactory, this concentration is suggested lowered to 0.3-0.6 ${}^{mg}/_{l}$ as the German regulation specifies, if the permit is assigned from the authorities. Taking the present political focus on swimming pool water treatment in consideration, to be granted an exemption is not expected to cause problems. The free chlorine concentration is controlled by a simple on/off regulation as described in section 5.3.2. The existing equipment for measurement of free chlorine in Spanien is able to supply this on/off signal to the power supply by minor modifications of the internal settings and the establishing of an additional wiring system. Furthermore, a thermal cut-out placed on the reactor should be installed and cut-out the power, if the temperature reaches 45 ºC, which indicates no flow through the reactor.

The temperature of the pool water is maintained at 34 ºC.

7.3 Run-in and monitoring

Subsequent to the installation, the system has to be tested and optimized before the swimming pool is reopened. The project group recommends that the process provided below is followed:

1. *NaCl* has to be added to the water (288 kg in 32 m^3 of water). In order to obtain full dissolution, the addition can be done to the equalisation tank, while recirculation at the normal flow of 64 m^3/h.

2. When all the salt is dissolved and a constant conductivity is measured, the reactor is switched on and adjusted to 24 A. According to the theory, it will take about 2.5 hours to reach a free chlorine concentration of 1.0 $^{mg}/_{l}$ in the pool. The project group suggests that the ability of maintaining a constant chlorine concentration is tested for about 3 days prior to the reopening of the swimming pool. The optimal procedure is to test three different concentrations, for instance 0.5 $^{mg}/_{l}$ (day 1), 1.5 $^{mg}/_{l}$ (day 2), and finally 1.0 $^{mg}/_{l}$ (day 3). The chlorine concentration should be monitored during the run-in period in order to evaluate the performance of the system.

3. The swimming pool is reopened and the concentrations of free chlorine, combined chlorine, pH, and *NaCl* are followed closely over a period of 4-6 weeks. During the same period, sampling for microbiological analysis occurs weekly. The project group suggests analysis for total germs 2-3 times a week and a full microbiological analysis once a week including *E. coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Legionella*, *Cryptosporidium*, and coliphage. Also samples for analysis of the concentration of THM are recommended to be conducted at least once a week.

If the chlorine concentration is easily controlled and maintained at 1.0 $^{mg}/_{l}$, the concentration of combined chlorine is kept below 0.2 $^{mg}/_{l}$, and the microbiological and THM analysis comply with the regulations provided by the Danish authorities during the 4-6 week period, the system is working as intended. If this is not the case, optimization of the system regarding applied current, flow, conductivity etc. has to be performed. In order to evaluate the performance of the tests, the analysis results from the 4-6 weeks of operation are compared to results from the old treatment system for the last 2 years, which are obtained by the technical staff in Spanien.

8 Conclusion

This present master thesis comprised two main topics; identification of the possibilities for practical test of alternative techniques in treatment of swimming pool water and an investigation of the chemical processes occurring in the electrochemical Watersafe reactor.

In the identification of test possibilities, the chemical test trailer developed by Rambøll and the project group was evaluated, and it was found applicable for the conduction of tests with ozone treatment of full scale swimming pools. In addition, tests with electrochemical treatment are possible. In a market search, investigating available swimming pool treatment applications and installations, experiences from the manufactures and distributors were collected and revealed that especially UV treatment is comprehensively investigated and documented. The treatment installation in MarselisborgCentrets Svømmebad was identified and found particular applicable for test purposes, since possibilities for membrane filtration, UV, photocatalytic, and stripping tests exist.

Literature studies revealed that in contrast to ozone and UV treatment, a very limited amount of published material concerning electrochemical treatment of swimming pools was available, which showed the need for further investigations. The performed laboratory test investigating the chlorine electrolysis revealed a chlorine production rate of $1.69 \cdot 10^{-4}\ ^{mol}/_{min \cdot A}$ in a 0.9 % $NaCl$ electrolyte. A current efficiency of 55-98 % and an energy efficiency of 6-12 % were obtained, which both increased with increasing $NaCl$ concentration. During the free chlorine electrolysis, the bulk pH increased with time, whereas dissolved oxygen decreased, either because of the formation of other oxidants or due to the dissolved oxygen being stripped out by the cathodic produced hydrogen gas.

During electrolysis, the hydrogen gas production rate was $3.82 \cdot 10^{-4}\ ^{mol}/_{min \cdot A}$, which is 2.3 times the chlorine production. The ratio strongly indicated the formation of other oxidants. The produced gas was qualitatively determined to consist of molecular hydrogen, maybe with minor amount of molecular oxygen. Chlorine gas was not found. Because of the hydrogen production, cautions should be made, when full scale systems are installed.

The electrochemical formation of hydroxyl radicals was investigated by the bleaching of p-nitrosodimethylaniline (RNO). A second order rate equation for the bleaching of RNO was obtained, with the observed rate constant, k_{obs} being a linear function of the applied current. The bleaching demonstrated the formation of hydroxyl radicals in the electrochemical process. According to the literature study, ozone and $HOCl$ induce RNO bleaching by hydroxyl radical reactions as well. The chemical bleaching test with $HOCl$ solutions showed a much slower reaction (15x – 86x) than the electrochemical bleaching, even though higher concentrations of $HOCl$ were applied. Test with a KNO_3 electrolyte resulted in a very slow zero order bleaching of RNO. From these two experiments it can be concluded that a synergetic effect between electrochemical treatment and either chloride or chlorine takes place and results in an enhanced bleaching.

Tests with inactivation of *E. coli* resulted in a logarithmic reduction as a function of applied current. At a contact time of 2.2 s, a log-3 reduction was obtained at a current of 9 A in a 0.9 % *NaCl* electrolyte, and 100 % killing was obtained at 20 A. By the Selleck-Collins model it was showed that the produced chlorine accounted for less than 1 % of the inactivation. The remaining 99 % is expected to be caused by hydroxyl radicals, ozone or other strong oxidants.

Finally, a full scale electrochemical treatment installation for a public swimming pool was designed and dimensioned. A full stream reactor for the 32 m^3 pool needs a power supply of 50A/20V and is expected to operate at 24A/8V in 0.9 % *NaCl* water. At an operating time of 12 $^{h}/_{day}$, the power consumption is estimated to be 2.3 $^{kWh}/_{day}$. The electrochemical system is not suitable for chock chlorination, because of the relative low maximal capacity in chlorine production.

Overall, the electrochemical reactor from Watersafe showed promising results regarding treatment of swimming pool water treatment, but further investigations in laboratory and full scale installations have to be carried out in order to fully understand the process and efficiency of the technique, and provide the requested documentation material.

