

## MASTER THESIS

# Degradation of model reactants as a chemical probe for cavitation induced hot spots in water treatment devices

in cooperation with



**Submitted by:**  
Daniel Vallant  
0935407

**Supervisors:**  
Ao. Prof. DI Dr. Christian Weiß  
MSc Joe Chiarelli

Leoben, 2/17/16

## **EIDESSTATTLICHE ERKLÄRUNG**

Ich erkläre an Eides statt, dass ich die vorliegende Masterarbeit/Bachelorarbeit selbständig und ohne fremde Hilfe verfasst, andere als die angegebenen Quellen und Hilfsmittel nicht benutzt und die den benutzten Quellen wörtlich und inhaltlich entnommenen Stellen als solche erkenntlich gemacht habe.

## **AFFIDAVIT**

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume.

2/17/16

---

## **ACKNOWLEDGEMENT**

Firstly, I would like to express my sincere gratitude to my advisor Prof. Christian Weiß for the continuous support, for his motivation and immense source of knowledge. His guidance helped me in all the time of research and writing of this thesis.

I would like to express my special appreciation and thanks to Dr. Tzahi Y. Cath, Colorado School of Mines, civil and environmental engineering department for the invitation to work at his department at the Colorado School of Mines, the access to the AQWATEC lab and for comments that greatly improved the manuscript.

My sincere thanks also goes to the team of Arisdyne Systems, especially Dr. Peter Reimers, MSc Joe Chiarelli, Dr. Oleg Kozyuk, Paul Mulhollem and Bill who provided me the opportunity to do this research, and who gave access to the laboratory and research facilities. Without their precious support and sharing their pearls of wisdom during the course of this research, it would have not been possible to conduct this thesis.

Besides my advisor, the team of Arisdyne Systems and the civil and environmental engineering department at the Colorado School of Mines, I would like to thank the Austrian Marshall Plan Foundation for funding my research stay with a scholarship and the Chair for Process Technology and Industrial Environmental Protection for financial support.

Finally, I must express my very profound gratitude to my family for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them. Thank you.

## Abstract

### Degradation of model reactants as a chemical probe for cavitation induced hot spots in water treatment devices

Cavitation is the formation, growth and implosion of vapor bubbles in a liquid medium (Capocelli et al. 2014a, p. 2566) causing localized high temperature (1000 - 10000 K) and pressure (100 - 500 bar) for a few nanoseconds (Suslick 1990). A number of studies show that these so called "hot spots" lead to the generation of free radicals like  $\dot{O}H$  and  $\dot{H}$ . They are produced through the homolytic dissociation of water and used to oxidize complex contaminants in waste water streams (Advanced Oxidation Process (AOP)). This is the point where in this thesis the term cavitation is strictly differentiated from the damaging event of cavitation. Two different kinds of cavitation are considered: The first, hydrodynamic cavitation (HC) is performed with the patented cavitation unit from Arisdyn systems Inc., which is implemented into a closed loop. The second is ultrasonic cavitation (UC) which is realized through an ultrasonic horn. To investigate the degradation and the existence of cavitation induced hot spots, three different model reactants are used for the experiments: The liberation of iodine (Weissler reaction), the oxidation of sulfite to sulfate and the metabolization of PNP (p-nitrophenol). Samples are prepared for photometric measurement (UV/VIS spectrometer) and the performance of the HC loop is compared with the UC setup. The HC is studied over the pressure range 1000 - 15000 psi and the results of all three model reactants demonstrate that an applied pressure of 1000 psi shows the biggest degradation effect. All HC results are compared with the UC under the same operating parameters like temperature and pH. On the one hand the findings of this study indicate the existence of cavitation induced hot spots through HC and on the other hand it provides a possibility to monitor them quantitatively. Future investigation will be about the scale-up of the used HC system and if it is suitable for different applications like the cracking of long-chained hydrocarbons in the oil industry or the removal of persistent contaminants in waste water streams.

## Kurzfassung

### Chemischer Nachweis für durch Kavitation erzeugte Hot Spots in Wasserbehandlungsanlagen durch den Abbau von Modellreaktanten

Unter Kavitation versteht man die Formation, das Wachstum und die Implosion von Dampfblasen in einer Flüssigkeit und die damit verbundenen kurzzeitig (einige Nanosekunden) lokal auftretenden hohen Temperaturen (1000 - 10000 K) und Drücke (100 - 500 bar). Mehrere Studien im industriellen Umweltbereich zeigen, dass es bei diesen sogenannten „Hot Spots“ durch homolytische Dissoziation von Wasser ( $H_2O$ ) zur Entstehung von freien Radikalen wie z.B.  $\dot{O}H$  und  $\dot{H}$  kommt, welche für die Reinigung von komplexen und mit herkömmlichen Mitteln schwer behandelbaren Abwässern eingesetzt werden. An dieser Stelle grenzt sich der in dieser Arbeit verwendete Begriff der Kavitation vom Schadensfall ab. Es werden zwei unterschiedliche Arten der Kavitation untersucht: Die hydrodynamische Kavitation (HC) wird durch die patentierte Kavitationseinheit von Arisdyn systems Inc. erzeugt, welche in einem vollkommen geschlossenen Kreislauf implementiert ist. Ultraschall Kavitation (UC) stellt die zweite Art dar und wird durch ein Ultraschallhorn erzeugt. Um die Effekte der Kavitationsarten zu untersuchen, werden drei unterschiedliche Modellreaktanten eingesetzt: Die Freisetzung von Jod (Weissler Reaktion), die Oxidation von Sulfid zu Sulfat und der Abbau von PNP (p-Nitrophenol). Die Proben werden photometrisch ausgewertet (UV/VIS Spektrometer) und die Ergebnisse des HC Kreislaufes mit denen des Ultraschallkavitations - Setups verglichen. Die HC wird in einem Druckbereich von 1000 - 15000 psi untersucht und die Ergebnisse zeigen, dass die Anwendung von 1000 psi die besten Abbauresultate erzielt. Unter gleichen Betriebsparametern wie pH und Temperatur werden die HC Ergebnisse mit den Ergebnissen der UC Tests verglichen. Einerseits deuten die Ergebnisse auf die Existenz der „Hot Spots“ hin und andererseits stellen sie eine Möglichkeit dar, diese kontrolliert einzusetzen. Zukünftige Untersuchungen werden zeigen, wie sich das angewendete System im Zuge eines Upscaling verhält und ob es z.B. für Anwendungen in der Ölindustrie wie das Cracken von langkettigen Kohlenwasserstoffen oder in der Reinigung von persistenten Schadstoffen in Abwasserströmen eingesetzt werden kann.

## Content

	Page
<b>1 INTRODUCTION.....</b>	<b>3</b>
<b>2 TASK .....</b>	<b>4</b>
2.1 Actual technological issues .....	4
2.2 Objective.....	5
<b>3 THEORY .....</b>	<b>6</b>
3.1 Ultrasonic cavitation.....	6
3.1.1 Generation of cavitation through ultrasound (Suslick 1990) .....	6
3.2 Hydrodynamic cavitation.....	7
3.2.1 Cavitation unit and the issue of comparability .....	8
3.2.2 Cavitation number.....	10
3.2.3 The effect of pressure .....	16
3.3 Another cavitation effect: Generation of radicals .....	16
3.4 Comparison between ultrasonic and hydrodynamic cavitation .....	17
3.5 Model reactants and associated reactions.....	17
3.5.1 Inorganic reactions.....	17
3.5.2 Organic reactions.....	18
<b>4 METHODOLOGY.....</b>	<b>19</b>
4.1 Chemical model reactions.....	19
4.1.1 Radical chemistry.....	19
4.1.2 Inorganic reactions.....	19
4.1.3 Organic reaction .....	20
4.2 Analytical procedure .....	21
4.2.1 Calibration method: Liberation of iodine .....	22
4.2.2 Calibration method: Oxidation of sulfite.....	24
4.2.3 Calibration method: Degradation of PNP .....	26
4.3 Experimental approach.....	29
4.3.1 Ultrasonic cavitation.....	29
4.3.2 Hydrodynamic cavitation:.....	30
4.4 Result Quantification.....	31
<b>5 RESULTS .....</b>	<b>32</b>
5.1 Liberation of iodine.....	32

5.1.1	Liberation of iodine: Calculation scheme HC.....	32
5.1.2	Liberation of iodine: Calculation scheme UC.....	42
5.1.3	Liberation of iodine: Results.....	45
5.1.4	Liberation of iodine: Comparison HC with UC .....	51
5.2	Oxidation of sulfite .....	55
5.2.1	Oxidation of sulfite: Calculation scheme HC.....	55
5.2.2	Oxidation of sulfite: Calculation scheme UC.....	58
5.2.3	Oxidation of sulfite: Results.....	58
5.2.4	Oxidation of sulfite: Comparison HC with UC .....	63
5.3	Degradation of PNP .....	66
5.3.1	Degradation of PNP: Calculation scheme HC .....	66
5.3.2	Degradation of PNP: Calculation scheme UC .....	69
5.3.3	Degradation of PNP: Results HC .....	69
5.3.4	Degradation of PNP: Results UC .....	75
5.3.5	Degradation of PNP: Comparison HC with UC.....	77
<b>6</b>	<b>CONCLUSION .....</b>	<b>82</b>
<b>7</b>	<b>DIRECTORIES.....</b>	<b>84</b>
7.1	Publication bibliography .....	84
7.2	Tables .....	87
7.3	Figures.....	89
<b>APPENDIX A: LIBERATION OF IODINE “HC“ .....</b>		<b>I</b>
<b>APPENDIX B: LIBERATION OF IODINE “UC“ .....</b>		<b>VI</b>
<b>APPENDIX C: OXIDATION OF SULFITE “HC“ .....</b>		<b>V</b>
<b>APPENDIX D: OXIDATION OF SULFITE “UC“ .....</b>		<b>XI</b>
<b>APPENDIX E: DEGRADATION OF PNP “HC“ .....</b>		<b>XVI</b>
<b>APPENDIX F: DEGRADATION OF PNP “UC“ .....</b>		<b>XXIII</b>

# 1 Introduction

The majority of people do not know the term “cavitation” because there are only a few fields that have to deal with that phenomenon. A field maybe nobody will think of the first time, is nature. A crab species called “mantis” uses self - made cavitation to stun their prey (Patek et al. 2004). Engineers who are designing pumps or ship’s propellers know “cavitation” because they want to avoid it at all costs. Bioengineers are using “cavitation” to control for example the growth of algae like *M. aeruginosa* (Li et al. 2014, p. 247). Generally there are only two points of view, the user wants cavitation or not. The mechanism to create cavitation is basically the same in both cases and is very important for this study.

The cavitation effect includes three steps, the **formation, growth and implosion of vapor bubbles in a liquid medium** (Capocelli et al. 2014a, p. 2566).

The phase change takes place at narrowly constant temperature which is quite the contrary to boiling (d'Agostino, Luca and Salvetti, Maria Vittoria 2007, p. 8).

Generally speaking there are four different types of cavitation based on the mode of its generation. Two modes which are rarely in use are optic cavitation where photons produced by high intensity light (e.g. laser) rupturing the liquid continuum, and particle cavitation where any other type of beam of elementary particles rupturing a liquid (bubble chamber) (Gogate 2002). The two most important forms of cavitation for this study are acoustic and hydrodynamic cavitation. If the cavitation effects are caused by the application of high frequency sound waves (e.g. ultrasound), then it is called acoustic or ultrasonic cavitation. Terms like “Sonochemistry” and “Sonoluminescence” base on this form of cavitation. Different pressures in the liquid stream due to a change in the geometry of the flowing system generates hydrodynamic cavitation (Li et al. 2015, p. 246). More detailed explanations can be found in chapter 3.1 and 3.2.

In both cases the implosion of the bubble creates a so called “hot spot” and products a dramatic increase of temperature and pressure inside the bubble. Early data referring to temperature and pressure is published by Suslick (1990). In his study, hot spots with intense local heating (1000 - 10000 K), high pressures (100 - 5000 bar) and very short lifetimes (few nanoseconds) are found. Other pertinent literature reports temperatures up to 14000 K and pressures between 10 and 25 kbar (14500 and 36000 psi), depending on the radius of the bubble (Leighton 1995). The values of these parameters are responsible for the use of cavitation to enhance or boost chemical reactions.

This study strictly differentiated itself from the damaging event of cavitation.

Much research (Capocelli et al., p. 2569, Kalumuck et al. 2003) in recent years has focused on waste water treatment using cavitation to remove different contaminants from the water. Numerous experiments have established that this energy is adequate to generate oxidizing species in form of radicals. A current focus in this field is to investigate the impact of this oxidizing species on chemical reactions and the upscaling to industrial applications.

## 2 Task

### 2.1 Actual technological issues

“Arisdyne systems Inc.”, a company from Ohio, Cleveland, is specialized in using cavitation for industrial applications. They successfully established their technology in several fields, like ethanol and biodiesel production, degumming of crude vegetable oil and waste water treatment. Several patents make it possible to control cavitation and avoid erosion. One very important property of cavitation itself, beside the generated energy, is the mixing and particle homogenization effect. Shear forces, created by cavitation, are able to disrupt agglomerates or lyse cells. In case of ethanol and biodiesel production, smaller particles mean higher surface areas. Through the application of controlled cavitation, the particle size distribution shows that particles with larger diameters get smaller and small particles stay at the same size. In case of biodiesel production, it is possible to reduce the catalyst consumption by 25 % and decrease the retention time which increases the capacity. Crude vegetable oils contain phosphatides or so-called gums and they have to be removed during the refining process. These contaminants lead to losses in oil yield and a high demand of acid and alkali. Arisdyn is using a compressing - decompressing jet atomization process (see also 3.2) which allows a reduction in chemical consumption and oil yield loss. A lot of customers have realized that this novel side-effect of cavitation works better than a stirrer for the applications mentioned above (Arisdyne Systems 2015).

Mixing, particle homogenization and atomization are not the only effects connected to cavitation. Evidence that the patented technology from Arisdyn is able to create the mentioned cavitation induced hot spots is non-existent. To get a foot into the waste water treatment field it is very important to prove that the application is able to boost chemical reactions. The generated oxidizing species should be able to treat waste water (e.g. pharmaceutical waste water). Another important aim of Arisdyn for the future is to cooperate with oil companies. An undisputed fact is that every oil distillation column produces oil residues which are collected as the bottom product. This oil residue is used for bitumen, asphalt or roofing. Further processing to increase the valuable output of crude oil like petrol for vehicles, jet fuel or diesel fuel, is beyond the economical limit of currently used technologies. A concept to be proven in the future is that the cavitation induced hot spots are strong enough to crack the long chained hydrocarbons in the residual to maximize the output stream of valuable products.

## 2.2 Objective

In the present study fundamental research plays an important role. To probe the existence of cavitation induced hot spots generated with the cavitation unit from Arisdyn<sup>1</sup>, chemical model reactions are required. A model reaction has a simple and well known reaction mechanism and experimental data is available from previous work. The aim of this thesis is to prove the existence of controlled cavitation induced hot spots by using three model reactants.<sup>2</sup> For each model different concentrations of the contaminant in a defined volume are used. These model reactants are investigated under acoustic cavitation and hydrodynamic cavitation conditions.<sup>3</sup> The changing of several parameters like temperature, pressure, concentration and pH leads to a wide range of covered reaction conditions.

The thesis is organized as follows: Chapter 3 deals with the theory of the different forms of cavitation and introduces the 3 model reactants. The Methodology in chapter 4 provides specific and precise details about the model reactants and their reactions, used materials and instruments. Further it includes the basic calculation methods, result quantification and it describes and justifies the choices made referring to several parameters. Chapter 5 deals with the calculation of the results and the chemical explanations of specific results of every single model reaction. Every calculation is described on the basis of one randomly chosen input data set. At the end of each section, possible implications and open issues are discussed. Chapter 6 ends the thesis with a conclusion of the whole study. It analyses the achievement, lines out the limitations and gives an outlook for future work and applications.

---

<sup>1</sup> See Cavitation unit and in 3.2.1 for more details.

<sup>2</sup> See chapter 3 for more details.

<sup>3</sup> See chapter 4 for the experimental approach.

## 3 Theory

This thesis distinguishes two types of cavitation: Acoustic and hydrodynamic cavitation. In the following chapters (4-6) the acoustic cavitation is called ultrasonic cavitation (abbreviation UC) and the abbreviation of hydrodynamic cavitation is HC. It should be noticed that the reactor design, geometry of the cavitation unit and the kind of pollutant are very important parameters for the performance of cavitation (Gogate (2002, p. 335), Gogate et al. (2001, p. 2526), Gogate et al. (2011, p. 1066), Suslick, M. mdleleni, Millan and T. Ries, Jeffrey (1997, p. 9303). Kumar, P.S. and Pandit, A.B. (1999, p. 1017), Chand et al. (2007, p. 357)).

### 3.1 Ultrasonic cavitation

Through the study of sonochemistry, scientists try to understand the effect of ultrasound in forming UC in liquids. As a result of ultrasound induced cavitation the chemical activity in the solution is increased. This proves the fact that the chemical effects of ultrasound do not come from a direct interaction with molecular species. The bubble collapse during cavitation is able to concentrate the diffuse energy of sound to a very small volume element in the liquid. This phenomenon is responsible for effects like sonochemistry and sonoluminescence (Suslick 1990). That means that it is not the ultrasound that changes the chemical activity in the solution, however, it is responsible for the creation, growth and implosion of the bubbles. The local energy release during bubble collapse changes the chemical properties in the solution. Another very interesting effect is sonoluminescence whereby a liquid excited by sound, emits short flashes of light from imploding bubbles. The effect can occur when a sound wave with sufficient intensity induces a gaseous cavity within a liquid to collapse quickly.

#### 3.1.1 Generation of cavitation through ultrasound (Suslick 1990)

The nucleation process for every cavitation event is the formation of cavities in liquids. The acoustic expansion wave has a negative and positive pressure half and both are combined to one acoustic cycle. Under typical laboratory conditions the theoretical tensile strength of a pure liquid is too high to simply form cavities from the negative pressure of an acoustic expansion wave. Weak points in the liquid are fundamental for the nucleation of bubbles, such as gas-filled crevices in suspended particles or from already existing microbubbles from prior cavitation events.

There are several different mechanisms for the bubble growth in an irradiated liquid. A small cavity or bubble may grow rapidly through inertial effects if high - intensity ultrasound is applied. If the rate of expansion is sufficiently fast, the bubble will not have enough time to recompress during the positive-pressure half of the acoustic cycle. Slow cavity growth can also occur at lower acoustic intensities and is called rectified diffusion. This kind of diffusion bases on the fact that the cavity's surface area is slightly greater during expansion than during compression and therefore, growth processes are slightly faster than shrinking processes. Simply said, over many acoustic cycles, the cavity will grow. If the cavity or bubble reaches a specific size (resonant size) it is able to efficiently absorb energy from the

sound field (acoustic wave). This size depends on the frequency of the ultrasound. In this study a frequency of 20 kHz is used and the critical size of the bubble is 170  $\mu\text{m}$  in diameter. In phase with the sound field, such a cavity is able to grow rapidly in the course of one single expansion cycle. Once the cavity is too big, it can no longer efficiently absorb energy from the sound field and can no longer maintain itself. The cavity implodes as the surrounding liquid rushes in. In the moment of collapse free radicals are formed through the homolytic dissociation of water because of the aforementioned high temperature and pressure conditions. Especially the  $\dot{O}H$  - radical is known to be a strongly oxidizing species.

### 3.2 Hydrodynamic cavitation

d'Agostino, Luca and Salvetti, Maria Vittoria (2007, p. 8) reported that a local pressure drop generated by the flow itself is required to initiate the formation and growth of bubbles. A local pressure drop is for example realized by a venturi nozzle (Figure 1). The transition from a larger to a small and again to a larger pipe diameter leads to a maximum velocity of the liquid flow at the constriction. According to the Bernoulli equation, the pressure is minimized at the throat and the chance to create cavitation is maximized, when the throat pressure is smaller than the vapor pressure of the liquid.

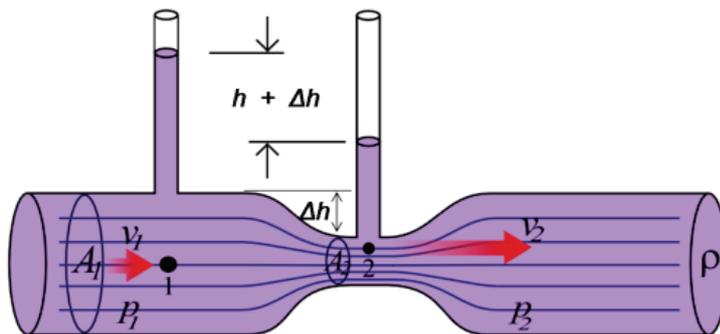


Figure 1: Venturi effect<sup>4</sup>; pressure drop due the diameter change from point 1 to point 2 results in an increased flow velocity in point 2.

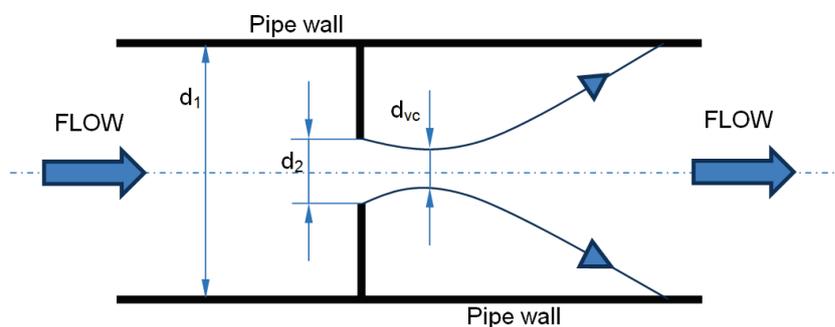


Figure 2: Orifice -  $d_1$  is the pipe diameter,  $d_2$  the opening size and  $d_{vc}$  vena contracta diameter.

<sup>4</sup> Wikipedia contributors. Venturi effect [Internet]. Wikipedia, The Free Encyclopedia; 2016 Jan 4, 16:56 UTC [cited 2016 Jan 9]. Available from: [https://en.wikipedia.org/w/index.php?title=Venturi\\_effect&oldid=698201539](https://en.wikipedia.org/w/index.php?title=Venturi_effect&oldid=698201539).

Very important examples for this study are orifices (Figure 2). Through enough throttling the pressure around the area of *vena contracta* can fall below the threshold pressure of cavitation. When this is the case, an uncountable number of cavities are generated. The threshold pressure is the required pressure to create cavitation and is normally defined as the vapor pressure of the medium at the operating temperature. After that local pressure drop the liquid jet expands and the pressure recovers which leads to the implosion or collapse of the cavities (Gogate et al. 2001). As reported for the UC, free radicals (oxidizing species) are formed at the time of implosion. In an earlier work, Kumar, P.S. and Pandit, A.B. (1999) reported two different applications referring to different inlet pressure: High inlet and recovered downstream pressure of the liquid through the venturi or orifice can be used to generate cavitation of higher intensity, necessary for influencing chemical reactions. Low inlet and recovered downstream pressure can be used to generate cavitation of low intensity required for applications, such as the removal of blue-green algae reported by Wu et al. (2012, p. 152).

### 3.2.1 Cavitation unit and the issue of comparability

As mentioned in the objective in 2.2, Arisdyne is using its own developed and patented cavitation unit. The company provides great flexibility by offering a range of different cavitation units in their product portfolio for miscellaneous applications. These cavitation or mixing units are following the principle technology of flow through orifices.

#### 3.2.1.1 Orifice dimensions

Number 5a and 5b in Figure 3 represent the mentioned units. These units are available in different sizes. In this study size 6/8 and 8/12 are used. The dimensions are the opening sizes in thousandths of an inch for one chamber (1 inch = 25.4 mm). That means unit 5a has an opening size of for example 6 thousandths and unit 5b of 8 thousandths of an inch. A 12 means twelve thousands of an inch.

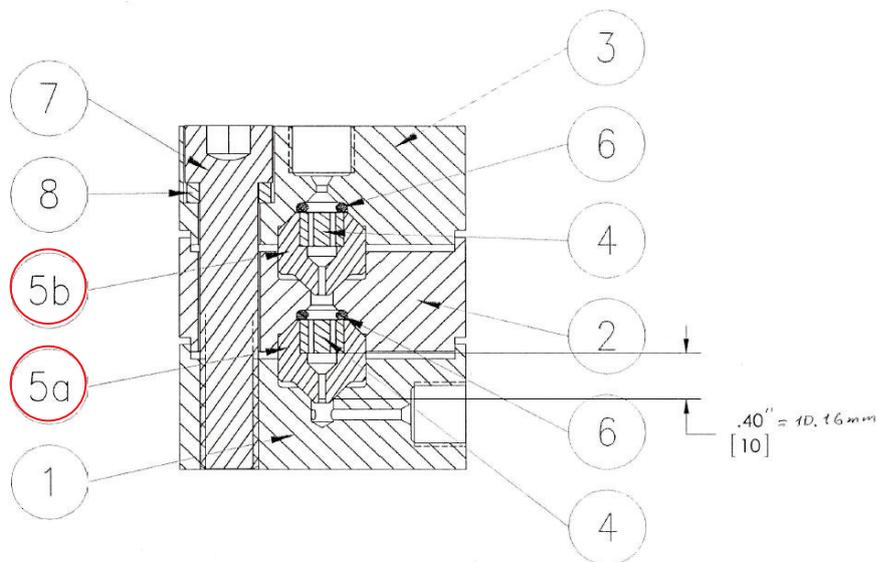


Figure 3: Original drawing of one cavitation chamber with two cavitation units; each chamber consists of two mixing units (5a and 5b) and two baffles (4) with four channels.

### 3.2.1.2 Retention time

The retention time describes the time the solution is treated with HC. Compared to UC, where the solution is treated under static conditions (without any macro - motion of the fluid except the motion through the induced ultrasound waves) the fluid is in constant motion in the HC system because it is pumped through the loop. With the HC system the cavitation is only created in a very specific location in the cavitation unit. In case of the UC system the effective volume is limited by the surface area of the transducer which creates the ultrasound (ultrasonic horn, ultrasonic flow cell and other different types of reactors (Gogate et al. 2011, p. 1067)) and the fluid volume in the boundary layer at the transducer surface is always much bigger in comparison with the effective fluid volume in the HC system.

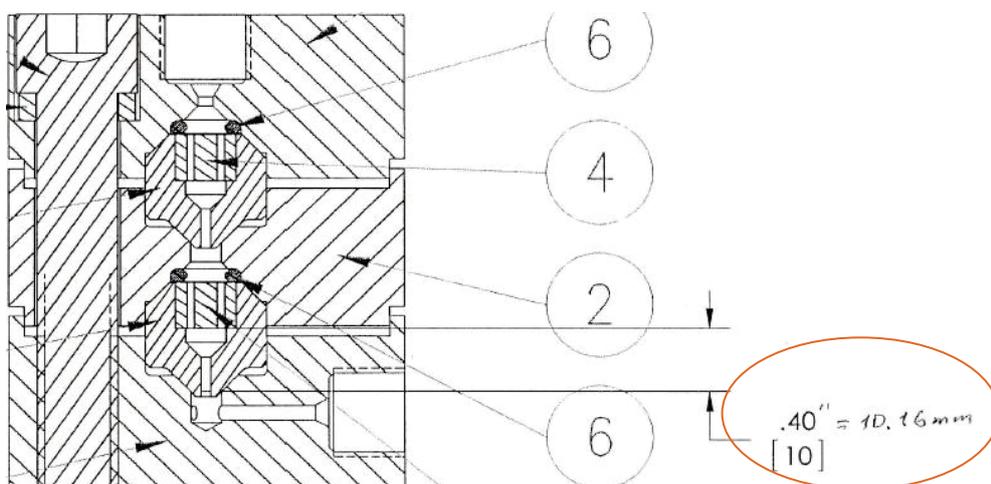


Figure 4: The marked value ( $h = 10.16 \text{ mm}$ ) indicates the length of the inlet channel.

Table 1: Calculated reactor volume (Equation 1) and retention time (Equation 2).

orifice dimension	diameter	area	reactor volume	reference pressure	reference pressure	volume flow	volume flow	retention time
thousands of an inch	d	A	VR	p	p	V_point	V_point	τ
-	m	m <sup>2</sup>	m <sup>3</sup>	psi	Pa	ml/min	m <sup>3</sup> /s	s
6	1.5E-04	1.8E-08	1.9E-10	2500	1.7E+07	142	2.4E-06	7.83E-05
				5000	3.4E+07	200.5	3.3E-06	5.55E-05
				10000	6.9E+07	283.5	4.7E-06	3.92E-05
				15000	1.0E+08	347.2	5.8E-06	3.20E-05
8	2.0E-04	3.2E-08	3.3E-10	2500	1.7E+07	142	2.4E-06	1.39E-04
				5000	3.4E+07	200.5	3.3E-06	9.86E-05
				10000	6.9E+07	283.5	4.7E-06	6.97E-05
				15000	1.0E+08	347.2	5.8E-06	5.69E-05
12	3.0E-04	7.3E-08	7.4E-10	1000	6.9E+06	167.3	2.8E-06	2.66E-04
				2500	1.7E+07	264.2	4.4E-06	1.68E-04

It should be noted that the values for the volume flow in Table 1 and Table 3 are for continuous flow and measured with new cavitation units (courtesy of Arisdyn). In this study a plunger pump<sup>5</sup> is used which means a pounding delivery of the liquid. These values can be used because the volume flow inside the cavitation chamber is the same in both cases. The same argument holds for the calculation of the cavitation number in 3.2.2.2. Table 1 presents the retention time for the HC system for one cavitation unit. According to Figure 3 and Figure 4 two units are used for the study, which results in a very short retention time for a very small liquid volume for the stated example where a 6/8 chamber is used.

$$V_R = \frac{d^2 * \pi}{4} * h = \frac{(1.5 * 10^{-4} m)^2 * \pi}{4} * 1.02 * 10^{-2} m$$

$$= 1.9 * 10^{-10} m^3$$

Equation 1

$$Retention\ time\ \tau = \frac{V_R}{\dot{V}} = \frac{1.9 * 10^{-10} m^3}{2.4 * 10^{-6} \frac{m^3}{s}} = 7.83 * 10^{-5} s$$

Equation 2

On the whole the results show that the retention time is extremely short compared to the retention time in the UC system.

## 3.2.2 Cavitation number

### 3.2.2.1 Definition and theory

The amount or intensity of cavitation is characterized by a non dimensional parameter, the cavitation number  $\sigma_c$ , defined by:

$$\sigma_c = \frac{(p_{ref} - p_v)}{(\frac{1}{2} * \rho * v_{th}^2)}$$

Equation 3

<sup>5</sup> See Figure 11 in 4.3.2.1.

In this expression,  $p_{ref}$  is a reference pressure taken at a given point in the liquid flow,  $v_{th}$  is a characteristic flow velocity,  $p_v$  is the vapor pressure and  $\rho$  the density of the liquid. The reference pressure and the flow velocity need to be precisely specified for each practical situation. Density and vapor pressure are temperature dependant parameters. Large values of the cavitation number imply a non cavitating flow. This is easy to understand because high reference pressures usually correspond to large values of the cavitation number but this is not the dominant parameter if the flow velocity is high enough. In the first case, it can be expected that the pressure will be everywhere above the vapor pressure of the liquid and the flow will remain free of cavitation. This number is a relevant scaling parameter only for cavitating flows and it measures the global extent of cavitation. Cavitation generally appears for a critical value of the cavitation number known as the incipient or beginning cavitation number  $\sigma_i$ . The point of cavitation inception can be reached either by decreasing the reference pressure or increasing the flow velocity which leads in both cases to smaller cavitation numbers. Any further decrease will lead to an additional development of cavitation. Increasing the reference pressure afterwards means that cavitation disappears for a critical cavitation number somewhat higher than  $\sigma_i$  (d'Agostino, Luca and Salvetti, Maria Vittoria 2007, p. 9).

### 3.2.2.2 Calculation

One example (orifice dimension 6, pressure 2500 psi and temperature 20°C) for the calculation of the cavitation number is shown. The equations and explanations can be found below Table 3.

There are 4 assumptions for the calculation of the cavitation number:

1. Constant volume flow through the mixing unit at the same point (Figure 5).
2. The data for vapor pressure and density are for water because of the low concentration of the model reactants in the initial solution (Table 2).

Table 2: Vapor pressure<sup>6</sup> and density<sup>7</sup> of water at different temperatures.

water temperature	vapor pressure	density water
$T_w$	$p_v$	$\rho$
°C	Pa	kg/m <sup>3</sup>
5	866.3	999.97
10	1221.2	999.70
20	2329.8	998.21
36	5927.2	993.69
42	8180.5	991.44
65	24949.1	980.55

3. Point where hydrodynamic cavitation occurs (Figure 5).
4. Pipe resistances are not considered.

<sup>6</sup> <http://www.endmemo.com/chem/vaporpressurewater.php>; requested 1/5/2016.

<sup>7</sup> <http://www.internetchemie.info/chemiewiki/index.php?title=Wasser-Dichtetabelle>; requested 1/5/2016.

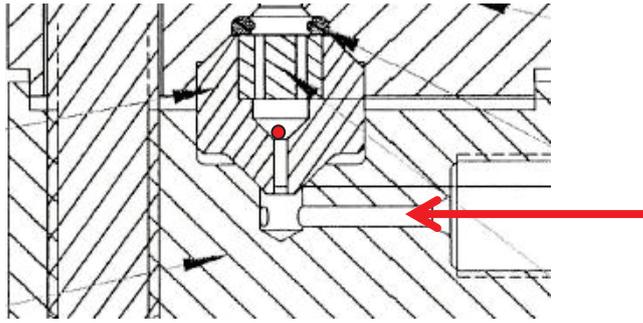


Figure 5: The red circle presents the relevant point for the calculation after the throat of the orifice where the smaller diameter changes to a bigger diameter; the red arrow shows the direction of flow.<sup>8</sup>

Table 3: Calculated outflow velocity from the throat.

orifice dimension	diameter	area	reference pressure	reference pressure	volume flow	volume flow	velocity
thousands of an inch	d	A	p	p	V_point	V_point	vth
-	m	m <sup>2</sup>	psi	Pa	ml/min	m <sup>3</sup> /s	m/s
6	1.5E-04	1.8E-08	2500	1.7E+07	142	2.4E-06	129.7
			5000	3.4E+07	200.5	3.3E-06	183.2
			10000	6.9E+07	283.5	4.7E-06	259.0
			15000	1.0E+08	347.2	5.8E-06	317.2
8	2.0E-04	3.2E-08	2500	1.7E+07	142	2.4E-06	73.0
			5000	3.4E+07	200.5	3.3E-06	103.0
			10000	6.9E+07	283.5	4.7E-06	145.7
			15000	1.0E+08	347.2	5.8E-06	178.4
12	3.0E-04	7.3E-08	1000	6.9E+06	167.3	2.8E-06	38.2
			2500	1.7E+07	264.2	4.4E-06	60.3

To calculate the flow velocity, the continuity equation (Equation 4) is transformed into Equation 6 ( $\dot{V}$  is the volume flow,  $A$  is the cross-sectional area and  $v_{th}$  the flow velocity). The area of the throat is calculated with Equation 5 ( $d$  is the opening diameter). This calculation is made for each orifice dimension for the full range of the applied pressures (Table 3).

$$\text{Continuity equation: } \dot{V} = A * v_{th} \quad \text{Equation 4}$$

$$A = \frac{d^2 * \pi}{4} = \frac{(1.5 * 10^{-4} \text{ m})^2 * \pi}{4} = 1.8 * 10^{-8} \text{ m}^2 \quad \text{Equation 5}$$

$$w = \frac{\dot{V}}{A} = \frac{2.4 * 10^{-6} \frac{\text{m}^3}{\text{s}}}{1.8 * 10^{-8} \text{ m}^2} = 129.7 \frac{\text{m}}{\text{s}} \quad \text{Equation 6}$$

The experimental setup, the geometry of the cavitation unit and the compared high inlet pressures indicate the existence of a critical pressure and consequential a critical mass flux.

<sup>8</sup> For details see Cavitation unit and the issue of comparability in 3.2.1.

Firstly, 3.2.2.3 shows the calculation of the critical pressure and associated mass flux and secondly, the calculation of the cavitation number.

### 3.2.2.3 Calculating critical mass flux (VDI Heat Atlas 2010, p. 1171)

If the pressure at the inlet cross section of a nozzle, an orifice, or any other duct is kept constant and the pressure at the exit cross section is reduced step by step, the mass flux increases. If the pressure falls below a certain value, no further increase in mass flux is observed and the mass flux is limited to the critical mass flux. In general the reason for critical flow is the compressibility of the fluid. Compressible effects are important for gaseous flow and even more for liquid - gaseous two phase flow; e.g. cavitating bubble flows. The potential energy contained in the pressurized gas phase at the inlet is transformed into kinetic energy of the two-phase flow. An exceedance of the critical mass flux  $\dot{m}_c$  is not possible because otherwise the kinetic energy in the exit cross section due to the high velocity would exceed the released potential energy. Thus, the mass flux is limited to the critical mass flux.

To calculate the critical mass flux, the Homogeneous Nonequilibrium Model is used. The related equations and transformations can be found in VDI Heat Atlas (2010, p. 1177). Under the given conditions the mass transfer between the liquid and gas phases is negligible. This is the case if the gas phase consists of a noncondensable gas and the vapor pressure  $p_{lg}$  of the liquid is comparatively low to the pressure levels along the stream path (downstream pressure is much higher than the vapor pressure). These conditions apply for the co-current flow of water and air because of the extremely short time interval for gas - liquid mass transfer, which is the case in the presented experiments.

The following assumptions are made for the model:

- No mass transfer takes place between the gas and liquid. In many cases, a remarkable amount of gas can be dissolved in the liquid and due to pressure reduction along the stream path, desorption can occur. Mostly, the time of residence inside the fitting is so short that the amount of desorbed gas can be neglected. The diffusive resistance of the gaseous component inside the liquid is comparatively high to the evaporation rate of a single component liquid and therefore, desorption does not play an important role.
- The liquid and gas have the same velocity, and the slip is one.
- The wall friction is zero.
- The change of conditions of the two-phase flow mixture between the inlet and exit of the fitting is adiabatic.

Figure 6 presents the situation in the cavitation chamber of Arisdyne, which is similar to Fig. 2 in VDI Heat Atlas (2010, p. 1172).

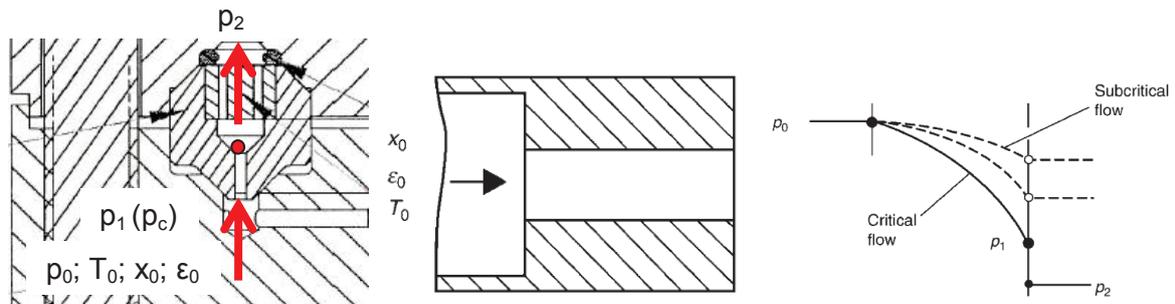


Figure 6: Left picture: Current situation at the cavitation unit. Middle picture: Used model for the Homogeneous Nonequilibrium Model ( VDI Heat Atlas 2010, p. 1171). Right picture: Pressure over distance and different types of flow for the given model.

$T_0$ ,  $p_0$ ,  $x_0$  and  $\epsilon_0$  are the parameters of the incoming flow,  $p_1$  the pressure in the smallest cross section and  $p_2$  the counterpressure in the exit cross section (Table 4 and Table 5).  $p_c$  is defined as the critical pressure and  $p_1 = p_c$  when  $p_2 < p_c$  which is true for the used system (the flow is critical).

Table 4: Constant values for the calculation acc. to the Homogeneous Nonequilibrium Model (VDI Heat Atlas 2010, p. 1177).

name	value	unit	comment
$p_2$	101325	Pa	counterpressure
$\epsilon_0$	0.006802721		volumetric gas fraction
$S_{O_2}$	9	mg/l	Solubility $O_2$ in water at 20°C
$\rho_{O_2}$	1.314	mg/ml	density oxygen at 20°C
	1.1894	kg/m <sup>3</sup>	density air at 20°C
$\rho_{H_2O}$	0.998207	g/ml	density water at 20°C
	998.207	kg/m <sup>3</sup>	
$V_{g,0}$	2.739726027	ml	initial volume gas
$V_{f,0}$	400	ml	initial volume fluid
$d_0$	5	mm	duct's diameter in front of the orifice
	0.005	m	

Table 5: Substance data for water<sup>9</sup> and oxygen<sup>10</sup> at the given pressure.

reference pressure		Water				Oxygen				
		density at 20°C	specific density at 20°C	heat capacity fluid	heat capacity fluid	density at 20°C	specific density at 20°C	heat capacity gas	heat capacity gas	isentropic coefficient
$p_0$	$p_0$	$\rho_f$	$V_f$	$C_{p,f}$	$C_{v,f}$	$\rho_g$	$V_g$	$C_{p,g}$	$C_{v,g}$	K
psi	Pa	kg / m <sup>3</sup>	m <sup>3</sup> / kg	kJ/kgK	kJ/kgK	kg / m <sup>3</sup>	m <sup>3</sup> / kg	kJ/kgK	kJ/kgK	
1000	6.9E+06	1001.29	1.0E-03	4.16	4.13	94.39	1.1E-02	1.04	0.67	1.54
2500	1.7E+07	1005.91	9.9E-04	4.13	4.10	241.75	4.1E-03	1.22	0.69	1.75
5000	3.4E+07	1013.40	9.9E-04	4.09	4.05	447.88	2.2E-03	1.34	0.71	1.88
10000 <sup>11</sup>	6.9E+07	1027.62	9.7E-04	4.02	3.96	573.60	1.7E-03	1.34	0.73	1.84

<sup>9</sup> Data water from [http://www.peacesoftware.de/einigewerte/wasser\\_dampf.html](http://www.peacesoftware.de/einigewerte/wasser_dampf.html); requested 1/5/2016.

<sup>10</sup> Data oxygen from <http://www.peacesoftware.de/einigewerte/o2.html>; requested 1/5/2016.

<sup>11</sup> Data for 15000 psi and 10000 psi are not available - the given data are for 500 bar (approx. 7200 psi).

Table 6: Calculated gas mass flow fraction and discharge coefficient for the fluid.

volume flow fluid	mass flow fluid	mass flow gas	gas mass flow fraction	duct's diameter	diameter orifice	Area	discharge coefficient fluid	diameter ratio
$\dot{V}_f$	$\dot{M}_f$	$\dot{M}_g$	$\dot{x}$	$d_0$	$d_1$	A	$C_{d,f}$	$\beta$
m <sup>3</sup> /s	kg/s	kg/s	-	m	m	m <sup>2</sup>	-	-
2.8E-06	2.8E-03	2.5E-08	9.0E-06	0.005	3.0E-04	7.30E-08	0.6142	0.061
2.4E-06	2.4E-03	2.1E-08	8.9E-06	0.005	2.0E-04	3.24E-08	0.6140	0.041
3.3E-06	3.4E-03	3.0E-08	8.9E-06	0.005	1.5E-04	1.82E-08	0.6139	0.030
4.7E-06	4.9E-03	4.3E-08	8.8E-06	0.005	1.5E-04	1.82E-08	0.6139	0.030

Table 7: Calculated critical pressure and mass flux.

two phase isentropic exponent	critical pressure ratio	critical pressure		critical mass flux	orifice dimension	pressure jump	void fraction	v1	v2	v3
$\Gamma$	$\eta_c$	$p_c$		$\dot{m}_c$	thous. of an inch	$\Delta p$	$\epsilon_{g,1}$	$K_N$	w	f
-	-	Pa	psi	kg/sm <sup>2</sup>	-	Pa	-			
1.007	0.1070	<b>7.4E+05</b>	<b>106.97</b>	<b>110958.7</b>	12	6.4E+05	4.06E-04	0.413	0.349	0.3028
1.009	0.1068	<b>1.8E+06</b>	<b>266.92</b>	<b>175946.2</b>	8	1.7E+06	1.33E-04	0.473	0.376	0.3023
1.011	0.1064	<b>3.7E+06</b>	<b>532.04</b>	<b>249833.9</b>	6	3.6E+06	6.62E-05	0.506	0.389	0.3022
1.016	0.1056	<b>7.3E+06</b>	<b>1056.21</b>	<b>355957.8</b>	6	7.2E+06	5.32E-05	0.494	0.385	0.3022

Table 8: Calculated discharge coefficient, flow velocity and cavitation number.

discharge coefficient	mass flow	volume flow	flow velocity	Temperature	vapor pressure	cavitation number
$C_d$	$\dot{M}$	$\dot{V}$	w	$T_w$	$p_v$	$\sigma_c$
	kg/s	m <sup>3</sup> /s	m/s	°C	Pa	-
0.765	6.19E-03	6.18E-06	<b>84.73</b>	20.0	2329.8	<b>0.2046</b>
0.767	4.38E-03	4.35E-06	<b>134.20</b>			<b>0.2029</b>
0.769	3.50E-03	3.46E-06	<b>189.50</b>			<b>0.2015</b>
0.769	4.99E-03	4.86E-06	<b>266.26</b>			<b>0.1999</b>

The values in Table 6 are required for the critical pressure and mass flux which are displayed in Table 7. Table 8 shows the corrected mass flow and flow velocity in combination with Equation 4, Equation 5 and Equation 6. The cavitation number is calculated with Equation 7 for the reference pressure of 1000 psi.

$$\sigma_c = \frac{(p_{ref} - p_v)}{\left(\frac{1}{2} * \rho * v_{th}^2\right)} = \frac{(7.4 * 10^5 - 2329.8) Pa}{\left(\frac{1}{2} * 1001.29 \frac{kg}{m^3} * (84.73 \frac{m}{s})^2\right)} \quad \text{Equation 7}$$

$$= 0.2046$$

As mentioned in 3.2.2.1, cavitation performance increases if the value for the cavitation number decreases. A cavitation number smaller than one means that hydrodynamic cavitation occurs (Kalumuck 2000). The results indicate that the used cavitation unit reaches

small cavitation numbers (Table 8) and the number increases by increasing the temperature and decreases by increasing the reference pressure. It should be noted that the value changes only slightly in both directions. The calculated velocities in Table 3 are theoretically true but the mass flow is limited and consequently the velocity changes. The trend of the cavitation number indicates that the increased inlet pressure has practically no influence on the cavitation performance. Generally speaking, the investigated cavitation unit creates cavitation in all applied settings.