9 Further work

During the present project, many different aspects in swimming pool treatment were reviewed with focus on electrochemical treatment, and the project group has been involved in several commercially contexts with different companies. The work carried out is not completed yet, since the final decision regarding the EPA examination project and the installation and test of the full scale electrochemical system are not scheduled before July 2007. However, the present report serves as introductory work for both the full scale installation and the EPA examination project, and the project group is further involved in both cases after the completion of this project.

Besides the follow up on the commercially aspects related to the present project report, the electrochemical reactor needs to be investigated in more details in the laboratory in order to fully understand the processes going on and the possibilities of improving the efficiency of the processes. The present project has provided some answers concerning the electrochemistry in the Watersafe reactor, but some of the experiments revealed results that need to be investigated in further details. Hopefully, a PhD programme concerning electrochemical processes will start-up later this year. Some of the areas to be investigated besides the ones treated in this report are reviewed below.

The anode material can be investigated with x-ray photoelectron spectroscopy (XPS) in order to investigate the elemental composition and the chemical state of the elements in the surface. This will reveal the oxidation state of the surface metals and the chemical state of oxygen; adsorbed water, lattice oxygen, hydroxyl groups etc. Also voltammetry, where information about an analyte is obtained by measuring the current as the potential is varied, can be applied in the investigation of the electrochemical processes in the reactor.

The present study concerning bleaching of RNO revealed indications of radical formation, which has to be investigated further. By using electron spin resonance (ESR) in combination with a spin trap, it might be possible to determine the presence and amount of radicals produced in the reactor. The RNO experimental method can also further be applied in the investigation of other oxygen radicals by the addition of different scavengers, and hence a comprehensive further work can be conducted just by the RNO method.

Ozone and hydrogen peroxide were not measured in the present project due to malfunctioning sensors. Further investigations need to concern measurements of these oxidants, either by new sensors or alternative analytical methods such as titration or test kits. Also the production of other chlorine species; chlorate, chlorite, chlorine dioxide etc. has to be performed, in order to determine the overall oxidation potential and in order to investigate possible health and safety issues caused by these compounds.

Electrochemical degradation tests, investigating the oxidation of THMs, chloramines, and precursors have to be carried out as well, in order to evaluate the efficiency concerning swimming pool water treatment.

Only very simple investigations of the produced gas have been conducted in the present project. More advanced gas analyses can reveal the exact composition of the produced gas and thereby determine the actual amount of oxygen and chlorine present in the gas.

Finally, more disinfection studies with different microorganisms and more variable parameters such as *NaCl* concentration, retention time, temperature etc. have to be performed, in order to ensure that the process is capable of inactivating the broad range of microorganisms found in swimming pools. Especially, further investigations considering the electrochemical disinfection of chlorine resistant bacteria, e.g. *Cryptosporidium*, are important.

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Appendix 1 – Free chlorine equilibrium

This appendix explains the dissociation of chlorine in water and shows the m-file programmed in Matlab in order to plot the chlorine species as a function of pH.

Dissociation

The dissociation of hypochlorous acid ($HOCl$) into hypochlorite (ClO^-) is pH depending:

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \tag{A-1}$$

$$HOCl \rightleftharpoons H^+ + ClO^- \tag{A-2}$$

Hypochlorous acid has an ionization constant of $3.7\cdot 10^{-8}$ $^{mol}/_{l}$ (25°C) [White, 1972].

$$K = 3.7\cdot 10^{-8}\ {}^{mol}\!/_{l} = \frac{[H^+]\cdot[ClO^-]}{[HOCl]} \Leftrightarrow [ClO^-] = \frac{K\cdot[HOCl]}{[H^+]} \tag{A-3}$$

The amount of $HOCl$ compared to ClO^- is calculated at a certain value of pH according to equation A-4:

$$HOCl(\%) = \frac{100\%\cdot[HOCl]}{[HOCl]+[ClO^-]} = \frac{100\%\cdot[HOCl]}{[HOCl]+\dfrac{K\cdot[HOCl]}{[H^+]}} = \frac{100\%}{1+\dfrac{K}{[H^+]}} \tag{A-4}$$

Vapour pressure

The phase equilibrium between gaseous and dissolved chlorine can be described by Henry's law [Downs and Adams, 1973]:

$$H = \frac{[Cl_2(aq)]}{p_{Cl_2}} = 4.805\cdot 10^{-6}\cdot e^{(\frac{2818.48}{T})} \tag{A-5}$$

A practical consequence of reaction A-1 and A-2 is that the chlorine vapour pressure over a solution depends on the solution pH. Increasing pH results in decreasing vapour pressure because of the increased formation of nonvolatile chlorine species.

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Matlab script file

The above expression, 4, can be included in a Matlab script file in order to obtain the graph showed in the report, Figure 2:

```
%Free chlorine
clc;

%Constants
K=3.7*10^-8;

%Calculations
pH=linspace(5,10,100);        %Creates a vector with 100 elements
                              %linearly spaced between 5 and 10

H=10.^(-pH);                  %Converts pH to [H+]

HOCl=100*(1+K2./H).^-1;       %Calculates [HOCl] as a function of [H+]
ClO=100-HOCl                  %Calculates [ClO]

%plot
hold on
axis([5 10 0 100]);
plot(pH,HOCl);
plot(pH,ClO);
xlabel('pH');
ylabel('%');
title('Free chlorine speciation');
```

Appendix 2 – Computational chemistry investigation

In order to investigate, why the wavelength specified by the manufactures as the ones primary applied in the degradation of chloramines, see Table A- 1, the energy levels in the molecular orbitals in the chloramines have been investigated through a computational chemistry investigation performed with the Gaussian v.03 software.

Table A- 1: Wavelength for optimal chloramine degradation and corresponding energy.

Substances	Wavelength [nm]	Energy [eV]
Monochloramine	245	5.061
Dichloramine	297	4.175
Trichloramine	260	4.769
	340	3.647

Source: [Wallace and Tiernan, 2004b]

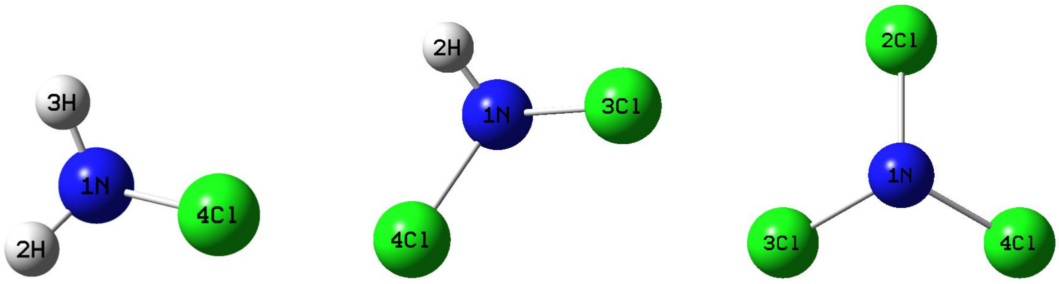
The two main elements constituting the chloramines are nitrogen and chlorine atoms. Their electron configurations in the ground states are seen in Table A- 2.

Table A- 2: The electron configurations of nitrogen, chlorine, and hydrogen atoms.

Element	Atomic no.	Electron configuration	Valence atomic orbital
Nitrogen	7	$1s^2$ $2s^2 2p^3$	p_x, p_y, p_z
Chlorine	17	$1s^2$ $2s^2 2p^6$ $3s^2 3p^5$	p_z
Hydrogen	1	$1s^1$	s

Source: [Linde, 1996]

In degradation of chloramines, which are showed in Figure A- 1, it is the nitrogen-chlorine bond, which is of interest, and only the valence atomic orbitals have to be considered. In monochloramine, the $1s^1$ atomic orbital of the hydrogen atom and the p_x- and the p_y-orbitals of the nitrogen bond in the sp2-hybridizated molecular orbitals, whereas the p_z-orbital of the nitrogen and the p_x-orbital of the chlorine atom combines in the bonding σ-orbital and the anti-bonding σ*-orbital.



(a) (b) (c)

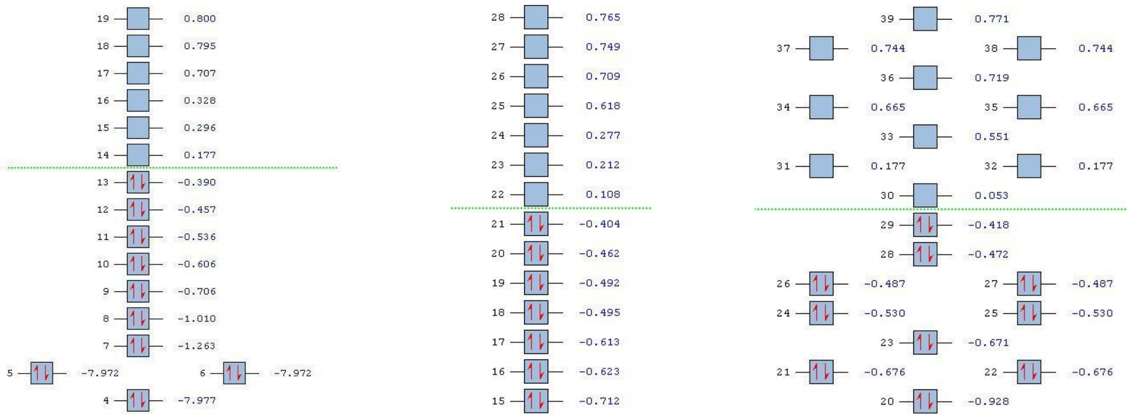
Figure A- 1: (a) monochloramine, (b) dichloramine, and (c) trichloramine.

By a simple consideration, the chloramine molecule is excited, when it absorbs the right quantum of UV light, by the transition of an electron from the bonding σ-orbital to the anti-bonding σ*-orbital. In fact, a range of other transitions from the upper occupied molecular orbitals to other anti-bonding orbitals are possible as well.

The project group has performed some computational calculations with the Gaussian v.03 software in order to determine the ground state energy of the respective chloramines, with the purpose of identifying the transition energies specified in Table A- 1. Applying computational chemistry with the purpose of predicting properties of molecules in research is however a tool in which the project group possess little experience, and the investigation has to be considered as part of a learning process in order to gain knowledge and be capable of applying the computational chemistry as a research tool in future work.

The calculations in Gaussian are based on the Hartree-Fock method, which is an iterative method of solving the Schrödinger wavefunction of a molecule. A detailed description of the Hartree-Fock algorithm will not be provided in the present project, but a comprehensive introduction is found in Sherril, 2000. The solutions of the orbital energies in the system obtained through the Hartree-Fock method are approximations, and the method makes some simplifications in order to complete the iterative calculation procedure. In Gaussian, the CIS (Configuration Interaction with Single excitation) method was applied in the calculation of the energy needed to excite the molecule using single-excitation.

The orbital energy levels, calculated for mono-, di-, and trichloramine, are seen in the diagrams in Figure A- 2. The green punctured lines indicate the zero level from which the relative orbital energies are calculated. The units of the relative orbital energies are provided in Hartree (1 Hartree = 27.211 eV).



(a) (b) (c)

Figure A- 2: Screenshots from Gaussian showing the calculated molecular orbital energy levels in the unit of Hartree. (a) monochloramine, (b) dichloramine, (c) trichloramine.

The calculations have been performed with chloramines in the singlet state, and the numbers indicate the orbital numbers. The excitation energies for chloramines calculated through the CIS method are showed in Table A- 3. The orbital excitation transitions are specified by Gaussian, but by manual comparison with the orbital energy levels in the diagrams, the energies can not be retrieved. The algorithm applied in the CIS method is not known by the project group, but it must consider parameters beside the orbital transition.

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Table A- 3: Results of the Gaussian calculations.

Molecule	Orbital transition	Symmetry Singlet-A’	Excitation energy [eV]	Wavelentgh [nm]
Monochloramine	13 → 14	0.66954	6.0257	205.76
	13 → 15	0.18678		
Dichloramine	19 → 23	-0.10723	5.2247	237.31
	21 → 22	0.68245		
Trichloramine	29 → 30	0.68565	4.6828	264.77

The calculations performed with the CIS method resulted in excitation energies higher than the ones specified by the manufacturers for the use of chloramine degradation. The difference is probably caused by several factors, as the lack of experience and knowledge of the project group concerning the use of computational quantum chemistry, approximations applied in the Hartree-Fock method and the CIS algorithm, the fact that Gaussian considers the molecules in vacuum, while the experimental absorption maximal wavelengths are obtained in aqueous solution, and maybe that the wavelength specified by the manufacturers refer to the energy needed for direct photolysis of the chloramines and not just excitation. The found excitation energies however correspond to the ones in Table A- 1 in the way that more energy is needed in order to excite the monochloramine than the trichloramine. This favours the UV induced reduction of chloramines in swimming pools, where the trichloramine is showed to be the most abundant.

The concluding remark to be attached to this computational chemistry investigation is that further knowledge about the applied algorithms and limitations of the calculation model has to be gained before more useful information can be drawn from investigations by this analysis tool. The project group however considers the applied procedure as an applicable introductory step, but the obtained results are not applicable in resolving the origin of the UV manufacturer specified wavelength.

Appendix 3 – Chlorine production

This appendix contains the raw data, obtained in the chlorine production test.