### 3.2.3 The effect of pressure

In case of HC the operating parameter “inlet pressure” is very important. This is the pressure the liquid medium is pumped into the cavitation chamber and through the cavitation unit. Referring to the continuity equation (Equation 4) a pressure increase at the inlet as well as decreasing the cross-sectional diameter leads to a flow velocity increase. High values for the flow velocity results in a turbulence regime after the orifice at the point of *vena contracta* (Figure 2). To define the turbulence regime the dimensionless Reynolds number is needed (Equation 8).  $Re_{crit}$  in Equation 9 shows the transition range where the laminar flow changes to the turbulence. It turns out that cavitation only occurs in the turbulent flow regime.<sup>12</sup>

$$Re = \frac{w * d * \rho}{\eta} \quad \text{Equation 8}$$

$$Re_{crit} \approx 2400 \mp 100 \quad \text{Equation 9}$$

An empirical look at cavitation shows that high inlet pressure and flow rates lower the bubble growth, the amount of captured vapor molecules and, as a consequent, the intensity of collapse but increases the number of cavities. The collapse intensity is affected because at higher pressure the flow rate increases, leaving less time for the bubble to grow and generating higher turbulence stresses which act against the expansion of the bubble. The increased number of cavities at higher  $p_{in}$  is the opposite of higher specific radical production at lower pressure. The relation between high and low pressure and the cavitation number is given in 3.2.2.1. The study from Capocelli et al. (2014a, p. 2569) introduces a slight dependence of radical production on initial radius of the bubble. In their study they stress that there is a strong dependence of the collapse bubble size on the turbulence intensity and, consequently, on  $p_{in}$ . The initial size of the bubble is of minor importance because the collapse is controlled by the inlet pressure at a fixed geometry of the bubble.

Higher inlet pressure induces more cavities but less production of radicals. Lower inlet pressure leads to an increased production of free radicals and the number of cavities is smaller, however the bubbles size is bigger (more vapor molecules).

## 3.3 Another cavitation effect: Generation of radicals

As mentioned in the Introduction, UC and HC cause high temperature and high pressure. In both cases this energy release is high enough for the dissociation of vapors trapped in the

<sup>12</sup> See Avila et al. 2011 for more details.

cavitating bubbles (Parag R. Gogate and Abhijeet M. Kabadi (2009)) and can therefore be used to provide extremely reactive species like  $OH^\cdot$ -,  $O^\cdot$ - and  $HOO^\cdot$ - radicals (Suslick 1990, Saharan et al. 2012, p. 1981). This finding has been implemented as an Advanced Oxidation Process (AOP) (Capocelli et al. 2014a, p. 2566). AOP can be defined as the process that involves formation and following attack of free radicals, which are capable of oxidizing organic compounds and attacking inorganic molecules. Beside cavitation, Saharan et al. (2012, p. 1981) reports alternative types of AOPs like photocatalytic oxidation (using UV light/sunlight in the presence of semiconductor catalyst), Fenton chemistry (using reaction between Fe-ions and hydrogen peroxide), and chemical oxidation (use of ozone and hydrogen peroxide).

### 3.4 Comparison between ultrasonic and hydrodynamic cavitation

The main differences between UC and HC referring to generation and flow mechanism are explained in 3.1 and 3.2. From the energy efficiency point of view, HC represents a cheaper and more energy efficient method for generating cavitation than UC (Capocelli et al. 2014b, p. 17). Kalumuck (2000, p. 466) and Gogate (2002) report that the equipment used for generating HC is more simple, flexible and the maintenance effort of such systems (loop and reactor) is very low. Pertinent literature also outlines the good scale - up properties from HC contrary to the corresponding problems with UC (Gogate et al. 2011, p. 1067).

### 3.5 Model reactants and associated reactions

This chapter is about the choice, applicability and limitations of the three model reactants and associated reactions used in this study.<sup>13</sup>

#### 3.5.1 Inorganic reactions

One inorganic model reactant that is suitable for this study is used by Gogate et al. (2001). In their study they investigate the *Weissler*<sup>14</sup> reaction to prove cavitation. Free radicals, formed under cavitating conditions, attack the KI (Potassium Iodide) and liberate iodine. The liberated iodine reacts, after a series of intermediate steps, to the tri-iodide complex  $I_3^-$ . Morison, K. and Hutchinson, C. (2009, p. 176) established limitations of the Weissler reaction referring to the comparability of UC and HC. They argue that this reaction is inappropriate because the  $I_3^-$ - complex may form during hydrodynamic flow, with and without cavitation. The potential limitations of this reaction led to the conclusion that a second inorganic model reaction is required. From a search for a suitable reaction system the oxidation from sulfite to sulfate as a model reaction turned out as a candidate. Free radicals, again formed under cavitating conditions, form hydrogen peroxide ( $H_2O_2$ ) which is an oxidizing agent capable oxidize sulfite to sulfate. This expected theoretical mechanism needs evidence. To the knowledge of the author of this thesis, currently no reference exists that describes the oxidation of sulfite forced by UC or HC.

<sup>13</sup> Chemism of the model reactions is explained in detail in chapter 4.

<sup>14</sup> Named after A. Weissler, H.W. Cooper, S. Snyder, J. Am. Chem. Soc. 72 (1950) 1769–1775.

### 3.5.2 Organic reactions

Beside the inorganic reactions it is very important to investigate the behavior of organic reactions under cavitating conditions. The third model reactant for this thesis is converted by an organic reaction and has been chosen from several authors like Capocelli et al. (2014a, p. 2568) and Kalumuck (2000, p. 467). They used the degradation of PNP (Para Nitrophenol) or 4-Nitrophenol for their study. In this case the free radicals form an oxidizing agent and this agent oxidizes the PNP to several products which are less harmful compared to the reactant.

## 4 Methodology

The purpose of this work is to prove the existence of cavitation hot spots. HC and UC are tested by the performance of three different model reactions.

### 4.1 Chemical model reactions

#### 4.1.1 Radical chemistry

A radical is an atom, ion or molecule that has unpaired valency electrons. Equation 10 shows the decomposition of water into hydrogen and hydroxyl radicals. Through a process called homolysis, which requires a certain amount of energy (homolytic bond dissociation energies), covalent bonds break. The break of the covalent bond can be realized by any process that puts enough energy into the water molecule (parent molecule). Previous work, for example from Kalumuck (2000), shows that the energy created by cavitation is enough to form free radicals.



The majority of the radicals are highly reactive towards themselves or other substances. Hydrogen peroxide, which is a strong oxidizing agent, is formed by hydroxyl radicals (Equation 11).



Because of their high reactivity the free radicals attack other substances. This form of "attack" is used in all three model reactions used in this thesis.

#### 4.1.2 Inorganic reactions

The fundamental chemism in 4.1.1 is a central step for the conversion of all model reactants and therefore should be kept in mind as basis for the following sections.

##### 4.1.2.1 Iodine liberation

Equation 12 presents the Weissler reaction which has been used for many years to indicate the presence of oxidizing species.



Alternatively, the free radicals attack the potassium iodide and liberate iodine (Equation 13). The complex  $I_3^-$  is formed after several steps (Equation 14, Equation 15 and Equation 16) and is responsible for the yellow and brown color of the samples. A high concentration of this complex is associated with a high intensity of the brown color in the solution.





When starch (Table 10) is added to the solution, a blue colored complex is formed. This blue color makes a photometric measurement<sup>15</sup> possible for concentrations as low as  $2 \times 10^{-5}$  mole/l at 20°C.<sup>16</sup> The mechanism of this reaction is not fully clarified, but scientists think that the iodine ( $I_3^-$  and  $I_5^-$  ions) fit inside the coils of amylose. The charge transfers between the iodine and the starch, and the level of energy spacings in the resulting complex, correspond to the absorption spectrum in the visible light region.

#### 4.1.2.2 Sulfite oxidation

Hydrogen peroxide reacts with the sulfite and oxidizes it to sulfate (Equation 17). This model reaction should prove the existence of cavitation induced hot spots generated in the cavitation unit.



The necessary reactant for the oxidation from sulfite to sulfate is an oxidation agent like hydrogen peroxide or oxygen.<sup>17</sup> Air consists of 21 % atmospheric oxygen. This oxygen has an impact on the reaction and accelerates the oxidation in an uncontrolled way. To avoid the contact, the whole process must be purged with an inert gas, for example nitrogen.<sup>18</sup>

#### 4.1.3 Organic reaction

##### 4.1.3.1 The degradation of PNP (Para - Nitrophenol)

**Reaction mechanism and removal pathway of PNP.** The advanced oxidation process (AOP) with pseudo-first order kinetics works better in an acidic environment but ions like  $HCO_3^-$ ,  $NO_3^-$  and  $Cl^-$  slow down the degradation. Intermediate products are hydroquinone, 1,2,4 - trihydroxybenzene, 4-nitropyrogallol and 4 - nitrocatechol (Zhang et al. (2003, p. 788)). Two different possible ways are proposed by Zhang et al. (2003, p. 793) where  $\dot{O}H$  radicals attack different positions in the benzene ring to form the mentioned hydroxylated compounds of PNP. One path describes a forming of molecules with no nitrogen ( $NO_2^-$  release through the free radical attack). The second one leads to small molecules which contain nitrogen. In both ways the PNP is subsequently oxidized by ring cleavage to yield compounds with and without nitrogen. This model reaction should again

<sup>15</sup> See chapter 4.2 for analytical procedure.

<sup>16</sup> Wikipedia contributors. Iodine test [Internet]. Wikipedia, The Free Encyclopedia; 2015 Dec 2, 16:35 UTC [cited 2016 Jan 9]. Available from: [https://en.wikipedia.org/w/index.php?title=Iodine\\_test&oldid=693443633](https://en.wikipedia.org/w/index.php?title=Iodine_test&oldid=693443633).

<sup>17</sup> It should be noticed that a free radical like  $\dot{H}$  or  $\dot{O}H$  is completely different compared to the cation  $H^+$  or anion  $OH^-$ . For example is the  $OH^-$  ion not a free radical because the unpaired electron is resolved by the addition of an electron.

<sup>18</sup> See chapter 4.3 for experimental setup.

prove the existence of cavitation induced hot spots and the ability of the used system to remove organic contaminants from water.

**Handling and application of PNP.** PNP normally occurs as a yellow powder and is a intermediate in the synthesis of paracetamol which is used in medication to reduce fever (Ellis 2002). This medication respectively the intermediates, get into the water circuit through the metabolism and finally excretion. PNP irritates the eyes, skin, and respiratory tract. It may also cause inflammation of those parts. It has a delayed interaction with blood and forms methaemoglobin which is responsible for methemoglobinemia, potentially causing cyanosis, confusion, and unconsciousness (Agency for Toxic Substances and Disease Registry U.S. Public Health Service 1992). As a solution it is used as a pH indicator. In a neutral state the solution is pale yellow and the intensity increases by increasing the pH. Under acidic conditions the solution turns into water clear appearance.

## 4.2 Analytical procedure

A calibration chart is required for each model reaction to calculate the concentration of the contaminant after HC and UC. The calibration charts base on the photometric measurement, realized by a UV/VIS spectrometer at different wavelengths for different contaminants. The calibration was established at Colorado School of Mines (Golden, Colorado, USA), Department for Civil- and Environmental Engineering (CEE), Coolbaugh Hall, AQWATEC<sup>19</sup> lab number 323. Table 9 shows the used instruments and lab equipment. The weighting is realized through a scale with high accuracy. Weighting papers and ships are used to put the chemicals into the beaker. An electronic digital pipette from RAININ is used for the small volumes from 0.01 to 4 ml. The manual pipette from HACH is used for volumes up to 10 ml. The beakers and any other glassware are covered with a stopper or PARAFILM to avoid contamination through the air. It should be noted that the samples from Arisdyn are mailed from Cleveland, Ohio to the CEE department.

Table 9: Instruments and lab equipment for all three model reactants with available manufacturer's data.

UV/VIS - Beckman Coulter DU 800 Spectrometer; computer program: DU 800 Spec
Scale - Mettler AE 163 (accuracy of 4 digits after the decimal point)
Electronic digital pipette 1000µl (edp RAININ)
pH meter accumet AB 81209951 (Fisher Scientific) with a VWR probe
Florence flasks 10, 50, 100, 250 ml from PYREX and VWR
Beakers 50, 250, 500 ml from PYREX, VWR and KIMAX
Small glassware
Pipette Hach 10 ml - TenSette Pipette
Washing bottle
Spatula
Bunsen burner

<sup>19</sup> <http://aqwatec.mines.edu/>; requested 1/5/2016.

Cuvettes

Funnel

Weighting paper

DI water creation device Ultrapure (Type1) water from Synergy UV-R (18,2 MΩ.cm 25°C)

PARAFILM

Each model reactant needs special chemicals for the calibration (Table 10). The reason the iodine solution with the expiration date 2000 has though been used needs a more detailed explanation. Oxidizing materials which could have contaminated the solution by mistake could decompose the iodine which is unlikely in relevant amount. A leaking bottle through wrong storage could lead to an evaporation of iodine and is also excluded because of the original sealing of the reagent bottle. The author and the supervisors of this thesis accepted the use of this iodine solution.

Table 10: Specific chemicals for the model reactions.

Liberation of iodine	Oxidation of sulfite	Degradation of PNP
Iodine solution 0.2 N (0.1 mole/l) Fisher Scientific SI106-1 UN2920 (Expiration date 2000)	DTNB (Ellman's reagent (5,5'-dithiobis-(2-nitrobenzoic acid))	4-Nitrophenol, 98 % (SIGMA - ALDRICH, 425753-1KG, CAS 100-02-7)
Starch (potato starch flour from SWAN)	HOAc (acetic anhydride 99 % Aldrich 320102)	Sodium Hydroxide, Pellet (MACRON - Fine Chemicals, 500 g, Batch No: 0000026134)
	Na <sub>2</sub> CO <sub>3</sub> (sodium carbonate anhydrous Fisher Scientific S263-3)	
	Na <sub>2</sub> SO <sub>3</sub> (Sodium sulfite anhydrous Fisher Scientific S 447-3)	

## 4.2.1 Calibration method: Liberation of iodine

### 4.2.1.1 Stock solution from the standard solution

The standard solution with a concentration of  $0.1 \frac{\text{mole}}{\text{l}}$  is used to prepare a stock solution. 3.94 ml (Equation 18 and Equation 19) from the standard solution are pipetted into a 100 ml flask and filled up with DI water to generate the stock solution with  $\frac{100 \text{ mg}}{100 \text{ ml}}$ .

$$C_{\text{standard}} = MW_{I_2} * C_{I_2} = 253.81 \frac{\text{g}}{\text{mole}} * 0.1 \frac{\text{mole}}{\text{l}} = 25.38 \frac{\text{g}}{\text{l}} \quad \text{Equation 18}$$

$MW_{I_2}$  is the molar weight of iodine and  $c_{I_2}$  is the given concentration from the manufacturer.

$$V_{\text{standard}} = c_{\text{wanted}} * V_{\text{wanted}} * \frac{1}{C_{\text{standard}}} \quad \text{Equation 19}$$

$$= \frac{100 \text{ mg}}{100 \text{ ml}} * 100 \text{ ml} * \frac{1000 \text{ ml}}{25380.9 \text{ mg}} = 3.94 \text{ ml}$$

$c_{\text{standard}}$  is the calculated standard concentration from Equation 18,  $V_{\text{standard}}$  the necessary volume,  $c_{\text{wanted}}$  the defined concentration and  $V_{\text{wanted}}$  the wanted amount of the standard

solution. To get a solution with  $1 \frac{mg}{l}$ , 10  $\mu l$  of the stock solution are pipetted into a 10 ml flask and filled up with DI water. This procedure works up to  $1000 \frac{mg}{l}$ , where 10000  $\mu l$  are pipetted into a 10 ml flask.

#### 4.2.1.2 Preparation of solutions for the calibration

For the analysis of the samples 10 ml of each solution is pipetted into small glassware (approx. 50 ml). To use the UV/VIS for the analysis it is necessary to add 4 ml of starch solution to each 10 ml sample.<sup>20</sup> The starch solution with a concentration of  $\frac{1 g}{100 ml}$  is boiled for approx. 15 minutes on a hot plate (Gogate et al. 2001, p. 2528). A filtration of the jelly and milky looking solution is necessary. After pipetting the starch solution to the samples the solution changes its color from copper brown to blue or purple. The intensity depends on the concentration. The last step is to fill it into the cuvette. The cuvette is the same for every test. After every test the cuvette is cleaned with two or three rinses of DI water. It is very important to keep the cuvette clean and not touch it without gloves.

#### 4.2.1.3 Measuring with the UV/VIS

For this calibration 10 solutions (Table 11) with different concentrations plus one blank (starch solution) are measured at a wavelength of 353 nm. The results are shown in Table 11 and the calibration chart in Figure 7.

Table 11: Liberation of iodine: concentration and extinction of the calibration solutions.

concentration	extinction
mg/l	-
50	0.3573
45	0.3379
40	0.306
35	0.2854
30	0.2346
25	0.1908
20	0.181
15	0.1698
10	0.1505
5	0.1393
0	0.127

<sup>20</sup> See 4.1.2.1 for more details about starch chemistry.

#### 4.2.1.4 Calibration chart

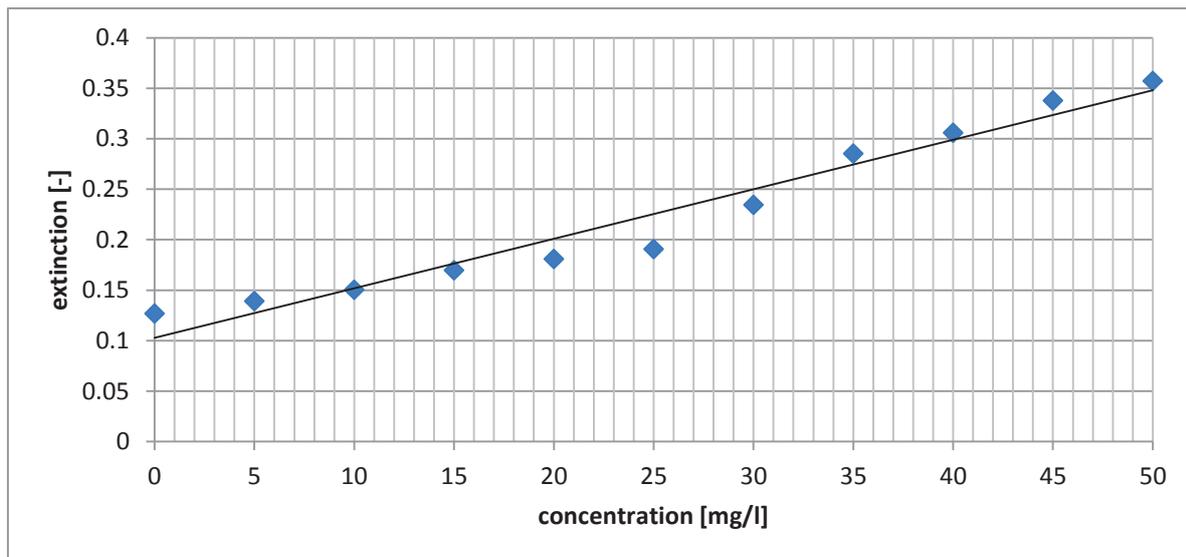


Figure 7: Liberation of iodine: calibration chart.

A linear regression (Equation 20) with a correlation coefficient (Equation 21) is made.

$$y = kx + d = 0.0049 * x + 0.1028 \quad \text{Equation 20}$$

$$R^2 = 0.9557 \quad \text{Equation 21}$$

#### 4.2.1.5 Measuring method for samples

For the analysis of the samples 10 ml of each solution is pipetted into small glassware. To use the UV/VIS for the analysis it is necessary to add 4 ml of starch solution to each 10 ml sample. The rest of the procedure is the same as explained in 4.2.1.2.

$$\frac{y - d}{k} = x \rightarrow C_{hc} = \frac{0.3573 - 0.1028}{0.0049} = 51.94 \frac{mg}{l} \quad \text{Equation 22}$$

Equation 22 where  $y$  is the extinction, is used to calculate the concentration  $x$  of the iodine complex  $I_3^-$  of the samples. The samples from Arisdyn are measured the exact same way.

### 4.2.2 Calibration method: Oxidation of sulfite

#### 4.2.2.1 Acetate - puffer pH 6

7 ml of 99 %  $HOAc$  are pipetted and 5.3 g of  $Na_2CO_3$  are weighted into a 500 ml beaker and filled up with DI water. The filling with DI water should be done under the airflow because of the exothermic reaction of  $Na_2CO_3$  with  $H_2O$ . Probably some more of the  $Na_2CO_3$  is needed to get a pH of 6. The pH of 6 is measured by an electronic pH meter.

#### 4.2.2.2 DTNB - Solution ( $10^{-3}$ mole/l)

99 mg of the DTNB powder are weighted into a 250 ml flask and then 8 ml of the acetate puffer is added. The function of the puffer is to dissolve the DTNB. At first, the flask is not completely filled up to the mark with DI water because swinging of it leads to an acceleration

of the dissolution. If there is no solid particle left in the solution the flask is filled up to the mark with DI water.

#### 4.2.2.3 Preparation of samples

2 ml of the DTNB solution and 4 ml of the acetate puffer are pipetted into small glassware (20 ml) for each calibration sample.

#### 4.2.2.4 Preparation of solutions for the calibration

Table 12 shows the chosen target concentrations for the calibration and the associated extinction. For example the solution with a concentration of 35 mmole/l, is prepared through weighing 1.10285 g of  $\text{Na}_2\text{SO}_3$  (Equation 23) into a 250 ml flask.

$$\begin{aligned}
 m_{\text{Na}_2\text{SO}_3} &= c_{\text{SO}_3^{2-}} * MW_{\text{Na}_2\text{SO}_3} * V \\
 &= 35 * 10^{-3} \frac{\text{mole}}{\text{l}} * 126.04 \frac{\text{g}}{\text{mole}} * 0.25 \text{l} \\
 &= 1.10285 \text{ g} = 1102.85 \text{ mg}
 \end{aligned}
 \tag{Equation 23}$$

The wanted volume of the solution  $V$  multiplied with the molar weight of sodium sulfite  $MW_{\text{Na}_2\text{SO}_3}$  and the wanted sulfite concentration  $c_{\text{SO}_3^{2-}}$ , results in the weight of sample taken  $m_{\text{Na}_2\text{SO}_3}$ .

After putting the powder with a funnel carefully into the flask, the flask is filled up to the mark with DI water after a complete dissolution. It is the same method and calculation for every other concentration in Table 12. To minimize the exposure time to the atmospheric oxygen, the samples are prepared previously (see 4.2.2.3). 10  $\mu\text{l}$  of each sample to measure is pipetted into one of the small glassware. At this point, the sulfite is bound as a complex and there is no further oxidation to sulfate. The last step is to fill the light yellow solution into the cuvettes. The cuvette is the same for every test. Previous experiments showed that it is essential to measure the prepared samples right after the filling into the cuvettes. After 2 hours there is a crucial different in the color of the solution. After every test the cuvette is cleaned with two or three rinses of DI water. It is very important to keep the cuvette clean and not touch it without gloves.

#### 4.2.2.5 Measuring with the UV/VIS

For this calibration 4 different solutions plus one blank (acetate puffer and DTNB solution) were measured at a wavelength of 430 nm. The results are shown in Table 12 and the calibration chart in Figure 8.

Table 12: Oxidation of sulfite: concentration and extinction of the calibration solutions.

concentration mmole/l	extinction
35	0.9633
30	0.8578
25	0.6596
20	0.5728
0	0.0185

#### 4.2.2.6 Calibration chart

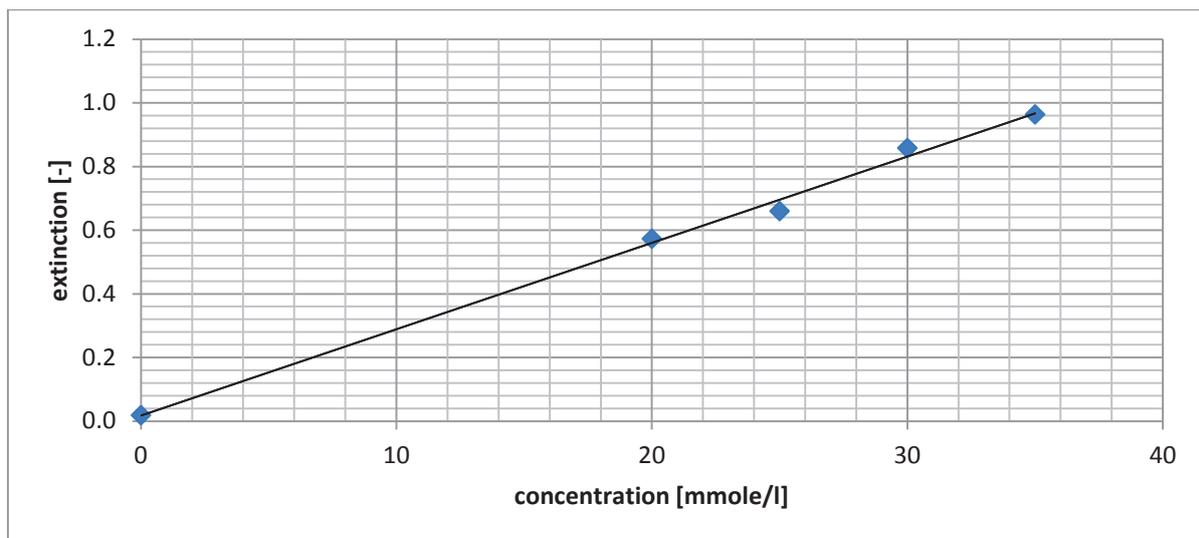


Figure 8: Oxidation of sulfite: Calibration chart.

A linear regression is made. The linear equation is  $y = 0.0271 * x + 0.0173$ . The coefficient of determination is  $R^2 = 0.996$ .

#### 4.2.2.7 Measuring method for samples

The samples from Arisdyn are prepared the exact same way as explained in 4.2.2.3. After that, 10  $\mu$ l of the sample is pipetted into the previous prepared small glassware (4.2.2.4, paragraph 3). The previously created calibration chart (Figure 8) with the related linear equation is used for calculating the concentration of the sulfite in the samples.

### 4.2.3 Calibration method: Degradation of PNP

#### 4.2.3.1 NaOH solution (5 %)

To change the pH (see 4.2.3.3) 5 % NaOH solution is used. This solution is created with NaOH - pellets (Table 10). 12.5648 g of the pellets are weighted into a 250 ml flask and filled up to the mark with DI water. To accelerate the dilution of the pellets a magnetic stirrer is in action. The concentration of 5 % was high enough to set the pH in an adequate time.

### 4.2.3.2 Preparation of the stock solution

A stock solution with a concentration of  $500 \frac{\mu\text{mole}}{\text{l}}$  is prepared to produce the concentrations for the calibration (Table 13).

$$\begin{aligned} m_{\text{PNP}} &= c_{\text{PNP}} * MW_{\text{PNP}} * V \\ &= 500 * 10^{-6} \frac{\text{mole}}{\text{l}} * 139.11 \frac{\text{g}}{\text{mole}} * 1 \text{ l} \\ &= 0.06956 \text{ g} = 69.56 \text{ mg} \end{aligned} \quad \text{Equation 24}$$

Equation 24 leads to  $m_{\text{PNP}}$  (the weight of sample taken) whereas  $c_{\text{PNP}}$  is the wanted PNP concentration,  $MW_{\text{PNP}}$  the molar weight of PNP and  $V$  the wanted volume. The slight difference between  $m_{\text{target}} = 0.06956 \text{ g}$  and  $m_{\text{being}} = 0.06948 \text{ g}$  is due to the inaccuracy of the manual weighing.

0.06948 g are weighted into a beaker and filled up to approx. 250 ml with DI water. To be sure that all of the PNP powder is dissolved, the solution is mixed with a magnetic stirrer. After that, the solution from the beaker is poured into a 1 l flask and filled up to the mark. Out of this stock solution, 8 solutions were made through dilution. One example, whereby  $V_2$  is the wanted volume to fill up to the target volume  $V_1$ ,  $c_1$  is the target concentration and  $c_2$  the concentration of the starting solution, is given by Equation 25.

$$V_2 = V_1 * \frac{c_1}{c_2} = 250 \text{ ml} * \frac{25 \frac{\mu\text{mole}}{\text{l}}}{500 \frac{\mu\text{mole}}{\text{l}}} = 12.5 \text{ ml} \quad \text{Equation 25}$$

12.5 ml of the stock solution are pipetted into a 250 ml flask and filled up to the mark with DI water. This solution has then a concentration of  $25 \frac{\mu\text{mole}}{\text{l}}$ . It is the same method, with other target concentrations, for the rest of the dilution series.

### 4.2.3.3 Preparation of solutions for the calibration

The pH of the solution after the complete dissolution depends on the concentration. For the measuring approx. 100 ml are poured into a beaker and a pH increase >11 (Kalumuck 2000, p. 467, Hua et al. 1995, p. 2336) is realized by carefully adding 5 % NaOH solution with a pipette (18 - 90  $\mu\text{l}$ ). During this the solution is mixed with a magnetic stirrer. The last step is to fill it into the cuvette. The cuvette is the same for every test. After every test the cuvette is cleaned with two or three rinses of DI water. It is very important to keep the cuvette clean and not touch it without gloves.

### 4.2.3.4 Measuring with the UV/VIS

For this calibration 8 different solutions plus one blank (DI water) are measured at a wavelength of 400 nm. The results are shown in Table 13 and the calibration chart in Figure 9.

Table 13: Degradation of PNP: concentration and extinction of the calibration solutions.

concentration	extinction
$\mu\text{mole/l}$	-
0	0
1	0.0183
5	0.0851
10	0.1823
15	0.2759
20	0.3693
25	0.4599
30	0.5529
50	0.9267

#### 4.2.3.5 Calibration chart

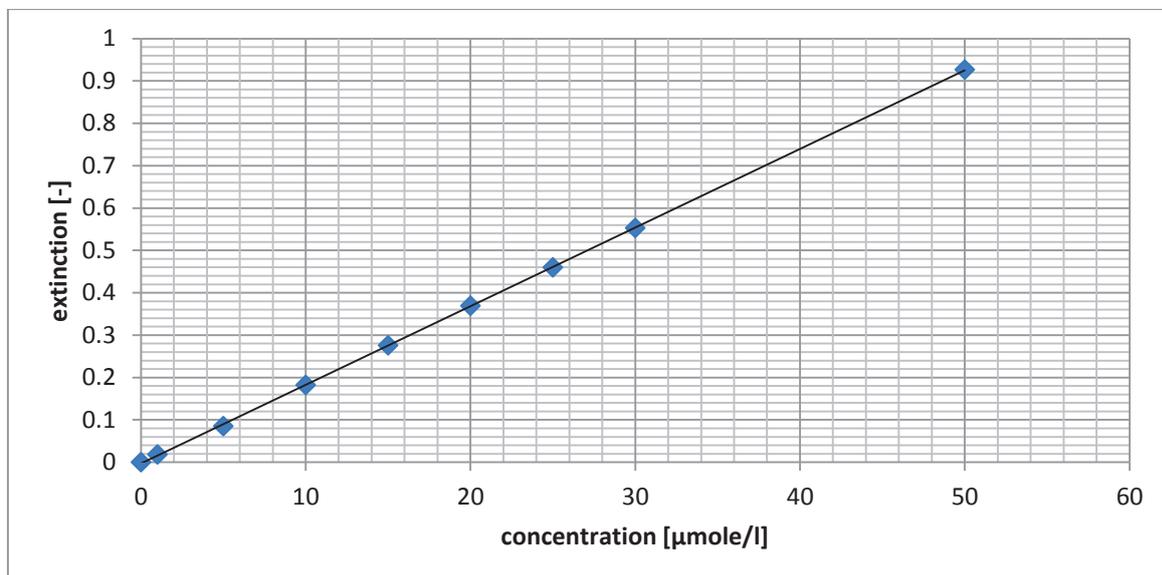


Figure 9: Degradation of PNP: calibration chart.

A linear regression is made. The equation is  $y = 0.0186 * x - 0.0028$ . This equation is used to calculate the concentration. The coefficient of determination is  $R^2 = 0.9999$ .

#### 4.2.3.6 Measuring method for samples

For the analysis of the samples from Arisdyn the whole sample volume, approx. 50 ml, is used. A pH increase  $> 11$  is realized by carefully adding 5 % NaOH solution with a pipette. The added amount (90 to 1700  $\mu\text{l}$ ) depends on the pH of the starting solution. The pH of each sample is measured before and after adding the base. The solution is mixed with a magnetic stirrer during adding NaOH. To be as accurate as possible the pH probe and the stirrer are rinsed with DI water after every sample. The last step is to fill up the cuvette and measure it with the UV/VIS at a wavelength of 400 nm.

### 4.3 Experimental approach

Basically there are two different experimental setups. The system for the UC is realized through an ultrasonic horn and a flow cell (Figure 10). For the HC system a completely closed cavitation loop is created (Figure 11 and Figure 12). The possibility to apply different temperature conditions is realized with a chiller or an oil heater. Table 14 displays the data about the used units for both systems.

Table 14: List of used units with available manufacture's data.

Unit	Manufacturer	Details
Plunger pump	Five Stars Technologies	CP300 (300 means a maximum pressure of 30000 psi)
Ultrasonic horn	Sonics & Materials Inc.	VC750, 750 W, 20kHz, 120 VAC, 15 A, Serial number: 52172Y
Water chiller	Thermo Electron	115V, 60Hz, 13.2 A
Oil heater	Ogden Manufacturing Co.	4500W, 240V, Phase 3,
Thermometer	Oakton - Eutech Instruments	Temp JKT

#### 4.3.1 Ultrasonic cavitation

Under assembled condition the UC system shows a small surface which is in contact with air. To avoid a longer impact in case of the sulfite oxidation the ultrasonic cell is again purged with N<sub>2</sub> through the gas valve in Figure 10. A relief valve is installed to secure safe operation conditions. The gas supply is not required for the other model reactants. The possibility to apply different temperature conditions is realized with a chiller or an oil heater. 50 ml glass vials are used to store the samples (Figure 10 - sample valve). To exclude contamination from previous runs, tap water and DI water are used to rinse the loop after every test.

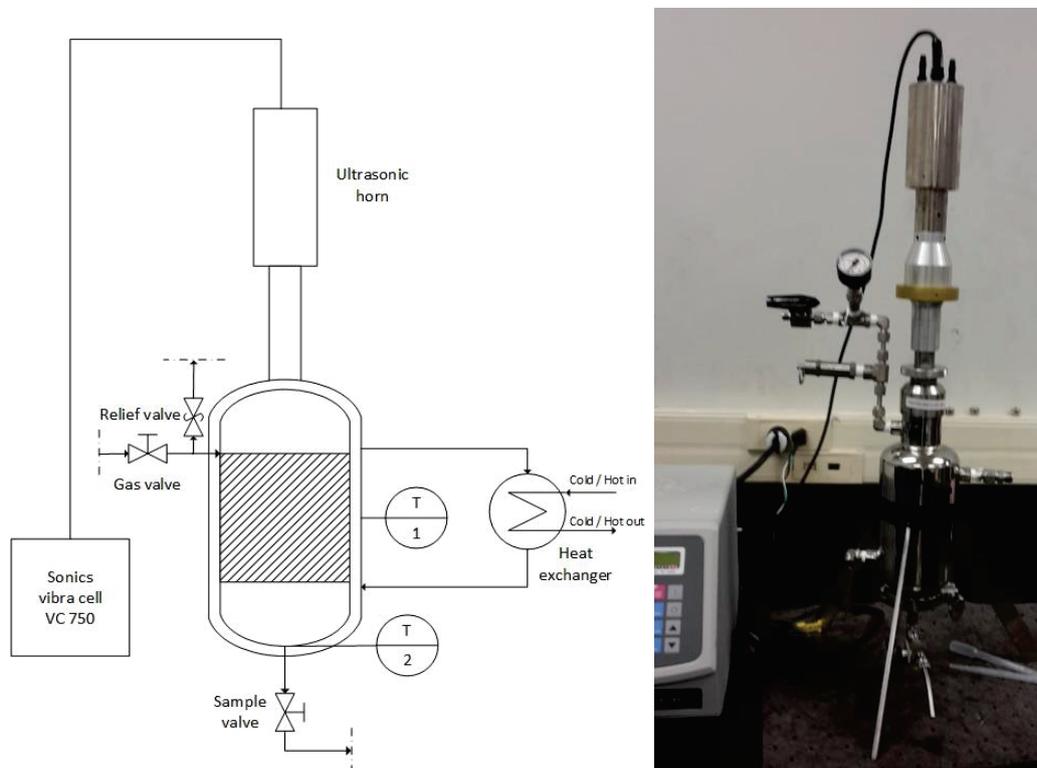


Figure 10: Flow chart and UC construction for all experiments.

## 4.3.2 Hydrodynamic cavitation:

### 4.3.2.1 Liberation of iodine and degradation of PNP

At the beginning of every test, the initial solution is poured into the hopper. A completely with  $N_2$  purged hydrodynamic cavitation loop is not required for these reactions (Figure 11 - gas valve is not used for these tests). The air compressor provides the plunger pump with the necessary air pressure.

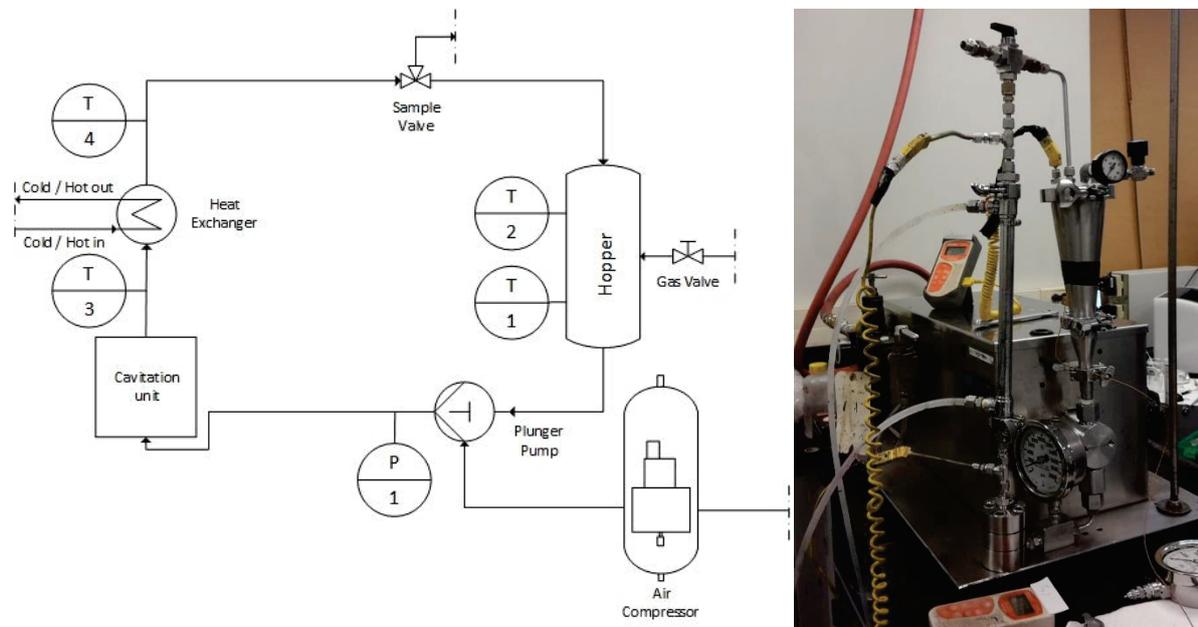


Figure 11: Hydrodynamic cavitation loop for the liberation of iodine and degradation of PNP.

A tubular heat exchanger provides constant temperature conditions inside the hopper. The samples are taken and stored in 50 ml glass vials.

### 4.3.2.2 Oxidation of sulfite

At the beginning of every test, the initial solution is again poured into the hopper. A completely with  $N_2$  purged HC loop is created to avoid the contact with the atmospheric oxygen (Figure 12). Every time a prepared sulfite solution has to be stored, the air above the surface is also driven out by  $N_2$ .

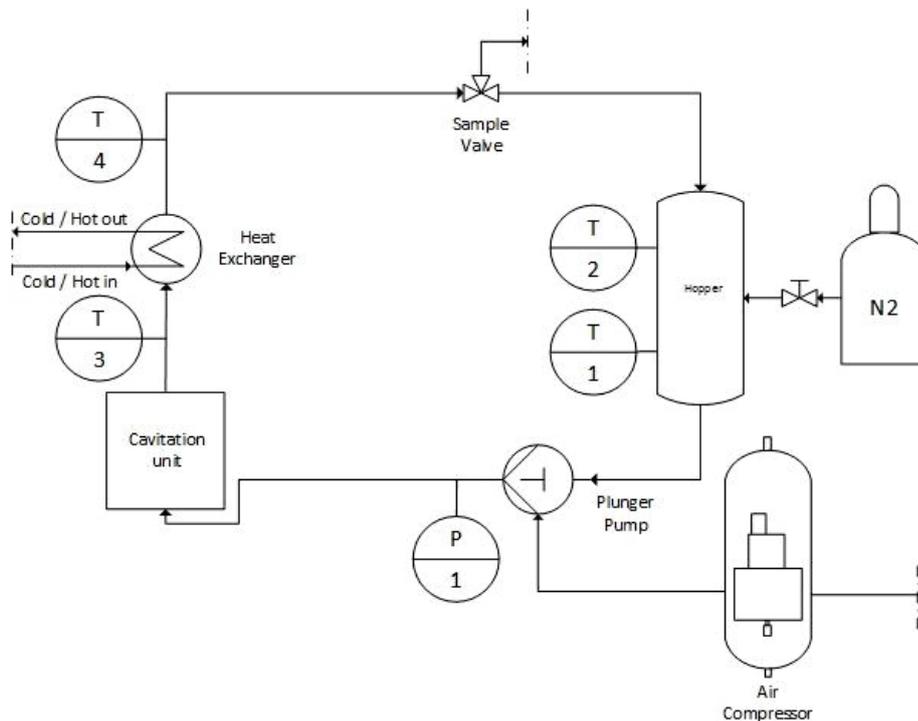


Figure 12: Hydrodynamic cavitation loop for the oxidation of sulfite to sulfate.

20 ml glass vials are used to store the samples (Figure 12- sample valve). The same step includes the use of a crimp tool to seal the vials with a stopper against the impact of atmospheric oxygen. Previous tests showed that the sealing is adequate. To exclude contamination from previous runs, tap water and DI water are used to rinse the loop after every test.

#### 4.4 Result Quantification

The most important question this study has to answer is the existence of hot spots on the one hand and on the other hand how much energy input is required to ensure a proper conversion of the reactants. To compare the UC with the HC system the exactly same parameters are used for a specific experiment for both systems. All experiments with the different settings are tested on both systems. Appropriate care and effort was taken to accurately establish always the same conditions. Time is the basic parameter for the UC. The number of passes<sup>21</sup> whereby one pass means one pass of the initial volume through the whole loop, provides a more understandable and workable parameter for the HC system. Basically passes are just converted time, which is important for the comparison of the two systems. Additional to passes and time the other working parameters are pressure for the HC, temperature and pH for the UC. The applied pressure stages are 15000, 10000, 5000, 2500 and 1000 psi (Suslick, M. mdleleni, Millan and T. Ries, Jeffrey 1997, p. 9303). The different values for the temperature and the pH are explained in the Results section.

<sup>21</sup>See chapter 5 for a more detailed explanation.

## 5 Results

### 5.1 Liberation of iodine

#### 5.1.1 Liberation of iodine: Calculation scheme HC

The test with the number 1.6 - 4.6 has been chosen as one example to show the calculation of the different parameters. The explanation and the associated equations for quantification of the parameters are separately shown below each table.