Experiment no. 1 (Introductory test; 10.0 V; 0.9 % *NaCl*)

Time [min]	Current [A]	ORP [mV]	pH	Conductivity $[^{mS}/_{cm}]$	DO $[^{mg}/_{l}]$	Temp. [°C]	Free chlorine $[^{mg}/_{l}]$
0	10.9	190	8.57	14.25	9.1	15.0	0
3	-	498	8.68	14.3	8.8	15.4	4
4	-	519	8.70	14.2	8.8	15.5	-
5	-	518	8.72	14.06	8.6	15.7	-
7	-	529	8.77	Unstable!	8.5	16.0	-
9	-	533	8.82		8.1	16.2	-
12	-	538	8.88		7.8	16.6	-
15	-	541	8.95		7.8	17.1	31
18	-	542	9.01		7.6	17.6	-
20	11.6	548	9.08		7.4	18.1	-
23	-	554	9.16		6.9	18.6	-
25	-	557	9.20		6.9	18.8	-
29	-	564	9.30		6.6	19.4	75
35	12.0	577	9.43		6.3	20.1	-
39	-	589	9.57		6.0	20.9	-
45	-	604	9.74		5.9	21.8	142
50	12.7	614	9.93		5.6	22.4	-
55	12.9	625	10.12		5.5	23.1	-
60	13.0	634	10.39		5.5	23.9	>200
61	Turned off						
65		642	10.59		5.6	23.9	-
68		647	10.70		5.7	23.8	-
70		644	10.75		5.7	23.8	-
72		651	10.81		5.8	23.7	-
75		655	10.90		5.8	23.7	-
77		658	10.98		5.9	23.6	-
122		692	12.33		6.4	22.7	-
125		698	12.41		6.4	22.6	-

Experiment no. 2 (Introductory test; 10.0 V; 0.9 % *NaCl*)

Time [min]	Current [A]	ORP [mV]	pH	DO $[^{mg}/_{l}]$	Temp. [°C]	Free chlorine $[^{mg}/_{l}]$
0	13.5	226	8.05	8.1	26.0	0.02
2	-	-40	8.24	7.7	26.1	-
5	-	-207	8.35	7.3	26.4	17.1
7	-	-235	8.41	6.9	26.7	-
10	-	Turned off				23
14	-		8.52	6.4	27.5	-
18	-		8.59	6.1	27.9	-
22	-		8.63	5.9	28.4	65
25	14.2		8.65	5.8	28.7	-
30	-		8.69	5.3	29.2	86
34	-		8.73	5.2	29.7	-
38	14.5		8.76	5.1	30.1	-

40	-	8.77	5.1	30.4	163
43	-	8.79	4.9	30.6	-
46	14.8	8.85	4.8	31.0	-
50	-	8.83	4.8	31.5	195
53	-	8.83	4.7	31.8	-
55	-	8.84	4.7	31.9	-
58	15.1	8.86	4.7	32.2	-
60	-	8.86	4.6	32.5	258

Experiment no. 3 (15.0 V; 0.9 % *NaCl*)

Time [min]	Current [A]	pH	DO [$^{mg}/_{l}$]	Temp. [°C]	Free chlorine [$^{mg}/_{l}$]
0	25.3	8.08	7.6	28.9	0
1	-	8.23	7.5	29.1	-
2	25.4	8.30	7.2	29.5	-
3	-	8.36	7.0	29.8	-
4	25.5	8.40	6.8	30.1	-
5	25.7	8.47	6.6	30.5	34
7	25.9	8.52	6.5	31.1	-
9	26.2	8.58	6.1	31.7	-
10	26.3	8.65	6.0	32.1	81
13	26.8	8.65	5.9	33.0	-
15	-	-	-	-	132
17	27.3	8.82	5.6	34.2	-
20	27.8	8.87	5.6	35.2	189
22	28.0	8.89	5.4	35.8	-
25	28.5	8.84	5.3	36.8	248
27	28.7	8.85	5.2	37.3	-
30	29.2	8.88	5.0	38.3	283
32	29.4	8.88	5.1	38.9	-
35	29.9	8.93	5.1	39.9	353
37	30.1	8.95	5.0	40.4	-
40	30.5	8.96	5.0	41.3	418
43	31.0	9.00	4.9	42.2	-
45	31.2	8.96	5.1	42.8	435
47	31.4	9.00	5.0	43.3	-
50	31.9	9.02	5.0	44.3	500
55	32.5	9.06	5.0	45.7	570
57	32.8	9.06	5.1	46.2	-
60	33.1	9.12	5.3	47.4	605
60	Turned off				
65	-	9.06	5.2	46.4	-
70	-	9.06	5.3	45.5	-
75	-	9.08	5.4	44.6	625
80	-	9.08	5.4	43.9	-

Experiment no. 4 (5.0 V; 0.9 % *NaCl*)

Time [min]	Current [A]	pH	DO [$^{mg}/_{l}$]	Temp. [°C]	Free chlorine [$^{mg}/_{l}$]
0	4.0	7.88	8.1	25.9	0
1	-	8.02	8.1	25.9	-
2	-	8.02	7.9	25.9	-
3	3.9	8.05	7.9	25.9	-
4	3.9	8.09	7.7	25.9	-

5	3.9	8.11	7.5	25.8	7.3
7	3.9	8.14	7.3	25.8	-
10	3.9	8.20	7.2	25.8	15.3
12	3.9	8.23	7.1	25.8	-
15	3.9	8.27	7.1	25.8	18
17	3.9	8.29	7.1	25.7	-
20	3.9	8.32	7.0	25.7	30
22	3.9	8.34	7.1	25.7	-
25	3.9	8.36	7.1	25.7	35
27	3.9	8.38	6.5	25.6	-
30	3.9	8.41	6.4	25.6	33
32	3.9	8.42	7.1	25.6	-
35	3.9	8.44	6.3	25.6	49
38	3.9	8.45	6.2	25.5	-
40	3.9	8.46	6.5	25.5	54
42	3.9	8.47	6.2	25.5	-
45	3.9	8.50	6.2	25.5	46
47	3.9	8.51	6.1	25.5	-
50	3.9	8.52	6.0	25.5	75
52	3.9	8.52	6.2	25.4	-
55	3.9	8.54	6.0	25.4	82
57	3.9	8.55	6.0	25.4	-
60	3.9	8.56	6.0	25.4	91

Experiment no. 5 (20.0 V; 0.9 % *NaCl*)

Time [min]	Current [A]	pH	DO [$^{mg}/_{l}$]	Temp. [°C]	Free chlorine [$^{mg}/_{l}$]
0	35.6	7.92	8.2	26.4	0
1	35.7	8.16	-	27.0	-
2	36.0	8.28	7.9	27.5	-
3	36.4	8.36	7.6	28.0	-
5	37.2	8.50	6.7	29.2	59
7	37.7	8.58	7.1	30.2	-
10	38.9	8.65	6.4	31.9	139
12	39.5	8.74	6.4	33.1	-
15	40.6	8.89	6.1	34.8	220
17	41.3	8.78	5.8	35.9	-
20	42.3	8.98	5.7	37.6	-
22	43.0	8.99	5.6	38.5	-
25	44.1	9.04	5.6	40.4	385
27	44.6	8.90	6.0	41.3	-
30	45.9	8.87	5.8	43.2	450
32	46.5	8.89	5.0	44.3	-
35	47.5	9.23	5.0	46.0	530
37	48.2	9.17	4.9	47.0	-
40	49.4	9.16	5.1	48.8	610
45	51.2	9.19	-	>50	745
50	-	-	-	>50	800

Experiment no. 6 (10.0 V; 0.9 % *NaCl*)

Time [min]	Current [A]	pH	DO [$^{mg}/_{l}$]	DO sat. [%]	Temp. [°C]	Free chlorine [$^{mg}/_{l}$]
0	13.2	7.9	8.2	99	25.4	0
1	13.2	8.08	8.1	98	25.5	-
2	13.2	8.13	7.8	95	25.6	-
4	13.2	8.19	7.5	92	25.8	-
5	13.3	8.24	7.3	89	26	20
7	13.3	8.29	7.0	87	26.2	-
10	13.4	8.37	6.7	83	26.5	45
12	13.5	8.40	6.5	81	26.7	-
15	13.6	8.46	6.2	78	27.1	77
17	13.6	8.47	6.2	78	27.3	-
20	13.7	8.53	6.0	76	27.7	96
22	13.8	8.54	6.0	76	27.9	-
25	13.9	8.58	5.6	72	28.2	124
27	13.9	8.60	5.6	72	28.4	-
30	14.0	8.63	5.5	71	28.8	166
32	14.0	8.65	5.6	73	29	-
35	14.1	8.67	5.5	72	29.3	145
37	14.2	8.68	5.5	72	29.5	-
40	14.3	8.71	5.5	72	29.9	200
42	14.6	8.72	5.4	71	30.0	-
45	14.4	8.74	5.4	71	30.4	218
47	14.4	8.74	5.3	70	30.6	-
50	14.5	8.75	5.4	72	30.9	260
52	14.6	8.77	5.2	70	31.1	-
55	14.7	8.78	5.2	71	31.4	288
57	14.7	8.79	5.1	69	31.6	-
60	14.8	8.80	5.1	69	31.9	313

Experiment no. 7 (10.0 V; 4.0 % *NaCl*)

Time [min]	Current [A]	pH	DO [$^{mg}/_{l}$]	DO sat. [%]	Temp. [°C]	Free chlorine [$^{mg}/_{l}$]
0	45.3	7.89	8.7	104	24.4	0
1	45.2	8.15	7.7	91	24.7	-
2	45.3	8.30	6.8	81	25.0	-
3	45.5	8.40	5.8	71	25.4	-
4	45.8	8.46	4.9	60	25.7	-
5	46.0	8.53	4.8	58	26.1	150
7	46.5	8.60	4.0	50	26.7	-
10	47.4	8.69	3.0	-	27.9	300
12	47.8	8.76	2.7	35	28.6	-
15	48.7	8.78	1.9	26	29.8	455
17	49.2	8.85	1.9	27	30.4	-
20	50.1	8.85	1.7	24	31.5	590
22	50.6	8.86	1.7	24	32.1	-
25	51.5	8.89	1.5	21	33.2	845
27	52.1	8.92	1.4	20	33.9	-
30	53.0	8.94	1.5	21	35.0	820

Experiment no. 8 (10.0 V; 2.0 % *NaCl*)

Time [min]	Current [A]	pH	DO [$^{mg}/_{l}$]	DO sat. [%]	Temp. [°C]	Free chlorine [$^{mg}/_{l}$]
0	27.0	7.96	8.4	102	25.6	0
1	26.9	8.20	7.1	87	25.9	-
2	26.7	8.27	7.1	87	26.1	-
3	27.0	8.34	6.5	77	26.3	-
5	27.2	8.49	5.4	67	26.8	64
7	27.4	8.57	4.8	59	27.2	-
10	27.9	8.64	4.2	53	27.9	150
12	28.1	8.67	3.7	49	28.3	-
15	28.5	8.73	3.4	43	29.1	220
17	28.7	8.80	3.3	42	29.5	-
20	29.1	8.83	2.9	38	30.2	285
22	29.4	8.88	3.0	40	30.7	-
25	29.7	8.90	2.8	38	31.3	365
27	29.9	8.93	2.8	38	31.8	-
30	30.2	8.93	2.7	37	32.5	453

Experiment no. 24 (Full scale trailer test; 100 A; 0.65 % *NaCl*)

Time [min]	Voltage [V]	ORP [mV]	Conductivity [$^{mS}/_{cm}$]	DO [$^{mg}/_{l}$]	Temp. [°C]	Free chlorine [$^{mg}/_{l}$]
0	48.0	323	11.41	8.64	11.6	0
5	47.2	1089	11.12	8.65	12.1	0.22
10	46.6	1096	11.14	8.30	12.6	19
18	46.0	1096	11.12	7.81	13.5	3
-	-	-	-	-	-	19
26	45.0	1086	11.13	7.41	14.4	29
32	44.7	1088	11.01	7.21	14.8	2
-	-	-	-	-	-	14.5
34	STOP					

Appendix 4 – Identification of oxidising agents

In this section, the data obtained in the experiments with bleaching of RNO is found. At first, the calibration curves applied in the spectrophotometric RNO analyses are presented.

RNO calibration curves

The calibration curves applied in the RNO spectrophotometric measurements are seen in Figure A- 3.

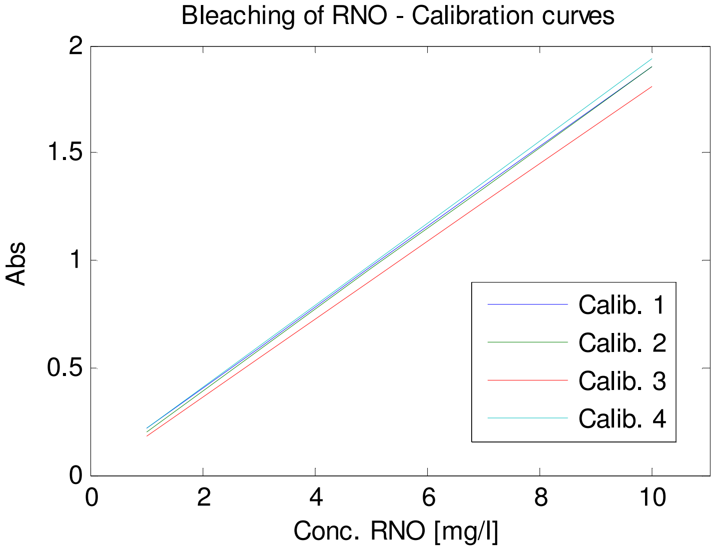

Figure A- 3: Calibration curves applied in the RNO measurements.