Table 15: Settings.

number. series	initial concentration, mass and volume				passes	inlet pressure	orifice dimension
	$C_0$	sample $m_{0s}$	sample real $m_{0sr}$	sample real corr. $V_{0src}$	$\Omega$	$p_i$	thousandths of an inch
	g/l	g	g	ml	-	psi	-
1.6	50	400	400.4	387.77	5	2500	6/8
2.6		350	350.9	339.83	15		
3.6		300	301.1	291.60	25		
4.6		250	251.1	243.18	35		

##### 5.1.1.1 number.series

The first number changes always from 1 to 4, whereas 1 means after 5, 2 after 15, 3 after 25 and 4 after 35 passes. The second number is for the same series always identical. In this case, 6 mean it is the sixth series with the HC system.

##### 5.1.1.2 Initial concentration, mass and volume

The concentration for the initial solution  $C_0$  is  $50 \frac{g}{l}$  and has been adopted from the work of Gogate et al. (2001, p. 2534). To use 400 g for the initial mass is due to the capacity of the hopper. "sample  $m_{0s}$ " is the wanted sample mass, "sample real  $m_{0sr}$ " the real mass after the measuring with the scale and "sample real corr.  $V_{0src}$ " is the conversion from mass into volume considering the density (Equation 26). To measure the density of the initial solution, 25 g are weighted into a 500 ml flask and filled up to the mark with DI water. Equation 27 shows the calculation of the density, where  $m_s$  is the mass of the solution,  $V_s$  the volume of the solution,  $\rho_{KI}$  the density of the solution,  $m_f$  the mass of the full flask and  $m_e$  is the mass of the empty flask.

$$V_{0src} = \frac{m_{0sr}}{\rho_{KI}} = \frac{400.4 \text{ g}}{1.03258 \frac{\text{g}}{\text{cm}^3}} = 387.77 \text{ ml} \quad \text{Equation 26}$$

$$m_s = V_s * \rho_{KI} \rightarrow \rho_{KI} = \frac{m_f - m_e}{V_s} = \frac{(681.81 - 168.52) \text{ g}}{500 \text{ ml}} \quad \text{Equation 27}$$

$$= 1.03258 \frac{\text{g}}{\text{cm}^3}$$

### 5.1.1.3 Passes

The range of passes is based on the time which is used in previous literature (Morison, K. and Hutchinson, C. 2009, p. 176). It was not possible to bring the samples back into the loop after the analysis because the analytic with the UV/VIS took place in the AQWATEC lap at CSM in Golden.<sup>22</sup>

### 5.1.1.4 Inlet pressure

The inlet pressure presents the pressure the liquid medium is entering the cavitation chamber. The influence of pipe friction is not considered. The maximum pressure of 15000 psi (approx. 1034 bar) based on the work from Suslick, M. mdleleni, Millan and T. Ries, Jeffrey (1997, p. 9303) where the range of  $I_3^-$  - production was investigated over the range 100 - 1500 bar. The minimum pressure is limited with 1000 psi (approx. 70 bar) because of the plunger pump's specification and the used pressure display.

Table 16: Calculated time and measured temperature.

min/pass	time	time real	time accumulated	T1 (vessel)	T2 (vessel skin)	T3 (after cav. unit)	T4 (after heat ex)
t/Ω	t	t <sub>r</sub>	t <sub>acc</sub>	T11/T12	T21/T22	T31/T32	T41/T52
min/pass	min	h:mm:ss	min	°C	°C	°C	°C
3.58	17.88	00:17:52	17.88	21.3/20.5	21.8/20.9	24.0/23.3	chiller 20°C
3.13	31.33	00:31:20	49.21	20.5/20.4	20.9/20.7	23.3/23.3	
2.69	26.88	00:26:53	76.09	20.4/20.2	20.7/20.7	23.3/23.4	
2.24	22.42	00:22:25	98.51	20.2/20.2	20.7/20.7	23.4/23.4	

### 5.1.1.5 min/pass, time, time real, time accumulated

To quantify the minutes per pass in Table 16, Equation 28 with the data from Table 17 is used. The data in Table 17 is created through the manual determination of the strokes per minute, executed by simply counting and a stopwatch, and the ml per stroke, realized by catching the volume per stroke with a measuring cylinder.

Table 17: Used orifice design and specific data of the plunger pump.

6/8					
1000	psi	19	strokes/min	3.5	ml/stroke
2500		32		3.5	
5000		42		3.9	
10000		54		4.3	
15000		63		4.2	
8/12					
1000	psi	30	strokes/min	4	ml/stroke
2500		46		4.1	
5000		61		4.4	
10000		78		4.6	

<sup>22</sup> See 4.2 for more details about the analytical procedure.

Because of the changing volume it is essential to use the difference of the passes. A certain volume needs certain strokes to get through the loop one time. Per stroke a certain volume is moved by the plunger pump. With Equation 29 the time  $t$  is calculated and the difference of passes is considered.  $t_r$  is  $t$  in a more clearly format and  $t_{acc}$  is the accumulated time of all passes. That means it takes 98.51 minutes for the entire series with a pressure of 2500 psi.

$$\frac{t}{\Omega} = \frac{V_{osrc}}{\frac{\text{strokes}}{\text{min}} * \frac{\text{ml}}{\text{stroke}}} = \frac{387.77 \text{ ml}}{32 \frac{\text{strokes}}{\text{min}} * 3.5 \frac{\text{ml}}{\text{stroke}}} = 3.58 \frac{\text{min}}{\text{pass}} \quad \text{Equation 28}$$

$$t = \frac{t}{\Omega} * \Delta\Omega = 3.58 \frac{\text{min}}{\text{pass}} * (5 \text{ passes} - 0 \text{ passes}) = 17.88 \text{ min} \quad \text{Equation 29}$$

### 5.1.1.6 Temperature T1 - T4

T1 to T4 are the temperatures at different locations in the loop (Table 16). "T4 (after heat ex)" is not always measured because after some runs it appears that the temperature after the heat exchanger is the same as the temperature inside the hopper ("T1 (vessel)").

Table 18: Measured results extinction and precipitation.

sample taken at Arisdyne	pH at CSM	extinction (without filtration)	extinction (after filtration)	volume to filter	filter paper weight - unused	filter paper weight - used	produced precipitation and concentration		sample weight at CSM
$m_{sAr}$	pH	$\zeta_{wf}$	$\zeta_{af}$	$V_f$	$m_{fpun}$	$m_{fpus}$	$m_p$	$m_{pc}$	$m_{sCSM}$
g	-	-	-	ml	g	g	g	mg/ml	g
49.5	7.69	0.3573	0.4195	35	0.0869	0.1039	0.0170	0.49	
49.8	7.98	0.3497	0.4136	36	0.0877	0.1044	0.0167	0.46	48.2
50	8.05	0.3341	0.3987	35	0.0878	0.1024	0.0146	0.42	47.6
50	8.16	0.307	0.3802	39	0.0887	0.1052	0.0165	0.42	50.98

### 5.1.1.7 Sample weight

Table 18 (Table 26 for the UC system) shows a difference between the sample taken at Arisdyne and the sample weight at CSM. The reason is that at Arisdyne a scale with a maximum weight of 20 kg and 1 digit and at CSM an analytical scale with a maximum of 160 g and 4 digits is used. The deviation is due to the higher accuracy of the analytical scale.

### 5.1.1.8 Excursion: Observed precipitation

Some kind of black precipitation appears in every sample after some time. This precipitation gets visible through its sedimentation to the ground of the sample glass. The first thought that the precipitation are iodine crystals turned out false because no color change to purple is observed after pouring some droplets of carbon tetrachloride ( $\text{CCl}_4$ ) or chloroform ( $\text{CHCl}_3$ ) on the dried filtration residue. Tests with different kind of acids like  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  failed because no decomposition occurs. After an intensive cleaning session of the HC loop with several rinses with DI water, a replicant test was performed (All equipment was cleaned with acid before the start of the experiments). The black precipitation still appears and this indicates that the black flakes come from the only possible source left, the seal of the plunger pump. This seal is a graphite ring. This conclusion is confirmed by the fact that

no precipitation is found in the samples created with the UC system. In the following, the short excursion discusses the relation between carbon, activated surfaces and free radicals.

**Liberation of iodine:** The produced radicals during the cavitation process attack the potassium iodide (KI) and the graphite seal of the plunger pump (Boehm 2012, p. 3154). The high pressure seems to be an additional factor but no carbon is found in the samples of the other two model reactions. In this case, mainly hydrogen and oxygen radicals are responsible for the activated carbon surface referring to cavitation (Xu et al. 2007, p. 1365). It is already known that due to their strongly oxidizing properties, free radicals enhance the intercalation of many products into the carbon (Schlöggl, R. and Boehm, H.P. 1988). Lau et al. (1986, p. 103) showed that there is an adsorption sequence at pH 7 of  $rH^+ > rK^+ > rLi^+ > rI^- > rNO_3^- > rOH^-$ , where  $r$  is the adsorption density in  $\frac{\text{mole}}{\text{m}^2}$ . The produced radicals are strong enough to intercalate the potassium ion. The potassium ion catalyzed the decomposition of the graphite surface (Billinge et al. 1984, p. 85). An immediate color change is not observed, because the iodide ion is also bound on the active surface of the carbon. After a specified time (weekend) these ions get dissolved in water and create the  $I_3^-$ -complex which is responsible for the color change. It depends on the oxidizing properties of the produced radicals how active the surface is and, later, how high the concentration of the dissolved  $I_3^-$ -complex is. **Oxidation of sulfite:** In this system the same radicals are created but no carbon precipitation occurs. No hint was found in the literature that sodium or sulfite is a catalyst like the potassium ion. An active carbon surface is also present but there is no decomposition because neither the  $Na^+$ -ions nor the  $SO_3^{2-}$ -ions are absorbed by or have any other impact on the graphite. There is no potassium or any other ion from the sequence mentioned above in the sulfite/sulfate - system. That suggests that different salts have different impacts on the graphite seal.

#### 5.1.1.9 Extinction without and after filtration

To investigate if the carbon flakes influence the concentration, a measuring of the extinction with and without the precipitation is required. This means a measuring before and after the filtration. The values in Table 18 show that there is a difference between the extinctions in this example. The extinction before filtration was taken on a Friday and also the filtration has been taken place on this day. The measuring of the second extinction was performed on the Monday after. The filtration caused an additional activation (additional liberation of iodine through radicals from the carbon) of the carbon after the weekend. This is just a theory and additional investigations are needed. The measuring of all the other samples was executed on the same day and they show slightly different values before and after the filtration.

#### 5.1.1.10 Produced precipitation and concentration

To quantify the existing amount of carbon flakes, Equation 30 is used. The used filter paper is dried in an oven for 30 minutes by  $50^\circ\text{C}$ . 30 minutes are enough because tests with a drying time up to 2 hours showed no difference in the weight of the filter residue. Generally the concentration increases by increasing the pressure. Weighing of the filter paper before

and after the filtration is required. To avoid contamination, it is absolutely necessary to handle the filter paper only with gloves and a forceps.

$$m_{pc} = \frac{m_{fpus} - m_{gpun}}{V_f} = \frac{(0.1044 - 0.0877) * 10^{-3} g}{36 ml} = 0.46 \frac{mg}{ml} \quad \text{Equation 30}$$

### 5.1.1.11 pH at CSM

The pH can be excluded as an influence factor for the occurring precipitation because all samples show a pH of approx. 8.

Table 19: Measured concentration and calculated production of the tri-iodide ( $I_3^-$ ) complex.

concentration $CCl_4$	concentration $I_3^-$		$I_3^-$ - production	$I_3^-$ - production total	rate of $I_3^-$ - production	rate of $I_3^-$ - production
$C_h$	$C_{nc}$	$C_{af}$	$n_p$	$n_{ptot}$	$n_p/\Omega$	$n_p/t$
g/l	mg/l	mg/l	$\mu\text{mole}$	$\mu\text{mole}$	$\mu\text{mole/pass}$	$\mu\text{mole/s}$
	51.94	64.6	25.89	69.77	5.18	2.41E-02
	50.39	63.4	20.56		2.07	1.10E-02
	47.20	60.4	14.75		1.48	9.15E-03
	41.67	56.6	8.48		0.85	6.30E-03

### 5.1.1.12 Concentration carbon tetrachloride ( $CCl_4$ )

The column "concentration  $CCl_4$ " in Table 19 is empty because no  $CCl_4$  is added in this series. 0.324 g  $CCl_4$  / l are added to those solutions which are used for the investigation of the impact of haloalkanes to cavitation.<sup>23</sup>

### 5.1.1.13 Blanks

Table 20 shows the results of the blank tests of the initial solution. There is a certain amount of the  $I_3^-$ -complex formed in these solutions without HC or any other treatment. The concentration of the initial solution  $C_{blank}$  for all samples is defined with 20.1 mg/l and represents the measurement directly after creating the solution. This is very important for further calculations.

Table 20: Different blanks to investigate the liberation without cavitation.

number.series	initial concentration, mass and volume			extinction without filtration	concentration $CCl_4$	concentration $I_3^-$	$I_3^-$ - production
	$C_0$	sample $m_{0s}$	sample real corr. $V_{0src}$	$\zeta_{wf}$	$C_h$	$C_{blank}$	$n_{p,blank}$
	g/l	g	ml	-	$g/dm^3$	mg/l	$\mu\text{mole}$
5.3 Blank	50	400	387.38	0.2367		27.33	27.81
KI Blank			387.38	0.2013		20.10	20.45
KI Blank			387.38	0.2623		32.55	33.12
KI Blank			387.38	0.2643	0.324	32.96	33.54

<sup>23</sup> See 5.1.3.2 for more details.

### 5.1.1.14 $I_3^-$ - production and $I_3^-$ - production total

To calculate the  $I_3^-$  - production (Table 19 and Table 20), Equation 31 is used. The total  $I_3^-$  - production is the summation of the produced amount of substance per volume or after 35 passes (Equation 32).

$$n_p = \mu\text{mole sample} - \mu\text{mole initial solution} = \quad \text{Equation 31}$$

$$\frac{C_{hc} * (V_{0src} - \frac{m_{SAr}}{\rho_{KI}})}{MW_{I_3^-}} - \frac{C_{blank} * V_{0src}}{MW_{I_3^-}}$$

$$= \left( \frac{\left( 51.49 * 10^{-3} \frac{g}{l} * \left( 387.77 - \frac{49.5}{1.03258} \right) * 10^{-3} l \right) - \left( 20.10 * 10^{-3} \frac{g}{l} * 387.77 * 10^{-3} l \right)}{380.71 \frac{g}{mole}} \right)$$

$$* 10^6 \mu\text{mole} = 25.89 \mu\text{mole}$$

$$n_{ptot} = n_{p,5\text{ passes}} + n_{p,15\text{ passes}} + n_{p,25\text{ passes}} + n_{p,35\text{ passes}}$$

$$= (25.89 + 20.65 + 14.75 + 8.48) \mu\text{mole}$$

$$= 69.77 \mu\text{mole} \quad \text{Equation 32}$$

### 5.1.1.15 Rate of $I_3^-$ - production

Equation 33 and Equation 34 are used to quantify the rate of  $I_3^-$  - production in  $\frac{\mu\text{mole}}{\text{pass}}$  and  $\frac{\mu\text{mole}}{s}$ .

$$\frac{n_p}{\Omega} = \frac{25.89 \mu\text{mole}}{5 \text{ passes}} = 5.18 \frac{\mu\text{mole}}{\text{pass}} \quad \text{Equation 33}$$

$$\frac{n_p}{t} = \frac{25.89 \mu\text{mole}}{17.88 * 60 s} = 2.41 * 10^{-2} \frac{\mu\text{mole}}{s} \quad \text{Equation 34}$$

Table 21: Efficiency and energy.

flow rate	power consumption $P=Q*\Delta P$	power consumption total	energy density	oxidation efficiency	oxidation efficiency total	enhancement of liberation	energy	energy costs
Q	P	P <sub>tot</sub>	$\rho_e$	O <sub>e</sub>	O <sub>etot</sub>	-	-	11.2 ¢/kWh
m <sup>3</sup> /s	W	W	J/ml	$\mu\text{mole}/J$	$\mu\text{mole}/J$	%	kWh	¢
1.81E-06	31.16	124.65	86.19	7.75E-04	9.47E-05	341.1	0.2	2.29
			172.38	3.53E-04				
			172.38	2.94E-04				
			172.38	2.02E-04				

### 5.1.1.16 Power consumption

Equation 35 describes the power consumption for a certain volume flow when a certain pressure is applied and Equation 36 calculates the flow rate. 1 psi is equal to approx. 6895 Pa. It should be noted that the flow rate for 15 passes represents the flow rate for 10

passes with the associated volume (Equation 37). The same is valid for 25 and 35 passes which results in the same power consumption after each stage.

$$P = \dot{Q} * \Delta p = 1.81 * 10^{-6} \frac{m^3}{s} * 2500 * 6895 Pa = 31.16 W \quad \text{Equation 35}$$

$$\begin{aligned} \dot{Q}_{5 \text{ passes}} &= \frac{\Omega * V_{0scr}}{t} = \frac{(5 \text{ passes} * 387.7710^{-6} m^3)}{17.88 * 60 s} \\ &= 1.81 * 10^{-6} \frac{m^3}{s} \end{aligned} \quad \text{Equation 36}$$

$$\begin{aligned} \dot{Q}_{15 \text{ passes}} &= \frac{\Omega * V_{0scr}}{t} \\ &= \frac{((15 \text{ passes} - 5 \text{ passes}) * 339.83 * 10^{-6} m^3)}{31.33 * 60 s} \\ &= 1.81 * 10^{-6} \frac{m^3}{s} \end{aligned} \quad \text{Equation 37}$$

The total power consumption over the full range of passes (35 passes) is the summation of the consumption per stage.

#### 5.1.1.17 Energy density

Equation 38 is used to calculate the energy density in  $\frac{J}{ml}$ . It describes, how much power is drawn per volume of the initial solution (Koh et al. 2014).

$$\rho_e = \frac{P * t}{V_{0scr}} = \frac{31.16 W * 17.88 * 60 s}{387.77 ml} = 86.19 \frac{J}{ml} \quad \text{Equation 38}$$

#### 5.1.1.18 Oxidation efficiency or cavitation yield

$$Y(t) = \frac{\text{moles degraded per second}}{\text{power consumption}} = \frac{\dot{Q} * (C_t - C_0)}{\dot{Q} * \Delta P} * \frac{10^3}{MW} \quad \text{Equation 39}$$

where  $\dot{Q}$  is the flow rate and  $\Delta P$  is the system pressure drop,  $C_t$  and  $C_0$  are the reagent concentration at time t and initial time, respectively (Capocelli et al. 2014a, p. 2570).

The cavitation yield, here practically oxidation efficiency (Equation 40) is calculated as  $\frac{\mu\text{mole}}{J}$  for a certain pressure and volume. Oxidation efficiency total in Equation 41 is defined for a certain pressure and over the full range of passes (35 passes). Series 1.1 - 3.1 and 1.2 - 3.2 with pressures of 2500 and 5000 psi are performed without constant temperature conditions. It is not possible to run the system without heat control at higher pressure because of the occurring high temperatures in the cavitation unit. The calculation of the energy efficiency by using the calorimetric method is only possible for these two HC series but all UC tests and is explained in 5.1.1.20 and 5.1.2.3.

$$O_e = \frac{n_p}{P * t} = \frac{32.43 \mu\text{mole}}{31.16 W * 17.88 * 60s} = 7.75 * 10^{-4} \frac{\mu\text{mole}}{J} \quad \text{Equation 40}$$

$$O_{etot} = \frac{n_{ptot}}{P_{tot} * \Sigma t} = \frac{94 \mu mole}{264.87 W * 98.51 * 60s} = 9.47 * 10^{-5} \frac{\mu mole}{J} \quad \text{Equation 41}$$

### 5.1.1.19 Enhancement of liberation and energy demand

The “enhancement of liberation” describes how much more of the  $I_3^-$ - complex is formed because of the cavitation. 100 % is the amount of  $I_3^-$  in  $\mu mole$  in the samples without cavitation or any other treatment (Table 20,  $n_{p,blank}$ ).

There is an increase of the liberated amount of about 340 % (Equation 42) for the given example with 2500 psi. Through cavitation 3.4 times more  $I_3^-$  ions are formed.

$$enhancement = \frac{100 \%}{20.45 \mu mole} * 69.77 \mu mole = 341.1 \% \quad \text{Equation 42}$$

The very important question of how much energy is needed for the given degradation, is answered by Equation 43 and Equation 44. The costs for the increased liberation of iodine are calculated with Equation 45. The specific electricity price for Colorado and Ohio is  $11.2 \frac{\text{¢}}{\text{kWh}}$ .<sup>24</sup>

$$1 kWh = 1000 Wh = 1000 \frac{J}{s} * 3600 s = 3600000 J \quad \text{Equation 43}$$

$$Ee = \frac{124.65 W * 98.51 * 60 s}{3600000 J} = 0.2 kWh \quad \text{Equation 44}$$

$$\text{¢} = 0.2 kWh * 11.2 \frac{\text{¢}}{\text{kWh}} = 2.29 \text{ ¢} \quad \text{Equation 45}$$

### 5.1.1.20 Power dissipated into the liquid (calculation scheme for HC and UC)

HC series 1.1 - 3.1 and 1.2 - 3.2 and UC series 1.1 - 4.1<sup>25</sup> are performed without constant temperature conditions. Calorimetric calculations are used to determine the dissipated power into the liquid. Table 22 shows the settings for the HC series whereas here the time is the main parameter.

<sup>24</sup> <http://www.npr.org/sections/money/2011/10/27/141766341/the-price-of-electricity-in-your-state> requested 1/8/2016.

<sup>25</sup> Only for the UC test the temperature of the solution decreases and the temperature of the vessel skin increases. The cavitation generated condensation heat has to be dissipated to the outside.

Table 22: Settings.

number. series	initial concentration, mass and volume				time	inlet pressure	orifice dimension	passes
#	$C_0$	sample $m_{0s}$	sample real $m_{0sr}$	sample real corr. $V_{0src}$	t	$p_i$	thousandths of an inch	$\Omega$
-	g/l	g	g	ml	min	psi	-	-
1.1	50	400	400.3	387.67	10	2500	6/8	2.80
2.1		350	400.3	387.67	20			5.60
3.1		300	400.3	387.67	30			8.40
1.2	50	400	400.2	387.57	10	5000	6/8	4.10
2.2		350	351.4	340.31	20			8.19
3.2		300	302.6	293.05	30			12.29

Because of measuring the temperature inside the vessel before and after the treatment it is possible to calculate the power dissipated into the liquid for the named HC series and for every UC series. A temperature increase at every measuring point can be observed from Table 23.

Table 23: Measured temperature.

temp. T1.1 (vessel)	temp. T1.2 (vessel)	temp. T2.1 (vessel skin)	temp. T2.2 (vessel skin)	temp. T3.1 (after cav unit)	temp. T3.2 (after cav unit)
T11	T12	T21	T22	T31	T32
°C	°C	°C	°C	°C	°C
22	26.2	22.4	27.2	23.2	28.1
26.2	28.6	27.2	30.1	28.1	31.1
28.6	30.6	30.1	32.4	31.1	32.8
23	34.4	23.2	36.9	28.4	39.9
34.4	40.2	36.9	43.7	39.9	47.1
40.2	44.6	43.7	49.1	47.1	53

The heat capacity for the KI solution is determined by Novikov (2014, p. 3). For the heat capacity of the sodium sulfite and PNP solution the heat capacity of water (4.186 J/gK at 20°C) is used. It is assumed that the low concentrations of the model reactants have no influence on the heat capacity.

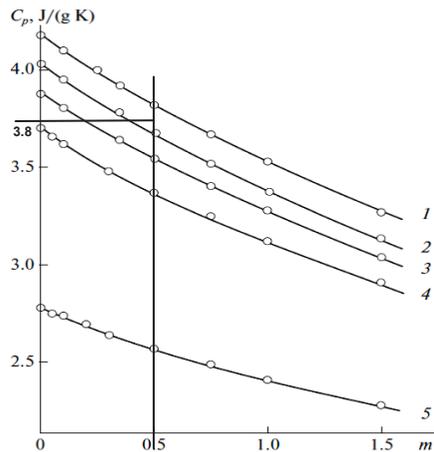


Figure 13: Concentration dependences of the specific heat capacities of potassium iodide solutions in water and mixed MP (N-methylpyrrolidone) - H<sub>2</sub>O solvent at 298.15 K and different values of xMP: (1) 0, (2) 0.025, (3) 0.05, (4) 0.10, (5) 0.33.

$$C_p = 3.8 \frac{J}{g \cdot K}$$

$$P = C_p * m * \frac{dT}{dt} = 3.8 \frac{J}{g \cdot K} * 400.3 g * \frac{(26.2 - 22.0)K}{10 * 60s} = 10.65 W \quad \text{Equation 46}$$

Equation 46, where  $C_p$  is the heat capacity,  $m$  the mass of the solution,  $dT$  the temperature difference and  $dt$  the time difference, is used to calculate the dissipated power.

Table 24: Calculated calorimetric and enhancement of liberation.

Power dissipated in the liquid	Power dissipated in the liquid	energy efficiency	energy efficiency total	enhancement of liberation
$P_{diss}$	$P_{disstot}$	$E_e$	$E_{etot}$	-
W	W	%	%	%
10.65	19.73	34.14	24.19	322.01
5.33		19.51		
3.75		16.26		
28.89	50.23	31.69	20.91	376.64
12.91		16.12		
8.43		12.23		

The positive values for the power dissipated into the liquid in Table 24 indicate that the cavitation process increases the temperature of the solution with increasing the treatment time.

### 5.1.2 Liberation of iodine: Calculation scheme UC

Basically, the calculation is the same as for the HC system but with some important differences. The declaration of the test series is the same as for the HC system and the example for the calculation scheme is the series 1.2 - 4.2. There is no counting of passes with the ultrasonic horn and the main parameter is time. The settings related to an amplitude of 25 % and a pulse of 4 seconds on, 2 seconds off, are based on the previous work from Chakinala et al. 2008, p. 166.

Table 25: Settings and measured temperature.

number .series	initial concentration, mass and volume			time	temp. 11 (jacket)	temp. 12 (jacket)	temp. 21 (inside)	temp. 22 (inside)
	$C_0$	sample $m_{0s}$	sample real corr. $V_{0src}$	t	T11	T12	T21	T22
	g/l	g	ml	min	°C	°C	°C	°C
1.2	50	300.0	290.53	5	20	20	24.4	24.8
2.2		249.7	241.82	10			25.3	27
3.2		300.2	290.73	20			25.1	27.8
4.2		250.6	242.69	30			27.8	30

After pouring the 300 g solution with a concentration of 50 g KI per liter into the ultrasonic cell, the horn is fixed by tighten the bolt. 300 g are chosen for the starting volume because of the limited space in the ultrasonic cell. For the first series a sample after 5 and 10 minutes is taken (second run with 5 minutes). The rest of the solution is drained through the valve at the bottom of the cell and the cell and horn are rinsed two times with DI water. The second series also consists of 300 g solution, with the only difference that the sample is taken after 20 and 30 minutes (second run with 10 minutes). That leads to a total runtime of 40 minutes for each series (Table 25). Table 25 also shows the location and the temperatures of the different measuring points at the ultrasonic cell. The temperature is measured and noted before and after the treatment. T11 and T12 are the same because of constant cooling. T21 and T22 are the temperatures inside the cell before and after the treatment.<sup>26</sup> They are measured with a thermo element on the bottom of the cell.  $m_{sAr}$  presents the weight of the sample which was taken at Arisdyn.

Table 26: Measured concentration.

sample taken at Arisdyne	pH at CSM	extinction	sample weight at CSM	concentration $CCl_4$	concentration after ultrasonic
$m_{sAr}$	pH	$\zeta_{uc}$	$m_{sCSM}$	$C_h$	$C_{uc}$
g	-	-	g	g/l	mg/l
50.3	6.95	0.3101	48.3092		42.31
50.1	7.06	0.3467	47.7735		49.78
49.6	7.01	0.3853	47.6932		57.65
49.7	7.06	0.4282	51.4015		66.41

<sup>26</sup> See 4.3.1 for the flow chart.

There is no significant increase or decrease of the pH after storage and shipping (Table 26). The procedure for measuring the extinction with the UV/VIS and calculating the concentration is the same for both systems.<sup>27</sup> The column "concentration CCl<sub>4</sub>" is again empty because no CCl<sub>4</sub> is added in this series as well. 0.324 g CCl<sub>4</sub> /l are added to those solutions which are used for the investigation of the impact of haloalkanes to ultrasonic cavitation.

Table 27: Calculated tri-iodide ( $I_3^-$ ) production.

$I_3^-$ - production	$I_3^-$ - production total	rate of $I_3^-$ - production
$n_p$	$n_{ptot}$	$n_p/t$
$\mu\text{mole}$	$\mu\text{mole}$	$\mu\text{mole/s}$
11.53	24.04	3.84E-02
12.50		2.08E-02
21.40	42.52	1.78E-02
21.12		1.17E-02

As already mentioned, a certain amount of the  $I_3^-$  complex is formed in these solutions without any kind of cavitation or treatment. To calculate the  $I_3^-$  production, Equation 31 is used. Table 27 shows the  $I_3^-$  production after 5, 10, 20 and 30 min. The total  $I_3^-$  production is the summation of the produced amount of substance after 10 and 30 minutes. Equation 34 is used to get the rate of the  $I_3^-$  production in  $\frac{\mu\text{mole}}{s}$ .

### 5.1.2.1 Power consumption

The use of a temperature regulating device (water chiller or oil heater) leads to positive values for the power dissipated into the liquid because of a constant temperature regime in the cell (Table 28, column 1). The calculation of the power dissipated into the liquid is explained in 5.1.1.20.

Table 28: Calculated power demand and enhancement.

power dissipated into the liquid	total power dissipated into the liquid	power consumption total	energy density	enhancement of liberation
$P_{diss}$	$P_{disstot}$	$P_{tot}$	$\rho_e$	-
W	W	W	J/ml	%
1.52	6.90	84.21	86.96	118
5.38		84.21	104.47	
2.57	6.06	84.05	173.47	208
3.49		84.11	207.93	

To get the energy efficiency, the electrical power consumption has to be calculated. The pulse of the horn causes a longer total runtime (Table 29). If the timer is set to for example 5

<sup>27</sup> See Measuring method for samples in 4.2.1.5.

minutes, the total runtime is 7 minutes and 28 seconds because of the pause of 2 seconds. The 5 minutes represents the effective time of treatment. During the additional 2 minutes and 28 seconds power is only needed for the instruments.

Table 29: Runtime ultrasonic horn.

effective ultrasonication (timer)	pause		total runtime	
$t_{eff}$	$t_p$		$t_{tot}$	
min	min	sec	min	sec
5	2	28	7	28
10	4	58	14	58
20	9	58	29	58

Equation 47 shows the needed electrical power for the ultrasonic horn.

$$P = \frac{U * I_{run} * t_{eff} + U * I_0 * t_p}{t_{tot}} =$$

$$\frac{120 \text{ Vac} * 0.9 \text{ A} * 5 * 60 \text{ s} + 120 \text{ Vac} * 0.3 \text{ A} * (2 * 60 + 28) \text{ s}}{(7 * 60 + 58) \text{ s}} = 84.21 \text{ W}$$

Equation 47

$U$  ... Voltage alternating current

$P$  ... total power

$I_{run}$  ... ampere when running

$I_0$  ... ampere for the instruments

### 5.1.2.2 Energy density and enhancement of liberation

Applying Equation 38 shows nearly the same energy density in all series. The slight difference occurs because always a little different volume of the initial solution is used and also the weight of sample taken is not always exactly the same. The enhancement of the liberation caused by UC is explained in 5.1.1.19 and calculated with Equation 42.

### 5.1.2.3 Energy efficiency

Energy efficiency (Equation 48) examines the question of how much of the energy is effectively dissipated into the system. This fraction of the total energy is used for the generation of cavitation and should be as high as possible (Gogate et al. 2001).

Table 30: Calculated energy and efficiency.

energy efficiency	energy efficiency total	oxidation efficiency	oxidation efficiency total	energy	energy costs
$E_e$	$E_{etot}$	$O_e$	$O_{etot}$	-	11.2 ¢/kWh
%	%	$\mu\text{mole/J}$	$\mu\text{mole/J}$	kWh	¢
1.15	5.22	4.28E-04	4.52E-04	0.02	0.08
4.07		2.38E-04			
1.94	4.59	1.81E-04	2.45E-04	0.07	0.25
2.65		1.24E-04			

$$E_e = \frac{P_{diss}}{P_{tot}} = \frac{1.52 \text{ W}}{132 \text{ W}} * 100 \% = 1.15 \% \quad \text{Equation 48}$$

$$E_{etot} = \frac{P_{disstot}}{P_{tot}} = \frac{6.90 \text{ W}}{132 \text{ W}} * 100 \% = 5.22 \% \quad \text{Equation 49}$$

Equation 49 is the total energy efficiency after 10 and 30 minutes. Equation 40 and Equation 41 are used for the calculation of the oxidation efficiency after 5, 10, 20 and 30 minutes. The total oxidation efficiency is calculated after 10 and 30 minutes, in other words, after every new initial solution. The total power consumption and consequently the energy demand and the arising costs are the same for every series. (Table 30 and Equation 43, Equation 44, Equation 45,).

### 5.1.3 Liberation of iodine: Results

The following results and discussion belong to the HC test series. The results of the UC tests are included in the comparison between HC and UC in 5.1.4. It should be kept in mind that the leading parameter of all the HC experiments is passes. After one pass the starting volume is pumped through the loop back into the hopper. The assumed range over passes is 5, 15, 25 and 35. The first sample is taken after 5 and the second after additional 10 passes, which consequently means after 15 passes. The same procedure applies for the samples after 25 and 35 passes.

#### 5.1.3.1 Different pressure

The different pressures, temperatures and orifice designs used for the HC tests are given in Table 31. The reason to change the orifice dimension from 6/8 to 8/12 bases on the shorter total runtime for 35 passes.

Table 31: Parameters; without the adding of  $\text{CCl}_4$ .

pressure	orifice dimension	temperature
$p_i$	-	T1
psi	thousandths of an inch	°C
15000	6/8	20
10000	6/8	20
5000	6/8	20
2500	6/8	20
1000	8/12	5/20

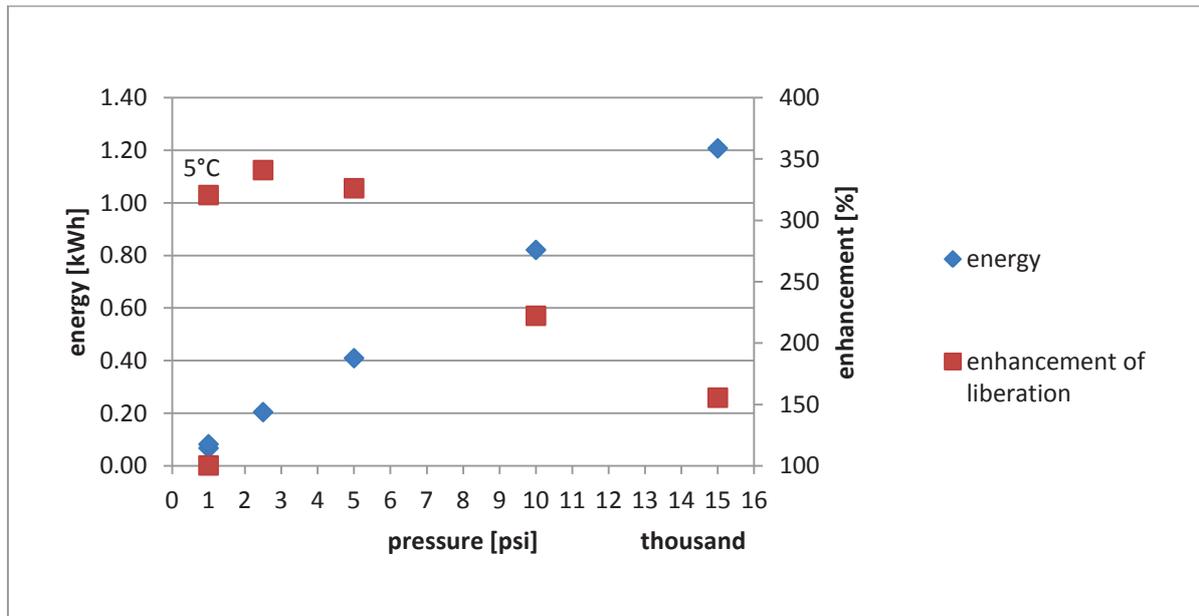


Figure 14: The enhancement of liberation decreases by increasing the pressure at 20°C, a starting concentration of 50 g KI/l and without adding any additional chemicals (CCl<sub>4</sub>); the two data points at 1000 psi are explained in the text below.

In general the results in Figure 14 display an increased enhancement by decreasing the pressure. The results of the tests with 1000 psi and different temperatures require a more detailed explanation. With 5°C the enhancement is an approx. 3.5 - fold and with 20°C no increase in production of  $I_3^-$ . This lower enhancement is due to the fact that the liberation of iodine and the following generation of the  $I_3^-$  - complex is chemically described as an oxidation. An oxidation is an exothermic reaction and decreasing the temperature shifts the equilibrium to the products. High inlet pressure generates a large number of cavities and the comparison of the test with 2500 psi and 20°C with the 1000 psi and 20°C indicates that the liberation of iodine requires a pressure between 2500 and 5000 psi ( $2500 \leq p_i < 5000$ ). The energy demand increases by increasing the pressure. It should be noticed that the displayed energy data point for the test with 1000 psi and 5°C does not consider the cooling energy.

### 5.1.3.2 Different pressure and carbon tetrachloride (CCl<sub>4</sub>)

Chakinala et al. (2008, p. 170) investigated how the use of haloalkanes impacts the cavitation effect whereas the use of CCl<sub>4</sub> shows the most promising effect. In a next series different pressures are applied and a small amount of CCl<sub>4</sub> is added to each starting solution (Table 32).

Table 32: Parameters; with CCl<sub>4</sub>.

pressure	orifice dimension	temperature	concentration CCl <sub>4</sub>
p <sub>i</sub>	-	T1	C <sub>h</sub>
psi	thousandths of an inch	°C	g/l
15000	6/8	20	0.324
10000	6/8		
5000	6/8		
1000	8/12		

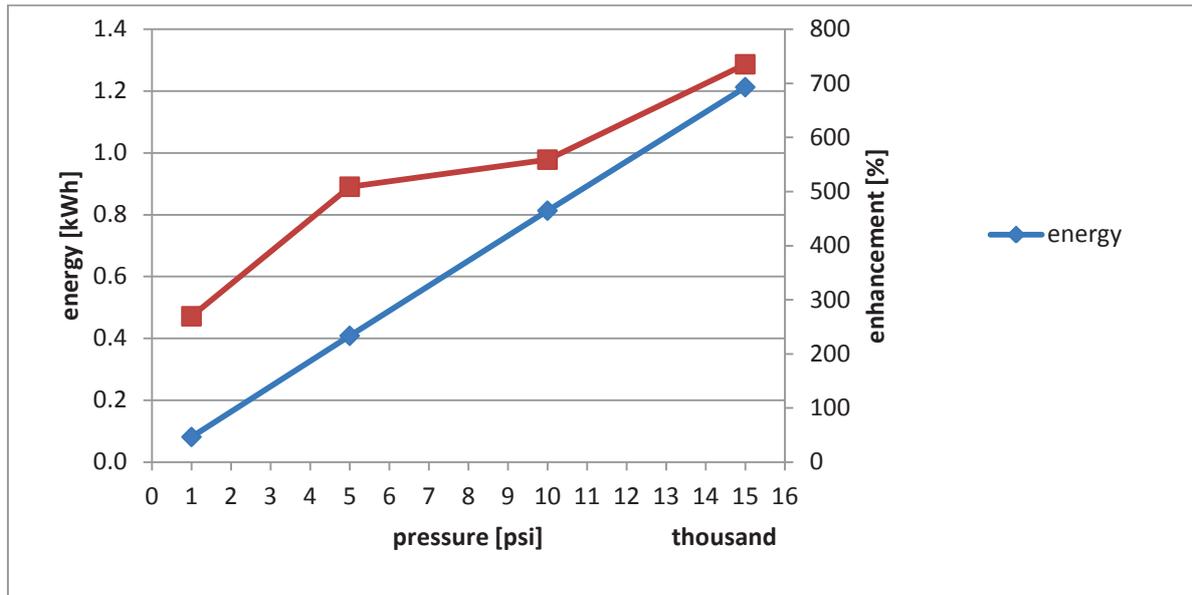


Figure 15: By adding CCl<sub>4</sub>, the enhancement of liberation increases by increasing the pressure at 20°C and a starting concentration of 50 g KI/l.

By adding a small amount of CCl<sub>4</sub>, the enhancement shows a peak at 15000 psi (Figure 15). In agreement with Suslick (1990), the current study found out that adding CCl<sub>4</sub> results in an increased output of the I<sub>3</sub><sup>-</sup> complex. Comparing the enhancement in Figure 14 and Figure 15, the adding of CCl<sub>4</sub> doubles the enhancement from a 3.5-fold to a 7-fold increasing production of I<sub>3</sub><sup>-</sup>. Cavitation induced hot spots lead to additional generation of  $\dot{C}l$  radicals. These additional radicals, beside  $\dot{O}H$  and  $\dot{H}$ , also attack the KI and further increase the intensity of I<sub>3</sub><sup>-</sup> production. By undergoing several series of recombination reactions, oxidizing agents like Cl<sub>2</sub> and HOCl are formed. These agents are much more stable than the free radicals and so they cause an additional overall intensification effect on the oxidation rates (Chakinala et al. 2008, p. 166).

Considering pressure, the results in Figure 14 and the findings of this series are the complete opposite. Through adding CCl<sub>4</sub>, a high pressure results in an increased enhancement. The same phenomenon was observed by Chakinala et al. (2008, p. 167). In their study the increased rates of oxidation are attributed to the higher inlet pressure which leads to higher intensity of cavitation (Gogate, Parag R. and Pandit, Aniruddha B. 2000). Higher intensity cavitation means enhanced degradation of the chloroalkanes generating higher amounts of the oxidizing agents (Cl, Cl<sub>2</sub> and HOCl). The results indicate a changed performance of HC

at high pressure and by adding  $\text{CCl}_4$ . The high pressure is needed to create the more stable oxidizing agents. This correlation of pressure and enhancement inevitably leads to higher energy costs.

### 5.1.3.3 Different pressure plus low pH

The idea to decrease the pH of the starting solution bases on the homolytic dissociation of water. Because of the decreased pH, hydrogen radicals should increase the liberation of iodine. Through adding a few drops of 10 % citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) the pH is set to 3.3. To increase the pH is excluded for the HC loop because of Figure 21 “UC pH 12.5”. The settings for this series are shown in Table 33.

Table 33: Parameters; low pH.

pressure	orifice dimension	temperature	acid	pH
$p_i$	-	T1	-	-
psi	thousandths of an inch	°C	-	-
5000	6/8	20	citric acid	3.3
2500	8/12			
1000	8/12			

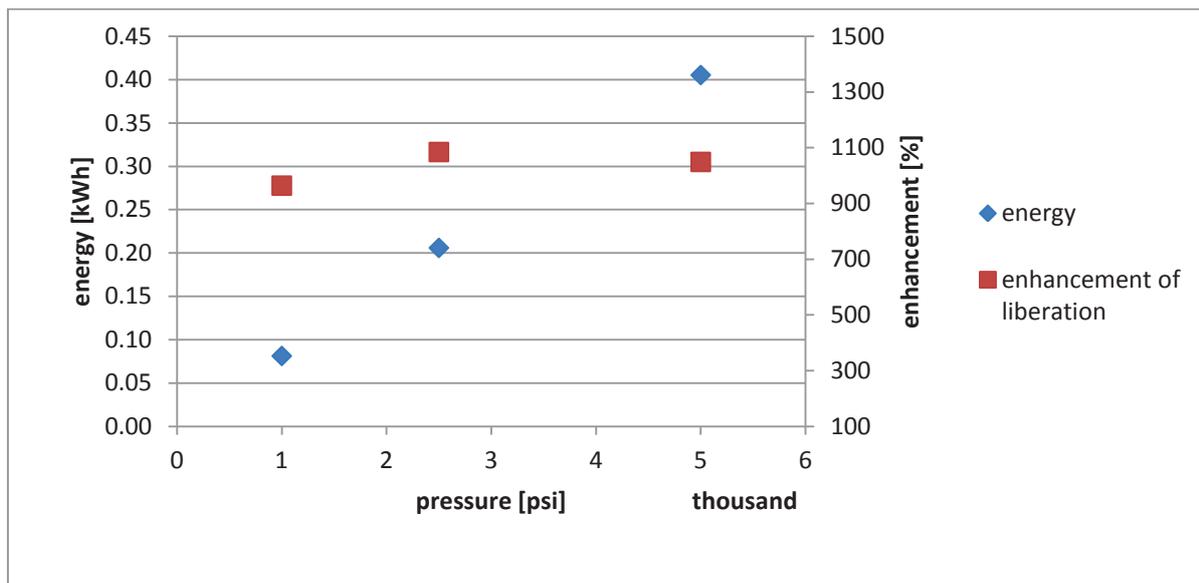


Figure 16: Citric acid (10 %) is used to set the pH to 3.3; the enhancement shows similar improvement by increasing the pressure at 20°C and a starting concentration of 50 g KI/l.