Experimental results – Bleaching of RNO

<u>Experiment no. 9 (5.0 V; 0.9 % *NaCl*)</u>

Time [min]	Voltage [V]	Abs.1	Abs.2	Time [min]	Voltage [V]	Abs.1	Abs.2
0	6.0	1.831	1.832	13	6.1	0.180	0.178
0.5	6.0	1.462	1.508	14	6.1	0.161	0.165
1	6.1	1.113	1.109	16	6.1	0.145	0.147
2	6.1	0.706	0.701	18	6.1	0.133	0.132
3	6.1	0.546	0.533	20	6.1	0.132	0.128
4	6.1	0.452	0.442	22	6.1	0.121	0.111
5	6.1	0.373	0.390	25	6.0	0.115	0.110
6	6.1	0.339	0.336	30	6.0	0.083	0.082
7	6.1	0.298	0.296	40	6.0	0.068	0.068
8	6.1	0.268	0.262	50	6.0	0.060	0.059
9	6.1	0.242	0.242	60	6.0	0.048	0.048
10	6.1	0.223	0.222		Turned off		
11	6.1	0.209	0.206	67	-	0.044	0.044
12	6.1	0.191	0.191				

Experiment no. 10 (Demonstration test; 20.2 V; 0.9 % *NaCl*)

Time [min]	Voltage [V]	Current [A]	Abs.1	Abs.2
0	20.2	30.6	-	-
0.5	20.2	31.1	-	-
3	20.2	34.3	-	-
6	20.2	38.4	-	-
8	20.2	-	0.043	0.041

Experiment no. 11 (1.0 V; 0.9 % *NaCl*)

Time [min]	Voltage [V]	Abs.1	Abs.2	Time [min]	Voltage [V]	Abs.1	Abs.2
0	3.4	1.972	2.002	12	3.5	0.589	0.592
0.5	3.4	1.883	1.916	14	3.6	0.527	0.526
1	3.5	1.823	1.842	16	3.6	0.473	0.473
2	3.5	1.702	1.715	18	3.6	0.432	0.423
3	3.5	1.506	1.518	20	3.6	0.383	0.382
4	3.5	1.340	1.347	22	3.6	0.345	0.344
5	3.5	1.134	1.140	25	3.6	0.298	0.305
6	3.5	0.948	0.957	30	3.6	0.271	0.255
7	3.5	0.805	0.814	40	3.6	0.187	0.191
8	3.5	0.749	0.755	50	3.6	0.165	0.166
9	3.5	0.704	0.712	60	3.6	0.143	0.133
10	3.5	0.666	0.672				

Experiment no. 12 (10.0 V; 0.9 % *NaCl*)

Time [min]	Voltage [V]	Abs.1	Abs.2	Time [min]	Voltage [V]	Abs.1	Abs.2
0	8.8	1.951	1.968	11	8.6	0.157	0.153
0.5	8.8	1.181	1.262	12	8.6	0.140	0.139
1	8.8	0.712	0.706	14	8.5	0.119	0.118
2	8.8	0.571	0.565	16	8.5	0.105	0.115
3	8.8	0.442	0.445	18	8.5	0.091	0.089
4	8.8	0.366	0.375	20	8.4	0.085	0.085
5	8.8	0.321	0.321	25	8.4	0.07	0.070
6	8.7	0.279	0.277	31	8.2	0.059	0.059
7	8.7	0.248	0.241	40	8.1	0.047	0.048
8	8.7	0.214	0.219	50	8.0	0.031	0.031
9	8.6	0.190	0.190	60	8.0	0.022	0.023
10	8.7	0.169	0.168				

Experiment no. 13 (add. *NaOCl* ; 0.9 % *NaCl*)

RNO + 750 $^{mg}/_{l}$			RNO + H_2O		
Time [min]	Abs.1	Abs.2	Time [min]	Abs.1	Abs.2
0	1.780	1.803	0	1.709	1.715
1	0.929	0.919	1	0.294	0.296
5	0.853	0.846	5	0.321	0.315
10	0.821	0.820	10	0.814	0.822
16	0.773	0.767	15	0.321	0.324
20	0.750	0.751	18	0.332	0.334

25	0.730	0.729	27	0.304	0.358
30	0.691	0.689	32	0.318	0.319
35	0.671	0.669	37	0.326	0.327
40	0.648	0.644	42	0.315	0.314
50	0.598	0.596	52	0.296	0.292
60	0.564	0.561	62	0.306	0.300
70	0.523	0.520	72	0.358	0.296
90	0.463	0.461	92	0.298	0.294
120	0.390	0.389	122	0.303	0.346
180	0.273	0.270	182	0.306	0.304

Experiment no. 14 (add. *NaOCl* ; 0.9 % *NaCl*)

RNO + 1310 $^{mg}/_{l}$			RNO + 655 $^{mg}/_{l}$			RNO + H_2O		
Time [min]	Abs.1	Abs.2	Time [min]	Abs.1	Abs.2	Time [min]	Abs.1	Abs.2
0	2.556	2.555	0	2.623	2.624	0	2.555	2.554
2	2.537	2.549	3	2.576	2.573	5	2.497	2.495
7	2.551	2.550	9	2.263	2.226	10	2.497	2.494
14	2.452	2.437	16	1.773	1.774	18	2.495	2.493
20	2.259	2.246	22	1.414	1.403	24	2.499	2.497
26	1.937	1.926	28	1.289	1.284	30	2.496	2.495
35	1.692	1.687	37	1.074	1.071	59	2.496	2.496
45	1.405	1.404	47	0.931	0.929	94	2.496	2.494
55	1.275	1.275	57	0.830	0.828	124	2.493	2.492
90	0.896	0.898	92	0.641	0.641	182	2.495	2.493
120	0.741	0.742	122	0.565	0.566	212	2.494	2.493
150	0.629	0.631	152	0.517	0.519			
180	0.563	0.564	182	0.491	0.494			
208	0.518	0.520	210	0.474	0.476			

Experiment no. 15 (add. *NaOCl* ; 0.9 % *NaCl*)

Solution 2			Solution 1			Blank		
Time [min]	Abs.1	Abs.2	Time [min]	Abs.1	Abs.2	Time [min]	Abs.1	Abs.2
0	1.937	1.937	0	1.964	1.964	0	1.970	1.970
1	0.139	0.118	2	0.068	0.059	10	1.003	1.048
3	0.070	0.065	4	0.032	0.036			
5	0.046	0.043	6	0.021	0.020			
7	0.033	0.033	8	0.016	0.016			
9	0.027	0.025	10	0.014	0.013			

Experiment no. 16 (20.2 V; 0.2 A ; 0.0 % *NaCl*)