Figure 16 presents that a decrease of the pH to 3.3 results in a 11-fold increase of  $I_3^-$  production at an applied pressure of 2500 psi because the additional  $\text{OH}^-$  and  $\text{H}^+$  ions lead to an increased amount of the formed strong oxidizing agent  $\text{H}_2\text{O}_2$ . In general the series with the low pH showed even at 1000 psi a better enhancement than the best result of the series where  $\text{CCl}_4$  is added.

### 5.1.3.4 Efficiency

Figure 17 shows the development of the efficiency (Equation 39) in  $\mu\text{mole}/\text{J}$  over the range of 35 passes. The parameter efficiency describes how many  $\mu\text{mole } I_3^-$  are formed per Joule.

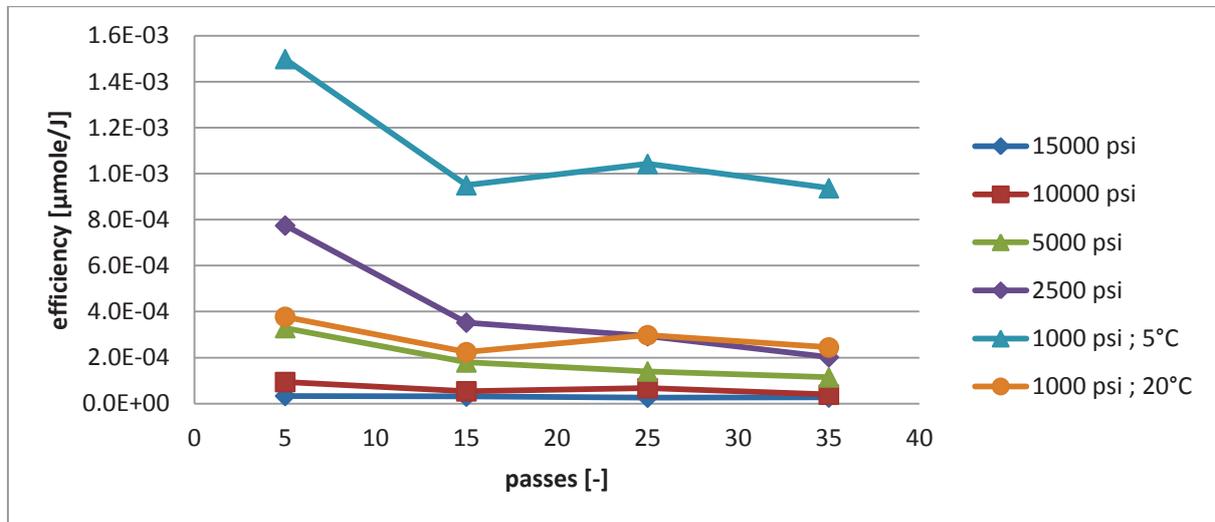


Figure 17: 50 g KI /l; different pressures; 20°C (except 5°C at 1000 psi); the efficiency combines the energy point of view with the enhancement of liberation and is plotted against the full range of passes.

The efficiency decreases from 5 to 35 passes because a high number of passes requires more electrical power. As mentioned before the additional energy for the cooling for the test with 1000 psi is not considered.

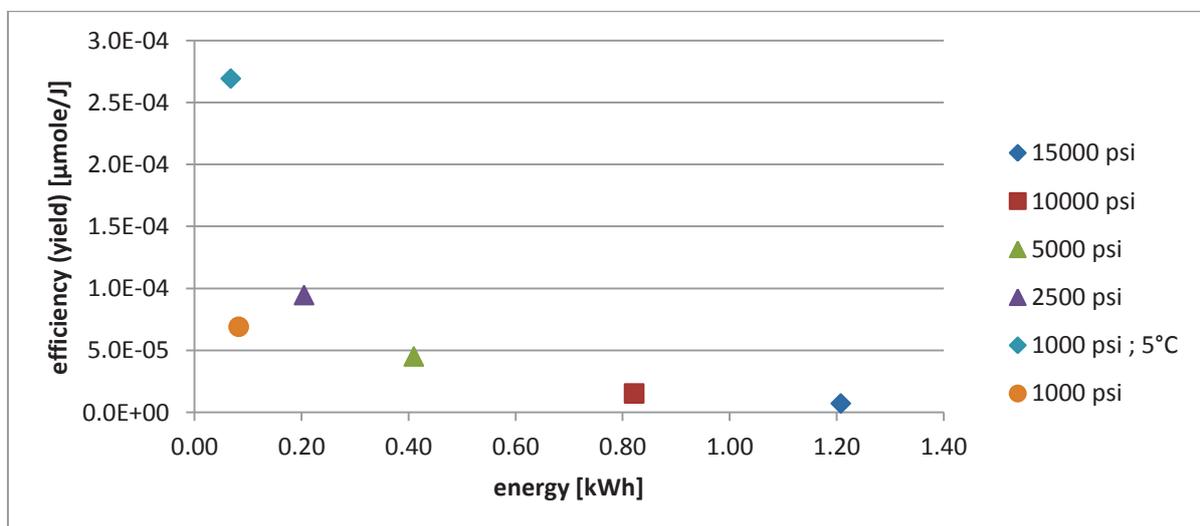


Figure 18: Efficiency vs. energy by investigating different pressures at 20°C.

By comparing the efficiency (yield) with the spent electrical energy (Figure 18), the results in Figure 17 are confirmed. Through decreasing the pressure the efficiency increases.

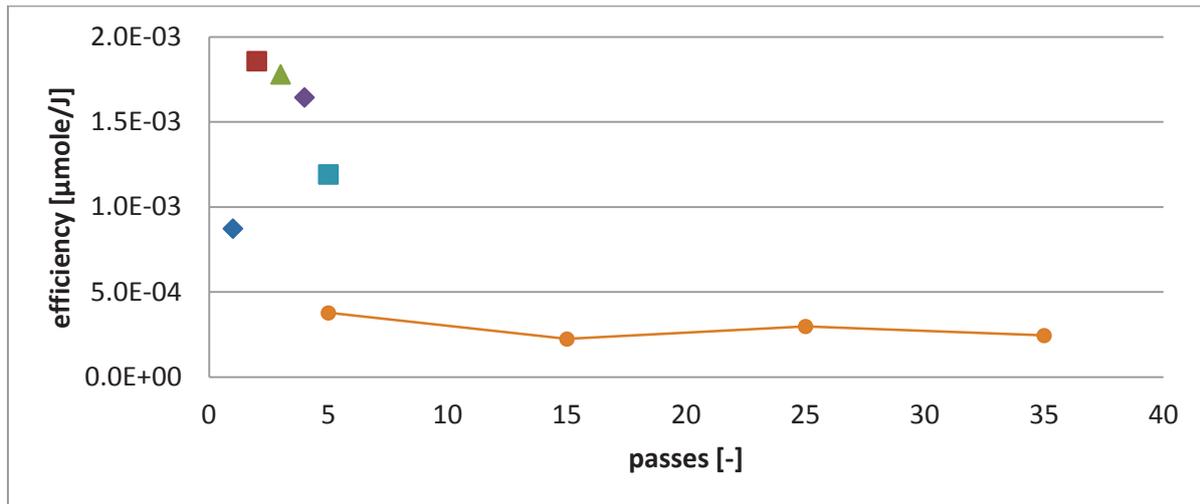


Figure 19: Closer inspection of the efficiency from the first to the fifth pass at 1000 psi, an operating temperature of 20°C and a starting concentration of 50 g KI /l; the efficiency shows a peak after two passes and decreases afterwards.

A closer look to the big gap from zero to five passes is given in Figure 19. The efficiency increases from the first to the second pass which indicates also the most efficient point of operation. From the third to the fifth pass the efficiency decreases. A reasonable explanation for the gap between the two points at 5 passes is the difference of the starting volumes (450 ml instead of 400 ml). Figure 20 examines the question of how much  $\mu\text{mole } I_3^-$  per ml are created over the range of passes and shows a step increase from the first to the second pass. The HC liberates approximately the same amount of iodine per ml after the second pass as after the fifth pass. The deviation between the samples after five passes is due to measurement uncertainty. From five to 25 passes the production rate increases and slightly decreases from 25 passes to 35 passes. The peak after 25 passes indicates a maximum number of passes under the given operating conditions.

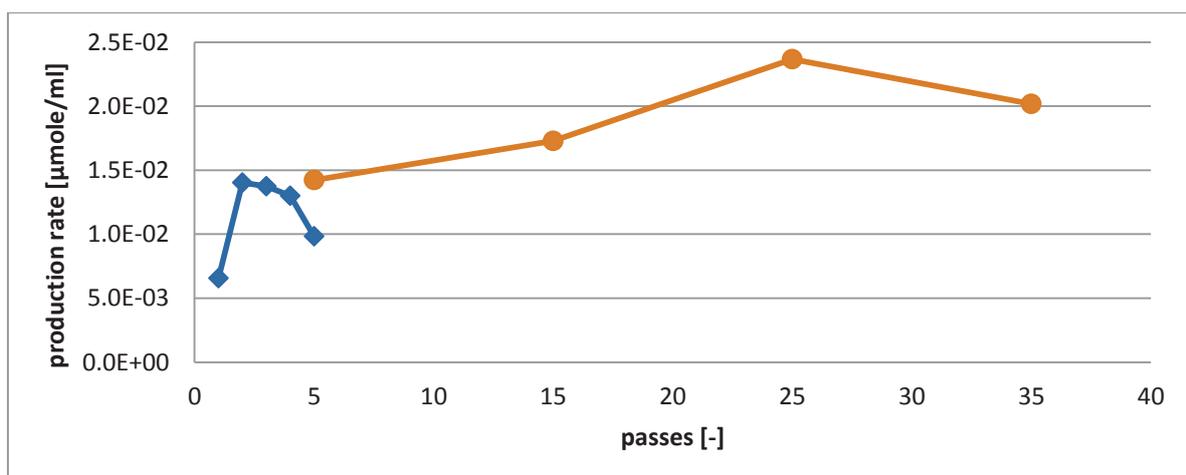


Figure 20: Starting concentration 50 g KI /l; 1000 psi; 20°C; after the second pass of the solution the cavitation unit creates approx. the same amount of  $\mu\text{mole}$  per ml than after the fourth or fifth pass; by increasing the number of passes the production rate increases from the fifth to the 25<sup>th</sup> pass and decreases afterwards.



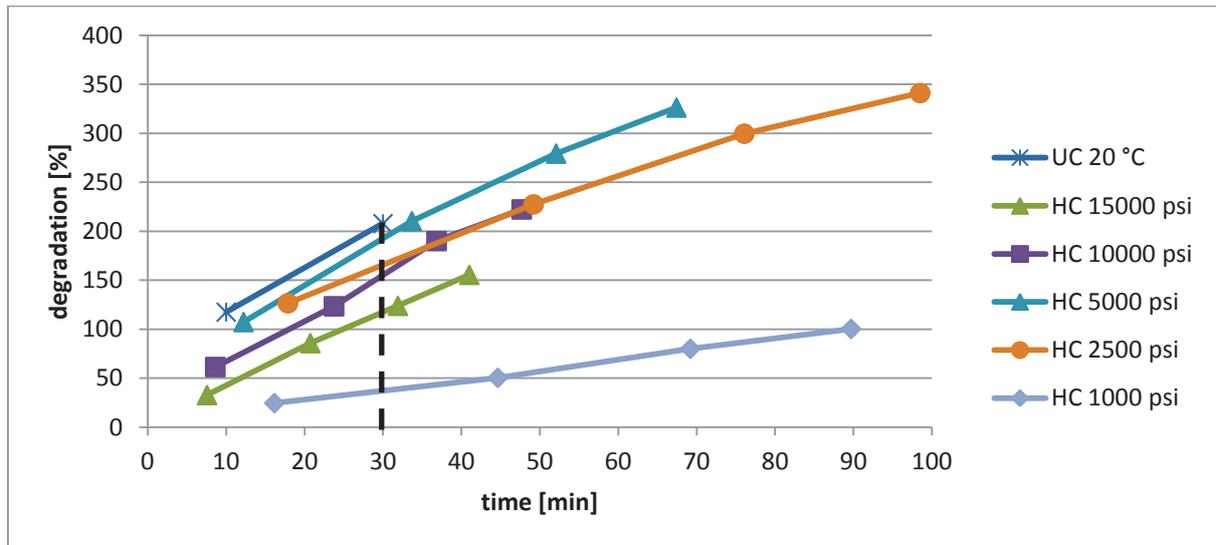


Figure 22: HC vs. UC by considering the degradation over time; all HC tests with different pressure at 20°C; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1.

The black dotted line in Figure 22 highlights the fact that the UC test shows a better enhancement after 30 minutes than all HC experiments. This could be caused on the one hand by the short retention time in case of HC or on the other hand by the high energy input through the ultrasonic horn.

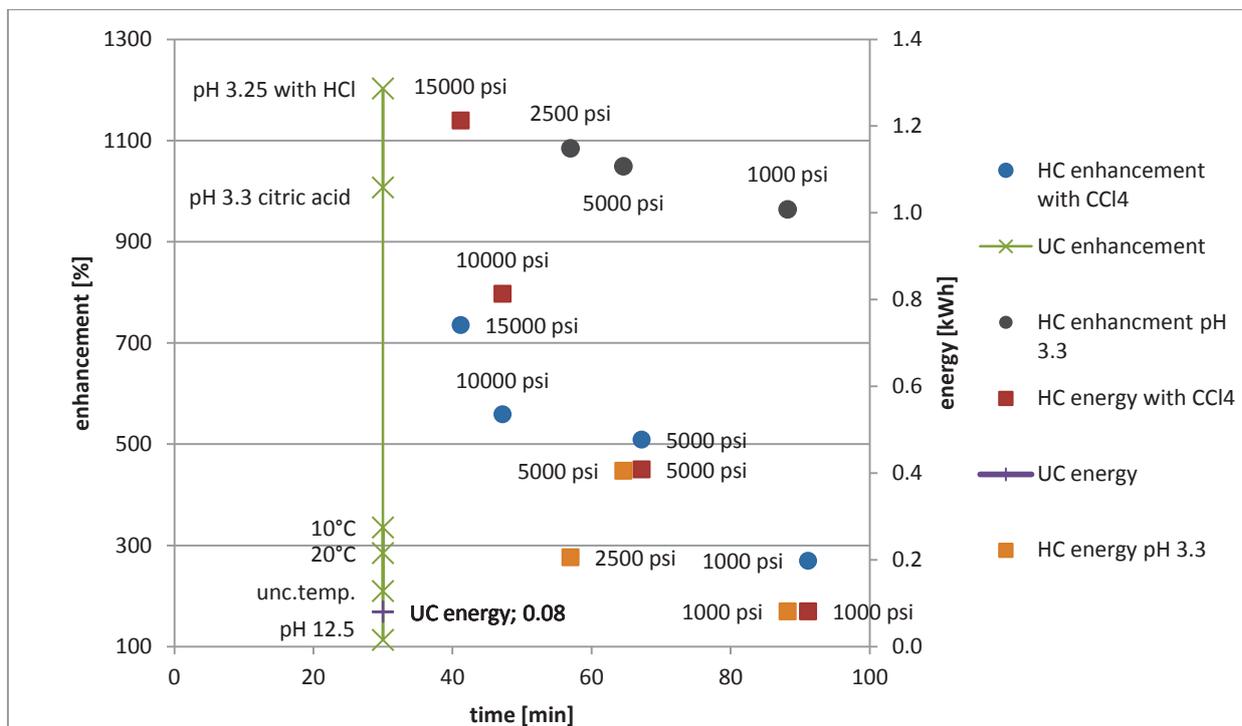


Figure 23: HC vs. UC by considering the adding of CCl<sub>4</sub> and different pH; Citric acid (10 %) is used to set the pH to 3.3; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1; the impact of the low pH is more weighty than the adding of CCl<sub>4</sub>.

A very interesting fact is represented by Figure 23. The enhancement in case of the low pH, set through citric acid, is for both systems approximately the same. The optimum for the HC system was found with a pressure of 2500 psi. The HC low pH (citric acid) shows an approx. 3 to 4 times better enhancement than at 15000 psi where  $\text{CCl}_4$  is added. The discussion referring to UC test with a pH 3.25 (with HCl) can be found on page 55. The adding of  $\text{CCl}_4$  or any other chemical in the applied low concentrations does not influence the energy demand. The deviation is due to the slightly different used starting volumes.

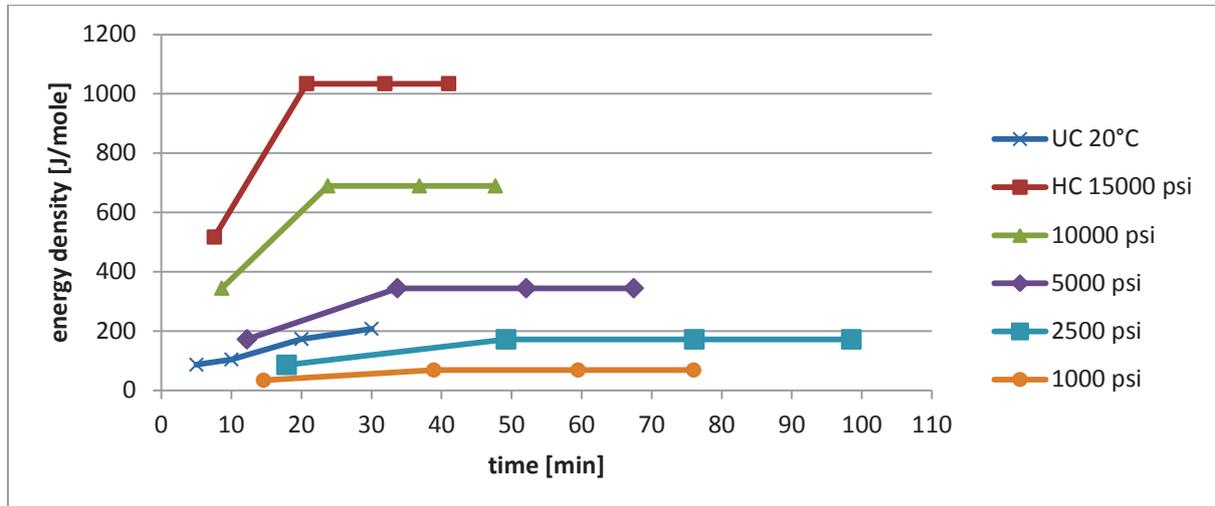


Figure 24: HC vs. UC by considering the energy density over time; all HC tests with different pressure at 20°C; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1.

The energy follows the already determined rule, the higher the pressure, the higher the energy density and the costs. The energy density of the UC test is positioned between the HC test with 2500 and 5000 psi. The energy input during the UC test increases much steeper over time than observed with the HC tests with 1000 and 2500 psi. This finding confirms the literature (Capocelli et al. 2014b, p. 17).



Figure 25: UC vs. HC to show the UC sample where CCl<sub>4</sub> is added and how big the difference is between the other samples considering the enhancement; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1.

An exception is pictured in Figure 25: The pH of 3.25 for the UC test is set through 0.1 M HCl. The use of HCl is not representative because it is a very strong acid and causes concentration gradients in the solution. Beside the supply of  $H^+$ - ions the hydrochloric acid also provides  $Cl^-$ - ions, which forms strong radicals under cavitation conditions.<sup>28</sup> Through cavitation chloride radicals are formed which are attacking the potassium iodide to liberate iodine. It should be noticed that the adding of 0.1 M HCl to the starting volume causes a formation of the  $I_3^-$ - complex without any cavitation. The effect with 10 % citric acid is also given, but the concentration is 3-times smaller which is due to the weaker acid. The coloring increases in both cases with time. A 20-fold increase of  $I_3^-$ - production was determined by Suslick (1990) after adding liquid  $CCl_4$  to the solution until saturation. The diagram in Figure 25 is required because of the UC test with  $CCl_4$ . It shows that this experiment stands alone with a 48-fold increase of  $I_3^-$ - production.

## 5.2 Oxidation of sulfite

To understand the analytic behind this calculation, it is important to know that the UV/VIS always measures the sulfite ( $SO_3^{2-}$ ) concentration. The difference between the initial mole of sulfite and the mole of sulfite after the treatment, based on passes or time, are the mole of sulfate ( $SO_4^{2-}$ ), respectively the oxidation output. The data of the parameters is given below (Table 34 - Table 37) for the series 1.9 - 4.9. The explanation of the identical parameters and calculated values are explained in 5.1. Parameters which are calculated in a different way are explained below the tables.

### 5.2.1 Oxidation of sulfite: Calculation scheme HC

Table 34: Settings.

number. series	initial concentration				passes	inlet pressure	orifice dimension	min/pass	time	time real	time accumulated
	$C_0$	sample $m_{0s}$	sample real $m_{0Sr}$	sample real corr. $V_{0src}$	$\Omega$	$p_i$	-	$t/\Omega$	t	$t_r$	$t_{acc}$
	mmole/l	g	g	ml	-	psi	thousandths of an inch	min/pass	min	h:mm:ss	min
1.9	25	300	301.4	301.47	5	5000	6/8	1.84	9.2	00:09:12	9.2
2.9		280	280.8	280.87	15			1.71	17.2	00:17:09	26.35
3.9		260	259.3	259.36	25			1.58	15.8	00:15:50	42.18
4.9		240	238.3	238.36	35			1.46	14.6	00:14:33	56.74

<sup>28</sup> See Different pressure and carbon tetrachloride ( $CCl_4$ ) in 5.1.3.2 for more details.

Table 35: Measured temperature and concentration.

T1 (vessel)	T2 (vessel skin)	T3 (after cav. unit)	T4 (after heat ex)	sample taken at Arisdyne	extinction	concentration $SO_3^{2-}$	$SO_3^{2-}$ - mole per sample
T11/T12	T21/T22	T31/T32	T41/T42	$m_{sAr}$	$\zeta_{HX}$	$C_{HC}$	$n_{SO_3^{2-}}$
°C	°C	°C	°C	g	-	mmole/l	µmole
21.3/20.4	22.2/20.9	29.5/27.4	chiller 20°C	20.6	0.4123	14.58	4093.82
20.4/20.4	20.9/20.9	27.4/27.1		21.5	0.4224	14.95	3877.03
20.4/20.4	20.9/20.9	27.1/27.0		21	0.4475	15.87	3783.81
20.4/20.4	20.9/20.9	27.0/27.1		21.8	0.4487	15.92	3447.25
						25	7536.81

The text “chiller 20°C” in Table 35 (column “T4 (after heat ex)”) means, that a chiller for constant temperature conditions is used. At Arisdyn e a scale with a maximum of 20 kg and 1 digit was used to weigh the samples. At CSM an analytical scale with a maximum of 160 g and 4 digits was in action. No back weights were made at CSM. The extinction is realized through measuring the absorbance of the samples with the UV/VIS at a wavelength of 430 nm.<sup>29</sup> The last two rows represent the initial concentration and multiplied with the starting volume, the moles of  $SO_3^{2-}$  of the reference solution.

### 5.2.1.1 $SO_3^{2-}$ - mole per sample

The column “ $SO_3^{2-}$  - mole per sample” in Table 35 describes the amount of mole in each sample after certain passes (Equation 50 and Equation 51).

$$n_{SO_3^{2-},initial} = C_0 * V_{0src} = 25 * 10^3 \frac{\mu mole}{l} * 0.30147 l \quad \text{Equation 50}$$

$$= 7536.81 \mu mole$$

$$n_{SO_3^{2-},5passes} = C_{HC} * V_{0src} = 14.58 * 10^3 \frac{\mu mole}{l} * 0.28087 l \quad \text{Equation 51}$$

$$= 4093.82 \mu mole$$

Table 36: Calculated production and percentage of oxidation.

$SO_4^{2-}$ - production	$SO_4^{2-}$ - production total	rate of $SO_4^{2-}$ - production	rate of $SO_4^{2-}$ - production	percentage of oxidation
$n_p$	$n_{ptot}$	$n_p/\Omega$	$n_p/t$	-
µmole	µmole	µmole/pass	µmole/s	%
3442.98	4089.56	688.60	6.24	54.26
216.79		21.68	0.21	
93.22		9.32	0.10	
336.56		33.66	0.39	

<sup>29</sup> See Measuring method for samples in 4.2.2.7.

### 5.2.1.2 $SO_4^{2-}$ - production

The  $SO_4^{2-}$  - production after certain passes and after 35 passes is calculated with Equation 52 and Equation 53. The different rates of  $SO_4^{2-}$  - production are calculated the same way as described in 5.1.1.15 for the liberation of iodine.

$$\begin{aligned} n_p &= n_{SO_3^{2-},initial} - n_{SO_3^{2-},5passes} && \text{Equation 52} \\ &= 7536.81 \mu\text{mole} - 4093.82 \mu\text{mole} \\ &= 3442.98 \mu\text{mole} \end{aligned}$$

$$\begin{aligned} n_{ptot} &= n_{SO_3^{2-},initial} - n_{SO_3^{2-},35passes} && \text{Equation 53} \\ &= 7536.81 \mu\text{mole} - 3447.25 \mu\text{mole} \\ &= 4089.56 \mu\text{mole} \end{aligned}$$

After 35 passes 4089.56  $\mu\text{mole}$  sulfate are created through cavitation.

### 5.2.1.3 Percentage of oxidation

The percentage of oxidation examines the question of how much of the initial moles of sulfite are oxidized to sulfate through HC. There are two possibilities to calculate the percentage (Equation 54 and Equation 55).

$$\begin{aligned} \text{percentage of oxidation} &= \frac{100}{n_{SO_3^{2-},initial}} * n_{ptot} && \text{Equation 54} \\ &= \frac{100}{7536.81 \mu\text{mole}} * 4089.56 \mu\text{mole} = 54.26 \% \end{aligned}$$

$$\begin{aligned} \text{percentage of oxidation} &= 100 - \frac{100}{n_{SO_3^{2-},initial}} * n_{SO_3^{2-},35passes} \\ &= 100 - \frac{100}{7536.81 \mu\text{mole}} * 3447.25 \mu\text{mole} && \text{Equation 55} \\ &= 54.26 \% \end{aligned}$$

More than 50 % of the initial sulfite is oxidized to sulfate over the range of 35 passes at the given pressure of 5000 psi and the temperature of 20°C.

Table 37: Calculated power and energy demand and oxidation efficiency.

flow rate	power consumption $n P = \dot{Q} * \Delta p$	power consumption total	energy density	energy	energy costs	oxidation efficiency	oxidation efficiency total
$\dot{Q}$	P	$P_{tot}$	$\rho_e$	-	11.2 ¢/kWh	$O_e$	$O_{etot}$
m <sup>3</sup> /s	W	W	J/ml	kWh	¢	$\mu\text{mole}/\text{J}$	$\mu\text{mole}/\text{J}$
2.73E-06	94.12	376.47	172.375	0.36	3.99	6.63E-02	3.19E-03
	94.12		344.75			2.24E-03	
	94.12		344.75			1.04E-03	
	94.12		344.75			4.10E-03	

### 5.2.1.4 Oxidation efficiency

The parameter “oxidation efficiency” in Table 37 is calculated the same way as described for the “liberation efficiency” in 5.1.1.18. It shows how many  $\mu\text{mole}$  are oxidized per Joule.

### 5.2.2 Oxidation of sulfite: Calculation scheme UC

The parameters and values for the sulfite oxidation caused by UC are calculated the same way as for the liberation of iodine in 5.1.2. The relevant differences referring to the experimental setup are the same as for the HC system.<sup>30</sup>

### 5.2.3 Oxidation of sulfite: Results

Table 38 shows the used pressure, orifice dimensions and temperatures for all HC tests. The test with an applied pressure of 1000 psi is executed with two different temperatures. An oxidation is an exothermic reaction ( $\Delta H_R$  is negative) and a temperature increase shifts the equilibrium to the left side. To investigate the performance of the oxidation at higher temperature, 42 °C has been chosen (Figure 29). The temperature T1 in Table 38 is the temperature in the hopper.<sup>31</sup> To get more volume per stroke of the plunger pump through the cavitation unit, orifice dimension 6/8 is used for 2500, 5000 and 15000 psi and dimension 8/12 is used for 1000 psi.

Table 38: Settings for HC tests.

pressure	orifice dimension	temperature
$p_i$	-	T1
psi	thousandths of an inch	°C
15000	6/8	20
5000	6/8	20
2500	6/8	20
1000	8/12	20/42

<sup>30</sup> See 4.3.2.2 and the paragraph below 5.2.

<sup>31</sup> See flow chart in 4.3.1.

The results of the HC tests with different pressures at 20°C are given in Figure 26. At very high pressure (red line, 15000 psi) the system produces about 4000  $\mu\text{mole}$  of  $\text{SO}_4^{2-}$  after five passes. Lower pressure like 1000, 2500 and 5000 psi causes a total  $\text{SO}_4^{2-}$ - production of about 3500  $\mu\text{mole}$  after 5 passes. After the first 5 passes the cavitation unit produces enough free radicals respectively  $\text{H}_2\text{O}_2$  to oxidize sulfite to sulfate. It is apparent that in all cases, the production is the highest after 5 passes and drops afterwards. It can be found that after 15, 25 and 35 passes the production is constant for all pressures. The data points at 15 and 35 passes for the tests with 15000 and 2500 psi are missing because of measurement inaccuracy but the general trend is nevertheless warranted.

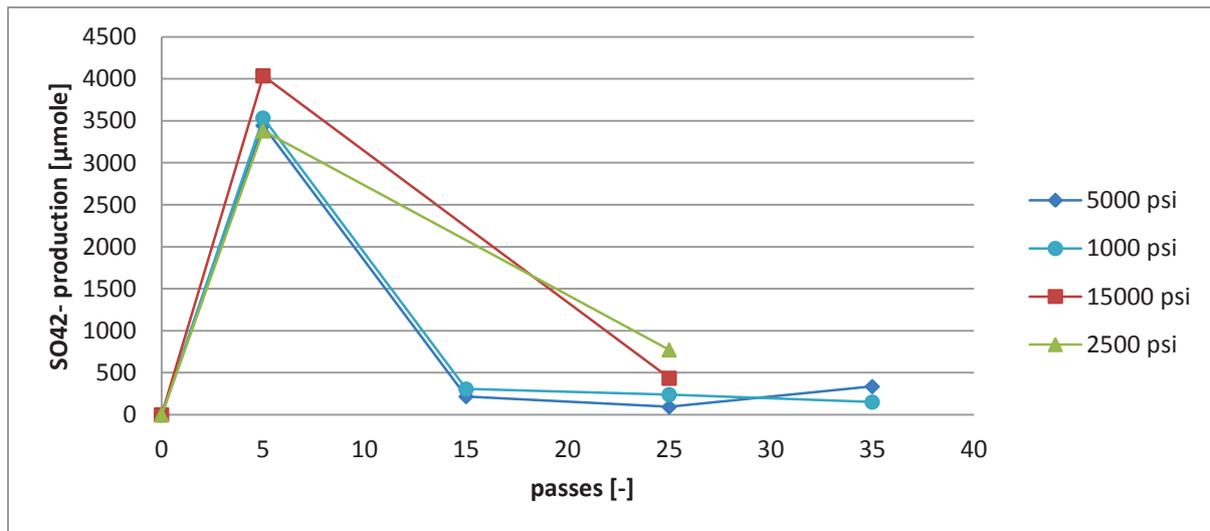


Figure 26: The sulfate production shows a peak after five passes and decreases significantly afterwards at all applied pressures, a starting concentration of 25 mmole/l and an operating temperature of 20°C.

It can be observed from Figure 26 that the production or oxidation is the highest by increasing pressure but the gap between the test with 1000 and 15000 psi is only about 500  $\mu\text{mole}$ .<sup>32</sup> This applied high pressure causes a high electrical input. As predicted and according to Figure 27, the efficiency for 15000 psi is very low. Comparing the data for 15000, 5000 and 2500 psi with 1000 psi from an economical point of view, it is clear that only the lower pressure is acceptable (red line, 1000 psi).

<sup>32</sup> See The effect of pressure in 3.2.3.

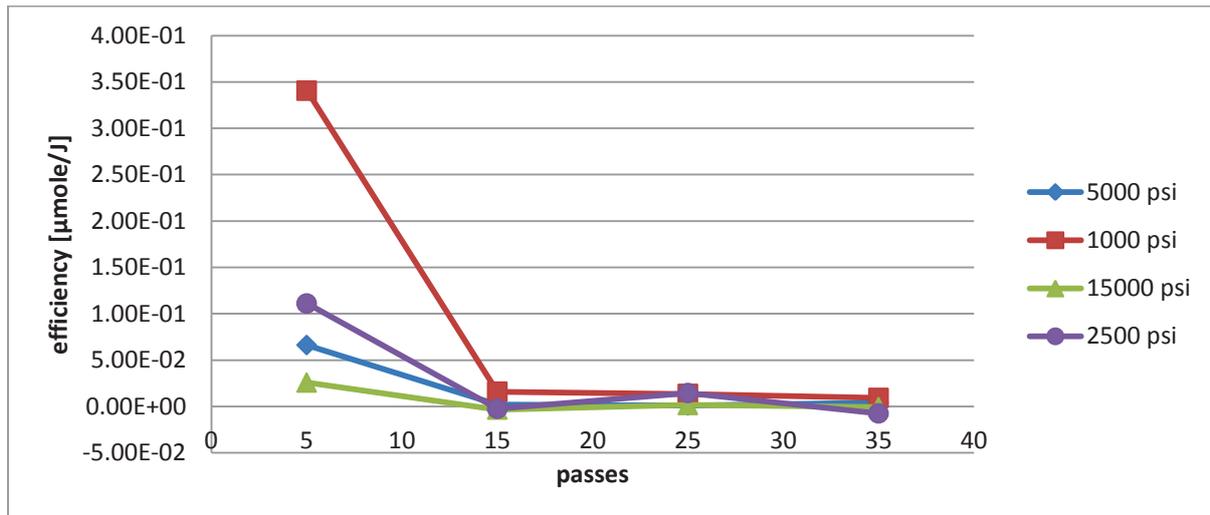


Figure 27: Efficiency over the full range of passes; samples with a starting concentration of 25 mmole/l, a different pressure range and an operating temperature of 20°C; the best efficiency shows the sample at 1000 psi.

The data in Figure 26 and Figure 27 suggest stopping the treatment after 5 passes. For industrial applications, where huge waste water volumes have to be treated, every circulation creates costs. It is useful to take a closer look at the performance of the treatment after the first, second, third, fourth and fifth pass. The results of this investigation are given in Figure 28. The efficiency after 1 pass is higher than the efficiency after 5 passes because of the very low electrical power input. The three points in the diagram (blue diamond, grey cross and orange dot) represent one experiment. In this test a sample is taken after every pass of the initial volume and stopped after the fifth pass. Two data points are missing because of measurement inaccuracy. The red line in Figure 28 presents an independent test with the same parameters. For both tests the efficiency after 5 passes matches within the measurement uncertainty. Generally speaking, a treatment with more than 5 passes can be excluded for future investigations.

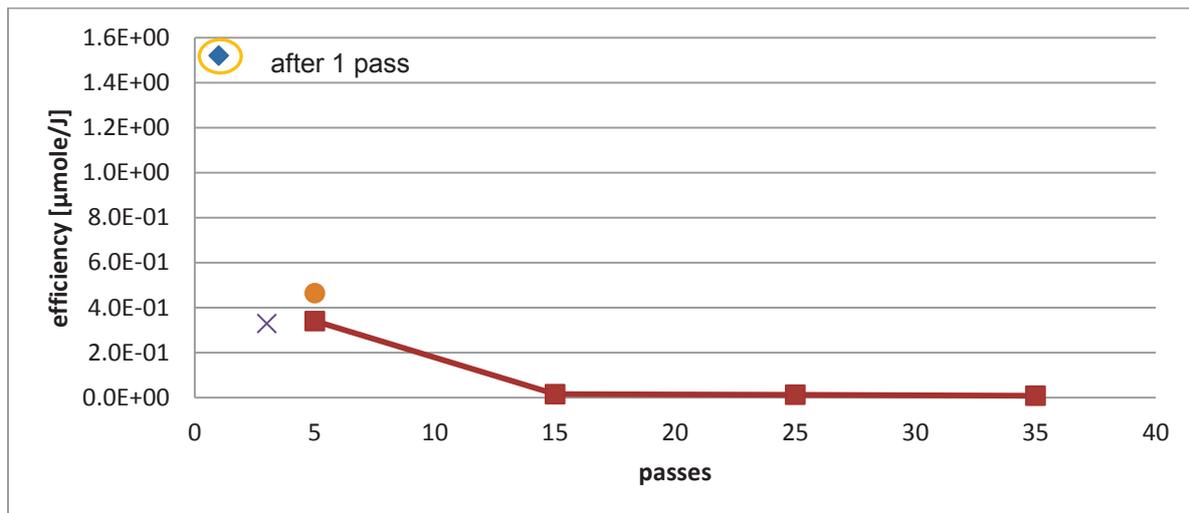


Figure 28: Closer look at the efficiency from the first to the fifth pass at 1000 psi, an operating temperature of 20°C and a starting concentration of 25 mmole/l; after one pass the efficiency is the highest and decreases by increasing the number of passes.

A certain amount of energy has to be supplied for a successful homolytic dissociation of water and further for the oxidation from sulfite to sulfate.<sup>33</sup> The required electrical energy input and the output as percentage of oxidation of the initial amount can be observed in Figure 29. At a pressure of 1000 psi and 20°C the oxidation has the highest value because at low inlet pressure the cavities have more time to generate free radicals.<sup>34</sup> On the whole, low pressure (5000, 2500 and 1000 psi) shows better results than high pressure. In consideration of the energy aspect, the application of high pressure, respectively 15000 psi can be excluded without any concerns.

<sup>33</sup> See 4.1.2.2 for more information about the oxidation.

<sup>34</sup> See 3.2.3 for more information about the different impacts of high and low pressure.

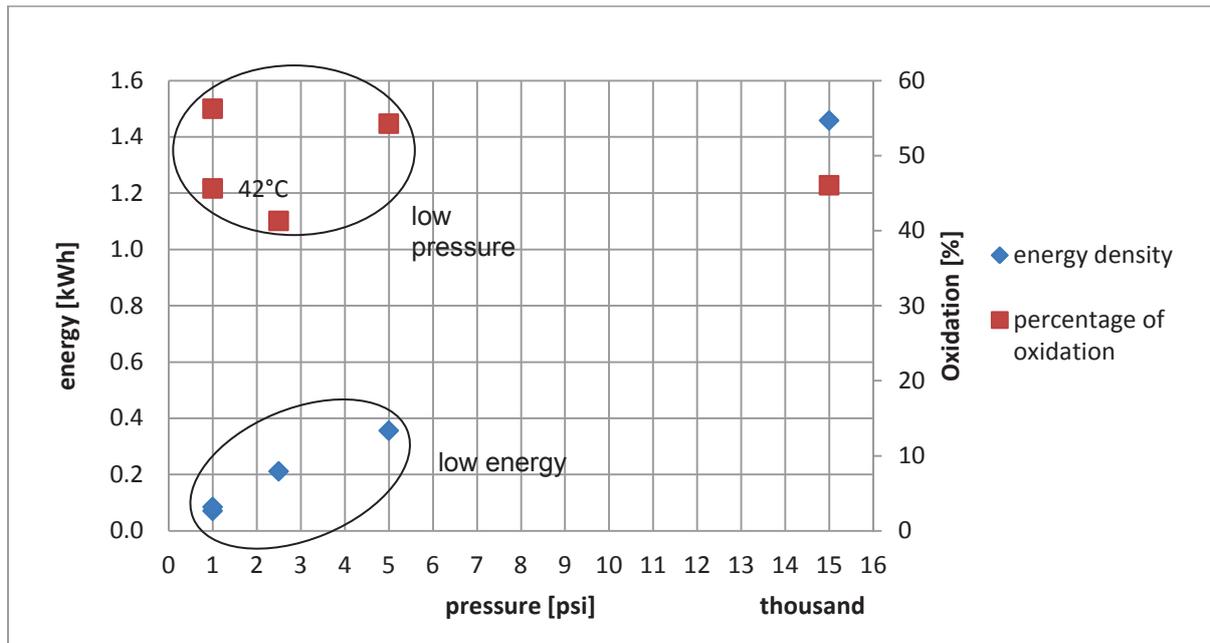


Figure 29: Starting concentration of 25 mmole/l; operating temperature of 20°C; one test with 42°C which show the negligible impact of increased operating temperature; low pressure (1000 - 5000 psi) implies low energy input with a better percentage of oxidation than the test with high pressure (15000 psi); number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1.

The findings in Figure 29 are confirmed through Figure 30. The test with 1000 psi shows the best efficiency and simultaneously lowest energy consumption.

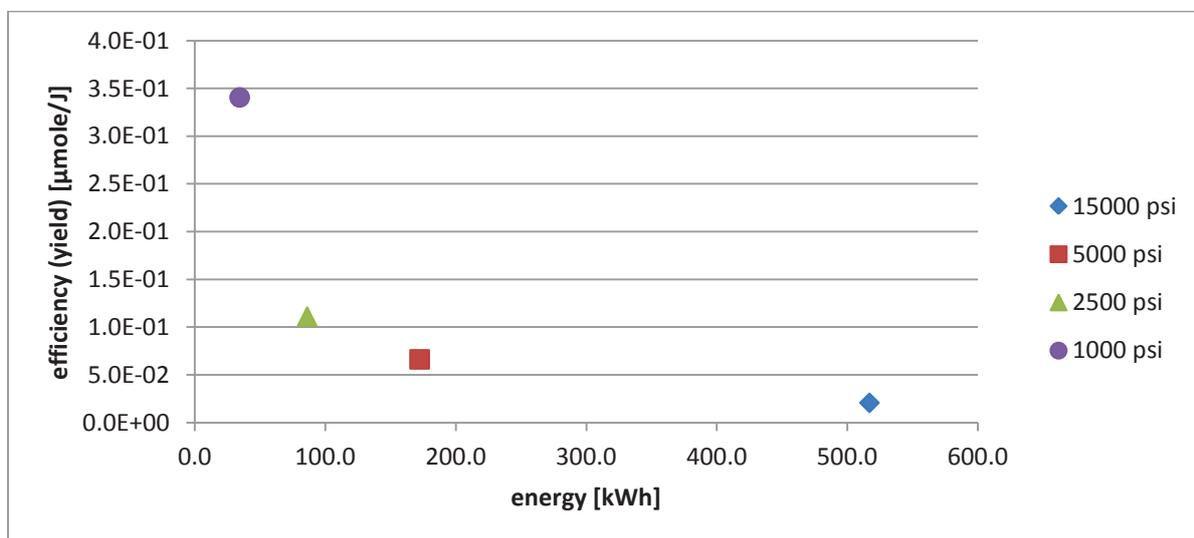


Figure 30: Efficiency vs. energy by considering different pressure; starting concentration 25 mmole/l; operating temperature 20°C; these findings are in line with the explanations in 3.2.2 and the pressure dependencies in 3.2.3.

Additionally to the efficiency and related energy, the rate of the  $SO_4^{2-}$ - production is of interest. As it can be seen from Figure 26, all tests show the highest number of produced  $\mu\text{mole}$  after the first 5 passes. According to this fact, Table 39 shows very high rates after 5

passes comparing to the other rates after more passes. The numbers in the brackets belong to the number of the series. A few cells are empty because of the measurement inaccuracy but the tendency is still the same in every test. The highest rate is presented by the test with 15000 psi. The application of this high pressure for further tests can be excluded because of the small additional gain between this test and the one with 1000 psi (approx. 45  $\mu\text{mole}$  per pass) and the very high energy consumption.

Table 39: Rate of  $\text{SO}_4^{2-}$  - production.

passes	rate of $\text{SO}_4^{2-}$ - production (1.14-4.14)	rate of $\text{SO}_4^{2-}$ - production (1.9-4.9)	rate of $\text{SO}_4^{2-}$ - production (1.16-4.16)	rate of $\text{SO}_4^{2-}$ - production (1.10-4.10)
$\Omega$	$n_p/\Omega$	$n_p/\Omega$	$n_p/\Omega$	$n_p/\Omega$
-	$\mu\text{mole/pass}$	$\mu\text{mole/pass}$	$\mu\text{mole/pass}$	$\mu\text{mole/pass}$
5	751.36	688.60	675.99	706.70
15	-	21.68	-	30.65
25	51.12	9.32	77.28	24.08
35	-	33.66	-	15.16

Referring to several literature references like Morison, K. and Hutchinson, C. 2009, p. 182 or Chakinala et al. 2008, p. 166, the more common way to describe the generation rate is in  $\mu\text{mole}$  per time unit, as illustrated by Figure 31. The graphs show the same courses as the values in Table 39 because  $\mu\text{mole}$  per seconds is just a different representation method for  $\mu\text{mole}$  per passes. Comparison of Figure 30 with Figure 31 shows that the generation rate is approx. 2  $\mu\text{moles}$  per second increased with the pressure of 15000 psi.

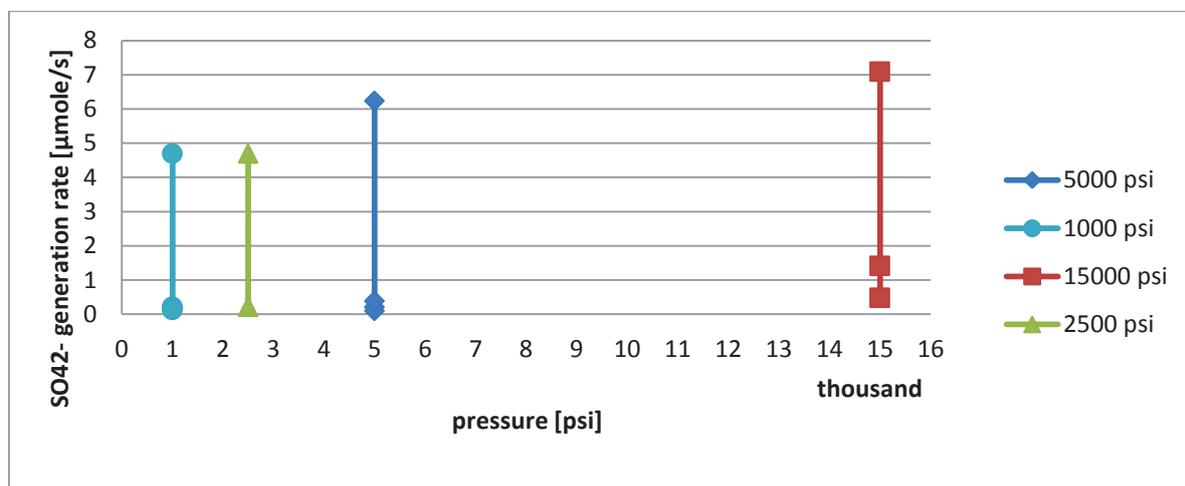


Figure 31:  $\text{SO}_4^{2-}$  generation rate over pressure shows the best rate at 15000 psi; starting concentration 25 mmole/l; different pressure; operating temperature 20 °C.

#### 5.2.4 Oxidation of sulfite: Comparison HC with UC

In this section, the two used cavitation systems are compared and the results of the UC tests are added (Figure 32).

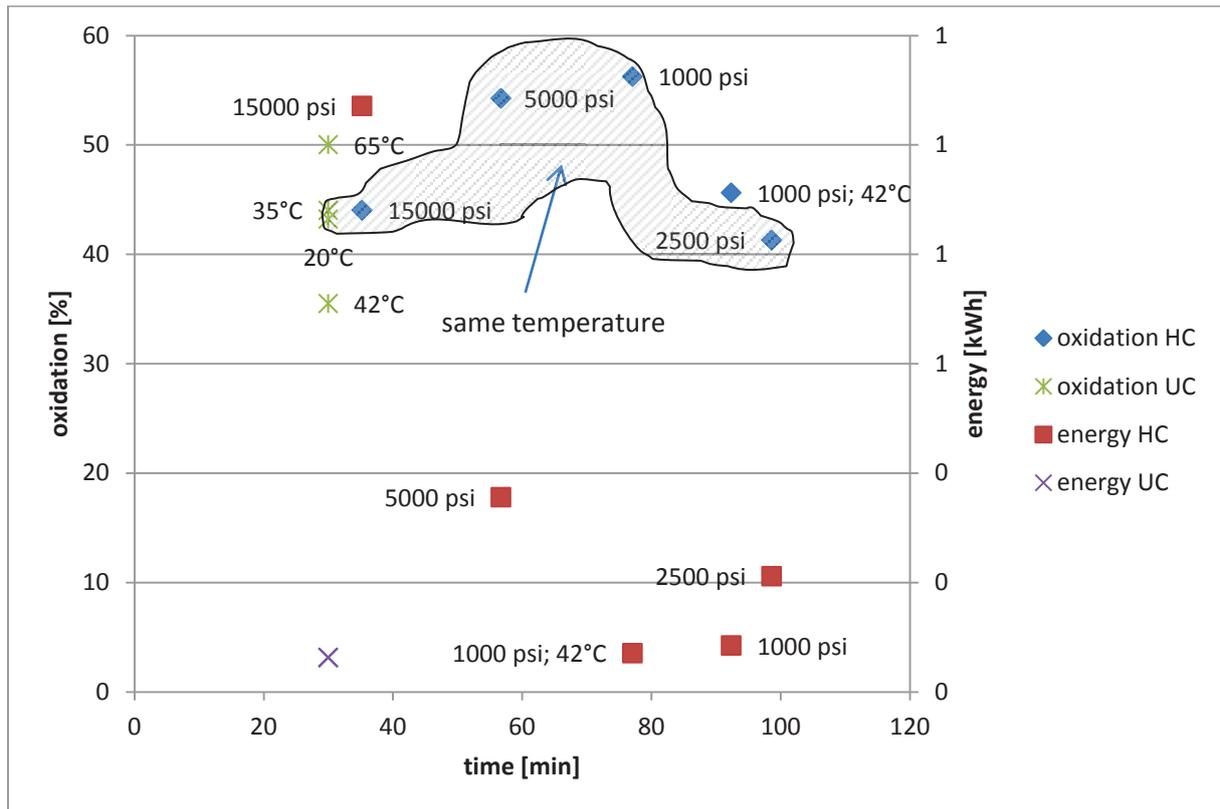


Figure 32: HC vs. UC with a starting concentration of 25 mmole/l for all tests; the marked HC tests are performed with different pressure at 20°C; UC tests with different temperature; the temperature effect on the UC samples does not show a specific direction; the percentage of oxidation increases by decreasing the pressure of the HC samples and shows an approx. 10 % improvement (1000 psi) compared to the UC sample at the same temperature.

The data points within the marked area in Figure 32 allow a comparison of the oxidation performance of the HC - system with the UC - system under the same temperature conditions. Inspection of Figure 32 indicates a further improvement of the oxidation performance of the UC tests by increasing the temperature from 35 to 65°C and deterioration with a temperature of 42°C. Under HC conditions the tendency occurs to be the opposite. Even the UC test with 65°C is not able to reach the performance of the HC test with 1000 psi at 20°C. The energy for all UC tests is the same because of the constant treatment settings. The energy for the HC system follows the already known course - high pressure causes a high energy demand.

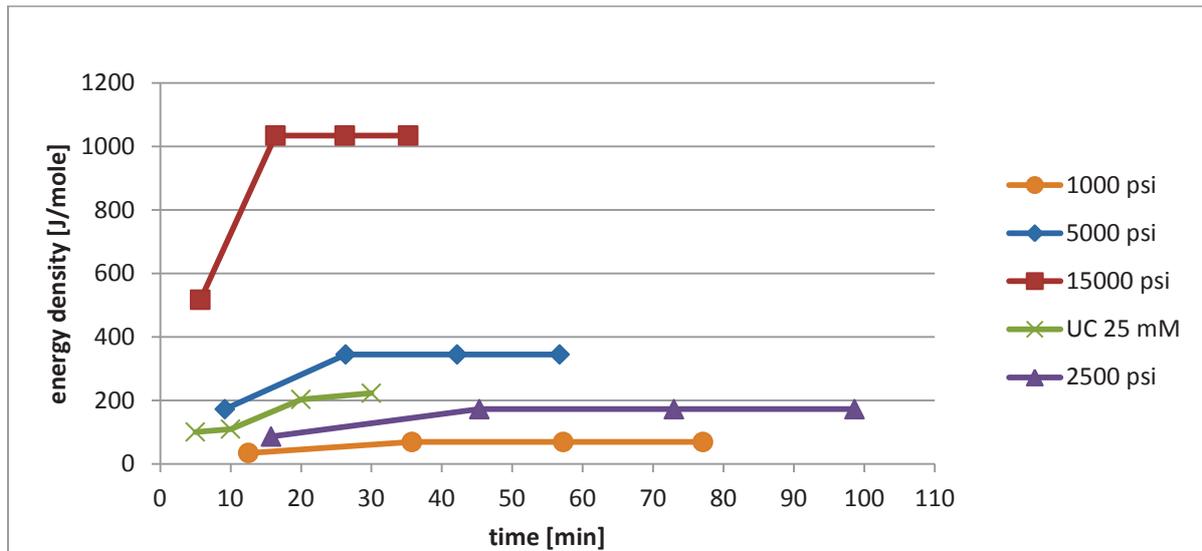


Figure 33: HC vs. UC by considering the energy density over time at the same operating temperature of 20°C and a starting concentration of 25 mmole/l; HC with different pressure; “mM” stands for mmole/l; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1.

The UC test with 20 °C can be found, referring to energy density, between the HC tests with high and low pressure.

### 5.3 Degradation of PNP

The UV/VIS measures the *PNP*- concentration. The difference between the initial mole of PNP and the mole of PNP after the treatment, based on passes or time, are the removed or metabolized mole of PNP respectively the oxidation output. The data of the different parameters is given below (Table 40 - Table 44) for the example series 1.5 - 4.5.

#### 5.3.1 Degradation of PNP: Calculation scheme HC

The parameters and values are calculated the same way as for the liberation of iodine in 5.1.1. Explanations for new parameters can be found below each specific table.

Table 40: Settings.

number series	initial concentration				passes	inlet pressure	orifice dimension	min/pass	time	time real	time accumulated							
	$C_0$	sample $m_{0s}$	sample real $m_{0Sr}$	sample real corr. $V_{0src}$								$\Omega$	$p_i$	-	$t/\Omega$	$t$	$t_r$	$t_{acc}$
	$\mu\text{mole/l}$	g	g	ml								-	psi	thousands of an inch	min/pass	min	h:mm:ss	min
1.5	25	400	400	401.4	5	1000	8/12	3.34	16.7	00:16:43	16.72							
2.5		350	350.8	352	15			2.93	29.3	00:29:20	46.06							
3.5		300	300	301	25			2.51	25.1	00:25:05	71.14							
4.5		250	247	247.8	35			2.07	20.7	00:20:39	91.79							

Table 41: Measured temperature and concentration.

T1 (vessel)	T2 (vessel skin)	T3 (after cav. unit)	T4 (after heat ex)	sample taken at Arisdyn	pH1	pH2	extinction	concentration of PNP	PNP-mole per sample
T11/T12	T21/T22	T31/T32	T41/T42	$m_{sAr}$	-	-	$\zeta_{HX}$	$C_{HC}$	$n_{PNP}$
°C	°C	°C	°C	g	-	-	-	$\mu\text{mole/l}$	$\mu\text{mole}$
20.8	21.1	23.1	chiller 20°C	49.2	6.9	11.1	0.4327	23.41	8.24
20.4	20.9	23		50.8	7	11.1	0.4347	23.52	7.08
20.3	20.8	22.7		53	6.9	11.1	0.434	23.48	5.82
20.3	20.8	22.7		50	6.9	11.1	0.4323	23.39	4.63

As mentioned in 4.1.3.1, PNP is very sensitive when the pH changes. The absorbance at a wavelength of 400 nm is measured with a UV/VIS.<sup>35</sup> Kalumuck (2000, p. 467) reports that the pH of the solution has to be set to 11 and refers to the study of Hua et al. (1995, p. 2336). In their study they prefer a pH of approx. 12. In this study the pH is set between 11 and 12. The

<sup>35</sup> See Measuring with the UV/VIS in 4.2.3.4.

parameters “pH1” and “pH2” in Table 41 describe the pH directly after the treatment and after adding NaOH to increase the pH.

### 5.3.1.1 PNP - mole per sample

The column “PNP- mole per sample” in Table 41 describes the amount of mole which stays in each sample after certain passes (Equation 56). The variable  $n_{PNP,5passes}$  examines the question of how many  $\mu\text{mole}$  are left in the solution after for example 5 passes. The volume  $V_{0src,2.5}$  is the solution volume after 5 passes and also after the sample was taken. The number 2.5 is the name of the series (Table 40).

$$\begin{aligned} n_{pNP,5passes} &= C_{HC} * V_{0src,2.5} = 23.41 \frac{\mu\text{mole}}{l} * 0.352 l \\ &= 8.24 \mu\text{mole} \end{aligned} \quad \text{Equation 56}$$

To review the initial concentration, a random sample from one of the initial solutions was taken. The result is listed in Table 42 and they confirm the calibration chart (Figure 9 in 4.2.3.5). The little deviation of the calculated and measured concentration is because of the measurement uncertainty of the UV/VIS ( $\sim 0.4\%$ ).

Table 42: The data represents the control of the initial solution; concentration  $25 \mu\text{mole/l}$ .

calculated concentration	pH1	pH2	extinction	measured concentration
$C_0$	-	-	$\zeta_{HC}$	$C_{HC,initial}$
$\mu\text{mole/l}$	-	-	-	$\mu\text{mole/l}$
25	6.25	11.00	0.464	25.0967

Table 43: Calculated PNP degradation and percentage of degradation.

PNP - degradation	PNP - degradation total	rate of PNP-degradation	rate of PNP-degradation	percentage of degradation	percentage of degradation total
$n_{deg}$	$n_{degtot}$	$n_{deg}/t$	$n_{deg}/\Omega$	-	-
$\mu\text{mole}$	$\mu\text{mole}$	$\mu\text{mole/s}$	$\mu\text{mole/pass}$	%	%
1.83	5.44	1.83E-03	3.66E-01	18.18	54.06
1.16		6.60E-04	1.16E-01	29.71	
1.26		8.37E-04	1.26E-01	42.22	
1.19		9.62E-04	1.19E-01	54.06	

### 5.3.1.2 PNP - degradation

The PNP - degradation after the first five passes is calculated with Equation 57.  $n_{PNP,initial}$  bases on the values from Table 42 and is used as reference for every series respectively for the degradation after certain passes. Equation 57 implies the procedure for the other passes.  $1.83 \mu\text{mole}$  and  $1.16 \mu\text{mole}$  are the amount of  $\mu\text{mole}$  which are removed or metabolized after 5 and 15 passes. The different rates of PNP - production are calculated identically as described in 5.1.1.15 for the liberation of iodine.

$$\begin{aligned}
 n_{deg,5\ passes} &= n_{pNP,initial} - n_{pNP,5\ passes} \\
 &= (C_{HC,initial} * V_{0src,1.5}) - n_{pNP,5\ passes} \\
 &= \left( 25.0967 \frac{\mu mole}{l} * 401.4 * 10^{-3} l \right) - 8.24 \mu mole \\
 &= 1.83 \mu mole
 \end{aligned}
 \tag{Equation 57}$$

$$\begin{aligned}
 n_{deg,15\ passes} &= n_{pNP,5\ passes} - n_{pNP,15\ passes} \\
 &= 8.24 \mu mole - 7.08 \mu mole = 1.16 \mu mole
 \end{aligned}
 \tag{Equation 58}$$

After 35 passes 5.44  $\mu mole$  PNP are removed in total through HC ( $n_{degtot}$ ).

### 5.3.1.3 Percentage of degradation

The initial amount of  $\mu mole$  PNP is the same within one series. In this case (1.5 - 4.5) it is 401.4 ml multiplied with the reference concentration (Table 42). With Equation 59 the degradation regarding to the initial amount after 5 passes is calculated.

$$\begin{aligned}
 \text{percentage of degradation after 5 passes} &= \frac{100}{n_{pNP,initial}} * n_{deg,5\ passes} \\
 &= \frac{100}{\left( 25.0967 \frac{\mu mole}{l} * 401.4 * 10^{-3} l \right)} * 1.83 \mu mole \\
 &= 18.18 \%
 \end{aligned}
 \tag{Equation 59}$$

The total percentage of degradation describes how much of the initial mole of PNP are removed through cavitation (Equation 60).

$$\begin{aligned}
 \text{percentage of degradation total} &= \frac{100}{n_{pNP,initial}} * n_{degtot} \\
 &= \frac{100}{\left( 25.0967 \frac{\mu mole}{l} * 401.4 * 10^{-3} l \right)} * 5.44 \mu mole \\
 &= 54.06\%
 \end{aligned}
 \tag{Equation 60}$$

More than 50 % of the initial PNP is removed or metabolized after 35 passes at the given pressure of 1000 psi and the temperature of 20°C.

Table 44: Calculated power demand, energy costs and efficiency of degradation.

flow rate	power consumption $P = \dot{Q} * \Delta p$	power consumption total	energy density	energy	energy costs	degradation efficiency	degradation efficiency total
$\dot{Q}$	P	$P_{tot}$	$\rho_e$	-	11.2 ¢/kWh	$D_e$	$D_{etot}$
m <sup>3</sup> /s	W	W	J/ml	kWh	¢	µmole/J	µmole/J
2.00E-06	13.79	117.22	34.475	0.18	2.01	1.32E-04	8.43E-06
3.00E-06	20.69		103.425			3.19E-05	
5.00E-06	34.48		172.375			2.43E-05	
7.00E-06	48.27		241.325			1.99E-05	

### 5.3.1.4 Degradation efficiency

The parameter “degradation efficiency”  $D_e$  in Table 44 is calculated with Equation 61. It shows how many µmole are removed per Joule.

$$D_e = \frac{n_{deg,5passes}}{P * t} = \frac{1.83 \mu mole}{13.79 W * 16.72 * 60 s} = 1.32 * 10^{-4} \frac{\mu mole}{J} \quad \text{Equation 61}$$

### 5.3.2 Degradation of PNP: Calculation scheme UC

The results for the PNP - degradation caused by UC are calculated the same way as in Liberation of iodine: Calculation scheme UC in 5.1.2. The relevant differences are explained in Liberation of iodine and degradation of PNP in 4.3.2.1.

### 5.3.3 Degradation of PNP: Results HC

This chapter shows the results of the HC tests and discusses their meaning. Operating parameters are pressure, pH and temperature.

#### 5.3.3.1 Different pressure at 20°C

In this stage of the study tests with the already known range of different pressures are performed to find out the optimal operating pressure. The first aim was to select the one sample which shows the highest yellow intensity<sup>36</sup> through simple optical inspection. The inspection outlined the samples at 2500 psi and 1000 psi as the two relevant candidates.

<sup>36</sup> See The degradation of PNP (Para - Nitrophenol) in 4.1.3.1.

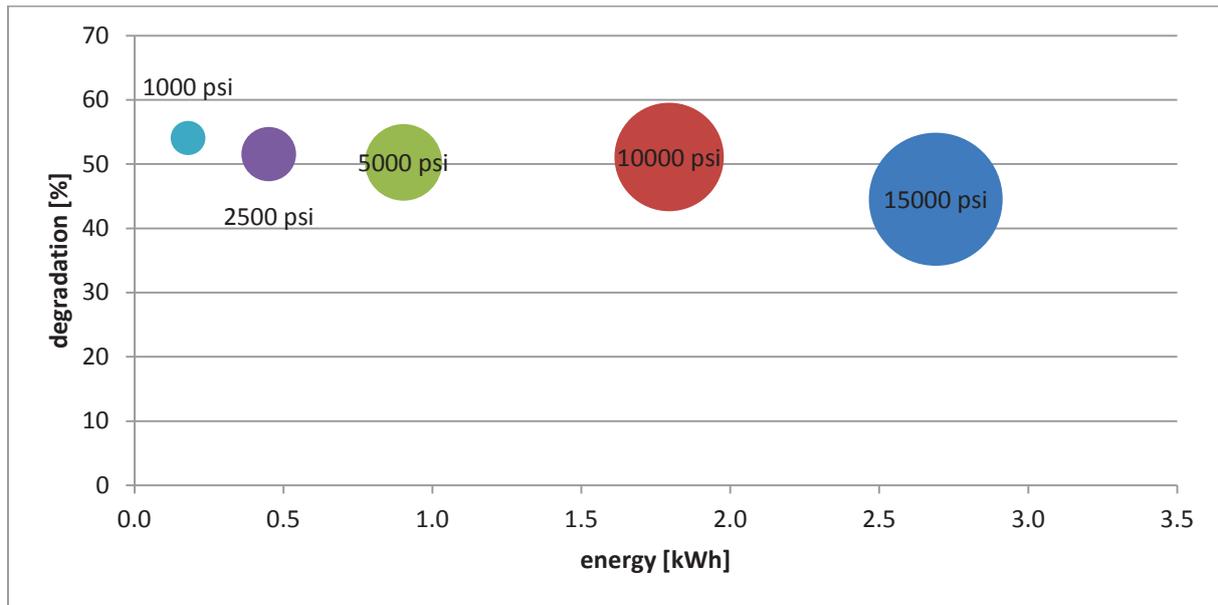


Figure 34: Percentage of degradation and the associated energy consumption over the applied pressure range; the size of the bubbles represent the pressure; the degradation of the samples (starting concentration of 25  $\mu\text{mole/l}$  and 20°C) slightly decreases by increasing the inlet pressure (see 3.2.3 for more details).

After considering the energetic aspect, a decision was made in favor of the sample with 1000 psi. The confirmation that the decision was the right one is given in Figure 34 and Figure 35. As explained in the theory section low pressure causes an increased production of free radicals.<sup>37</sup> The test with an applied pressure of 1000 psi shows a degradation of approx. 54 % and the best degradation efficiency. This result strongly supports the theory in 3.2.3 (see also the explanation below Figure 37).

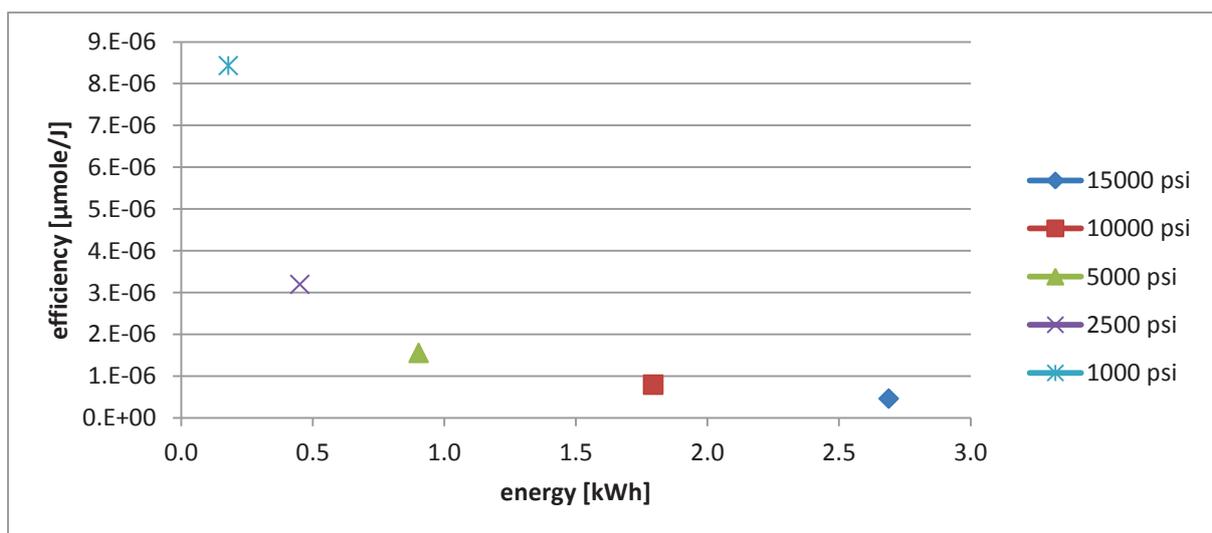


Figure 35: Efficiency over energy consumption by considering the applied pressure range; all tests have a starting concentration of 25  $\mu\text{mole/l}$  and an operating temperature of 20°C; the best efficiency is presented by the test with 1000 psi.

<sup>37</sup> See chapter 3 for more details and explanations.

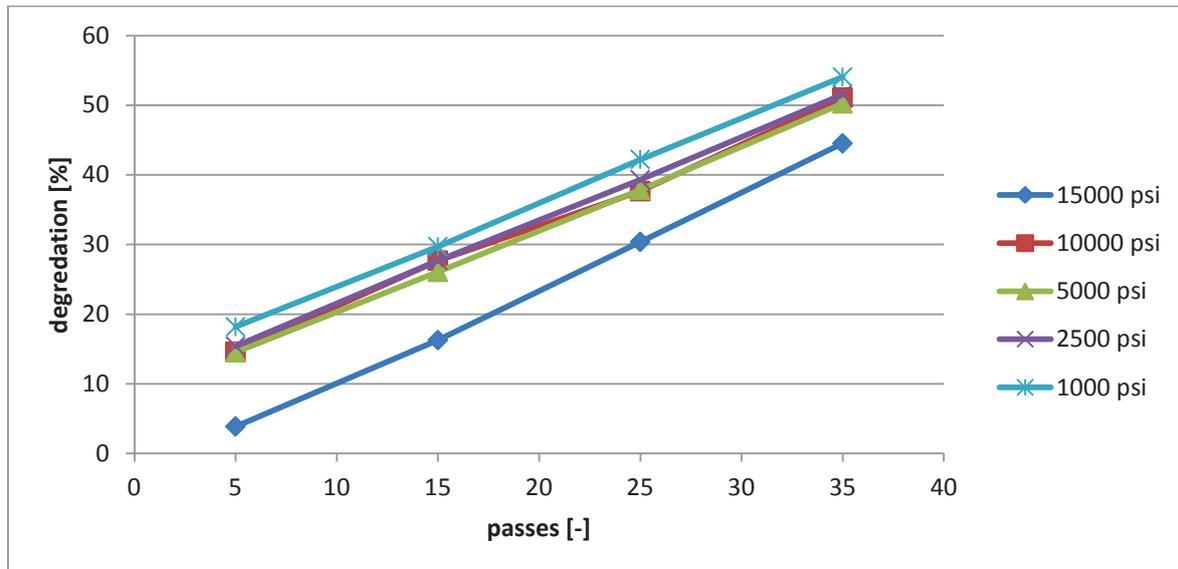


Figure 36: Degradation over the full range of passes and different pressures shows an increase by increasing the number of passes; steepest course with 1000 psi; starting concentration of 25  $\mu\text{mole/l}$ ; operating temperature of 20°C.

In all cases the degradation increases linear from 5 to 35 passes (Figure 36). As reported in chapter 4, the splitting of water through cavitation forms free radicals which attack the benzene ring. The more often the volume runs through the HC loop (Figure 11) the more radicals attack and form intermediate products.<sup>38</sup>

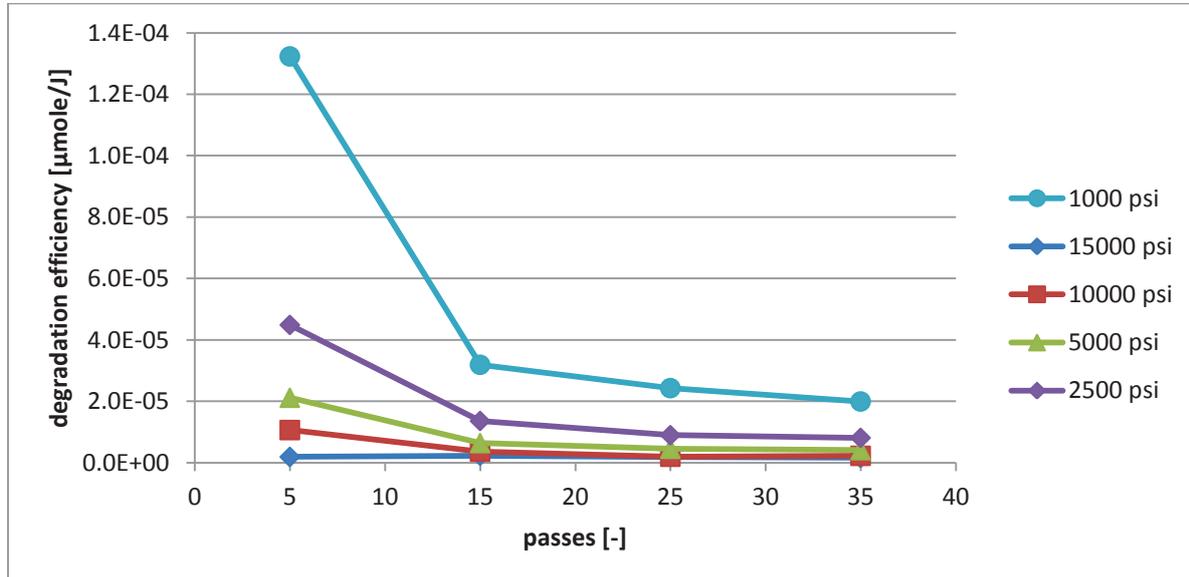


Figure 37: Degradation efficiency over the full range of passes combines the degradation and the energy aspect; starting concentration of 25  $\mu\text{mole/l}$ ; different inlet pressures; operating temperature of 20°C.

<sup>38</sup> See The degradation of PNP (Para - Nitrophenol) in 4.1.3.1 for more details about the metabolism of PNP.

It is important to reiterate that high pressure means high energy input. It can be identified from Figure 37 and Figure 35 that the test with 1000 psi has the best efficiency. On the whole the efficiency decreases strongly from 5 to 15 passes and flattens from 15 to 35 passes.

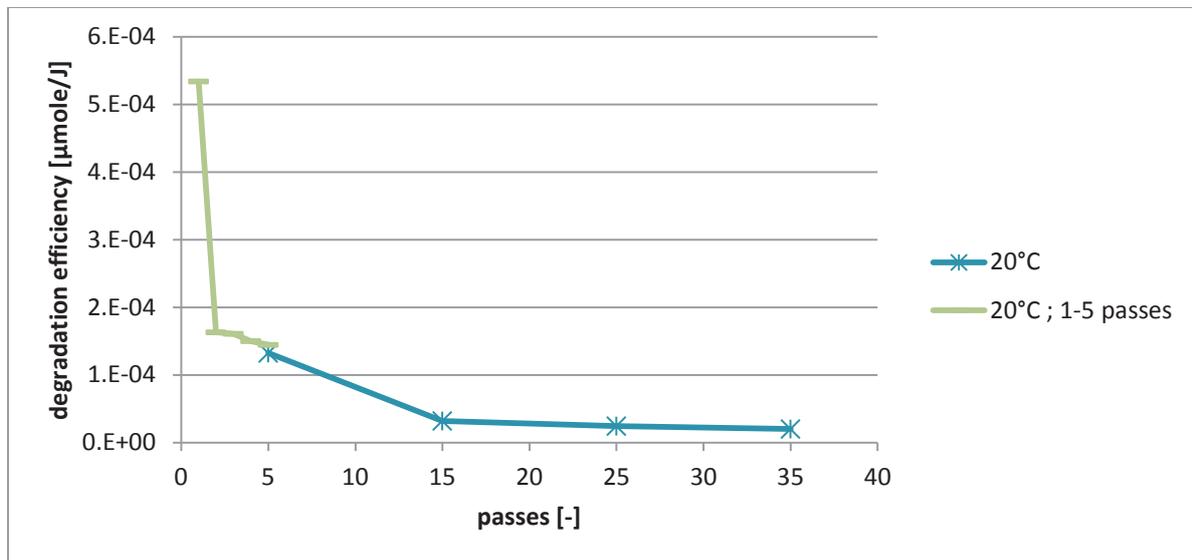


Figure 38: From the energy point of view it is useful to have a closer look at the first five passes; after the first pass the efficiency shows a peak and steeply decreases afterwards; starting concentration 25 µmole/l; inlet pressure 1000 psi; operating temperature 20°C.

As already discussed it is very important to minimize the required passes of the volume through the system because a high number of passes of huge volumes causes a high energy demand and therefore creates high costs. Figure 38 shows a closer look at the performance of the cavitation system within the first five passes. It can be observed that the graph peaks after one pass and drops afterwards. After the first pass the cavitation metabolizes more PNP - molecules per Joule as after every following pass. One logical result of this statement would be to stop the treatment after one pass of the volume, which is true if only the energy aspect is considered. By considering the degradation aspect and comparing Figure 36 with Figure 37, it is clear that a longer treatment time means on the one hand a better removal of PNP but on the other hand an increased energy demand.

### 5.3.3.2 Variable temperature and pH at 1000 psi: degradation efficiency

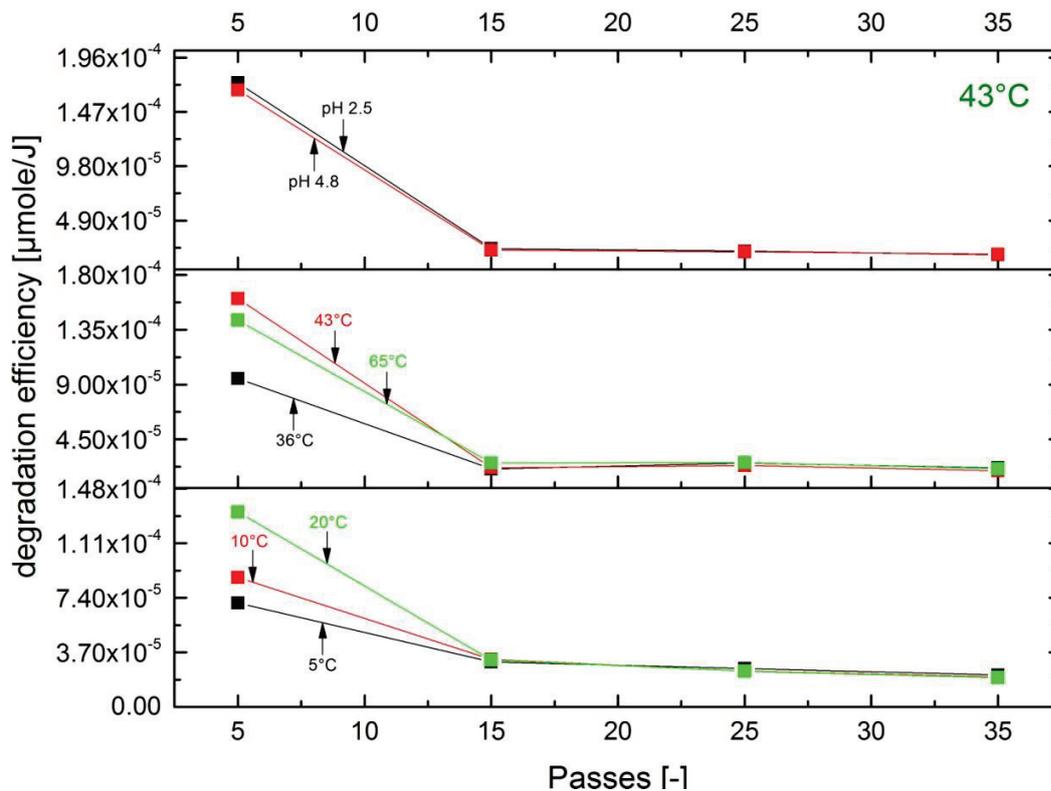


Figure 39: Degradation efficiency over the full range of passes by considering low and high operating temperature and different pH; the efficiency strongly decreases by increasing the number of passes from five to 15 passes; starting concentration 25 µmole/l.

All results regarding to degradation efficiency within the predefined passes range can be found in Figure 39. The best results can be observed from layer one with an operating temperature of 43°C and pH of 2.5 or 4.8. Both tests show an efficiency of approx.  $1.7 \cdot 10^{-4}$  µmole per Joule. This finding is in good agreement with the work of Kalumuck (2000). At high temperature the test with 43°C in layer two shows a higher efficiency compared to the tests with 36°C and 65°C. At low temperature the test with 20°C in layer three shows better results than the lower temperatures 10°C and 5°C. If the additional energy for heating or cooling is considered, the favorite test is the one with 20°C.

### 5.3.3.3 Variable temperature and pH at 1000 psi: degradation

The discussion is about the comparison of how many µmole are metabolized after certain passes. From Figure 40 it can be seen that within one test the number of removed PNP molecules is the highest after 5 passes. The number drops to its minimum after 15 passes and slightly increases from 15 to 25 passes and is stable for the last ten passes. This course demonstrates that there is still a removal or degradation of molecules after 35 passes because of the ongoing production of free radicals. The remarkable results in Figure 40 are divided into two parts as follows: Part one contains the tests with 43 °C and pH 2.5 (first layer), 43°C (second layer) and 20°C (third layer). The results from part one are promising if

industrial applications are considered (explanation below Figure 38). This investigation found evidence to suggest that the value for the ideal operating temperature is between 20 and 43°C. Compared to the results for the UC tests in 5.3.4, this tendency is quite the opposite and suggests that the metabolization reaction shows a different reaction pattern if the degradation is caused by HC. Further investigations are required to find out more details about the potential metabolization path ways (cf. section 4.1.3.1). Part two contains the rest of the results whereas these tests, performed at higher and lower temperature, can be excluded for further considerations. The tests with a pH of 2.5 and 4.8 are also excluded because compared to the test with 43°C these tests show only an increased degradation of approx. 10 % and the adding of chemicals and additional heating energy decrease the efficiency.

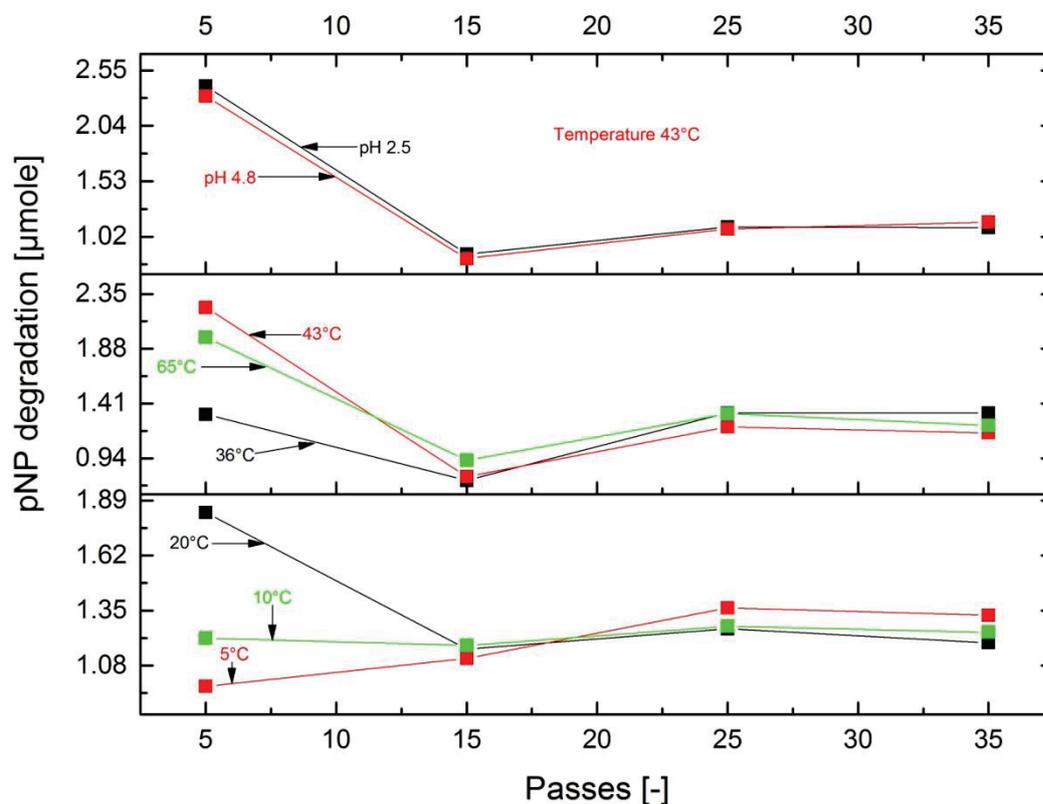


Figure 40: Absolute PNP - degradation over the full range of passes by considering different temperatures and pH; the degradation increases within the first five passes, decreases to its minimum after 15 passes and slightly increases by increasing the number of passes; the exceptions are the tests with a temperature below 20°C where the lower starting temperature boosts the degradation by increasing the number of passes; starting concentration 25 µmole/l.

It is apparent that in the majority of cases, HC is able to remove or metabolize more than 40 % of the initial PNP molecules (Figure 41) after 35 passes. This is more than reported by Capocelli et al. (2014a, p. 2571) who reached a removal percentage of 24 % with an applied pressure of approx. 65 psi (approx. 0.45 MPa). This is due to the fact that the efficiency and intensity of cavitation strongly depends on the experimental setup and the geometry of the

cavitation unit (Gogate (2002, p. 347) and Capocelli et al. (2014a, p. 2566)) as well as the operating pressure.

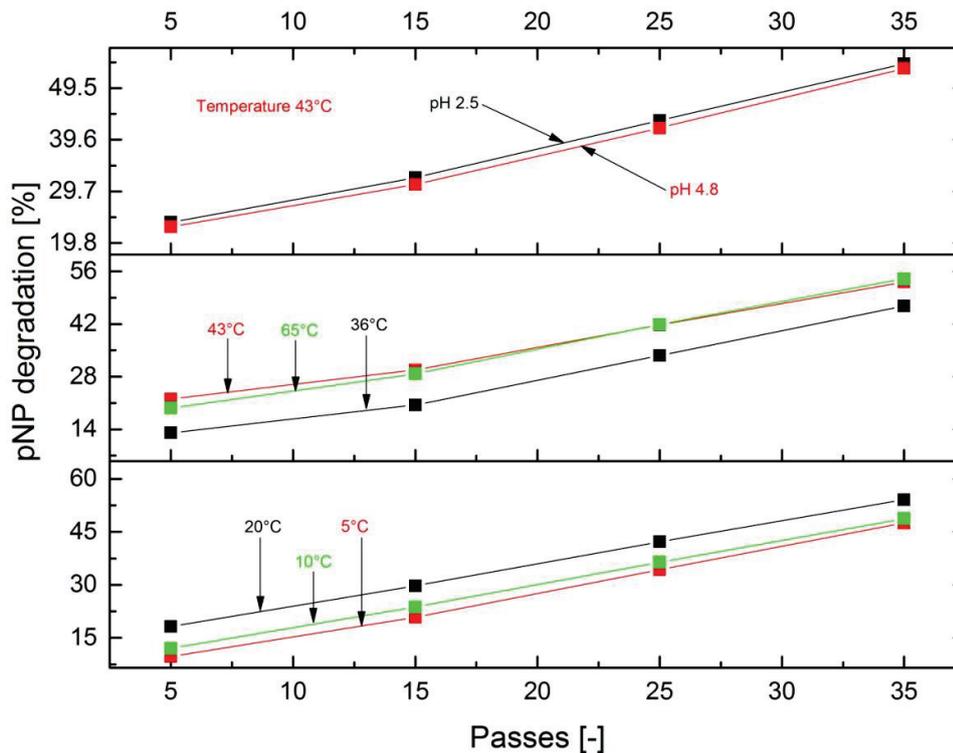


Figure 41: Percentage of degradation over the full range of passes by considering different temperatures and pH; the HC increase the degradation by increasing the number of passes; the course of the findings indicate an ongoing increase of degradation after 35 passes; starting concentration 25  $\mu\text{mole/l}$ .

Both tests (Figure 41 - test from layer one with 43°C and pH 2.5 and test from layer three with 20°C) have the same degradation percentage of approx. 50 % if the measurement uncertainty and inaccuracy are considered.

### 5.3.4 Degradation of PNP: Results UC

The results of the tests with the UC system are shown in Figure 42 and Figure 43. The graphs in both figures need further explanation: The first graph in each layer on the left side shows the result of the test for a runtime of 10 minutes. Afterwards a second solution with the same volume for the test with a runtime of 30 minutes is used (second graph on the right side).

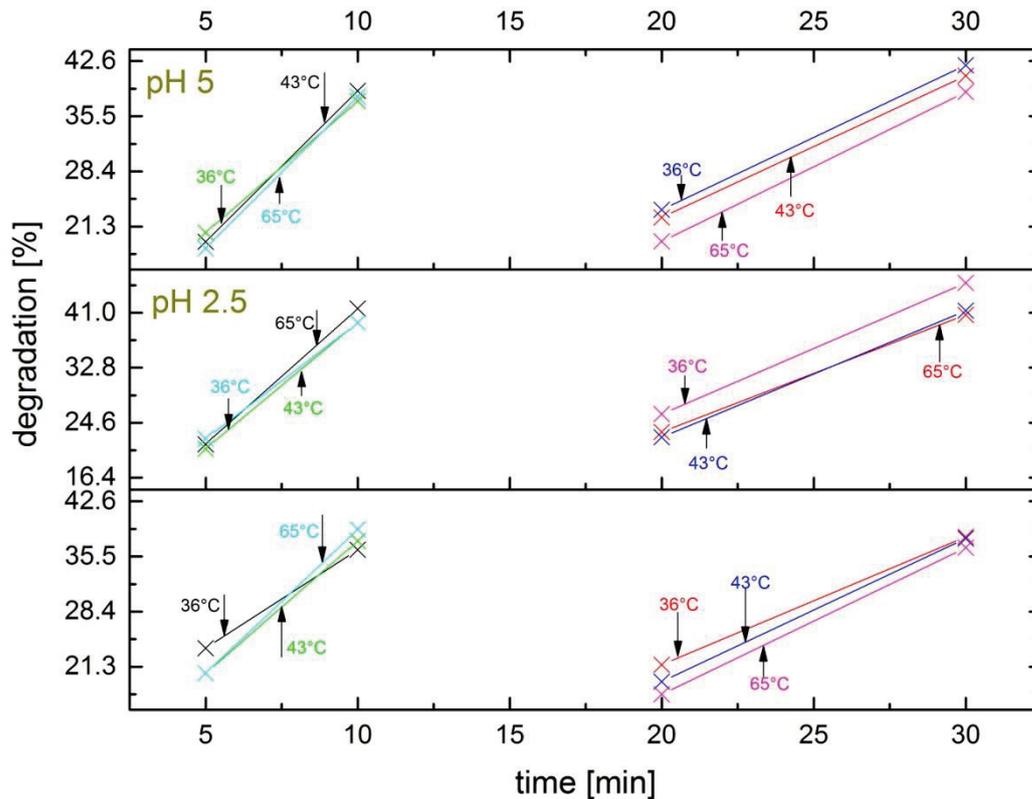


Figure 42: Percentage of degradation over time by considering high temperature and different pH; the gap between the data points in each layer is due to the use of a fresh starting solution after 10 minutes; starting concentration 25  $\mu\text{mole/l}$ .