Time [min]	Abs.1	Abs.2
0	1.967	1.968
1	1.999	2.009
2	2.003	2.012
4	2.001	2.009
8	2.002	2.009
10	1.999	2.008

Experiment no. 17 (power on/off; 0.9 % *NaCl*)

Time [min]	Current [A]	Voltage [V]	Abs.1	Abs.2
0	1.0	3.4	1.977	1.991
1	1.0	3.5	1.942	1.950
2	1.0	3.5	1.845	1.859
3	1.0	3.5	1.720	1.729
4	1.0	3.5	1.565	1.573
5	1.0	3.5	1.391	1.402
6	0.0	0.0	1.245	1.247
7	0.0	0.0	1.214	1.216
8	0.0	0.0	1.210	1.213
9	0.0	0.0	1.205	1.206
10	0.0	0.0	1.200	1.203
11	0.0	0.0	1.195	1.199
12	1.0	3.5	1.192	1.195
13	1.0	3.5	1.164	1.167
14	1.0	3.5	1.072	1.070
15	1.0	3.5	0.985	0.979
16	1.0	3.5	0.907	0.902
17	1.0	3.5	0.837	0.827
18	0.0	0.0	0.771	0.762
19	0.0	0.0	0.722	0.716
20	0.0	0.0	0.696	0.692
21	0.0	0.0	0.671	0.668
22	0.0	0.0	0.652	0.643
23	0.0	0.0	0.632	0.633
24	1.0	3.5	0.620	0.619
25	1.0	3.6	0.595	0.592
26	1.0	3.5	0.562	0.559
27	1.0	3.5	0.529	0.527
28	1.0	3.5	0.502	0.498
29	1.0	3.5	0.474	0.471
30	1.0	3.5	0.448	0.446

Experiment no. 18 (0.9 % KNO_3)

Time [min]	Current [A]	Voltage [V]	pH	DO [$^{mg}/_{l}$]	Abs.1	Abs.2
0	0.0	0.0	6.19	9.0	1.969	1.982
1	1.0	3.4	6.55	9.5	1.988	1.996
2	1.0	3.4	6.80	9.6	1.995	2.002
3	1.0	3.4	7.42	9.9	1.998	1.999
4	1.0	3.4	8.37	10.3	1.999	2.004
5	1.0	3.4	8.75	10.5	1.995	1.989
6	1.0	3.4	8.97	10.7	1.991	1.991
8	1.0	3.4	8.97	10.7	1.986	1.992
10	10.0	10.9	9.22	11.3	1.969	1.981
11	10.0	10.9	9.84	12.1	1.973	2.005
12	10.0	10.7	10.13	12.3	1.956	1.965
14	10.0	10.7	10.42	13.2	1.946	1.950
16	10.0	10.6	10.59	13.7	1.927	1.932
20	10.0	10.4	10.83	14.4	1.876	1.882
25	10.0	10.2	10.98	14.8	1.843	1.849
27	20.0	17.0	11.03	14.3	1.818	1.823
30	20.0	16.5	11.10	13.5	1.765	1.771
36	20.0	15.5	11.02	12.1	1.668	1.676
41	20.0	15.0	11.13	11.7	1.566	1.562

Appendix 5 – Gas production

In this section, the results obtained in the gas production test are found.

Experiment no. 19 (0.9. 1.8 and 3.6 % *NaCl*)

Conductivity [$^{mS}/_{cm}$]	Current [A]	Voltage [V]	Time [s]	Volume [ml]
15.30	5.0	5.3	90	50
-	-	-	170	100
-	-	-	250	150
15.30	10.0	10.1	36	50
-	-	-	73	100
-	-	-	107	150
-	-	-	143	200
15.30	15.0	10.1	23	50
-	-	-	47	100
-	-	-	71	150
-	-	-	95	200
-	-	-	119	250
-	-	-	143	300
-	-	-	166	350
-	-	-	190	400
15.57	20.0	12.5	17	50
-	-	-	35	100
-	-	-	54	150
-	-	-	70	200
-	-	-	89	250
-	-	-	107	300
-	-	-	124	350
-	-	-	142	400
15.57	30.0	16.8	10	50
-	-	-	21	100
-	-	-	31	150
-	-	-	44	200
-	-	-	55	250
-	-	-	65	300
-	-	-	77	350
-	-	-	87	400
27.22	5.0	4.4	125	50
-	-	-	244	100
-	-	-	363	150
27.22	10.0	5.8	48	50
-	-	-	98	100
-	-	-	149	150
-	-	-	199	200
27.22	15.0	7.3	27	50
-	-	-	53	100
-	-	-	81	150
-	-	-	109	200
28.08	20.0	8.5	22	50
-	-	-	41	100
-	-	-	62	150
-	-	-	82	200

-	-	-	102	250
-	-	-	122	300
-	-	-	143	350
-	-	-	163	400
28.08	30.0	11.1	12	50
-	-	-	25	100
-	-	-	37	150
-	-	-	49	200
-	-	-	61	250
-	-	-	73	300
-	-	-	85	350
-	-	-	98	400
14.73	5.0	5.4	87	50
-	-	-	163	100
-	-	-	238	150
14.73	10.0	7.8	36	50
-	-	-	69	100
-	-	-	107	150
-	-	-	140	200
14.73	15.0	10.1	25	50
-	-	-	47	100
-	-	-	72	150
-	-	-	94	200
-	-	-	117	250
15.08	20.0	12.7	17	50
-	-	-	35	100
-	-	-	52	150
-	-	-	69	200
-	-	-	86	250
15.08	30.0	17.0	11	50
-	-	-	22	100
-	-	-	32	150
-	-	-	43	200
-	-	-	54	250
-	-	-	65	300
-	-	-	76	350
27.51	5.0	4.4	86	50
-	-	-	169	100
-	-	-	256	150
27.51	10.0	5.8	41	50
-	-	-	80	100
-	-	-	120	150
-	-	-	159	200
-	-	-	199	250
27.51	15.0	7.1	27	50
-	-	-	53	100
-	-	-	78	150
-	-	-	105	200
-	-	-	131	250
-	-	-	157	300
27.9	20.0	8.6	18	50
-	-	-	36	100
-	-	-	54	150
-	-	-	71	200

-	-	-	90	250
-	-	-	109	300
-	-	-	128	350
27.9	30.0	11.1	11	50
-	-	-	23	100
-	-	-	36	150
-	-	-	47	200
-	-	-	58	250
-	-	-	70	300
49.3	5.0	3.8	132	50
-	-	-	250	100
-	10.0	4.7	50	50
-	-	-	99	100
-	-	-	149	150
-	-	-	199	200
49.3	15.0	5.5	27	50
-	-	-	57	100
-	-	-	87	150
-	-	-	114	200
-	-	-	144	250
-	-	-	174	300
-	-	-	204	350
-	-	-	233	400
50.2	20.0	6.3	19	50
-	-	-	38	100
-	-	-	57	150
-	-	-	77	200
-	-	-	96	250
-	-	-	115	300
50.2	30.0	7.9	12	50
-	-	-	24	100
-	-	-	36	150
-	-	-	48	200
-	-	-	61	250
-	-	-	74	300