Figure 42 belongs to high temperature conditions and two different pH values. Citric acid (10 %) is used to set the pH. Generally speaking there is a strong increase of the degradation over time. Within the period of the first ten minutes approx. 40 % are metabolized. Further investigations are needed to explain the fact that in some cases (for example 65°C) the UC is able to remove more of the PNP after ten minutes than after 20 minutes and that the percentage of degradation is always lower after 20 minutes than after 10 minutes. Measurement uncertainty is only one possibility. With a treatment time of 30 minutes the degradation is in most of the cases higher (approx. 2 %) than with a treatment time of 10 minutes. The longer the treatment time, the more PNP molecules are metabolized. Zhang et al. (2003, p. 793) reported that more than 98 % of PNP are removed after 12 minutes by adding hydrogen peroxide into the solution.

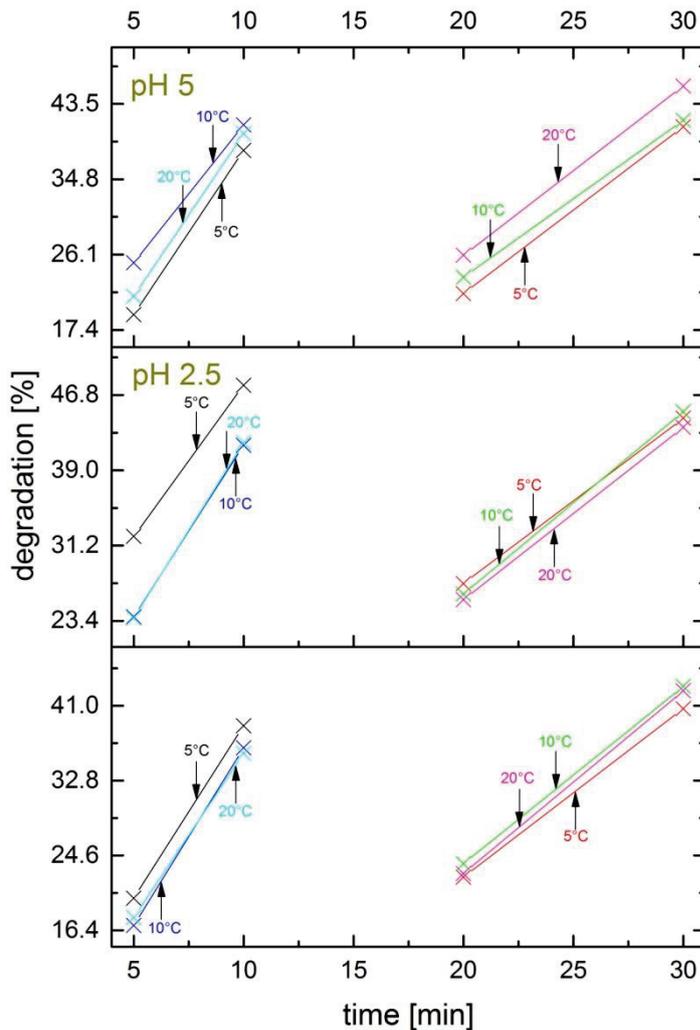


Figure 43: Percentage of degradation over time by considering low temperature and different pH; the gap between the data points in each layer is due to the use of a fresh starting solution after 10 minutes; starting concentration 25  $\mu\text{mole/l}$ .

From the labeling in Figure 43 it can be observed that they belong to low temperature conditions and also two different pH values. The required energy for UC is 0.08 kWh for all tests. Comparing Figure 42 and Figure 43 shows that a higher degradation percentage (approx. 45 %) is reached at low pH and low temperature because an oxidation is an exothermic reaction and a temperature decrease shifts the equilibrium of the reaction to the products. It is evident from the results that the ultrasonic system shows good results after a short runtime with normal temperature (20°C) conditions and a low pH value.

### 5.3.5 Degradation of PNP: Comparison HC with UC

For further applications it is important to know which system leads to a better removal of PNP. Energy input and degradation output are the main parameters. The UC system creates a “static” treatment respectively the liquid is not in motion and the only motion comes from the induced ultrasound. In principle the ultrasonic treatment time is equal to the retention time. For the hydrodynamic system the situation is not that transparent. The liquid is always

in motion by pumping it through the cavitation unit or the loop. However, the true retention time, defining the time the liquid actually is under the action of cavitation, is very short.<sup>39</sup> This fact should be always kept in mind when comparing the results of the two systems (Figure 44 - Figure 48).

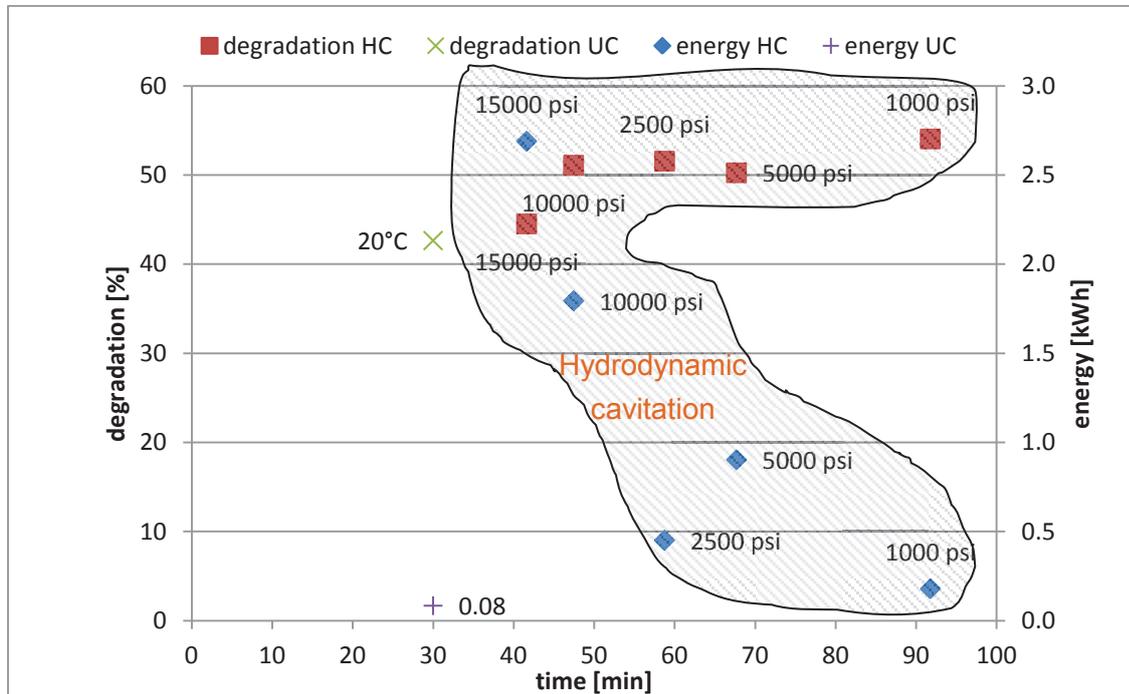


Figure 44: HC vs. UC at 20°C; the marked area represents the HC tests with different pressures; the percentage of degradation of the HC samples is always (over the full range of the applied pressure) higher than the UC sample; starting concentration 25  $\mu\text{mole/l}$ .

Figure 44 illustrates the comparison of the HC system with different pressures with the UC system at 20°C. Referring to percentage of degradation, the experiment with 1000 psi (54 %) shows approx. a 12 % better degradation than the UC test. As mentioned before the total runtime is 3 times longer with the HC system than with the UC. From the energetically point of view the HC systems follows the already known linear pressure law: High pressure means high electrical power input.

<sup>39</sup> See also Cavitation unit and the issue of comparability in 3.2.1.

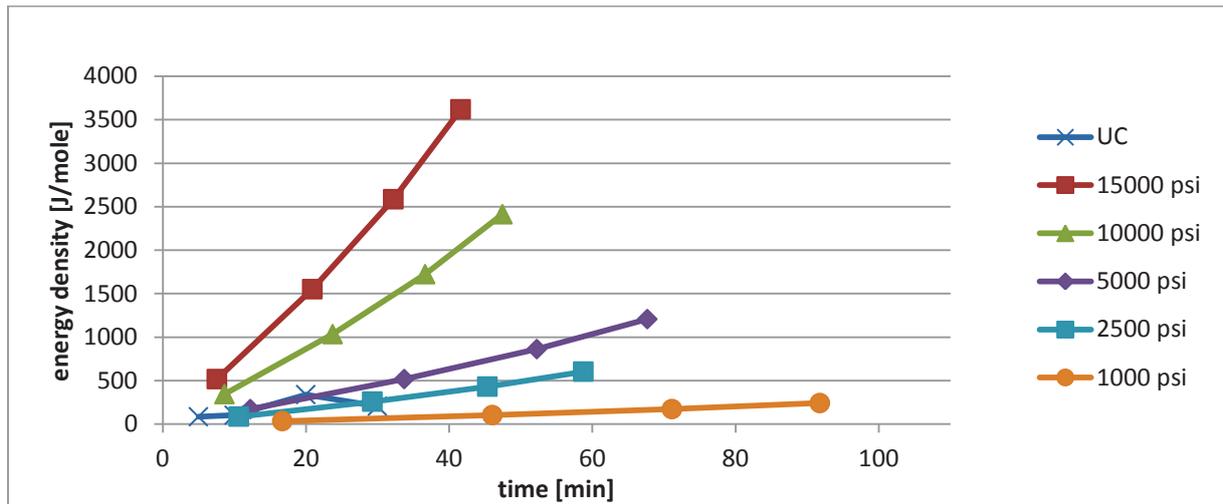


Figure 45: HC vs. UC by considering the energy density over time at the same operating temperature of 20°C and a starting concentration of 25  $\mu\text{mole/l}$ ; HC with different pressure; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1.

One of the most important questions to answer is how high is the energy demand of the two systems to remove a certain amount of PNP. Figure 45 displays a comparison between the systems and it is apparent that the UC test has a higher energy density than the HC tests with 2500 and 1000 psi. On the one hand the UC system is able to metabolize about 40-45 % of the initial PNP molecules after a short treatment time (30 minutes) but on the other hand it requires a high energy input. At 1000 psi the HC system reaches a degradation of approx. 50 % and compared to the UC test, the energy density is still lower after a treatment time of approx. 90 minutes.

Figure 46, Figure 47 and Figure 48 correspond to different operating parameters which have been tested on both systems. The black dotted line is explained below Figure 48.

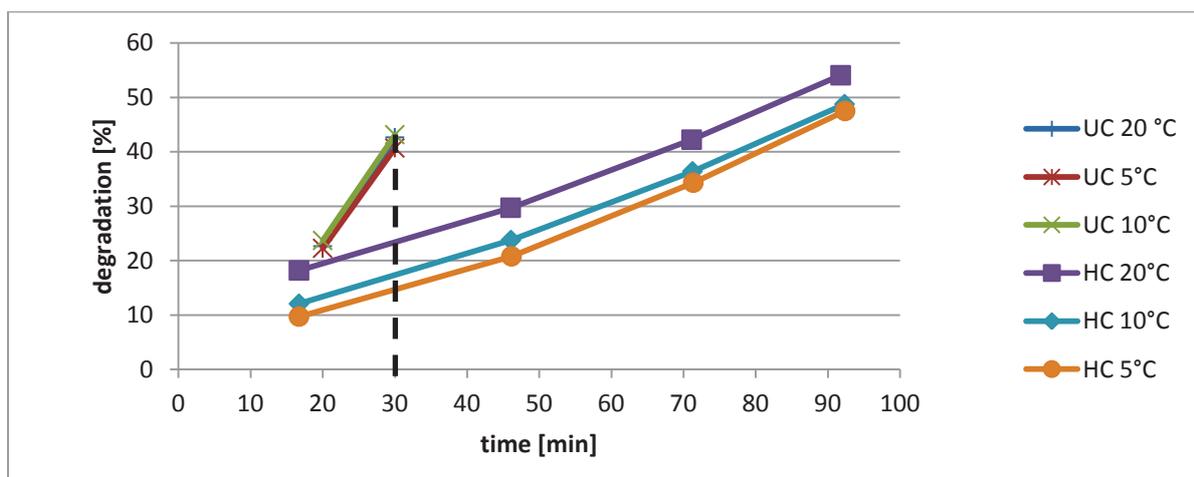


Figure 46: HC vs. UC - comparison of degradation at low temperature; starting concentration 25  $\mu\text{mole/l}$ ; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1; the explanation of the black dotted line can be found below Figure 48.

Comparing Figure 46 (low temperature) and Figure 47 (high temperature) shows that the UC system works better at low temperatures. The temperature influence in case of HC is negligible because the majority of the experiments show a percentage of degradation of approx. 50 % after 35 passes (displayed as time).

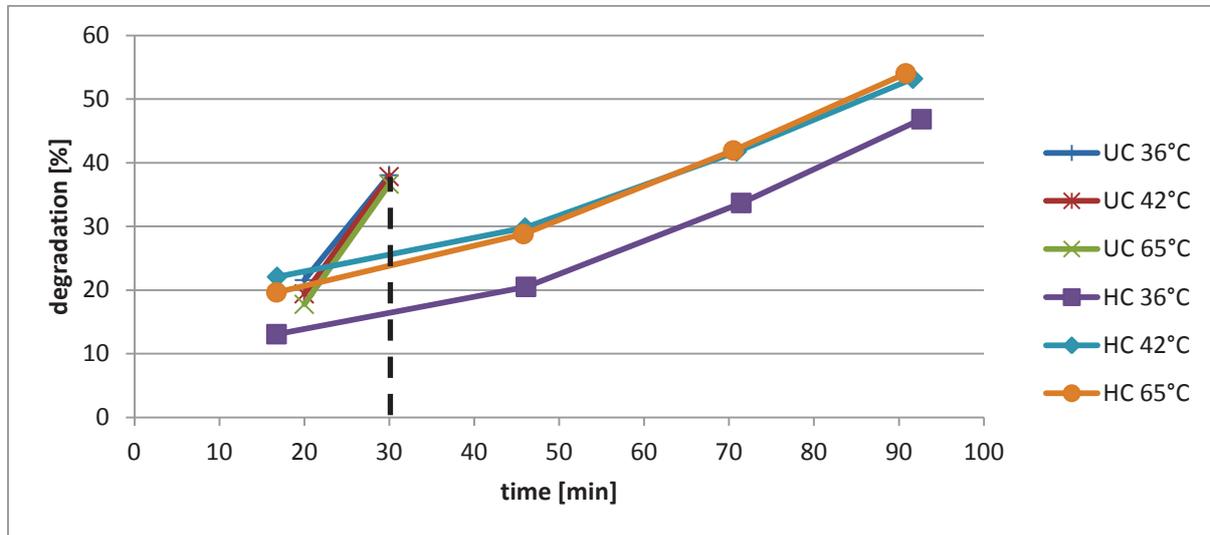


Figure 47: HC vs. UC - comparison of degradation at high temperature; starting concentration 25  $\mu\text{mole/l}$ ; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1; the explanation of the black dotted line can be found below Figure 48.

For constant temperature conditions an additional aggregate is required. High or low temperature is realized through a heater or a chiller.

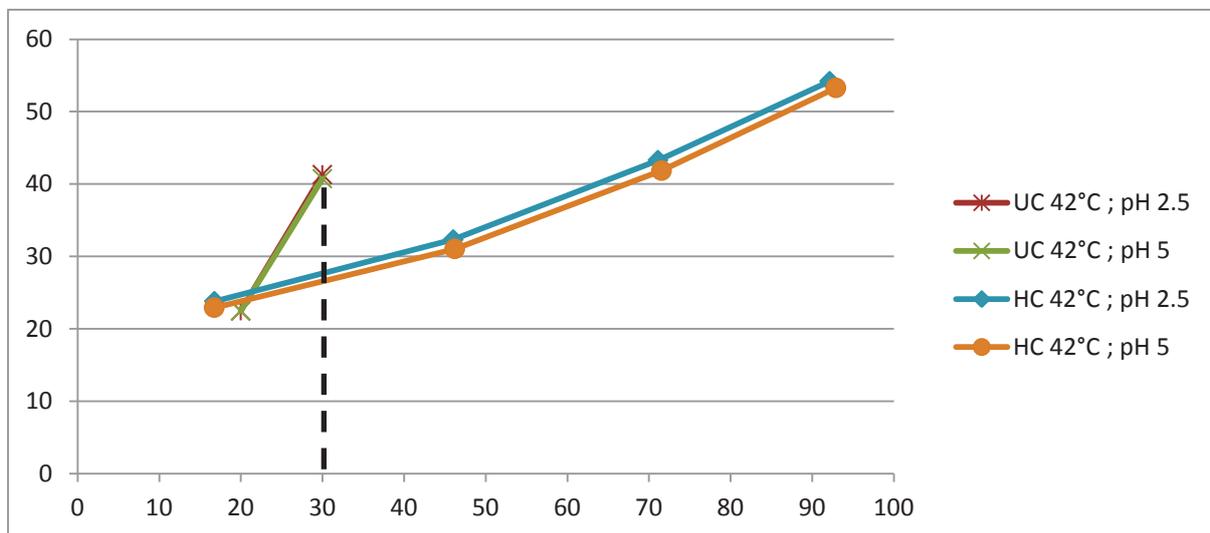


Figure 48: HC vs. UC - comparison of degradation at 42°C and different pH; the difference between pH 2.5 and pH 5 is negligible; starting concentration 25  $\mu\text{mole/l}$ ; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1; the explanation of the black dotted line can be found in the text.

The black dotted line in all three figures (Figure 46, Figure 47 and Figure 48) should highlight the fact that all UC tests show a much better (approx. 20 %) percentage of degradation after

30 minutes than the HC experiments. This could be caused on the one hand by the short retention time (“true” treatment time) in case of HC and on the other hand by the high energy input through the ultrasonic horn.

Kalumuck (2000) reported a big difference between the application of a pH of 2.5 and 5. In his work the oxidation efficiency is 5 times higher for the test with a pH of 2.5 compared to a pH of 5. Inspection of Figure 39 and Figure 48 indicates that the influence of the pH is not that strong in both of the used systems. As mentioned before it is difficult to compare systems which do not have the identically experimental setup.

## 6 Conclusion

This study confirms the predicted generation of cavitation induced hot spots. Three model reactants, the liberation of iodine (Weissler reaction), the oxidation of sulfite to sulfate and the degradation of PNP are used in two different cavitation systems. The first system generates HC through the patented cavitation unit from Arisdyn systems Inc. which is fully implemented into a closed loop. The second system creates UC through an ultrasonic horn (source of ultrasound) which immerses into a flow cell. Similar setups can be found in pertinent literature (Kumar, P.S. and Pandit, A.B. 1999; Capocelli et al. 2014a, p. 2566). In their studies researchers often used different devices like orifices, high speed homogenizer or venturi pipes to create cavitation. In this study ideal operating conditions within the predefined range are developed through varying parameters like pressure and passes for the HC system and temperature and pH for the UC system. The performed tests on both systems are compared under the same conditions. By comparing the two systems it should be noticed that there is a difference between the treatment and retention times. In case of the UC system, the retention time respectively the time the whole liquid volume actually is treated, equals the total runtime. The retention time in case of HC is much shorter because the HC takes place at a very specific point inside the cavitation unit and only a small fluid volume is affected by cavitation per pass. Beside the retention time the energy aspect has to be considered. The costs rise and the energy efficiency decrease rapidly when a higher pressure or additional heating or cooling is used. The main task is to find a trade - off between additional chemicals, operational energy costs for heating or cooling and reaction output. Further it should be noticed that the total runtime of the HC tests is always higher than of the UC tests. After a total runtime of 30 minutes, the UC tests show a better enhancement, percentage of oxidation<sup>40</sup> and degradation than the HC tests after the same time. As confirmed through previous literature and the results of this study, the energy input is much higher in case of UC. The key results of the three model reactants and the associated reactions are listed in three sections as follows:

**Liberation of iodine.** The HC tests show better results referring to liberation than the UC tests. The adding of citric acid or in general a decrease of the pH seems to be a very promising application. An 11-fold increase of  $I_3^-$  - production at a pressure of 2500 psi and a 9.5-fold increase at 1000 psi are reached at 20°C with a pH of 3.3. The adding of any additional chemical to contaminated waste water, as well as probably heating or cooling, creates additional costs. Without any additional supply the HC system reaches a 3.5-fold increase in  $I_3^-$  - production at an applied pressure of 2500 psi and an operating temperature of 20°C. Under the same circumstances the UC system reaches only a 2-fold increase.

**Oxidation of sulfite.** To our knowledge, the data of all this tests are the first of its kind. No reference has been found that describes a sulfite oxidation forced by UC or HC under different conditions (temperature and pressure). Because of the N<sub>2</sub> purge in both systems the experimental setup is unaffected by atmospheric oxygen. This indicates that the oxidation occurs because of the formation of free radicals through cavitation induced hot spots. The

<sup>40</sup> Further tests are required to support this statement.

main statement of the results is that approx. 50 % of the initial sulfite is oxidized to sulfate at low pressure (1000 psi), room temperature (20°C) and after the first five passes. This finding is promising in terms of developing and investigating possible industrial applications.

**Degradation of PNP.** The data show that good results (percentage of degradation approx. 50 %) can be achieved under economical temperature and pressure conditions like 20°C and 1000 psi. Considering pressure level, it must be indicated however, that comparing the 1000 psi in this study with the pressure used in previous work ( (Capocelli et al. 2014a, p. 2568), (Chakinala et al. 2008, p. 167)), 1000 psi is indeed very high. The optimal operating conditions in terms of degradation efficiency are 43°C and a pH between 2.5 and 4.8. The results are in general agreement with previous studies (Capocelli et al. (2014a, p. 2571), Kalumuck (2000)) but the pH influence in the findings is far less sensitive. The study of Zhang et al. (2003, p. 788) outlined that the pH should be in an acidic range.

At 1000 psi the retention time has the highest number (Table 1). This information, the information from 3.2.2, together with the explanations in 3.2.3 support the results of this study. Future work should focus on the performance at pressure below 1000 psi and long - term tests regarding to time (UC system) and passes (HC system). The maximum possible percentage of liberation, oxidation and degradation should be explored. It is known from the literature (Gogate et al. 2011, p. 1067; Morison, K. and Hutchinson, C., p. 182) and an accepted fact that there are differences referring to chemism between the upscaling sizes from the lab - scale over the pilot - scale to the operating plant. It is recommended for future work to perform tests on pilot-scale plants to investigate possible deviations to the lab - scale. The findings in this study make it possible to treat water contaminants with controlled cavitation induced hot spots generated by the investigated technology from Arisdyne. The application of HC in the chemical industry has great potential. Future investigations will show if the energy created through cavitation induced hot spots is strong enough to enhance new and emerging fields of application, e.g. the cracking of long-chained hydrocarbons in oil residues.<sup>41</sup>

Some of the aforementioned topics, exemplary the carbon precipitation and the potential interaction of activated carbon with radicals formed by the cavitation still have the status of a current working hypothesis. Further tests are required to investigate the impacts of this effect on possible water treatment applications.

---

<sup>41</sup> ExxonMobil Research and Engineering Company (EMRE) signed a Joint Development Agreement with Arisdyne Systems Inc. - <http://www.businesswire.com/news/home/20150107005688/en/Arisdyne-ExxonMobil-Research-Engineering-Company-Sign-Agreement>; requested 1/8/2016.

## 7 Directories

### 7.1 Publication bibliography

Agency for Toxic Substances and Disease Registry U.S. Public Health Service (1992): Toxicological Profile for Nitrophenols: 2-Nitrophenol and 4-Nitrophenol.

Arisdyne Systems (2015): Technologies. Edited by Arisdyn Systems. Ohio, Cleveland. Available online at <http://www.arisdyn.com>, updated on 12/8/2015, checked on 12/8/2015.

Avila, Kerstin; Moxey, David; Lozar, Alberto de; Avila, Marc; Barkley, Dwight; and Hof, Björn (2011): The Onset of Turbulence in Pipe Flow. In *Science* 333 (6039), pp. 192–196.

Billinge, B.H.M.; Docherty, Josephine B.; and Bevan, M. J. (1984): The Desorption of Chemisorbed Oxygen from Activated Carbons and its Relationship to Ageing and Methyl Iodide Retention Efficiency. In *Carbon* 22 (1), pp. 83–89.

Boehm, H. P. (2012): Free radicals and graphite. In *Carbon* 50 (9), pp. 3154–3157. DOI: 10.1016/j.carbon.2011.10.013.

Capocelli, Mauro; Musmarra, Dino; Prisciandaro, Marina; Lancia, Amedeo (2014a): Chemical effect of hydrodynamic cavitation: Simulation and experimental comparison. In *AIChE J.* 60 (7), pp. 2566–2572. DOI: 10.1002/aic.14472.

Capocelli, Mauro; Prisciandaro, Marina; Lancia, Amedeo; Dino Musmarra (2014b): Comparison Between Hydrodynamic and Acoustic Cavitation in Microbial Cell Disruption. In *Chemical Engineering Transactions* 38, pp. 13–18. DOI: 10.3303/CET1438003.

Chakinala, Anand G.; Gogate, Parag R.; Chand, Rashmi; Bremner, David H.; Molina, Raúl; Burgess, Arthur E. (2008): Intensification of oxidation capacity using chloroalkanes as additives in hydrodynamic and acoustic cavitation reactors. In *Ultrasonics Sonochemistry* 15 (3), pp. 164–170. DOI: 10.1016/j.ultsonch.2007.02.008.

Chand, Rashmi; Bremner, David H.; Namkung, Kyu C.; Collier, Phillip J.; Gogate, Parag R. (2007): Water disinfection using the novel approach of ozone and a liquid whistle reactor. In *Biochemical Engineering Journal* 35 (3), pp. 357–364. DOI: 10.1016/j.bej.2007.01.032.

d'Agostino, Luca and Salvetti, Maria Vittoria (2007): Fluid Dynamics of Cavitation and Cavitating Turbopumps: Springer Wien New York.

Ellis, Frank (2002): Paracetamol. A curriculum resource. Cambridge: Royal Society of Chemistry.

Gogate, Parag R. (2002): Cavitation: an auxiliary technique in wastewater treatment schemes. In *Advances in Environmental Research* 6 (3), pp. 335–358. DOI: 10.1016/S1093-0191(01)00067-3.

Gogate, Parag R.; Shirgaonkar, Irfan Z.; Sivakumar, M.; Senthilkumar, P.; Vichare, Nilesh P.; and Pandit, Aniruddha B. (2001): Cavitation reactors: Efficiency assessment using a model reaction. In *AIChE J.* (11), pp. 2526–2538.

Gogate, Parag R.; Sutkar, Vinayak S.; Pandit, Aniruddha B. (2011): Sonochemical reactors: Important design and scale up considerations with a special emphasis on heterogeneous systems. In *Chemical Engineering Journal* 166 (3), pp. 1066–1082. DOI: 10.1016/j.cej.2010.11.069.

Gogate, Parag R. and Pandit, Aniruddha B. (2000): Engineering design methods for cavitation reactors II: Hydrodynamic cavitation. In *AIChE J.* Volume 46 (Issue 8), pp. 1642–1649.

Hua, Inez; Höchemer, Ralf H.; Hoffmann, Michael R. (1995): Sonolytic Hydrolysis of p-Nitrophenyl Acetate: The Role of Supercritical Water. In *J. Phys. Chem.* (99), pp. 2335–2342.

Kalumuck, K. M. (2000): The use of cavitating jets to oxidize organic compounds in water. In *Journal of Fluids Engineering (ASME)* (122), pp. 465–470.

- Kalumuck, K. M.; Chahine, G. L.; C-T Hsiao; J-K Choi (2003): Remediation and disinfection of water using jet generated cavitation. In *Fifth International Symposium on Cavitation (Cav03-OS-2-2-003)*, pp. 1–4.
- Koh, Li Ling A.; Chandrapala, Jayani; Zisu, Bogdan; Martin, Gregory J. O.; Kentish, Sandra E.; Ashokkumar, Muthupandian (2014): A Comparison of the Effectiveness of Sonication, High Shear Mixing and Homogenisation on Improving the Heat Stability of Whey Protein Solutions. In *Food Bioprocess Technol* 7 (2), pp. 556–566. DOI: 10.1007/s11947-013-1072-1.
- Kumar, P.S. and Pandit, A.B. (1999): Modeling Hydrodynamic Cavitation. In *Chem. Eng. Technol.* (22), pp. 1017–1027.
- Lau, A. C.; Furlong, D. N.; Healy, T. W.; and Grieser, F. (1986): The Electrokinetic Properties of Carbon Black and Graphitized Carbon Black Aqueous Colloids. In *Colloids and Surfaces* (18), pp. 93–104.
- Leighton, T.G (1995): Bubble population phenomena in acoustic cavitation. In *Ultrasonics Sonochemistry* 2 (2), pp. S123-S136. DOI: 10.1016/1350-4177(95)00021-W.
- Li, Pan; Song, Yuan; Yu, Shuili (2014): Removal of *Microcystis aeruginosa* using hydrodynamic cavitation: Performance and mechanisms. In *Water Research* 62, pp. 241–248. DOI: 10.1016/j.watres.2014.05.052.
- Li, Pan; Song, Yuan; Yu, Shuili; Park, Hee-Deung (2015): The effect of hydrodynamic cavitation on *Microcystis aeruginosa*: Physical and chemical factors. In *Chemosphere* 136, pp. 245–251. DOI: 10.1016/j.chemosphere.2015.05.017.
- Morison, K. and Hutchinson, C. (2009): Limitations of the Weissler reaction as a model reaction for measuring the efficiency of hydrodynamic cavitation. In *Ultrasonics Sonochemistry* 16 (1), pp. 176–183. DOI: 10.1016/j.ultsonch.2008.07.001.
- Novikov, A. N. (2014): Heat capacity and density of potassium iodide solutions in mixed N-methylpyrrolidone-water solvent at 298.15 K. In *Russ. J. Phys. Chem.* 88 (10), pp. 1621–1625. DOI: 10.1134/S0036024414100252.
- Parag R. Gogate and Abhijeet M. Kabadi (2009): A review of applications of cavitation in biochemical engineering/biotechnology. In *Biochemical Engineering Journal* (Volume 44), pp. 60–72.
- Patek, S. N.; Korff, W. L.; Caldwell, R. L. (2004): Biomechanics: deadly strike mechanism of a mantis shrimp. In *Nature* 428 (6985), pp. 819–820. DOI: 10.1038/428819a.
- Saharan, Virendra Kumar; Pandit, Aniruddha B.; Satish Kumar, Panneer Selvam; Anandan, Sambandam (2012): Hydrodynamic Cavitation as an Advanced Oxidation Technique for the Degradation of Acid Red 88 Dye. In *Ind. Eng. Chem. Res.* 51 (4), pp. 1981–1989. DOI: 10.1021/ie200249k.
- Schlögl, R. and Boehm, H.P. (1988): Photochemical Intercalation in Graphite. In *Synthetic Metals* (23), pp. 407–413.
- Suslick, Kenneth S. (1990): Sonochemistry. In *Science* 247 (4949), pp. 1439–1450.
- Suslick, Kenneth S.; M. mdleleni, Millan and T. Ries, Jeffrey (1997): Chemistry Induced by Hydrodynamic Cavitation. In *Journal American Chemical Society* (119), pp. 9303–9304.
- VDI Heat Atlas (Ed.) (2010). VDI-Gesellschaft Verfahrenstechnik und Chemieingenieurwesen. 2<sup>nd</sup> ed. Berlin Heidelberg: Springer Verlag.
- Wu, Zhilin; Shen, Haifeng; Ondruschka, Bernd; Zhang, Yongchun; Wang, Weimin; Bremner, David H. (2012): Removal of blue-green algae using the hybrid method of hydrodynamic cavitation and ozonation. In *Journal of Hazardous Materials* 235-236, pp. 152–158. DOI: 10.1016/j.jhazmat.2012.07.034.

Xu, S. C.; Irle, S.; Musaev, D. G.; Lin, M. C. (2007): Quantum Chemical Study of the Dissociative Adsorption of OH and H<sub>2</sub>O on Pristine and Defective Graphite (0001) Surfaces. Reaction Mechanisms and Kinetics. In *J. Phys. Chem. C* 111 (3), pp. 1355–1365. DOI: 10.1021/jp066142i.

Zhang, Wenbing; Xiao, Xianming; An, Taicheng; Song, Zhiguang; Fu, Jiamo; Sheng, Guoying; Cui, Mingchao (2003): Kinetics, degradation pathway and reaction mechanism of advanced oxidation of 4-nitrophenol in water by a UV/H<sub>2</sub>O<sub>2</sub> process. In *J. Chem. Technol. Biotechnol.* 78 (7), pp. 788–794. DOI: 10.1002/jctb.864.

## 7.2 Tables

Table 1: Calculated reactor volume (Equation 1) and retention time (Equation 2). .....	10
Table 2: Vapor pressure and density of water at different temperatures. ....	11
Table 3: Calculated outflow velocity from the throat. ....	12
Table 4: Constant values for the calculation acc. to the Homogeneous Nonequilibrium Model (VDI Heat Atlas 2010, p. 1177). ....	14
Table 5: Substance data for water and oxygen at the given pressure. ....	14
Table 6: Calculated gas mass flow fraction and discharge coefficient for the fluid. ....	15
Table 7: Calculated critical pressure and mass flux. ....	15
Table 8: Calculated discharge coefficient, flow velocity and cavitation number. ....	15
Table 9: Instruments and lab equipment for all three model reactants with available manufacturer's data. ....	21
Table 10: Specific chemicals for the model reactions. ....	22
Table 11: Liberation of iodine: concentration and extinction of the calibration solutions. ....	23
Table 12: Oxidation of sulfite: concentration and extinction of the calibration solutions. ....	26
Table 13: Degradation of PNP: concentration and extinction of the calibration solutions. ....	28
Table 14: List of used units with available manufacture's data. ....	29
Table 15: Settings. ....	32
Table 16: Calculated time and measured temperature. ....	33
Table 17: Used orifice design and specific data of the plunger pump. ....	33
Table 18: Measured results extinction and precipitation. ....	34
Table 19: Measured concentration and calculated production of the tri-iodide ( $I_3^-$ ) complex. ....	36
Table 20: Different blanks to investigate the liberation without cavitation. ....	36
Table 21: Efficiency and energy. ....	37
Table 22: Settings. ....	40
Table 23: Measured temperature. ....	40
Table 24: Calculated calorimetric and enhancement of liberation. ....	41
Table 25: Settings and measured temperature. ....	42
Table 26: Measured concentration. ....	42
Table 27: Calculated tri-iodide ( $I_3^-$ ) production. ....	43
Table 28: Calculated power demand and enhancement. ....	43
Table 29: Runtime ultrasonic horn. ....	44
Table 30: Calculated energy and efficiency. ....	44
Table 31: Parameters; without the adding of $CCl_4$ . ....	45

Table 32: Parameters; with CCl <sub>4</sub> .....	47
Table 33: Parameters; low pH. ....	48
Table 34: Settings.....	55
Table 35: Measured temperature and concentration. ....	56
Table 36: Calculated production and percentage of oxidation. ....	56
Table 37: Calculated power and energy demand and oxidation efficiency. ....	57
Table 38: Settings for HC tests. ....	58
Table 39: Rate of S042 -- production. ....	63
Table 40: Settings.....	66
Table 41: Measured temperature and concentration. ....	66
Table 42: The data represents the control of the initial solution; concentration 25 μmole/l. ....	67
Table 43: Calculated PNP degradation and percentage of degradation.....	67
Table 44: Calculated power demand, energy costs and efficiency of degradation.....	69

## 7.3 Figures

Figure 1: Venturi effect; pressure drop due the diameter change from point 1 to point 2 results in an increased flow velocity in point 2. ....	7
Figure 2: Orifice - $d_1$ is the pipe diameter, $d_2$ the opening size and $d_{vc}$ vena contracta diameter. ....	7
Figure 3: Original drawing of one cavitation chamber with two cavitation units; each chamber consists of two mixing units (5a and 5b) and two baffles (4) with four channels. ....	9
Figure 4: The marked value ( $h = 10.16$ mm) indicates the length of the inlet channel. ....	9
Figure 5: The red circle presents the relevant point for the calculation after the throat of the orifice where the smaller diameter changes to a bigger diameter; the red arrow shows the direction of flow. ....	12
Figure 6: Left picture: Current situation at the cavitation unit. Middle picture: Used model for the Homogeneous Nonequilibrium Model ( VDI Heat Atlas 2010, p. 1171). Right picture: Pressure over distance and different types of flow for the given model. ....	14
Figure 7: Liberation of iodine: calibration chart. ....	24
Figure 8: Oxidation of sulfite: Calibration chart. ....	26
Figure 9: Degradation of PNP: calibration chart. ....	28
Figure 10: Flow chart and UC construction for all experiments. ....	29
Figure 11: Hydrodynamic cavitation loop for the liberation of iodine and degradation of PNP. ....	30
Figure 12: Hydrodynamic cavitation loop for the oxidation of sulfite to sulfate. ....	31
Figure 13: Concentration dependences of the specific heat capacities of potassium iodide solutions in water and mixed MP (N-methylpyrrolidone) - $H_2O$ solvent at 298.15 K and different values of xMP: (1) 0, (2) 0.025, (3) 0.05, (4) 0.10, (5) 0.33. ....	41
Figure 14: The enhancement of liberation decreases by increasing the pressure at 20°C, a starting concentration of 50 g KI/l and without adding any additional chemicals ( $CCl_4$ ); the two data points at 1000 psi are explained in the text below. ....	46
Figure 15: By adding $CCl_4$ , the enhancement of liberation increases by increasing the pressure at 20°C and a starting concentration of 50 g KI/l. ....	47
Figure 16: Citric acid (10 %) is used to set the pH to 3.3; the enhancement shows similar improvement by increasing the pressure at 20°C and a starting concentration of 50 g KI /l. ....	48
Figure 17: 50 g KI /l; different pressures; 20°C (except 5°C at 1000 psi); the efficiency combines the energy point of view with the enhancement of liberation and is plotted against the full range of passes. ....	49
Figure 18: Efficiency vs. energy by investigating different pressures at 20°C. ....	49
Figure 19: Closer inspection of the efficiency from the first to the fifth pass at 1000 psi, an operating temperature of 20°C and a starting concentration of 50 g KI /l; the efficiency shows a peak after two passes and decreases afterwards. ....	50
Figure 20: Starting concentration 50 g KI /l; 1000 psi; 20°C; after the second pass of the solution the cavitation unit creates approx. the same amount of $\mu$ mole per ml than after the fourth or fifth	

pass; by increasing the number of passes the production rate increases from the fifth to the 25 <sup>th</sup> pass and decreases afterwards. ....	50
Figure 21: HC vs. UC; different pressure and same temperature of 20°C (except the two data points at 1000 psi) in case of HC; different temperature and one data point with an increased pH in case of the UC; every sample without CCl <sub>4</sub> ; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1. ....	51
Figure 22: HC vs. UC by considering the degradation over time; all HC tests with different pressure at 20°C; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1. ....	52
Figure 23: HC vs. UC by considering the adding of CCl <sub>4</sub> and different pH; Citric acid (10 %) is used to set the pH to 3.3; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1; the impact of the low pH is more weighty than the adding of CCl <sub>4</sub> . ....	52
Figure 24: HC vs. UC by considering the energy density over time; all HC tests with different pressure at 20°C; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1. ....	53
Figure 25: UC vs. HC to show the UC sample where CCl <sub>4</sub> is added and how big the difference is between the other samples considering the enhancement; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1. ....	54
Figure 26: The sulfate production shows a peak after five passes and decreases significantly afterwards at all applied pressures, a starting concentration of 25 mmole/l and an operating temperature of 20°C. ....	59
Figure 27: Efficiency over the full range of passes; samples with a starting concentration of 25 mmole/l, a different pressure range and an operating temperature of 20°C; the best efficiency shows the sample at 1000 psi. ....	60
Figure 28: Closer look at the efficiency from the first to the fifth pass at 1000 psi, an operating temperature of 20°C and a starting concentration of 25 mmole/l; after one pass the efficiency is the highest and decreases by increasing the number of passes. ....	61
Figure 29: Starting concentration of 25 mmole/l; operating temperature of 20°C; one test with 42°C which show the negligible impact of increased operating temperature; low pressure (1000 - 5000 psi) implies low energy input with a better percentage of oxidation than the test with high pressure (15000 psi); number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1. ....	62
Figure 30: Efficiency vs. energy by considering different pressure; starting concentration 25 mmole/l; operating temperature 20°C; these findings are in line with the explanations in 3.2.2 and the pressure dependencies in 3.2.3. ....	62
Figure 31: S042 – generation rate over pressure shows the best rate at 15000 psi; starting concentration 25 mmole/l; different pressure; operating temperature 20 °C. ....	63
Figure 32: HC vs. UC with a starting concentration of 25 mmole/l for all tests; the marked HC tests are performed with different pressure at 20°C; UC tests with different temperature; the temperature effect on the UC samples does not show a specific direction; the percentage of oxidation increases by decreasing the pressure of the HC samples and shows an approx. 10 % improvement (1000 psi) compared to the UC sample at the same temperature. ....	64

- Figure 33: HC vs. UC by considering the energy density over time at the same operating temperature of 20°C and a starting concentration of 25 mmole/l; HC with different pressure; “mM” stands for mmole/l; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1. .... 65
- Figure 34: Percentage of degradation and the associated energy consumption over the applied pressure range; the size of the bubbles represent the pressure; the degradation of the samples (starting concentration of 25 µmole/l and 20°C) slightly decreases by increasing the inlet pressure (see 3.2.3 for more details). .... 70
- Figure 35: Efficiency over energy consumption by considering the applied pressure range; all tests have a starting concentration of 25 µmole/l and an operating temperature of 20°C; the best efficiency is presented by the test with 1000 psi. .... 70
- Figure 36: Degradation over the full range of passes and different pressures shows an increase by increasing the number of passes; steepest course with 1000 psi; starting concentration of 25 µmole/l; operating temperature of 20°C. .... 71
- Figure 37: Degradation efficiency over the full range of passes combines the degradation and the energy aspect; starting concentration of 25 µmole/l; different inlet pressures; operating temperature of 20°C. .... 71
- Figure 38: From the energy point of view it is useful to have a closer look at the first five passes; after the first pass the efficiency shows a peak and steeply decreases afterwards; starting concentration 25 µmole/l; inlet pressure 1000 psi; operating temperature 20°C. .... 72
- Figure 39: Degradation efficiency over the full range of passes by considering low and high operating temperature and different pH; the efficiency strongly decreases by increasing the number of passes from five to 15 passes; starting concentration 25 µmole/l. .... 73
- Figure 40: Absolute PNP - degradation over the full range of passes by considering different temperatures and pH; the degradation increases within the first five passes, decreases to its minimum after 15 passes and slightly increases by increasing the number of passes; the exceptions are the tests with a temperature below 20°C where the lower starting temperature boosts the degradation by increasing the number of passes; starting concentration 25 µmole/l. 74
- Figure 41: Percentage of degradation over the full range of passes by considering different temperatures and pH; the HC increase the degradation by increasing the number of passes; the course of the findings indicate an ongoing increase of degradation after 35 passes; starting concentration 25 µmole/l. .... 75
- Figure 42: Percentage of degradation over time by considering high temperature and different pH; the gap between the data points in each layer is due to the use of a fresh starting solution after 10 minutes; starting concentration 25 µmole/l. .... 76
- Figure 43: Percentage of degradation over time by considering low temperature and different pH; the gap between the data points in each layer is due to the use of a fresh starting solution after 10 minutes; starting concentration 25 µmole/l. .... 77
- Figure 44: HC vs. UC at 20°C; the marked area represents the HC tests with different pressures; the percentage of degradation of the HC samples is always (over the full range of the applied pressure) higher than the UC sample; starting concentration 25 µmole/l. .... 78

- Figure 45: HC vs. UC by considering the energy density over time at the same operating temperature of 20°C and a starting concentration of 25 µmole/l; HC with different pressure; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1. .... 79
- Figure 46: HC vs. UC - comparison of degradation at low temperature; starting concentration 25 µmole/l; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1; the explanation of the black dotted line can be found below Figure 48..... 79
- Figure 47: HC vs. UC - comparison of degradation at high temperature; starting concentration 25 µmole/l; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1; the explanation of the black dotted line can be found below Figure 48..... 80
- Figure 48: HC vs. UC - comparison of degradation at 42°C and different pH; the difference between pH 2.5 and pH 5 is negligible; starting concentration 25 µmole/l; number of passes for the HC data points is converted to treatment time acc. to explanation in section 5.1.1; the explanation of the black dotted line can be found in the text. .... 80

## Appendix A: Liberation of iodine "HC"

number. series	initial concentration, mass and volume				passes	inlet pressure	orifice dimension
	$C_0$	sample $m_{0s}$	sample real $m_{0Sr}$	sample real corr. $V_{0src}$	$\Omega$	$p_i$	thousandths of an inch
	g/l	g	g	ml	-	psi	-
1.3	50	400	400	387.38	5	15000	6/8
2.3		350	348.7	337.70	15		
3.3		300	295.4	286.08	25		
4.3		250	241.1	233.49	35		
1.4	50	400	400.2	387.57	5	10000	6/8
2.4		350	351.5	340.41	15		
3.4		300	303.7	294.12	25		
4.4		250	252	244.05	35		
1.5	50	400	400.3	387.67	5	5000	6/8
2.5		350	351.6	340.51	15		
3.5		300	301.3	291.79	25		
4.5		250	251.5	243.56	35		
1.6	50	400	400.4	387.77	5	2500	6/8
2.6		350	350.9	339.83	15		
3.6		300	301.1	291.60	25		
4.6		250	251.1	243.18	35		
1.7*	50	350	350	338.96	5	1000	8/12
2.7*		300	291.6	282.40	15		
3.7*		250	247.3	239.50	25		
4.7*		200	198	191.75	35		
1.15	50	400	400.2	387.57	5	15000	6/8
2.15		350	348.1	337.12	15		
3.15		300	295.2	285.89	25		
4.15		250	246.2	238.43	35		
1.16	50	400	401.7	389.03	5	10000	6/8
2.16		350	348.7	337.70	15		
3.16		300	300.1	290.63	25		
4.16		250	246.3	238.53	35		
1.17	50	400	401.5	388.83	5	5000	6/8
2.17		350	350.6	339.54	15		
3.17		300	299.7	290.24	25		

4.17		250	249.7	241.82	35		
1.18*	50	400	401.4	388.74	5	1000	8/12
2.18*		350	348.4	337.41	15		
3.18*		300	299.2	289.76	25		
4.18*		250	245.3	237.56	35		
1.8	50	400	399.2	386.60	5	1000	8/12
2.8		350	345.8	334.89	15		
3.8		300	298.2	288.79	25		
4.8		250	249.2	241.34	35		
1.9	50	400	402	389.32	5	2500	8/12
2.9		350	354.6	343.41	15		
3.9		300	303.7	294.12	25		
4.9		250	250.1	242.21	35		
1.10	50	400	400.9	388.25	5	5000	6/8
2.10		350	349.3	338.28	15		
3.10		300	295.8	286.47	25		
4.10		250	246.7	238.92	35		
1.11	50	450	450.3	436.09	1	1000	8/12
2.11		400	398.5	385.93	2		
3.11		350	350.9	339.83	3		
4.11		300	301.9	292.37	4		
5.11		250	253.5	245.50	5		
1.12	50	400	400.3	387.67	5	1000	8/12
2.12		350	353.1	341.96	15		
3.12		300	304.2	294.60	25		
4.12		250	254.1	246.08	35		

min/pass	time	time real	time accumulated	T1 (vessel)	T2 (vessel skin)	T3 (after cav. unit)	T4 (after heat ex)
t/Ω	t	t <sub>r</sub>	t <sub>acc</sub>	T11/T12	T21/T22	T31/T32	T41/T52
min/pass	min	h:mm:ss	min	°C	°C	°C	°C
1.51	7.56	0:07:34	7.56	21.7/20.4	22.3/21.1	26.7/42.7	chiller 20°C
1.32	13.18	0:13:11	20.74	20.4/20.5	21.1/20.9	42.7/42.7	
1.12	11.16	0:11:10	31.90	20.5/20.3	20.9/20.7	42.7/42.6	
0.91	9.11	0:09:07	41.01	20.3/20.2	20.7/20.7	42.6/42.5	
1.72	8.62	0:08:37	8.62	21.4/20.2	22.1/20.9	33.4/35.1	chiller 20°C
1.51	15.14	0:15:08	23.76	20.2/20.3	20.9/20.8	35.1/35.3	
1.31	13.08	0:13:05	36.83	20.3/20.2	20.8/20.8	35.3/35.2	
1.09	10.85	0:10:51	47.69	20.2/20.4	20.8/20.9	35.2/35.1	

2.44	12.22	0:12:13	12.22	21.2/20.5	21.9/20.9	19.0/27.4	chiller 20°C
2.15	21.47	0:21:28	33.68	20.5/20.5	20.9/20.8	27.4/27.4	
1.84	18.39	0:18:24	52.08	20.5/20.4	20.8/20.8	27.4/27.4	
1.54	15.35	0:15:21	67.43	20.4/20.4	20.8/20.9	27.4/27.4	
3.58	17.88	0:17:52	17.88	21.3/20.5	21.8/20.9	24.0/23.3	chiller 20°C
3.13	31.33	0:31:20	49.21	20.5/20.4	20.9/20.7	23.3/23.3	
2.69	26.88	0:26:53	76.09	20.4/20.2	20.7/20.7	23.3/23.4	
2.24	22.42	0:22:25	98.51	20.2/20.2	20.7/20.7	23.4/23.4	
2.92	14.58	0:14:35	14.58	21.2/11.6	21.8/9.9	27.5/11.6	chiller 5°C
2.43	24.30	0:24:18	38.88	11.6/11.0	9.9/9.3	11.6/11.4	
2.06	20.61	0:20:37	59.49	11.0/11.0	9.3/9.1	11.5/10.8	
1.65	16.50	0:16:30	75.99	11.0/11.0	9.1/9.1	10.8/10.8	
1.51	7.56	0:07:34	7.56	21.3/20.8	21.8/21.0	27.0/42.7	yes
1.32	13.16	0:13:09	20.72	20.8/20.8	21.0/21.0	42.7/42.8	
1.12	11.16	0:11:09	31.87	20.8/20.7	21.0/20.9	42.8/42.9	
0.93	9.30	0:09:18	41.18	20.7/20.7	20.9/20.9	42.9/42.5	
1.73	8.65	0:08:39	8.65	21.7/20.9	22.2/21.2	31.5/35.5	yes
1.50	15.02	0:15:01	23.67	20.9/20.2	21.2/20.2	35.5/34.7	
1.29	12.92	0:12:55	36.59	20.2/20.1	20.2/20.2	34.7/34.7	
1.06	10.61	0:10:36	47.20	20.1/20.2	20.2/20.2	34.7/34.6	
2.45	12.26	0:12:15	12.26	21.6/20.9	22.1/21.1	28.7/27.5	yes
2.14	21.40	0:21:24	33.66	20.9/21.0	21.1/21.0	27.5/27.4	
1.83	18.30	0:18:18	51.96	21.0/20.9	21.0/21.0	27.4/27.7	
1.52	15.24	0:15:15	67.20	20.9/20.9	21.0/21.0	27.7/27.6	
3.35	16.73	0:16:43	16.73	22.2/20.9	22.6/21.0	23.8/21.2	yes
2.90	29.03	0:29:02	45.76	20.9/20.8	21.0/20.9	21.2/21.1	
2.49	24.93	0:24:56	70.69	20.8/20.9	20.9/20.9	21.1/21.2	
2.04	20.44	0:20:26	91.13	20.9/20.9	20.9/21.0	21.2/21.3	
3.22	16.11	0:16:07	16.11	20.1	20.3	22.3	chiller 20°C
2.79	27.91	0:27:54	44.02	20.1	20.4	22.7	
2.41	24.07	0:24:04	68.08	20.2	20.3	22.6	
2.01	20.11	0:20:07	88.19	20.1	20.5	22.5	
2.06	10.32	0:10:19	10.32	20.5	20.4	25.2	chiller 20°C
1.82	18.21	0:18:13	28.53	20.5	20.5	25	
1.56	15.59	0:15:36	44.12	20.4	20.5	25.1	
1.28	12.84	0:12:51	56.97	20.1	20.7	25.2	
2.37	11.85	0:11:51	11.85	19.6	19.5	28.6	chiller 19°C
2.07	20.65	0:20:39	32.50	19.2	19.7	28.2	
1.75	17.49	0:17:29	49.99	19.5	19.9	28.7	
1.46	14.59	0:14:35	64.58	19.4	19.9	28.6	
3.63	3.63	0:03:38	3.63	21.5	21.9	24.3	chiller 20°C
3.22	3.22	0:03:13	6.85	20.7	21	23.7	
2.83	2.83	0:02:50	9.68	20.3	20.7	23.4	
2.44	2.44	0:02:26	12.12	20.4	20.6	23.2	

2.05	2.05	0:02:03	14.16	20.4	20.7	23.1	
3.23	16.15	0:16:09	16.15	20.5	20.5	23.1	chiller 20°C
2.85	28.50	0:28:30	44.65	20.3	20.5	22.9	
2.46	24.55	0:24:33	69.20	20.4	20.5	23	
2.05	20.51	0:20:30	89.71	20.3	20.7	22.9	

sample taken at Arisdyn	pH at CSM	extinction (without filtration)	extinction (after filtration)	volume to filter	filter paper weight - unused	filter paper weight - used	produced precipitation and concentration		sample weight at CSM
$m_{sAr}$	pH	$\zeta_{wf}$	$\zeta_{af}$	$V_f$	$m_{fpun}$	$m_{fpus}$	$m_p$	$m_{pc}$	$m_{sCSM}$
g	-	-	-	ml	g	g	g	mg/ml	g
51.3	8.23	0.2530	0.2530	39	0.0880	0.1031	0.0151	0.39	
53.3	8.02	0.2897	0.2887	37	0.0883	0.1040	0.0157	0.42	
54.3	7.95	0.2858	0.2841	34	0.0886	0.1047	0.0161	0.47	
50	8.02	0.2922	0.2913	40	0.0886	0.1048	0.0162	0.41	
48.7	8.36	0.2839	0.2795	36	0.0892	0.1088	0.0196	0.54	
47.8	8.13	0.2972	0.2864	34	0.0881	0.1052	0.0171	0.50	
51.7	8.08	0.3256	0.3178	38	0.0875	0.1058	0.0183	0.48	
50	8.11	0.2887	0.2847	39	0.0874	0.1045	0.0171	0.44	
48.7	8	0.3353	<sup>42</sup>	34	0.0871	0.1045	0.0174	0.51	
50.3	7.92	0.3524	0.3388	38	0.0871	0.1053	0.0182	0.48	
49.8	8.06	0.3288	0.3145	36	0.0881	0.1041	0.0160	0.44	
50	8.06	0.3176	0.3093	25	0.0894	0.1049	0.0155	0.62	
49.5	7.69	0.3573	0.4195	35	0.0869	0.1039	0.0170	0.49	
49.8	7.98	0.3497	0.4136	36	0.0877	0.1044	0.0167	0.46	48.20
50	8.05	0.3341	0.3987	35	0.0878	0.1024	0.0146	0.42	47.60
50	8.16	0.3070	0.3802	39	0.0887	0.1052	0.0165	0.42	50.98
58.4	6.94	0.3367	0.3762	37	0.0885	0.1003	0.0118	0.32	
44.3	7.13	0.3630	0.4256	36	0.0871	0.0991	0.0120	0.33	48.38
49.3	7.43	0.3933	0.4534	35	0.0879	0.1016	0.0137	0.39	47.65
50	7.62	0.3958	0.4585	40	0.0879	0.1013	0.0134	0.34	52.36
52.1	7.26	0.375	0.3708	38	0.0896	0.1070	0.0174	0.46	51.28
52.9	7.3	0.4762	0.4556	40	0.0897	0.1072	0.0175	0.44	52.81
49	7.41	0.5565	0.5199	35	0.0899	0.1047	0.0148	0.42	48.66
49.5	7.48	0.6113	0.5641	36	0.0871	0.1030	0.0159	0.44	49.20
53	7.68	0.3738	0.3719	40	0.0883	0.1025	0.0142	0.36	52.18
48.6	7.93	0.425	0.425	35	0.0877	0.1018	0.0141	0.40	48.59
53.8	7.87	0.4563	0.4492	40	0.0875	0.1025	0.015	0.38	52.25
53.9	7.94	0.465	0.458	41	0.0898	0.1086	0.0188	0.46	52.47
50.9	7.67	0.3683	0.3647	40	0.0898	0.1058	0.016	0.40	50.42
50.9	7.63	0.4122	0.4017	35	0.0889	0.101	0.0121	0.35	48.41
50	7.7	0.4469	0.4312	36	0.0882	0.1057	0.0175	0.49	47.94
50.7	7.95	0.389	0.3812	39	0.089	0.1066	0.0176	0.45	49.37
53	8.24	0.2929	0.2986	38	0.0884	0.1051	0.0167	0.44	49.13
49.2	8.19	0.3114	0.3089	34	0.0885	0.1062	0.0177	0.52	45.72
53.9	8.13	0.3429	0.348	39	0.0892	0.1036	0.0144	0.37	51.69
54.9	8.06	0.3449	0.3469	41	0.0888	0.1059	0.0171	0.42	52.65
53.4		0.5266	-	-	-	-	-	-	-

<sup>42</sup> The measurement was not possible because starch contaminated the solution.

47.6		0.588	-	-	-	-	-	-	-
49		0.5569	-	-	-	-	-	-	-
		0.5145	-	-	-	-	-	-	-
47.4		0.5106	-	-	-	-	-	-	-
50.9		0.6357	-	-	-	-	-	-	-
53.6		0.6128	-	-	-	-	-	-	-
		0.5918	-	-	-	-	-	-	-
51.6		0.5155	-	-	-	-	-	-	-
53.5		0.6071	-	-	-	-	-	-	-
49.1		0.6035	-	-	-	-	-	-	-
		0.6043	-	-	-	-	-	-	-
51.8		0.2268	-	-	-	-	-	-	-
47.6		0.2418	-	-	-	-	-	-	-
49		0.2439	-	-	-	-	-	-	-
48.4		0.2453	-	-	-	-	-	-	-
50		0.2446	-	-	-	-	-	-	-
47.2		0.242	-	-	-	-	-	-	-
48.9		0.2506	-	-	-	-	-	-	-
50.1		0.2666	-	-	-	-	-	-	-
50		0.2646	-	-	-	-	-	-	-

concentration $\text{CCl}_4$	concentration $I_3^-$		$I_3^-$ - production	$I_3^-$ - production total	rate of $I_3^-$ - production	rate of $I_3^-$ - production
$C_h$	$C_{hc}$	$C_{af}$	$n_p$	$n_{\text{ptot}}$	$n_p/\Omega$	$n_p/t$
g/l	mg/l	mg/l	$\mu\text{mole}$	$\mu\text{mole}$	$\mu\text{mole/pass}$	$\mu\text{mole/s}$
	30.65	30.65	6.74	31.83	1.35	1.49E-02
	38.14	37.94	10.83		1.08	1.37E-02
	37.35	37.00	7.80		0.78	1.16E-02
	38.65	38.47	6.46		0.65	1.18E-02
	36.96	36.06	12.58	45.48	2.52	2.43E-02
	39.67	37.47	12.68		1.27	1.40E-02
	45.47	43.88	13.62		1.36	1.74E-02
	37.94	37.12	6.61		0.66	1.01E-02
	47.45		21.97	66.74	4.39	3.00E-02
	50.94	48.16	21.06		2.11	1.64E-02
	46.12	43.20	14.10		1.41	1.28E-02
	43.84	42.14	9.61		0.96	1.04E-02
	51.94	64.63	25.89	69.77	5.18	2.41E-02
	50.39	63.43	20.65		2.07	1.10E-02
	47.20	60.39	14.75		1.48	9.15E-03
	41.67	56.61	8.48		0.85	6.30E-03
	47.73	55.80	17.51	65.61	3.50	2.00E-02
	53.10	65.88	18.49		1.85	1.27E-02
	59.29	71.55	17.21		1.72	1.39E-02
	59.80	72.59	12.39		1.24	1.25E-02
0.324	55.55	54.69	28.73	150.38	5.75	6.33E-02
	76.20	72.00	39.42		3.94	4.99E-02
	92.59	85.12	42.89		4.29	6.41E-02
	103.78	94.14	39.34		3.93	7.05E-02
0.324	55.31	54.92	28.52	114.32	5.70	5.49E-02
	65.76	65.76	32.37		3.24	3.59E-02

	72.14	70.69	29.85		2.99	3.85E-02
	73.92	72.49	23.58		2.36	3.71E-02
0.324	54.18	53.45	27.79	104.08	5.56	3.78E-02
	63.14	61.00	30.21		3.02	2.35E-02
	70.22	67.02	29.28		2.93	2.67E-02
	58.41	56.82	16.80		1.68	1.84E-02
0.324	38.80	39.96	13.86	55.11	2.77	1.38E-02
	42.57	42.06	14.59		1.46	8.37E-03
	49.00	50.04	15.28		1.53	1.02E-02
	49.41	49.82	11.39		1.14	9.28E-03
-	86.49		55.67	197.11	11.13	5.76E-02
-	99.02		57.43		5.74	3.43E-02
-	92.67		43.50		4.35	3.01E-02
-	84.02		40.52		4.05	3.36E-02
-	83.22		54.51	221.79	10.90	8.80E-02
	108.76		65.89		6.59	6.03E-02
	104.08		50.69		5.07	5.42E-02
	99.80		50.70		5.07	6.58E-02
-	84.22		54.34	214.53	10.87	7.64E-02
	102.92		59.58		5.96	4.81E-02
	102.18		49.00		4.90	4.67E-02
	102.35		51.61		5.16	5.90E-02
-	25.31		2.63	17.07	2.63	1.20E-02
	28.37		4.94		4.94	2.56E-02
	28.80		4.17		4.17	2.45E-02
	29.08		3.32		3.32	2.27E-02
	28.94		2.02		2.02	1.64E-02
-	28.41		5.05	20.53	1.01	5.21E-03
	30.16		5.29		0.53	3.09E-03
	33.43		6.05		0.61	4.11E-03
	33.02		4.15		0.42	3.37E-03

flow rate	power consumption $P=Q*\Delta P$	power consumption total	energy density	oxidation efficiency	oxidation efficiency total	enhancement of liberation	energy	energy costs
Q	P	$P_{tot}$	$\rho_e$	$O_e$	$O_{etot}$	-	-	11.2 ¢/kWh
m <sup>3</sup> /s	W	W	J/ml	µmole/J	µmole/J	%	kWh	¢
4.27E-06	441.71	1766.85	517.13	3.36E-05	7.32E-06	155.6	1.21	13.53
4.27E-06	441.71		1034.25	3.10E-05				
4.27E-06	441.71		1034.25	2.64E-05				
4.27E-06	441.71		1034.25	2.68E-05				
3.75E-06	258.42	1033.67	344.75	9.42E-05	1.54E-05	222.4	0.82	9.20
3.75E-06	258.42		689.50	5.40E-05				
3.75E-06	258.42		689.50	6.72E-05				

3.75E-06	258.42		689.50	3.93E-05				
2.64E-06	91.15	364.59	172.38	3.29E-04	4.52E-05	326.3	0.41	4.59
2.64E-06	91.15		344.75	1.79E-04				
2.64E-06	91.15		344.75	1.40E-04				
2.64E-06	91.15		344.75	1.14E-04				
1.81E-06	31.16	124.65	86.19	7.75E-04	9.47E-05	341.1	0.20	2.29
1.81E-06	31.16		172.38	3.53E-04				
1.81E-06	31.16		172.38	2.94E-04				
1.81E-06	31.16		172.38	2.02E-04				
1.94E-06	13.35	53.42	34.48	1.50E-03	2.69E-04	320.8	0.07	0.76
1.94E-06	13.35		68.95	9.50E-04				
1.94E-06	13.35		68.95	1.04E-03				
1.94E-06	13.35		68.95	9.37E-04				
4.27E-06	441.71	1766.85	517.13	1.43E-04	3.44E-05	735.2	1.21	13.58
4.27E-06	441.71		1034.25	1.13E-04				
4.27E-06	441.71		1034.25	1.45E-04				
4.27E-06	441.71		1034.25	1.60E-04				
3.75E-06	258.42	1033.67	344.75	2.13E-04	3.91E-05	558.9	0.81	9.11
3.75E-06	258.42		689.50	1.39E-04				
3.75E-06	258.42		689.50	1.49E-04				
3.75E-06	258.42		689.50	1.43E-04				
2.64E-06	91.15	364.59	172.38	4.15E-04	7.08E-05	508.9	0.41	4.57
2.64E-06	91.15		344.75	2.58E-04				
2.64E-06	91.15		344.75	2.93E-04				
2.64E-06	91.15		344.75	2.01E-04				
1.94E-06	13.35	53.42	34.48	1.03E-03	1.89E-04	269.4	0.08	0.91
1.94E-06	13.35		68.95	6.27E-04				
1.94E-06	13.35		68.95	7.65E-04				
1.94E-06	13.35		68.95	6.95E-04				
2.00E-06	13.79	55.16	34.48	4.18E-03	6.75E-04	963.7	0.08	0.91
2.00E-06	13.79		68.95	2.49E-03				
2.00E-06	13.79		68.95	2.18E-03				
2.00E-06	13.79		68.95	2.43E-03				
3.14E-06	54.18	216.73	86.19	1.62E-03	2.99E-04	1084.3	0.21	2.30

3.14E-06	54.18		172.38	1.11E-03				
3.14E-06	54.18		172.38	1.00E-03				
3.14E-06	54.18		172.38	1.21E-03				
2.73E-06	94.12	376.47	172.38	8.12E-04	1.47E-04	1048.8	0.41	4.54
2.73E-06	94.12		344.75	5.11E-04				
2.73E-06	94.12		344.75	4.96E-04				
2.73E-06	94.12		344.75	6.27E-04				
2.00E-06	13.79	68.95	6.90	8.74E-04	2.91E-04	83.5	0.02	0.18
2.00E-06	13.79		6.90	1.86E-03				
2.00E-06	13.79		6.90	1.78E-03				
2.00E-06	13.79		6.90	1.64E-03				
2.00E-06	13.79		6.90	1.19E-03				
2.00E-06	13.79	55.16	34.48	3.78E-04	6.92E-05	100.4	0.08	0.92
2.00E-06	13.79		68.95	2.24E-04				
2.00E-06	13.79		68.95	2.98E-04				
2.00E-06	13.79		68.95	2.45E-04				

## Appendix B: Liberation of iodine "UC"

number .series	initial concentration, mass and volume			time t	temp. 11 (jacket) T11 °C	temp. 12 (jacket) T12 °C	temp. 21 (inside) T21 °C	temp. 22 (inside) T22 °C
	C <sub>0</sub>	sample m <sub>0s</sub>	sample real corr. V <sub>0src</sub>					
	g/l	g	ml	min	°C	°C	°C	°C
1.1 <sup>43</sup>	50	300.10	290.63	5	21.7	22.1	22.4	20.1
2.1		249.70	241.82	10	22.1	23.9	20.1	19.1
3.1		300.20	290.73	20	23.1	27.5	23.1	15.7
4.1		248.60	240.76	30	27.5	29.4	15.7	13.5
1.2	50	300.0	290.53	5	20	20	24.4	24.8
2.2		249.7	241.82	10			25.3	27
3.2		300.2	290.73	20			25.1	27.8
4.2		250.6	242.69	30			27.8	30
1.3	50	300.00	290.53	5	10	10	34.3	38
2.3		246.40	238.63	10			38	38.2
3.3		301.80	292.28	20			27.8	35.3
4.3		251.00	243.08	30			35.3	38.1
1.4	50	299.90	290.44	5	20	20	24.6	26.3
2.4		248.60	240.76	10			26.3	28
3.4		300.10	290.63	20			24.1	25.7
4.4		247.80	239.98	30			25.7	28
1.5	50	300.30	290.82	5	20	20	22.8	21.6
2.5		248.50	240.66	10			21.6	24.5
3.5		300.00	290.53	20			21.6	24.5
4.5		249.20	241.34	30			24.5	28.1
Blank		300.00	290.53					
1.6	50	300.50	291.02	5	20	20	24.1	24.4
2.6		248.60	240.76	10			24.4	26.3
3.6		300.50	291.02	20			24.2	24.5
4.6		249.70	241.82	30			24.5	25.5
Blank		300.00	290.53					
1.7 <sup>44</sup>	50	300.7	291.21	5	18.6	18.7	20	19.9
2.7		249.84	241.96	10	18.7	18.6	19.9	19.9
3.7		301.2	291.70	20	18.7	18.7	20.5	19.9

<sup>43</sup> Uncontrolled temperature conditions.

<sup>44</sup> 10 % citric acid to set the pH is used.

4.7		243.97	236.27	30	18.7	18.7	19.9	19.9
-----	--	--------	--------	----	------	------	------	------

sample taken at Arisdyne	pH at CSM	extinction	sample weight at CSM	concentration CCl <sub>4</sub>	concentration after ultrasonic
m <sub>sAr</sub>	pH	ζ <sub>uc</sub>	m <sub>sCSM</sub>	C <sub>h</sub>	C <sub>uc</sub>
g	-	-	g	g/l	mg/l
50.4	7.02	0.2913	48.1741		38.47
50.1	6.98	0.3049	49.4463		41.24
51.6	7.04	0.3359	49.7861		47.57
51.1	7.07	0.3709	49.3858		54.71
50.3	6.95	0.3101	48.3092		42.31
50.1	7.06	0.3467	47.7735		49.78
49.6	7.01	0.3853	47.6932		57.65
49.7	7.06	0.4282	51.4015		66.41
53.6	6.88	0.3396	51.1377		48.33
53.7	6.9	0.3616	51.9563		52.82
50.8	6.98	0.4216	48.9905		65.06
50.6	7.02	0.4626	48.1881		73.43
51.3	6.68	0.715	52.5145	0.243	124.94
50.1	6.38	1.244	47.7387		232.90
52.3	4.22	4.5	50.2227		897.39
51.2	3.81	4.5	49.3542		897.39
51.8	3.65	1.3672	50.6475		258.04
54	3.63	1.4192	52.9822		268.65
50.8	3.57	0.9883	49.7502		180.71
50.5	3.58	1.1552	48.9093		214.78
	3.42	1.3186			248.12
51.9	12.13	0.2718	51.3731		34.49
51	12.14	0.2962	53.4049		39.47
50.8	12.13	0.2807	49.2001		36.31
51	12.12	0.2841	49.6754		37.00
	12.11	0.2409			28.18
50.86		0.6803			117.86
57.1		0.7246			126.90
57.23		0.8574			154.00
50		1.0172			186.61

$I_3^-$ - productio n	$I_3^-$ - production total	rate of $I_3^-$ - production	Power dissipated into the liquid	total power dissipated into the liquid	power consumpti on total	energy density	enhancement of liberation
$\eta_p$	$\eta_{ptot}$	$\eta_p/t$	$P_{diss}$	$P_{disstot}$	$P_{tot}$	$\rho_e$	-
$\mu\text{mole}$	$\mu\text{mole}$	$\mu\text{mole/s}$	W	W	W	J/ml	%
14.02	27.45	0.04673833	-8.74	-11.91	84.21	86.93	134
13.43		0.02238273	-3.16		84.21	104.47	
20.98	42.87	0.01748076	-7.03	-10.50	84.05	173.47	210
21.89		0.01216019	-3.46		84.11	209.61	
11.53	24.04	3.84E-02	1.52	6.90	84.21	86.96	118
12.50		2.08E-02	5.38		84.21	104.47	
21.40	42.52	1.78E-02	2.57	6.06	84.05	173.47	208
21.12		1.17E-02	3.49		84.11	207.93	
14.95	28.24	0.04983331	14.06	14.68	84.21	86.96	138
13.29		0.02215036	0.62		84.21	105.87	
26.11	50.71	0.02175701	7.17	11.62	84.05	172.55	248
24.60		0.01366508	4.45		84.11	207.60	
63.67	168.56	0.21224723	6.46	11.81	84.21	86.99	824
104.89		0.17481327	5.35		84.21	104.94	
550.32	986.45	0.45860387	1.52	5.13	84.05	173.53	4823
436.12		0.24228956	3.61		84.11	210.28	
147.76	267.97	0.49253371	-4.56	4.56	84.21	86.87	1310
120.21		0.2003563	9.13		84.21	104.98	
99.22	195.03	0.0826805	2.76	8.44	84.05	173.58	954
95.82		0.05323097	5.68		84.11	209.10	
174.01							
6.44	13.57	0.28	1.14	84.21	84.21	86.81	66
7.13		1.45	5.98	84.21	84.21	104.94	
7.69	13.63	0.28	0.29	84.05	84.05	173.29	67
5.93		0.77	1.58	84.11	84.11	208.68	
6.17							
59.53	108.97	0.19842228	-0.38	-0.38	84.21	86.76	533
49.44		0.08240206	0.00		84.21	104.42	
80.17	159.77	0.06680989	-0.57	-0.57	84.05	172.89	781
79.60		0.0442237	0.00		84.11	213.58	

energy efficiency	energy efficiency total	oxidation efficiency	oxidation efficiency total	energy	energy costs
$E_e$	$E_{\text{tot}}$	$O_e$	$O_{\text{tot}}$	-	11.2 ¢/kWh
%	%	$\mu\text{mole/J}$	$\mu\text{mole/J}$	kWh	¢
-10.38	-7.07	5.55E-04	2.72E-04	0.03	0.31
-3.76		5.32E-04			
-8.37	-6.24	2.08E-04	1.42E-04	0.08	0.94
-4.12		4.34E-04			
1.80	4.09	4.56E-04	2.38E-04	0.03	0.31
6.38		4.95E-04			
3.05	3.60	2.12E-04	1.40E-04	0.08	0.94
4.15		4.19E-04			
16.70	8.72	5.92E-04	2.79E-04	0.03	0.31
0.74		5.26E-04			
8.53	6.91	2.59E-04	1.68E-04	0.08	0.94
5.29		4.87E-04			
7.67	7.01	2.52E-03	1.67E-03	0.03	0.31
6.36		4.15E-03			
1.81	3.05	5.46E-03	3.26E-03	0.08	0.94
4.29		8.64E-03			
-5.42	2.71	5.85E-03	2.65E-03	0.03	0.31
10.84		4.76E-03			
3.28	5.02	9.84E-04	6.44E-04	0.08	0.94
6.76		1.90E-03			
1.36	50.00	2.55E-04	1.34E-04	0.03	0.31
7.10		2.82E-04			
0.34	49.98	7.63E-05	4.50E-05	0.08	0.94
1.88		1.18E-04			
-0.45	-0.23	2.36E-03	1.08E-03	0.03	0.31
0.00		1.96E-03			
-0.68	-0.34	7.95E-04	5.28E-04	0.08	0.94
0.00		1.58E-03			

## Appendix C: Oxidation of sulfite "HC"

number.series	initial concentration				passes	inlet pressure	orifice dimension	min/pass	time	time real	time accumulated
	$C_0$	sample $m_{0s}$	sample real $m_{0sr}$	sample real corr. $V_{0src}$	$\Omega$	$p_i$	-	$t/\Omega$	$t$	$t_r$	$t_{acc}$
	mmole/l	g	g	ml	-	psi	thousandths of an inch	min/pass	min	h:mm:ss	min
1.8	25	400	400.8	400.90	5	15000	6/8	1.52	7.58	0:07:35	7.58
2.8		380	378.7	378.79	15			1.43	14.32	0:14:19	21.89
3.8		360	355.7	355.79	25			1.34	13.45	0:13:27	35.34
4.8		340	333.8	333.88	35			1.26	12.62	0:12:37	47.96
0.1					0						
1.9	25	300	301.4	301.47	5	5000	6/8	1.84	9.20	0:09:12	9.20
2.9		280	280.8	280.87	15			1.71	17.15	0:17:09	26.35
3.9		260	259.3	259.36	25			1.58	15.83	0:15:50	42.18
4.9		240	238.3	238.36	35			1.46	14.55	0:14:33	56.74
0.2					0						
1.10 <sup>45</sup>	25	300	300.9	300.97	5	1000	8/12	2.51	12.54	0:12:32	12.54
2.10		280	278.6	278.67	15			2.32	23.22	0:23:13	35.76
3.10		260	257.8	257.86	25			2.15	21.49	0:21:29	57.25
4.10		240	238	238.06	35			1.98	19.84	0:19:50	77.09
0.3					0						
1.11	250	300	300.5	293.06	5	1000	8/12	2.44	12.21	0:12:13	12.21
2.11		280	279.3	272.38	15			2.27	22.70	0:22:42	34.91
3.11		260	258.5	252.10	25			2.10	21.01	0:21:00	55.92
4.11		240	236.4	230.54	35			1.92	19.21	0:19:13	75.13
0.4					0						
1.12	250	300	300.5	293.06	5	5000	6/8	1.79	8.95	0:08:57	8.95

<sup>45</sup> Orifice change from 6/8 to 8/12.

2.12		280	278.7	271.80	15			1.66	16.59	0:16:36	25.5 4
3.12		260	258.2	251.80	25			1.54	15.37	0:15:22	40.9 1
4.12		240	236.3	230.45	35			1.41	14.07	0:14:04	54.9 8
0.50					0						
1.13	250	300	301.3	293.84	5	15000	6/8	1.11	5.55	0:05:33	5.55
2.13		280	278.7	271.80	15			1.03	10.27	0:10:16	15.8 2
3.13		260	256.4	250.05	25			0.95	9.45	0:09:27	25.2 7
4.13		240	235.7	229.86	35			0.87	8.69	0:08:41	33.9 6
0.60					0						
1.14 <sup>46</sup>	25	300	302	302.07	5	15000	6/8	1.14	5.71	0:05:42	5.71
2.14		280	282.4	282.47	15			1.07	10.68	0:10:41	16.3 8
3.14		260	260.4	260.46	25			0.98	9.84	0:09:51	26.2 3
4.14		240	238.2	238.26	35			0.90	9.00	0:09:00	35.2 3
0.70					0						
1.22	25	350	351.7	351.78	5	1000	8/12	2.93	14.66	0:14:39	14.6 6
2.22		330	332.4	332.48	15			2.77	27.71	0:27:42	42.3 6
3.22		310	310.4	310.47	25			2.59	25.87	0:25:52	68.2 4
4.22		290	289.5	289.57	35			2.41	24.13	0:24:08	92.3 7
1.14 <sup>47</sup>	25	350	350.5	350.58	5	15000	6/8	1.32	6.62	0:06:37	6.62
2.14		330	323.2	323.28	15			1.22	12.22	0:12:13	18.8 4
3.14		310	301	301.07	25			1.14	11.38	0:11:23	30.2 2
4.14		290	278.7	278.77	35			1.05	10.54	0:10:32	40.7 6
1.16	25	350	353	353.08	5	2500	6/8	3.15	15.76	0:15:46	15.7 6
2.16		330	331.2	331.28	15			2.96	29.58	0:29:35	45.3 4
3.16		310	309.4	309.47	25			2.76	27.63	0:27:38	72.9 7
4.16		290	287.2	287.27	35			2.56	25.65	0:25:39	98.6 2

<sup>46</sup> Replication of 1.8 - 4.8.<sup>47</sup> Replication of 1.8 - 4.8.

1.15	25	350	350	350.08	1	1000	8/12	2.92	2.92	0:02:55	2.92
2.15		330	328.4	328.48	2			2.74	2.74	0:02:44	5.65
3.15		310	308.7	308.77	3			2.57	2.57	0:02:34	8.23
4.15		290	287.1	287.17	4			2.39	2.39	0:02:24	10.6 2
5.15		270	266.1	266.16	5			2.22	2.22	0:02:13	12.8 4

T1 (vessel)	T2 (vessel skin)	T3 (after cav. unit)	T4 (after heat ex)	sample taken at Arisdyn	extinction	concentration $SO_3^{2-}$	$SO_3^{2-}$ - moles per sample
T11/T12	T21/T22	T31/T32	T41/T42	$m_{sAr}$	$\zeta_{HX}$	$C_{HC}$	$n_{SO_3^{2-}}$
°C	°C	°C	°C	g	-	mmole/l	µmole
21.7/20.7	22.3/21.0	28.3/42.3	yes	22.1	0.5037	17.95	6798.67
20.7/20.4	21.0/20.9	42.3/42.6		23	0.4426	15.69	5583.60
20.4/20.3	20.9/20.4	42.6/41.9		21.9	0.4858	17.29	5772.06
20.3/20.2	20.4/20.7	41.9/41.9		21.7	0.4867	17.32	5407.19
						25.00	10022.41
21.3/20.4	22.2/20.9	29.5/27.4	yes	20.6	0.4123	14.58	4093.82
20.4/20.4	20.9/20.9	27.4/27.1		21.5	0.4224	14.95	3877.03
20.4/20.4	20.9/20.9	27.1/27.0		21	0.4475	15.87	3783.81
20.4/20.4	20.9/20.9	27.0/27.1		21.8	0.4487	15.92	3447.25
						25.00	7536.81
21.7/20.4	22.4/20.7	22.5/21.0	yes	22.3	0.4054	14.32	3990.80
20.4/20.2	20.7/20.6	21.0/20.6		20.8	0.4045	14.29	3684.28
20.2/20.2	20.6/20.6	20.6/20.6		19.8	0.4093	14.46	3443.48
20.2/20.3	20.7/20.7	20.6/20.7		20.2	0.4268	15.11	3291.90
						25.00	7524.31
22.1/20.6	22.7/20.9	34.1/41.9	yes	19.6	0.3546	12.45	3515.73
20.6/20.5	20.9/20.9	41.9/41.9		22	0.4845	17.24	4490.34
20.5/20.4	20.9/20.8	41.9/42.0		22.2	0.4785	17.02	4054.77
20.4/20.4	20.8/20.8	42.0/42.2		20.5	0.5433	19.41	4226.58
					0.4780	25.00	7551.81
42.1	<sup>48</sup>	38.3	43.6	19.3	0.376	13.24	4400.76
42.5		42.3	44.1	22	0.5152	18.37	5704.25
41.9		41.8	43.6	20.9	0.528	18.85	5456.94
41.9		41.2	43.6		0.4648	16.51	4781.64
						25.00	8794.61

<sup>48</sup> Data was not correct, skin was hot to touch.

21.4	21.4	44.8	chiller 18°C	27.3	0.4371	15.49	5007.82
21.3	21.5	45		22.2	0.5022	17.89	5387.08
21.3	21.6	45.1		22.3	0.4913	17.49	4875.85
21.3	21.7	45			0.5098	18.17	5066.15
						25.00	8764.60
20.6	20.8	25.1	chiller 20°C	21.8	0.4629	16.44	5447.16
20.6	21	25		21.8	0.5064	18.05	5585.38
20.8	20.8	25.1		22.2	0.4713	16.75	4812.55
20.6	21	25.2			0.5061	18.04	5181.44
						25.00	8827.12
21.2	21.1	23.9	chiller 20°C	21.6	0.4367	15.48	5083.54
20.8	21.2	24		19.7	0.5191	18.52	5717.45
20.8	21.1	23.7		21.6	0.4906	17.46	5015.39
20.6	21	23.3		21	0.5988	21.46	5711.34
20.5	21.1	23			0.512	18.25	4858.72
						25.00	8752.10

SO <sub>4</sub> <sup>2-</sup> - production	SO <sub>4</sub> <sup>2-</sup> - production total	rate of SO <sub>4</sub> <sup>2-</sup> - production	rate of SO <sub>4</sub> <sup>2-</sup> - production	percentage of oxidation
n <sub>p</sub>	n <sub>ptot</sub>	n <sub>p</sub> /Ω	n <sub>p</sub> /t	-
μmole	μmole	μmole/pass	μmole/s	%
3223.74	4615.21	644.75	7.09	46.05
1215.07		121.51	1.41	
-188.46		-18.85	-0.23	
364.87		36.49	0.48	
3442.98	4089.56	688.60	6.24	54.26
216.79		21.68	0.21	
93.22		9.32	0.10	
336.56		33.66	0.39	
3533.51	4232.41	706.70	4.70	56.25
306.51		30.65	0.22	
240.80		24.08	0.19	
151.58		15.16	0.13	
4036.08	3325.23	807.22	11.78	44.03
-974.60		-97.46	-1.52	
435.57		43.56	0.74	
-171.81		-17.18	-0.32	

4393.85	4012.97	878.77	5.00	45.63
-1303.50		-130.35	-0.78	
247.31		24.73	0.16	
675.31		67.53	0.47	
3756.78	3698.45	751.36	9.45	42.20
-379.26		-37.93	-0.52	
511.23		51.12	0.75	
-190.30		-19.03	-0.30	
3379.95	3645.68	675.99	3.57	41.30
-138.22		-13.82	-0.08	
772.83		77.28	0.47	
-368.89		-36.89	-0.24	
3668.56	3893.38	3668.56	20.96	44.49
-633.90		-633.90	-3.86	
702.06		702.06	4.55	
-695.95		-695.95	-4.85	
852.62		852.62	6.41	

flow rate	power consumption $n P = \dot{Q} * \Delta p$	power consumption total	energy density	energy	energy costs	oxidation efficiency	oxidation efficiency total
$\dot{Q}$	P	$P_{tot}$	$\rho_e$	-	11.2 $\phi/kWh$	$O_e$	$O_{etot}$
$m^3/s$	W	W	J/ml	kWh	$\phi$	$\mu mole/J$	$\mu mole/J$
4.41E-06	456.10	1824.42	517.125	1.46	16.33	1.56E-02	8.79E-04
4.41E-06	456.10		1034.25			3.10E-03	
4.41E-06	456.10		1034.25			-5.12E-04	
4.41E-06	456.10		1034.25			1.06E-03	
2.73E-06	94.12	376.47	172.375	0.36	3.99	6.63E-02	3.19E-03
2.73E-06	94.12		344.75			2.24E-03	
2.73E-06	94.12		344.75			1.04E-03	
2.73E-06	94.12		344.75			4.10E-03	
2.00E-06	13.79	55.16	34.475	0.07	0.79	3.41E-01	1.66E-02
2.00E-06	13.79		68.95			1.60E-02	
2.00E-06	13.79		68.95			1.35E-02	
2.00E-06	13.79		68.95			9.23E-03	
4.41E-06	456.10	1824.42	517.125	1.07	12.00	2.58E-02	8.62E-04
4.41E-06	456.10		1034.25			-3.34E-03	

4.41E-06	456.10		1034.25			1.62E-03	
4.41E-06	456.10		1034.25			-6.97E-04	
2.00E-06	13.79		34.475			3.62E-01	
2.00E-06	13.79		68.95			-5.69E-02	
2.00E-06	13.79	55.16	68.95	0.08	0.95	1.16E-02	1.31E-02
2.00E-06	13.79		68.95			3.38E-02	
4.41E-06	456.10		517.125			2.07E-02	
4.41E-06	456.10		1034.25			-1.13E-03	
4.41E-06	456.10	1824.42	1034.25	1.24	13.88	1.64E-03	8.29E-04
4.41E-06	456.10		1034.25			-6.60E-04	
1.87E-06	32.18		86.1875			1.11E-01	
1.87E-06	32.18		172.375			-2.42E-03	
1.87E-06	32.18	128.71	172.375	0.21	2.37	1.45E-02	4.79E-03
1.87E-06	32.18		172.375			-7.45E-03	
2.00E-06	13.79		6.895			1.52E+00	
2.00E-06	13.79		6.895			-2.80E-01	
2.00E-06	13.79	68.95	6.895	0.01	0.17	3.30E-01	7.33E-02
2.00E-06	13.79		6.895			-3.51E-01	
2.00E-06	13.79		6.895			4.65E-01	

## Appendix D: Oxidation of sulfite "UC"

number .series	initial concentration, mass and volume			time	temp. 11 (jacket)	temp. 21 (inside)	temp. 22 (inside)
	$C_0$	sample $m_{0s}$	sample real corr. $V_{0src}$	t	T11/T12	T21	T22
	mmole/l	g	ml	min	°C	°C	°C
1.8	25	250.9	251.0	5	20	18.2	20.2
2.8		230.2	230.3	10	20	20.2	21.5
3.8		248.2	248.3	20	20	21.5	21
4.8		226.5	226.6	30	20	21	22
1.9	250	241.9	235.9	5	20	22.1	21.6
2.9		221.3	215.8	10	20	21.6	21.1
3.9		259.1	252.7	20	20	22.1	21
4.9		238.1	232.2	30	20	21	21
1.10	2.5	251.1	252.0	5	20	21.7	21.1
2.10		230.4	231.2	10	20	21.1	21
3.10		242.2	243.0	20	20	21.4	21.1
4.10		221.2	222.0	30	20	21.1	21.2
1.11	25	300	301	5	44.5/44.6	42.6	42.6
2.11		280	279.63	10	44/44.6	38.6	42.6
3.11		300	300	20	51.4/45.5	42.1	42.4
4.11		280	278.4	30	45.5/44.4	42.4	42.4
1.12 <sup>49</sup>	25	300	300.7	5	66.8/63.0	56.4	56.8
2.12		280	279.76	10	63.0/64.8	56.8	59.3
3.12		260	259.06	20	64.8/65.3	59.3	59.9
4.12		240	238.46	30	65.3/64.2	59.9	59.5
1.13	25	300	301.9	5	38.8/36.9	36.7	36.1
2.13		280	280.9	10	36.9/37.1	36.1	36.2
3.13		260	260.2	20	37.1/36.3	36.2	35.4
4.13		240	239.44	30	36.3/36.5	35.4	36.8
1.8 rep	25	300	300	5	18.3/17.7	19.4	19
2.8 rep		280	279.3	10	17.7/17.9	19	19.2
3.8 rep		260	261.17	20	17.9/18.3	19.2	19.2
4.8 rep		240	239.1	30	18.3/18.6	19.2	19.2

<sup>49</sup> The starting solution is not changed after 10 minutes. The samples are taken from the same starting solution after 5, 10, 20 and 30 minutes.

sample taken at Arisdyn e	extinction	concentration $SO_3^{2-}$ <sup>50</sup>	$SO_3^{2-}$ - moles per sample <sup>51</sup>	$SO_4^{2-}$ - production	$SO_4^{2-}$ - production total	rate of $SO_4^{2-}$ - production	percentage of oxidation
$m_{sAr}$	$\zeta_{HX}$	$C_{HC}$	$n_{SO_3^{2-}}$	$\eta_p$	$\eta_{ptot}$	$\eta_p/t$	-
g	-	mmole/l	$\mu\text{mole}$	$\mu\text{mole}$	$\mu\text{mole}$	$\mu\text{mole/s}$	%
20.7	0.3989	14.08	3242.27	3031.74	2454.58	10.1058	39.1
19.4	0.5082	18.11	3819.43	-577.16		-0.9619	
21.7	0.4504	15.98	3620.69	2585.80	2814.41	2.1548	45.3
20.3	0.463	16.45	3392.08	228.61		0.1270	
		25.00	6274.01				
		25.00	6206.49				
20.6	3.5439	106.13	22905.34	36071.64	43575.00	120.2388	73.9
21.6	3.5439	106.13	20669.66	2235.68		3.7261	
21	3.3977	101.92	23665.87	39504.60	45135.13	32.9205	71.4
22.1	3.3977	101.92	21469.25	2196.62		1.2203	
		250.00	58976.98				
		250.00	63170.47				
20.7	0.0222	0.89	205.06	424.86	402.77	0.6835	63.9
20.6	0.0228	0.94	197.71	7.35		0.3295	
21	0.0269	1.30	287.59	342.33	352.48	0.2397	58.0
20.2	0.0157	0.32	64.89	222.69		0.0361	
		2.50	629.92				
		2.50	607.59				
21.37	0.5905	21.15	5914.54	1610.46	2664.28	5.3682	35.4
20.17	0.525	18.73	4860.72	1053.82		1.7564	
21.6	0.6225	22.33	6217.26	1282.74	2662.87	1.0690	35.5
20.25	0.5251	18.74	4837.13	1380.13		0.7667	
		25.00	7525.00				
		25.00	7500.00				
20.94	0.5086	18.13	5071.81	2445.69	3760.63	8.1523	50.0
20.7	0.5157	18.39	4764.41	307.40		0.5123	
20.6	0.5074	18.08	4312.52	451.89		0.3766	
20.77	0.485	17.26	3756.87	555.64		0.3087	

<sup>50</sup> The values of 250, 25 and 2.5 mmole/l are the concentration of the starting solution.