Experiment no. 20

NaCl [%]	Conductivity $[^{mS}/_{cm}]$	Current [A]	Free chlorine $[^{mg}/_{l}]$
0.9	15.44	30.0	0.07
4.0	65.70	30.0	0.08

Experiment no. 25 (10.0 A, 20.0 A; 0.9 % *NaCl*)

Tid [s]	Current [A]	Voltage [V]	Conc. H_2 [pA]	Temp. [°C]	Current [A]	Voltage [V]	Conc. H_2 [pA]	Temp. [°C]
0	10	8.2	12	26.5	20	-	9	-
20	10	-	57	-	20	-	54	-
40	10	-	127	-	20	-	93	-
60	10	-	196	-	20	-	168	-
80	10	-	335	-	20	-	240	-
100	10	-	356	-	20	14.0	308	-
120	10	-	411	-	20	-	385	-
140	10	8.2	476	27.0	20	-	456	-
160	10	-	535	-	20	-	530	-
180	10	-	595	-	20	13.7	594	-
200	10	-	638	-	20	-	654	-
220	10	-	684	-	20	-	710	-
240	10	8.2	744	27.3	20	-	760	-
260	10	-	780	-	20	-	806	-
280	10	-	817	-	20	-	855	-
300	10	-	857	-	20	-	897	-
320	10	-	895	-	20	-	936	-
340	10	-	930	-	20	-	975	-
360	10	-	965	-	20	-	1008	-
380	10	8.1	997	27.8	20	-	1062	-
400	10	-	1029	-	20	-	1078	-
420	10	-	1108	-	20	-	1200	-
440	10	-	1135	-	20	-	1176	-
460	10	-	1321	-	20	-	1182	-
480	10	-	1190	-	20	-	1220	-
500	10	-	1358	-	20	-	1400	-
520	10	-	1269	-	20	-	1280	-
540	10	8.1	1265	28.2	20	-	1285	-
560	10	-	1288	-	20	-	1308	-
580	10	-	1308	-	20	-	1337	-
600	10	-	1306	-	20	13.2	1358	-
620	10	-	1323	-	20	-	1376	-
640	10	-	1339	-	20	-	1385	-
660	10	-	1355	-	20	-	1400	-
680	10	8.0	1370	28.6	20	-	1432	-
700	10	-	1386	-	20	-	1444	-
720	10	-	1400	-	20	-	1458	-
740	10	-	1415	-	20	-	1470	30.4
760	10	-	1428	-	20	-	1474	-
780	10	-	1441	-	20	-	1491	-
800	10	8.0	1453	29.0	20	-	1493	30.8
820	10	-	1464	-	20	12.5	1500	31.1
840	0	-	1474	-	0	-	1505	-
860	0	-	1477	-	0	-	1481	-
880	0	-	1472	-	0	-	1444	-
900	0	-	1463	-	0	-	1412	-
920	0	-	1455	-	0	-	1385	-
940	0	-	1449	-	0	-	1350	-
960	0	-	1438	-	0	-	1320	-
980	0	-	1429	-	0	-	1309	-

1000	0	-	1422	-	0	-	1290	-	
1020	0	-	1411	-	0	-	1259	-	
1040	0	-	1402	-	0	-	1244	-	
1060	0	-	1392	-	0	-	1200	-	
1080	0	-	1383	-	0	-	1181	-	
1100	0	-	1373	-	0	-	1166	-	
1120	0	-	1364	-	0	-	1157	-	
1140	0	-	1355	-	0	-	1134	31.1	
1160	0	-	1348	-	0	-	1116	-	
1180	0	-	1340	-	0	-	1100	-	
1200	0	-	1331	-	-	-	-	-	
1220	0	-	1320	-	-	-	-	-	
1240	0	-	1310	-	-	-	-	-	
1260	0	-	1201	-	-	-	-	-	
1280	0	-	1271	-	-	-	-	-	
1300	0	-	1248	-	-	-	-	-	
1320	0	-	1223	-	-	-	-	-	
1340	0	-	1200	28.8	-	-	-	-	
1360	0	-	1176	-	-	-	-	-	
1380	0	-	1148	-	-	-	-	-	
1400	0	-	1123	-	-	-	-	-	
1420	0	-	1100	-	-	-	-	-	

Appendix 6 - Disinfection of *E. coli*

In this section, the results obtained in the disinfection experiments are found.

Experiment no. 21 (OD = 5.9; 0.9 % *NaCl*)

Dissolution Current [A]	1:1	1:10	1:100	1:1000	1:10000	Free chlorine [$^{mg}/_{l}$]
0.0	n.c./n.c.	n.c./n.c.	n.c./n.c.	133/48	32/0	0.02
1.0	74/7	24/1	25/27	59/21	59/n.c.	0.30
5.0	1/2	4/1	4/4	4/1	2/5	2.38
10.0	2/1	2/1	2/1	12/2	29/8	8.30
20.0	0	0	1	4/1	10/2	-
0.0	-	-	-	5/0	29/20	-

White/yellow, n.c. = not countable

Experiment no. 22 (OD = 5.65; 0.9 % *NaCl*)

Dissolution Current [A]	1:1-1	1:1-2	1:1-3	1:1-4	1:1-5	1:10-1	1:10-2	1:10-3
0.0	106	102	154	-	80	-	-	-
0.5	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
1.0	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.
1.5	n.c.	n.c.	n.c.	n.c.	n.c.	-	-	-
2.0	n.c.	n.c.	n.c.	n.c.	n.c.	-	-	-
3.0	n.c.	n.c.	n.c.	n.c.	n.c.	-	-	-
5.0	n.c.	n.c.	n.c.	n.c.	n.c.	-	-	-

n.c. = not countable

Experiment no. 23 (OD = 5.15; 0.9 % *NaCl*)

Dissolution Current [A]	1:1-1	1:1-2	1:10-1	1:10-2	1:100-1	1:100-2	1:1000-1	1:1000-2	1:10000-1	1:10000-2	10000-3
0.0	-	-	-	-	-	-	386	-	70	71	64
2.0	n.c.	n.c.	n.c.	n.c.	n.c.	n.c.	245	236	17	26	-
5.0	n.c.	n.c.	n.c.	n.c.	194	155	19	12	1	0	-
10.0	305	261	31	27	6	5	0	0	0	0	-
20.0	0	0	0	0	0	0	0	0	0	0	-
30.0	0	0	0	0	0	0	0	0	0	0	-

n.c. = not countable

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