<sup>51</sup> The moles per sample for the starting solution are different because of the different volume of the starting sample.

		25.00	7517.50				
21	0.401	14.16	3977.17	3570.33	3322.34	11.9011	44.0
20.7	0.5164	18.42	4792.10	-814.93		-1.3582	
20.76	0.4881	17.37	4159.72	632.38		0.5270	
21.17	0.5419	19.36	4225.16	-65.44		-0.0364	
		25.00	7547.50				
20.7	0.5172	18.45	5152.11	2347.89	3241.55	7.8263	43.2
18.13	0.4918	17.51	4572.88	579.22		0.9654	
22.07	0.5637	20.16	4820.82	-247.94		-0.2066	
20.32	0.5448	19.46	4258.45	562.38		0.3124	
		25.00	7500.00				

Power dissipated into the liquid	total power dissipated into the liquid	power consumption total	energy density	energy efficiency	energy efficiency total
$P_{diss}$	$P_{disstot}$	$P_{tot}$	$\rho_e$	$E_e$	$E_{etot}$
W	W	W	J/ml	%	%
7.00	11.18	84.21	100.67	8.31	6.64
4.18		84.21	109.72	4.96	
0.43	2.01	84.05	203.14	0.52	1.20
1.58		84.11	222.75	1.88	
-1.69	-3.23	84.21	107.09	-2.00	-1.92
-1.54		84.21	117.06	-1.83	
0.99	0.99	84.05	199.59	1.18	0.59
0.00		84.11	217.33	0.00	
-2.10	-2.42	84.21	100.27	-2.50	-1.44
-0.32		84.21	109.28	-0.38	
0.25	0.41	84.05	207.51	0.30	0.24
0.15		84.11	227.35	0.18	
0.00	15.63	84.21	83.93	0.00	9.28
15.63		84.21	90.35	18.56	
-0.31	-0.31	84.05	168.11	-0.37	-0.19
0.00		84.11	181.26	0.00	
1.67	11.32	84.21	84.02	1.99	3.36
9.77		84.21	90.31	11.60	
0.54		84.11	194.80	0.65	
-0.67		84.11	211.63	-0.80	

-2.51	-0.50	84.21	83.68	-2.98	-0.15
0.39		84.21	89.94	0.46	
-0.73		84.11	193.94	-0.86	
2.34		84.11	210.76	2.79	
-1.67	-0.89	84.21	84.21	-1.99	-0.27
0.78		84.21	90.46	0.93	
0.00		84.11	193.22	0.00	
0.00		84.11	211.06	0.00	

oxidation efficiency	oxidation efficiency total	energy	energy costs
$O_e$	$O_{\text{etot}}$	-	11.2 ¢/kWh
$\mu\text{mole/J}$	$\mu\text{mole/J}$	kWh	¢
1.20E-01	2.43E-02	0.08	0.94
-2.28E-02			
2.56E-02	9.30E-03		
4.53E-03			
1.43E+00	4.31E-01	0.08	0.94
8.85E-02			
3.92E-01	1.49E-01		
4.35E-02			
1.68E-02	3.99E-03	0.08	0.94
2.91E-04			
3.39E-03	1.16E-03		
4.41E-03			
6.37E-02	2.64E-02	0.08	0.94
4.17E-02			
1.27E-02	8.80E-03		
2.73E-02			
9.68E-02	1.86E-02	0.06	0.70
1.22E-02			
8.95E-03			
1.10E-02			
1.41E-01	1.64E-02	0.06	0.70
-3.23E-02			
1.25E-02			
-1.30E-03			
9.29E-02	1.60E-02	0.06	0.70

2.29E-02			
-4.91E-03			
1.11E-02			

## Appendix E: Degradation of PNP "HC"

number series	initial concentration				passes	inlet pressure	orifice dimension	min/passes	time	time real	time accumulated
	$C_0$	sample $m_{0s}$	sample real $m_{0Sr}$	sample real corr. $V_{0src}$	$\Omega$	$p_i$	-	$t/\Omega$	$t$	$t_r$	$t_{acc}$
	$\mu\text{mole/l}$	g	g	ml	-	psi	thousands of an inch	min/passes	min	h:mm:ss	min
1.1*	25	400	400	401.4	5	15000	6/8	1.52	7.58	0:07:35	7.58
2.1		350	351.6	352.8	15			1.33	13.33	0:13:20	20.92
3.1		300	298.2	299.2	25			1.13	11.31	0:11:18	32.23
4.1		250	247.8	248.6	35			0.94	9.40	0:09:24	41.62
1.2	25	400	400	401.4	5	10000	6/8	1.73	8.64	0:08:39	8.64
2.2		350	349.6	350.8	15			1.51	15.11	0:15:06	23.75
3.2		300	299	300.0	25			1.29	12.92	0:12:55	36.67
4.2		250	249.9	250.7	35			1.08	10.80	0:10:48	47.47
1.3	25	400	400	401.4	5	5000	6/8	2.45	12.25	0:12:15	12.25
2.3		350	350.9	352.1	15			2.15	21.50	0:21:30	33.75
3.3		300	302.3	303.3	25			1.85	18.52	0:18:31	52.26
4.3		250	252	252.9	35			1.54	15.44	0:15:26	67.70
1.4	25	400	400	401.4	5	2500	8/12	2.13	10.64	0:10:38	10.64
2.4		350	350.6	351.8	15			1.87	18.65	0:18:39	29.29
3.4		300	302	303.0	25			1.61	16.07	0:16:04	45.36
4.4		250	251.8	252.7	35			1.34	13.40	0:13:24	58.76
1.5	25	400	400	401.4	5	1000	8/12	3.34	16.72	0:16:43	16.72
2.5		350	350.8	352.0	15			2.93	29.33	0:29:20	46.06
3.5		300	300	301.0	25			2.51	25.08	0:25:05	71.14
4.5		250	247	247.8	35			2.07	20.65	0:20:39	91.79
1.6	25	400	400	401.4	5	1000	8/12	3.34	16.72	0:16:43	16.72
2.6		350	352.2	353.4	15			2.94	29.45	0:29:27	46.17
3.6		300	301.4	302.4	25			2.52	25.20	0:25:12	71.37
4.6		250	251.5	252.4	35			2.10	21.03	0:21:02	92.40
1.7	25	400	400	401.4	5	1000	8/12	3.34	16.72	0:16:43	16.72
2.7		350	351.3	352.5	15			2.94	29.37	0:29:22	46.10
3.7		300	300.9	301.9	25			2.52	25.16	0:25:10	71.26
4.7		250	252.1	253.0	35			2.11	21.08	0:21:05	92.34

1.13	25	450	444.2	445.7	1	1000	8/12	3.71	3.71	0:03:43	3.71
2.13		400	393.3	394.6	2			3.29	3.29	0:03:17	7.00
3.13		350	344.6	345.8	3			2.88	2.88	0:02:53	9.88
4.13		300	297.2	298.2	4			2.49	2.49	0:02:29	12.37
5.13		250	249	249.8	5			2.08	2.08	0:02:05	14.45
1.17	25	400	400.5	401.9	5	1000	8/12	3.35	16.74	0:16:45	16.74
2.17		350	351.2	352.4	15			2.94	29.37	0:29:22	46.11
3.17		300	303.1	304.1	25			2.53	25.34	0:25:21	71.45
4.17		250	253.9	254.8	35			2.12	21.23	0:21:14	92.68
1.18	25	400	402.1	403.5	5	1000	8/12	3.36	16.81	0:16:49	16.81
2.18		350	349.2	350.4	15			2.92	29.20	0:29:12	46.01
3.18		300	297.9	298.9	25			2.49	24.91	0:24:55	70.92
4.18		250	248.2	249.0	35			2.08	20.75	0:20:45	91.67
1.19	25	400	400.3	401.7	5	1000	8/12	3.35	16.74	0:16:44	16.74
2.19		350	347.8	349.0	15			2.91	29.08	0:29:05	45.82
3.19		300	295.5	296.5	25			2.47	24.71	0:24:43	70.53
4.19		250	242.8	243.6	35			2.03	20.30	0:20:18	90.83
1.20	25	400	401.2	402.6	5	1000	8/12	3.35	16.77	0:16:46	16.77
2.20		350	350.1	351.3	15			2.93	29.27	0:29:16	46.05
3.20		300	299.9	300.9	25			2.51	25.08	0:25:05	71.12
4.20		250	251.6	252.5	35			2.10	21.04	0:21:02	92.16
1.21	25	400	400.6	402.0	5	1000	8/12	3.35	16.75	0:16:45	16.75
2.21		350	352.5	353.7	15			2.95	29.47	0:29:28	46.22
3.21		300	303.1	304.1	25			2.53	25.34	0:25:21	71.57
4.21		250	255.5	256.4	35			2.14	21.36	0:21:22	92.93

T1 (vessel)	T2 (vessel skin)	T3 (after cav. unit)	T4 (after heat ex)	sample taken at Arisdyn	pH1	pH2	extinction	concentration of PNP	PNP left in the samples
T11/T12	T21/T22	T31/T32	T41/T42	m <sub>sAr</sub>	-	-	ζ <sub>HX</sub>	C <sub>HC</sub>	Π <sub>PNP</sub>
°C	°C	°C	°C	g	-	-	-	μmole/l	μmole
21.5	21.5	45.5	20°C	48.4	6.61	11.21	0.5077	27.45	0.41
21.3	21.1	45.4		53.4	6.62	11.09	0.5215	28.19	0.70
21.1	21	45		50.4	6.8	11.21	0.5218	28.20	0.99
21.3	21.1	45		50	6.74	11.1	0.5205	28.13	-0.42
20	20.2	36.6	20°C	50.4	6.75	11.19	0.4533	24.52	0.37
20.3	20.2	36.1		50.6	6.67	11.41	0.4488	24.28	0.61

19.9	20.2	36.2		49.1	6.83	11.17	0.463	25.04	0.88
20.4	20	36.3		50	6.61	11.14	0.4536	24.54	-0.37
19	19.2	27.3	20°C	49.1	6.79	11.3	0.452	24.45	0.37
19.6	19.9	28.2		48.6	6.73	11.15	0.4538	24.55	0.61
19.6	19.9	28.2		50.3	6.71	11.13	0.4577	24.76	0.87
19.5	20	28.4		50	6.8	11.1	0.4566	24.70	-0.37
19.6	19.9	24.4	20°C	49.4	6.67	11.18	0.4477	24.22	0.36
20.4	20.7	25.1		48.6	6.81	11.12	0.4443	24.04	0.60
20.5	20.4	25		50.2	6.85	11.15	0.4472	24.19	0.85
20.3	20.7	25.2		50	6.8	11.1	0.4451	24.08	-0.36
20.8	21.1	23.1	20°C	49.2	6.87	11.1	0.4327	23.41	0.35
20.4	20.9	23		50.8	6.97	11.07	0.4347	23.52	0.59
20.3	20.8	22.7		53	6.85	11.06	0.434	23.48	0.82
20.3	20.8	22.7		50	6.86	11.11	0.4323	23.39	-0.35
7.1	8.7	12.1	4°C	47.8	6.86	11.22	0.4759	25.74	0.39
6.4	8.4	10.4		50.8	6.96	11.08	0.488	26.39	0.66
6.2	10.3	10		49.9	7	11.12	0.4849	26.22	0.92
6.1	9.7	10		50	6.82	11.07	0.4834	26.14	-0.39
11.7	13	15.1	9°C	48.7	6.83	11.21	0.4646	25.13	0.38
10.3	12	14.1		50.4	6.91	11.13	0.4703	25.44	0.64
10.4	11.8	14		48.8	6.83	11.14	0.4683	25.33	0.89
10.3	13	14		50	6.8	11.12	0.4704	25.44	-0.38
21.3	22.5	24	20°C	50.9	6.5	11.15	0.4471	24.19	0.05
20.5	22.3	23		48.7	6.78	11.21	0.463	25.04	0.08
20.5	22.3	23.3		47.4	6.6	11.21	0.4656	25.18	0.10
20.7	22.4	23.1		48.2	6.54	11.16	0.4642	25.11	-1.11
20.6	22.5	23.1		50	6.51	11.14	0.4657	25.19	-1.13
34.1	data was not correct, skin was hot to touch	33.1	36°C	49.3	6.64	11.14	0.46	24.88	0.37
36.7		37.3	36.3	48.1	6.68	11.17	0.4876	26.37	0.66
35.9		36.6	36.4	49.2	6.56	11.18	0.4856	26.26	0.92
35.7		36.6	36.2	50	6.79	11.15	0.4843	26.19	-0.39
41.7	data was not correct, skin was hot to touch	39.3	43°C	52.9	6.71	11.14	0.4161	22.52	0.34
41.9		41.8	43	51.3	7.06	11.15	0.4395	23.78	0.59
41.9		42.1	43	49.7	6.95	11.19	0.4377	23.68	0.83
42.3		42.5	44.2	50	6.94	11.11	0.4401	23.81	-0.36

58	data was not correct, skin was hot to touch	52.1	65°C	52.5	7.04	11.14	0.429	23.22	0.35
59.5		57.1	61.5	52.3	7.25	11.12	0.4475	24.21	0.61
58.9		56.7	61.2	52.7	7.29	11.1	0.4442	24.03	0.84
58.1		56	60.3	50	7.41	11.16	0.4423	23.93	-0.36
41.6	data was not correct, skin was hot to touch	40.7	43°C	51.1	2.69	11.99	0.4048	21.91	0.33
41.5		41.6	42.4	50.2	2.62	11.77	0.4198	22.72	0.57
41.9		41.2	42.8	48.3	2.63	11.75	0.4193	22.69	0.79
41.9		40.4	43.8	50	2.63	11.42	0.4223	22.85	-0.34
40.9	data was not correct, skin was hot to touch	38	43°C	48.1	5.29	11.21	0.4061	21.98	0.33
42.5		41	43.6	49.4	5.2	11.12	0.4227	22.88	0.57
42.6		41.7	44.7	47.6	5.43	11.16	0.4228	22.88	0.80
42.5		41.8	43.1	50	5.31	11.08	0.422	22.84	-0.34

PNP - degradation	PNP - degradation total	rate of PNP- degradation	rate of PNP- degradation	percentage of degradation	percentage of degradation total
$n_{deg}$	$n_{degtot}$	$n_{deg}/t$	$n_{deg}/\Omega$	-	-
$\mu\text{mole}$	$\mu\text{mole}$	$\mu\text{mole/s}$	$\mu\text{mole/pass}$	%	%
0.39	4.48	8.57E-04	7.80E-02	3.87	44.52
1.25		1.56E-03	1.25E-01	16.27	
1.42		2.10E-03	1.42E-01	30.38	
1.42		2.53E-03	1.42E-01	44.52	
1.47	5.15	2.84E-03	2.94E-01	14.60	51.10
1.32		1.45E-03	1.32E-01	27.68	
1.00		1.30E-03	1.00E-01	37.66	
1.35		2.09E-03	1.35E-01	51.10	
1.46	5.06	1.99E-03	2.93E-01	14.53	50.26
1.16		9.02E-04	1.16E-01	26.08	
1.19		1.07E-03	1.19E-01	37.85	
1.25		1.35E-03	1.25E-01	50.26	
1.55	5.19	2.43E-03	3.10E-01	15.41	51.55
1.24		1.10E-03	1.24E-01	27.69	
1.17		1.22E-03	1.17E-01	39.32	
1.23		1.53E-03	1.23E-01	51.55	
1.83	5.44	1.83E-03	3.66E-01	18.18	54.06

1.16		6.60E-04	1.16E-01	29.71	
1.26		8.37E-04	1.26E-01	42.22	
1.19		9.62E-04	1.19E-01	54.06	
0.98	4.78	9.74E-04	1.96E-01	9.71	47.49
1.12		6.31E-04	1.12E-01	20.78	
1.36		9.02E-04	1.36E-01	34.31	
1.33		1.05E-03	1.33E-01	47.49	
1.21	4.91	1.21E-03	2.43E-01	12.06	48.74
1.18		6.69E-04	1.18E-01	23.76	
1.27		8.43E-04	1.27E-01	36.39	
1.24		9.83E-04	1.24E-01	48.74	
1.64	6.15	7.36E-03	1.64E+00	14.66	55.00
0.89		4.49E-03	8.86E-01	22.59	
1.15		6.65E-03	1.15E+00	32.86	
1.23		8.27E-03	1.23E+00	43.88	
1.24		9.95E-03	1.24E+00	55.00	
1.32	4.72	1.31E-03	2.63E-01	13.06	46.83
0.75		4.25E-04	7.50E-02	20.49	
1.33		8.74E-04	1.33E-01	33.67	
1.33		1.04E-03	1.33E-01	46.83	
2.23	5.39	2.22E-03	4.47E-01	22.07	53.19
0.78		4.47E-04	7.83E-02	29.80	
1.21		8.10E-04	1.21E-01	41.75	
1.16		9.30E-04	1.16E-01	53.19	
1.98	5.45	1.97E-03	3.96E-01	19.63	54.03
0.92		5.29E-04	9.23E-02	28.79	
1.32		8.93E-04	1.32E-01	41.92	
1.22		1.00E-03	1.22E-01	54.03	
2.40	5.48	2.39E-03	4.81E-01	23.80	54.20
0.86		4.90E-04	8.61E-02	32.33	
1.11		7.36E-04	1.11E-01	43.29	
1.10		8.73E-04	1.10E-01	54.20	
2.31	5.37	2.30E-03	4.62E-01	22.92	53.28
0.82		4.63E-04	8.18E-02	31.03	
1.09		7.18E-04	1.09E-01	41.85	
1.15		8.99E-04	1.15E-01	53.28	

flow rate	power consumption $P=\dot{Q}\cdot\Delta p$	power consumption total	energy density	energy	energy costs	degradati on efficiency	degradati on efficiency total
$\dot{Q}$	P	$P_{tot}$	$\rho_e$	-	11.2 $\phi/kWh$	$D_e$	$D_{tot}$
$m^3/s$	W	W	J/ml	kWh	$\phi$	$\mu mole/J$	$\mu mole/J$
4.41E-06	456.10	3876.89	517.125	2.69	30.12	1.88E-06	4.63E-07
6.62E-06	684.16		1551.375			2.28E-06	
1.10E-05	1140.26		2585.625			1.84E-06	
1.54E-05	1596.36		3619.875			1.58E-06	
3.87E-06	266.84	2268.11	344.75	1.79	20.10	1.06E-05	7.97E-07
5.81E-06	400.25		1034.25			3.63E-06	
9.68E-06	667.09		1723.75			1.94E-06	
1.35E-05	933.93		2413.25			2.24E-06	
2.73E-06	94.12	799.99	172.375	0.90	10.11	2.12E-05	1.56E-06
4.10E-06	141.18		517.125			6.39E-06	
6.83E-06	235.29		861.875			4.54E-06	
9.56E-06	329.41		1206.625			4.10E-06	
3.14E-06	54.18	460.56	86.1875	0.45	5.05	4.49E-05	3.20E-06
4.72E-06	81.27		258.5625			1.36E-05	
7.86E-06	135.46		430.9375			8.97E-06	
1.10E-05	189.64		603.3125			8.09E-06	
2.00E-06	13.79	117.22	34.475	0.18	2.01	1.32E-04	8.43E-06
3.00E-06	20.69		103.425			3.19E-05	
5.00E-06	34.48		172.375			2.43E-05	
7.00E-06	48.27		241.325			1.99E-05	
2.00E-06	13.79	117.22	34.475	0.18	2.02	7.07E-05	7.36E-06
3.00E-06	20.69		103.425			3.05E-05	
5.00E-06	34.48		172.375			2.62E-05	
7.00E-06	48.27		241.325			2.18E-05	
2.00E-06	13.79	117.22	34.475	0.18	2.02	8.78E-05	7.56E-06
3.00E-06	20.69		103.425			3.23E-05	
5.00E-06	34.48		172.375			2.45E-05	
7.00E-06	48.27		241.325			2.04E-05	
2.00E-06	13.79	206.85	6.895	0.05	0.56	5.34E-04	3.43E-05
4.00E-06	27.58		13.79			1.63E-04	
6.00E-06	41.37		20.685			1.61E-04	

8.00E-06	55.16		27.58			1.50E-04	
1.00E-05	68.95		34.475			1.44E-04	
2.00E-06	13.79	117.22	34.475	0.18	2.03	9.51E-05	7.25E-06
3.00E-06	20.69		103.425			2.06E-05	
5.00E-06	34.48		172.375			2.54E-05	
7.00E-06	48.27		241.325			2.16E-05	
2.00E-06	13.79	117.22	34.475	0.18	2.01	1.61E-04	8.35E-06
3.00E-06	20.69		103.425			2.16E-05	
5.00E-06	34.48		172.375			2.35E-05	
7.00E-06	48.27		241.325			1.93E-05	
2.00E-06	13.79	117.22	34.475	0.18	1.99	1.43E-04	8.53E-06
3.00E-06	20.69		103.425			2.56E-05	
5.00E-06	34.48		172.375			2.59E-05	
7.00E-06	48.27		241.325			2.08E-05	
2.00E-06	13.79	117.22	34.475	0.18	2.02	1.73E-04	8.45E-06
3.00E-06	20.69		103.425			2.37E-05	
5.00E-06	34.48		172.375			2.14E-05	
7.00E-06	48.27		241.325			1.81E-05	
2.00E-06	13.79	117.22	34.475	0.18	2.03	1.67E-04	8.22E-06
3.00E-06	20.69		103.425			2.24E-05	
5.00E-06	34.48		172.375			2.08E-05	
7.00E-06	48.27		241.325			1.86E-05	

## Appendix F: Degradation of PNP "UC"

number .series	initial concentration, mass and volume			time	pH at Arisdyne	temp. (jacket)	temp. 21 (inside)	temp. 22 (inside)
	C <sub>0</sub>	sample m <sub>0s</sub>	sample real corr. V <sub>0src</sub>	t	-	T11/T12	T21	T22
	g/l	g	ml	min	-	°C	°C	°C
1.1 <sup>52</sup>	25	299.11	298.1	5		34.3/34.4	28.3	33.3
2.1		241.12	240.31	15		34.4/34.1	33.3	34.9
3.1		299.41	298.4	20		25.6/34.5	34.1	34.2
4.1		249.09	248.25	30		34.5/34.3	33.7	34.3
1.2	25	299.81	298.8	5		40.2/40.6	30.2	37.8
2.2		246.35	245.52	10		40.9/41.0	37.8	39.5
3.2		297.50	296.5	20		45.1/44.4	40.6	42.6
4.2		245.93	245.1	30		44.4/44.8	42.6	43.1
1.3	25	296.90	295.9	5		65.6/55.5	57.6	52.9
2.3		239.61	238.8	10		65.5/66.8	58.1	60.4
3.3		294.69	293.7	20		66.8/66.1	58	60.2
4.3		240.11	239.3	30		66.1/66.2	60.1	60.3
1.4	25	296.50	295.5	5	2.51	66.2/66.0	58	59.7
2.4		239.99	239.18	10		66.0/66.8	59.7	60.4
3.4		299.21	298.2	20		65.7/65.8	57.3	60.2
4.4		249.64	248.8	30		65.8/67.0	60.2	60.8
1.5	25	296.70	295.7	5	2.5	45.1/43.5	42.5	41.8
2.5		241.51	240.69	10		43.5/43.3	41.8	41.9
3.5		296.80	295.8	20		44.6/43.1	39.3	41.5
4.5		243.23	242.41	30		43.1/44.0	41.5	42
1.6	25	301.32	300.3	5	2.5	38/37.1	34	35.8
2.6		250.45	249.6	10		37.1/36.6	35.8	35.9
3.6		301.32	300.3	20		39.0/35.7	34.6	35
4.6		244.12	243.3	30		35.7/35.8	35	35
1.7	25	294.69	293.7	5	5	43.2/43.9	39.7	41.3
2.7		241.38	240.57	10		43.9/44	41.3	42.1
3.7		294.69	293.7	20		43.9/44.1	40.3	41.9
4.7		238.12	237.32	30		44.1/44.3	41.9	42.4
1.8	25	297.81	296.8	5	5	38.1/37.6	33.2	35.9

<sup>52</sup> The color of the first samples are cloudy.

2.8		243.87	243.05	10		37.6/36.6	35.9	35.5
3.8		298.11	297.1	20		39.4/36.9	33.6	35.8
4.8		239.90	239.09	30		36.9/36.8	35.8	36.1
1.9	25	305.53	304.5	5	5	63.9/64.8	57	58
2.9		255.90	255.04	10		64.8/65.6	58	59.5
3.9		296.80	295.8	20		64.8/65.9	57	60.2
4.9		246.21	245.38	30		65.9/65.7	60.2	60.2
1.10	25	302.84	301.82	5		19.1/20.7	20.5	21.4
2.10		246.84	246.01	10		20.7/19.7	21.4	20.7
3.10		301.02	300	20		19.7/19.8	21.4	20.7
4.10		247.50	246.66	30		19.8/19.9	20.7	20.8
1.11	25	300.30	299.29	5		8.2/8.3	11.2	11.4
2.11		251.14	250.29	10		8.3/7.4	11.4	10.4
3.11		304.38	303.35	20		7.2/7.3	11.1	10.6
4.11		244.84	244.02	30		7.3/7.4	10.6	10.7
0								
1.12	25	301.99	300.97	5		3.6/3.9	7.1	7.4
2.12		249.55	248.71	10		3.9/3.8	7.4	7.7
3.12		302.62	301.6	20		3.6/3.8	8	7.5
4.12		251.96	251.11	30		3.8/3.2	7.5	7.7
0								
1.13	25	301.94	300.92	5	2.7	3.1/3.2	7.8	7.8
2.13		250.68	249.83	10	2.5	3.2/3.4	7.8	7.7
3.13		302.05	301.03	20	2.55	2.2/2.8	7.6	7.1
4.13		250.01	249.17	30	2.5	2.8/2.7	7.1	7
1.14	25	302.23	301.21	5	2.5	6.9/7.0	11	10.7
2.14		246.09	245.26	10		7.0/7.2	10.7	10.7
3.14		301.07	300.05	20		7.2/7.2	10.9	10.7
4.14		250.84	249.99	30		7.2/7.0	10.7	10.7
1.15	25	301.50	300.48	5	2.55	18.1/18.6	18	19.9
2.15		251.26	250.41	10		18.6/18.6	19.9	20
3.15		301.05	300.03	20		18.5/18.7	21.3	20.1
4.15		250.12	249.28	30		18.7/18.6	20.1	20.1
1.16	25	301.37	300.35	5	5	18.5/18.5	20.6	20.3
2.16		248.46	247.62	10		18.5/18.6	20.3	20.2
3.16		301.93	300.91	20		18.5/18.9	20.7	20.4
4.16		250.69	249.84	30		18.9/18.7	20.4	20.3
1.17	25	302.15	301.13	5	5	6.8/6.4	10.9	10

2.17		250.27	249.43	10		6.4/6.4	10	10
3.17		301.46	300.44	20		6.9/6.4	10.7	10
4.17		252.99	252.14	30		6.4/6.8	10	10.1
1.18	25	301.22	300.2	5	5	2.4/1.9	7.2	6.2
2.18		250.94	250.09	10		1.9/1.7	6.2	6.2
3.18		301.21	300.19	20		1.5/1.8	7.8	6.2
4.18		251.01	250.16	30		1.8/1.8	6.2	6.2

sample taken at Arisdyn	pH 1	pH 2	extinction	concentration after ultrasonic	PNP left in the samples	PNP - degradation	PNP - degradation total
$m_{sAr}$	pH	pH	$\zeta_{uc}$	$C_{uc}$	$n_{PNP}$	$n_{deg}$	$n_{degtot}$
g	-	-	-	$\mu\text{mole/l}$	$\mu\text{mole}$	$\mu\text{mole}$	$\mu\text{mole}$
57.79	6.33	11.1	0.4405	23.83	5.73	1.78	2.73
50.56	6.58	11.11	0.4655	25.18	4.78	0.95	
50.15	6.82	11.2	0.4388	23.74	5.89	1.62	2.86
53.44	6.82	11.17	0.4418	23.90	4.66	1.24	
53.28	6.88	11.15	0.4506	24.38	5.98	1.54	2.82
52.67	6.83	11.17	0.4509	24.39	4.70	1.28	
51.4	6.75	11.16	0.4539	24.55	6.02	1.45	2.82
54.25	6.58	11.15	0.4497	24.33	4.64	1.38	
57.1	6.72	11.19	0.4588	24.82	5.93	1.52	2.90
57.53	6.8	11.1	0.4638	25.09	4.55	1.38	
54.4	6.86	11.15	0.47	25.42	6.08	1.31	2.71
54.17	7.05	11.11	0.4681	25.32	4.69	1.40	
56.32	3.06	12.05	0.4521	24.46	5.85	1.59	3.10
59.96	3.03	11.72	0.4481	24.24	4.34	1.50	
49.4	3.04	11.57	0.4282	23.17	5.77	1.74	3.06
58.41	3.06	11.1	0.4322	23.39	4.45	1.31	
55.01	3.14	11.56	0.4534	24.53	5.90	1.54	2.95
57.08	3.24	11.23	0.4531	24.51	4.50	1.40	
53.39	3.04	11.1	0.4404	23.83	5.78	1.67	3.08
53.33	3.04	11.12	0.4273	23.12	4.37	1.40	
50.7	2.73	12.17	0.4356	23.57	5.88	1.68	2.99
59.97	2.71	11.51	0.4458	24.12	4.57	1.31	
57	2.73	11.16	0.4255	23.03	5.60	1.96	3.44
61.84	2.71	11.38	0.4197	22.72	4.12	1.48	
53.13	6.18	11.17	0.4585	24.80	5.97	1.43	2.87

58.21	6.02	11.15	0.459	24.83	4.53	1.44	
56.38	5.96	11.04	0.4467	24.17	5.74	1.66	3.01
56.75	5.94	11.13	0.4487	24.27	4.38	1.35	
53.75	5.89	11.16	0.4517	24.44	5.94	1.53	2.80
54.66	5.86	11.2	0.4586	24.81	4.67	1.27	
58.01	5.6	11.13	0.4427	23.95	5.73	1.75	3.15
57	5.6	11.1	0.4398	23.80	4.33	1.39	
49.46	5.93	11.2	0.453	24.51	6.25	1.42	2.92
61.3	5.66	11.07	0.4533	24.52	4.75	1.50	
50.42	5.81	11.18	0.4525	24.48	6.01	1.44	2.88
58.4	5.74	11.11	0.452	24.45	4.57	1.43	
55.81	6.44	11.07	0.4694	25.39	6.25	1.35	2.72
52.46	6.58	11.1	0.4661	25.21	4.88	1.37	
53.34	6.62	11.1	0.4379	23.69	5.84	1.71	3.22
63.91	6.53	11.02	0.4382	23.71	4.33	1.51	
49		11.11	0.4623	25.01	6.26	1.28	2.74
57.96		11.01	0.4608	24.92	4.79	1.46	
60.36		11	0.4415	23.89	5.83	1.81	3.30
61.97		11.01	0.441	23.86	4.34	1.49	
52.26		11.02	0.4511	24.40	6.07	1.51	2.94
57.93		11.06	0.4493	24.31	4.64	1.43	
50.49		10.96	0.4346	23.52	5.91	1.69	3.09
57.83		11.06	0.4307	23.31	4.50	1.40	
51.09		11.07	0.3799	20.58	5.14	2.44	3.62
58.32		11.43	0.3812	20.65	3.95	1.19	
51.86		12.19	0.4087	22.12	5.51	2.07	3.37
60		11.46	0.4116	22.28	4.21	1.30	
55.95		11.84	0.4354	23.56	5.78	1.81	3.15
59.01		11.1	0.4397	23.79	4.43	1.35	
50.06		12.05	0.4121	22.31	5.58	1.98	3.41
63.03		11.15	0.4101	22.20	4.15	1.43	
50.07		12	0.4259	23.05	5.77	1.80	3.17
61.22		11.04	0.4297	23.25	4.40	1.37	
50.75		11.7	0.4166	22.55	5.62	1.93	3.28
59.59		11.05	0.4161	22.52	4.27	1.35	
52.73	5.72	11.2	0.4443	24.04	5.95	1.61	3.03

59.82	5.32	11.1	0.4462	24.14	4.53	1.42	
51.07	5.58	11.14	0.4145	22.44	5.61	1.97	3.45
63.17	5.23	11.08	0.4082	22.10	4.12	1.48	
51.7	5.7	11.25	0.4205	22.76	5.68	1.91	3.12
58.93	5.49	11.12	0.4333	23.45	4.47	1.21	
48.3	5.63	11.03	0.4242	22.96	5.79	1.78	3.15
58.21	5.78	11.14	0.4208	22.77	4.42	1.37	
50.11	5.04	11.19	0.4516	24.43	6.11	1.45	2.88
59.42	4.83	11.15	0.4534	24.53	4.68	1.43	
50.03	5.45	11.26	0.4378	23.69	5.93	1.63	3.09
62.8	5.06	11.1	0.4409	23.85	4.47	1.46	

rate of PNP-degradation	percentage of degradation	Power dissipated into the liquid	total power dissipated into the liquid	power consumption total	energy density	energy efficiency	energy efficiency total
$n_{deg}/t$	-	$P_{diss}$	$P_{disstot}$	$P_{tot}$	$\rho_e$	$E_e$	$E_{etot}$
$\mu\text{mole/s}$	%	W	W	W	J/ml	%	%
5.93E-03	23.70	20.80	23.48	84.21	84.46	24.70	13.94
1.06E-03	36.36	2.68		84.21	209.55	3.19	
1.35E-03	21.56	0.10	1.14	84.05	336.88	0.12	0.68
6.87E-04	38.03	1.04		84.11	202.59	1.24	
5.13E-03	20.46	31.69	37.51	84.21	84.27	37.63	22.27
2.13E-03	37.48	5.82		84.21	102.55	6.92	
1.21E-03	19.40	2.07	2.92	84.05	339.03	2.46	1.74
7.64E-04	37.81	0.85		84.11	205.20	1.02	
5.08E-03	20.47	-19.41	-11.74	84.21	85.09	-23.04	-6.97
2.30E-03	38.97	7.66		84.21	105.44	9.10	
1.09E-03	17.75	2.25	2.59	84.05	342.27	2.68	1.54
7.75E-04	36.63	0.33		84.11	210.17	0.40	
5.31E-03	21.39	7.01	9.35	84.21	85.21	8.32	5.55
2.51E-03	41.61	2.34		84.21	105.27	2.77	
1.45E-03	23.22	3.02	4.06	84.05	337.10	3.59	2.41
7.29E-04	40.70	1.04		84.11	202.15	1.24	
5.14E-03	20.72	-2.89	-2.55	84.21	85.15	-3.43	-1.52
2.34E-03	39.56	0.34		84.21	104.61	0.40	
1.39E-03	22.46	2.27	3.12	84.05	339.84	2.70	1.85
7.80E-04	41.30	0.85		84.11	207.47	1.01	
5.60E-03	22.20	7.54	7.89	84.21	83.85	8.96	4.68
2.18E-03	39.52	0.35		84.21	100.88	0.41	
1.63E-03	25.91	0.42	0.42	84.05	334.74	0.50	0.25

8.23E-04	45.49	0.00		84.11	206.72	0.00	
4.76E-03	19.33	6.56	9.24	84.21	85.73	7.79	5.49
2.40E-03	38.78	2.69		84.21	104.66	3.19	
1.38E-03	22.45	1.64	2.47	84.05	342.27	1.95	1.47
7.51E-04	40.73	0.83		84.11	211.92	0.98	
5.12E-03	20.54	11.18	9.83	84.21	84.83	13.28	5.83
2.11E-03	37.47	-1.36		84.21	103.60	-1.61	
1.46E-03	23.46	2.28	2.78	84.05	338.35	2.71	1.65
7.74E-04	42.08	0.50		84.11	210.36	0.59	
4.73E-03	18.49	4.25	9.59	84.21	82.69	5.05	5.69
2.50E-03	38.04	5.34		84.21	98.73	6.34	
1.20E-03	19.36	3.30	3.30	84.05	339.84	3.93	1.96
7.97E-04	38.62	0.00		84.11	204.96	0.00	
4.52E-03	17.83	3.79	1.39	84.21	83.42	4.50	0.82
2.28E-03	35.80	-2.40		84.21	102.35	-2.85	
1.43E-03	22.64	-0.73	-0.56	84.05	335.08	-0.87	-0.33
8.40E-04	42.64	0.17		84.11	203.90	0.20	
4.26E-03	16.96	0.84	-2.66	84.21	84.13	0.99	-1.58
2.44E-03	36.39	-3.49		84.21	100.60	-4.15	
1.51E-03	23.69	-0.53	-0.36	84.05	331.38	-0.63	-0.21
8.25E-04	43.14	0.17		84.11	206.11	0.20	
5.03E-03	19.92	1.26	2.30	84.21	83.66	1.50	1.37
2.39E-03	38.81	1.04		84.21	101.24	1.24	
1.41E-03	22.25	-0.53	-0.18	84.05	333.30	-0.63	-0.10
7.78E-04	40.69	0.35		84.11	200.29	0.42	
8.12E-03	32.17	0.00	-0.35	84.21	83.67	0.00	-0.21
1.98E-03	47.82	-0.35		84.21	100.78	-0.41	
1.72E-03	27.28	-0.53	-0.70	84.05	333.93	-0.62	-0.42
7.21E-04	44.40	-0.17		84.11	201.85	-0.21	
6.02E-03	23.82	-1.26	-1.26	84.21	83.59	-1.50	-0.75
2.25E-03	41.58	0.00		84.21	102.66	0.00	
1.65E-03	26.20	-0.21	-0.21	84.05	335.02	-0.25	-0.12
7.92E-04	45.07	0.00		84.11	201.18	0.00	
5.98E-03	23.72	7.97	8.32	84.21	83.80	9.46	4.94
2.29E-03	41.86	0.35		84.21	100.55	0.41	
1.61E-03	25.60	-1.26	-1.26	84.05	335.05	-1.49	-0.75
7.49E-04	43.46	0.00		84.11	201.76	0.00	
5.37E-03	21.30	-1.26	-1.60	84.21	83.83	-1.49	-0.95
2.36E-03	40.06	-0.35		84.21	101.68	-0.41	
1.64E-03	26.03	-0.31	-0.49	84.05	334.07	-0.37	-0.29
8.22E-04	45.56	-0.17		84.11	201.30	-0.21	
6.35E-03	25.14	-3.78	-3.78	84.21	83.62	-4.49	-2.25
2.02E-03	41.10	0.00		84.21	100.95	0.00	

1.48E-03	23.49	-0.73	-0.56	84.05	334.59	-0.87	-0.33
7.62E-04	41.62	0.18		84.11	199.47	0.21	
4.83E-03	19.18	-4.19	-4.19	84.21	83.87	-4.97	-2.49
2.39E-03	38.14	0.00		84.21	100.68	0.00	
1.36E-03	21.61	-1.68	-1.68	84.05	334.87	-1.99	-1.00
8.09E-04	40.88	0.00		84.11	201.05	0.00	

degradation efficiency	degradation efficiency total	energy	energy	energy costs
$D_e$	$D_{etot}$	$E_e$	$E_{etot}$	11.2 $\phi$ /kWh
$\mu\text{mole/J}$	$\mu\text{mole/J}$	kWh	kWh	$\phi$
7.04E-05	1.80E-05	1.05E-02	0.08	0.94
1.88E-05		1.05E-02		
1.61E-05	9.44E-06	4.20E-02		
2.45E-05		2.10E-02		
6.09E-05	2.79E-05	1.05E-02	0.08	0.94
5.07E-05		1.05E-02		
1.44E-05	9.33E-06	4.20E-02		
2.72E-05		2.10E-02		
6.04E-05	2.87E-05	1.05E-02	0.08	0.94
5.46E-05		1.05E-02		
1.30E-05	8.95E-06	4.20E-02		
2.77E-05		2.10E-02		
6.30E-05	3.06E-05	1.05E-02	0.08	0.94
5.96E-05		1.05E-02		
1.73E-05	1.01E-05	4.20E-02		
2.60E-05		2.10E-02		
6.11E-05	2.92E-05	1.05E-02	0.08	0.94
5.55E-05		1.05E-02		
1.66E-05	1.02E-05	4.20E-02		
2.78E-05		2.10E-02		
6.65E-05	2.96E-05	1.05E-02	0.08	0.94
5.18E-05		1.05E-02		
1.94E-05	1.14E-05	4.20E-02		
2.93E-05		2.10E-02		
5.66E-05	2.84E-05	1.05E-02	0.08	0.94
5.69E-05		1.05E-02		
1.65E-05	9.95E-06	4.20E-02		

2.68E-05		2.10E-02		
6.08E-05	2.77E-05	1.05E-02	0.08	0.94
5.01E-05		1.05E-02		
1.74E-05	1.04E-05	4.20E-02		
2.76E-05		2.10E-02		
5.61E-05	2.89E-05	1.05E-02	0.08	0.94
5.93E-05		1.05E-02		
1.43E-05	9.50E-06	4.20E-02		
2.84E-05		2.10E-02		
5.36E-05	2.69E-05	1.05E-02	0.08	0.94
5.41E-05		1.05E-02		
1.70E-05	1.06E-05	4.20E-02		
2.99E-05		2.10E-02		
5.06E-05	2.71E-05	1.05E-02	0.08	0.94
5.80E-05		1.05E-02		
1.79E-05	1.09E-05	4.20E-02		
2.94E-05		2.10E-02		
5.98E-05	2.91E-05	1.05E-02	0.08	0.94
5.67E-05		1.05E-02		
1.68E-05	1.02E-05	4.20E-02		
2.78E-05		2.10E-02		
9.65E-05	3.59E-05	1.05E-02	0.08	0.94
4.70E-05		1.05E-02		
2.05E-05	1.11E-05	4.20E-02		
2.57E-05		2.10E-02		
7.15E-05	3.12E-05	1.05E-02	0.08	0.94
5.33E-05		1.05E-02		
1.96E-05	1.13E-05	4.20E-02		
2.83E-05		2.10E-02		
7.11E-05	3.13E-05	1.05E-02	0.08	0.94
5.43E-05		1.05E-02		
1.92E-05	1.08E-05	4.20E-02		
2.67E-05		2.10E-02		
6.38E-05	3.00E-05	1.05E-02	0.08	0.94
5.62E-05		1.05E-02		
1.96E-05	1.14E-05	4.20E-02		

2.93E-05		2.10E-02		
7.55E-05	3.08E-05	1.05E-02	0.08	0.94
4.79E-05		1.05E-02		
1.76E-05	1.04E-05	4.20E-02		
2.72E-05		2.10E-02		
5.74E-05	2.85E-05	1.05E-02	0.08	0.94
5.67E-05		1.05E-02		
1.62E-05	1.02E-05	4.20E-02		
2.89E-05		2.10E-02		